Indian Journal of Pure & Applied Physics
Vol. 46, June 2008, pp. 439-442

Dielectric properties and surface morphology of proton irradiated ferric oxalate dispersed PVC films

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Received 28 October 2007; accepted 8 April 2008

Different concentrations of organometallic compound (ferric oxalate) have been dispersed in polyvinyl chloride (PVC) films. PVC has been synthesized by solution polymerization technique. These films have been irradiated with 3 MeV protons at a fluence of 1×10^{13} ions/cm^2. The frequency response of dielectric behaviour has been studied both in pristine and irradiated samples using LCR meter in the frequency range100 Hz-10MHz. The results so obtained are explained using the universal law of dielectric behaviour ($\varepsilon \; \alpha \; f^{\,n-1}$). The results are also explained on the basis of intra-cluster motion. It is observed that the log conductivity increases with increase in metal concentration and also with the fluence. The dielectric constant/loss shows frequency dependent behaviour. SEM studies show that the particle size of metal compound decreases upon irradiation.

Keywords: Proton irradiation, PVC, Organometallics, Dielectric properties, Universal power law, SEM

1 Introduction

Polymer composites are made by mixing two or more constituents in the polymer to make up some disadvantages in single material[1-3]. Polymer composites are potentially important over the traditional polymers because of their enhanced electrical, mechanical and magnetic properties. Metal particles embedded in polymer matrix have excellent potential for dielectric devices, packaging and data storing devices. The dielectric property of the composites depends on the volume fraction, size and shape of conducting fillers, and also on other factors such as, preparation method, interface and interaction between fillers and the polymers[4,5]. It is well established that the effective utilization of filled polymers depends strongly on the ability to disperse the particles homogeneously throughout the matrix[6]. Generally, polyvinyl chloride (PVC) is being used for the consumer products like cables, pipes, window frames, packaging, bottles, credit cards, and audio recording. It is also used in car interiors and in hospital as medical disposables. The presence of chlorine in the PVC structure is the reason of its better properties like fire resistance and durability. Purpose of metal compound doping is to enhance the adhesion possibility of metal and polymer as it contains large number of functional groups. Different concentrations of organometallic compound were dispersed in PVC and films of composites were prepared by solution casting method. Overall, the reasonable dispersion and improvement in dielectric properties achieved which is promising for the use of these films as dielectric material. High energy ion beam irradiation of polymers is a novel technique for the generation of active sites for surface physical and chemical modifications of polymers so as to enhance the properties like conductivity and solubility[7]. Interaction of high energy ion beam with polymers results in the formation of gaseous products, accompanied by polymer cross-linking, the chain-scissioning and some other secondary processes.

In the present work, radiation induced modification in *ac* dielectric properties and surface morphology are studied at a fluence of 1×10^{13} ions/cm^2 by means of LCR meter and Scanning Electron Microscopy (SEM) respectively.

2 Experimental Details

Polymer composites of organometallic compound/ ferric oxalate dispersed in PVC are prepared. Ferric oxalate was formed by taking 6.24 g of oxalic acid and 5.24 g of 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. Different concentrations (e.g. 5, 10 and 15%) of ferric oxalate (f_o) were dissolved in PVC using acetone and the solution was stirred thoroughly for about an hour and poured on clean, uniform glass trough. The solvent was evaporated at room temperature to get film of thickness 150 μm[8]. 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 nA/cm^2 and irradiated at a fluence of 1×10^{13} ions/cm^2. All irradiations were performed in vacuum (10^{-6} torr) at ambient temperature. The dielectric properties of all the samples were measured using an LCR meter/impedance-phase analyzer (General Radio, USA, Modal 1689/Solartron-1260). Conductivity of the material was calculated using the relation

$$\sigma=2\pi f C_p D t/A \text{ (S/m)}$$

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 $C_0=\varepsilon_0 A/t$, A and t are the cross-sectional area of the electrode and thickness of the sample respectively. ε_o (permittivity of vacuum) = 8.85×10^{-12} F/m. The Scanning electron micrographs of the polymer films were recorded using Oxford_INCA Energy dispersive X-ray spectrometer.

3 Results and Discussion

3.1 *ac* Conductivity

The *ac* electrical conductivity of pure polymer and ferric oxalate doped PVC is shown in Fig. 1 for (a) pristine and (b) irradiated films on the logarithmic scale. It is observed from the plots that conductivity increases with the increase of frequency as well as with the concentration of ferric oxalate in PVC. It is assumed that an electrical conducting path and network could be formed in the composites with increasing the concentration of fillers[9].

For irradiated samples further increase in conductivity is observed. Irradiation is expected to promote the metal to polymer bonding and convert polymer structure into hydrogen depleted carbon network. An *ac* field of sufficiently high frequency may cause a net polarization, which is out of phase with the field. This results in increase of conductivity at higher frequency.

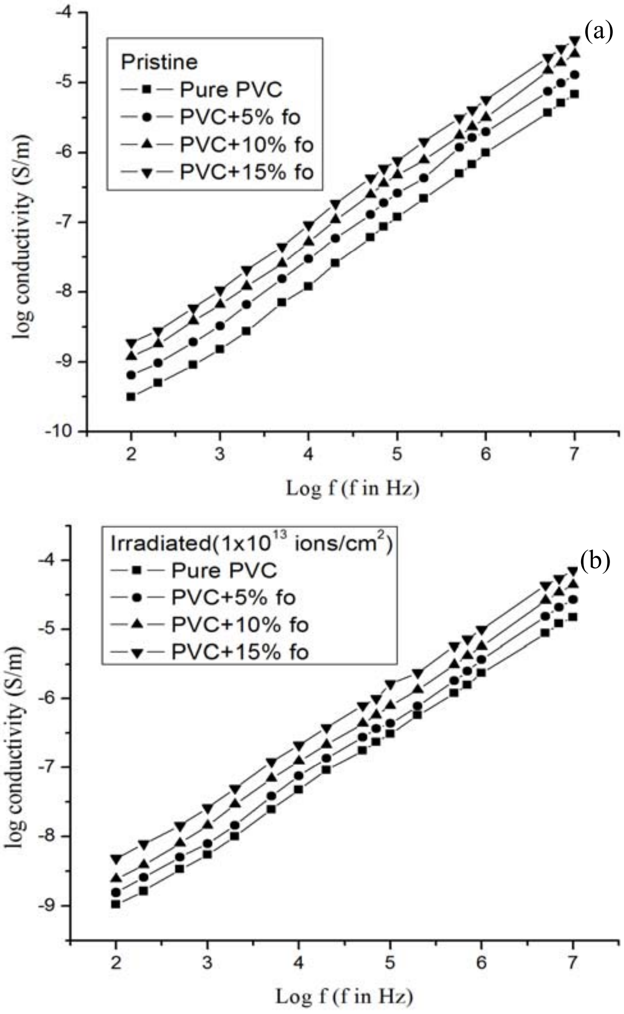

Fig. 1 — Log conductivity versus log frequency of (a) pristine and (b) irradiated films of composites

3.2 Dielectric constant

It is observed from Fig. 2 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 a defect site. They induce an opposite charge in its vicinity, as a result of which, motion of charge carriers is slowed down and the value of dielectric constant decreases. According to Dissado and Hill theory at high frequency, a single cluster dipole moment relaxation takes place[10]. This reduces the dielectric constant at higher frequency. The decrease in dielectric constant at higher frequency can be explained by Jonscher's power law[11] i.e. $\varepsilon \propto f^{n-1}$ where $0<n<1$. When the doping is done, the quantity of the accumulated charge will increase because of the polarization of the polymer/metal at interfaces.

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[9]. The experimental results of the present study also support this explanation as seen in Fig. 2. It is observed that the value of *n* increases from 0.76 to 0.92 upon irradiation for pure PVC. Similar results are also obtained for doped PVC. This may be due to the dominance of metal to polymer bonding due to irradiation, which reduces the dipole polarization.

3.3 Dielectric loss

Figure 3 represents the loss factor versus log frequency for pristine and irradiated samples. It is observed that the loss factor decreases exponentially with the increase of frequency. It is also observed that loss factor increases upon irradiation and with increase in filler concentration. The increase in dielectric loss is attributed to chain scissioning at higher fluences, resulting in an increase of free radicals, unsaturations.

3.4 Scanning Electron Microscopy

Figure 4 represents the SEM images for (a) pristine and (b) irradiated samples of 15% fo dispersed PVC films.

No significant change in pure PVC films before and after irradiation has been observed. But the surface morphology of composite shows appreciable change after ion beam irradiation. The particle size of the filler is observed to reduce after ion beam irradiation[12]. The high energy ion beam irradiation makes the surface smoother than the pristine film[13].

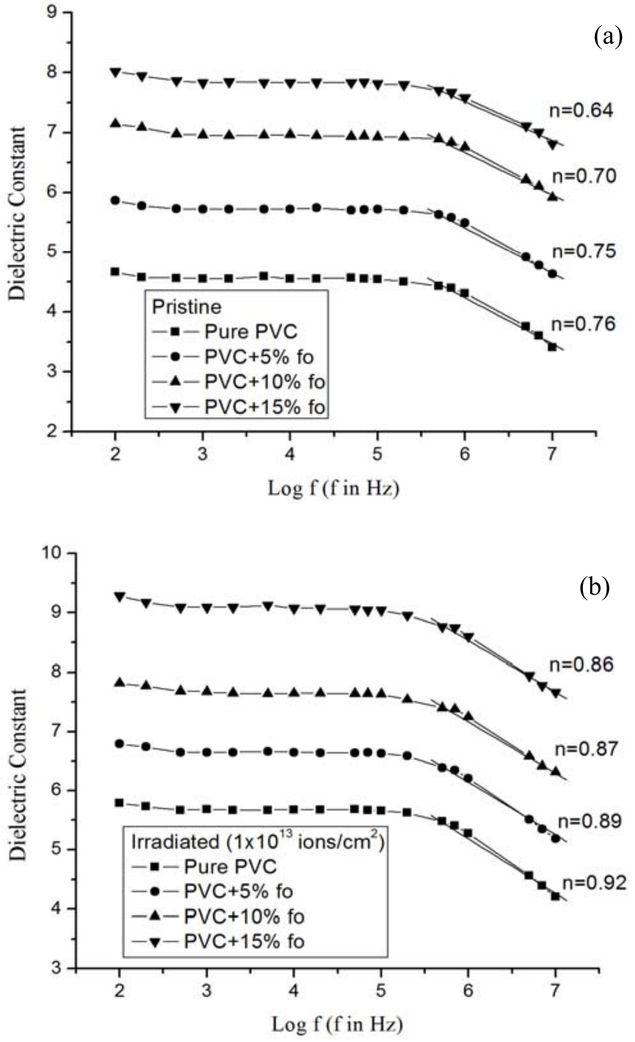

Fig. 2 — Dielectric constant vs. log frequency for (a) pristine and (b) irradiated films of composites

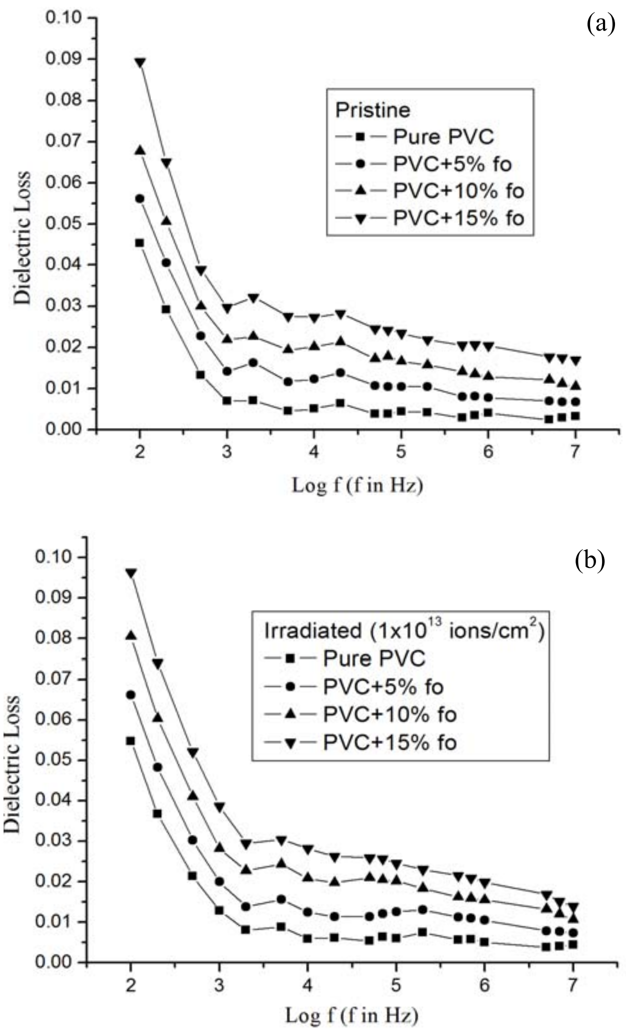

Fig. 3 — Dielectric loss vs. log frequency for (a) pristine and (b) irradiated films of composites

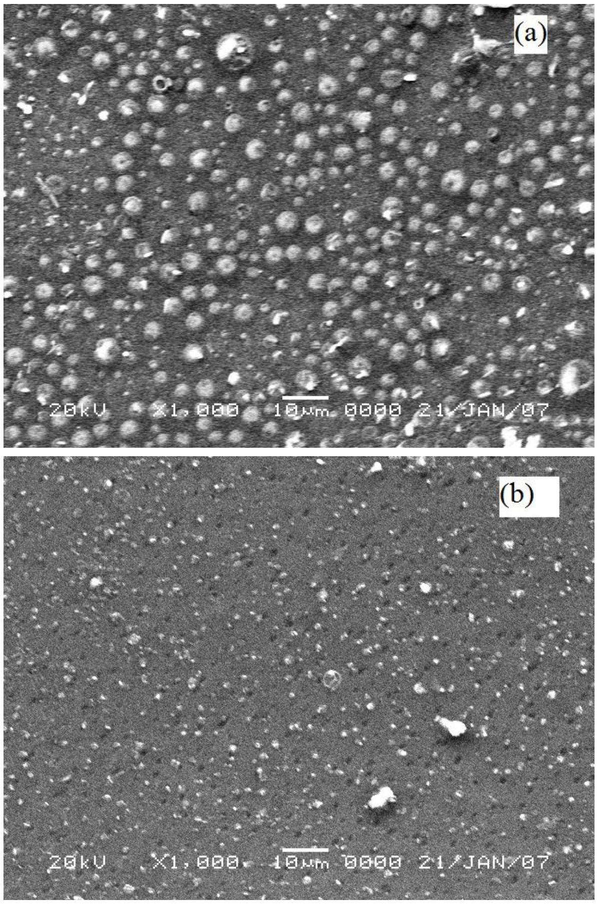

Fig. 4 — SEM images for (a) pristine and (b) irradiated 15% to dispersed PVC films

4 Conclusions

Ion irradiation has shown significant enhancement in dielectric properties of organometallic compound dispersed PVC films. It may be attributed to metal/polymer bonding and conversion of polymeric structure in to hydrogen depleted carbon network due to irradiation. The dielectric constant/loss shows the frequency dependence behaviour and obeys universal law of dielectric. Surface morphology as well as size of the particle is observed to change due to irradiation.

Acknowledgement

Authors are thankful to the staff of Cyclotron crew members, Punjab University, Chandigarh for providing irradiation facility. Financial support given by Inter University Accelerator Centre, New Delhi is gratefully acknowledged.

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