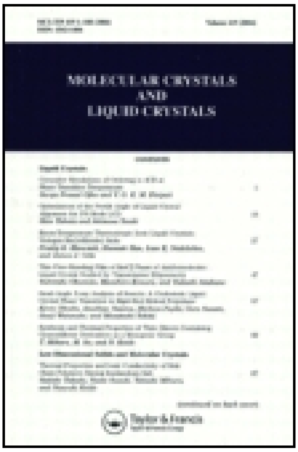

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Surface Properties of Poly(ethylene terephthalate) Films Modified by Inductively Coupled Plasma with Ar/N_2 Mixture Gases

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We have investigated the effects of an inductively coupled plasma (ICP) treatment using Ar and N_2 gas mixtures on the surfaces properties of poly(ethylene terephthalate) (PET) films. The Ar/N_2 ICP-modified PET surfaces have been characterized by X-ray photoelectron spectroscopy, atomic force microscopy, and contact angle measurements. The experimental results reveal that ICP treatment with Ar/N_2 mixture gas induces physical and chemical changes of PET surface, showing the increases of surface roughness and hydrophilic functional groups in the surface Also, the contact angle of distilled water on the surface becomes smaller with increasing RF power applied to ICP antenna, resulting in higher adhesion energy.

Keywords Adhesion energy; Ar/N_2 mixture gas; inductively coupled plasma; plasma surface treatment; poly(ethylene terephthalate)

Introduction

Poly(ethylene terephthalate) (PET) is one of the most widely used materials in the micro-electronics industry and a good candidate for the substrates of flexible optoelectronic devices such as flexible displays and solar cells [1–5]. The important reasons

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are that it offers high optical transmission in the visible range, good resistance to corrosion, and relatively inexpensive to produce. In application to the flexible optoelectronic devices, despite above excellent characteristics, PET polymeric films require surface treatment in order to improve surface wetting and adhesion properties due to their low surface energies [6].

It has been reported plasma surface treatment should only modify the surface of polymeric substances without affecting their bulk properties especially the cohesion strength at the surface [7]. Among the plasma treatment techniques, inductively coupled plasma (ICP) has unique advantages, including low-temperature, highly charged species, and high density plasma. This results in an effective surface treatment involving both short treatment time and compact treatment per unit area [8,9]. Recently, we have reported [10] that oxygen ICP treatment on the surface of PET films efficiently led to hydrophilic surfaces with oxygen containing moieties. However, in the ICP treatments, the changes of physical and chemical properties of the treated PET surface strongly depend on the species of discharge gas.

Thus, this study has examined the surface properties of PET treated by ICP using Ar and N_2 mixtures as reactive gas. By action of these active species, new distinctive functional groups can be generated and grafted on the surface. The surface chemical bonding states, surface roughness, and contact angle of PET treated by Ar/N_2 ICP have been investigated with respect to a range of Ar/N_2 gas mixtures and RF power applied to ICP antenna.

Experimental

Experiments were performed on PET film with thickness of 100 μm. Prior to plasma treatments, the films were ultrasonically washed in isopropyl alcohol during 2 min and then dried in air. The surface modifications of PET films have been performed by an ICP reactor at room temperature, varying Ar/N_2 flow rate ratio and RF power applied to ICP antenna. The details of the experimental set up used for the ICP treatment of PET films have been described elsewhere [10]. The base pressure in the reactor was adjusted to 5.0×10^{-6} Torr and the pressure during the treatment was maintained at 10 m Torr regardless of N_2 fraction in Ar and N_2 gas mixture. The mixture gas flow rate and treatment time were fixed at 50 sccm and 90 sec, respectively.

X-ray photoelectron spectroscopy (XPS) (K-Alpha, ThermoFisher) examination was conducted to analyze the surface chemical compositions of PET films. 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. The contact angles were measured with de-ionized water using a contact angle measurement (DSA 100, Kruss). In the experiment, 5-point measurements on each sample were performed at regions selected at random. All measurements were carried out at room temperature.

Results and Discussion

Figure 1 shows the surface contact angle of PET treated by Ar/N_2 ICP at 200 W of applied RF power with varying N_2 flow rate. It is shown that the contact angle of the treated PET film decreases with increasing N_2 flow rate up to 30 sccm and increases above 30 sccm. It is, therefore, found that when Ar/N_2 flow rate is 20/30 sccm, the gas mixture is the best combination to use for improving wettability on the surface of

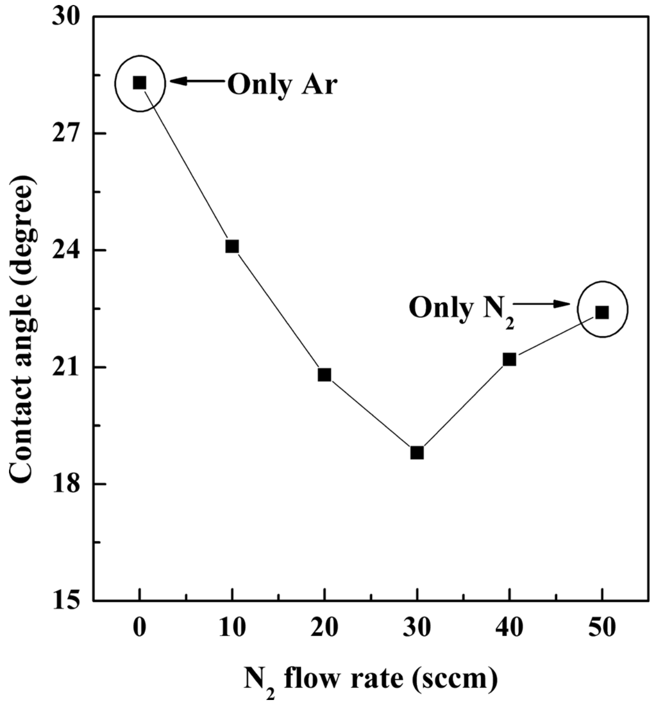

Figure 1. Contact angles of distilled water on the PET surface treated by Ar/N_2 ICP with varying N_2 flow rate.

PET in our experiments. Generally, it is known that the interactions between the plasma and polymer surface include the physical bombardments by energetic particles and the surface chemical reactions. Due to various energetic species are generated with the N_2 flow rate, each gas mixture may have a different treatment effect such as surface morphology and chemical bonding structure. Moreover, the considerable reduction in contact angle of the film means that large number of hydrophilic groups is generated in the surface. Based on the above result, therefore, the surface of PET film treated at 30 sccm of N_2 flow rate has highest wettablilty, and the subsequent investigation on the changes in chemical and morphology on the surface is conducted.

Figure 2 shows the XPS wide scan spectra of the pristine and Ar/N_2 ICP-treated PET surfaces. In the Figure 2(a), the spectrum for pristine surface of PET contain C1 s and O1 s peaks.

For the treated PET surface, a new intense peak is observed at about 400 eV due to N1 s electrons. In addition, the C1 s peak decreases while the content of O1 s increases. The results imply that a small amount of nitrogen indicates the surface grafting of reactive species in ICP and the oxygen component is incorporated in the PET surface during treatment.

For the precise investigation, XPS spectra of the C1 s core level in PET surfaces are shown in Figure 3. All spectra have referred to the C1 s peak for the carbon atom with assigned value of 284.6 eV, and have corrected for the charging effect due to the insulating character of the PET. Based on some published data [11–13], the fitting of the complex C1 s peak is performed using a non-linear least-squares routine with

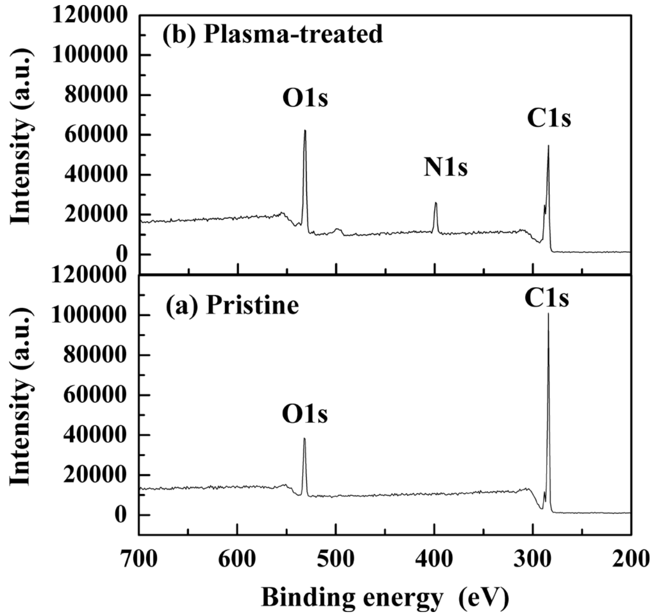

Figure 2. XPS wide scan spectra of the pristine (a) and Ar/N_2 ICP-treated PET surfaces (b).

Gaussian-Lorentzian function. The measured C1 s peak of the untreated PET can be decomposed into three peaks which originates from C–C and C–H bonds, C–O bond, and O=C–O bond, as shown in Figure 3(a). Due to the creation of N1 s peak after the plasma treatment, the C1 s spectrum of the treated PET surface can be deconvoluted to the four components such as C–C and C–H bonds, C–O and C–N bonds, O=C–NH_2 bond, and O=C–O bond. Compared to pristine PET, it is found that for the treated surface, the band associated with C–C and C–H bonds decreases, whereas the bands corresponding to oxygen containing-functional groups

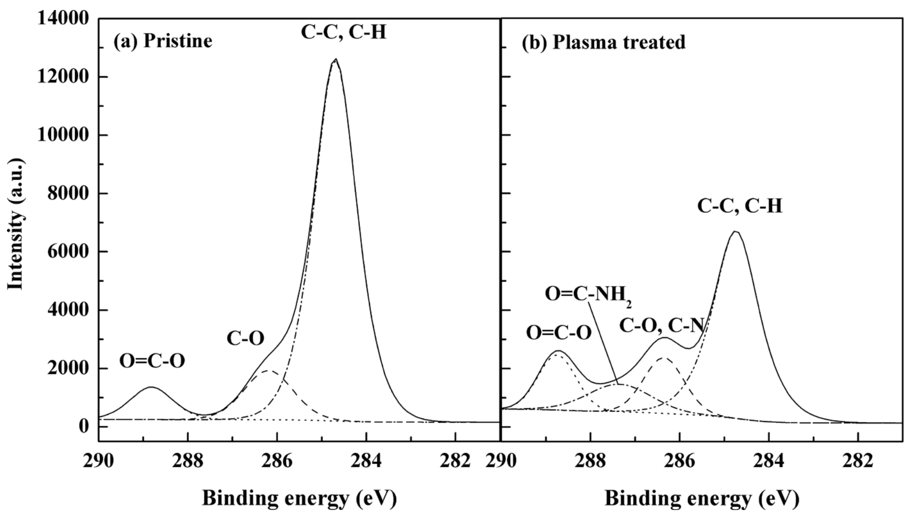

Figure 3. XPS spectra of C1 s core level in the PET surface treated by Ar/N_2 ICP.

such as C–O and O–C=O becomes higher. These results can be explained as follows: some of the C–C and C–H bonds in the surface may be broken by the plasma treatment, and the broken C–C and C–H bonds recombine with oxygen atoms, resulting in the production of oxygen-containing groups. Also, as shown in Figure 3(b), the peaks from C–N and O=C–NH_2 bonds is occurred, indicating newly formed functional groups due to reactive nitrogen gas in the ICP. 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 [13].

Figure 4 shows the surface roughness of PET film treated by ICP using Ar/N_2 gas mixture with varying RF power applied to ICP antenna. For reference, AFM image for pristine PET is inserted. It is observed that the surface roughness of PET increases from 9 nm to 28.4 nm under applied RF power to 400 W, and the surface becomes significantly rougher. This result may be attributed to the increase in incident ion flux on the PET in the ICP. It has been known that the wettability on polymeric substances is strongly dependent on the changes in surface roughness [14]. With respect to only surface roughness, if the contact angle of pristine surface is less than 90°, the rougher surface of the same material brings about the smaller contact angle. Therefore, it is noted that the increase of the surface roughness with RF power can be expected to become the improving wettability on the surface of PET. It is also worth noting that surface roughness of PET film under Ar/N_2 ICP treatment is smaller than that under O_2 ICP [10]. It is wisely accepted that characteristics of transparent conducting oxide films on polymeric substrate are known to be easily affected by the properties of substrate surface, and subsequently surface uniformity of the films is one of the crucial factors for determining the lifetime and performances

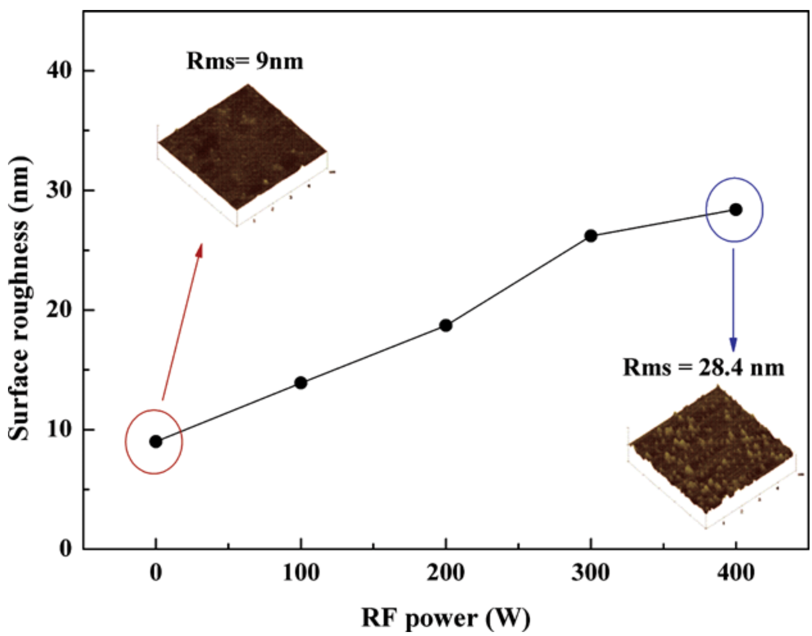

Figure 4. Surface roughness of the PET treated by treated by Ar/N_2 ICP. The inserted are the AFM images of pristine and the treated PET surfaces.

of the devices [15]. Accordingly, surface treatment of PET by Ar/N_2 ICP may have priority to O_2 ICP.

Figure 5 shows the changes in the contact angle and adhesion energy of the PET films at different applied RF power. The contact angle of pristine PET films is 70, which is corresponding to a lower surface energy. When the PET surface was exposed to the Ar/N_2–ICP, the contact angle is decreased rapidly with applied RF power. As seen in Figure 3, from pristine PET, the peaks from C–O and C–N bonds, O=C–NH_2 bond, and O=C–O bond, which are hydrophilic functional groups, account for 17.3, 0, and 13.4% of the total C1 s band area, respectively. After plasma treatment, the corresponding peaks increase to 19.6, 19.2, and 18.2%, respectively. Accordingly, the decrease of contact angle represents a number of hydrophilic functional groups is inserted into the surface of the original hydrophobic PET film due to the Ar/N_2–ICP treatment. Also, it cannot be disregarded that the PET surface is simultaneously bombarded by an incident ion flux to provide the changes in the surface topography, as mentioned above. The contact angles of the modified surface are dropped to 9.3° at RF power 400 W, representing a higher surface energy. The adhesion energy of PET surfaces is estimated from the measured contact angle by the following equation

$$E_{ad} = \gamma_{water}(1 + \cos\theta),$$

where E_{ad}, γ_{water}, and θ are adhesion energy, surface tension of pure water ($\gamma_{water} = 72.8\,mJ/m^2$), and contact angle of PET surface, respectively [16]. The

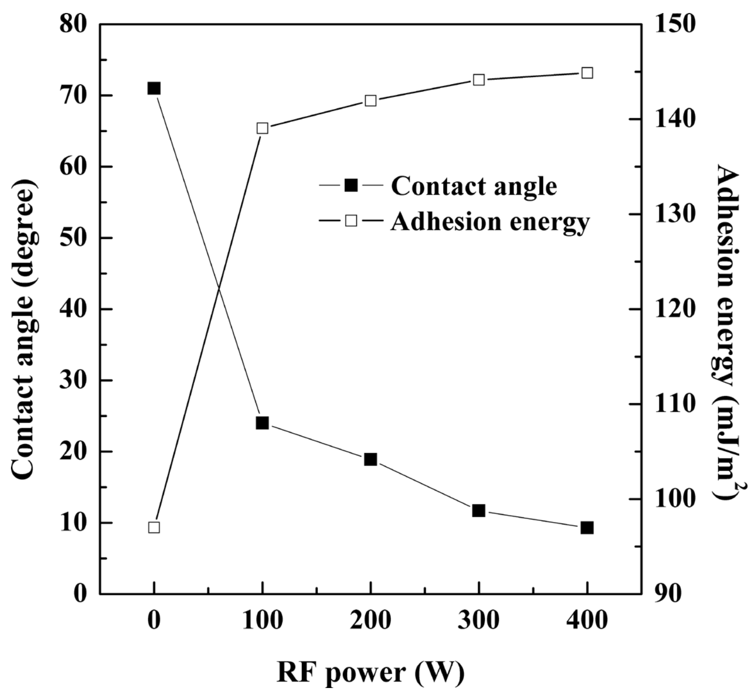

Figure 5. Contact angles of distilled water and adhesion energies on the PET surface treated by treated by Ar/N_2 ICP.

adhesion energy of pristine PET films is 97 mJ/m^2. With an increasing RF power, the adhesion energy is increased to about 49%, reaching up to 144.9 mJ/m^2. It is obvious that 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. It is worth noting that compared with the results for O_2–ICP [10], although the rms value of surface roughness of PET treated by Ar/N_2–ICP is smaller, the adhesion energy is enlarger at the same applied RF power. Hence, our study suggested that the surface modifications of PET by ICP using Ar and N_2 mixture gases make to the film more hydrophilic and adhesion increasing under lower ion damages.

Conclusions

The surface modification of PET films was performed by using ICP with Ar/N_2 gas mixture at different nitrogen flow rate and RF power applied to the ICP antenna. The study reveals that the lowest contact angle is observed at 30 sccm of N_2 flow rate. After PET film expose to Ar/N_2 ICP, the enlargement in oxygen containing-functional groups and the creation of newly functional groups on the surface is found. Under constant ratio of N_2 gas flow rate, when the RF power increases, surface roughness of the film increases. As a result, the wetting angle of distilled water on the Ar/N_2 ICP-treated surface decreases with RF power and adhesive energy increases simultaneously, indicating superior to O_2-ICP. Therefore, the study suggest that the changes in PET surfaces by ICP using Ar/N_2 as precursor gas can be a possible approach to be more hydrophilic and adhesion increasing suitable for flexible optoelectronic applications.

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References

[1] Chang, H., Chen, T. L., Huang, K. D., Chien, S. H., & Hung, K. C. (2010). *J. Alloys. Compd.*, *504*, S435.
[2] Kwak, D.-J., Kim, J.-H., Park, B.-W., Sung, Y.-M., Park, M.-W., & Choo, Y.-B. (2010). *Curr. Appl. Phys.*, *10*, S282.
[3] Laskarakis, A., Logothetidis, S., Kassavetis, S., & Papaioannou, E. (2008). *Thin Solid Films*, *516*, 1443.
[4] Li, J., Hu, L., Liu, J., Wang, L., Marks, T. J., & Grüner, G. (2008). *App. Phys. Lett.*, *93*, 083306.
[5] Cheon, K.-E., Lee, D.-Y., Cho, Y.-R., Song, P.-K., & Lee, G.-H. (2008). *J. Kor. Phys. Soc.*, *53*, 396.
[6] Upadhyay, D. J., Cui, N. Y., Anderson, C. A., & Brown, N. M. D. (2004). *Appl. Surf. Sci.*, *229*, 352.
[7] Eom, J. S., & Kim, S. H. (2008). *Thin Solid Films*, *516*, 4530.
[8] Kim, H., Jung, S. J., Han, Y. H., Lee, H. Y., Kim, J. N., Jang, D. S., & Lee, J. J. (2008). *Thin Solid Films*, *516*, 3530.

[9] Lieberman, M. A., & Lichtenberg, A. J. (1994). *Principles of Plasma Discharges and Materials Processing*, John Wiley & Sons: New York.
[10] Han, D. C., Choi, Y. C., Shin, H. J., Son, S., Kim, J. H., Sohn, S. H., & Lee, D. K. (2010). *Mol. Cryst. Liq. Cryst.*, *532*, 148.
[11] Watts, J. F., & Wolstenholme, J. (2003). *An Introduction to Surface Analysis by XPS and AES*, John Wiley & Sons: New York.
[12] Cryst, B. V. (2000). *Handbook of Monochromatic XPS Spectra*, John Wiley & Sons: Chichester.
[13] Vesel, A., Mozetic, M., & Zalar, A. (2008). *Vacuum*, *82*, 248.
[14] Wenzel, R. N. (1936). *Ind. Eng. Chem.*, *28*, 988.
[15] Woo, B.-J., Hong, J.-S., Kim, S.-T., Kim, H.-M., Park, S.-H., Kim, J.-J., & Ahn, J.-S. (2006). *J. Kor. Phys. Soc.*, *48*, 1579.
[16] Fujinami, A., Matsunaka, D., & Shibutani, Y. (2009). *Polymer*, *50*, 716.