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PRELIMINARY REPORT ON PROPERTIES AND INTERACTION OF LAYERS IN "BOARD-BIODEGRADABLE PRIMER-PRINTING INK" SCREEN-PRINTED SYSTEM

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Abstract: *Surface phenomena in printing are extremely important for understanding and optimizing the interaction of materials involved in the process of graphic reproduction. In order to protect absorbent printing substrates from moisture penetration, to strengthen mechanical properties or to ensure better adhesion of the printing ink to the substrate, the substrates are often coated with protective coatings (primers) before printing. The adhesion parameters between the coating and the printing ink then become extremely important for assessing the durability, but also the quality of the print. In this research, biodegradable primers (polycaprolactone and polylactic acid) were applied on a board substrate with the primary aim of reducing the permeability to water vapour in combination with printed ink layers. Two types of water-based screen printing inks were printed on the primed substrates: ink prepared using the transparent base, and the ink prepared using the opaque white base. Two meshes with different screen count were used (32 l/cm and 60 l/cm). The research focused on the possibility of reducing the water vapour transmission rate using the inks and biodegradable primers, and at the same time analysing the interaction of biodegradable primers and printing inks by determining the surface and interfacial properties in the "printing substrate-primer-printing ink" system. The results of the research have contributed to the optimization of the screen-print quality on the primed absorbent and porous substrates.*

Key words: biodegradable primer, PCL, PLA, screen printing

1. BACKGROUND AND MOTIVATION FOR THE RESEARCH

The development of biodegradable and functional materials for the application in graphic and other industries have led to the modification of the conventional printed products (Anselmann, 2001; Khwaldia, Arab-Tehrany & Desobry, 2010). In packaging, printed products need to protect their content and be visually appealing to the potential customer (Kovačević, Brozović & Itrić Ivanda, 2019; Sharma et al., 2017). In order to improve the properties, quality and visual appeal of the printed product, primers are often applied on the board substrates before the printing. Primers can be applied during the board production, or just before the printing. Some board coatings are intended for the products that will not be printed (Tang et al., 2012; Rastogi & Samyn, 2015) - however, if a board substrate with the applied primer is undergoing the printing process, printability is of crucial importance. The properties of the board primer and its interaction with that particular printing substrate greatly influence the suitability of the primed board for the graphic reproduction when using specific printing techniques and inks (Hudika et al., 2020).

Board primers can improve the visual properties of the substrate such as gloss, but they often improve the mechanical and other properties, as well. In some cases, they serve as a barrier to the gas and liquid substances. In addition to the protective purposes and improvement of the print quality, primer can also enable the increase of the printing speed, easier and faster further processing of the print, and add value to the printed product (Lavoine et al., 2016).

For more than a hundred years, polymers have been indispensable in almost every segment of the practical application of materials. Polymers obtained from renewable sources and biodegradable polymers are attracting more and more attention, and one of the main reasons is primarily the care for the environment. The application of biodegradable materials became widespread because they can be utilized in different industries, given their wide range of properties.

In order to facilitate the recycling process of the board substrate, biodegradable polymers were used as board primers in this research: poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA). PLA is one of the most widely applied biodegradable polymers today. It is classified as thermoplastic polyester. It can be obtained from lactic acid by the process of fermentation of agricultural crops. Melting temperature of PLA is 170 °C and the glass transition temperature is 60 ° (Priselac et al., 2017). PCL is a biodegradable

polymer of synthetic origin with hydrophobic and a semi-crystalline structural property. It has a melting point of 60 °C, and the glass transition temperature of −60 °C.
There is a wide range of applications for PLA. Some of the most common applications include plastic foils, bottles, and biodegradable medical devices (e.g., screws, needles, rods, and plates that are expected to degrade within 6-12 months). PLA shrinks under heat and is therefore suitable for use as a wrapping material. In addition, the ease with which PLA melts allows for some interesting applications in 3D printing. On the other hand, its low glass transition temperature makes many types of PLA (for example, plastic cups) unsuitable for holding hot liquid (Ilyas et al., 2022).
PCL is often used in the production of food packaging and due to its excellent biocompatibility has been researched as a building material in tissue engineering (tissue regeneration and stem cell transplantation). In order to improve its mechanical and thermal properties, it can be mixed with other polymers, such as cellulose acetate, butyrate and polylactic acid. Pure PCL requires two to four years to completely disintegrate, depending on the molecular weight of the polymer (Woodruff & Hutmacher, 2010; Priselac et al., 2017).
Previous research on PCL and PLA as primers on paper substrates proved them as suitable solution for the improvement of print properties in offset printing technique (Hudika *et al.*, 2020). Furthermore, PCL/PLA composites have been successfully applied as the materials for relief printing plate production (Poljaček et al., 2021; Priselac et al., 2022).
PLA and PCL were used in this research as primers on the board substrate, with the motivation of having beneficial effect on reducing the permeability to water vapour, and possibly improving the characteristics of the print such as the edge of the printed motive and adhesion parameters between layers on the print.
The research hypotheses were as follows:

1. The adhesion parameters between biodegradable primers and prepared printing inks will differ depending on the type of materials, but will indicate the optimal acceptance of printing inks on primed printing substrates.
2. Biodegradable primers and printed ink layers will reduce the permeability of the board printing substrate to water vapour.
3. Biodegradable primers will not diminish the definition of the edges of printed elements.

2. RESEARCH METHODOLOGY AND FINDINGS

2.1 Methodology

In this research, the interaction of screen printing inks based on opaque and transparent base, and biodegradable primers applied to the board printing substrates, was analysed. Used printing inks were water-based. Uncoated offset board Sappi Tauro was used as a printing substrate. Uncoated board was chosen specifically because of the application of the PCL and PLA primers prior to the printing process. Polymer/solvent solutions were prepared by stirring the mixtures using magnetic stirrer in air-tight container for 120 minutes to obtain the homogeneous solution. The primers were applied using K202 Control Coater in controlled conditions defined by the ISO 187:1990 standard and using rod number 4. Printing process was performed using a screen-printing machine by Bochonow (Drucktisch 2000 50/70). Printed samples were air-dried for 48 h at a temperature of 25 ± 2 °C after the printing process.
Basic properties of the materials used in this research are given in Table 1.

Table 1: Properties of the printing substrate, primers and inks

Printing substrate	Primers	Printing inks
● Sappi Tauro ● grammage: 300 g/m^2 ● uncoated offset board	● PLA by InegoTM, 3251D (10% weight, dissolved in ethyl-acetate) ● PCL 6800 Capa (10% weight, dissolved in chloroform)	● water-based ● TBI: 5 g of black process K print pigment + 95 g Midrol Transparente transparent base ● WBI: 5 g of black process K print pigment + 95 g Midrol Bianco white opaque base

In order to analyse the interaction of biodegradable primers and screen printing ink, after the selection of the screens with optimal mesh counts (32 l/cm and 60 l/cm) applicable for the full-tone prints on the given printing substrate, coating the substrate with biodegradable coatings and printing on the coated substrate using two types of screen printing inks was performed. After that, the following methods of measurement and analysis were performed:

- measurement of the roughness of printing substrate, primed printing substrate and the prints;
- calculation of water vapour transmission rates;
- measurements of the contact angles of the referent liquids on all samples in order to calculate the surface free energy (SFE) components of the printing substrate, primed printing substrates and the prints;
- from the SFE values, the adhesion parameters in the system "printing substrate-biodegradable primer-printing ink" were calculated;
- 2D microscopy of the prints.

Surface roughness of the substrate, primed substrates and prints was measured to define the influence of the primers and mesh count on the surface topography of the prints. The profiling method was defined by ISO 11562, DIN 4777, and DIN 4762 standards. Ra and Rz parameters were displayed for all measured samples. The device MarSurf PS 10 with the stylus method was used for the roughness measurements. The diameter of a stylus was 2 µm and measuring force was 0.00075 N. Measurement was performed ten times on each sample.

Thickness of the printed ink layers was measured using SaluTron D4-Fe device. SaluTron D4-Fe works on the principle of magnetic induction and can measure the thickness of layers on non-magnetic surfaces. The results of the printed ink layers' thickness obtained using different inks and printed on different primers were used as an indication of the decrease of the substrate's absorptiveness after the application of the primers.

Water vapour transmission rate was calculated using the cup method. Distilled water (50 ml) was poured into the container. The opening at the lid had a diameter of 35 mm. The samples fixed onto containers were placed in a desiccator in which (50 ± 5)% of relative humidity was set. The surrounding temperature was (23 ± 1) ∘C. The container with the lid and the sample was weighed before putting it into the desiccator. The weighing of the samples was performed after 24 and 48 h. The measured weights were included in Equation (1) to obtain the water vapour transmission rate (WVTR).

$$WVTR = \frac{\Delta m}{\Delta t * A}, \quad (1)$$

where Δm is the difference in sample mass (in grams), Δt is the time period (in days) and A is the area of lid opening (in m^2). The calculated coefficient WVTR presents the weight of water vapour that passed through an area of 1 m^2 in one day (unit of measurement is $g/day \cdot m^2$) (Cigula, Hudika & Tomašegović, 2021). Obtained values for all samples were presented as relative percentages, where the percentage of 100% was allocated to the WVTR of the board.

Surface free energy (SFE) of unprimed and primed board, as well as of the prints, was calculated using the OWRK method. Water, glycerol and diiodomethane were used for calculation of SFE. The conductivity of water was γ = 2,0 μScm^{-1}, the dispersive component of the water's surface tension γ_l^D = 21.80 mJm^{-2}, the polar component of the surface tension γ_l^P = 51.00 mJm^{-2} and the total surface tension of the water was γ_l = 72.80 mJm^{-2}. Glycerol has equal amount of polar and dispersive surface tension components (γ_l^P = 34.0 mJm^{-2}, γ_l^D = 30.0 mJm^{-2}) and total surface tension γ_l = 64.0 mJm^{-2} and diiodomethane is a dispersive liquid with total surface tension, $\gamma_l = \gamma_l^D$ = 50.8 mJm^{-2} ('Future Fibres: Coir', n.d.; Tomašegović *et al.*, 2021). Sessile drop method was used for the contact angle measurement, and the volume of the drops was 1 µl. All measurements of the contact angle on the samples were performed at the same moment after the droplet touched the sample surface (with a delay of 10 frames) and the average value of ten measurements was calculated. The measurements were performed using goniometer Data Physics OCA 30. Adhesion parameters (thermodynamic work of adhesion, interfacial tension and wetting coefficient) were calculated from the obtained total, dispersive and polar components of SFE (Priselac *et al.*, 2022).

Microscopy of the edges of printed elements was used to visually assess the influence of the primers on the line edge of the printed motives. Microscope Olympus BX 51 was used, and magnification was set to 50x.

2.2 Overview of the results

Tables 2 and 3 present the results of the Ra and Rz parameters, and the thickness of the printed ink layers on unprimed and primed substrates in micrometers, respectively.

PLA and PCL layers on the board without additional printed ink layer do not have a significant effect on the roughness of the substrate since they are partially absorbed into the board (Table 2). The lowest values of Ra and Rz were measured on a WBI print obtained using the screen of 60 l/cm on unprimed substrate, while the highest values of Ra and Rz were measured on unprimed substrate with TBI print, obtained using a screen of 32 l/cm.

Table 2: Ra and Rz roughness parameters of the surfaces

Board	Ra = 2.34 ± 0.18, Rz = 14.56 ± 0.99			
PLA on board	Ra = 2.24 ± 0.12, Rz = 14.62 ± 0.84			
PCL on board	Ra = 2.50 ± 0.09, Rz = 14.98 ± 0.65			
	32 l/cm		60 l/cm	
	Ra (µm)	Rz (µm)	Ra (µm)	Rz (µm)
TBI	3.02 ± 0.21	16.85 ± 1.65	2.80 ± 0.34	15.29 ± 1.70
TBI on PLA	2.55 ± 0.19	13.98 ± 1.12	2.17 ± 0.15	12.98 ± 0.85
TBI on PCL	2.34 ± 0.22	13.44 ± 1.36	2.10 ±0 0.17	12.35 ± 1.48
WBI	1.94 ± 0.18	9.67 ± 0.98	1.50 ± 0.19	8.55 ± 0.82
WBI on PLA	1.67 ± 0.16	10.02 ± 1.25	1.56 ± 0.15	8.90 ± 0.58
WBI on PCL	1.71 ± 0.24	10.15 ± 1.21	1.62 ± 0.23	8.66 ± 1.55

It is observable that both PLA and PCL primers cause the increase of the printed ink layer thickness compared to the prints on the unprimed board.

Table 3: Thickness of the ink layers on unprimed and primed substrates (µm)

	TBI	TBI on PLA	TBI on PCL	WBI	WBI on PLA	WBI on PCL
32 l/cm mesh	24.75 ± 3.20	37.00 ± 2.94	32.10 ± 2.10	30.60 ± 2.30	37.25 ± 2.50	35.80 ± 2.17
60 l/cm mesh	13.20 ± 1.71	15.60 ± 2.04	14.00 ± 3.74	15.40 ± 3.21	22.80 ± 3.11	23.40 ± 2.88

Table 4 shows the relative water vapour transmission rates in relation to the rates of the board itself, for which the value of WVTR was set to 100%. It can be seen that TBI as a layer on the substrate has the most expressed property of reducing the WVTR compared to other layers. Therefore, TBI obviously has the most pronounced water vapour barrier properties. On the other hand, PCL, WBI, and WBI on PLA have displayed the highest WVTR percentages and thus contribute the least to the desired effect of reducing WVTR.

Table 4: Water vapour transmission rates (WVTR) of the primed or/and printed substrates, expressed in (%)

	PLA	PCL	TBI	TBI on PLA	TBI on PCL	WBI	WBI on PLA	WBI on PCL
32 l/cm mesh	81.4	71.1	43.17	42.03	39.77	60.44	72.98	50.98
60 l/cm mesh			36.9	57.80	56.47	77.00	62.36	55.32

Surface free energy results were used to calculate the adhesion parameters between the unprimed/primed board and the printed ink layers.

From the obtained results of the calculated adhesion parameters, it was possible to conclude that the adhesion between PLA and WBI, compared to other combination of the interfaces, had the most optimal

interfacial tension (0.04 mN/m), very good thermodynamic work of adhesion (60.22 mN/m) and wetting with the coefficient closest to zero (-0.27 mN/m) regardless of the negative coefficient. Interfacial tension was highest between PCL and TBI (4.88 mN/m). As far as the thermodynamic work of adhesion is concerned, it was highest between PCL and WBI (72.94 mN/m). It was concluded that the adhesion parameters between biodegradable primers and prepared printing inks differ significantly depending on the types of used materials.
Furthermore, after the analysis of two-dimensional microscopic images, it was concluded that the primers did not affect the appearance of the line edge printed using TBI. When WBI and 32 l/cm screen were used, and the ink was printed on the PLA-primed board, the disappearance of the gradient present on the edge of the line printed with the same ink and screen on the unprimed board, was observed.

3. CONCLUSION

After the performed research and obtained results, hypotheses of the research were partially of completely confirmed:

1. The adhesion parameters between biodegradable primers and prepared printing inks will differ depending on the type of materials, but will indicate the optimal acceptance of printing inks on primed printing substrates.
   The first hypothesis has been partially confirmed. Research has shown that the adhesion parameters are most optimal between PLA and WBI, but not when using PLA in combination with TBI. On the other hand, due to the extremely negative wetting coefficient, PCL is not recommended as a board coating for either WBI or TBI but should be tested for the application when printing with other types of inks (solvent-based or UV-curable).
2. Biodegradable primers and printed ink layers will reduce the permeability of the board printing substrate to water vapour.
   The second hypothesis was confirmed. Specifically, it was established that PLA, as a primer on a board substrate, has the least effect on the reduction of water vapour permeability. The mentioned permeability of board with a PLA layer was about 80%. The similar was true for PCL primer, with a value of about 70% WVTR. Significant reduction in WVTR occurred when the biodegradable primers were combined with TBI, because it apparently contained the most favourable water vapour barrier properties.
3. Biodegradable primers will not diminish the definition of the edges of printed elements.
   This hypothesis was confirmed – the biodegradable primers did not decrease the quality of the printed line edge but have caused the decrease in the appearance of the gradient on the line edge present on the unprimed substrate due to the ink absorption into the board.

4. REFERENCES

Anselmann, R. (2001) Nanoparticles and nanolayers in commercial applications. *Journal of Nanoparticle Research*. 3 (4), 329–336. Available from: doi: 10.1023/A:1017529712314.

Cigula, T., Hudika, T. & Tomašegović, T. (2021) Lightfastness, surface and interfacial properties of colour-printed paper substrates coated with PCL/ZnO and PCL/TiO2 nanocomposites. *Surfaces and Interfaces*. 27, 101522. Available from: doi: 10.1016/J.SURFIN.2021.101522.

Food and Agriculture Organization of the United Nations (n.d.) *Future Fibres: Coir*. Available from: https://www.fao.org/economic/futurefibres/fibres/coir/en/ [Accessed 27th June 2022]

Hudika, T., Tomašegović, T., Cigula, T. & Prša, M. (2020) Polycaprolactone primers with zinc oxide and silicon dioxide nanoparticles for paper substrates: Influence on the properties of cyan and magenta offset prints. *Coloration Technology*. 136 (5), 435–449. Available from: doi:10.1111/cote.12487 [Accessed: 19th December 2020].

Ilyas, R.A., Zuhri, M.Y.M., Aisyah, H.A., Asyraf, M.R.M., Hassan, S.A., Zainudin, E.S., Sapuan, S.M., Sharma, S., Bangar, S.P., Jumaidin, R., Nawab, Y., Faudzi, A.A.M., Abral, H., Aseofi, M., Syafri, E. & Sari, N.H. (2022) Natural Fiber-Reinforced Polylactic Acid, Polylactic Acid Blends and Their Composites for Advanced Applications. *Polymers.* 14 (1), 202. Available from: doi: 10.3390/POLYM14010202.

Khwaldia, K., Arab-Tehrany, E. & Desobry, S. (2010) Biopolymer Coatings on Paper Packaging Materials.

Comprehensive Reviews in Food Science and Food Safety. 9 (1), 82–91. Available from: doi: 10.1111/j.1541-4337.2009.00095.x.

Kovačević, D., Brozović, M. & Itrić Ivanda, K. (2019) Eco-mark on product packaging and its effect on the perception of quality. *Journal of graphic engineering and design*. 10 (2), 17–24. Available from: doi: 10.24867/jged-2019-2-017.

Lavoine, N., Guillard, V., Desloges, I., Gontard, N. & Bras, J. (2016) Active bio-based food-packaging: Diffusion and release of active substances through and from cellulose nanofiber coating toward food-packaging design. *Carbohydrate Polymers*. 149, 40–50. Available from: doi: 10.1016/j.carbpol.2016.04.048.

Mahović Poljaček, S., Priselac, D., Stankovič Elesini, U., Leskovšek, M. & Leskovac, M. (2021) Preparation, properties, and laser processing of poly(ε-caprolactone)/poly(lactic acid) blends with addition of natural fibers as a potential for printing plates application. *Polymer Engineering & Science*. 61 (9), 2295–2310. Available from: doi:10.1002/PEN.25758.

Priselac, D., Mahović Poljaček, S., Tomašegović, T. & Leskovac, M. (2022) Blends Based on Poly(ε-Caprolactone) with Addition of Poly(Lactic Acid) and Coconut Fibers: Thermal Analysis, Ageing Behavior and Application for Embossing Process. *Polymers.* 14 (9), 1792. Available from: doi:10.3390/POLYM14091792.

Priselac, D., Tomašegović, T., Mahović Poljaček, S., Cigula, T. & Leskovac, M. (2017) Thermal, surface and mechanical properties of PCL/PLA composites with coconut fibres as an alternative material to photopolymer printing plates. *Tehnički glasnik*. 11 (3), 111–116. Available from: https://hrcak.srce.hr/index.php?show=clanak&id_clanak_jezik=275277 [Accessed: 19th February 2018].

Rastogi, V.K. & Samyn, P. (2015) Bio-based coatings for paper applications. *Coatings*. 5 (4), 887–930. Available from: doi: 10.3390/coatings5040887.

Sharma, C., Dhiman, R., Rokana, N. & Panwar, H. (2017) Nanotechnology: An untapped resource for food packaging. *Frontiers in Microbiology*. Available from: doi: 10.3389/fmicb.2017.01735.

Tang, X.Z., Kumar, P., Alavi, S. & Sandeep, K.P. (2012) Recent Advances in Biopolymers and Biopolymer-Based Nanocomposites for Food Packaging Materials. *Critical Reviews in Food Science and Nutrition*. 52 (5), 426–442. Available from: doi: 10.1080/10408398.2010.500508.

Tomašegović, T., Mahović Poljaček, S., Strižić Jakovljević, M. & Marošević Dolovski, A. (2021) Properties and Colorimetric Performance of Screen-Printed Thermochromic/UV-Visible Fluorescent Hybrid Ink Systems. *Applied Sciences.* 11 (23), 11414. Available from: doi: 10.3390/APP112311414.

Woodruff, M.A. & Hutmacher, D.W. (2010) The return of a forgotten polymer—Polycaprolactone in the 21st century. *Progress in Polymer Science*. 35 (10), 1217–1256. Available from: doi: 10.1016/J.PROGPOLYMSCI.2010.04.002.