INDUSTRIAL CORONA PRE- AND POST-TREATMENT FOR ENHANCED SILICONE COATING OF PAPER USED AS RELEASE LINER

ŠTĚPÁNOVÁ Vlasta[1], KOVÁČIK Dušan[1], GALMIZ Oleksandr[1], TUČEKOVÁ Zlata[1], ZEMÁNEK Miroslav[1], STUPAVSKÁ Monika[1], KELAR Jakub[1], VALLADE Julien[2], ČERNÁK Mirko[1]

[1]*Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic, EU*

[2]*Coating Plasma Industrie, ZA du Verdalaï 30 impasse du Nid, Peynier, France, EU*

vstepanova@mail.muni.cz

Abstract

In this work, atmospheric pressure, ambient air plasma was used for pre-treatment of clay coated paper before silicone coating as well as for post-treatment to prepare the release liner with low adhesion. As a plasma source "industrial corona" in roll-to-roll configuration was used for plasma treatment. The aim of the study was to evaluate the effect of plasma pre- and post-treatment time on adhesive properties of silicone layer sprayed on the paper. Plasma pre-treated paper was sprayed with silicone oil of different amounts using spray gun and subsequently plasma post-treated for defined repetition. Surface of silicone sprayed paper was analyzed by water contact angle measurement immediately after oil spraying procedure. The possible changes in morphology were characterized by scanning electron microscopy, chemical composition by X-ray photoelectron spectroscopy and the adhesion by measuring tape peel force. The silicone coated paper was characterized by increase of hydrophobicity and decrease of release factor with significant impact of plasma post-treatment.

Keywords: Release liner paper, atmospheric pressure plasma, industrial corona, silicone coating, adhesion

1. INTRODUCTION

Release liner papers are used in various self-adhesive applications such as hygiene products, envelopes, bar code labels, packaging tapes, postage stamps, etc. The main function of the release liner is to protect the adhesive layer in the product [1]. It has to stick to the adhesive, but also be easily removed from it. However, a typical problem for silicone based release liners is transfer and migration from the release coating on surfaces they come into contact. In the presented work atmospheric pressure plasma was used for pre-treatment of clay coated paper before silicone coating as well as for post-treatment to prepare the release liner with low adhesion. Oil spraying without plasma pre- and post-treatment leads to the high peel force necessary for removing the sticker from oil sprayed paper. Moreover, the oil sprayed paper used as carrier leaves oil residue on stickers after their removal from paper. Oil spraying ensures non-adhesive surface however oil spraying itself is not sufficient to decrease the peel force. Our idea is to solve this problem using plasma treatment before and also after oil spraying. As known, plasma treatment enables to improve the hydrophilic properties of paper surface [2-3], wettability [4,5], therefore sprayed oil will be soaked more effectively into the paper after pre-treatment. Post-treatment serves for so call hardening of sprayed oil and better incorporation of them to the paper. The aim of this study was to optimize the oil spraying procedure following plasma pre-treatment and finishing by plasma post-treatment for preparing the release liner paper with sufficiently low release factor.

2. EXPERIMENTAL

2.1. Material, plasma treatment and silicone oil spraying procedure

For optimization of silicone oil spraying procedure, the A4 size sheets of clay coated paper provided by Crown Van Gelder company (CVG, Holland) were used. Clay coated paper consists of a thin layer of pigment coating on one side of paper, which makes the surface very consistent in comparison with the opposite non-coated side. In experiments, we focused on the coated side of paper which was pre-treated by plasma, oil sprayed and plasma post-treated. As a source of atmospheric pressure plasma for pre- and post-treatment of paper volume dielectric barrier discharge (vDBD), often referred to as “industrial corona”, in roll-to-roll configuration from Ahlbrandt System GmbH (Germany) was used. The electrode system consists of four high-voltage strip electrodes and a grounded cylindrical electrode, all isolated by a thin ceramic layer, as illustrated by photo in **Figure 1a**. Plasma is generated in adjustable gap (1 - 3 mm) between rotating cylinder and detachable electrodes as shown in **Figure 1b**. The dimensions of effective area of generated non-equilibrium plasma are 7 cm × 21 cm. During experiments corona was operating at input power 380 W, supplying voltage frequency was 24.3 kHz and as a working gas ambient air of room temperature was used. The distance between treated paper sample taped on the roller and high-voltage electrodes was set to the value of 2 mm, velocity of rotating cylinder was 18 m/min. The effect of plasma pre- and post-treatment was investigated at three different exposure times 0.25 s, 0.5 s, and 5 s

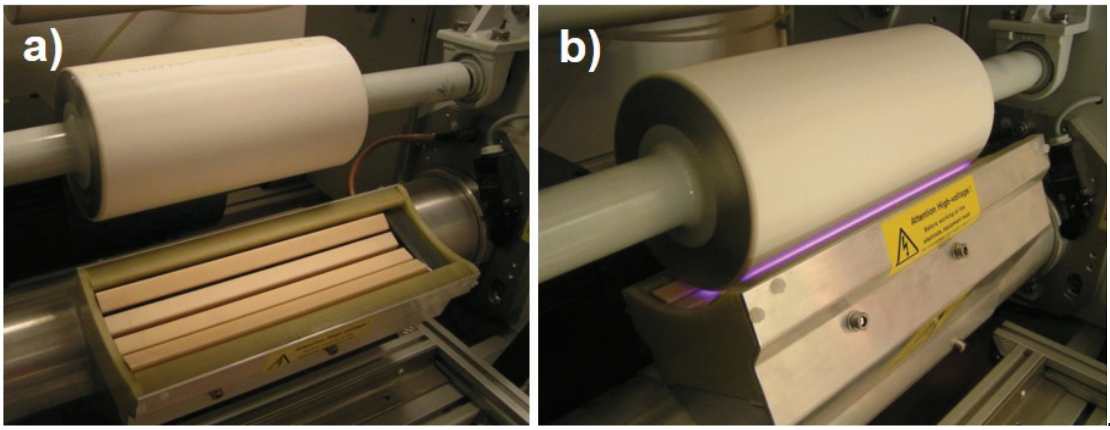

Figure 1 Photos illustrating a) the electrode system of industrial corona, and b) ambient air plasma burning in 2 mm gap between electrodes

Plasma pre-treated paper was sprayed with silicone oil (0.25 or 0.5 ml/A4 size) using spray gun with subsequent plasma post-treatment. Silicon oil was purchased from Sigma Aldrich. Various exposure times of plasma pre- and post-treatment as well as repeated spraying procedures (1-3 runs) were combined.

2.2. Analytical methods

To determine the adhesion of paper with sprayed silicone oil layer the tape peel test at angle 180° was realized. Measurement was carried out using the test machine AR-1000 Adhesion/Release tester (ChemInstruments, Fairfield, Ohio, USA) at peeling speed 300 mm/min, force range 0.045 - 45 N and the adhesive tape Tesa 7475 at controlled temperature 23°C and humidity 40-50%. Parameters such as peel force, transfer peel force, and percentage of initial peel force value were obtained as results from measurement. Peel force represents force necessary to remove the adhesive tape from the paper sample under above mentioned controlled conditions. Transfer peel force means force necessary to remove used adhesive tape from previous test from reference paper. Initial value of transfer peel force represents conditions when non-used adhesive tape was peeled off from reference sample of paper. This method demonstrates what amount of oil remained on used adhesive tape. It approximates the real situation for oil remaining on the sticker peeled off from release liner paper and its ability to be stuck on target surface. Parameter “percentage of initial value” compared the measured value of transfer peel force for certain sample with value of peel force for reference sample. Contact angle measurements were carried out with a See System (Surface Energy Evaluation) analyzer (Advex Instruments, Brno, Czech Republic). A drop of distilled water (1 µl) was dropped on the coated side of paper surface. The value of the contact angle was calculated as a mean value of at least ten drops. The X-ray photoelectron spectroscopy (XPS) measurements were done on an ESCALAB 250Xi (Thermo Fisher

Scientific, East Grinstead, United Kingdom). An X-ray beam with power of 200 W (650 microns spot size) was used. The survey spectra were acquired with a pass energy of 50 eV and a resolution of 1 eV. In order to compensate for charges on the surface, an electron flood gun was used. Spectra calibration and processing were done using Avantage software. Surface morphology was studied using Scanning Electron Microscope (SEM) Mira3 (Tescan, Brno, Czech Republic) with maximal resolution 1 nm and maximal magnification 1 000 000. Detector of secondary electrons and accelerating voltage of 5 kV was used. To prevent any charging of the sample, paper samples were coated with 10 nm of gold layer.

3. RESULTS

3.1. Adhesion - tape peel test

Results of tape peel tests revealed the effect of plasma pre-treatment and post-treatment on adhesive properties of silicone layer sprayed on clay coated paper. Observed parameters were peel force (N/cm), transfer peel force (N/cm), and percentage of initial value [%]. Peel force of paper with silicone oil sprayed layer without plasma pre- and post-treatment corresponds to the value of 5.5 N/cm. Adhesion measurement showed that both plasma pre- and post-treatment have a benign influence on the low adhesion of paper with silicone oil layer. It was observed, that repetition of silicone oil spraying and post-treatment process for 3 times led to decrease of peel force to the value of 3.5 N/cm in case of 0.25 ml of sprayed oil (**Table 1**). As expected, the same trend was confirmed also for higher amount of sprayed oil (0.5 ml) and longer pre- and post-treatment times of 0.5 s when obtained peel force was the lowest at all (2.1 N/cm). The effect of pre-treatment and post-treatment time is demonstrated in **Table 2**. As can be seen, long pre-treatment (5 s) led to undesirable increase of peel force up to the value 3.8 N/cm. Importance of post-treatment can be represented by the fact that the plasma pre-treated clay coated paper with the sprayed silicone oil layer but without plasma post-treatment was characterized again by high peel force value of 5.8 N/cm. Transfer peel force is logically lower than initial peel force because of reuse of the same adhesive tape, however transfer peel force is still high enough for good adhesion of tape (sticker) on target surface. Percentage representing the ratio between transfer peel force and initial peel force corresponds to the values of 83-91%. Permanency of plasma treatment and whole oil spraying procedure is essential for shelf life of oil sprayed paper. Therefore, peel force was investigated on the same (aged) samples after 3 months and was almost the same as immediately after the plasma treatment. This finding is crucial for potential industrial application.

Table 1 The results of tape peel test presenting the adhesion properties of paper with silicone oil layer for different number of spraying runs and volume of sprayed oil

Sample (pre-treatment, volume of sprayed oil, post-treatment)	Peel force (N/cm)	Transfer peel force (N/cm)	Percentage of initial value [%]
Reference	5.5 ± 0.1	-	-
0.25 s + (0.25 ml) + 0.25 s, **1 run**	4.3 ± 0.1	5 ± 0.1	91
0.25 s + (0.25 ml) + 0.25 s, **2 runs**	3.9 ± 0.1	4.6 ± 0.3	83
0.25 s + (0.25 ml) + 0.25 s, **3 runs**	3.5 ± 0.1	5 ± 0.1	91
0.5 s + (0.5 ml) + 0.5 s, **1 run**	2.9 ± 0.1	5 ± 0.2	91
0.5 s + (0.5 ml) + 0.5 s, **2 runs**	2.6 ± 0.1	4.9 ± 0.1	89
0.5 s + (0.5 ml) + 0.5 s, **3 runs**	**2.1 ± 0.1**	4.7 ± 0.1	86

Table 2 The results of tape peel test illustrating the influence of plasma pre-treatment and post-treatment time on the adhesion properties of paper with silicone oil layer

Sample (pre-treatment, volume of sprayed oil, post-treatment)	Peel force (N/cm)	Transfer peel force (N/cm)	Percentage of initial value [%]
0 s + (0.5 ml) + 0.5 s, 1 run	2.7 ± 0.1	4.9 ± 0.1	89
0.5 s + (0.5 ml) + 0.5 s, 1 run	2.9 ± 0.1	5 ± 0.2	91
5 s + (0.5 ml) + 0.5 s, 1 run	3.8 ± 0.1	4.9 ± 0.1	89
0.25 s + (0.5 ml) + **0.25 s**, 1 run	3 ± 0.1	4.9 ± 0.1	90
0.25 s + (0.5 ml) + **0.5 s**, 1 run	3 ± 0.1	4.9 ± 0.1	89
0.25 s + (0.5 ml) + **5 s**, 1 run	3.4 ± 0.1	5 ± 0.1	90

3.2. Water contact angle and peel force

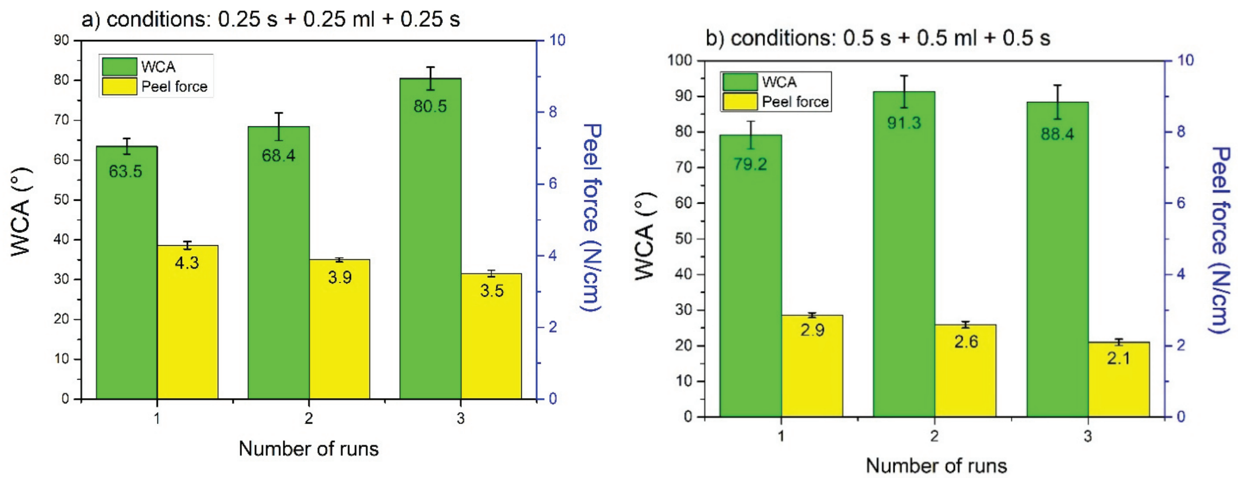

Figure 2 WCA and peel force in dependence on volume of sprayed silicone oil and number of runs

Wettability change of paper after plasma treatment and silicone oil spraying was evaluated. Promising combination of plasma pre-treatment and post-treatment was determined from previous experiments. Initial value of water contact angle (WCA) for reference paper was 76.1° ± 1.4°. Plasma pre-treatment led to hydrophilization of paper surface with WCA value around 40° depending on exposure time. Subsequent oil spraying resulted in hydrophobization and post-treatment led to better incorporation of oil into paper. Silicone oil spraying procedure is a complex process which affects surface wettability as well as the adhesion properties. Therefore, the results from WCA measurements and peel test were investigated together. WCA and peel force values in dependence on number of spraying and post-treatment runs for shorter (0.25 s) and longer (0.5 s) plasma pre- and post-treatment, and lower (0.25 ml) and higher volume (0.5 ml) of sprayed silicone oil are presented in **Figure 2**.

The effect of various times of plasma pre-treatment and post-treatment is demonstrated in **Figure 3**. The best result (combination of highest WCA and lowest peel force) was obtained for 0.5 s pre-treatment, 0.5 ml silicone oil spraying, and 0.5 s post-treatment in 2 repetitions.

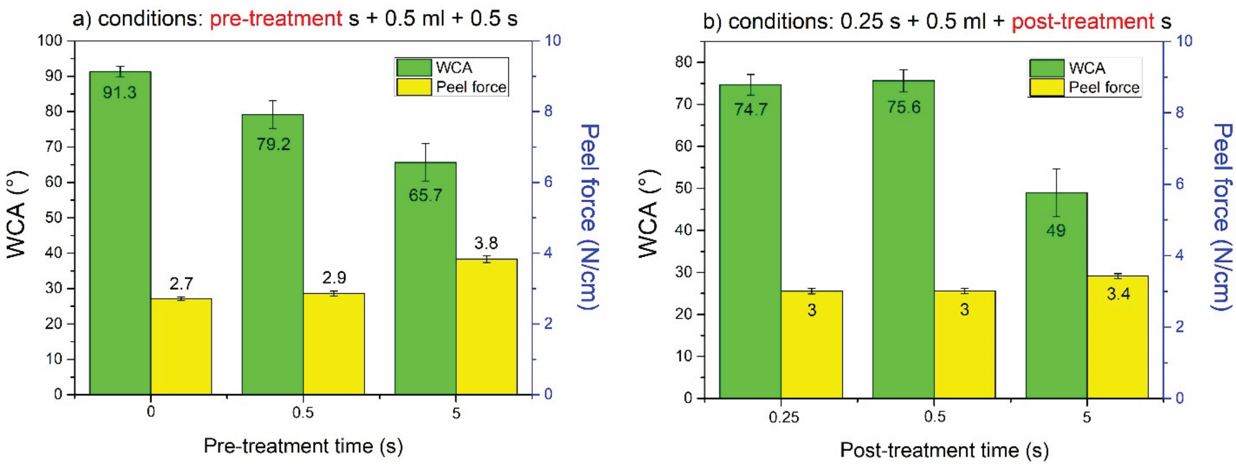

Figure 3 WCA and peel force in dependence on plasma pre- and post-treatment exposure time

3.3. Surface chemistry (XPS)

Surface chemical composition of reference (clay-coated paper), industrial corona treated paper (0.5 s, 5 s) and silicone oil (0.5 ml) sprayed paper (including pre- and post-treatment) was investigated using XPS. For plasma pre-treatment two different exposure times (0.5 s, 5 s) were used. Plasma post-treatment with exposure time 0.5 s was chosen based on the results of previous tape peel test. Results of chemical composition are presented in **Table 3** and indicate that plasma treatment led to oxidation of paper surfaces. Plasma pre-treatment for 0.5 s led to increase of oxygen from 34% to 43%, on the other hand, led to decrease of carbon amount from 47% to 36%. Plasma treatment without oil spraying had only minor effect on total amount of silicon (Si) which corresponded to the value approx. 10%. A trace level (< 0.5%) of nitrogen and calcium was detected for all samples. Silicone oil spraying procedure caused the increase of silicone to 23-24% and slightly decrease of alumina to 4-5%. This can be explained by covering the treated paper surface with silicone oil layer resulting in decrease of alumina content on the native surface. Plasma treatment made the surface hydrophilic to be able to absorb the sprayed oil as indicated by increase of O/C ratio from 0.7 to 1.8. Subsequent silicone oil spraying following by post-treatment promoted the hydrophobic properties of paper surface (decrease of O/C ratio from 1.8 to 1).

Table 3 Surface chemical composition of plasma treated and silicon oil sprayed paper at different conditions

Sample	O	C	Si	Al	Na	O/C	Si/C
Reference	34	47	9	8	2	0.7	0.2
0.5 s	43	36	10	8	3	1.2	0.3
5 s	49	27	11	10	3	1.8	0.4
0.5 s + (0.5 ml) + 0.5 s	37	35	24	4	0	1.1	0.7
5 s + (0.5 ml) + 0.5 s	36	36	23	5	0	1	0.6

3.4. Surface morphology (SEM)

No morphological changes were observed after plasma treatment on paper surface. **Figure 4** illustrates the appearance of paper surface a) clay coated paper - as received, b) plasma treated, c) plasma pre-treated, oil sprayed and post-treated. Paper surface after silicone oil spraying procedure is more conductive, therefore charging of relief edges occurred.

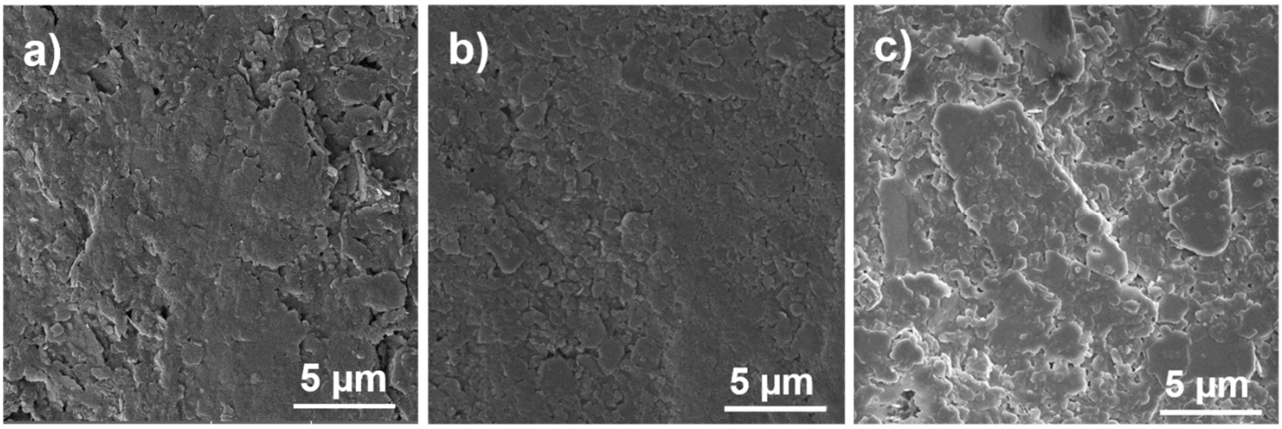

Figure 4 Surface morphology of clay coated paper samples: a) reference (as received), b) plasma treated for 5 s, c) 5 s pre-treated + 0.5 ml of sprayed oil + 5 s post-treated paper

4. CONCLUSION

WCA measurement of clay coated paper samples with sprayed silicone oil layer revealed its increase from initial value 76.1°± 1.4° indicating the lower adhesion of oil sprayed paper. The lowest peel force value (2.1 ± 0.1) N/cm and the highest WCA (91.3 ± 4.5)° was achieved for paper sample corona pre- and post-treated for 0.5 s in 3 repetitions of silicone oil spraying and post-treatment. Long pre-treatment (5 s) caused increase of peel force, therefore shorter pre-treatment time (0.25 s, 0.5 s) should be used. Peel force measured 3 months after plasma treatment and oil spraying was almost the same as immediately after treatment. XPS results indicate that plasma treatment led to oxidation of paper surfaces demonstrated by increase of O/C ratio. Oil spraying caused decrease of O/C ratio and increase of Si content. Surface morphology was not changed by plasma treatment and oil spraying as confirmed by SEM. It can be concluded that ambient air industrial corona pre- and post-treatment leads to chemically binding of the stable silicone oil layer on the paper surface resulting in low values of peel force.

ACKNOWLEDGEMENTS

This research has been supported by the project 7D16003 funded by EUROSTARS 2 and project LO1411 (NPU I) funded by Ministry of Education Youth and Sports of Czech Republic.

REFERENCES

[1] VANGENEUGDEN, D., DUBREUIL, M., BONGAERS, E., HENDRIX, W. Atmospheric DBD plasma Deposition of ECO-Friedly Release Liners for Pressure Sensitive Adhesive Tapes. *Contributions to Plasma Physics,* 2009, vol. 49, pp. 648-654.

[2] SKÁCELOVÁ, D., KOVÁČIK, D., HOMOLA, T., ČECH, J., ČERNÁK, M. *Atmospheric Pressure Plasmas: Processes, Technology and Applications*, *1st ed.* New York: Nova Science Publishers, Inc., 2016. pp. 227-236.

[3] FANG, Z., XIE, X., TAJIMA, S., KOMVOPOULOS, K., MORENT, R., DE GEYTER, N. Modification of ink-jet paper by oxygen-plasma treatment. *Journal of Physics D: Applied Physics,* 2007, vol. 40, pp. 3689-3696.

[4] BALU, B., KIM, J. S., BREEDVELD, V., HESS, D. W. Design of Superhydrophobic Paper/Cellulose Surfaces *via* Plasma Enhanced Etching and Deposition. *Contact Angle, Wettability and Adhesion,* 2009, vol.6, pp. 235-249.

[5] JIANG, Q., LI, Y., XIE, J., SUN, J., HUI, D., QIU, Y. Plasma functionalization of bucky paper and its composite with phenylethynyl-terminated polyimide. *Composites: Part B. Engineering,* 2012, vol. 45, no. 1, pp. 6-12.