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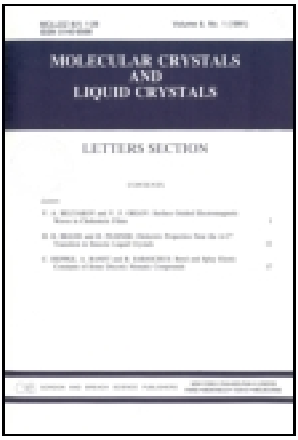

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Enhancing the Surface Wettability of Poly(Ethylene Terephthalate) Film by Atmospheric Pressure Plasma Treatment with Ar and N_2Gas Mixture

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Enhancing the Surface Wettability of Poly(Ethylene Terephthalate) Film by Atmospheric Pressure Plasma Treatment with Ar and N_2 Gas Mixture

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In this work, the specific influences of atmospheric pressure plasma (APP) treatment on the surface modifications of poly(ethylene terephthalate) (PET) polymeric film have been explored. The APP was generated using dielectric barrier discharge in the ambient of Ar and N_2 gas mixture. Experimental results of the surface properties are presented for the PET film before and after the APP treatment. The exposure of PET films to APP leads to the roughening surface. Also, the APP-induced modifications are associated with incorporation of polar oxygen and nitrogen containing groups on the PET surface. Due to the changes of chemical composition and topology on the surface by the APP treatment, the contact angle of distilled water on the surface becomes smaller, resulting in higher surface wettability.

Keywords Ar and N_2 gas mixture; atmospheric pressure plasma; plasma surface treatment; poly(ethylene terephthalate); surface wettability

Introduction

Poly(ethylene terephthalate) (PET) is one of the most widely used materials in the microelectronics industry and a good candidate for the substrates of flexible optoelectronic devices such as flexible displays and flexible solar cells [1–3]. In application to the flexible optoelectronic devices, an important issue for the plastic substrate is the weak adhesion between the inorganic thin film and the polymeric substances because the reliability and durability of thin films largely depend on their adhesion to the substrates [4–7].

The surface wettability enhancement of PET by plasma treatment technology can be a very excellent way for adhesion improvement. Recently, we have reported [8] that the inductively coupled plasma treatment with Ar and N_2 gas mixtures on the surface of PET films efficiently leads to hydrophilic surfaces.

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On the other hand, among the plasma treatment techniques, research on the use of atmospheric pressure plasma (APP) treatment at the surface of plastic substrates has grown in interest because of its simple structure, high productivity and easy configuration for an in-line process [9–11]. In particular, APP generated by dielectric barrier discharge is non-thermal plasmas, which can be very promising to use in the industry. APP processing can be carried out using noble and/or chemically reactive gases. The changes of physical and chemical properties of the modified PET surface by the plasma treatments strongly depend on the species of discharge gas. Up to now, most of the APP treatments have been performed by using oxygen-containing gases. Although the possibility of APP treatments as the surface modifications of PET has been introduced, there are few reports on the detailed investigation for the effects of APP with Ar and N_2 gas mixture on the surface properties of PET. In order to understand the effects of APP treatment on PET surface, the physical and chemical interactions of the APP with the surface are most important. These are based on that the wettability of PET film is governed by both the chemical composition and the geometrical structure of surface.

Hence, this study has examined the surface properties of PET treated by APP with varying stage speed using Ar and N_2 mixtures as reactive gas. The wettability of APP-modified PET surfaces have been characterized by atomic force microscopy, X-ray photoelectron spectroscopy, surface free energy, and contact angle measurements.

Experimental

Experiments were performed on PET film with thickness of 200 μm. Plasma surface treatment on PET was carried out at atmospheric pressure using a dielectric barrier discharge system. A schematic diagram of the plasma configuration is represented in Fig. 1. The discharge is produced between two planar electrodes covered with ceramic plate and the

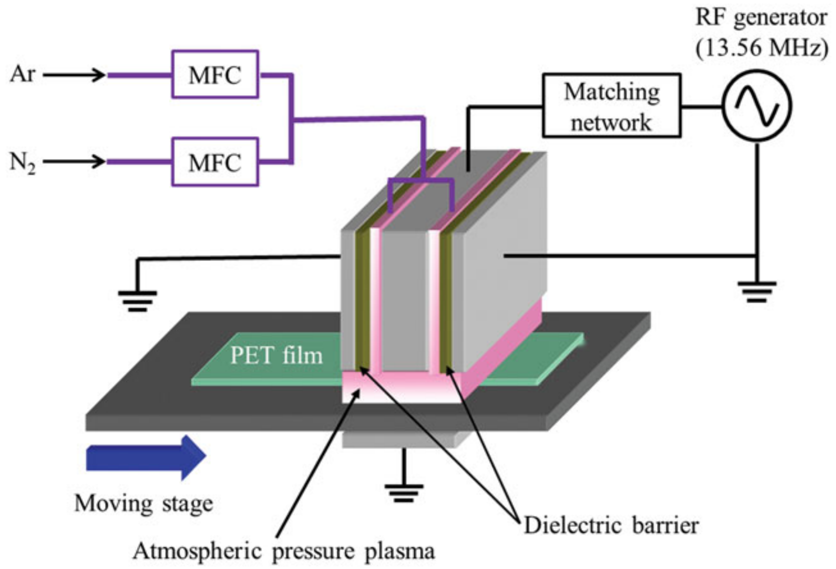

Figure 1. Schematic diagram of the APP reactor used in this study.

inter-electrode distance is set to 1.5 mm. The PET films were placed on the lower ceramic plate that moves forth at controlled speed with distance of 2 mm from electrodes. Prior to plasma treatments, the films were ultrasonically washed in isopropyl alcohol during 2 min. and then dried in the air flow method. The surface modifications of PET films have been performed at room temperature with Ar and N_2 gas mixture, varying the stage speed. The gas flow rates for Ar and N_2 are controlled and monitored by the mass flow controllers, which are typical flow rates of 5 slm and 5 sccm, respectively. The applied power with radio frequency was fixed at 400 W.

Surface morphology of the film was monitored with an atomic force microscopy (AFM) (XE-100, Park system). Surface roughness was expressed in terms of root mean square (RMS) value. X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo-Fisher) examination was conducted to analyze the surface chemical compositions of PET films. The contact angles were measured with de-ionized water using a contact angle measurement (DSA 100, Kruss). The adhesion energy of PET surfaces is estimated from the measured contact angle by the following equation

$$\mathrm{E}_{\mathrm{ad}} = \gamma_{\mathrm{water}}(1 + \cos\theta),$$

where E_{ad}, γ_{water}, and θ are adhesion energy, surface tension of pure water ($\gamma_{\mathrm{water}} = 72.8\ \mathrm{mJ/m^2}$), and contact angle of PET surface, respectively [12]. The surface free energy was calculated as sum of the dispersive energy and the polar energy by the Owens-Wendt geometric mean method [13] with DI water and diiodomethane. All measurements were carried out at room temperature.

Results and Discussion

Figure 2 shows the variation of surface roughness with respect to the stage speed for the APP-treated PET film. The RMS values of surface roughness for the APP-treated PET film are higher than that of surface roughness for the pristine film. This represents the structure modifications on the surface of PET by the APP treatment. The wettability on polymeric substances has been known to be strongly dependent on the changes in surface roughness, which is called Wenzel model [14]. Wenzel's model is based on the assumption that the water completely penetrates into the valleys of the surface texture. For a rough surface, water may enter and fill the grooves of the film, leaving only the up part of the film. Therefore, the rougher surface of PET film can be expected to enhance the surface wettability of the film. It is also found that the surface roughness of the APP-treated PET decreases from 16.3 to 12.1 nm with the increase of stage speed from 2 to 10 mm/sec. The faster stage speed means the shorter expose time to APP of PET film. Hence, the decrease in the surface roughness of the APP-treated PET with the increasing stage speed is attributed by the decrease in the expose time of APP.

Figure 3 shows the XPS wide scan spectra of the pristine and APP-treated PET surfaces. The spectrums for pristine PET contain C1s and O1s peaks which may be identified at 285 eV and 533 eV, respectively. After the APP treatment, the C1s peak decreases while the content of O1s increases. In addition, a new intense peak is observed at about 400 eV due to N1s electrons. The elemental composition and ratio in the APP-modified surface of the PET films are summarized in Table 1. The O/C atomic ratio for the pristine film is equal to 24.8%, while the O/C ratio for the APP-treated film is increased to 39.2%. The increase in O/C atomic ratio suggests that additional oxygen-containing groups are formed on the surface of PET film after APP treatment. Also, the APP treatment leads to the increase in

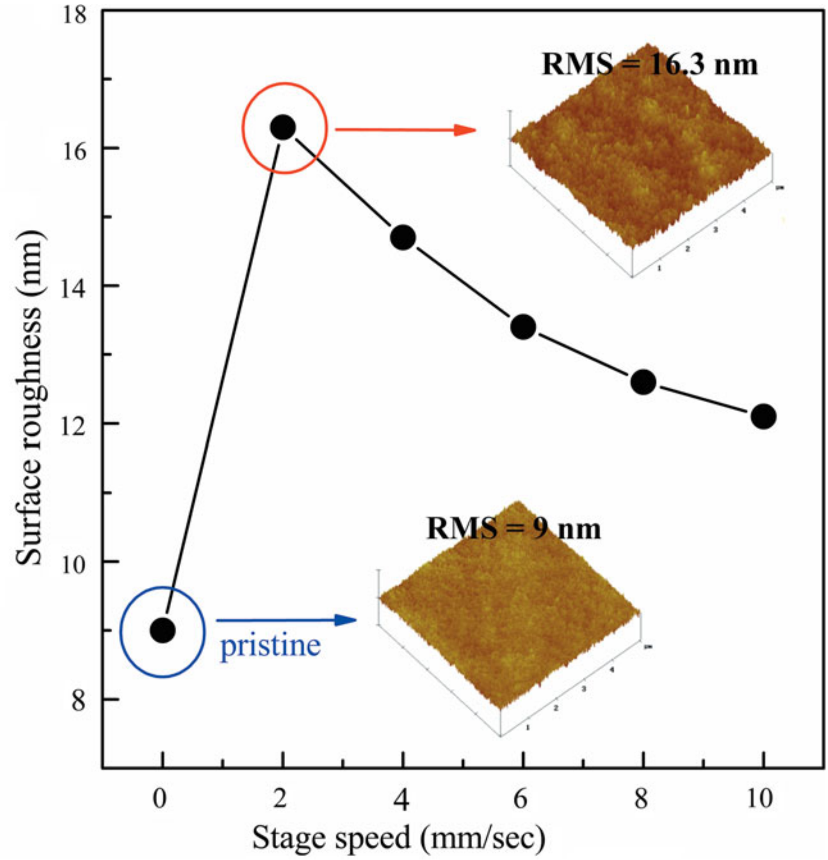

Figure 2. Surface roughness of the PET film treated by APP.

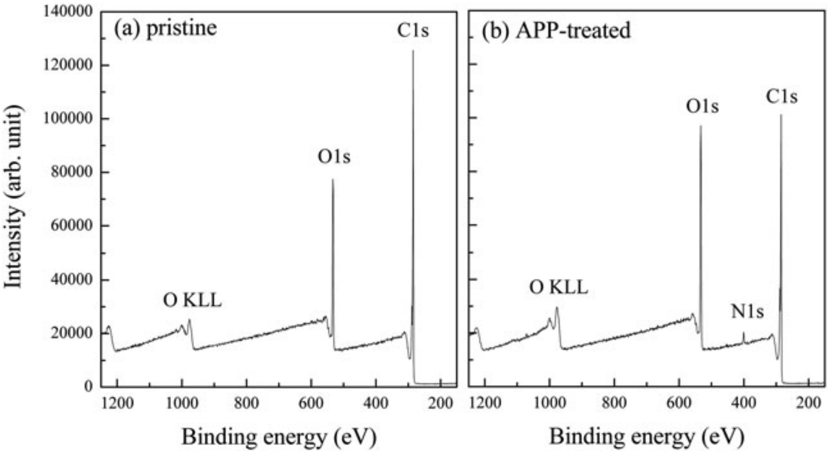

Figure 3. XPS wide scan spectra of the pristine and APP-treated PET surfaces.

Table 1. The elemental composition and ratio in the APP-modified surface of the PET films

	Elemental composition (%)			Elemental ratio (%)	
Stage speed (mm/sec)	C1s	O1s	N1s	O/C	N/C
pristine	80.1	19.9	—	24.8	—
2	70.2	27.5	2.3	39.2	3.3
6	72.2	25.8	2	35.7	2.8

the N/C atomic ratio up to 3.3%. This is suggested that new nitrogen-containing functional groups are formed on the PET surfaces after APP treatment. Accordingly, the changes in the atomic ratios imply that a small amount of nitrogen indicates the surface grafting of reactive species in APP and the oxygen component is incorporated in the PET surface during the treatment [8]. The introduction of oxygen and nitrogen-containing polar groups in the surface exposed to APP can result in the hydrophilic improvement.

Information on how oxygen and nitrogen are implanted on the PET surface as a consequence of APP treatment can be obtained from deconvolution of XPS spectra for the C1s core level in PET surfaces. Figure 4 presents the high resolution spectra of the C1s core level in the pristine and APP-treated PET surfaces. The C1s spectrum for the pristine PET can be decomposed into three peaks which originates from C—C/C—H bonds, C—O bond, and O=C—O bond, as shown in Fig. 4(a). After the APP treatment, the band associated with C—C/C—H bonds decreases, whereas the band corresponding to oxygen containing-functional O=C—O bond becomes higher. The C—O bond may be converted to C—O/C—N bonds by the virtue of the C—N bond creation, and the intensity is larger. Also, it is observed that the C=O/C=N bonds are generated due to the increase in N/C atomic ratio after the APP treatment. These results indicate that some of the weak C—C/C—H bonds in PET surface may be broken by the APP treatment. Then the C-dangle bonds caused by the broken of C—C/C—H chemically recombine with O and N elements. Thus, oxygen and nitrogen containing-functional groups such as C—O/C—N bonds, O=C—O bond, and

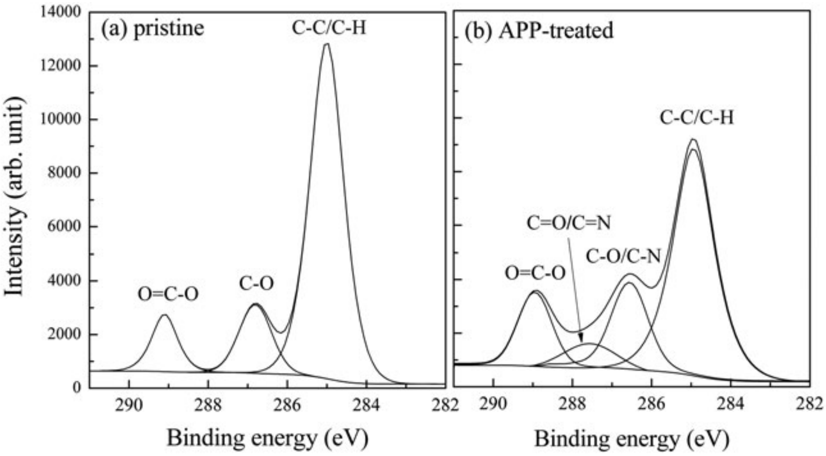

Figure 4. XPS spectra of C1s core level in the PET surface treated by APP.

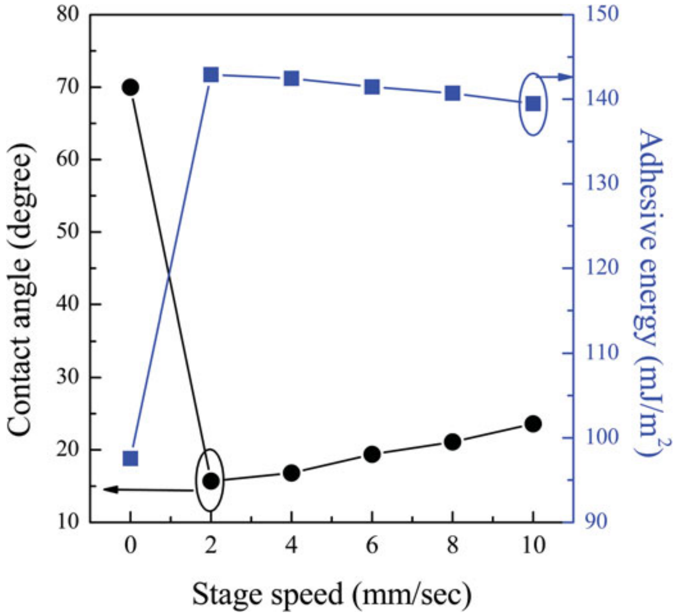

Figure 5. Contact angles of distilled water and adhesion energies on the PET surface treated by APP.

C=O/C=N bonds may then be produced on the surface. These polar functional groups which are associated with high value-dipole moment binding energy states contribute to the decrease of contact angle and improvement of the hydrophilicity on the surfaces [15].

Figure 5 shows the changes in the contact angle and adhesion energy of the PET films at different moving stage speed. The contact angle of pristine PET films is 70°, which is corresponding to the adhesion energy of 97.6 mJ/m^2. The contact angles of the APP-modified surface are dropped to 15.7° at the moving stage speed of 2 mm/sec, representing the adhesion energy of 142.9 mJ/m^2. On the basis of the above analysis, the decrease of contact angle represents that a number of hydrophilic functional groups may be inserted into the surface of the original hydrophobic PET film due to the APP treatment. Also, it is considered that the PET surface is simultaneously bombarded by an incident ion flux to provide the changes in the surface topography. Because the adhesion energy is deeply related to the surface wattability, the increasing adhesion energy is attributed to the changes in the contact angle, resulting from the variations of both hydrophilic functional groups and surface roughness. When the stage speed increases from 2 to 10 mm/sec, the contact angle increases from 1.57 to 23.6°, whereas adhesion energy decreases from 142.9 to 139.5 mJ/m^2. This may be originated in the decreases in the exposure time of PET surface under the APP.

The surface free energy of APP-treated PET film with respect to stage speed is shown in Fig. 6. The surface free energy for pristine PET is about 39 mJ/m^2. For the PET films treated by APP, all surface free energy are higher than that of the pristine film, indicating the enhancement of wettability. Also, the surface free energy of the APP-treated films decreases from about 71.3 to about 65.4 mJ/m^2 with the increase in the stage speed from 2 to 10 mm/sec. These features of surface free energy for the films are very similar to that of the adhesive energy, as shown in Fig. 5. It can be observed that the dispersive energy represents a small variation with respect to stage speed. However, the polar energy has the

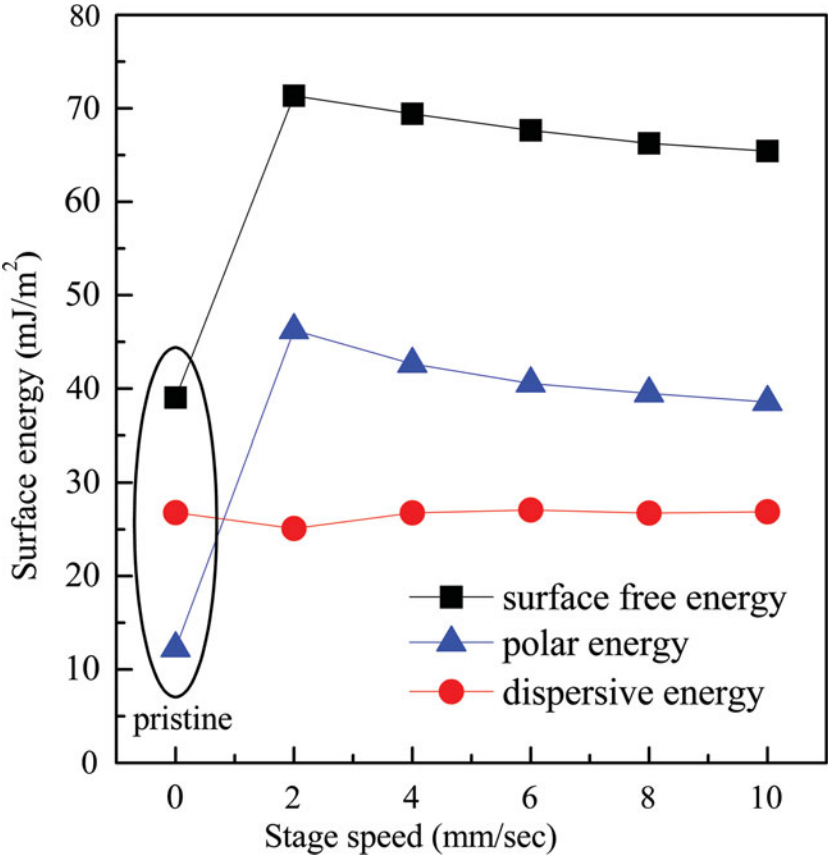

Figure 6. Surface free energy of APP-treated PET as a function of stage speed.

similar tendency with surface free energy. It is obvious that the polar energy contributes more to surface free energy than dispersive energy. Hence, the increase in surface free energy by the APP treatment is mainly due to the incorporation of the polar functional groups onto the PET surface. Since water is the liquid of polar character, the polar part of the surface free energy is associated to the decrease of water contact angle. Therefore, because the water contact angle and surface free energy is strongly related to surface wettability, higher enhancement in wettability on the PET surface can be achieved after APP treatment with lower stage speed.

Conclusions

The surface modification of PET films was performed by using APP with Ar and N_2 gas mixture at different stage speed. After PET films are exposed to APP, significant morphological and chemical changes in the surface are produced. Under the slower stage speed, hydrophilic functional groups on the film increases. As a result, the wetting angle of distilled water on the PET surface treated by APP decreases with lower stage speed and surface free energy increases simultaneously. On the basis of this work, therefore, we think that the changes in PET surface by APP with low stage speed can be a possible approach to be the enhancing wettability suitable for flexible optoelectronic applications.

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