Asian Journal of Chemistry; *Vol. 23, No. 2 (2011), 863-866*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Influence of Dielectric Barrier Discharge treatment on Adhesion Properties of Platinum Coated Polypropylene Foil and Polypropylene Fabrics

S. SHAHIDI[1,*], J. WIENER[1], M. GHORANNEVISS[2] and M. ŠTEPÁNKOVÁ[1]

[1]Department of Textile Chemistry, Faculty of Textile, Technical University of Liberec, Liberec, Czech Republic
[2]Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, P.O. Box: 14665-678, Tehran, Iran

*Corresponding author: E-mail: shahidish@yahoo.com; sheila.shahidi@tul.cz

(*Received*: 1 June 2010; *Accepted*: 14 October 2010) AJC-9183

This work report, the effects of low temperature plasma treatment on physical and chemical properties of polypropylene fabrics and foils. We have used a dielectric barrier discharge (DBD), working in an atmospheric pressure air. More polar functional groups were present on the substrate surface after dielectric barrier discharge pretreatment. The effects of plasma treatment on the adhesion properties of polypropylene samples were also studied. It is shown that the adhesion of fabrics and foils of polypropylene to platinum, when deposited on them, have been improved after plasma treatment.

Key Words: Dielectric barrier discharge, Film, Fabric, Polypropylene.

INTRODUCTION

Polypropylene (PP) and polyethylene terephthalate (PET) fibres are used for a wide variety of applications in many technological fields because they have some excellent bulk properties, such as high strength-to-weight ratio, good resistance to corrosion and relatively inexpensive production[1]. These materials are frequently used as films and foils for packaging, protective coatings and sealing applications[2]. However, polymers are hydrophobic, low-surface energy materials and thus they do not adhere well to other materials. Metallization of polymeric substrates is currently widely investigated because of various applications in microelectronics, packaging, optics and medical implants[3]. Recently, nano-structured materials based on nano-metal particles have also been studied extensively for various applications on account of their attractive physical, chemical and catalytic properties[4-6].

In this field, the adhesive property between film and substrate is one of the most important properties because the film delaminating should be suppressed during manufacturing process. So it is desirable to modify polymer surfaces and increase the surface free energy while keeping their no-change bulk properties for many commercial applications. Traditional methods of surface treatment are mostly chemical processes. However the ecological requirements force the industry to search alternative environmental safety methods[1,7].

The technique of plasma treatment is an effective surface modification way to save processing cost and to avoid environmental pollution problem[8-14].

Recently, surface modification using atmospheric pressure plasma treatment is being widely used and it can be realized in air with no vacuum system. The last two decades, dielectric barrier discharges (DBDs) are widely used as a surface modification tools[15].

There has been growing interest in investigation of the industrial applications of the barrier discharge technology. This type of discharge has advantages over many other types of discharges that dielectric barrier discharges require no vacuum system and can be used for processing of large samples[16].

In this research work we have investigated the effects of using a dielectric barrier discharge (DBD) device on modifying the surface properties of polypropylene foils and fabrics and specially in studying the adhesive properties of these material to platinum.

EXPERIMENTAL

In this research work, we studied the effects of dielectric barrier discharges treatment on the commercial polypropylene foil (Tatrafan KX-30 μm) and polypropylene fabrics. The samples first cleaned and extract with chloroform, the cleaned samples were treated by a dielectric barrier discharge (DBD) for up to 10 min. The experimental set up is shown in Fig. 1. This device is applied for treating plane materials at an atmospheric pressure. The reactor mainly contains an Al_2O_3 ceramic electrode (active area 9 cm × 20 cm) and a high power supply unit (500 W). The electrode is cooled by a circulated oil system which is operated by a pump.

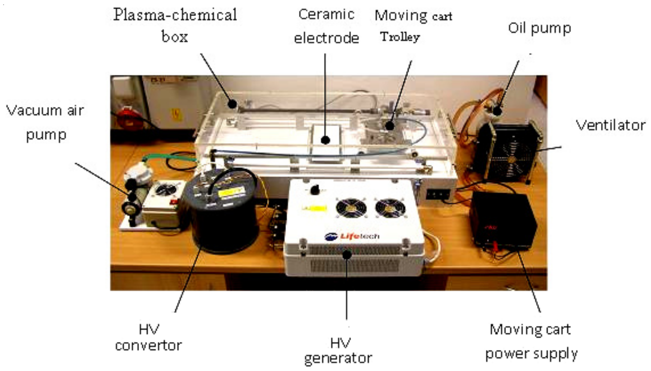


Fig. 1. Experimental setup

The condition chosen for device to operate was an alternating voltage of 20 kV and a power of 300 W. The gap between the electrodes could be adjusted in the range of 0.5-2.5 mm.

The system worked in air at an atmospheric pressure, though it was also possible to use different kinds of gases as the discharge medium. Samples were attached to a movable trolley by means of a vacuum sucker. The movable trolley which supplies a linear displacement is responsible for moving the samples to get contact with plasma.

After plasma treatment, surface roughness of polypropylene foils was measured by atomic force microscope (AFM) (Park Scientific Instrument). Atomic force microscope images were obtained with the silicon nitride probe mounted on a cantilever. Imaging was performed in contact mode. The morphology of the fabric samples was observed by a scanning electron microscope (SEM) using a LEO 440 I with an accelerating voltage of 20 kV. The resolution of 3 μm was chosen. The samples were pre coated with gold, using a sputter coater. The magnification of the image was set in the range of 3000X.

Fourier transform infrared spectroscopy (FTIR) was also used for investigation of the chemical structure of the foils and fabrics. Infrared spectra of the samples were obtained using a Perkin-Elmer, FTIR spectrometer. For coating the samples with platinum a Sputter Anlage für REM-Proben SCD 030 was used. The time of coating and electric current were: 120 s, 15 mA, respectively. The wet ability of the samples were evaluated by water drop test according to AATCC 79-2000 standard, in which drops of controlled size were placed at a constant rate upon the fabric surface and the duration of the time required for them to penetrate to the fabrics were measured. The adhesion properties were measured using abrasion (Martindale 2000, Shirley Ltd.) and rubbing tests were done according to the European standard ISO 105-X12: textiles-tests for colour fastness-colour fastness to rubbing. Samples were rubbed by dry wiping fabric and the staining of wiping fabrics was evaluated according to the grey scale.

RESULTS AND DISCUSSION

The samples of polypropylene foils and fabrics were treated under different time intervals duration up to 10 min and then analyzed by FTIR, SEM and AFM to compare the results. It is found that, under a power of 300 W and voltage of 20 kV a duration of 8 min gives the best results. In shorter time no significant changes occurred on the samples and in longer exposure time, some parts of the samples were melted.

Fourier transform infrared spectroscopy: The modified polypropylene was characterized by FT-IR in order to give better understanding of the enhanced adhesive properties. As shown in Fig. 2, as-received polypropylene fabric exhibits some peaks at 840, 890, 960, 1180, 1370, 1450 and 2900 cm^{-1}, which are well matched to those reported in the handbook[17]. But upon dielectric barrier discharge treatment, an extra peak appears around 1708 cm^{-1}, which can be attributed to C=O stretching, moreover, absorption in the range of 1628-1593 cm^{-1} is related to resonance C-O bonds[17-21].

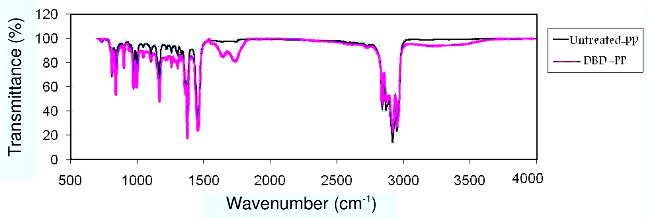


Fig. 2. FTIR spectra of untreated and DBD treated PP fabric

To achieve a high rubbing fastness, a strong adhesion between the adhesive and the substrate is essential. This requires the formation of covalent bonds between the molecules of the adhesive and the adherent and thus a good match between the functional groups of the substrate surface and the adhesive material. The formation of additional functional groups at the surface is probably the most significant contribution of the plasma treatment to the adhesion improvements. Probably both the oxygen groups and the large variety of functional groups produced, contribute to this improvement. Variety of functional groups can be especially an advantageous when different types of adhesives are to be used. Incorporation of oxygen is also responsible for the increase in surface energy.

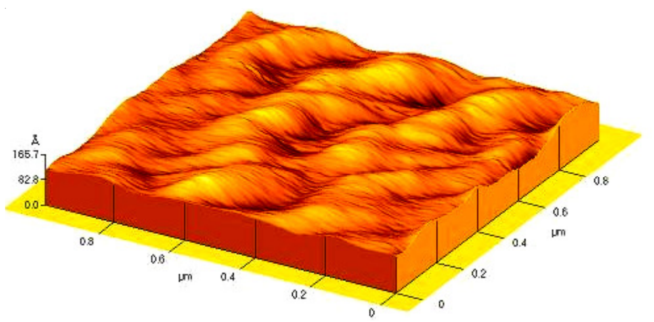
Water drop test: When polypropylene surfaces were treated by plasma, their surface free energy considerably increased and their wet ability improved. The results shown in Table-1, in which the absorption times have been recorded for different treated and original samples. As seen after plasma treatment the water absorption time is much decreased. The decrease of water-absorption time can be attributed to introduction of polar groups such as hydroxyl and carboxyl groups due to plasma chemical modification and morphological changes. Time of absorption for untreated polypropylene fabrics is about 14 min and by coating the samples with platinum, this time is increased more than 1 h.

TABLE-1
ABSORPTION TIME OF TREATED AND UNTREATED FABRICS

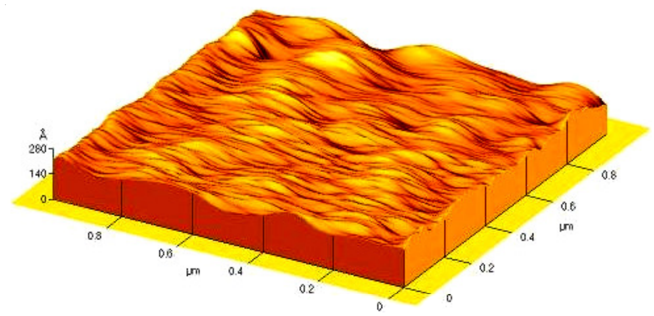
Sample	Absorption time
Untreated	14 min
DBD treated polypropylene fabric for 120 s	2 s
DBD treated polypropylene fabric for 480 s	1 s
Untreated-Pt coated	75 min
DBD treated-Pt coated	75 min

Atomic force microscope (AFM): Adhesion properties are strongly influenced by the surface topology. A microscopic and nano metric roughness can also lead to a mechanical interlocking between the two partners of the adhesive joint.

The surface topology of original polypropylene and also treated films were measured with atomic force microscope, the results are shown in Fig. 3. The average surface roughness (Ra) has increased from 9.4 nm for the original polypropylene surface to 18.3 nm, for treated specimens. This investigation revealed that the roughness of the films has been increased due to the dielectric barrier discharge treatment. Surface roughening of polymer substrate can result from the difference in etching rates between crystalline and amorphous regions of the polymer during reactive ion etching[22,23]. It is believed that complete wetting samples is primarily caused by a large increase in surface roughness induced by an ion bombardment together with the generation of oxygen containing functional groups. Surface micro-roughness produces a greater surface area leading to increased total surface area and as a result reduced contact angles even though it is difficult to differentiate the effect of surface roughness and surface functional groups on the measured wetting time.



polypropylene-untreated



PP-DBD treated

Fig. 3. Atomic force microscope images of untreated and DBD treated polypropylene foil

Scanning electron microscopy: Fig. 4 shows the photographs obtained by an scanning electron microscope from the treated fibers, as well as of non-treated ones. As shown the treated samples have suffered some morphological changes on their surfaces, with the formation of ripple-like patterns. Also some of the spots on the surface of original polypropylene have disappeared due to the treatment.

Adhesion properties: For measuring the adhesive properties, both treated and untreated samples were coated with platinum using sputtering system and the results were compared with rubbing and abration testers. The adhesion properties of Pt-coated dielectric barrier discharge treated polypropylene samples and Pt-coated untreated samples were evaluated in terms of the fastness towards rubbing and abrasion, using the gray scale according to ISO standard recommendations of which the results are given in Table-2. Assessment of fastness involves a visual determination of either change in shade or staining of an adjacent material. The graduation of the gray tones in the scales is defined as the smallest difference in depth, which is of commercial significance.

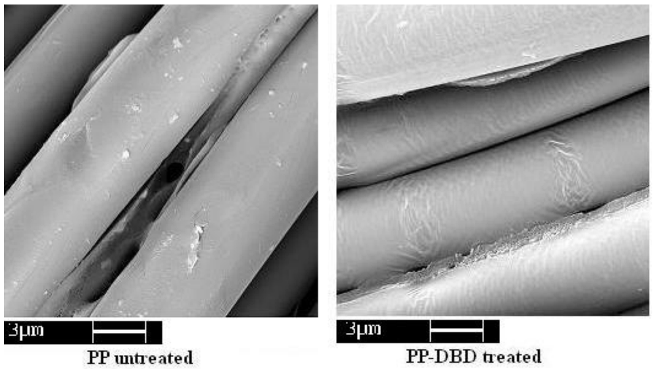


Fig. 4. SEM images of untreated and DBD treated polypropylene fabric

TABLE-2
RESULTS OF RUBBING AND ABRASION FASTNESS OF BOTH TREATED AND UNTREATED POLYPROPYLENE FOILS AND FABRICS

Samples	Degree of rubbing fastness	Degree of abrasion fastness
Untreated polypropylene foil	3	2
DBD treated polypropylene foil for 120 s	4	3
DBD treated polypropylene foil for 480 s	5	4-5
Untreated polypropylene Fabric	3	3
DBD treated polypropylene Fabric for 120 s	3-4	3-4
DBD treated polypropylene fabric for 480 s	5	5

Thus, as given in Table-2, the dielectric barrier discharge treatment on polypropylene samples has caused an increase in the adhesion of the platinum particles to the sample fibers as compared to untreated samples. This is due to the creation of some functional groups and some morphological changes on the surface of the samples after the dielectric barrier discharge treatment which has caused the surface energy of samples to be increased. An observed correlation between the increase in the RMS surface roughness and the adhesion properties (Table-2) in this study also confirms the effectiveness of surface roughening on the significant adhesion improvement. It is also found that by increasing the time of dielectric barrier discharge treatment till to an optimums value (8 min) this feature improves, however treating more than 10 min would lead to melt and destroy the fibers.

Conclusion

Atmospheric pressure plasmas are an interesting alternative to other pretreatment methods (*e.g.*, low-pressure plasma or wet chemical treatment) because of in-line process capabilities, relatively low costs and low requirements on personal and environmental safety. In present report, we have studied the effects of a dielectric barrier discharge device working at atmospheric pressure on physical and chemical properties of polypropylene. The results from the atomic force microscope and wetting time measurements showed a gradual increase in the surface roughness of plasma-treated surface with the time of exposure increased. The wettability of polypropylene samples is strongly improved after dielectric barrier discharge pre-treatment. As expected, a higher etching rate of the surface after dielectric barrier discharge treatment was observed. The adhesion strength between platinum layer and polypropylene substrates is increased significantly. In addition to the increased formation of functional groups such as C=O and C-O-C by the plasma treatment, surface roughening is ascribed to the increase in the measured adhesion strength due to increased surface area and the largely roughened morphological effects induced by surface etching in the present experimental conditions.

ACKNOWLEDGEMENTS

This research has been supported by KAN 101630651.

REFERENCES

1. C. Cheng, Z. Liye and R.-J. Zhan, *Surface Coating Tech*., **200**, 6659 (2006).
2. N. De Geyter, R. Morent, C. Leys, L. Gengembre and E. Payen, *Surface Coating Tech.*, **201**, 7066 (2007).
3. C. Bao, D. Xu, S.-Z. Yang and C. Liu, *Mater. Chem. Phys*., **61**, 163 (1999).
4. S. Kim, Y. Jung and S.-J. Park, *Colloids Surf. A: Physicochem. Eng. Asp.*, **313-314**, 189 (2008).
5. O. Paschos, P. Choi, H. Efstathiadis and P. Haldar, *Thin Solid Films*, **516**, 3796 (2008).
6. A. Mackova, V. Svorcik, P. Sajdi, Z. Stryhal, J. Pavlik, P. Malinsky and M. Slouf, *Vacuum*, **82**, 307 (2008).
7. H.-Y. Nie, M.J. Walzak, B. Berno and N.S. McIntyre, *Appl. Surface Sci*., **144-145**, 627 (1999).
8. M.H. Han, J.P. Jegal, K.W. Park, J.H. Choi, H.K. Baik, J.H. Noh, K.M. Song and Y.S. Lim, *Surface Coatings Tech.*, **201**, 4948 (2007).
9. M. Tahara, N.K. Cuong and Y. Nakashima, *Surface Coating Tech*., **173-174**, 826 (2003).
10. C.-K. Jung, I.-S. Bae, S.-B. Lee, J.-H. Cho, E.-S. Shin, S.-C. Choi and J.-H. Boo, *Thin Solid Films*, **506-507**, 316 (2006).
11. M. Noeske, J. Degenhardt, S. Strudthoff and U. Lommatzsch, *Int. J. Adhesion Adhesives*, **24**, 171 (2004).
12. S. Shahidi, M. Ghoranneviss, B. Moazzenchi, A. Anvari and A. Rashidi, *Surface Coating Tech.*, **201**, 5646 (2007).
13. S. Shahidi, M. Ghoranneviss, B. Moazzenchi, A. Rashidi and D. Dorranian, *Fibers Polym*., **8**, 123 (2007).
14. M. Ghoranneviss, S. Shahidi, B. Moazzenchi, A. Anvari, A. Rashidi and H. Hosseini, *Surface Coatings Tech*., **201**, 4926 (2007).
15. N. De Geyter, R. Morent, C. Leys, L. Gengembre, E. Payen, S. Van Vlierberghe and E. Schacht, *Surface Coating Tech.*, **202**, 3000 (2008).
16. N.-Y. Cui, D.J. Upadhyay, C.A. Anderson, B.J. Meenan and N.M.D. Brown, *Appl. Surface Sci*., **253**, 3865 (2007).
17. C.J. Pouchert, The Aldrich library of FT-IR spectra, vol. 2, edn. 1, p. 115 (1985).
18. C. Oehr, *Nucl. Instrum. Methods Phys. Res. B*, **208**, 40 (2003).
19. M.J. Tsafack and J. Levalois-Grützmacher, *Surface Coating Tech*., **201**, 2599 (2006).
20. D.R. McKenzie, K. Newton-McGee, P. Ruch, M.M. Bilek and B.K. Gan, *Surface Coatings Tech.*, **186**, 239 (2004).
21. R.E. Farsani, S. Raissi, A. Shokuhfar and A. Sedghi, *World Acad. Sci. Eng. Tech.*, **50**, 430 (2009).
22. A.M. Ektessabi and S. Hakamata, *Thin Solid Films*, **377-378**, 621 (2000).
23. S.H. Kim, S.W. Na, N.-E. Lee, Y.W. Nam and Y.-H. Kim, *Surface Coatings Tech.*, **200**, 2072 (2005).