The effect of film thickness and concentration of SIO_2 nanoparticles in PCL coatings on color change of tonal value increase

Josip Bota[1], Zlata Hrnjak-Murgić[2], Maja Brozović[1]

[1] Faculty of Graphic Arts, Zagreb; [2] Faculty of Chemical Engineering and Technology, Zagreb

E-mail: josip.bota@grf.hr

Abstract

This work presents research on the effects of polycaprolactone (PCL) and PCL modified with silica (Si_2) nanoparticles, on the color change of offset printed paperboard. The nanocomposite was prepared with three different concentrations (1%, 2% and 3%) of SiO_2, and applied in four different coating thicknesses (4 µm, 24 µm, 40 µm and 80 µm). The color values of the printed sample were measured before and after the coating application to facilitate the measurement and comparison of the results. The research shows an overall preview of the effects of coating thickness and the influence of SiO_2 modification on color change. Implementing silica particles in PCL improves the optical properties of the coating while adding additional beneficial properties to the paperboard.

Keywords: Polycaprolactone, SiO_2, coating, color change, paperboard, offset print

1. Introduction

Paperboard is a renewable material, widely available, cost-efficient with excellent potential for use in numerous applications, and has a wide range of properties which can be achieved simply by choosing appropriate manufacturing conditions (Teisala et al., 2010; Mäkelä et al., 2011; Stepien et al., 2012). Polymer coatings are used to improve mechanical and chemical properties of paperboard such as: strength, flexibility, gloss, printability, resistance to ware and tare, barrier and optical properties, etc. (Andersson, 2008; Hong and Kim, 2013). Biopolymers are widely investigated with a goal to reduce and replace use of synthetic polymers which are known to have a negative impact on the environment (Khwaldia et al., 2010). To achieve the desired properties, biopolymers are usually modified using nanoparticles (Cava et al., 2006). Embedded in the polymer matrix they can add additional beneficial properties such as: antibiotic properties, hydrophobic properties, provide a barrier to gasses (for example oxygen) or moisture, protect from exposure to UV rays etc. (Mittal, 2011; Rhim et al., 2013). The main goal is to extend the use of paperboard and/or to improve quality without neglecting environmental aspect.

Varnishes used in print are usually styrene-acrylate copolymer based which have a high molecular weight; so the polymer should not readily biodegrade (Nie and Miller, 1997) and has a negative impact on mechanical properties of paper (Soltani et al., 2013). Polycaprolactone (PCL), on the other hand, is a semi-crystalline biodegradable linear aliphatic polyester susceptible to undergo auto-catalyzed bulk hydrolysis and slow degradation (Woodruff and Hutmacher, 2010). PCL has a good water, oil, solvent and chlorine resistance and is commonly used for specific applications in the human body (Wu et al., 2012). This polymer is commonly used as an additive for resins to improve their processing characteristics and their end use properties. It is found that thicker coating in some polymers can improve the mechanical properties of paperboards (Morsy and El-Sherbiny, 2004).

Silica (SiO_2) is used as an additive for rubber and plastics (Hong and Kim, 2013). The nanoparticles fully disperse in plastic raw materials and can significantly improve strength, toughness, permeability, wear resistance and aging resistance of plastics (Saladino et al., 2012; Ribeiro et al., 2014). Silica in a plastic film is used to provide a barrier to gasses (for example oxygen), or moisture, and is commonly used for packaging (Finson and Felts, 1994).

Polymer nanocomposite materials have attracted considerable attention due to their potential in creating new high performance materials for optical, electrical and other application. As the organic and inorganic substances usually have very different diffraction index, when combined in inorganic-organic composite they can be optically transparent due to the nanoscale size of present particles (Salamone, 1996). This advantage is used to obtain optical coatings with high refractive index.

Color change is common in printing industry so colorimetry is used to check and achieve the uniformity of print. Adding overprint varnishes and coatings usually change the color properties of a print. PCL modified with SiO_2 nanoparticles changes the optical and mechanical properties of coating. This work investigates the extend PCL and PCL nanocomposite coatings impact the color change due to difference in SiO_2 concentration and coating thickness.

2. Material and methods

Color test card was developed via spectrophotometric software and offset printed on paperboard. A pseudo solvent PCL dispersion for coating was made (Hong and Kim, 2013). The color values of the printed sample were measured before and after the coating application to facilitate the measurement and comparison of the results. The coatings applied on the printed sample were three different concentrations of silica nanoparticles in PCL biopolymer.

2.1. Materials

Paperboard of 230 g/m², GD2 grade (Umka color®) as a commonly used material in the packaging industry and was cut into 30cm x 35cm sheets samples. The coating has been made from polycaprolactone (PCL) biopolymer, (molecular mass: Mn ~80,000) Aldrich®. As the nanofiller hydrophobic fumed silica (AEROSIL® R 8200), SiO_2 content > 99.8, specific surface area (BET) 220 ± 25 m²/g, was used. The ethyl-acetate solvent ($C_4H_8O_2$) (99.5%), T.T.T. d.o.o.® was used for the coating preparation.

2.2. Print sample preparation (Color test card)

The examined colors were basic colors of subtractive color synthesis and key black (CMYK) with a tonal value increase (TV) scale from 10-100% with a step every 10%. Color test card were prepared via X-rite Color Port® software and exported as a TIFF file. Prepress was sent to be printed with implemented Process Standard Offset printing developed by Fogra® (ISO 12647-2) to ensure good print quality. The color test card was 20cm x 25cm in size.

2.3. Coating preparation

The coating was prepared by dissolving 10g of PCL polymer granulates in 90g of etil-acetate solvent, solution was heated at 40°C, stirred 30 min to get a homogenous 10% solution, using a magnetic stirrer. The coatings on the printed color test card samples were prepared from PCL polymer solution by varying the concentrations of silica nanoparticles. Four different coatings were prepared, without silica (pure PCL) and by adding 1 mass% (PCL 1%SiO_2), 2 mass% (PCL 2%SiO_2), 3 mass% (PCL 3%SiO_2) of silica; dispersing them with a homogenizer for 8 min at 15000 rpm.

2.4. Coating application

The coating was applied using the K202 Control Coater® in controlled condition defined by the ISO 187:1990 standard. The wet coating thickness was defined with the standard coating bars to 4μm, 24μm, 40μm and 80μm. All coatings were applied on the printed side of the paperboard.

2.5. Measurement procedure

The Color test on the printed color test card samples was carried out by spectrophotometric software, the X-Rite i1 Pro2® spectrophotometer. The exact CIE LAB colorimetric values for forty color areas were measured before and after the application of the tested coatings. The results were obtained as an average of ten measurements for each of coating sample.

3. Results and discussion

Spectrophotometer results were measured before and after coating. The results are obtained in the CIE Lab color space and the color change is expressed using ΔE_{00} formula. It has been reviewed by several authors and confirmed that when selecting a conventional color difference formula for predicting color difference involving different magnitudes, ΔE_{00} should be used (Wang et al., 2012).

$$\Delta E^{*}_{00} = [(\Delta L^{*}/k_L S_L)^2 + (\Delta C^{*}/k_C S_C)^2 + (\Delta H^{*}/k_H S_H) + R_T\,(\Delta C^{*}/k_C S_C)\,(\Delta H^{*}/k_H S_H)]^{1/2}$$

$$\Delta a^{*} = a_1^{*} - a_2^{*}$$

$$\Delta b^{*} = b_1^{*} - b_2^{*}$$

$$\Delta C_{ab} = [(a_2 - a_1)^2 + (b_2 - b_1)^2]^{1/2} = C_1^{*} - C_2^{*}$$

$$\Delta H^{*} = (\,\Delta a^{*2} + \Delta b^{*2} - \Delta C^{*}_{ab}{}^{2}\,)^{1/2}$$

$$\Delta L^{*} = L_2^{*} - L_1^{*}$$

R_T - A hue rotation term to deal with the problematic blue region (hue angles in the neighborhood of 275°) Compensation for neutral colors (the primed values in the $L^{*}C^{*}h$ differences)

S_L - compensation for lightness=1

S_C - compensation for chroma =1+ $K_1\, C_1^{*}$

S_H - compensation for hue=1+ $K_2\, C_1^{*}$

K_1 - graphic arts= 0.045

K_2 - graphic arts= 0.015

Coating paperboard with neat PCL (Fig. 1) and PCL silica nanocomposites (Fig. 2-4) induces a color change of the print. An overall view shows that implementation of SiO_2 in the PCL matrix reduces the amount for color change in comparison with neat PCL coating. Nanocomposite coatings show less deviations in-between different concentrations of silica (Fig. 2-4). Color change does not affect all colors with the same amount due to different properties of the inks colors and coatings. Black tones show the highest values for color change, followed by magenta and cyan while yellow tones have the least amount of color change. Figure 1 shows values for tonal values increase from 10% to full tone (100%). An inverted u-type curve is observed in tonal value increase (TV) of cyan, magenta and black so the highest values of color change are in the mid tones. Yellow tones appear more as a monotonic non-linear curve where the highest amount of color change is in the light tones. Similar trend can be observed in all coatings types and thicknesses.

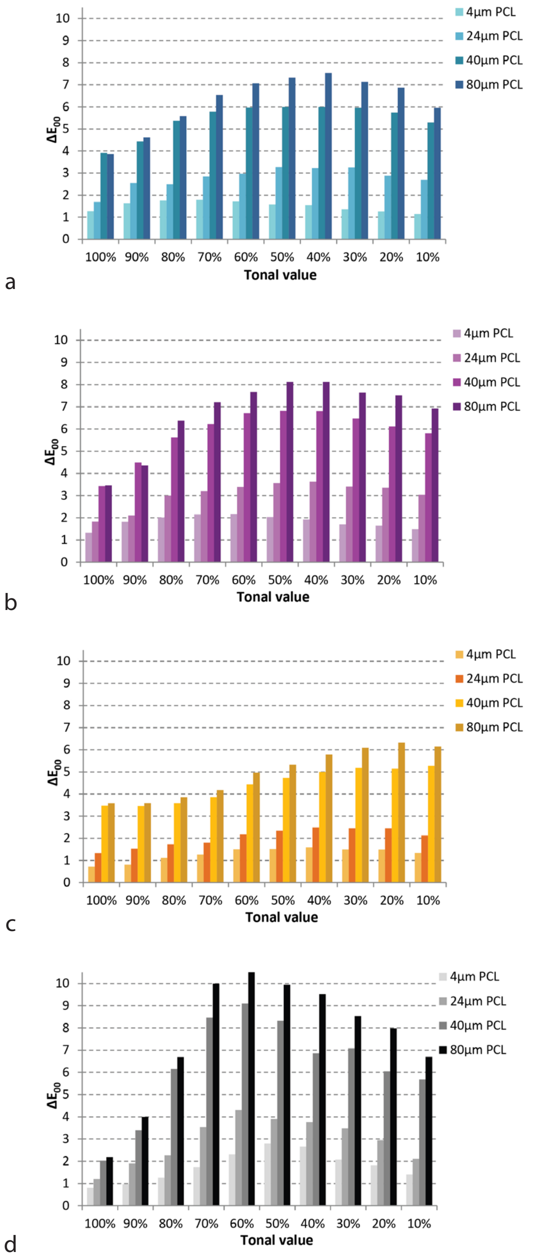

Figure 1. Coating thickness and color difference (ΔE_{00}) of tonal values increase (TV) of neat PCL coated paperboard for: a) cyan; b) magenta; c) yellow; d) black

ΔE values below 3.5 are not visible to an untrained eye, while values up to 6 are acceptable but there is an obvious color change and values beyond 6 are visible and unacceptable (Fernandez-Maloigne, 2013) Most of the CMYK ΔE values for 40 µm and 80 µm neat PCL coating exceed the 3.5 benchmark, and cyan, magenta and black 10% - 70% tonal values exceed the unacceptable ($\Delta E_{00} > 6$) benchmark (Fig. 1). Samples with PCL nanocomposite (Fig. 2-4) show a lower amount of color change. Only magenta (10% - 60%) and black (20% - 70%) tones for 40 µm and 80 µm thickness, exceed the acceptable benchmark ($\Delta E_{00} > 3.5$). Silica is known (Bogoslovov et al., 2008) to enhance the polymer surface interaction so a higher transparence rate caused with better adhesion properties and homogenous dispersion of the nanofiller in the PCL matrix (Avella et al., 2001; Christmann et al., 2013; Zhou and Wu, 2015).

Coating thickness shows also influences to the color change. The peaks in color change in relations to the tonal values are shown in Table 1. From Table 1 it is visible that thickness has some impact on position (TV) and oscillation of the ΔE_{00} values, no matter the concentrations of silica. ΔE_{00} peaks in 4µm coating thickness show a deviation in comparison to other thicknesses. The ΔE_{00} oscillations in that case are much smaller and values for all TV are ±0.4. This can cause the peak values to shift.

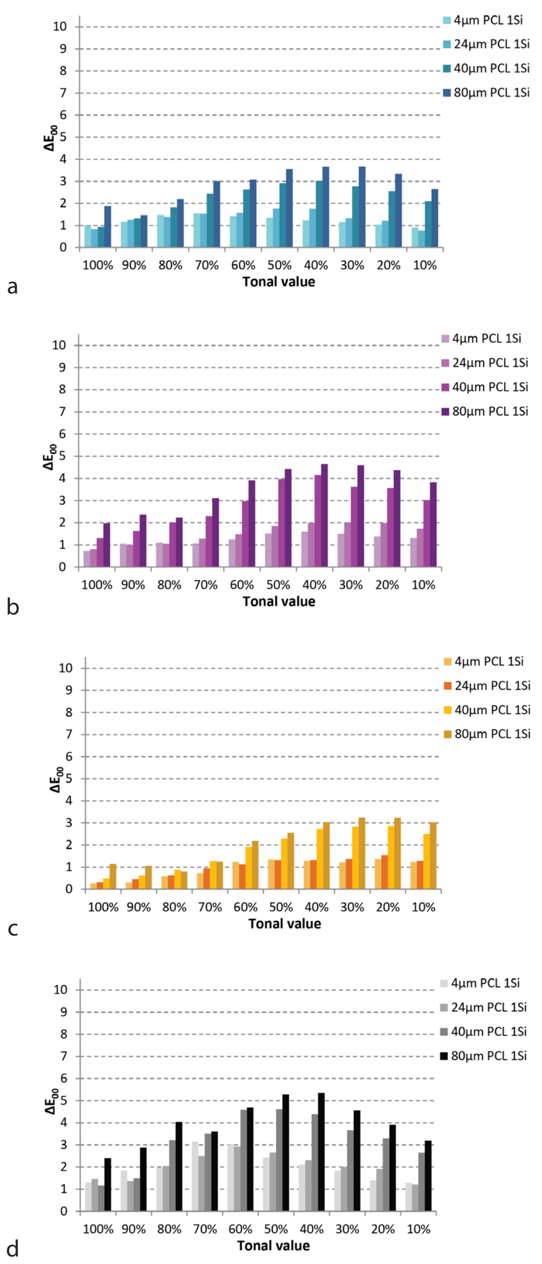

Figure 2. Coating thickness and color difference (ΔE_{00}) of tonal values increase (TV) of PCL 1% SiO_2 nanocomposite coated paperboard for: a) cyan; b) magenta; c) yellow; d) black

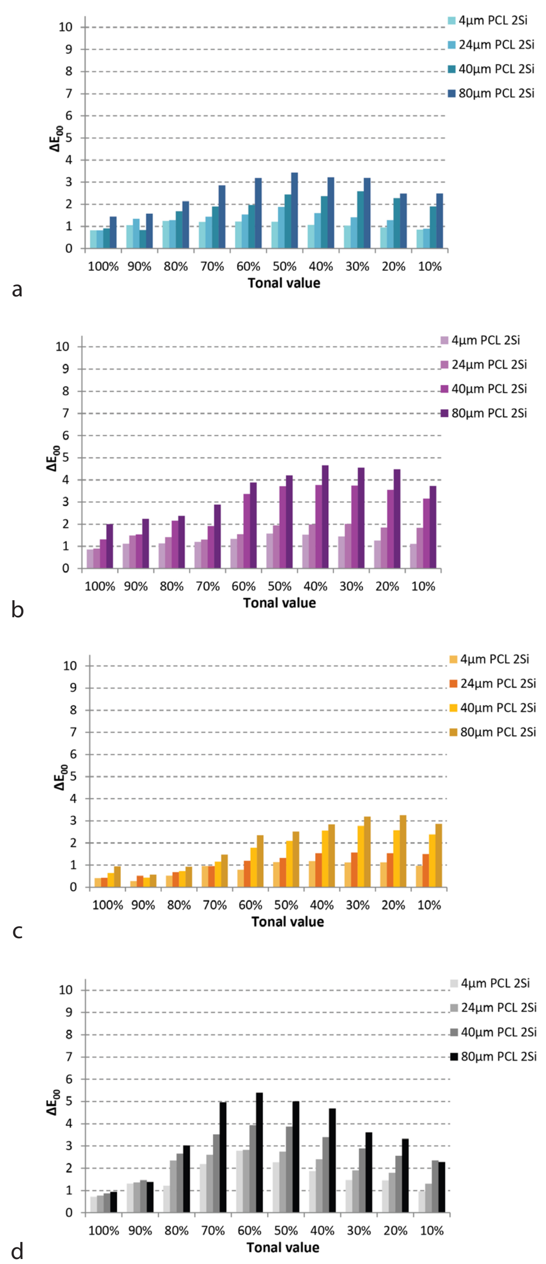

Figure 3. Coating thickness and color difference (ΔE_{00}) of tonal values increase (TV) of PCL 2% SiO_2 nanocomposite coated paperboard for: a) cyan; b) magenta; c) yellow; d) black

Table 1. Peaks of ΔE_{00} values in relation to tonal value increase and color.

	4 μm	24 μm	40 μm	80 μm
Cyan	70%-80%	50%	30%-50%	40%-50%
Magenta	40%-60%	30%-50%	40%-50%	40%-50%
Yellow	20%-40%	20%-30%	10%-30%	20%-30%
Black	50%-70%	60%	50%-60%	40%-60%

Tones in the 40%-60% TV range commonly produce difficulties in print production. In that value span the raster has the greatest dot gain, so any optical quality decrease should have the highest impact in that area. Presumably, this is a result of refraction, absorption and/or scattering of light caused by the coating. Yellow tones repetitively show a ΔE_{00} peak position at 20%-30% TV and overall lower values of color change. Both of these observations can be explained with a hue shift of the PCL coating. The yellow shift caused by the coating has a higher influence on tonal values where there is a bigger area of background and affecting the whiteness of the paperboard. That same shift has less effect on ΔE_{00} and it is annulated for yellow 40%-100% tonal values. Overall inspection of coating thickness shows that a higher intensity of color change can be observed between 24 μm and 40 μm commonly observed at the ΔE_{00} peak positions.

Figure 4.d shows that in the 100% and 90% TV of the 4μm and 80 μm coating thickness color change does not follow the linear increase. This can be explained with a higher concentration of SiO_2 nanoparticles tend to agglomerate thus having a higher impact on the optical properties (Jin et al., 2012; Ribeiro et al., 2014).

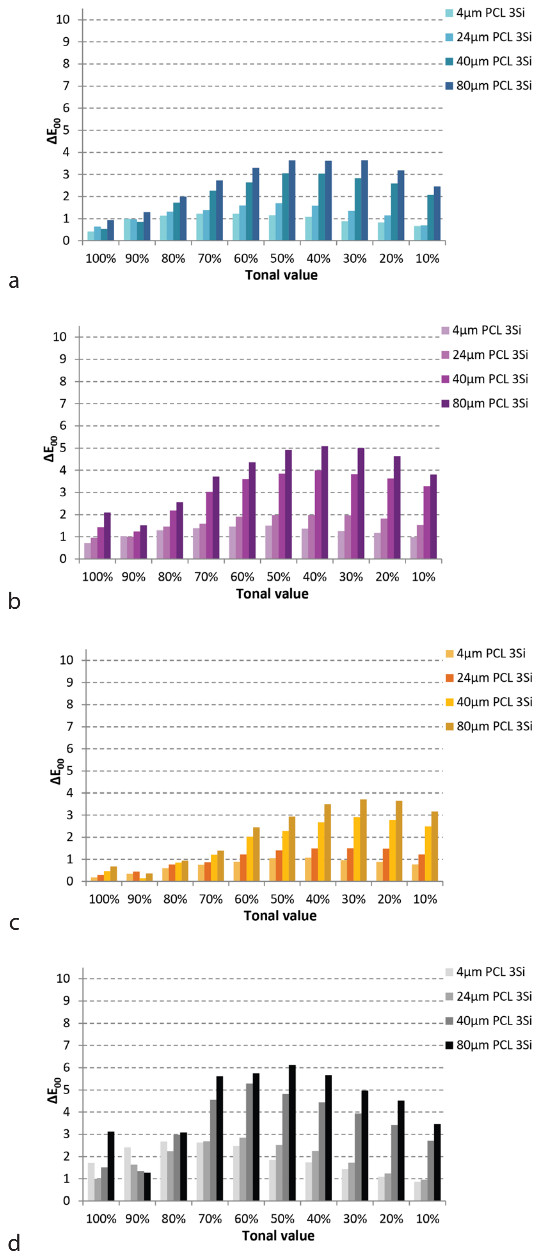

Figure 4. Coating thickness and color difference (ΔE_{00}) of tonal values increase (TV) of PCL 3% SiO_2 nanocomposite coated paperboard for: a) cyan; b) magenta; c) yellow; d) black

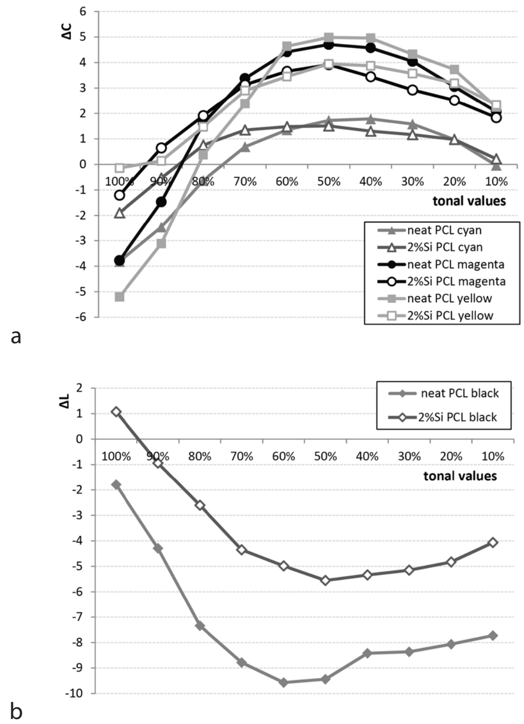

Figure 5. Example of chroma and lightness difference (ΔC, ΔL) of tonal values increase (TV) for 40 μm thick neat PCL and 2% SiO_2 PCL nanocomposite coatings: a) chroma difference; b) lightness difference

Adding varnish type coatings to print have the biggest influence on chroma and lightness (Simonot and Elias, 2004). After drying the PCL and PCL nanocomposite coating have a mat finish, so a decrease in lightness (ΔL) was expected, which is mostly observed in the black tones (Fig. 5.b). The same decrease can be seen in cyan and magentas but the major effect to the color difference is the chroma decrease in the full tones (100% and 90%), and increase in the 80%-10% range of tonal values (Fig. 5.a). The silica modification of the PCL reduces the chroma change of CMY and lightness change of black, so an overall improvement can be observed.

There is also an indication of a improvement of the correlation between thickness of coating and color change of full tones when PCL is modified with a 2% of SiO_2. According to literature (Liu et al. 2015; Zhou and Wu 2015) an optimal concentration of silica particles reduces agglomeration which can change mechanical and optical properties of polymer/nanoparticle composite. Other research coherently shown that 2% of SiO_2 achieve the best results in mechanical, thermal properties (Saladino et al., 2012) as well as optical properties (Christmann et al., 2013; Bota et al., 2014).

4. Conclusions

When applying PCL coating on offset printed paperboard, a color change can be expected. Color change in tonal value increase differs in different (CMYK) colors. The most amount of color change appears in the mid the lighter tonal values. Adding 1%-3% silica nanoparticles improves the optical properties of the PCL coating, while adding additional beneficial properties to the paperboard. The amount of color change is also relative to the coating thickness. The highest recommended thickness value is 24 μm due to the color change increase at thicker coatings. If there is a need for thicker coatings the 40 μm thicknesses are still optically acceptable, but thicker coatings should be avoided.

Modifying PCL with 2% of silica achieves slight better results in optical properties which can indicate better mechanical properties of the coating. This concentration also showed the most repetitive ΔE_{00} peak value when comparing to other silica concentrations.

To achieve color change compensation in a new varnish type coating, it is preferable to establish individual characterization data. This could be done by appropriate data adjustments based on the newly provided data sets. This color profiling could compensate the color change in mid and lighter tonal values.

References

1. Andersson, C., 2008. New ways to enhance the functionality of paperboard by surface treatment - A review. *Packaging Technology and Science*, 21(6), pp.339–373.
2. Avella, M. et al., 2001. Properties/Structure Relationships in Innovative PCL-SiO2 Nanocomposites. *Macromolecular Symposia*, 169(1), pp.201–210.
3. Bogoslovov, R.B. et al., 2008. Effect of silica nanoparticles on the local segmental dynamics in polyvinylacetate. In *AIP Conference Proceedings*. pp.1315–1317.
4. Bota, J., Brozović, M. and Hrnjak-Murgić, Z., 2014. Influence of silica nanoparticles in pcl overprint coating on the color change of offset print. In D. Novaković, ed. *INTERNATIONAL Symposium on Graphic Engineering and Design GRID*. Novi Sad: Faculty of Technical Sciences, Department of Graphic Engineering and Design, pp.225–232.
5. Cava, D. et al., 2006. Comparative Performance and Barrier Properties of Biodegradable Thermoplastics and Nanobiocomposites versus PET for Food Packaging Applications. *Journal of Plastic Film and Sheeting*, 22(4), pp.265–274.
6. Christmann, A., Longuet, C. and Lopez Cuesta, J.-M., 2013. Transparent Polymer Nanocomposites. In *Nanomaterials and Surface Engineering*. Hoboken, NJ USA: John Wiley & Sons, Inc., pp.31–52.
7. Fernandez-Maloigne, C. ed., 2013. *Advanced Color Image Processing and Analysis*, New York, NY: Springer New York.
8. Finson, E. and Felts, J., 1994. Transparent SiO_2 Barrier Coatings: Conversion and Production Status. *37th Annual Technical Conference Proceedings - Society of Vacuum Coaters*, pp.139–143.
9. Hong, S.G. and Kim, G.H., 2013. Mechanically improved electrospun PCL biocomposites reinforced with a collagen coating process: preparation, physical properties, and cellular activity. *Bioprocess and Biosystems Engineering*, 36(2), pp.205–214.
10. Jin, J. et al., 2012. Silica nanoparticle-embedded sol-gel organic/inorganic hybrid nanocomposite for transparent OLED encapsulation. *Organic Electronics: physics, materials, applications*, 13(1), pp.53–57.
11. Khwaldia, K., Arab-Tehrany, E. and Desobry, S., 2010. Biopolymer Coatings on Paper Packaging Materials. *Comprehensive Reviews in Food Science and Food Safety*, 9, pp.82–91.

12. Liu, J. et al., 2015. Effects of fumed and mesoporous silica nanoparticles on the properties of sylgard 184 polydimethylsiloxane. *Micromachines*, 6(7), pp.855–864.
13. Mäkelä, J.M. et al., 2011. Nanoparticle Deposition from Liquid Flame Spray onto Moving Roll-to-Roll Paperboard Material. *Aerosol Science and Technology*, 45(7), pp.827–837.
14. Mittal, V., 2011. Nanocomposites with Biodegradable Polymers: *Bio-nanocomposites: future high-value materials*, Oxford University Press, UK, 2011, pp 1–27.
15. Morsy, F.A. and El-Sherbiny, S., 2004. Mechanical properties of coated paper: Influence of coating properties and pigment Blends. *Journal of Materials Science*, 39(24), pp.7327–7332.
16. Nie, X.S. and Miller, J.D., 1997. The effect of ink types and printing processes on flotation deinking. In *1997 RECYCLING SYMPOSIUM*. pp.131–165.
17. Rhim, J.W., Park, H.M. and Ha, C.S., 2013. Bio-nanocomposites for food packaging applications. *Progress in Polymer Science*, 38(10-11), pp.1629–1652.
18. Ribeiro, T., Baleizão, C. and Farinha, J., 2014. Functional Films from Silica/Polymer Nanoparticles. *Materials*, 7(5), pp.3881–3900.
19. Saladino, M.L. et al., 2012. The effect of silica nanoparticles on the morphology, mechanical properties and thermal degradation kinetics of PMMA. *Polymer Degradation and Stability*, 97(3), pp.452–459.
20. Salamone, J.C., 1996. *Polymeric Materials Encyclopedia, Twelve Volume Set*, Taylor & Francis. Available at: https://books.google.hr/books?id=sod-oOKb10QC [Accessed on Jaunuary 22nd 2016].
21. Simonot, L. and Elias, M., 2004. Color change due to a varnish layer. *Color Research and Application*, 29(3), pp.196–204.
22. Soltani, M. et al., 2013. UV-Curable Coating Process on CMYK-Printed Duplex Paperboard, Part I: Mechanical and Optical Properties. *BioResources*, 9(1).
23. Stepien, M. et al., 2012. Surface chemical characterization of nanoparticle coated paperboard. *Applied Surface Science*, 258(7), pp.3119–3125.
24. Teisala, H. et al., 2010. Development of superhydrophobic coating on paperboard surface using the Liquid Flame Spray. *Surface and Coatings Technology*, 205(2), pp.436–445.
25. Wang, H. et al., 2012. Evaluation of colour-difference formulae for different colour-difference magnitudes. *Color Research & Application*, 37(5), pp.316–325.
26. Woodruff, M.A. and Hutmacher, D.W., 2010. The return of a forgotten polymer—Polycaprolactone in the 21st century. *Progress in Polymer Science*, 35(10), pp.1217–1256.
27. Wu, F. et al., 2012. Fabrication and properties of porous scaffold of zein/PCL biocomposite for bone tissue engineering. *Composites Part B: Engineering*, 43(5), pp.2192–2197.
28. Zhou, S. and Wu, L., 2015. Transparent Organic-Inorganic Nanocomposite Coatings. In *Functional Polymer Coatings*. Hoboken, NJ: John Wiley & Sons, Inc, pp.1–70.