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PCL-TiO_2 NANOCOMPOSITE TO IMPROVE AGEING OF OFFSET PRINTS

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Abstract: *UV radiation or sunlight can affect the printed sample by fading the ink surface and therefore the product losses it's decorative purpose and becomes less desirable to the customer. To create the efficient protective coating, titanium dioxide (TiO_2) will be used as a well-known compound that should lower the effects of UV radiation. TiO_2 should lower the colour fade after UV radiation and this will be determined by densitometric and colorimetric (CIE L*a*b*) measurements. In addition, measurement of print gloss will also be conducted to evaluate visual appearance of the sample. Biopolymer Polycaprolactone (PCL) was the base of the PCL-TiO_2 composite in which TiO_2 nano sized. To determine influence of the amount of TiO_2, three composites were prepared by adding different weight ratio of the TiO_2. The prepared nanocomposites were then applied onto the offset prints on gloss art print paper and on the uncoated paper. The results have shown that TiO_2 coating does affect ink's density, colorimetric properties and print gloss after initial coating. The change in chroma due to the accelerated ageing is most visible on yellow ink, cyan and magenta proved to be the more stable. Accelerated ageing caused change in the L* of black. On all colours, increase of the TiO_2 weight ratio improved resistance of colour to change. Coated gloss paper was more resistant to density change where uncoated had lower change in chroma. It could be concluded that TiO_2 has the ability to protect the prints in the measured time interval but it has to be noted that concentration of the TiO_2 particles also causes colour difference and must be observed when defining composure of the nanocomposite.*

Keywords: Nanocomposite, offset, coating, biopolymer, PCL, TiO_2

1. INTRODUCTION

Cardboard packaging has a vast share in the packaging industry. Regardless of the general opinion, the packaging industry is supposed to grow in the period of 2018 – 2022 up to 3.1% annually, according to Smithers-Pira (Smithers-Pira, 2018.) Industries are faced with the new trends, such as eco-friendly and "green" industry development and packing is no exception (Kovačević et al, 2019). Nevertheless, application of these concepts must not degenerate its basic purpose and requirements which are product protection and aesthetics (Makower, 2006).

Paperboard itself has some weak points and therefore usage of synthetic materials is growing in general use but those materials do have some disadvantages in terms of recyclability and biodegradation (Vukoje, 2018). Paper based materials are more suitable to meet those environmental-friendly requirements but they lack the good barrier properties, resistance to colour fading when exposed to UV radiation, tensile strength and more (Bota et al, 2018). One of solutions is to coat with overprint varnishes (OVPs) in order to improve their downsides. A number of currently used OVPs are not eco-friendly, which leads to the research of substitute materials (Bota, 2017).

Biodegradable materials such as biopolymers are increasingly applied as coating materials (Rastogi et al, 2015). The surface of the paper can be coated with polymer layer that contains nanoparticles which could fulfil the requirements of the OVP (Uglesic, 2015). The surface properties such as wettability, strength, water-vapor permeability as well as the optical properties (colour resistance to colour fading, ink density and print gloss (Afsharpour et al, 2017).

To improve properties of the biodegradable material one usually adds some chemical compounds. Recently, nanomaterials are widely used in composition of these materials (Fithriyah et al, 2015). Mechanical and optical properties are largely dependent on the nanoparticle's degree of dispersion in the biopolymer solution. Depending on the weight ratio of nanoparticles in the mixture, nanocomposites can display different properties as well.

In order to lower degradation of prints due to the UV radiation or general sunlight titanium-dioxide (TiO_2) nanoparticles could be used (Miklečić et al, 2015). Titanium dioxide, also called titania (TiO_2) is a white, opaque, naturally occurring mineral which exists in the number of crystalline forms. Its most important and useable forms are rutile and anatase. The most important function in the powder form is the pigment used for whiteness and opacity. Titanium-dioxide is also used to protect materials from UV radiation (ex.

inks from fading) due to its ability to absorb ultraviolent light. In this paper PCL-TiO_2 composites will be investigated to determine its usability as an OVP.

2. MATERIALS AND METHODS

For the purpose of this research, the most common paper types, coated and uncoated, were chosen – gloss art print paper (coated) with production name UPM Finesse gloss paper and offset paper (uncoated) with production name Tauro offset, both of 300g/m^2. The samples were printed by means of sheetfed offset printing press KBA Rapida 105 with quickset process inks (Novavit Supreme Bio, Flintgroup) in compliance with the Fogra PSO 2016 printing process (Kipphan, 2001).
The nanocomposites were prepared by dissolving PCL (6800 Capa) in ethyl acetate with heated magnetic stirrer in air-tight container for 120 minutes, TiO_2 nanoparticles (Sigma Aldrich rutile) were added with weight ratios of 0.10%, 0.25% and 0.50%, samples designated as Ti010, Ti025, Ti050 while sample where coating process was not conducted is designated as ORG. The nanoparticles were homogenized into PCL solution with ultrasound dispenser Hirrlscher UP100H for 10 minutes at 100% amplitude and 100% power.
The polycaprolactone or PCL is a biodegradable polymer with a low melting point around 60 degrees Celsius. Its common use is as an additive to resins, modelling via 3D printer and with its high level of compatibility with other materials also as a base for primers or coatings (Rastogi et al, 2015).
Nanocomposites were applied to printed samples using K202 Control Coater in controlled conditions defined by the ISO 187:1990 while the wet OVP's thickness was approx. 24 µm, as defined by the coating bar standard bar 3.
After drying and characterization, the varnished samples were placed into Cofomegra Solarbox 300 Xenon Test chamber (Cofomegra, 2020). The samples were subjected to indoor exposure (sunlight through a glass window, ATSM 3424-11 2011). Exposure in the test chamber was divided into intervals of 2 (0 - 10 hours) and 5 hours (10 - 25 hours).
The prepared samples were analysed by measuring colorimetric coordinates in compliance with CIE L*a*b* colour space and relative print density (D). The results were obtained by Techkon SpectroDens spectrophotometer (Techkon Spectrodensitometer, 2020).
The instrument settings for colorimetric measurements were light source D50, standardized observer 2^o, no polarization filter, filter M1 and calibrated on absolute white. Densitometric measurements' settings were density filter status E, light source D50, polarization filter included, calibrated on paper sample. In addition, after measuring CIE L*a*b* coordinates, colour difference ΔE_{ab} was calculated (Mokrzycki et al, 2014). Although there are newer colour difference formulas, the ΔE^*_{ab} is an important feature for graphic reproduction. It is still used to evaluate compliance to the international standard (ISO 12647-2:2013), which provides tolerances in the reproduction of process colours ($\Delta E^*_{ab} < 5$) (Sharma et al, 2005). Measurements were conducted in every of 2 (0 - 10 hours) and 5 hours (10 - 25 hours) of accelerated ageing.
The print gloss was measured with the use of Elcometer 407 statistical gloss meter at the angle of 60 degrees (Elcometer n.d.). The intensity of the light depends on the measured material and the angle of illumination. In the case of non-metals (coating, plastics), the amount of reflected light increases with increased angle of illumination which mimics the human eye (Hunter, 2012). The remaining part of the light penetrates into the material and is absorbed or diffused (Van der Walle et al, 1999).

3. RESULTS

The relative density measurement is more used in process control on the printing machine, but could provide us information about ink layer, indirectly to the strength of a process colour. In this research ink density could give a quick response about ink fading. Fading as phenomena can be explained as a change in ink's density measured via reflectiveness (Wang et al, 2018).

3.1 Ink density on coated paper

In Table 1 one could see that ink density is generally decreasing for all four inks when increasing weight ratio of TiO_2 in coating.

Table 1: Density for all four inks with and without nanocomposite coating before ageing process

	ORG	Ti010	Ti025	Ti050
Cyan	1.43	1.41	1.44	1.39
Magenta	1.51	1.52	1.49	1.46
Yellow	1.33	1.32	1.30	1.24
Black	1.77	1.74	1.70	1.66

Decrease of the density value is largest on the black (achromatic colour) and lowest on the cyan. As the TiO_2 is a white powder increases reflection of the light from the surface and therefore causing decrease of the ink film density on a substrate (Kumar et al, 2012). In Figure 1, one can diagrams for density change (D') of the cyan and magenta ink during accelerated ageing process. Density change (D') is calculated using Equation (1).

$$D' = \frac{D_0}{D_i} \quad (1)$$

where D_0 is the initial density value before ageing process and D_i is the density value after certain period (i) of the accelerated ageing process.
Observing Figures 1 and 2 one could see that density change of cyan and black are almost none while on magenta and yellow one could see increasing trend of density change over accelerated ageing change.

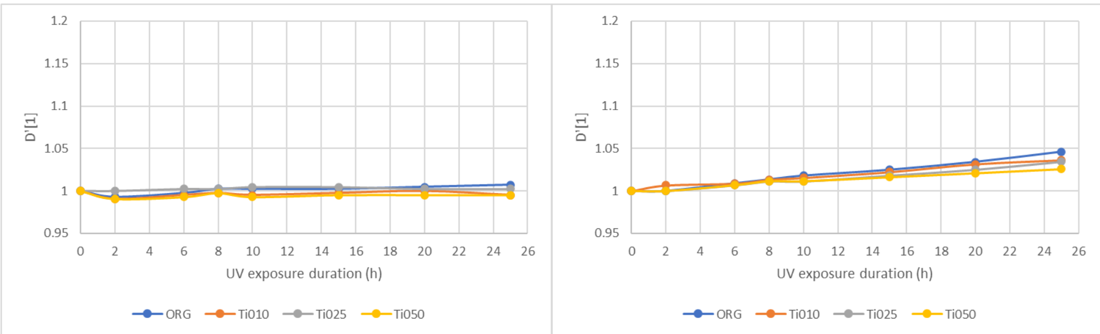


Figure 1: Ink density change (D') – cyan (left) and magenta (right)

Although less visible on black and cyan, on all printed samples is the protection by the nanocomposite noticed. Furthermore, increasing the weight ratio of the TiO2 in a nanocomposite increases protective role to the ink film over time. This behavior is most likely a consequence of the UV light absorbance of the TiO2 (Hongying et al, 2004) which then disables degradation of the colour under the nanocomposite layer.

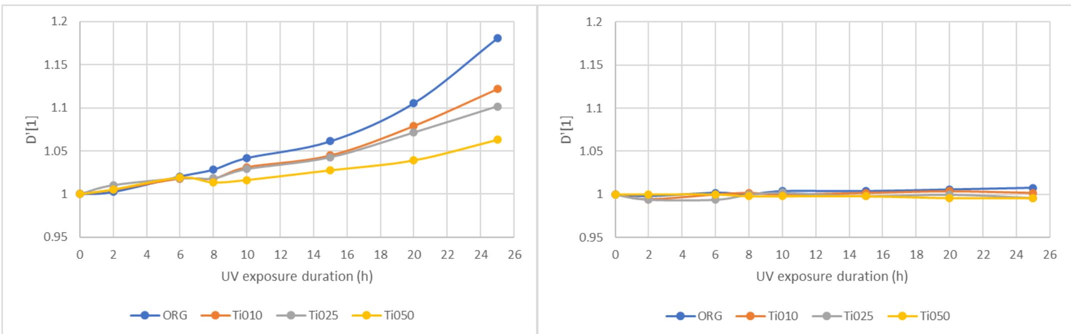


Figure 2: Ink density change (D') – yellow (left) and black (right)

3.2 Ink density on uncoated paper

Ink density on uncoated substrates is lower from the one found on gloss substrates. In Table 2 one could see the ink's density of printed samples before the ageing process. As mentioned before, fading as phenomena can be explained as a change in ink's density measured via reflectiveness which in this case due to surface properties is very low as the substrate itself is matte (Kappel et al, 2008).

Table 2: Density for all four inks and concentration before ageing process

	ORG	Ti010	Ti025	Ti050
Cyan	0.97	0.95	0.98	0.96
Magenta	0.98	0.99	1.00	1.01
Yellow	0.91	0.90	0.91	0.91
Black	1.27	1.24	1.26	1.25

On diagrams in Figure 3, cyan and magenta are presented in entire tested accelerated aging period. The density change of cyan is increasing, i.e. the ink is lowering the density value, but in a very small amount regardless on application of nanocomposite coating. Magenta's results do show that ink is decreasing density faster than observed at cyan.

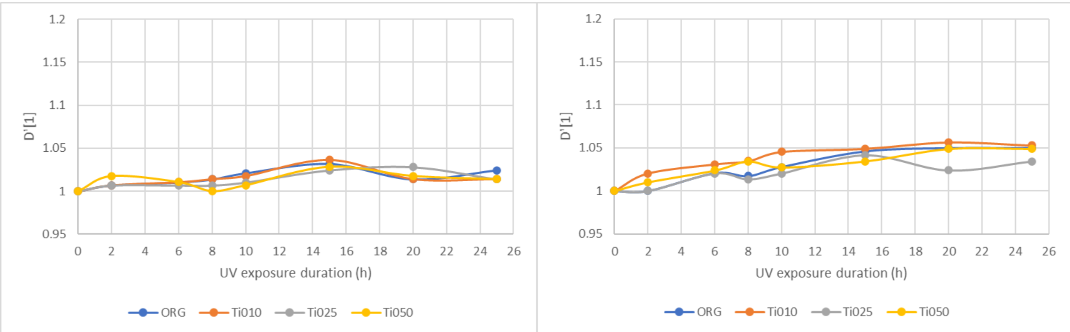


Figure 3: Ink density change (D') – cyan (left) and magenta (right)

The biggest density decay has occurred on original yellow samples on uncoated samples and most stable ink in this accelerated ageing process was black (Figure 4). On both inks it is clearly visible that nanocomposite protects them from change in density. Different to the coated paper, on the uncoated paper protection role of the nanocomposite coating is not so connected with the weight ratio of the TiO_2 in it as smallest density change on yellow is obtained by the nanocomposite with 0.25% TiO_2, on black this is achieved by nanocomposite with 0.10% TiO_2.

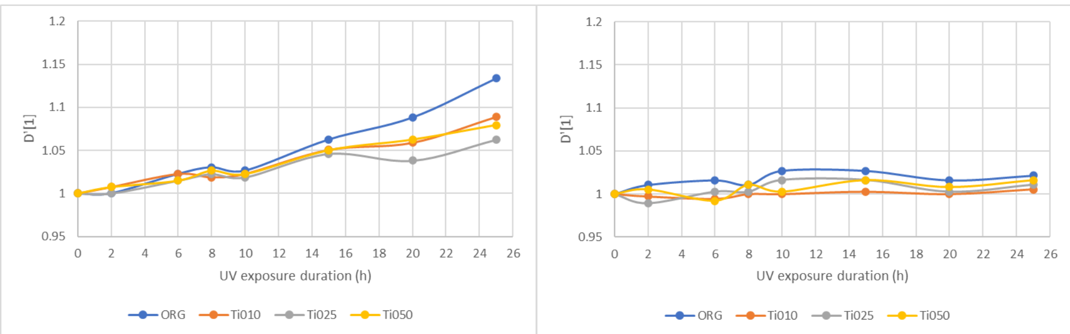


Figure 4: Ink density change (D') – yellow (left) and black (right)

The different effect of prepared nanocomposites on the print's protection during accelerated ageing is most probably due to the absorption of the uncoated paper in comparison to the coated paper. The micro-unevenness on the uncoated paper causes the absorption of the nanocomposite in the coating process leaving nanoparticles trapped in the paper and disabling them to absorb part of the light, i.e. disable fading of the inks.

3.3 Colorimetric analysis on coated paper

In this paragraph colorimetric measurements are presented. The colour difference is presented between average measured colour coordinates in the CIE L*a*b* colour space and colour coordinates provided by Fogra PSO 2016.

In Table 3, are presented colour differences ΔE_{ab} before accelerated ageing. It can be seen that all the printed inks on the original (before coating) are in compliance to the Fogra PSO, but magenta is very close to the allowed tolerance (ΔE_{ab} < 5). The colour difference of the coated samples are out of the allowed difference on magenta samples and black coated with nanocomposite in which weight ratio of TiO_2 is 0.5%. The used magenta ink has a bit high b* coordinate (b* = -1) than defined by the standard (b* = -5) which even increases with coating, On the other hand, increasing the amount of the TiO_2 particles will lead to the increase of lightness of the sample, which influences black most.

Table 3: ΔE_{ab} for all four inks and concentration before ageing process

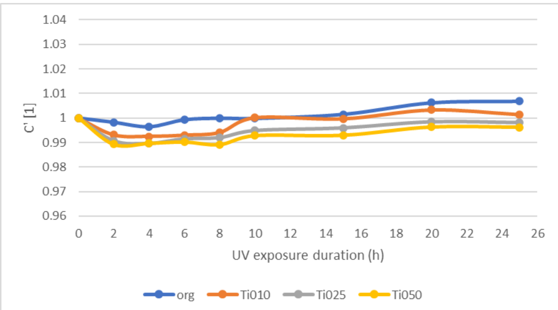
	ORG	Ti010	Ti025	Ti050
Cyan	1.61	1.98	1.38	1.92
Magenta	4.17	6.65	7.24	7.58
Yellow	2.56	3.43	1.77	1.52
Black	3.18	2.05	2.67	5.91

As previously investigated (Havlínová et al, 2002) the ageing process highly influences lightness of black and chromatic components of other process colours. Therefore, to determine influence of the accelerated ageing on the prepared samples, calculation of the chroma (C) and chroma change (C') was performed for the cyan, magenta and yellow and lightness change (L') for black. The chroma change was calculated by the following Formula (2):

$$C' = \frac{C_0}{C_i} \tag{2}$$

Where C_0 is chroma before the accelerated ageing and the C_i is chroma on the sample after certain period (i) of the accelerated ageing process.

In the Figures 5 and 6 are presented values of calculated chroma change on the samples printed on coated paper. If the chroma change (C') is lower than 1 means that the chroma of the sample increased and C' higher than 1 means that chroma of the sample is lower than on the beginning.



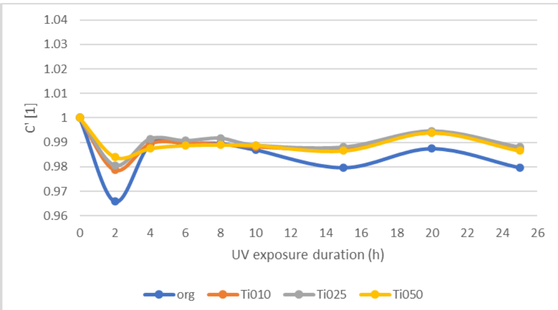


Figure 5: Chroma change - cyan (left) and magenta (right)

As seen in the Figure 5, the chroma of the magenta ink is stable regardless on the accelerated ageing time and nanocomposite used. On the other hand, on cyan and yellow ink it is clearly seen decrease of the chroma with the duration of the accelerated ageing process (Figure 6). In addition, on both inks there is visible trend that chroma change is lower with the increase of the added TiO_2 particles in the nanocomposite proving the positive effect of the added nanoparticles.

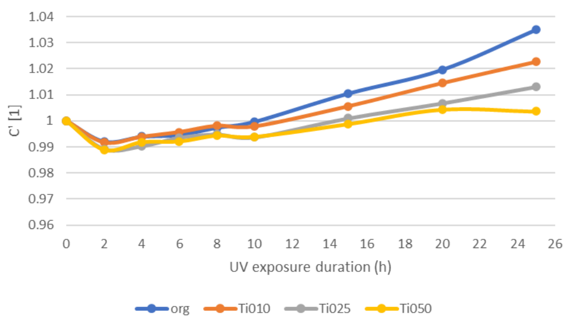


Figure 6: Chroma change - yellow

The TiO_2 as a nanoparticle has various application among others is ability to absorb UV light and therefore could be used as part of the protective coating (Khitab et al, 2018). The changes that occurred with the black ink were tracked via L* coordinate as to black being achromatic and therefore the change in a* and b* coordinate is less relevant. The diagram in Figure 6 shows the lightness change (L'). The lightness change (L') was calculated using the following Formula (3):

$$L' = \frac{L_0}{L_i} \tag{3}$$

where L_0 is chromatic value at the beginning and L_i is lightness of the colours after defined (i) accelerated ageing period.

Same as the chroma change, results in the Figure 7 mean that lightness of the sample is lower than initial if the L' is higher than 1 and lower than initial if L' is higher than 1. As with the chroma of the cyan and yellow it is visible that increasing weight ratio of the TiO_2 in composite provides better protection of the sample colour and reduces change of the lightness of the black ink (L' nearer to 1). Although it was expected that black ink without protection would get lighter, results show opposite, the L* is decreasing during accelerated ageing process. This change is low and is close to the instrument repeatability (SpectroDens, 2020), but the trend could be noticed.

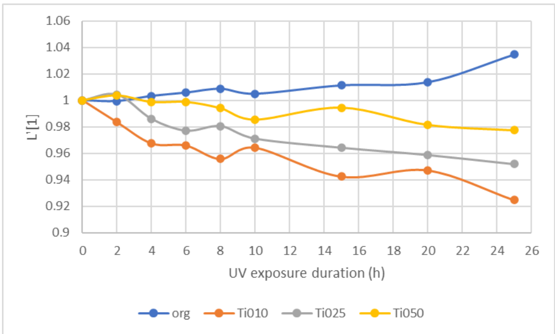


Figure 7: Lightness change - black

3.4 Colorimetric analysis on uncoated paper

The uncoated paper is more resistant to colour change after varnishing as to its counterpart – coated gloss paper. This phenomena is linked to the uncoated paper's surface which is more rough and absorptive, leading to the lower ink densities which are present through reflectiveness (Kappel et al, 2008). The colour difference is presented between average measured colour coordinates in the CIE L*a*b* colour space and colour coordinates provided by Fogra PSO 2016. In Table 4, are presented colour differences ΔE_{ab} before accelerated ageing. It can be seen that all the printed inks on the original (before coating) are in compliance to the Fogra PSO. Moreover, TiO_2 coating did lower the ΔE_{ab} on magenta, yellow and black which is because PCL coating itself lowers lightness of the colours (Golik, 2020).

Table 4: ΔE_{ab} for all four inks and concentration before ageing process

	ORG	Ti010	Ti025	Ti050
Cyan	3.62	3.256	2.33	3.05
Magenta	1.71	1.08	1.45	1.79
Yellow	3.56	3.09	2.18	2.54
Black	3.85	1.64	0.75	1.69

On diagram in the Figure 8, one can see that cyan had very low change in chroma change during the tested and measured period of time. If the chroma change (C') is lower than 1 means that the chroma of the sample increased and C' higher than 1 means that chroma of the sample is lower than on the beginning.

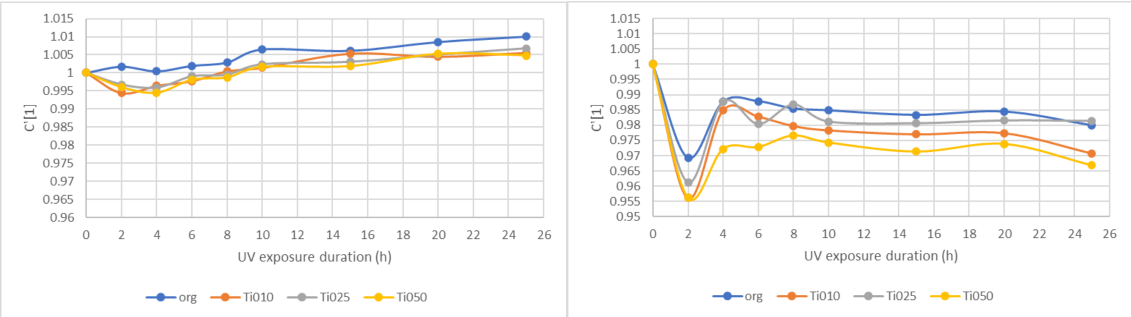


Figure 8: Chroma change - cyan (left) and magenta (right)

Observing Figures 8 and 9 one could see that accelerated ageing influences prints on the uncoated paper differently to the ones on the coated paper. Only cyan is decreasing chroma by exposed to the light in the accelerated ageing process, but the decrease is lower on the samples coated with nanocomposites (Figure 7). Magenta and yellow increase chroma, with yellow being less affected by nanocomposite coating, i.e. chroma change of all yellow samples are similar to the 10 hours of accelerated ageing. The yellow and magenta are inks with predominant chromatic coordinates in CIE L*a*b* colour space with magenta dominant in +a* and yellow with dominant +b*. The opposite coordinate (b* by magenta and a* by yellow) is of low value and with having in mind lower ink film on rough and absorptive uncoated paper, the varnishing and/or ageing process causes changes in coordinates which could compensate the chroma change. In this research, magenta decreases slightly a* coordinate, but increases b*, while by yellow was the opposite (the change itself was small ≈1).

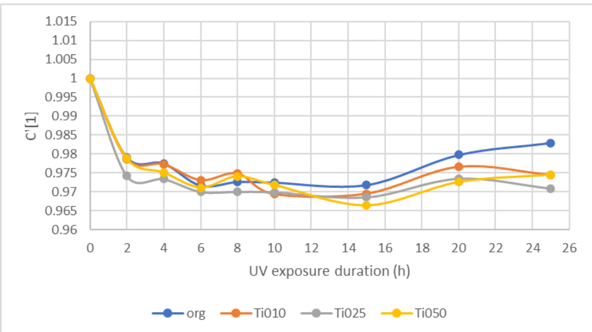


Figure 9: Chroma change - yellow

Same as the chroma change, results in the Figure 10 mean that lightness of the sample is lower than initial if the L' is lower than 1 and higher than initial if L' is higher than 1. Although it was expected that only the black ink without protection would get lighter, results do show the opposite. All measured results are scattered throughout the diagram meaning that TiO_2 was probably soaked into the substrate as there is no trend. Black did undergo the biggest colour change (ΔE_{ab}) in the initial measurement provided in the Table 4 above and this both phenomena can be linked.

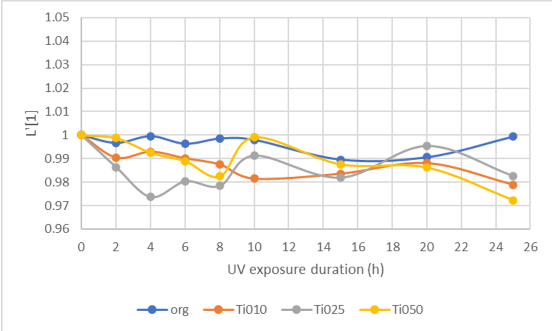


Figure 10: Lightness change - black

3.5 Print gloss analysis on coated paper

Print gloss as an important visual aspect was measured to see the dependence of the gloss to the accelerated ageing process. In Figure 11, cyan and magenta gloss unit diagrams are shown. The print gloss values are expressed in gloss units (GU) measured by means of previously mentioned glossmeter (Landy, 2007). It can be noted that gloss is widely effected by the weight ratio of TiO_2. The uncoated, cyan printed sample has 71.1 GUs at the beginning while the value goes down in an almost linear with increase of weight ratio of TiO_2. The accelerated ageing impacts the overall print gloss of the uncoated sample the most, while samples protected by nanocomposites deteriorate less. Magenta had lower GU value at the beginning, compared to the cyan. The nanocomposite coating also lowered the initial gloss.

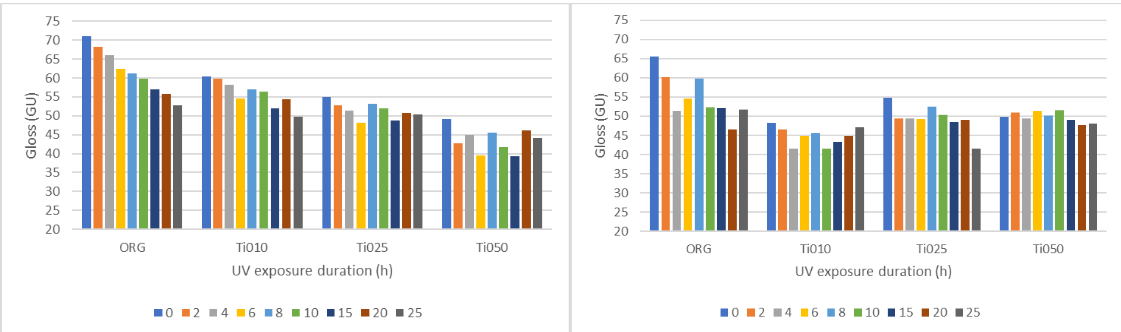


Figure 11: Print gloss – cyan (left) and magenta (right)

On yellow and black one can see similar behaviour with nanocomposites lowering the initial gloss and stabilizing it throughout the entire ageing interval (Figure 12). One can see from this diagrams that the bigger the nanoparticle concentration, lower the gloss units. Black sample's ink gloss was most affected by the 0,5% concentration where initial gloss was lowered in a substantial amount. This could be the consequence of agglomeration of the particles leading to the more uneven surface of the print sample.

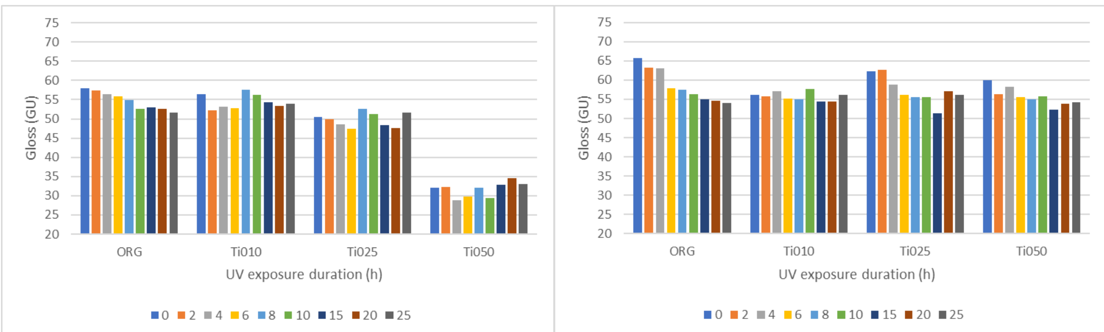


Figure 12: Print gloss – yellow (left) and black (right)

3.6 Print gloss analysis on uncoated paper

Print gloss measured on the uncoated offset paper is very low due to the substrate surface properties. According to the ISO 2813 all measured values under 10 are considered matte while over 3 GU difference on very matte surface is visible to human eye (Landy, 2007). On Figure 13 and 14, diagrams for print gloss on uncoated paper can be seen. The change on all measured inks are barely visible and therefore irrelevant on macro scale. On micro scale one can notice that UV radiation does not influence the ink or the coating in the terms of print gloss on uncoated paper.

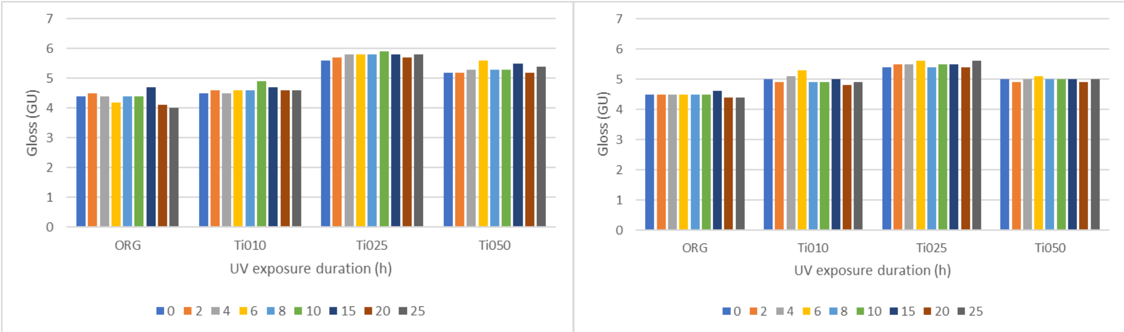


Figure 13 Print gloss – cyan (left) and magenta (right)

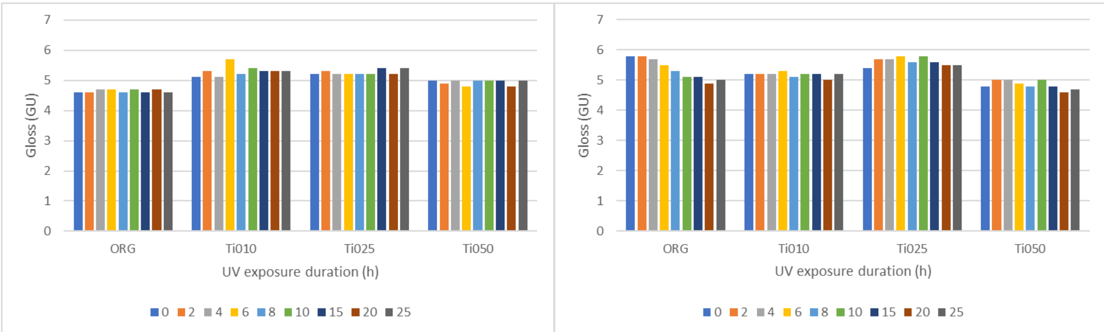


Figure 14: Print gloss – yellow (left) and black (right)

4. CONCLUSION

The change in the appearance of the graphics is a problem to battle when producing items made to be used or stored for a longer period of time. The aim of this paper was to determine if a PCL-TiO2 nanocomposite can be used to protect the offset prints in a simulated ageing.

For the purpose of this research samples of process colours were prepared on coated and uncoated papers. The prepared samples were then coated by PCL-TiO2 nanocomposites in which weight ratio of nanoparticles (TiO2) was changed. The samples were then exposed to the accelerated ageing for 25 hours. Investigation of the changes included optical measurements (print gloss) and determining optical density and color coordinates in CIE L*a*b* colour space.

The results of the research showed that accelerated ageing caused significant change in optical density of the yellow ink on both papers while cyan and black experienced almost no change in optical density. Nanocomposites proved their role in preserving inks, which is more visible on coated papers. The increase in weight ratio of TiO2 improves the protective effect, which can clearly be seen on coated paper, a bit less on uncoated paper. When determining colour difference to the standardized values, it could be seen that nanocomposite do not cause colours to be outside the allowed tolerances on uncoated paper, but shift the magenta outside the tolerance on coated paper. Although the change between samples is not high, magenta was close to the tolerance before coating process. Similar to the optical density, chroma of the yellow ink on coated paper decreased most by the ageing process. Results of the print gloss determination showed that print gloss decreases by coating with nanocomposites, but in the ageing process all concentrations of the TIO2 stabilize the print gloss to the initial value after coating process.

This research proved the protective role of the nanocomposite in the investigated accelerated ageing process, but showed the need for better colour control of the initial printing, especially magenta. The protection role is higher with more nanoparticles in coating so there must be further researched. e.g. SEM to detect possible agglomeration and absorption on the papers and FTIR to detect influence of the TiO_2 changes by UV irradiation, to achieve optimal concentration.

5. ACKNOWLEDGMENTS

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6. REFERENCES

[1] Afsharpour, M., Imani, S.: "Preventive protection of paper works by using nanocomposite coating of zinc oxide", Journal of Cultural Heritage 25,142-148, 2017. doi: 10.1016/j.culher.2016.12.007.
[2] Bota, J., "Optimisation of Coated Paperboard Packaging Properties According to Design", PhD thesis, University of Zagreb, 2017.
[3] Bota, J., Vukoje, M., Brozovic, M., Hrnjak-Murgic, Z.: "Reduced water permeability of biodegradable PCL nanocomposite coated paperboard packaging", Chemical and Biochemical Engineering Quarterly 31, 417-424, 2018. doi: 10.15255/CABEQ.2017.1126.
[4] Cofomegra, Solarbox, A family of two sizes and four models tabletop xenon test chambers,
[5] URL: https://cofomegra.it/download/SOLARBOX%20XENOTEST%20depliant%20eng.pdf (last request: 2020-09-18).
[6] Fithriyah, N., Erdawati, M.: "Influence of nanoparticles coating on paper durability", Journal of Engineering Science and Technology 10(10), 1-11, 2015.
[7] Golik M.: "Functional PCL coating with the addition of ZnO nanoparticles as print protection", Bachelor thesis, University of Zagreb, 2020.
[8] Havlínová, B., Babiaková, D., Brezová, V., Ďurovič, M., Novotná, M., Belányi, F.: "The stability of offset inks on paper upon ageing", Dye Pigment 54, 173-188, 2002. doi: 10.1016/S0143-7208(02)00045-1.
[9] Hunter, R.: "Methods of determining gloss", Journal of Research of the National Institute of Standards and Technology 18, 14-16, 2012.
[10] Hongying, Y., Sukang, Z., Ning, P.: "Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme", Journal of applied polymer science 92, 5-10, 2004. doi: 10.1002/app.20327.
[11] Kappel, C., Hirn, U., Donoser, M., Bauer, W.: "Measurement of Printing Ink Penetration in Uncoated Papers and Its Influence on Print Quality", 94th Annual Meeting of Pulp and Paper Technical Association Canada 94, 539-542, 2008.
[12] Khitab, A., Ahmad, S., Munir, M., Kazmi, S., Arshad, T., Khushnood, R.: "Synthesis and applications of nano titania particles", Reviews on advanced materials science 53, 90-105, 2018. doi: 10.1515/rams-2018-0007.
[13] Kipphan, H.: "Handbook of Print Media", (Heidlberg publication, 2001), pages 206-224.
[14] Kovačević, D., Brozović, M., Itric Ivanda, K.: "Eco-mark on product packaging and its effect on the perception of quality", Journal of Graphic Engineering and Design 10, 17-24, 2019. doi: 10.24867/JGED-2019-2-017.
[15] Kumar, S., Verma, K., Singla, M.: "Size dependent reflective properties of TiO2 nanoparticles and reflectors made thereof", Digest Journal of Nanomaterials and Biostructures 7, 607-619, 2012.
[16] Landy, M.: "Visual perception: A gloss on surface properties". Nature 447, 158-159, 2007. doi: 10.1038/nature05714.
[17] Makower, J.: "How green printing can make a good impression", 2006,
[18] URL: https://grist.org/article/printing/ (last request: 2020-09-20).
[19] Miklečić, J., Blagojević, S., Petrić, M., Jirous-Rajković, V.: "Influence of TiO2 and ZnO nanoparticles on properties of waterborne polyacrylate coating exposed to outdoor conditions", Progress in Organic Coatings 89, 67–74, 2015. doi: doi.org/10.1016/j.porgcoat.2015.07.016.

[20] Mokrzycki, W., Tatol, M.: "Color difference Delta E-A survey Colour difference ΔE-A survey", Machine Vision and Applications 1, 14-18, 2014.
[21] Rastogi, V., Samyn, P.: "Bio-based coatings for paper applications", Coatings 5, 887-930, 2015. doi: 10.3390/coatings5040887.
[22] Sharma, G., Wu, W., Dalal E.: "The CIEDE2000 color-difference formula: Implementation notes, supplementary test data, and mathematical observations", Color Research and Application 30, 21–30, 2005. doi: 10.1002/col.20070.
[23] Smithers-Pira, Inkjet printing builds towards $100 billion market, URL: https://www.smithers.com/resources/2018/oct/inkjet-printing-builds-towards-$100-billion-market (last request: 2020-06-15).
[24] Techkon Spectrodenistometer, URL: https://www.techkon.com/files/downloads/prospekte/SpectroDens%20Manual%20Web.pdf (last request: 2020-09-17).
[25] Uglesic, P.: "Biodegradable Polymers and application", Bachelor thesis, University of Zagreb, 2015.
[26] Vukoje, M.: "The influence of adhesion parameters on material and organic recycling of thermochromic prints", PhD thesis, University of Zagreb, 2018.
[27] Van der Walle, G., Buisman, H., Weusthuis, A., Eggink, G.: "Development of environmentally friendly coatings and paints using medium-chain-length poly(3-hydroxyalkanoates) as the polymer binder", International Journal of Biological Macromolecules 25, 123-128, 1999. doi: 10.1016/S0141-8130(99)00025-2.
[28] Wang, Z, Elsayed, E.: "Degradation Modeling and Prediction of Ink Fading and Diffusion of Printed Images", IEEE Transactions on Reliability 67, 184-195, 2018. doi: 10.1109/TR.2017.2780170.