The Influence of Atmospheric Pressure Plasma Treatment on Surface Properties of Polypropylene Films

Andrea Oravcova, Ivan Hudec

Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, Bratislava 812 37, Slovakia

xoravcovaa@stuba.sk

Abstract

In this work the influence of the atmospheric pressure plasma treatment on the surface properties of polypropylene (PP) films was investigated. The film samples were modified by atmospheric pressure plasma treatment by diffuse coplanar surface barrier discharge (DCSBD) using ambient air as working gas. The contact angle measurement, the test pen method, atomic force microscopy (AFM) and attenuated total reflection technique Fourier transformed infrared spectroscopy (ATR-FTIR) were applied to analyze the changes of the surface of the polymer film. In all experiments, the contact angle of the treated polypropylene samples decreased and the surface energy of the samples increased in comparison with the plasma untreated samples. The proper surface energy for printing using solvent-based inks was detected by all the samples. There were not observed any significant changes in mechanical properties of the films after plasma treatment by measuring their tear parameters.

Key words: plasma treatment, polypropylene film, surface energy, wetting

Introduction

Atmospheric-pressure, non-equilibrium plasmas produced by the dielectric barrier discharge are very attractive for various industrial applications because of their low-cost, high speed and the ability to operate without vacuum. Depending on the gas composition and plasma conditions, ions, electrons, fast neutrals, radicals and VUV radiation contribute to the polymer treatment, resulting in etching, activation and/or cross-linking (Hegemann, 2003). Plasma surface activation means usually plasma treatment when non-polymerizing working gases are used. The chemical surface modification is initiated by the radical reaction of plasma species and the polymer surface. In atmospheric pressure plasmas, the surface activation typically takes places with oxygen-containing gas mixtures such as ambient air. Low-functionality polypropylene surfaces become more reactive by enhancing the concentration of polar groups on the surface.

The advantage of the plasma treatment is the ability to change the surface properties of the most external layers of the material without modifying its bulk characteristics (Inagaki, 1996). It means there is no change in mechanical properties, too.

The aim of this work was to improve surface energy and wettability of the films before printing. The printability of polymer materials is dependent upon the chemical and physical properties of the polymers. The surface of polypropylene consists solely of carbon and hydrogen. Using appropriate plasma treatment, the surface of the non-polar polymer material may be activated to contain the variety of functional groups including oxygen-based functionalities (carbonyl, carboxyl, ether, peroxide etc.) or nitrogen- based groups resulting in modification of the surface properties.

The result of plasma modification of the polymer film is the increase of the surface energy of the polymer and the improvement of surface wetting by liquid. The minimum value of the surface free energy of the material being printed using the solvent-based inks is 38 mJ m^{-2} (Panak et al., 2008).

Materials and Methods

The transparent PP film (monoaxially oriented polypropylene, 30 μm thickness, CHEMOSVIT FOLIE, a.s. Svit) determined for packaging various food products was studied. The films were activated by atmospheric pressure plasma treatment by diffuse coplanar surface barrier discharge DCSBD (350W input) using ambient air as working gas. The treatment time varied from 1s to 5s.

Wetting was characterized by the contact angle measurement of sessile drop (4μl, testing liquids; water, glycerol, α-bromonaphthalene, formamide, ethylene glycol) using CCD camera (SEE software 6.1, MU Brno, Czech Republic). The calculation of surface energy was performed by using Owens - Wendt regression method. The test pen Quick Test 38 was also used to confirm changes in wetting of the films. The functional groups of the polypropylene surface after plasma treatment were monitored by the attenuated total reflection (ATR) technique of FTIR spectroscopy (Excalibur, FTS 3000MX, Digilab, USA). Atomic force microscopy (AFM, IC-mod, Veeco Di CP-II) was applied to analyze the changes in morphology of the samples. Mechanical properties were measured and calculated by Zwick Tensile tester (by STN ISO 527).

Results and Discussion

The surface properties of the plasma-treated PP films were monitored by using contact angle measurements in testing liquids with different polarity and surface free energy calculation. As it can be seen in the Fig.1, polar liquids, such water, do not wet the surface of the untreated hydrophobic PP film in comparison with the treated film sample (Fig.2).

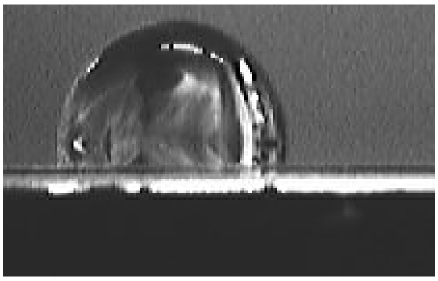


Fig.1 A drop of water on the PP film **before** treatment

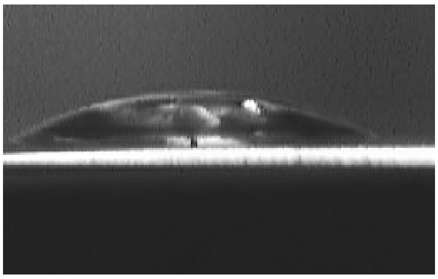


Fig.2 A drop of water on the PP film plasma **after** plasma treatment (5s)

The angles of water and other testing liquids on PP film are largely decreased with increasing treatment time, it means that the values of total surface energy, calculated by Owens-Wendt regression method, are increased, as shown in Fig.3. There is a significant increase in the polar (AB) component of surface energy.

The required surface energy for printing using solvent-based inks (38 mJ/m^2) was detected by all the investigated samples. Printing ink-wettability was also confirmed by the test pen Quick Test 38. In the image Fig.4 is shown untreated and wettable 5s-plasma treated film.

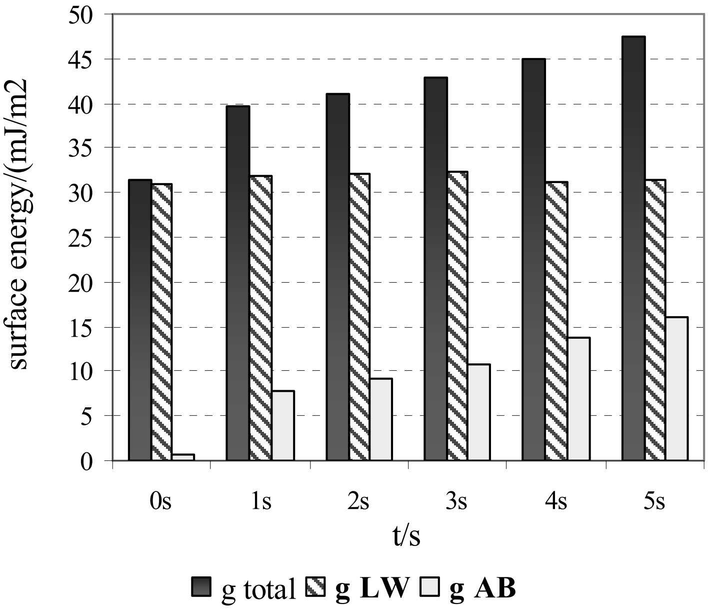
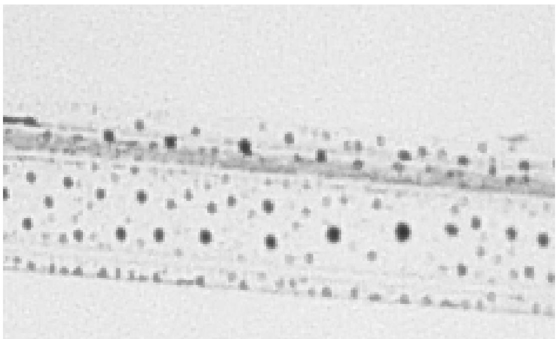


Fig.3 Influence of the time of plasma treatment on the surface energy



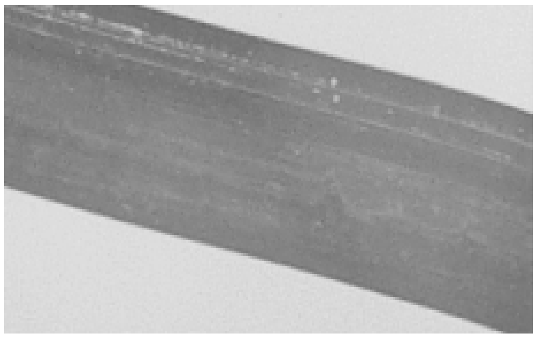


Fig.4 Test by Quick Test 38

untreated **5s plasma treated film**

AFM technique was used to study changes in morphology of PP films as it can be seen in Fig.5 and Fig.6. There are changes in roughness, the value of middle roughness (RSM) increased (RSM=3.1nm for untreated film sample) after plasma treatment (RSM=24nm for 5s plasma treated film sample). It can be caused by thermal effects of plasma or chemical reactions and sputtering.

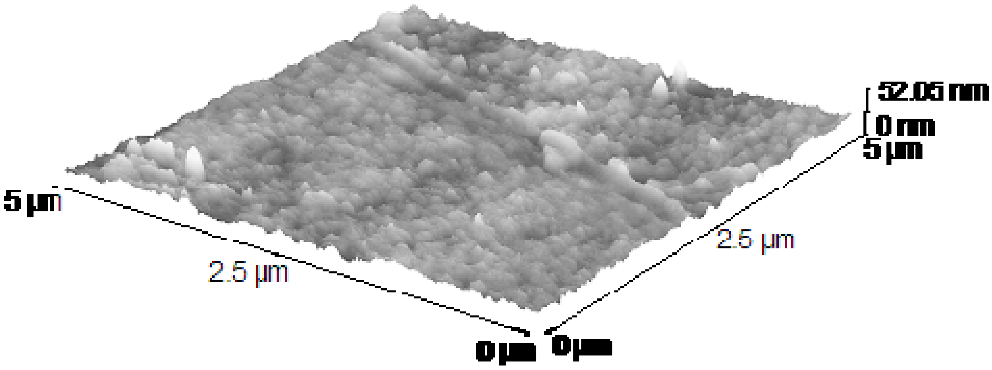


Fig.5 AFM image of the untreated film, RSM= 3.1nm

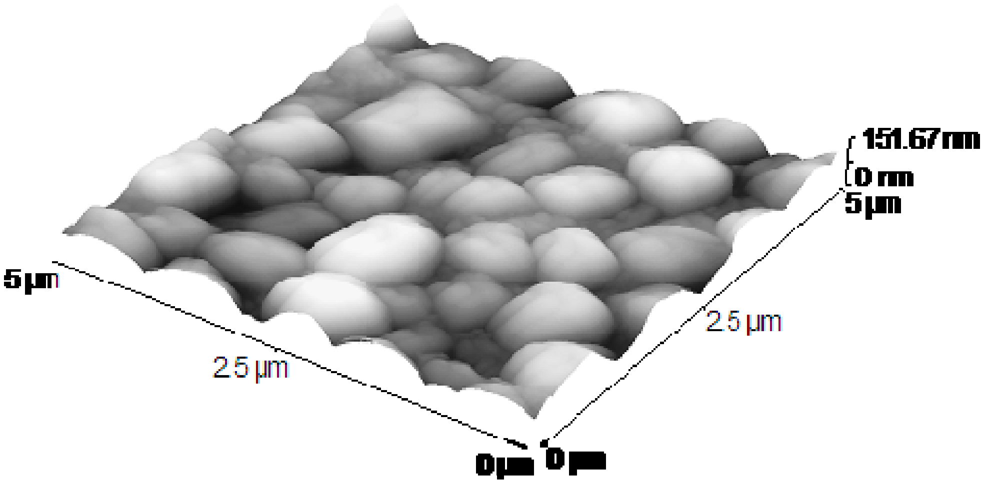


Fig.6 AFM image of the 5s plasma treated film, RSM= 24nm

The surface functionalities were also detected by ATR-FTIR spectroscopy. Fig.7 shows the influence of plasma discharge on chemical composition of surface of polypropylene films.There are some small surface changes of PP films, before and after plasma treatment, in the region of carbonyl and carboxyl groups (1520-1750 cm^{-1}). It confirms creation of small amount of polar functional groups on the film.

As it was expected, plasma treatment has no significant influence on mechanical properties ("bulk properties"). The values of tensile strength at break varied from 21.9 (3s) to 23 MPa (1s), the value for untreated sample was 23 MPa.

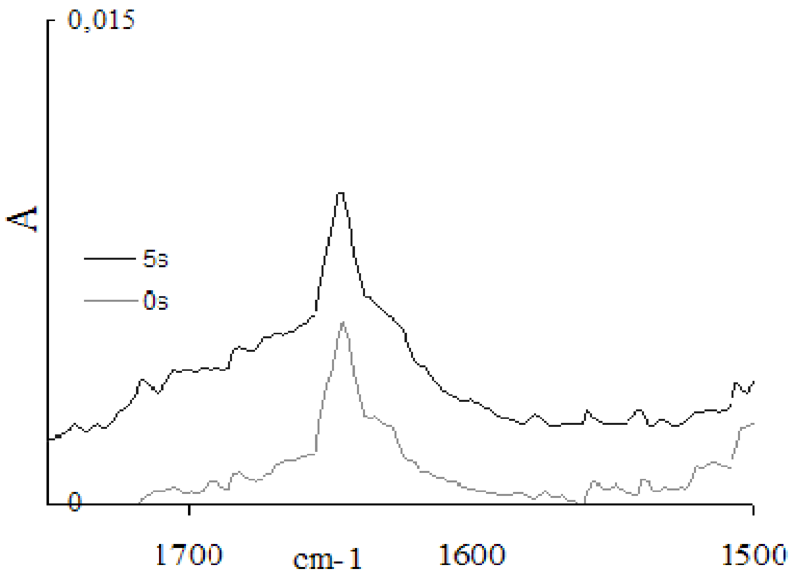


Fig.7 ATR-FTIR spectrum of untreated (0s) and plasma treated (5s) PP films

Conclusion

Based on obtained results it is possible to note that the plasma treatment at atmospheric pressure by diffuse coplanar surface barrier discharge seems to be a successful technique for improving wettability of hydrophobic polymer film materials.

As performed experiments showed, the contact angle of the treated biaxially oriented polypropylene films decreased and the surface energy of the samples increased in comparison with the plasma untreated samples. Improved wettability of the samples was also obtained by using the test pen. The proper surface energy for printing using solvent-based inks (38 mJm^{-2}) was detected by all the investigated samples after plasma treatment in ambient air. It was confirmed that plasma treatment has no significant influence on mechanical properties of polypropylene films, too.

References

Hegemann, D., Brunner, H., Oehr,Ch.:(2003) Nucl. Instr. And Meth. In Phys. Res B 208:281-286

Inagaki N.: (1996) Plasma Surface Modification and Plasma Polymerization, CRC Press, London

Panák J., Čeppan,M., Dvonka,V., Karpinský, Ľ., Kordoš, P., Mikula,M., Jakucewicz,S.: (2008) Polygrafické minimum, TYPOSET, Bratislava, 169