SVEUČILIŠTE U ZAGREBU
GRAFIČKI FAKULTET
ZAGREB, Getaldićeva 2

Postupak ocjene doktorskog rada

DOKTORAND/ICA:	Dino Priselac, mag. ing. techn. graph.

NASLOV RADA na hrv. jeziku:	Razvoj novih materijala za izradu tiskovnih formi za visoki tisak
NASLOV RADA na engl. jeziku:	Development of new materials for the production of letterpress printing plates

SAŽETAK:

U ovom doktorskom radu istražena je mogućnost primjene biorazgradivih polimernih mješavina na bazi polilaktida (PLA) i polikaprolaktona (PCL), uz dodatak nanočestica silicijeva dioksida (SiO_2), kao održive alternative konvencionalnim materijalima za izradu tiskovnih formi za visoki tisak. Polazište rada nalazi se u potrebi za ekološki prihvatljivijim materijalima koji bi mogli zamijeniti polioksimetilen (POM), standardni, ali neobnovljivi i nebiorazgradivi materijal koji se trenutačno koristi u industriji. Cilj istraživanja bio je ispitati utjecaj različitih udjela PLA-a i PCL-a te koncentracija nanočestica SiO_2 na kemijska, morfološka, površinska, toplinska, mehanička i funkcionalna svojstva dobivenih mješavina, kao i ocijeniti njihovu prikladnost za izradu reljefnih tiskovnih formi. Eksperimentalni dio obuhvatio je pripravu dvokomponentnih (PLA/PCL) i trokomponentnih (PLA/PCL/SiO_2) mješavina, izrađenih metodom taljenja i prešanja u standardizirane pločice. Provedena su ispitivanja FTIR spektroskopije, SEM i SEM-EDS analize, određivanja slobodne površinske energije, diferencijalne pretražne kalorimetrije (DSC), termogravimetrijske analize (TGA), dinamičko-mehaničke analize (DMA) te mehaničkih ispitivanja rastezanja i tvrdoće. Funkcionalna svojstva ispitana su laserskim graviranjem kako bi se simulirao proces izrade tiskovne forme te procijenila kvaliteta dobivenih reljefnih elemenata. Rezultati su pokazali da dodatak PCL-a povećava elastičnost PLA-a, dok nanočestice SiO_2 poboljšavaju mješljivost dvaju polimera te doprinose povećanju krutosti, žilavosti i toplinske stabilnosti. SEM analiza potvrdila je povoljniju morfologiju pri dodatku nanočestica, osobito u uzorcima s većim udjelom PLA-a, gdje su sferne čestice PCL-a smanjene ili djelomično uklonjene. Površinska energija povećala se dodatkom SiO_2, što ukazuje na povoljnije uvjete adhezije. DSC i TGA analize pokazale su porast stupnja kristalnosti i bolju toplinsku stabilnost kod nanočesticama modificiranih uzoraka, dok su DMA i mehanička ispitivanja potvrdila povećanje modula elastičnosti i tvrdoće. Najbolja svojstva pokazale su mješavine PLA/PCL/SiO_2 80/20/3 i 90/10/3, koje su ostvarile stabilnost tiskovnih elemenata pri laserskom graviranju, minimalna oštećenja slobodnih površina te stabilna mehanička i toplinska svojstva. Dobiveni rezultati potvrđuju da je pravilnim odabirom omjera PLA-a, PCL-a i SiO_2 nanočestica moguće dobiti funkcionalan i održiv materijal pogodan za primjenu u izradi tiskovnih formi za visoki tisak.

Ključne riječi: polilaktid, polikaprolakton, nanočestice silike, biorazgradive polimerne mješavine, tiskovne forme

EXTENDED ABSTRACT:

This doctoral thesis investigates the development and characterization of biodegradable polymer blends based on polylactic acid (PLA) and polycaprolactone (PCL), with the addition of silica nanoparticles (SiO_2), with the aim of evaluating their potential use as alternative materials for relief and hot foil stamping printing plates. The motivation for this research stems from the growing need for environmentally sustainable materials that could replace polyoxymethylene (POM), a conventional but non-biodegradable polymer commonly used for producing printing plates. As PLA and PCL have complementary mechanical and thermal characteristics but are mutually immiscible, the research focuses on understanding how their ratio and the presence of silica nanoparticles influence the final properties relevant for printing plate applications. The blends were prepared by melt mixing and compression molding in predefined mass ratios. PLA was used as the matrix due to its stiffness and thermal resistance, while PCL served as the dispersed phase, contributing toughness and flexibility. Silica nanoparticles were incorporated at 1 wt% and 3 wt% as potential compatibilizers expected to improve the interfacial adhesion between the polymers. The prepared samples were subjected to a comprehensive set of characterization methods to evaluate their chemical structure, morphology, surface behavior, thermal characteristics, mechanical performance, and functional suitability for relief printing and hot foil stamping.

Chemical characterization using FTIR spectroscopy confirmed that blending PLA with PCL and incorporating silica nanoparticles did not result in the formation of new chemical bonds or functional groups. The characteristic spectra of both polymers remained unchanged, indicating that the interactions between components are primarily physical. Minor variations in band intensities observed in samples containing 3 wt% silica can be attributed to changes in crystallinity rather than chemical modifications. These findings are consistent with the assumption that silica acts mainly as a physical compatibilizer and reinforcing filler, without altering the polymer backbone.

Morphological observations obtained from SEM and SEM-EDS analyses revealed pronounced differences among the blends depending on the PLA/PCL ratio and the presence of silica nanoparticles. Binary blends exhibited clear phase separation, with co-continuous structures at higher PCL contents and “sea–island” morphologies in PLA-rich compositions. In blends without silica, inadequate interfacial adhesion and the presence of voids at the polymer–polymer boundary were frequently observed. The introduction of silica nanoparticles, particularly at 3 wt%, significantly improved the morphology, resulting in more uniform structures and reduced size of PCL droplets in PLA-rich blends. These improvements indicate enhanced compatibility between the phases, supporting the intended function of silica nanoparticles.

Surface property analysis included contact angle measurements, determination of surface free energy, and calculation of adhesion parameters for both binary and ternary systems. Contact angle results showed an increase in surface hydrophobicity in blends containing SiO_2 nanoparticles, which was contrary to initial expectations given the use of hydrophilic Aerosil 200 silica. This behavior can be explained by the surface chemistry of SiO_2, which contains hydrophilic silanol groups (Si–OH) and hydrophobic siloxane bridges (Si–O–Si). At elevated temperatures, silanol pairs begin to deactivate and condense into siloxane structures, gradually increasing the hydrophobic character of the silica surface. As a result, blends containing SiO_2 exhibited higher water contact angles. Surface free energy measurements further indicated that the addition of silica nanoparticles reduced the total surface free energy of the blends, with a more pronounced decrease observed at 1 wt% SiO_2. These findings suggest that the surface free energy of PLA/PCL blends can be tuned through controlled nanoparticle incorporation. Adhesion parameter calculations confirmed that the nanoparticles preferentially localize within the PCL phase, which is consistent with SEM–EDS observations. Previous studies support this behavior, noting that hydrophilic nanoparticles such as Aerosil 200 tend to migrate into the dispersed phase, whereas hydrophobic nanoparticles are more likely to accumulate at the polymer–polymer interface.

Thermal analyses further highlighted the influence of composition and nanoparticle content. DSC measurements showed that PLA crystallinity, although inherently low, increased in the presence of both PCL and silica nanoparticles, suggesting a nucleating effect. The effect varied across compositions but was most pronounced in blends containing 3 wt% silica. TGA results revealed two-step degradation behavior characteristic of immiscible polymer systems, corresponding to the degradation of PCL and PLA. However, blends containing silica exhibited higher onset temperatures and improved thermal stability. DMA analysis confirmed the presence of two relaxation processes associated with the glass transitions of PLA and PCL, but also showed an increase in storage modulus in nanoparticle-modified blends, indicating enhanced rigidity.

Mechanical testing supported the observed morphological and thermal trends. PLA-rich blends exhibited higher stiffness and hardness, while PCL contributed to improved elongation at break. The addition of silica nanoparticles further increased the modulus and, in certain compositions, improved toughness. Among all investigated formulations, PLA/PCL/SiO_2 blends with ratios of 80/20/3 and 90/10/3 demonstrated the most balanced set of mechanical properties, including sufficient rigidity, resistance to deformation, and adequate elasticity for practical use.

Functional evaluation through laser engraving tests provided a direct assessment of the blends’ applicability for relief and hot foil stamping printing plates. Binary blends often exhibited surface defects, deformation, or irregular relief geometry due to insufficient thermal stability. In contrast, PLA-rich blends containing 3 wt% silica produced well-defined relief structures with clear height differences between printing and non-printing areas. The surfaces remained stable under thermal loading, and the engraved structures retained their geometry without significant damage. These compositions also performed well in subsequent printing tests, consistently transferring the printing medium and maintaining motif fidelity.

Overall, the results of this research demonstrate that PLA/PCL/SiO_2 blends, particularly those with higher PLA content and 3 wt% silica, represent a promising biodegradable alternative to conventional printing plate materials. By optimizing the polymer ratio and nanoparticle concentration, it is possible to produce materials whose chemical, morphological, surface, thermal, mechanical, and functional properties approach those of POM, while offering the advantages of biodegradability and a more sustainable origin. The findings confirm the initial research hypotheses and provide a foundation for further development of biodegradable polymer systems tailored for advanced applications in the graphic arts industry.

Keywords: polylactic acid, polycaprolactone, silica nanoparticles, biodegradable polymer blends, printing plates

Zagreb, 15.12.2025.