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Properties and interaction of layers in board-biodegradable primer-printing ink screen-printed system

ABSTRACT

Surface interactions of the materials during and after the printing process are extremely important for understanding and optimizing the process of graphic reproduction. In screen printing on porous and absorbent substrates, mesh type and ink composition significantly influence the properties of the printed product. To protect the absorbent printing substrates such as board from moisture penetration and to ensure the optimal interaction of the printed ink layer and the substrate, board substrates can be coated with protective primers before printing. In this research, biodegradable primers made of poly(ε-caprolactone) and poly(lactic acid) were applied on the board substrate which was then screen-printed using two screen rulings of the mesh and two different types of water-based printing inks on unprimed and primed board substrates. Printed ink layer thickness, surface roughness, water vapor transmission rate, surface free energy and adhesion parameters were measured/calculated on all produced samples. Microscopy of the printed elements was performed to visualize the influence of the primers on the printed line edge. Results of the research have shown that the primers influence the roughness reduction of the printed ink layer. Furthermore, thickness of the printed ink layers increased when the primers were applied on the substrate, pointing to the decreased permeability of the board, which was confirmed by the reduced water vapor transmission rate of the primed and printed substrates. The surface free energies of the tested surfaces and the adhesion parameters between biodegradable primers and prepared printing inks differed depending on the type of the ink and primer, pointing to the optimal combination of the primer and ink for the favorable acceptance of printing ink on the substrate. Results of this research have enabled the optimization of the quality of screen-printed board product.

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Introduction

Modern packaging production has a significant share on the market of printed products (Kipphan, 2001). In recent years, packaging industry has faced the new trends in terms of design, ecology, protection, and the added value of the printed products while at the same time maintaining or even increasing the quality of the packaging products (Makower, n.d.). Printed packaging products have to protect the product they contain, while being visually appealing to the end customer (Sharma et al., 2017; Kovačević, Brozović & Itrić Ivanda, 2019). Furthermore, the trends regarding the application of biodegradable and other new functional materials have resulted with the modification of the conventional printed packaging products (Khwaldia, Arab-Tehrany & Desobry, 2010; Anselmann, 2001). Board printing substrates generally have acceptable printability properties, but due to their surface and physical properties, they often need to be coated before the printing to ensure all their intended purposes in the lifespan of the final product. Board coatings (primers) can improve the visual, as well as mechanical, surface, and other properties of the substrate. They can have a purpose of a barrier to the gas and liquid. However, primers applied to the board substrates must preserve, or even improve the printability of the substrate, since the properties of the printing substrate greatly influence its suitability for the commercial graphic reproduction techniques (Mahajan & Bandyopadhyay, 2020).

Considering the increasing use of biodegradable materials in many industries with the aim of reducing the environmental impact of conventional materials, the need to switch to environmentally friendly processes and materials has arisen in the printing industry, as well (Vruno, n.d.; Wilson, n.d.). The advantage of biodegradable polymers over the conventional ones is their ability to degrade faster than conventional polymers (Song et al., 2009; Tokiwa et al., 2009).

Therefore, chosen primers for the board printing substrate used in this research consisted of biodegradable polymers: poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA). PCL is a synthetic biodegradable polymer with hydrophobic properties and a semi-crystalline structure. Its melting point is as 60°C, and its glass transition temperature is −60°C (Kelly et al., 2013). PCL has excellent elastic deformability. One of the most interesting properties of PCL is relatively good miscibility and compatibility with other polymers (López-Rodríguez et al., 2006; Woodruff & Hutmacher, 2010).

In polymer blends, the addition of PCL can improve the resistance to cracking of the material. PLA is one of the most widely applied biodegradable polymers today. It is obtained from lactic acid by the process of fermentation of agricultural crops.

Melting temperature of PLA is 170°C and the glass transition is at 60°C. PLA is very often used in packaging, agriculture, medicine, and in 3D printing application as a filament (Tokić, Fruk & Jemrić, 2011; Chavalitpanya & Phattanarudee, 2013; Nampoothiri, Nair & John, 2010; Rasal, Janorkar & Hirt, 2010).

Previous research on PCL and PLA proved them as suitable board primers when using offset printing technique (Hudika et al., 2020). PCL/PLA composites have also been successfully applied as alternative materials for the relief printing plate production (Poljaček Mahović et al., 2021a; Priselac et al., 2022).

The aim of this research was to improve the physical and surface properties of the board printing substrate, specifically the water vapor permeability and adhesion between the printing ink and the substrate by application of PCL and PLA primers prior to the printing process. By printing on the primed substrates in screen printing technique and using two types of water-based printing inks, it was possible to determine the influence of the applied biodegradable primers on the printed boards' properties of interest.

Materials and methods

Preparation of the samples

In this research, uncoated offset board Sappi Tauro with grammage of 300 g/m^2 was used as a printing substrate. Uncoated board was chosen for this research specifically because of the application of the PCL and PLA primers prior to the printing process. Board was stored in conditioned environment at temperature of (23 ± 1)°C and (50- 55)% relative humidity prior to the application of the primers, printing and measurements.

Biodegradable primes were prepared by stirring the PCL/ethyl acetate mixture, and PLA/chloroform using magnetic stirrer in air-tight container for 120 min to obtain the homogeneous solution. Primers were prepared by dissolving 10 grams of poly(ε-caprolactone) 6800 Capa in 90 grams of ethyl acetate; and by dissolving 10 grams of poly(lactic acid) by InegoTM, 3251D, in chloroform. The prepared biodegradable coatings were applied on board samples using K202 Control Coater in controlled conditions defined by the ISO 187:1990 standard, using the rod number 4 (Hudika et al., 2020).

Printing inks used in this research were prepared by mixing 5 grams of black process K print pigment in 95 grams of water-based Midrol Bianco or water-based Midrol Transparente screen printing bases, produced by EPTA Inks. In this way, two types of screen printing inks were prepared: one ink with the transparent base, denoted TBI, and the other ink with opaque white base, denoted WBI. Printing process was performed using two screens with different mesh counts: 32 l/cm and 60 l/cm.

Meshes were produced by SEFAR® and made of polyethylene terephthalate. Printing process was performed using a screen-printing machine Bochonow Drucktisch 2000 50/70. Printed samples were air-dried for 48 h after the printing, at a temperature of 25 ± 2°C.

Methods of measurement and analysis

Surface roughness of the board, primed board and prints were measured to define the influence of the primers and different screens on the surface of the prints. The profiling method for the roughness measurements was defined by international standards (ISO 11562, DIN 4777, DIN 4762).

Two basic roughness parameters were measured: Ra- the arithmetic mean deviation of the profile, and Rz- mean height of unevenness in ten points, numerically the difference in mean height between the five highest peaks and the five lowest peaks within the reference length. The device MarSurf PS 10 (Mahr GmbH, Germany) with the stylus method was used for the measurements. The diameter of a stylus was 2 µm and measuring force was 0.00075 N. Measurements were performed ten times in two directions (in the grain direction and in the opposite direction), on each sample and the results of the mean values with standard deviation were presented.

Thickness of the printed ink layer was measured using SaluTron D4-Fe device, using the principle of magnetic induction for measuring the thickness of layers on non-magnetic surfaces. The results of the printed ink layers' thickness obtained using different inks and by printing on different primers were used to determine the possible decrease of the substrate's absorptiveness after the application of the primers.

Water vapour transmission rate (WVTR) is an important indicator of the efficiency of absorbent packaging materials such as board (Song, Xiao & Zhao, 2014). The higher the water vapour permeability of the material, the faster the vapour passes through it, i.e., the higher the WVTR. In this research, the 'cup method' was used to analyse the permeability of the unprimed, primed and printed board substrates to water vapour. Detection of the water vapour leaving the cup through the board samples was performed on unprimed, primed and printed substrates, using the same experimental setup and following the procedure described in (Cigula, Hudika & Tomašegović, 2021): the container was filled with 50 ml of water. Then, the lid with the hole (diameter of 35 mm) was put on the container and tightly covered with test sample. The samples fixed onto containers were placed in a desiccator containing silica, with (50 ± 5) % relative humidity after the initial weighing The temperature of the environment was (23 ± 1) °C. After the weighing of the samples, performed after one and two days, water vapour transmission rate (WVTR) was calculated using Equation (1) (Cigula, Hudika & Tomašegović, 2021).

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

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 vapor that passed through an area of 1 m^2 in one day (unit of measurement is $g \cdot m^{-2} \cdot day^{-1}$).

Contact angles of the referent liquids and surface free energy (SFE) of the samples were analysed using the Data Physics OCA 30 goniometer. Three referent liquids with known SFE were applied on the board, primed board and printed samples: water, diiodomethane, and glycerol. SFE of the referent liquids and their contact angles on the samples were used to calculate the SFE of the solid substrates. Contact angles were measured by sessile drop method, ten times on each sample, at different positions. The shape of the drop was a spherical cap, and the volume of the drop was 1 µl. All measurements of the contact angles were performed at 0.4 s (10 frames) after the drop had touched the sample surface, due to the absorption of the liquids in some samples. SFE was calculated using a well-known OWRK method. From the calculated SFE components, the adhesion parameters between the layers in the "board-primer-printing ink" system were calculated (Azarhoosh, Moghadas Nejad & Khodaii, 2017). The work of adhesion (W_{12}) (Equation (2)) between the layers in contact was defined in order to predict the strength of interactions (Żenkiewicz, 2007; Tomašegović et al., 2021):

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}, \qquad (2)$$

where the subscript refers to SFE of the solids in contact and the γ_{12} denotes the surface free energy of the interphase. Surface free energy of the interphase (γ_{12}) was calculated according to Equation 3:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \qquad (3)$$

The wetting coefficient (S_{12}) indicates the spontaneity of spreading on the solid surface if the value is positive or equal to zero, while the negative value implies that the wetting is not complete (Equation (4)):

$$S_{12} = \gamma_1 - \gamma_2 - \gamma_{12}, \qquad (4)$$

where γ_1 and γ_2 denote SFE of the solid layers in contact (board and printed ink layer), and γ_{12} denotes SFE of their interface.

Finally, 2D microscopy of the edges of printed elements was used to visually analyze the influence of the primers on the edges of the printed motives using both water-based inks. Microscope Olympus BX 51 was used, and magnification was set to 50x.

Results and discussion

Roughness of the printed surfaces

Roughness parameters Ra and Rz of the board substrate were measured before the priming and printing: Ra = 2.34 ± 0.18 µm, Rz = 14.56 ± 0.99 µm. After coating the board with biodegradable PLA and PCL primers, no significant effect on Ra and Rz was observed, due to the evaporation of the solvents and partial absorption of the primer solutions in the porous surface layer of the board.

Specifically, Ra of the board coated with PLA primer was 2.24 ± 0.12 µm, and Rz was 14.62 ± 0.84 µm. Ra of the board coated with PCL primer was 2.50 ± 0.09 µm, and Rz was 14.98 ± 0.65 µm.

Ra and Rz parameters of the printed unprimed and primed surfaces are shown in Figure 1.

The lowest values of Ra were measured on a board substrate printed with WBI (Figure 1a), using screen with 60 l/cm (1.56 µm for WBI on board, 1.50 µm for WBI on PLA, and 1.62 µm for WBI on PCL). Highest values of Ra were measured on a board substrate printed with TBI (3.02 µm for 32 l/cm screen, and 2.80 µm for 60 l/cm screen).

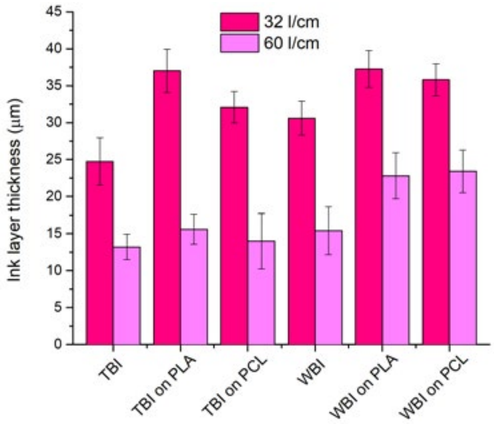
Similar trend of the results is visible when observing the parameter Rz (Figure 1b). The lowest values of Rz were measured on a board substrate printed with WBI, using screen with 60 l/cm (8.55 µm for WBI on board, 8.90 µm for WBI on PLA, and 8.66 µm for WBI on PCL). Highest values of Rz were measured on a board substrate printed with TBI (16.85 µm for 32 l/cm screen, and 15.29 µm for 60 l/cm screen).

With the addition of a layer of PLA or PCL primer under the TBI, the roughness of the printed surface decreased. Essentially, a smoother print due to the improved wetting of TBI on primed substrate (Figure 4c) was obtained compared to the TBI printed directly on board. Since TBI has lower values of SFE than WBI, (Table 1), the interaction of TBI with the substrates was favorable for obtaining a smoother and ink layer on the substrate. Biodegradable primers did not affect the roughness of WBI layer significantly. WBI is initially much denser than TBI and has SFE values closer to the values of the substrates it was printed on, which had a direct effect on the spreading of the ink on the substrate during the printing process.

Thickness of the printed ink layers

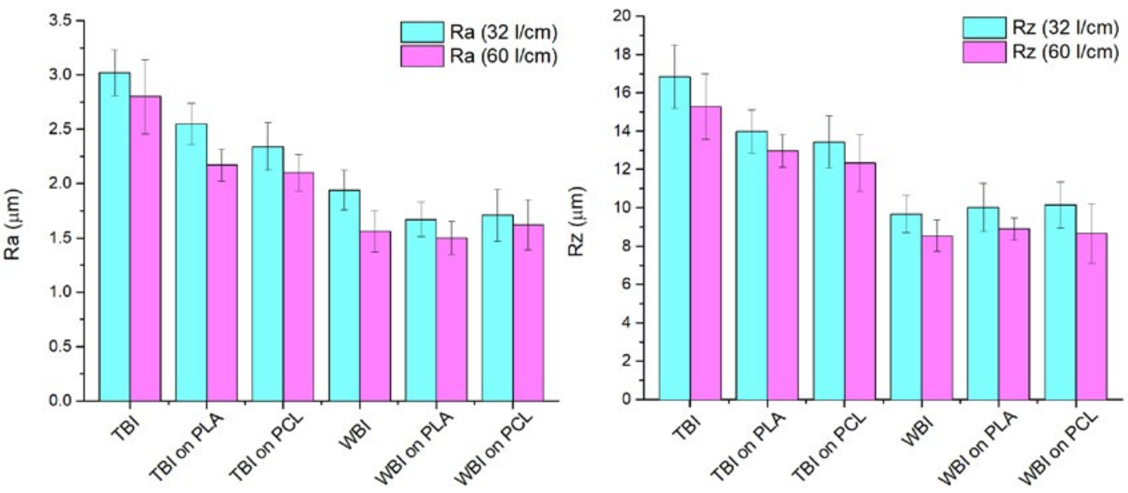
Printed ink layer thickness values are presented in Figure 2. The thickness of PLA and PCL on board could not be measured, since the primer layers were very thin due to their absorption in the board surface.

When observing the results presented in Figure 2, one can see that PCL and PLA primers had an effect of the increase of both TBI and WBI layer thicknesses. This effect can be related to the decreased absorptiveness of the board printing substrate after coating with PCL or PLA primers.



» **Figure 2:** *Thickness of the printed ink layers*

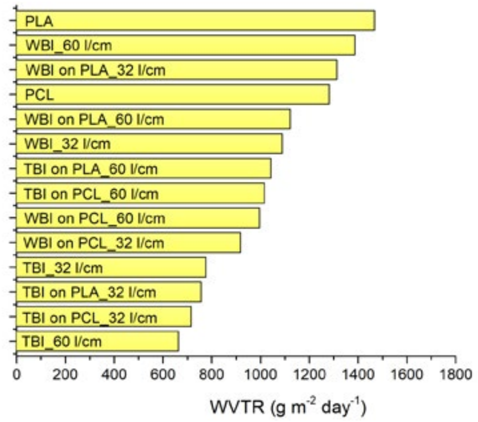
Furthermore, screen count had a noticeable effect on the thickness of the printed TBI and WBI layers. There is a clear and stable difference between the ink layers obtained using 23 l/cm and 60 l/cm screens. Furthermore, all printed WBI layers had higher thickness compared to the corresponding TBI layers, regardless of the applied primers or screen count. This occurrence is related to different compositions of transparent base and white base, which is thicker.



» **Figure 1:** *Roughness parameters of the printed surfaces: a) Ra, b) Rz*

Water vapor transmission rate

Figure 3 presents the relative WVTR in relation to the WVTR of the board without any primers or printed ink layers.



» **Figure 3:** *Water vapor transmission rate of the board, primed board and the samples with printed ink layers*

Calculated WVTR of the plain board was 1804 g·m^{-2}·day^{-1}. In Figure 3, the descending path is shown, ranging from the sample with the highest WVTR to the sample with the lowest WVTR. It is clearly visible that TBI as a layer on the board has the leading property of reducing the permeability to water vapor. The most expressed reductions of WVTR were achieved for four samples which contained a TBI layer and ranged from 663.54 g·m^{-2}·day^{-1} for TBI on board (60 l/cm screen) to 777.04 g·m^{-2}·day^{-1} for TBI on board (32 l/cm screen). Water vapor barrier properties of TBI can be related to the composition of TBI, where plastisol is present (Poljaček Mahović et al., 2021b).

On the other hand, PLA together with WBI presented the highest permeability to water vapor and thus contributed the least to the desired effect of reducing WVTR. Highest WVTR was calculated for PLA on board and amounted 1468.75 g·m^{-2}·day^{-1}. Similar results were obtained for WBI on board, obtained using 60 l/cm screen (1387.06 g·m^{-2}·day^{-1}), and for WBI on PLA, using the screen of 32 l/cm (1313.68 g·m^{-2}·day^{-1}). Due to its water vapor permeability (Halász, Hosakun & Csóka, 2015), PLA benefited from the combination with the printing inks used in this research, especially TBI. Furthermore, PCL alone on the board substrate was not the best solution for decreasing WVTR because its water vapor permeability was 1281.66 g·m^{-2}·day^{-1}. Similar to PLA, its combination with TBI or WBI improved the WVTR.

Although the PLA and PCL primers alone did not decrease the WVTR as much as TBI layer, their application on the board substrate was significant for the improvement of the ink adhesion, presented in 3.4.

Surface properties and interactions of layers in "board-biodegradable primer-printing ink" system

Although the contact angles were measured on the surfaces of all samples, no distinction between the same ink layers obtained using different screen counts was made when calculating SFE. Since the thickness of all printed layers was enough to achieve the uniform and complete coverage of the board, no effect of the screen count on the contact angle values was observed. According to the results of SFE calculations, presented in Table 1, the highest total SFE was calculated for the PCL primer (44.32 mN/m), and the lowest SFE was calculated for TBI layer (20.24 mN/m). Furthermore, it can be observed that all surfaces had a dominant dispersive component of SFE.

Table 1
SFE components of the layers in "board-biodegradable primer-printing ink" system

	Total SFE (mJ/m²)	**Dispersive SFE (mJ/m²)**	**Polar SFE (mJ/m²)**
Board	24.00	23.98	0.02
PLA layer	30.25	29.65	0.60
PCL layer	44.32	43.24	1.09
TBI layer	20.24	20.14	0.10
WBI layer	30.01	29.09	0.92

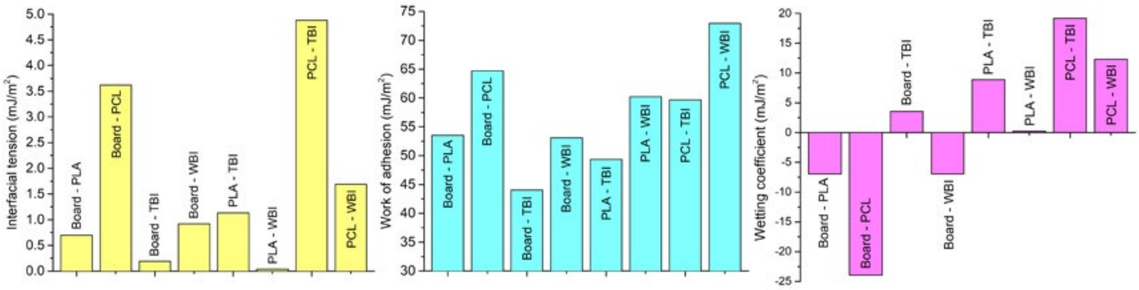
PLA and PCL primers have increased SFE of the board, which is an indication that the wetting and adhesion of the used inks on primed board should be improved.

In order to analyze the effect of the surface interactions of the primed board and the used inks and compare it to the interactions of unprimed board and the inks, adhesion parameters were calculated and presented in Figure 4.

Optimal adhesion is achieved when all three adhesion parameters meet the following criteria: the interfacial tension (γ_{12}) should be minimal, i.e., as close as possible to 0, the thermodynamic work of adhesion (W_{12}) should be maximal, and, finally, wetting coefficient (S_{12}) should be positive.

When observing Figure 4a, it can be seen that γ_{12} is closest to 0 for PLA and WBI (0.04 mJ/m^2), followed by γ_{12} between board and TBI (0.19 mJ/m^2). The highest, and least favorable γ_{12}, was calculated between PCL and TBI (4.88 mJ/m^2). W_{12} was highest between PCL and WBI (72.94 mJ/m^2), followed by W12 of 64.69 mJ/m^2, achieved between board and PCL (Figure 4b).

This means that the highest work is needed to separate these two pairs of layers. Lowest work of adhesion was calculated between board and TBI (44.04 mJ/m^2), pointing to the weaker adhesion between these two layers.



» **Figure 4:** *Adhesion parameters in "board-biodegradable primer-printing ink" system: a) interfacial tension, b) work of adhesion, c) wetting coefficient*

The last adhesion parameter, S_{12}, (Figure 4c), is positive for all combinations of primers and inks, pointing to the optimal adhesion of the inks and both PLA and PCL primer. Negative S_{12} is present between the board and the primers, as well as between the unprimed board and WBI. Negative S_{12} indicates that the spreading of the observed primer/ink layer on the board is not spontaneous, and could pose a problem with the mechanical properties and durability of the print (Tomašegović et al., 2021; Aydemir, Altay & Akyol, 2021).

However, in the case of PLA and PCL primers, this would not be the case, since they were applied on the porous, uncoated board substrate in the form of a solution which was partially absorbed in the surface of the board.

Furthermore, when assessing the adhesion performance, all three parameters should be considered at once. From the given results, it could be concluded that the best adhesion was achieved between PLA and WBI, and PCL and WBI.

Therefore, the primers had the most expressed effect on improving the adhesion of WBI ink on the board substrate. The adhesion of TBI ink on the board did not benefit from the application of the primers as much as WBI.

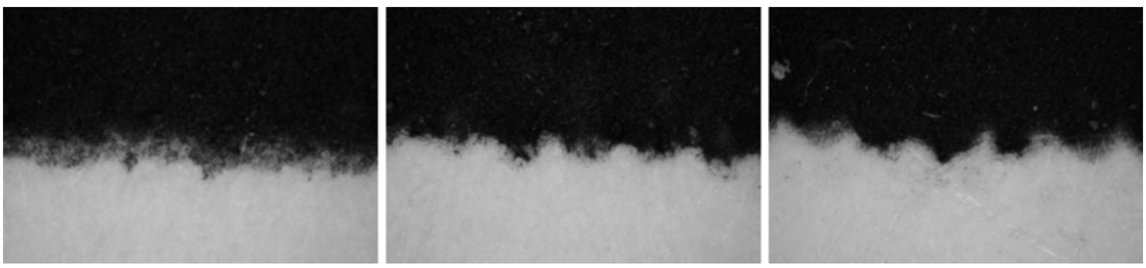
Nevertheless, W_{12} between TBI and the substrate was increased when the board was primed with PLA or PCL.

Microscopy of printed elements' edges

Figure 5 shows the chosen images of the printed element edges obtained by Olympus BX 51 microscope, with magnification of 50x. There was no noticeable difference between the printed element's edge when comparing TBI and WBI, and the effect of the PLA and PCL primers on the element's edge was more noticeable on the prints obtained using 32 l/cm screen. Therefore, the prints obtained using TBI and 32 l/cm screen were chosen for the comparison and presented.

When comparing the Figures 5a-c, it can be noticed that the gradient transition between the ink and board present on the print of the TBI on unprimed board, has disappeared when the ink is printed on the primed board. This can be attributed to the reduction of the board's absorbency after the application of the primers.

When comparing the edges of the printed elements, it can be seen that the realistic edge of the printed element is significantly more noticeable when the ink was printed on the primers (Figure 5b-c). The uneven character of the line edge is common in the screen printing and is a result of the mesh structure. This occurence is more pronounced when using the screens with lower mesh count, such as in this research. If the screen for the reproduction of the fine lines, with high mesh count, would be used, the prints on the primed board would have clearer line edges if the board was primed with PCL or PLA, compared to the prints on the plain board.



» **Figure 5:** *2D microscopy of printed elements' edges: a) TBI on board (no primer), 32 l/cm, b) TBI on PLA, 32 l/cm, c) TBI on PCL, 32 l/cm*

Conclusion

The aim of this research was to analyze the effect of biodegradable primers made of PLA and PCL on the properties of the uncoated board, in terms of the interaction with two types of common water-based screen printing inks (ink with the transparent base- TBI, and ink with opaque white base- WBI) and their influence on the permeability to water vapor.

Thickness and roughness of ink layers (printed using different inks and screen counts), as well as surface free energies and water vapor transmission rates, were measured/calculated. Surface free energy components were used to calculate the adhesion parameters between the layers in contact. 2D microscopy of the printed elements' edges was performed to visualize the effect of the primers on the line edge definition. From the obtained results, the following conclusions can be made:

- The addition of PLA and PCL primers under TBI caused the decrease of the roughness of the printed surface, but did not affect the roughness of WBI layer significantly;
- As expected, mesh count had a noticeable effect on the thickness of the printed TBI and WBI layers. Furthermore, PCL and PLA primers had an effect of increasing both TBI and WBI layers' thickness. The effect can be related to the decreased absorptiveness of the board after coating with PCL or PLA primers;
- TBI as a layer on the board had the leading property of reducing the permeability to water vapor, while PLA together with WBI presented the highest permeability to water vapor.
- Although PLA and PCL primers alone did not decrease the WVTR as significantly as TBI layer, or the combination of the primers and TBI ink, application of the primers on the board substrate was significant for the improvement of the ink adhesion,
- The best adhesion was achieved between PLA and WBI, and PCL and WBI. Therefore, the primers had the most expressed effect on improving the adhesion of WBI ink on the board substrate.

The results of the research have contributed to the optimization of the screen printed ink layers on the primed absorbent and porous substrates. They have described the important properties of the print obtained using two common types of water-based screen printing inks on the board substrate primed with PLA and PCL, specifically regarding the water vapor transmission rate and interaction of the biodegradable primers and printing inks for screen printing, thereby enabling the optimization of the quality of screen-printed board product.

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