Chemical and Physical Properties of Laser-Modified Polymers

D. S. Dunn and A. J. Ouderkirk*

3M Corporate Research Process Technologies Laboratory, 208-1-01 3M Center, St. Paul, Minnesota 55144. *Received April 28, 1989; Revised Manuscript Received July 3, 1989*

ABSTRACT: Pulsed UV laser irradiation alters the physical and chemical properties of polymer surfaces.[1,2] These property changes have a dominant effect on the production of texture in laser-etched polymers. The chemical and physical nature of the laser-modified surface of poly(ethylene terephthalate) (PET) has been studied by infrared spectroscopy in the work reported here. These studies show that chemical and physical modification occurs in distinctly different power regions. When the infrared absorption intensities of the laser-modified PET are monitored as a function of depth in the polymer, the depth profile of the physical and chemical changes has also been measured. These measurements will be related to excimer laser texturing of semicrystalline polymers.

Introduction

Excimer laser etching of polymer films and fibers is capable of producing maskless texturing of surfaces. The tendency to produce texture is particularly strong in semicrystalline polymers such as poly(ethylene terephthalate) (PET) and natural keratin fibers and films.[3,4] The relationship between crystallinity and laser-induced texturing is an important issue, since the form and degree of polymer crystallinity may be used to control laser-induced texturing. This control is critical for many applications of laser etching. In some applications such as dry patterning, texturing limits the ultimate resolution, finish, and etching efficiency. In other applications such as improvement of adhesion to polymers, texturing is desirable to increase surface area and, because of the cost sensitivity typical in these applications, is ideally created with minimal laser exposure.

Recently, it has been shown that oriented, semicrystalline PET tends to texture after multiple laser pulses during laser etching much more readily than amorphous, unoriented PET.[5] It has been suggested that the etch rate of amorphous PET is higher than that for semicrystalline PET. These results imply that texturing is a result of the different etching rates between the amorphous and crystalline areas. Laser etching of semicrystalline polymer fibers, however, suggests that the formation of texture is the result of polymer relaxation.[4]

The dependence of laser-etched texture on polymer crystallinity and orientation indicates that texture does not arise from optical effects (although optical effects may enhance and modify texture). Rather, the formation of texture is critically dependent on the thin layer of laser-modified polymer at the freshly created polymer surface after each laser pulse. Therefore, as part of any mechanistic study on laser texturing, the effects of subetching fluences (<15–20 mJ/cm^2 at laser wavelengths of 193 and 248 nm) on polymers must be studied. In particular, the effect of laser light on polymer morphology and chemistry, along with the depth of the interaction, needs to be established. This is the subject of the work reported in this paper.

Experimental Section

The semicrystalline PET (27 000 MW) used in this work was 100-μm thick biaxially oriented (3.5 by 3.5) film. This film was heat set and had a crystallinity of about 50% as determined by density. The amorphous PET that was used was 300 μm thick and was prepared by extrusion and quenching on a casting cylinder. Both films had high clarity. IR measurements were made on PET films spin cast from *o*-chlorophenol solution on either Al- or Au-coated polished silicon wafers. Amorphous spin cast films were prepared by drying the cast films in a vacuum oven at about 75 °C for 2 h. Semicrystalline films were prepared by thermal crystallization of the dried, amorphous films at 200 °C under vacuum for 2 h. Final PET film thicknesses were 100–170 nm.

A Lambda Physik 201 MSC excimer laser with a stable resonator was used to treat the PET samples. The nominal pulse width was 20 ns. All laser exposures were done in air. The infrared absorption measurements were made in the reflection-absorption configuration using an IBM Instruments IR44 FTIR spectrophotometer. The spectra were acquired using a variable angle reflection attachment with a beam angle of 78°. Surface analysis was done with a Physical Electronics model 5100 XPS. UV–visible spectra were taken with a Perkin-Elmer Lambda 9 spectrophotometer. The UV–visible reflectivity measurements were made by using an integrating sphere configuration to collect both diffuse and specularly reflected light.

Results and Discussion

Figure 1 compares the transmission spectrum at normal incidence in the visible and near IR spectral regions of excimer laser treated biaxially oriented PET to the spectrum of untreated polymer. The figure shows that the transmission of the PET increases from 88 to 92% in the visible region when treated on both sides with one pulse of 17 mJ/cm^2, 248-nm light. As described in ref 1, the increased transmission is accompanied by an equal decrease in reflectivity of the polymer, indicating that the laser treatment is creating a surface on the PET that is antireflective.

The observed antireflectivity is due to the formation of a thin layer of low refractive index polymer by the excimer laser light. The thickness of this thin layer can be estimated by fitting a numerical thin film optical model to measured transmission spectra such as those shown in Figure 1. In the optical model used here the individual optical layers were assumed to be homogeneous with plane parallel boundaries. The reflectivity and the transmission of the optical structure was then calculated from the Fresnel reflection coefficients at each interface in the structure using the optical constants of the individual layers. An estimate of the thickness of the antireflective layer was determined from these calculations by placing a film of variable thickness and refractive index profile on a substrate that had the refractive index of biaxially oriented PET (n = 1.64). The optical modeling results along with the experimental change in the transmission spectrum of PET on laser treatment at a wavelength of 193 nm are shown in Figure 2. The calculated transmission changes suggest that the excimer laser reduces the

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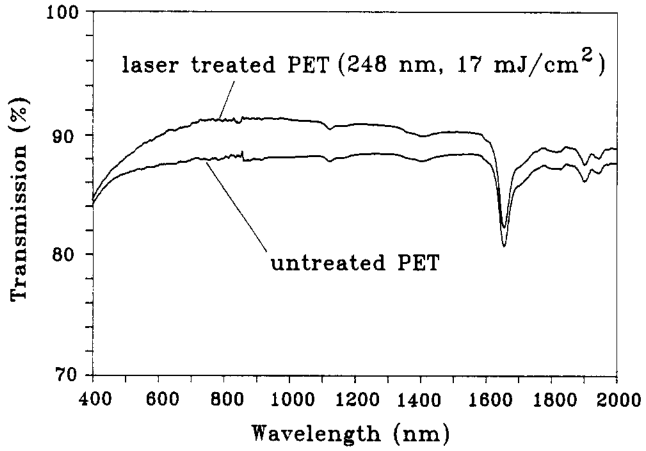

Figure 1. Transmission spectra of untreated and excimer laser-treated biaxially oriented PET film.

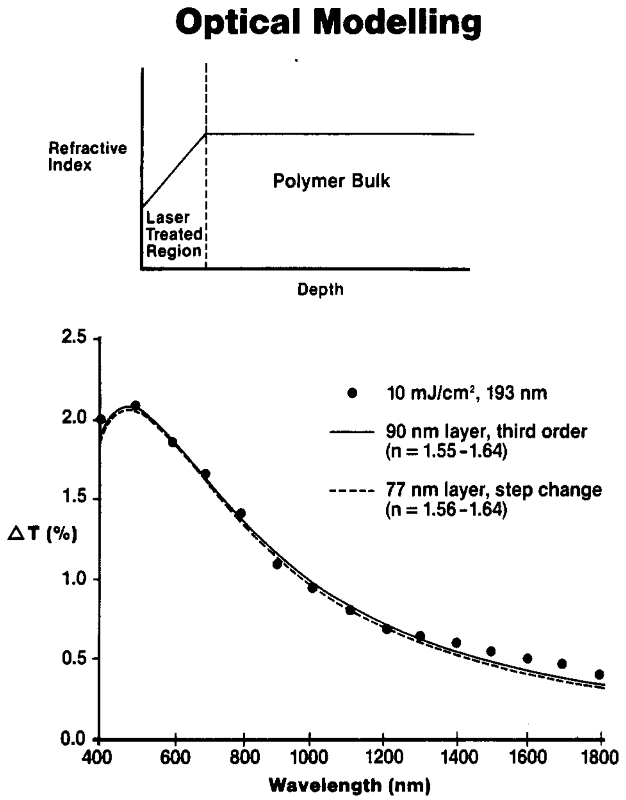

Figure 2. Optical modeling results. The material configuration modeled is shown schematically at the top of the figure. Measured changes in transmission are shown by the circles. Calculated changes in transmission are given by the solid and dashed lines.

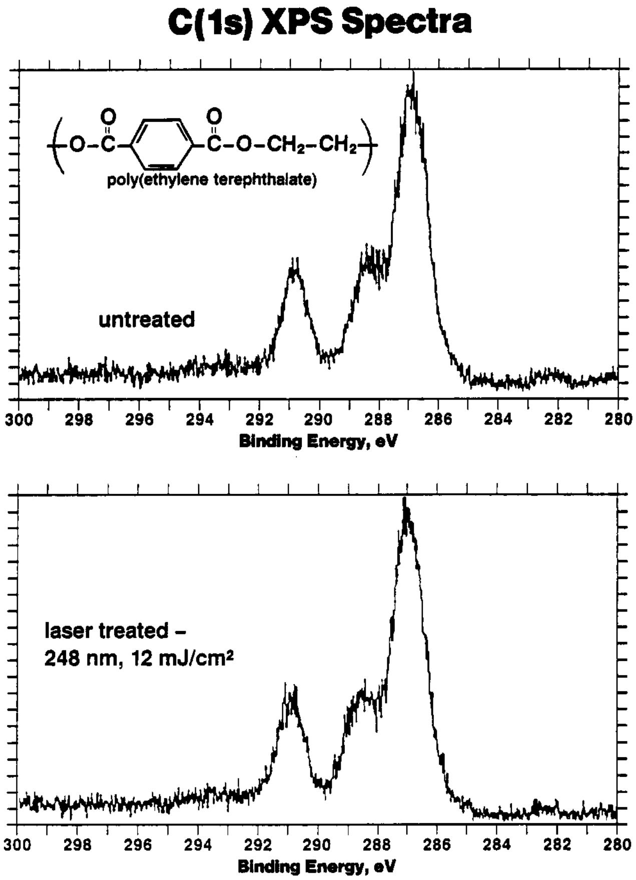

Figure 3. XPS spectra in the C(1s) region of untreated (top) and laser-treated (bottom) biaxially oriented PET.

refractive index of 80 to 90 nm of PET from the initial value of 1.64 to about 1.55 at the PET surface. The optical model also shows that there is little detectable difference between a step change in refractive index (dashed line in Figure 2) or a graded refractive index profile (solid line in Figure 2) on going from the laser-modified to the unmodified layers of the polymer. Ellipsometric measurements, described in ref 1, support the depth of modification and change in refractive index determined by the optical model. The depth of modification is also reasonable on the basis of the absorptivity of PET at 193 nm (absorbance of 1/e for a 50-nm thick film).

The change in refractive index of PET described above is quite substantial. There are at least three mechanisms in which the laser can cause this large a change in refractive index: 1, polymer cross-linking or bond scission; 2, texturing or increased porosity; 3, altering polymer morphology. Reference 1 shows that XPS, water contact angle, and gel permeation chromatography indicate that at low fluences, laser exposure causes very little change in polymer chemical structure or molecular weight. Figure 3 shows XPS spectra in the C(1s) region of biaxially oriented PET before and after laser treatment at a wavelength of 248 nm and a fluence of 12 mJ/cm². The spectra in Figure 3 show that both before and after laser exposure the PET is composed of only three kinds of carbon atoms in a 3:1:1 ratio consistent with the chemical structure of the ideal PET repeat unit. In addition, examination of the O(1s) spectral region showed that the C/O ratio is invariant on laser exposure at a value of 2.66 which is in good agreement with the theoretical value of 2.5. These results suggest that mechanism 1, cross-linking or bond scission, is not the dominant cause of the observed laser-induced antireflectivity.

In Figure 4, SEM analysis of PET before and after laser treatment shows no change in polymer texture. This rules out mechanism 2, an increase in polymer texture, as the cause of the PET antireflectivity. A change in polymer morphology due to amorphization of a thin layer at the PET surface, mechanism 3, is therefore the preferred mechanism. This is in agreement with the observation that laser treatment of amorphous PET, at fluences that make semicrystalline PET antireflective, has no effect on the optical properties of the amorphous polymer. This is shown by the data in Figure 5. Amorphization of the polymer surface region is further supported by the similarity of the refractive index of laser modified polymer (determined by ellipsometry at a wavelength of 632.8 nm and computer models) to the reported refractive index in the visible of 1.576 of amorphous

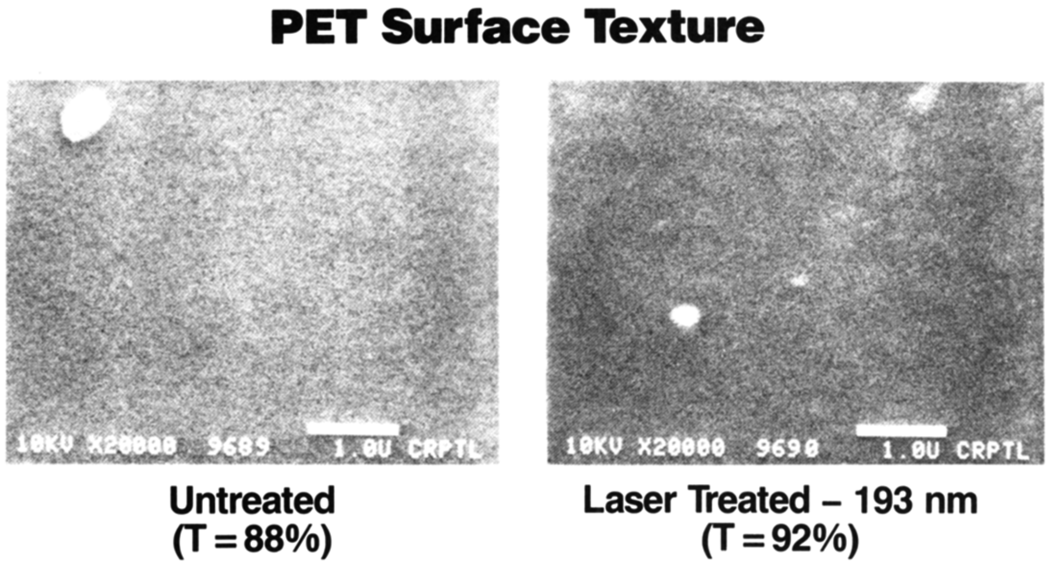

Figure 4. Scanning electron micrographs of untreated and excimer laser-treated biaxially oriented PET. The length of the white bar in each photograph is 1 μm.

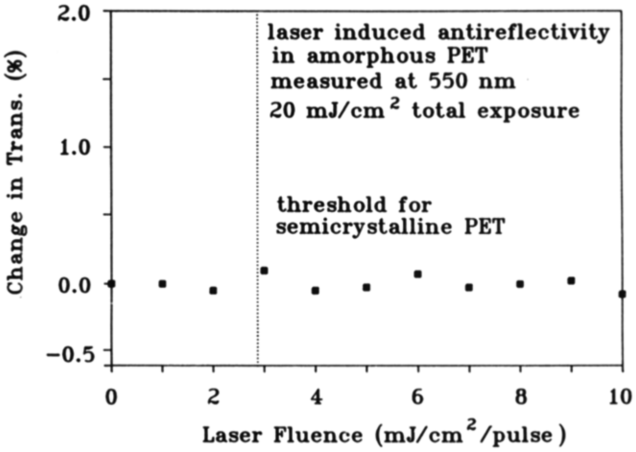

Figure 5. Plot of the change in transmittance, measured at 550 nm, of cast amorphous PET as a function of laser fluence at 248 nm.

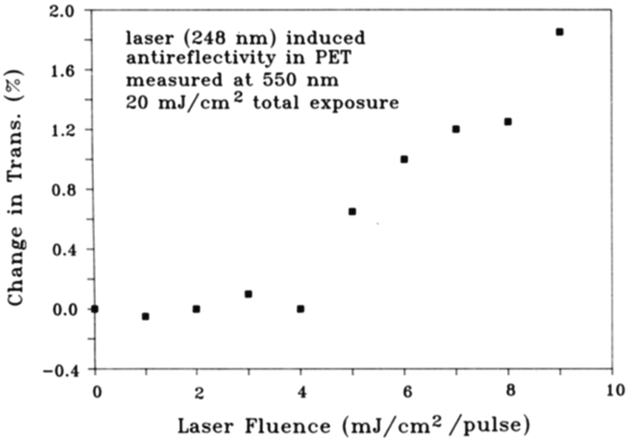

Figure 6. Plot of the change in transmittance, measured at 550 nm, of biaxially oriented PET as a function of laser fluence at 248 nm.

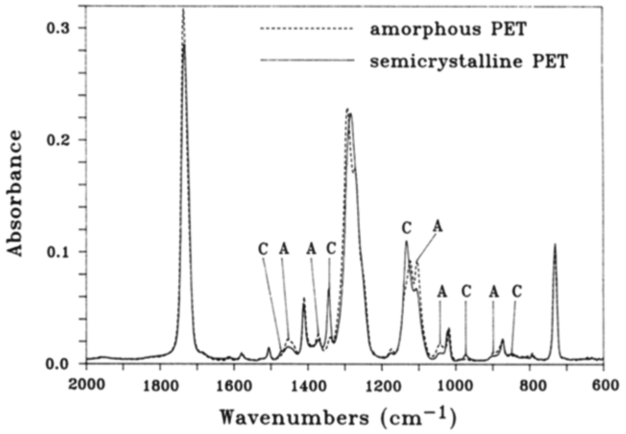

Figure 7. Infrared absorption spectra of 100-nm thick amorphous and semicrystalline PET films (A = absorption bands characteristic of amorphous PET; C = absorption bands characteristic of crystalline PET).

PET.[6] Finally, the effect of excimer laser light on the optical transparency of semicrystalline PET shows a strong threshold fluence, as can be seen in Figure 6. Since the total UV exposure was approximately constant at 20 mJ/cm^2 for the data shown in Figure 6, the effect of the laser light on PET can most easily be described by a nonlinear process such as thermal melting followed by quenching of the melt. A linear, photochemical process would have resulted in the same antireflectivity for all the laser fluences used. As Figure 6 shows, this is clearly not the case.

IR spectroscopy provides a very convenient method for studying laser modification of polymer surfaces. Because of the sensitivity of molecular vibrations to bond strengths and configurations, IR spectroscopy is a sensitive method for determining both the extent of morphological change and photodecomposition occurring in a polymer on laser exposure. Unfortunately, the depth of laser modification of the PET sample is small compared to the thickness of commercially available PET film. Therefore, standard transmission IR measurements on laser-treated polymers do not reveal any useful information.[7] IR reflection absorption spectroscopy (IRRAS), however, provides a method for studying thin supported films.[8] This technique is highly sensitive and has allowed us to study polymer films as thin as 10 nm. Since film thicknesses can now be chosen that are equal to the laser penetration depth, the IRRAS spectra are unencumbered by spectral features of the untreated polymer.

Figure 7 shows the IR spectra of cast amorphous PET and the same film after thermal crystallization. The

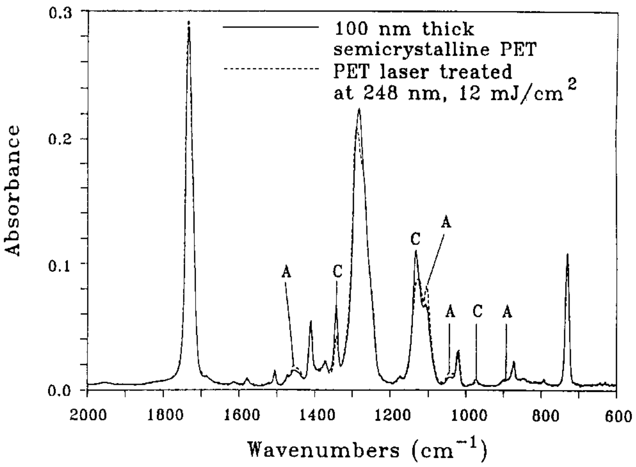

Figure 8. Infrared absorption spectra of 100-nm thick semicrystalline PET film before and after excimer laser exposure (A = absorption bands characteristic of amorphous PET; C = absorption bands characteristic of crystalline PET).

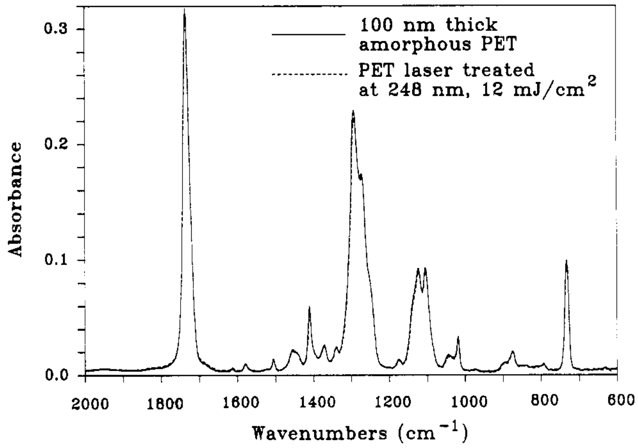

Figure 9. Infrared absorption spectra of 100-nm thick amorphous PET film before and after excimer laser exposure.

changes in IR absorption due to crystallization are well documented, and the major crystalline and amorphous IR absorption bands are indicated in the figure (A = absorbance characteristic of amorphous PET; C = absorbance characteristic of crystalline PET). Figure 8 shows the IR spectrum of the crystalline film of Figure 7 after laser treatment with two pulses of 248-nm light at 12 mJ/cm^2 per pulse. The spectral changes shown in Figure 8 indicate that the laser converts a large fraction of the crystalline film to amorphous polymer. The IR spectra in Figure 8 also show that there is very little photodecomposition. This is seen more clearly from the IR spectra of an amorphous PET film before and after laser treatment shown in Figure 9. Here there is no detectable spectral change, indicating a complete absence of photodecomposition. These IR measurements on amorphous PET have been repeated on laser-treated films as thin as 10 nm and show that laser amorphization is not accompanied by photodegradation for laser exposure at 248 nm. In addition, laser-amorphized PET films can be thermally recrystallized to yield films whose IR spectra are nearly identical with the spectrum of a semicrystalline film, such as that shown in Figure 7. This indicates that there is very little cross-linking of the polymer during laser exposure.

The nature of the IRRAS samples also allows the effect of laser treatment on PET to be depth profiled. By depth profiling the laser treated samples, the true extent and depth of laser amorphization can be unequivically determined. We have developed a technique for determining the IR spectra of thin sections of the 100–200-nm thick PET films. The technique will be described in more detail in a future publication. Briefly, oxygen sputter etching is used to etch away layers of the PET while the sample is in the IR beam path. When spectra are subtracted before and after etching, IR spectra can be produced for the section of film etched away. It has been previously shown that for the conditions used here sputter etch damage (i.e., oxidation, cross-linking) to the PET films has an equivalent thickness of less than 5 nm and therefore does not significantly alter the spectra of 100–200-nm thick films.[9] In addition, the small amount of damage that does occur during oxygen sputter etching comes to equilibrium in very short etching times (10–15 s). The effects of these etch products on each IR spectrum can then be removed when successive spectra are subtracted to produce the spectrum of the film that has been etched away in each etching step.

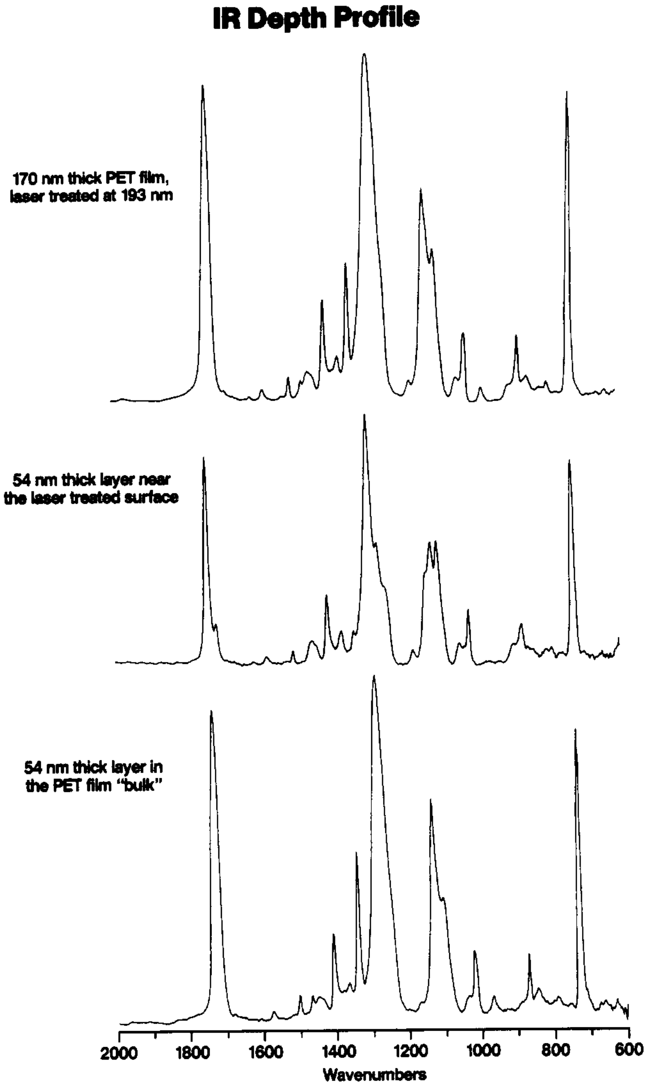

Figure 10. Infrared absorption spectra of 170-nm thick excimer laser treated semicrystalline PET film: upper, spectrum of entire film; middle, spectrum of a 54-nm thick section of the film at the surface; lower, spectrum of a 54-nm thick section near the film/substrate interface.

A 170-nm thick PET film that had been treated with one, 7 mJ/cm^2 pulse from a 193-nm excimer laser was IR depth profiled as described above. The IR spectrum of this film before depth profiling is shown by the upper spectrum in Figure 10. The IR spectrum of a 55-nm thick section near the surface of this laser-treated film is shown

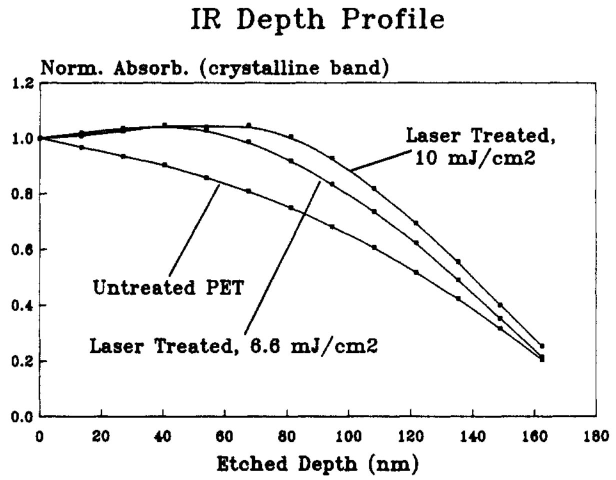

Figure 11. Plot of the peak absorbance of the crystalline absorption band at 1344 cm^{-1} of the PET remaining as a function of the polymer thickness etched off for an untreated semicrystalline PET film and two laser-treated semicrystalline films.

by the middle spectrum in Figure 10. This spectrum shows that the PET near the surface is completely amorphous. This is particularly easy to see by the weak absorption intensity of the band at 1344 cm^{-1} that is characteristic of crystalline PET (cf. Figure 7). The IR spectrum of a section of this same PET near the substrate, shown by the lower spectrum in Figure 10, however, indicates that the PET in this region is highly crystalline. The PET at this depth in the film is beyond the effective penetration depth of the laser for a fluence of 7 mJ/cm^2.

The change in polymer crystallinity vs depth in the film can also be seen from the data shown in Figure 11. In this figure the peak intensity of the crystalline absorption band at 1344 cm^{-1} for the PET remaining after each etching step is plotted as a function of etch depth for an untreated film and films laser treated at 7 and 10 mJ/cm^2. This figure shows that the total absorbance of the crystalline peak decreases uniformly as polymer is etched off of the untreated PET film.[10] The crystalline regions in the untreated film are homogeneously distributed throughout the polymer depth. For the two laser-treated films, however, the crystalline absorbance is initially constant with etching time. Laser exposure has completely amorphized the surface region of these films so there is no crystalline material removed during the initial stages of etching. As the laser-treated films are more extensively etched, the crystalline absorbance finally starts to decrease due to removal of polymer that was beyond the effective penetration depth of the laser. From the data in Figure 11, a depth of amorphization of 70–80 nm is obtained for laser treatment at a fluence of 10 mJ/cm^2. This depth is in good agreement with the value suggested by the optical analysis of thicker, laser-modified PET films shown in Figure 2.

Conclusion

Semicrystalline PET is amorphized to a depth of 60–90 nm (dependent on laser fluence) by excimer laser treatment at fluences below the threshold for etching. Therefore, in a laser etching process only the first excimer laser pulse exposing the polymer surface will etch semicrystalline material. Subsequent pulses will etch amorphous polymer modified by the preceding laser pulse. Since the first pulse causes only minor texturing, the origin of laser texturing of polymers is not due to differential etching of crystalline and amorphous areas. This conclusion is further supported by the observation that the crystallite size in biaxially oriented PET is much smaller than the minimum size of the topological features formed by laser texturing (30 nm vs 500 nm, respectively).

The laser amorphization reported here is extremely rapid, occurring during the laser pulse. On the basis of the difference in density between amorphous and crystalline PET, the laser-induced polymer melting should be accompanied by a 5–10% increase in volume. This expansion will be accompanied by polymer relaxation that will cause anisotropic expansion of the polymer. The creation of texture in laser-etched semicrystalline polymer films is, therefore, most likely a result of this anisotropic strain created in the laser amorphization process.

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References and Notes

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(10) Optical calculations show that the nonlinearity in the plot of absorbance vs etched depth in Figure 11 for the untreated PET film is due to variations in the electric field strength of the spectrophotometer beam in the film as the thickness is decreased by the etching process.