

Effect of Ar⁺ Ion Beam in the Process of Plasma Surface Modification of PET Films

JINHO HYUN,¹ PHILIP BARLETTA,¹ KWANGOK KOH,¹ SANGDUK YOO,² JAEHWAN OH,² DAVID E. ASPNES,² JEROME J. CUOMO¹

¹ Department of Materials Science and Engineering, NCSU, Raleigh, North Carolina 27695-7907

² Department of Physics, NCSU, Raleigh, North Carolina 27695-8202

Received 28 October 1999; accepted 14 October 1999

ABSTRACT: In general, plasma modified polymer surfaces tend to show short aging time and rapid hydrophobic recovery after treatment. To prevent reorientation from the surface to the bulk, appropriate crosslinking is necessary among the polymer chains. In this work, an Ar⁺ ion beam was used to provide crosslinking to the surface. Crosslinking was shown by spectroscopic ellipsometry, AFM, and FTIR. Contact angle measurements were performed to see the aging of the modified surfaces. The surface modified with Ar⁺ ion beam followed by RF plasma treatment exhibited reduced chain mobility and a highly stable hydrophilic surface. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1679–1683, 2000

Key words: polymer; plasma; ion beam; crosslinking; hydrophilic

INTRODUCTION

Increased wettability of polymers as a result of plasma treatment has been known for a long time. Among the methods, O₂ plasma surface treatment has been studied extensively because it can effectively provide hydrophilic functional groups to the polymer surface.^{1–3} However, the properties of plasma-modified surfaces are time dependent, and recover their hydrophobicity partially or even completely in a few hours or days.⁴ This aging of plasma-modified surfaces can be detrimental to device performance. Hydrophobic recovery appears to result from a reorientation of surface hydrophilic groups away from the surface or migration of treated polymer chains from the surface to the bulk. To understand the chain mobility, several studies have been done in the last few years.^{5–8}

In this work, we use Ar⁺ ion beam irradiation prior to O₂ plasma treatment in an attempt to reduce polymer chain mobility from the surface to the bulk.

EXPERIMENTAL

Commercial PET (ROHM and HAAS, 0.005" × 40" × 10' clear polyester, crystallinity 30%, M_w 18,000) film was surface modified. Prior to treatment, PET specimens were ultrasonically washed in ethanol and deionized water for 5 min.

The ion beam system used is shown schematically in Figure 1. Specimens were mounted on a flat sample holder and the chamber was evacuated to the base pressure of 10⁻⁶ Torr or better. Treatment was performed for 1 min at a running pressure of 2 × 10⁻⁴. The RF plasma system is a commercially available, capacitively coupled equipment with 13.54-MHz RF power and a quartz-made reaction chamber. Pumping down was done with a Trivac[®] rotary pump using a

Correspondence to: Jinho Hyun.

Journal of Applied Polymer Science, Vol. 77, 1679–1683 (2000)
© 2000 John Wiley & Sons, Inc.

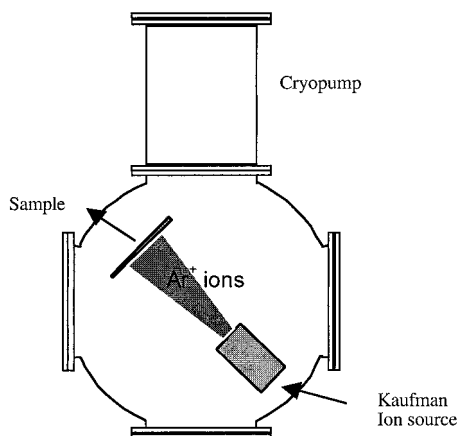


Figure 1 Schematic diagram of the ion bombardment system.

mass trap. All RF plasma treatments were done under 100 mTorr oxygen pressure for 1 min and at a RF power of 180 W.

All treated samples were immediately used for water contact angle measurements and stored in air. The contact angles between the distilled water and the plasma or ion beam-modified polymer films were measured at room temperature using a Goniometer (Rame-Hart, Model 100-00 115 1119), with a droplet technique.⁹ Ellipsometric spectra were recorded from 1.5 to 4.0 eV to obtain information about the dielectric response of the polymer surfaces with a rotating analyzer ellipsometer.⁵ FTIR spectroscopy was performed with a Nicolet 750 spectrometer on the ion beam-irradiated PET films and RF plasma-modified PET films.¹⁰ The incoming source was a KBr laser, and 64 scan spectra were recorded from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Polymer surfaces undergo crosslinking when they are irradiated by Ar^+ ions at energies above 250 eV, which create free radicals in the absence of oxygen or other free radical scavengers. The ions attack the polymer surface and break C—C and C—H bonds, leaving radicals on the surface.¹⁴ If there is any flexibility in the polymer chain, or if the radicals can migrate on the chains, then recombination, unsaturation branching, or crosslinking can occur. The latter effect may improve the chemical resistance, barrier property, hardness, optical density, tribological property, cohesive strength of the surface, and other surface properties.¹⁵

Figure 2 shows the refractive indices of PET samples obtained in the two-phase model. The refractive index can be obtained from the dielectric functions, which were measured from a rotating analyzer spectroscopic ellipsometer. Throughout we used the standard physics convention where a complex dielectric function [$\epsilon(\omega) = \epsilon_1 + i\epsilon_2$] lies in the upper half plane, and the complex refractive index [$\tilde{n}(\omega) = (n + ik)$] lies in the first quadrant.

As can be seen in Figure 2, the refractive indices increase as the irradiation energies increase. From this, we can infer that the layers formed at the surface of the treated PET films are more dense.⁷ The increase in the refractive index may be attributed to a surface densification, and indeed, crosslinking is expected to produce a denser structure. While double or triple bonds are formed if two neighboring radicals in the same chain react, crosslinking occurs when two free dangling ion or radical pairs on neighboring chains unite.

The density change can also be inferred by the observation of polymer structure shrinkage. Free volume is defined as a molecular scale gap or opening of sufficient size to accommodate a migrating molecule. The size, concentration, and mobility of such free volume elements are critical to the surface dynamics of polymers. However, a direct, unambiguous measurement of free volume and free volume distribution in polymers is not available. The most common characterization of solid state chain packing is average fractional

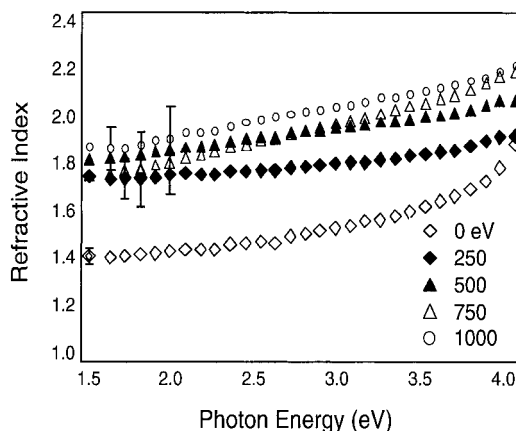


Figure 2 Refractive index data for PET films irradiated with Ar^+ ion at different energies as indicated. The base pressure was 10^{-6} Torr, the running pressure was 10^{-4} Torr, the flow rate was 25 sccm, and the treatment time was 1 min.

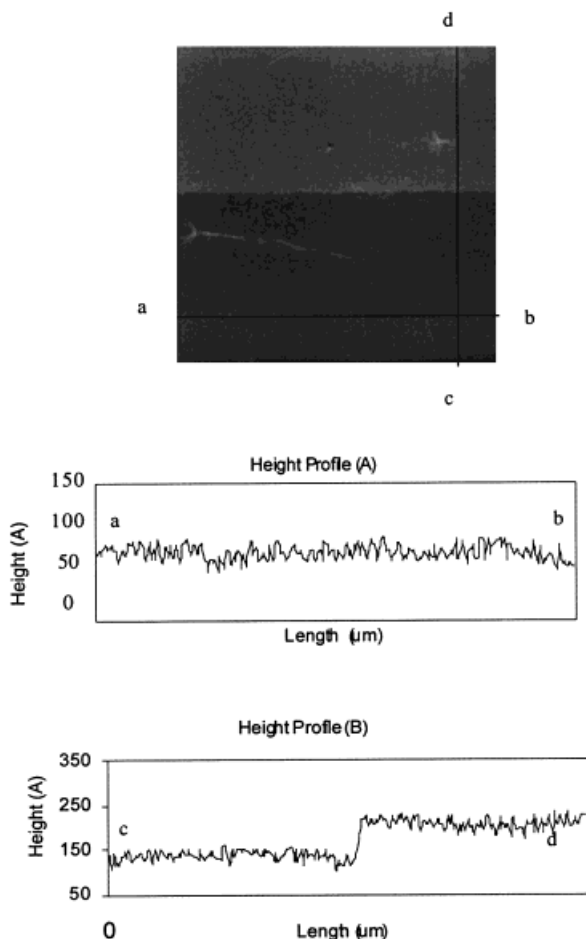


Figure 3 AFM image of the PET surface. The dark region was ion beam irradiated, and the light region is untreated.

free volume, FFV, which is defined as follows: $FFV = (V - V_o)/V$, where V is the polymer specific volume, and V_o is the so-called occupied volume of the polymer. The accessible free volume depends on the efficiency of chain packing and polymer segmental mobility. In general, the free volume of polymers is largely influenced by their chemical structure.¹⁶ When the polymer is irradiated by the ion beam having high energy, reactive radicals or functional groups are formed on the polymer chains. Crosslinking occurs through two adjacent reactive sites, and the polymer chains become highly packed. As can be seen in the AFM image of Figure 3, the difference of height between masked and irradiated films is a good evidence that the density of the irradiated surface area increases. From the profile, it can be seen that the height of the surface irradiated with the ion beam decreases about 100 angstroms with

respect to the surface of the masked film. This shrinkage occurs due to the crosslinking in the surface region and it is in accordance with other results of density increase. The film also shows an apparent contrast between ion beam irradiated and masked PET film. The light region is for the image of a masked PET and the dark region is for the ion beam irradiated. One of the reasons for the contrast on the polymer surface is the existence of color centers in the polymer. The optical density of treated PET films increases due to the formation of color centers like crosslinkings or conjugated double bonds by irradiation.¹¹ The loosely bound delocalized electrons in the conjugated bonds are more mobile than the covalently bonded electrons. In addition, the loosely bound electrons can be excited by the energies of visible light, and color changes result from the absorption of light when it passes through. The color change is generally irreversible, but some color centers such as structurally related radicals, can be reduced or removed by annealing. In this study, however, ion beam-irradiated films did not show a significant change of color after 12 h annealing test at over 120°C. The cause for this may be the formation of permanent color centers with reaction of radical sites during the ion beam treatment. The reflectance of ion beam-irradiated polymers calculated from the data of Figure 2 is shown in Figure 4.

The FTIR survey spectra in Figure 5 display existence of crosslinking in the modified surface. PET samples are unsaturated as indicated by the C=C absorption around 1650 cm^{-1} . As ion beam energy increases from 250 to 750 eV, there is an increase in the C=C absorption band intensity. The peaks of *t*-butyl in hydrocarbons, which are

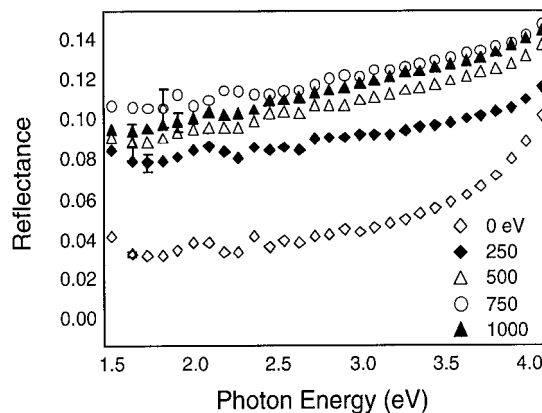


Figure 4 Reflectance of Ar⁺ ion beam treated PET films calculated from the data of Figure 2.

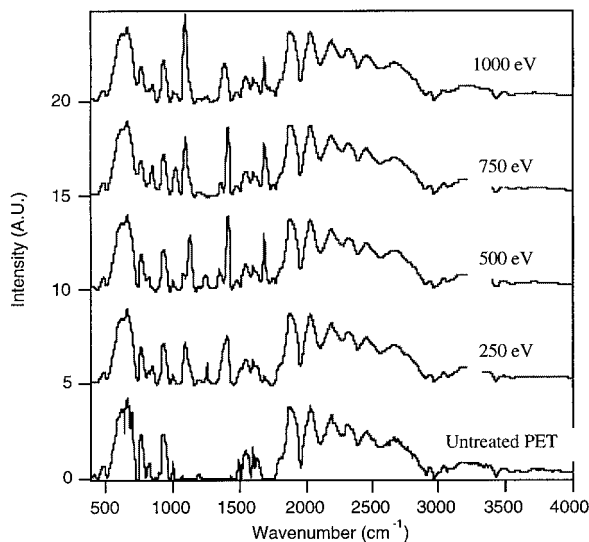


Figure 5 FTIR spectra of Ar^+ ion beam treated PET films.

assigned at 1240 and 1380 cm^{-1} , are also observed in the spectra of Ar^+ ion beam treated PET films.¹² The intensity in the C—O band between 1000 to 1100 cm^{-1} is higher in the 250 eV irradiation and decreases slightly as ion beam energy increases, this band gives the most reliable indication of the formation of C—O—H or C—O—C groups.¹³

Plasma treatments of polymer materials cause a marked increase in the surface oxygen content, which then decays with time after the treatment. In the case of a pure O_2 plasma, ions, atoms, ozone, and metastables of atomic and molecular oxygen, as well as electrons and a broad electromagnetic spectrum, can lead to the observed incorporation of oxygenated functional groups in the surface reaction.² However, O_2 plasma-treated surfaces generally show short aging times and recover hydrophobicity partially or even completely. The possible mechanisms for this are believed to be reorientation or migration of treated polymer chains from the surface to the bulk. The driving force is the minimization of interfacial energy, and this irreversible recovery is found in most plasma-treated polymer surfaces. Although immediately after each plasma treatment the water contact angles show a highly wettable surfaces the surfaces recover original contact angles in a few hours.⁴ Migration from the bulk is most likely to occur if low molecular weight unreacted polymer chains are present. Because these low molecular weight materials usually have lower surface tensions than the higher molecular

weight polymer components, energetic grounds such low molecular weight material should accumulate at the air/polymer surface of both the untreated and the plasma-treated polymer.¹⁷ Such a mechanism should eventually fail by depletion of the low molecular weight species. One of the possible ways to overcome this could be to provide crosslinking in the surface region by ion beam pretreatment.

The effect of ion beam pretreatment on the aging of O_2 plasma-treated PET films is shown in Figure 6. In the case of Ar^+ ion beam pretreatment, the degree of hydrophobic recovery after O_2 plasma treatment is apparently reduced. As the ion beam energy increases, lower contact angle is seen. This may be because of crosslinking between mobile polymer chains. The small amount of hydrophobic recovery may be due to the low molecular chain fragments in the process of O_2 plasma treatment.^{2,4}

CONCLUSION

The effect of Ar^+ ion beam irradiation on the polymer surface and the aging behavior have been discussed. Because most polymers have high mobility, and the migration of polymer chains from the bulk to the surface during hydrophobic recovery, plasma surface modification tends to produce transient effects. This is especially true in the case of low molecular weight materials which, having low surface tension, can easily migrate to the surface. To pre-

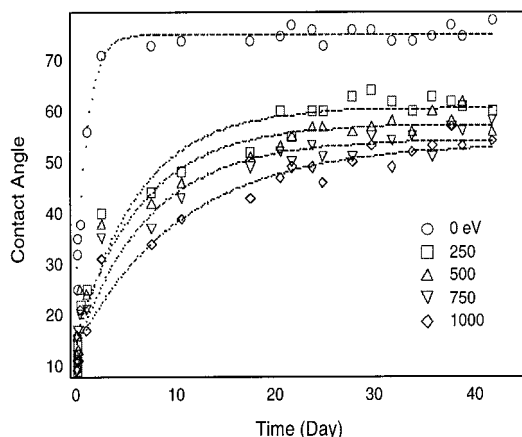


Figure 6 Time dependence of air/water contact angles of Ar^+ ion beam treated PET films followed by O_2 plasma treatment. The base pressure was 10^{-3} Torr, the running pressure was 10^{-1} Torr, the flow rate was 18 sccm , and the treatment time was 1 min .

vent the reorientation of polymer chains, ion beam irradiation was used. The evidences of crosslinking were shown by observing the increase of refractive index, the change of surface profile, and FTIR spectra. The hydrophobic recovery can be slowed down considerably by increasing crosslinking with Ar⁺ ion beam irradiation prior to the O₂ plasma surface treatment.

The authors thank Dr. B. Farcas for goniometry.

REFERENCES

1. Pochan, J.; Gerenser, L.; Elman, J. *Polymer* 1986, 27, 1058.
2. Conrad, J. R.; Radk, J. L.; Dodd, R. A.; Wrzala, F. J. *J Appl Phys* 1987, 62, 4591.
3. Greenwood, O. D.; Hopkins, J.; Badyal, J. P. S. *Macromolecules* 1997, 30, 1091.
4. Stewart, M. T.; Urban, M. W. *Polym Mater Sci Eng* 1988, 59, 334.
5. Aspnes, D. E.; Studna, A.A. *J Optic Soc Am* 1974, 64, 812.
6. Frank, B.; Gast, A. P.; Russel, T. P.; Brown, H. R. *Macromolecules* 1996, 29, 6531.
7. Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys Lett* 1994, 27, 59.
8. Yasuda, T.; Yoshida, K.; Okuno, T. *J Polym Sci Polym Phys Ed* 1988, 26, 2061.
9. Chan, C. M. In *Polymer Surface Modification and Characterization*; Hanser/Gardner: New York; 1994, p. 57.
10. Urban, M. W. *J Adhes Sci Technol* 1993, 7, 1.
11. Nassau, K. In *The Physics and Chemistry of Color*; John Wiley & Sons; New York, 1983, p. 109.
12. van der Mass, J. H. In *Basic Infrared Spectroscopy*; Heyden/Sadtler: Philadelphia, 1969.
13. Danilich, M. J.; Marchant, R. E. *J Appl Polym Sci Appl Polym Symp* 1994, 54, 77.
14. Yasuda, H. *J Macromol Sci Chem* 1976, A10, 383.
15. Schonhorn, H.; Hansen, R. H. *J Polym Sci* 1966, B4, 203.
16. Young, R. J.; Lovell, P. A. In *Introduction to Polymers*, Chapman and Hall: London, 1991, p. 294, 2nd ed.
17. Mills, A. P.; McKenzie, C. A. *J Am Chem Soc* 1954, 76, 2672.