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ANALIZA TRAGOVA TROŠENJA CIJEVI LOVAČKOG ORUŽJA

ANALYSIS OF WEAR TRACKS OF HUNTING RIFLE BARREL

Marin Ambrušec¹, Suzana Jakovljević¹

¹Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Ivana Lučića 5, 10000 Zagreb, Hrvastka.

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Sažetak

U radu je ispitan uzorak cijevi lovačkog oružja kalibra 8x57 mm koji se danas koristi kao najučestalije oružje za lov na raznoliku vrstu divljači. Provedeni su postupci mjerenja tvrdoće po Vickersu, analizirana mikrostruktura uzorka svjetlosnim mikroskopom te tragovi trošenja SEM-om.

Ključne riječi: cijev lovačkog oružja, trošenje, SEM

Abstract

In the thesis has been examined a sample of hunting weapon's barrel 8x57mm that is today most commonly used as the hunting weapon for various kinds of venison. Procedures measuring firmness have been carried out by Vickers, the microstructure is analyzed by light microscope and mechanisms of wear is analyzed by SEM.

Key words: hunting barrel, wear, SEM

1. LOVAČKO ORUŽJE

Lovačko oružje je vatreno oružje kojim se smije loviti divljač. Dijeli se prema vrstama i kalibrima. Glavna podjela lovačkih pušaka je prema njihovoj vrsti:

- 1. Lovačka puška s glatkim cijevima (sačmarica)
- 2. Lovačka puška s užljebljenim cijevima

1.1 Lovačka puška s glatkim cijevima (sačmarica)

Lovačke puške sačmarice su vrsta lovačkog oružja čije cijevi nisu užljebljene nego su glatke, a streljivo koje se koristi za puške sačmarice je drugačijeg sastava nego kod pušaka s užljebljenim cijevima, patrona. Sastoji se od velikog broja kuglica olovne šačme različite veličine (veličina ovisi o promjeru sačme.) Ispaljivanjem patrone iz puške sačmarice formira se sačmeni snop koji postiže određenu brzinu i ubojitost. Puške sačmarice mogu biti s dvije cijevi, slika 1 ili s jednom cijevi(slika 2). Ove se puške još nazivaju i "prelamače" zato što se prilikom svakog opaljenja puška mora prelomiti tj. otvoriti kako bi se stavila nova patrona [1].



Slika 1: Puška sačmarica s dvije cijevi literatura, [1].



Slika 2: Puška sačmarica s jednom cijevi literatura, [1].



1.2. Lovačka puška s užljebljenim cijevima

Najbitnija razlika u odnosu na puške sačamirce je da se ne koristi patrona nego zrno. Tijekom opaljenja zrno je prisiljeno prilikom pravocrtnog kretanja duž cijevi postići i rotaciju oko svoje uzdužne osi. Žlijebovi nisu usporedni s osi kanala cijevi, nego se uvijaju pod određenim kutom uvijanja, slika 3.



Slika 3: Pogled u kanal užljebljene cijevi, [1].

Osnovna razlika u odnosu na puške sačmarice je u izradi cijevi. Cijevi ovih pušaka su spiralno uzdužno izbrazdane, najčešće s po 4 – 6 polja i žljebova, tako da zrno kroz nju napravi krug od 360 stupnjeva, što zrnu daje rotirajuće kretanje, da bi na svom putu kroz prostor do cilja lakše savladao sile koje na njega djeluju i održao željeni pravac. Kod lovačkih pušaka s užljebljenim cijevima postoji spremnik u kojem se nalazi ležište za municiju, ležište zatvarača, zatvarač i mehanizam za okidanje (slika 4). Spremnik karabina čvrsto spaja cijev s kundakom. Kundak lovačkih karabina može biti rađen od drveta ili plastike. Ima istu svrhu i osobinu kao i kod pušaka sačmarica. [1].



Slika 4: Primjer mehanizma puške s užljebljenim cijevima [3].



2. CIJEV LOVAČKOG ORUŽJA

ožljebijeni dio cijevi cijev barutna komora prijelazni konus kanal cijevi

Na slici 5 prikazan je poprečni presjek užljebljene cijevi lovačkog oružja.

Slika 5: Uzdužni presjek cijevi lovačkog oružja, [1].

Barutna komora je glatki dio kanala cijevi, a namijenjena je za smještaj zrna i za početno izgaranje barutnog punjenja. Tipično zrno za lovačku pušku prikazano je na slici 6. Kod većine lovačkih pušaka barutno punjenje se nalazi u mjedenoj čahuri. Barutna komora za naboj s čahurom blago je konusnog oblika.



Slika 6: Primjer zrna kalibra 8x57 mm sa mjedenom čahurom proizvođača Lapua, [1].

Prijelazni konus je dio cijevi između barutne komore i vodećeg dijela cijevi. Osnovna mu je namjena da osigura postupno uvođenje zrna u vodeći dio cijevi, ali samim time i uvijek jedan i točan položaj zrna prije opaljenja. Kod užljebljenih cijevi prijelazni konus je na prvoj trećini svoje duljine gladak, a zatim počinje urezivanje žlijebova. Dubina žlijebova postepeno raste pa oni na kraju same cijevi postižu punu konstrukcijsku dubinu [1].

Prema literaturi [1] treba se postići optimalan tlak barutnih plinova (ni previsok ni prenizak) kako ne bi došlo do smicanja vodećeg prstena- užljebljeni dio cijevi s košuljice zrna. Zbog toga prijelazni konus ne smije biti prestrm. Računski i praktično je utvrđeno da bi trebao biti u omjeru 1:10 ili 1:20.

Vodeći dio cijevi se prostire od prijelaznog konusa do usta cijevi. Kod lovačkih pušaka s užljebljenim cijevima je užljebljen, a kod lovačkih pušaka s glatkim cijevima je gladak. Na poprečnom presjeku vodećeg dijela cijevi prikazana su polja i žlijebovi, slika 7.





Slika 7: Poprečni presjek vodećeg dijela cijevi, [1].

3. VAŽNI ZAHTJEVI I TRIBOLOŠKE ZNAČAJKE CIJEVI LOVAČKOG ORUŽJA

Cijev lovačkog oružja mora svojom ukupnom kvalitetom zadovoljiti stroge zahtjeve [2]:

- nakon opaljenja, uz ostvarivanje maksimalnog tlaka barutnih plinova i velikog udarnog opterećenja, ne smije doći do trajnih deformacija u cijevi,
- progib cijevi uslijed vlastite težine mora biti u dopuštenim granicama,
- proces opaljenja u cijevi mora se odvijati prema predviđenim parametrima unutarnje balistike,
- cijev mora imati visoku otpornost na korozijsko i mehaničko trošenje,
- proizvodnja cijevi mora biti tehnologična,
- održavanje cijevi mora biti jednostavno.

3.1 Proces opaljenja

Proces opaljenja lovačkog oružja je složeni proces kod kojega se kemijska energija baruta pretvara, u vrlo kratkom vremenu, najprije u toplinsku energiju barutnih plinova, a zatim u kinetičku energiju zrna i pokretnih dijelova oružja. Proces opaljenja se odvija u sustavu koji se sastoji od: cijevi, zrna, barutnog punjenja i zatvarača slika 8 [3].



Slika 8: Sustav opaljenja zrna [1].



Proces opaljenja lovačkog oružja sastoji se od tri osnovna procesa:

- proces izgaranja baruta i stvaranja barutnih plinova vrlo visoke temperature i visokog tlaka,
- proces pretvaranja toplinske energije barutnih plinova u kinetičku energiju kretanja sustava zrno-punjenje-cijev,
- proces kretanja plinova, barutnog punjenja, zrna i cijevi.

Svi gore navedeni procesi su povezani i odvijaju se istodobno.

Tlak barutnih plinova nastalih izgaranjem barutnog punjenja djeluje na sve površine barutne komore. Kao rezultat toga nastaju dvije glavne sile F_z i F_p .

 F_{P} - sila barutnih plinova koja prisiljava zrno na kretanje prema ustima cijevi

F_z- sila barutnih plinova na čelo zatvarača koja svojim djelovanjem preko zatvarača izaziva kretanje ostalih dijelova oružja i same cijevi. To kretanje same cijevi se odvija u suprotnom smjeru u odnosu na smjer kretanja zrna i naziva se trzanjem cijevi [1].



Slika 9 prikazuje proces opaljenja lovačkog oružja.



3.2 Tribološke značajke procesa opaljenja

Na trošenje cijevi veliki utjecaj imaju izgorene barutne čestice, okolna atmosfera te sami utjecaj zrna. Prilikom kretanja zrna kroz cijev lovačkog oružja, na dodirnim površinama kanala cijevi i prstenova projektila- prednji dio zrna se stvara pritisak i sila trenja klizanja. To je posebno izraženo kod oružja s užljebljenom cijevi, gdje se košulja zrna utiskuje u profil žlijebova i polja kanala cijevi. Košulja zrna izrađena je od čistog elektrolitičkog bakra ili od mjedi. Prilikom kretanja projektila kroz cijev, čestice bakra ili mjedi se odvajaju od projektila i mikrozavaruju na čeličnu površinu kanala cijevi. Taj proces se naziva pobakrivanjem.

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Zbog topline koja se oslobađa prilikom izgaranja barutnog punenja dolazi do zagrijavanja cijevi. To uzrokuje promjene strukture materijala i njegovih mehaničkih svojstava. Naglo zagrijavanje pri opaljenju može dovesti do spontanog pougljičenja i zakaljenja površinskih slojeva kanala cijevi zbog prostrujavanja hladnog okolnog zraka kroz cijev. Zbog nejednolikog zagrijavanja po presjeku dolazi do stvaranja toplinskih naprezanja na površini kanala. Nakon većeg broja opaljenja ta naprezanja dovode do pojave površinskih mirkopukotina, a međusobne kemijske reakcije stvaraju vrlo agresivnu atmosferu za materijal cijevi [2].

4. ZAGRIJAVANJE PRI PROCESU OPALJENJA

Zagrijavanje cijevi pri samom procesu gađanja nije ravnomjerno ni po dužini cijevi tako ni po debljini stjenke cijevi. Kanal cijevi je temperaturno najopterećeniji, pa zbog takvog neravnotežnog opterećenja dolazi do pojave unutrašnjih naprezanja cijevi [4].

Nepoželjne posljedice pri zagrijavanju cijevi :prema [4]:

- smanjenje trajnosti cijevi,
- pogoršanje mehaničkih svojstva materijala i smanjenje otpornosti stjenke prema visokim pritiscima u cijevi,
- povećava se čeoni zazor- unutarnji promjer zadnjeg dijela cijevi, zbog povećane temperature stijenki, što nepovoljno utječe na funkciju oružja,
- otežano je ciljanje zbog povećanog titranja zagrijanog zraka u cijevi,
- savijanje cijevi zbog neravnomjernog zagrijavanja,
- mogućnost samoopaljenja metka ako se duže drži u ležištu.

5. EKSPERIMENTALNI DIO

U ovom radu analiziran je uzorak cijevi lovačkog oružja kalibra 8x57 mm, slika 10. Prva brojka označava promjer cijevi, a druga brojka dužinu zrna. Dužina cijevi iznosi 55 mm, a unutarnji promjer cijevi (kalibar) iznosi 8 mm.



Slika 10: Uzorak cijevi za ispitivanje

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Vizualnim pregledom uočeno je loše stanje cijevi koja više nije za upotrebu. Vidljivi su tragovi korozije po cijeloj površini cijevi. Cijev nije čuvana u primjerenim uvjetima (suha područja, područja bez agresivnih medija, sobna temperatura.) i nije prikladno održavana i vidljive su promjene prikazane na slici 11.



Slika 11: Prikaz mjesta uzimanja uzorka za analizu

Cijev je fotografirana i izrezan je reprezentativni uzorak koji se koristi u daljnim ispitivanjima (slika 11). Uzorak je izrezan iz početnog dijela cijevi. U tom dijelu se javljaju najveći tlakovi i naprezanja. Na početku opaljenja je najveće trošenje i prisutnost barutnih ostataka. Uzorak cijevi je zaliven u polimernu masu te brušen sa brusnim papirima SiC (s 5 različitih finoća papira od P320 do P40000). Za poliranje je korištena dijamantna pasta sa zrncima promjera 0,2 µm. Uzorak je nagrižen sa 3% NITAL-om u trajanju od 5 sekundi. Mikrostruktura je analizirana u Laboratoriju za materijalografiju na Fakultetu strojarstva i brodogradnje – Zagreb na svjetlosnom mikroskopu Olympus GX51, (sl.12).



izlučivanje cementita





Na slici 12 vidi se mikrostruktura popuštenog martenzita što odgovara podacima iz prethodno navedene literature [1]. Cijev za lovačko oružje izrađuje se od čelika za poboljšavanje. Na slici je vidljivo izlučivanje karbida popuštanja unutar martenzitne mikrostrukture i izlučivanje cementita po granicama zrna (slika 12). Do izlučivanja cementita je došlo zbog pojave visokih temperatura pri opaljenju zrna. Ovi procesi karakteristični su za nelegirane i niskolegirane čelike za poboljšavanje od kojih je najvjerojatnije izrađena ispitivana cijev.

5.1 Mjerenje tvrdoće uzorka u laboratoriju za toplinsku obradu

Tvrdoća je mjerena Vickersovom metodom u Laboratoriju za toplinsku obradu na uređaju **Wilson Volpert Tukon 2100 b** (Tablica 1). Opterećenje je 9,81 N.

Niz 1	Niz 2	
HVı	HV 1	
292	302	
308	302	
299	304	
304	299	
301	306	

Tablica 1. Rezultati mjerenja tvrdoće na navedenom uređaju

Proračunom srednje vrijednosti dobiva se da je tvrdoća 300 HV1 koja je nešto niža od uobičajenih vrijednosti tvrdoće visokotemperaturnog popuštenog martenzita kod čelika za poboljšavanje . Sniženje tvrdoće posljedica je ugrijavanja cijevi prilikom opaljenja zrna.

Tragovi trošenja na unutrašnjoj strani cijevi analizirani su skenirajućim elektronskim mikroskopom Tescan Vega 5136 mm u Laboratoriju za materijalografiju, FSB, Zagreb. Na slici 13 prikazana je analiza trošenja cijevi lovačkog oružja.





Slika 13: Analiza trošenja cijevi

Na SEM slici uzorka cijevi vidljiv je dominantan mehanizam trošenja - umor površine. U cijevima lovačkih puški prisutna su različita opterećenja kao što je zagrijavanje cijevi i barutne čestice. Takva opterećenja izrazito utječu na trošenje cijevi. Uz navedena opterećenja u cijevi puške došlo je do ovakvog ubrzanog trošenja cijevi. Također, ovdje nisu pravilno poštivana uputstva za održavanje cijevi (redovno čišćenje i podmazivanje) te je i zbog tih razloga došlo do znatnog ubrzanog trošenja cijevi.

6. ZAKLJUČAK

Najvažniji dio same lovačke puške je cijev. Zbog vrlo složenih mehaničkih, toplinskih i kemijskih procesa koji su vrlo intenzivni njezino stanje se mora vrlo pomno pratiti i primjereno održavati. Provedenim ispitivanjima na odabranom uzorku prikazano je da je materijal cijevi lovačke puške niskolegirani čelik za poboljšavanje u kaljenom i popuštenom stanju tvrdoće 300 HV1. Za bolju otpornost na sniženje tvrdoće i dulji vijek trajanja cijevi preporučuje se cijev izraditi od visokolegiranog čelika za poboljšavanje.





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KARAKTERIZACIJA ULTRAFILTRACIJSKIH KERAMIČKIH MEMBRANA S ORGANSKIM MARKERIMA PRI OBRADI OTPADNE VODE TEKSTILNE INDUSTRIJE

CHARACTERIZATION OF ULTRAFILTRATION CERAMIC MEMBRANES WITH ORGANIC MARKERS IN TEXTILE WASTEWATER TREATMENT INDUSTRY

Maja Zebić Avdičević^{1*}, Krešimir Košutić², Slaven Dobrović¹

¹ UniZg, Faculty of mechanical engineering and naval architecture, Ivana Lučića 5, Zagreb, Croatia ² UniZg, Faculty of chemical engineering and technology, Marulić square 19, Zagreb, Croatia

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Sažetak

Racionalno i održivo korištenje te upravljanje vodama globalni je izazov uzrokovan ograničenim prirodnim vodenim resursima, povećanom potrošnjom vode te sve strožim zakonskim propisima. Membranske tehnologije pripadaju skupini tehnologija prvog izbora pri obradi vode zbog svoje visoke separacijske učinkovitosti, nedestruktivnosti i ekološke održivosti. Rad membranskog sustava redovito je popraćen u većoj ili manjoj mjeri pojavom blokiranja pora membrana uslijed prisustva organskih, anorganskih i bioloških tvari u sustavu. Posljedice ovog fenomena su smanjenje protoka, promjene u separacijskoj učinkovitosti membrane (membranskog sustava), učestalo fizikalno-kemijsko čišćenje te time povećani troškovi rada i održavanja sustava. Aktivni sloj membrane definira fluks i stupanj separacije, a njegovu nominalnu graničnu molarnu masu moguće je odrediti stupnjem zadržavanja organskih tvari (otopina markera) koji je proporcionalan njihovoj molarnoj masi. U ovom radu prikazana je karakterizacija komercijalnih keramičkih membrana različitih veličina pora separacijom otopina polietilen glikola (PEG) i polietilen oksida (PEO) različitih molarnih masa. Karakterizirane membrane namijenjene su za obradu otpadnih voda tekstilne industrije. Rezultati separacije modelnih otopina i otpadne vode iz mercerizacije tekstila su pokazali da membrana s većim porama pokazuje veću sklonost blokiranju pora.

Ključne riječi: keramičke membrane, karakterizacija, stupanj zadržavanja, otpadna voda tekstilne industrije

Abstract

Rational and sustainable water use and management is a global challenge caused by limited natural water resources, increased water consumption and stringent legal regulations. Membrane technologies are the first-choice water treatment technologies due to their high separation efficiency, non-destructivity and ecological sustainability. The application of the membrane system is accompanied with membrane blockage because presence of organic, inorganic and biological substances. The consequences of this phenomenon are flux decline and change in separation efficiency of membrane (membrane system), frequent physical-chemical cleaning and thus increased operating and maintenance costs. Membrane active layer defines the flux and separation efficiency and its molecular weight cut-off can be determined by the retention efficiency of the marker solutions, which is proportional to their molecular weight. This paper presents the characterization of commercial ceramic membranes of different pore sizes by separating solutions of polyethylene glycol (PEG) and polyethylene oxide (PEO) of various molecular weight. Used membranes are intended for textile wastewater treatment. The results of the separation of the model solutions and mercerization wastewater showed that the membrane with larger pores shows a greater tendency to pore blockage.

Keywords: ceramic membranes, characterization, solute rejection, textile wastewater

1. INTRODUCTION

Membrane technologies are the first choice of water treatment technologies, and the application of membrane material with a defined pore size allows the separation of individual components in addition to obtaining the product of desired quality [1]. Permeate flux and selectivity of the membrane depend on the membrane pore size and the thickness of the active membrane layer [2]. Initial membrane selection is usually based on the molecular weight cut-off (MWCO) specified by the manufacturer and the purpose of membrane characterization is to predict membrane performance regarding flux and rejection of a solutes. The MWCO of the membrane can be determined based on observed rejection of markers, ie. dilute solutions containing the uncharged solutes and the retention rate proportional to their molar mass. The nominal MWCO value of the membrane [3-9]. Sieving curve is obtained from the plot of the efficiency of solute retention to the molar mass [6].

Textile wastewater is considered as one of the most polluted in all industrial sectors [10] and also, textile industry process generate a large quantities of wastewater [11]. Mercerization is first stage of textile treatment which includes the treatment of textile with highly caustic alkaline solution of sodium hydroxide which improves the textile fiber strength and dye process efficiency [12]. During textile mercerization process, alkaline wastewater is generated. Membrane technology can be used for fiber removal from generated wastewater, and permeate can be reused in new mercerization cycle in place of fresh water [13]. Polymeric membranes are the most commercially used [10], but ceramic membranes have higher thermal, chemical and mechanical stability compared to polymeric membranes [10, 14-19]. Since wastewater from mercerization process is extremely alkaline, ceramic membranes could be solution for its treatment and potential reuse in the process.

Membrane fouling is main phenomena affecting the economic and technological viability of ultrafiltration processes, which essentially depend on the permeate fluxes and their stability with time [20]. If the membrane pores are larger than the size of the solute molecules, these molecules can enter the membrane pores causing irreversible fouling. Contrary, if membrane pores are smaller than the size of the solute molecules present in the feed solution, these molecules accumulate over the membrane surface causing pore blocking and/or the formation of a gel layer [21]. Finally, solute molecules of a similar size to that of the membrane pores may result in a partial blocking of them [20].

Polyethylene glycol (PEG) solutions can be used for determination of pore size and results can be presented by log-normal distribution [2]. As it was previously reported [4, 7, 8] MWCO can be determined using PEG solutions for commercial and laboratory prepared membranes. Platt et al. [6] identified MWCO commercial membranes with PEG solutions and showed that the experimentally obtained separation values differed from those given by the manufacturer.

This paper provides a comparative study of the characterization of two tubular ceramic membranes of different pore size 2 kDa and 500 kDa MWCO using PEG and polyethylene oxide (PEO) solutions of different molecular weight. On the base of flux decline during the separation cycle of markers solutions, the fouling study was carried out. The performance of both tested membranes in experiments with textile wastewater was represented and the



effectiveness of filtration treatments was assessed by monitoring the permeate quality and the permeate flux decline.

2. MATERIALS AND METHODS

2.1. Membrane modules and membrane separation unit

During separation tests permeate fluxes (J_p) at specific transmembrane pressure (TMP) for PEG and PEO solutions, and mercerization wastewater were measured and these results were used to determinate MWCO of membranes and investigate the fouling mechanisms. Separation experiments were carried out on two commercially available ceramic membranes produced by Likuid Nanotek S.L., Spain. The membranes are multi-channel tubular type with dimensions of 200 mm in length, outer diameter of 25 mm, and channel diameter of 3.5 mm. Both membranes have 19 inside-out channels with a total membrane surface of 0.0418 m², placed in stainless steel housing. MWCO of ceramic membrane given by the manufacturer are 2 kDa and 500 kDa. Membranes are composed of an alumina oxide supporting layer, and zirconium oxide, alumina oxide and titanium oxide active layer for 500 kDa, and zirconium oxide for 2 kDa membrane. Pure permeate water flux (J_w) and TMP were experimentally tested at 20°C for each membrane using deionized water. Normalized pure water flux for 2 kDa membrane was 75.89 L m⁻² h⁻¹ bar ⁻¹ (R^2 =·0.9969) and for 500 kDa membrane was 432.39 L m⁻² h⁻¹ bar⁻¹ (R^2 =·0.9966). Both membranes are operated in a same filtration unit in crossflow separation mode described in detail elsewhere [22] along with the data collection procedures and TMP flux calculations. Membranes characteristics are represented in table 1.

Membrane	2 kDa	500 kDa		
Manufacturer	Likuid Nanotek			
Туре	Tubular mu	ılti-channel		
Active layer	ZrO ₂	Al ₂ O ₃ , ZrO ₂ , TiO ₂		
Support layer	Al	2 0 3		
Molecular weight cut off (MWCO)	2	500		
Number of channels	19			
Number of tubes/fibers	1			
External diameter (mm)	2	5		
Channel diameter (mm)	3	-5		
Length (mm)	200			
Thermal stability (°C)	<300			
Effective filtration area (m ²)	0.0418			
Pure water permeability* (L m ⁻² h ⁻¹ bar ⁻¹)	75.89 432.39			

2.2. Membrane characterization solutions

The membrane characterization was carried out with PEG and PEO solutions with various molecular weight (MW): 600, 950-1050, 2050, 4000, 6000 and 8000 g mol⁻¹ for 2 kDa membrane and 20000, 35000, 100000, 300000 and 600000 g mol⁻¹ for 500 kDa membrane

supplied by Sigma Aldrich. The solutions were prepared by dissolving of PEG and PEO of the appropriate MW in demineralized water to achieve concentration of 0.25 g L⁻¹.

2.3. Wastewater sample

The textile wastewater samples were supplied by textile industry from Zagreb (Unitas Co.), Croatia. The textile mercerization process includes immersion of textile in 25% sodium hydroxide solution and 1-2% of wetting agent; and then rinse with hot water and cold water of 80 °C and 18-20 °C respectively. The wastewater from washing after mercerization process was collected and used for membrane separation tests represented in this paper. To determine the process efficiency, permeate quality was defined by measuring pH, total suspended solids (TSS), turbidity and total organic carbon (TOC). The wastewater from mercerizing process contains approximately 1.4% of sodium hydroxide, pH value is 13.3, TSS is 100 mg L⁻¹, turbidity 14.6 NTU and the TOC 499.2 mg L⁻¹. For the purpose of this research, original mercerization wastewater was used without any changes or additions.

For chemical cleaning of the membranes the technical grade NaOH and NaOCI were used.

2.4. Analytical methods

Membrane characterization was done based to the measured TOC values for model solution and permeates. Concentration of PEG solutions was measured using a TOC analyzer (SHIMADZU TOC-VCPH) and expressed as non-purgeable organic carbon by NPOC method. TOC was also determinated for the wastewater samples and permeates. Temperature was determined using Pt-100 temperature transducers (MA TERM MWT 410) and laboratory Pt-100 sensor.

pH values were determinated using a pH-meter (Mettler Toledo), TSS values were determinated gravimetrically according the Standard Methods 2540 D and turbidity was measured using a HACH turbidimeter 2100 AN.

3. EXPERIMENTAL PROCEDURES

3.1. Membrane characterization

PEG solutions for membrane characterization were selected respect to MWCO according to the membrane manufacturer (2 kDa and 500 kDa). During ultrafiltration tests with PEG solutions, permeate flux and TMP evolution were measured in 120 min separation cycle. Initial flux for all experiments was 70-80 L m⁻² h⁻¹, the temperature was 20 °C ± 1 °C, and cross flow velocity was 2 m s⁻¹. The temperature of the solutions was adjusted with a spiral heat exchanger that was regulated with a thermostatic bath (Lambda) and controlled by Pt-100 sensors. Samples of the initial PEG solution and permeate were taken and TOC values were measured. Characterization of the membrane was done regarding to the observed separation efficiency (R, %) of PEG for a given molar mass which was calculated according to TOC values in the PEG input solution and in the permeate for specific PEG according to the Equation 1.

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$$R = \frac{C_f - C_p}{C_f}$$

Where C_p and C_f are solute concentrations in permeate and feed solutions respectively [23].

3.2. Flux decline experiments

During the 120 min for PEG solutions and 30 min for wastewater separation tests changes in flux and TMP values were observed. Normalized permeate flux for deionized water $(J_{DW,n})$ was determined before each experiment by measuring the pure water flux (J_{DW}) for adequate measured TMP value. Normalized demineralized water flux was calculated according to the Equation 2.

$$J_{DW,n} = \frac{J_{DW}}{TMP}$$
(2)

After each filtration test, membranes were flushing with deionized water on a pressure side in order to assess the degree of irreversible fouling and/or to achieve a satisfactory level normalized flux recovery [24]. The process of flushing with deionized water was not sufficient to reach a satisfactory level of normalized flux recovery. To achieve nearly a complete flux recovery, a thorough chemical cleaning was conducted using cleaning in place (CIP) procedure with sodium hydroxide and sodium hypochlorite as previously reported [22]. After chemical cleaning the normalised flux value for demineralised water was determinated and compared to initial value.

4. RESULTS AND DISCUSSION

4.1. Membrane characterizations

Characterization of the 2 kDa and 500 kDa ceramic membranes was performed with PEG solutions of different molar mass according to the MWCO declared by manufacturer. The results of the membrane separation efficiency are given graphically in Fig. 1. as a cumulative log-normal distribution function.







Based on the obtained results observed rejection efficiency higher than 90% was not achieved after separation of tested PEG solutions. The separation efficiency was up to 78% for 6000 g mol⁻¹ PEG solution for 2 kDa membrane and up to 68% for 60000 g mol⁻¹ for 500 kDa membrane. The deviation from the declared value of the manufacturer can be explained by the structure of the non-spherical PEG molecule; it is elongated and can be "tapped" through the membrane pores. In addition, in the characteristics of the ceramic membrane obtained by the manufacturer, substance to which separation efficiency was expressed was not provided. This is in accordance with data find in the literature [3] which described similar studies involved with characterization of membranes with PEG solutions, which showed the differences between declared values of MWCO by manufacturers and those obtained by experiment, depending on the operational conditions.

4.2. Flux decline study

Example of separation tests is represented in Fig. 2. It gives the flux, normalized flux and TMP evaluation during the ultrafiltration cycle of 2 kDa ceramic membrane with 8000 g mol⁻¹ polyethylene glycol (PEG) solution, T=20 °C, CFV 2 m s⁻¹.







Fig. 2: Normalized permeate flux (J_{Pn}), permeate flux (J_P), and transmembrane pressure (TMP) evaluation of 2 kDa ceramic membrane (PEG :8000 g mol⁻¹ , *T*=20 °C, CFV= 2 m s⁻¹)

Evaluation of membrane normalized flux, J_{Pn} measured with PEG solutions 600 - 600000 g mol⁻¹ is represented in Fig. 3 and Fig. 4 respectively.





Fig. 3: Normalised flux evaluation of 2 kDa ceramic membrane (PEG solutions: 600 - 8000 g mol⁻¹, *T*=20 °C, CFV=2 m s⁻¹

According to the results, it is obvious that the decrease of the normalized flux is sensitive to the molar mass of the PEG molecule. The difference from flux decline for all tested solutions is 10-17% of initial value. The Fig. 3 shows that the normalized flux decline is lowest for the lowest PEG molar mass solution (10%) and the most intensive for the PEG solution for highest molar mass (17%). PEG molecules smaller than membrane pore size do not pass through the membrane, they are retained within the pores and membrane fouling occurs which results in the flux decline and TMP increase.

Tab. 2: Evolution of the normalized permeate flux of 2 kDa membrane after forward flushing and CIP
(PEG solutions: 600-8000 g mol ⁻¹ , <i>T</i> =20°C)

MW _{PEG} [g mol ⁻¹]	600	1000	2000	4000	6000	8000
J _{DW} (initial) [L m ⁻² h ⁻¹ bar ⁻¹]	76	78	78	78	77	78
J _{DW} (after separation) [L m ⁻² h ⁻¹ bar ⁻¹]	72	72	67	71	72	70
Flux recovery, [%]	95	92	86	91	94	90
J _{DW} (after chemical cleaning) [L m ⁻² h ⁻¹ bar ⁻¹]	78	78	78	77	78	78
Flux recovery, [%]	>100	100	100	99	>100	100

Table 2 represents the values of the normalized flux for demineralised water obtained prior to the PEG solution and after each experiment. Based on the results, after tests with PEGs solutions flux recovery higher than 86% was achieved by flushing with demineralised water. Complete flux recovery wasn't obtained because the fouling phenomena occurred; PEG molecules which were retained by the membrane surface caused fouling intermediate and

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standard pore blockage. After chemical cleaning normalized flux recovery was more than 99% for all tested solutions.



Fig. 4: Normalised flux evaluation of 500 kDa membrane (PEG solutions: 20000 - 60000 g mol⁻¹, *T*=20 °C, CFV= 2 m s⁻¹)

In case of 500 kDa membrane, flux decline was more intense for all tested solutions; it was 15-39% lower than the initial flux, depending on MW of the solute. Regardless that size of the membrane pore is higher than PEG molecule, PEG molecules are retained on the membrane surface and in the membrane pores causing decline of flux and increase of TMP. Therefore, the difference between flux decline for solution lower and higher molar mass than the membrane MWCO can be clearly seen from the results. For PEGs with molar mass higher than 35000 g mol⁻¹, flux decline is more intensive because the more intensive fouling phenomena on the membrane surface occurred.

Tab. 3: Evolution of the normalized permeate flux of 500 kDa membrane after forward flush and CIP	using
the PEG and PEO solutions 20000-600000 g mol ⁻¹ ($T=20^{\circ}$ C)	

Mw(PEG/PEO) [g mol ⁻¹]	2000	35000	100000	300000	600000
J _{DW} (initial) [L m ⁻² h ⁻¹ bar ⁻¹]	264	264	260	264	254
J _{DW} (after separation) [L m ⁻² h ⁻¹ bar ⁻¹]	200	226	154	121	126
Flux recovery, [%]	76	85	59	45	50
J _{DW} (after chemical cleaning) [L m ⁻² h ⁻¹ bar ⁻¹]	264	260	264	254	264
Flux recovery, [%]	98	>100	>100	96	>100



Table 3 represents the values of the normalized flux for demineralised water obtained prior to the PEG solution and after each experiment. Satisfactory flux recovery wasn't achieved by flushing with demineralised water because the fouling phenomena occurred; PEG molecules were retained on membrane surface caused pore blockage and probably gel layer formation on the membrane surface. After chemical cleaning normalized flux recovery was more than 96% for all tested solutions.

Both ceramic membrane show the tendency for fouling phenomena even for separation of solutions with smaller PEG molar mass values than their declared MWCO. It can be assumed that blockage inside the pores occurs first, then the formation of molecules on the surface and the formation of cake. Lower membrane fouling phenomena for 2 kDa membrane was probably the result of favourable relationship between CFV, pore size and rejected matter. In case of the 500 kDa MWCO, probably the intermediate pore blocking occurs but does not rule out the possibility of other blocking types. These results are in concordance with other researchers [10] who also observed a higher decrease of permeate flux for the membrane of higher MWCO when applying ultrafiltration.

4.2. Textile wastewater study

Experiments with the ceramic membranes were conducted with the raw mercerization wastewater at a CFV of 2 m s⁻¹ and T=20 °C. Forward flush and CIP were conducted to achieve a minimal flux recovery of 90%. Fig. 5. shows the normalized permeate flux decrease after 30 min separation which is 2% for 2 kDa membrane and 18% for 500 kDa membrane. Membrane with higher pore size (500 kDa) showed higher tendency for fouling phenomena, which is in accordance with previously investigated fouling effect using PEG and PEO solutions represented in previous chapter.







Fig. 5: Normalised flux evaluation of 2 kDa and 500 kDa membrane for mercerization

wastewater, (*T*=20 °C, CFV= 2 m s⁻¹)

Table 4 represents the flux recovery data after forward flush and CIP cleaning procedures after mercerization separation tests. Forward flush was not efficient to fully recover the demineralized flux and it was 80% for 2 kDa membrane and 87% for 500 kDa membrane. After CIP, complete flux recovery was achieved.

Tab. 4: Evolution of the normalized permeate flux of 2 kDa and 500 kDa membrane after forward flush

Membrane	2 kDa	500 kDa
J _{DW} (initial) [L m ⁻² h ⁻¹ bar ⁻¹]	76	347
J _{DW} (after separation) [L m ⁻² h ⁻¹ bar ⁻¹]	61	300
Flux recovery, [%]	80	87
J _{DW} (after chemical cleaning) [L m ⁻² h ⁻¹ bar ⁻¹]	75	329
Flux recovery, [%]	99	95

and CIP using the mercerization wastewater (T=20°C)

The effects of using the tested membranes in the ultrafiltration process are determined by the rejection rates of the evaluated parameters represented in table 5. As it was expected, the greatest reduction in TSS, TOC and turbidity removal was achieved for 2 kDa membrane. According to expectations, the pH values for both tested membrane permeates were approximately the same because the membrane pores are too large to maintain the dissolved sodium hydroxide that affect most these pH values.

Tab. 5: Characteristics of permeate samples and rejection rates of total suspended solids (TSS), turbidity

Marahrana	2 kDa		500 kDa	
Membrane		R,%		R,%
рН	13.04	-	13.13	-
TSS [mg L⁻¹]	26	74.0	48	52.0
Turbidity [NTU]	0.27	98.2	2.57	82.4
TOC [mg L ⁻¹]	243.5	51.2	398.47	20.2

Although the separation efficiency of organic compounds and solids that contribute to the turbidity was higher in case of 2 kDa membrane, it showed much less fouling intensity than the 500 kDa membrane which is probably the result of intensive fouling effect inside of the membrane material.

Both membrane showed similar behaviour according to the flux decline study for all tested inlet waters; PEG and PEO solutions and real wastewater. Study of fouling phenomena using marker solutions can give a good insight for overview of membrane fouling behaviour, and could be comparable to real wastewater treatment study.



5. CONCLUSION

The experimentally determined MWCO values of the tested 2 and 500 kDa ceramic membranes differ from those given by the manufacturer. Deviation from the declared value of the manufacturer can be explained by the structure of the non-spherical PEG molecule, which caused the fouling inside the membrane structure. In addition, in the characteristics of the membranes obtained by the manufacturer, no mention is made of the substance, which refers to the separation efficiency.

In case of 2 kDa membrane after flushing with demineralized water, the flux regeneration decreases with the increase in the molar mass of the PEG molecule. Therefore, after chemical cleaning the regeneration for all test solutions is higher than 99%. For 500 kDa membrane, regeneration of the flux is higher for the PEG solution with a lower molar mass and after chemical cleaning the regeneration rate for all test solutions is higher than 96%. During the experiments with PEG solutions of lower molar mass a significant decrease in normalized flux occurs which is the result of intermediate and/or standard pore blockage due to accumulation molecule within the pores and on the membrane surface.

For wastewater separation test, lower membrane fouling level was noticed for the membrane with lower pore size, but the complete flux recovery could be accomplished only by application of intensive chemical cleaning.

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APPLICATION OF FRATTINI TEST AND SATURATED LIME TEST TO ASSESS POZZOLANIC ACTIVITY OF DIFFERENT ALUMINOSILICATE MATERIALS

Damir Barbir, Pero Dabić, Ljubica Tunjić

University of Split, Faculty of Chemistry and Technology, Department of Inorganic Technology, Ruđera Boškovića 35, 21000 Split, Croatia

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Abstract

In this study the pozzolanic activity of aluminosilicate materials (waste container glass, natural zeolite and waste building brick) with particles size <125 μ m was tested using Frattini test and saturated lime test. For Frattini test three samples were prepared with Portland cement/pozzolan ratio 80:20. Samples were thermostated for 8 days at 40 °C. For saturated lime test 12 samples were prepared. The samples contained 1g of puccolan and 75 mL of saturated lime solution (2g Ca(OH)₂ in 1L of demineralised water). Samples were thermostated for 1, 3, 7 and 28 days at 40 °C. After each period of hydration, samples were filtered through Büchner's funnel using a vacuum pump and liquid phase was separated from the solid phase. Total alkalinity and CaO concentration in aqueous solutions were determined by titration with HCl and EDTA. The results showed that waste container glass, natural zeolite and waste brick of particles size <125 μ m are pozzolanic active materials and they can be use as supplementary cementitious materials. The results did not confirm the correlation between the Frattini test and saturated lime test.

Keywords: portland cement, lime, waste container glass, waste construction brick, natural zeolite, pozzolanic activity, aluminosilicate materials

1. INTRODUCTION

The pozzolanic materials consist of reactive silicon dioxide, SiO_2 and aluminum (III) oxide, Al_2O_3 . The pozzolans do not have binding properties, but in fine-grained form and the presence of water they react with lime or cement and form new compounds having binding properties [1,2]. They were named after the city of Pozzuoli near Naples, where the pozzolanic activity of the material was observed. These are the first cementitious materials that have been used since the time of the first civilizations for the construction of most important historical buildings.

The main reasons for the use of pozzolan materials in cement and concrete are: reducing the amount of cement in cement composites, resulting in reduced costs [3], reduced heat of hydration [4], improved workability of cement composites, achieving the desired strength after 28 days of hydration and improving the resistance to sulphate attack [5-8].

The pozzolanic materials are divided into three groups:

- natural pozzolans (eg. volcanic ash),
- artificial pozzolans (eg. fly ashes from thermal power plants) and
- activated pozzolans (eg. activated clays).

The natural pozzolans are: the Naples pozzolans, the volcanic tuffs, the Santorini earth, the diatomaceous earth, the trans, the opal, the grit and the crystalline zeolites.

Artificial pozzolans are byproducts of some industries. The most famous artificial pozzolans used as cement additives are: precipitated SiO_2 , silica fume and fly ash from coal-fired thermal power plants.

Activated pozzolans are obtained by targeted production, sintering of natural materials that do not normally have pozzolanic properties but are obtained after thermal treatment. In this type of pozzolans there are activated clays and shale clays [9].

Although pozzolanic materials have some properties similar to cement, they are not of sufficient quality to be used as a binder alone, but are added to cement and improve the cement composite properties (durability, strength, resistance). Due to the pozzolanic reaction, new C-S-H phases fill up the remaining space in the cement composition, thus altering the structure of the pores of the composite system. The proportion of tiny pores increases, resulting in a reduction in the permeability of the concrete. C-S-H phases increase the durability of the cement composite.

Reactive SiO_2 is responsible for the pozzolanic reaction, which may be free or contained in aluminosilicate. The higher the SiO_2 content, the pozzolanic activity of the material is higher.

In the literature, there is a whole range of methods by which pozzolanic activity is determined. All of these methods can be divided into direct and indirect methods. Direct methods follow the content of calcium hydroxide and its depletion by the pozzolanic reaction using analytical methods such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) or classical chemical titration.

The Frattini test is the most commonly used direct method which involves the determination of concentrations Ca²⁺ and OH⁻ ions in a solution containing ordinary Portland cement and tested pozzolan using classical chemical titration. This test has been used to determine the pozzolanic activity of metacaolinite [10], ground brick [11] and fly ash [12].



The saturated lime test is a simplified version of the Frattini test in which pozzolan is mixed with a solution of saturated lime instead of ordinary Portland cement and water. The amount of lime that binds to the pozzolan is determined by measuring the amount of residual dissolved calcium. The literature shows the results of the saturated lime method for waste paper from the paper industry [13], sugar cane waste [14] and waste from the industry of iron alloys [15].

Indirect methods measure the physical properties of a sample that demonstrate the degree of pozzolanic activity. Most of this method measures pressure strength, specific conductivity, or the amount of heat released during time of reaction. The results of indirect methods should be confirmed using direct methods [16].

In this paper, the investigation of pozzolanic activity of aluminosilicate materials - waste container glass, waste building brick and natural zeolite was carried out using direct methods of determination of pozzolan activity: Frattini test and saturated lime test.

2. EXPERIMENTAL

2.1. Materials

In this paper, Portland cement CEM I 42.5 R was used. This was commercial product of CEMEX Croatia cement plant. Mark CEM I signifies ordinary Portland cement with a 95-100% clinker content. This cement is certified according to the requirements of HRN EN 197-1: 2012 and HR 197-2: 2014. Table 1 shows the chemical composition and physico-mechanical properties of Portland cement used. The cement was dried for 2 hours at 105 °C to constant mass.

Composition	Content, wt. %	Physico-mechanical properties and measurement size	Value
SiO₂	22.85	Specific surface according to Blaine, cm ² g ⁻¹	
Al ₂ O ₃	4.81	Standard consistency, mas. %	26
Fe₂O ₃	2.79	Setting time - start, min	
CaO	65.23	Setting time - end, min	
MgO	1.61	Average flexural strength, MPa	
SO ₃	3.00	- after 3 days	
K₂O	1.89	- after 28 days	8.44
Ті	0.37	Average compressive strength, MPa	
Mn ₂ O ₃	0.12	- after 3 days	
Cr ₂ O ₃	0.04	- after 28 days	50.70
Loss of ign.	0.04		

Tab. 1: Chemical	composition ar	nd physico	-mechanical r	properties o	of Portland	cement CEM I	42.5 R [17]

As pozzolanic materials waste glass, waste brick and natural zeolites were used. Natural zeolites were dried at 60 °C to constant mass for 2 hours, and the brick and glass were dried for 2 hours at 105 °C. Glass, brick and zeolite were sieved through a laboratory sieve with a



pore size <125 μ m. The chemical composition of waste container glass, waste brick and natural zeolite is shown in Table 2.

Composition, wt. %	Container glass	Building brick	Natural zeolite
SiO₂	72.75	63.42	64.93
Al ₂ O ₃	2.54	15.36	13.39
MgO	1.18	2.99	1.08
K ₂ O	1.15	3.03	1.30
CaO	15.60	6.60	2.00
Fe₂O ₃	-	6.18	2.07

Tab. 2: Chemical composition of waste container glass, waste building brick and natural zeolite

2.2. Preparation of samples for the determination of pozzolanic activity

2.2.1 Frattini test

For the Frattini test, 3 samples of a constant mass 20 g were prepared. The ratio of cement and pozzolan (glass, brick and zeolite) in the sample was 80:20. The cement and pozzolan mixture was transferred to a plastic bottle. Thereafter, 100 mL of boiled demineralised water was added to each sample and cooled to 40 °C. Samples were thermostated for 8 days at 40 °C. After 8 days, the samples were cooled to room temperature. The solutions were filtered through a vacuum pump through a Büchner funnel where a liquid phase was separated from the solid. For each sample in the filtrate, the concentration of hydroxide ions (total alkalinity) and the concentration of calcium oxide were determined by titration.

2.2.2 Saturated lime test

Prepared samples for pozzolanic activity testing by saturated lime test contained 1 g of pozzolan and 75 mL of saturated calcium hydroxide solution. 12 samples were prepared, 4 samples of each pozzolan (waste glass, waste building brick and natural zeolite) for monitoring the pozzolanic activity of the samples for 28 days. The saturated lime solution was prepared by dissolving 2 g of hydrated lime (98% purity) in 1 L of demineralised water. Samples were thermostated for 1, 3, 7 and 28 days at 40 °C. After each period, the samples were filtered and total alkalinity and concentration of calcium oxide determined.

2.3. Determination of pozzolanic activity

Pozzolanic activity is based on the determination of the total alkalinity and concentration of calcium ions present in the aqueous solution after contact with pozzolan or with a mixture of pozzolan and cement.

The total alkalinity shown as [OH⁻] ion concentration is determined by the acidometric titration.

To 50 mL of filtrate, five drops of the methylorange indicator were added and titrated with 0.1 mol/L hydrochloric acid. The equivalence point corresponded to the change of color from yellow to orange.

The total alkalinity expressed as the concentration of hydroxide ions is calculated according to the equation 1:

$$[OH^{-}] = \frac{1000 \cdot 0.1 \cdot V1 \cdot f1}{50} = 2 \cdot V1 \cdot f1$$
(1)

where is:

 $[OH^{-}]$ – concentration of hydroxide ions, mmol/L V1 – volume of HCl solution (c = 0.1 mol/L) for titration, mL f1 – factor of the HCl solution (c = 0.1 mol/L).

After determination of total alkalinity or concentration of [OH⁻] ion in the solution, a few drops of 30% sodium hydroxide solution and a murexide indicators were added to the solution. The sample was titrated with EDTA concentration of 0.025 mol/L to change the purple color in violet. For a visible change of color, the pH value must be above 12 and during titration is maintained by addition of sodium hydroxide.

The calcium oxide concentration is calculated according to the equation 2:

$$[CaO] = \frac{1000 \cdot 0.025 \cdot V2 \cdot f2}{50} = 0.5 \cdot V2 \cdot f2$$
(2)
$$36$$

where is:

[CaO] – concentration of calcium oxide, mmol/L

V2 – volume of EDTA (c = 0.025 mol/L) for titration, mL

 $f_2 - factor of the EDTA solution (c = 0.025 mol/L).$

The amount of calcium oxide removed is calculated according to the equation 3:

where is:

[CaO] – concentration of calcium oxide calculated according to the equation 1,

mmol/L

[CaO]_{max} – maximum concentration of calcium oxide in the sample, mmol/L

According to the saturated lime test, the maximum concentration of calcium oxide in the sample is calculated at the equation 4:


$[CaO]_{max} = \frac{n}{V}$ (4)

where is:

n – mole of Ca(OH)₂, mmol

V – volume of saturated lime solution, L.

According to the Frattini test, the maximum CaO concentration is calculated at the equation 5:

$$[CaO]_{max} = \frac{350}{[OH] - 15}$$

(5)

3. RESULTS AND DISCUSSION

During the determination of pozzolanic activity of different materials, it is very important which method is used. It is common to use more than one method for the determination of pozzolanic activity, but at least one must be qualitative and must show the consumption of calcium hydroxide over time. By comparing the different methods, the main factors in the estimation of activity are the temperature and time of sampling.

3.1 The Frattini test results

Table 3 shows the consumption of HCl and EDTA during titration and the concentration of hydroxide ions and calcium oxide calculated according to equations 1 and 2.

Pozzolan	HCl, mL	[OH ⁻], mmol/L	EDTA, mL	[CaO], mmol/L
Glass	32.10	64.20	8.50	4.25
Brick	22.50	45.00	8.20	4.10
Natural zeolite	23.20	46.40	9.60	4.80

Tab 3: Consuption of HCl and EDTA during titration and the concentration of hydroxide ions and calcium oxide after 8 days

Table 4 shows theoretical maximum calcium oxide concentration calculated according to equation 5 and percentage of calcium oxide removed after 8 days calculated according to equation 3.



Pozzolan	[CaO] _{max} , mmol/L	CaO removed, %
Glass	7.11	40.23
Brick	11.67	64.87
Natural zeolite	11.15	56.94

Tab. 4: Maximum calcium oxide concentration and content of calcium oxide removed after 8 days

Table 3 and 4 show that the highest measured concentration of calcium oxide in binary mixtures of natural zeolite and cement, which means that the least calcium hydroxide was reacted with silicon dioxide from natural zeolite. The lowest measured CaO concentration in binary mixtures of brick and cement, ie the most Ca(OH)₂ was reacted with SiO₂ from brick. The experimental points in Figure 1 are below the Ca(OH)₂ solubility curve, which means in the active pozzolan area. The lowest point below the solubility curve corresponds to the brick sample, and the highest point corresponds to the zeolite.



Fig. 1: Ca(OH)₂ solubility curve and dependence of total alkalinity on calcium oxide concentration for glass (Sample 1), brick (Sample 2) and natural zeolite (Sample 3) samples

The Frattini test showed that all the materials used in the test were active pozzolans, brick was the most active pozzolan, and the natural zeolite was the least active pozzolan.



3.2. The saturated lime results

Table 5 shows concentrations of hydroxide ions and calcium oxide for samples of waste container glass, waste building brick and natural zeolite. It can be seen that the concentration of CaO and total alkalinity drops for 28 days for each sample, meaning that the resulting $Ca(OH)_2$ is reacted with SiO₂ from pozzolan. It is apparent that CaO concentrations decrease over time, and the fastest decline was observed over the first 7 days, meaning that the most $Ca(OH)_2$ reacted in that initial period.

Tab. 5: Concentration of hydroxide ions and calcium oxide of waste container glass, waste building brick
and natural zeolite

	Pozzolan						
Time, days	Glass		Brick		Natural zeolite		
	[OH ⁻],	[CaO] ,	[OH ⁻],	[CaO] ,	[OH ⁻],	[CaO] ,	
	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	
1	35.00	23.60	30.00	18.10	25.40	16.25	
3	29.80	19.70	19.60	13.10	15.00	8.45	
7	27.20	17.20	12.60	8.00	11.00	5.30	
28	17.40	9.45	8.00	4.40	4.00	0.95	

Figure 2 shows the amount of calcium oxide removed depending on time. It can be noticed that the most CaO was removed from the sample of natural zeolite and lime, and at least from the sample of glass and lime.



Fig. 2: Amount of calcium oxide removed depending on the time



The saturated lime test showed that glass, brick and natural zeolite were pozzolan active materials. The most active pozzolan according to this test is natural zeolite, and the least active waste glass.

The Frattini test and saturated lime test have shown that glass, brick and zeolite are pozzolan active materials, but there is no correlation between these two tests. According to Frattini test the most active pozzolan is the brick and the least active natural zeolite while the saturated lime test shows that natural zeolite was most active, and the least active was glass.

The most important factor compared to the tests is the lime:pozzolan ratio. It is very difficult to accurately determine the amount of calcium hydroxide produced by the hydration of Portland cement, although it is a rule that about 25% Ca(OH)₂ is produced from the total mass of cement after complete hydration. Furthermore, at the Frattini test, every 4 grams of pozzolan comes with 16 grams of cement, and the lime:pozzolan ratio is 1. For saturated lime test, 1 g of pozzolan is mixed with 75 mL of saturated lime solution containing 0.15 g of Ca(OH)₂ and gives a much lower lime:pozzolan ratio of 0.15. Precisely because of the low lime:pozzolan ratio, saturated lime test tends to show positive pozzolanic activity compared to Frattini test.

The biggest difference between the tests was for natural zeolite samples, where the saturated lime test showed very positive pozzolanic activity while the Frattini test showed the lowest pozzolanic activity. Saturated lime test has shown that natural zeolite has the ability to bind large amounts of lime in a short time, but the mechanism itself is constrained by its capacity. The results of the Frattini test have shown that during the hydration of the cement in the saturated lime solution the same mechanism does not occur. The same conclusions came from scientists Donatello et al. [16].

4. CONCLUSION

Based on the results presented it can be concluded that:

- According to the Frattini test and the saturated lime test, waste glass, waste brick and natural zeolite are pozzolan active materials if their particle size is <125 μm.
- There is no correlation between the Frattini test and the saturated lime test. The Frattini test shows that waste brick is the most active pozzolan, and the least active pozzolan is natural zeolite, while the saturated lime test shows that natural zeolite is the most active pozzolan and the least active is waste glass.
- Waste container glass, waste brick and natural zeolite with particle size <125 µm can be used as additives for Portland cement because they are active pozzolan and during hydration create new hydraulic properties.

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PREGLED POSTOJEĆIH PRISTUPA I METODA ZA PROCJENU CIKLIČKIH I ZAMORNIH PARAMETARA MATERIJALA

OVERVIEW OF EXISTING APPROACHES AND METHODS FOR ESTIMATION OF CYCLIC AND FATIGUE PARAMETERS OF MATERIALS

Robert Basan¹, Tea Marohnić¹, Sunčana Smokvina Hanza¹

University of Rijeka, Faculty of Engineering, Vukovarska 58, 51000 Rijeka, Croatia

<u>Review paper / pregledni rad</u>

Sažetak

Pravilan odabir materijala jedna je od najvažnijih odluka koje treba donijeti tijekom razvoja proizvoda. Za pravilno modeliranje i simulaciju odziva opterećenih struktura i komponenti potrebno je poznavati ponašanje materijala i odgovarajuće parametre koji ga definiraju. Eksperimentalno određivanje njihovih vrijednosti je najpreciznije, ali se zbog dugotrajnosti i visokih troškova ne može izvesti u ranoj fazi razvoja proizvoda. U literaturi su predloženi različiti pristupi i metode za procjenu cikličkog i zamornog ponašanja i pripadnih parametara materijala na osnovi njihovih monotonih značajki. U radu se daje kratak pregled metoda temeljenih na empirijskom pristupu i onih temeljenih na strojnom učenju te se ukazuje na neke od njihovih glavnih značajki, prednosti i nedostataka.

Ključne riječi: ponašanje materijala, cikličko opterećenje, zamor, parametri, metode procjene, umjetne neuronske mreže

Abstract

Proper selection of the material is one of the most important design decisions, which must be made during the product development. Material behaviour and corresponding parameters that define it must be known in order to enable proper modelling and simulation of loaded structures and components' response. The experiment-based determination of material behaviour and parameters is certainly the most accurate but, due to the long duration and high expenses, it cannot be performed in early phase of product development. Various methods for estimation of cyclic and fatigue behaviour and parameters of the material utilising simple, monotonic properties, have been developed and proposed in the literature. This paper provides a brief overview of empirically-based and machine learning-based methods, and points out some of their main features, advantages and drawbacks.

Keywords: material behaviour, cyclic loading, fatigue, parameters, estimation methods, artificial neural networks

1. Uvod

U suvremenom razvoju proizvoda, već se u tzv. konceptualnoj fazi, definira približno 80 % ukupnih troškova razvoja, proizvodnje, eksploatacije te zbrinjavanja proizvoda na kraju njegovog životnog ciklusa. U skladu s tim, sve se više složenih razvojnih aktivnosti poput računalnog modeliranja i simuliranja ponašanja proizvoda, određivanja opteretivosti i trajnosti proizvoda te odabira materijala nastoji izvoditi u ranoj fazi razvoja, dok su izmjene lako izvedive i jeftine. Jedan od ključnih alata u tim aktivnostima i podrška donošenju ispravnih odluka je računalno modeliranje ponašanja materijala za koje je potrebno poznavati značajke i parametre materijala kojima se definira njihovo ponašanje u stvarnim uvjetima (različite temperature, vrste i brzine opterećenja, itd.).

Eksperimentalno određivanje vrijednosti parametara je najpreciznije, ali se zbog dugotrajnosti i visokih troškova ne može izvoditi za veći broj materijala kandidata, posebice ne u spomenutoj ranoj fazi razvoja proizvoda kad su promjene još česte. U cilju prevladavanja navedenih poteškoća, još se od sredine 1960-tih godina razvijaju i u literaturi predlažu različiti pristupi i metode za procjenu cikličkog i zamornog ponašanja i pripadnih parametara materijala na osnovi njihovih monotonih značajki poput tvrdoće, granice razvlačenja $R_{\rm e}$, vlačne čvrstoće $R_{\rm m}$, stvarnog naprezanja pri lomu $\sigma_{\rm f}$, stvarnog istezanja pri lomu $\varepsilon_{\rm f}$, koeficijenta deformacijskog očvršćivanja K, eksponenta deformacijskog očvršćivanja n itd. [1,2,3,4,5,6,7].

Metode procjene kao praktično, brzo i dovoljno točno rješenje ubrzano dobivaju na važnosti sa sve većom primjenom simulacija i analiza opteretivosti i vijeka trajanja temeljenih na deformaciji, koje su već uobičajene u automobilskoj, zrakoplovnoj i energetskoj industriji za procjenu trajnosti visokoopterećenih metalnih dijelova i konstrukcija [8]. U nastavku je dan kratak pregled metoda procjene cikličkih odnosno zamornih parametara temeljenih na empirijskom pristupu i onih temeljenih na strojnom učenju, ponajprije umjetnim neuronskim mrežama, te se ukazuje na neke od njihovih glavnih značajki, prednosti i nedostataka.

2. Cikličko i zamorno ponašanje te pripadni materijalni parametri

Problematika i metodologija procjenjivanja cikličkih i zamornih parametara materijala na osnovi njegovih monotonih značajki ponajprije se odnosi na pristup karakterizaciji cikličkog odziva i zamaranja materijala temeljenom na deformaciji (engl. strain-based approach). U tom pristupu povezuje se broj izmjena opterećenja do otkazivanja $2N_{\rm f}$ s amplitudom ukupne deformacije $\Delta \varepsilon/2$ koju čine dvije komponente: amplituda elastične deformacije $\Delta \varepsilon_{\rm e}/2$ i amplituda plastične deformacije $\Delta \varepsilon_{\rm p}/2$ (slika 1). Ovim pristupom moguća je detaljna analiza zamora i u područjima gdje naprezanja prelaze cikličku granicu razvlačenja $R_{\rm e}'$ materijala te je on prikladniji za procjenu trajnosti u slučaju niskocikličkog zamora kad u ukupnoj deformaciji prevladavaju plastične deformacije. Pristupom temeljenim na deformaciji uspješno se karakterizira i visokociklički zamor pa se on primjenjuje za karakterizaciju zamaranja većine metalnih materijala [9,10].

Cikličke krivulje naprezanje–deformacija većine metalnih materijala dovoljno se dobro mogu opisati cikličkim Ramberg–Osgoodovim izrazom:

$$\frac{\Delta\varepsilon}{2} = \frac{\Delta\varepsilon_{\rm e}}{2} + \frac{\Delta\varepsilon_{\rm p}}{2} = \frac{\Delta\sigma}{2E} + \left(\frac{\Delta\sigma}{2K'}\right)^{\frac{1}{n'}}$$

(1)



gdje su $\Delta \varepsilon/2$, $\Delta \varepsilon_e/2$ i $\Delta \varepsilon_p/2$ vrijednosti amplituda ukupne, elastične i plastične deformacije, $\Delta \sigma/2$ amplituda naprezanja, *E* Youngov modul, *K*' koeficijent cikličkog deformacijskog očvršćivanja, a *n*' eksponent cikličkog deformacijskog očvršćivanja.

Za procjenu broja izmjena opterećenja do otkazivanja $2N_f$, za veliku većinu metalnih materijala, uspješno se primjenjuje integralni pristup opisan Basquin–Coffin–Mansonovim (BCM) izrazom, koji povezuje amplitudu ukupne deformacije $\Delta \varepsilon/2$ s brojem izmjena opterećenja do otkazivanja $2N_f$:

$$\frac{\Delta\varepsilon}{2} = \frac{\Delta\varepsilon_{\rm e}}{2} + \frac{\Delta\varepsilon_{\rm p}}{2} = \frac{\sigma_{\rm f}'}{E} (2N_{\rm f})^b + \varepsilon_{\rm f}' (2N_{\rm f})^c \,. \tag{2}$$

gdje su $\sigma_{\rm f}$ ' koeficijent dinamičke čvrstoće, *b* eksponent dinamičke čvrstoće, $\varepsilon_{\rm f}$ ' koeficijent cikličkih deformacija, a *c* eksponent cikličkih deformacija. Parametri $\sigma_{\rm f}$ ', *b*, $\varepsilon_{\rm f}$ ' i *c* još se nazivaju i zamornim parametrima i u potpunosti određuju međusobnu ovisnost ukupne amplitude deformacije $\Delta \varepsilon/2$ i broja izmjena opterećenja do otkazivanja 2*N*_f (Slika 1).



Broj izmjena opterećenja do inicijacije pukotine, $2N_{\rm f}$ (log)



3. Konvencionalne, empirijske metode procjene

Metode procjene materijalnih parametara (kako monotonih tako i cikličkih te zamornih) temelje se na pronalaženju i karakterizaciji odnosa između veličina na osnovi kojih se vrši procjena (nezavisnih, prediktorskih varijabli) i parametara čija se vrijednost traži (zavisnih, kriterijskih varijabli). Kod konvencionalnih, empirijskih metoda prvenstveno je riječ o regresijskim modelima pri čemu je češće riječ o jednostavnoj linearnoj ili nelinearnoj regresiji, a rjeđe višestrukoj. U literaturi je predložen niz empirijskih metoda za procjenu cikličkih [11,12,13,14,15,16,17,18] i zamornih [1,2,3,4,5,6,7] parametara. Monotoni parametri ili konstante na osnovi kojih se u odabranim metodama procjenjuju vrijednosti Basquin–Coffin–Mansonovih zamornih parametara navedeni su u tablici 1, a oni na osnovi kojih se određuju vrijednosti cikličkih Ramberg–Osgoodovih parametara dani su tablici 2. Za sve metode

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naveden je i broj materijala na osnovi kojih su razvijane ukoliko je ta informacija bila dostupna.

Tablica 1. N	/Ionotoni param	ietri na osnovi	kojih se p	ojedinim meto	odama pro	cjenjuju v	rijednosti za	imornih
	•				•			

Metoda procjene	<i>σ</i> _f ′	Ь	&	с
Metoda univerzalnih nagiba krivulja (1965) - svi materijali [1] Broj materijala: 29	R _m	-0,12	क्ष	-0,6
Korelacijska metoda četiriju točaka (1965) - svi materijali [1] Broj materijala: 29	b, Ε, R _m , ε _f	क्ष	C, ମ	b, Ε, R _m , ε _f
Mitchellova metoda (1977) - čelici [2]	R _m	R _m	क्ष	-0,5(-0,6)
Modificirana metoda univ. nagiba krivulja (1988) - svi materijali [3] Broj materijala: 47	E, R _m	-0,09	E, R _m , &	-0,56
Uniformni materijalni zakon (1990) - nelegirani i niskolegirani čelici [4] Broj materijala: 125	R _m	-0,087	E, R _m	-0,58
Uniformni materijalni zakon (1990) - Al i Ti slitine [4] Broj materijala: 125	R _m	-0,095	0,35	-0,69
Modificirana korelacijska metoda četiriju točaka (1993) - svi materijali [5] Broj materijala: 49	<i>R</i> m, <i>&</i>	E, Rm	æ	E, Rm, ε, σ
Metoda tvrdoće (2000) - čelici [6] Broj materijala: 69	HB (R _m)	-0,09	E, HB	-0,56
Metoda medijana (2004) - čelici [7] Broj materijala: 724	R _m	-0,09	0,45	-0,59
Metoda medijana (2004) - Al slitine [7] Broj materijala: 81	R _m	-0,11	0,28	-0,66

parametara materijala [20]

Tablica 2. Monotoni parametri na osnovi kojih se pojedinim metodama procjenjuju vrijednosti cikličkih parametara materijala [10]

Metoda procjene	Dodatna podjela	К'	n'
Zhang et al. (2009.) — čelici, Al- i Ti- slitine	α < 5% i 10% ≤ α < 20%	K ili σ _f , ε _f , n	R _m , R _{po,2} , n ili R _m , R _{po,2} , σ _f , ε _f
(dodatna podjela u podgrupe s obzirom na parametar α) [15]	5% < α < 10%	К ili Rm, Rpo,2, σf, εf, n	R _m , σ _f , n ili R _m , R _{po,2} , σf, εf
Broj materijala: 22	α > 20%	Κ ili R _m , R _{po,2} , σ _f , ε _f , n	R _m , R _{po,2} , σ _f , n ili R _m , R _{po,2} , σ _f , ε _f
Basan et al. (2010.) — niskolegirani čelik 42CrMo4 [16] Broj materijala: 40	-	НВ	0,1087
	-	-	n ili R _e /R _m
Proi materijala 422	$R_{\rm m}/R_{\rm e} \leq 1,2$	HB ili R _m ili K	<i>R</i> e , <i>R</i> m
	$R_{\rm m}/R_{\rm e} > 1,2$	HB ili R _m ili K	Re, Rm
Li et al. (2016.) – čelici [18]	$R_{\rm m}/R_{\rm e} \leq 1,2$	R _m	<i>R</i> _e ', <i>K</i> '

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Broj materijala: 27	1,2 < <i>R</i> m/ <i>R</i> e < 1,4	Rm	<i>R</i> e', <i>K</i> '
	<i>R</i> m/ <i>R</i> e≥1,4	R _m	<i>R</i> e', <i>K</i> '

Iz tablica 1 i 2 uočljivo je da je većina metoda (pogotovo starijih) pretežno razvijana na vrlo skromnom broju podataka o materijalima.

Usprkos činjenici da cikličku krivulju definiraju 2 parametra (K' i n') odnosno zamornu krivulju 4 parametra (σ_i', α_i', b i c), postojeće metode procjene temelje se na utvrđivanju postojanja i karakterizaciji izravne, nezavisne veze između monotonih značajki materijala i pojedinačnih cikličkih/zamornih parametara (uglavnom za koeficijente K', σ_i' i α' te eksponent n'). U slučaju nemogućnosti utvrđivanja i karakterizacije takve povezanosti, cikličkim/zamornim parametrima (uglavnom eksponentima b i c) pridaju se prosječne, konstantne vrijednosti ili medijani vrijednosti parametara grupa materijala na osnovi kojih su razvijane.

Pregledima i analizama postojećih metoda procjene cikličkih i zamornih parametara materijala, provedenima u [19,20,21] utvrđeni su njihovi dodatni nedostaci. Većina postojećih metoda procjene zanemaruje razlike u ponašanju i parametrima različitih grupa materijala (čelika, aluminijevih i titanijevih legura) odnosno pojedinih podgrupa unutar njih (nelegirani, niskolegirani i visokolegirani čelici) te se temelje na univerzalnim izrazima za procjenu njihovih cikličkih i zamornih parametara. Novije metode, počevši od [4] razmatraju glavne grupe metala zasebno (čelici, aluminijeve slitine, titanijeve slitine). Statističkom analizom [20] i formalno su potvrđene statistički značajne razlike u zamornom ponašanju navedenih grupa materijala, ali i podgrupa čelika, kao i između njihovih zamornih parametara što ukazuje na mogućnost točnijih procjena uz uvažavanje specifičnosti pojedinih skupina materijala.

U slučaju svih metoda procjene, monotone značajke na osnovi kojih se procjenjuju ciklički i zamorni parametri, tj. ponašanje materijala, odabrane su bez prethodno provedene statističke analize kojom bi se utvrdila relevantnost pojedine monotone značajke.

4. Napredne metode procjene primjenom umjetnih neuronskih mreža

Empirijske metode procjene cikličkih i zamornih parametara na osnovi monotonih značajki materijala zbog svoje su praktičnosti, jednostavnosti i brzo dostupnih rezultata i danas u širokoj upotrebi, no s porastom dostupnosti postojećih podataka o materijalima i mogućnosti računalnih sustava, težište razvoja metoda procjene pomiče se od analitičkih metoda prema sofisticiranijim računalnim metodama temeljenim na strojnom učenju, posebice umjetnim neuronskim mrežama.

Za razliku od jednostavnijih regresijskih modela koji su osnova većine konvencionalnih metoda procjene, metodama strojnog učenja poput umjetnih neuronskih mreža moguće je identificirati kompleksnije odnose između nezavisnih, prediktorskih varijabli i zavisnih, kriterijskih varijabli. Zahvaljujući većoj dostupnosti podataka o materijalima i razvoju računalnih resursa i alata, te činjenici da omogućavaju lakšu manipulaciju većim brojem prediktorskih varijabli i većim brojem podataka, umjetne neuronske mreže već neko vrijeme predstavljaju jedan od glavnih smjerova razvoja metoda procjene cikličkih i zamornih parametara na osnovi monotonih značajki materijala [22,23,24,25,26,27].

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Već je u prethodnom poglavlju spomenut problem odabira monotonih značajki na osnovi kojih će se procjenjivati ciklički i zamorni parametri, tj. ponašanje materijala. Pregledom radova u kojima su postojeće metode predložene, utvrđeno je da se u pravilu odabiru bez prethodno provedene sustavne i detaljne statističke analize kojom bi se precizno utvrdila relevantnost pojedine monotone značajke i njen doprinos procjeni pojedinog cikličkog ili zamornog parametra čelika [19]. Navedeno posebno dobiva na važnosti kod razvoja metoda procjene temeljenih na primjeni strojnog učenja poput umjetnih neuronskih mreža. Budući da je to moguće, brojna rješenja i metode predložene u literaturi predlažu neselektivno korištenje svih dostupnih monotonih značajki. Često uočljiv nedostatak takvih rješenja je da su razvijana na premalom broju podataka što u velikoj mjeri dovodi u pitanje njihovu točnost, pouzdanost i sposobnost generalizacije. Zbog toga je odabir samo relevantnih varijabli iznimno bitan za procjenu cikličkih i zamornih parametara primjenom umjetnih neuronskih mreža i za olakšavanje njihovog korištenja.

Detaljnom statističkom analizom provedenom u [19], za analizirani skup podataka o čelicima podijeljenim u 3 podgrupe (nelegirane, niskolegirane i visokolegirane čelike), za svaku su podgrupu utvrđene monotone značajke relevantne za procjenu njihovih cikličkih i zamornih parametara. U tablicama 3 i 4 na razini svake podgrupe čelika i za svaki ciklički odnosno zamorni parametar navedene su monotone značajke za koje je utvrđeno da su statistički relevantne za njihovu procjenu.

Podgrupa čelika	Zavisna (zamorni parametar)	varijabla	Nezavisne (monotone značajke)	varijable
	<i>σ</i> , ′		Re, Rm, K, σ τ	
Nalagirani čalici	Ь		R _m /R _e , Z, <i>о</i> ғ	
	&f'		analiza neprovediva	
	с		analiza neprovediva	
	σ _f '		Rm , Z, K	
Niskologirani čolici	Ь		Rm/Re, Rm/E, Z, K	
	&		analiza neprovediva	
	с		R _m /R _e , Z, n	
	σť		<i>R</i> _m / <i>R</i> _e , <i>R</i> _m / <i>E</i>	
Visokologirani čolici	Ь		<i>R</i> e, <i>R</i> m, <i>R</i> m/ <i>E</i>	
	<i>ੜ</i> '		R _m /E	
	С		R _e , R _m	

Tablica 3. Pregled monotonih značajki relevantnih za procjenu zamornih parametara nelegiranih, niskolegiranih i visokolegiranih čelika [10,19]

Tablica 4. Pregled monotonih značajki relevantnih za procjenu cikličkih parametara nelegiranih,

niskolegiranih i visokolegiranih čelika [10,19]

Podgrupa čelika	Zavisna (ciklički parametar)	varijabla	Nezavisne (monotone značajke)	varijable
Nelegirani čelici	К'		R _e , R _m , n	

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	n'	R _e , R _m /R _e , n
Niskolegirani čelici	К'	Rm, Z
	<i>n</i> ′	R _m /R _e , n
Visokolegirani čelici	К'	R _m /E
	<i>n</i> ′	Re, Rm/Re

Na temelju pretpostavke da se umjetnim neuronskim mrežama, razvijenim posebno za svaku skupinu čelika, podijeljenih prema udjelu legirajućih elemenata, i to samo na osnovi relevantnih monotonih značajki, može točnije procijeniti cikličke i zamorne parametre odnosno cikličko i zamorno ponašanje čelika, predlaže se i razvija [10,27] novi pristup procjeni cikličkih i zamornih parametara te ponašanja nelegiranih, niskolegiranih i visokolegiranih čelika. Za razvoj umjetnih neuronskih mreža korištene su samo monotone značajke čija je relevantnost za procjenu pojedinih parametara utvrđena detaljnim statističkim analizama [10, 19].

Rezultati dobiveni umjetnim neuronskim mrežama u čiji su razvoj integrirana saznanja iz prethodnih statističkih analiza relevantnosti pojedinih značajki, vrednovani su usporedbom s eksperimentalnim vrijednostima cikličkih i zamornih parametara, te vrijednostima dobivenim odabranim empirijskim metodama procjene.

Uspješnost pristupa razvijenog u [10,27] jasno je vidljiva iz rezultata procjene eksponenta dinamičke čvrstoće *b*, kojem velika većina empirijskih metoda dodjeljuje konstantnu vrijednost zbog nemogućnosti utvrđivanja zadovoljavajuće koreliranosti s monotonim značajkama. Detaljniji rezultati procjene eksponenta dinamičke čvrstoće *b* nelegiranih, niskolegiranih i visokolegiranih čelika korištenjem umjetnih neuronskih mreža (UNM) razvijenih u [10] uspoređeni su s rezultatima dobivenim odabranim empirijskim metodama procjene: Modificiranom metodom univerzalnih nagiba krivulja (Modif. UNP) [3], Uniformnim materijalnim zakonom (UMZ) [4], Metodom tvrdoće [6] i Metodom medijana [7]. Dijagrami na slici 2 za svaku metodu prikazuju postotke procijenjenih vrijednosti eksponenta dinamičke čvrstoće *b* koje od eksperimentalnih vrijednosti odstupaju do ±10 %, ±20 % i ±30 %.



Slika 2. Postotak vrijednosti *b* nelegiranih, niskolegiranih i visokolegiranih čelika procijenjenih empirijskim metodama procjene [3,4,6,7] i umjetnim neuronskim mrežama koje odstupaju do 10, 20 i 30 % od eksperimentalnih vrijednosti [10]

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Na slici 3. prikazani su postotci odstupanja vrijednosti eksponenta dinamičke čvrstoće *b* procijenjenih odabranim empirijskim metodama i UNM razvijenom za sve čelike zajedno od eksperimentalnih vrijednosti.



Slika 3. Postotak vrijednosti *b* procijenjenih empirijskim metodama [3,4,6,7] i umjetnim neuronskim mrežama primijenjenim na sve čelike zajedno koje odstupaju 10, 20 i 30 % od eksperimentalnih vrijednosti [10]

Umjetnim neuronskim mrežama uspješno je ustanovljeno postojanje funkcionalnih zavisnosti eksponenta dinamičke čvrstoće *b* i monotonih značajki za razliku od empirijskih metoda procjene koje mu dodjeljuju konstantnu vrijednost, čak i za skupinu visokolegiranih čelika koju karakteriziraju vrlo veliki rasap i razlike u vrijednostima zamornih (i cikličkih) parametara.

5. ZAKLJUČAK

U radu je dan pregled postojećih glavnih pristupa i metoda procjene cikličkih i zamornih parametara materijala na osnovi monotonih značajki. I pored značajnih prednosti, prilikom njihovog korištenja posebno je potrebno voditi računa o nedostacima od kojih su najznačajniji:

- zanemarivanje razlika između pojedinih grupa/podgrupa materijala te njihovih specifičnosti,
- dodjeljivanje konstantnih vrijednosti pojedinim parametrima materijala uslijed nemogućnosti određivanja korelacije između prediktorskih i zavisnih varijabli,
- razvoj metoda na malom broju podataka o materijalima,
- procjenjivanje cikličkih i zamornih parametara na osnovi (pre)malog broja monotonih značajki,
- neselektivno korištenje svih dostupnih monotonih značajki za procjenu odnosno neprovođenje prethodnih statističkih analiza za utvrđivanje relevantnosti monotonih značajki za procjenu,
- korištenje više međusobno koreliranih monotonih značajki.

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Osim prilikom odabira metoda za procjenu potrebnih parametara materijala, o navedenim nedostacima valja voditi računa i pri razvoju novih, poboljšanih metoda procjene te oni u tom smislu mogu predstavljati i svojevrsne smjernice za razvoj boljih rješenja neovisno o tome je li riječ o empirijskim metodama procjene ili metodama temeljenim na nekoj od metoda strojnog učenja.

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KARAKTERIZACIJA ČESTICA NA RECIKLIRANIM LISTOVIMA PAPIRA DOBIVENIM OD OTISNUTE KARTONSKE AMBALAŽE ZA LIJEKOVE

CHARACTERIZATION OF PARTICLES ON RECYCLED PAPER SHEETS OBTAINED FROM CARDBOARD PHARMACEUTICAL PACKAGING

Ivana Bolanča Mirković¹; Mia Klemenčić¹; Nenad Bolf²

¹ Sveučilište u Zagrebu, Grafički fakultet, Getaldićeva 2, Zagreb, Hrvatska
²Sveučilište u Zagrebu, Fakultet kemijskog inženjerstva i tehnologije, Trg Marka Marulića 19, Zagreb, Hrvatska

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Sažetak

Ambalaža za lijekove prati trendove u ambalažnoj industriji. Takvi ambalažni proizvodi prvenstveno mora zadovoljavati stroge odredbe kvalitete ambalaže farmaceutskih proizvoda, međutim bitan je i njegov dizajn. Na tržištu je sve prisutnija laminirana kartonska ambalaža, koja ima privlačniju sjajniju površinu. Međutim, laminirana kartonska ambalaža stvara dodatne probleme u procesu reciklaže iskorištenog proizvoda. Broj ljepljivih čestica, ali i sijanih čestica se uvelike povećava. Ovaj rad dat će karakterizaciju i usporedbu čestica nečistoća na površini listova načinjenih od recikliranih vlakanaca dobivanih od kartonske i laminirane kartonske ambalaže. Metodom slikovne analize čestice nečistoća će se razvrstati po broju i površini unutar definiranih klasa veličina. Doprinos ovih istraživanja je optimizacija procesa reciklaže, primjena kod dizajniranja ambalažnog proizvoda i bolja formulacija ambalažnih materijala.

Ključne riječi: Ambalaža za lijekove, reciklaža, čestice nečistoća

Abstract

A Pharmaceutical packaging follows trends in the packaging industry. Such packaging products must primarily satisfy stringent regulations on the quality of pharmaceutical product packaging, but its design is also important. On the market there is more and more laminated cardboard packaging, which has an attractive glossy surface. However, laminated cardboard packaging creates additional problems in the recycling process of the used product. The number of sticky particles, but also the shiny particles is greatly increased. This paper characterize and compare the particles of impurities on the surface of the handsheets made from recycled fibres obtained from cardboard and laminated cardboard packaging. With the method of image analysis will be sorted of impurities by number and surface within defined size classes. The contribution of these researches is the optimization of the recycling process itself, the application in designing the packaging product and the better formulation of packaging materials.

Keywords: Pharmaceutical packaging, recycling, particles of impurities.

1. UVOD

Povezivanjem dva ili više različitih materijala nastaje višeslojni ili laminirani materijali. Spomenuti materijali su kvalitetniji od pojedinačnih materijala koji su u slojevima, jer se odlikuju pozitivnim svojstvima svakog pojedinog materijala. Vanjski sloj višeslojnih materijala uvijek odlikuju dobra tiskovna svojstva. Laminirani ambalažni materijali za lijekove mogu se sastojati od slojeva papira ili kartona i aluminija. Kombiniranjem spomenutih materijala pogotovo u kombinaciji s filmom metalizirane plastike dolazi do poboljšanja svojstva barijere i zaštiti od vlage, ulja, zraka i mirisa. Vanjsku površinu spomenutih laminatnih materijala odlikuje visoki sjaj koji kupci vole.

Papir ili karton se može laminairati s aluminijem na dva načina. Nanošenje tankog sloja aluminijske folije na papir pomoću ljepila, što se više ne primjenjuje tako često kao prije. U upotrebi je samo kod pakiranja slatkiša, žvakaćih guma, duhana i kozmetike. Za pakiranje farmacetuskih proizvoda papir ili karton laminiran je s metaliziranim filmom. Film je obično polipropilen ili poliester, metaliziran aluminijem. Sloj se na papir ili karton nanosi ljepilom [1]. Laminirana ambalaža privlačnija je kupcima zbog svog sjaja i ističe proizvod među sličnim proizvodima [2].

U prošlosti se iskorišteni laminirani proizvodi nisu upotrebljavali u tvornicama za recikliranje papira, jer su se aluminij i folija smatrala zagađivalima[1]. Razina onečišćenja u papiru ili kartonu uvelike ovisi o porijeklu celuloznih vlakanca iz kojih se papir odnosno karton izrađuje. Izrada papira ili kartona od djevičanskih vlakana zahtjeva rafiniranje. To je postupak u kojemu se uz pomoć raznih kemijskih sredstava, boja, lakova te premaza dobiva kvalitetna tiskovna podloga. Takva tiskovna podloga nije održiva, ali potencijalno sadrži manji broj zagađivala od tiskovne podloge načinjene od recikliranih vlakanca. Reciklirana vlakanca mogu sadržavati određene količine kemijskih onečišćivala kao što su aldehidi, alkani, ketoni, ftalati i teški metali [3]. Vlakanca spomenutog porijekla mogu sadržavati tvari koje su bile dodane u papire od djevičanskih vlakanaca radi poboljšanja njihovih svojstva kao što su kalibracijska sredstava i premazi [4]. Zagađivala na kojima će se najviše temeljiti istraživanja u ovom radu su ostatci i sastojci tiskarskih bojila, folije i aluminija.

Folija sa četicama aluminija kao i ostatci i sastojci tiskarskih bojila u reckliranim vlakancima čine nečistoće koje se moraju ukloniti iz estetskih razloga, kvalitete tiskovne podloge i optičke homogenosti podloge. Metalne čestice povezane s ljepilom s vlakancima celuloze koje se nalaze na/u recikliranom papiru, a vidljive su, stvaraju mrlje i prozirne točke u papirnoj ili kartonskoj tiskovnoj podlozi. Takve pojave se kolokvijalno nazivaju i "riblje oči" ("fish-eyes") u gotovom papiru odnosno kartonu[1]. Takvim tiskovnim podlogama značajno pada kvaliteta. Spomenute pojave izazvane ljepljivim česticama izazivaju velike probleme kod sušenja papirne trake u procesu proizvodnje papira pri čemu nastaju rupe, papirna traka puca u toku procesa tiska. Spomenute nečistoće mogu zabrtviti opremu u proizvodnji papira.

O površini i broju ljepljivih čestica odnosno čestica nečistoća u papirnoj pulpi ovisiti će efikasnost izdvajanja u procesu alkalne deinking flotacija. Karakterizacija čestica utvrđuje se pomoću slikovne analize, a spomenute čestice grupiraju se u dvije osnove skupine veličina, u vidljive i nevidljive čestice ljudskom oku [6].



2. EKSPERIMENTALNI DIO

U radu su korišteni ofsetni otisci (tisak iz arka) načinjeni na kartonskoj tiskovnoj podlozi jednostrano premazanoj, gramature 300 g/m². Uzorci su laminirani (oznaka uzoraka u1 i u3) i ne laminirani (oznaka uzoraka u2 i u4). Za otiskivanje su korištena pantone bojila.

Uzorci su nakon otiskivanja podvrgnuti oporabi na dva različita načina. Na dijelu uzoraka je provedena oporaba prema metodi kemijske deinking flotacija po standardnoj metodi INGEDE 11 [7]. Druga korištena metoda je oporaba uz pomoć uređaja za odjeljivanje ljepljivih čestica Somerville tester prema metodi TAPPI T 275 sp-078 [8].



Slika 1. Dijagram toka oporabe iskorištene otisnute ambalaže

Uzorci laboratorijskih listova papira su izrađeni na uređaju za automatsku izradu listova papira Rapid- Köthen, proizvođača Frank – PTI, prema standardnoj metodi ISO 5269, 2017 [9].

Za slikovnu analizu laboratorijski izrađenih listova korišten je Apologee SpecScan[®], a distribucija čestica na laboratorijskim listovima utvrđena je u području od 0,001-5.00 mm².

3. REZULTATI

Klase veličina čestica promatra se kako slijedi: čestice manje od o,o4mm² i veće od o,o4mm². Razlog takve podjele pronalazi se u optičkim svojstvima izrađenog laboratorijskog lista papira. Čestice koje su manje od o,o4mm² utječu na sivoću laboratorijskih listova, dok one veće od o,o4mm² utječu na njihovu optičku nehomogenost.

U ovom radu nisu prikazane sve klase veličina čestica, jer nisu utvrđene čestice nečistoća veće od 0,2mm². Općenita karakteristika ofsetnih nelaminiranih otisaka s konvencionalnim CMYK

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bojilima je velik broj manjih čestica koje se mogu uspješno odvojiti procesom alkalne kemijske deinking flotacije u ovisnosti o relevantnim čimbenicima, što je prikazano u ranijim radovima[10].

Glavni cilj ovih istraživanja je utvrđivanje utjecaja laminirane podloge i pantone bojila na efikasnost reciklaže i karakteristike recikliranih vlakanaca, što prikazuje rezultati koji slijede.



Slika 2. Prikaz raspodjele broja čestica nečistoća manjih od 0,04mm² po klasama na laboratorijskom listu papira

Broj čestice nečistoće na laboratorijskom papiru u klasama manjim od o,o4mm² povećava se uglavnom nakon postupka odvajanja čestica. Razlog tome može se naći u procesu fragemtacije većih čestica u manje u postupku neposredno prije njihovog uklanjana. Samo se smanjuje broj česticama manjih od o,oo6mm² postupkom lužnate deinking flotacije nakon postupka odvajanja kada se postupak provodi na kartonu koji nije laminiran. Takav rezultat pokazuje jako dobro odvajanje čestica u spomenutoj klasi te vezanje čestica nečistoća na mjehuriće zraka.



Slika 3. Prikaz raspodjele površine čestica nečistoća manjih od 0,04mm² po klasama na laboratorijskom listu papira

Oba postupka odvajanja čestica nečistoća uglavnom doprinose smanjenju ukupne površine čestica po klasama (slika 3). Što samo potvrđuje da su se čestice u oba postupka fragmentirale

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u čestice s manjom površinom što je uzrokovalo i povećanjem njihove brojnosti što se vidi i na slici 2. Takvi rezultati pokazuju da je efikasnost odvajanja čestica nečistoća dobra što potvrđuje i slika 4.



Slika 4a) Broj odvojenih čestica nečistoća manjih od 0,04mm² iz papirne pulpe, 4b) Površina odvojenih čestica nečistoća manjih od 0,04mm² iz papirne pulpe

Kada se proučava broj odvojenih čestica nečistoća manjih od o,o4mm² na laboratorijskom listu papira lako se može zaključiti da se u klasama od o,oo1-o,oo6mm² i o,oo6-o,o13mm² odvajanje čestica nečistoće najveće, ali kada se proučava površina odvojenih čestica najmanje tri klase čestica imaju najveću uspješnost odavanja. Kada se uspoređuju postupci odvajanja čestica nečistoća manjih od o,o4mm² iz papirne pulpe vidljivo je da je postupak odavanja s uređajem za odvajanje ljepljivih čestica efikasniji kada se radi s laminiranim i nelaminiranim otisnutim uzorkom kartona (slika 4a i4b).





Slika 5. Prikaz raspodjele broja čestica nečistoća većih od 0,04mm² po klasama na laboratorijskom listu papira

Efikasnost odvajanja čestica nečistoća klasa većih od 0,04mm² je velika, broj čestica smanjuje se dva do tri puta. U zadnje dvije klase veličina 0,1-0,15 mm² te 0,15-0,20 mm² čestice se u potpunosti odvajaju u nekim vrstama postupaka. Papirna pulpa iza postupaka odvajanja čestica ne sadrži velike čestice koje uzrokuju optičku nehomogenost papira.



Slika 6. Prikaz raspodjele površine čestica nečistoća većih od 0,04mm² po klasama na laboratorijskom listu papira

Kada se promatra površina čestica nečistoća zaostalih na laboratorijskim listovima papira vidljivo je iz slike 6. da se površina značajno smanjuje pogotovo nakon postupka odvajanja čestica postupkom pomoću uređaja za odvajanje ljepljivih čestica.

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Slika 7a) Broj odvojenih čestica nečistoća većih od 0,04mm² iz papirne pulpe, 7b) Površina odvojenih čestica nečistoća većih od 0,04mm² iz papirne pulpe

Kada se proučava efikasnost odvajanja čestica nečistoća većih od o,o4mm² iz papirne pulpe vidljivo je da je uspješnost odvajanja velika. Iz slika 7a i 7b može se utvrditi da čestice nečistoća nastale u pulpi dobivenoj od laminiranog uzorka kartona imaju veću efikasnost izdvajanja postupkom izdvajanja pomoću uređaja za izdvajanje ljepljivih čestica. Vidljivo je također da su najveće površine i broj čestica nečistoća većih od o,o4mm² nakon postupka izdvajanja izmjerene na listovima koji su načinjeni iz pulpe dobivene iz laminiranog otisnutog kartona. Takva papirna pulpa u sebi ima veću količinu ljepila koje je ostalo od apliciranja polimerne folije na površinu kartona što kasnije u postupku deinking flotacije dovodi do problema nastanka ljepljivih čestica aglomerata, koje se taško mogu vezati za mjehuriće zraka i izdvojiti.



4. ZAKLJUČAK

Na osnovu rezultata istraživanja mogu se izvesti slijedeći zaključci.

U procesu oporabe laminirane tiskane ambalaže za farmaceutske proizvode nastaju nešto veće čestice onečišćenja, maksimalno do o, 20 mm² u odnosu na one tiskane u istoj tehnici tiska na nelaminiranoj podlozi. Korištenjem metode oporabe koja uključuje uređaj za odvajanje ljepljivih čestica, čestice nečistoća nastale u pulpi dobivenoj od otiska na laminiranom kartonu imaju veću efikasnost izdvajanja. Unatoč toga najveće površine i broj čestica nečistoća većih od o, 0,4mm² nakon postupka izdvajanja su izmjerene na listovima koji su načinjeni iz pulpe dobivene iz laminiranog otisnutog kartona. Ta problematika se može tumačiti površinskim svojstvima nastalih čestica onečišćenja i hidrodinamikom opisanog sustava.

Provedena istraživanja su znanstveni doprinos u pojašnjenju efikasnosti oporabe, karakteristikama dobivenih sekundarnih vlakanaca, te koje klase čestica/nečistoća su zastupljenije u kartonskoj pulpi dobivenoj od otisaka s pantone bojilom na nelaminiranom i laminiranom kartonu, namijenjenog za pakiranje proizvoda farmaceutske industrije, koristeći u proizvodnji ambalaže nove grafičke materijale i postupke u tisku, uključujući u tom segmentu domenu ekološke održivosti.

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POSTOJANOST FOTOGRAFIJA U DEFINIRANIM UVJETIMA UBRZANOG

STARENJA

DURABILITY OF PHOTOGRAPHY UNDER DEFINED CONDITIONS OF ACCELERATED AGEINGPAPER TITLE

Ivana Bolanča Mirković¹; AntonioKralj¹, Marina Vukoje¹, Zdenka Bolanča²

¹Sveučilište u Zagrebu Grafički fakultet, Getaldićeva 2, 10000 Zagreb, Hrvatska ²Hrvatska akademija tehničkih znanosti

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Sažetak

Fotografije se koriste kao sredstvo dokumentacije događaja s posebnim značajem, važnog predmeta, odnosno eksponata, poznate osobe, te bilježenje obiteljskih događaja. Fotografija je vizualna umjetnost, a jedno od područja je umjetnička fotografija. Umjetnici – fotografi na fotografijama izražavaju trenutni osjećaj, ambijentalni doživljaj ili fotografiraju portrete. Zbog svega nabrojanog trajnost i postojanost fotografskog ispisa vrlo je značajna.

U ovom radu promatra se utjecaj ubrzanog starenja u kontroliranim uvjetima na fotografije, koje sadrže pune tonove RGB boja. Proces ubrzanog starenja izvodi se prema ISO standardu 18909, korištenjem ksenonske komore uz definirane parametre. Navedeno istraživanje može doprinijeti razvoju novih formulacija materijala na tom području sa većom trajnost i postojanost ispisa bez posebnih postupaka zaštite fotografije ili korištenja posebnih načina arhiviranja fotografija.

Ključne riječi: fotografija, ubrzano starenje, postojanost

Abstract

Photographs are used as a means of documenting events of special importance, important objects, i.e. exhibits, celebrities, and recording of family events. Photo is a visual art, and one of the areas is art photography. Artists - photographs in photographs express instant feelings, ambience, or portraits. Due to all of the mentioned durability and stability of photographic printing, it is very important.

This paper examines the influence of accelerated aging in controlled conditions on photographs that contain RGB full tons. The accelerated aging process is carried out in accordance with ISO standard 18909, using a xenon chamber with defined parameters. This research can contribute to the development of new material formulations in the area with greater durability and stability without special procedures for photographs protection or the use of special methods of archiving photographs.

Keywords: photography, accelerated aging, durability





KVANTITATIVNA ANALIZA CMY REPRODUKCIJE OTISNUTE INKJET SUBLIMACIJSKIM TISKOM NA POLIESTERSKOJ TKANINI

QUANTITATIVE ANALYSIS OF CMY REPRODUCTION CLEAN INKJET WITH SUBLIMATION TISSUE ON POLYESTER TANK

Franka Žuvela Bošnjak¹, Igor Majnarić², Suzana Kutnjak-Mravlinčić¹

¹Sveučilište u Zagrebu, Tekstilno-tehnološki fakultet, Studij Varaždin, Hallerova aleja 6, 42000 Varaždin, Hrvatska
²Sveučilište u Zagrebu, Grafički fakultet, Getaldićeva 2, 10 000 Zagreb, Hrvatska

<u>Original scientific paper / Izvorni znanstveni rad</u>

Sažetak

Inkjet tisak spada u jednu od najjednostavnijih tehnika otiskivanja gdje se tekuća boja direktno nanosi na podlogu. Sublimacijski Inkjet tisak kao metoda obojavanja temelji se na postupku zagrijavanja pri čemu se čestice krutih nosioca obojenja provode u plinovito stanje te sublimiraju u doticaju s tretiranom podlogom. U ovom radu izvršena je detaljna kolorimetrijska analiza otisaka ostvarenih sa sublimacijskim piezoelektričnim Inkjet strojem uz određivanja devijacija nastalih tijekom svih tranzicijskih faza. Pritom je određena uspješnost tiska na sublimcijski papir, uspješnost transferiranja papira na PES tkaninu i ostatka kolorne reprodukcije na potrošenom papiru za sublimaciju. Rezultati pokazuju da uspješnost tranzicije obojenja ovisi o primjenjenim bojama pri čemu žuta ostvaruje najmanju kolornu promjenu. Razlog tomu je mala devijacija tonova ostvarenih po kromatičnosti C*. Kolorne promjene DE za procesnih boja iznose: C=12,49, M=11,00, Y=6,92.

Ključne riječi: Sublimacijski Inkjet tisak, PES tknina, sublimacijski papir, CIE LAB DE

Abstract

Inkjet printing is one of the simplest printing techniques where the liquid color is directly applied on printing substrate. Sublimation Inkjet printing use dyeing method based on the heating process whereby the solid ink particles will be transferred on gaseous state and sublimated in printing substrate. This paper represents colorimetric analysis of the textile prints made with the sublimation piezoelectric Inkjet machine, with definition of colour deviations created during all transition process. Results show success of printing on sublimation paper, the success of transferring paper to the PES fabric and the remain of ink on sublimation paper. Success of the transition of color depends on the applied inks, whereby the yellow is the least colour deviation. The reason for this is the small deviation of the tones realized in the chroma. Color changes (DE) for process colors are: C = 12.49, M = 11.00, Y = 6.92.

Keywords: Sublimation Inkjet Printing, PES textile, Sublimation Paper, CIE LAB DE

1. UVOD

Sublimacija je postupak pri kojem se zagrijavanjem medija i nositelji obojenja, (na temperaturi oko 200°C) provode migracije bojila iz krutog u plinovito stanje uz osiguran kontakt s tretiranom podlogom. Sublimacijski tisak Inkjet uglavnom se upotrebljavaju u tekstilnoj industriji. Razlog tomu je porozna tekstilna podloga koja se teško obojava s viskoznim bojilim. Piezo ispisne glava omogućuju uspješno nanošenje sublimacijskog inkjet bojila na tiskovnu podlogu. Međutim kako dobiveni otisci nisu kromatski zadovoljavajuće zasićenosti potrebna je dodatna termalna obrada. Da bi se postiglo stabilan otiska (sublimacije boje na tekstil) otisnuti prijenosni materijal potrebno je kalandrirati valjcima.[1,2] Zbog ostvarenih zasičenih otisaka ova tehnika omogućuje tisak odjevnih materijala, zastava, tekstilnih reklama, POS programa, dresova, a u zadnje vrijeme se otvara mogućnost dekorativnog tiska. Međutim, doradne mašine za ovu tehnologiju su neophodne.[3]

2 TEORETSKI DIO.

2.1. Sublimacijska boja (boja prilagođena za Inkjet tisak)

Tiskovne podloge pogodne za sublimacijski transfer su poliesterske tkanine ili podloge koje su presvučene polimerim slojevima. Razlog tome je što poliester u odnosu na papir ima veći sublimacijski afinitet i bolji prodor bojila u strukturu molekula poliesterskog materijala. Ostale pogodne podloge su: poliamid (PA 6, PA 6.6), poliakrilonitril (PAN), triacetat (HAT), tkanine s 60% udjela gore navedenih tkanina. Svi oni ostvaruju briljantne otiske, otporane na UV zračenje i ne iritacijom ljudske kože.

Prve sublimacijske boje u području sublimacijskog toplinskog transfer tisaka primjenila je tvrtka ICI (Imperial Chemical Industries). U ovoj tehnici tiska, sublimacijske boje ugrađene su u ribone koji su se pomoću termičke glave ispisivale (taložile) na bijelu tiskovnu podlogu. [4] Ostvarena rezolucija ispisa bila je mala (100-400 dpi) uz relativno visoki trošak proizvodnje tiskarske ribone (širina max ispisa 350 mm). Međutim, svi ovi nedostaci riješeni su primjenom Inkjet tiska s sublimacijskim bojama. Sublimacijske boje za Inkjet tisak mogu se nanašati sa dva različita tiskarska procesa: direktni tisak i transferni (prijenosni) tisak.

U slučaju direktnog tiska provodi se postupak zagrijavanja sublimacijskih boja zajedno sa tiskarskom podlogom. Ovisno o sastavu upotrijebljenih boja, tipu i toplinskom kapacitetu tiskovne podloge, te o opremi za kalandriranje (metodi zagrijavanja), tipično vrijeme djelovanja topline može varirati od 20 sekundi do nekoliko minuta. Temperatura fiksiranja je između 175 °C i 210 ° C, uzmehanički pritisak od 1,03 do 4,14 bara. [5] Prilikom izvođenja direktnog tiska sublimacijskim bojama primjenjuju se slični parametri kao kod transfernog tiska da bi se osigurala potpuna penetracija molekula boje u podlogu. Osim na tekstilu moguća je primjena i na ostalim tiskovnim podlogama.

Tablica 1: Parametri	prijenosa top	oline kod sublima	acijskog tran	sfernog tiska

proizvod	parametri procesa
tekstilni materijal/ odjeća	204 °C, 35-65 s, 2. 76 bar
keramičke šalice/pločice	175-204 °C, 150-210 s, 2.76-4.14 bar
premazane polimerne	204 °C, 60 s, 2.76 bar
podloge	





Termalni transfer sublimacijske boje na podlogu izvoditi se u tri osnovne faze: a) kruta boja zagrijava se iznad temperature sublimacije, b) oslobođeno plinovito bojilo se isparava u područje između prijenosnog papira i polimerne podloge, c) taloženje na površini, gdje će plinovito obojene molekule boje nastaviti migriraciju i prodor u unutrašnjost polimera. [6]

Sublimacijske boje koje se koriste u Inkjet tisku pripadaju skupini disperznih boja. To su organske boje koje nemaju značajnu topivost ni u vođenim i u organskim otapalima. Disperzne boje su stabilne i ne reagiraju s materijalom. Samim time ne dolazi do kovalentnih veza između boje i materijala, niti dolazi do promjene strukture materijala. Sublimacijske boje koje sadrže antrakinon, kvinopalmon ili azo/dijazo grupa disperznih boja, neionske su sintetske molekule s konjugiranom strukturom i funkcionalnim skupinama. Kao takve karboksilne ili sulfonske skupine nemaju mogućnost otapanja u vodi. [7]

Kako bi se osiguralo učinkovito sublimiranje, molekularna masa ovih boja mora biti manja od 500 g/mol. Većina ovih molekula je plosnatog oblika i bez dugačkih alifatskih lanaca, što osigurava ulazak i sidrenje u polimernu matricu tkanine za vrijeme sublimacijskog procesa. Od gotovo 1000 komercijalnih dispeznih boja samo manji broj ima mogućnost uspješnog sublimacijskog procesa bojanja. Kemijski, sublimacijske boje korištene u digitalnom tisku tako pripadaju grupaciji spojeva kao što su antrakinon, kvinopalmon, azo spojevi, stiril, oksazin, ksanten, metin ili azometin disperzije. Ove boje imaju afinitet povezivanja s hidrofobnim sintetičkim polimernim materijalima kao što su poliester i najlon. Kemijske strukture procesnih sublimacijskih boja koje se koriste u digitalnom tisku prikazane su na slici 1.



Slika 1. Strukture sublimacijske boje koje se koriste u sublimacijskom tisku: a) crvena 60, Cl60756. b) plava 3, Ci61505. c) žuta 54, Cl47020

Sublimacijske boje se mogu podijeliti i prema razinama sublimacijske energije. Tako postoje niske, srednje i visoko energetske sublimacijske boje. Boje s nižom razinom energije lakše sublimiraju pri transfernom tisku. Međutim, one imaju relativno nisku postojanost obojenja jer proces vezivanja između molekula boje i strukture polimera uključuje samo Van der Walsove sile i vodikovu vezu. Drugim riječima osnovni čimbenici u sublimacijskom tisku su temperatura sublimacije i sublimacijska čvrstoća gotovog otiska. Viša temperatura ili dulje vrijeme potrebno je da se postigne zadovoljavajuće sublimacija, a samim time i viša kategorija razine energije sublimacijske boje. CMYK sublimacijske Inkjet boje (osnovne

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procesne bioje) mogu se koristiti za direktni termalni tisak, kao i za prijenosni (industrijske) termalni tisak. Sublimacijske boje za Inkjet tako moraju imati usklađen kemijski sastav i udjele komponenti, da bi omogućili najbolju moguću kompatibilnost tekućih kemijskih i fizikalnih svojstava. Da bi se dobio odgovarajući disperzni sustav potrebno je kontrolirati faktore kao što su: veličina čestica, distribuciju čestica, solventnost, kiselost, vodljivost, udio zraka, viskoznost, površinsku napetost, učinkovitost prijenosa boja. U tablici 2. prikazana su svojstava za vodene Inkjet sublimacijske boje koje se nanašaju s DOD piezoelektričnim Inkjet printerom.

svojstva boje	granične vrijednosti			
viskoznost (cp, 6o rpm)	3 - 10			
površinska napetost (mN/m)	> 30			
pH vrijednost	6 - 11			
vodljivost (μS)	1-6			
srednja veličina čestica (μm)	0.1 - 0.5			
otopljeni zrak (ppm)	< 20			

Tablica 2.	Svoistva	vodene su	blimaciiske	boie kod	DOD piezo	električnoa	Inkiet tiska
rabiica zi	510,5114	rouene be	, o nin a cijok c	boje kou	DOD piczo	erencereg	initjee cibika

Tijekom sublimacijskog procesa odvija se i proces reverzne difuzije sa otisnute podloge. Pritom se provodi migracija molekule bojila iz unutrašnjosti supstrata na površinu. Zbog molekulske težine i razlika u temperaturi, primjenjena boja se mora spojiti s istom ili sličnom razinom energije. Na njihov točan omjer tako utječe parcijalni tlak obojene pare, temperatura zagrijavanja i vrijeme djelovanja. To je posebice važno pri primjeni CMY bojila. Za primjenu na obojenim tiskovnim podlogama ponekad se primjenjuje i bijela pri čemu se primjenjuju različite metode maskiranja. [8,9]

Ovim parametrima upravlja kemijski sastav sublimacijskog bojila. Zbog toga u krutom agregatnom stanju moraju pronaći i dodatne komponente kao što su: tenzidi, ovlaživači, puferi, pH pufer i sredstva za kelatiziranje) Načelno, tradicionalna veziva nisu potrebna u sublimacijskom tisaku, osim ako se ne želi postići promjena viskoziteta. Oblik pigmenata ima puno važniju ulogu tijekom prijenosnog sublimacijskog tiska. Pri visokim temperaturama (iznad točke sublimacije) dolazi do staklastog prijelaza polimera (Tg). To rezultira sa popunjavanjem otvora polimernih tekstilnih materijala. Pritom će se molekule pigemata plosnatog oblika boje povezati i migrirati u polimernu strukturu. Hlađenjem na sobnoj temperaturi struktura polimera će se zatvoriti, a molekule boje ostaju u njenoj unutrašnjosti. [10,11]

3. EKSPERIMENTALNI DIO

U ovom radu provedena je analiza kolorne reprodukcije provedene piezoelektričnim Inkjet sublimacijskim tiskom. Analiza je napravljena na 2 uzorka. To su uzorak U1 (otisak na papir za sublimaciju 95 g/m2) te uzorak U2 (otisak na PES tkanini nakon provedenog tiskanja). Tiskani uzorci imali su 378 polja otisnutih s CMY bojama. Za otiskivanje koristio se je Inkjet pisača Roland Texart RT-640 8C koji koristi RIP TEXART 14.1.8.5703. Dobiveni otisak je zajedno s tekstilnom poliesterskom podlogom i papirnom podlogom pušten kroz kalender za uprešavanje HT-1742 T2B s vremenom sublimiranja od 10 minuta i pri temperaturi od 200 °C. Kako je jedan dio boje prešao je i na podložnu papirnu podlogu, i ona je kolorimetrijski

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analizirana (U3). Svi proizvedeni uzorci su izmjerena kolorimetrom i spektrofotometrom X-Rite eXact te digitalnim mikroskopom Dino-Lite. [12,13,14]



Slika 2: Tijek izvršenog eksperimenta

4. REZULTATI I RASPRAVA

Postupkom indirektnog sublimacijskog transvernog postupka otisak se formira na specijalno prilagođenom materijalu (sublimacijski papir) s kojeg se otisak djelovanjem topline, prenosi na konačnu tekstilnu podlogu. Djelovanjem vanjske temperature (200°C) i ovisno o strukturi (gustoći tkanja) ostvaruje se veći ili manji kolorni intenzitet otisaka. Rezultat toga moguće je vidjeti na ostacima sublimacijskog papiru. Na slici 3, slici 4. I slici 5 prikazani su 3D Lab dijagrami procesnih boja CMY i ostvarena njihova razlika u obojenju ΔE2000.

Kod cijan boje razlika u obojenju (ΔE) se povećava povećanjem rastera tonske vrijednosti (RTV). Što je veća pokrivenost površine veća je i nastala promjena u obojenju. Raspon razlika u bojenju od 3,5 do 5 govori da je ona izrazito velika (kritična za primjenu). Kolorne razlike iznad 5, govore da je došlo do potpune promjene tona. Nakon početnog otiskivanja te izvršenog transfera, na sublimacijskom papiru ostvaruje se prosječna promjena cijan tona od $\Delta E_{U_1-U_2} = 13,96$. To je uzrazito velika kolorna razlika. Dodatnom obradom i aktivacijom temperaturom od 200 °C sublimacijska boja povećava svoju zasićenost stvarajući potom

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razliku u obojenju cijana od $\Delta E_{U_1-U_3} = 12,49$. Ostaci sublimacijskog papira i otiska na poliesterskoj tkanini tako ostvaruju veliku razliku u iznosu od $\Delta E_{U_2-U_3} = 24,08$. Otisci i krivulje reprodukcije postaju sve duže a tonovi zasićeniji.



Slika 3. a) 3D Lab dijagrami cijan boje, b) ΔE razlika u obojenju cijan boje; c). mikroskopske fotografije cijan boje, uzoraka U1, U2, U3, (uvećane 60 puta)

Druga separacija (magenta) zadržava u potpunosti istu tendenciju kao i cijan. Međutim, ostvarene razlike su nešto niže. Magenta boje na sublimacijskom papiru ostvaruje izrazito veliku prosječna promjena magenta tona od $\Delta E_{U_1-U_2} = 13,18$. Razlika u obojenju između sublimacijskog papira s uzorkom za tisak i sublimacijskog papira nakon tiska iznosi $\Delta E_{U_1-U_2} = 13,18$.





11,00; a razlika ostataka iznosi ΔE_{U2-U3}= 23,41. Ove vrijednosti su niže od vrijednosti dobivenih kod cijan boje, te je magenta boja vidljivo reaktivna. Trendovi povećanja linija (slika 4a) su isti kod obe procesne boje. Tako najduža linija prikazuje najveći raspon obojenja.



Slika 4. a) 3D Lab dijagrami magenta boje, b) ΔE razlika u obojenju magenta boje; c). mikroskopske fotografije magenta boje, uzoraka U1, U2, U3, (uvećane 60 puta)

Žuto sublimacijsko bojilo pokazuje najmanje kolorne promjene ΔE . Ona ne prelazi granicu od 20. Zbog male kolorne promjene ne postoji pravilnost u krivuljama DE2000 reprodukcije. S obzirom da je žuta najsvjetlija boja mala je promjena u kromatičnosti kao i u samoj svjetlini. Kod žute boje na sublimacijskom papiru se ostvaruje prosječna kolorna razlika od $\Delta E_{U1-U2} = 8,65$. Razlika u obojenju između sublimacijskog papira za tisak i sublimacijskog papira nakon tiska iznosi $\Delta E_{U1-U2} = 6,92$. Samim time kolorna razlika ostatka iznosi (ΔE) $_{U2-U3} = 14,89$.

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C) **UZORAK1** UZORAK 2 **UZORAK 3** žuta_U1_25%_RTV žuta_U2_25%_RTV žuta_U3_25%_RTV žuta_U1_50%_RTV žuta_U2_50%_RTV žuta_U3_50%_RTV žuta_U1_75%_RTV žuta_U2_75%_RTV žuta_U3_75%_RTV žuta_U2_100%_RTV žuta_U3_100%_RTV žuta_U1_100%_RTV podloga_U1 podloga_U2 U3_podloga

Slika 5. a) 3D Lab dijagrami žute boje, b) ΔE razlika u obojenju žute boje; mikroskopske fotografije magenta boje, uzoraka U1, U2, U3, (uvećane 60 puta)

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5. ZAKLJUČAK

Od tri mjerena uzorka (otisnuti sublimacijski papir, otisak na PES-u, ostatak boje na sublimacijskom papiru nakon transfera) najveće kromatske vrijednosti će imati PES otisak. Svi Inkjet otisci na sublimacijskom papiru će djelovanjem topline ostvariti povećanje u a* i b* koordinatama i manje promjene u L* koordinate.

Cijan Inkjet otisak na sublimacijskom papiru će djelovanjem topline ostvariti povećanje u a* i b* koordinatama za 89,9 i 40,4 %. Analogno tome dolazi i do pada u svjetlini cijan otiska L* od 22,2%. U odnosu na tekstilni uzorak efikasnost transfernog procesa je vrlo velik. U odnosu na izmjerene koordinate cijan ostataka na potrošenom sublimacijskom papiru ona iznosi: a* koordinata 94,4%; b* koordinata 90,7%: L* koordinata 62%.

Magenta Inkjet otisak otisnut na sublimacijskom papiru će tijekom sublimacijskog procesa također ostvariti povećanje u a* i b* koordinatama (a*= 39,4% i b*=78,1%). Analogno tome dolazi i do pada u svjetlini cijan otiska L* od 18,5%. U odnosu na tekstilni uzorak efikasnost transfernog procesa je nešto manji. U odnosu na izmjerene koordinate cijan ostataka na potrošenom sublimacijskom papiru ona iznosi: koordinata a* za 73,0%; koordinata b* za 66,5% i koordinata L*za 63,6%.

Najsvjetlija komponenta žuta će u sublimacijskom tisku ostvariti najmanje kolorno odstupanje. Tako će žuti nosioci obojenja djelovanjem topline ostvariti povećanje u a* i b* koordinatama za 53,4% i 26,4 %. Analogno tome dolazi i do pada u svjetlini žutog otiska minornih L*= 4,4%. U odnosu na tekstilni uzorak efikasnost transfernog procesa je kromatski dobar što se ne može reći za svjetlinu. U odnosu na izmjerene koordinate žuti ostataka na potrošenom sublimacijskom papiru ona iznosi: a* koordinata 91,6%; b* koordinata 81,8% i koordinata L* za 8,2%.

Da bi se efikasnost trensferiranja povećala u narednim istraživanjima izvršiti će se testiranje utjecaja temperature (tisak sa većim temperaturama transfera) i tlaka (povećavanje sile pritiska u transfernoj zoni).

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MEHANIČKA SVOJSTVA I SVJETLOSTALNOST KARTONA PREMAZANIH PCL NANOKOMPOZITIMA

MECHANICAL PROPERTIES AND LIGHTFASTNESS OF PAPERBOARD COATED WITH PCL NANOCOMPOSITES

Josip Bota¹, Zlata Hrnjak-Murgić², Dubravko Banić¹, Maja Brozović¹

¹ University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, Zagreb, Croatia

² University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia

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Sažetak

U ovom radu istražena su mehanička svojstva kartona (GD2, gramature: 230 g/m², 280 g/m² i 350 g/m²) s nanesenim biorazgradljivim polimernim premazom (polikaprolatonom) u svrhu unapređenja svojstava materijala. Polikaprolaktonski (PCL) premaz je dodatno modificiran dodavanjem nanočestica aluminijevog oksida (Al₂O₃), silicijevog dioksida (SiO₂) i cinkovog oksida (ZnO). Istražena mehanička svojstva su prekidna čvrstoća, prekidno istezanje, otpornost na savijanje, otpornost na obostrano savijanje, te otpornost na pucanje i otiranje. Pripremljeni uzorci premazanih kartona su izloženi ubrzanoj degradacije (120h). Tijekom tog vremena svaka 24h određena su kolorimetrijska svojstva kako bi se ispitala svjetlostalnost otiska. Nakon provedenog istraživanja ustanovljeno je da mehanička svojstva premazanih kartona nisu narušena. Rezultati prekidne čvrstoće, prekidnog istezanja, otpornosti na savijanje, otpornosti na obostrano savijanje, te otpornost na pucanje unapređenje svojstava kartona. Premazi su evidentno povećali otpornost na otiranje otisaka čime je postignuta veća razina zaštite otiska. Svi uzorci s nanočesticama su postigli određeno povećanje svjetlostalnosti.

Ključne riječi: polikaprolakton (PCL), karton, nanokompozit, svjetlostalnost

Abstract

This paper investigated the mechanical properties of paperboards (GD₂, grammage: 230 g/m², 280 g/m² and 350 g/m²) with biodegradable polymer coating (polycaprolaton) in order to improve the properties of the material. Polycaprolactone (PCL) coating is further modified by the addition of nanoparticles of alumina (Al₂O₃), silicon dioxide (SiO₂) and zinc oxide (ZnO). The investigated mechanical properties were tensile strength, tensile elongation, bending resistance, double folding resistance, and burst resistance and abrasion test. Prepared samples of coated paperboards were exposed to accelerated degradation (120h). During this time every 24h, colorimetric properties were measured to examine the lightfastness of the print. The study proved that the mechanical properties of the coated paperboard were not impaired. Results of tensile strength, tensile elongation, bending resistance, double folding resistance, and burst resistance, and burst resistance point to a minor improvement of paperboard properties. There is an evident increase of abrasion resistance thereby achieving better protection of the print. All samples with nanoparticles have achieved a certain increase of lightfastness.

Keywords: polycaprolactone (PCL), paperboard, nanocomposite, lightfastness print

1. INTRODUCTION

The life span of packaging can range from one day to several months or years. It is generally considered that short-term packaging has a greater negative impact on the environment due to the large amount of daily waste that needs to be disposed of before disposal. The advantages of cellulosic material include: low-cost production, biodegradability, recyclability, simple graphics processing, coating, ease of formation, lightness and ease of improving the properties of the manufacturing process [1–3] The use of fiber-based material has many advantages compared with plastic packaging, such as sustainability, recyclability, and the stiffness-to-weight ratio[4]. However, due to the insufficiency of the carton (high porosity, moisture absorption, and low mechanical stability) it is necessary to explore the possibility of its advancement. Polymer coated paperboard layer, and in particular nano-coating polymer can significantly improve mechanical properties of the main roles of packaging is marketing used to communicate consumer value products as well as information on content and usage. Therefore, in the printing industry print quality as well as its stability is of utmost importance and the subject of many investigations [6].

In recent years, there is an increasing attention to the selection of packaging materials that are environmentally more suitable. Research is mostly focused on replacing synthetic raw materials with biodegradable and/or sustainable raw materials from natural sources [1]. Pure biopolymer coatings generally have insufficient properties to fully replace synthetic polymers. For this reason, a large number of researches focuses on mixing biopolymers (combining multiple types of biopolymers to achieve new properties) and biopolymer (nano) composites (modification of biopolymers with nanoparticles) [5,7,8]. Most research on biopolymer coatings based on the analysis of chemical properties of paperboard packaging in order to protect the product (barrier properties) and the preparation of paper and paperboard for printing (production process) [1,8–13]. Under-explored area is the effect of varnishes (coatings applied after printing on print) on mechanical properties of paperboard and quality print and print degradation. According to available literature, only a few studies investigating the effect of the coating on the optical properties of the print [14–17] while only one is investigates the improvements to paperboard properties [18]. No scientific work has been found that explores biopolymer in the role of varnishes. Hence the need for research and improvement of biopolymer after print coatings for environmental sustainability, and improvement of packaging materials.

The aim of this research was to develop and describe the state of PCL and PCL nanocomposite coated paperboard in order to improve mechanical, aesthetic and usable properties of the packaging materials.

1.1. Hypotheses

H1 nanoparticles in the PCL polymer matrix will improve the mechanical properties of the paperboard

H2 PCL coating modified with nanoparticles that absorb the UV part of the spectrum will slow down the process of print degradation

H3 Coating applied as a varnish will improve rubbing resistance of the print






2. METHODOLOGY

2.1. Materials

- *GD2 paperboard*, (Umka color®) Umka d.o.o.

Three different grammages of GD₂ paperboards where used in this research (230 g/m², 280 g/m²) and 350 g/m²). Thicknesses are shown in Table 1.

Grammage	230 g/m²	280 g/m²	350 g/m²
Thickness	0,28 mm	o,36 mm	o,48 mm

- offset ink (CMYK) Novavit® F 918 SUPREME BIO - Flint Group produced on the basis of renewable raw materials.

- ethyl acetate p.a. (C₄H₈O₂), T.T.T. doo[®] (solvent)
- *polycaprolactone* (C₆H₁₀O₂), Sigma Aldrich[®] (polymer)

- nanoparticles:

Silica (SiO₂) AEROSIL® R 8200, Evonik, SiO2 content>99.8%, surface area (BET) 220± 25 m2/g;

Aluminum oxide (Al_2O_3) Aeroxide[®] Alu C, Evonik, molecular weight: 101.96 g/mol, particle size of 13 nm, content > 99.8%, surface area (BET) 85-115 m2/g

Zinc oxide (ZnO) ZH4810000, Lach-ner d.o.o., molecular weight 81.39 g/mol

2.2. Sample preparation

Printed paperboard

Paperboard samples are printed by offset printing using the Fogra[®] standard for offset printing (ISO 12647-2) that ensures high quality prints.

Color chart

The color fields where prepared using pure process colors (CMYK). The defined sample chart ranges from 10% to 100% rastertonal values (RTV). With pure surface color, there were a total of 41 fields.

PCL nanocomposites

The coatings were prepared by dissolving 10 g of PCL polymer in 100 mL (90 g) ethyl acetate. The dissolution process was carried out at 40 °C by stirring the magnetic stirrer for 30 min to give a 10 wt.% homogeneous solution. Then, to the so-prepared PCL polymer solution nanoparticles (Al₂O₃, SiO₂ and ZnO) were added and dispersed with a homogenizer (IKA T₂₅ digital TURRAX) for 8 minutes at a speed of 15,000 rpm.





Sample	E-A	Р	Al	Si	Zn
K/o	-	-	-	-	-
K/P	90	10	-	-	-
K/P/1Al	89	10	1	-	-
K/P/2Si	88	10	-	2	-
K/P/2Zn	88	10	-	-	2

Tab. 2: PCL nanocomposite ingredient ratios (mas%)

 $\textbf{K}-\text{Karton}, \textbf{E-A}-\text{etil-acetat}, \textbf{P}-\text{PCL}, \textbf{Al}-\text{Al}_2\text{O}_3, \textbf{Si}-\text{SiO}_2, \textbf{Zn}-\text{ZnO}$

Coating the samples

The coating was applied to the coating (K202 Control Coater) under controlled conditions as defined by the ISO 187: 1990 standard. For the application of the coating film a standard rod (24 μ m coating thickenss) was used, and it allows the formation of a uniform film thickness according to ASTM D823 - 95 (2001). All coatings were applied to the printed side of the paperboard. The dry thickness of the coatings was 6.1 μ m. Thickness of coating film was measured by micrometer Enrico Toniolo S.r.l. DGTB001, range of 0-10 mm gauge with a precision of 0.001 mm

Accelerated aging

Paperboard samples with and without coating were exposed in an accelerated aging chamber (Cofomegra Solarbox 3000 Xenon Test Chamber of Commerce). Xenon lamp 2500 W, SX07 Outdoor UV filter + IR coating, long life, 550W/m² BST 50 was the source of radiation. During radiation, the temperature inside the chamber was 50 °C. The samples were irradiated 5 days (120 hours).

2.3. Methods

2.3.1. Mechanical properties

All measurements of the mechanical properties of tested samples of packaging paperboards were carried out under the defined conditions: temperature (23 °C ± 1 °C) and humidity (RV 50% ± 2%) according to ISO 187: 1990 standard.

Tensile strength and tensile elongation

Tensile strength (S) and tensile elongation (ϵ) was performed on the FRANK mechanical tester according to ISO 1924-2. Dimensions of the paperboard samples were 250 x 15 mm, the spacing between the grips was 180 mm and the breaking speed was 50 mm/min. The results are expressed as the mean values of twenty measurements. Tensile strength was determined for both directions of cellulose fibers (cross direction-CD and machine direction-MD of the fibers). The calculations where made according to the formulas 1–4

S=F/w (1)

S – tensile strenght (N/mm)

F – tensile force (N)

w – sample width (mm)

l=S/g·1000 (2)

I - tensile index (Nm/g)





$$\varepsilon = \Delta l/l_i$$
 (3)
 $\Delta l = l - l_i$ (4)

 ε – tensile elongation (%)

 Δl – total elongation of the sample (mm)

l – length of the sample after breaking (mm)

 l_i – starting length of the sample (mm)

Burst strength

Burst strength (p) and burst index (x) are determined with the Lorentzen & Wettre Bursting Strength Tester. The dimensions of the tested packaging carton samples were diameters Ø= 100 mm, the measuring area was diameter Ø = 50mm and the elastic diaphragm was Ø = 33.1 mm in diameter. At the site of the diaphragm there is a gradual increase in pressure on the sample until bursting. The maximum pressure at the time of cracking is the burst strength. The pressure range of the device is 70 kPa to 1400 kPa, in accordance with ISO 2759-2001. Burst strength determined for both sides of the paperboard as one side of the cardboard is printed. The calculations where made according to the formula 5

x=p/g (5)

x – burst index (kPa•m²/g) p – burst strenght (kPa)

g - grammage (g/m²)

Bending resistance

Lorentzen & Wettre Bending Tester was used to measure the bending force (F) needed to reach the defined bending angle. The device measures the resistance forces in millimeters (mN) that occurs when bending the test sample (dimensions $_{38 \times 76}$ mm) by 15 ° along longer side. The device measures paperboard resistance in the range of 20 to 10000 mN and in accordance with ISO 2493. The results are expressed as the mean values of twenty measurements for both fiber directions (CD and MD).

Folding resistance

The paperboard sample (dimensions 140 x 15 mm) is attached to the grips by passing through the vertical slit of a metal plate. Tiles move forward and back that leads to double fold of the sample which is stretched with a constant force of 9.81 N. The result is shown as the total number of double folds performed prior breaking of the test sample. The results are expressed as the mean values of twenty measurements for both fiber directions (CD and MD).

Rubbing resistance

Rubbing resistance of the print and coating was conducted on the Hanatek Rub and Abrasion Tester. A plane GD₂ paperboard (110 mm diameter) was used as a referent rubbing surface. On the test head of the device, the sample size of the printed paperboard (50 mm diameter)



is set face down and the sampling procedure is activated. The test head was loaded with weights of that are equivalent to 3447.38 Pa, 6894.76 Pa and 13789.5 Pa of pressure and the rate of rotation was 60 rpm for 10 revolutions. The results are presented as a visual comparison of the reference substrate. After a visual examination, a grade from 0 to 5 was assigned based on the degree of ink transfer from the tested sample, where 0 is absent ink, and 5 are high degrees of ink transfer. The print and coating damage was also observed and presented. The metering method is in accordance with the BS 3110 standard.

2.3.2. Optical properties

Spectral values of the color chart was measured using i1Publish Pro spectrophotometer. The spectral measurement range was 380 - 730 nm (visible spectrum), resolution 10 nm, according to ISO 13655: 2009 standard, with M1 measurement conditions (D50 according to ISO 13655: 2009). When scanning the sample, the measurement frequency was 200 measurements per second. Devices display the data as the amount of wavelength reflection converted to the CIE Lab colorimetric color system. The results were compared using the calculated color change values (ΔE). The description of ΔE values and the tolerances according to ISO 12647-2(2013) are presented it Tables 3.-5.

ΔE value	Meaning
0 - 1	change invisible to the human eye
1-2	very little deviation (visible to a trained observer)
2 - 3.5	medium deviation visible to the average observer
3.5 - 5	visible deviation
5 <	very visible deviation

Tab. 3: Description of the ∆E value

Tab. 4: Allowed tolerance for full (CMYK) tones acording to ISO 12647-2(2013)

	С	М	Y	Κ
ISO 12647-2 deviation tolerance ΔE_{∞}	3,5	3,5	3,5	5
ISO 12647-2 variation tolerance ΔE_{oo}	2,8	2,8	3,5	5

Tab. 5: Allowed tolerance for rastertonal values (CMYK) tones acording to ISO 12647-2(2013)

	deviation tolerand	ce (ΔE₀₀)	variation tolerance (ΔE_{\circ}		
Rastertonal values (%)	profile (proof) print	OK print	production print		
40 ili 50	3	4	4		
75 ili 80	2	3	3		
maximum deviation of RTV	4	5	5		

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3. RESULTS AND DISCUSSION

3.1. Results and discussion for tensile strength and elongation

Figure 1 shows the results of the tensile strength of coated and uncoated paperboard samples (S). Tests were performed on three grammages of paperboard (230 g/m², 280 g/m² and 350 g/m²) with PCL coating modified using Al_2O_3 , SiO₂ and ZnO and nanoparticles, whereby the tensile strength was determined for both fiber direction (CD and MD). As expected, the strengths determined for the CD are considerably lower and range from 0.23 N/mm to 0.45 N/mm for all paperboard weights and values for MD range from 0.75 N/mm to 1.08 N/mm. It may be noted that the tensile strength and MD and CD increases with the increase of paperboard weight. Further, the paperboards with PCL nanocomposite coating have slightly increased strength when comparing with uncoated samples for the MD samples. Thus, the coatings did not impair the mechanical properties, on the contrary they slightly improved them. It was expected that the tensile strength would be moslty improved in CD, but the obtained results did not show this.



Fig. 1: Tensile strenght of samples according to fiber direction and grammage





				CD		MD				
	Sample	St dev	F min (N)	F max (N)	CoV (%)	St dev	F min (N)	F max (N)	CoV (%)	
	K/o	0,8	51,9	54,9	1,5	4,1	162,7	178,4	2,4	
۳²	K/P	1,5	51,0	56,9	2,7	4,2	167,7	182,4	2,4	
)g (K/P/1Al	1,4	49,0	53,9	2,6	3,7	165,8	180,5	2,2	
530	K/P/2Si	0,8	53,0	54,9	1,6	3,2	165,7	176,5	1,9	
	K/P/2Zn	0,7	53,0	54,9	1,2	3,4	168,7	179,5	1,9	
	K/o	2,0	57,8	64,7	3,2	4,5	198,1	211,8	2,2	
m²	K/P	0,9	61,6	66,6	1,3	3,8	201,0	213,8	1,8	
<u> </u>	K/P/1Al	0,5	61,8	63,7	0,8	4,4	201,0	213,8	2,1	
280	K/P/2Si	3,0	58,8	66,7	4,8	3,6	208,9	219,7	1,7	
	K/P/2Zn	1,5	66,7	70,6	2,1	3,6	200,1	211,8	1,8	
	K/o	1,4	98,0	102,9	1,4	6,8	226,3	249,9	2,7	
_۳	K/P	0,7	100,0	102,0	0,7	4,8	233,2	249,4	2,0	
/ɓ c	K/P/1Al	1,1	96,1	100,0	1,1	8,2	218,7	253,0	3,4	
350	K/P/2Si	1,5	98,1	103,0	1,5	6,7	227,5	257,9	2,7	
	K/P/2Zn	1,0	97 , 1	100,0	1,0	4,4	237,3	251,1	1,8	

Tab. 6: Statistical values of tensile strenght test

From the results it can be concluded that the coated samples tested do not have significant deviations compared to the results of uncoated. Table 6 shows the statistical values of the test results of the tensile strenght test of three different grammages of paperboards regard to the fiber direction and the investigated coatings.

The tensile index represents the characterization of paperboard strenght, and is calculated from the ratio of the tensile strength and the grammage of the paperboard. The results of the tensile index for the tested samples are shown in Table 7. The CD results are in the range of 14.7 N·g/m to 19.2 N·g/m and 45.3 N·g/m to 51.3 N·g/m for MD. 230 g/m² i 280 g/m² paperboards show a significal lower values in the CD. At the same time, the tensile index values the 350 g/m² samples for the MD are lower than those for the less grammage. From these results it can be presumed that the 350 g/m² paperboards have a higher degree of fibrous interlocking in both directions, resulting in a greater number of fibers oriented transversely in the direction that should contain dominantly longitudinal fibers.

		I _{CD} (N∙g/m)		I _{MD} (N⋅g/m)			
sample	230 g/m²	280 g/m²	350 g/m²	230 g/m²	280 g/m²	350 g/m²	
K/o	15,2	14,7	19,0	49,1	48,7	45,5	
K/P	15,6	15,0	19,2	49,7	49,8	45,3	
K/P/1Al	15,1	14,9	18,8	49,2	49,6	45,5	
K/P/2Si	15,6	14,9	19,0	50,8	51,3	46,5	
K/P/2Zn	15,5	16,4	18,8	50,4	49,1	46,6	

Tab.	7:	Tensile	index	of sa	mples	accord	lina to	fiber	direction	and	aramma	ae
	1 -										3	<u> </u>

When determining the tensile strength the material also deformes before breaking, consisting of elastic and plastic deformation (extension) of the material. The sum of the

elastic and plastic elongation at the point where the material breaks is called the tensile elongation (ε) shown in Figure 2. Paperboard samples with a PCL nanocomposite coating exhibit a significantly higher percentage of extension with respect to the CD, from 4.3% to 5.8%, while the MD samples resulted in a much smaller elongation of 1.8% to 2.8%.



Fig. 2: Tensile elongation of samples according to fiber direction and grammage

		CD						MD	
	sample	St dev	ε min (%)	ε max (%)	CoV (%)	St dev	ε min (%)	ε max (%)	CoV (%)
	K/o	0,8	4,2	5,8	8,8	0,4	1,7	2,5	9,0
m²	K/P	1,2	3,9	5,8	13,0	0,2	1,9	2,3	5,7
) g (K/P/1Al	0,9	4,2	5,6	9,9	0,3	1,7	2,2	8,4
230	K/P/2Si	0,9	5,2	6,7	8,6	0,5	1,7	2,5	13,6
	K/P/2Zn	0,5	5,3	6,1	4,5	0,3	1,7	2,2	8,7
	K/o	0,6	3,9	4,9	7,5	0,2	2,5	2,8	3,9
"m	K/P	o,8	3,9	5,3	9,4	0,4	2,2	2,8	8,4
60	K/P/1Al	o,8	4,1	5,3	8,9	0,3	2,1	2,5	6,7
280	K/P/2Si	0,6	3,4	4,7	7,4	0,2	1,8	2,2	4,8
	K/P/2Zn	0,8	4,2	5,6	8,6	0,3	2,2	2,8	6,8
	K/o	0,7	3,9	5,6	9,1	0,2	2,2	2,7	5,5
m²	K/P	0,5	4,2	5,0	6,2	0,2	2,1	2,7	5,5
/ɓ c	K/P/1Al	0,5	3,9	5,0	6,2	0,5	1,7	2,5	14,9
350	K/P/2Si	0,5	4,2	5,0	6,5	0,4	1,8	2,7	9,3
	K/P/2Zn	0,4	3,8	4,4	4,9	0,6	1,7	2,5	16,2

Tab. 8: Statistical values of tensile elongations

Some small improvement of the elastic/plastic properties of the coated paperboards was observed CD, and decreased in MD samples. It is also apparent that the influence of the coating is uniform with the MD samples independent of gramature, as opposed to the CD.



Most noted increase of tensile elongation is observed in the paperboard sample coated with PCL-SiO₂ coating. The increase of +1% apears in the lightest paperboard (230 g/m²) for CD samples. The percentage of elongation of CD is lesser when the grammage is higher. It can be observed that the addition of PCL-SiO₂ and PCL-ZnO coatings to a lighter paperboard can positively influences the elongation of the material for forces in the CD and negatively in the MD. Table 7 shows the statistical values of the test results of the tensile elongation of three different grammages of paperboards regarding to the fiber direction.

3.2. Results and discussion for burst strength

Burst strenght was conducted with two directions of force acting on the samples. The burst strenght results from the side without coating (outward burst strenght) (Figure 3) show the effect of force on the back of the paperboard, opposite to the coated side. This simulates the cardboard resistance to the effect of the force that would cause the product on the inside of the packaging. Inward burst strenght simulates the reverse action force i.e. the resistance of the packaging on external forces. The results are presented in Figure 4.





From te inward and outward burst strenght results it can be observed that values proportionaly increase according to grammage. It is also important to note that the overall burst resistance is greater when the force direction is oppostite to the position of print and coating. This fact points to the existence of greater strength of material on the printed side of the material. Most often the upper layers of paperboard contain new or recycled cellulosic fibers improving the optical and mechanical properties when compared to other layers [19]. This procedure provides a brighter finishing of the paperboard. The increase of bursting strenght is most visible in samples with PCL-SiO₂ coatings. Unlike outward resistance, the results of inward resistance point to a uniform trend. Samples with PCL nanocomposte coating (K/P/1Al, K/P/2Si, K/P/2Zn) result in a higher inward burst strenght when compared with pure paperboard and pure PCL sample. Table 9 shows the statistical values of the test

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results of the burst strenght of three different grammages of paperboards regarding the force direction.



Fig. 4: Inward burst strenght of samples according to grammage

		Coating side Opposite coatir					oating side	5	
	sample	St dev	max (kPa)	min (kPa)	CoV (%)	St dev	max (kPa)	min (kPa)	CoV (%)
	K/o	12,2	260	220	5,1	11,7	272	237	4,5
m²	K/P	8,8	255	229	3,6	8,7	275	240	3,3
230 g/	K/P/1Al	8,6	267	236	3,4	10,9	285	253	4,2
	K/P/2Si	17,1	252	205	6,8	13,4	373	332	5,0
	K/P/2Zn	11,0	268	229	4,4	14,9	288	239	5, ⁸
	K/o	11,3	343	310	3,5	16,9	371	318	4,8
'm²	K/P	13,7	351	302	4,2	13,5	366	321	3,9
/ɓ c	K/P/1Al	15,2	370	312	4,4	15,9	365	319	4,7
280	K/P/2Si	15,7	390	328	4,4	15,9	390	328	4,5
	K/P/2Zn	14,3	359	319	4,2	12,4	367	333	3,5
	K/o	22,8	468	391	5,3	31,6	538	437	6,6
m²	K/P	19,1	460	403	4,4	24,1	516	431	5,1
/ɓ (K/P/1Al	25,5	464	393	5,7	34,3	552	429	7,2
350	K/P/2Si	23,2	478	403	5,3	33,5	534	431	6,8
	K/P/2Zn	17,4	462	395	4,2	25,0	509	436	5,4

Tab. 9: Statistical values of burst strenght test

Bursting index also describes the strenght of a paperboard. It si calculated from the ration of burst strenght and grammage. The results are shown in Table 10. Unlike tensile index the burst index clearly shows that the resistance grows with the increase of grammage. The PCL- SiO_2 sample showed the highest values for all three grammages and both directions of the applied force. The 280 g/m² inward burst index is equal to the outward and is the highest value





when compared to the other samples. The values of the inward burst index are generally lower for all coating samples and grammages.

	Inv	vard Burst ind x _i (kPa·m²/g)	ndex Outward Burst index				
sample	230 g/m²	280 g/m²	350 g/m²	230 g/m²	280 g/m²	350 g/m²	
K/o	1,12	1,24	1,36	1,03	1,16	1,23	
K/P	1,14	1,24	1,34	1,05	1,17	1,24	
K/P/1Al	1,14	1,22	1,37	1,09	1,24	1,25	
K/P/2Si	1,15	1,27	1,41	1,09	1,27	1,27	
K/P/2Zn	1,11	1,26	1,36	1,09	1,22	1,23	

Tab. 10: Burst index of samples according to force direction and grammage

3.3. Results and discussion for bending resistance

The bending resistance values of the tested samples are given in Figure 5 for CD and Figure 6 with respect MD. As expected, fibers with CD have significantly lower bending resistance than MD. The values in bending resistance increase the larger the grammage which shows that stiffnes grows. The trend of growth seems exponetial. Thus, it can be seen that bending resistance values for the 230 g/m² range from 30 to 40 N for 280 g/m² of paperboard samples from 70 to 80 N and for 350 g/m² of 175 to 190N. Furthermore, by comparing the results of all the samples, it can be noticed that the application of the coating on paperboard has no significant effect on the increase or decrease bending resistance. The only bigger change is visible in the PCL coated paperboard for MD where there is a decrease in stiffness. There is no clear explanation for this irregularity and it needs to be thoroughly explored.



Fig. 5: Bending resistance of samples according to grammage (CD)





Fig. 6: Bending resistance of samples according to grammage (MD)

			C	D		MD				
	anmala	st	Fmax	F min	CoV	st	Fmax	F min	CoV	
	sample		(mN)	(mN)	(%)	dev	(mN)	(mN)	(%)	
	K/o	1,7	37	31,8	4,8	3,3	107	97,3	3,2	
m²	K/P	2,1	33,7	28,1	6,8	2,1	93,9	86,5	2,3	
/ɓ c	K/P/1Al	1,3	43	38,2	3,2	3,2	110	99,1	3,0	
230	K/P/2Si	1,5	40,8	36,7	3,9	3,9	111	97,9	3,7	
	K/P/2Zn	2,6	42,6	34,8	6,7	2,9	110	98,8	2,8	
	K/o	3	81,7	69,8	3,9	6	208	191	3,0	
m²	K/P	5	87,2	70,9	6,3	8	202	180	4,2	
)g c	K/P/1Al	6,8	83,5	65,3	9,2	9	213	180	4,6	
280	K/P/2Si	6,5	80,9	57,1	9,2	8	207	179	4,0	
	K/P/2Zn	4,9	88,8	72	6,2	7	205	181	3,6	
	K/o	5	200	184	2,6	14	464	423	3,2	
35o g/m²	K/P	5	195	177	2,7	16	434	388	3,9	
	K/P/1Al	8	213	189	4,5	15	467	419	3,4	
	K/P/2Si	8	197	175	4,3	16	474	426	3,6	
	K/P/2Zn	6	203	185	3,1	16	468	416	3,6	

Tab. 11: Statistical values of bending resistance test

The method of testing stiffness or bending strength determines the force required to bend the paperboard to the defined angle. Significant influence on the bending resistance has the length, flexibility and strength of the fibers in relation to the bond strength between the fibers [20]. This method gives an insight into the plastic deformation of the tested samples, or in other words, determining the stiffness of the paperboard with respect to the type of PCL nanocomposite coatings. The disadvantage of this kind of testing is that the results are significantly influenced by the asymmetric distribution of the tensile and pressure forces of the cardboard and the different properties of the web (dual sides). For this reason, the measurements were carried out with respect to both directions of the orientation of the

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cellulose fibers and an equal number of measurements was used using force from the front and back of the cardboard. Table 11 shows the statistical values of the test results of the bending resistance of three different grammages of paperboards regarding to the fiber direction.

3.4. Results and discussion for folding resistance

Figure 7 shows the number of double folds needed to break the CD sample. The results present the three grammages and paperboards with different coating types.



Fig. 7: Number of double folds according to grammage (CD)

The results do not show any consistency in the number of folds, grammage or sample type. The gotten values cannot point to any conclusion because the low values and there was a large dispersion of the results. This is because the folding is paralel to the CD of the fibers, so this can result in a fast tear.

Figure 8 presents the number of double folds for the MD of the samples. It can be observed that the number of double folds do not differ for the 280 g/m² and 230 g/m². It is assumed that in the case of a 280 g/m² paperboard, the ratio of the forces inside (and between) the cellulose fibers and the thickness causes a reduced resistance to folding, leading to an earlier burst. The same property was not noticed with a grammage (350 g/m²). A significant increase in the number of double bending is visible on the 350 g/m² samples. The largest deviation occurs in K/P and K/P/2Si samples, while the other results are similar to the reference value (K/o). A large impact on double folds has the fiber length and/or the ratio of recycled fibers in the paperboard, so it is expected to have a deviation between identical samples. The results of MD are more important because this simulates the opening fold of the packaging. Table 12 shows the statistical values of the test results of the folding resistance of three different grammages of paperboards regarding to the fiber direction.





Fig. 8: Number of double folds according to grammage (MD fiber direction)

		CD fiber direction			MD fiber direction				
	Sample	St dev	min	max	CoV (%)	St dev	min	max	CoV (%)
) g/m²	K/o	10,6	22	57	344	56,9	217	395	567
	K/P	4,8	26	40	696	43,1	210	322	618
	K/P/1Al	5,8	22	39	516	59,2	191	362	488
230	K/P/2Si	8,4	28	55	439	57,3	218	382	489
	K/P/2Zn	8,8	19	48	348	45,4	226	354	5 ⁸ 7
	K/o	9,5	12	39	272	85,7	200	451	347
m²	K/P	6,5	10	30	295	99,4	122	403	255
/g c	K/P/1Al	8,7	9	36	252	154,9	78	570	151
280	K/P/2Si	6,4	14	32	348	79,3	232	434	395
	K/P/2Zn	6,7	20	46	443	127	128	554	198
	K/o	16,3	9	64	212	138	1011	1445	850
350 g/m²	K/P	17,9	16	85	156	282,6	1110	1993	515
	K/P/1Al	21,4	25	92	254	264,5	770	1564	415
	K/P/2Si	20,3	15	83	185	163,8	1088	1491	811
	K/P/2Zn	24,3	33	102	268	286,7	807	1684	407

According to the results of the mechanical properties if the tested samples the H1 hypothesis can be partally confirmed, because some properties have been slightly improved while others were kept unchanged.

3.5. Results and discussion for rubbing resistance

This test gave an insight into the changes of the print as a result of rubbing against other packaging that can ocure durring transport. Figure 9 shows the results of the visual evaluation of the rubbing transfer for the tested samples relative to the reference. Samples were tested under three different loads (a=3447,38 Pa, b=6894,76 Pa i c=13789,5 Pa) after 10 rotations. By increasing the load, an increase in the degree of ink transfer is apparent, but not as expected as the load has tripled. The non-coated sample had the expected highest degree of ink transfer. Samples with a coating have a much smaller degree of rubbing transfer because the coating must firsty be mechanically descaled.





Fig. 9: Visual assesment of rubbing resistance test

Samples with the PCL-SiO₂ coating showed slightly worse results. Example of the rubbing test on a referent sample is visable in Figure 10. The visual assessment results confirms the H_3 hypothesis.



Fig. 10: Example of rubbing against referent sample; a) before rubbing b) after rubbing

In this case, besides the substrate analysis, it was important to investigate the surface of the sample after testing to gain insight into the mechanical abrasion of the tested carton sample with the coating. The non-coating paperboard is visually more acceptable with the appearance of damage only in the color fields, while the other samples have visible traces of locally removed coatings that are caused by mechanical forces.





Fig. 11: Example of rubbed sample; a) without coating b) with coating

Figure 11 shows examples of damage to the print and coating surface due to mechanical abrasion. For non-coating samples, ink removal was observed, while coatings with the coating showed visible wear of the coating layer.

The rubbing resistance test show mixed results. The ink transfer due to rubbing does not occur on the coated samples but descaling of the coating decreases the estetical properties of the sample.



3.6. Results and discussion for lightfastness

The samples were exposed to accelerated ageing to observe the lightfastness of the print after coating. The ageing of the referent sample (without coating) is presented in Figure 12.



Fig. 12: Color deviation of RTV values during accelerate ageing of pure paperboard; a) Cyan, b) Magenta, c) Black, d) Yellow

Minimum deviations were observed in the black RTV values (Figure 12 c). Approximately 85% of all black colorants have charcoal as the primary pigment consisting of hydrocarbon particles of 100 to 200 nm that are very stable to light effect [21,22]. From the results it can also be seen that the yellow (Figure 12d) RTV have the greatest color deviation, then magenta (Figure 12b) and cyan (Figure 12a).

It is known that most color pigments (which are not black or white) contain chromophores which, when cumulative exposed to sunlight, can be damaged and lose their propeties [23]. The obtained results of the examined samples confirm the current research of lightfastness of offset print [23–25]. These studies has proven that colors fade with time in a way that their CIE L values incerase (become lighter), and CIE a i b values move towards zero (lose their saturation). From the results it is also apparent that smaller RTV of cyan, magenta and black



have a larger color change than full tones. It is known from the literature that pigments degrade less when they have greater optical density relative to low optical density, meaning that a lower percentage of RTV will result in a greater degree of color loss. This fact suggests that light energy can simultaneously affect only a small part of the chromophore at the same time and that the chromophores in a certain way prevent the penetration of light [23]. The opposite phenomenon can be observed in yellow color results; decreasing the optical density (RTV) of the print reduces color decay due. This can be explained by the fact that yellow as the brightest of the four process colors of the printing press is also the closest to the color of paperboard. Low percentages of RTV of brighter colors, such as yellow, result in a smaller color deviation compared with darker colors. Also, the fact that paper due to degradation changes the tone from white neutral to yellow contributes to this case [19,26].

Figure 13 shows the results of offset color change of different RTV after accelerated degradation for samples of with pure PCL coatings. There are visible differences compared to the reference sample. In all cyan RTV (Figure 13a) there are slightly lower ΔE deviations in all exposure times. The difference is approximately equal in all RTV to the reference values. The difference of magenta (Figure 13b) in the range of 60% to 100% RTV are consistent with the results of the non-coated carton, but better results are visible at the last measurement (after 120 hours). The 40% and 50% RTV improvement occurs after 96 hours, and in the range of 10% to 30% RTV a slight difference is visible after 24 hours. The yellow tones (Figure 13d) after total exposure to the irradiation in the chamber show an increased deviation compared to the reference. Slight improvement was observed in the range of 70% to 100% after 48 hours and in the 90% and 100% RTV area after 72 hours of exposure.





Fig. 13: Color deviation of RTV values during accelerate ageing of paperboard with pure PCL coating; a) Cyan, b) Magenta, c) Black, d) Yellow

The results of samples coated PCL-Al₂O₃ are shown in Figure 14. After the complete exposure of the sample to accelerated degradation cyan tones (Figure 14a) result in greater color difference (from 0.4 for full tones to 2.8 for lighter tones) than the reference sample (uncoated sample). Slight improvement is only visible in the range of 10% to 60% of RTV within the first 48 hours. Magenta tones (Figure 14b) have the same trend in the range of 10% to 60% RTV as well as cyan colors, while a more significant improvement is visible in the range of 90% to 100% of RTV after five days of irradiation. Black tones (Figure 14c) show no improvement in deviations except in the range of 10% to 50% of RTV within the first 96 hours and within the last 24 hours of exposure, these tones suddenly result in increased levels of fading. Yellow tones (Figure 14d) have less color deviation in the range of 70% to 100% RTV, while lighter tones generally have similar results as the reference sample. Most pigments (non-black or white) contain chromophores that are known to be more or less damaged when cumulative exposure to sunlight [23]. In the PCL-Al₂O₃ sample it has been observed that the lighter tones of cyan, magenta and black have more color change. The obtained results are





in contrast to the theoretical assumptions [23-25] so it is assumed that Al_2O_3 nanoparticles in the PCL nanocomposite coating partly inteact with UV radiation. In this sample, it has been observed that in lighter tones of cyan, magenta and black there is a greater difference in color. A possible explanation is that the nanocomposite coating acts as a catalyst.



Fig. 14: Color deviation of RTV values during accelerate ageing of paperboard with PCL-Al₂O₃ nanocomposite coating; a) Cyan, b) Magenta, c) Black, d) Yellow

Color difference for the PCL-SiO₂ nanocomposite sample is shown in Figure 15. The results of cyan (Figure 15a) and black tones (Figure 15c) for the whole radiation period show lower values, from 0.1 for full tones to 1.3 for lighter tones compared to the reference sample. Magenta tones (Figure 15b) show a total improvement in color change generally found in the 60% to 100% RTV range, and it is visible after five days of exposure, while in the range of 10% to 20% RTV color changes after the first 24 hours. The results of the yellow tones show a greater color difference of 0.9 to 2.4 compared to the reference sample. Lower values of yellow color changes can only be observed after the first 48 hours in the range of 70% to 100% RTV.

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Fig. 15: Color deviation of RTV values during accelerate ageing of paperboard with PCL-SiO₂ nanocomposite coating; a) Cyan, b) Magenta, c) Black, d) Yellow

Samples with PCL-ZnO (Figure 15) show significantly less color change for all RTV of cyan, magenta, and black tones. Largest deviation from the reference sample is in the area of lighter tones. These results confirm significant UV absorption in the range of 280 to 375 nm resulting in less color fading [27]. Comparing the results of the yellow tones (Figure 15d) with the reference sample, a decrease in color difference is visible in the 70% to 100% RTV range after 120h of irradiation. After 96 hours of radiation, the improvement is visible in the range of 50% to 70% RTV, while the remaining yellow tones throughout the exposure time are mostly consistent with the reference values.





Fig. 16: Color deviation of RTV values during accelerate ageing of paperboard with PCL-ZnO nanocomposite coating; a) Cyan, b) Magenta, c) Black, d) Yellow

The results indicate that the ZnO nanoparticle percentage was not large enough to reduce the cyan, magenta and black color fading, but large enough to reduce the effect of degradation in yellow tones. Other studies have shown that a higher ZnO nanoparticle content in the coating causes a higher degree of absorption of UV light and thus reduces degradation and fading of color [28]. The same conclusion can be drawn from UV-Vis results that indicate that a smaller portion of ZnO nanoparticle in PCL coating results in less absorption of UV irradiation. For UV absorption most commonly used are zink oxide, titanium oxide or cerium oxide (with an energy consumption greater than $_3$ eV), but photocatalytic activity predominantly depends on the nature of the polymer-filler-air behavior [29]. Therefore, modification of the nanoparticles ZnO and Al₂O₃ potentially enables the reduction of photocatalytic action on the color and improves their lightfastness. The results confim hypothesis H₂ that PCL coating modified with nanoparticles that absorb the UV part of the spectrum will slow down the process of print degradation

Unfortunately, the whole mechanism of the color degradation is not yet fully clarified. As pigments make up inks, their lightfastness plays an important role in the degradation



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mechanism. In inks, the pigments are dispersed within the emulsion composed of fillers and solvents, and they are 5-25% of the color composition. It is also assumed that the fillers and additives can contrubute degredation effect [23]. So each research in the field of color degradation contributes understanding and overall picture.

4. CONCLUSION

Research results presented in this paper can conclude that:

- mechanical properties of PCL and PCL nanocomposite coatings did not decrease the mechanical properties of GD₂ paperboard.
- because of the large coating-to-material thickness ratio no major improvement was achieved but there was a slight increase in mechanical properties of PCL-SiO₂ samples in tensile strength (CD direction) and inward bursting strength.
- the coated samples improved the rubbing resistance, and preserved the print (the downside is that the damaged coating can also negatively influence on the esthetical perception of the packaging)
- all nanocomposite coatings improved the lightfastness of the print. The least amount of color change was observed in the PCL-ZnO coating because of its absorption properties of UV radiation.

The obtained results can serve as an objective feature of assessing visual durability due to color degradation of the investigated coatings. Further research should investigate other biopolymers and nanocomposites in order to achieve the best results for durability, improvement of mechanical and optical properties as well as sustainability.



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DETERMINATION OF DEGRADATION KINETICS OF PHARMACEUTICALS

Matija Cvetnić, Lidija Furač, Dajana Kučić Grgić, Šime Ukić, Marinko Markić, Hrvoje Kušić, Ana Lončarić Božić, Tomislav Bolanča

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia

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Abstract

Due to the increasing use of pharmaceuticals in everyday life, there is growing water pollution. Particularly expressed are their increased concentrations in surface, underground and drinking waters that can not be reduced by conventional processing processes. For that reason, advanced oxidation processes (AOPs) can be used because of their effective removal rate of recalcitrant organic compounds. In this paper, removal rate from water for ten pharmaceuticals was measured by two AOP processes: UV/H_2O_2 and UV/PS. The following pharmaceuticals include desloratadine, desvenlafaxine, donepezil hydrochloride, etodolac, febuxostat, hydrochlorothiazide, memantine hydrochloride, omeprazole, silver sulfadiazine and tulathromycin. Experimental first order pseudokinetics were obtained for different concentrations of oxidant - hydrogen peroxide (H_2O_2) and sodium persulfate (PS). With the competitive reference compound, para-chlorobenzoic acid (pCBA), the second order rate of pharmaceutical removal was calculated.

Keywords: Dexamethasone, adsorption, RSM, chemicals of emerging concern

1. INTRODUCTION

Essential resource for sustaining humanity and life in general is water. Nowadays intensive pollution issues, and consequently lack of water quality in many areas in the world have raised awareness about the importance of water. Therefore, many conventions, directives, and protocols related to better water quality and management have been adopted during the last 20 years. Thus, European Union (EU) introduced in 2000 a list of 33 priority substances to control the chemical quality of water (Water Framework Directive, 2000/60/EC) (EU, 2000) which was later updated to 45 substances in 2013 (Directive 2013/39/EU) [1]. Furthermore, a special "watch list" was adopted in 2015 [2]. The list includes substances omitted in the Directive for which evidence suggested a possible risk to environment and for which a temporary monitoring was required. The Directive (and the "watch list") includes various pesticides and pharmaceuticals, particularly interested due to their applications; to be biologically active and persistent toward atmospheric conditions. Such properties suggest on their long-term stability and potential adverse effects in the environment. Hence, these artificial products can be considered as contaminants of emerging concern (CECs) [3].

The persistence of contaminants in water depends on their chemistry, as well as on the environment conditions and applied treatment for their elimination prior the discharge into natural environment. The later can be accomplished by several methods. Common (waste)water treatment plants (WWTP), based on primary (physical) and secondary (biological) methods, have showed fairly limited effectiveness in CECs removal [4]. On the other hand, chemical methods, particularly advanced oxidation processes (AOPs), showed much higher potential for CECs degradation and eventual elimination from the environment. One of the important characteristics of AOPs, besides the optimization of conditions applied in such multi-parameter systems, are the knowledge on the process kinetics determined by the rate constants between involved species. The knowledge on degradation rate constants of CECs, particularly newly introduced pollutants, with the most common reactive species generated by AOPs, hydroxyl (HO·) and sulfate (SO₄:-) radicals, are still scarce [5, 6, 7].

This research is aimed at determining the key structural features of CECs responsible for their susceptibility to be degraded by radical driven reactions occurring within AOPs. Hence, comparative methodology was applied to calculate the second-order degradation kinetics by HO· and SO₄·⁻ for CECs, more specifically pesticides and pharmaceuticals. However, our study is exclusively limited on the CECs and includes sulfate radicals based chemistry as well, which is according to available literature sources, rather scarce.

2. EXPERIMENTAL

Pharmaceuticals were all purchased from Sigma-Aldrich, USA or Acros Chemicals, USA and used as model pollutants. Information (names, formulae, CAS# and purities) are summarized in Tab. 1. The model solutions of the studied aromatics were prepared by dissolving respective quantities in deionized water (conductivity <1 μ S cm⁻¹). The degradation rate of was monitored by HPLC (Series 10, Shimadzu, Japan) equipped with UV–DAD (SPD-M1oAVP, Shimadzu, Japan) using XBridge BEH C18 column (13 nm, 3.5 mm, 2.1 mm x 150 mm), Waters, USA. The mobile phase was operated by isocratic flow at 0.5 mL min⁻¹ in all cases, while the ratio of organic (CH₃OH) and polar phase (0.1% HCOOH) was 50%:50%. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements. Initial pH was adjusted to pH = 7±0,1 with 0.01M NaOH or 0.01 M



 H_2SO_4 . Reactions with both oxidants were performed in 4 oxidant concentration ranges 0.2 mM, 0.5 mM, 1.0 mM and 2.0 mM while in all experiments, initial concetration of pharmaceuticals were 0.01 mM.

3. RESULTS AND DISCUSSION

Advanced oxidation processes have very complex mechanism, so it is very unlikely that reactive hydroxyl and sulphate radicals react only with the observed compound of the pharmaceuticals. For that reason, the reaction kinetics does not obey first-order kinetics, but actually pseudo-first-order kinetics what is presented on Fig. 1. for UV/H_2O_2 while for UV/PS system this is presented in Fig. 2. From the obtained values it can be concluded that higher kinetics values are achieved using persulfate as the oxidant in all compounds.

The second order kinetics is determined from the slope of linear curve which is shown graphically in Fig. 4. In order to obtain a constant value, the slope should be multiplied with the known kinetics of the reference compound, pCBA. For the UV/H₂O₂ system, the reference value for the reference compound is $k_{OH•}$, pCBA = $5 \cdot 10^9 M^{-1} s^{-1}$, whereas for the UV/PS system this value for pCBA is k_{SO4-} , pCBA = $3.6 \cdot 10^9 M^{-1} s^{-1}$ [8]. The equations for calculation second order kinetics are shown in equations 1 and 2:

$$k_{R,S} = k_{R,pCBA} \cdot \left(\frac{ln(\frac{c_t(S)}{c_0(S)})_T - ln(\frac{c_t(S)}{c_0(S)})_{UV-C}}{ln(\frac{c_t(pCBA)}{c_0(pCBA)})_T - ln(\frac{c_t(pCBA)}{c_0(pCBA)})_{UV-C}} \right)$$
(1)

where $k_{R,S}$ is calculated second order kinetics, $k_{R,pCBA}$ is second order rate of pCBA from literature, $c_t(S)$ is concentration of CEC in time t, $c_o(S)$ is initial concentration of CEC, $c_t(pCBA)$ is concentration of pCBA in time t, $c_o(pCBA)$ is initial concentration of pCBA.

This equation 1 can be simplified:

$$k_{R,S} = k_{R,pCBA} \cdot \left(\frac{k(S)_T - k(S)_{UV-C}}{k(pCBA)_T - k(pCBA)_{UV-C}}\right)$$
(2)

where $k_{R,S}$ is calculated second order kinetics, $k(S)_T$ is first-order kinetics of CEC, $k(S)_{UV-C}$ is first-order kinetics of CEC degradated by UV-C only, $k(pCBA)_T$ is first-order kinetics of pCBA, $k(pCBA)_{UV-C}$ is first-order kinetics of pCBA degradated by UV-C only

The obtained values of the pseudo-first-order kinetics are dependent on the oxidant concentration what is shown in Fig. 3. and in Tab. 1. As can be seen from values in Tab. 1., first order kinetics are linearly increasing with the increament of an oxidant with different slope. That slope has to be calculated in order to determine second order rate constants.

Taken into consideration that degradation of CECs by hydroxyl (HO·) and sulfate (SO₄·⁻) radicals are completely different oxidation mechanisms, first and second order kinetics are different for both of them, sulfate (SO₄·⁻) radicals degradated organic structure via electron transfer mechanism, while hydroxyl (HO·) radicals combines processes of addition and H-abstraction [8]. As can be seen from Tab. 2, Tulathromycin has the lowest kinetics for both processes, so that means that that compound is the most recalcitrant. It can be because of its large and compact structure without halogen elements. Similar observation can be applied for donepezil hydrochloride where electrons are localized within benzene ring. For every other compound, the values are similar with the same pattern. Second order rates are higher

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for HO· radicals due to addition of hydroxyl group to the compound. Because of the properties of this choosen CECs, their stability is very high and because of that, degradation by SO_4 ·- radicals are slower.



Fig. 1: Degradation of Desloratadine by UV/H₂O₂



Fig. 2: Degradation of Desloratadine by UV/PS



Fig. 3: Testing the rate of degradation kinetics of Desloratadine by UV/H₂O₂ and UV/PS







Spoj	c _{oxidant} , mM	k _{UV/H2O2} , s ⁻¹	k _{UV/PS} , s⁻¹
	0,2	0,084	0,106
Desloratadine	0,5	0,089	0,119
	1,0	0,097	0,143
	2,0	0,113	0,284
-	0,2	0,029	0,032
Desvenlafaksin –	0,5	0,035	0,080
-	1,0	0,050	0,140
	2,0	0,062	0,167
Donenezil	0,2	0,005	0,041
hidroklorid	1.0	0,005	0,002
	2,0	0,009	0,135
	0.2	0.070	0.142
	0,5	0,088	0,182
Etodolac –	1,0	0,093	0,240
	2,0	0,095	0,309
	0,2	0,094	0,114
Febuweetet	0,5	0,103	0,131
rebuxustat	1,0	0,110	0,203
	2,0	0,120	0,261
_	0,2	0,030	0,045
Hydrochlorothiazid	0,5	0,043	0,059
е	1,0	0,055	0,114
	2,0	0,062	0,256
_	0,2	0,042	0,090
Memantine HCl	0,5	0,050	0,139
	1,0	0,071	0,177
	2,0	0,082	0,233
_	0,2	0,081	0,075
Omeprazole –	0,5	0,091	0,107
	1,0	0,107	0,166
	2,0	0,121	0,204
_	0,2	0,035	0,121
Silver sulfadiazine	0,5	0,044	0,250
_	1,0	0,052	0,441
	2,0	0,061	0,494
	0,2	0,025	0,060
Tulathromycin	0,5	0,034	0,096
	1,0	0,040	0,127
	2,0	0,044	0,149

Tab. 1: Results of pseudo-first-order kinetics of pharmaceuticals

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Fig. 4 is graph representation of equation 2, where it is important to see that $\left(\frac{k(S)_T - k(S)_{UV-C}}{k(pCBA)_T - k(pCBA)_{UV-C}}\right)$ is a slope of linear line. Determination of that slope is important information about pseudo-first order kinetics. From that value, second order kinetics is calculated. The slope is after that multiplied by second order rate of pCBA to get second order rate of CEC (literature data) [8].

Table 2 shows the values of the slopes for the observed compounds and the corresponding second order kinetics. The second order kinetics are obtained in the manner described previously in text. The high values of R^2 indicate the the model selection is correctly applied.

Compound	Slope	R ²	<i>k</i> он•/10 ⁹ М ⁻¹ s ⁻¹	Slope	R ²	<i>k</i> _{SO4-} ./10 ⁹ M ⁻¹ s ⁻¹
Desloratadine	0,4116	0,8171	2,058	2,4467	0,8965	0,934
Desvenlafaxine	0,5062	0,8962	2,531	1,808	0,8983	0,651
Donepezil HCl	0,1430	0,7106	0,715	1,2988	0,9847	0,468
Etodolac	0,3959	0,9383	1,980	2,2732	0,9883	0,818
Febuxostat	0,3854	0,9534	1,927	2,1250	0,9899	0,765
Hydrochlorothiazide	0,4997	0,9922	2,499	2,9716	0,9598	1,070
Memantine HCl	0,6340	0,9152	3,170	1,8592	0,9554	0,669
Omeprazole	0,6106	0,9316	3,053	1,7867	0,9603	0,643
Silver sulfadiazine	0,3916	0,9652	1,958	5,0723	0,0886	1,826
Tulathromycin	0,2965	0,9998	1,483	1,1535	0,8976	0,415

Tab. 2: Statistical parameters of slopes and corresponding second order kinetics

4. CONCLUSION

The aim of this paper was to remove desvenlafaxine, donepezil hydrochloride, etodolac, febuxostat, hydrochlorothiazide, memantine hydrochloride, omeprazole, silver sulfadiazine and tulatromycin from the aquatic environment and to monitor the reaction behaviour in the study.

Advanced oxidation processes of UV photolysis and UV with hydrogen peroxide and sodium persulfate as an oxidant have been used. For the four concentrations of each oxidant, the values of the decomposition kinetics of the first order were obtained. While with using the reference compound, pCBA, second order kinetics were obtained.

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DEXAMETHESONE REMOVAL SIMULATION BY ADSORPTION ON IRON(III) HYDROXIDE

Matija Cvetnić, Dora Furač, Lidija Furač, Dajana Kučić Grgić, Šime Ukić, Marinko Markić, Hrvoje Kušić, Ana Lončarić Božić, Tomislav Bolanča

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia

<u>Original scientific paper / Izvorni znanstveni rad</u>

Abstract

Pharmaceuticals, listed as chemicals of emerging concers are new class of pollutants. Theirs extremely stable organic structure, toxicity to the living world and resistancy to biological and photolytic degradation are forthcoming issue. Conventional wastewater treatment methods have been insignificantly efficient for their removal. Therefore, it is necessary to explore and develop additional methods to improve the efficiency of their removal. The aim of this work was to investigate the removal of pharmaceutical dexamethasone by adsorption on iron(III) hydroxide at different pH values and different concentration of the adsorbent. The intention was to reduce level of the pollution in effluent of wastewater treatment process. The experiments indicated that efficiency of pesticide removal was affected by both tested parameters. Based on the obtained results, the removal was described by the response surface methodology and the optimal process conditions were determined. An ANOVA analysis was performed to evaluate the validity of the developed model. The experimental design, statistical analysis, and ANOVA were performed using thesoftware package Design Expert 10.0, StatEase, USA.

Keywords: Dexamethasone, adsorption, RSM, chemicals of emerging concern

1. INTRODUCTION

Water has always been receiver of solid and liquid waste to the human population in history [1]. The increase in population and industrial and technological progress have led to an increase in the volume of discharged municipal and industrial wastewaters, as well as the pollution of surface and groundwater [2]. The pollution of the water environment is becoming the burning problem of all humanity, it posible has a harmful effect on human health and a food chain globally [3]. For the purpose of protecting the environment and human population, before discharging wastewater into recipient it is necessery to treat that water. Elimination of main sources of pollution is defined by legal regulations and subjected to monitoring. However, with development of pharmaceutical industry, the presence of new and mutually distinct synthetic chemical compounds has not been sufficiently explored and are considered potentially toxic to the environment and human health [4]. European Union Environmental Legislation has identified this problem and in the long term defined a water policy strategy in the European area through the Water Framework Directive [5]. Its Annex X. contains a list of priority substances suspected of being contaminants that pose a potential risk to the aquatic environment. A large proportion of pharmaceuticals are listed on the "watch list" and scientific researches are carried out to determine their toxicity, wastewater disposal, bioaccumulation and biodegradation, in order to define the environmental effect on those priority substances [6].

Dexamethasone (DXT) is a synthetic hormone with an anti-inflammatory effect. It is often used for the treatment of humans and animals and is one of the most used glucocorticoid drug in the last few decades. The main issue about DXT is that its properties and wide consumption can give negative effect on the environment, human and animal health [7].

In order to reduce the water load at the effluent in the wastewater treatment plant terciary processes must be added. The way to avoid this adjustment of the wastewater treatment plant is to investigate the possibilities to reduce pharmaceuticals in pre-existing process. One way is to investigate the adsorption of pharmaceutical dexamethasone on iron(III) oxides salts, such as iron(III) sulphate heptahydrate ($Fe_2(SO_4)_3 \cdot 7H_2O$) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$). These chemicals have common usage as a coagulants added in aqueous solutions where they hydrolyze by creating soluble monomers, dimers or polymer hydroxymethyl complexes that destabilize colloidal particles, Fig. 1 [8-10].



Fig. 1: Schematic of processes coagulation and flocculation

The purpose of this paper is to investigate the removal of dexamethasone pharmaceutical by adsorption onto iron(III) hydroxide ($Fe(OH)_3$) at different pH values and different concentrations of adsorbents. On the basis of the obtained results, the removal is described by the response surface model and the optimal process conditions are determined. An



analysis of the variance was carried out for the purpose of the validation of the developed model. Design of experiment, statistical analysis and variance analysis were carried out using the Design Expert 10.0, StatEase, USA, program package.

2. EXPERIMENTAL

Dexamethasone (DXT) were purchased from Sigma-Aldrich, USA and used as model pharmaceutical pollutant. The model solution of dexamethasone were prepared by dissolving respective quantities in deionized water (conductivity <1 μ S cm⁻¹). The degradation rate of was monitored by HPLC (Series 10, Shimadzu, Japan) equipped with UV–DAD (SPD-M10AVP, Shimadzu, Japan) using XBridge BEH C18 column (13 nm, 3.5 mm, 2.1 mm x 150 mm), Waters, USA. The mobile phase was operated by isocratic flow at 0.5 mL min⁻¹ in all cases, while the ratio of organic (CH₃OH) and polar phase (0.1% HCOOH) was 50%:50%. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements.

3. RESULTS AND DISCUSSION

The aim of this paper was to remove dexamethasone from aqueous solution by adsorption using $Fe(OH)_3$ and to determine the effect of process parameters on the DXT removal efficiency. pH-value varied from 4 to 10, and the concentration of adsorbents expressed as the ratio of the concentration of priority pollutants and adsorbents, was varied from 1:1, 1:10 and 1:20 (designated in equation 1 as c(OX). In Tab. 2. are presented coded and real values of the process variables according to the design of experiments. Results of the DXT removal were obtained through analysis by HPLC and presented in Tab. 2 in form of removal conversion in percentage.

No. exp.	coded	рН	coded	[PO]:[Fe(OH) ₃], mM	Conversion, %
1	-1	4	-1	1:20	85.4
2	0	7	-1	1:10	81.1
3	1	10	-1	1:1	82.7
4	-1	4	0	1:20	88.6
5	0	7	0	1:10	84.1
6	1	10	0	1:1	86.2
7	-1	4	1	1:20	92.9
8	0	7	1	1:10	83.9
9	1	10	1	1:1	87.7

Tab. 1: Coded and real values of the process variables and adsorption removal of DXT	by design
of experiments	_

From results from Tab. 2 multi-regression analysis of the design matrix and corresponding response were resulted in the second-order polynomial equation (model, equation 1) for predicting the behavior of the observed system:



$$X = 83,4889 - 1,71667 * pH + 2,55 * c(OX) - 0,625 * pH * c(OX) + 4,21667 * pH^2 - 0,68333 * c(OX)^2$$
(1)

According to the model, the optimal adsorption conditions of DXT in water are pH = 4 and with $[PO]:[Fe(OH)_3] = 1:20$. The analysis of variance (ANOVA) is a test of the ability of a developed model to observe the variability of the data and their significance. The analysis of variance has resulted and statistical model parameter parameters are presented in Tab. 2.

Analysis of variance									
Factor	SS	df	MSS	F	р	PRESS	R²		
Model	94.75	5	18.95	10.14	0.04	64.38	0.9441		
рН	17.68	1	17.68	9.46	0.05				
c(OX)	39.02	1	39.02	20.87	0.01				
pH · с(ОХ)	1.56	1	1.56	0.84	0.43				
рН²	35.56	1	35.56	19.02	0.02				
с(ОХ)²	0.93	1	0.93	0.50	0.53				

Tab. 2: Statistical parameters for model of the design matrix

SS – sum of error squares; df – degrees of freedom; MSS – mean of sum of error squares; F – F-value of model; p – probability; PRESS – predicted residual error sum of squares; R^2 – coefficient of determination

Based on the *p*-value of the model, which must be less than 0.05, it is concluded that the model significantly describes the variability of the dependent variable with model is *p*-value of 0.04. High value of the regression coefficient: $R^2 = 0.9441$, indicates that 94.41% of the variance is a consequence of changes in the value of independent variables, while the remaining 5.59% is the result of the error. Considering the low *p*-values of for both process parameters (pH and [PO]:[Fe(OH)₃]), it can be concluded that the pH of the solution and the adsorbent concetration significantly influence the DXT adsorption. The combined effect of the process parameters is shown in the three-dimensional view in Fig. 2.





Fig. 2: Combined effect of the process parameters on DXT removal

In order to resolve the adsorption mechanism and to explain the obtained results, it should be noted that in all adsorption processes, the pH of the solution directly affects the properties of the adsorption surface and the ionic forms of the pharmaceutical in the solution. The type and ionic state of the functional group of pharmaceuticals and adsorbent surfaces are the main factors that will depend on the effectiveness of the removal or the adsorption process. DXT contains several functional groups (carbonyl: C=O, carboxylic: -COOH, and hydroxyl: -OH) wherein the largest dipole produces oxygen in the carbonyl C=O group due to two free electronic pairs, and the pharmaceuticals are adsorbed precisely through this group. The pK_a value of DXT is 6 and is protonated up to this value, and above pH=6 is in deprotonated form.

In order to determine the effect of pH, three values of pH 4, 7 and 10 were selected. From Fig. 2 it is visible that the DXT removal efficiency increases in lower pH region and that the maximum is at pH = 4. If we look at the distribution diagram of the species for $c(Fe^{3+}) = 2 \text{ mM}$ (Fig. 3.), it is evident that at pH 4 the monomeric hydrolytic products of $Fe(OH)^{2+}$ and $Fe(OH)_{2^+}$ predominate in equal proportions. At pH 7, only one monomer hydrolytic species and $Fe(OH)_{2^+}$ are present, and at a pH of 10, the monoclear type of the negative charge $Fe(OH)_{4^-}$. From the above, it can be concluded that in the acidic region at a lower pH of 4 a higher number of H⁺ ions in the solution, and therefore the adsorption surfaces of the flocculation are positively charged. The positively charged surface with strong electrostatic forces attracts DXT via oxygen dipole on the carbonyl group. In the neutral pH range, the number of H⁺ ions decreases, and adsorption decreases because the surface is neutrally charged. In the alkaline region, at pH 10, the concentration of OH⁻ ions increases, but at the same time deprotonation of dexamethasone is positively charged, and therefore electrostatic adsorption is more than in the neutral region.






Fig. 3: Fe_3^+ species through whole pH range

For the determination of the effect of adsorbents, three different concentrations are shown that are expressed through the ratio of dexamethasone and adsorbents, and are $[PO]:[Fe(OH)_3] = 1:1, 1:10$ and 1:20. An increase in the adsorbent concentration increases the efficiency of removal as the number of floating adsorption sites increases on the surface of the flocculation.

From the above, it is concluded that the maximum adsorption effect, ie the dexamethasone removal, is most effective at the lowest pH and above the adsorbent concentration, which model shows: pH = 4 and the ratio [PO]: $[Fe(OH)_3] = 1:20$. For the purpose of determining the exact DXT adsorption mechanism for the further research should be carried out.

4. CONCLUSION

The aim of this paper was to remove dexamethasone from aqueous solution by adsorption using $Fe(OH)_3$ and determine the effect of process parameters on the processing efficiency. The combined influence of process parameters is shown by the response surfaces methododology and the optimal process conditions are determined: pH = 4 and $[PO]:[Fe(OH)_3] = 1:20$. The coefficient of regression coefficient $R^2 = 0.9441$ points the ability of the model to describe 94.41% of the variation of the dependent variable.

Based on the results, two mechanisms of adsorption of dexamethasone are proposed, protonated surface $Fe(OH)_3$ ligand binding by electrostatic attraction via the carboxyl group and hydrogen bond through polar functional total (hydroxyl, carbonyl or carboxyl).

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QSAR MODELS FOR PREDICTION OF BIODEGRADABILITY OF PHARMACEUTICALS IN WATER

Matija Cvetnić, Ana Tolić, Marija Sigurnjak, Dajana Kučić Grgić, Šime Ukić, Marinko Markić, Hrvoje Kušić, Ana Lončarić Božić, Tomislav Bolanča

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia

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Abstract

Increment of pharmaceutical usage has resulted in accumulation of active substances and their metabolised byproducts in the aquatic environment. The accumulation of such substances carries out a whole range of negative consequences for the entire ecosystem. The European REACH Directive advocates the development of the QSAR/QSPR models which can lead to reduction in the number of experiments thereby saving valuable time and money so as minimizing testings on animals. The aim of this paper is to develop a model for predicting the biodegradability of pharmaceuticals in water. For that purpose, biodegradability for 18 pharmaceuticals has been determined experimentally. Biodegradability is defined as a BOD5/COD ratio. Obtained pharmaceutical biodegradability values were correlated with their structural properties using the QSAR methodology. According to the statistical analysis, threevariable model was taken as the most appropriate for prediction of biodegradibility. The acquired models were internally and externally validated and the given values of the statistical parameters for the prediction of biodegradation are: R2 = 0,9320, Q2 = 0,7989 for the training set, and R2 = 0,6490 in the validation set.

Keywords: QSAR modelling, biodegradation, pharmaceuticals, chemicals of emerging concern

1. INTRODUCTION

There is an essential human need for clean water and a functional environment, which is threatened by mostly man-made various pollutants such as reactants, products and wastes of various industries. These possiblly toxic chemicals reach the aquatic environment resulting in a serious threat to flora, fauna and humans [1, 2]. One of the most relevant groups of micropollutants are pharmaceuticals due to their possible adverse effect on aquatic ecosystems. Chemo-physical properties of the pharmaceuticals engineered to remain unchanged during their transfer through the human body, can cause a lots of environmental problems. These difficulties are also correlated to their capacity of being incompletely reduced after purification in WWT plants [3-6]. Pharmaceuticals in the environment are detected worldwide, both groundwater and surface water [7] and even drinking water [8]. Therefore, European Parliament and Council lays down a strategy against the pollution of water amending the Directives 2000/60/EC and 2008/105/EC with the latest update known as Directive 2013/39/EU. Preventive actions, the identification of pollution causes, dealing with emissions of pollutants at the source, and development of innovative water/wastewater treatment technologies is promoted by Directive [9]. Besides the Directive, the European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), requires the information on ready biodegradation as a screening test for assessing biodegradability of chemicals. Simultaneously, REACH encourages the use of alternatives to time- and money consuming experimental analyses, which sometimes require animal testing [10]. The alternative, throughout providing fast and reliable data, is guantitative structureactivity relationship (QSAR) modeling, which is based on direct relationship between pollutant structural characteristics and targeted biological activity such as biodegradability and toxicity. Recent literature suggests that QSAR may be utilized to predict toxicity in a variety of chemical classes towards different test organisms [11-13], while the corresponding biodegradability data are relatively scarce. Several QSAR studies dealt with the biodegradability prediction in order to estimate the fate and ecological hazard of targeted chemical classes [10, 14-16].

Accordingly, the goal of this study is to develop quantitative models for accurate prediction of the biodegradability as an important water quality parameter. For this purpose, we selected 18 different type of pharmaceutical compounds, and determined their biodegradability in terms of BOD₅/COD ratio. Values obtained were afterwards used as the representative responses in QSAR modeling; the obtained models were then internally and externally verified to gain accuracy result.

2. EXPERIMENTAL

Pharmaceuticals were all purchased from Sigma-Aldrich, USA or Acros Chemicals, USA and used as model pollutants. Information (names, formulae, CAS# and purities) are summarized in Tab. 1. The model solutions of the studied aromatics were prepared by dissolving respective quantities in deionized water (conductivity <1 μ S cm⁻¹). The measurements of chemical (COD) and biochemical oxygen demand (BOD5) of model solutions prior and after the treatment were performed by colorimetric method using HACH DR2800 spectrophotometer, Hach Lange, USA, equipped with a barcode reader. In COD analysis, Lange reagent kit LCK514 was used. For BOD measurements, Lange reagent kit LCK554 was used. The biodegradability was expressed as BOD5/COD ratio.





Pharmaceutical	Molecular formula	CAS #	Purity	Log (BOD5/COD)
Desloratadine	$C_{19}H_{19}CIN_2$	100643-71-8	>98%	-1,013
Desvenlafaxine hydrochloride	$C_{16}H_{25}NO_2$	93413-62-8	>98%	-1,129
Enroflaxacin	$C_{19}H_{22}FN_3O_3$	93106-60-6	>99,0%	-1,067
Etodolac	C ₁₇ H ₂₁ NO ₃	41340-25-4	>98%	-1,222
Febuxostat	$C_{16}H_{16}N_2O_3S$	144060-53-7	>98%	-0,978
Hydrochlorothiazide	$C_7H_8CIN_3O_4S_2$	5 ⁸ -93-5	>98%	-0,893
Hydrocortisone	$C_{21}H_{30}O_5$	50-23-7	>98%	-1,144
Carfilzomib C ₄₀ H ₅₇ N ₅ O ₇		868540-17-4	97%	-0,757
Levamisole	$C_{11}H_{12}N_2S$	14769-73-4	>98%	-0,942
Lidocaine	C ₁₄ H ₂₂ N ₂ O	137-58-6	>98%	-1,093
Omeprazole	$C_{17}H_{19}N_3O_3S$	73590-58-6	>98%	-1,249
Procaine C13H20N2O2		59-46-1	>98%	-0,358
Silver(I) sulfadiazine C10H9AgN4O2S		22199-08-2	98%	-0,630
Sulfadiazine C ₁₀ H ₁₀ N ₄ O ₂ S		68-35-9	98%	-0,898
Sulfaguanidine C ₇ H ₁₀ N ₄ O ₂ S		57-67-0	>99%	-0,602
Sulfamethazine	C ₁₂ H ₁₄ N ₄ O ₂ S	57-68-1	99,0%	-0,754
Tetramisole	$C_{11}H_{12}N_2S$	5036-02-2	99%	-1,642
Tobramycin	C ₁₈ H ₃₇ N ₅ O ₉	32986-56-4	>99,0%	-1,831

Tab. 1: List of pharmaceuticals with included technical data and biodegradability of pollutants transformed logaritmically

2.1. Calculations

Molecular structures of studied pharmaceuticals were built using Chem₃D Pro software (ChemOffice 15.0, Perkin Elmer, USA) and optimized by RM1 method using MOPAC2012 interface. The molecular descriptors have been calculated by DRAGON 6.0 software (Milano chemometrics & QSAR research group, TALETE, Italy). The correlation between targeted QSAR responses, i.e. biodegradability and structure related descriptors (DRAGON generated and computed in a semiempirical quantum chemical fashion) was obtained using the variable selection Genetic Algorithm (GA) and Multiple Linear Regression Analysis (MLRA) methods. The combination of the GA-MLRA technique was applied for the selection of descriptors and construction of 1-, 2-, and 3-variable models using QSARINS 2.2. (QSAR Group, University of Insubria, Italy). GA variable selection technique started with a population of 200 random models and 2000 iterations to the evolution with the mutation probability specified as 20%. The selection and validation of models was performed by comparing values of selected statistical model performances: R (the correlation coefficient of regression); R^2 (the model explained variance); F (F-ratio between the variances of observed and calculated property/activity); p (probability value for calculated F); Q^2 (the leave-one-out crossvalidation coefficient); s (standard error); and SPRESS (standard error of the predictive residue of sum of squares). The validation of models, selected as the best for each chosen response, was also performed using Leave Many Out (LMO) and "Y-scrambling" tests.





3. RESULTS AND DISCUSSION

For aforementioned pharmaceuticals, biodegradability has been experimentally determined. Pharmceutical water solutinos were prepared in concentration of 0,1 mM. From the results obtained, only procaine is easy biodegradable (BOD5/COD > 0,4), carfilzomib, silver(I) sulfadiazine, sulfamethazine and sulfaguanidine are slightly biodegradable (0,2 < BOD5/COD < 0,4). The rest of pharmaceuticals are not biodegradable ((BOD5/COD < 0,2). Pharmaceutical biodegradability was correlated with structural features of every compound. Validation set has 3 randomly chosen compounds while training set is consisted of 15 compounds. For developing QSAR models, whole set of descriptors (gained by Dragon software) were set as an independent variables while dependent variable was logarithmic value of biodegradability in GA-MLRA. Statistical parameters for best 1-, 2- and 3-variable QSAR models are shown in Tab. 2.

MODEL	STATISTICAL PARAMETERS				
1-variable	R ²	Ra²	Q ²	F	S
BIC4	0,5764	0,5438	0,4417	17,6865	0,2576
2-variable					
VR2_B(i), H-053	0,7985	0,7650	0,6722	23,7810	0,1849
3-variable					
nRo5, VR2_B(i), H-053	0,9320	0,9135	0,7989	50,2874	0,1122

Tab. 2: Statistical parameters for best 1-, 2- and 3-variable QSAR models

Complexicity of models increases by increasing the number of variables, hence 3-variable model has been chosen as the best. High values of R^2 , R_a^2 and Q^2 demonstrate the accuracy and reliability of the model with predictive capabilities. The model significance is proved through *p*-value of all variables included in model, Tab. 3. Model robustness is proved through LOO and LMO internal methods with values of Q_{LMO^2} and Q_{LOO^2} 0,799 and 0,831, respectively. In order to show that the model is not the result of random correlation, an *Y*-scrambling test was applied, Fig. 1.

DESCRIPTOR	COEFFICIENT	RMSE	<i>p</i> -value
Intercept	3,1173	0,7843	0,0016
nRo5	-0,2611	0,0562	0,0005
VR2_B(i)	-3,7752	0,7603	0,0003
Н-053	-0,2858	0,0293	0,0002

Tab. 3: Statistical	parameters	of 3-variable	QSAR model
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Fig. 1: Y-scramble test of a 3-variable QSAR model

In the last step of QSAR model development, graphical representation of the predicted data relative to the experimental is analyzed, Fig. 3, this is fundamental for accepting the model as a predictive one. The distribution of points is near to the line y=x which confirms the reliability of the model. The use of Williams plot, gives graphical evidence that there is no outlier in the training set nor validation set. It was concluded that the data set used in this study is appropriate for the investigation carried out, Fig. 4.



Fig. 2: Experimental vs predicted values of the 3-variable model





Fig. 3: Williams plot of the 3-variable model

QSAR model equation is represented in the Eq. 1.

$$\log\left(\frac{\text{BPK}_{5}}{\text{KPK}}\right) = -0,2611 \cdot (\pm 0,0562) \cdot nR05 - 3,7752 \cdot (\pm 0,7603) \cdot VR2 B(i)$$

$$-0,2858 \cdot (\pm 0,0293) \cdot H - 053 + 3,1173 \cdot (\pm 0,7843)$$
(1)

Equation 1 shows descriptors with their coefficients. The first descriptor, nRo5, denotes the number of five-membered rings. It belongs to a group of constitutional descriptors. This descriptor group is based on simple structural facts completely independent of the conformation of the molecule and the connection of the atom [17]. In this case, the negative index of its coefficient means that the compounds with a high value of nRo5 (molecules with a higher number of five-membered rings) will have less biodegradability. Descriptor H-053 denotes the number of hydrogen atoms attached to the sp³ carbon atom with two heteroelectronegative atoms (e.g. O, N, S, P, halogens) that are attached to the adjacent carbon atom. According to the type of information it carries, H-053 belongs to a group of "atomcentered fragments" (ACF). Such descriptors are obtained by decomposing the molecule into structural moieties, wherein each non-hydrogen atom molecule acts as an ACF center. ACF varies with respect to the link length of a central atom with adjacent atoms (including hydrogen) and is described by the elements and the connection environment [18]. Also, this descriptor is in a negative relationship with biodegradability. Higher H-053 value will contribute with lower biodegradability of the compound. According to the dimension of the information it carries, it belongs to the 1D group of descriptors that provide information on the number and properties of substituents, fragments of these functional groups. The last descriptor VR2_B(i) belongs to the group of 2D descriptors. It is defined as the Randic index

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based on the inherent Burden matrix vector weighted by the ionization potential. These descriptors are calculated on the basis of the so-called elements. graph-theoretical matrix using several algebraic operations [19]. The negative coefficient of this descriptor indicates lower biodegradability of the compound with higher value of the descriptor. The first two descriptors, nRo5 and H-o53, indicate that the biodegradability of the compound is influenced by the number and type of substituents. However, the described biodegradability of the compound according to this model can only be explained by the synergistic action of the descriptor, i.e. the explanation of the biodegradability individually with each descriptor is not complete and precise enough.

4. CONCLUSION

The aim of this paper was to develop a model according to experimentally determined biodegradability which was quantified over the ratio of biochemical oxygen demand, BOD5 and chemical oxygen demand, COD. Developed QSAR models can predict the biodegradability of the non-tested compounds.

Also, obtained QSAR models reveal the main factors that affect biodegradability and they include:

- 2D structure of the compound,
- Type and number of supstituents,
- Ionization potential.

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INFLUENCE OF THE STRESS RATE ON THE RESULTS OF TENSILE TESTING

Danko Ćorić¹, Matija Sakoman¹, Roman Dragojević¹

¹ University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture

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Abstract

In this paper the influence of testing rates on the results of tensile test was investigated. At different stress rates in the range of 2 to 100 MPa·s⁻¹, the values of proof strength, tensile strength and percentage elongation after fracture have been determined. Tests shown a significant influence on the testing rate on the values of the measured properties. At higher testing rates, the value of the proof strength and tensile strength increases as the material ductility decreases. Increase in stress rate causes an increase in strain rate during elongation of the test piece on the testing machine, which induces higher material strengthening by cold working (strain hardening) mechanism that is reflected in the increase in mechanical characteristics. The correlation between the tested properties in relation to the testing rate has been successfully determined through the conducted tests. The test results indicate that elastic materials such as aluminum, characterized by more pronounced deformation increase during elongation on the testing machine must be examined at lower stress rates, due to lower influence of strain hardening.

Keywords: tensile testing, stress rate, strain rate, mechanical properties, aluminium

1. INTRODUCION

The properties of the material in general, including mechanical, are closely related to the microstructure of the tested material which is determined by its chemical composition and the technological process of producing it. Establishing a correlation between the properties and the structure of the material is possible only with ideal substances. For real materials that contain various irregularities of crystal structure which have a significant effect on their properties, it is not possible by mathematical models to quantify the influence of every single factor influencing the properties. Therefore, the properties of real materials are determined solely by experimental tests in conditions that imitate environmental conditions. [1, 2]

One of the most important material properties are the mechanical properties that are crucial in selecting materials for a technical application. These mechanical properties will represent the durability of materials under short- or long-term static, dynamic or impact load at a certain temperature or specific ambient conditions. The mechanical properties of the material are determined by various tests, and one of the basic tests is the tensile test in accordance with HRN EN ISO 6892-1: 2016. The test determines the behavior of the material under uniaxial tensile load, where the elastic and plastic deformation of the material under load is monitored. During the tensile test, the basic mechanical properties quantifying the mechanical resistance of the material are determined. For the validity of the test results, it is important to properly adjust the test parameters, which among other include the testing rate. [4-7] According to the mentioned standard, the speed of testing is determined in accordance with two methods:

- 1. testing rate based on strain rate control (method A),
- 2. testing rate based on stress rate (method B) [3].

In this article, method B has been selected according which has the testing rate based on the rate of stress increase in the test piece during the tensile test on the testing machine. Unless otherwise specified, any convenient speed of testing may be used up to a stress equivalent to half of the specified yield strength or proof strength. The testing rates above this point depend on the specific stresses which are determined by testing. In the case of measuring proof strength (plastic extension) R_p , the rate of separation of the crossheads of the machine shall be kept as constant as possible and within the limits corresponding to the stress rates (\dot{R}) in Table 1 within the elastic range. [3]

	-	
Modulus of elasticity	Stress rate, <i>R</i>	
of the material, <i>E</i>		
MPa	MPa·s⁻¹	
	min.	max.
< 150000	2	20
	C	<u> </u>

T	ab.	1:	Stress	rate	[3]
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It is obvious that the stress rate within the elastic range shall conform to the requirements depending on the nature of the material and its stiffness determined by modulus of elasticity. Typical materials having a modulus of elasticity smaller than 150000 MPa include

magnesium, aluminum alloys, brass, and titanium. Typical materials with a modulus of elasticity greater than 150000 MPa include wrought iron, steel, tungsten, and nickel-based alloys [8].

Within the plastic range and up to the proof strength (plastic extension), the strain rate shall not exceed 0.0025 s⁻¹. If the testing machine is not capable of measuring or controlling the strain rate, a crosshead separation rate equivalent to the stress rate given in Table 1 shall be used until completion of yield. After determination of the required yield/proof strength properties, the test rate may be increased to a strain rate (or equivalent crosshead separation rate) no greater than 0.008 s⁻¹. [3]

The assumption of this article is that the higher stress rates will cause higher work hardening and by doing so will increase the rise in mechanical properties of a material.

2. MATERIALS AND METHODS

- Experimental testing was carried out on aluminum test pieces tensile loaded at different stress rates.

- The test pieces were made of unalloyed aluminum with a purity of 99.5% according to EN 1050. For testing purposes, test pieces with coefficient of proporcionality k = 11.3 with shoulder heads were used, dimensions of the test part as follows: parallel length (L_c) 135 mm, original gauge length (L_o) 100 mm and original diameter (d_o) 10 mm, Figure 1.



Fig. 1: Aluminum test piece

Original cross-sectional area of the parallel length of test piece (S_0) is determined from the eguation [3]:

$$S_o = \frac{d_o^2 \cdot \pi}{4} (\text{mm}^2) \tag{1}$$

- When loading the test piece on the testing machine the basic mechanical properties of material are characterized such as [3]:

• proof strength for 0.2 plastic extension, *R*_{p0.2}:

$$R_{p0.2} = \frac{F_{p0.2}}{S_o} \text{ (MPa)}$$
(2)

where $F_{po.2}(N)$ proof (yield) force,

• tensile strength, *R*_m:

$$R_m = \frac{F_m}{S_o}$$
(MPa) (3)





where $F_{m}(N)$ maximum force,

percentage elongation after fracture, A_{11.3}:

$$A_{11.3} = \frac{\Delta L_f}{L_o} \cdot 100$$
 (%) (4)

where $\Delta L_f(mm)$ extension at fracture.

- All the tests were carried out on a hydraulic testing machine (manufacturer: WPM, Germany; type: EU 40mod; measuring system: pressure transducer, digital scale, measuring range: 0 - 400 kN; class of machine range: 1) with electronic extensometer (type: MFA 2; electric resistance: 350Ω m; output signal maximum value: 2mV/V; maximum measurement length: 2 mm) that was used to precisely determine the extension at each specific force in real time. For conducted tests the gap between the contact points in the extensometer (extensometer gauge length, L_e) was set to 50 mm.

- Tensile testing was carried out at various testing rates based on stress rates which amounted 2, 5, 10, 20, 30, 50 and 100 MPa·s⁻¹. The first four of the stress rates (2, 5, 10, 20 MPa·s⁻¹) correspond to the values specified in Table 1, while the higher test speeds 30, 50 and 100 MPa·s⁻¹ exceed the permissible values and are allowed only at stiffer materials (E \geq 150000 MPa), except for 100 MPa·s⁻¹. On each of the above mentioned rates three test pieces were tested.

- The specified stress rates cause smaller or larger strain rates within the plastic range. After determination of the proof strength properties with the strain rate equivalent to the default stress rate, the test rate is primarily characterized by the strain rate (\dot{e}_{Lc}) determined by the equation:

$$\dot{\mathbf{e}}_{Lc} = \left(\frac{\Delta L_m}{L_c}\right) : t_m \,,\,\mathsf{S}^{-1} \tag{5}$$

where is:

 ΔL_{m} - extension at maximum force, mm

L_c - parallel length of the test piece, mm

 $t_{\rm m}$ – time to achieve of a maximum force, s.

- The range of strain rates for the considered stress rates is shown in Table 2.

Stress rate, <i>R</i>	Strain rate over the parallel length, <i>ė</i> Lc		
MPa·s ⁻¹	S ⁻¹		
2	0.0010 - 0.0020		
5	0.0037-0.0041		
10	0.0049 - 0.0063		
20	0.0073 – 0.0076		
30	0.0246 - 0.0266		
50	0.0347 - 0.0363		
100	0.0391 - 0.0408		

ab. 2: Strain rate ov	er the parallel	length
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3. RESULTS AND DISCUSSION

- Figure 2 shows the F - ΔL curves for some samples tested at different stress rates in the range of 2 to 100 MPa·s⁻¹.



Fig. 2: F - ΔL curves at different stress rates

Based on these diagrams the values of characteristic forces - proof (yield) force ($F_{po.2}$) and maximum force (F_m) were measured and used to determine the values of analysed stresses: proof strength ($R_{po.2}$) and tensile strength (R_m). From these curves the value of extension at fracture (ΔL_f) for calculating the percentage elongation after fracture ($A_{11.3}$) was determined. Figures 3, 4 show a change in the proof strength and tensile strength that occurs by varying the stress rates in the range from 2 to 100 MPa·s⁻¹. The points in these diagrams represent the mean values of three repeated measurements at each test rate. Differences in the form of standard deviation are also shown.



Fig. 3: Dependency of proof strength regarding to the stress rate

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Fig. 4: Dependency of tensile strength regarding to the stress rate

It is obvious that higher test rates cause an increase in the proof strength ($R_{po.2}$) and tensile strength (R_m). Their growth can be well described with the power regression function with a high correlation coefficient which in case of proof strength is R²=0.968 and for the tensile strength R²=0.895. By comparing the mean values of the proof strength at least and the highest stress rate, an increase in absolute value of 10.66 MPa was established. A slightly smaller increase in noted with tensile strength. R_m at a testing rate of 100 MPa·s⁻¹ was increased by 6.47 MPa.

In accordance with the increase in characteristic stresses, the ductility of the material exhibited through the elongation decreases at higher stress rates, Figure 5.



Fig. 5: Dependency of percentage elongation after fracture regarding to the stress rate

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The absolute difference between the elongation value at the stress rate of 2 MPa \cdot s⁻¹ and 100 MPa \cdot s⁻¹ is 10.67%.



Changes of considered properties, but in relative amount, are shown in Figure 6. Variations of properties were calculated in relation to the values recorded at the lowest testing rate.

Fig. 6: Relative change of properties regarding to the stress rate

Obviously, the increase in stress rate is accompanied by a more intense increase in proof strength than tensile strength. A grow in proof strength at \dot{R} =100 MPa·s⁻¹ is 29.9%, while for tensile strength at the same speed it is only 8.2%. The relative difference between the percentage elongation after fracture values at stress rates 2 MPa·s⁻¹ and 100 MPa·s⁻¹ is 29.2%, which roughly corresponds to the increase in $R_{po.2}$.

4. CONCLUSION

The results of the conducted tests clearly indicate an increase in the mechanical resistance of the examined aluminum with an increase in stress rate. Higher testing rates especially affect the increase in the proof strength ($R_{p0.2}$) while the increase in tensile strength (R_m) is somewhat milder. At the same time, with the increase of characteristic stresses, the material ductility is decreased through the percentage elongation after fracture ($A_{11.3}$). The relative decrease of $A_{11.3}$ recorded at higher stress rates is in correlation with the percentage increase of $R_{p0.2}$.

Changes in mechanical properties due to varying stress rates are the result of work hardening, also known as strain hardening. This hardening mechanism is particularly prone to metals with a face centered cubic (FCC) structure that is characteristic for the tested aluminium as well. Work hardening that occurs in the process of stretching the test piece is especially visible at higher stress rates. Therefore, more elastic materials, such as aluminum, with a 70 GPa modulus of elasticity, must be tested at lower stress rates, thus achieving acceptable strain rates which in the case of aluminum vary in the range from 0.0010 s⁻¹ for \dot{R} =2 MPa·s⁻¹ and all the way to 0.0076 s⁻¹ za \dot{R} =20 MPa·s⁻¹. Testing rates greater than 20 MPa·s⁻¹ within the plastic



range result in very large strain rates that can go up to 0.040 s⁻¹ for \dot{R} =100 MPa·s⁻¹, resulting in multiple accumulation of structural defects, especially dislocations, which significantly influence on the stress value required for plastic flow, so that additional energy is required in the form of external stress, which is evident to the outside as a hardening of the material and a reduction in its ductility.

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PROCJENA PRIHVATLJIVOG DODATKA ZEOLITA ZASIĆENOG IONIMA CINKA U CEMENTNIM PASTAMA, CEM I, PRAĆENJEM SPECIFIČNE ELEKTRIČNE PROVODNOSTI I ELEKTRODNOG POTENCIJALA Pb-Cu ELEKTRODE

ASSESSMENT OF THE APPROVED ADDITION OF ZEOLITE SATURATED WITH ZINC IONS IN CEMENT PASTES, CEM I, WITH MONITORING OF SPECIFIC ELECTRICAL CONDUCTIVITY AND Pb-Cu ELECTRODE POTENTIAL

Pero Dabić, Damir Barbir, Josipa Lovrić

University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, Split, Croatia

<u>Original scientific paper / Izvorni znanstveni rad</u>

Sažetak

Prema hrvatskim normama HRN EN 196-3 obvezno je provesti ispitivanje vremena početka i kraja vezivanja cementnog materijala pomoću Vicatova aparata. Točno vrijeme početka vezivanja teško je odrediti jer se metoda temelji na povremenom puštanju igle aparata kroz cementnu pastu. Praktično rješenje je primjena kontinuiranih mjerenja pojedinih svojstava cementne paste koja se mijenjaju početkom vezivanja cementne paste. Takva mjerenja omogućava konduktometrija i mjerenje elektrodnog potencijala Pb-Cu elektrode. U radu je ispitivan utjecaj dodatka zeolita zasićenog Zn²⁺ ionima na vrijeme vezivanja cementnih pasti pripravljenih od CEM I mjerenjem specifične električne provodnosti i elektrodnog potencijala Pb-Cu elektroda. Cementne paste pripremljene su uz dodatak zeolita zasićenog Zn²⁺ ionima od o, 5, 10, 15, 20, 25 i 30 mas. % i uz omjer voda/kruto, V/K =0,5. Mjerenja su provedena pri konstantnoj temperaturi od 20 °C. Dobivene krivulje specifične električne provodnosti – vrijeme imaju karakterističan maksimum provodnosti nakon koga provodnost naglo opada. Pojava maksimuma provodnosti odgovara vremenu početka vezivanja cementnih pasti. Slično se može uočiti i na krivuljama promjene elektrodnog potencijala Pb-Cu elektrode s obzirom na količinu dodanog zasićenog zeolita.

Ključne riječi: Cementna pasta, zasićeni zeolit, vrijeme vezivanja, konduktometrija, Pb-Cu

Abstract

According to the Croatian standard HRN EN 196-3 it is necessary to carry out the testing of the start time and the end of the binding of the cement material carried out by the Vicat apparatus. The exact starting time is difficult to determine because the method is based on the occasional release of the needle through the cement paste. A practical solution is the use of continuous measurements of certain properties of cement paste that change at the start of the binding of the cement paste. Such measurements enable conductometry and measurement of the electrode potential of the Pb-Cu electrode. The paper investigated the effect of zeolite saturated with Zn2+ ions at the binding time of cement paste prepared from CEM I by measuring specific electrical conductivity and electrode potential of Pb-Cu electrodes. Cement pastes were prepared with o, 5, 10, 15, 20, 25 and 30 wt.% of zeolite saturated with Zn2+ ions and with water/solid ratio, W/S=0.5. The measurements were carried out at a constant temperature of 20 °C. Specific electrical conductivity drops quickly. The appearance of the maximum conductivity corresponds to the start of binding of the cement pastes. Similarly, it can be seen in the curves of changing the electrode potential of the Pb-Cu electrode over time. Mathematical dependence on the occurrence of maximum specific conductivity and potential of the Pb-Cu electrode saturated zeolite.

Keywords: cement paste, saturated zeolite, binding time, conductometry, Pb-Cu electrode potential

1. UVOD

Velike količine otpadnih anorganskih materijala, troske, pepela iz termoelektrana, muljeva iz pojedinih industrija te otpadnog građevinskog materijala nastalog nakon rušenja pojedinih objekata odlagano je nekontrolirano u okoliš te su predstavljali ekološki problem. Takav otpad ugrožava zdravlje ljudi, biljnog i životinjskog svijeta i narušava izgled okoliša. Otpadni materijali koji sadrže teške metale i druge ione koji su opasni za okoliš, kao i materijali koji te ione primaju kroz različite fizikalne i kemijske procese (ionska izmjena i sl.) ne smiju se odlagati u okoliš nekontrolirano, nego se moraju stabilizirati i zbrinuti na takav način da se spriječi ispuštanje opasnih iona u okoliš iznad dopuštene vrijednosti tijekom dugog vremenskog razdoblja. Cementni kompoziti predstavljaju veliki potencijal u zbrinjavanju otpadnih anorganskih materijala iz drugih industrija. Neki od otpadnih materijala imaju i vezivna svojstva pa je moguće zamijeni dio veziva, cementa, a da pri tome nastali cementni kompozit zadrži potrebna svojstva i ima uporabnu vrijednost. To doprinosi smanjenju energije potrebne za proizvodnju cementa i emisije CO₂. Istraživanja stabilizacijskih procesa u industrijskom otpadu i sličnim materijalima koji sadrže štetne ione upućuju na to da se mogu uspješno stabilizirati skrućivanjem u cementnim kompozitima. Na taj način komponente opasnog otpada su i fizički i kemijski vezane u cementnom kompozitu.[1,2,3] Pri obradi otpadnih voda pojedinih industrijskih pogona opterećenih ionima teških metala često se kao relativno učinkovito i jeftino rješenje primjenjuju prirodni ili sintetski zeoliti koji ionskom izmjenom vežu ione teških metala. Grade se filtri, barijere ili zeolitne brane kroz koje se propušta voda opterećenja ionima teških metala i pri tome se oni zasićuju i gube funkciju izmjene te je potrebno primijeniti novu količinu nezasićenog zeolita.[4] Optadni zeolit, zasićen ionima teških metala, potencijalno je štetan za okoliš pa se vrše ispitivanja njegovog trajnog zbrinjavanja u cementnim vezivima. [5,6] Potrebna svojstva cemenata, kao temeljnih građevinskih materijala, vrlo dobro su opisana normama te se postavljene granice moraju poštovati. Za praktičnu primjenu cementnih veziva bitna svojstva su početak i kraj vezivanja, prema HRN EN 196-3 i na kraju procesa hidratacije, kada materijal otvrdne, bitna je postiguta čvrstoća nastalog materijala prema HRN EN 196-1. Neki dodatci djeluju kao ubrzivači hidratacije, neki kao usporivači što ograničava prihvatljivi udjel dodatka u cementnom kompozitu.[3] Vremena vezivanja mogu biti vrlo različita u odnosu na vezivo bez dodatka i potrebno je ispitati i po mogućnosti dati matematički opis djelovanja dodatka na ispitivano svojstvo. U ovome radu ispitivan je utjecaj dodatka zeolita zasićenog cinkovim ionima u iznosima od o-30 mas. % na početak i kraj vezivanja cementnih pasti pripremljenih od portladskog cementa CEM I. Određivanje vremena vezivanja prema normi vrši se diskontinuirano, Vicatovim aparatom, a moguće je procijeniti vremena vezivanja i kontinuiranim mjerenjima pojedinih svojstava cementnih pasti koje u trenutku početka vezivanja prelaze iz stanja paste u kruto stanje. Pri tom procesu smanjuje se broj iona u sustavu, OH⁻ i Ca²⁺, jer dolazi do precipitacije portlandita, Ca(OH)₂ i nastajanja netopljivih CSH faza (kalcijevih silikatnih hidrata).[7,8] Odrađivanjem specifične električne provodnosti moguće je precizno odrediti trenutak početka vezivanja, tj. kada dolazi do smanjenja broja iona koji provode elektricitet u sustavu. Radi smanjenja iona u sustavu mijenja se i potencijal Pb-Cu elektrode. Mehanizam se temelji na procesu da se na površini metala Pb i Cu koji služe kao elektrode, a uronjene su u cementnu pastu, stvara oksidni sloj pri čemu se elektrode nalaze u ravnoteži s tekućom fazom, što se općenito može opisati Nernstovim izrazima za svaku elektrodu. Za bakarnu elektrodu vrijedi:

$$E_{Cu} = E_{Cu}^0 + \frac{RT}{zF} \ln K_p(Cu)$$

(1)



a za olovnu elektrodu:

$$E_{Pb} = E_{Pb}^0 + \frac{RT}{zF} ln K_p(Pb)$$
⁽²⁾

gdje je:

 $K_p(Cu)$ – konstanta ravnoteže stanja oksidacije na bakrenoj elektrodi $K_p(Pb)$ – konstanta ravnoteže stanja redukcije na olovnoj elektrodi.

Ukoliko se proučavaju elektrokemijski procesi koji se odvijaju na granici faza elektroda – elektrolit, treba uzeti u obzir da u konstantu ravnoteže ulazi i aktivnost OH⁻ iona. Elektromotorna sila iz ovog elektrokemijskog sustava može se prikazati i kao :

$$EMS = \Delta E = E_{Cu} - E_{Pb} \tag{3}$$

a ukoliko se sredi jednadžba dobije se izraz:

$$EMS = \Delta E = (E_{Cu}^{0} - E_{Pb}^{0}) + \frac{RT}{zF} ln \frac{K_{p}(Cu)}{K_{p}(Pb)}$$
(4)

Potencijal svake elektrode je određen odnosom oksidiranog i reduciranog oblika. Aktivnost iona koji sudjeluju u elektrokemijskoj reakciji na različitim elektrodama je različita. Uslijed stvaranja oksidnog sloja na površini Cu elektrode, u trenutku početka procesa vezivanja cementa, dolazi do promjene potencijala na samoj elektrodi. U svježoj cementnoj pasti olovna elektroda se jako brzo oksidira, jer na njenoj površini nastaju produkti oksidacije i to u najvećoj mjeri plumbiti koji dovode do promjene potencijala Pb-elektrode. S obzirom da navedena promjena potencijala nije značajno izražena, ista se može zanemariti. Prema tome, svekukupna promjena EMS u sustavu Pb-Cu elektrode bit će jednaka promjeni potencijala Cu-elektrode, iz čega slijedi izraz:

odnosno,

$$EMS = \Delta E = E_{Cu} = E_{Cu}^0 + \frac{RT}{zF} lnK_p(Cu)$$
(6)

 $EMS = \Delta E = E_{Cu}$

U ovome radu za određivanje vremena vezivanja pri hidrataciji cementnih pasti primijenjena su kontinuirana mjerenja, konduktometrijska i mjerenja određivanja potencijala Pb-Cu elektrode.[9] Analizom dobivenih rezultata određena su vremena početka i kraja vezivanja cementnih pasti te je određena matematička ovisnost vremena vezivanja o udjelu dodatka zasićenog zeolita.

2. EKSPERIMENTALNI DIO

2.1. Primijenjeni materijali

Za pripremu cementnih pasti korišten je portland cement CEM I 42,5 R, Cemex, Kaštel Sućurac, Hrvatska; prirodni zeolit, s osnovnim mineralom klinptilolitom je iz nalazišta Donje Jesenje, Hrvatska; aditiv tipa superplastifikatora, Kemament L10, KEMA d.o.o, Puconci, Slovenija i destilirana voda specifične električne provodnosti od 4 2 Scm⁻¹.

2.1.1. Portland cement CEM I 42,5 R

U radu je korišten portland cement cementare CEMEX Hrvatska iz Kaštel Sućurca koji je usklađen s normom HRN EN 197-1 i HRN EN 197-2 te označen kao CEM I 42,5 R. Ovu vrstu cementa odlikuju visoka rana i konačna čvrstoća, kratak period početka vezivanja, optimalna obradivost te znatan razvoj topline hidratacije. Tipična svojstva za CEM I 42,5 R su prikazana u Tablici 1.

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(5)

Tipična sv	Zahtjev norme	
Gubitak žarenjem	2,0 ± 0,5%	≤ 5,0
Netopivi ostatak	0,25 ± 0,05 %	≤ 5,0
% SO₃	3,2 ± 0,30 %	≤ 4 , 0
Kloridi	0,02 ± 0,01 %	≤0,1
Vrijeme vezivanja (početak)	125 ± 35 min	≥ 60
Rana čvrstoća (2 dana)	28 ± 2 MPa	≥ 20
Normirana čvrstoća (28 dana)	53 ± 2 MPa	≥ 42,5; ≤ 62,5
Tipičan s	Zahtjev norme	
Klinker (K) + gips (G)	96,5 %	95 – 100 %
Ostalo	3,5 %	0 -5%

Tablica 1. Tipična svojstva za CEM I 42,5 R pri temperaturi T = 20 °C. [10]

2.1.2. Prirodni zeolit zasićen Zn²⁺ ionima

Klinoptilolit, pojednostavljene formule (Na,K)₆Si₃₀Al₆O₇₂·24H₂O najrasprostranjeniji je prirodni zeolit u svijetu. U Hrvatskoj se naslage klinoptilolita nalaze u poroznim stijenama u Donjem Jesenju. Udjel klinoptilolita je 50-60 %. Kemijski i mineraloški sastav prirodnog zeolita iz Donjeg Jesenja, prikazan je u tablici 2.

Kemijski sastav (%)		Mineraloški sastav – kvalitativni
SiO ₂	64,93	Glavna komponenta:
Al ₂ O ₃	13,66	- klinoptililit
Fe ₂ O ₃	2,03	Primjese:
K ₂ O	1,88	- muskovit
Na ₂ O	3,66	- ilit
CaO	2,99	- feldšpat
MgO	1,10	- sepiolit
Gubitak žarenjem	9,84	- kvarc

Tablica 2. Kemijski i mineraloški sastav prirodnog zeolita

Prirodni zeolit zasićen Zn²⁺-ionima dobiven je zasićivanjem prirodnog zeolitnog tufa otopinom koja sadrži 9,0 mmol/dm³ ZnSO₄, nakon čega je osušen pri 60 °C, usitnjen i prosijan kroz standarno sito s 4900 očica/cm², tako da su njegove čestice po veličini slične česticama cementa.

2.1.3. Aditiv superplastifikator, KEMAMENT L 10

Primjenjeni aditiv KEMAMENT L 10 je visokoaktivni univerzalni superplastifikator za pripremu betona, mortova i prenapregnutih betona. KEMAMENT L 10 (melment) je bezklorni kemijski dodatak na osnovi sulfatoniziranih polikondenzacijskih produkata melamina. U reakcijski sustav dodan je sa stalnim masenim udjelom od 0,3 % (0,3 % krutog aditiva odgovara 1,5 % KEMAMENT L 10 na masu krutog cementa). Prema preporuci proizvođača, aditiv je dodan istovremeno s vodom. Osnovna uloga primijenjenog superplastifikatora je doprinos povećanoj obradljivosti cementnih pasti. [11,12]

2.2. Priprema uzoraka

Cementne paste za konduktometrijska mjerenja i određivanje početka i kraja vezanja elektrokemijskom metodom pripremljene su miješanjem portland cementa CEM I 42,5R i prirodog zeolita zasićenog Zn²⁺ ionima s destiliranom vodom s 0,3 %-tnim dodatkom

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superplastifikatora. Vodocementni omjer, tj. omjer voda/kruto iznosi V/K = 0,5 pri konduktometrijskim mjerenjima, odnosno V/K = 0,3 pri mjerenju elektrodnog potencijala Pb-Cu elektrode. Na analitičkoj vagi izvaže se točno 100 g uzorka, a zasićeni zeolit se dodaje u udjelima: w = 5, 10, 15, 20, 25, 30 mas. % u odnosu na ukupnu masu krutog uzorka. Nakon vaganja smjesi se pomoću pipete doda količina destilirane vode koja odgovara V/K omjeru. Uzorak se zatim prenese u držač uzorka i termostatira pri temperaturi 20 °C. U međuvremenu se pokrene računalni program kojim se prati i upisuje vrijednost specifične provodnosti svake 2 minute. Referentni uzorak bez dodatka zasićenog zeolita nosi oznaku Coo. U tablici 3 prikazani su različiti udjeli prirodog zeolita zasićenog Zn²⁺ ionima i portland cementa u masi uzorka od 100 g.

Oznaka uzorka	m (uzorka) g	w (cementa) %	w (zasićenog zeolita) %	w (superplast.) %
Coo	100	100	0	0,3
Co5	100	95	5	0,3
C10	100	90	10	0,3
C15	100	85	15	0,3
C20	100	80	20	0,3
C25	100	75	25	0,3
C30	100	70	30	0,3

Tablica 3. Priprema uzoraka cemetnih pasti s udjelima zasićenog zeolita i superplastifikatora

2.3. Aparature za mjerenje i izvedba mjerenja

2.3.1. Konduktometrija

Za provođenje konduktometrijskih mjerenja korišten je digitalni konduktometar ISKRA MA 5964 koji je povezan s osobnim računalom preko RS 232 C. Elektroda konduktometrijske ćelije je od nehrđajućeg čelika s vrijednosti konstante ćelije C = 0,2654 cm⁻¹. Pripremljeni uzorak cementnih paste koji se nalaze u plastičnoj čašici, prenese se u termostatiranu staklenu posudu s dvostrukom stijenkom kroz koju cirkulira voda temperature 20 °C. Zatim se u tako pripremljene uzorke uranja elektroda od nehrđajućeg čelika, te se mjeri specifična provodnost u vremenskim intervalima od 2 minute. Mjerenje se provodi dok vrijednosti specifične provodnosti ne počnu kontinuirano padati. Na slici 1 prikazana je aparatura za provođenje konduktometrijskih mjerenja.



Slika 1. Aparatura za kontinuirano praćenje specifične električne provodnosti: a)konduktometar MA 5964 povezan s osobnim računalom za pohranjivanje i obradu podataka; b) ćelija za termostatiranje i elektroda od nehrđajućeg čelika.⁸

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2.3.2. Određivanje vremena vezanja cementa i cementnih kompozita pomoću Pb – Cu elektrodnog para

Sustav se sastoji od olovne i bakrene elektrode, koje se nalaze uronjene u cementnu pastu. Početak vremena vezivanja ukazuje nagla promjena, tj. porast elektrodnog potencijala, a kraj vezivanja njegov pad, stabilizacija te konačna vrijednost. Promjena potencijala je vrlo izražajna i ona tijekom vezivanja iznosi od 300 mV na početku vezivanja pa do oko 500 mV na kraju vezivanja. Aparatura za izvođenje određivanje vremena vezanja ovom metodom prikazana je na slici 2.



Slika 2. Shema aparature za određivanje vremena vezanja Pb — Cu elektrodom 1 — Pb — Cu elektroda, 2 — držač elektrode, 3 — držač uzorka, 4 — Cu elektroda, 5 — Pb elektroda, uzorak, 7 — termostat, 8 — Data Logger

3. REZULTATI I RASPRAVA

3.1. Rezultati konduktometrijskih mjerenja

Grafički prikaz izmjerenih podataka specifične električne provodnosti prikazan je na slici 3, a na slici 4 prikazana je ovisnost vremena za postizanje maksimalne specifične električne provodnosti cementnih pasti o udjelu zasićenog zeolita.





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Vrijednost specifične električne provodnosti za cementnu pastu bez zasićenog zeolita uz dodatak 0,3 % melmenta je 21,3 mS/cm, vrijeme maksimalne provodnosti postiže se nakon 202 minute. Dodatkom zeolita od 5 do 30 mas. % vrijednosti specifične električne provodnosti opadaju od 19,9 do 11,02 mS/cm, a maksimalna provodnost postiže se u vremenskom periodu od 234 do 362 minute. Povećanje udjela zasićenog zeolita u cementnom sustavu usporava hidrataciju, maksimumi se odgađaju, a vrijednosti maksimalne provodnosti su niže. Sa slike 3 očitana su vremena potrbna za postizanje maksimalne specifične električne provodnosti cementnih pasti za određeni dodatak zasićenog zeolita te su vrijenosti prikaazane na slici 4.



Slika 4. Grafički prikaz ovisnosti specifične električne provodnosti cementnih pasti o udjelu zasićenog zeolita

Određena je matematička funkcija ovisnosti specifične električne provodnosti cementnih pasti o dodatku zasićenog zeolita kao:

gdje je y – vrijeme pojave maksimalne specifične električne provodnosti, min, a x – dodatak zasićenog zeolita, mas. %. Slaganje matematičkog modela s eksperimentalnim podacima potvrđuje vrijednost R² koja iznosti R² = 0,9919.

3.2. Rezultati određivanja vremena vezivanja cementnih pasti pomoću Pb-Cu elektrodnog para

Mjerni podatci pohranjeni u data loggeru preneseni su u računalo te su obrađeni u Excelu. Grafički prikaz rezultata mjerenja prikazan je na slici 5.



Slika 5. Prikaz ovisnosti promjene elektrodnog potencijala Pb-Cu elektrode o vremenu hidratacije za cementne paste s 0,3 % dodatkom melmenta, (M) i o - 30 mas. % zasićenog zeolita, (ZZ)

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Naslici 5 vidi se da nema pravilnosti vrijednosti platoa potencijala Pb-Cu elektrode u ovisnosti o udjelu dodatka zasićenog zeolita. Vjerojatni razlog za ovo je velika osjetljivost početnog potencijala s obzirom na stanje poliranosti površine metala, posebice bakra, načina uronjenosti elektrode u cementnu pastu i trenutne vlažnosti u zraku, jer je bakreni dio elektrode dijelom na zraku. Očitana vremena vremena početka i kraja vezivanja cementnih pasti prikazana su u tablici 4.

Dodatak M	Dodatak ZZ	Vrijeme do max. Pb-Cu potencijala	Vrijeme do max. Pb-Cu potencijala
%	%	početak, min	kraj, min
0,0	0,0	205	262
٥,3	0,0	252	276
٥,3	5,0	248	263
٥,3	10,0	270	278
٥,3	15,0	270	285
٥,3	20,0	302	325
0,3	25,0	301	314
0,3	30,0	344	350

Tablici 4. Određena vremena vezivanja uzoraka cementnih pasti s različitim udjelima zasićenog zeolita, (ZZ)

Grafički prikaz podataka iz tablice 4 poslužio je za određivanje matematičkog modela ovisnosti početka vezivanja cementnih pasti o udjelu zasićenog zeolita (slika 7).





Matematička ovisnost početka i kraja vezanja cementnih pasti o dodatku zasićenog zeolita može se opisati izrazima:

$$y_p = 0,0008x^4 - 0,0483x^3 + 0,9398x^2 - 4,1424x + 251,95$$

$$y_k = 0,0009x^4 - 0,0606x^3 + 1,3494x^2 - 8,4258x + 276,7$$
(8)

gdje je x – dodatak zasićenog zeolita, mas. %, y
p $_{\rm P}$ – početak vezanja, min, y
k- kraj vezanja, min.

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(9)



4. ZAKLJUČAK

Kondutometrijom je moguće određivanje početka vezivanja cementnih pasti uz dodatak o-30 mas. % cinkom zasićenog zeolita. Cementne paste s povećanim udjelom zeolita imaju niže vrijednosti specifične električne provodnosti, a maksimumi provodnosti se događaju u kasnijim vremenima. Iz ove činjenice može se zaključiti da cinkom zasićeni zeolit usporava hidrataciju cementa. Mjerenjem potencijala Pb-Cu elektrode moguće određivanje početka i kraja vezivanja cementnih pasti uz dodatak zasićenog zeolita, ali je potrebno uvijek osigurati istu pripremljenost površine elektrode te iste radne uvjete u laboratoriju. Dobiveni rezultati, slično konduktometriji, upućuju da se početak i kraj vezivanja cemetnih pasti događaju u kasnijim vremenima. Za praktičnu primjenu ovakvih kompozita, ovisno o namjeni, od velike pomoći je imati matematički model ovisnosti vremena vezanja i količine dodatka te se vrlo brzo može procijeniti vrijeme vezanja za bilo koji udio dodatka.



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INFLUENCE OF THE PROCESSING ROUTE ON THE MICROSTRUCTURE FORMATION AT SEMI-SOLID TEMPERATURES FOR ALUMINUM ALLOY A₃80

Ivana Dumanić¹, Jure Krolo¹, Sonja Jozić¹, Branimir Lela¹, Dražen Bajić¹, Ljumović Petar¹

¹ University of Split, Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, Ruđera Boškovića 32, 21000 Split, Hrvatska

<u>Original scientific paper / Izvorni znanstveni rad</u>

Abstract

In this study, the influence of the material processing route for semi-solid thixoforming process was investigated. The main aim of this research was to achieve globular microstructure during samples heating at semi-solid temperatures. In order to achieve globular microstructure equal channel angular pressing (ECAP) was used to deform originally casted dendritic microstructure. During reheating of the cold worked billet in the semi-solid temperature range, partial remelting should result with extremely fine, uniform, and nondendritic spherical microstructure. Therefore, ECAPed specimens were subsequently heated at the appropriate temperatures above solidus to get a globular structure of A₃80 (AlSi₉Cu₃(Fe)) aluminum alloy. The microstructural evolutions during semi-solid heating at different holding times were carried out utilizing optical microscope. Conclusion indicated that the microstructure was significantly influenced by holding time. Also, it was demonstrated that slurry composed of spheroidal solid primary particles within a liquid matrix could be achieved by reheating (in semi-solid range) of the heavily deformed specimens. Finally, it was confirmed that ECAP is a promising route for processing of the semi-solid raw materials for thixoforming.

Keywords: Semi-solid, aluminum, ECAP, globular microstructure, thixoforming.

1. INTRODUCTION

Semi-solid metal (SSM) processing technologies involve the formation of metal alloys between solidus and liquidus temperatures providing the final component with enhanced properties. These technologies have some advantages such as lower energy consumption and cost [1], prolonged die life due to less thermal shock [2], limitation the risk of gas entrapment due to laminar flow [3]. SSM technologies are generally categorized into two groups: rheo-routes and thixo-routes. The rheo-route refers to the preparation of an SSM slurry directly from a liquid phase and its direct injection into a die or a mould for component shaping. The thixo-route refers to the preparation of a feedstock material, reheating of a feedstock material between solidus and liquidus temperatures and its shaping [4], [5]. It is necessary to get globular microstructure when the material is cooled (rheo-routes) or heated (thixo-routes) into semi-solid state. Such structure is required in order to achieve thixotropic properties of slurries. The fluid which surrounds solid globules acts as a lubricant and hence a better flow and lower viscosity and deformation forces are achieved [6]. Physical basics of thixotropy are: when the slurry is at rest, gravity will bring the particles into contact and the semi-solid will support its own weight and can be handled like a solid; during a deformation, shear breaks the bonds and viscous flow of material occurs [6].

In order to prepare suitable globular microstructure, numerous routes have been tested, e.g. rheo-route techniques: mechanical stirring, the cooling slope process, new rheocasting process; thixo-route techniques: thermomechanical treatments, spray casting, thixomolding [5]. One of the thermomechanical treatments routes, which has been proved to be capable to produce thixo feedstock, is severe plastic deformation technique (SPD) [5]. In severe plastic deformation (SPD) techniques high plastic strain is applied to a solid sample. As a result, the dendritic microstructure is deformed and bonds are broken. This structure, after heating at a semi-solid temperature, could be changed to the globular structure. Lately, one of the SPD techniques that has been gaining attention is equal channel angular pressing (ECAP) [5], [7], [8]. In this process, plastic deformations are achieved by pressing feedstock through channels of the same cross-sectional area. Channels are bent at an angle typically as 90 ° Or 120 °.

Several researchers investigated the microstructure of aluminum alloy produced by ECAP process. Nedjadj et al. [9], Meidani et al. [10] and Moradi et al. [11] concluded that ECAP followed by isothermal heating A356 alloy in the semi-solid range was suitable to produce semi-solid feedstock with the spheroidal solid phase. Ashouri et al. [12] and Moradi et al. [13] investigated the effects of the route and the number of passes in ECAP process for A356 alloy. It was observed that, if considering an industrial application, one-pass treated material was a good choice for semi-solid forming process. Campo et al. [14] presented that samples prepared by ECAP route have the most suitable characteristics for thixoforming A356 alloy in comparison with five various routes (commercial product, direct casting with and without electromagnetic stirring and grain refining, direct casting with mechanical vibration, direct casting followed by one ECAP pass). Aghaie-Khafri and Azimi-Yancheshme [15] concluded that for AI-Fe-Si alloy, ECAP and semi-solid heating resulted in an enhanced microstructure and mechanical properties. Also, they have found that mechanical properties of Al-Si-Fe samples after ECAP and semi-solid process were improved among the as received and only ECAPed samples [16]. Meshkabadi et al. [17] found that by processing ECAP route BA up to five passes and isothermally heating at 630 °C for 15 min, the most suitable microstructure of 7075 aluminum alloy will be achieved. Torres et al. [18], [19] compared the two processing



routes for production of raw material for thixoforming. They concluded that the more suitable microstructure of Al-4.owt%Si-2.5wt%Cu and Al-7.owt%Si-2.5wt%Cu alloy was achieved by ECAP process than electromagnetic stirring process.

It is evident from the literature study, that no studies were found on the use of ECAP in semisolid processing aluminum alloy A₃80. Therefore, the goal of this work is to produce feed material with globular structure by ECAP process followed by heating in semi-solid range for A₃80 alloy.

2. EXPERIMENTAL PROCEDURE

Selected alloy for the research was aluminum alloy A₃80 with the chemical composition given in Tab. 1.

Elements	Fe	Si	Mn	Ni	Cr	Ti	Cu	Pb	Mg	Zn	Sn
Min Max. (%)	1.3	8 - 11	0.55	0.55	0.15	0.25	2 - 4	0.35	0.05 - 0.55	1.2	0.15

Tab. 1: Chemical composition of aluminum alloy A380 (Wt. %)

A first experimental step was to cast selected aluminum alloy A₃80 (EN AC - AlSi₉Cu₃(Fe)) in the form of the round bar. Aluminum was melted at 700 °C and poured into the steel die to form round bars with 15 mm in diameter and 100 mm in length, Fig. 1. After casting samples were annealed to increase ductility at 350 °C temperature in duration of 5 hours. Samples were cooled in a closed furnace. Aluminum melting and annealing were performed in the 3 kW furnace "Demiterm Easy" with maximum working temperature of 1150 °C.



Fig. 1: Aluminum alloy A380 after casting

After samples annealing, they were processed with equal channel angular pressing (ECAP). This processed is well known as severe plastic deformation (SPD) process. Main characteristics of the SPD processes are significant crystal grain refinement and unique mechanical and physical properties improvement. In this research, ECAP process was mainly used for introduction of the significant amount of plastic deformation and cold work inside casted samples. ECAP tool used in this research has two intersecting channels with 15.1 mm in diameter. At the channel intersection, it is of the main importance to define inner and outer die angle. Die angle determines which amount of the plastic deformation will be introduced into processed material. Inner die angle for the ECAP tool used in this work is 90°, and outer die angle is 12° which is defined with 3 mm radius. According to the Iwahashi et al. [20] analytical approach, this tool geometry gives total plastic shear strain around 1. Graphite grease was used for the process lubrication. ECAP tool used for this research is presented in Fig. 2.

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Fig. 2: ECAP tool utilized for severe plastic deformation

After ECAP process samples were heated at the appropriate semi-solid temperature. The selected temperature will define solid fraction inside samples, where 50 % of the solid fraction is a good selection for the thixoforming process [21]. According to the Birol et al. [21], the temperature to achieve 50% solid is estimated to be 567 °C for A380 alloy. Therefore, for this research selected temperature for semi-solid heating was 570 °C ± 3 °C to fit into mentioned solid fraction range. Six casted, annealed and ECAPed samples were prepared for heating at the semi-solid temperature. Samples were held at semi-solid temperature for different times in order to determine an optimal time to achieve optimal semi-solid globular microstructure. Selected times were 1 min, 2 min, 2 min and 40 seconds, 5 min, 8 min and finally 12 min and 30 seconds, for samples A, B, C, D, E, F and G, respectively. In order to achieve good repeatability, surface temperature was measured on all sample with contact thermometer DT 02 and type K thermocouple probe. Average heating rate for all samples to reach the desired semi-solid temperature on the surface was 1,6 °C/s (average 6 minutes). After that samples were heated at the above-mentioned times. For metallography analysis, optical microscope "OPTON Axioskop" and computer software "BIOVIS MP2000" were utilized. In the first preparation step samples where manually grinded and polished. However, to obtain high-quality metallographic images, samples where electropolished with "Struers LectroPol-5" device with two component A2 electrolyte. Finally, samples were etched with 0.5% HF (hydrofluoric acid) reagent in a duration of 10 s at room temperature.

3. RESULTS ANALYSIS AND DISCUSSION

After casting, annealing, ECAP and semi-solid process, samples were cut on the metallographic cutter to avoid any heat influence. Fig. 3 a shows microstructure of the cast sample A. According to Fig. 3 a characteristic dendritic structure appeared in as cast sample and even after annealing dendritic microstructure was also preserved, Fig. 3 b. Eutectic was formed in the needle like structure. After the ECAP process, dendritic structure was highly deformed and a significant amount of the distortion energy was introduced into the samples, Fig. 3 c. These heavily distorted regions would create the location of the recrystallization nucleus. During samples reheating, recrystallization occurs in the solid state and new grains nucleate and grow with high angle grain boundaries. When the temperature rises to above solidus, the high-energy grain boundaries of these new grains are penetrated by liquid, leading to the fragmentation of original grains to small equiaxed grains. The presence of liquid causes grain growth and spheroidization of the newly formed grains [13].





a) Cast sample b) Annealed sample c) ECAPed sample Fig. 3: Dendritic microstructure of as cast aluminum A380, cast and annealed sample and heavily deformed ECAPed sample

In order to determine optimal holding time at semi-solid temperature six samples were held at semi-solid temperature for a 1 min, 2 min, 2 min and 40 seconds, 5 min, 8 min and finally 12 min and 30 seconds which corresponds to the samples A, B, C, D, E, F and G, respectively, Fig. 4. Fig. 4 a shows sample A which was held only for one minute at semi-solid temperature and already characteristic ECAPed and heavily deformed microstructure disappeared. That indicated that the recrystallization process and partial remelting already take significant effect. However, despite the fact that dendrite structure had completely disappeared for sample A, still there is no clear sign of globular microstructure formation. The same observation can be given and for sample B and C with 2 min and 2 min and 40 seconds holding times, respectively, Fig. 4 b and c. However, with 5 min holding time (sample D), larger white areas started to form which should correspond to the solid α – aluminum matrix. Solid areas were surrounded with liquid of low melting phase, Fig. 4 d. Further holding time increment (8 min) results with the formation of the very small solid globular areas for sample E, Fig. 4 e. However, these formed globules are somewhat inhomogeneous and small which suggested that even longer holding times should be introduced for semi-solid homogeneous globular microstructure formation and larger globules. There is no sign of any dendritic microstructure. Desired globules size for thixoforming process are usually under 100 µm [22]. Therefore, finally holding time of 12 min and 40 s for sample F was used. An obtained microstructure with homogeneously dispersed globular structure was achieved, Fig. 4 f. Furthermore, according to the Gecu et al. [23], for aluminum alloy A380 low melting eutectic phase should be surrounding globular solid α – Al. Furthermore, for same alloy, after thixoforming process, usual formed phases are α (Al), eutectic and polyhedral Si phases and additionally Fe-rich and Cu-rich phases [23]. Microstructure of the sample F with 500 x magnification is shown in figure 5.



a) Sample A (1 min)

b) Sample B (2 min)

c) Sample C (2 min and 40 s)



d) Sample D (5 min) e) Sample E (8 min) f) Sample F (12 min and 30 s) Fig. 4: Microstructure evolution of the aluminum alloy A380 during different holding times at semi-solid temperature

Morphology of the as cast needle like eutectic is changed into smaller size eutectic which surrounding globular solid α – Al. There is no sign of any large-scale silicon or Fe- rich based particles. Therefore, sample F with obtained microstructure should be excellent feedstock material for thixoforming process for A₃80 aluminum alloy. For future work, obtained phases determination with scanning electron microscopy and energy dispersive x-ray spectroscopy should be done. Furthermore, influence of heat treatment on obtained samples microstructure should be investigated.



Fig. 5: Globular microstructure of the sample F with 500 x magnification

4. CONCLUSION

In the present work, equal channel angular pressing (ECAP) technique is used to produce thixo feedstock. By this thixo-route method, a high plastic strain is applied to a solid feedstock. By heating in semi-solid range, this deformed structure is changed to the structure consisted of globular solid particles surrounded with liquid. The homogenous distribution of α – Al and eutectic phase of A₃80 alloy is achieved by heating ECAPed samples at semisolid temperature for 12 min and 30 sec. Hence, the explained process is good enough for producing thixo feedstock.

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TRACEABILITY FOR STYLUS INSTRUMENT MEASUREMENTS

Maja Grbavac¹, Gorana Baršić¹, Vedran Šimunović¹

¹ University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Department of Quality, Ivana Lucica 5, Zagreb, Croatia

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Abstract

The state of product surface roughness is an important feature that affects its functionality through wear resistance, friction and lubrication, corrosion resistance, etc. Although the measure of surface roughness can be characterised by numerous measuring devices, stylus instruments are most frequently used. To ensure reliable and traceable measurement results it is necessary to calibrate measuring devices periodically. Artefacts used to calibrate stylus instruments are defined in standard ISO 5436-1:2000 Geometrical Product Specifications (GPS) - Surface texture: Profile method; Measurement standards - Part 1: Material measures.

This standard defines five types of artefacts to be used for calibration of stylus instruments and each type has a limited range of application according to its own characteristics and those of the instrument to be calibrated. When calibrating a stylus instrument with roughness standards, laboratories are using only a few artifacts of different nominal values resulting in insufficient values of different amplitudes and wavelengths.

Due to recognized limitations of the current traceability chain, national metrology institutes invest efforts to develop a new calibration approaches, particularly for different amplitude and wavelength values, which cannot be achieved using artefacts defined by ISO 5436-1 standard.

Motivated by previously defined limitations of contemporary calibration chain, in the Laboratory for precise measurements of length at Faculty of mechanical engineering and naval architecture, Zagreb a research of a novel method for calibration of stylus instrument using displacement tranducer (piezo capacitive sensors) has been investigated. Measurement setup included the following elements: Stylus instrument Perthometer S8P using a probe without skid with 10 μ m radius, Piezo actuator P-621.ZCD, Piezo Amplifier & Servo-Controller E-625.CR LVPZT, Software PZTControl and a wafer.

Two different geometries were simulated - a sequence of regular triangular and a sequence of regular rectangular structures with the total heights of roughness profile of 0.4 μ m, 4 μ m and 40 μ m. Also, 5 discrete step heights on primary profile have been simulated: 1 μ m, 5 μ m, 10 μ m, 25 μ m, and 50 μ m. In the future research implementation of a probe with a better resolution should be investigated, as well as, possibilities to generate a larger number of points that will define more precisely the simulated measurement structures.

Keywords: Surface roughness, Traceability, Roughness standards, Displacement tranducer





KONCEPT PROVJERE TOČNOSTI POZICIONIRANJA NUMERIČKI KONTROLIRANIH OSI 3D OPTIČKIM SKENIRANJEM

CONCEPT OF POSITIONING ACCURACY TESTING OF NUMERICALLY CONTROLLED AXIS WITH 3D SCANNING SYSTEM

Marko Horvatek¹, Vedran Šimunović¹, Gorana Baršić¹, Nenad Drvar²

¹ University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Department of Quality, Ivana Lucica 5, Zagreb, Croatia

² Topomatika d.o.o., Ilica 231, HR-10000 Zagreb, Croatia

Expert paper / Stručni rad

Sažetak

U cilju određivanja točnosti alatnog stroja potrebno je provesti provjeru točnosti pozicioniranja, ponovljivosti i provjeru geometrijskih značajki toga stroja. Tradicionalno korišteni uređaji za provođenje navedenih ispitivanja su komparatori, kutnici, lineali, precizne libele, laserski mjerni sustavi i dr. Posljednjih godina zabilježen je izrazit rast u primjeni tehnologija optičkog 3D skeniranja u svim granama industrije. Tomu je pridonio ubrzani razvoj računalne industrije kao i sve precizniji optički sustavi. Ovim napretkom otvaraju se nova područja istraživanja i primjene optičkih mjernih sustava te se oni nameću kao alternativa klasičnim mjernim tehnikama.

U ovom radu obrađena je alternativa klasičnom načinu provjere točnosti pozicioniranja CNC strojeva korištenjem tehnologije optičkog 3D skeniranja. Opisan je način rada sustava, ponuđen je plan mjerenja, navedena su ograničenja sustava, te su prikazani preliminarni rezultati provjere točnost pozicioniranja CNC glodalice pomoću GOM 3D optičkog sustava.

Ključne riječi: Mjerenje, Provjera točnosti, Optički sustavi, CNC, GOM Aramis

Abstract

In case when accuracy determination of machine tool is needed, it is necessary to perform determination of accuracy and repeatability of numerically controlled axis as well as geometrical accuracy tests. Traditionally used measuring equipment for this tasks are comparators, squares, levels and laser measurement systems, etc. In the past couple of years, significant increase in usage of optical 3D scanning technologies has been recorded in all branches of the industry. These changes were caused by the rapid development of the computer industry and increased accuracy of optical 3D scanning systems. That improvements opened new fields of application where optical measurement systems can be used as an alternative to existing measurement techniques.

In this paper an alternative way of CNC machine positioning accuracy testing using 3D optical scanning technology is presented. Detailed description of measurement system with measurement plan and limiting factors is given. Preliminary results of positioning accuracy of CNC milling machine obtained using GOM 3D optical system are shown.

Keywords: Measurement, Machine accuracy, Optical systems, CNC, GOM Aramis

1. INTRODUCTION

Machine tool manufacturers as well as users are encouraged to perform geometrical testing and determination of accuracy and repeatability and of their machine at certain time periods in order to detect condition of critical machine parts such as machine axis, turning table, machine beds etc. International standards for geometry testing of the machine tools such as ISO 230-1:2012 [2] proposes guidelines regarding measurements equipment and methods in order to ensure valid and reliable measurement results.

Common equipment for this measurement task are laser interferometers that, in addition to displacement measurements, are used for measurements of numerous features such as straightness, flatness, parallelism, squareness, etc. with high accuracy. However, with those measuring systems it is possible to perform one measurement at a time what makes geometry testing rather time consuming task.

When information on the complete geometry of a product or tool is needed optical scanners are commonly used measuring system. [4,5]

With the increasing development of optical 3D scanning technologies, it is reasonable to expect greater use of this technology in field of machine testing in future. Possibility of determination of tool machine geometric deviations from just one set of measurements is a step forward and a good motivation for future research.

This new approach opens the possibility of testing of the entire geometry of the tool machine in no-load conditions, as well as, under the load conditions in short period of time.

2. CHARACTERISTIC OF CNC MILLING MACHINE LEO 9050

The tests were carried on the custom made CNC-controlled milling machine LEO 9050. It is a three-axis portal mill, mainly intended for woodworking. The milling machine has a vertically positioned milling head, Fig. 1 [1].



Fig. 1: LEO 9050 milling machine

The milling machine is controlled by a computer that processes the G-code and sends the control signals to the control unit of the machine. Stepping motors and motor spindle are controlled by control unit according to received signals. The milling machine uses 4 stepping

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motors for axis movement. Two motors are used for the x-axis drive, and one per y-axis and z-axis drive. Characteristics of LEO 9050 are given in Table 1.

LEO 9050					
Dimensions, mm	1200 x 850 x 300				
Weight, kg	95				
Working space, mm	900 X 500 X 200				
Processing materials	Wood, aluminum, polymers				
Maximum load, kg	50				
	Working table				
Dimensions, mm	1000 X 525				
Material	Aluminum EN AW 6063 / T66				
Positioning accuracy					
X (900 mm)	0,2 mm				
Y (500 mm)	0,15 mm				
Z (200 mm)	0,15 mm				

Tab. 1: Characteristics of milling machine LEO 9050

3. MEASUREMENT CONDITIONS

Measurements were carried using 3^{rd} generation of GOM ATOS Triple Scan with measuring volume MV700 (700 mm x 530 mm x 520 mm). GOM Reference points with diameter of 3 and 5 mm were used.

Working parameters are presented in Table 2.

Tab. 2: Working parameters

Maximum speed	1000 mm/min
Maximum acceleration	700 mm²/min
Temperature	20°C ± 4 °C
Compensations	All off
Preheated time	30 min

Spindle was removed in order to simplify measurement process.

4. MEASUREMENTS

During the test relative movement of two components of the machine were monitored: surface of the machine base (stationary part) and surface of the spindle mount (moving part). Large number of reference points had been previously attached on the machine base surface in order to extrapolate reference plane needed for definition of measurement coordinate system. The spindle mount position was monitored by tracking of 16 reference points. Positions of the reference points attached on the machine can be seen in Fig. 2.



Reference points on stationary machine base

Fig. 2: Position of reference points and monitoring (spindle mount) points

Adapters GOM ADC05-3140 and GOM ADC03-3088 [Fig.3] were used to extrapolate center axis of the machine tool X guide.



Fig. 3: GOM magnetic adapters

The reference coordinate system was created by 3-2-1 alignment in the ATOS Professional 2017 program. The z-axis was defined as the normal to machine base, the x-axis direction was aligned with the guide center axis. Positive directions of the reference coordinate system were aligned with positive directions of machine axis. Reference coordinate system can be seen in Fig. 4. After the coordinate system was set, spindle reference points and reference coordinate system were used as an input to the ARAMIS Professional program where displacement of the spindle mount (in the referent coordinate system) was measured for each measurement position. Reference points on spindle mount were used to create one point that represents position of the spindle mount.



Fig. 4: Coordinate system and displacement of spindle monitoring points





4.1. Measurement plan

Measurement plan for positioning accuracy was adopted from ISO 230-2:2014 [3]. Target positions for x-axis are shown in Table 3.

x–axis								
i	1	2	3	4	5	6	7	8
P _i [mm]	10	60	110	160	210	260	310	360
Direction	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Tab. 3: Measurement target positions

4.2. Positioning accuracy measurement

Positioning accuracy measurements were performed in ARAMIS professional program. Deviation of spindle reference point from target position in direction of x-axis was in accordance by ISO 203-2:2014 [3].

Results of positioning accuracy of LEO 9050 milling machine in x-axis direction are given in Fig. 5.



Fig. 4: Results of positioning accuracy of LEO9050

4.3. Straightness measurement

In order to show that the same dataset (positions of spindle reference points) can be used for straightness measurements, x-axis straightness in y-axis direction were measured in ARAMIS professional software. Results of measurement are given as an arithmetic mean of five repeated measurement for each direction, as shown on Fig. 5.





Fig. 5: Results of straightness of X axis

5. CONCLUSION

This paper presents an alternative to classical methods of measuring positioning accuracy and the straightness of machine tools axis. The test procedure was successfully performed using the GOM's ATOS optical scanners. The main advantage of this method is that coordinates of referent and tracking points are recorded during the measurement process. This functionality allows that the data from a single measurement set can be used for the determination of various geometric relations.

Optical 3D scanners offer the ability to measure positions with accuracy of several micrometres. Modern tool machines often have declared accuracy higher than the accuracy of the optical scanners that makes optical scanners unfitting measuring systems (for verification of the tool machine geometry) at the present moment. However with the rapid development of optical digitalization technology it is reasonable to expect more advanced scanners with the sufficient accuracy in the near future.

Accuracy of measuring result depend on a number of factors, such as the number of referent points, position of the scanner, determination of the coordinate measuring system, etc. As far as authors are aware, there are no guidelines that would give the directions to active the reliable and comparable measuring result.

In this paper proof of concept for the positioning accuracy of the custom made CNC milling machine using GOM 3D optical system have been presented.





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MODIFIKACIJA BIOLOŠKIH SVOJSTAVA TITANIJA ZA BIOMEDICINSKU PRIMJENU

THE MODIFICATION OF BIOLOGICAL PROPERTIES OF TITANIUM FOR BIOMEDICAL APPLICATION

Hrvoje Ivanković¹, Anamarija Rogina¹, Ivona Košić¹, Maja Antunović¹, Marica Ivanković¹

¹University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10000 Zagreb, Croatia

Conference abstract / Kongresno priopćenje

Sažetak

Gubitak kosti uslijed ozlijeda ili bolesti predstavlja značajan problem u ortopedskoj kirurgiji. Titanij (Ti) i njegove legure uvelike se koriste kao koštani implantati. Nedostaci titanija kao implantirajućeg materijala su visoki Youngov modul te manjak biokompatibilnosti koji uzrokuju "zasjenjenje naprezanja" (eng.stress shielding) i onemogućuju vezanje implantata za okolno tkivo. Obećavajući pristup modifikaciji titanija je primjena hidroksiapatita (HAp), bioaktivne keramike mineraloškog sastava sličnog sastavu prirodne kosti. Nedostatak metalurgije praha kao jednostavne metode priprave Ti/HAp kompozita je toplinska razgradnja hidroksiapatitne faze tijekom sinteriranja pri temperaturi iznad 800 °C. Iz tog razloga, u ovom radu priprava Ti/HAp kompozita provedena je uz dodatak titanijeva hidrida (TiH₂) kao agensa za sinteriranje što je omogućilo sinteriranje titanija pri nižoj temperaturi (800 °C), a time i zadržavanje stabilnosti apatita. Istražen je utjecaj različitog udjela HAp-a u Ti/HAp kompozitu na mineraloški sastav, mikrostrukturu, fizikalna i biološka svojstva kompozita. XRD analiza ukazala je na stabilnost HAp faze tijekom vakuum sinteriranja te na blagu oksidaciju titanija tijekom pripreme kompozita. Veći udio HAp-a doveo je do smanjenja gustoće uz istovremeno povećanje poroznosti zbog prisutnih mikro- i makro-pora stvorenih ugradnjom HAp čestica unutar titanijske matrice. Bioaktivnost Ti/HAp kompozita istražena standardnim in vitro testom u simuliranoj tjelesnoj tekućini povećala se s većim udjelom HAp-a u kompozitu. Nadalje, dobra vijabilnost Hek293 stanica tretiranih ekstraktom materijala ukazuje da Ti/HAp kompoziti nisu citotoksični.

Ključne riječi: Titanij, hidroksiapatit, citotoksičnost.

Abstract

The major issue in clinical orthopaedics is a large bone loss caused by trauma or diseases. Titanium (Ti) and its alloys are widely used as hard tissue replacements. The most limiting features of titanium are high Young's modulus and lack of biocompatibility. Such properties result in stress shielding and implant's inability to bond to the surrounding tissue. One of the promising approaches is modification of titanium by hydroxyapatite (HAp), a bioactive ceramic with mineralogical composition similar to one of the human bone. Powder metallurgy is a simple method to produce Ti/HAp composites; however, with possible thermal decomposition of hydroxyapatite phase during sintering above 800 °C. With this in mind, in this work Ti/HAp composites have been prepared using titanium hydride as a sintering agent to provide titanium sintering at lower temperatures (800 °C) and to preserve stability of apatite phase. Different HAp amounts were applied in order to investigate its influence on mineralogical composition, microstructure, physical and biological properties of Ti/HAp composites. The XRD analysis indicated thermal stability of HAp during vacuum sintering and slight oxidation of titanium. Higher HAp content resulted in decreased density and higher porosity due to formation of microand macro-pores caused by the integration of HAp particles into titanium matix. The bioactivity of Ti/HAp composites performed in simulated body fluid (SBF) by standard in vitro test was increased with higher HAp content. Moreover, good viability of Hek293 cells exposed to materials extracts indicated no cytotoxicity of Ti/HAp composites.

Keywords: Titanium, hydroxyapatite, cytotoxicity





KINETIC ANALYSIS OF THERMAL DEGRADATION OF THE POLYVINYL CHLORIDE/MAGNESIUM HYDROXIDE BLENDS

Miće Jakić, Jelena Jakić, Iva Radonić

University of Split, Faculty of chemistry and technology, Ruđera Boškovića 35, Split, Croatia

<u>Original scientific paper / Izvorni znanstveni rad</u>

Abstract

Thermal stability of poly(vinyl chloride)/magnesium hydroxide (PVC/Mg(OH)₂) blends has been investigated by thermogravimetric analysis (TG) in dynamic heating regime. PVC/Mg(OH)₂ blends were prepared by hot-melt extrusion (HME). According to TG analysis, PVC as well as PVC/Mg(OH)₂ blends decomposes in two degradation stages. In order to evaluate the effect of Mg(OH)₂ addition on the thermal stability of PVC, different criteria were used. It was found that by addition of Mg(OH)₂ the degradation of PVC starts at higher temperatures and therefore Mg(OH)₂ enhances the thermal stability of the PVC even at small loads up to 10%. By using multiple heating rate kinetics the activation energies of the PVC/PEO blends thermal degradation were calculated by isoconversional integral Flynn-Wall-Ozawa and differential Friedman method. According to dependence of activation energy on degree of conversion the complexity of degradation processes was determined. The addition of Mg(OH)₂ increased the apparent activation energy value of the thermal degradation of PVC. However, the exception is blend 95/5 which showed the lowest value.

Keywords: activation energy, fire retardant, magnesium hydroxide, poly(vinyl chloride), thermal degradation

1. INTRODUCTION

Polyvinyl chloride (PVC) is probably one of the most versatile and oldest thermoplastic polymers. It is the polymer with which a person comes into contact within minutes of their birth and accompanies us through life: from toys to drinking water pipes. One of the most outstanding characteristics of PVC is its enormous longevity with an almost unchanged functionality [1]. However, during polymerization of vinyl monomer to PVC defects may occur. The most important defects are tertiary chlorine atoms (from branch formation during polymerization) and allylic chlorine atoms (form by termination of the polymerization reaction). The degradation of PVC starts at these defect sites called the initiation sites of degradation. The degradation of PVC is called dehydrochlorination because hydrochloric acid (HCl) is split off during the process. The split-off of HCl generates new defects. If no stabilizer intervenes, this process continues in a zipper-like fashion. Hydrochloric acid and conjugated double bonds form (polyene sequences). Once six to seven conjugated double bonds have formed, a slight yellowing of the PVC can be observed. This yellow discoloration grows darker with increasing length of conjugation, from red to brown and finally to black. The problem of the flammability of PVC-based products is becoming increasingly central in modern society [2]. On its own, polyvinyl chloride ignites with great difficulty on account of its high chlorine content (56%). In addition, it actually prevents fires both starting and spreading because of its inherent flame retardant nature. Therefore, it can be used as wire and cable insulation in various machines, transmission cables, fiber optics, and construction materials [3]. Furthermore, PVC is characterized by the lowest value of heat of combustion compared to other polymer materials, which notably limits the risk of fire. Although many common applications of rigid PVC do not require the use of flame retardants, investigations are undertaken to additionally enhance its fire resistance and reduce its smoke generation ability. Aluminum hydroxide and magnesium hydroxide are most often used flame retardants for this purpose. The latter is used more often in the processing of unplasticized PVC due to its higher decomposition temperature. Magnesium hydroxide (Mg(OH)₂) also contributes to a considerable reduction of the amount of generated smoke and lightening of its color during a fire, and makes the smoke less corrosive because it also scavenges the hydrochloric acid which is formed during combustion [4]. According to the available literature [1-7], Mg(OH)₂, usually reagent grade (95%), used as a flame retardant was purchased from different producers, e.g. Darmstadt (Germany), Sigma Aldrich (USA), Tianjin Kermel Chemical Reagent Co. (China), Dead Sea Bromine Compounds Ltd. (Israel), Dead Sea Periclase (Israel), Kyowa (Japan), Magnifin (Austria). In this work magnesium hydroxide was obtained by substoichometric precipitation from seawater. Seawater used for the precipitation of magnesium hydroxide in this study was taken from the location nearby the Oceanographic Institute in Split, Croatia. Procedure details can be found in works of Jakić et al. [8-9]. An additional advantage of this technological process lies in huge reserves of seawater (1 m³ contains 0.945 kg of magnesium) [10].

However, in spite of a number of positive advantages, to achieve the necessary degree of fire resistance, the content of $Mg(OH)_2$ in the composite must be 40-50%. Such a content of inorganic filler, increasing the flame resistance, lowers the physicomechanical properties of the plasticised material considerably [2, 5]. Hence, in order to gain information how addition of magnesium hydroxide from seawater (content up to 10%) affects the thermal degradation of rigid polyvinyl chloride, non-isothermal thermogravimetry in an inert atmosphere was used. Thermogravimetry (TG) has demonstrated to be very appropriate and reliable





methodology to monitor the influence of degradation phenomena on polymeric materials. The results of the non-isothermal thermogravimetry are often used for determination of thermal stability of polymers and kinetic analysis. In this work the isoconversional integral Flynn-Wall-Ozawa (FWO) and differential Friedman (FR) methods were applied in order to determine dependence of apparent activation energy on conversion and, consequently, the kinetic scheme of thermal degradation process of PVC/Mg(OH)₂ blends.

2. EXPERIMENTAL

2.1. Materials

The powder of PVC (Ongrovil S5258) was purchased from BorsodChem (Hungary) and used as recived. The used Mg(OH)₂, specifications and the experimental procedure were described in detail in already published work [8-9]. PVC/Mg(OH)₂ blends of different compositions (100/0, 99/1, 98/2, 95/5 and 90/10) were prepared by mixing powders in a laboratory extruder (Dynisco, Qualitest, North America) at 175 °C and screw speed 150 rpm. In order to prevent thermal degradation of PVC during the sample preparation 2 wt.% Ca/Zn stabilizer (Reapack B-NT/7060) was added.

2.2. Thermogravimetric analysis

Thermogravimetric measurements of the PVC/Mg(OH)₂ blends were conducted by using PerkinElmer Pyris 1 TGA thermobalance at the heating rates of 5, 10 and 20 °C min⁻¹ in a temperature range 50 – 650 °C under a steady flow of nitrogen (20 cm³min⁻¹). Samples weighing approximately 10±0,5 mg for the analysis were used. To evaluate the thermal stability of the investigated polymers different criteria can be used. From TG and DTG curves the following characteristics were determined: the onset temperature (T_{onset}), the temperature at 5% mass loss ($T_{5\%}$), the temperature at the maximum degradation rate (R_{max}), the final mass (m_f) and the mass loss (Δ m) for the corresponding degradation steps.

2.3. Nonisothermal degradation kinetics analysis

The nonisothermal TG data can be used for the kinetic analysis of the investigated process. Kinetic analysis of the solid-state reactions that are ruled by a single process is based on Eq. (1):

$$\frac{d\alpha}{dt} \cong \beta \frac{d\alpha}{dT} = A \cdot \exp(-\frac{E}{RT}) \cdot f(\alpha)$$
(1)

where α is the degree of conversion, β is the linear heating rate (°C min⁻¹), *T* is the absolute temperature (K), *R* is the general gas constant (J mol⁻¹K⁻¹) and *t* is the time (min). *A* and *E* are Arrhenius parameters, the preexponential factor and the activation energy, respectively. Activation energy is often interpreted as the energy barrier opposing the reaction and preexponential or frequency factor as a measure of the probability that a molecule having *E* will participate in reaction. *f*(α) is a reaction model and together with *A* and *E* makes the kinetic triplet. Since *E* is associated with the energy barrier, it is suggested that prior to any

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kinetic analysis one should investigate the complexity of the process by determining the dependence of *E* on α by isoconversional methods [11-12]. Namely, this dependence is considered as a reliable criterion of the process complexity and isoconversional methods are considered as the most reliable methods for the calculation of E and E vs. α dependence of thermally activated reactions. If *E* does not depend on α , the investigated process is simple (overall single-stage) and can be described by unique kinetic triplet. Otherwise, the process is complex and the shape of the *E* vs. α curve indicates the possible reaction mechanism [11-12]. Therefore, E values and E vs. α dependence have been calculated by means of isoconversional method which can determine them without knowledge or assumption of kinetic model (model-free). Isoconversional methods enable determination of E directly from experimental α - T data ($\alpha = (m_o - m)/(m_o - m_f)$), where m_o , m and m_f refer to the initial, actual and residual mass of the sample obtained at several heating rates without the knowledge of $f(\alpha)$. The experimentally determined E is appropriate to call "effective", "apparent", "empirical", or "global" to stress the fact that it can deviate from the intrinsic activation energy of a certain individual stage [11-12]. Isoconversional integral Flynn-Wall-Ozawa (FWO) and differential Friedman (FR) methods have been used. FWO method is a linear integral method based on Eq. (2):

$$\log \beta = \log \frac{AE}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E}{RT}$$
(2)

FR method is a linear differential method based on Eq. (3):

$$\ln\left[\beta\frac{d\alpha}{dT}\right] = \ln A + \ln f(\alpha) - \frac{E}{RT}$$
(3)

The plots $log \ \theta$ vs. 1/T, and $ln[\ \theta \ d\alpha/dT]$ vs. 1/T obtained for α = const. from α - T curves recorded at several heating rates should be straight lines whose slopes allow calculation of E by means of FWO and FR method, respectively.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric analysis

The dynamic thermogravimetric (TG) curves (mass versus degradation temperature), and corresponding derivative thermogravimetric (DTG) curves (mass loss rate versus temperature) of PVC/Mg(OH)₂ blends obtained at 5 °C min⁻¹ are shown in Fig. 1. Collected data from TG/DTG curves (tabulated in Table 1) were used to assess the effect of Mg(OH)₂ additon on the degradation pattern of PVC. A two-stage degradation pattern is seen in the case of PVC (Fig. 2(a)). The first stage begins at 246 °C (T_{onset1}) and ends at 375 °C with a peak temperature at 264 °C (T_{max1}). This corresponds to a weight loss of 58.3%, which is slightly greater than the stoichiometric amount of HCl contained in PVC (cca 56%) indicating the existence of a parallel reaction. The second stage of degradation begins at 427 °C (T_{onset2}) and ends at 600 °C with a peak temperature of 460 °C (T_{max2}). The total weight loss at this stage is found to be 78.9%.

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PVC/Mg(OH) ₂	<i>Т</i> _{5%} (°С)	T _{onset} (°C)	T _{max} (°C)	<i>R</i> _{max} (%min⁻¹)	<i>m</i> f (%)	∆ <i>m</i> (%)
First stage						
100/0	233	246	264	9.5	41.7	58.3
99/1	243	248	268	8.2	43.1	56.9
98/2	246	249	268	8.2	43.8	56.2
95/5	252	253	267	10.1	46.8	53.2
90/10	251	254	270	8.6	50.0	50.0
Second stage						
100/0	-	427	460	1.6	21.1	20.6
99/1	-	429	466	1.7	20.6	22.5
98/2	-	430	461	1.7	21.5	22.3
95/5	-	428	459	1.6	24.7	22.1
90/10	-	432	463	1.7	27.2	22.7

Tab. 1. The characteristics of thermal degradation curves of PVC/Mg(OH)₂ blends (heating rate 5 °C min⁻¹).

In addition, S. Moulay [13] has exposed that PVC degradation takes place in a three successive stages: (1) HCl formation occurred in the first two stages within 220–370 °C; (2) benzene was exclusively produced in the first stage (220–290 °C) in parallel with HCl, and (3) the remaining aromatics were developed in the last stage (beyond 370 °C).

The degradation of all PVC/Mg(OH)₂ blends is found to follow similar pattern as PVC and shows two-stage degradation. As the Mg(OH)₂ content is increased, a total increase of onset temperature by 8 °C is observed. Likewise, the temperature at 5% mass loss and peak temperature also show the same changes indicating that Mg(OH)₂ enhances the thermal stabilty of the PVC. On the other hand, maximum rates of degradation don't change dramatically upon Mg(OH)₂ addition. The only exception is sample with 5% of Mg(OH)₂ content, showing the highest value (10.1 %min⁻¹) in the first degradation stage. The mass loss in the first degradation stage, Δm , decreased linearly as the Mg(OH)₂ content increased in the blend, while mass loss in the second degradation stage increased by 1.9% upon 1% Mg(OH)₂ addition and after that remained almoust unchanged. The final masses in the first and second stage increased linearly upon Mg(OH)₂ addition.

The TG/DTG curves scanned at higher heating rates (10 and 20 °Cmin⁻¹) are similar to those at 5 °Cmin⁻¹ and shifted to higher temperatures. At higher heating rates, polymer decomposition processes are more vigorously and consequently result to higher maximum rates of degradation.





Fig. 1. TG (a) and DTG (b) curves of PVC/Mg(OH)₂ blends thermal degradation at heating rate of 5 °C min⁻¹.

By reviewing available literature [1-7], many papers can be found investigating the Mg(OH)₂ as flame retardant in the processing of unplasticized PVC. From the results reported in the abovementioned literature, the conclusion is unambiguous: the Mg(OH)₂ addition indeed enhances the PVC fire resistance. Hence, from characteristic of thermal degradation curves it could be concluded that by addition of Mg(OH)₂ the degradation of PVC starts at higher temperatures and therefore Mg(OH)₂ enhances the thermal stabilty of the PVC even at small loads up to 10%.





Fig. 2. TG and DTG curves of PVC/Mg(OH)₂ blends 100/0 (a) and 90/10 (b) thermal degradation at different heating rates.

3.2. Nonisothermal degradation kinetics analysis

Collected data from non-isothermal thermogravimetric analysis of PVC/Mg(OH)₂ blends were used to assess the effect of Mg(OH)₂ addition on the degradation mechanism of PVC. Firstly, the dependence of *E* on α is established using isoconversional integral Flynn-Wall-Ozawa and differential Friedman methods. For each selected α =const., the corresponding plots (Figs. 3 and 4) according to Eqs. (2) and (3) are obtained and from their slopes values of

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E are calculated. Dependence of *E* on α obtained for PVC/Mq(OH)₂ blends is presented in Fig. 5. It can be concluded from Fig. 5 that *E* depends on α in a whole conversion range for all investigated samples, indicating complex degradation mechanism. Since E depends on α , the process cannot be described adequately by a single reaction model and a single pair of Arrhenius parameters. It is advised to resort to a multi-step kinetic analysis that would yield an individual reaction model and a pair of Arrhenius parameters for each of the reaction steps. Such an analysis can be accomplished by using the model fitting multivariate non-linear regression method [11, 12]. The presence of two or more inflection points or maximums for all investigated samples (Fig. 4) indicates that degradation takes place at least in two main steps, which is consistent with TG and DTG results (Figs. 1 and 2). Upon detailed examination of apparent activation energy of degradation of PVC calculated by FWO and FR methods one can notice three areas with different E values. As expected, other investigated samples also showed three different areas of apparent activation energy (Fig. 5). Conversion region from 0.01 to 0.99 was used to calculate the values of activation energy and the average values of the three apparent degradation stages are shown in Table 2. This is in an agreement with investigation of Moulay [13] who has established that PVC degradation takes place in a three successive stages. It should be emphasized that, in case when *E* changes with α , Friedman method is recommended as more reliable method then FWO [14].

Method	Sample	Conversion, α	E₁/ kJmol⁻¹	Conversion, α	E₂/ kJmol⁻¹	Conversion, α	E₃/ kJmol⁻¹
	100/0		119.6		144.8		360.3
	99/1		133.0		216.1		347.6
FWO	98/2	0.01 - 0.65	131.3	0.65 - 0.8	162.3	0.80 - 0.99	343.2
	95/5		117.5		162.1		294.0
	90/10		127.2		175.8		421.6
	100/0		114.1		157.1		360.2
	99/1		127.0		214.2		333.1
FR	98/2	0.01 - 0.60	127.9	0.60 - 0.8	200.2	0.80 - 0.99	338.1
	95/5		103.3		180.2		284.7
	90/10		126.5		187.2		403.6

Tab. 2. Range of apparent activation energy values of thermal degradation of PVC/Mg(OH)₂ blends obtained by Flynn-Wall-Ozawa and Friedman method.

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Fig. 3. FWO plots for the thermal degradation of PVC/Mg(OH)₂ blends: 100/0 (a), 99/1 (b), 98/2 (c), 95/5 (d) and 90/10 (e).

In the first degradation stage dehydrochlorination of PVC is the main degradation process and the average values of activation energy are 25-43 kJmol⁻¹ lower than in the second and 240-246 kJmol⁻¹ lower than in the third stage. Higher values for the second and third stages could be accounted by the higher collision frequencies at the higher degradation temperatures [15]. In the literature different values of *E* for neat PVC degradation can be found. Sánchez-Jiménez et al. [16] have obtained *E* values of 125 and 190 kJmol⁻¹ for first and second stage of degradation of PVC, respectively. In our previous study [17] thermal stability of neat PVC has been investigated and *E* values calculated by isoconversional methods FWO/FR are 146.3/125.6 kJmol⁻¹ (first stage) and 221.6/224.9 kJmol⁻¹ (second stage) respectively.





Fig. 4. FR plots for the thermal degradation of PVC/Mg(OH)₂ blends: 100/0 (a), 99/1 (b), 98/2 (c), 95/5 (d) and 90/10 (e).

Likewise, the average apparent activation energy of the first stage of thermal degradation of investigated PVC/Mg(OH)₂ blends calculated by isoconversional methods FWO/FR amounts in the range 103.3/117.5 – 127.9/133.0 kJmol⁻¹. Evidently, the addition of 1mas.% Mg(OH)₂ increased the *E* value after which *E* value remained more-less the constant. However, the exception is blend 95/5 which showed the smalest *E* value of 103.3/117.5 kJmol⁻¹ (Tab. 2). This exception is particulary evident on Fig. 5(b) for FR method. Usually, the lower value of apparent activation energy indicates the lower thermal stability of the sample. Althgouh, characteristic of thermal degradation curves proved that addition of Mg(OH)₂ enhances the thermal stability of the PVC, from the TG/DTG data it was concluded that sample with 5% of Mg(OH)₂ content is showing the highest value od R_{max} (10.1 %min⁻¹) in the first degradation stage. This means that this sample degrades faster than others, which is in accordance with the smalest *E* value.





Fig. 5. Activation energy as a function of conversion for PVC/Mg(OH)₂ blends calculated by means of Flynn-Wall-Ozawa (a) and Friedman (b) method.

In the second and third degradation stages the *E* values increased by the addition of 1mas.% $Mg(OH)_2$. Upon $Mg(OH)_2$ content increase the *E* values didn't follow linear trend and once again blend 95/5 showed the smalest *E* value. The observed anomaly is very interesting and

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should be further explored. Possibly, preparation of PVC/Mg(OH)₂ blends with greather Mg(OH)₂ content (> 10%) could give additional informations.

From the computational standpoint, the purpose of kinetic analysis of thermally stimulated processes is to establish mathematical relationships between the process rate, the extent of conversion, and the temperature [11-12]. This can be accomplished by determining a kinetic triplet. Hence, in order to fully describe the kinetic process of thermal decomposition of PVC/Mg(OH)₂ blends, it would be necessary to calculate other components of kinetic triplet (A and $f(\alpha)$), which will be the subject of future research.

4. CONCLUSIONS

In order to gain information how addition of magnesium hydroxide from seawater in small quantities (up to 10%) affects the thermal degradation of rigid polyvinyl chloride, nonisothermal thermogravimetry in an inert atmosphere was used. A two-stage degradation pattern is seen in the case of PVC. The degradation of all PVC/Mg(OH)₂ blends is found to follow similar pattern as PVC and shows two-stage degradation. As the Mg(OH)₂ content is increased, the degradation of PVC starts at higher temperatures and therefore Mg(OH)₂ enhances the thermal stabilty of the PVC even at small loads up to 10%. In this work the isoconversional integral Flynn-Wall-Ozawa (FWO) and differential Friedman (FR) methods were applied in order to determine dependence of apparent activation energy on conversion of thermal degradation process of PVC/Mg(OH)₂ blends. It can be concluded that *E* depends on *α* in a whole conversion range for all investigated samples, indicating complex degradation mechanism. Since *E* depends on α , it is advised to resort to a multi-step kinetic analysis that would yield an individual reaction model and a pair of Arrhenius parameters for each of the reaction steps. Upon detailed examination of apparent activation energy of degradation of PVC and its blends one can notice three areas with different E values. The addition of Mq(OH)₂ increased the apparent activation energy value of the thermal degradation of PVC. However, the exception is blend 95/5 which showed the lowest value. The observed anomaly is very interesting and should be further explored. Ultimately, in order to fully describe the kinetic process of thermal decomposition of PVC/Mg(OH)₂ blends, it would be necessary to calculate other components of kinetic triplet (A and $f(\alpha)$), which will be the subject of future research.

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TROŠENJE ALATA ZA IZVLAČENJE ELIPSI NA METALNOM LIMU

WEAR OF TOOLS FOR DRAWING ELIPSIS ON METAL SHEETS

Suzana Jakovljević¹, Krešimir Grilec¹, Ivica Antolković¹

¹ Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Ivana Lučića 5, Zagreb, Hrvatska

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Sažetak

Izvlačenjem elipsastih izbočina na metalnim limovima onemogućuje se klizanje osobnih vozila te njihov jednostavniji i sigurniji smještaj pri prijevozu na teretnim vozilima. Prilikom izvlačenja elipsi dolazi do trošenja površine alata za izvlačenje elipsi na mjestu dodira alata i metalnog lima. U ovom radu je analizirano trošenje alata za izvlačenje elipsi metalnog lima. Ispitana je tvrdoća materijala alata, analizirana je mikrostruktura uzorka alata i SEM-om je analizirana površina potrošenog dijela alata.

Ključne riječi: trošenje, tvrdoća, alatni čelik.

Abstract

By drawing elipsis on metal sheets, the antislip properties of the vehicles and their easier and safer transport on the cargo vehicles can be achieved. During drawing elipsis the wear of tools is occured on the contact of tool and metal sheet. In this paper were analyzed the wear of tools for drawing elipsis on metal sheets. The hardness, microstructure and topography of tool steel were tested

Keywords: wear, hardness, tool steel.

1. UVOD

Povećani razvoj automobilske industrije početkom 20 stoljeća uzrokovao je i povećanje potražnje automobila. Zbog tog razloga, važna je dobra organizacija transporta automobila od tvornice do auto-kuća, odnosno kupaca. Prijevoz automobila zahtijeva visoku razinu sigurnosti transporta. Važno je na propisani način onemogućiti pokretanje vozila prilikom transporta na kamionu kako ne bi došlo do oštećivanja vozila, ali i da se izbjegne ugrožavanje ostalih sudionika u prometu. Jedan od najvažnijih čimbenika sigurnosti prilikom transporta vozila su platforme na koje se navoze automobili, slika 1.



Slika 1: Kamion za prijevoz automobila [1]

Na površini platforme nalazi se mnoštvo eliptičnih izbočina koje imaju višestruku važnost. Elipse imaju protuklizno svojstvo - spriječavaju pomicanje vozila prilikom transporta i omogućuju lakši navoz automobila, a omogućuju i pričvršćivanje traka za vezanje tereta na platformi jer uz točne dimenzije elipsa omogućeno je i lako stavljanje i vađenje trake iz elipse. Sve navedene prednosti omogućuju sigurnost transporta i uštedu vremena. [2]

Za izradu platformi koriste se limovi za hladno preoblikovanje s visokom granicom razvlačenja EN10149-2/EN10051, kvalitete S420MC i debljine 2,5mm ili 4 mm. Ovisno o teretu, limovi debljine 2,5 mm koriste se za izradu platformi za prijevoz automobila, dok se limovi debljine 4 mm koriste za platforme za prijevoz kamiona i većih vozila. [2]

Proces probijanja se sastoji od tri faze, analogno fazama u procesu odrezivanja. U prvoj fazi je materijal pod djelovanjem tlačne sile prosjekača izložen naprezanju na elastično savijanje. To savijanje u određenom trenutku prelazi u plastično savijanje kod kojeg dolazi do deformacije materijala. U drugoj fazi nastaju znatne deformacije ispod prosjekača tj. materijal se savija i utiskuje u otvor prstena za prosijecanje kod kojeg dolazi do plastične deformacije zbog utjecaja vanjskih sila. U trećoj fazi zbog vrlo male debljine prstenastog elementa koji se deformira dolazi do prekoračenja stupnja deformacije. Javljaju je prve napukline ispred reznih rubova alata te dolazi do loma materijala i istiskivanja jezgre. Najveća relativna dubina prodiranja prosjekača kod koje dolazi do vrsti naterijala ovisi o vrsti i debljini materijala te o stanju reznih oštrica. U ovisnosti o vrsti materijala s povećanjem tvrdoće pada dubina prodiranja. Ako rezne oštrice nisu oštre, potrebna je veća dubina prodiranja prije pojave pukotina [3]. Nakon probijanja, na istoj probijačici, mijenja se alat i slijedi postupak izvlačenja lima.

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Izvlačenjem se pomoću posebno dizajnirane matrice (žiga) dobiva konačni oblik elipse s točno propisanim dimenzijama. Oblik i dimenzije alata definirani su dimenzijama elipse. Alati za izvlačenje i probijanje izrađuju se od alatnih čelika. Zbog visokih opterećenja u radu i specifičnih funkcija alata, od čelika se zahtijevaju i posebna svojstva kao npr. visoka tvrdoća i otpornost na trošenje, postojanost tvrdoće pri povišenim radnim temperaturama i druga [4]. Alatni čelici se, u pravilu, primjenjuju u toplinski obrađenom stanju, primarno zakaljeni i popušteni. Dodatno se provode i neki od postupaka za oplemenjivanje površine, npr. cementiranje.

2. EKSPERIMETALNI DIO

U radu je analizirano trošenje alata za utiskivanje elipsi, slika 2a. Očekivani broj udaraca na probijačici, tj. broj probijanja je 700 000-800 000. Međutim, ispitivani alat nije postigao projektirano vrijeme trošenja jer već nakon 150 000 probijanja oblik elipse nije odgovarao zahtijevanim dimenzijama kupca [2]. Zbog neodgovarajućih dimenzija elipse, proizvođač je prisiljen ponovno prilagoditi alat traženim zahtjevima i brušenjem oblikovati alat na definirane dimenzije te nakon toga ponovno provesti postupak toplinske obrade. Nakon tog postupka, alat je moguće koristiti još neko vrijeme, ali usprkos dodatnoj obradi dolazi do trošenja alata i pogrešnih dimenzija obratka.

2.1. Priprema uzorka

Za analizu mikrostrukture i tragova trošenja potrebno je odabrati i pripremiti reprezentantni uzorak zadovoljavajućih dimenzija. Alat je izrezan na manje dijelove te je izuzet jedan uzorak prikladan za daljnju pripremu, slika 2b.



Slika 2. a) Alat probijačice izrezan na dijelove; b) Uzorak za ispitivanje



2.2. Mjerenje tvrdoće

Mjerenje tvrdoće provedeno je Vickers metodom na tvrdomjeru INSTRON Wilson-Wolpert Tukon 2100B u Laboratoriju za toplinsku obradbu na Fakultetu strojarstva i brodogradnje, Zagreb. Rezultati mjerenja tvrdoće prikazani su u Tablici 1.

780			
773			
752			
75 ²			
719			
671			
598			
557			
532			
494			
417			
406			
404			
369			

Tablica 1. Iznosi izmjerenih tvrdoća

Na temelju izmjerenih tvrdoća napravljen je dijagram niza kaljenja, slika 3, te je određena efektivna dubina cementiranja prema normi HRN ISO 15787:2001 koja iznosi 0,74mm.





Slika 3. Raspored tvrdoća od ruba prema jezgri

2.3. Analiza mikrostrukture

U Laboratoriju za materijalografiju Fakulteta strojarstva i brodogradnje u Zagrebu, odabrani ispitni uzorak zaliven je u polimernu masu, brušen (brusni papiri P120, P320, P500, P1000, P2400 i P4000) i poliran (dijamantna pasta 3µm i 1µm). Nakon nagrizanja 3%-tnom otopinom nitala, mikrostruktura ruba i jezgre uzorka alata analizirana je svjetlosnim mikroskopom Olympus GX51, slika 4 i 5.





Slika 4. Mikrostruktura ruba uzorka alata



Slika 5. Mikrostruktura jezgre uzorka alata

Slika 4 prikazuje martenzitnu mikrostrukturu površine uzorka. U mikrostrukturi jezgri, slika 5, dominira gornji bainit što je potvrđeno mjerenjem tvrdoće na udaljenosti od ruba većoj od 10 mm – 368HV1. Dobivene mikrostrukture odgovaraju zahtjevima i svojstvima alatnih čelika (alata za izvlačenje elipsi) tj. žilavost i otpornost na trošenje.



2.4. SEM analiza

Skenirajućim elektronskim mikroskopom TESCAN VEGA 5136 MM u Laboratoriju za materijalografiju, FSB, provedena je analiza tragova trošenja na površini alata.



Slika 6. SEM slika površine potrošenog dijela alata

Na SEM slici površine uzorka, slika 6., jasno je vidljiv velik broj iščupanih dijelova površine alata i pukotina što dovodi do brzog trošenja alata i upućuje da je glavni mehanizam trošenja ovog alata umor površine, a do kojeg je došlo zbog kontinuiranog udarnog rada alata.

4. ZAKLJUČAK

Nakon detaljne analize uzorka alata probijačice koja je obuhvatila SEM analizu površine alata, analizu mikrostrukture svjetlosnim mikroskopom i mjerenje tvrdoće po Vickersu (HV1), može se zaključiti da:

Tvrdoća ruba uzorka alata iznosi 780HV1, a tvrdoća jezgre na udaljenosti 10mm od ruba 368HV1. Mikrostruktura odgovara izmjerenim tvrdoćama, odnosno, u rubnom sloju je martenzitna mikrostruktura, dok je mikrostruktura jezgre bainitna s mogućim udjelima martenzite i feritne faze te je niže tvrdoće što čini jezgru žilavom.

- SEM analiza ukazuje da je glavni mehanizam trošenja umor površine do kojeg dolazi zbog kontinuiranog udarnog rada alata te nastaju mikropukotine i dolazi do odvajanja dijelova alata.

- Efektivna dubina cementiranja iznosi 0,74 mm što nije dovoljno za uvjete rada ovog alata.

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Do prebrzog trošenja alata za izvlačenje elipsi metalnog lima, tj. do nepostizanja projektiranog vijeka trajanja alata dolazi zbog nedovoljne dubine cementiranog sloja. Vrijeme cementiranja je bilo prekratko pa se nije postigla dovoljna debljina cementiranog sloja što uzrokuje prebrzo trošenje alata te bi se iz tog razloga trebala provesti duža toplinska obrada. Tim postupkom dobila bi se veća efektivna dubina cementiranja što bi ispunilo zadane uvjete rada probijačice.

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PREPARATION AND THERMAL ANALYSIS OF POLYLACTIC ACID/MAGNESIUM HYDROXIDE COMPOSITES

Sanja Perinović Jozić, Anamarija Stoilova, Jelena Jakić, Branka Andričić

University of Split, Faculty of chemistry and technology, Ruđera Boškovića 35, Split, Croatia

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Abstract

Modification of polylactic acid (PLA) was performed by the addition of magnesium hydroxide $(Mg(OH)_2)$ prepared from seawater. Composites with satisfying homogeneity were made by previous preparation of PLA fibres from pellets and their subsequent milling. Differential scanning calorimetry (DSC) was used to study the thermal transitions and crystallinity of PLA/Mg(OH)₂ composites. Inorganic filler reduces PLA crystallinity, so doesn't work like a nucleating agent in PLA composites. The content of Mg(OH)₂ from 15 to 20% represents the amount after which the filler has an opposite impact on the thermal properties of PLA. The thermal stability of all samples was investigated by the nonisothermal thermogravimetric analyses (TG). Degradation of PLA and Mg(OH)₂ includes only one degradation stage while degradation of PLA/Mg(OH)₂ composites have up to six degradation stages. With an increase of Mg(OH)₂ content in the composites their thermal degradation becomes more complex and their thermal stability is getting worse.

Keywords: processing procedure, PLA/Mg(OH)₂ composites, thermal properties, thermal stability

1. INTRODUCTION

The main sources for the production of synthetic polymers are petrochemicals. Although these polymers significantly contribute to the development of modern society, the technical advantages of such polymers fall into the second plan, since the most of them after usage ends up in landfills or discarded in the environment and endanger human and animal health. The society, limited in sources of fossil fuels, such as coal and oil, is now focused on the new sources, such as renewable sources and the synthesis of biodegradable polymers.

By using biodegradable polymers, whose decomposition in controlled conditions results in a low molecular weight non-toxic compounds and biomass, the emission of harmful substances in the environment has been reduced. The most prominent representatives of the biodegradable polymers are polylactic acid (PLA) and poly(3-hydroxybutyrate) (PHB) [1]. Today, the highest degree of commercialization has been achieved by the production of PLA. This biodegradable polymer can be synthesized from lactic acid that is produced by a biotechnological process from starc rich raw materials [2]. Despite the great interest, PLA production is lower than expected due to large production costs (about 3 US \$ per kg in 2006.) [3]. The price of PLA, as one of the main drawbacks, can be reduced with additives and in the first place with fillers. It is a great advantage if these additives are cheap. By modification of biodegradable polymers, it is possible to extend their application areas and achieve properties of the commodity plastic (poly(vinyl chloride), polystyrene, polypropylene, polyethylene, etc.).

 $Mg(OH)_2$ is a nontoxic, noncorrosive, thermally stable and environment-friendly flame retardant in composite materials. It has been successfully applied in many fields, such as flame retardant in polymers [4], as a neutralizer in the treatment of acid wastewater and gases rich in sulfuric oxides [5], as an antacid excipient in pharmaceutics [6], in pulp and paper industry and as fertilizer additive. Various methods have been developed to synthesize magnesium hydroxide but the precipitation crystallization method is the most economical method for industrial continuous production with the simple process and low energy consumption [7]. The process involves the chemical reaction between magnesium ions of seawater with dolomite lime to produce a magnesium hydroxide precipitate [8]. Seawater represents a major reservoir and an inexhaustible source of magnesium hydroxide due to the high mass concentration of magnesium in seawater, which averages 1.35 g dm⁻³ i.e. 0.13% magnesium in the total mass of seawater [8].

PLA is now used in medicine such as surgical thread, in dialysis, pharmacy, automotive industry, aerospace, packaging industry and more recently in $_{3}D$ printing [9]. Today, more than ten companies around the world produce PLA [10]. This research work is based on the preparation of Mg(OH)₂ from seawater, production of PLA/Mg(OH)₂ composites on horizontal single-screw extruder in order to extent PLA application range. The main focus is on their thermal properties and thermal stability. Positive results will direct further investigations into the study of flame resistance properties.

2. EXPERIMENTAL

2.1. Materials

Polylactic acid (PLA), NatureWorks IngeoTM 3100HP in pellet form was obtained from Resinex Croatia d.o.o. (Croatia). PLA pellets were melted using horizontal single-screw extruder (Dynisco LME 230, Qualitest, Canada). The optimum rotation speed was 120 rpm and the





optimum temperature was 180 °C. The molten PLA was extruded in the form of the thin fibres and then milled. The finest milled PLA particles were separated with a sieve shaker; the particles on the sieve diameter of 0.37 mm were used for the sample preparation.

Seawater used for the precipitation of magnesium hydroxide in this study was taken from the location of the Oceanographic Institute in Split, Croatia. The content of MgO and CaO in seawater, determined complexometrically, was 2.3397 g L⁻¹ and 0.6505 g L⁻¹, respectively. Dolomite lime was obtained by the calcination of dolomite (location Dipalo-Sini, Croatia) at 950 °C for 5 h. The composition of dolomite lime used as the precipitation agent was as follows: 40.69 wt % MqO; 59.03 wt % CaO; 0.1083 wt % SiO₂; 0.0705 wt % Fe₂O₃; 0.0925 wt % Al₂O₃. Seawater was pre-treated with sulphuric acid in order to remove bicarbonate (HCO₃⁻) and carbonate (CO_3^{2-}) ions, followed by the removal of the liberated carbon dioxide (CO_2) by aeration in a desorption tower. The flow rate of the induced air was 120 L h⁻¹ and the volumetric flow rate of seawater through the desorption tower was 6 L h⁻¹. After the pretreatment of seawater, a calculated amount of dolomite lime was added to the magnesium hydroxide precipitate. The experiments were carried out with substoichiometric precipitation, with the addition of 120% of the stoichiometric quantity of dolomite lime. The precipitation reaction took 30 min under magnetic stirring. Sedimentation was improved by the addition of the optimum amount (4.8 cm³/2L) of the anionic 130A flocculent (polyacrylamide) (Hercules, Netherland). After sedimentation of the magnesium hydroxide, the precipitate was decanted and rinsed 5 times with distilled water (pH = 5.86). Rinsing by decanting was performed with about 1 dm³ of the rinsing agent. The duration of contact with the rinsing agent was about 30 min, i.e. until the precipitate settled again before the next decanting. After rinsing by decanting, the samples were rinsed in the process of filtering on multiple funnels using repeated rinsing (5 times) with distilled water. The rinsed precipitate was dried in an oven at 105 °C. The contents of MgO and CaO in the samples of magnesium hydroxide product (120% precipitation) were 95.16 wt % and 2.95 wt %, respectively. The average particle diameter is 127,14 µm with a standard deviation of 32,58 µm. PLA pellets and Mq(OH)₂ powder were dried in a vented oven at 100 °C for 4 h prior to processing to remove moisture.

2.2. Sample preparation

The milled PLA fibres were blended with various amounts of Mg(OH)₂, as shown in Table 1, using horizontal single-screw extruder (Dynisco LME 230, Qualitest, Canada). The optimum rotation speed was 120 rpm and the optimum temperature was 180 °C.



Sample	Composition / wt %				
Sumple	PLA	Mg(OH) ₂			
PLA o	100	0			
PLA 2	98	2			
PLA 4	96	4			
PLA 6	94	6			
PLA 8	92	8			
PLA 10	90	10			
PLA 15	85	15			
PLA 20	80	20			
PLA 30	70	30			
PLA 40	60	40			
PLA ₅ 0	50	50			
Mg(OH)₂	0	100			

Tab. 1: Composition of PLA/Mg(OH)₂ composites

2.3. DSC analysis

The thermal characteristics of the composites were determined using differential scanning calorimeter (DSC 823°, Mettler-Toledo), equipped with an intracooler. The measurements were performed in the closed aluminium pans under nitrogen atmosphere (flow rate was 30 cm³ min⁻¹). Approx. 10 mg samples were heated from 25 °C to 205 °C at 20 °C min⁻¹ (first heating scan), than cooled from 205 °C to 0 °C at 20 °C min⁻¹ (cooling scan), kept at 0 °C for 5 min and finally heated from 0 °C to 205 °C at 20 °C min⁻¹ (second heating scan). The cold crystallization temperature (T_{cc}), the premelting crystallization temperature (T_{pmc}), the melting temperature of the cold crystallization exotherm, the premelting crystallization exotherm, respectively, whereas the glass transition temperature (T_g) was taken as the inflection point of the specific heat decrement at the glass transition. Degree of crystallinity (X_c) of PLA was calculated according to Eq. (1) [11]:

$$X_{c}(\%) = \frac{\Delta H_{m} + \sum \Delta H_{c}}{\Delta H_{100\%} \times w_{PLA}} \times 100$$
(1)

where $\Delta H_{\rm m}$ is the melting enthalpy of the sample, $\Delta H_{\rm c}$ is the crystallization enthalpy of the sample, $\Delta H_{100\%}$ is the melting enthalpy of 100% crystalline PLA (93 J g⁻¹) and w is the weight fraction of PLA in the sample.





2.4. TG analysis

The thermal degradation of the composites was investigated thermogravimetrically (Pyris 1 TGA, Perkin-Elmer). Sample mass was 5.0 \pm 0.1 mg. TG analysis was carried out in the temperature range from 50 to 500 °C under nitrogen atmosphere (flow rate was 20 cm³ min⁻¹) at the heating rate of 10 °C min⁻¹.

3. RESULTS AND DISCUSSION

3.1. DSC analysis

Using DSC analysis, the influence of the inorganic filler on the thermal properties and PLA crystallinity was investigated. The DSC curves of PLA/Mg(OH)₂ composites are shown in Fig. 1, 2 and 3. The first heating scan curves reflect the influence of the thermal history of the composites and the influence of the filler on the thermal properties of PLA. But, the curves of the second heating scan show the influence of the filler only. Index 1 and 2 on the thermal characteristic represent the first and the second heating scan, respectively.



Fig. 1: DSC curves of the first heating scan for PLA, Mg(OH)₂ and PLA/Mg(OH)₂ composites





Fig. 2: DSC curves of the cooling scan for PLA, Mg(OH)₂ and PLA/Mg(OH)₂ composites



Fig. 3: DSC curves of the second heating scan for PLA, Mg(OH)₂ and PLA/Mg(OH)₂ composites

The values of the thermal characteristics obtained from DSC curves are presented in Tab. 2, 3 and 4. The cold crystallization temperature (T_{cc1}) slowly increases with the increase of inorganic filler content up to 15% from 102 °C to 107 °C. With further increase of Mg(OH)₂ content, the composites with Mg(OH)₂ content higher than 15%, T_{cc1} decreases to 104 °C. The cold crystallization enthalpy (ΔH_{cc1}) is almost the same for pure PLA and the composites with Mg(OH)₂ up to 10%. For the composites with 15 and 20% percent of the filler, the values of ΔH_{cc1} are slightly lower, around 28 J g⁻¹, but the further increase of the filler content reduces

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ΔH_{cc1} to 13.2 J g⁻¹. From the aforementioned DSC thermal characteristics, it can be concluded that Mg(OH)₂ content from 15 to 20% represent the amount after which the filler has an opposite impact on the thermal properties of PLA. The premelting crystallization temperature (T_{pmc1}) doesn't change with the increase of Mg(OH)₂ content in the composites, Tab. 2. The premelting crystallization enthalpy gradually decreases with the increase of Mg(OH)₂ and at 40 and 50% percent of Mg(OH)₂ it doesn't occur. The melting temperature (T_m) doesn't change up to 20% percent of Mg(OH)₂, but the further increase of the filler in the composites decreases T_m from 180 to 174 °C. Again, the content of Mg(OH)₂ of 20% represents the amount after which the filler has an opposite impact on the thermal properties of Mg(OH)₂ content from 43.4 to 16.1 J g⁻¹. From the change of degree of crystallinity (X_{c1}), it is difficult to conclude how Mg(OH)₂ affects the crystallization of PLA. Generally, is noticed that pure PLA has higher value of X_{c1} (14.4%) than PLA in the composites, with the exception of the composite with 6% of Mg(OH)₂ (18.9%).

Sample	T_{cc1}	ΔH_{CC1}	Tpmc1	ΔH_{pmc1}	Tmi	$-\Delta H_{m1}$	X _{C1}
Sample	/°C	/J g-1	/°C	/J g-1	/°C	/J g-1	/%
PLA o	102	29.0	166	1.0	182	43.4	14.4
PLA 2	102	29.2	165	1.2	182	41.6	12.3
PLA 4	104	30.6	166	1.1	182	41.0	10.4
PLA 6	104	29.4	164	0.8	181	46.7	18.9
PLA 8	105	30.6	165	0.9	180	39.3	9.1
PLA 10	106	31.0	165	0.7	180	40.2	10.2
PLA 15	107	27.4	164	0.4	180	37.6	12.4
PLA 20	106	28.0	165	0.2	180	33.6	7.3
PLA 30	105	21.8	164	0.1	179	26.6	7.2
PLA 40	104	17.9	1	1	177	19.1	2.2
PLA50	105	13.2	1	1	174	16.1	6.2

Tab. 2: Thermal characteristics of PLA and PLA/Mg(OH)₂ composites from the first heating scan

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Camala	T _{mc}	ΔH_{mc}
Sample	/°C	/J g⁻¹
PLA o	97	27.4
PLA 2	92	8.7
PLA 4	92	5.5
PLA 6	91	4.9
PLA 8	91	2.6
PLA 10	90	1.9
PLA 15	1	1



PLA 20	1	/
PLA 30	1	/
PLA 40	1	/
PLA ₅ 0	1	1

Tab. 4: Thermal characteristics of PLA and PLA/Mg(OH)₂ composites from the second heating scan

Comple	T _{mg2}	Δc_{p_2}	T _{cc2}	ΔH_{cc2}	T _{pmc2}	ΔH_{pmc2}	T _{m2}	$-\Delta H_{m_2}$	X _{c2}
Sample	/°C	/J g ⁻¹ ° C ⁻¹	/°C	/J g ⁻¹	/°C	/J g ⁻¹	/°C	/J g ⁻¹	/%
PLA o	65	0.2	97	1.9	165	1.1	178	42.5	42.3
PLA 2	63	0.4	101	17.8	162	2.4	176	43.1	24.7
PLA 4	63	0.4	104	22.8	162	1.7	175	40.6	17.6
PLA 6	63	0.4	105	24.7	162	1.3	177	40.3	15.9
PLA 8	63	0.4	109	29.4	161	0.2	177	37.0	8.2
PLA 10	62	0.4	109	32.1	1	1	174	36.5	4.8
PLA 15	62	0.5	109	30.6	1	1	175	34.5	4.3
PLA 20	62	0.3	108	25.6	1	1	173	31.8	7.9
PLA 30	62	0.3	108	18.2	1	1	173	25.7	11.1
PLA 40	60	0.3	109	15.1	1	1	168	20.0	8.2
PLA50	59	0.2	110	10.1	1	1	164	12.8	5.4

Tab. 3 shows the thermal characteristics of DSC cooling scan curves for all composites. The crystallization from the melt occurs only in the composites with Mg(OH)₂ content up to 10%. The melt crystallization temperature (T_{mc}) decrease about 6 °C with the addition of Mg(OH)₂, but the further increase of Mg(OH)₂ content doesn't change it significantly. The melt crystallization enthalpy (ΔH_{mc}) significantly decrease with the addition of Mg(OH)₂ from 27.4 to 8.73 J g⁻¹. Increase of Mg(OH)₂ content results in a gradual decrease of ΔH_{mc} from 8.73 to 1.93 J g⁻¹. It can be concluded that Mg(OH)₂ doesn't act as a nucleation agent of PLA crystallization but just the opposite, prevents it. If the melt crystallization even occurs, it starts later, and it is independent on the filler content.

DSC curves of the second heating scan of PLA/Mg(OH)₂ composites are used to obtain the thermal characteristics that are presented in Tab. 4. The glass transition temperature (T_{g2}) slowly decreases from 65 to 59 °C with the increase of Mg(OH)₂ content in the composites. Tab. 4 also shows the specific heat capacity (Δc_{p2}) which increases with the increase of Mg(OH)₂ up to 15%, but with a further increase of the filler content, it decreases. The value of T_{cc2} increased by 4 °C with the addition of Mg(OH)₂, but with the increase of Mg(OH)₂ content it continues to grow but with lower intensity, Tab. 4. The cold crystallization enthalpy of pure PLA is quite low (1.8 J g⁻¹) and the addition of only 2% of Mg(OH)₂ rapidly increased it to 17.6 J g⁻¹. Further, increase of Mg(OH)₂ up to 10% increase the value of ΔH_{cc2} from 17.6 to 32.08 J g⁻¹, but with the addition of Mg(OH)₂ content less than 8% and there are very



small transitions. The value of T_{pmc2} decreased by 3 °C with the addition of Mg(OH)₂ but an increase of Mg(OH)₂ content doesn't change it, Tab. 4. The value of ΔH_{pmc2} slightly increase by the addition of Mg(OH)₂ but increases of the filler content decrease it. The value of T_{m2} decreases with the increase of Mg(OH)₂ content in the composites from 178 to 164 °C. The melting enthalpy decreases with the increase of Mg(OH)₂ content from 42.5 to 12.8 J g⁻¹. At the second heating scan of PLA/Mg(OH)₂, X_{c2} of the composites decreases with the increase of Mg(OH)₂ up to 15% (from 42.3 to 4.3%) followed by an irregular increase of X_{c2} , Tab. 4. From the obtained characteristics of DSC curves of the second heating scan, it can be also concluded that Mg(OH)₂ content from 15 to 20% is the amount after which the filler has an opposite influence on the thermal properties of PLA. In the further research, it is necessary to prepare the composites with Mg(OH)₂ content between 15 and 20% to better determine the filler limit content after which its influence on the thermal properties of PLA changes.

The results obtained coincide with the appearance of surface roughness, i.e. surface roughness occurs in the samples containing more than 20% of Mg(OH)₂. In the literature, Mg(OH)₂ content in some other composites may range from 40 to 70% [12], which is very doubtful if based on the results of this research. The appearance of PLA/Mg(OH)₂ composite samples with higher filler content questions the mechanical properties, but also some other properties of these composites. Mg(OH)₂ doesn't act as a nucleation agent of PLA crystallization but prevents its crystallization. As the filler particles are very large, PLA crystallization is disrupted because macromolecular motions in that environment are limited. Modification of Mg(OH)₂ surface could improve the adhesion between the polar filler and the nonpolar matrix and enhance the material properties, or even increase the optimum content of the filler.

3.2. TG analysis

Thermal stability of PLA has great importance because during processing the polymer is exposed to a temperature above its melting point where degradation may occur. In a more complex system, eg. PLA/Mg(OH)₂ composites, the thermal stability must be well known not only for the processing but also for the final application. TG and associated DTG curves are shown in Fig. 4 and 5.





Fig. 4: TG curves of the nonisothermal degradation of PLA, Mg(OH)₂ and PLA/Mg(OH)₂ composites





Generally, PLA shows fast and almost complete degradation (residual weight of the sample $(m_f) < 1\%$) with one degradation stage, Fig. 4 and 11. The temperature at 5% weight loss ($T_{5\%}$), the onset temperature (T_{onst}) and the temperature at maximum degradation rate (T_{max}) for PLA are 269.7; 334.0 and 366.6 °C, respectively (Fig. 4 and 8-10). On DTG curve of PLA (Fig. 5), apart from the major degradation stage, there are small weight losses at the very beginning of the degradation, or small "shoulders" at the main decomposition peak in the range of 300 to 350 °C. Other authors also observed this thermal degradation at about 300 °C that can be attributed to the aluminium-catalyzed depolymerization due to the residual



aluminium catalysts in PLA sample [13]. The main degradation products of PLA are oligomers, lactide, acetaldehyde, carbon dioxide, carbon monoxide and ketene [14,15].

The inorganic filler, Mg(OH)₂, decomposes through one degradation stage and its degradation occurs much later than PLA, Fig. 4. The values of $T_{5\%}$, T_{onset} and T_{max} are 364.3, 370.0 and 401.2 °C. The residual weight of Mg(OH)₂ is 71.59%. Since it is a material that serves as a flame retardant, i.e. during degradation releases water that should prevent the ignition of the material that contains it, its degradation should take place before degradation of PLA [16]. From TG curves of the polymer and the filler, Fig. 4, it is a questionable action of Mg(OH)₂ as a flame retardant for PLA and it is necessary to analyse the results obtained from their composites so that a definite conclusion can be drawn. It is also necessary to conduct combustion tests with appropriate instrument techniques and methods.

PLA/Mg(OH)₂ composites decompose in several degradation stages what is visible in Fig. 4 and 5, but for better observation of this stages Fig. 6 and 7 is shown, too (Roman numerals I-VI signify degradation stages as they come up in temperature range of the experiment, because the composites do not exhibit the same degradation stages). By reviewing the literature that deals with a similar subject as this paper, it was found a paper in which PLLA/Mg(OH)₂ nanocomposite were prepared by the film casting method. The nanoparticles of Mg(OH)₂ and PLLA were synthesized by the authors and the nanocomposites decompose in two degradation stages [17]. The filler in this paper doesn't have nano dimensions and the composites have a very complex degradation which cannot be fully explained without additional analysis and DTG curves give a better insight into it. Fig. 4 and 5 show the degradation of all composites include the composite with 8% of Mg(OH)₂. This sample was excluded from further analysis because its curve coincides with the curve of PLA 10 composite. This pointed out the problem during the preparation of this composite.

The first and the biggest degradation stage (I) occurs in the range of 225 to 300 °C of all composites and represents the degradation of PLA. It has been observed that with the increase of Mg(OH)₂ content degradation temperatures $T_{5\%}$, T_{onset} and T_{max} of PLA decreases from 296.7 to 219.7 °C, 334.0 to 224.0 °C and 366.2 to 242.0 °C (Fig. 8-10), respectively. Decomposition of the composites is very complex and attention is focused only on the degradation beginning, i.e. the influence of the filler on the thermal stability of the polymer (stage I). Thermal stability of PLA gets worse by the addition of Mg(OH)₂ because the degradation temperatures $T_{5\%}$, T_{onset} and T_{max} move to lower temperatures. This result was not expected due to the better thermal stability of Mg(OH)₂ than PLA, Fig. 4 as well as the results of C. H. Kum and his associates [17].









Fig. 6: DTG curve of the nonisothermal degradation of PLA/Mg(OH)₂ composite with 4% of Mg(OH)₂



Fig. 7: DTG curve of the nonisothermal degradation of PLA/Mg(OH)₂ composite with 50% of Mg(OH)₂

The second degradation stage (II) occurs only in the composites with 4 and 6% of Mg(OH)₂, Fig. 5 and 6. DTG curves of these compositions also show a small "shoulder" along with the main degradation peak, i.e. the degradation peak of PLA, and it is around 270 °C. In the temperature range of 300 to 375 °C, the third degradation stage (III) occurs in all compositions except for the composite with 2% of Mg(OH)₂, Fig. 5. The fourth degradation stage (IV) is observed after the content of Mg(OH)₂ is increased above 10%. The temperature interval of this degradation stage is from 375 to 400 °C, Fig. 5. The fifth degradation stage (V) occurs only in the composite with 50% of Mg(OH)₂, Fig. 5 and 7. The temperature range of this stage is from 440 to 460 °C and it can be considered as a shoulder on the sixth degradation stage. The sixth degradation stage (VI) is observed in all PLA/Mg(OH)₂ composites except for the composite with 2% of Mg(OH)₂, Fig. 5, and occurs in the range of 430 to 500 °C.

Fig. 8-12 illustrates the characteristics of TG and DTG composite curves to make detection of the filler impact on the thermal stability of the polymer easier. The maximum degradation



rate of PLA ($(dm/dT)_{max}$) increase with the addition of 2% of Mg(OH)₂ in the composites from 23.36 to 37.54 % °C⁻¹ but a further increase of the filler content lowers it, Fig. 12. The filler moves decomposition of PLA to the lower temperature and accelerates it too. In Fig. 12, the dependence of $(dm/dT)_{max}$ on Mg(OH)₂ content with and without PLA 4 and PLA 6 composites is shown because these composites have degradation stage II which doesn't appear in other composites. The value of m_f increases with the increase of Mg(OH)₂ content in the composites, almost linearly, Fig. 11. The obtained values of m_f are in a good agreement with the theoretical calculation of m_f which indicates good preparation of the composite.



Fig. 8: Dependence of $T_{5\%}$ on Mg(OH)₂ content in the composites



Fig. 9: Dependence of Tonset on Mg(OH)₂ content in the composites





Fig. 10: Dependence of $T_{\rm max}$ on Mg(OH)₂ content in the composites



Fig. 11: Dependence of $m_{\rm f}$ on Mg(OH)₂ content in the composites



Fig. 12: Dependence of (dm/dT)_{max} on Mg(OH)₂ content in the composites

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4. CONCLUSION

The milled PLA fibres and Mg(OH)₂ powder was successfully prepared and the homogeneous PLA/Mg(OH)₂ composites were obtained. Prepared composites with Mg(OH)₂ content above 20% have a rough surface making the quality of the prepared composites questionably, i.e. primary their mechanical properties. The reason could be in large particles of Mg(OH)₂. The filler has a complex effect on the thermal properties of PLA. From DSC curves it can be concluded that Mg(OH)₂ content from 15 to 20% is the amount after which the filler has opposite influence on the thermal properties of PLA. In the further research, it is necessary to prepare the composites with $Mq(OH)_2$ content between 15 and 20% for better determination of the filler limiting content after which its influence on the thermal properties of PLA changes. The filler, Mg(OH)₂, doesn't act as a nucleation agent of PLA crystallization but prevents its crystallization. TG and DTG curves show one degradation stage for PLA and $Mq(OH)_2$ while PLA/Mq(OH)_2 composites have up to six degradation stages. It's a very complex decomposition that can't be fully explained without additional instrument techniques. Thermal degradation of PLA is accelerated with the addition of Mg(OH)₂ and its thermal stability is worsened. From the obtained data, the action of Mg(OH)₂ as a fire retardant for PLA is guestionable.

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PRIMJENA METODE SEPARACIJE POGREŠKE VOĐENJA NA MJERENJE ODSTUPANJA OD PRAVOCRTNOSTI

APPLICATION OF ERROR SEPARATION METHOD ON STRAIGHTNESS MEASUREMENT

Marko Katić¹, Helena Tubić¹, Jakov Baričević¹

¹ Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Ivana Lučića 5, Zagreb, Hrvatska

<u>Original scientific paper / Izvorni znanstveni rad</u>

Sažetak

Ovaj rad opisuje inicijalna mjerenja novog 2D mjernog sustava u Laboratoriju za precizna mjerenja duljina (LFSB). Odstupanje od pravocrtnosti linearnih vodilica jedan je od primarnih utjecaja na točnost budućih mjerenja pomoću ovog sustava. Kako bi se utvrdilo odstupanje od pravocrtnosti, provedena su ponovljena mjerenja ovih vodilica pomoću dvije različite mjerne metode. Dodatno, provedena je i drugačija metoda mjerenja odstupanja od pravocrtnosti: metoda separacije pogreške vođenja. Metoda razdvajanja pogreške može pružiti još veću točnost nego uobičajene mjerne metode mjerenja odstupanja od pravocrtnosti. Ova metoda je detaljno opisana, a rezultati te metode se uspoređeni s mjerenjima dobivenim uobičajenim metodama mjerenja odstupanja od pravocrtnosti, laserskim interferometrom i autokolimatorom.

Ključne riječi: Odstupanje od pravocrtnosti, metoda separacije pogreške, Mjeriteljstvo duljine, Sljedivost.

Abstract

This paper describes initial measurements of a new 2D measurement system at Laboratory for precise measurement lengths (LFSB). Straightness deviation of two linear guides is one of the primary influences on the accuracy of future measurements using this system. In order to determine straightness deviation, these linear guides have been repeatedly measured using two different measurement methods. Additionally, a different method of straightness measurement was also carried out: reversal error separation. Reversal error separation method could provide even higher accuracy than typically used straightness measurement method. This method has been described in detail, and its measurements were compared to measurements obtained with typicall straightness measurement methods, a laser interferometer and an autocollimator.

Keywords: Straightness measurement, Error separation method, Length metrology, Traceability.

1. INTRODUCTION

Precision engineering relies on several fundamental concepts that are defined across several ISO standards, most notably in ISO 1101:2018 (Geometrical tolerancing - Tolerances of form, orientation, location and run-out) [1]. Among other tolerances of form, straightness is relatively simple to define; but in light of recent developments in precision manufacturing methods, it is becoming increasingly difficult to measure. Error separation techniques [2], [3], are therefore becoming important, not only to achieve highest accuracy levels which are required, but also because these methods can provide high accuracy results without the use of state-of-the-art measurement equipment.

Typical measurement setup for straightness measurement uses an LVDT sensor mounted on a precision linear guide, which measures relative deviation of the measured surface relative to the linear guide, Figure 1. Results need to be corrected for misalignment of measured surface and external datum, usually using linear regression with least-squares method. However, any straightness error in the external datum itself will remain in the results, so the accuracy of the external reference is the limiting factor in this type of measurement. This error can be separated from the measurement results if additional measurements are made, usually by rotating the direction of the measured surface.

Contactless methods include, among others, laser interferometer and autocollimator, both of which are state-of-the-art methods able to provide highest accuracy. Since the external reference in these methods is an optical axis, they succeefully eliminate any influence of straightness errors of the external reference. However, they are limited by accuracy of calculation of index of air referaction [4] and vibration.

All of these methods were applied to determine the straightness of a precision linear guide, which is a part of a new 2D measurement system in Laboratory for precise measurement of dimensions (FSB-LPMD) shown in Figure 2. Laser interferometer and autocollimator results were used as reference for comparison with error separation results, which were obtained with an LVDT sensor.



Fig. 1: Schematic representation of straightness measurement.



2. MEASUREMENT RESULTS

2.1. Reference measurements

Straightness of a precision linear guide was measured over 800 mm, using both an autocollimator and a laser interferometer configured for straightness measurement. Unidirectional straightness was measured, with 7 repeated measurements over the course of several months for both methods [5]. Results shown in Table 1 and Figure 3 indicate good agreement between these methods.



Fig. 2: A part of a new 2D measurement system in FSB-LPMD, showing linear guide for which straightness was measured.

	Interferometer		Autocollimator		
Nominal position /mm	Straightness deviation /µm	Standard deviation of the result /µm	Straightness deviation /µm	Standard deviation of the result /µm	
0	-3.12	0.70	-3.10	0.30	
100	-1.30	0.30	-1.63	0.25	
200	0.73	0.50	0.16	0.20	
300	4.92	0.20	4.83	0.40	
400	3.16	0.30	3.50	0.40	
500	0.45	0.50	-1.80	0.50	
600	-2.61	0.20	-4.59	0.10	
700	-3.74	0.20	-2.83	0.30	
800	1.50	0.20	3.83	0.20	

Tab. 1: Results of reference straightness measurements.

According to results shown in Table 1, straightness deviation measured with interferometer and autocollimator is equal to 8.66 μ m and 9.42 μ m, respectively.





Fig. 3: Results of reference straightness measurements.

2.2. Error separation measurements

Error separation methods are typically used to separate form error of external datum from the form error of measured object. Numerous approaches to solving this objective have been introduced, with reversal error separation ("Donaldson reversal") being the simplest to implement [2]. Reversal technique for error separation is schematically shown in Figure 4, and its application to a granite straightedge used in this work is shown in Figure 5.





If $I_1(x)$ is the straightness measurement result obtained in initial probe orientation, and $I_2(x)$ is the result obtained after reversal of both probe and straightedge, then external datum straightness deviation G(x) and measurement object straightness deviation R(x) can be separated using the following formulas:

$$G(x) = \frac{I_1(x) - I_2(x)}{2}$$
(1)

$$R(x) = \frac{I_1(x) + I_2(x)}{2}$$
(2)





Fig. 5: Initial and reversed measurement orientations.

Measurements were made over the same length and nominal position on the linear guide, with spacing of data points reduced to 50 mm in order to obtain a more robust error separation result [6]. The goal of this experiment was not to determine the straightness deviation of the granite slide, but rather to use it as a stable "transfer artefact" for determination of the straightness error of the linear guide. Results are shown in Table 2 and a graphical comparison with reference measurements is shown in Figure 6.

Nominal position /mm	Straightness deviation (initial orientation) /µm	Straightness deviation (reverse orientation) /μm	External datum straightness deviation G(x) /µm	Measurement object straightness deviation R(x) /μm
0	-4.32	0.81	-2.57	-1.45
50	-3.71	1.79	-2.75	-0.62
100	-3.02	2.94	-2.98	0.08
150	-2.79	3.12	-2.96	0.50
200	-2.13	3.18	-2.66	1.48
250	-0.22	1.41	-0.82	2.24
300	3.07	-1.04	2.06	2.17
350	5.38	-3.96	4.67	1.74
400	7.44	-6.2	6.82	0.85
450	7.9	-6.77	7.34	-0.02
500	6.73	-6.12	6.43	-1.03
550	4.07	-3.07	3.57	-1.05
600	0.98	-0.44	0.71	-1.63
650	-2.81	2.02	-2.42	-1.98
700	-5.97	5.07	-5.52	-0.89
750	-6.84	5.58	-6.21	0.92
800	-3.75	1.68	-2.72	0.84

Tab. 2: Results of error separation straightness measurements.







Fig. 6: Comparison of reference and error-separated results.

Straightness deviation of the linear guide, determined using error separation method, was equal to 13.55 μ m.

3. CONCLUSION

A comparison of reference straightness measurements (using an interferometer and an autocollimator) with results obtained with error separation method was carried out. Even though the difference between reference straightness measurements (8.66 μ m and 9.42 μ m) and error-separated straightness measurements (13.55 μ m) is not large, it will be investigated in further research. It is possible (see Figure 6) that a relative shift in nominal positions between reference and error-separated measurements has occurred, and that could influence the straightness values as well. Additionally, error separation methods produce corrected results at the exact location of the motion axis, while all other methods introduce an offset between the motion axis and the measurement result.

With these considerations in mind, it was shown that results obtained with error separation method are comparable to state-of-the-art methods, using only widely available equipment.

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KRUŽNO GOSPODARSTVO I VEZA AMBALAŽA/HRANA

CIRCULAR ECONOMY AND FOOD PACKAGING/FOOD NEXUS

Lidija Runko Luttenberger¹

¹ University of Rijeka, School of Polytechnics , Sveučilišna avenija 4, Rijeka, Hrvatska

<u>Review paper / Pregledni rad</u>

Sažetak

Postojeće je stanje da još uvijek prevladava linearno gospodarstvo u sektoru hrane i plastične ambalaže, na štetu okoliša, resursa, ekosustava i zdravlja ljudi. U radu se analizira povezanost između ambalaže i hrane i predlažu mogući načini postizanja kružnog gospodarstva, posebno korištenje materijala na biološkoj osnovi koji su i biorazgradivi. Raspravlja se o održivosti takvih materijala kada se koriste kao ambalaža za hranu. Poseban naglasak je na stanje u Hrvatskoj koja se suočava s problemom gospodarenja plastičnim otpadom i nema proaktivan pristup za smanjenje ambalaže, nalaženje inovativnih rješenja za kompostabilnu ambalažu na biološkoj osnovi u plasmanu lokalno proizvedene hrane, te reguliranje ambalaže, posebno korištenjem instrumenta zelene javne nabave.

Ključne riječi: kružno gospodarstvo, ambalaža, bioplastika, hrana, dizajn za okoliš

Abstract

Linear economy for both food and plastics presently prevails to the detriment of the environment, resources, ecosystems and public health. The paper analyses the nexus between food packaging and food and proposes possible pathways to achieving circular economy, particularly the use of biobased materials that are also biodegradable. Sustainability of such materials when used for food packaging is discussed. Reference is made in particular to the situation in Croatia which is confronted with plastic waste management problem and is still not taking a proactive approach in reducing the packaging, finding innovative solutions for biobased compostable packaging for marketing locally produced food, and regulating the packaging, particularly through the use of green public procurement instrument.

Keywords: circular economy, packaging, bioplastic, food, design for environment

1. INTRODUCTION

The goals of design for environment (DFE) is the practice of designing products are protecting environmental systems from harm, protecting human health and safety, with the sustainability of natural resources applying over the entire life cycle. Its practice focuses on reduction of the use of hazardous substances, minimum possible consumption of resources and energy, reduction of waste, and extending the life cycle of products through recycling and reuse. With regard to packaging, three characteristics are relevant to DFE: type of material used, amount of material used, and whether the packaging is reusable. The substances used for packaging material should avoid non-renewable resources and toxic emissions and should preferably be made from renewable materials that can be composted after use. Challenges remain because while this packaging can be composted in a commercial composting process, it does not break down when buried in a landfill [1].

The paper makes parallel analysis of the linearity in food and plastics sectors, describes the concept of sustainable packaging, and provides definitions concerning bioplastics. In the chapter dealing with bio-based economy, the role of soil as carbon sink is described and how food sector connects all the Sustainable Development Goals. Sustainability criteria for bio-based and biodegradable plastics are specified and finally a particular situation in Croatia is considered.

2. LINEAR ECONOMY IN FOOD AND PLASTICS SECTORS

Various reports of recent date provide a status of plastic waste situation and prevention in Europe [2,3]. Measures should be applied to reduce the use of plastic products, such as plastic packaging waste, being the single largest plastic waste stream in Europe [4] and significant source of marine litter. EU recently introduced new measures to address plastic waste and pollution through 2018 European strategy for plastics in a circular economy [5] and Single Use Plastics Directive proposal [6].

When it comes to food as one of the most common objects of packaging, the very nature of food production that is presently "linear" (see fig. 1) extracts finite resources such as phosphorus, potassium and fossil fuels. It is wasteful as 1/3 of all edible food go uneaten, while less than 2% of valuable nutrients in food by-products and human waste generated in cities is valorised. Bulk of nutrients are destined for landfill, incinerators or open dumps or are released untreated, thus polluting the environment by pesticides and synthetic fertilizers. Mismanagement of manure exacerbates air pollution, contaminates soils and leaches chemicals into water supplies. Long-term exposure to low levels of pesticides for farm workers is linked to serious health problems and significant costs [7].

In a circular economy for food, the ingredients considered unsafe for cycling should be "designed out". Food ingredients and plastic packaging can contaminate organic material streams and make it challenging to extract valuable nutrients.

With regard to conventional plastics in use, it was a series of accidental discoveries that had demonstrated that it is not inert as has commonly been assumed. For instance, some of the chemicals leaching from plastics are hormonally active. As plastics has found its way into every corner of our lives, there is thus a constant great risk of chronic exposure to hormone disruptors. Plastics enclose the products from soda to cooking oil and line metal cans, not to say that are the preferred material for children's toys. It is not likely that all plastics are hazardous, but because of manufacturers' claims of trade secrets, chemical composition of

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plastic containers remains unknown [8]. Endocrine disrupting ingredients in plastics are phthalates and bisphenol A. Phthalates give PVC plastic flexibility and have turned up in foods, especially those with high fat content, such as eggs, milk, cheese, margarine, and seafood. And they have also turned up in us. As for organochlorines, besides those deliberately constructed, they are synthesized when water containing decayed leaves is chlorinated or when chlorinated plastics are burned [9].



Fig. 1: The flow of materials in the food systems is overwhelmingly linear [7]

3. SUSTAINABLE PACKAGING

Besides introducing food product delivery models which can eliminate some packaging needs altogether and also decentralised systems that separately collect biological nutrients as close to the point of source are possible, technical innovations can help create compostable packaging. The packaging that preserves food can be made from materials that can compost as safely and easily as the food it contains such as Cassava plant [10] or compostable cellulose from wood [11]. Hemp could be an option for packaging and also composites [12].

In addition, co-producing bio-based plastics and food is feasible, ensuring more secure markets for farmers. Also, some bio-based plastics like have barrier properties which ensure that food may stay fresh longer [13].

The use of bio-based plastics in place of conventional, fossil-based consumes less nonrenewable energy and produces less greenhouse gases, although a problem with land-use change may occur, be it direct or indirect. Also, bio-based plastics have an impact both on eutrophication and acidification [13].



4. DEFINITIONS IN USE

Bioplastic as a term refers both to bio-based origin or to the biodegradable character of a plastic. Bio-based and biodegradable are therefore not synonyms (see fig. 2).

	Petrochemical	Partly bio-based	Bio-based	
Non-biodegradable	PE, PP, PET, PS, PVC	Bio-PET, PTT	Bio-PE	
Biodegradable	PBAT, PBS(A), PCL	Starch blends	PLA, PHA, Cellophane	

Fig. 2: Bio-based versus petrochemical plastics and biodegradable versus nonbiodegradable plastics [13]

Plastics industry converts uses about 7% of petroleum produced [14]. The feedstock for plastics production may as well be biomass.

Biodegradability of materials (ability to be broken down by microorganisms into water, CO_2 , CH_4) and biomass) depends on the environmental conditions such as temperature, presence of microorganisms, oxygen and water. Thus, biodegradability and rate of biodegradation differs, depending on environmental component and conditions - in the soil, on the soil, humid or dry climate, surface water, the sea, or in composting conditions [15, 16].

Industrial composting requires elevated temperature (55-60°C), high relative humidity and oxygen presence. The compliance with EN13432 standard is considered to be a good measure for industrial compostability of packaging materials. The material should be naturally biodegradable in a composting process, it must not negatively affect the process of composting and compost quality.

The conditions prevailing in home composting are characterized by lower temperature that is also less constant due to lesser quantity of material, all that resulting in slower degradation rate when compared to industrial composting [13].

European standard EN 13430 and EN 16848 defines material recycling. Besides mechanical recycling, there is also chemical recycling, for instance the process were PLA is hydrolysed to lactic acid [17]. Directive 94/62/EC [18] considers composting and anaerobic digestion (biogasification) as being a specific form of material recycling, or 'organic recycling'. Not considered as recycling is the energy recovery and using the product as fuel.

The durability depends on the type of chemical structure of a polymer and not on the origin of the feedstock. Plastic materials are sometimes referred to as durable, that being contrary to biodegradable. For instance, PLA can be durable at indoor conditions, while biodegradable in conditions of industrial composting [13].

The most commonly used bio-based plastics are polylactic acid (PLA), (biodegradable) starch based plastics, and cellophane. Biodegradable (and bio-based) polyesters are predominantly based on fossil fuels.

Figure 3 shows bio-based plastics (orange boxes), intermediates (blue boxes), and raw materials (green boxes).





Blue boxes coloured grey are intermediates that are fossil-based, but could be produced from bio-based resources as well. Future evolution is shown by green dotted lines.

5. BIO-BASED ECONOMY AND SUSTAINABLE DEVELOPMENT GOALS

In terrestrial systems, soil is the major organic carbon resource and plays a crucial role in global carbon cycle. The most relevant component in terms of carbon sink effect of the soil is humus. Promoting sustainable agriculture as crucial part of bioeconomy [20] would result in an annual increase of 4‰ organic carbon stocks in agricultural stocks globally. Expected results is complete neutralization of anthropogenic fossil emissions of CO₂. Therefore, one of the aims is the use of compost on agricultural land, whereby an emphasis should be put on the synergy that exists between composting and solid waste management system. In that way organic fraction management is harmonized with quality compost market and sustainable agricultural practice, resulting in bio-based economy, fig. 4.



Fig. 3: Bio-based plastics, their intermediates and raw resources [19]





*by 2030: increase of demand +50% (LCA FOOD 2010, Bari Italy)



It should also be pointed out that food connects all the Sustainable Development Goals (SDG). The "wedding cake" shown in fig. 5 presents a new way of viewing the SDGs and how they are all linked to food. It implies that economies and societies are seen as embedded parts of the biosphere.



Fig. 5: How food connects all the SDGs [22]



6. SUSTAINABILITY OF BIO-BASED AND BIODEGRADABLE PLASTICS

Suitability of bio-based and biodegradable plastics for food packaging basically depends on the impact of such plastics on food products shelve life and on how safe such plastics is [13].

However, there are also other natural resources that should be taken in consideration when assessing sustainability of bio-based plastics: fertile land and land-use change, both direct and indirect, water, phosphate, and energy. The use of biodegradable bio-based plastics in packaging applications and for food waste carriers may significantly increase the quantity of separately collected food and garden waste. It may also reduce contamination of compost by non-biodegradable plastics. With such co-benefits its usage becomes attractive. However, in order to ensure correct disposal, packaging and food carriers should use appropriate logo. Also, the input of virgin plastics required in food packaging can be provided from sustainable agriculture sources. Thus, bio-based plastics which has low carbon footprint and is sourced sustainably may link bio-based economy to circular economy. Therefore, biodegradability represents an asset for specific purposes – agricultural and in stimulating separate food waste collection [19].

7. SITUATION IN CROATIA

Croatia is not proactive with regard to sustainable packaging, being concerned mainly with end-of-pipe solutions, however inefficiently. Prevention, as the top priority measure in waste hierarchy is not tackled at all. At the same time, about 400.000 tons of food is thrown annually in Croatia [23]. Also, current Waste management plan and waste prevention programme [24] incorporated therein do not place significant emphasis neither on packaging nor composting. Draft proposal of food waste prevention plan [25] has undergone public consultation in 2019.

A turnaround in waste policy and alignment with circular concept was undertaken in 2016 through Draft Waste Management Plan 2016-2022 [26] which involved source separation, numerous local sorting facilities, home and municipal composting and biogas production for estimated 390,000 tons of bio waste, with minimum resources left for disposal.

An important contribution in reducing marine litter, particularly in a country that relies heavily on tourism with all its seasonality and periodical pressures on public services would be implementing the policies to reduce and modify packaging, the materials used therefor and to avoid one-use and disposable plastic materials of all types. Such an approach obviously implies the change of habits, intervention in supply chain and increasing domestic supply of agricultural goods in particular [27].

Using the instrument of public procurement, public authorities at all levels and entities should show the way of purchasing the products which are least harmful for natural ecosystems, the people and the climate [28].

8. CONCLUSION

Achieving sustainability and resilience which commands for material efficiency greatly depends on the circularity in food sector and plastic sector, as they both presently exert a great impact on resources, waste, climate, soil, and pollution. Sustainable production and use of degradable bioplastics would greatly contribute to returning the resources contained in food waste to the soil. Biodegradable plastics would also decrease the amount of microplastics ending in the sea.



Croatia should make significant strides towards achieving circularity in order to meet its international obligations and to preserve its environment. Such an undertaking presents great opportunities for academia, innovators, SMSs and consequently quality employment.

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KVALITETA REPRODUKCIJE ETIKETA NA RAZLIČITIM KONSTRUKCIJAMA STROJEVA

LABEL REPRODUCTION QUALITY ON DIFFERENT MACHINE CONSTRUCTIONS

Ivana Ljevak¹, Eduard Galić², Igor Zjakić³

¹ Meteor Grupa – Labud d.o.o., Radnička cesta 173r, Zagreb, Croatia

² Stega tisak d.o.o., Heinzelova 60/1, Zagreb, Croatia

³ University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, Zagreb, Croatia

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Sažetak

U ovom istraživačkom radu analizirali su se parametri koji utječu na kvalitetu tiska etiketa i vizualni dojam gotovog grafičkog proizvoda. Predmet istraživanja su uzorci višebojnih etiketa tiskanih na istoj tiskovnoj podlozi a različitim ofsetnim tiskarskim strojevima. Analiza se provodila na uzorcima iz različitih naklada. Prva naklada tiskana je na ofsetnom tiskarskom stroju iz arka, dok je druga naklada tiskana na ofsetnom tiskarskom stroju iz role. Postojanost otiska na tiskovnoj podlozi zavisna je o njezinoj strukturi te karakteristikama strojeva koji se međusobno razlikuju po svojoj konstrukciji. Na uzorcima su provedena denzitometrijska i spektrofotometrijska mjerenja, te je promatran utjecaj parametara koji dovode do deformacije resterskog elementa i prirasta rastertonske vrijednosti.

Ključne riječi: ofsetni strojevi, etikete, kvaliteta tiska

Abstract

In this research the parameters that affect the quality of the label print and the visual impression of the finished graphic product were analyzed. The subject of the study is the samples of multicolored labels printed on the same printing substrate and various offset printing machines. The analysis was carried out on samples from different editions. The first edition was printed on offset printing press from offset sheetfed, while the second edition was printed on offset printing machine from rolls. Print durability on the printing substrate depends on its structure and characteristics of the machines that differ in their construction. Densitometric and spectrophotometric measurements were carried out on the samples, and the influence of parameters causing the deformation of the raster element and increase the dot gain was observed.

Keywords: offset machines, labels, print quality





OPTIČKA SVOJSTVA I APLIKACIJE EPOKSIDNE SMOLE

EPOXY RESIN OPTICAL PERFORMANCE AND ITS APPLICATION

Lana Makovec¹, Antun Lovro Brkić², Katja Petric Maretić¹, Mateja Cindrić³

¹ Faculty of Graphic Arts, University of Zagreb, Getaldićeva 2, Zagreb, Croatia

² Institute of Physics, Zagreb, Croatia

³ University of Zagreb, Faculty of science, Department of physics, Zagreb, Croatia.

Preliminary notice / Prethodno priopćenje

Sažetak

Jednostavni optički elementi poput leća i prizmi imaju veliku primjenu u svakodnevnom životu i primarno se proizvode od stakla. Kompleksna proizvodnja čini cijeli proces vrlo skupim i obično fokusiranim na fiksnim veličinama i karakteristikama. U ovom radu razvijamo metodu izgradnje leća i prizmi koristeći brzo rastuće područje 3D printanja i lako dostupne materijale (kalupni silikon i epoksidna smola), istražujući njihova svojstva i performanse. Ovaj pristup nam omogućuje individualiziranu proizvodnju optičkih elemenata raznih karakteristika i namjena. Predstavljena metoda dopušta jednostavno unapređenje kvalitete uvođenjem specijalizirane smole, dok u trenutnom izdanju omogućuje niske troškove. To je čini prihvatljivom za proizvodnju različitih optičkih elemenata višestruke namjene i primjenjivom u školama, približujući učenicima inače apstraktne i teško zamislive pojmove.

Ključne riječi: optika, epoksidna smola, prizma, leća.

Abstract

Simple optical elements such as lenses and prisms are widely used in everyday life and are primarily made from glass. Complex manufacturing makes the whole process very expensive and usually focused on fixed sizes and characteristics. In this paper we develop a method for lens and prism manufacturing using fast growing area of 3D printing combined with accessible materials (mould silicone and epoxy resin), exploring their properties and performance. This approach enables us an individualization of the manufacturing process, creating optical elements with various features and uses. The method presented in this paper allows for simple improvement of quality using higher grade epoxy resin, while in the current form it provides lower cost. This makes it acceptable for producing different optical elements of multiple purpose and applicable in schools, where students' understanding of optics is based on abstract concepts if no observation is possible.

Keywords: optics, epoxy resin, prism, lenses

1. UVOD

Epoksidna smola je vrlo poznat i raširen materijal koji ima mnoge primjene. Dok se najčešće pronalazi kao dvokomponentno ljepilo unutar svakog doma, njegovu primjenu možemo naći u elektronici, umjetnosti, te kao sastavni dio raznih boja i zaštitnih preljeva.

Iako je puno lakše proizvesti optički element koristeći epoksidnu smolu nego staklo, za njezinu primjenu u optici ne postoji jedinstvena metoda koja nudi brzu i jeftinu proizvodnju optičkih elemenata proizvoljnih svojstava. Cilj ovog rada je istraživanje optičkih svojstva lako dostupne epoksidne smole, proučavanje procesa izrade i predstavljanje nove, jednostavne i pristupačne metode za izradu proizvoljnih leća koristeći 3D ispis i silikonske kalupe.

2. METODA

2.1. Model leća i prizme

Modele prizmi i leća željenih dimenzija i karakteristika možemo napraviti pomoću programa za 3D modeliranje. U ovom radu korišten je program Fusion360 zbog mogućnosti precizne izrade, koji je dostupan kao freeware svim studentima. Kod izrade modela za kalup potrebno je najprije odrediti dimenzije objekta modeliranja. Presjekom dviju sfera izradili smo bikonveksnu leću s polumjerima zakrivljenosti 10 cm gdje upravo taj presjek predstavlja model leća. Na model leće dodaje se postolje s otvorom kroz koji će se kasnije ulijevati epoksidna smola. Posljedni korak u modeliranju je dizajniranje kućišta, odnosno potpore kalupa koje će silikonskom kalupu dati oblik i stabilnost. Prikaz modela u programu Fusion360 može se vidjeti na slici 1 i 2.





Slika 1: 3D model leće i kalupa

Poznavajući parametre zakrivljenosti postavljene u programu za 3D modeliranje, možemo izračunati indeks loma epoksidne smole sljedećim izrazom:

$$J = (n-1)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$$
(1)

gdje je *J* jakost leće, *n* indeks loma, a $R_1 i R_2$ su odabrani polumjeri sfera čijim presjekom smo dobili željeni oblik leće. Kako bi se smanjila mogućnost deformacije silikona, a time i završnog proizvoda potrebna je potpora oko kalupa za leće širine 2 *cm*. Iako smo u ovom radu koristili predloženi model leća kako bi jednostavno odredili svojstva materijala, u budućem istraživanju proučavat ćemo parabolični model leća.

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Baza modela za prizme je trokut, u našem slučaju jednakostraničan duljine osnovnog brida od 3*cm*, a visina prizme je 3*cm*. Ove mjere nisu fiksne već se prilagođavaju s obzirom na to kakvu prizmu želimo dobiti na kraju procesa (Slike 3-5). Konačni rezultat sa spomenutim mjerama je prizma s kutom prizme (ϕ) od 60°, ali može se postići bilo koji željeni kut (kao što se kod leća može dobiti zadani polumjer zakrivljenosti). Kod modela prizme razmak između modela prizme i kućišta kalupa može biti manji za razliku od kalupa za leće kako bi se smanjila potrošnja materijala. Ispod modela prizme dodaje se podloga širine 1 mm i oko podloge zidovi također širine 1mm.



Slika 2: 3D model prizme i kalupa

2.2. 3D printanje

Razvoj 3D tehnologija koje koriste UV osjetljivu smolu i set lasera (SLA/LFS) ili UV lampu sa lcd zaslonom (DLP/MSLA) omogućilo je uvođenje preciznije izrade plastike. Dobro poznati FFF (eng. Fused filament fabrication) printeri rade na principu rastapanja plastike (obično pri temperaturama od 220°*C*) i ograničeni na mlaznicu veličine 400 μ m, te na visinu sloja od 200 μ m, što sa sobom povlači odstupanja do 70 μ m. Prelaskom sa tehnologije koja rastapa plastiku unutar mesingove mlaznice (FFF) na printanje koristeći UV osjetljivu smolu na kojoj iscrtava 405*nm* laser (SLA) postignut je manji teoretski maksimum za "širinu mlaznice" i visinu sloja (85 μ m i 25 μ m), ali i smanjeno je odstupanje koje je za korišteni printer (Formlabs Form 2) manje od 25 μ m. Navedene karakteristike omogućavaju nam preciznu izradu pozitiva leća, od kojih se vrlo jednostavno može napraviti silikonski kalup čiji konačni proizvod zahtijeva minimalnu mehaničku doradu.

2.3. Silikonski kalup

Nakon što se model isprinta u njega se ulijeva kalupni silikon. Kalupni silikon naprije treba pripremiti za korištenje/lijevanje. Kalupni silikon sastoji se od dva dijela (baza i katalizator) koji se miješaju u masenom omjeru 100:3. Smjesu je potrebno miješati 5 minuta, no tijekom miješanja u smjesu uvodimo zrak koji treba ukloniti kako u konačnom proizvodu ne bi bilo nepravilnosti. Zrak možemo ukloniti tako da smjesu stavljamo u vakuumsku komoru na vrijeme od 10 minuta jer tada nema rizika od stvrdnjavanja slikona unutar vremena određenog prema proizvođaču (za slikon korišten u ovom istraživanju maksimalno vrijeme je 30 min od miješanja komponenti). Kad je silikon spreman za korištenje, kistom se na model nanosi tanki sloj silikona kako bi se smanjio rizik od nastanka mjehurića uz stijenke modela. Silikon je poželjno ulijevati s veće visine jer će na taj način izaći i ostali mjehurići zraka iz smjese. Na slici 3 može se vidjeti konačan izgled silikonskih kalupa.







Slika 3: Silikonski kalupi

2.4. Epoksidna smola

Epoksidna smola je dvokomponetno epoksidno ljepilo koje se sastoji od dvije komponente A i B (dihidroksifenilpropan i epiklorhidrin) koje povezivanjem tvore visokomolekulske polimerne materijale (epoksidni polimeri). Miješanjem ovih dviju komponenti u masenom omjeru 2:1 dobiva se prozirna tekuća smjesa koja se s vremenom učvrsti, a u potpunosti je čvrsta nakon 48 sati. Kao i silikon smola se stavlja u vakuumsku komoru kako bi se uklonili mjehurići zraka i kako bi na taj način gotovi proizvodi imali što manje nepravilnosti. Primjer leća napravljenih sa smolom prije i nakon obrade s vakuumskom pumpom možemo vidjeti na slici 4.



Slika 4: Leća od epoksidne smole izlivene prije (lijevo) i nakon (desno) vakuumske komore

Poželjna okolina za rad sa smolom je pri nižim temperaturama budući da se prilikom viših temperature ubrzava proces učvršćivanja.

2.5. Završna obrada

Spomenuta odstupanja kod 3D ispisa na kraju ostavljaju površine koje je potrebno još dodatno obraditi. Obrada se može napraviti ili pomoću premaza za veću preciznost površine, ili pomoću mehaničke obrade, koja je korištena u ovom radu. Zbog toga se obradom proizvoda pokušava ukloniti nepravilnosti ili barem učiniti da te nepravilnosti ne utječu na performanse proizvoda. Jedan od načina obrade je brušenje i poliranje površine optičkih elemenata kako bi oni bili što prozirniji. Za brušenje se koriste brusni papiri (od 1500 do 3000 jakosti) namijenjeni za korištenje s vodom. Postepeno se brusi počevši s najgrubljim papirom i kreće se prema najmekšem. Nakon brušenja, površine se obrađuju polir pastom. Gotova prizma prije brušenja i poliranja može se vidjeti na slici 7 (lijevo), dok prizma sa svim završnim obradama prikazana je na slici 7(desno).

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Slika 5: Prizma prije mehaničke dorade (lijevo) i nakon mehaničke dorade (desno)

3. REZULTATI

Mjerenje fokusa leće računa se prema prije spomenutoj formuli no u ovome radu je zbog toga što je $R_1 = R_2 = R$ korištena je sljedeća izvedena formula:

$$n=\frac{R}{2f}+1,$$

gdje se pripadno odstupanje računa prema:

(2)

$$\sigma_n = \sqrt{\left(\frac{\partial n}{\partial f} \times \sigma_f\right)^2} = \left|\frac{R}{2f^2} \times \sigma_f\right|.$$
(3)

Fokus leće f se računa preko veličina a i b, gdje je a udaljenost od izvora svjetla do leće, a b udaljenost od leće do zastora na kojemu nastaje slika. Nakon 10 mjerenja, konačni iznos za žarišnu duljinu iznosi:

$$f = (10.4 \pm 0.2) \text{ cm}$$
.
(4)

Izračunate vrijednosti žarišne duljine leće i njene standardne devijacije (4), uvrstimo u formule (2) i (3) pa time dobivamo pripadni indeks loma epoksidne smole:

$$n = (1.48 \pm 0.04)$$
(5)

Vidimo da je indeks loma korištene epoksidne smole usporediv s indeksima loma najčešće korištenih stakala (1.49 za akrilno staklo, 1.52 za krunsko staklo te 1.46 za silicijsko staklo). Usporediv indeks loma omogućuje nam jednostavnu kopiju postojećih staklenih leća i prizmi (koristeći istu metodu bez 3D printanja i mehaničke obrade) s minimalnim podešavanjem optičkog sustava.

Dobiveni indeks loma je zapravo srednja vrijednost indeksa loma budući da on ovisi o valnoj duljini upadne svjetlosti. Koristeći izmjerenu vrijednost za indeks loma, prizmu te spektroskop odredili smo promjenu indeksa loma o valnoj duljini. Rezultati se mogu vidjeti na grafu 1.

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Graf 1: Indeks Ioma u ovisnosti o valnoj duljini

4. ZAKLJUČAK

Uvođenje novog materijala unutar nekog područja može rezultirati mnogim korisnim i novim primjenama. Epoksidna smola pokazuje odlične karakteristike kao optički medij. Uz metodu i primjenu predloženu u ovome radu za izradu leća i prizmi može poslužiti i za druge primjene, poput popravka staklenih leća, kopiranje postojećih optičkih sustava i još mnogo toga. Mehanička svojstva materijala i njegova pristupačna cijena čine upravo leće načinjene od epoksidne smole kao idealno rješenje u školama i ostalim edukacijskim ustanovama.

Buduća istraživanja temeljimo na korištenju kompleksinijh modela leća i prizmi, te u izradi programskog rješenja koji će automatski generirati 3D modele željenih optičkih medija koristeći odabrana svojstva.

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ELECTROLESS NICKEL-PHOSPHOROUS LAYERS ON AUSTENITIC STAINLESS STEEL SUBSTRATE

Mauro Maretić, Dario Iljkić, Sunčana Smokvina Hanza, Milenko Jokić, Loreta Pomenić, Božo Smoljan

University of Rijeka - Faculty of Engineering, Vukovarska 58, 51000 Rijeka, Croatia

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Abstract

An electroless deposition of nickel-phosphorous coatings on austenitic stainless steel substrate was investigated. Electroless deposited coatings have a uniform thickness on a complex-shaped objects. Study has been focused on electroless deposition mechanism, microhardness and uniformity of electroless nickel-phosphorous coatings. Microstructure was analyzed by optical and scanning electron microscopy. Based on experimental results, it can be concluded that electroless nickel-phosphorous layers deposited by proposed procedure have high adhesivity and microhardness.

Keywords: Electroless, Deposition, Coatings, Heat treatment, Stainless Steel, Micro-hardness

1. INTRODUCTION

Electroless plated metal substrates can have high hardness, high wear resistance, and acceptable ductility [1, 2]. Substrate surface could be pre-treated to catalyze the reduction reaction by initiation of nickel deposition. When electroless process starts, nickel itself becomes the catalyst of the nickel deposition on substrate surface, and process proceeds as "autocatalytic" process [2-4]. Because of this chemical process, the obtained coatings have a uniform thicknesses. This property is very important in plating of engineering components with complex shape. This uniform thickness and composition of the coating results in uniform mechanical and physical properties of surface layer [3]. Besides that, nickel-phosphorous alloy coatings deposited by electroless process can have good adhesivity and high hardness [5].

It is known that nickel-phosphorous alloy coatings deposited by electroless process on austenitic stainless steel as substrate usualy have poor mechanical properties. After electroless coating process, nickel-phosphorous alloy coatings can be heat treated [4], preferably because of increasing their adhesivity and hardness. Improving of properties of nickel-phosphorous alloy coatings deposited by electroless process on austenitic stainless steel AISI 316, as a substrate was desirable subject of study in this paper. This study should be focused on study of microhardness of nickel-phosphorous alloy coatings deposited by electroless process.

When nickel layer is formed on surface by activation with a weak acid etch, i.e., nickel strike, electroless nickel-phosphorous alloy coating should be applied [6]. Novelty of this paper is replacement of nickel strike process with involving special activation by electrode prior to electroless process.

2. ELECTROLESS PROCEDURE AND METHODS

Quality of the nickel-phosphorous alloy coatings deposited by electroless process depends on their microstructural characteristics which are controlled by phosphorous content [5].

An important characteristic of plating metals is the strength of the bond that can develop between the base metal and the coating. Removing foreign contaminants (soil, dirt, corrosion products, oxides, tarnish, and others), and eliminating mechanically distorted surface layers from the base metal surface should be done [7].

Appropriate heat treatment processing of nickel-phosphorous alloy coatings have a significant impact on their mechanical properties [3]. With prolonged tempering at high temperatures, electroless deposited nickel-phosphorous coatings begin to crystallize and to lose its preferable amorphous character [5]. In the same time higher hardness on stainless steel is obtained [5]. Moreover, hardness of electroless deposited nickel-phosphorous coatings can increase because of the precipitation of Ni₃P phase [8].

Hardness of the nickel-phosphorous coatings decreases by increasing the phosphorus content in it. In industrial application, nickel-phosphorous alloy coatings deposited by electroless process usually contain from 5 to 13 wt. % phosphorous [3, 9].

The basic classification of the nickel-phosphorous layers with respect to the phosphorus content, microcrystalline structure and hardness is shown in Table 1 [5].





Type of coating	Mass content of phosphorus/%	Hardness HV	Structure
Low content	14	560810	crystalline
Medium content	410	430490	crystalline
High content	10.514	400480	amorphous

 Tab. 1: Classification of the nickel-phosphorous coatings with respect to the phosphorus content,

 microcrystalline structure and hardness [5]

Grain size of nickel-phosphorous alloy composite coatings deposited by electroless process could have the significant influence on hardness.

Stainless steels surfaces are not suitable for electroless nickel-phosphorous alloy coating. To achieve better results of electroless nickel-phosphorous alloy coating with stainless steels as substrate, its surface usualy should be additionally prepared by a nickel strike before electroless deposition (Figure 1) [6]. In this work surface of stainless steel stainless steel as substrate was polished, degreased and activated using the special electrode.



Fig. 1: Flow chart diagram of recommended pre-treatment procedure of substrate surface [6]

In applied experimental procedure work, cylindrical specimens of austenitic steel AISI 316 were used as substrate. Chemical composition of steel specimens is given in Table 2. Diameter of cylindrical specimens was equal to 8 mm and their length was equal to 50 mm. Before electroless process, surface of specimens has been cleaned and prepared in accordance with pre-treatment procedure of substrate surface shown on Figure 1, but instead nickel strike pre-coating treatment activation by electrode was applied. Specimens were at first mechanically polished by using Kemipol T-12, with Al_2O_3 grains of 14 µm. This has been followed by degreasing the surface of the sample by cleaning agent UNICLEAN 253, which is composed of the silicate, hydroxide and biodegradable surfactants. After that, the substrate surfaces were washed and activated in activation agent UNICLEAN 675. When the surfaces were cleaned, substrate surfaces were "activated" by pre-coating treatments. After rinsing, the main electroless deposition process has been applied (Figure 2). Electroless nickel plating process has been carried out by nickel bath based on an aqueous solution of sodium hypophosphite.



Tab. 2: Chemical composition of steel substrate



Fig. 2: Flow chart diagram of the electroless process nickel plating on austenitic steel AISI 316 substrate

After the electroless processing samples have been tempered at 400 °C for 60 min in air furnace atmosphere. Aging was conducted not longer than 24 hours after applying the electroless processing on specimens.

Nickel-phosphorous alloy coating layers of heat treated samples have been tested by microhardness indentation technique. The Vickers microhardness testing of each sample has been determined as the average of five test results by Vickers tester Struers Duramin 2. Microstructure analysis of nickel-phosphorous alloy coating layers were obtained by optical microscope Olympus BX51 and by scanning electron microscope FEG FEI QUANTA 250 SEM. X-ray Diffraction (XRD) analysis of the heat treated electroless coating was carried out by instrument BRUKER AXS D8-Advance, Vertical Theta-Theta goniometer with Co radiation.

3. RESULTS

The obtained microhardness of the heat treated electroless nickel-phosphorous alloy coating was 853 HV0.01. From Figure 3 it can be seen that the electroless nickel-phosphorous alloy coating is following the surface morphology of the sample. The uniform nickel-phosphorous alloy coatings deposited by electroless process was formed on surface of heat treated substrate. Absence of the Ni-P alloy coating was not observed in heat treated specimens. The thickness nickel-phosphorous alloy coating is equal to 7.5 μ m (Figure 4).

Content of the iron, chromium, nickel and phosphorus of the surface layer was evaluated by SEM and EDS mapping (Figure 5). It was obtained that surface layer have about 9 % of phosphorous. Segregation of phosphorous is not visible.




Fig. 3: Micrograph of cross section of heat treated nickel-phosphorous alloy coating on austenitic stainless steel AISI 316 substrate



Fig. 4: Thickness of the electroless nickel-phosphorous alloy coating on austenitic stainless steel AISI 316

substrate







Fig. 5: SEM and EDS mapping of cross section of nickel-phosphorous alloy coatings deposited by electroless process on austenitic stainless steel AISI 316 substrate of the heat treated sample

The test of adhesivity of Ni-P coatings was done using a Vickers indenter. The indentation of Vickers pyramid on specimen treated by pre-coating activation of surface is shown in Figure 6a. Indentation of specimen treated by pre-coating activation of surface + electroless coating + aging at 500 °C is shown in Figure 6b. In Figure 6c, is shown indentation on samples treated by ordinary electroless coating + aging at 500 °C.



Fig. 6: Indentation results of adhesivity of nickel-phosphorous coatings, mag. 35:1, a) chemical precoating treatment of surface + electroless coating, b) pre-coating treatment of surface + electroless coating + aging at 500 °C, c) electroless coating + aging at 500 °C

It is visible that proper activation of surface has most important rule in adhesivity of Ni-P layer. After the heat treatment, structure of coating is more crystalline, moreover the intermetallic nickel phosphide (Ni₃P) phase are appearing [8]. Hardness of coating can increase by appearance of intermetallic Ni₃P phase, and by higher crystallinity of nickel-phosphorous coatings [6, 8]. For more precise definition of possible mechanism of hardening of the coating by heat treatment, further study of electroless nickel-phosphorous coatings was done using X-ray diffraction analysis. X-ray diffraction analysis was done on heat treated and non heat treated specimens. In Figure 7 and Figure 8 the results of X-ray diffraction analysis of heat treated and non heat treated electroless coating are shown. It can be seen that Ni₃P phase is formed in heat treated electroless coating. The Ni₃P phase was not obtained in non-heat treated electroless coating. Figure 9 shows microstructure of heat

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treated Ni-P layer. Microstructure is consisted of Ni_3P precipitates in fine grained nickel matrix.



Fig. 7: X-ray spectra of the heat treated electroless nickel-phosphorous coating

(111) Intensity (200) (311) (222)(220) 2θ

Fig. 8: X-ray spectra of the non-heat treated electroless nickel-phosphorous coating

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Fig. 9: Microstructure of heat treated electroless nickel-phosphorous coating, 94 Kalling's 2 reagent

4. CONCLUSION

The new electroless process deposition of nickel-phosphorous alloy coatings on austenitic steel AISI 316 was studied. Surfaces of austenitic steel AISI 316 substrate were activated by special electrode before depositing the nickel-phosphorous alloy coatings. Investigated coatings are following the surface morphology of the sample. The uniform nickel-phosphorous alloy coatings deposited by electroless process was formed.

By X-ray diffraction analysis it was found out that the Ni₃P phase was formed by heat treatment of samples. In the same time, it was found out that hardness and adhesivity of heat treated nickel-phosphorous layers are very high.

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IDENTIFIKACIJA POTPISA AUTORA KORIŠTENJEM PCA NA STARIM SLIKAMA

IDENTIFICATION OF AUTHOR'S SIGNATURE BY USING PCA ON OLD PAINTINGS

Damir Modrić¹, Antun Lovro Brkić², Sanja Zlatić³, Jana Žiljak Gršić⁴

¹ Faculty of Graphic Arts, University of Zagreb, Getaldićeva 2, Zagreb, Croatia

² University of Zagreb, Institute of Physics, Zagreb, Croatia

³ University of North - University Center Varazdin, Varaždin, Croatia

⁴ University of Applied Sciences, Zagreb, Croatia

<u>Original scientific paper / Izvorni znanstveni rad</u>

Sažetak

Analiza glavnih komponenti (PCA - Principal component analysis) jedna je od statističkih tehnika koje se koriste u obradi signala kako bi se reducirale dimenzije podataka ili njihova dekorelacija. Prikazani rad se bavi redukcijom boje slike, dok su višestruke komponente boje, dobivene multispektralnom analizom, reducirane na one koje sadrže veći dio informacija. Za prethodnu detekciju objekata mogu se koristiti različite metode. Kvaliteta segmentacije slike podrazumijeva rezultate procesa ocjenjivanja objektne orijentacije na temelju PCA. Prezentirani rad u početku ukratko uvodi PCA teoriju i prikazuje rezultate dešifriranja potpisa na slici nepoznatog majstora.

Ključne riječi: PCA, multispektralna analiza, očuvanje kulturne baštine.

Abstract

Principal component analysis (PCA) is one of the statistical techniques used in signal processing to reduce data dimensions or their decorations. The present paper deals with image color reduction, while multiple color components, obtained by multispektral analysis, are reduced to those that contain most of the information. Different methods can be used for previous detection of objects. The image segmentation quality implies the results of the object orientation process based on the PCA. Presented work initially briefly introduces PCA theory and displays the results of decryption of signatures in an image of an unknown master.

Keywords: PCA, multispectral analysis, cultural heritage conservation.

1. UVOD

Multispektralno snimanje jedna je od najrasprostranjenijih tehnika za proučavanje kulturne baštine i arheoloških slika [1-5]. Iako je spektralna rezolucija ove vrste analize općenito vrlo ograničena, količina informacija koja se može dobiti je izuzetno visoka, s obzirom na visoku prostornu razlučivost slika koje se mogu dobiti vrlo jednostavnim eksperimentalnim postavkama. U svojoj jednostavnijoj primjeni, multispektralno snimanje podrazumijeva akviziciju boje i infracrvenih slika u najmanje četiri spektralna područja (tri u vidljivoj regiji, RGB i jedna u infracrvenom, IR). Iako se statistička metoda koje će biti razmatrana u ovom radu, u načelu može primijeniti na manje, više ili različite spektralna područja, čak je i minimalni skup RGB i IR slika dobar primjer kako multispektralno snimanje može pružiti informacije koje nisu vidljive oku (infracrveno područje) koje nisu trivijalne za vizualizaciju zajedno s RGB vidljivom informacijom. U posljednjih nekoliko desetljeća predloženo je nekoliko tehnika za izvlačenje informacija iz skupa multispektralnih slika o materijalima korištenim za realizaciju slike [6-9] ili za dokazivanje skrivenih uzoraka kroz razradu digitalnih slika [10-11]. Pristupi koji se normalno koriste podrazumijevaju smanjenje broja spektralnih vrpci koje treba vizualizirati, za iskorištavanje mogućnosti vizualizacije rezultata kao (lažne) slike u boji [12-14] ili u svakom slučaju linearne kombinacije multispektralnih slika za dokazuje obrasce i sličnosti [10-11,15].

U nastavku ćemo raspraviti o primjeni PCA statističke metode koje se koristi, s ciljem da jednoznačno odredimo autora jedne slike temeljem njegovog potpisa.

2. ANALIZA GLAVNIH KOMPONENTI (PCA – Principal component analysis)

Analiza glavnih komponenti je statistička tehnika za reduciranje dimenzije podataka. Glavni aspekti PCA analize su sažimanje i analiza linearne povezanosti većeg broja multivarijatno distribuiranih, kvantitativnih, međusobno koreliranih varijabli u smislu njihove kondenzacije u manji broj komponenti, novih varijabli, međusobno nekoreliranih, sa minimalnim gubitkom informacija. U literaturi je prvi puta spominje Pearson 1901, ali samo ime i tehniku kakvu poznajemo danas razradio je Hotelling 1933. i 1936. Šira primjena ove tehnike, zbog kompleksnog računa, pričekala je dostupnost elektroničkih računala. [16-20]

Cilj PCA je ekstrahirati maksimalnu varijancu iz seta podataka sa svakom komponentom. Prva glavna komponenta linearna je kombinacija promatranih vrijednosti koja maksimalno razdvaja subjekte maksimizirajući varijancu njihovih komponentnih vrijednosti. Druga se komponenta oblikuje iz rezidualnih korelacija; to je linearna kombinacija promatranih varijabli koja ekstrahira maksimalnu varijabilnost koja ne korelira s prvom komponentom. Sljedeće komponente također ekstrahiraju maksimalnu varijabilnost iz rezidualnih korelacija i ortogonalne su na sve prethodno ekstrahirane komponente. Glavne se komponente poredaju, tako da prva komponenta ekstrahira najviše varijance, a posljednja komponenta najmanje. Rješenje je matematički jedinstveno i, ako se zadrže sve komponente, točno reproducira promatranu korelacijsku matricu. Nadalje, s obzirom da su komponente ortogonalne, njihovo korištenje u drugim analizama može uvelike olakšati tumačenje rezultata. PCA je optimalno rješenje za istraživača koji je prvenstveno zainteresiran za smanjenje velikog broja varijabil na manji broj komponenta. [21]

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Ulazni podatci za PCA analizu čine p varijabli i n opažanja i imaju oblik $p \times n$ matrice. Cilj analize je kreiranje p linearnih kombinacija izvornih varijabli koje se nazivaju glavne komponente [20]. Ovisno o problemu, tipu varijabli i skali mjerenja, u početku, PCA metoda izračunava matricu kovarijance ili matricu korelacije a zatim pronalazi svojstvene vrijednosti i svojstvene vektore te matrice koji se također nazivaju i glavne komponente [20,22]. Dakle, iz velikog boja izvornih varijabli kreirano je nekoliko glavnih komponenti koje nose većinu informacija dok se varijable koje imaju malu varijancu zanemaruju i kaže se da je to *šum*. [20]

3. EKSPERIMENT

Tijekom provođenja konzervatorsko-restauratorskih radova na slici 1 pokazalo se da je potpis autora koji se nalazi u doljnjem desnom kutu nečitak što je onemogućilo atribuciju slike.



Fig. 1: Žena za klavirom; Autor: R. ili K. (?) Rose; (1642. ili 1842. (?)); ulje na platnu; 31 x 22,7 cm Objekt: iz zbirke Željka Šunjića [24]

To nas je ponukalo da pokušamo odrediti autora (preko potpisa) koristeči multispektralnu analizu i PCA.



Fig 2.: Detalj s potpisom nakon restauracije slike

Sustav za multispektralno snimanje sastoji se od Projectina PAG B50 digitalnog fotoaparata u boji [23] (razlučivost od 5 megapiksela), dizajniran od strane Projectina AG s 24 uskopojasna filtera: N (dnevne svjetlosti), 280, 385, 400, 420, 455, 475, 495, 515, 530, 550, 570, 590, 610, 630, 645, 665, 695, 715 735, 780, 830, 850 i 1000 nm su spojeni pomoću firewire 1394a u PIA-7000 softver za snimanje slika. Dakle, naš slog slika sastojao se od 23 slike koje su dobivene

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snimanjem kroz uskopojasne filtere u kameri. Rezultat inicijalnog mjerenja prikazan je na slici (Fig.3)



Fig. 3: Slog slika (Image stack) dobivenih snimanjem s kamerom Projectina PAG B50 [18]. Ispod slike je centralna vrijednost filtera u nm.



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Fig. 4: Potpis: na svakoj slici se nazire potpis, ali nije razlučiv. Slike su pretvorene u 8-bitne.

To dovodi do tehnike analize glavnih komponenti [17-19] (PCA), kroz koje skup od N multispektralnih kanala proizvodi N slika koje predstavljaju međusobno nekorelirane obrasce. PCA analizi prethodilo je sređivanje inicijalnog sloga slika. Naime, prilikom slikanja došlo je do manjih pomaka što je dovelo do toga da se slike ne prekrivaju u potpunosti, te je trebalo to ispraviti. Iako svaka slika sadrži svoj set informacija, karakteristike slike (poput rubova, sjena i izvora svijetlosti) su očuvane. Uspoređivajući dvije fotografije najbliže po valnim duljinama, razlika u normaliziranoj fotografiji neće biti velika. Uspoređivajući matrice dviju slika, vidimo da pozicija preklapanja odgovara najmanjoj spektralnoj normi njihovih razlika. Postepeno slažući susjedne slike, vidimo da kao rezultat dobivamo sustav slika koji dijele karakteristike.

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Fig. 5: Potpis nakon PCA: potpis se nazire na prvih par slika, a ostale daju samo šumi ne donose nikakvu novu informaciju. Iz ove slike se jasno vidi redukcija dimenzija pomoću PCA

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No, da bi izvukli traženu informaciju potrebno je odrediti koje ćemo slike dalje koristiti, a koje odbaciti. Taj kriterij je najlakše vidjeti na grafu:



Fig.6: Korisna vizualna pomoć za određivanje odgovarajućeg broja glavnih komponenti.

Ovaj graf može biti korisna vizualna pomoć za određivanje odgovarajućeg broja glavnih komponenti. Broj komponenata ovisi o točki tzv. "koljena" u kojoj su preostale vlastite vrijednosti relativno male i sve približno iste veličine. Ova točka nije jako vidljiva na grafu, ali još uvijek možemo reći da je četvrta točka naša točka laktova. Iz grafa se vidi da prve četiri slike dobivene nakon PCA analize sadrže 60% informacije. Nažalost metoda nije polučila željene rezultate zahvaljujući nedovoljnoj kvaliteti slika koje smo dobili u multispektralnoj analizi. To je očekivani rezultat jer prilikom snimanja nije u potpunosti uklonjeno ambijentalno svjetlo. Kamera se teško fiksira pa prilikom promjene filtera dolazi do pomicanja što dovodi do potrebe računalnog prekrivanja fotografija u slogu.

4. REZULTATI

Multispektralne slike obično se koriste za detaljnu analizu svojstava datog objekta. U teoriji, PCA transformacija utječe na klasifikaciju multispektralnih slika. Sada ćemo procijeniti rezultate klasifikacije PCA opsega uspoređujući ih s rezultatima dobivenim na izvornim slikama.

Iznenađujuće, i teorijske i eksperimentalne studije pokazuju da PCA bendovi s manjim svojstvenim vrijednostima (ili niskim redovima PCA) mogu sadržavati naizgled vidljive informacije koje su korisne i mogu doprinijeti klasifikaciji slika. Zapravo, Mather [25] je sugerirao da se zaključak ne može temeljiti isključivo na veličinama svojstvenih vrijednosti, a vizualna provjera dobivenih PCA vrpci je neophodna i važna.

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Ova rekonstrukcija pomoću prve četiri glavne komponente (vidi sliku 10 (b)) može se postići korištenjem svojstvenih vektora koji odgovaraju prvim četirima glavnim komponentama u matrici transformacije i primjenom sljedeće jednadžbe.

X '= A'Y' + M (1) X '= Rekonstruirani vektor

A'= Nova matrica transformacije

Y '= Matrica sa samo četiri glavne komponente

M = matrica srednjih vrijednosti

Slika 7a) pokazuje rezultat dobiven gore navedenom procedurom, a radi usporedbe stavljena je slika snimljena u IR dijelu spektra (Fig. 7b)). Na slikama c) i d) prikazan je potpis dobiven nakon segmentacije koju smo napravili pomoću programa ImageJ.



Fig.7: Slike potpisa c) i d) dobivena nakon segmentacije slike a). za usporedbu b) slika snimljena u IR dijelu spektra

Analizom dobivenih rezultata zaključili smo da bi moguće ime autora bilo – Julija ili muška verzija Julijus.

5. ZAKLJUČAK

Ovo istraživanje otkriva da je PCA pristup korisna tehnika predobrade za klasifikaciju multispektralnih slika. Između svih dobivenih PCA komponenti, prvih nekoliko (u našem slučaju oko 5) komponenti mogu sadržavati većinu informacija sadržanih u cjelokupnim multispektralnim slikovnim podacima.



Budući da je korištena metoda osmišljena kako bi se izbjegao korak binarizacije, evaluacija je također provedena na neobrađenim slikama, što je rezultiralo značajnim lošijim brzinama identifikacije.

Drugi problem koji treba riješiti je pronaći postupak za procjenu kvalitete rezultata. Prema našem iskustvu, pronalaženje apsolutne mjere za vrednovanje performansi algoritma u velikoj mjeri ovisi o konačnim ciljevima i, posljedično, o količinama slika (informacija) odabranim za evaluaciju. Za virtualnu restauraciju dokumenata, slika, freski, itd. krajnji cilj je savršeno uklanjanje posljedica starenja, atmosferskih utjecaja, neadekvatnog skladištenja ili očuvanja. Gdje god se to ne može postići, mjera djelotvornosti može se definirati na temelju poboljšanja koje se može postići u nekom kasnijem zadatku.

Svi ovi nalazi sugeriraju da je uporaba PCA pristupa za multispektralnu klasifikaciju slika korisna i učinkovita. To značajno smanjuje količinu podataka kojima se rukuje i postiže praktično prihvatljive i točne rezultate klasifikacije koji su usporedivi s rezultatima dobivenim korištenjem cjelokupnih multispektralnih slikovnih podataka.

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BUDUĆNOST I SMJER TRENDOVA U GRAFIČKOJ INDUSTRIJI

THE FUTURE AND DIRECTION OF TRENDS IN THE GRAPHIC INDUSTRY

Marko Morić¹

¹Sveučilište Sjever, Sveučilišni centar Varaždin, Jurja Križanića 31b, Hrvatska

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Sažetak

Trendovi u grafičkoj industriji se mijenjaju s obzirom na trženja tržišta, odnosno krajnjih kupaca kao i raznih servisa koji izravno i neizravno utječu na pristup tržištu i krajnjem kupcu. Kad pogledamo iza sebe, vidljivo je da je grafička industrija u zadnjih 20-ak godina doživjela velike promjene. Iako još uvijek zbog kvalitete i brzine dominiraju klasične tehnologije otiskivanja (ofsetni i fleksotisak). Kad sagledamo istraživanja koja se bave kretanjem trendova u budućnosti, uočavaju se novi trendovi tiska s NIP (Non Impact Printing) tehnologijama. Smanjenje naklada je negativno utjecalo na dio proizvodnje s konvencionalnim tehnikama tiska, dok se predstavnici digitalnih tehnika tiska kao što je Inkjet i elektrofotografija sve više primjenjuju na tržištu. Zbog toga su digitalne tiskarske tehnologije danas, a i u budućnosti će biti sve više tražene. Grafički proizvodi razvrstani u tri osnovne skupine doživjeli su promjene u broju otisaka, a kako će se trendovi u tiskarskoj industriji kretati u budućnosti dalo je nekoliko istraživanja od kojih se izdvaja istraživanje Smithers PIRA-e kao globalnog čimbenika za istraživanje kretanja tržišta grafičke industrije u svijetu.

Ključne riječi: Smithers PIRA, grafička industrija, ofset, fleksotisak, digitalni tisak, trendovi.

Abstract

Trends in the graphics industry are changing with regard to market penetration, like end customers as well as various services that directly and indirectly affect access to the market and the end customer. When we look behind it, it is evident that the graphics industry has undergone great changes in the last 20 years. Although classical printing technology (offset and flexo printing) is still dominated by quality and speed. When we look at researches that deal with trends in the future, new printing trends with NIP (Non Impact Printing) technologies are noticed. Reduction of the print has negatively affected part of production with conventional printing techniques, while representatives of digital printing techniques such as Inkjet and Electrophotography are increasingly being applied on the market. That is why digital printing technologies today, and in the future, will be increasingly demanded. Graphic products classified into three core groups have experienced changes in the number of prints, and how trends in the printing industry will move in the future have led to several researches outlining the Smithers PIRA research as a global factor to explore the world's graphics market trends.

Keywords: Smithers PIRA, graphic industry, offset, flexo printing, digital printing, trends





ANALIZA .OBJ FORMATA ZAPISA U PROCESU ADITIVNE PROIZVODNJE

ANALYSIS OF .OBJ FILE FORMAT IN ADDITIVE MANUFACTURING PROCESS

Josip Nef¹, Marko Maričević¹, Mile Matijević¹, Krunoslav Hajdek²

¹ Sveučilište u Zagrebu, Grafički fakultet, Getaldićeva 2, Zagreb 10000, Hrvatska

² Sveučilište Sjever, Hrvatska

<u>Original scientific paper / Izvorni znanstveni rad</u>

Sažetak

Sve bržim razvojem i mogućnostima aditivne proizvodnje, primarno FFF (Fused filament fabrication) tehnologija, dolazi do razvoja sve veće zajednice korisnika uključenih u razvoj i primjenu ove tehnologije. Samim time stvaraju se online digitalni repozitoriji gdje su korisnici slobodni dijeliti i objavljivati svoje modele i radove. Iako postoji veliki broj formata u kojima se modeli zapisuju i koriste u raznim programima za rezanje odnosno pripremu za 3D tisak, najčešće korišteni oblik zapisa je .stl (Standard tessellation language). Drugi format po popularnosti je .obj zapis. U ovome radu će se analizirati .obj format zapisa prilikom uporabe u aditivnoj proizvodnji, s naglaskom na FFF tehnologiju i koje su potencijalne prednosti i mane korištenja ovog formata zapisa u usporedbi sa .stl formatom zapisa modela.

Ključne riječi: .obj format zapisa, aditivna proizvodnja, 3D tisak, programi za rezanje

Abstract

With growing popularity of additive technologies, primarily FFF (Fused filament fabrication) technology, community of users involved in the development and application of this technology is rapidly expanding. With growing demand for models and blueprints, online digital repositories appeared, where users are free to share and publish their work. Although, there are a large number of formats in which the models are written, shared and used, the most commonly used one is .stl (standard tessellation language) file format. Second widest adopted file format is considered to be .obj file format. In this paper, .obj file format will be analyzed in context of additive manufacturing with emphasis on FFF additive process. It strengths and weaknesses will be compared to .stl file format.

Keywords: .obj file format, aditive manufacturing, 3D print, slicers

1. UVOD

Razvojem popularnosti 3D printera i aditivnih tehnologija općenito, posljedično dolazi do razvoja cijele aditivne industrije. Trenutačno se sami proizvođači natječu u utrci novih funkcija, dok se znanstvenici fokusiraju na pronalaženje novih materijala. U koju god se stranu gledalo, svi su u žurnoj potrazi za novim tehnikama i funckijama [1]. Osim tehničkog razvoja aditivnih procesa, stalna je potreba i za razvojem različitih programa koji omogućuju aditivnu proizvodnju ili je optimiziraju na određeni način. Samim time je na tržištu veliki broj različitih programa za rezanja, te programa za optimizacijom modela nastalih u jednom od različitih programa za modeliranje [2, 3].

Samim time, kako ne postoji jedan univerzalan program za modeliranje u svrhu aditivne proizvodnje, tako se koriste mnogi različiti programi različitih proizvođača. Kako bi se diferencirali jedni od drugih, osim razlika u programima, stvaraju razlike u samim formatima zapisa modela. Iz toga razloga se zadnjih godina pojavljuju različite inicijative za stvaranjem novih formata zapisa 3D modela koji bi primarno bili korišteni u svrhe aditivne proizvodnje. Kako se tehnologije aditivne proizvodnje razvijaju, tako se nadodaju i određene nove funkcije koje nisu podržane u današnjim programima za rezanje, pa ni u samim zapisima modela, pa se stoga radi sve veći pritisak da se postave neki novi standardi za razmjenu takvih formata i njihovo efikasnije korištenje [4, 5].

S time u vidu, dok se neki novi formati zapisa 3D modela ne pokažu kao novi industrijski standardi će se koristiti dobro uhodani modeli, a zajednica će se morati potruditi kako bi se ta promjena ostvarila. Trenutačno je standard .stl format zapisa koji je relativno jednostavan u svojem načinu zapisivanja informacija o modelu razbijanjem ploha na trokute, te je iz toga razloga podržan u mnogim procesima [6].

2. ANALIZA .OBJ FORMATA ZAPISA

Format zapisa .obj je primarno razvila kompanija Wavefront Technologies kako bi se koristio u njihovom paketu za modeliranje i animaciju. Sami format napisan linijom otvorenog koda, pe je s vremenom postao gotovo univerzalno prihvaćen oblik zapisa modela. Zbog toga su ga u svoje programe implementirale razne druge kompanije, te je tako postao vrlo popularan format za razmjenu modela, posebice u industriji video igara i animaciji. Iako je njegova primarna funkcija vrlo slična .stl formatu zapisa, osim samih informacija o geometriji modela, podržava mnoge druge funckije. Jedna od značajki ovog zapisa je da podržava informacije o teksturama i bojama kada se kombinira sa .mtl (Material template library) zapisom koji je također razvila Wavefront Technologies kompanije u obliku otvorenog koda. Druga od bitnih značajki ovoga zapisa je njegova podrška za različite oblike krivulja i površina toga tipa, s najčešćim predstavnikom NURBS krivulja [7].

Unatoč raznim mogućnostima ovog tipa zapisa modela, trenutačno je za aditivne procese jedino bitna informacija o položaju same geometrije. Također se često postavljaju pitanja koliko su određene naprednije funkcije ovog zapisa podržane od strane proivođača programa za modeliranje i programa za rezanje.

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v -50.000000 -50.000000 0.000000	vn -0.5773
v -50.000000 0.000000 0.000000	vn -0.7071
v 0.000000 0.000000 0.000000	vn 0.00000
v 0.000000 -50.000000 0.000000	vn 0.00000
v 50.000000 0.000000 0.000000	vn 0.70710
v 50.000000 -50.000000 0.000000	vn 0.57735
v -50.000000 50.000000 0.000000	vn -0.5773
v 0.000000 50.000000 0.000000	vn 0.00000
v 50.000000 50.000000 0.000000	vn 0.57735
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v 50.000000 50.000000 100.000000	vn 0.57735
v 0.000000 -50.000000 50.000000	vn 0.00000
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v 50.000000 -50.000000 50.000000	vn 0.70710
v 50.000000 0.000000 50.000000	vn 1.00000
v 50.000000 50.000000 50.000000	vn 0.70710
v 0.000000 50.000000 50.000000	vn 0.00000
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v -50.000000 0.000000 50.000000	vn -1.0000
# 26 vertices	# 26 vertex

350 -0.577350 -0.577350 07 0.000000 -0.707107 00 0.000000 -1.000000 00 -0.707107 -0.707107 07 0.000000 -0.707107 50 -0.577350 -0.577350 350 0.577350 -0.577350 00 0.707107 -0.707107 50 0.577350 -0.577350 350 -0 577350 0 577350 00 -0.707107 0.707107 00 0.000000 1.000000 07 0.000000 0.707107 50 -0.577350 0.577350 07 0.000000 0.707107 00 0.707107 0.707107 350 0.577350 0.577350 50 0.577350 0.577350 00 -1.000000 0.000000 07 -0.707107 0.000000 07 -0.707107 0.000000 0000000 0.000000 00 07 0.707107 0.000000 00 1.000000 0.000000 07 0.707107 0.000000 000000.0 000000.0 000 # 26 vertex normals

o simple cube g simple cube f 1//1 2//2 3//3 4//4 f 4//4 3//3 5//5 6//6 f 2//2 7//7 8//8 3//3 f 3//3 8//8 9//9 5//5 f 10//10 11//11 12//12 13//13 f 11//11 14//14 15//15 12//12 f 13//13 12//12 16//16 17//17 f 12//12 15//15 18//18 16//16 f 1//1 4//4 19//19 20//20 f 4//4 6//6 21//21 19//19 f 20//20 19//19 11//11 10//10 f 19//19 21//21 14//14 11//11 f 6//6 5//5 22//22 21//21 f 5//5 9//9 23//23 22//22 f 21//21 22//22 15//15 14//14 f 22//22 23//23 18//18 15//15 f 9//9 8//8 24//24 23//23 f 8//8 7//7 25//25 24//24 f 23//23 24//24 16//16 18//18 f 24//24 25//25 17//17 16//16 f 7//7 2//2 26//26 25//25 f 2//2 1//1 20//20 26//26 f 25//25 26//26 13//13 17//17 f 26//26 20//20 10//10 13//13 #24 polygons

Figure 1: Primjer .obj zapisa na modelu kocke s podjelom na svakoj stranici

U priloženom primjeru [slika o1.] se može vidjeti kako izgleda model jednostavne kocke s podjelom svakog lica na četri jednaka dijela. Zapise .obj se može čitati i manipulirati putem programa za uređivanje teksta. Ukoliko su zapisani u ASCII formatu će biti prikazani kao u gore navedenom primjeru, no mogu se zapisati i u binarnom [8].

Na prvi pogled sam zapis može djelovati konfuzno, no zapravo je riječ o relativno jednostavnom tipu zapisa. Redovi nanzančeni s prefiksom "v" označavaju koordinate svake točke (engl. vertex) koja se nalazi u trodimenzionalnom prostoru. Konvencija prilikom zapisivanja koordinata se zadržala na pravilu desne ruke. S time u vidu, brojevi označavaju x, y i z pozicije u trodimenzionalnom prostoru. Kada se koriste racionalne krivulje i površine, na kraju zapisa svake točke se nadopisuje još jedna vrijednost, težine (engl. weight) [8].

Redovi naznačeni s prefiksom "vn" su također dio podataka koji opisuju točke, u ovome slučaju pozicije normala točaka. Kada je riječ o poligonalnim površinama, tada se koriste normale točaka umjesto normale samih površina [8]. Pravilna orijentacija normala je jedan od ključnih parametara, bilo u klasičnim digitalnim vizualizacijama ili u aditivnim procesima. Ukoliko dođe do nepravilnih orijentacija normala, programi za rezanje neće moći pravilno interpretirati zadanu geometriju, što može uzrokovati poteškoćama prilikom reprodukcije.

Ostali tipovi podataka vezanih za same točke najčešće još obuhvaća prefikse "vp" i "vt", gdje prefiks "vt" označava informacije o apliciranim teksturama, a prefiks "vp" označava parametre točaka kod slobodnih krivulja [8].



Treći stupac (u originalnom zapisu se stupci nalaze jedan ispod drugoga, a ovdje su prikazani jedan pored drugoga radi bolje preglednosti) označava elemente. Unutar .obj zapisa mogu se zapisati elemetni poput točaka, linija i lica, te krivulja, krivulja na površinama, te povrišine. U ovome slučaju se koristi prefiks "f" koji označava lica, a potom ga slijede grupacije brojeva s kosim crtama. Brojevi koji su zapisani u svakom zasebnom paru ili tripletu su, redom, geometrijska točka, točka teksture i normala točke. Kao što se može vidjeti, u ovome primjeru ne postoje aplicirane teksture tako da je riječ o parovima brojeva koji označavaju geometrijsku točku i normalu točke. Sami brojevi zapravo referiraju o kojoj točki je zapravo riječ [8].

lako ovaj tip formata zapisa ima još mnogo različitih sintaksi koje se koriste prilikom zapisivanja određenih tipova geometrija, krivulja i površina, gore navedeni primjer je jedan jedan od najčešće susretanih kada je riječ o aditivnoj proizvodnji. Samim time je korisno poznavanje određenih osnova zapisa kako bi pomoglo krajnjem korisniku otkriti određene probleme, ukoliko ih ima, a nema pristupa originalnom dokumentu ili programu za modeliranje koji podržava unos .obj formata.

3. PRIMJENA .OBJ FORMATA ZAPISA U ADITIVNOJ PROIZVODNJI

U nastavku će biti prikazani različiti modeli kocke spomenute u prijašnjem paragrafu, koje će biti pripremljene na više različitih načina. Neke od njih će se razlikovati u geometriji koja ih opisuje, dok će se neki razlikovati po određenom algoritmu koji je na njih apliciran. S takvim relativno jednostavnim modelima će se usporediti razlika između .stl i .obj formata zapisa, te će se razmotriti kakvu stvarnu primjenu ima .obj format u aditivnoj proizvodnji.



Figure 2: Prikaz testnih modela s odgovarajućim nazivima





Figure 3: Simulacija pripremljenih modela .obj formata u Cura programu za rezanje



Figure 4: . Simulacija pripremljenih modela .stl formata u Cura programu za rezanje

	FEDORA 25						CURA 15.04.4				
FILE FORMAT	FILE NAME	FILE SIZE	LOADED FROM DISK	FACE COUNTS	VERTEX COUNTS	SLICED MODEL	GENERATED LAYER PARTS	GENERATED INSET	GENERATED UP/DOWN SKIN	WROTE LAYERS	TOTAL TIME
	simplebox_mesh	2.6 kB	0.001s	48	144	0.001s	0.001s	0.003s	0.006s	0.01s	0.02s
	simplebox_meshsmooth	40.4 kB	0.003s	768	2 304	0.003s	0.001s	0.018s	0.025s	0.04s	0.09s
	simplebox_nurbs	1.5 kB	0.002s	24	72	0.000s	0.000s	0.002s	0.003s	0.01s	0.01s
	simplebox_nurms	2.7 kB	0.001s	48	144	0.000s	0.000s	0.002s	0.004s	0.01s	0.01s
OBJ	simplebox_patch	16.9 kB	0.003s	432	1 296	0.001s	0.001s	0.004s	0.005s	0.01s	0.02s
	simplebox_patch_relax	22.4 kB	0.002s	432	1 296	0.002s	0.001s	0.010s	0.017s	0.02s	0.06s
	simplebox_poly	2.6 kB	0.001s	48	144	0.000s	0.000s	0.002s	0.002s	0.01s	0.01s
	simplebox_solid	2.7 kB	0.001s	48	144	0.000s	0.000s	0.002s	0.002s	0.00s	0.01s
	simplebox_turbosmooth	11.9 kB	0.001s	240	720	0.002s	0.001s	0.016s	0.026s	0.03s	0.07s
	simplebox_mesh	11.4 kB	0.002s	48	144	0.000s	0.000s	0.002s	0.002s	0.00s	0.01s
	simplebox_meshsmooth	199.3 kB	0.003s	768	2 304	0.002s	0.001s	0.013s	0.017s	0.02s	0.06s
	simplebox_nurbs	6.2 kB	0.001s	24	72	0.000s	0.001s	0.002s	0.002s	0.01s	0.01s
	simplebox_nurms	201.5 kB	0.003s	768	2 304	0.002s	0.001s	0.013s	0.019s	0.02s	0.06s
STL	simplebox_patch	113.2 kB	0.002s	432	1 296	0.001s	0.001s	0.003s	0.004s	0.01s	0.02s
	simplebox_patch_relax	112.7 kB	0.002s	432	1 296	0.002s	0.001s	0.011s	0.021s	0.02s	0.06s
	simplebox_poly	12.4 kB	0.002s	48	144	0.000s	0.000s	0.002s	0.004s	0.01s	0.02s
	simplebox_solid	12.5 kB	0.002s	48	144	0.001s	0.000s	0.003s	0.002s	0.00s	0.01s
	simplebox_turbosmooth	200.2 kB	0.002s	768	2 304	0.002s	0.001s	0.014s	0.021s	0.02s	0.06s

Figure 5: Mjerenja procesa rezanja svakog modela zasebno ovisno o formatu



Kako se moglo očekivati, poznavanjem teorije oba formata, dolazi do određene razlike između ova dva tipa zapisa prilikom aplikacije u aditivnim procesima. Iako se kod svih modela, na prvi pogled ne može očitati vizualna razlika, tablica s mjerenjima [tablica o1] će pružiti detaljniji uvid.

Očitavanjem rezultata dobivenih mjerenjem raznih aspekata procesa rezanja, može se zaključiti da .obj format zapisa, u pravilu, zauzima puno manje prostora za istu količinu informacija u usporedbi sa .stl formatom zapisa. Kod prvog reda modela [slika o2, o3, o4] (najudaljeniji red s obzirom na kadar) može se primijetiti da nije došlo do značajne razlike u interpretaciji modela, te da nema većih odstupanja kada se promatraju mjerenja u tablici [slika o5].

Kod sljedećeg reda modela [slika o2, o3, o4] (srednji red modela) se na samoj interpretaciji također vrlo teško može razlučiti razlika. S drugre strane, gledajući u tablicu [tablica o1], može se zaključiti kako je .obj format zapisa drastično manji u usporedbi sa .stl formatom zapisa iako sadržavaju jednake informacije o zadanom modelu. Unatoč tome, vremena računanja rezanja su im gotovo jednaka.

Kod zadnjeg reda modela [slika o2, o3, o4], na kojima su aplicirani različiti algoritmi se može pratiti drastična promjena u samom izgledu interpretiranih modela. Razlika je posebice vidljiva na modelu simplebox_nurms kod kojeg je .stl zapis pravilno interpretiran, dok je .obj zapis prikazan kao klasičan model kocke. Također se može iščitati iz tablice [tablica o1] da je došlo do svojevrsnih razlika u zapisu modela, gledajući broj poligona i vremena samog računanja procesa rezanja. Kod simplebox_turbosmooth modela se također može vidjeti razlika između samih modela. Kod .obj zapisa je došlo do laganog pucanja modela, iako bi se ova simulacija trebala potvrditi punom reprodukcijom samog modela. I u ovome slučaju se može primjetiti razlika u samom zapisu kada se proučavaju vrijednosti mjerenja. U tome redu je jedino model simplebox_meshsmooth simuliran identično korištenjem oba formata zapisa s jedinom razlikom veličine samih zapisa.

4. ZAKLJUČAK

Postoji određena razlika između ova dva tipa zapisa, koja se može prikazati na samim reprodukcijama, te mjeriti različitim duljinama vremena rezanja u određenim programima.

Pregledom ovih informacija se može zaključiti da .obj format zapisa uglavnom zauzima manje prostora nego njegova .stl verzija. No, također je pokazao određene negativne interpretacije samih modela dok je .stl verzija uspješno reproducirala sve modele. S druge strane, mogu se vidjeti određeni parametri i mogućnosti .obj formata s obzirom na podršku različitih algoritama. Također treba napomenuti da kada se .stl format zapisa vraća u programe za modeliranje, prikazuje model setom trokuta koji su vrlo nezahvalni za manipulacije dok kod .obj postoji veća fleksibilnost.

U ovome trenutku bi se vrlo teško moglo preporučiti .obj zapis naspram .stl zapisa za aditivnu proizvodnju, no ne iz razloga jer je neadekvatan zapis, već bi se trebalo napraviti puno detaljnije ispitivanje. Ono bi uključivalo različit broj strojeva, programa za rezanje i modeliranje kako bi se pravilno prikazalo. Razlog tome je što je teoretski moguće da korišteni program za rezanje ili modeliranje ne podržava sve funkcije samog .obj formata zapisa. No u konačnici je ovakav eksperiment pokazao da bi se sami postojeći zapisi trebali detaljnije



istražiti kako bi se pokazao njihov puni potencijal ili kako bi se korisne funkcije bolje implementirale u buduće nove formate zapisa.

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3D TISAK TAKTILENE FOTOGRFIJE

3D PRINTING OF TACTILE POTHOGRAPHY

Fabijan Nushi, Iva Vasiljev, Ana Agić, Miroslav Mikota

Sveučilište u Zagrebu Grafički fakultet, Getaldićeva 2, Zagreb, Hrvatska

Preliminary notice / Prethodno priopćenje

Sažetak

Razvoj tehnologije 3D ispisa i računalnih softvera omogućuje inovativan pristup fotografiji kao trodimenzionalnom mediju. Fotografija tako postaje multisenzorni doživljaj koji uz vizualni omogućuje i taktilni podražaj. Uvođenje taktilnog podražaja u ovaj isključivo vizualni medij, fotografiju približava i osobama s oštećenim vidom. Za izradu takve taktilne fotografije, koriste se softveri za pretvaranje digitalnih slika u reljefe koji se mogu prevesti u stvarne, opipljive objekte, ispisom na 3D pisačima. Cilj rada je utvrditi optimalnu rezoluciju za 3D ispis određene vrste fotografije (portret, pejzaž ili arhitektura), te usporediti kvalitetu 3D ispisa različitih fotografija s obzirom na prikazani motiv i količinu detalja, odnosno informacija koje sadrže. Odabrani materijal za ispis 3D fotografije jest biorazgradivi termoplast PLA, koji je odabran upravo zbog svojih povoljnih ekoloških svojstava, te povoljnih mehaničkih svojstava.

Ključne riječi: 3D tisak, multisenzorski mediji, taktilna fotografija, PLA

Abstract

The development of 3D printing as well as computer softwares allows us an innovative approach to photography as a three dimensional media. A photograph then becomes a multi sensory experience that offers, not only a visual but a tactile stimulus. Implementing a tactile stimulus to a primarily visual media, brings photography closer to individuals with certain visual impairments. In order to create this type of tactile photography, we use softwares that convert digital images into reliefs that can be translated into real, palpable object, by printing them using 3D printers. The main goal is to determine an optimal resolution for 3D printing, for a specific type of photograph (portrait, landscape or architecture), and then comparing the quality of the 3D print between various photographs, taking in consideration the motives, details and information that they hold. The chosen material for 3D printing is a biodegradable thermoplastic PLA, which was selected because of its ecologically acceptable components, as well as mechanical properties.

Keywords: 3d printing, multisession media, tactile photography, PLA

1. UVOD I TEORIJSKI DIO

Većina ljudi navikla je fotografiju promatrati kao dvodimenzionalni mediji. Danas je fotografija izrazito zastupljen i vrlo popularan medij, dostupan gotovo svima. Iako daleko od svojih skromnih početaka, fotografija je još uvijek ograničena svojom dvodimenzionalnošću. Razvojem tehnologije, razvijala se i fotografija, od "camere obscure" preko tamnih komora, sve do digitalne fotografije, kako bi se približila što većem broju korisnika.

Razvoj fotografije ne ide samo u smjeru digitalnog razvoja odnosno obrade fotografija, nego se nastoje poboljšati i pojednostaviti ispisi fotografija, bez kompromitiranja njihove kvalitete. Danas dostupna tehnologija omogućava novi smjer pristupa fotografiji, odnosno njezin prelazak u opipljivi, reljefni 3D objekt. Takva fotografija koja kombinira vizualni podražaj i dodir, naziva se taktilna fotografija. Taktilna fotografija pruža promatraču novo multisenzorno iskustvo, te približava fotografiju ljudima s oštećenjem vida. [1]

Stvaranjem reljefne strukture uz pomoć različitih materijala kao što su to drvo, metal, tkanina i staklo umjetnici su pokušavali fotografiju približiti slijepima. Iako ovakav pristup daje relativno dobre rezultate, njegov glavni nedostatak je ograničenost reprodukcije. Zahvaljujući naprednim računalnim softverima za obradu slika i sve dostupnijim tehnikama 3D ispisa, omogućuje se brži razvoj taktilne fotografije.

Do sada je u ranijim istraživanjima klasificiran cijeli spektar mogućnosti pretvorbe na temelju dimenzionalnosti (iz 2D u 2.1D, 2.5D ili 3D), te su ispitani programi i algoritmi pretvorbe dvodimenzionalnih fotografija u reljefne modele [2]. Također su ispitani različiti načini dobivanja reljefa pomoću računalnih softvera, odnosno količina detalja koji će se prikazivati te način njihovog prikazivanja [3].

U ovom radu ispituje se optimalna rezolucija FDM tehnike 3D ispisa s biorazgradivom plastikom PLA, za određene vrste fotografija (portret, pejzaž ili arhitektura). Nadalje, uspoređuje se kvaliteta 3D ispisa različitih fotografija s obzirom na prikazani motiv i količinu detalja, odnosno informacija, koje sadrže.



2. EKSPERIMENTALNI DIO I METODOLOGIJA ISTRAŽIVANJA

U ovom istraživanju korišten je 3D printer Prusa i3 MK3, koji printa FDM (fused deposition modeling) tehnologijom (slika 1). FDM je aditivna tehnologija proizvodnje pomoću koje se 3D objekti grade sloj po sloj, novi sloj materijala dolazi na postojeći sve dok se ne izgradi 3D objekt. Filament (materijal za ispis) obično dolazi o obliku tankih niti (1.75 mm) koje se zagrijavaju do temperature taljenja i rastaljeni materijal se istiskuje kroz mlaznicu koja se tijekom ispisa pokreće uzduž tri osi (x, y i z), po unaprijed računalno definiranoj stazi. [4]



Slika 1. 3D printer Prusa i3 MK3

FDM tehnologija kombinira 3D pisače i termo-plastiku s ciljem izrade čvrstih, dimenzionalno stabilnih i izdržljivih objekata. Ova tehnologija je čista i jednostavna za uporabu, a proizvodi su mehanički stabilni i ekološki prihvatljivi. [5]

U ovom radu za ispis je korišten plastični filament PLA (poli-laktična kiselina). PLA je biorazgradivi polimer koji se proizvodi iz ekološki obnovljivih izvora, kao što su to kukuruzni škrob ili šećerna trska. [6] Jedan je od najzastupljenijih filamenta kod FDM tehnologije 3D ispisa zbog svojih povoljnih ekoloških svojstva. Tijekom ispisa ne ispušta neugodne mirise, a isparavanja nisu opasna, te stoga nisu potrebne posebne mjere opreza (npr. nije potrebna dodatna ventilacija), čime se pojednostavnjuje sam proces ispisa. Temperatura taljenja PLA je u rasponu od 180° do 230°C. [4]

Cilj istraživanja je utvrditi optimalnu rezoluciju za 3D ispis određene vrste fotografije (portret, pejzaž ili arhitektura), te usporediti kvalitetu 3D ispisa različitih fotografija s obzirom na prikazani motiv i količinu detalja, odnosno informacija koje sadrže. Također, se uz provedbu optimalne rezolucije provodi i usporedba vremena potrebnog za ispis uzoraka različitih rezolucija, jer i vremenski faktor ima značaju ulogu kod odabira optimalnog prototipa. Tijek istraživanja prikazan je na dijagramu na slici 2.



Slika 2 . Dijagram tijeka istraživanja





Za potrebe istraživanja odabrane su tri fotografije različitih motiva, kao predstavnici tri različita tipa fotografije, portret, priroda i arhitektura. Za arhitekturu je odabrana fotografija Taj Mahala (slika 3), za prirodu/pejzaž fotografija suncokreta (slika 4), a za portret fotografija Nikole Tesle (slika 5).



Slika 3 . 3D Taj Mahala



Slika 4 . 3D Suncokret





Slika 5 . Nikola Tesla

Fotografije su obrađene u Photoshopu CS6, gdje je napravljena njihova konverzija iz RGB u grayscale. Obrađene fotografije se zatim otvaraju u programu za rezanje (slicing program) Ultimaker Cura, gdje se vrši izrada 3D reljefa iz odabranih slika. [7]

Pretvorba fotografije u 3D reljef vrši se definiranjem nekoliko ključnih stavki, kao što su maksimalna visina objekta, njegove dimenzije (12 x 8 cm), te način konverzije. Maksimalna visina svih uzoraka je 2 cm, a njihove dimenzije su 12x8 cm. Konverzija u reljef napravljena je na principu razlike u tonovima, što znači da svjetliji tonovi na slici imaju veću visinu od tamnijih. Maksimalna visina od 2 cm postiže se samo za potpuno bijele elemente (R=B=G=255).

Definiranjem navedenih parametara softver automatski generira putanje koje će 3D pisač slijediti tijekom printa, odnosno stvara g-kod. G-kod je jezik koji ljudi koriste kako stroju rekli kako nešto učiniti, sam kod sadrži naredbe za premještanje, to jest pozicioniranje mlaznice tijekom ispisa. [8]

Nakon pretvorbe formata zapisa u g-kod, sve tri fotografije su ispisane na 3D pisaču u dvije različite rezolucije (0.1 mm i 0.3 mm). Printano je na 3D printeru Prusa i3 MK3, čiji je promjer mlaznice 0.4 mm, na temperaturi od 205°C.

Isprintani 3D modeli ispitani su preko taktilnog i vizualnog podražaja. Ispitanicima su prikazane obje verzije fotografija, te je od njih zatražena usporedba uzoraka na temelju vizualne razlike i razlike u osjetu.

U ovom istraživanju sudjelovalo je ukupno 63 ispitanika. Ispitanici su studenti Grafičkog fakulteta Sveučilišta u Zagrebu, od čega je 52,5% (39) žena i 47,5% (24) muškaraca, u dobi od 20 do 25 godina. Anketa je provedena u prostornima fakulteta pod dnevnim svijetlom, gdje su ispitanicima dane dvije varijante svakog od triju uzoraka, na kojima su usporedili taktilni podražaj te vizualnu razliku između samih uzorka.





3. REZULTATI ISTRAŽIVANJA

Usporedbom pejzažne fotografije (Suncokret) rezolucija 0,1 mm i 0,3 mm uočena je znatna razlika. Većina ispitanika ustvrdila je kako taktilna fotografija rezolucije 0,1 mm ima glađu teksturu pirikom dodira i izraženije detalje u odnosu na taktilnu fotografiju rezolucije 0,3 mm. Nadalje, taktilna fotografija rezolucije 0,3 mm ima hrapaviju teksturu i slabije izražene elemente. Nakon provedenog ispitivanja, utvrđeno je kako je razlika između dvije rezolucije za pejzažnu fotografiju znatna, kod rezolucije 0.1 mm, i vizualno i taktilno uočeno je više detalja.

Taktilna fotografija arhitekture (Taj Mahal), također, je ispitanicima dana u dvije rezolucije (0,1 mm i 0,3 mm). Ispitanici su na ovom uzorku, na temelju vizualne usporedbe, zamijetili nešto više detalja na taktilnoj fotografiji rezolucije 0,3 mm. Međutim razlika između uzoraka ispitivana taktilnim podražajem je znatno manja nego kod pejzažne taktilne fotografije, iako je zamijećeno da model isprintan u rezoluciji 0.1 mm ima nešto glađu strukturu, od modela u rezoluciji 0,3 mm.

3D prototip taktilne fotografije portreta (Nikola Tesla) potrebno je ponovo računalno obraditi jer njegov ispis nije bio uspješan. Iako je na prototipu potrebno izvršiti popravak, svejedno je dan ispitanicima na vizualnu i taktilnu usporedbu. Vizualnom usporedbom ispitanika, utvrđeno je kako značajne vizualne razlike između uzoraka nema, ali je kod taktilnog podražaja uočeno da uzorak rezolucije 0,3 mm djeluje glađe u odnosu na uzorak rezolucije 0,1 mm.

Uz provedbu usporedbe taktilnog i vizualnog podražaja, provedena je i usporedba vremena potrebnog za ispis svake varijante uzoraka. Na temelju dobivenih rezultata (tablica 1) uočeno je kako su prototipovi taktilnih fotografija rezolucije 0,3 mm imali znatno kraće vrijeme ispisa, jer se u vremenu koje je potrebno za ispis jednog sloja kod rezolucije od 0,1 mm, kod ispisa u rezoluciji od 0,3 mm isprintaju tri sloja.

	Vrijeme potrebno za ispis				
Fotografije	rezolucija 0,1 mm	rezolucija 0,3 mm			
Pejzaž (Suncokret)	6 h 53 min	2 h 32 min			
Arhitektura (Taj Mahal)	7h 57 min	2 h 53 min			
Portret (Nikola Tesla)	11 h 45 min	4 h 10 min			

Tablica 1.	Tablica ispisa	za rezolucije o.:	1 mm i 0 <i>.</i> 3 mm.
raonea ±i	i abiica ispisa	La recordenje of	





4. ZAKLJUČAK

Na temelju rezultata ispitivanja utvrđeno je postojanje razlike kod ispisa različitih rezolucija. Uzorci isprintani u rezoluciji 0,3 mm su na dodir glađi, ali se na uzorcima rezolucije 0,1 mm vizualno uočava više detalja. S obzirom na to da su razlike dobivene vizualnim i taktilnim podražajem relativno male, glavni utjecaj u odabiru optimalnog 3D modela za izradu taktilne fotografije na kraju je bio vremenski faktor, jer se pri ispisu modela rezolucije 0,3 mm vrijeme znatno smanjilo, a detalji su i dalje ostali dovoljno izraženi.

Buduće istraživanje će se usmjeriti k ispitivanju kvalitete taktilne fotografije dobivene različitim tehnikama ispisa na 3D printerima (FDM, prah), te kombinacijama 3D ispisa s UV ink-jet tehnikama ispisa. Usporedba će se vršiti s obzirom na tehniku ispisa, a ispitivanje će uključivati i taktilnu percepciju fotografije kroz nekoliko različitih grupiranih skupina (ljudi s normalnim vidom, slabovidni i slijepi), sukladno dobivenim rezultatima izabrat će se najoptimalniji modeli i napraviti izložba na fakultetu.

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ISTRAŽIVANJA UTJECAJA MALIH PROMJENA VRIJEDNOSTI RGB KANALA NA FOTOGRAFSKU REPRODUKCIJU BOJE LJUDSKE KOŽE

RESEARCHES OF THE IMPACT OF SMALL CHANGES OF RGB CHANNELS VALUES ON PHOTOGRAPHIC REPRODUCTION OF SKIN COLOR

Ivana Pavlović, Miroslav Mikota, Petra Ptiček, Teo Žeželj

¹University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, Zagreb, Croatia

Conference abstract / Kongresno priopćenje

Sažetak

Kroz ovaj se rad prikazuju istraživanja promjena poruka koje portretna fotografska slika prenosi konzumentu–promatraču, a koje nastaju ciljanim promjenama vrijednosti R, G, B kanala digitalnog zapisa te slike. Pri tome se istražuju granice u kojima portretna fotografska slika zadržava svoju ikoničnost, tj. konzument-promatrač ju prihvaća kao realni prikaz modela te se promjene poruke promatraju upravo unutar tih granica promjene vrijednosti R, G i B kanala zapisa. Kao glavni modulator promjene poruke se ističe reprodukcija boje ljudske kože, a istraživanja povezuju tehničke i doživljajne vrijednosti promatranih promjena.

Ključne riječi: digitalni zapis fotografske slike, portretna fotografija, boja ljudske kože, R,G,B vrijednosti

Abstract

Paper presents researches of messages changes that portrait photographic image transmit to the consumer-observer, arising by targeted changes of the R, G, B channels values of the recorded image. The boundaries in which the portrait photographic image retains its iconic nature is explored, ie the consumer-observer accepts it as a realistic model view, and the message changes are observed within these boundaries of of the R, G and B channel changes. The main modulator of the message changes is the reproduction of the skin color, and the researches links the technical and experiential values of the observed changes.

Keywords: digital photographic image, portrait photography, skin color, R, G, B values





ČVRSTOĆA ADHEZIJSKIH NANO-MODIFICIRANIH POLIVINIL-ACETATNIH SPOJEVA USLIJED PROMJENE TEMPERATURE I VLAGE

STRENGTH OF NANO-MODIFIED POLYVINYL-ACETATE ADHESIVE JOINTS AT TEMPERATURE AND HUMIDITY CHANGES

Gorana Petković¹, Ivana Bolanča Mirković¹, Suzana Pasanec Preprotić¹

¹ Sveučilište u Zagrebu Grafički fakultet, Getaldićeva 2, 10000 Zagreb, Hrvatska

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Sažetak

Polivinil-acetatni (PVAc) adhezivi na bazi vode upotrebljavaju se pri proizvodnji malih naklada grafičkih proizvoda. Kako bi se prevladali nedostaci PVAc-a, kao što je niska otpornost na vremenske uvjete i vlagu, ali i povećala čvrstoća polivinil-acetatnih adhezijskih spojeva povode se brojna istraživanja o modifikacijama PVAc adheziva nanočesticama. Cilj ovog rada je povećati čvrstoću polivinil-acetatnih adhezijskih spojeva dodavanjem 1 % silika (SiO₂) nanočestica i 1 % titan-dioksid (TiO₂) nanočestica u adhezijskom sustavu papir-papir. Ispituje se i utjecaj promjene temperature i vlage (63 °C i 12 % RV; o °C i 50 % RV) na čvrstoću adhezijskih spojeva, kao i uspješnost modifikacije PVAc-a nanočesticama u svrhu povećanja otpornost adhezijskih spojeva na spomenute promjene. Evaluacija čvrstoće ispitivanih adhezijskih spojeva i modifikacije PVAc adheziva temelji se na rezultatima testova ljuštenja (*T-peel test*), za pet vrsta papira različitog sastava, namjene i gramature (bezdrvni nepremazani, bezdrvni premazani, voluminozni, uredski i 100 % reciklirani uredski papir; 80 – 115 g/m²).

Ključne riječi: polivinil-acetatni adheziv, adhezijski spoj, test ljuštenja, nanočestice, nano-adhezivi.

Abstract

Polyvinyl-acetate (PVAc) adhesives are used in short run production of graphic products. In order to overcome PVAc disadventages, such as low resistance to weather and moisture, and to increase the strength of polyvinyl-acetate adhesive joints, numerous studies on PVAc adhesive modification by adding nanoparticles were carried out. The aim of this research is to increase the strength of polyvinyl-acetate adhesive joints by adding 1 % of silica (SiO₂) nanoparticles and 1 % of titanium dioxide (TiO₂) nanoparticles in paper-paper adhesive system. In addition, the strength of adhesive joints at temperature and humidity changes (63 °C i 12 % RH; o °C i 50 % RH) is investigated, as well as enhancement of adhesive joints resistance on above-mentioned conditions due to PVAc modification with nanoparticles. The evaluation of adhesive joints strength and modification of PVAc adhesive is based on the peeling test results (T-peel test), for five types of paper with different paper composition, purpose and grammage (woodfree uncoated, woodfree coated, bulky, office and 100 % recycled office paper; 80 - 115 g/m²).

Keywords: polyvinyl-acetate adhesive, adhesive joint, peel test, nanoparticles, nano-adhesives.

1. UVOD

Odabir vrste adheziva ovisi o svojstvima adherenata, dostupnoj tehnologiji, samom procesu lijepljenja te veličini proizvodnje. U doradnoj grafičkoj proizvodnji, a posebno u knjigoveštvu, upotrebljevaju se polivinil-acetatni (PVAc) adhezivi na bazi vode, taljivi etilen vinil-acetatni (EVA) i reaktivni taljivi poliuretanski (PUR) adhezivi. PVAc adhezivi pogodni su za sljepljivanje papira, plastike, metalnih folija, koža, tkanina i drva. Glavne prednosti PVAc-a su njihova jednostavna upotreba, široka primjena i dostupnost, mala cijena, elastičnost osušenog adhezijskog spoja te ekološka i zdravstvena ispravnost. Kako bi se prevladali glavni nedostaci PVAc-a, kao što su niska otpornost na vremenske uvjete i vlagu te sporo sušenje, te kako bi se povećala čvrstoća adhezijskih spojeva [1]–[4], u posljednjih nekoliko godina provode se brojna istraživanja vezana uz modifikacije PVAc-a nanočesticama. Uz učinkovitu disperziju nanočestica u odabranom adhezivu, postizanje značajnih promjena moguće je uz veoma malen udio nanočestica, čime polimerni nanokompoziti nalaze svoju primjenu i dobivaju na značaju u različitim industrijama. Nanokompoziti kombiniraju pozitivne karakteristike anorganskih čestica s prednostima odabranih polimernih materijala [5]-[9]. Uspješnost modifikacije PVAc-a nanočesticama moguće je evaluirati kroz cijeli niz mjernih, ali i vizualnih analiza. U ovom radu, utjecaj modifikacije PVAc adheziva nanočesticama silika (SiO₂) i titandioksida (TiO₂) ispituje se provedbom testova mehaničke čvrstoće adhezijskih spojeva testovima ljuštenja (T-peel test). Provedbom testova čvrstoće u standardnim uvjetima, ali i uvjetima povećanja, odnosno smanjenja temperature i vlage, donose se zaključci o uspješnosti modifikacije PVAc-a nanočesticama, odnosno pozitivnom utjecaju nanočestica na povećanje otpornosti adhezijskih spojeva na promjene temperature i vlage. Testovima ljuštenja nastoje se simulirati uvjeti kranjeg korištenja ispitivanih adhezijskih spojeva. Dobiveni rezultati najčešće se koriste za uspoređivanje mehaničke otpornosti različitih vrsta adheziva pri istoj aplikaciji, a ne za brojčano definiranje čvrstoće spoja [10], [11]. Rezultati ovise o mnogo faktora, kao što su kut ljuštenja, svojstva adheziva, mehaničke i fizikalne karakteristike substrata, temperatura okoline i relativna vlažnost zraka, postupcima kondicioniranja te kohezijskim svojstvima substrata i adheziva [12], [13].

2. MATERIJALI I METODE

2.1. Papir

Pri formiranju adhezijskih spojeva, u svrhu procjene njihove čvrstoće, upotrebljeno je pet vrsta papira različitog sastava, namjene i gramature: bezdrvni nepremazani (AMBER GRAPHICS), bezdrvni premazani (GARDA GLOSS), voluminozni (MUNKEN WHITE), uredski (NAVIGATOR UNIVERSAL) i 100 % reciklirani uredski papir (RECY OFFICE). Standardiziranim metodama odredila se debljina (ISO 534:2011), površinska upojnosti (T441 om-13), sadržaja pepela (T413 om-17) i mehanička (vlačna) čvrstoće (ISO 1924-2:2008) ispitivanih papira. Gramature i hrapavosti papira navedene su prema tehničkim listovima ispitivanih papira. Svojstva papira i njihove oznake korištene u ovom radu prikazane su u Tablici 1.



Naziv papira: AMBEI GRAPHI		GARDA GLOSS	MUNKEN WHITE	NAVIGATOR UNIVERSAL	RECY OFFICE
Vrsta papira:	bezdrvni nepremazani	bezdrvni premazani	voluminozni	uredski	uredski, 100% reciklirani
Oznaka:	WFU	WFC	CW	WFoffice	CRoffice
Gramatura [g/m²]:	100	115	90	80	80
Hrapavost (Bendtsen) [ml/min]:	160	80	300	120	225
Debljina [μm]:	122 ± 1	84 ± 2	134 ± 1	109 ± 1	100 ± 1
Upojnost (Cobb)	A: 30,19 ± 2,26	A: 64,86 ± 1,16	A: 29,10 ± 0,93	A: 41,43 ± 1,63	A: 25,28 ± 1,80
[g/m²]:	B: 29,33 ± 2,15	B: 65,66 ± 2,30	B: 30,14 ± 1,48	B: 41,27 ± 2,52	B: 26,03 ± 2,96
Pepeo [%]:	16,47 ± 0,23	30,75 ± 0,56	13,62 ± 0,44	13,67 ± 0,79	16,62 ± 0,32
Mehanička čvrstoća [kN/m]:	MD: 4,71 ± 0,28 CD: 2,33 ± 0,24	MD: 3,64 ± 0,24 CD: 2,12 ± 0,08	MD: 4,11 ± 0,13 CD: 1,53 ± 0,11	MD: 6,08 ± 0,18 CD: 2,28 ± 0,09	MD: 3,29 ± 0,12 CD: 1,12 ± 0,27

Tablica 1: Svojstva ispitivanih papira

2.2. Adheziv

Za potrebe ovog istraživanja odabran je adheziv komercijalnog naziva SIGNOKOL L na bazi vodene disperzije polivinil-acetata, 45 ± 2 % sadržaja suhe tvari s mogućnošću korekcije viskoziteta dodatkom do 5 % vode na ukupnu masu adheziva. S obzirom na već provedena preliminarna ispitivanja optimalnog udjela vode (0 %, 2,5 % i 5 %) mjerenjem kontaktnog kuta metodom viseće kapi na goniometru, u svrhu procjene površinske energije ispitivanih uzoraka papira i adheziva, te na temelju rezultata o najučinkovitijem prijanjanju PVAc adheziva s o % vode [14], u ovom istraživanju PVAc adhezivu nije dodavana voda.

2.3. Nanočestice

U svrhu modifikacije PVAc adheziva nanočesticama odabrane su hidrofobne silika (SiO₂) AEROSIL R 8200 nanočestice i hidrofilne titan-dioksid (TiO₂) AEROXIDE P25 nanočestice. Obje vrste čestica su u praškastom obliku, visoke čistoće (≥ 99.8 % Sio₂; ≥ 99.5 % Tio₂), bijele boje i bez mirisa, ali različite specifične površine (BET) (135-185 m² g⁻¹ SiO₂; 35-65 m² g⁻¹ TiO₂).

2.4. Priprema adheziva

Postizanje značajnih promjena i poboljšanje učinkovitosti PVAc-a moguće je uz veoma malen udio nanočestica. Na temelju provedenih preliminarnih ispitivanja optimalnog udjela nanočestica (1 %, 2 % i 3 %) mjerenjem kontaktnog kuta, ali i analizom morfološke strukture pretražnim elektronskim mikroskopom (SEM) te infracrvenom spektroskopijom s Fourierovom transformacijom (FTIR), optimalni udio nanočestica SiO₂ i TiO₂ za potrebe ovog istraživanja je 1 %. Kako bi se ostvario puni potencijal nanokompozita, učinkovita disperzija nanočestica u PVAc adhezivu postignuta je miješanjem IKA T 25 ULTRA-TURRAX



homogenizatorom u trajanju od 15 minuta. Prvih 5 minuta brzina miješanja se kontinuirano povećavala do 7000 okr/min, a potom je 10 minuta bila stalna - 7000 okr/min.

2.5. Priprema uzoraka

Za pripravu uzoraka prema ASTM D1876-08(2015)e1 standardu svi arci su izrezani na iste dimenzije - 210 x 70 mm. Dva istovrsna papira sljepljivana su 40 mm po visini, pazeći na smjer toka vlakanaca, kako bi se formirali adhezijski spojevi prikladni za ispitivanje ljuštenja (*peel test*). Za svaku ispitivanu skupinu spojeva, pripremljeni su uzorci u uzdužnom (*machine direction* - MD) i poprečnom smjeru (*cross direction* – CD) toka vlakanca. Postupak sljepljivanja uključivao je nanos adheziva kistom na samo jednu papirnu podlogu, sljepljivanje s drugom papirnom podlogom te prešanje i sušenje tako nastalih adhezijskih spojeva (*T-peel panels*). Nakon jednosatnog prešanja pritisnom silom od 3 Pa i ukupnog vremena sušenja od 48 h, rezanjem dobivenih adhezijskih spojeva na trakice širine 25 mm, dobiveni su standardni uzorci potrebni za provedbu testa ljuštenja (*T-peel test stripes*). Izgled dobivenih uzoraka prikazan je na Slici 1. Za svaku ispitivanu skupinu pripremljeno je više od 50 uzoraka, za oba smjera toka vlakanaca, nakon čega je mjerenjem debljine nanosa adheziva (53,6 ± 0,4 µm (CD), 63,5 ± 1,4 µm (MD)) provedena selekcija po 30 uzoraka, za svaki smjer toka vlakanaca potrebnih za provedbu testiranja čvrstoće adhezijskih spojeva.



Slika 1: Shematski prikaz uzorka za provedbu testa ljuštenja

2.6. Test ljuštenja

Određivanje čvrstoće adhezijskih spojeva, usporedba čvrstoće spojeva prilikom upotrebe PVAc i nano-PVAc adheziva te ispitivanje otpornosti čvrstoće spojeva pri promjeni temperature i vlage, temelji se na rezultatima testova ljuštenja (*T-peel test*). Testovi ljuštenja provode se prema ASTM D1876-08(2015)e1 metodi za oba smjera toka vlakanaca papira, pomoću MARK 10 ES30 uređaja opremljenog digitalnim uređajem za mjerenje sile i paralelnim hvataljkama tipa G1015-1. Prema spomenutoj metodi, otpornost adhezijskih spojeva na ljuštenje opisuje se kao sila po jedinici širine, mjerena duž linije veza, a potrebna za razdvajanje ispitivanog adhezijskog spoja. Kako bi se ispitala otpornost adhezijskih

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spojeva na promjenu temperature i vlage, prema metodi ASTM D 1151-oo, sve skupine adhezijskih spojeva testirane su u standardnim uvjetima, ali i uvjetima povišene, odnosno smanjene temperature i vlage. Nakon izrade uzoraka potrebnih za provedbu testova, uzorci su sedam dana kondicionirani u standardnim uvjetima (50 ± 2 % RV; 23 ± 1 °C). Nakon kondicioniranja, trećina svih skupina uzoraka podvrgnuta je ispitivanju čvrstoće adhezijskih spojeva, čime je omogućena usporedba čvrstoća PVAc i nano-PVAc adheziva, ali i dobivanje referentnih vrijednosti potrebnih za ispitivanje otpornosti adhezijskih spojeva na promjenu temperature i vlage. Preostali uzorci izloženi su temperaturama od 63 °C i 12 % relativne vlažnosti zraka, odnosno o °C i 50 % relativne vlažnosti zraka, u trajanju od sedam dana. Ispitivanje čvrstoće tih adhezijskih spojeva provedeno je nakon četiri sata kondicioniranja uzoraka u standardnim uvjetima.

3. REZULTATI I ANALIZA

Čvrstoća adhezijskih spojeva pri standardnim uvjetima (23 °C, 50 % RV) prikazana je u Tablici 2. Prikazane su čvrstoće adhezijskih spojeva svih ispitivanih papira, za oba smjera toka vlakanaca te tri vrste adheziva – PVAc adheziv, PVAc adheziv modificiran s 1 % SiO₂ nanočestica te PVAc adheziv modificiran s 1 % TiO₂ nanočestica. Uz rezultate, prikazan je i postotak poboljšanja čvrstoće veze za svaku ispitivanu kombinaciju papira i nanomodificiranog adheziva u odnosu na čvrstoću adhezijskih spojeva s polivinil-acetatom.

		ADHEZIV							
		PVAc	PVAc	: + SiO₂	PVAc				
		Čvrstoća	Čvrstoća Poboljšanje		Čvrstoća	Poboljšanje	-		
		[N/m]	[N/m]	[%]	[N/m]	[%]			
	WFU	224 ± 19,60	232 ± 13,27	+ 3,57	238 ± 24,41	+ 6,25	MD		
		154 ± 20,10	176 ± 14,97	+ 14,29	168 ± 27,13	+ 9,10	CD	히	
APIR	WFC	129 ± 13,11	150 ± 24,08	+ 16,28	148 ± 18,33	+ 14,73	MD	<u> </u>	
		100 ± 8,94	106 ± 9,17	+ 6,00	104 ± 8,00	+ 4,00	CD	aka	
	CW	228 ± 20,40	280 ± 17,89	+ 22,81	282 ± 24,41	+ 23,68	MD	ana	
		168 ± 16,00	198 ± 14,00	+ 17,86	172 ± 25,61	+ 2,38	CD	ICa	
_	WFoffice	234 ± 42,00	270 ± 44,05	+ 15,38	238 ± 36,28	+ 1,71	MD	[M]	
		134 ± 20,1	166 ± 28,36	+ 23,88	140 ± 12,65	+ 4,48	CD	P	
	CRoffice	226 ± 18,00	256 ± 33,23	+ 13,27	230 ± 20,50	+ 1,77	MD	Ē	
		144 ± 13,42	154 ±22,00	+ 6,94	152 ± 9,80	+ 5,55	CD		

Tablica 2: Čvrstoća adhezijskih spojeva pri standardnim uvjetima (23 °C, 50 % RV) uz izračun postotka poboljšanja čvrstoće spojeva modifikacijom PVAc adheziva nanočesticama

Prema rezultatima u Tablici 2, zabilježno je poboljšanje čvrstoće kod svih ispitivanih adhezijskih spojeva dodatkom nanočestica u PVAc adheziv. Poboljšanje čvrstoće za spojeve s nano SiO₂-PVAc adhezivom u većini slučajeva bilo je nešto veće u odnosu na spojeve s nano TiO₂-PVAc adhezivom. Adhezijskih spojeve sa silika nanočesticama imali su povećanje u iznosu od 3,57 % - 22,81 % za uzdužni smjer toka vlakanca (MD), odnosno 6 % - 23,88 % u poprečnom smjeru (CD). Dodatak titan-dioksid nanočestica rezultirao je povećanjem od 1,71 % - 23,68 % u uzdužnom smjeru (MD), odnosno 2,38 % - 9,10 % u poprečnom smjeru (CD). Uzimajući u obzir svojstva papira prikazana u Tablici 1 i čvrstoću PVAc adhezijskih spojeva iz Tablice 2, može se zaključiti kako hrapavost papira i sadržaj pepela najviše utječu na njihovu



čvrstoću. Spojevi s papirima veće hrapavosti i manjim sadržajem pepela ostvarili su veću čvrstoću (WFoffice – CW – CRoffice – WFU – WFC (MD); CW – WFU – CRoffice – WFoffice - WFC (CD)). Dodatkom SiO₂ nanočestica u adheziv najviše se povećala čvrstoća spojeva s CW papirom u uzdužnom smjeru toka vlakanaca (22,81 %), odnosno WFoffice papirom u poprečnom smjeru (23,88 %). Dodavanjem TiO₂ naočestica, u uzdužnom smjeru se također najviše povećala čvrstoća spojeva s CW papirom (23,68 %), dok se u poprečnom smjeru najviše povećala čvrstoća spojeva s WFU papirom (9,1%).

		ADHEZIV							
		PVAc Čvrstoća [N/m]		PVAc + SiO₂		PVAc + TiO₂			
				20/ + 17 //	182 + 14.00	214 + 25 28	10/ + 28 26	MD	
	WFU	190 ± 20,91	1/4 - 25/30	204 - 1/,44	102 ± 14,00	214 - 25,30	194 - 20,30		-
		134 ± 9,17	84 ± 8,00	152 ± 13,27	114 ± 18,00	156 ± 17,44	136 ± 23,32	CD	
	WFC	112 ± 22,27	108 ± 9,80	140 ± 15,49	132 ± 22,27	144 ± 21,54	140 ± 15,49	MD	,
		84 ± 8,00	70 ± 10,00	100 ± 12,65	84 ± 8,00	102 ± 22,72	78 ± 28,91	CD	vlal
PAPIR	CW	176 ± 34,41	176 ± 35,55	214 ± 22,00	200 ± 17,89	235 ± 46,64	234 ± 32,31	MD	cana
		120 ± 15,50	130 ± 20,50	154 ± 23,75	174 ± 20,10	156 ± 12,00	134 ± 15,62	CD	lca [
	WFoffice	172 ± 16,00	134 ± 15,62	200 ± 21,91	140 ± 36,24	207 ± 19,84	154 ± 22,00	MD	MD,
		104 ± 8,00	90 ± 13,42	130 ± 13,42	114 ± 12,81	132 ± 22,27	112 ± 22,27	CD	<u>[</u>]
	CRoffice	188 ± 27,13	188 ± 18,33	210 ± 27,20	202 ± 28,91	212 ± 13,27	216 ± 30,73	MD	
		122 ± 14,00	102 ± 6,00	128 ± 20,40	124 ± 8,00	136 ± 14,97	138 ± 18,87	CD	
		63 °C 12 % RV	ہ °C 50 % RV	63 ℃ 12 % RV	ہ ℃ 50 % RV	63 °C 12 % RV	ہ ℃ 50 % RV		

Tablica 3: Čvrstoća adhezijskih spojeva pri promjeni uvjeta (63 °C i 12 % RV; o °C i 50 % RV)

U Tablici 3 prikazane su vrijednosti čvrstoće adhezijskih spojeva pri promjeni temperature i vlage. Prema standardu ASTM D 1151-00, čvrstoća spojeva ispitana je za sve adhezijske spojeve nakon povećanja temperature na 63 °C te smanjenja relativne vlažnosti zraka na 12 %, odnosno nakon smanjenja temperature na o °C uz zadržavanje relativne vlažnosti zraka od 50 %. Smanjenje čvrstoće, u odnosu na čvrstoću u standardnim uvjetima, zabilježeno je kod svih ispitivanih uzoraka. Iz priloženih rezultata može se zaključiti kako na smanjenje čvrstoće spojeva, ovisno o vrsti adheziva, vidljivo je da je čvrstoća adhezijskih spojeva pri promjeni temperature i vlage veća prilikom korištenja adheziva s nanočesticama, a vrijednosti čvrstoće adhezijskih spojeva s nano TiO₂-PVAc adhezivom veće su u odnosu na nano SiO₂-PVAc adheziv, neovisno o vrsti papira, smjeru toka vlakanaca ili ispitivanim temperaturnim i vlažnim uvjetima.

Tablica 4 prikazuje smanjenje čvrstoće adhezijskih spojeva uslijed promjene temperature i vlage, za svaku ispitivanu kombinaciju papira i adheziva, izraženu u postocima u odnosu na vrijednosti čvrstoće istih spojeva pri standardnim uvjetima.


		ADHEZIV							
		PV Smanje	/Ac enje [%]	PVAc Smanje	+ SiO₂ enje [%]	PVAc Smanje	+ TiO₂ enje [%]		
PAPIR	WFU	- 11,61	- 22,32	- 12,07	- 21,55	- 10,08	- 18,49	MD	
		- 12,99	- 45,45	- 13,64	- 35,23	- 7,14	- 19,05	CD	
	WFC	- 13,18	- 16 , 28	- 6,67	- 12,00	- 2,70	- 5,41	MD	Tç
		- 16,00	- 30,00	- 5,66	- 20,75	- 1,92	- 25,00	CD	vlak
	cw	- 22,81	- 22,81	- 23,57	- 28,57	- 16,67	- 17,02	MD	cana
		- 28,57	- 22,62	- 22,22	- 12,12	- 9,30	- 22,09	CD	ıca [
	WFoffice	- 26,50	- 42,74	- 25,93	- 48,15	- 13,03	- 35,29	MD	MD/
		- 22,39	- 32,84	- 21,69	- 31,33	- 5,71	- 20 , 00	CD	Ð
	CRoffice	- 16,81	- 16,81	- 17,97	- 21,09	- 7,83	- 6,09	MD	
		- 15,28	- 29 , 17	- 16,88	- 19,48	- 10,53	- 9,21	CD	
		63 °C 12% RV	o °C 50% RV	63 °C 12% RV	۰ °C 50% RV	63 °C 12% RV	ہ °C 50% RV		

Tablica 4: Izračun postotka smanjenja čvrstoće pri povećanju/smanjenju temperature i vlage

Pri povećanju temperature na 63 °C i smanjenju relativne vlažnosti zraka na 12 %, čvrstoća PVAc adhezijskih spojeva smanjila se za od 11,61 % do 28,57 %. Smanjenje čvrstoće nano SiO₂-PVAc adhezijskih spojeva bila je nešto niža, od 5,66 % do 25,93 %. Adhezijski nano TiO₂-PVAc spojevi pokazali su se kao najotporniji na temperaturne promjene i promjene vlage sa smanjenjem od 1,92 % do 16,67 %. Prilikom smanjenju temperature na o °C i zadržavanja uvjeta relativne vlažnosti zraka, smanjenje čvrstoće PVAc adhezijskih spojeva bilo je od 16,28 % do 45,45 %. Čvrstoća nano SiO₂-PVAc adhezijskih spojeva smanjila se za od 12 % do čak 48,15 %, a nano TiO₂-PVAc spojevi opet su se pokazali najotporniji sa smanjenjem od 5,41 % do 35,29 %. Temperaturne promjene i promjene vlage najmanje su utjecale na adhezijske spojeve s WFC papirom u oba smjera toka vlakanaca, a najviše na spojeve s WFOffice u uzdužnom, odnosno na spojeve s WFU papirom u poprečnom smjeru toka vlakanaca papira.

Zbog velike količine podataka, a u svrhu bolje interpretacije rezultata, čvrstoće svih ispitivanih adhezijskih spojeva u standardnim uvjetima te u uvjetima promjenjene temperature i relativne vlažnosti zraka, prikazani su na Slici 2.









Slika 2: Čvrstoća svih ispitivanih adhezijskih spojeva u oba smjera toka vlakanaca

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4. ZAKLJUČCI

Zbog velikog broja interakcija koje se javljaju prilikom formiranje adhezijskih spojeva u ispitivanom adhezijskom sustavu papir-papir, međuovisnosti ispitivanih parametara te nekoliko nedostataka vezanih uz upotrebljene metode, nije lako jednostavno i nedvosmisleno interpretirati dobivene rezultate. Procjena kvalitete i čvrstoće adhezijskih spojeva je veoma složen proces koji se mora sastojati od velikog broja mjernih, ali i vizualnih analiza. Cilj ovog rada je ispitati utjecaj modifikacije PVAc adheziva nanočesticama silike i titan-dioksida na čvrstoću adhezijskih spojeva isključivo, za pet vrsta papira različitog sastava, namjene i gramature te utjecaj nanočestica na povećanje otpornosti adhezijskih spojeva prilikom promjene temperature i relativne vlažnosti zraka. Dodavanje nanočestica u PVAc adheziv rezultiralo je povećanjem čvrstoće adhezijskih spojeva, pri standardnim uvjetima (23 °C; 50 % RV), kod svih ispitivanih uzoraka i to u rasponu od 1,71 % do 23,88 %. Poboljšanje čvrstoće dodatkom 1 % SiO₂ nanočestica bilo je nešto veće u odnosu na rezultate čvrstoće prilikom dodavanja 1 % TiO₂ nanočestica. Spojevi papira veće hrapavosti i manjeg sadržaja pepela ostvarili su bolje rezultate čvrstoće. Sukladno većoj mehaničkoj čvrstoći papira u uzdužnom smjeru toka vlakanaca i rezultati čvrstoće adhezijskih spojeva u uzdužnom smjeru, prilikom testa ljuštenja, bili su veći u odnosu na poprečni smjer. Povećanjem temperature na 63 °C i smanjenjem relativne vlažnosti zraka na 12 %, odnosno smanjenjem temperature na o °C i zadržavanjem postojeće relativne vlažnosti zraka, došlo je do značajnog smanjenja čvrstoće adhezijskih spojeva. Na smanjenje čvrstoće spojeva nepovolinije je utjecalo snižavanje temperature (smanjenje od 5,41 % do 48,15 %), nego povećanje temperature i smanjenje relativne vlažnosti zraka (smanjenje od 1,92 % do 28,57 %). Upotrebom nano-PVAc adheziva povećala se otpornost adhezijskih spojeva na promjenu čvrstoće spojeva prilikom temperaturnih promjena i promjena relativne vlažnosti zraka. Nano TiO₂-PVAc adheziv pokazao se otpornijim pri promjeni temperature i vlage u odnosu na nano SiO₂-PVAc adheziv, neovisno o vrsti papira, smjeru toka vlakanaca ili ispitivanim temperaturnim uvjetima.

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KOMUNIKACIJA BOJOM U TURISTIČKOJ MEDIJSKOJ KAMPANJI

COLOR COMMUNICATION IN TOURISTIC MEDIA CAMPAIGN

Petra Ptiček, Ivana Žganjar, Nikola Mrvac, Miroslav Mikota

Sveučilište u Zagrebu Grafički fakultet, Getaldićeva 2, Zagreb, Hrvatska

Preliminary notice / Prethodno priopćenje

Sažetak

Konkurentnost turističke ponude oslanja se na razvojne mjere temeljene na strateškim dokumentima. Informacijsko komunikacijsku tehnologiju Strategija razvoja turizma Republike Hrvatske do 2020. godine je prepoznala kao vrlo važan tehnološki čimbenik, čiji se pozitivan trend rasta s vremenom sve više odražava na konkurentu sposobnost razvoja turizma. Na odluke turista utječu tehnološke promjene koje se vide u novim oblicima informiranja o destinaciji, novi mediji, materijali, aktivnosti, društvene i političke promjene, a odražavaju se na doživljaj destinacije. Cilj rada je utvrditi u kojoj mjeri novi informacijsko komunikacijski trendovi i primjena turističke medijske kampanje, temeljeno na boji vizualnoj karakteristici mrežnih stranica utječe na odabir turističke destinacije.

Ključne riječi: boja, turistička medijska kampanja, mrežne stranice

Abstract

Competitiveness of tourist offer relies on development measures based on strategic documents. Croatian Tourism Development Strategy untill 2020 has recognized Information Communication Technology as a very important technological factor, whose positive growth trend over time reflects increasingly on the competitive ability of tourism development. Tourism decisions affect the technological changes seen in new forms of information about destination, new media, materials, activities, social and political changes, and reflect on the destination experience. The aim of the paper is to determine to what extent the new information communication trends and the use of touristic media campaign based on the color of the visual characteristics of web pages affect the choice of tourist destination.

Keywords: color, touristic media campaign, web pages

1. UVOD

Turistička medijska kampanja u današnje vrijeme doživljava velike promijene, a odražava se na promovirani proizvod kao posljedica specifičnih potreba turista te razvoja informativnog medija. Kroz različite oblike informacijsko komunikacije tehnologije turistička medijska kampanja razvija se s ciljem boljeg povezivanja sa svojim korisnicima. Komunikacija oslonjena na tehnologije omogućava individualiziranu komunikaciju u realnom vremenu, oslanjajući se na brojnu tehnološku podršku, naročito interaktivnost. Komunikacija u realnom vremenu kao dio turističke medijske kampanje podržava potrebu suvremenog čovjeka da određenu informaciju dobije odmah, bez uloženog vremena u istraživanje i provjeru točnosti iste informacije. Korisnici se oslanjaju na vjerodostojnost informacije putem društvenih mreža kao pomoćne promocijske aktivnosti, a koja čini važan segment integrirane marketinške komunikacije. Integrirana marketinška komunikacija kroz osnovni koncept objedinjuje utjecaj na ponašanje korisnika s ciljem da promotivna poruka potakne korisnika na odlazak u turizam. Sinergijski učinak komunikacije vidljiv je od samog početka korisničke komunikacije, kako bi namijenjena promotivna poruka došla do korisnika te izgradnjom dugoročnih odnosa s korisnicima, koji za posljedicu imaju stabilnost poslovanja i gospodarski rast.

2. TEORETSKI DIO

2.1. Komunikacija u turističkoj medijskoj kampanji

U kontekstu prepoznatljivosti kroz turističku medijsku kampanju "Strategija razvoja turizma RH do 2020. godine" predstavlja krovni razvojni dokument hrvatskog turizma, koji daje odgovor na pitanje kakav turizam Hrvatska želi i treba razvijati te utvrđuje ključne aktivnosti turističke politike za poboljšanje konkurentske sposobnosti hrvatskog turizma koristeći vrijednosni sustav održivog razvoja i konkurentske strategije EU na području turizma. [1]

Unutar toga je prepoznata nedovoljno jasno utvrđena nadležnost komercijalizacije i razvoja turističkih proizvoda, kroz sustav promocije hrvatskog turizma koji je baziran pretežno na offline oglašavanju, a premalo online. Zastarjeli vizualni identitet i promotivne poruke zasnovane na nacionalnom turističkom brandu otežavaju poziciju na tržištu; nedostaje sustav posebnih oznaka kvalitete koji bi osiguravali prepoznatljivost ponude. Hrvatski turizam nema konzistentnu, hijerarhijski ustrojenu i efikasnu web platformu, općenito je pasivan odnos prema elektroničkom marketingu i mrežnim društvenim servisima, uz nedovoljno poznavanje primjera dobre prakse, kao novih smjerova kretanja u marketingu i prodaji. [2]

Primjena informacijske i komunikacijske tehnologije, pokretača globalizacijskih procesa i razvoja svjetskog gospodarstva kroz razvoj turizma jedne od najznačajnijih i najbrže rastućih gospodarskih grana pridonosi praćenju i prilagođavanju suvremenim i inovativnim trendovima i individualiziranim zahtjevima turista. [3]

Mrežne stranice definiraju se u odnosu na karakteristike mrežnih alata te je neophodno utvrditi u kolikoj su mjeri namijenjene promotivnim aktivnostima turističke medijske kampanje.

Stupanj optimizacije sadržaja mrežnih alata namijenjenih promotivnim aktivnostima turističke medijske kampanje obuhvaća kategorije podijeljene u tri tematska sklopa: tehničke

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karakteristike, vizualna obilježja i prisutnost sadržaja s izraženom perspektivom razvoja. Pod tehničkim karakteristikama utvrđuju se prilagođenost mrežnih portala temeljenih na mrežnim alatima za najčešće korištene mrežne preglednike; umreženošću i interakcijom utvrđuje se u kojoj mjeri su stranice povezane s najčešće korištenim društvenim mrežama. Analiza vizualnog sadržaja obuhvaća elemente dizajna u digitalnom okruženju: boja, pokret, fotografija, prisutnost logotipa te upotreba simbola i njihove osnovne karakteristike. Treći tematski sklop prisutnost sadržaja s izraženom perspektivom razvoja utvrđuje se na način da se zadovolji nacionalni, regionalni, lokalni i specifični kriterij.

Boja može imati velik utjecaj na doživljaj stranice, određuje atmosferu i usmjerava poruku. Boja može pojačati neku poruku, ali ona sama po sebi može biti i nositelj poruke. Boja povećava učinak zapažanja i budi emocije. Ona je ono što prvo uočavamo, prije povezivanja viđenih informacija i stavljanja u određeni kontekst. Boja može biti i društvena, kulturna i ideološka kategorija. Bez obzira da li boja označava društvene ili osobne osjećaje, ljudi uvijek interpretiraju vizualnu poruku pod utjecajem boja, bilo njihovo značenje uvjetovano odgojem, kulturom, navikama ili iskustvom. Ljudi ne razmišljaju o bojama, ali ih osjećaju. [4]– [11]

2.2. Boja kao element komunikacije

Boje se često opisuju kao isključivo optički fenomen, ignorirajući ostala osjetila, ali ako boje mogu posjedovati toplinu ili hladnoću, biti oštre i meke, zasićene ili nezasićene, ako glazbeni tonovi imaju boju, može se zaključiti da se u percepciji boja ipak koristi sva osjetila. Preplavljeni smo bojama sa svih strana pa ih konstantno koristimo u komunikaciji. Ljudska je komunikacija nezamisliva bez utjecaja elementa boje. One se doživljavaju kao simbol i koriste se kao jezični pojmovi u komunikaciji.[3] Boje su u našoj svakodnevici prisutne i utječu na nas u brojnim aspektima našeg života. Imaju podsvjesni utjecaj na našu svakodnevicu: utječu na vizualnu, estetsku i prostornu percepciju svijeta oko nas, imaju psihološko djelovanje, utječu na naše raspoloženje i emocije, definiraju naše preferencije putem marketinga, a sve se više vjeruje da imaju i iscjeliteljsko djelovanje pa se mogu koristiti i u zdravstvene svrhe. Zahvaljujući bojama lakše se diferencira različite kulture, religije, političke asocijacije, društvene grupe, sportski klubovi ili brandovi, a pomažu i interpretirati pojedine podražaje.[12]

Razvojem društava, religija, vjerovanja i tradicije, pojavila se potreba za definiranjem simbolizma boja koji se gradio kroz čitavu ljudsku povijest. [13] Pri tome utjecaj na definiranje boje kao nositelja informacije utjecaj imaju različiti čimbenici – kako psiho-fizički tako i civilizacijsko-kulutrološki: u skladu se s time pojedinim bojama pripisuju različite karakteristike: [14]

Crvena - Ljudi su vrlo rano naučili dobivati i rabiti crvenu boju pa su se stoljećima predmeti crvene boje smatrali lijepima. U mnogim kulturama crvena je najvažnija boja, privlači pažnju, a označava - ljubav, strast, energiju, želju, toplinu, snagu, vatru, opasnost, moć, odlučnost, bijes, radost , osjećajnost. Ubrzava disanje i podiže krvni tlak.

Narančasta - Kombinacija crvene i žute, ne smatramo se niti negativnom niti pozitivnom. Ima neutralno značenje – radost, razigranost, entuzijazam, kreativnost, odlučnost, privlačnost, uspjeh, ohrabrenje, poticaj, fascinaciju, sreću, povjerenje, pristupačnost, neformalnost.





Žuta - Ima najveću refleksiju pa se prva primjećuje. Povezuje se sa Sunčevom svjetlošću, potiče mentalnu aktivnost povezuje se uz hranu. Značenje žute je duhovnost, radost, sreća, optimizam, nada, energija, intuicija, svjesnost, mudrost, inteligencija, čast, vedrina, prestiž, bogatstvo (zlatna). S druge strane predstavlja ljubomoru, kukavičluk, izdaju, obmanu, opasnost, bolest, zavist, propadanje.

Zelena - Boja prirode, djeluje smirujuće. Simbolizira rast, svježinu, obnovu, harmoniju, mir, sigurnost, prosperitet, nadu, sigurnost, novac, ambiciju, zdravlje i plodnost. S druge strane povezuje sesa zavisti, pohlepom, ljubomorom, neiskustvom, dotrajalosti i bolesti.

Plava - Boja neba i mora. Plava se povezuje sa spokojnošću, mirom i duhovnošću, dubinom, snagom, stabilnosti, povjerenjem, uspjehom. Ona predstavlja čistoću, prazninu, mudrost, nadu, zdravlje, odanost, samopouzdanje, inteligencija, istinitost, stručnost, usamljenost, autoritet, konzervatizam, hladnoću, daljinu, formalnost, strogost.

Magenta - Boja umjerenosti, sačinjena je od jednakog omjera crvene i plave. Najteža je boja za razlikovanje ljudskom oku, rijetka u prirodi. To je boja aristokracije koja simbolizira nesvjesno, maštu, kreativnost, inspiraciju, hrabrost, plemstvo, bogatstvo, dekadenciju, luksuz, ambiciju, ekstravaganciju, mudrost, dostojanstvo, kreativnost, mističnost, romantičnost, nostalgičnost, tugu. Negativne asocijacije s kojima se povezuje su uobraženost, pompoznost, okrutnost, arogancija, smrt, žalovanje, nestabilnost, frustracija, ekcentričnost i nezrelost.

Crna – Definira se kao akromatska, odnosno "neboja", jer crni predmeti apsorbiraju sve boje vidljivog spektra. Simbolizam crne najčešće se veže uz negativan aspekt. Kao negacija svih boja najčešće se povezuje s tamom, noći, strahom, smrti, zlom, grijehom. Simbol je tuge, umjerenosti, poniznosti, skromnosti i suzdržanosti. Danas je crna i boja prestiža. Predstavlja eleganciju, moć, misterioznost, povezuje se uz konvencionalnost, konzervativnost, ozbiljnost, formalnost, misteriju, depresiju i kriminal.

Bijela – Akromatska "neboja". Apsolutna je boja koja nema drugih varijacija osim onih koje idu od prigušenog do sjajnog pa označava ili odsutnost ili zbroj boja. Reflektira sve boje vidljivog spektra. Simbolizira pojmove poput čistoće i nevinosti, djevičanstva, neokaljanosti, mira i blaženstva, dobrote, uspješan početak, krhkost, neplodnost, izolaciju i hladnoću, mudrost, blaženstvo i unutarnji mir.

3. METODOLOGIJA IREZULTATI ISTRAŽIVANJA

Anketno ispitivanje provedeno na 30 ispitanika budućih stručnjaka u području izrade mrežnih stranica pokazalo je da su vizualne karakteristike mrežnih stranica najvažniji element definiranja mrežnih stranica s ciljem kvalitetne komunikacije u turističkoj medijskoj kampanji. Unutar ove kategorije, dominantna boja najvažnija je vizualna karakteristika, zatim zastupljenost fotografija, prisutnost i karakteristike logotipa i prisutnost pokreta (flash i video).









Pod tehničkim karakteristikama utvrđuju se prilagođenost mrežnih portala temeljenih na mrežnim alatima za najčešće korištene mrežne preglednike; umreženošću i interakcijom utvrđuje se u kojoj mjeri su stranice povezane s najčešće korištenim društvenim mrežama. Analiza vizualnog sadržaja obuhvaća elemente dizajna u digitalnom okruženju: boja, pokret, fotografija, prisutnost logotipa te upotreba simbola i njihove osnovne karakteristike. Treći tematski sklop prisutnost sadržaja s izraženom perspektivom razvoja utvrđuje se na način da se zadovolji nacionalni, regionalni, lokalni i specifični kriterij.



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4. ZAKLJUČAK

Integrirana turistička medijska kampanja treba se bazirati na dostupnim komunikacijskim alatima u okviru koordinirane strategije razvoja hrvatskog turizma, kako bi se željena promotivna poruka prenijela do krajnjeg korisnika, a temeljeno na smjernicama za izradu mrežnih stranica u okviru turističke medijske kampanje doprinijelo bi se konzistentnosti na u izgradnji slike Republike Hrvatske.

Unatoč izuzetnim potencijalima hrvatskog turizma razvoj kroz primjenu informacijske i komunikacijske tehnologije se u nedovoljnoj mjeri oslanja na potporu i primjenu novih tehnologija. Turistička medijska kampanja bazirana na primjeni suvremenih informacijskih i komunikacijskih tehnologija i inovacija turističku ponudu čini atraktivnijom i konkurentnijom. Turistička medijska kampanja treba staviti bitno veći naglasak na 'nove medije', odnosno na internet i mobilne uređaje kao kanale s izuzetno brzim rastom broja korisnika te nizom prednosti poput dostupnosti, informativnosti, mogućnosti multimedijalne komunikacije i mogućnosti prodaje usluga. U tom se procesu posebna pozornost posvećuje: provjeri kvalitete i unapređenju web stranica sustava turističkih zajednica, intenzivnijem korištenju društvenog weba te intenzivnijem razvoju aplikacija za mobilne uređaje.





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DEVELOPMENT OF FATIGUE TESTING RIG FOR WOOD SPECIMENS

Denis Rajh¹, Bojan Gospodarič¹ and Gorazd Fajdiga¹

¹ University of Ljubljana, Biotechnical faculty, Department of Wood Science and Technology, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

Preliminary notice / Prethodno priopćenje

Abstract

In product design the focus is increasingly shifted towards optimization and improving the efficiency of the development process. We can accomplish this by using advanced numerical tools, but these methods require precise knowledge of material properties. One of the desired property is the dynamic load behaviour of wood, which we intend to investigate. For this cause, we developed a pneumatic fatigue rig for testing wood and wood composites at Department of wood technology. By implementing deflection-measuring systems along thermal imaging, we can thoroughly analyse the fatigue process in those materials. The results are going be used to further predict the duration of a product and estimate the probability of material failure due to load cycling for real life applications.

Keywords: Material properties, Wood, Fatigue, Cyclic loading

1. INTRODUCTION

Predicting the life expectancy is crucial in every step of product development. To accomplish this we need to conduct systematic and elaborate testing methods for materials used in production. Whereas the fatigue behaviour in most materials like for example in metals, polymers and ceramics is very well studied due to material uniformity in quality and therefore repeatability, the effect by cyclic loading and unloading wood is way more challenging. That is why the research in this matter was ignored until the second half of the 20th century [1] and has gained focus with increased demand for wood product in recent years with its low environmental impact and renewability [2]–[7].

As a natural grown resource, wood is subject to many factors like growth, harvesting and processing, which ultimately affect its structure and suitability as a raw material [8]. Nevertheless the fatigue in wood is very present and is seen in many structures and products like furniture [9], roof structures, wind turbine blades [10], bridges, etc., where load is cyclically applied. That is why this topic is very important nowadays and will continue to be increasingly noteworthy for future applications and use of wood to predict its life expectancy in various products.

In this paper, we intend to present a self-constructed pneumatic rig to study fatigue behaviour of wood and a promising analysis technique to evaluate the process – thermal imaging. Due to relative simplicity of the construction itself and the following analysis, the decision was made on a tree-point bending fatigue setup.

2. FATIGUE RIG SETUP

The basis of the fatigue rig is a rigid frame made of aluminium strut profiles, which allows for an easy and accessible placement of the measuring system and the pneumatics (Fig. 1). Wooden specimens are placed on two fixed supports with height adjustment to accommodate for various thicknesses. Distance between supports is limited to a maximum of 673 mm due to the size of the frame. Load to the specimen is applied by a pneumatic cylinder with a diameter of 63 mm, which can produce a peak force of 2200 N, when accounted for a 7 bar maximum pressure.

Fatigue cycling is achieved by switching the solenoid pressure valve with a programmable logic controller (PLC) and is set to apply load for 1 second followed by a 0.7-second relaxation period (pulsating loading, R=0). The described dynamics for the fatigue setup was chosen to be ideal for our application. With higher frequencies, the deflection of the sample would not reach its maximum position and other loading profiles are not possible due to mechanical constraints of the constructed system.

During the experimental run, the deflection is measured with a laser distance meter positioned above the third roller, which exerts load, and a pressure sensor on the compressed air supply line is used to keep record of the applied force (Fig. 2). The PLC also acts as a simple counter to keep track of the elapsed cycles, though the main analysis is performed on the collected data using LabVIEW at a later point.







Fig. 1: Self-constructed fatigue rig for testing wooden specimens.

For safety reasons we have set the deflection limits, minimum and maximum measuring distances for the laser system, which when exceeded stop the complete testing machine. This function also serves as the general halt function for the individual experiment, when the specimen breaks due to fatigue failure.



Fig. 2: Laser system for measuring deflections (left). The upper portion of the fatigue rig: compressed air regulation (1), pressure sensor (2), PLC (3) and solenoid valve (4) (right).

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3. THERMAL PROFILE

With the increased availability of thermal imaging cameras in research, it is sensible to use them in fields where material dynamics is studied. For this reason, we conducted some fatigue runs, using the department's thermal camera.



Fig. 3: Optris PI – in experiment used thermal imaging camera (left). Due to fatigue testing fractured *Picea abies* (Norway spruce) samples (right).

The results are presented in contrast on two extreme cases with samples No. 13 and No. 4. Both samples were made of *Picea abies* (Norway spruce) wood, with dimensions 24 x 44 x 800 mm (Fig. 3). The specimens were oriented with tangential planes facing the bottom and top side, while the grain ran parallel along the full length. Prior testing all samples were conditioned at 20 °C and 65 % relative humidity for two weeks.

The loading force was applied transversely to the tangential surface at the mid-span of the sample and was set constant to 1600 N for the entire running time of the fatigue experiment (Fig. 4). Such load should suit to around 90 % of the modulus of rupture (MOR), the value which we determined prior fatigue testing according to standard ISO 13061-3 (2014) [11].







Fig. 4: Photograph showing the fatigue process on sample No. 4, while monitoring its thermal profile.

Each loading cycle caused deflections between 20 and 35 mm, which correspond to deformations in plastic regions. After removing the load, the amount of the deflection does not recover fully, and the excessive energy is released as heat [12], which can be effectively captured with a thermal imaging camera (Fig. 5).



Fig. 5: An example of released heat due to cyclic loading. Regions with higher temperatures are coloured yellow and red with peak values in white, right under the loading area.

Sample No. 13

The occurrence of increased heat in this case is already noticed in the very first cycle, as spots in the vicinity of the loading area (Fig. 6). With the ever-increasing cycle count, the heat only intensified in these localised regions, until the material eventually failed. During the final phase of the fatigue session, the thermal profile showed a 10 degree centigrade rise above the initial temperature of the sample in areas, where wood ultimately fractured. The eminent



failure is also apparent from the last image in the series, where a splinter at the bottom side is about to chip off.



Fig. 6: Sequence of thermal images for sample No. 13 according to cycle count. Already in the initial cycles, spots with higher temperature are formed.

Sample No. 4

Although the initial conditions were the same and the samples did not differ visually nor in their density, the response to the loading in first cycle for sample No. 4 differs greatly. The heat is released more evenly, without any high temperature spots (Fig. 7). Therefore, we suspect that the plastic deformation translates to a broader area, where structure is less affected to damage compared to the previous sample. In this run, the fatigue process had to be prematurely stopped at 1500th cycle, because the integrity of the sample was still sound and there were no evident indication that if will fail any time soon. At the last cycle, we recorded only a 3 degree centigrade increase in temperature on the hottest region.





Fig. 7: Sequence of thermal images for sample No. 4, where released heat spreads more evenly along its surface.



4. CONCLUSION

Despite the observation of fatigue process on two almost the same and therefore comparable samples made from same batch of wood, the results vary. Not only by the cycle count until failing, but also by the thermal image profile.

The thermal profile endorses the fact that the low endurance to the dynamic loading process induces permanent damage to the wood structure locally, where it will eventually fail and fracture. Because those deflections are in majority plastic, the excessive energy is released in form of heat. Therefore, by examining the thermal images, we could estimate how severe is the damage and approximate the durability of the sample to the cyclic loading.

From the overview, we can conclude, that the self-constructed fatigue rig with addition to thermal camera, can be a useful tool to predict durability of dynamically loaded wood and wood composites.

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STANDARDIZACIJA KAO GLOBALNA MARKETINŠKA STRATEGIJA

STANDARDIZATION AS A GLOBAL MARKETING STRATEGY

Ante Rončević¹, Damira Keček¹, Matija Konjić¹

¹ Sveučilište Sjever, Sveučilišni centar Varaždin, Jurja Križanića 31b, 42000 Varaždin, Hrvatska

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Sažetak

Globalni marketing jedan je od važnijih dijelova opće strategije poslovanja poslovnih organizacija. Poslovne organizacije su uvidjela moć koju dobivaju ostvarivanjem većih prihoda na globalnom tržištu. Stoga se na dinamične globalne marketinške strategije gleda kao na stupanj do kojeg poduzeće globalizira svoje marketinško ponašanje u različitim zemljama kroz standardizaciju marketinških aktivnosti i integraciju marketinških koraka na različitim tržištima. Takve strategije nastoje osigurati poduzeću poboljšanje performansi na globalnoj razini. U ovom je radu analizirana globalizacija tržišta, globalni marketing te globalne marketinške strategije. Također, prikazan je utjecaj kulturoloških razlika na globalne marketinške strategije. Nadalje, analiziran je proces standardizacije na međunarodnom tržištu te važnost odabira optimalnog marketinškog puta kojim će poduzeća plasirati svoje proizvode na tržište. Prikazana je važnost korištenja marketing miksa kako bi se zadovoljile potrebe stranih tržišta te ostvarila konkurentska prednost.

Ključne riječi: globalna tržišta, globalni marketing, globalne marketinške strategije, standardizacija

Abstract

Global marketing is one of the most important part of general business strategy of business organizations. Business organizations have seen the power they gain by generating more revenue on the global market. Therefore, a dynamic global marketing strategy is viewed as the degree to which the company globalizes its market behavior in different countries through standardization of market activities and integration of market steps on different markets. Such strategies seek to provide enterprise performance improvement globally. In this paper market globalization, global marketing and global marketing strategy are analyzed. Also, the impact of cultural differences on the global marketing strategy has been demonstrated. Furthermore, the process of standardization on the international market has been analyzed as well as importance of choosing the optimal marketing path for companies to place their products on the market. The importance of using marketing mix to fulfill foreign markets and to achieve competitive advantage has been demonstrated.

Keywords: global markets, global marketing, global marketing strategy, standardization

1. UVOD

Svijet se opet globalizira. Padom Berlinskog zida označene su brojne političke, zakonodavne, kulturološke i tehnološke promjene koje su se manifestirale kroz procese deregulacije, privatizacije i liberalizacije tokova informacija, novca, usluga, roba i ljudi. U tim i takvim uvjetima razvijale su se i nove marketinške strategije kako na lokalnim tako i na inozemnim tržištima. Tako globalne marketinške strategije osiguravaju poslovnim organizacijama poboljšanje performansi na globalnoj razini te ostvarenje većih prihoda na globalnom tržištu. Globalne marketinške strategije predstavljaju stupanj do kojeg poduzeće globalizira svoje marketinško ponašanje na međunarodnom tržištu kroz proces standardizacije i adaptacije radi integracije na različitim tržištima.

Osim uvoda i zaključka rad se sastoji od kratke analize globalnog tržišta, prikaza globalnog marketinga te razvrstavanja globalnih marketinških strategija. U trećem poglavlju prikazan je utjecaj kulturoloških razlika na globalne marketinške strategije, dok četvrto poglavlje analizira proces standardizacije na međunarodnom tržištu.

2. GLOBALNE MARKETINŠKE STRATEGIJE

Današnje ekonomsko okruženje oblikuju brojne političke, zakonodavne, kulturološke, demografske, a posebno tehnološke promjene. Nije poželjno ako tvrtke danas razmišljaju samo u okvirima domaćeg tržišta. Ubrzani tempo globalizacije, turbulentne ekonomske i političke promjene te dominacija multinacionalnih kompanija preuzimaju globalna tržišta. Širenje globalne kulture zasnovano je na: profiliranju multinacionalnih kompanija, razvoju globalnog kapitalizma, raširenoj težnji za posjedovanjem materijalnih dobara i homogenizaciji globalne potrošnje [1].

Globalizacija tržišta obilježena je visokim stupnjem dostupnosti dobara i usluga, novca, ljudi i tehnologije diljem svijeta. Sve to zasniva se na razvoju prometa, telekomunikacija i informacijske tehnologije. Gledano s toga aspekta, globalna orijentiranost postaje potreba u suvremenom društvu. Marketing se definira kao proces planiranja i provođenja te stvaranja ideja, proizvoda i usluga; određivanja njihovih cijena te promocije i distribucije kako bi se obavila razmjena koja zadovoljava ciljeve pojedinaca i organizacije. Pridruživanje međunarodne dimenzije marketingu omogućuje definiranje međunarodnog, tj. globalnog marketinga. [1]

Prema Američkom udruženju za marketing, međunarodni ili globalni marketing je multinacionalni proces planiranja i sprovođenja koncepcije, određivanja cijena, promocije i distribucije ideja, roba i usluga za stvaranje razmjena koji zadovoljavaju ciljeve pojedinca i organizacije [2]. Odgovor poslovne organizacije na globalne tržišne mogućnosti u velikoj mjeri ovisi o stavovima i pretpostavkama menadžmenta. Naime, globalno poslovanje i globalni marketing podrazumijevaju uvažavanje načela održivog razvoja koji dugoročno doista može ispuniti glavni cilj globalizacije, a to je svjetsko blagostanje [3]. Sve marketinške aktivnosti, od istraživanja tržišta do marketinške strategije, usmjerene su na međunarodno tržište, pri čemu je svako tržište specifično i ima vlastite potrebe koje je potrebno prepoznati i zadovoljiti.

Kao i svaka druga strategija poduzeća, tako i globalni marketing ovisi o promjenjivim i nepromjenjivim elementima, kontroliranim elementima i elementima koji se ne mogu kontrolirati. U prvu skupinu elemenata koje tvrtka kontrolira i usmjerava ulaze elementi marketing miksa: proizvod, distribucija, promocija i cijena, vlastiti kapaciteti, iskustvo i



znanja marketinga te financijska sposobnost tvrtke. U drugu skupinu ulaze elementi na koje tvrtka nema utjecaja, a to su: snaga međunarodnog i nacionalnog okruženja (ekonomska, politička, pravna i kulturna) i međunarodna konkurencija. [1] Na spomenute elemente tvrtka ne može utjecati, ali ih treba konstantno analizirati, upoznati ih i te spoznaje koristiti u izradi marketinških planova, kao i u predviđanju budućih događaja i tendencija.

Razlike među nacionalnim tržištima u svijetu vrlo su važne za određenu skupuni proizvoda pa je potrebno poznavati i poštivati te razlike kod izrade marketinških planova. No, kod tržišta za druge proizvode i usluge razlike među pojedinim nacionalnim tržištima su minimalne što međunarodnom poduzeću omogućuje korištenje globalne marketinške strategije za sva takva tržišta ili svjetsko tržište u cjelini.

Organizacije su s vremenom postale svjesne moći koju mogu dobiti ostvarivanjem većih prihoda na globalnom tržištu. Na dinamične globalne marketinške strategije gleda se kao na stupanj do kojeg tvrtka globalizira svoje marketinško ponašanje u različitim zemljama kroz standardizaciju marketinških aktivnosti i integraciju marketinških koraka na različitim tržištima. Cilj tih dinamičnih globalnih marketinških strategija je osigurati tvrtki poboljšanje performansi na globalnoj razini, te mogućnost da se tvrtke koje ju provode prilagode silama koje ubrzano kruže globalnim tržištem [1].

Dakle, nastupanje poduzetnika na međunarodnom tržištu gotovo je nezamislivo bez dobro pripremljene strategije koja obuhvaća plan i program koji će poduzetniku omogućiti da postane uspješan konkurent na ciljanom stranom tržištu. Kvalitetna strategija podrazumijeva pažljivi odabir tržišta na kojima poduzetnik može konkurentno plasirati svoje proizvode, pri čemu je također potrebno pažljivo odabrati vrijeme ulaska, obujam poslovanja, proizvode koji će biti plasirani i način ulaska na strano tržište [4].

Strategije za poslovanje na stranim tržištima su:

- etnocentrična strategija – poduzetnik je orijentiran na domaće tržište, a na međunarodno tržište plasira proizvode superiornih karakteristika koji mogu uspjeti na tom tržištu, pritom se od poduzetnika ne zahtijeva neka posebna strategija nastupa;

- policentrična strategija - odnosi se na poslovanje poduzetnika koja su orijentirani na svega nekoliko stranih tržišta; potrebno je pažljivo analizirati pojedino tržište i za svako tržište, radi njihove specifičnosti, definirati strategiju poslovanja;

- regiocentrična strategija - razvija se sukladno s karakteristikama i zahtjevima pojedine regije u kojoj poduzeće posluje; utjecaj regionalno orijentiranog poslovanja se povećava i ima sve veću važnost staranjem europskih integracija kao što su Europska unija, NAFTA, ASEAN i druge regionalne organizacije;

- geocentrična ili globalna strategija jedinstvena je na čitavom svjetskom tržištu i svijet smatra jedinstvenim tržištem; globalna strategija je orijentirana na stvaranje novih proizvoda ili usluga koji imaju globalnu uporabu i pretvaranje već postojećih proizvoda u globalne, a za njezinu primjenu potrebni su poprilični resursi, iskustvo i obranjiva konkurentnost. [4]

Modeli izlaska na strana tržišta su dio međunarodne teorije poslovanja koji objašnjavaju način na koji poduzetnici mogu internacionalizirati svoje poslovne aktivnosti. Pritom niti jedan model ne predstavlja pravilo koje će u potpunosti dovesti poduzeće do uspješnog međunarodnog poslovanja, jer modeli ne uzimaju u obzir individualne utjecaje donositelja odluka kao ni sociokulturna ni politička okruženja na stranom tržištu. [5]



Različiti načini poslovanja na nekom tržištu zahtijevaju različite stupnjeve poslovnog iskustva i financijskih investicija. U početku poslovanja na stranom tržištu poduzetnik se može osloniti na izvozne aktivnosti da bi stekao uporište na tom tržištu, no ako se odluči za dugotrajniji izlazak na neko strano tržište, može se odlučiti za izravno strano ulaganje ili udružiti kapital u međunarodno zajedničko ulaganje sa stranim partnerom.

3. UTJECAJ KULTUROLOŠKIH RAZLIKA NA GLOBALNE MARKETINŠKE STRATEGIJE

Premještanje na globalna tržišta omogućava poduzećima da postignu ekonomiju obujma i ekonomiju razmjera, ali i da iskoriste prednosti koje nosi niska cijena faktora proizvodnje, a posebno niski troškovi radne snage. No, s druge strane povećana razina izloženosti globalnim tržištima donosi nove izazove za međunarodni rast i razvoj te veću kompleksnost i diferencijaciju. Geografske, psihološke, ekonomske, administrativne i kulturološke razlike stvorile su potrebu za globalnom integracijom i koordinacijom. Stoga, mnoge tvrtke moraju u obzir uzeti uvjete okruženja u svim zemljama u kojima posluju, istodobno se boreći s velikim pritiskom da prodaju svoje proizvode i usluge širom svijeta. [1]

Kultura je i dalje jedan od najkritičnijih faktora koje marketinški stručnjaci moraju razmotriti prije uvođenja novog proizvoda na strana tržišta, jer bi u protivnom mogla ometati tvrtkinu globalnu integraciju i koordinaciju s globalnom marketinškom strategijom. Stoga je sve više tvrtki u svoj marketing uvrstilo razvoj međunarodnih istraživačkih timova koji prikupljaju dostupna znanja o kulturi koja se istražuje. Svakako je poželjno razvijati timove sastavljene od istraživača iz različitih zemalja i različite kulturološke pozadine.

Na području globalnog marketinga, standardizacija je privukla zapravo najviše pažnje, a posebno u segmentu oglašavanja na globalnim tržištima. Oglašavanja u različitim kulturama u većini slučajeva pokazuju i temeljne vrijednosti koje se smatraju važnima. Za tvrtke, prednost standardizacije obuhvaća kreiranje slike korporativnog branda i korištenje svih prednosti ekonomije obujma kao i mogućnost veće kontrole i iskorištavanje ekstremno dobrih ideja. S druge strane, prilagodba dopušta tvrtkama da po mjeri kroje svoje oglase prema potrebama i ukusima svake od lokalnih kultura. [1]

4. STANDARDIZACIJA NA MEĐUNARODNOM TRŽIŠTU

Za neko poduzeće važno je odrediti je li bolje da u svom međunarodnom poslovanju primjenjuje globalnu, odnosno standardiziranu strategiju ili lokalnu, odnosno adaptacijsku strategiju. Neovisno o kojem elementu miksa se radi, postoji puno čimbenika koji utječu na takve odluke kod primjene marketinga u međunarodnom poslovanju, uključujući čimbenike okoliša, karakteristike tržišta, ponašanje potrošača i sl.

Globalni pristup obuhvaća standardizaciju marketinškog programa na način da međunarodno poduzeće nudi isti proizvod s istom markom, ambalažom, cijenom i uslugom i prodaje ga preko istih ili sličnih distribucijskih kanala, te ga na isti način promovira na svjetskom tržištu. S druge strane, lokalna strategija pretpostavlja prilagodbu marketinških programa lokalnim obilježjima svakoga pojedinog stranog tržišta [1].

Standardizacija predstavlja proces proširenja i djelotvorne primjene domaćeg ciljano tržišno diktiranog proizvoda prema standardima materijalnih ili nematerijalnih atributa stranog okruženja. Sljedbenici standardizacijskog pristupa smatraju da prakticiranjem sličnih marketinških strategija svijet može dati sljedeće prednosti za tvrtku: značajnu uštedu troškova, usklađenost s kupcima, poboljšano planiranje i distribuciju, veću kontrolu nad državnim granicama, ekonomiju razmjera u proizvodnji i promociji. Ipak, tvrde da provedba

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standardizirane marketinške strategije možda neće biti moguća kada postoje razlike u državnim propisima, koji obuhvaćaju i zahtjev za ispunjavanje propisa o zaštiti okoliša, sigurnost proizvoda prema standardima ili zahtjevima lokalnog sadržaja.

Adaptacija podrazumijeva obaveznu izmjenu domaćih ciljeva tržišno diktiranih standarada proizvoda, u smislu opipljivih ili nematerijalnih atributa prema izvedbi proizvoda pogodnog za inozemne okolišne uvjete na inozemnom tržištu.

Putem standardizacije se mogu smanjiti troškovi, poslovati jednostavnije, te se može stvoriti prepoznatljivi imidž u svijetu, dok se adaptacijom pokazuje briga za različitosti međunarodnih tržišta, za drukčije vrijednosti koje su bitne potrošačima na tim tržištima, te se stvara viša vrijednost za potrošače. Naime, briga za poštovanje kulturoloških razlika ja vrlo važna. Također, značajnu ulogu imaju ekonomske, pravne i političke različitosti koje su važan dio adaptacije marketing miksa na međunarodnom tržištu. Obavezni razlozi za adaptaciju na međunarodnom tržištu su: pravni razlozi, porezi i pristojbe, tehnički zahtjevi, nacionalizam, klima [6]. Kulturološki razlozi za adaptaciju na međunarodnom tržištu su: ukusi potrošača, raspoloživi dohodak, različitosti potrošača, jezik, estetika.

Upravljanje marketing miksom u međunarodnom marketingu zahtijeva formiranje tj. oblikovanje i upravljanje kombinacijom: predmeta razmjene, njegove cijene, prodajnih i distribucijskih kanala i marketinških komunikacijskih aktivnosti, koja će u najvećoj mjeri zadovoljiti potrebe i želje pojedinih ciljnih skupina potrošača i segmenata stranih tržišta [7].

Važno je korištenje marketinga miksa da bi se zadovoljile potrebe stranih tržišta na takav način da se ostvari konkurentska prednost. Pritom treba uzeti u obzir međunarodnu konkurenciju i na najbolji način se nastojati uklopiti u međunarodno okruženje.

Marketing miks podrazumijeva specifičnu kombinacija elemenata koji se koriste za istovremeno postizanje ciljeva poduzeća i zadovoljavanje potreba i želja ciljanih tržišta. Sastoji se od četiri varijable: proizvod, distribucija, cijena i promocija, a proširenu verziju kod uslužnih djelatnosti čine još: ljudi, proces pružanja usluga i fizički dokaz [8]. Svaki element je potrebno definirati i planirati u skladu s određenim međunarodnim tržištem. Uz navedeno, važna je integracija sveukupnih elemenata da bi njihova primjena u organizaciji i provedbi međunarodnog marketinga bila uspješna.

Vanjski čimbenici, tj. čimbenici okruženja, kao što su politička i ekonomska stabilnost, značajno utječu na mogućnosti standardizacije. Standardizacija osigurava poboljšanje prodajnih margina. Strateški elementi standardizacije marketing miksa koji se sastoji od proizvoda, cijene, promocije i distribucije su važan faktor smanjenja troškova i povećanja zarade tvrtki. Strateška kontrola distribucije i promocije ograničujući je faktor standardizacije za neke tvrtke. Sposobnost standardizacije proizvoda i tržišta pojavljuje se kao odvojeni faktor standardizacije.

Potrošači na različitim nacionalnim tržištima zahtijevaju proizvode koji reflektiraju njihov ukus, a pritom kulturno, političko, pravno i gospodarsko okruženje utječe na preferencije potrošača i industrijskih kupaca širom svijeta. Standardizacija proizvoda je bitna, jer osim smanjenja troškova i jednostavnosti, donosi prepoznatljivost i imidž, te kvalitetu.

5. ZAKLJUČAK

Globalni marketing predstavlja jedan od važnih dijelova opće strategije poslovanja poduzeća. Poduzeća su uvidjela moć koju dobivaju ostvarivanjem većih prihoda na globalnom tržištu. Stoga se na dinamične globalne marketinške strategije gleda kao na stupanj do kojeg tvrtka

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globalizira svoje marketinško ponašanje u različitim zemljama kroz standardizaciju marketinških aktivnosti i integraciju marketinških koraka na različitim tržištima. Takve strategije nastoje osigurati tvrtki poboljšanje performansi na globalnoj razini.

Za uspješno nastupanje poduzetnika na međunarodnom tržištu potrebna je dobro pripremljena strategije koja obuhvaća plan i program koji će poduzetniku omogućiti da postane uspješan konkurent na ciljanom stranom tržištu. Također, potrebna je prilagodba marketing miksa uvjetima na međunarodnom tržištu. Pri izlasku na međunarodno tržište, poduzeća se odlučuju uglavnom ili za proces standardizacije ili adaptacije, a pritom mnogi čimbenici utječu na donošenje te odluke, kao npr. čimbenike okoliša, karakteristike tržišta, ponašanje potrošača i slično.

Globalni pristup obuhvaća standardizaciju marketinškog programa tako da međunarodno poduzeće nudi isti proizvod s istom markom, ambalažom, cijenom i uslugom i prodaje ga preko istih ili sličnih distribucijskih kanala, te ga na isti način promovira na svjetskom tržištu. Standardizacija marketing miksa obuhvaća centralizirani organizacijski dizajn, a adaptacija podrazumijeva usvajanje decentraliziranog dizajna. Različite tvrtke i čimbenici, specifični za određenu zemlju, mogu utjecati na odluku o standardizaciji ili adaptaciji marketing miksa. Uglavnom se preferira standardizacijski pristup, jer se polazi od toga da postoji snažna slika proizvoda na različitim tržištima diljem svijeta, a većina je tvrtki u mogućnosti povećati prodaju. Svaki od elemenata marketing miksa se tada mora prilagoditi, a svaki od elemenata ima jedinstvene karakteristike po kojima se razlikuje u tom stupnju prilagodbe globalnom tržištu.

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ZAHTJEVI NA POVRŠINSKU HRAPAVOST KOROZIJSKI POSTOJANIH ČELIKA OPĆE NAMJENE

THE REQUIREMENTS ON SURFACE ROUGHNESS OF STAINLESS STEEL FOR GENERAL PURPOSES

Biserka Runje¹, Vesna Alar¹, Amalija Horvatić Novak¹, Matko Stanković¹, Ante Ajduković¹

¹University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Ivana Lučića 5, Zagreb, Croatia

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Abstract

Considering the various applications of stainless steels, there exists a wide range of surface quality demands. Stainless steel surface quality can be expressed in a variety of ways, both qualitatively and quantitatively. In this paper the surface quality of stainless steel was evaluated using surface roughness parameters. Surface roughness is a component of surface texture which includes short surface irregularities and it is defined as a microgeometric state of the surface. In this paper, the surface roughness of steels belonging to several categories was measured and observed, in accordance with the EN 10088-2:2014 standard.

Keywords: Surface roughness, stainless steel, corrosion, EN 10088:2-2014.

Sažetak

S obzirom na razne primjene nehrđajućih čelika, javljaju se različiti zahtjevi na kvalitetu površine. Kvaliteta površine nehrđajućih čelika može se izraziti na više načina, kvalitativno i kvantitativno. U radu je kvaliteta površine nehrđajućih čelika ocijenjena parametrima hrapavosti. Površinska hrapavost je komponenta teksture koja uključuje kratkovalne nepravilnosti površine, a definira se kao mikrogeometrijsko stanje površine. Hrapavost je posljedica proizvodnog procesa odnosno rezultat je postupka obrade. U radu je mjerena i promatrana površinska hrapavost čelika svrstanih u kategorije materijala sukladno međunarodnoj normi EN 10088-2:2014.

Ključne riječi: Površinka hrapavost, nehrđajući čelici, korozija, EN 10088:2-2014.

1. INTRODUCTION

Nowadays, stainless steels have been used in many sectors such as construction, mechanical engineering, medical and household appliances, food industry, pharmaceutical industry, etc. The reason for such a broad application lies in their high resistance to corrosion attacks, reasonable cost and excellent mechanical properties. By definition, stainless steels are steels with a minimum of 12 % chromium content by mass and a maximum of 1.2 % carbon content by mass [1]. Nowadays, a distinction is made between a large variety of stainless steels whose properties depend on the addition alloying elements such as nickel, molybdenum and titanium. By adding alloying elements, it is possible to act on the mechanical properties of the material and its corrosion resistance [2]. Stainless steels are protected from corrosion due to the presence of chromium which forms a passive chromium oxide film Cr₂O₃ on the metal surface [3]. In such a case when the surface of the stainless steel is damaged, the thin oxide film on the surface is rapidly formed and the onset of oxygen and corrosion is prevented. Since its wide application in many sectors, especially in the food and pharmaceutical industry, the requirements on surface quality are of special interest. Due to the different applications of stainless steels, different surface quality requirements exist. International standards, from the EN 10088 group of standards, define technical requirements for the delivery of corrosion-resisting steels. More specifically, the standard EN 10088-2:2014 provides technical delivery conditions for the sheet/plate and strip of corrosion resisting steels meant for general purposes. This standard also sets requirements for the quality of stainless steel surfaces. The standard defines the surface quality and the conditions for stainless steel sheets, plates and strips in the cases of:

- Hot rolled finish.
- Cold rolled finish.
- Special finish.

Each material is marked with a number (1 or 2) and a letter. Numbers are used to denote the process of obtaining material surfaces, where 1 refers to the hot rolled finish and 2 refers to the cold rolled finish. The letter in each of the individual symbols indicates the sequence of different processing operations. Table 1 shows a description of the surface finish as proscribed by the EN 10088-2:2014 standard. In this paper the surface quality of stainless steel was evaluated using surface roughness parameters. Surface roughness is the measure of the finely spaced micro-irregularities on the surface texture [5]. The surface texture is composed of three components, namely roughness, waviness, and form [5]. Surface roughness is a result of the production process, i.e. material processing. Surface roughness can affect increased surface wear, reduced dynamic durability, adhesion to the base surface, accelerated surface corrosion, etc. Considering how surface roughness has a great impact on occurrence of surface corrosion, the definition of the quality of stainless steel should also include the allowed roughness parameters. Therefore, this paper emphasizes the quality of stainless steel surface expressed by amplitude surface roughness parameters. The paper investigates the surface roughness of the AISI 304 stainless steels sheets with different thickness and AISI 430 stainless steel, and determines their roughness parameters.





	Symbol	Description of surface finish
	ıU	Covered with rolling scale
Hot rolled surfaces	ıC	Covered with rolling scale
Hot folled sollaces	ıЕ	Free of scale
	ıD	Free of scale
	2H	Bright
	2C	Smooth with scale from heat treatment
	2E	Free of scale
Cold rolled surfaces	2D	Smooth
Cold Tolled Sofraces	2B	Smoother than 2D
	2A	Smoother and more reflective than 2D
	2R	Smooth, bright, reflective
	2Q	Free of scale
	1G or 2G	Surfaces finsh can vary
	1J or 2J	Surfaces finsh can vary
	1K or 2K	Surfaces finsh can vary
	1P or 2P	Surfaces finsh can vary
Spacial finishes surfaces	2F	Uniform nonreflective matt surface
Special finishes sofraces	ıМ	Surfaces finsh can vary
	2M	Surfaces finsh can vary
	2W	Design to be agreed
	2L	Colour to be agreed
	1 S or 2S	-

Tab. 1. Requirements on surface finish according to EN 10088:2-2014 [4]

2. MEASUREMENTS AND RESULTS

Measurements of surface roughness were conducted with use of the Taylor Hobson Surtronic 25 device and the Taly Profile Silver software for roughness measurements. Surface roughness measurements were conducted according to requirements specified in ISO 4288:1996. The following roughness parameters were observed: arithmetic average height (*Ra*), maximum height of profile within sampling length (*Rz*), maximum profile peak height within sampling length (*Rp*) and largest profile valley depth within sampling length (*Rv*).

With the aim to determine the surface quality expressed by the surface roughness parameters, different surfaces were examined on AISI 304 stainless steels samples with different thickness, and on AISI 430 samples of sheets with 0.8 mm thickness.



The first part of the surface roughness inspection was performed on three stainless steel samples made of AISI 304, whose dimensions were equal to 100 mm x 70 mm x 1.5 mm. The prepared samples were electropolished and then colorized by electropolishing. After the surface treatment, parameters of surface roughness on all samples were measured. Different surfaces were observed on the same sample: basic material (untreated), electropolished surface and colored surface. Figure 1 illustrates sample 1.



Fig. 1: Sample 1 after surface treatments

The surface of the basic material can be classified as belonging to either the 2K class, in accordance with the EN 10088-2:2014 standard. Figure 2 illustrates the roughness profile of the supplied (basic) material, while measurement results for the same surface are given in Table 2.





Measurement No.	1	2	3
Ra, μm	0.204	0.204	0.205
Rz, μm	1.82	1.90	1.51
<i>Rp</i> , μm	0.633	0.48	0.503
<i>Rv</i> , μm	1.19	1.42	1.00

Tab. 2: Measured roughness parameters of the basic material

Roughly half of the sample plate was electropolished and the surface roughness of the plate was measured. The process of electropolishing was performed on materials intended to be used primarily in the food and pharmaceutical industry. The electropolish works to smooth the surface, reducing the roughness and enabling the dirt and microorganisms to be trapped on the material surface. Table 3 demonstrates measured surface roughness parameters obtained from the electropolished parts. The surface quality attained after electropolishing can be classified as belonging to group 2D in accordance with the EN 10088-2:2014 standard.

Measurement No.	1	2	3
Ra, µm	0.187	0.163	0.159
Rz, μm	0.957	1.38	1.66
<i>Rp</i> , μm	0.497	0.567	0.87
<i>Rv</i> , μm	0.46	0.817	0.793

Tab. 3: Measured roughness parameters of the electropolished surface

After electropolishing, the samples were chemically coloured. Except for the decorative effect, colouring the samples increases their surface passive layer, which increases the corrosion resistance of the material. The increase of corrosion resistance of coloured surfaces, as opposed to electropolished surfaces, is too small to affect long-term efficiency [6]. If the material is put in an aggressive environment, corrosion can occur. In that case, the corrosion present on uncoloured steels can be mechanically removed without significantly affecting the visual appearance of the surface. On the other hand, removing the corrosion from coloureded surfaces significantly affects their appearance. The procedure of electrochemical colouring was carried out by submerging the samples into acid and via the subsequent hardening of the applied paint in a separate fluid while exposed to the effects of a direct current. Following this process, the surface which was subjected to electro-chemical colouring turned blue (Figure 1). After having their surfaces coloured, the tested materials can be classified as belonging to the 2L category of materials, in accordance with the EN 10088:2-2014 standard (Table 4).



Measurement No.	1	2	3
Ra, µm	0.144	0.162	0.108
<i>Rz</i> , μm	0.90	1.43	0.727
<i>Rp</i> , μm	0.426	0.590	0.273
<i>R</i> ν, μm	0.474	0.843	0.453

Tab. 4: Measured roughness parameters of the colored surfaces

The second part of the research included roughness measurements for two stainless steels, one belonging to the AISI 304 classification and the other belonging to AISI 430 classification. Observed were stainless steels sheets with thickness of 0.8 mm. Three samples of each of these materials were prepared and measurements were subsequently conducted on all of them. Measurements of the Ra and Rz parameters were conducted for all samples. The values of the roughness parameters displayed in the following section represent parameter arithmetic means which were derived from measurements conducted upon samples possessing equal quality of material (Table 5).

Tab. 5: Measured roughness parameters on 0.8 mm thick stainless steel sample
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	AISI 304	AISI 430
Ra, μm	0.27	0.28
<i>Rz</i> , μm	1.62	1.63

According to the EN 10088:2-2014 standard, AISI 304 sample belongs to the 2B group of materials, while AISI 430 sample belongs to 1J or 2J group.

3. DISUSSION AND CONCLUSION

Stainless steels have a large application in many different industries. The reason for the high use of stainless steels lies in their corrosion resisting properties. The quality of a stainless steel surface is of great importance both in terms of corrosion resistance and surface appearance. Due to the large application of stainless steels, different demands on surface quality, purity, color and gloss of surface appear. The EN 10088-2:2014 standard defines the quality of stainless steel surfaces as well as the technical delivery conditions for the sheet/plate and strip, of general purpose corrosion resistant steels. The quality of steel, as defined by this standard, includes the surface appearance. With the aim of better classifying general purpose stainless steels, measurements of samples possessing varying degrees of surface roughness were conducted. As a result, the amplitude surface roughness parameters *Ra* and *Rz* were observed. In the case of surface roughness measurement conducted for steels belonging to the AISI 304 classification, a reduction of the level of surface roughness was

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observed for the sample surfaces exposed to electropolishing and colouring procedures. Furthermore, a reduction of the *Ra* parameters was observed after the sample surfaces were exposed to the electropolishing and colouring procedures, as opposed to their prior base state. In the case of the measurements conducted for the surface roughness samples of the AISI 304 and AISI 430 steels with thickness of 0.8 mm, similar results of parameters *Ra* and *Rz* were obtained. Although both samples have similar roughness parameters, they are classified in different groups of materials. Considering the appearance of the samples, first sample (AISI 304) belongs to 2B group of material, while second sample (AISI 430) belongs to 1J or 2J group of material (in accordance with the EN 10088:2-2014 standard). In order to define the quality of the materials more specifically, the next step in the research should involve measurements of other surface roughness parameters (such as amplitude, spacing, hybrid, bearing ratio curve parameter). Also, a new revision of the standard should implement information about the recommended surface roughness parameters for general purpose corrosion resisting steels.

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DEVELOPMENT OF ADVANCED CEMENTED CARBIDE CUTTING TOOLS – TRENDS IN INDUSTRY AND SCIENCE

Matija Sakoman^{1,} Danko Ćorić¹

¹ University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture

Invited lecture / Pozvano predavanje

Abstract

In the next decade we will be celebrating over 100 years of cemented carbides and over 60 years of existence of coated cutting tools successfully employed in the industry. Despite the "retirement age" of these two topics, the scientific papers mostly funded by industrial research are written on a daily basis, and small improvements in understanding the material as well as complex architecture coating systems which are applied on them are visible. In 2019th 85% of all cemented carbide tools are coated, and the demand for efficient tools is ever-growing. Continuous increase of productivity in dealing well as new challenges arriving with modern materials being machined is a "holy grail" of the industry.

The value of the global industry in 2019 is expected to be over 17 billion USD. The cutting technologies are present in a nearly constant ratio, around 39 % goes on milling technology, and turning represents around 30 % of the market. However, the drilling share is rising due to advanced production of microdrills. As a material, cemented carbide represents around 50 % of the cutting tool's market and it's market share is slowly decreasing due to the advancements in other materials such as PCD and CBN. Nowadays the cooling of the cutting tool is trending towards "greener technologies" and the quantity of the coolant being used is decreasing. The main reason for that are the advanced cutting tools themselves that have excellent mechanical properties, mainly hardness at high temperatures, as well as good tribological properties.

CVD coatings used from 1979., in modern and highly reactive nanostructured cemented carbides are being more and more of a problem due to their high coating temperature, creating Eta phase causing a decrease in toughness of the tool. The PACVD coatings are yet to be investigated in detail. Multilayer gradient coating systems such as TiN/TiCN, TiN/TaN, TiN/NbN, TiN/AIN, TiN/TiBN, TiN/CrN have shown to have a high potential in dealing with high demands of the industry.





PRIMJENA ADITIVNH TEHNOLOGIJA U IZRADI CoCr DENTALNIH FIKSNO-PROTETSKIH KONSTRUKCIJA

APPLICATION OF ADDITIVE TECHNOLOGY IN COCR DENTAL FIXED-PROSTHETIC CONSTRUCTIONS

Sanja Šolić¹, Zdravko Schauperl², Amir Ćatić³, Vlado Tropša¹

¹ Sveučilište Sjever, J. Križanića 31b, 42000 Varaždin, Hrvatska

² Fakultet strojarstva I brodogradnje Sveučilišta u Zagrebu, I. Lučića 5, Zagreb, Hrvatska

³ Stomatološki fakultet Sveučilišta u Zagrebu, Gundulićeva 5, Zagreb, Hrvatska

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Sažetak

CoCr legure koriste se za široku primjenu u dentalnoj medicine, od mobilnih djelomičnih proteza do fiksnih nosača sinterirane estetske keramike, radi svojih odličnih mehaničkih svojstava i otpornosti na koroziju. Uz klasične postupke proizvodnje i oblikovanja aditivni tehnološki postupak selektivnog laserskog taljenja – SLM posljednjih godina bilježi sve veću upotrebu u izradi CoCr dentalnih fiksno-protetskih konstrukcija. U ovom radu prikazani su najvažniji postupci aditivne proizvodnje te utjecaj parametara selektivnog laserskog taljenja na mikrostrukturu i mehanička svojstva CoCr legura u usporedbi sa lijevanim legurama za istu namjenu u dentalnoj medicini.

Ključne riječi: CoCr dentalne legure, aditivne tehnologije, SLM, mikrostruktura

Abstract

CoCr alloys are widely used in dental medicine, from mobile partial prostheses to fixed carriers of sintered aesthetic ceramics for their excellent mechanical properties and corrosion resistance. Along with the classic production and shaping processes, the adventitious technological process of selective laser melting - SLM has been increasingly used in the development of CoCr dental fixed-prosthetic constructions in recent years. This paper presents the most important methods of additive production and the influence of selective laser melting parameters on the microstructure and mechanical properties of CoCr alloys compared to cast alloys for the same purpose in dental medicine.

Keywords: CoCr dental alloys, additive technologies, SLM, microstructure

1. UVOD

Aditivne tehnologije obuhvaćaju tehnologije brze izrade prototipa i 3D print koje omogućuju konstrukcijsku slobodu, minimizaciju otpada obrade, mogućnost jednostavne izrade kompleksnih geometrija kao i brzu izradu modela i proizvoda. Aditivnim proizvodnim postupcima izrađuju se trodimenzionalni dijelovi postupnim nanošenjem tankih slojeva materijala vođenih računalnim modelom. Ta jedinstvena značajka omogućuje izradu kompleksnih te namjenski prilagođenih i unikatnih dijelova direktno iz konstrukcijskog računalnog modela bez potrebe izrade skupih alata i dijelova kao što su kalupi, ukovnji ili gravure, čime se smanjuje potreba za velikim brojem koraka u proizvodnom procesu. Ovim postupcima moguće je također izraditi dijelove kompleksne geometrije i oblika u jednom koraku bez ograničenja klasičnih postupaka proizvodnje (npr. izbjegavanje oštrih prijelaza, dubokih provrta, koncentratora naprezanja itd.) ili klasičnih oblika polaznog materijala (puni profili, cijevi, pločevine standardnih dimenzija) čime se značajno smanjuje i broj potrebnih pozicija za izradu takvih dijelova klasičnim tehnologijama kao i linija na kojima se takvi proizvodi sklapaju do gotovog oblika. Također, dijelove je moguće proizvesti direktno prema zahtjevu čime se smanjuje potreba za skladištenjem većeg broja proizvoda, a smanjuje se i kritično vrijeme potrebno za zamjenu istrošenih ili dotrajalih dijelova strojeva i proizvodnih linija kod preventivnog i reparaturnog održavanja. Radi navedenog, aditivne tehnologije danas su prihvaćene kao model za konstrukciju i proizvodnju visoko učinkovitih dijelova za zrakoplovnu, automobilsku i energetsku industriju te medicinsku primjenu. Medicinski i stomatološki implantati kao i dentalne fiksno-protetske konstrukcije proizvedene aditivnim postupcima nude značajna poboljšanja s aspekta osteointegracije i biokompatibilnosti te mogućnosti izrade implantata i dentalnih fiksno-protetskih konstrukcija potpuno prilagođenih anatomiji samih pacijenata. Međutim, preciznost izrade implantata i fiksnoprotetskih konstrukcija kao i njihova mehanička svojstva značajno ovise o točnosti ili rezoluciji uređaja te značajno o parametrima postupka (brzini lasera, količini energije, debljini materijala nanesenog u jednom prolazu itd). Optimiranjem parametara postupka moguće je utjecati na dobivanje različitih mehaničkih svojstava i mikrostrukture na točno određenim mjestima same konstrukcije i na taj način postići optimalna svojstva na točno određenom dijelu samog proizvoda.

2. ADITIVNI POSTUPCI PROIZVODNJE

Aditivne tehnologije i postupci razvijaju se u svrhu proizvodnje kompleksnih struktura i geometrija u visokoj rezoluciji odnosno visoke točnosti dimenzija. Brzo prototipiranje, sposobnost izrade velikih dijelova, smanjenje grešaka pri taloženju i poboljšanje mehaničkih svojstava neki su od ključnih faktora koji su potaknuli razvoj aditivnih tehnologija. Najraširenija metoda 3D izrade danas, koja uglavnom koristi polimerne niti poznata je kao *postupak taložnog srašćivanja* (eng. Fused deposition modelling - FDM). Osim ovog postupka, aditivne tehnologije proizvodnje u praškastoj komori *selektivnim laserskim sinteriranjem* (eng. Selective laser sintering - SLS), *selektivnim laserskim taljenjem* (eng. selective laser melting - SLM) ili *umrežavanje polimera iz tekuće faze u trodimenzionalni proizvod* (3DP), kao i *stereolitografija* te *direktno taloženje izvorom energije* (eng. Direct energy deposition - DED) i izrada laminiranih proizvoda (eng. Laminated object manufacturing - LOM), danas su glavni postupci aditivne proizvodnje koji su ukratko opisani u ovom radu [1]. Osim ovih postupaka razvijaju se i novi za specifične aplikacije, kao što su dvo-fotonska polimerizacija (two-photon polymerization - TPP), projekcijska mikro stereolitografija (PµSLA), elektrohidrodinamička


izrada/print (EHDP) koji su detaljno prikazani u [2] te bezkontaktni mikro i nano postupci taloženja, opisani u [3].

2.1 Taložno srašćivanje (Fused Deposition Modelling – FDM ili Fused Filament Fabrication FFF)

Postupak taložnog srašćivanja (FDM) najpoznatiji je i najrašireniji aditivni postupak, poznat i pod nazivom 3D print odnosno 3D izrada. Kod ovog postupka kontinuirana nit plastomera koristi se za izradu trodimenzionalnog oblika proizvoda oblikujući ga nanošenjem polimera u slojevima (Slika 1a). Polimerna nit ugrijava se u sapnici u tjestasto stanje te se ekstrudira na radnu platformu na prethodno nanesene slojeve. Termoplastičnost polimera ključno je svojstvo postupka koje omogućava srašćivanje odnosno staljivanje polimernih niti prilikom nanošenja u homogeni materijal, te skrućivanje homogenog materijala do sobne temperature. Debljina sloja, širina, te orijentacija niti kao i eventualna zračnost između polimernih niti pri depoziciji (unutar sloja koji se nanosi ili između slojeva) najvažniji su parametri postupka koji značajno utječu na mehanička svojstva izratka. Kao glavni uzrok loših mehaničkih svojstava pokazala se upravo neravnomjernost materijala unutar nanesenih slojeva te šupljine unutar i između slojeva [1, 4]. Niska cijena te velika brzina i jednostavnost glavne su prednosti ovog postupka. S druge strane, loša mehanička svojstva proizvoda, vidljivost slojeva u strukturi i loša kvaliteta površine [5] te ograničen broj polimera adekvatnih svojstava, glavna su ograničenja FDM postupka [6]. Razvoj vlaknima ojačanih kompozita za primjenu u FDM postupku utjecao je na poboljšanje mehaničkih svojstava proizvoda, ali orijentacija vlakana, veza između vlakna i matrice te formiranje praznina pri depoziciji glavni su problemi koji se pojavljuju kod 3D izrade kompozitnih dijelova ovim postupkom.

2.2 Srašćivanje praškastog materijala u komori (Powder bed fusion)

Postupak srašćivanja materijala u komori kao polazni materijal koristi komoru ispunjenu prahom (metalnim ili polimernim) koji se u vrlo tankim slojevima povezuje vezivom ili sinterira pomoću lasera na nosaču. Daljnji slojevi praha valjaju se na prethodne, tale te se na taj način gradi konačni 3D oblik proizvoda (Slika 1d). Najvažniji parametri ovog postupka su granulacija praha te mogućnost ravnomjernog nanošenja i kompaktiranja o čemu direktno ovisi gustoća gotovog proizvoda. Sinteriranje praha može se koristiti samo za prahove s nižom temperaturom tališta/sinteriranja, a za ostale prahove potrebno je koristiti vezivo u tekućem stanju. Selektivno sinteriranje laserom (SLS) može se koristiti za različite vrste polimernih i metalnih prahova dok se selektivno taljenje laserom (SLM) može koristiti samo za određene čelike i aluminij. U SLS postupku laser ne tali u potpunosti prah već ga ugrijava na temperaturu pri kojoj se ostvaruje povezivanje kuglica praha na molekularnom nivou [7]. U SLM postupku laser u potpunosti tali prah pri nanošenju slojeva te se tim postupkom dobivaju proizvodi izvrsnih mehaničkih svojstava [8]. Kod ovih postupaka najvažniji parametri su snaga lasera i brzina, odnosno posmak lasera. Kod postupaka koji koriste tekuće vezivo, kemijska i reološka svojstva veziva, veličina i oblik čestica praha, brzina nanošenja praha, veza između praha i veziva te naknadne obrade ključni su parametri o kojima ovise svojstva proizvoda (Slika 1b). Glavne prednosti ovih metoda su dobra rezolucija tj. točnost dimenzija i visoka kvaliteta izratka s aspekta mikrostrukture i mehaničkih svojstava, što ih čini pogodnim za izradu proizvoda kompleksne geometrije. Koriste se u raznim industrijskim granama, od avionske industrije, za elektroničke komponente, u bioinženjerstvu pri izradi umjetnih tkiva, ćelijastih konstrukcija itd. Glavni nedostatak ovih postupaka je veliko vrijeme izrade proizvoda te visoka cijena, a kod postupka sa tekućim vezivom i veliki porozitet izratka [1].





Slika 1: a) Postupak taložnog srašćivanja (FDM); b) Srašćivanje praškastog materijala vezivom (Powder bed fusion); c) stereolitografija; d) Postupak Selektivnog sinteriranja/taljenja laserom (SLS/SLM) [1]

2.3 Stereolitografija (eng. Stereolithography - SLA)

Stereolitografija je jedan od prvih aditivnih postupaka proizvodnje koji je razvijen 1986. godine. Kod ovog postupka koristi se izvor UV zračenja (ili snop elektrona) koji potiče umrežavanje slojeva polimera u obliku smole ili otopine monomera (najčešće na bazi akrila ili epoksija). Nakon polimerizacije i očvrsnuća sloja polimera inicira se reakcija umrežavanja daljnjeg sloja. Višak neumreženog polimera odstranjuje se nakon postupka te ostaje oblik gotovog proizvoda. Za postizanje boljih mehaničkih svojstava proizvodi se podvrgavaju naknadnim grijanjima ili daljnjem UV zračenju. Ovim postupkom također se izrađuju i kompoziti s različitim česticama kao ojačalom. (Slika 1c). Proizvodi dobiveni ovim postupkom visoke su kvalitete i jako dobre rezolucije odnosno točnosti dimenzija do 10 μ m [9]. S druge strane, postupak je relativno spor i skup te s vrlo ograničenim brojem materijala pogodnih za ovaj postupak. Također, kinetika polimerizacije i umrežavanja materijala je vrlo kompleksna, a ima vrlo velik utjecaj na kvalitetu i mehanička svojstva proizvoda. Ovaj postupak uspješno se koristi za izradu kompleksnih nanokompozita [10].

2.4 Direktno taloženje izvorom energije (DED)

Ovaj postupak koristi se za izradu kompleksnih proizvoda visokih mehaničkih svojstava od super legura. Poznat je i pod nazivima LENS – Laser Engineered Net Shaping, LSF – laser solid forming, DMD – direct metal deposition, aditivna proizvodnja elektronskim snopom (EBAM) te aditivna proizvodnja električnim lukom i žicom (WAAM). Direktno taloženje izvorom energije koristi laser ili snop elektrona koji se usmjerava na malu površinu te istovremeno tali materijal koji se nanosi (u obliku praha ili žice). Rastaljeni materijal se nanosi i spaja s rastaljenom podlogom te skrućuje nakon odmicanja izvora energije. Razlika između ovog

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postupka i SLM je što se ne koristi komora ispunjena prahom, a materijal koji se nanosi tali se prije nanošenja (slično kao u FDM postupku ali uz značajno veću količinu potrebne energije za taljenje metala). Ovaj postupak pogodan je za reparaturne radove, a omogućuje više-osno nanošenje materijala kao i kombiniranje različitih materijala istovremeno. Materijali koji se koriste pri ovim postupcima su titanij, Inconel, nehrđajući čelici te aluminij sa legurama. Brzina postupaka je relativno velika (od 0,5 kg/h za LENS do 10 kg/h za WAAM) kao i mogućnosti izrade dijelova velikih dimenzija (do 6 m x 1,4 m x 1,4 m). Moguće je postići izvrsna mehanička svojstva, kontroliranu mikrostrukturu i točan kemijski sastav proizvoda. Nedostaci su relativno loša točnost dimenzija (0,25 mm), slaba kvaliteta površine te nemogućnosti izrade složenijih geometrija. Generalno, ovi postupci se koriste za jednostavne dijelove većih dimenzija te za reparaturu složenijih i velikih komponenata [1].

2.5 Izrada laminiranih proizvoda (LOM)

Ovaj aditivni postupak jedan je od prvih komercijalnih postupaka koji se temelji na rezanju i laminiranju limova ili traka materijala, sloj po sloj. Ovim postupcima izrađuju se različite kompozitne sendvič konstrukcije.

3. CoCr LEGURE ZA DENTALNE NAMJENE

Kobalt – krom legure koriste se za široku primjenu u dentalnoj medicini, od mobilnih djelomičnih proteza do fiksnih nosača sinterirane estetske keramike, radi svojih odličnih mehaničkih svojstava i otpornosti na koroziju. Ove legure također se koriste i za naprave za fiksiranje kostiju kao i pri totalnoj ili djelomičnoj zamjeni kuka ili koljena i to u lijevanom i gnječenon stanju te su vrlo bitne u medicinskim primjenama. Loše strane ovih legura su skupa proizvodnja i zahtjevna obradivost (lijevanje, rezanje i plastična deformacija) radi visoke temperature tališta (1623 K – 1723 K), visoke tvrdoće i ograničene duktilnosti [11, 12]. Od navedenih postupaka aditivne proizvodnje, SLM postupak posljednjih godina bilježi sve veću upotrebu u izradi CoCr dentalnih fiksno-protetskih konstrukcija. Obzirom na navedene prednosti postupka u 2.2 objavljeno je nekoliko radova s rezultatima ispitivanja osnovnih mehaničkih i korozijskih svojstava dentalnih konstrukcija proizvedenih aditivnim SLM postupkom [11, 13, 14]. U radu [14] ispitivana je usporedba čvrstoće veze CoCr legure dobivene SLM postupkom i lijevane legure s estetskom keramikom pri čemu su rezultati pokazali da nema značajne razlike u čvrstoći veze estetske keramike i lijevane CoCr legure te SLM CoCr legure. Površinsko i unutarnje prianjanje metal-keramičkih krunica proizvedenih SLM postupkom ispitano je in vivo, a rezultati su pokazali da krunice proizvedene SLM postupkom pokazuju i dimenzijsku točnost u području implementacije u kosti, koja je usporediva s konvencionalnim proizvodnim postupcima [15]. Ispitivanja mehaničkih svojstava SLM CoCr legura ukazuju na mogućnost postizanja viših vrijednosti vlačne čvrstoće i konvencionalne granice razvlačenja od CoCr legura dobivenih klasičnim postupcima [13]. Razlike u mikrostrukturi, koja ima najveći utjecaj na mehanička svojstva materijala, CoCr dentalnih fiksno-protetskih konstrukcija dobivenih SLM postupkom također su detaljno razrađene u literaturi [15 - 17]. CoCr legure za dentalnu namjenu imaju standardizirani raspon kemijskog sastava što ima velik utjecaj na mikrostrukturu i na mehanička svojstva i kod lijevanih legura stoga je od velikog značaja poznavati utjecaj svih parametara na strukturu i svojstva CoCr legura dobivenih SLM postupkom.

U radu [12] ispitivan je utjecaj parametara aditivnog SLM postupka na mikrostrukturu, mehanička svojstva i korozijsku postojanost Co-29Cr-6Mo legure. U eksperimentu je

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mijenjana snaga lasera od 75 W do 200 W te posmak od 0,1 mm do 0,3 mm. Brzina lasera i debljina sloja praha bili su konstantni i iznosili 50 mm/s i 0,05 mm. Kod ispitivanja mehaničkih svojstava autori su promatrali i utjecaj anizotropije SLM gradnje materijala te su izradili epruvete pod kutem 0°, 45° i 90° na smjer staljivanja i rasta epruvete. Mikrostrukturnu analizu autori su napravili pomoću svjetlosne i elektronske mikroskopije. Mikrostruktura uzoraka varirajući snagu lasera od 75 W do 200 W i posmak od 0,1 mm do 0,3 mm prikazana je na Slici 2 [12].



Slika 2: Mikrostruktura uzoraka u ovisnosti o snazi lasera (75 W do 200 W) i posmaku lasera (0,1 mm do 0,3 mm) [12]

Na Slici 2 su vidljivi širi tragovi područja staljivanja materijala s povećanjem posmaka posebno kod korištenih većih snaga lasera. Vidljivo je također da je postignuta veća gustoća materijala bez prisutnog poroziteta kod većeg unosa energije, iznad 400 J/mm³, a porozitet se u materijalu pojavljuje u većoj mjeri kod unosa energije manjeg od 150 J/mm³.

Usporedba mikrostruktura dentalnih CoCr legura dobivenih različitim tehnološkim postupcima predmet je mnogih istraživanja. U radu [18] uspoređivana je mikrostuktura dentalne CoCr fiksno protetske konstrukcije dobivene lijevanjem, glodanjem iz gnječenog pripremka, SLM postupkom te post sinteriranjem (nakon oblikovanja kostrukcije glodanjem) i prikazane su na Slici 3.



Slika 3: Mikrostruktura CoCr dentalne fiksno protetske konstrukcije izrađene: a) lijevanjem; b) glodanjem iz gnječenog pripremka; c) SLM postupkom; d) post sinteriranjem (nakon oblikvanja kostrukcije glodanjem [18]

Na Slici je vidljiva velika razlika između mikrostruktura legure istog kemijskog sastava dobivene različitim postupcima proizvodnje. Ispitivanja mehaničkih svojstava pokazala su da



najbolja svojstva iskazuje legura dobivena SLM postupkom zatim post sinterirana, lijevana te glodana [18].

Slika 4 pokazuje usporedbu lijevane i SLM CoCr dentalne legure gdje je također vidljiva heterogena struktura lijevanog uzorka s tipičnom dendritnom mikrostrukturom dok SLM uzorak iskazuje homogenu i kompaktnu mikrostrukturu [19].



Slika 4: Mikrostruktura dentalne CoCr legure na svjetlosnom mikroskopu: (a) lijevano; (b) SLM postupak [19]

4. ZAKLJUČAK

Kobalt – krom legure koriste se za široku primjenu u dentalnoj medicini, od mobilnih djelomičnih proteza do fiksnih nosača sinterirane estetske keramike, radi svojih odličnih mehaničkih svojstava i otpornosti na koroziju. Preciznost izrade implantata i fiksnoprotetskih konstrukcija kao i njihova mehanička svojstva značajno ovise o točnosti ili rezoluciji uređaja te značajno o parametrima postupka (brzini lasera, količini energije, debljini materijala nanesenog u jednom prolazu itd). Optimiranjem parametara postupka moguće je utjecati na dobivanje različitih mehaničkih svojstava i mikrostrukture na točno određenim mjestima same konstrukcije i na taj način postići optimalna svojstva na točno određenom dijelu samog proizvoda.

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FATIGUE LIFE MODELS OF WOOD – A REVIEW

Matjaž Šraml¹, Srečko Glodež² and Gorazd Fajdiga³

¹ University of Maribor, Faculty of Civil Eng., Transportation Eng. and Architecture, Smetanova 17, 2000 Maribor, Slovenia

² University of Maribor, Faculty of Mech. Engineering, Smetanova 17, 2000 Maribor, Slovenia

³ University of Ljubljana, Biotechnical Faculty, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

Review paper / Pregledni rad

Abstract

The objective of this paper is to report on the fatigue life models (FLM) of wooden structures. Lately, wood became widely use in different areas of everyday living, as a constructing material, subjected to cycling loading, as well. Therefore, some of the wood (timber) structures are subjected to dynamic loading, which call for deep investigation regarding the fatigue life prediction models. The paper focusing on an overview of existed and possible (analytical and numerical) modelling of fatigue life models (FLM). Experimental part of fatigue life models will be presented in the paper Fajdiga et al. also at "Matrib 2019".

Keywords: Wood, Fatigue, Analythical models

1. Introduction

Wood is a material with mechanical properties that vary markedly, both within a tree and among trees. Products made from biological materials such as wood often have a complex mechanical behaviour. Although such materials have been utilised for thousands of years, full knowledge of their mechanical behaviour has yet to be achieved. They often vary in their properties from sample to sample and exhibit a nonlinear mechanical behaviour at higher loading. Moisture changes lead to shrinkage or swelling and modify the mechanical properties. Wood also shows a loading-rate dependency, such as creep and viscoelasticity [1]. Anyway, recently, we can (again) find wood as a construction material, widely us as a sustainable material. Although, a wood is typical heterogeneous material, we used wood as a construction material which can also be subjected to the cycling (fatigue) loading.

Fatigue failure of a wood components results from cyclic application of stress which is lower if compare to the stress under monotonic loading conditions. The one of the first study related to the fatigue of woods was done by Wood [2] who presented so-called "Madison curve" as a relationship between the working stress and the duration of loading (Fig. 1). Over recent years many investigations have been proposed to explain the fatigue phenomena of wood [3-5]. The general conclusion of these studies is the fact that the fatigue properties of wood are significantly affected ba thy amount of water comprised in wood. Furthermore, the dynamic strength of wood is by pulsating loding (R=0) higher if compare to the complete reversed loading (R = -1) at the same peak stress.



Fig. 1: Relationship of working stress to duration of loading [2]

In the last period, researchers have analysed different influencing parameters on the fatigue behaviour of wood. However, research focused on wood fatigue is scarce owing to inherent difficulties. Namely, wood is a natural and anisotropic material with significant variability in its mechanical properties. In timber construction, wood members are generally connected to each other by means of dowels or screws, which represent the stress concentrations due to holes, notches etc. This notch effect has a negative influence on the fatigue behaviour of wood member espetially in high cycle fatigue regime [6]. Liu and Ross [7] developed a

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mathematical model for prediction the fatigue strength of Douglas-fir wood beams under. They concluded that for a given mean stress, fatigue life decreases with an increase of the amplitude stress. Furhermore, for a given stress amplitude, fatigue life decreases with an increase of the mean stress. The authors also found out that the fatigue life was almost independent on the loading frequency. Yildirim et al [8] investigated the fatigue behaviour of Scots pine and beech wood using a three point bendig test at different stress levels (from 40 to 80 % of material's ultimate static strength). Authors concluded that the fatigue strength of beech is higher if compare to the Scots pine. Mejri et al [9] have analysed the influence of the hygrothermal aging on the fatigue behaviour of wood fibre composites under bending loading. The authors concluded that damage mechanisms are directly influenced by aging. When analysing the fatigue behaviour of wood components, some authors also considered the fracture mechanics and fatigue crack growth theories. The proposed approaches are related to the Mode-I [10-12], Mode-II [13-15] or Mixed-Mode-I+II [16] fatigue crack growth.

The objective of this work is a short overview of the main avialabe mathematical models which can be used to describe the fatigue behaviour of wood components. The proposed models could be extended or improved with the consideration of scientific results related to the further investigations on the fatigue behaviour of wood.

2. Wood fatigue life modells

In the following chapter, an overview and possible implementation of already existed fatigue life models (FLM) applicate for wood structures will be discussed and analysed. Majority of them are discussed in [17], which is also main reference of presented overview paper.

Wood structures are not the first in mind when fatigue is discussed. And at a conversational level the authors of the present work have often been let to feel that the subject indeed was among the more "exotic". However, fatigue loaded wood constructions exists and the timber construction code includes an informative annex on fatigue.

Normally fatigue is described by number of load oscillations to failure at a given stress level. In wood where the static strength is a function of the duration of load, fatigue may also comprise static fatigue, i.e. fatigue where the failure is obtained within the first load cycle. Static fatigue is not just a special case of fatigue; when the strength depends on the duration of load the number of cycles to failure will depend on the load frequency.

The influence of duration of load divides the literature on wood fatigue into two fundamentally different main lines. The first main approach is a traditional number of cycles, *N*, quantification. According to this approach Wöhler curves can be used to state fatigue resistance in *N* and stress level. The second main approach is a traditional duration of load quantification. According to this approach fatigue failure is not directly a function of the number of load oscillations counted by *N*, but is explained by the total accumulated time under load, summarized over all load cycles. However, the truth may be in between, i.e. wood fatigue is governed by a combination of number of cycles and time under load.

Following, some of possible useful fatigue life prediction models for wooden structures are discussed. Amin references used there is reported in [17].

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2.1 Damage accumulation [17]

Damage accumulation laws have been proposed in various forms in order to model time to failure. The main goal for these models is to model the duration of load phenomenon adequately. The basic form of damage accumulation laws is proposed by Gerhards, reported in [18]. The rate of damage could be expressed as:

$$\left(\frac{da}{dt}\right) = \exp\left(-a + b\frac{\sigma(t)}{\sigma_s}\right),\tag{1}$$

where α is the damage degree ($0 \le \alpha \le 1$), t is time, $\sigma(t)$ is load history, σ_s is strength, and α and b are empirically constants for a given wood population. When neglecting the initial ramp loading the time to failure, T_c , at constant load conditions, σ_c , can be expressed using Eq. (2):

$$T_c = \exp\left(a - b\frac{\sigma_c}{\sigma_s}\right),$$
(2)

Barrett and Foschi [19] represents a damage accumulation law where the rate of damage growth is also dependent on the damage degree, following the Eq. (3):

$$\left(\frac{d\alpha}{dt}\right) = a \left(\frac{\sigma(t)}{\sigma_s} - \frac{\sigma_0}{\sigma_s}\right)^b + \lambda \alpha(t), \tag{3}$$

where σ_o is a stress threshold below which no damage occurs, and the parameters a, b and λ are empirical constants for a given wood material. In proposed model (Eq. 3) the damage rate is dependent on the degree of damage due to the term $\lambda \alpha(t)$. As reported by Foschi and Yao in [20], this term leads to exponential growth of damage when damage is present and the load is just larger than the threshold value. In order to avoid this fact, the model is improved by aplying λ as a function of stress level

$$\frac{d\alpha}{dt} = a \left(\frac{\sigma(t)}{\sigma_s} - \frac{\sigma_0}{\sigma_s}\right)^b + c \left(\frac{\sigma(t)}{\sigma_s} - \frac{\sigma_0}{\sigma_s}\right)^n \alpha(t),$$
(4)

where *c* and *n* are empirical constants for a given wood population.

Irrespective of the different forms of the damage accumulation laws, the models defined with Eqs. (1), (3) and (4) unite in seeing damage rate as being only time dependent. With respect to fatigue this may be a model flaw as damage introduced due to repetitive loading is only accounted for by time dependent damage. This is evident from a discussion of cyclic loading at constant amplitude proposed by Barrett and Foschi in [21], where it is explicitly stated that number of cycles to failure is proportional to the frequency of the load cycles. Hence, an ideal square load cycle only contributes to damage due to the time under constant load. In other words, the models cannot account for the effect due to the load oscillation phenomenon usually associated with fatigue phenomena.

2.2 Energy based models [17]

Fatigue models exploiting energy based failure criteria have been applied to wood by, e.g. Bach (1975) [22], and Philpot et al [23]. Energy based failure criteria are expressed as a critical

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value of a specific energy quantity, w, which is calculated as an integral of a stress component, σ , times the corresponding strain, ε , increment:

$$w = \int \sigma \cdot d\varepsilon \tag{5}$$

The stress component can be identified with the stress in an element of a rheological model (Fig. 1). Due to the time dependent properties of wood, energy based failure criteria can be expressed in rates of stress (e.g. time direvatives d/dt denoted by `), $\dot{\sigma}$, and strain, $\dot{\varepsilon}$, or generally stress work rate, \dot{w} :

$$w(t_f) \int_0^{t_f} \sigma \varepsilon + \sigma \dot{\varepsilon} dt = \int_0^{t_f} \dot{w} dt$$
(6)

A simple theoretical basis can be a four element viscoelastic rheological material model, proposed by Burger, reported in [17] and presented in Fig. 2, representing the three strain components: elastic strain, ε_{E} , viscoelastic strain, ε_{VE} and viscous strain, ε_{V} . Integrating all stress and strain components of the model (presented at Fig. 2) yields the total stress work (Eq. 6). An elaborate energy failure criterion was put forward by Reiner and Weisenberg in [24]. The criterion has furthermore been theoretically exploited in 90' by Liu & Ross in [7]. According to the Reiner-Weisenberg theory failure will occur when the strain work, w_c , due to the recoverable part of the deformation attains a critical value. Hence, the dissipation rate of non-elastic energy, \dot{D} , is subtracted from the work integral, presented in Eq. 7:



Fig. 2: The four element viscoelastic Burger's model [17]

The Reiner-Weisenberg theory (Eq. 7), states failure at a critical value of the energy stored due to $\varepsilon_{\rm E}$ and $\varepsilon_{\rm VE}$. However, the Reiner-Weisenberg theory does not include stress relaxation failure as reported in [25]. Stress relaxation failure occurs at constant strain condition due to redistribution of the strain components. To include stress relaxation failure, Bach in [26] proposed a modification of previos model, reported in [25] and defined with Eq. (7). The modified criterion includes only the energy stored due to $\varepsilon_{\rm VE}$, hence the instantaneously recoverable elastic energy at failure, $w_c^E(t_f)$, is excluded. The criterion takes the form, presented in Eq. (8):





$$w_{c}^{VE}(t_{f}) = -w_{c}^{E}(t_{f}) + \int_{0}^{t_{f}} (\dot{w} - \dot{D}) dt$$
(8)

Bach [22] attempted to verify the criterion (Eq. 8) experimentally in low cycle fatigue (LCF) testing. However, Bach found that failure was best expressed by a time under load criterion. Philpot et al. [23] discuss energy based failure models. In a work density model failure is suggested identified with a critical value of the total work, (Eq. 6), due to all strain components (Fig. 2). However, this model has the theoretical obstacle of rupture at almost any magnitude of load under repeated loading due to creep recovery, i.e. regain of ε_{VE} in periods without load. Hence, a modification is suggested which omits the work corresponding to creep recovery, i.e. the energy corresponding to the closed part of the hysteresis loop in a load cycle. The modification takes an empirical form and essentially the modified work density model in [23] is a stress level dependent criterion on the maximum strain.

2.3 Number of cycles criterion (NOC) [17]

Fatigue characterization in number of cycles to failure is the traditional and general approach to fatigue in engineering materials. In the NOC-approach Wöhler curves, or S–N diagrams, describe fatigue resistance by a critical number of load cycles, *N*, leading to failure at a given stress level, *SL*, i.e.:

$$(\log(N)) = A + B \cdot \log(SL)$$

where the coefficients A and B depend on the factor R, which is determined as $R = \sigma_{min}/\sigma_{max}$, where σ_{min} and σ_{max} are the minimum respectively maximum stress level in a cycle. The approach origins from empirical observation that number of cycles to failure in dependency of stress level can be described by a relation of the form (Eq. 9). However, steady state crack growth due to stress variations can be given an interpretation within linear elastic fracture mechanics. Well known Paris law assumes a relation between crack growth rate and the stress intensity factor of the following form:

$$\frac{da}{dN} = C\left(\Delta K\right)^m \tag{10}$$

where *a* is crack length, *N* is number of cycles, ΔK is the variation of the stress intensity factor in the crack tip, and *C* and *m* are material constants. If ΔK is given as function of stress variation, $\Delta \sigma$, and number of cycles, *N*, as a continuous variable an integration of Eq. (10) will give the number of cycles, *N*, corresponding to catastrophic/critical crack length, defined with following Eq. (11):

$$N = C'(\Delta\sigma)^m \tag{11}$$

Relation between number of cycles and stress level or stress level variation, presents in Eq. (11), is equivalent to idea, presents in Eq. (9), and gives a linear relation between number of cycles to failure and stress level in a double logarithmic diagram. Wöhler curves of this form establish the design basis at constant amplitude conditions. For load conditions with different amplitudes the Palmgren-Miner summation (PMS) rule is often assumed. The summation rule, presents in Eq. (12), states that the fatigue life consumed due to *n* cycles at condition *i*,

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(9)

e.g. n_i , is a fraction of the number of cycles to failure at this condition, e.g. N_i . The impact at k different stress levels is safe if following relation is valid:

$$\sum_{i=0}^{k} \frac{n_i}{N_i} \le 1 \tag{12}$$

A wood fatigue life prediction analysis based on Wöhler curves is presented in [27]. An explanation of the fatigue phenomena is not fully established, however the underlying theory for the empirical fits is a Paris law relation, placing all emphasis on *N* according to the fracture mechanical approach presented in [28]. However, the Wöhler approach is not able to distinguish between fatigue loading at different frequencies. That is the crack length grows with the number of cycles irrespective of the duration of each load cycle. This is a problem with respect to wood fatigue where duration of load phenomena may also be present.

Some results/hints of possible solution for fatigue life of wooden structures are presented in [29]. An informative annex gives guidelines for a simplified fatigue verification method. The method considers only number of cycles, *N*. According to the proposed method it should be verified that:

$$\Delta \sigma \le f_{fat,d} \tag{13}$$

where the stress range of the fatigue loading is determined by $\Delta \sigma = \sigma_{max} - \sigma_{min}$. The fatigue strength $f_{fat,d}$ is determined in dependency of the number of imposed load cycles according to:



Fig. 3: Fatigue reduction factor proposed in Eurocode [29]

The fatigue strength reduction factor, k_{fat} , is determined using the diagram in Fig. 3, and values for $k_{fat,\infty}$ corresponding to the fatigue limit is given (empirically) with the value 0.6 for compression perpendicular and parallel to grain, 0.3 for bending, tension and reversed tension/compression and 0.2 for shear.

2.4 Damaged viscoelastic material theory

The Damaged Cracked Viscoelastic Material (DVM) theory to describe the mechanical behaviour of wood subjected to constant loads was first first introduced by Nielsen in [30].

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Furthermore, in a number of papers, like [31, 32] the theory is further developed to cover harmonic load variations. A basic assumption behind the theory is that all mechanical behaviour of wood is governed by fracture mechanics, irrespective of loading mode. This assumption may be too bold, e.g. in compression parallel to grain the damage morphology is such that no free surfaces are produced and hence the concept of strain energy release rate should not be invoked. However, in tension perpendicular to grain, which is the subject of this thesis, fracture mechanics seems most appropriate.

Although several FLM were discussed in Ch. 2, there is no general model exist, yet. However, for more appropriate and credible analysis of fatigue life of wood/wooden structures, experimental procedures should be applied.

3. CONCLUSION

Rather low cases of fatigue life models exist, dealing with wood and/or wood structures. The main goal of the present paper was to analyse and present some of them. In general, FLM can be based on either experiments, numerical methods and/or analytical approach. However, due to a fact, that many different wooden structures exist, one cannot expect a unique methodology of FLM for this purpose. Therefore, in present paper, some of most prompt FLM for wooden structures are discussed. We can conclude, that there is no general FLM of wooden structures, although some of them presented and discussed in Ch. 2, are of great usefulness and will be used in our further research.

Finally, first experimental procedures, which will be obtained for this purpose, is discussed in paper at Matrib 2019 conference, Fajdiga et al.

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UTJECAJ OJAČALA NA SVOJSTVA DENTALNIH AKRILATA

INFLUENCE OF REINFORCEMENT ON PROPERTIES OF DENTAL ACRYLIC RESIN

Dalibor Viderščak¹, Zdravko Schauperl¹, Amir Ćatić², Bruno Babić¹

¹ Fakultet strojarstva i brodogradnje Sveučilišta u zagrebu, Ivana Lučića 5, Zagreb, Hrvatska

² Stomatološki fakultet Sveučilišta u Zagrebu, Ivana Gundulića 5, Zagreb, Hrvatska

Expert paper / Stručni rad

Sažetak

U radu je ispitan utjecaj ojačavala na mehanička svojstva polimera koji se primjenjuje u stomatologiji za izradu protetskih nadomjestaka. U istraživanju je korišten komercijalni polimer za izradu baze mobilnih proteza (poli(metil-metakrilat)-PMMA), a kao ojačavalo su upotrebljena neimpregnirana i impregnirana staklena vlakna. Impregnacija je napravljena s materijalom za poboljšanje adhezije s PMMA. Iz tih materijala izrađena su ispitna tijela za ispitivanje udarnog rada loma, statičkog rasteznog pokusa i savijanja u tri točke prema propisanim normama, te su provedena laboratorijska ispitivanja kako bi se odredila sljedeća svojstva: energija utrošena na lom (E_c), rastezna čvrstoća (R_m), savojna čvrstoća (σ_{ms}). Rezultati su pokazali značajan utjecaj ojačanja na sva ispitivana svojstva odnosno ojačavalo je doprinijelo značajnom povećanju vrijednosti ispitanih svojstava (E_c , R_m , σ_{ms}).

Ključne riječi: mobilne proteze, mehanička svojstva, PMMA, staklena vlakna

Abstract

In this paper is described the influence of reinforcement on the mechanical properties of the polymer used in dentistry to produce prosthetic substitues. In the Study was used a commercial polymer which is used to produce a base of mobile prostheses (PMMA), and as reinforcement were used unimpregned and impregned glass fiber. Material was impregnated to improve adhesion with PMMA. Test specimen were made from these material for the testing: fracture impact, static tensile test and three-point bending to the prescribed norms, and laboratory tests were conducted to determine the following characteristics: spendend energy on fracture (E_c), tensile stenght (R_m) and flexural strength (σ_{ms}). Results showed significance impact of reinforcement to all examined characteristics, reinforcement improves all characteristics (E_{cr}, R_m, σ_{ms}).

Keywords: Mobile Prostheses, Mechanical Properties, PMMA, Glass Fibre

1. UVOD

Kroz cijelu povijest postoji potreba za izradom nadomjestaka koji bi uspješno preuzeli funkciju izgubljenih zubi. Za izradu tih mobilnih i fiksnih proteza upotrebljavali su se i upotrebljavaju se svi dostupni materijali kao što su drvo, kosti, tuđi zubi, slonovača, a u novije vrijeme metali, polimeri, keramika i kompoziti. Od navedenih materijala svaki ima neke prednosti ali i nedostatke koji ograničavaju njihovu upotrebu [1].

1.1. Upotrebljeni materijali i zahtjevana svojstva

Kao i u cijeloj tehnici, revoluciju u izradi mobilnih i fiksnih proteza donio je razvoj i široka primjena polimernih materijala. Trenutno se na tržištu nalazi veliki broj različitih polimera za primjenu u stomatološkoj protetici, ali svima je zajedničko da posjeduju brojna dobra svojstva koja ih čine praktički nezamjenljivima u toj grani stomatologije. Tu su prvenstveno biokompatibilnost s tkivom, kemijska stabilnost i netopivost u usnoj šupljini, mala gustoća, dimenzijska stabilnost, te dobra tehnološka svojstva ali i estetski dojam [2].

Mehanička svojstva polimera su zadovoljavajuća, ali značajno lošija u usporedbi s većinom drugih konstrukcijskih materijala za primjenu u protetici. To posebno dolazi do izražaja kod mobilnih proteza, gdje se baze rade od polimernih akrilata i koje trebaju biti što tanje kako ne bi stvarale probleme prilikom primjene. Međutim zbog relativno niske čvrstoće akrilata i male debljine baze proteze često dolazi do njenog loma što zahtjeva ili reparaturu ili izradu nove proteze [3].

Kako bi se spriječila ta pojava, odnosno kako bi se smanjila mogućnost loma baze proteza razvijena su brojna ojačavala namijenjena za ugradnju u akrilat. Na tržištu se danas nalaze i komercijalno su dostupne metalne mrežice izrađene od različitih materijala kao što su zlato, Co-Cr legure i slično [4]. Obzirom na bolja mehanička svojstva metalnih materijala u odnosu na polimere za očekivati je da primjena takvih ojačavala značajno doprinosi povećanju čvrstoće i trajnosti baze same proteze. Međutim u zadnje vrijeme na tržištu se javljaju i ojačala protetskih akrilata izrađena od staklenih vlakna. To je relativno novi konstrukcijski materijal koji se najčešće upotrebljava kao ojačavalo u proizvodnji polimernih kompozita u brodogradnji, zrakoplovstvu i automobilskoj industriji [5]. Osnova staklenih vlakna je SiO₂, ali dodavanjem različitih minerala tijekom njihove proizvodnje moguće je postići široki raspon svojstava od kojih su najvažnija visoka rastezna čvrstoća i skoro 4 puta niža gustoća od čelika. Tako dobra kombinacija mehaničkih svojstava čini ovaj materijal izvrsnim izborom za

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ojačanje baze mobilnih proteza i nije neobično da su danas na tržištu komercijalna dostupna ojačavala izrađena od staklenih vlakana [6,7].

2. EKSPERIMENTALNI DIO

Analizirajući opterećenja koja se javljaju na bazu proteze tijekom primjene, odlučeno je da se ispitivanja fokusiraju na tri svojstva: rassteznu čvrstoću, savojnu čvrstoći i žilavost. Ispitivanja su provedena prema normama prikazanima u tablici 1.

Norma	Ispitivanje	Svojstvo
HRN EN ISO 527-4:2008	Statički rastezni pokus	Rastezna čvrstoća (<i>R</i> _m)
HRN EN ISO 179-2:2012	Udarni rad loma	Energija utrošena za lom (<i>Ec</i>)
HRN EN ISO 14125:2005	Savijanje u 3 točke	Savojna čvrstoća ($\sigma_{ m ms}$)

Tablica 1. No	orme korištene	prilikom	ispitivanja	ı [8]
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2.1. Ispitivanja

Ispitna tijela za ispitivanje su napravljena prema zahtjevima navedenih normi ali su umjesto normirane debljine od h = 4 mm, ispitna tijela izrađena s debljinom h = 1,2 mm što odgovara realnoj debljini baze zubne proteze. Prilikom izrade upotrebljen je hladno polimerizirajući komercijalno dostupan PMMA.

Izrađene su dvije grupe ispitnih tijela: neojačani i ojačani. Kod ojačanih ispitnih tijela upotrebljeno je komercijalno dostupno ojačavalo za protetske nadomjestke. Izrađeno je po tri ispitna tijela od ojačanog i neojačanog polimera za svako ispitivanje kako je definirano i u normama. Ispitno tijelo za ispitivanje udarnog rada loma je bilo izrađeno bez zareza.

Ispitna tijela pripremljena za ispitivanja prikazana su na slici 1.





Slika 1. Ispitna tijela za laboratorijska ispitivanja: a) statički rastezni pokus i b) savijanje u tri točke i udarni rad loma

Ispitivanja su provedena na *Fakultetu strojarstva i brodogradnje* u *Laboratoriju za polimere i kompozite* prema normama iz tablice 1 na *Charpy-jevom* batu (energija utrošena za lom) i univerzalnoj kidalici *VEB Thüringer Industriewerk* (savojna čvrstoća σ_{ms} i rastezna čvrstoća R_m).

Detalji tijekom ispitivanja prikazani su na slici 2.



a)



b)



Slika 2. Detalji ispitivanja: a) Udarni rad loma, b) Savijanje u tri točke, c) Statički rastezni pokus



2.2. Rezultati ispitivanja

Svako ispitivanje je provedeno na tri ispitna tijela ojačanog i tri ispitna tijela neojačanog polimera. Na temelju dobivenih rezultata izračunata je srednja vrijednost ispitanih svojstava (R_m , σ_{ms} , E_c) i pripadna standardna devijacija (σ) odnosno srednje odstupanje od aritmetičke sredine. Rezultati su prikazani u tablici 3.

Svojstvo	Uzorak	Srednja vrijednost svojstva	Standardna devijacija (σ)
Rastezna čvrstoća (<i>R</i> m)	Neojačan	46,4 MPa	3,92
	Ojačan	91,9 MPa	10,94
Savojna čvrstoća (σ _{ms})	Neojačan	98,5 MPa	23,5
	Ojačan	194,3 MPa	41,5
Energija utrošena za Iom (<i>E</i> _c)	Neojačan	0,019 J	0,004
	Ojačan	0,353 J	0,075

Tablica 3. Rezultati laboratorijskih ispitivanja

Dobiveni rezultati iz tablice 3 prikazani su i grafički na slici 3.





Na slici 3 su grafički prikazane izmjerene vrijednosti mehaničkih svojstava te se može vidjeti da postoji veoma velika razlika u vrijednostima između ispitnih tijela koja su izrađena bez ojačavala i sa ojačavalom. Ojačavala bitno utječu na vrijednosti ispitivanih svojstava, odnosno dolazi do značajnog porasta vrijednosti mehaničkih svojstava.



3. ZAKLJUČAK

Provedena ispitivanja pokazuju da se uporabom komercijalno dostupnih ojačavala za protetske nadomjeste može značajno utjecati na njihova mehanička svojstva. Dobiveni rezultati pokazuju da se primjenom komercijalno dostupnog ojačavala značajno povećavaju sva mehanička svojstva akrilata koja su odgovorna za njegovu otpornost na lom. Posebno je značajno povećanje udarnog rada loma materijala odnosno energije utrošene na lom materijala koja je najzanimljivije svojstvo u dentalnoj praksi jer ukazuje na maksimalnu apsorpciju energije prije loma materijala. Može se zaključiti da ojačavala za protetske nadomjestke značajno poboljšavaju mehanička svojstva te samim time produžuju radni vijek protetskih radova.

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STUDIJA STABILNOSTI I DEGRADACIJSKIH MEHANIZAMA TERMOKROMNIH OFSETNIH OTISAKA

STABILITY STUDIES AND DEGRADATION MECHANISMS OF THERMOCHROMIC OFFSET PRINTS

Marina Vukoje¹, Rahela Kulčar¹, Ivana Krajnović¹, Mirela Rožić¹

¹University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, Zagreb, Croatia

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Sažetak

Termokromne tiskarske boje danas nalaze primjenu u različitim aplikacijama, od ambalaže, komercijalnog tiska, zaštićenih dokumenata, keramike do tekstila. Njihova slaba stabilnost pri izlaganju UV zračenju ograničava njihovu stabilnost u vanjskim uvjetima. Stabilnost polimernih proizvoda prema oksidaciji i hidrolizi jedan je od važnih čimbenika. U ovom istraživanju, jedna termokromna ofset boja otisnuta je na dva različita papira (bezdrvni premazani i bezdrvni nepremazani). Otisci su bili izloženi testu ubrzanog starenja i biorazgradnje kako bi se razumjeli mehanizmi degradacije otisaka u različitim okruženjima. Na svim zorcima promjene su praćene FT-IR spektroskopijom i kolorimetrijskim svojstvima. FTIR spektroskopija pokazala je veće promjene i degradaciju tijekom testa biorazgradnje (uglavnom u slučaju nepremazanog papira), što je značilo veću brzinu hidrolize i oksidacije veziva boje i samog papira u usporedbi s ubrzanim starenjem (UV zračenjem). Spektrofotometrijska mjerenja boje pokazala su veću stabilnost termokromnog otiska na nepremazanom papiru tijekom UV degradacije.

Ključne riječi: termokromna ofset boja, premazani papir, nepremazani papir, ubrzano starenje, biorazgradnja, FTIR, kolorimetrijske karakteristike

Abstract

Thermochromic printing inks are nowdays used in a wide range of different applications, from packaging, commercial printing, protected documents, ceramics to textiles. Their poor stability when exposed to UV radiation limits their stability in external conditions. The stability of polymeric products towards oxidation and hydrolysis is one of the important factors. In this study, one thermochromic offset printing ink was printed on two different papers (wood free coated and wood free uncoated). The prints were exposed to accelerated aging and biodegradation test in order to understand the mechanisms of prints degradation in different environments. All the samples were evaluated for changes by FT-IR spectroscopy and colorimetric properties. FTIR spectroscopy showed higer changes and degradation during biodegradation test (mostly in the case of uncoated paper), implying higer rate of ink binder hydrolysis and oxidation compared to accelerated aeging test. Colorimetric measurements showed higer stability of thermochromic print on uncoated paper during UV degradation.

Keywords: thermochromic offset ink, coated paper, uncoated paper, accelerated aging, biodegradation, FTIR, colorimetric properties

1. INTRODUCTION

Within the frame of the sustainable development, new materials are being designed in order to to preserve natural resources and reduce the pollution. Today, new materials must be designed with high resistance during their use and must have biodegradable properties at the end of their life and it is of great challeng today to design new materials for long duration with low environmental impact [1]. Polymeric materials that are exposed to outdoor conditions (weather, ageing) can undergo transformations (mechanical, light, thermal, and chemical) more or less important. These are called abiotic parameters and they contribute to weakening of the polymeric structure. Sometimes, these abiotic parameters are useful either as a synergistic factor, or to initiate the biodegradation process. It is necessary to study the involvement of the abiotic conditions for a better estimation of the durability of polymeric materials. Photodegradation is the most efficient abiotic degradation occurring on the environment [1]. Biodegradability tests are necessary to estimate the environmental impact [1].

Thermochromic printing inks, as smart, functional and attractive materials, serve as a media for providing consumers with the necessary information about the products based on the colour of the ink they are seeing. Reversible thermochromic organic materials usually consist of at least three components namely a colour former (leuco dye), colour developer and solvent. Reversible colour change occurs via two competing reactions namely that between dye and developer and the other between solvent and developer [2]. A thermochromic printing ink is a mixture of thermochromic pigments (microcapsules) and a binder. The microcapsules are typically 3-5 μ m which is >10-times larger than conventional pigment particles. The decolourisation/colourisation reactions are regarded to be reversible and it is believed that the process can be repeated several thousand times [2]. The temperature at which decolourisation/colourisation occurs is commonly called activation temperature (T_A).

Thermochromic (TC) printing inks have quite short pot life and poor stability of TC colour due to the chemical stability of the ink formulation. In addition, TC inks have low light fastness of the entirely organic TC composite [3]. UV absorbers were proposed as effective stabilisers preventing the photofading of leuco dyes and organic TC pigments [2] or the or selection of the appropriate printing substrate such as paper with natural zeolite clinoptilolite tuff as a filler [4]. In addition, it was shown thaht different physical and chemical properties of paper doesn't affect the value of the thermochromic ink characteristic temperature but it can affect the shape of the thermochromic ink hysteresis curve [5]. For the evaluation of biodegradability potential, studies showed that polymerized ink vehicle (vegetable oil + resin) in thermochromic offset ink is more stable than the polymer resin present in UV curable screen printing thermochromic ink (polyurethane acrylate) [6,7]. Likewise, SEM micrographs indicated a notably higher stability of offset ink binder and accordingly lower deformation of the microcapsules.

Degradation of paper and cellulose has been widely studied by Fourier transform infrared spectroscopy (FTIR) [8–10]. In addition, FTIR spectroscopy has recently been used to study the distribution of offset ink components onto coated paper [11,12], for the evaluation of distribution of cold-set ink components on the surface and the inside of newspaper [13], the analysis of paper-ink interactions in digital prints [14] as well as mechanism of prints biodegradation [6,7,15].





2. EXPERIMENTAL

2.1. Materials

In the preparation of experiment, two different paper substrates (wood-free coated and wood-free uncoated) printed with offset thermochromic ink were exposed to anaerobic soil conditions. Wood-free, high quality coated paper (WFC) Maxi satin 115 g/m² and wood free uncoated (WFUC) Amber graphic 80 g/m². For the printing of paper samples one leuco dye based thermochromic offset printing ink was used (Chromatic Technologies, Inc.), with activation temperature of 45°C. Below its activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow (GY). The printing trials were carried out using Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm³ ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. All the samples were printed in the full tone.

2.2. Soil burial experiments

Laboratory soil burial experiments were conducted at room temperature 25 ± 2 °C by placing the printed paper substrates (size 4 x 5 cm) horizontally in field soils in in 2L volume laboratory glass containers. The paper substrates were buried for 50 and 150 days. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. The commercial available reagent Anaerocult A (Merck) was used in order to allow the development of anaerobic conditions.

2.3. UV radiation of the prints by xenon light

For accelerated aging of the prints, Solarbox 1500e device (CO.FO.ME.GRA) was used. This device enables the simulation of environmental conditions in an open or closed space, and ensures the control of temperature and radiation. All the samples were exposed to filtered xenon light for a period of 6 and 12 hours at a BST temperature of 60 °C. The indoor filter was used for the simulation of conditions of internal exposure (equivalent to sunrays filtered through a window pane). The UV filter was used to change the xenon spectral curve into the ultraviolet range.

2.4. Fourier transform infrared (FTIR) spectroscopy

The ATR spectra of the cardboard samples, unprinted as well as printed with the ink before and after the soil burial, were measured using Shimadzu FTIR IRAffinity-21 spectrometer with the Specac Silver Gate Evolution as a single reflection ATR sampling accessory with a ZnSe flat crystal plate (index of refraction 2.4). The IR spectra were recorded in the spectral range between 4000 and 400 cm-1 at 4 cm-1 resolution and averaged over 15 scans.

2.5. Colorimetric Measurements

Spectral reflectance was measured by using Ocean Optics USB2000+ spectrometer using 30mm wide integrating sphere under (8:di) measuring geometry (diffuse geometry, specular

component included). The printed samples were heated/cooled on the full-cover water block (EK Water Blocks, EKWB d.o.o. Slovenia). Its temperature was varied by thermostatically controlled water block. Reflectance spectra were measured in one heating/cooling cycle by heating them from 15 to 50°C and then cooling them back to 15°C. The measurements were performed in the steps of 1nm for the spectral region from 400 to 750 nm. Ocean Optics SpectraSuite software was used for the calculation of the CIELAB values from measured reflectance. The D50 illuminant and 2° standard observer were applied in these calculations.

3. RESULTS

In the FTIR spectra of wood-free coated paper, a broad band centred at about 1386 cm⁻¹ is detected, followed by the peaks around 1087, 1029, 1002, 914, and 700 cm⁻¹ indicating the presence of kaolin in the coating formulation (Fig. 1A) [16]. The bands observed at 871 and 711 cm⁻¹ (shoulder) can be attributed to the out-of- phase CO₃ bending vibration and the inplane CO₂ bending vibration of calcium carbonate. The FTIR spectra of wood-free uncoated paper shows vibrational bands of calcium carbonate (873, 709 cm⁻¹) and distinctive bands of cellulose (1421, 1160-987, 898 cm⁻¹) (Fig. 1B) [10]. The broad band around 3300 cm⁻¹ in the spectrum of the WFUC paper were assigned to the OH stretching of hydroxyl groups in cellulose, while a weak broad band at 1643 cm⁻¹ confirmed also the presence of water.

The previous study showed that the observed vibrational bands most likely originate from the thermochromic ink binders (vegetable oils,) and were not the result of the vibrational modes of the thermochromic composites within the microcapsules [6]. The IR spectra of the thermochromic ink on the WFC and WFUC paper were very similar, although the difference in intensity indicated a thinner layer of the thermochromic ink on the uncoated (WFUC) paper when compared to the coated paper (WFC).



Fig. 1: FTIR spectra of A) wood-free coated paper (WFC) and printed WFC paper (WFC-GY) and B) woodfree uncoated paper (WFUC) and printed WFUC paper (WFUC-GY)

The bands at 2920 and 2848 cm⁻¹ were assigned to the stretching modes of CH, CH₂, and CH₃ groups in aliphatic chains of fatty acids, while the carbonyl stretching band at 1730 and 1732 cm⁻¹ accompanied by the bands at 1232, 1155 cm⁻¹ points to the ester group in the case of WFC-GY (Fig 1), and 1234 cm- in the case of WFUC-GY paper. A significant contribution of



the cellulose bands, especially in the 1450-1200 and 1160-1000 cm⁻¹ range was obtained in the spectrum of the ink print on the WFUC paper, due to penetration of the ink into the paper structure (Fig 1B). In addition, in the case of WFC paper a significant contribution of coating vibrational bands can be observed, excpecially in the range 1500 – 900 cm⁻¹.

The carbonyl stretching band of the thermochromic ink at at 1730 cm⁻¹ and 1732 cm⁻¹ for the prints on the WFC and WFUC paper, decreases in the intensities during biodegradation test implying ester oxidation (Fig 2A and 2B). The spectral changes were also observed in the spectral range 1450 - 900 cm⁻¹ for the degraded print on WFUC paper. These changes may also point to cellulose degradation in paper, caused by long term degradation of the ink binder. In addition, in the case of both prints the changes were noticed in the spectral range of 2920 and 2848 cm⁻¹ pointing to the oxidation of the aliphatic chains. Previous study showed that the ink penetration into the paper structure is a very important property for the biodegradation [7]. The more the microcapsules are exposed ot bacteria, i.e. covered with a thinner layer of ink binder, the higher rate of biodegradation will be. On non absorbent paper, the microcapsules are covered with a thicker layer of polymer resin making them less exposed to bacteria [7].



Fig. 2: FTIR spectra of A) printed WFC paper (WFC-GY) and B) printed WFUC paper (WFUC-GY) afer 50 and 150days of biodegradation

During UV irradiation, no siginificatn changes were observed in the case of both papers (Fig 3A and 3B). The highest changes were noticed in the spectral range of 2920 and 2848 cm⁻¹ pointing to the oxidation of the aliphatic chains. Somewhat higer changes were observed in the case of print on uncoated paper (WFUC-GY) In the case of print on WFUC paper, the intensitie of vibrational band at 1234 cm⁻¹ corresponding to the ester group, decreases after 12 h of UV irradiation, implying ester oxidation. Due to thickher layer of ink on the surface of WFC paper and smaller changes of FTIR spectra it may be concluded that the ink binder is more stable to oxidation.





Fig. 3: FTIR spectra of A) printed WFC paper (WFC-GY) and B) printed WFUC paper (WFUC-GY) afer 6 and 12 h of UV irradiation

The second method of biodegradability and UV irradiation stability estimation is based on their dynamic colorimetric properties.



Fig. 4: *L* * values for samples before and afer 50 and 150 days of biodegradation during heating from 15°C up to 55°C and cooling down to 15 °C

Figure 4 shows colour hysteresis of prints before and after 50 and 150 days of biodegradation. Colour hysteresis describes temperature dependence of colour for *L** component of colour. Samples appear differently during the two reversible TC reactions (change of colour from green to yellow). This is probably because by heating, the microcapsules change their shape and position, they may become larger or more on surface, so for the opposite effect of the cooling process it is necessary to invest more energy for the same effect, i.e. lower temperature are needed to bring the colour of the sample into its initial state. After 50 days of biodegradation, only a slightly changes occurred. However, after 150 days of biodegradation significant changes were observed – the TC effect is almost destroyed in WFC-GY sample, whereas on the WFUC-GY sample small dynamic colour change is still present.



The simplest way to evaluate dynamic colour properties of TC inks is by measuring the colour in its two states as a function of exposure time. Projections of these values on the (a^*,b^*) plane are shown in Figure 5 and 7. Colour degradation of WFC-GY sample is significant, while lower colour degradation was observed on WFUC-GY sample (Fig 5). Based on the obtained results it can be concluded that the biodegradability of the prints depends mainly on the used paper substrates and the penetration of the binder into the paper.





Fig. 5: Dependence of colour of TC sample during heating and cooling in the (*α**,*b**) plane for WFC-GY and WFUC-GY sample before and afer 50 and 150 days of biodegradation



Fig. 6: *L* * values for samples before and afer 6 and 12 h of UV irradiation during heating from 15°C up to 55°C and cooling down to 15 °C



The results of UV radiation show that light exposure influences both samples in a relatively short time. Exposure for 12 h especially affects the WFC-GY sample. It completely destroys the colour of sample and its dynamic colour change (Fig 6 and 7). A TC sample is considered to work properly if its total colour contrast is large enough to be clearly recognised. Exposure to light diminishes the dynamic of colour of TC samples, and therefore the area between the heating and cooling trajectories in CIELab space becomes smaller.



Fig. 7: Dependence of colour of TC sample during heating and cooling in the (a^*,b^*) plane for WFC-GY and WFUC-GY sample before and afer 6 and 12 hours of exposure to UV radiatio

4. CONCLUSION

When designing the graphic products containing thermochromic offset printing inks, it is important to choose absorbent paper as printing substrate. This study has shown that when the thermochromic ink is printed on absorbent (uncoated) paper, a higher UV stability is achieved. In addition, one day when the product becomes discarded and ends up as waste, the thermochromic prints on absorbent paper will be more rapidly biodegraded with respect to the prints made on non absorbent paper, in this case coated paper. FTIR spectroscopy shows vibrational bands of the thermochromic ink binder and mostly degradation of the thermocromic printing ink binder, but it doesn't show the change and degradation of the microcapsules, whereas colorimetric measurements showed the loss of thermochromic effect, pointing to the degradation of the microcapsule. The result of FTIR spectroscopy show higher rate of the ink binder oxidation on the absorbent (uncoated) paper. By measuring

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dynamic colorimetric properties of thermochromic prints, it can be accurately determined when the thermochromic effect stops in the studied stability tests. In this case, the results show that the greatest colour degradation during UV irradiation is observed for the print obtained on the coated paper, but lower rate of biodegradation was noticed.

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NOVA VRSTA GRAFITNG KOMPOZITA ZA PRIMJENU U IZMJENJIVAČIMA TOPLINE

NEW TYPE OF GRAPHITE COMPOSITE FOR HEAT EXCHANGE APPLICATIONS

Mateja Šnajdar Musa^{1,} Jurica Huljev²

¹ University of Rijeka, Department of Polytehnics, Sveučilišna avenija 4, 51000 Rijeka, Croatia ..., Fakultet... , Adresa, Grad, Država ² Polytechnic of Zagreb, Vrbik, 10000 Zagreb, Croatia

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Abstract

This study of new thermally conductive composite was conducted as a part of EU project: "Development of new generation of Eco Smart products for Oprema d.d. KK.01.2.1.0104." Main objective was to develop a composite material that would replace existing cast aluminium heat exchanger dry blocks used in beer dispenser cooling units with satisfying multiple demands set on material properties such as: thermal conductivity comparable to the aluminium, lower material cost and suitability for company's production line capabilities. Aluminium blocks currently used, faced major issues due to casting process applied which firstly caused incomplete block interior infiltration due to complex pipe arrangement in the block. Secondly casting process at high temperature made usage of copper pipes in the block itself impossible so austenitic corrosion resistant steel pipes were used which would then have to be joined with copper pipes outside of the block by soldering, yielding extra production costs. All that taken in consideration implied that obtaining heat conductive yet cost and production effective composite material without high temperatures needed for production was crucial. Natural graphite was chosen as a basis of composite to be developed. The investigation was conducted in two major iterations, first regarding choice of the optimal mixture of different graphite powder granulations with heat conductivity set as key demanded property in laboratory conditions. In the second phase of study chosen graphite powder mixtures with defined weight ratios of each granulation were used along with wide array of different biding agents. Obtained materials were casted in real dry blocks with identical geometry of piping used so far in aluminium blocks. Detailed investigation of heat transfer properties in real life conditions conducted on all mixtures and compared to the reference Al block. The testing was conducted on Pro Event equipment provided by Oprema d.d. Along with thermal properties consistency changes during drying of the composite in order to check if any cracking occurred which would strongly reduce heat transfer in the block. All the obtained results showed ability of produced graphite-based composite to substitute aluminium.

Key words: graphite, composite, heat exchange, conductivity