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Effects of MeV Ions on PE and PVDC

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Abstract

We studied the effects of 3.5 and 5.0 MeV alpha bombardment on polyethylene and polyvinylidene chloride both of which have simple chemical structures. Using a thin polymer film stacking technique, we were able to map the effects of the MeV alpha particles in their track. The first layer of the thin polymer film stack experienced most of the effects of the electronic energy deposited and the last layer received most of the effects of the nuclear stopping. Using Raman microprobe analysis and measuring the ratio of the formation of graphene structures (G-line) to the disordered (amorphous) carbon line (D-line), we were able to separate the severed bond effects in the end of the alpha particles' track in the last polymer film layers from the effects of the electronic energy deposited in the first polymer film layers. The results are in agreement with our other measurements of each polymer film using FTIR, RBS and resistance measurements.

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Introduction

The electronic (ϵ_e) and nuclear (ϵ_n) stopping powers are interactions of bombarding ions, moving through target material, with the electrons and nuclei of the surrounding atoms [1]. Both ϵ_e and ϵ_n of MeV ions can be mapped using the thin polymer film stacking technique [2]. Stopping power profiles for MeV ions show that ϵ_e dominates at shallower penetration depths compared with ϵ_n which is maximum at the end of the ions' track. Each stopping power induces different effects in the target material due to the particular mechanisms and quantities of energy deposited. These deposited energies, effected by the stopping powers, can and have been used to enhance electrical conductivity and increase optical absorption in polymers by changing the chemical structures [3-6]. Studies have shown increases in electrical conductivity as much as eight orders of magnitude [4, 6, 7]. The transfer of energy from the ions to the surrounding material results in a complex combination of polymer chain scissoring, covalent bond breaking and cross-linking.

Polyvinylidene chloride (PVDC) $\{\text{CH}_2\text{-CCl}_2\}_n$, a copolymer, and polyethylene (PE) $\{\text{CH}_2\}_n$, a homopolymer are commercially available household plastic food wraps known as Saran® Wrap and Glad® Cling Wrap, respectively. They possess simple linear chain chemical structures which helped to keep the number of variables in the study as low as possible. This, combined with their readily available thin film forms, made them suitable polymers for this investigation. The objective was to develop an understanding of the effects of MeV ions in their track using the thin polymer film stacking technique.

Experimental Procedure

Helium ions, having energy values on the order of mega electronvolts, were bombarded on to stacked thin films of PVDC (13 μm) and PE (10 μm). SRIM (the 1996 version of TRIM)

computer simulation code [1] was used to select the energies of the incident ions to ensure that the ion tracks would not extend beyond the last laminae of the film stacks. SRIM predicted that 3.5 MeV alpha particles would penetrate to a depth of 18 μm in PVDC and 21 μm in PE, requiring two layers of thin polymer films for PVDC and three layers for PE. SRIM predicted a penetration depth of 29 μm in PVDC and 34 μm in PE for the 5.0 MeV alpha particles, requiring three layers of thin polymer films for PVDC and 4 for PE. Film stacking resulted in the first layers experiencing most of the effects of the deposited electronic energy and the last layer receiving almost all of the effects of the nuclear stopping power.

A rastered incident ion beam delivered 3.5 and 5.0 MeV alpha particles, at fluences of 10^{13} , 10^{14} , 10^{15} and 10^{16} ions/cm², to the target. The beam current density was kept below 35 nA/cm² to allow sufficient time for volatile gases, produced by the decomposing polymer, to diffuse out of the films and to allow shrinking without cracking. The films were attached to aluminum substrates using silicone grease which allowed the films to slide along the surface of the substrate during shrinking. Ion ranges for the 3.5 MeV alpha-particles extended to 2 layers while the 5 MeV alpha-particles allowed us to increase the number of irradiated layers which gave us better control over resolving the stopping powers.

Changes in the electrical properties of each layer at the different fluences were studied by direct resistance measurements across the films, while the chemical composition and structures were analyzed by Raman microprobe analysis, Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectrometry (RBS).

Results and Discussion

The two regions of interest in the Raman microprobe analysis are at 1595 cm^{-1} (G-line) and at 1350 cm^{-1} (D-line). The G-line is attributed to graphene structure formation in the material and the D-line is attributed to amorphous structure or "disorder" in the material. Figure 1, selected for the 5 MeV alpha irradiated PE (5×10^{15} ions/cm²), shows peaks at the G and D lines in the Raman spectra for all three layers. For each fluence received the D/G ratios increase progressively from the top to the bottom layers and is typical of the other irradiated stacked films. This is attributed to the effects of the nuclear stopping which accounts for most of the molecular dissociation and bond breakage, contributing to greater disorder in the material. All other layers but the last, having lower D/G ratios, tend to be more ordered as they experience mostly the effects of the electronic stopping power. The increase in the irradiating fluences also resulted in higher D/G ratios, as illustrated in Figure 2.

The FTIR spectra, shown in Figures 3 and 4, illustrate differences in the optical absorption for various irradiated layers and compare them with the virgin film. The characteristic absorption bands for the CH₂ bonds appear in the 2900-2840, 1460-1370 and 740-720 cm⁻¹ regions [8]. Figure 3, which shows spectra from the irradiated PVDC films, indicates the disappearance of the C-H bonds and a complete removal of the C-Cl bonds around the 866 cm⁻¹ region. It also shows that both CH₂ and CCl₂ bonds are reduced more in the first two layers than in the third one where the 5.0 MeV alpha particles are stopped. Figure 4, FTIR spectra from irradiated PE films, clearly indicates the disappearance of the absorption peaks associated with C-H bonds in the first and second irradiated layers, while in the third layer it shows a small reduction in the number of these bonds. The superposition of these three spectra would have been the spectra from a thicker PE film, which is in agreement with the results obtained in reference [8]. This can be attributed to the

scissoring and reforming or 'stitching' of the bonds by the electronic energy deposited in the ion track.

Darkening of the irradiated films at higher fluences and in the deeper layers has been attributed to beam induced carbonization [9] and we suspect that this results in the formation of chromophores, which are light-absorbing groups of conjugated polyenes [10]. Evidence of this is shown in the FTIR results as the double peak formation at 1780 cm^{-1} . The increase in the absorption bands in the 1640 cm^{-1} and the 1780 cm^{-1} regions, due to irradiation, has been attributed to the creation of unsaturated --C=C-- bonds for the first one and a beginning of polymer oxidation for the second [8]. The formation of the absorption peak at the $3600\text{--}3700\text{ cm}^{-1}$ region signifies the formation of N-H bonds at the lower end and O-H bonds at the higher end. Nitrogen appears because of the N_2 gas used to vent the implantation chamber.

Measured resistances of the 5.0 MeV and 3.5 MeV alpha irradiated PE and PVDC films are shown in Table 1. Changes in the layers' resistances for each fluence is related to phase changes in which the number of conjugated polymer chains, caused by the energy deposited in the ion track, increase. This increases the number of free electrons, which enhances the electrical conductivity. A competing process, in which there is an increase in the disordering of the polymer chains, disrupts the polymer chains to the extent that resistance increases as the movement of the free electrons are impeded. The intersection of these competing processes corresponds to a critical fluence at which there is a rapid reversal in the conductivity of the ion irradiated polymers [9]. The presence of chlorine enhanced the carbonization and the electrical resistance of PVDC was reduced more than PE for the same ion fluence which resulted in comparatively lower resistances in these layers where ϵ_n dominates. In PE the absence of chlorine, combined with polymer-chain

dissociation, in the ϵ_n dominated regions resulted in a rapid increase in the resistances from the first to the last layers in the 5 MeV bombarded PE and slight increases in the 3.5 MeV bombarded PE. The changes in the PE resistances are not as dramatic in the 3.5 MeV irradiated films as in the 5.0 MeV irradiated films because, in the former, the separate effects of the stopping powers are insufficiently resolved. This can also be seen in the high fluence PVDC films.

RBS analysis on the layers of the 3.5 MeV alpha irradiated PVDC showed that the concentration ratios of chlorine to carbon is less in the last layers and greater in the first. The chlorine-carbon bonds which are weakest break first, liberating the chlorine. More chlorine is liberated in the last layers where the effects of the nuclear stopping is greatest.

Conclusion

Raman microprobe analysis results clearly separated the effects of MeV alpha particles in their track. The FTIR and resistance measurement of each thin polymer film revealed a complex disordering of the chemical structure in the polymers. The changes in the properties at shallower, compared with deeper, depths of penetration suggest distinct modifying mechanisms which are attributed to the separated effects of ϵ_e and ϵ_n . As ϵ_n increases to a maximum in the last layers the corresponding increase in the disorder of the polymer chains results in increasing resistances and is most evident at the higher fluences. A comparison of the resistances from the 3.5 and 5.0 MeV irradiated layers suggests that increasing the beam energies and including more layers would further resolve the effects of ϵ_e and ϵ_n . The boundaries corresponding to the effects of ϵ_e and ϵ_n shift as the chemical structure of the PVDC and PE changes during irradiation. This complicates

the resolution of the effects of ϵ_e and ϵ_n because both stopping powers depend on the chemical composition of the target.

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Figure 1

Figure 2

Figure 3

Figure 4

Table 1. Resistance values for virgin and 3.5 MeV and 5 MeV α -irradiated PVDC and PE films.

		PVDC Resistance ($\times 10^9 \Omega$)						
		Layer 1	Layer 2	Layer 3	PE Resistance ($\times 10^9 \Omega$)			
		Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Layer 3	
3.5 MeV	Virgin	15 700	15 700	15 700	Virgin	5 830	5 830	5 830
	5E13	5 660	1 240	-	5E13	5 140	7 040	-
	5E14	1 050	1 440	-	5E14	7 600	9 760	-
	5E15	400	27.9	-	5E15	4 200	6 100	-
5 MeV	5E13	19.3	15.2	7.1	5E14	1 080	506.7	3 490
	5E14	230	5 590	1 140	5E15	12.3	66.5	1 690
	5E15	38.9	4.1	0.4	3.28E16	0.01	9.9	160

Figure Captions

- Figure 1. Raman spectra from all layers of the 5 MeV α -irradiated PE films at a fluence of 5×10^{15} ions/cm², showing the D/G ratios for each.
- Figure 2. Raman spectra from the first layers of the 5 MeV α -irradiated PE films at fluences of 5×10^{15} and 3×10^{16} ions/cm², showing the D/G ratios for each.
- Figure 3. FTIR spectra obtained from the layers of 5.0 MeV α -irradiated PVDC films at a fluence of 5×10^{15} ions/cm².
- Figure 4. FTIR spectra obtained from the layers of 5.0 MeV α -irradiated PE films at a fluence of 3×10^{16} ions/cm².

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