

Ion Irradiation of Polypropylene

INTRODUCTION

Ion irradiation of polymers has recently received increasing attention. The possibility of making microelectronic components by ion-beam lithography is documented in the literature.¹⁻³ Fundamental studies have been published¹⁻⁹ dealing with the effect of ion irradiation on poly(methyl methacrylate) (PMMA), which is the commonly used resist material. The creation of a hydrophilic surface on hydrophobic polymers such as polypropylene or polyethylene is another potentially interesting area.

When polymers are subjected to electrical discharges, ions are formed which are responsible, at least to some extent, for the degradation of the polymer which precedes the final breakdown. Hence, knowledge of the mechanisms for the interaction between ions and polymer and the succeeding reactions within the polymer is required for an understanding of the process involved in electrical breakdown of polymers.

The dominating mechanism for energy transfer from ions to polymer is inelastic collisions, referred to as *electronic stopping*, which affect the energy level of the electrons.⁹ The electron excitations lead to the formation of free radicals and subsequent chemical reactions in the polymer. This paper presents data obtained by infrared spectroscopy, ESCA and scanning electron microscopy on isotactic polypropylene which has been subjected to varying irradiation doses of helium and argon ions. These data are compared with results from a computer simulation of the penetration of ions in the polymer. The mechanisms involved in the degradation of the polymer are discussed.

EXPERIMENTAL

Films, $25 \pm 3 \mu\text{m}$ thick, were compression-molded from a commercial isotactic polypropylene grade (Propathen GWE23, ICI, U.K.; density = 905 kg/m^3). IR spectroscopy showed that this polymer contained 0.1% (w/w) of antioxidant [1,1,3-tris-(4-hydroxy-2-methyl-5-*t*-butylphenyl)butane]. Ion irradiation of the films with helium and argon was carried out in a 100 keV (16.2 fJ) isotope separator (pressure: 0.47 mPA, temperature: 294 K). The energy of the helium and argon ions was 70 keV (11.2 fJ) in all experiments and the irradiation dose was varied between 10^{14} and 10^{16} at./cm^2 .

The irradiated films with an approximate diameter of 15 mm were analyzed by reflection infrared (ATR-IR) spectroscopy (Perkin-Elmer 1710 Fourier transform infrared spectrometer; each spectrum is based on 50 scans), electron spectroscopy for chemical analysis (ESCA; Leybold Heraeus ESCA/Auger Spectrometer LH 2000), and after gold sputtering by scanning electron microscopy (SEM; ISI Mini Super SEM).

The depth of penetration of the ions was calculated by simulation using the TRIM Monte Carlo computer program.⁸ The calculations were carried out for ^4He and ^{40}Ar particles with an energy of 70 keV (11.2 fJ). The density of the PP material was taken to be 910 kg/m^3 and the molecular composition C_3H_6 . Bragg's law of linear additivity of the stopping cross sections for each individual element was assumed to be valid. In each calculation, 1000 particle trajectories in the solid material were simulated.

RESULTS AND DISCUSSION

Typical IR spectra for samples irradiated by He ions are shown in Figure 1. Three major absorption peaks develop: 1640 cm^{-1} (vinyl groups), 1685 cm^{-1} (α,β -unsaturated ketones), and $1720\text{--}1735 \text{ cm}^{-1}$ (aldehydes and ketones). The assignment of these absorptions bands is made according to Luongo.¹⁰ Two minor absorption peaks located at 1597 and 1653 cm^{-1} were observed in the spectra of the irradiated samples. Comparison of the absorbance value (A_{1700}) of

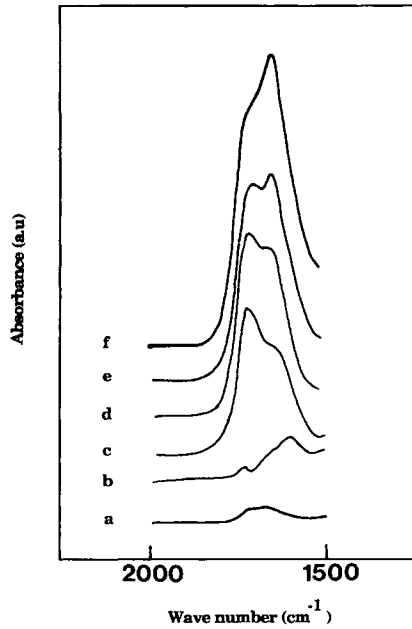


Fig. 1. Infrared spectra of samples irradiated by He^+ at the following dose levels (at./cm^2): (a) 0; (b) 2×10^{14} ; (c) 5×10^{14} ; (d) 1×10^{15} ; (e) 2×10^{15} ; (f) 5×10^{15} .

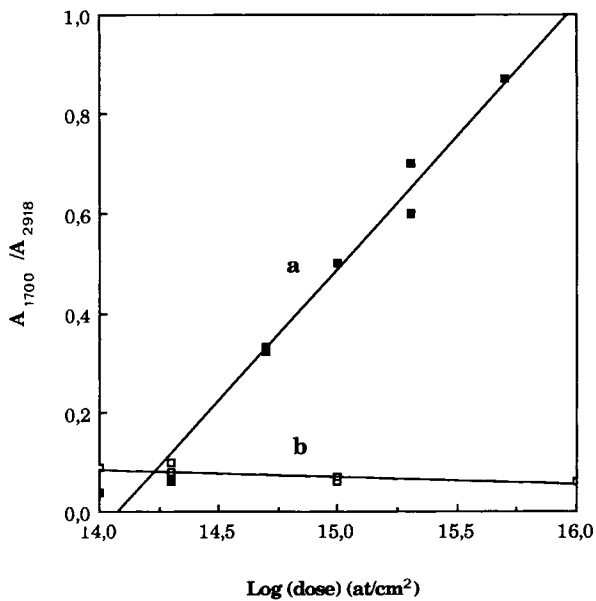


Fig. 2. Carbonyl-vinyl index (A_{1700}/A_{2918}) for samples irradiated by He^+ (a) and Ar^+ (b) plotted as a function of dose of irradiation.

the major absorption peak in this frequency domain with the absorption band corresponding to the —CH band at 2918 cm^{-1} (A_{2918}) enabled a carbonyl-vinyl index A_{1700}/A_{2918} to be established. It should be noted that the three absorption band (1640 , 1685 , and $1720\text{--}1735\text{ cm}^{-1}$) are severely overlapping and that A_{1700} is a composite value dependent on all three bands. Figure 2 presents data for the carbonyl–vinyl index as a function of irradiation dose for both He and Ar ions.

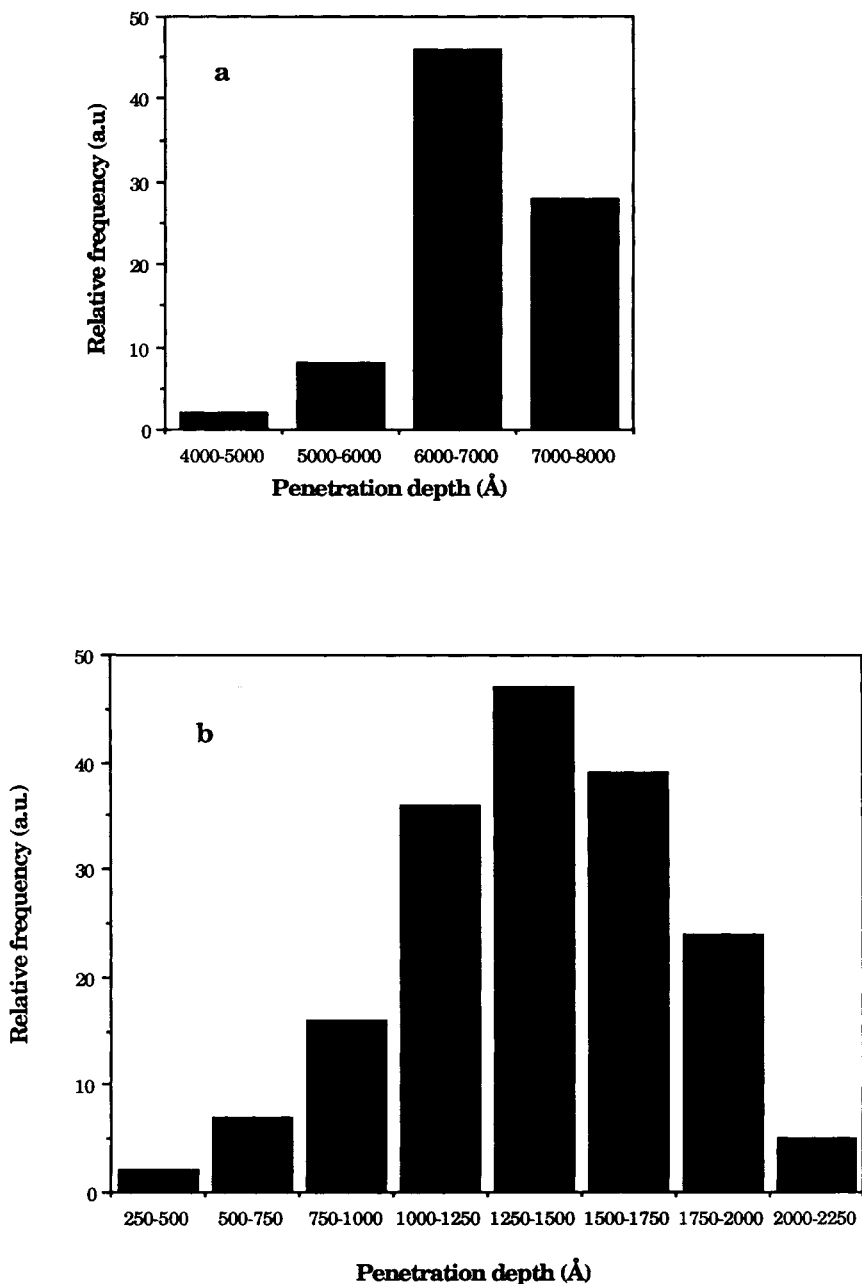


Fig. 3. Calculated penetration profile of (a) He⁺ and (b) Ar⁺. Energy of the ions: 70 keV (11.2 fJ).

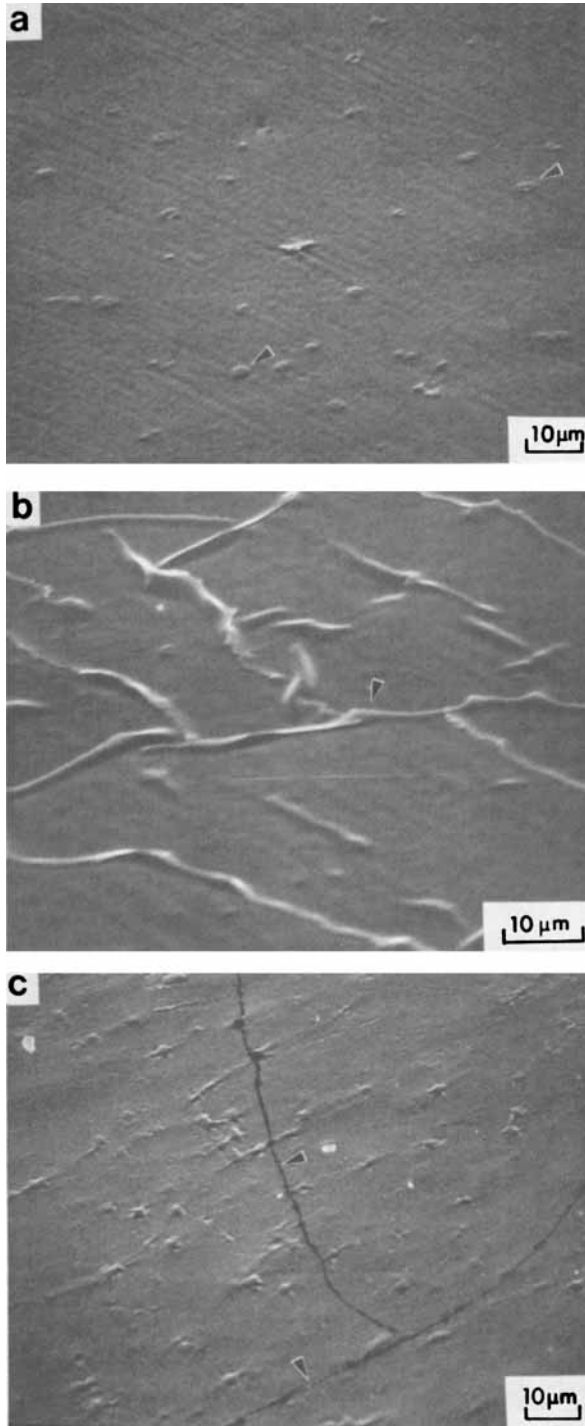


Fig. 4. Scanning electron micrographs of a sample irradiated with He⁺ displaying: (a) voids due to release of gases; (b) corrugations due to excess heat; (c) surface cracks.

The carbonyl-vinyl index of samples irradiated with He⁺ increases strongly with the irradiation dose. For samples irradiated with Ar⁺ the maximum carbonyl-vinyl index is only about 10% of the corresponding value for samples irradiated with He⁺. Furthermore, the carbonyl-vinyl index does not change appreciably with irradiation dose for samples irradiated with Ar⁺. It is important to note that the IR spectra presented in this paper are from reflection-IR experiments which reveal the molecular structure of the 0.1–1 μm top layer of the samples.¹¹

ESCA showed that the oxygen/carbon ratio in the 1–2 nm top layer¹¹ is 0.15 ± 0.01 for the samples irradiated with He⁺ and Ar⁺ of the same dose (10¹⁵ at./cm²).

The penetration profiles for the ions calculated by the TRIM Monte Carlo program were very different for the two ions used in our experiments (Fig. 3). The mean penetration depth was 0.67 μm for He⁺ but only 0.14 μm for Ar⁺. SEM revealed that the surfaces of irradiated samples display three types of characteristic features: surface voids indicating the formation of gases (Fig. 4(a)), partial melting [Fig. 4(b)], and cracking [Fig. 4(c)]. The electronic stopping causes excitation of the electrons and succeeding radical reactions in the polymer. The formation of carbonyl groups revealed by IR indicates the presence of dissolved oxygen in the polymer prior to the

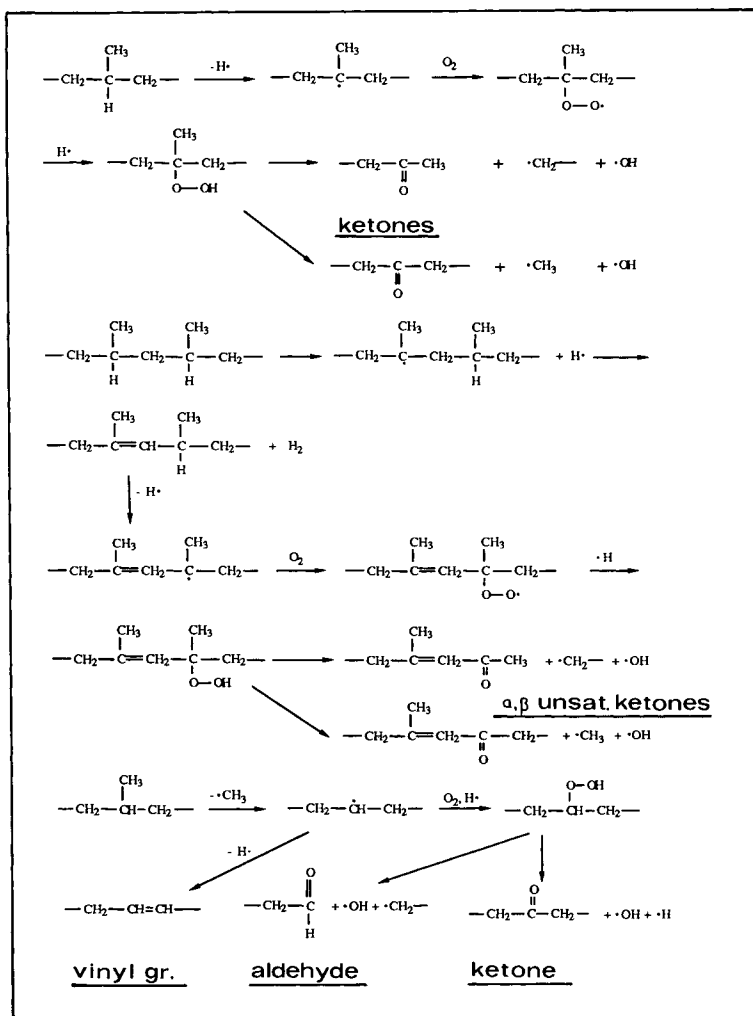


Fig. 5. Proposed mechanism for degradation of PP by ion irradiation. This mechanism has been originally suggested by Kagiya et al.,¹² Klee et al.,¹³ and Rabek and Rånby¹⁴ for degradation of PP by γ irradiation and thermal oxidation.

irradiation. Vinyl groups are also formed by the ion irradiation. Figure 5 presents a proposed mechanism for the degradation which is consistent with the IR spectra obtained for the irradiated samples.

The very high oxygen content values shown by ESCA probably indicate the existence of long-life radicals in the surface which react with oxygen in the air after the irradiation. The major difference in carbonyl-vinyl index data between samples irradiated with He⁺ and with Ar⁺ (see Fig. 2) is probably due to the difference in penetration depth of the ions, the limited access to oxygen in the polymer, and the existence of a "saturation" level of carbonyl and vinyl groups in the polymer. The argon ions transfer their energy to a relatively thin surface layer of polymer with respect to the thickness of the part of the sample which contributes to the recorded IR spectra. The "saturation" content of carbonyl and vinyl groups is reached at very low doses of irradiation. Increasing the irradiation dose above that level should therefore have no effect on the carbonyl-vinyl index and the measured carbonyl-vinyl index should be comparatively low. The He ions, on the other hand, transfer their energy to a much thicker surface layer and the saturation content of carbonyl and vinyl groups is not reached at the dose levels used in the reported experiments.

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