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Improving the electrical performance and mechanical properties of conductive ink on thin compound substrate

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Abstract

In printed electronics applications, very often conductive lines have to be printed and there are several ink/paste and substrate combinations to choose from. Silver ink is usually used due to its high electrical conductivity. Carbon black and PEDOT:PSS are also very common. Substrates are available in a broad variety. Flexibility, good adhesion of the ink, processability, and a maximum processing temperature compatible with the curing temperature of the functional inks is important. If barrier properties, e.g. against the permeation of oxygen, carbon dioxide or water vapour are required, a compound substrate may be necessary, consisting of two or more layers of different materials. The motivation for this investigation was the need for improving the stability and processability of a given substrate chosen for printed batteries. The substrate consists of three layers, namely polyethylene (PE), aluminium and polyethylene terephthalate (PET). This compound foil is rather thin (100 μm) and very flexible. This is a major requirement for the application. The aluminium sandwiched between two polymer layers provides sufficient barrier properties. PET is commonly used as a substrate for printed electronic applications. PE is not as easy to print on, but with e.g. plasma treatment the adhesion of printing inks is sufficient. The weldability of PE is beneficial for the screen-printed battery application, although poor printability without surface treatment and the thermal mismatch of the asymmetric polymer compound (PE–PET) renders processing rather difficult. In this work, the authors examined a route for printing on PE without the need of pre-treatment of the substrate with plasma or corona. Instead, it was found that an UV-ink layer used as adhesion promoter provided sufficient adhesion and improved mechanical stability, i.e. cohesion of the successively printed silver ink layer. Additionally, the thermal treatment of the conductive ink was optimized by comparing heat press and hot stamp curing with batch oven curing.

Keywords: printed electronics, printed battery, conductive ink, UV-curing, laminated substrate

1. Introduction and background

The choice of substrate in the field of printed electronics is very important. If one considers organic light emitting diodes (OLED) or – as in the underlying case – printed batteries, it is necessary to ensure the encapsulation of the chemical system during manufacturing and lifetime of the device. Without the appropriate barrier materials, the lifetime is drastically lower (Bülow et al., 2014; Park et al., 2011; Wendler, Krebs and Hübner, 2010; Yoshida et al., 2001). Usually, the application determines the inks, the substrates and the preferable printing method. Trade-offs have to be made, if requirements are conflicting. The authors chose a compound laminate consisting of polyethylene, aluminium and polyethylene terephthalate layers (PE-Al-PET) as substrate for printed batteries as part of a research project (KoSiF, 2013). The conflict in choosing this substrate lies in the favourable weldability and the poor printability of PE. Due to wettability reasons, printing on PET is uncomplicated, whereas printing on PE is quite difficult. Pre-treatment of the PE surface is necessary in order to achieve adhesion of the print layer on the polymer (Rossmann, 1956; Lommatzsch et al., 2007). In roll-to-roll production lines, corona or plasma pre-treatment devices can be implemented. However, if a sheet-fed lab machine is used and the available plasma/corona device has a limited spatial work area or if even no corona or plasma device is accessible at all, another approach to the problem may be useful.

One part of this paper is the examination of an ink layer that promotes the adhesion of silver ink on PE without prior application of corona or plasma treatment. An UV-curing printing ink is used as an adhesion agent, since the processability is very good as well as the adhesion of silver ink on top of the UV-ink layer. The second part of the paper reports on the examination of alternative thermal processes that are capable of curing electrical conductive printing inks. The thermal treatment after printing is essential for optimizing the electrical conductivity.

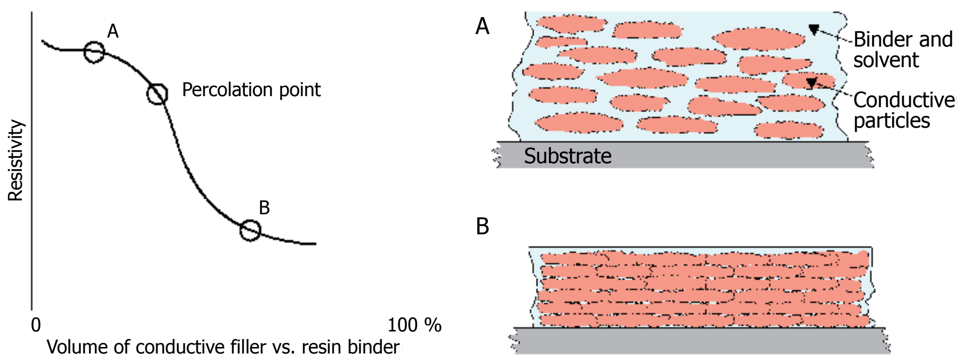

Figure 1: Pigment filled conductive inks need thermal treatment in order to establish electrical pathways between the single particles, modified from Banfield (2000)

The mechanism behind metal particle filled inks requires thermal post-treatment after printing (Banfield, 2000). A curing temperature of 120 °C for at least 10 minutes is mostly stated as the minimum requirement for achieving a reasonable conductivity. The conductance, the reciprocal of the ohmic resistance, increases with higher temperature and longer curing time. It is usually the substrate, what limits the maximum processing temperature, e.g. PET substrates do not withstand temperatures higher than 150 °C. According to Figure 1, the evaporation of the solvent and the shrinkage of the binder reduce the height of the ink layer, thus increasing the contact area of the conductive particles. The maximum continuous service temperature of some polymers, e.g. PE and PP, is below 100 °C. Thus, the compound foil examined in this paper (PE-Al-PET) is very prone to thermal stress; especially the asymmetry (PE–PET) leads to a pronounced tendency to curl.

Since the composite film used for the investigation was provided on a roll, it already showed distinct memory curl if cut in sheets for processing on a flatbed screen printing press. To prevent the curling of the substrate during the investigations completely, the compound films were laminated on a rigid carrier substrate, which can withstand temperatures of at least 120 °C for several minutes without deforming.

1.1 Preliminary tests

In a preliminary test series, the materials listed in Table 1 were examined. Without lamination to a carrier the compound foil curls immediately even when heated at low temperature, starting already from 40–50 °C. The substrate carrier supports the compound foil, which is laminated onto the carrier by printed adhesives. As can be seen in Figure 2, if the adhesion of the foil to the carrier is not good enough the foil delaminates and curls severely. Two adhesives were printed in three different patterns. The honeycomb pattern showed good adhesion, but the pattern was visible in the image printed on the laminated compound foil. Rigid substrate carriers like the phenolic paper improve the processability, whereas the cardboard used here also tended to curl (see Figure 3). Both adhesives performed similar and showed promising results. The solvent-based adhesive was chosen for further tests because of ease of use. Based on the results of the preliminary tests the examination of alternative thermal techniques that avoid oven treatment and maybe curl gains more and more attractiveness.

1.2 Alternatives to thermal treatment in an oven

Looking for alternative technologies for the thermal treatment of functional layers is a constant topic of research in the field of functional coatings and especially in the field of nanoparticles (German, 1996). Processes such as e.g. microwave (Perelaer, de Gans and Schubert, 2006), or IR-treatment (Tobjörk et al., 2012) and others have been tested. In this investigation, two techniques of applying heat have been tried. These two devices, which are commonly used in the graphic arts industry – a heat press usually used for

Table 1: Preliminary tests for identifying the main problems of processing the PE-Al-PET compound foil

Substrate carrier	Cardboard or phenolic paper
Adhesive	Water based dispersion or solvent based
Adhesive pattern	Full area, frame or honeycomb pattern
Screen mesh	Sefar PET 1500 120-34 or Sefar PET 1500 77-48
UV ink	SunChemical SunTronic 680 or Marabu Ultraswitch UVSW
Silver ink	Acheson Electrodag® PM-406

textile prints and a hot stamping machine – in the following are compared to oven drying. Both devices provide temperature and pressure at the same time. The pressure, however, was neglected in this examination and was set to a minimum. The heat press applies heat and pressure on an area of 37.5 cm × 27.5 cm. The hot stamping machine utilizes interchangeable stamps such that only the area of interest is pressed and heated.

The stamp used in the tests was of the same size as the test structure. This is considered as a major advantage of the hot stamping process, because the thermal loading to the substrate and the dimensional instability is assumed being less with the hot stamping. The thermal and mechanical impact on the printed layers may also have positive impact on the adhesion to the investigated substrate.

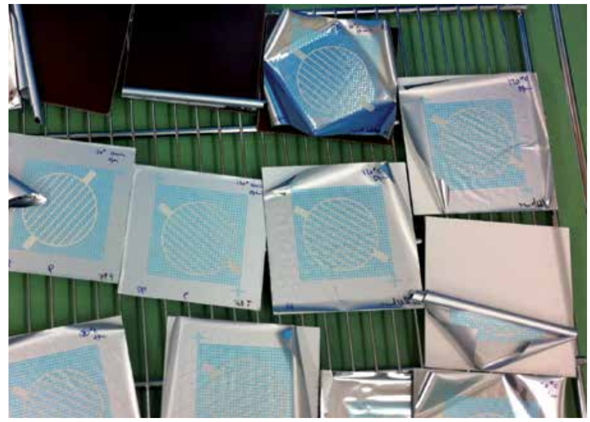

Figure 2: Effect of oven treatment on the dimensional stability of the laminated substrate; if the adhesion to the carrier was too weak, the samples pulled off and curled

a) b) c)

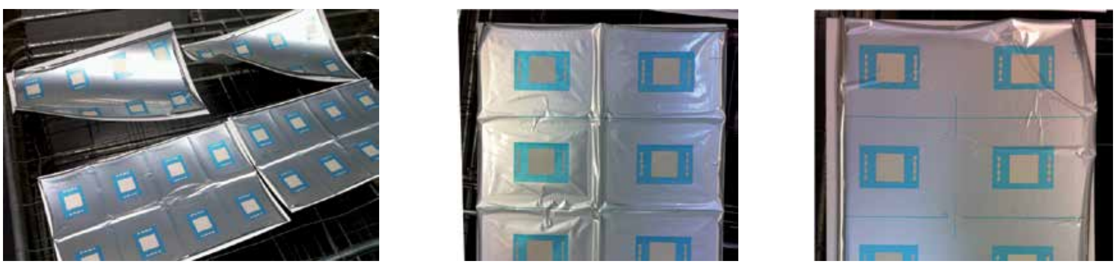

Figure 3: The full area adhesive sheets on cardboard are curling – two samples in rear of a) and sample in c), whereas the adhesive free parts of the frame laminated substrates at two foremost samples in a) and b) act as a kind of "expansion joint" due to different shrinkages

2. Materials and methods

2.1 Materials

The materials and patterns that were chosen for further experiments were based on the preliminary tests. The experiment setup is listed in Table 2.

The cardboard laminates were susceptible to the temperature impact in the batch oven. Since the investigation is aiming towards less temperature loading to the substrate, cardboard is a good indicator for excessive thermal loading.

The frame-patterned adhesive allows for better removal of the attached substrate, whereas the full area printed adhesive may show improved stability during printing and further processing.

2.2 Methods

The UV-curing ink is printed on the substrate without plasma treatment. In the preliminary tests, the Sun Chemical ink provided good results. Other UV inks and solvent-based inks were not able to adhere to the untreated PE surface. The silver ink test patterns – as shown in Figures 3 and 4 – are used for electrical measurements with a four-point probe setup. The printed square was used for crosscut tests. The ink layer thickness was measured with an optical 3D-microscope and

Table 2: Materials and adhesive patterns

Substrate Carrier	Cardboard
Adhesive	Solvent based KIWOPRINT TC 2500/1
Adhesive pattern	Full area or frame
UV Ink	SunChemical SunTronic 680
Silver Ink	Acheson Electrodag® PM-406

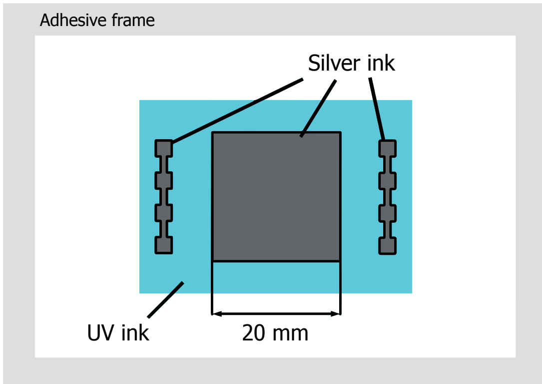

Figure 4: The test layout consisting of an adhesive frame (or full area printed adhesive, not shown), UV curing ink and silver ink test structure (1 mm width – left; 0.75 mm width – right) for four point probe measurement and area for crosscut tests

verified with a mechanical thickness tester. The electrical measurements were performed with a digital multimeter.

The samples were printed on cardboard reinforced PE-Al-PET compound foil with an EKRA X-1 screen printer (EKRA GmbH, Germany). Prior to printing the test samples, the adhesive KIWOPRINT TC 2500/1 was printed onto the cardboard substrate carrier and laminated with the compound foil. The screens were tensioned with PET 1500 120-34 and 77-48 meshes (SEFAR AG, Switzerland). The stencils were made of AZOCOL Z 160 HV emulsion (Kissel + Wolf GmbH, Germany). The UV curing dielectric ink SunTronic 680 (Sun Chemical Corporation, USA) was used as the adhesion agent. The silver ink Acheson Electrodag® PM-406 (Henkel AG & Co. KgaA, Germany) was used for electrical characterization of the print samples. Plasma treatment was performed with a desktop ambient atmosphere plasma-device (Plasmatreat GmbH, Germany). The oven-cured samples were processed in a batch oven (Binder, Germany). The heat press picollo plus (Walter Schulze GmbH, Germany) and the hot stamping press (Robertshaw, USA) were used for examining alternative thermal treatment. Four point probe measurements were performed with spring-loaded round-shaped probe heads (Feinmetall, Germany) and a digital multimeter M3510A (Picotest Corp., USA). Adhesion was tested with a Cross-Cut-Tester, 1 mm, DIN/ISO (BYK-Gardner GmbH, Germany). The thickness of the layers and overall roughness were determined with an optical microscope Infinite Focus (Alicona Imaging GmbH, Austria).

3. Results and discussion

3.1 Effect of thermal process on ohmic resistance

Thermal treatment of conductive inks printed on sheet-fed material is mostly performed in batch ovens. These allow curing of functional inks from room temperature up to roughly 300 °C. Curing temperature and time are limiting factors for manufacturing processes in printed electronics. In this specific scenario, the temperature is even more critical, since it causes dimensional distortion due to the low maximum processing temperature of PE and mismatch in the thermal shrinkage behaviour of the two polymer layers. This results in registration difficulties of the successively printed ink layers. The batch oven curing process is therefore not useful for processing this specific substrate. Samples, which were cured in the batch oven, are the reference samples to compare with the alternative processes. The negative impact (curl, pronounced shrinkage) of the batch oven curing is shown in Figures 2 and 3.

Figure 5 shows the ohmic resistance results of the reference samples for the two different line widths (0.75 and 1 mm) of the silver printed line patterns (see Figure 4).

In Figure 6, the influence of the heat press is illustrated. The effect of temperature is shown in the diagram in Figure 6a. The higher the temperature, the lower is the ohmic resistance. In Figure 6b, the effect of pressing time is shown at 5, 10 and 15 seconds, which is in accordance to the literature (Xu et al., 2013). As expected, the ohmic resistance is linearly decreasing with increasing process time. The way the compound foil is attached to the substrate carrier seems to influence the ohmic resistance as well. At least there is a tendency of increased ohmic resistance when the adhesive for laminating the compound foil on the carrier covers the full area. The samples which are laminated by using only a frame of adhesive surrounding the image area show slightly lower ohmic resistances.

The same effect of processing time on the ohmic resistance is evident in the case of the hot stamping processed print samples. In Figure 7, the percentage of ohmic resistance reduction is plotted. In Figure 7a of the diagram the influence of the processing temperature is shown, whereas Figure 7b shows the effect of the processing

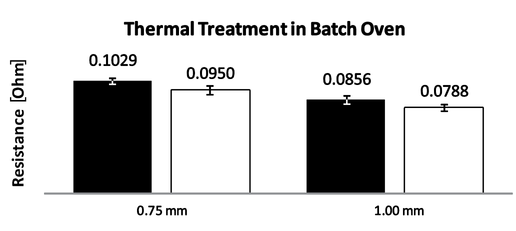

Figure 5: The thermal treatment in the batch oven is the reference for alternative curing processes

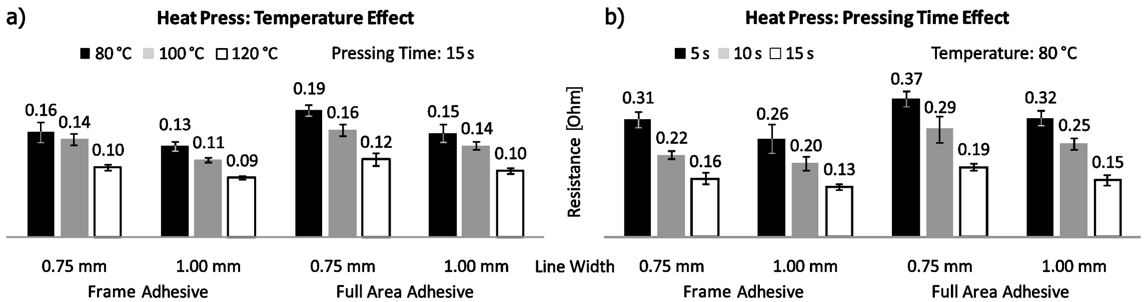

Figure 6: The heat press is capable of reducing the ohmic resistance, where the achievable resistance is in the same order of magnitude as with oven-dried samples

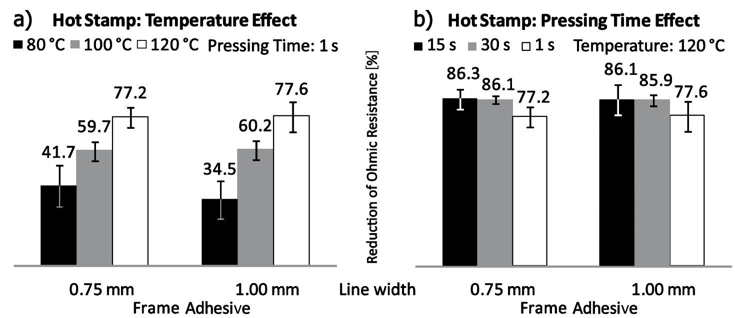

Figure 7: The process of hot stamping provides an efficient way of reducing the ohmic resistance

time. Even at a low temperature of 80 °C and with a very short processing time of one second, the reduction is very high, achieving ~ 40 % ohmic resistance reduction. At higher temperatures and longer pressing times of 15 seconds, the ohmic resistance is reduced about 86 %. Increasing the impact time from 15 to 30 seconds or even to 60 seconds does not reduce the ohmic resistance any further. It seems reasonable that at this point the maximum percolation of the conductive particles is achieved. Moreover, the print samples are deformed when pressing for 60 seconds.

As depicted by Figure 8, the samples dried at room temperature show the highest ohmic resistance. The resistances of the heat press samples are slightly higher than the batch oven results. The lowest ohmic resistance is achieved by the hot stamp samples. The advantage of hot stamping is faster processing and less impact on the substrate. The heat press is less efficient and more harmful to the substrate than hot stamping.

3.2 Impact of stress on morphological parameters

In order to identify the mechanical stress of the heat pressing and hot stamping on the printed layers, the morphological properties were measured. Important parameters are the surface roughness, layer thickness and adhesion to the underlying substrate. Roughness and

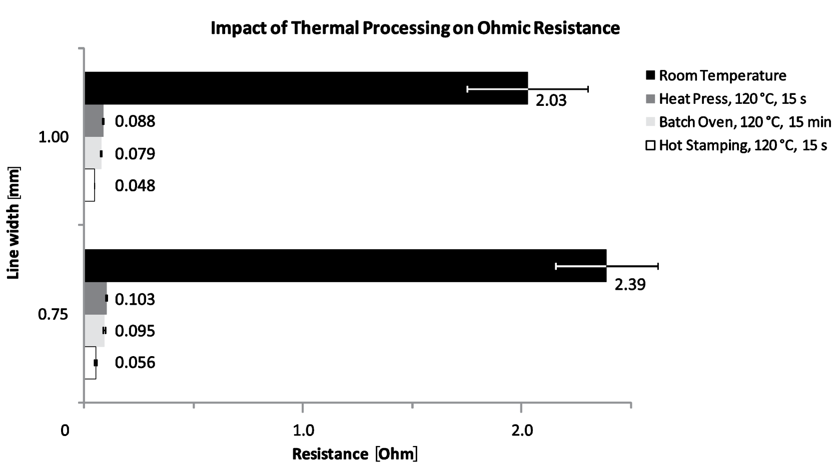

Figure 8: Comparison of the investigated routes for post-treatment of conductive silver ink

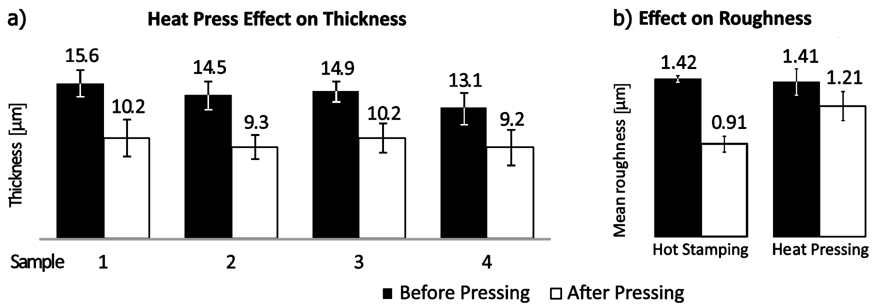

Figure 9: Decreased layer thickness after heat pressing at 120 °C for 15 s a), and the heat pressing effect on the roughness Sz maximum height parameter b)

thickness values were obtained by optical 3D-microscope measurements based on focus variation (Alicona infinite focus). Thickness and roughness data were obtained before and after the treatment with heat pressing and hot stamping at 120 °C for 15 seconds. The adhesion strength of the ink layer was tested in crosscut and tape-tests.

3.2.1 Thickness and roughness

The heat press processed samples showed thickness differences after pressing. Reliable thickness data could only be obtained from the samples, which were processed with the heat press. The results of the thickness measurements for a process temperature of 120 °C and a processing time of 15 seconds are given in Figure 9a. The samples were printed on full area laminated substrates.

On average, the layer thickness decreased about 30 %. Values dropped from roughly 13–15 µm to about 9–10 µm. The heat press process did not damage the samples, whereas visual inspection clearly showed the impact of the hot stamp on the samples (imprint of the stamp). It is likely that the pressing process leads to a densification of the silver layer that decreases the overall thickness. This observation is supported by the fact that the surface roughness changed, too.

After thermal treatment by hot stamping or heat pressing, the roughness of the silver layer decreased noticeably. The overall mean roughness seems to be lower for the samples which were processed with the hot stamp. Deviations in terms of surface roughness (*Sz*, maximum height of the surface) are in the range of 15 % for the heat pressed samples and up to 35 % for the hot stamped samples.

It is assumed that the significantly higher pressure of the hot stamping influenced the surface of the samples largely, what can be observed visually. An image, which clearly shows the imprint of the stamp on the sample, is given in Figure 10.

3.2.2 Crosscut, tape test and creasing test

The general adhesion of the ink on the substrate was tested in two experiments: crosscut-test and tape test.

Samples were crosscut in a 90° angle. This led to 25 equally shaped squares. The test procedure is in accordance with ISO 2409 and ASTM D 3359-97 (Byk-Gardner, 2015; Deutsches Institut für Normung, 2013). This partially removed the small squares from the surface. Figure 11 shows the count of removed squares giving an indication of the adhesion of the ink.

Crosscut-tests on samples which had atmospheric plasma pre-treatment showed very good adhesion on the underlying substrate. The crosscut did not influence the adhesion at all.

a) *b)*

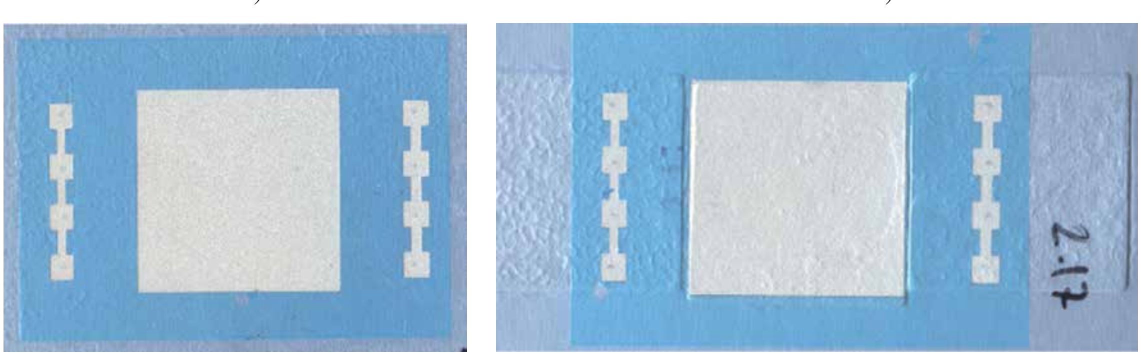

Figure 10: Heat press a) and hot stamping b), where the impact of the stamp is clearly visible

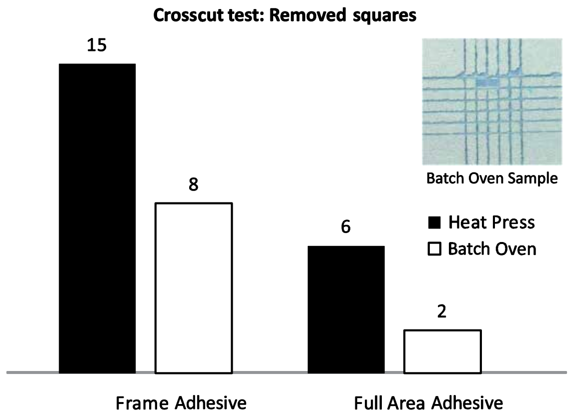

Figure 11: Crosscut test on heat press and oven-dried samples (120 °C, 15 min)

The patterning of the adhesive layer (full area or frame laminated) seems to have an effect on the adhesion. According to Figure 11, the full area adhesive samples show fewer failures.

The adhesion of the ink layer seems to be temperature dependent as well. Samples which were heat pressed at 80 °C for 15 seconds showed less adhesion to the substrate compared to samples which were pressed at 120 °C for the same time. However, this test was done manually and thus slight variations in downwards pressure and cutting speed cannot be avoided. This could be optimized by an automatic crosscutting machine, which was not available. Further tests need to be done in order to prove this.

3.2.3 Tape test

A tape test was carried out, which partially or fully removed the ink layers from the substrate. This was true for all samples except for samples that were treated with plasma prior to printing. No tendency in terms of temperature related adhesion could be noticed regarding the tape test.

3.2.4 Creasing test

A manual crease roller was used to simulate mechanical stress on the functional ink layers. After creasing the samples, the compound foil and the substrate carrier were bent by 180°. A four-point probe measurement was performed after re-flattening the samples.

The increase in ohmic resistance was massive, but most of the samples still showed electric conductivity. It is only possible to judge the outcome of this test qualitatively, because the ohmic resistance measurement showed no consistently repeatable results and lacked reliability, as indicated by the huge error bars in Figure 12. Thus, the creasing test only provides the mere result of continuity or discontinuity of the electric pathway. However, as shown with this crease roller test, even a quite violent handling of the print layers does not destroy the functionality.

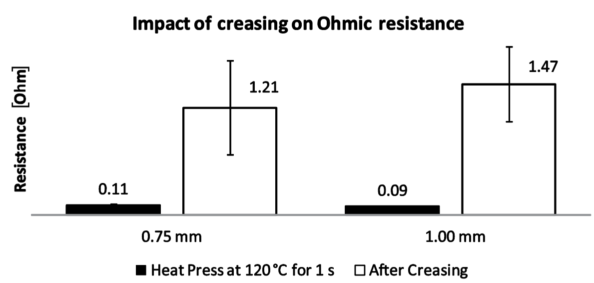

Figure 12: Creasing the printed structures and bending the compound film on the substrate carrier resulted in a massively increased ohmic resistance

4. Conclusions

The goal of this examination was to establish a route for screen printing electrically conductive structures on PE-Al-PET substrate. These structures are part of a printed battery that benefits from the properties of the compound substrate, i.e. the PE-weldability and the thin substrate thickness.

An UV-curing ink was introduced to act as an adhesion agent. This UV-ink improved the mechanical stability of the print samples. The formerly crumbling silver layers gained elasticity by the underlying UV-ink layer. The adhesion to the untreated substrate improved as well, but it is certainly less effective than a plasma treatment.

The heat press and hot stamping curing as an alternative to oven treatment showed also an improvement of the adhesion to the untreated substrate. Additionally, the ohmic resistances of the pressed samples were comparable (heat press) to or lower (hot stamping) than the samples post-treated in the batch oven at 120 °C for 15 minutes. The average thickness and roughness of the screen-printed silver layers seem to be influenced by the hot stamping and the heat pressing process, respectively. The crosscutting and tape test showed certain tendencies that need to be further investigated. Especially the influence of the temperature on the adhesion needs to be considered.

Acknowledgements

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