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Electrical and thermal behavior of proton irradiated polymeric blends

N.L. Singh[a,*], Nilam Shah[a], K.P. Singh[b], C.F. Desai[a]

[a]*Department of Physics, M.S. University of Baroda, Vadodara 390002, India*
[b]*Department of Physics, Panjab University, Chandigarh 160014, India*

Abstract

Polymeric blends of polyvinyl chloride (PVC) and polyethylene terephthalate (PET) have been irradiated with 3 MeV proton beam at different fluences. The radiation induced changes in electrical and thermal properties were investigated by the LCR meter in the frequency range 0.1–100 kHz, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy.

It is found that AC conductivity increases exponentially with log of frequency. The dielectric constant/loss are observed to change significantly due to the irradiation. TGA study indicates the degradation of polymer under proton irradiation and makes it to start decompose earlier than pristine sample. The DSC measurements exhibit significant change in their melting behavior. FTIR spectra reveal that material suffers serious degradation through bond breaking at the fluence of 10^{14} ions/cm^2 and above.

Keywords: Proton irradiation; Blend of PVC and PET; AC frequency response; TGA; DSC; FTIR

1. Introduction

The significant advantages of polymer blends are that the properties of the finished product can be tailored to the requirements of the applications, which cannot be achieved alone by one polymer. Polyvinyl chloride (PVC) is an important material in cable insulation and sheathing; there is a much greater emphasis today on the use of non-halogenated materials in electrical insulation. An extremely important factor in the selection of insulation and sheathing materials is the flammability, smoke evolution and toxicity of the evolved gases. Although PVC has very good electrical properties, polyethylene terephthalate (PET) was chosen because of its very good mechanical strength due to the presence of the aromatic ring in polymer structure.

The blending of PVC and PET was prepared in equal composition by weight in a two roll mill. Ion irradiation of polymers can induce irreversible changes in their macroscopic properties. Electron excitation, ionization, chain scission and cross-links as well as mass losses are considered as the fundamental events that give rise to the observed macroscopic changes (Venkatesan et al., 1987, Lee, 1999). The aim of the present work is to investigate the modifications induced by 3 MeV proton beam in the electrical and thermal behavior of blending polymer and to analyze the effect as a function of proton fluence.

2. Experimental details

The polymer blend of thickness 460 μm was prepared in the laboratory in equal proportion of PVC (IPCL make, India) with commercially grade PET (Garware make, India) in a two roll mill. The PVC and PET were taken in granules form as well as in pure form (wt/wt). The mixture

* Corresponding author. Tel.: +91 265 2783924; fax: +91 265 2787556.
E-mail address: singhnl_msu@yahoo.com (N.L. Singh).

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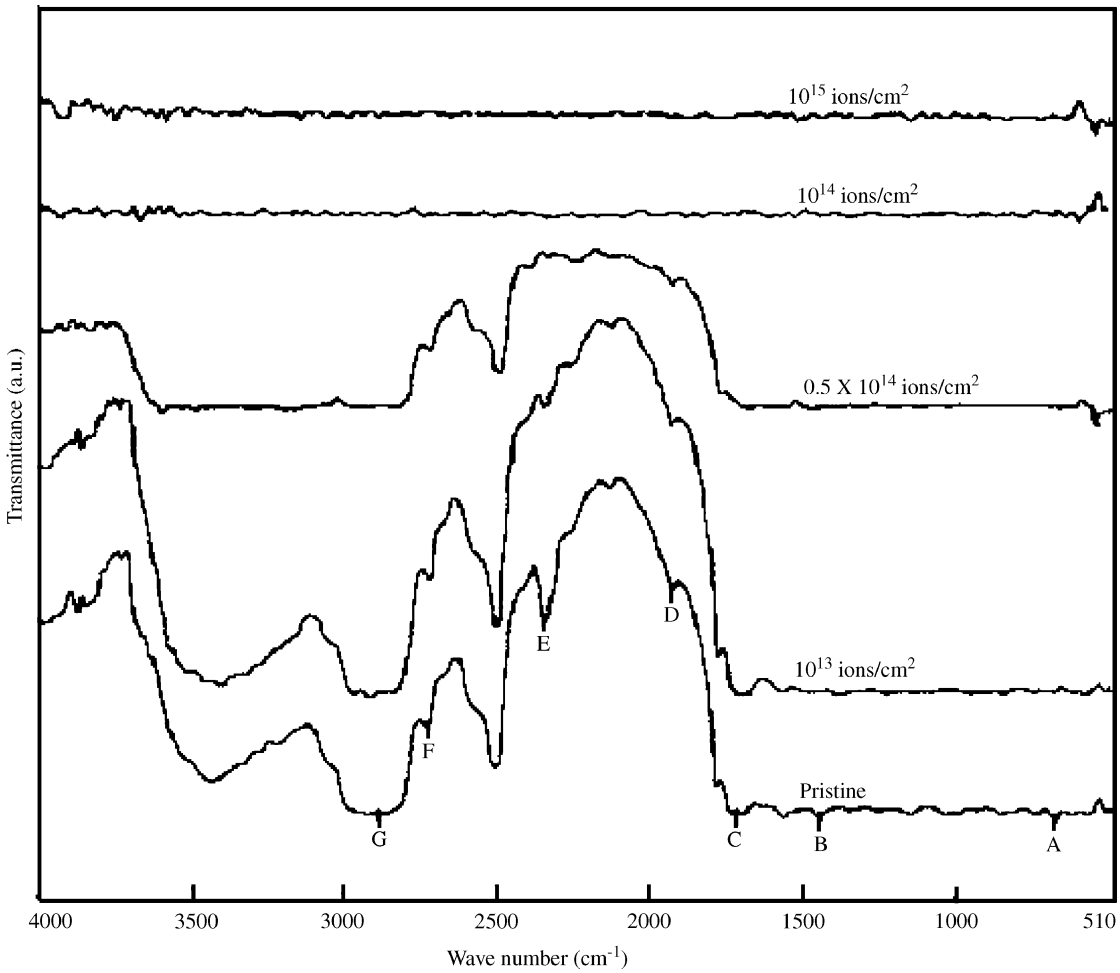

Fig. 1. FTIR spectra of pristine and proton irradiated polymeric blend films.

was transformed into sheet at around 125 °C for half an hour. Four pieces of size 1.5 × 1.5 cm^2 were cut from blended sheet. These samples were irradiated with 3 MeV protons at Physics Department, Chandigarh, India. The beam current density was of the order of 35 nA/cm^2 and irradiated at four different fluences, 10^{13}, 0.5×10^{14}, 10^{14} and 10^{15} ions/cm^2. The proton beam was propagating perpendicular to the target of diameter 6 mm. All irradiations were performed in vacuum (10^{-6} Torr) at room temperature. To study the structural changes including the alteration in position and intensity of the characteristic bands, the Fourier transform infrared (FTIR) spectroscopy of all samples were recorded in the wave number range 4000–500 cm^{-1}. The resistance, dielectric loss (tan δ) and capacitance measurements were carried out using an LCR meter (General Radio, USA, Model 1689) over the frequency range 0.1–100 kHz at room temperature. The AC conductivity was calculated using the relation $\sigma=(2\pi f C_p Dt)A^{-1}$ (Ω cm^{-1}). The dielectric constant was calculated using the relation $\varepsilon=C_p/C_0$, where C_p is capacitance measured and $C_0=\varepsilon_0 A/t$, where ε_0 is the permittivity of vacuum, D, f, A and t are the dielectric loss, frequency, cross-sectional area of the electrode and thickness of the sample, respectively. The thermogravimetric analysis (TGA) was recorded using the SIEKO thermal analysis (TGA-220) system in the presence of air from room temperature to 550 °C at a predetermined heating rate of 10 °C/min. The differential scanning calorimetry (DSC) measurement was carried out by a SIEKO Calorimeter (DSC-220), calibrated through the melting points of indium and tin. About 10 mg of pristine as well as irradiated blending polymer were scanned in the temperature range of 40 °C to 325 °C at a predetermined heating rate of 10 °C/min.

3. Results and discussion

The projected range of the 3 MeV proton beam in the blending polymer was calculated to be 128 μm using

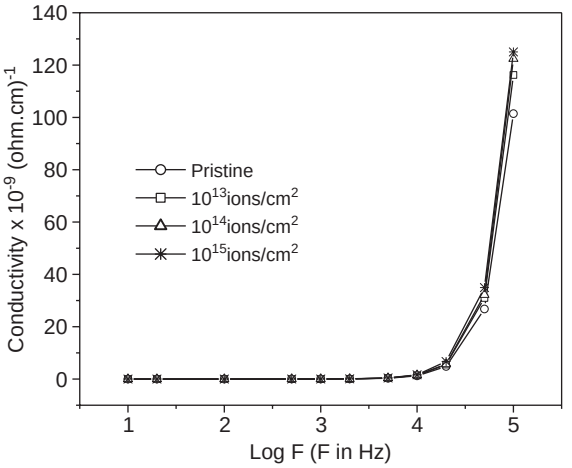

Fig. 2. AC conductivity versus log frequency plot for pristine and proton irradiated polymeric blend films.

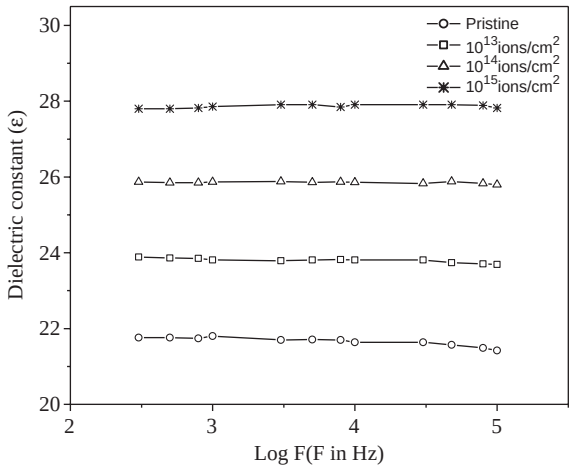

Fig. 3. Plot of dielectric constant versus log frequency for pristine and proton irradiated polymeric blend films.

SRIM-2000 (Ziegler, 2000). The thickness of the sample is 3.6 times more than the projected range. The electronic stopping power $(dE/dx)_e$ and nuclear stopping power $(dE/dx)_n$ were found to be 1.08×10^{-1} eV/Å and 6.48×10^{-5} eV/Å, respectively. It was found that 99.94% of energy is lost due to the electronic interaction.

3.1. FTIR analysis

The FTIR spectra of the pristine and irradiated samples are shown in Fig. 1. The absorption bands as obtained from the pristine spectrum are identified as (A) 800 cm^{-1}: C–Cl stretching vibration; (B) 1485 cm^{-1}: C–H bending vibration; (C) 1730 cm^{-1}: C═O stretching vibration; (D) 1950 cm^{-1}: C═C stretching vibration; (E) 2335 cm^{-1}:vibration of CO_2; (F) 2700 cm^{-1}: O–H stretching vibration; (G) 2850 cm^{-1}: C–H stretching vibration. It is observed that there is no significant change in the intensities up to the fluence of 10^{13} ions/cm^2. It is found that the absorption bands characteristic of all above functional groups decline, confirming their destruction by irradiation. These functional groups vanish gradually as irradiation proceeds. This might be attributed to breakage of chemical bonds and the formation/emission of low molecule gases and radicals due to irradiation (Biswas et al., 1999).

3.2. AC electrical frequency response

The AC conductivity measurement was performed for irradiated and pristine samples as shown in Fig. 2. A sharp increase in conductivity at 20 kHz has been observed in pristine as well as irradiated samples. It is observed that conductivity increases as fluence increases. The increase in conductivity due to irradiation may be attributed to scissioning of polymer chains and as a result an increase of free radicals,

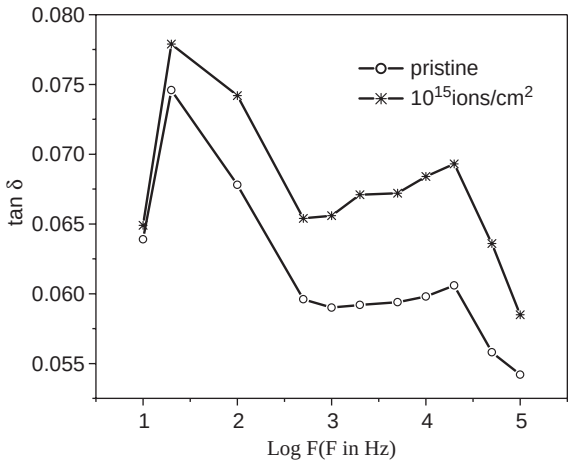

Fig. 4. Variation of tan δ with log frequency for pristine and proton irradiated polymeric blend films.

unsaturation, etc. An AC field of sufficiently high frequency applied to metal–polymer–metal structure may cause a net polarization, which is out of phase with the field. This results in AC conductivity that appears at frequency greater than that at which traps are filled or emptied (Jonscher, 1977).

Fig. 3 shows the variation of dielectric constant with log frequency for the pristine and irradiated samples. It can be seen that the dielectric constant remains almost unchanged over a wide frequency range and increases as fluence increases (Shah et al., 2003). This indicates that the motion of the free charge carriers is constant at these frequencies and so the dielectric constant does not change.

Fig. 4 shows the variation of tan δ with log frequency for pristine and irradiated samples. It reveals that the loss factor

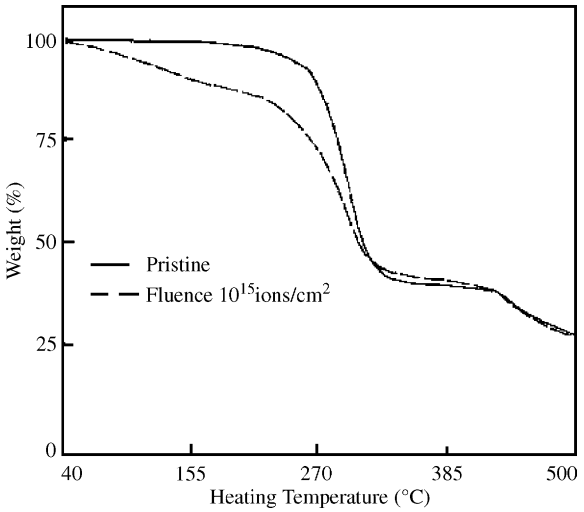

Fig. 5. TGA thermograms of the pristine and irradiated polymeric blend films.

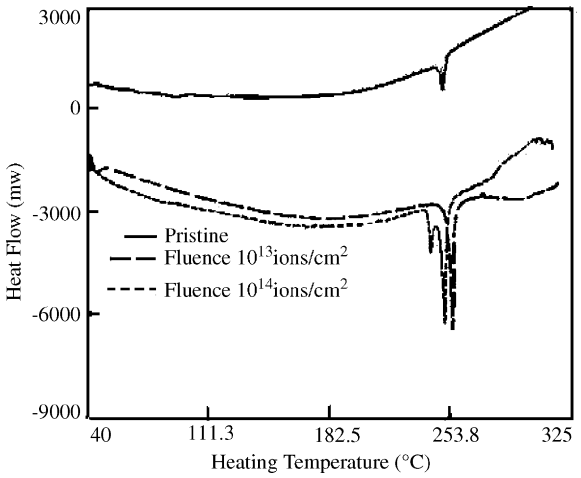

Fig. 6. DSC thermograms of the pristine and irradiated polymeric blend films.

(tan δ) drops as the frequency increases. It is also observed that the loss factor increases as fluence increases. The tan δ has positive values indicating the dominance of inductive behavior.

3.3. TGA analysis

The decomposition behavior of the polymer was examined by TGA as shown in Fig. 5. The thermogram shows two-step decomposition. As depicted in the figure, the stable zone disappeared for the irradiated (10^{15} ions/cm^2) polymer, which was observed up to 169 °C for pristine polymer. TGA thermograms indicate a degradation of the polymer matrix under proton irradiation making it to decompose earlier than the pristine sample, which is also corroborated by FTIR spectra. No significant change has been observed in the second stage. The weight loss of the pristine sample has been observed to amount to 57% at 328 °C in the first step of decomposition whereas, in the second step decomposition shows a weight loss of 75% at 500 °C. The weight loss for the irradiated (fluences of 10^{15} ions/cm^2) sample has been observed to be about 54% at 319 °C in the first step, whereas in the second step of decomposition, it is 70% at 500 °C. It is observed that the thermal decomposition of the polymer depends upon the fluence of the proton beam (Mishra et al., 2003).

3.4. DSC analysis

Fig. 6 shows the DSC thermograms of pristine and irradiated ($\sim 10^{13}$ and 10^{14} ions/cm^2) polymer films. The peak representing endothermal behaviors, i.e., heat absorption for the pristine film was observed at 249 °C. By increasing the fluence the endotherm shifts to slightly higher temperature and then decreases to lower temperature on further increase of the fluence. This change clearly indicates that up to the fluences of 10^{13} ions/cm^2, the system remains reasonably organized but gets quite disorganized with some residual energy when a fluence of 10^{14} ions/cm^2 is used. From the analysis of DSC curves, it is observed that the endotherm consists of two peaks at the fluences of 10^{14} ions/cm^2, one at high and constant temperature related to the unchanged material and the other at low temperature related to damage material. This may be due to decrease in molecular weight (Calcagno et al., 1994).

4. Conclusions

The proton irradiations of blended polymers lead to chain scission and as a result there are changes in the dielectric properties. There is an exponential increase in conductivity with log frequency and the effect is significant at higher fluences. The DSC measurement of irradiated blended polymer shows significant changes in its melting property. This indicates that the melting temperature first increases with fluence, and then decreases again. When ion track overlapping sets in, competing processes such as amorphization overtake, leading to a reduction of the melting point. The TGA thermogram indicates a degradation of the polymer matrix under proton irradiation making it to decompose earlier than the pristine sample, which is also corroborated by FTIR spectra. However, chain scission by proton irradiation at higher fluence seems to be the dominant process.

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