Mol. Cryst. Liq. Cryst., Vol. 532: pp. 148/[564]–155/[571], 2010
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.497061

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Surface Modification of Poly(ethylene terephthalate) Polymeric Films by Inductively Coupled Oxygen Plasma

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In this study, the surfaces of poly(ethylene terephthalate) (PET) films have been modified by high density inductively coupled plasma (ICP) using the oxygen gas. The ICP-modified PET surfaces have been characterized by atomic force microscopy, X-ray photoelectron spectroscopy, and contact angle measurement as a function of RF power applied to ICP antenna. The experimental results reveal that the exposure of PET films to ICP leads to the roughening surface and the increase of oxygen containing-functional groups such as O–C=O and C–O at the surface. Also, the contact angle of distilled water on the surface decreases with increasing RF power, resulting in the increase in the adhesion energy.

Keywords Adhesion energy; inductively coupled plasma; oxygen plasma treatment; poly(ethylene terephthalate); surface modification

Introduction

The polymer materials such as poly(ethylene terepthalate), polyether sulphone, poly carbonate, and poly(ethylene naphthalate) have been considered as flexible substrates in next generation display technologies [1]. The important reasons are that they offer high optical transmission in the visible range and good resistance to corrosion, and are relatively inexpensive to produce. Among the polymer materials, 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 [2–4].

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In application to the flexible devices, despite of above excellent characteristics, PET polymeric films require a surface treatment to improve surface wetting and adhesion properties due to their low surface energies [5]. 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 [6]. Up to now, capacitively-coupled plasmas [7,8] are predominantly studied because the gas glow discharge between two parallel electrodes is known to be the simplest method for generating plasmas. But, it has a drawback of limited process control of the ion energy and the plasma density.

The use of inductively coupled plasma (ICP) technique [9] is another promising method in the surface treatment because the plasma with high density and large area uniformity is obtained under a relatively low pressure and can offer faster etch rates at lower ion energies than conventional capacitively coupled discharges. In addition, the density and energies of the charged reactive species incident onto the film during treatment can be easily controlled. Nevertheless, studies on the surface properties of ICP-modified PET films have been still limited.

Hence, in this work, the surface modifications of PET treated by high density ICP with a reactive oxygen gas have been studied. In particular, effects of RF power applied to the ICP antenna on the surface properties of ICP-modified PET films are investigated.

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 the air flow method. The surface modifications of PET films have been performed by an ICP reactor with pure O_2 gas, as seen in Figure 1.

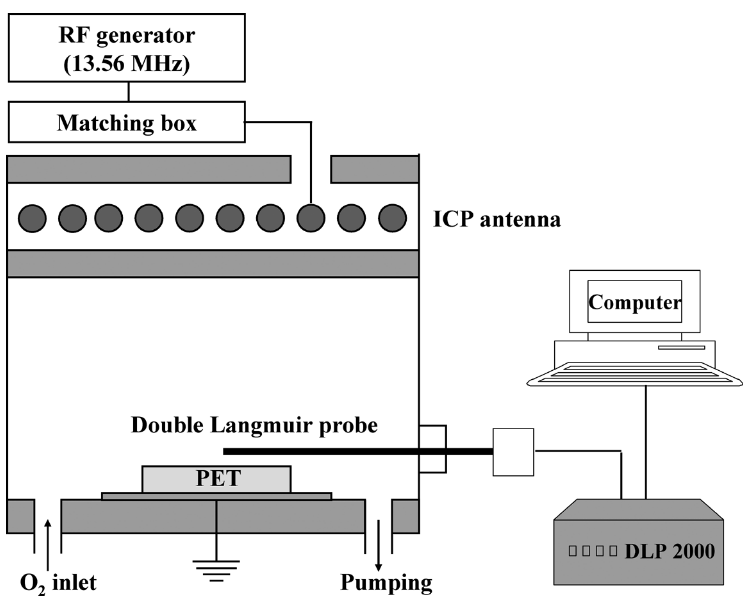

Figure 1. Schematic diagram of the inductively coupled plasma reactor used in this study.

Table 1. The conditions of the inductively coupled plasma treatment

Inlet gas	Pure oxygen
Base pressure	5×10^{-6} Torr
Gas flow rate	50 sccm
Working pressure	10 m Torr
Treatment time	90 sec
RF power	50~400 Watt

The conditions of the plasma surface treatment for PET films by high density ICP are summarized in Table 1.

The ion density in the O_2 plasma was measured by a double Langmuir probe plasma diagnostic system (DLP 2000, PLASMART). The contact angles were measured with de-ionized water using a contact angle measurement (DSA 100, Krüss). In the experiments, 5-point measurements on each sample were performed at regions selected at random. X-ray photoelectron spectroscopy (XPS) (K-Alpha, ThermoFisher) examination was conducted to analyze the surface chemical composition of the films. Surface morphology of PET was monitored by an atomic force microscopy (AFM) (XE-100, Park system). Surface roughness was expressed in terms of root mean square (RMS). All measurements were carried out at room temperature.

Results and Discussion

Figure 2 shows the influence of RF power applied to ICP antenna on the ion density in oxygen plasma. It can be seen that the ion density increases almost linearly with increasing applied RF power. At a RF power of 400 W, the ion density is

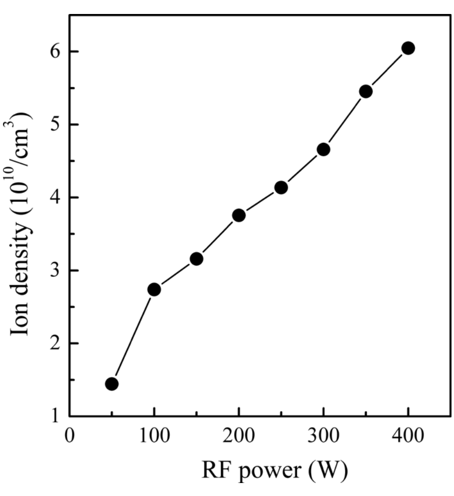

Figure 2. Variation of the ion density in inductively coupled oxygen plasma as a function of RF power.

about $6 \times 10^{10}\,cm^{-3}$, indicating the formation of the high density plasma. The increase in ion density with RF power may be due to an enhancement of the electron-neutral collision rate caused by the increasing path of energetic electron driven by the magnetic field induced at ICP antenna. It is of interest that high ion density implies sufficiently generations of atomic species such as ion and reactive radical [10], which can be effective in the plasma surface treatment for polymeric films.

Figure 3 illustrates the AFM images on the surface of PET film treated by O_2-ICP gas plasma. For comparison, AFM image for pristine PET is also included in

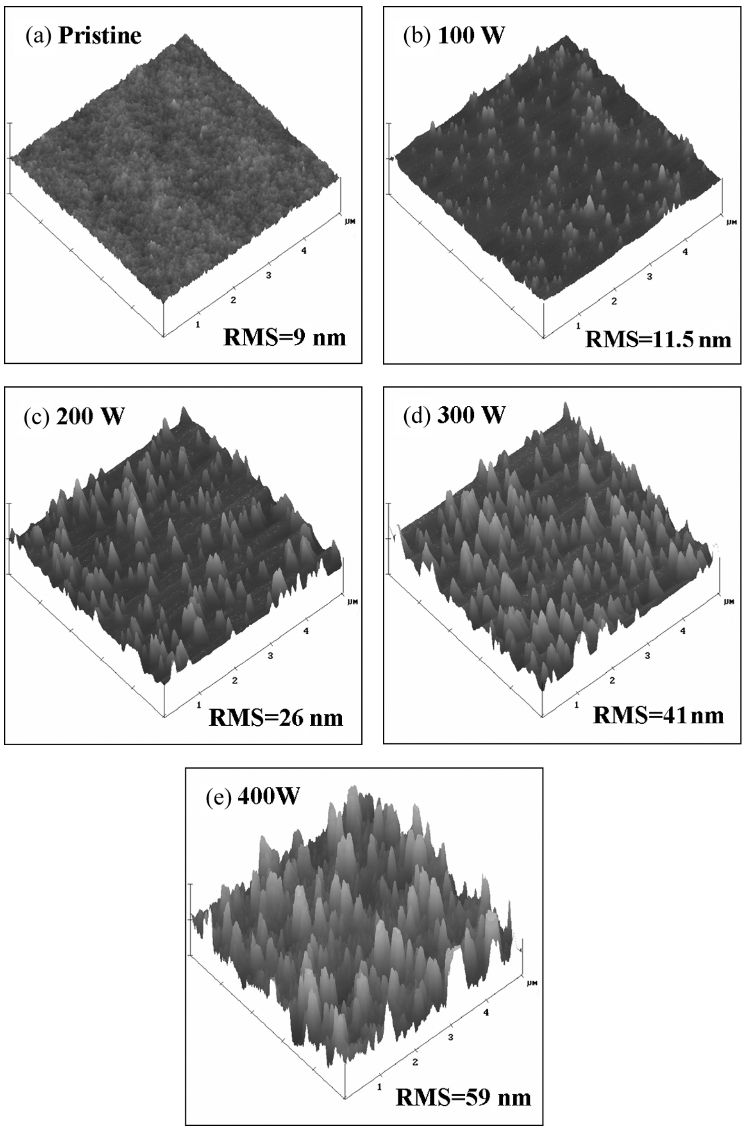

Figure 3. AFM images of inductively coupled oxygen plasma-treated PET surfaces.

the figure. It is observed that the original surface of untreated polymer is relatively smooth with roughness of about 9 nm. After exposure to the O_2 plasma, the protuberances with conical shapes appear on the PET surface. Hence, the surface roughness of PET increases remarkably with increasing RF power, and the surface becomes significantly rougher. The corresponding RMS values increase to 59 nm for a RF power of 400 W. It is well known that the reactive etching due to the bombardments of energetic oxygen ions and reactive radicals in the plasma on PET surface leads to the roughening of surface morphology. Accordingly, the increase in surface roughness with RF power may be attributed to the increase in the number of incident atomic species on the PET owing to the enhancement of the ion density in the ICP. It has been known that the wettability on polymeric substances is strongly dependent on the changes in surface roughness [11]. It is worth noting that the increase in the surface roughness with RF power yields an improving wettability on the surface of PET.

XPS spectra of the C1s core level in PET surfaces treated by ICP with O_2 gas are presented in Figure 4. The C1s spectrum of the untreated PET is decomposed into the following important bands [12]: the band centered at about 284.1 eV due to the C–C and C–H bonds, the band centered at about 285.5 eV due to the C–O bonds, and the band centered at about 288 eV due to the O–C=O bonds, as shown in Figure 4(a). It is found that after the plasma treatment, the band associated with C–C and C–H bonds decreases, whereas the bands corresponding to oxygen containing-functional groups such as C–O and O–C=O increase. These results can be explained by the surface chemical activation [13], which is originated from the fact that 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

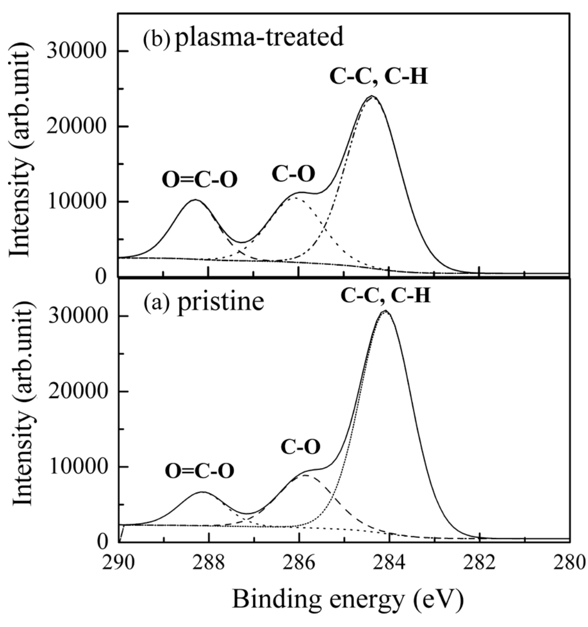

Figure 4. XPS spectra of C1s core level in the PET surface treated by inductively coupled oxygen plasma.

ions and/or reactive radicals, resulting in the production of oxygen-containing groups. Additionally, the increase of the ion density in the plasma may arise to enlargement of the incorporation of oxygen ions or radicals into the films under the ICP-O_2 gas plasma. These polar functional groups which are associated with high value-dipole moment binding energy states contribute to the decrease in the contact angle and improvement of the hydrophilicity on the surfaces [12].

Figure 5 shows the variation in the contact angle of PET film treated at different RF power. The contact angle of pristine PET films is 70°. It is seen from Figure 5 that when RF power increases to 400 W, the contact angle decreases to 12°. As indicated in Figure 2, the increasing RF power results in higher concentration of reactive oxygen species in the ICP. The enlargements of reactive etching and functionalization on the PET can be induced by the supplementation of a larger amount of oxygen species in the plasma. Thus, the decrease in the contact angle with increasing RF power is attributed possibly to the increase in the surface energy of PET films, owing to the increasing surface roughness and the formation of hydrophilic groups on the surface due to the increase of concentration of oxygen species, as previously mentioned.

Figure 6 represents the adhesion energy of PET surfaces, which can be obtained by using Eq. (1).

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

where E_{ad}, γ_{water}, and θ are the adhesion energy, the surface tension of pure water ($\gamma_{water} = 72.8\,mJ/m^2$), and the contact angle of PET surface, respectively [14]. The adhesion energy of untreated PET substrate is $97\,mJ/m^2$. The adhesion energy of ICP-treated PET surfaces increases with increasing RF power, reaching up to $143\,mJ/m^2$. It is obvious that because the adhesion energy is deeply related to the surface wettability, the increasing adhesion energy is due to the changes in both the surface composition and roughness, as explained in Figure 5.

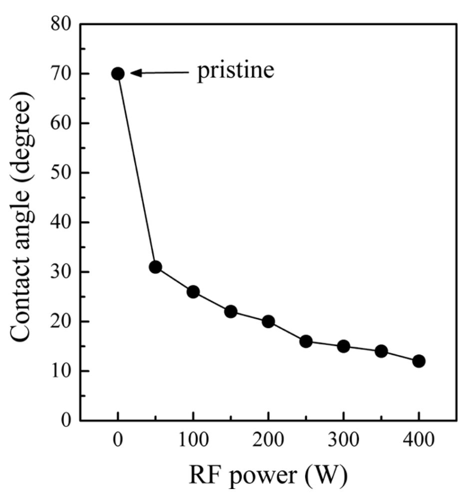

Figure 5. Contact angles of distilled water on the PET surface treated by inductively coupled oxygen plasma.

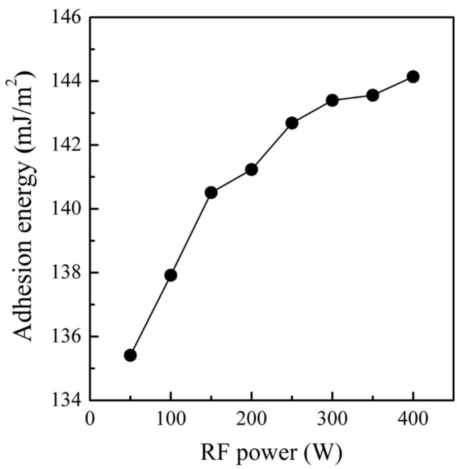

Figure 6. Adhesion energies of the PET surface treated by inductively coupled oxygen plasma.

Conclusions

Effects of oxygen ICP treatment on the surface modification of PET films have been investigated with regard to RF power. The study reveals that when RF power increases, the surface roughness of the film increases due to the increasing ion density in O_2 plasma. Also, the increase in oxygen containing-functional groups on the surface with increasing RF power is found. As a result, the wetting angle of distilled water on the PET surface decreases with increase of RF power and the adhesive energy increases simultaneously, resulting from increasing polar functional groups and roughening surface. Therefore, the study suggest that the changes in PET surfaces by ICP using the O_2 gas make the films more hydrophilic, resulting in larger adhesion suitable for flexible display applications.

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