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Dielectric response of proton irradiated polymer composite films

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Abstract

Different concentration of ferric oxalate (organometallic compound) was dispersed in polymethyle methacrylate (PMMA) films. PMMA was synthesized by solution polymerization technique. These films were irradiated with 3 MeV protons at a fluence of 1×10^{13} ions/cm^2. The frequency dependent dielectric behavior was studied both in pristine and irradiated samples in the frequency range from 100 Hz to 10 MHz. The contribution to the dielectric response is due to the conductive phase formed by organometallic compound. From the analysis of frequency dependence of dielectric constant it was observed that the dielectric response in both pristine and irradiated samples obey Jonscher's power law. These results were corroborated with structural changes observed in Fourier transform infrared (FTIR) spectra of pristine and irradiated samples.

Keywords: Proton irradiation; PMMA; Organometallics; Dielectric loss; Dielectric permittivity; AC conductivity

1. Introduction

Metallized polymers are widely used in the packaging industry, data storing devices, microelectronics components etc. In such applications, a good adhesion between polymer and metal is required. Some work has been done on the metal dispersed polymer composites during last few years to study the different aspects of metal/polymer interphase like ion beam surface modification of metallized polymer (Bertrand et al., 1997), magnetic inclusion formation (Khaibullin et al., 2000) and metal ion diffusion in polymer (Fink et al., 2000). Metal dispersed polymer matrix is a special arrangement of active metal compound and passive polymer materials. Purpose of metal compound doping is to enhance the adhesion possibility of metal and polymer as it contains large number of functional groups. High energy ion irradiation induces significant modification in the materials by electronic excitation or ionization. The dielectric response of solids provides information about the orientational adjustment of mobile charges present in the dielectric medium to an applied electric field. Polymethyl methacrylate (PMMA) is transparent plastic having outstanding optical properties. The pure PMMA polymer was dispersed with different concentration of ferric oxalate (FO) compound and irradiated with 3 MeV proton beam at a fluence of 1×10^{13} ions/cm^2. The AC electrical frequency response was studied in the frequency range from 100 Hz to 10 MHz by an LCR meter.

2. Experimental

PMMA $(C_5O_2H_8)_n$, density 1.19 g/cm^3, was prepared using solution polymerization technique. Proper amount of benzoyl peroxide (initiator) dissolved with inhibitor free MMA monomer in ethyl acetate solvent in a round bottom flask. This solution was properly refluxed for about 5 h at 75 °C. PMMA was precipitated out in another beaker containing methanol. The precipitated PMMA was allowed to dry at room temperature for 2 h. FO was formed by taking oxalic acid and ferric chloride with ethanol as a solvent in a round bottom flask, and it was refluxed for 4 h at 60 °C. The excess ethanol was distilled out and the substance was dried at 75 °C for 3 h in an oven. FO was then dissolved in PMMA using acetone and the solution was stirred thoroughly for about an hour and poured on clean, uniform glass trough (Qureshi et al., 2006). The solvent was evaporated at room temperature to get film of thickness 130 μm. The films of polymer with different concentrations of

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FO compound viz. 5%, 10% and 15% were prepared. Samples of the size $1.5 \times 1.5\,\mathrm{cm}^2$ were cut from these sheets for irradiation. These samples were irradiated with 3 MeV proton beam using cyclotron facility of Physics Department, Panjab University, Chandigarh. The beam current density was of the order of $20\,\mathrm{nA/cm}^2$ and the samples were irradiated at a fluence of $1 \times 10^{13}\,\mathrm{ions/cm}^2$. All irradiations were performed in vacuum (10^{-6} torr) at ambient temperature. The dielectric properties of all samples were measured using an LCR meter/impedance-phase analyzer (General Radio, USA, Modal 1689/Solartron-1260). Resistivity of the material was calculated using equation $\rho = A/(2\pi f C_p D t)$ $(\Omega\,\mathrm{m})$ and dielectric permittivity $\varepsilon = C_p/C_0$, where C_p is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and the C_0 the vacuum capacitance$=\varepsilon_0 A/t$, A and t are the cross-sectional area of the electrode and thickness of the sample, respectively. ε_0 is the permittivity of vacuum$=8.85 \times 10^{-12}\,\mathrm{F/m}$. To study the structural changes due to ion beam irradiation, Fourier transform infrared (FTIR) spectra of pristine and irradiated PMMA were recorded in the wave number range 4000–$500\,\mathrm{cm}^{-1}$ (Bomem Canada, model-104) with a resolution of $4\,\mathrm{cm}^{-1}$.

3. Results and discussion

3.1. AC electrical resistivity

AC electrical resistivity versus frequency for pure polymer and 5%, 10%, 15% FO doped PMMA is shown in Fig. 1 for pristine and irradiated (at a fluence of $1 \times 10^{13}\,\mathrm{ions/cm}^2$) samples in the logarithmic scale. It was observed that resistivity decreases with increasing frequency. It was also observed that resistivity decreases with increasing the concentration of dispersed FO in pristine PMMA (Fig. 1(a)) as well as those irradiated at a fluence of $1 \times 10^{13}\,\mathrm{ions/cm}^2$ (Fig. 1(b)). The

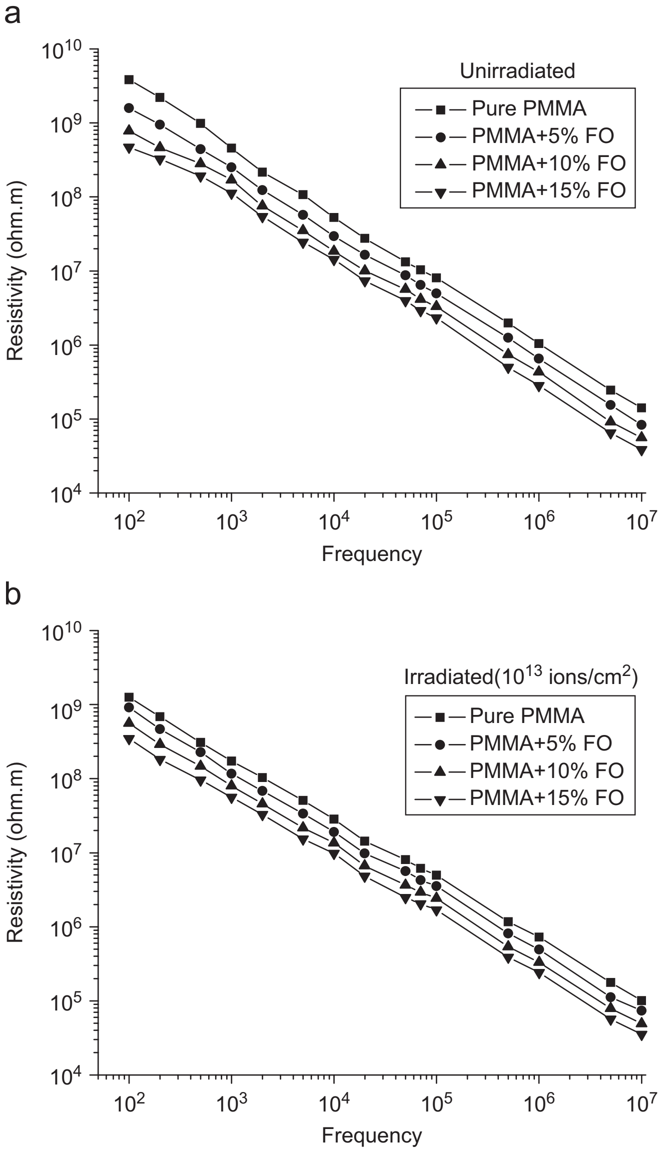

Fig. 1. AC Resistivity versus frequency for pure and FO dispersed PMMA for (a) pristine and (b) irradiated films.

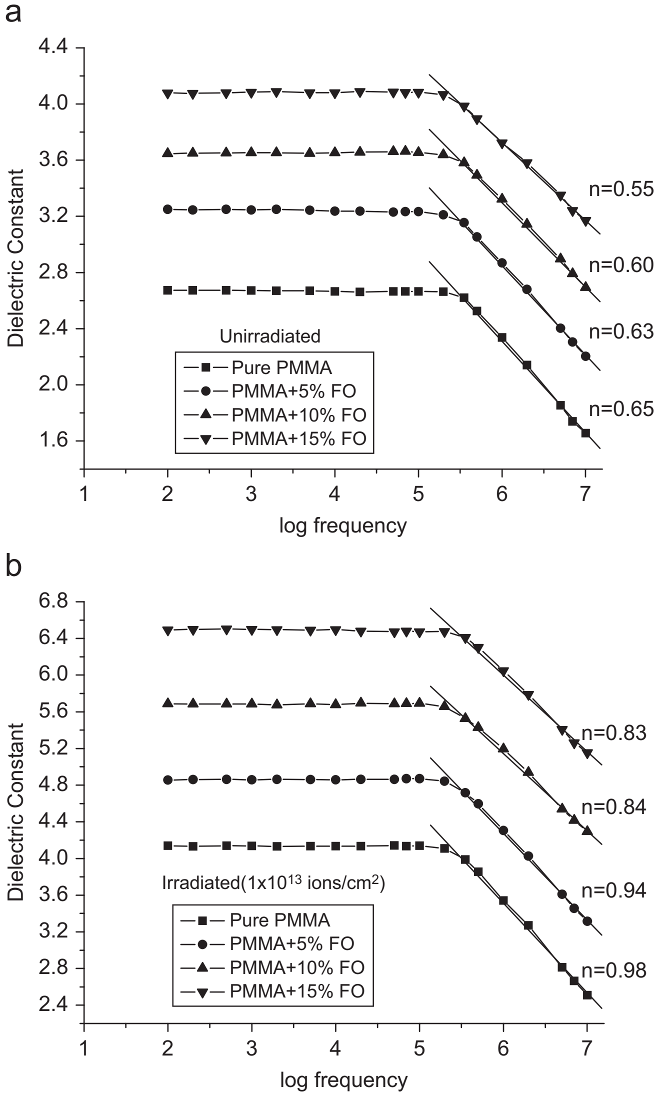

Fig. 2. Plot of dielectric constant versus log frequency for pure and FO dispersed PMMA for (a) pristine and (b) irradiated films.

decrease in resistivity with different FO concentrations for pristine samples may be attributed to the conductive phase formed by the dispersed compound in a polymer matrix. It is known that electrical conductivity of such composites depends on the type and concentration of the dispersed compound (Mamunya et al., 2002). As a result the resistivity of dispersed films decreases on increasing the concentration of FO compound in the polymer matrix. Fig. 1(b) shows that the resistivity decreases further due to irradiation with the concentration of the dispersed compound. Irradiation is expected to promote the metal to polymer adhesion and convert polymeric structure to a hydrogen depleted carbon network. It is this carbon network that is believed to make the polymer more conductive (Wang et al., 2004).

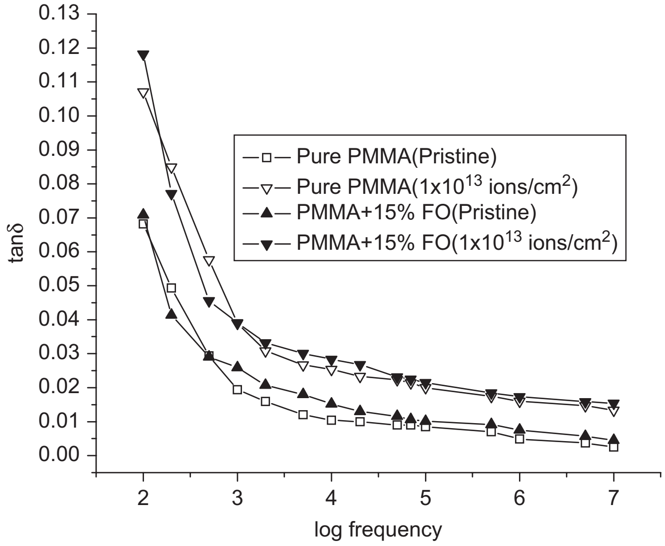

Fig. 3. Plot of dielectric loss versus log frequency for pure and 15% FO dispersed PMMA for pristine irradiated films.

3.2. Dielectric permittivity

It is observed that the relative dielectric permittivity is almost constant in the wide frequency range up to 100 kHz. This is because of the constant motion of free charge carriers at these frequencies. As the frequency increases further, the charge carriers migrate through the dielectric and get trapped against defect sites. They induce an opposite charge in its vicinity, as a result the motion of charge carriers is slowed down and the value of dielectric constant decreases. The decrease in dielectric constant at higher frequency can be explained by Jonscher's power law, i.e. $\varepsilon \alpha f^{n-1}$ where $0 < n < 1$. When the doping is done, the quantity of the accumulated charge will increase because the polarization of the polymer/metal interphases. The polarization makes an additional contribution to the charge quantity. From this point of view, the dielectric constant of the composites will be higher than the pure polymer (Dang et al., 2004). Our experimental results also support this explanation as seen in Fig. 2. It is observed that the value of n increases from 0.65 to 0.98 with ion fluence for pure PMMA. Similar results are also obtained for doped PMMA. This may be due to the dominance of metal to polymer bonding due to irradiation, which reduces the dipole polarization and as a result slop (n) increases.

3.3. Dielectric loss

The dielectric loss is the power dissipated in a dielectric as heat when the dielectric is exposed to an electric field. Dielectric loss tangent (tan δ) is defined as a ratio of energy lost

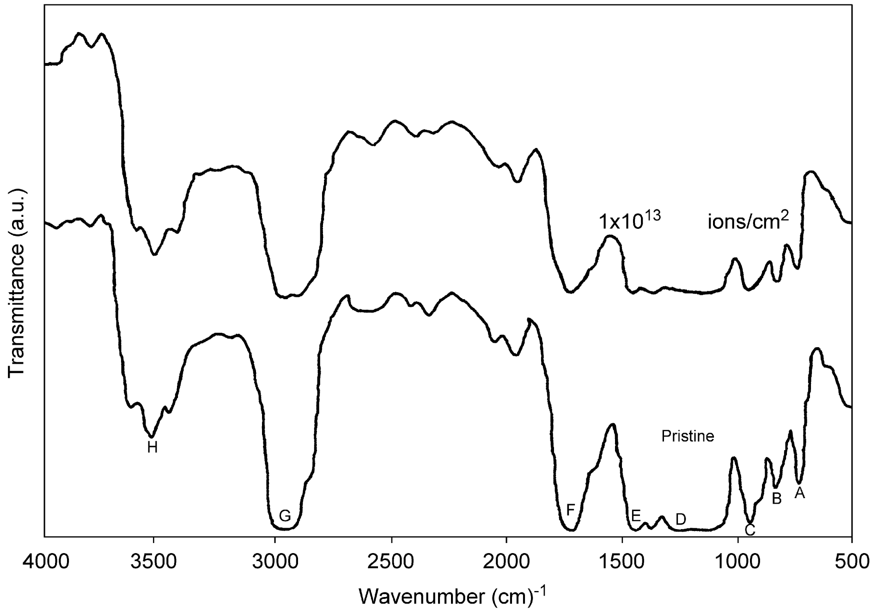

Fig. 4. FTIR spectra of pristine and irradiated PMMA.

or dissipated per cycle to the energy stored. It was measured directly using an LCR meter/impedance gain phase analyzer. Fig. 3 represents the dielectric loss versus log frequency for pristine and irradiated samples. It is observed that the dielectric loss decreases exponentially with the increasing the frequency. It is also observed that loss factor increases with FO concentration and also with the ion fluence. The growth in tan δ and thus decrease in resistivity is brought about by an increase in the conduction of residual current and absorption current (Jonscher, 1977).

3.4. FTIR analysis

Fig. 4 shows the spectra of pristine and irradiated PMMA samples. The absorption bands are obtained from the pristine spectrum are identified as (A) 730 cm^{-1}: CH_2 (C–H rocking), (B) 816 cm^{-1} : CH_3 (C–H rocking), (C) 950 cm^{-1}: carboxylic ester (D) 1270 cm^{-1}: C–C–O stretching, (E) 1438–1465 cm^{-1}: carboxylic ester, (F) 1715 cm^{-1}: R–C = O (kepton of ester) (G) 3900–3000 cm^{-1}: C–H stretching and (H) 3500 cm^{-1}: OH free stretching vibration (Fink et al., 1994). It is observed that there is no significant change in the overall structure of the polymer but changes in peak intensities were observed after irradiation. The reduction in peak intensities of the irradiated sample is attributed to the breakage of chemical bonds and formation/emission of low molecule gases and radicals due to irradiation.

4. Conclusion

The enhancement in dielectric properties of organometallic compound dispersed PMMA films is attributed to conductive phase formed by metal–polymer bonding and also emission of volatile gases such as hydrogen and other low molecule gases due to ion beam irradiation. The FTIR spectra also reveal the breakage of bonds and scissioning of polymer chain due to ion beam irradiation.

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