

ION BEAM MODIFICATION OF PVDC AND PE POLYMERS

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ABSTRACT

The electronic and nuclear stopping effects produced by MeV ion bombardment in polyvinylidene chloride (PVDC) and polyethylene (PE) are separated by stacking thin films of the polymers. The resulting multi-layer laminates of each polymer were bombarded with 3.5 MeV alpha particles. The energy of the incident ions was selected, using TRIM, such that the first layers experienced most of the effects of the electronic energy deposited and the last layers received most of the effects of the nuclear stopping power. The changes in the conductance and the chemical structure of each layer were measured by direct resistivity measurements and Raman microprobe analysis.

INTRODUCTION

Polymers are becoming increasingly useful and, as such, their importance has increased very rapidly over the past years. Although they do not exhibit the wide range of electrical and optical properties exhibited by inorganic materials, their ease of production and relatively low cost make them suitable materials for modification by ion beams.

It is known that ion-beam irradiation of certain polymer materials leads to the formation of new carbonaceous materials which exhibit enhanced electrical conductivity and an increase in the optical absorption [1-10]. Changes in the appearance of the polymers after bombardment is attributed to the modification of the chemical bonds. It has been shown that the darkening is due to the increase in the absorption in the near UV and shifts gradually toward the red region of the visible spectrum [11]. Ion bombardment causes physical damage which includes breaking covalent bonds, scissoring polymer chains, cross-linking and releasing of volatile species.

Studies have shown that ion-modified regions can be produced with enhanced mechanical and electrical properties as much as six orders of magnitude, owing to the rapid change in the structure of the polymers chosen [2, 12]. The formation of these regions is shown to be due to the electronic process during ion bombardment rather than the recoil process by nuclear stopping power [13]. The effects caused by the electronic and nuclear stopping cross-sections are inherent in ion-beam irradiation and are related to the energy loss of the incident ions as they traverse their target [14]. We decided to investigate the separate effects of these two stopping powers on the electrical and optical properties of two commercially available, relatively cheap polymers: polyvinylidene chloride (PVDC) and polyethylene (PE).

EXPERIMENTAL PROCEDURE

We selected the energy of the incident ions using the TRIM 93 [14] computer simulation code, such that the first layer experienced most of the effects of the electronic energy deposited and the last layer received most of the effects of the nuclear stopping power, illustrated in Figure 1. The dotted line separates the first layer from the second.

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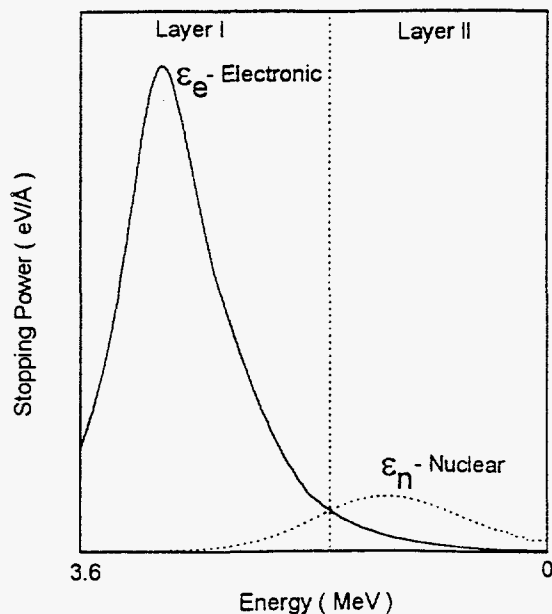


Fig. 1. Illustration of the electronic and nuclear stopping powers and the α energies which were determined by TRIM.

Clear plastic film samples of PVDC (trade name: Saran wrap) manufactured by the DOW Chemical Company, Midland, MI, and PE (trade name: Glad cling wrap) manufactured by First Brands Corporation, Danbury, CT, were placed on aluminum substrates. Silicone grease held the 1.5 cm^2 film samples to the substrate while allowing the films to shrink without breaking during the irradiation process. We stacked the aluminum substrates containing the $12.5 \text{ }\mu\text{m}$ thick PVDC and the $10.5 \text{ }\mu\text{m}$ thick PE samples respectively and oriented the stacks normal to a rastered incident alpha beam. We employed a $3/4$ " diameter circular aperture to ensure a uniform area of implanted He^{2+} ions on all samples. Irradiated samples received fluences of 10^{13} , 10^{14} and 10^{15} ions/ cm^2 from the 3.5 MeV alpha-particle beams. We used low currents (~ 2 nanoamperes) in the initial stages of the bombardment to avoid damage to the samples as a result of rapid heating.

Changes in the electrical properties of each layer at the different fluences were studied by employing direct resistivity measurements, while the chemical structures were analyzed by Raman microprobe analysis.

RESULTS AND DISCUSSION

After bombardment some film samples became darker in color, depending on the fluence received: generally, the higher the fluence, the darker the film appears. PVDC showed a greater sensitivity to the irradiation, turning dark at lower fluences compared with PE and was completely black at 10^{15} ions/ cm^2 . PE, however, seemed more robust and possessed a transparent dark amber color at 10^{15} ions/ cm^2 . This darkening has been attributed to beam induced carbonization [15,16].

Figure 2 illustrates a behavior in the electrical properties similar to that previously obtained from other ion-irradiated polymers [17]. There is a 1 to 2 order of magnitude reduction in the resistivity at fluences of 5×10^{15} ions/ cm^2 for the PVDC, which is a result of a change of phase in the implanted area. This phase change is an increase in the number of conjugated polymer

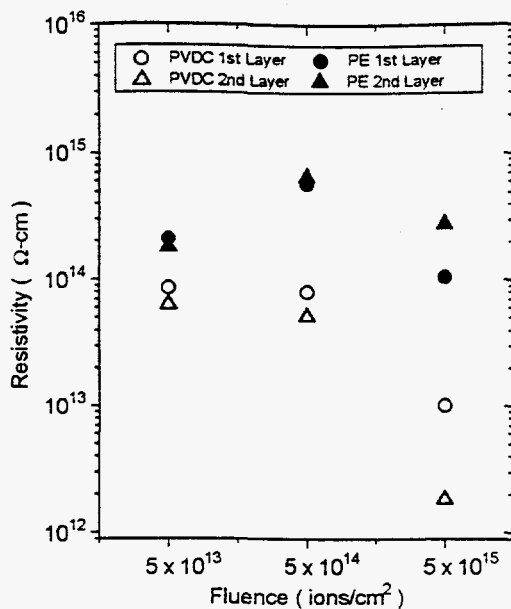


Fig. 2. Resistivity of PVDC and PE after α -irradiation to 10^{13} , 10^{14} , 10^{15} ions/cm².

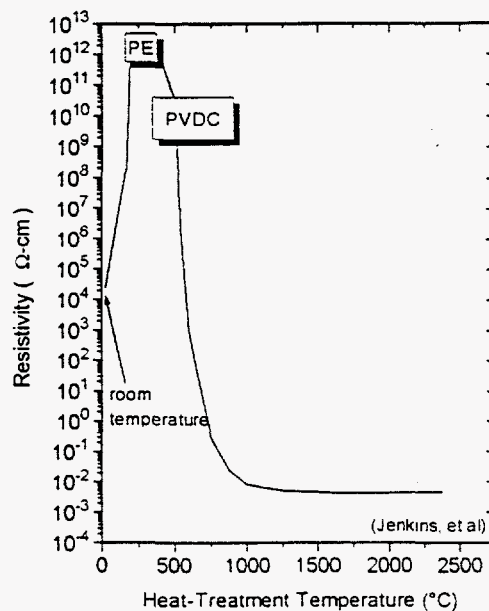


Fig. 3. The effect of heat-treatment temperature on the electrical resistivity of PF-resin.

chains caused by the energy deposited in the ion track and results in the increase of free electrons, which enhances the electrical conductivity. In fact, it is enough to have only one modified region to change its phase and form a conjugated structure to suddenly decrease the resistivity. The figure also shows that at the same fluence, this phase change has not yet occurred in PE which shows more resistance to the effects of ion irradiation. The apparent rise in the resistivity of PE at 5×10^{14} ions/cm² is also exhibited by other ion irradiated polymers at lower fluences before the resistivity decreases drastically. We predict that PE would also show a significantly sharp drop in its resistivity at higher fluences. Figure 3 shows the relationship between the electrical resistivity and heat treatment temperature of polymeric carbon [18]. The relative positions of the resistivities of the PVDC and PE, irradiated to 10^{15} cm², are indicated.

The Raman spectra of the irradiated PVDC and PE (Figures 4 and 5) contain two peak growths at around 1595 cm^{-1} (G-line) which is attributed to in-plane vibrations of aromatic layers as graphene structures are developed, and at 1350 cm^{-1} (D-line), which is attributed to "disorder" in such layers [19], but could also be related to lower stiffness in bonds at the edges of aromatic layers. The D/G ratios for PVDC and PE are shown in Table 1, along with their resistivity values. The D/G ratios are generally higher in the second layers for each fluence received. This is attributed to the effects of the nuclear stopping which accounts for most of the molecular dissociation and bond breakage, implying greater disorder in the material. The first layers, having lower D/G ratios, tend to be more ordered as they experience only the effects of the electronic stopping power. Both PVDC and PE appear to have lower ratios in the second layers at 5×10^{15} ions/cm². We suggest that at these higher fluences, as the chemical structure of the polymer changes, the energies at which the electronic effects dominate decrease and consequently increase for the nuclear effects. The first layers, at the higher fluences, experience greater effects of the nuclear stopping, resulting in molecular dissociation and bond breakage and hence greater disorder.

The change in the deposited energy is also reflected in the consistent increase in the difference between the resistivities of the first and second layers for each fluence received by the

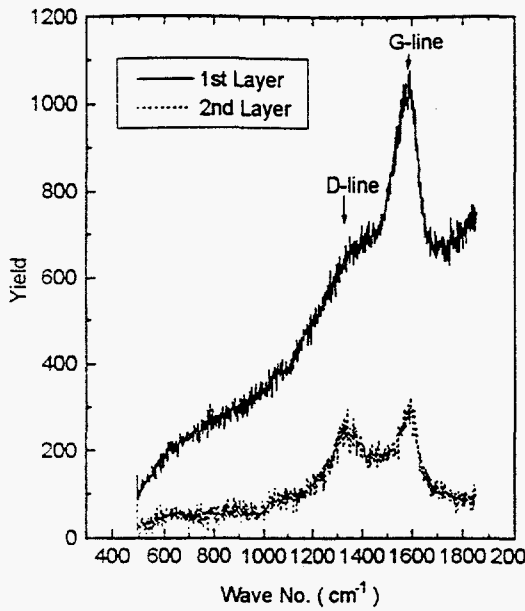


Fig. 4. Raman spectra from 3.5 MeV α -irradiated PVDC films (5×10^{13} ions/cm²).

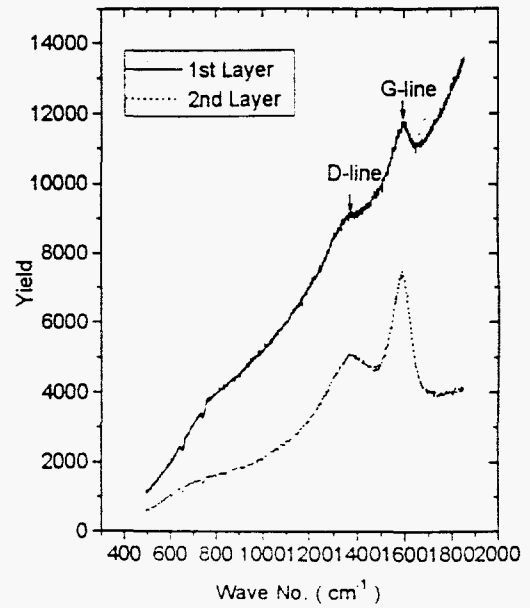


Fig. 5. Raman spectra from 3.5 MeV α -irradiated PE films (5×10^{13} ions/cm²).

PVDC (Table 1). The resistivity values for PE fluctuate too much to be of any significance at these fluences. However, PVDC promotes conjugation more readily at lower fluences than does PE.

	FLUENCE (cm ⁻²)	LAYER	D/G	Restivity (Ω -cm)
PVDC	5×10^{13}	1	0.25	9×10^{14}
		2	0.94	6.5×10^{14}
	5×10^{14}	1	0.78	8.9×10^{14}
		2	1.18	5.5×10^{14}
	5×10^{15}	1	1.01	1.1×10^{13}
		2	0.64	1.9×10^{12}
PE	5×10^{13}	1	-	1.9×10^{14}
		2	-	2.2×10^{14}
	5×10^{14}	1	-	5.7×10^{14}
		2	-	6.6×10^{14}
	5×10^{15}	1	0.66	1.1×10^{14}
		2	0.62	2.8×10^{14}

Table 1. D/G ratios and resistivity values for ion-irradiated PVDC and PE.

CONCLUSION

The carbonized volumes were analyzed by Raman microprobe spectroscopy which showed that the strongest graphitic (G-line) and distorted (D-line) Raman signals observed were from the volume with the lowest resistivity. The resistivity results, along with the Raman D/G ratios, indicate that there are differences in the layers of each irradiated stack; differences that are attributed to the distinguishing effects of the electronic and nuclear stopping powers. However, the changing chemical structure of the PVDC and PE, during irradiation, causes the dividing line between ϵ_c and ϵ_p , in Figure 1, to shift.

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