Surface Modification of Polyethylene and Polypropylene by Ion Implantation

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SYNOPSIS

The creation of oxidized structures and double bonds in polyethylene (PE) and polypropylene (PP) samples implanted with P^+ ions was studied. The surface polarity and the electrical conductivity of the ion-implanted polymers were also examined. As a result of the ion implantation, the polymer macromolecules are broken up and the material is degraded. An oxygen penetration into the radiation-damaged polymers is also observed, with PE being more vulnerable to the oxidation. The ion-implanted PP exhibits higher surface polarity and sheet conductivity compared to that of PE. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ion implantation is one of the most powerful techniques for surface modification of organic and inorganic materials. A great advantage of the method is that the space localization of the dopant may be precisely controlled. As the thickness of the surface layer affected by ion implantation does not exceed several tenths of micrometers, the mechanical properties of the exposed material are practically not changed.

By ion implantation, the electrical conductivity of polymers can be increased by 14 orders of magnitude, i.e., to the level comparable with that of conductive inorganic materials.[1] It has been demonstrated that by ion implantation the surface polarity of originally nonpolar polymers (e.g., polypropylene) can be increased.[2] As a result, the wettability and the sticking properties of the polymers are also improved.[2,3] The penetration of energetic ions leads to the degradation of the polymer,[2] which is often denoted as carbonization.[4-6]

In this study, we examined the effect of ion implantation on the chemical structure, surface polarity, and electrical conductivity of polypropylene (PP) and polyethylene (PE).

EXPERIMENTAL

The experiments described below were done on 10 μm-thick foils of PE with molecular weight (M_n) equal to 180,000 and the density (ρ) equal to 0.945 g cm^{-3} and of PP, 150,000 and 0.901 g cm^{-3}, respectively. The samples were implanted with 150 keV F^+ ions to the fluences of 1×10^{11}–1×10^{15} cm^{-2}. The ion implantation was performed at room temperature with residual pressure in the implanter target chamber of 10^{-6} Torr. The ion beam current density was kept below 50 nA cm^{-2} to avoid thermal degradation of the samples. The samples were implanted from both sides to strengthen expected changes in optical absorbance.

The polar component of the free surface energy, γs^p, was determined from the contact angle of the polymer surface measurement using a reflection goniometer. Hexane as a nonpolar and water as a polar liquid were utilized.[2,3,7] The UV-visible and IR spectra were obtained using standard spectrophotometers. The surface structure of the ion-implanted polymers was also studied using the standard Rutherford backscattering (RBS) technique with 1.3–2.0 MeV alpha particles. The particles scattered under

120°–160° angles were registered with a Si(Au) semiconductor detector (fwhm = 15 keV). The sheet conductivity was determined using a standard four-point probe method.

RESULTS AND DISCUSSION

It has been shown that during ion implantation polymeric materials oxidize and carbonyl groups are created.[2,8] In Figure 1(a), the increase of the 1720 cm^{-1} absorption band (ΔA_{1720}), which is a characteristic maximum for the carbonyl group, is shown as a function of the F^+ ion fluence ϕ. The concentration of the carbonyl group increases with increasing ion fluence and the concentration vs. fluence dependence becomes steeper at higher ion fluences. The later effect is more pronounced in PE samples. Also, the total concentration of the carbonyl group is higher in PE than in PP. It may be concluded that the oxidation of PE is more intensive.

These findings were confirmed also by RBS measurements of the same samples. In PP, the oxidation initially limited to the radiation-damaged surface layer proceeds steadily inward and a homogeneously oxidized layer is built up. The well-defined sharp interface between the oxidized layer and the bulk PP moves inside with a mean velocity of 4.0×10^{-5} nm s^{-1}. The ion-implanted PE samples are homogeneously oxidized from the sample surface up to the depths accessible to the RBS technique. The surface ratio of oxygen and carbon atomic densities in ion-implanted PP and PE samples increases from about 0.06 for the ion fluences below 1×10^{14} cm^{-2} to about 0.17 for higher ones. As the PE samples are fully oxidized, the total oxygen content in the PE surface layer is several times higher than in the PP samples implanted to the same ion fluence.

The presence of the carbonyl $C = O$ groups observed in the IR spectra indicates that a significant part of the oxygen atoms is chemically bound. The characteristic absorption maximum of the $C - F$ group was not found in the IR spectra and no fluorine atoms (above the RBS detection limit) were observed in RBS measurements. It is therefore supposed that the implanted fluorine atoms are mobile in the radiation-damaged polymer and their initially sharp depth distribution is smeared out by a diffusion process.

In the next experiment, the increase of the 1650 cm^{-1} absorption band amplitude (ΔA_{1650}) was determined as a function of the implanted ion fluence [Fig. 1(b)]. This band is characteristic for double bonds in polyolefins.[8] It is clearly seen from Figure 1(b) that the double-bond concentration is an in-
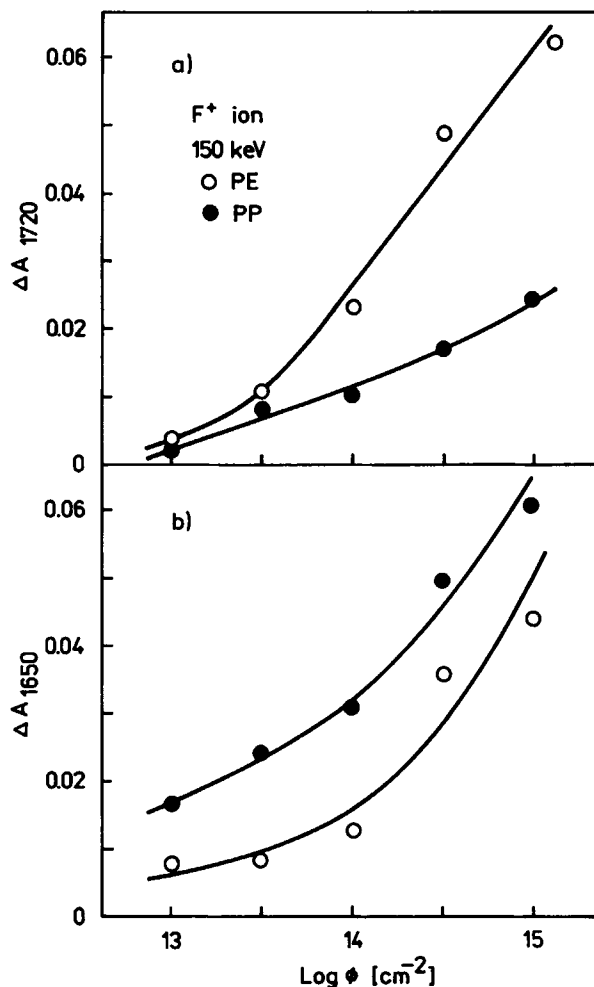

Figure 1   The dependence of the absorbance increase (ΔA) on the fluence of the implanted F^+ ions in the (○) PE and (●) PP samples: (a) absorption band at 1720 cm^{-1}; (b) absorption band at 1650 cm^{-1}.

creasing function of the ion fluence. For the same fluence, the concentration of double bonds in PP is higher compared to that in PE.

The arrangement of the double bonds in the molecule significantly affects the chemical structure of the polymer. It is well known that the polymer absorbance is affected by the presence and the degree of conjugated double bonds in the molecular chain. It has been reported[9] for UV-visible spectra that absorption maxima are observed in conjugated systems having a higher number of double bonds. The UV-visible spectra for the PE and PP samples implanted to the different ion fluences are shown in Figure 2. With increasing ion fluence, the concentration of the double bonds increases and the degree of conjugation becomes larger. The effect is more pronounced for the PP samples.

The sheet conductivity was also measured on the
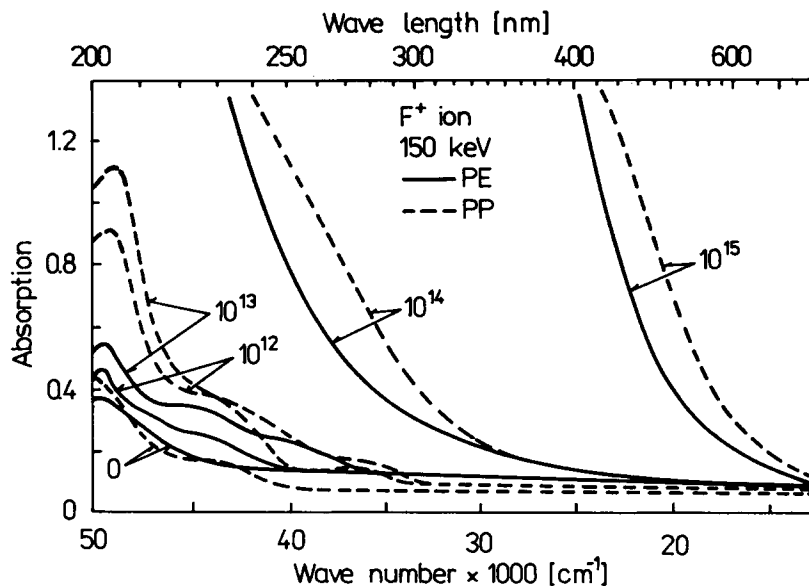
Figure 2   UV-visible spectra measured on the PE and PP samples implanted with the F^+ ions to different ion fluences. The numbers along the curves give the ion fluences in cm^{-2}.

PE and PP samples implanted to the different ion fluences. For the samples implanted to the fluences lower than 1×10^{15} cm^{-2}, the sheet conductivity was below 1×10^{-12} S. For the PE and PP samples implanted to the fluence of 1×10^{15} cm^{-2}, the measured sheet conductivities were 2×10^{-11} and 3×10^{-10} S, respectively. This result compared with the data shown in Figures 1(b) and 2 (higher concentration of conjugated double bonds and higher conductivity by PP) supports the proposed hopping mechanism[10] of the electrical conductivity of doped polymeric materials.

As mentioned above, the surface polarity of initially nonpolar polymers can be increased by ion implantation. The dependence of the polar component of the free surface energy, γs^P, for the PE and PP samples implanted with F^+ ions on the ion fluence is shown in Figure 3. The polar component increases with increasing ion fluence. The higher polar values for PE implanted to lower fluences can be explained by the presence of light stabilizers in the PE samples. The surface polarity of PP increases much faster with increasing ion fluence, and for the fluence above about 5×10^{13} cm^{-2}, it exceeds that of PE. This means that the concentration of the polar groups (e.g., $C = O$) created as a result of the ion implantation on the PE surface is lower than in the case of the PP samples. The surface degradation of the PP samples exposed to the F^+ ion beam is stronger but the PE samples are degraded to larger depths.

During the ion implantation, the polymer macromolecules are split and the average molecular weight of the sample surface layer decreases. PE
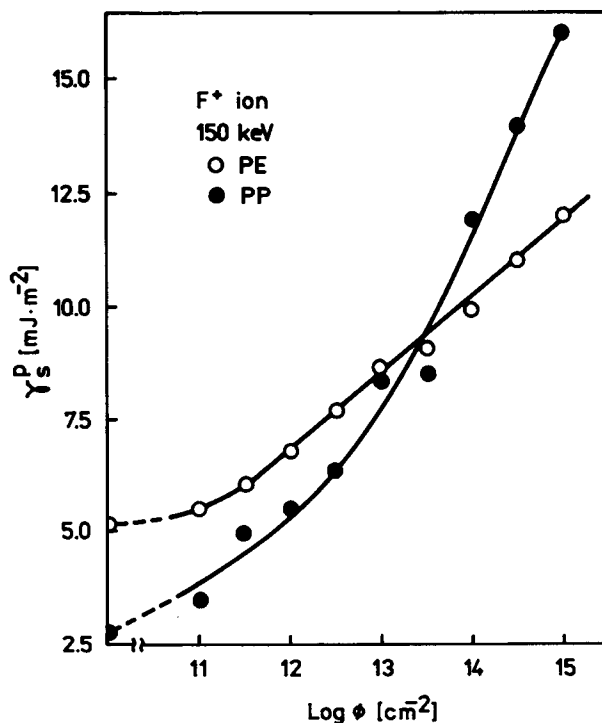
Figure 3   The dependence of the polar component of the surface free energy on the F^+ ions implanted into ($\bigcirc$) the PE and ($\bullet$) PP samples.
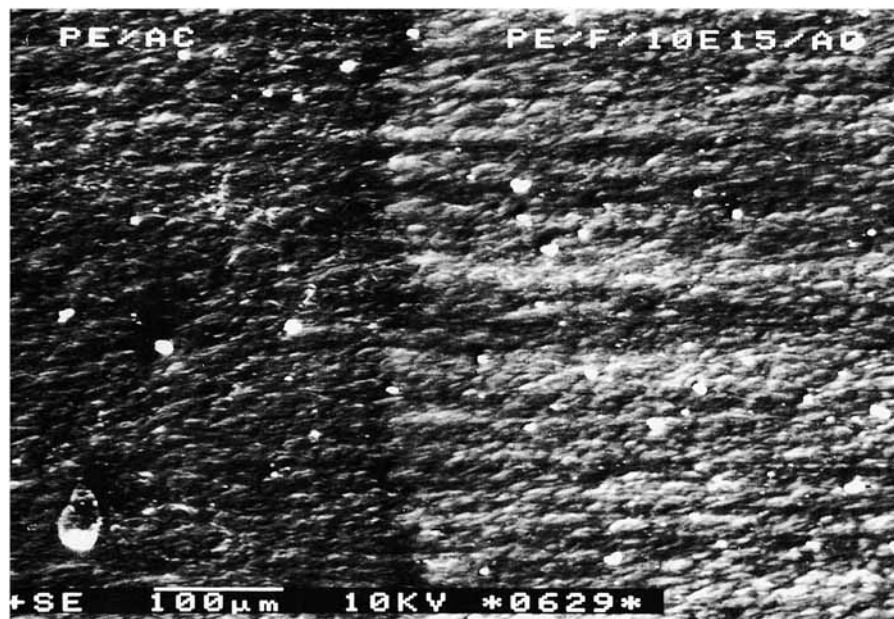
Figure 4 SEM photographs of the PE samples etched in acetone for 15 min. PE/AC = pristine, unimplanted PE sample; PE/F/10E15/AC-PE sample implanted to the fluence of 1×10^{15} cm^{-2}.

and PP are known to be generally insoluble in common solvents. The molecular fragments can be transferred into solution more easily. The dissolution of the pristine and the ion-implanted PE samples was studied and the results are shown in Figure 4. On the etched PE samples, the oriented domains of macromolecules are observed. This phenomenon confirms the molecular splitting and the subsequent dissolution of the radiation-damaged surface layer.

CONCLUSION

The implantation of F$^+$ ions into the PE and PP samples results in the splitting of molecular bonds plus creation of conjugated unsaturated bonds and oxidized structures. The surface degradation of the PP is stronger compared to that of the PE, but the PE is degraded to larger depths. The higher sheet conductivity of the ion-implanted PP in comparison with that of the PE is explained by the higher concentration and a higher degree of conjugated double bonds in the former material. The present results support the supposed hopping mechanism of the electrical conductivity of ion-exposed polymers.

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