Investigating the effects of plasma on the surface free energy of biaxially-oriented polypropylene with a focus on the alterations of surface morphology

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Abstract: Gliding arc plasma was utilized in different durations for surface modification of BOPP. Surface Free Energy values (SFE) of the surfaces were calculated through Contact Angle Measurement(CAM).Moreover, morphology was studied by Atomic force microscopy (AFM) and Scanning electron microscopy(SEM). Plasma smoothened the surface initially, followed by applying significant roughness. Meanwhile, SFE had a steady growth trend. In conclusion, the rise in the SFE was not happening as a consequence of increased roughness.

Keywords: gliding arc, plasma, polypropylene, roughness, surface free energy, morphology

1. Introduction

Biaxially-oriented polypropylene (BOPP) is extensively used in the packaging industry due to its numerous advantages. However, it suffers from an important drawback that makes challenges for the consumers. This problem refers to surface hydrophobicity and poor wetting on their surfaces which leads to none-printable surfaces. Over time, several methods have been proposed to overcome this challenge such as flame treatment, organic solvents' etching, UV radiation, laser, and plasma modifications.

Surface experiences different physical and chemical changes after the plasma modification. Plasma is produced by charged (electrons and ions) and neutral (ground state and excited molecules) species. These species affects the polymer chains through crosslinking, bridging, Hydrogen-Abstraction (H-Abstraction), and chain scission. As a result of these phenomena on the surface and creation of polar groups, functionalization on the surface takes place. Simultaneously, it applies changes on the surface through roughening. This leads to growth in the SFE and hydrophilicity. In most of the literature considering the plasma surface modification of polyolefins, it has been reported that the increased treatment time caused a steady rise in the surface roughness. Leroux et al. [1]. Observed an increase in the average surface roughness of PP from 5.8 nm to 12.9 after corona plasma treatment of the surface. Nai-Yai Cui treated the PP surface via air dielectric barrier discharge (DBD) plasma and has reported enhanced roughness up to 74 nm. Navaneetha Pandiyaraj et al. [2]. Modified the surface of PP film by air plasma (in glow discharge regime) in the duration from 2 to 20 minutes and observed a regularly growing root-mean-squared (RMS) roughness of the surface. Siriporn Theapsak et al. [3]. Applied air plasma (via DBD reactor) to polyethylene (PE) surface for 10 seconds and the roughness increased from 29 nm to 37 nm. In the publications in this area, there are very rare studies referring to fluctuations in the surface roughness during the modification. T.Felix[4]. has reported fluctuations in the roughness values; however, the roughness of all samples was higher than the untreated sample. In this article, the surface roughness alterations of BOPP due to the surface treatment by gliding arc plasma (working gas: air) has been investigated. The striking point about the roughness of the current material after the treatments was the lower roughness values of the treated surface until a specific duration of treatment and in some durations, very level and smooth surface profiles were observed. With extended durations of plasma exposure, the roughness values increased. SFE was reckoned as an essential criterion for determining the effectiveness of plasma modification and degree of applied hydrophilicity.

2. Experimental

A commercial grade BOPP film (Polex 221S Polfilm Co., Iran) fabricated for packaging applications was used in this study. Before treatments, BOPP film specimens were ultrasonically washed with acetone and deionized water and blown-dried in a vacuum chamber with nitrogen flow. In the treatment step, specimens were surface processed with air gliding arc plasma. Gliding arc is a type of plasma reactor consisting of two diverging electrodes. Here, plasma is created by conducting a high voltage in the area that two electrodes have the closest distance to each other. The produced plasma included small sparks that start to slip out on the electrodes by out coming gas flow from the nozzle. Therefore, the gas flow causes movement of the plasma produced species on the surface of the diverging electrodes. Thus, the length of the formed spark increases and this causes a fall in the current density of each spark (formation of non-thermal spark). The produced sparks are responsible for the surface treatment and doing the surface etching, ablation, cleaning, and functionalization with high efficiency. Fig. 1 illustrated a schematic representation of the utilized gliding arc plasma. In this equipment, the distance between nozzle and surface of the polymer was 15 mm. The frequency and power of the plasma reactor were 50 Hz and 300 w, respectively. For evaluating the voltage alteration, Tektronix P6015 (V) high-voltage probe, was employed and the data was displayed on an oscilloscope. The probe was capable of measuring up to 12 kV in DC voltages and up to 42 kV in AC voltages (measurement accuracy: 2%). The measured peak-peak potential difference was 27 kV. The analysis was performed three hours after finalizing the treatment procedure.

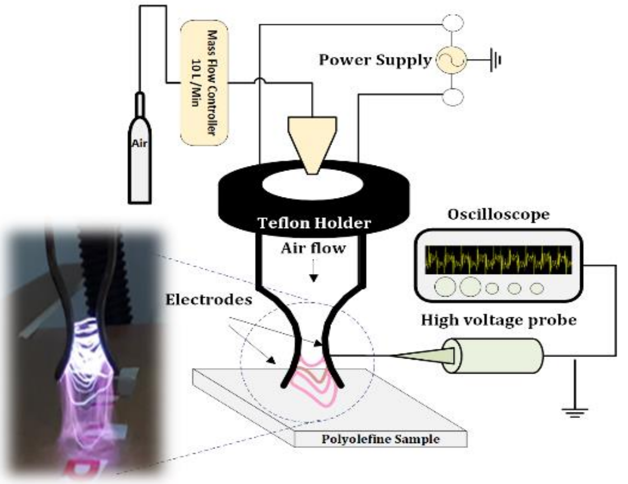

Fig. 1. Schematic of the utilized gliding arc plasma reactor

For investigating the surface topography and calculating the surface roughness parameters, AFM analysis was performed in ambient air with a scan rate of 2 Hz. An Ambios Technology USPM Atomic Force Microscope (USA) equipped with a 180 kHz resonant frequency silicon cantilever was utilized in tapping mode for this purpose. For capturing the morphology micrographs of the specimens, FE-SEM was used by means of a MIRA 2 LMU FE-SEM produced by Tescan (Brno, Czech Republic). The accelerating voltage of the microscope was 15 kV. Static contact angle values of two test liquids (De-ionized (DI) water and Diiodomethane) were measured on the surfaces of samples in the sessile drop method. The Owens-Wendt-Rabel-Kaelble approach was employed [5,6] according to ASTM D 7490-08 standard test method to calculate the polar and dispersive components of the SFE. Equation 1 presents the mathematical formulation of this approach.

$$\left[\frac{1+cos\theta}{2}\right] \times \left[\frac{\gamma_L}{(\gamma_L^d)^{0.5}}\right] = (\gamma_S^p)^{0.5} \times \left[\frac{\gamma_L^p}{\gamma_L^d}\right]^{0.5} + (\gamma_S^d)^{0.5} \qquad (1)$$

3. Results and discussion

The variations of surface free energy are along with the changes in the morphology of the surface. Fig. 2 presents the alterations of RMS and R_p roughness versus the plasma treatment time. Topography images of the untreated and treated for different durations samples. Fig 3. When the high energy plasma species impacts the polymer surfaces cause surface etching, crosslinking, branching, and chain scission on the top nonmetric layer of the surface. The initial decreasing and then rising trend in Fig. 2, which is a different trend than the most reported ones in the literature, can be described with a model introduced by [7]. In this model, surface roughness exerted by plasma etching is categorized into three regimes associated with the degree of. In the first Regime, the rate of crosslinking is relatively low in comparison with chain scission, so that aggregation and thus surface roughness are minimal. In the second regime, the rate of crosslinking is comparable to the rate of chain scission, inducing aggregation that leads to surface roughening. In the third regime, the rate of crosslinking is high, leading to an extensive crosslinked layer, suppressing mobility and aggregation, thus resulting in low surface roughness. The roughness on the untreated specimen was 8.86 nm. After the plasma treatment for 60 s, the roughness reaches to a value lower than the untreated one. However, after 90 s and 120 s of treatment, it increases. This happens in a condition that the surface free energy for all of the duration of treatment is higher than the untreated specimen.

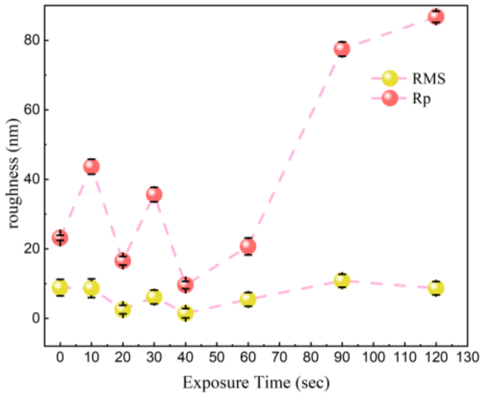

Fig. 2. Root-mean-squared (RMS) roughness and Maximum profile peak height (Rp) of the plasma-treated samples with different treatment durations

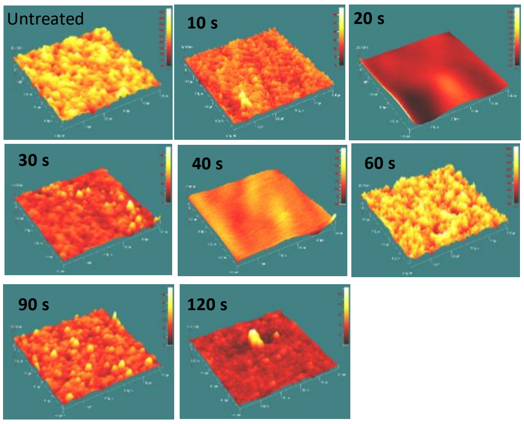

Fig. 3. AFM topography images of the untreated and treated for different durations samples

According to Wenzel theory, for the surfaces with contact angle values of less than 90°, surface roughening causes more hydrophilicity on the surface. In the obtained results, the roughness value was declined from 8.86 nm to 1.5 nm, whereas, surface free energy possess a growing trend. Therefore, the Cassie–Baxter, that considers chemical heterogeneity in the smooth surface is more applicable in the current study [4]. As can be seen in Fig. 2, roughness decreased about 90% only with 20 s of surface treatment. This can be associated with the high rate of crosslinking, decrement in the mobility, and aggregation of the chains (third regime). Fig. 4 illustrates the FESEM micrographs of the untreated and 120 s treated specimens. It can be observed that 120 s treated sample has a greater number of areas with higher height. This corroborated the obtained Rp values from the AFM analysis. For the sample with 120 s of treatment, the highest Rp amount was recorded that indicated the existence of high peaks on the surface of this sample. This unusual trend, i.e., smoothening up to 60 s and roughening after that, is a complicated subject that a clear response has not been addressed to it yet. Probably this can be described by this fact that with increasing the treatment time, high energy plasma species can obtain a higher chance for surface etching and chain scission, which per se increase the possibility of the penetration to the lower layers. Accordingly, the chains located there are affected by crosslinking and branching that leads to aggregation and roughening.

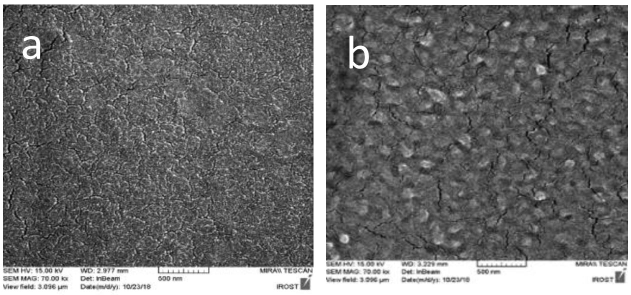

Fig. 4. FE-SEM micrographs of the a) untreated and b) 120 s treated specimens

The variations of SFE are shown in Fig. 5. It can be deduced that in the first 10 s of the plasma treatment, SFE increased significantly.

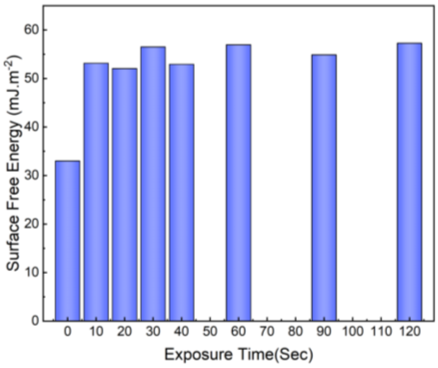

Fig. 5. SFE of the plasma-treated samples with different treatment durations

Surprisingly, in the areas that their roughness decreased, SFE did not decline considerably and always was higher than the untreated specimen. Although the roughness increased in 90 s and 120s of treatment, SFE did not increase. These results proofed that surface roughness cannot be the sole determining factor of surface hydrophilicity, and this is in line with Cassie–Baxter theory [8].

4. Conclusion

Air plasma is an efficient method for improving the printability of the surface of polyolefins (e.g. PP). This method could increase the surface free energy up to 70 $mJ.m^{-2}$ (approximately doubled). Even in a very short times of exposure (less than 10 s), it is capable of altering the surface free energy to a noticeable extent. This indicated that plasma is a very fast treatment. Moreover, it was deduced that plasma changed the topography of the samples. Overall, it was concluded with the Cassie–Baxter theory is more applicable in studying the wetting results in the current study.

5. References

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