Thin films of ferric oxalate dispersed in polyvinyl chloride (PVC) were synthesized. Ferric oxalate was dispersed in PVC films at various concentrations. These films were irradiated with 80 MeV O\(^{6+}\) ions at a fluence of \(1 \times 10^{11}\) ions/cm\(^2\). The radiation induced changes in dielectric properties, microhardness and surface roughness have been studied in the paper. It is observed that hardness and dielectric properties of the film increase with the concentration of dispersed ferric oxalate and also with the fluence. This suggests that ion beam irradiation promotes the metal to polymer adhesion, and converts the polymeric structure into hydrogen depleted carbon network, which make polymer harder and more conductive. Atomic force microscopy shows that the average roughness of the irradiated films is lower than that of un-irradiated films.

Keywords: Ion beam modification, Polymer composites, Polyvinyl chloride, Dielectric properties, Microhardness, AFM

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1 Introduction

Polymer composites filled with metal fillers are of interest of many fields of engineering. It is widely used for different applications: packaging, decorative, coatings, capacitors, magnetic tapes, electromagnetic interface (EMI) shielding, adhesives, sensors etc\(^1,2\). The use of organic and inorganic fillers is a common practice in the polymer industry to improve the mechanical properties of thermoplastic materials such as heat distortion temperature, hardness, roughness, stiffness and mold shrinkage or to decrease other properties such as permeability and often material price. The filler effect on the composite properties strongly depends on its shape, size, aggregation state, surface characteristics, and degree of dispersion. Ion beam modification is well known established and economical method for modifying the properties of polymer composites. The important properties of such polymer composites, i.e. mechanical property, thermal stability, chemical resistance, melt flow, process ability and surface properties can be significantly improved by ion beam irradiation\(^3,4\). A filled polymer differs substantially from the free one in wide range of properties. These materials can be cross-linked by radiation to obtain useful properties. Our interest in dispersion of organometallic compound is mainly because of ion irradiation induced enhancement of both electrical conductivity and mechanical (microhardness) properties of polymers. In this study, the PVC films were dispersed with different concentrations (i.e. 5, 10 and 15%) of ferric oxalate compound and irradiated with 80 MeV O\(^{6+}\) ions at a fluence of \(1 \times 10^{11}\) ions/cm\(^2\). We have studied the mechanical property (i.e. microhardness), surface roughness and electrical properties by means of Vickers’ microhardness indentation, atomic force microscopy and LCR meter, respectively.

2 Experimental Details

As an organometallic compound, the compound ferric oxalate is used. It was formed by taking 6.24g of oxalic acid and 5.24g of ferric chloride with ethanol as a solvent in a round bottom flask, and it was refluxed for 4h at 60°C. The excess of ethanol was then distilled out and the substance was dried at 75°C for 3h in an oven. The PVC and ferric oxalate compound of 5, 10, and 15% were dissolved using toluene and the solutions were mixed and stirred thoroughly for about an hour and poured on clean glass trough. The solvent was evaporated at room temperature (25± 1°C) to get thin films (thickness \(~50\mu m\)) of dispersed PVC with 5, 10, and 15% concentration of ferric oxalate compound. The films

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were used for irradiation. All films were irradiated with 80 MeV O\(^+\) ions at a fluence of 1 \(\times 10^{11}\) ions/cm\(^2\) using 15 UD Pelletron of Nuclear Science Centre (NSC), New Delhi. A Carl Zeiss microscope and accessories were used to investigate Vickers' microhardness of all samples. The electrical properties of all samples were measured in the frequency range 0.05-100kHz at ambient temperature using variable frequency LCR meter (General Radio, USA; model-1689). The conductivity was calculated using the relation \(\sigma = t/R A\) (\(\Omega^{-1}\) cm\(^{-1}\)), where \(R\) is resistance measured, \(A\) the cross-sectional area of the electrode and \(t\) is the thickness of the polymeric film. The dielectric constant was calculated using the relation \(\varepsilon = C_p/C_0\), where \(C_p\) is capacitance measured using the LCR meter and \(C_0 = \varepsilon_0 A/t\), where \(\varepsilon_0\) is the permittivity of vacuum.

3 Results and Discussion

3.1 ac electrical frequency response

The ac electrical measurement was performed for pristine and irradiated samples. Fig.1 shows the variation of conductivity with log of frequency for the pristine and irradiated samples at different ferric oxalate concentrations. A sharp increase in conductivity was observed around 10 kHz for dispersed pristine and irradiated samples. It is also observed that conductivity increases with increasing concentration of dispersed ferric oxalate compound [Fig.1(a)] as well as irradiated one at the fluence of 1\(\times10^{11}\) ions/cm\(^2\) [Fig.1(b)], respectively.

The increase in conductivity with different ferric oxalate concentrations for pristine samples may be attributed to the conductive phase formed by...
dispersed organometallic compound in polymer matrix. It is known that electrical conductivity of such composites depends on the type and concentration of the dispersed compound. As a result, the conductivity of dispersed films increases on increasing the concentration of ferric oxalate compound in the polymer matrix. It is also observed from Fig.1(b) that after the irradiation the conductivity increases with increasing the concentration of dispersed organometallic compound. It is expected to promote the metal to polymer bonding and convert the polymeric structure to a hydrogen depleted carbon network. It is this carbon network that is believed to make the polymers more conductive.

Fig. 2(a and b) show the plot of dielectric loss versus log frequency for pristine and irradiated samples at different ferric oxalate concentrations. It is observed that tanδ decreases exponentially as log frequency increases. It is also observed that tanδ increases as ferric oxalate concentration increases. Fig. 3 (a and b) show the plot of dielectric constant versus log frequency for pristine and irradiated samples at different ferric oxalate concentrations. As
3.2 Microhardness

Fig. 5 presents the Vickers hardness (Hv) values for both pristine and irradiated films. The AFM images of dispersed ferric oxalate in PVC films show clear differences in the microstructure, likely due to the increased crystallinity of the irradiated films.

It is evident that the load has become a constant for the pristine films, and the microhardness has increased almost constantly. The irradiated films show a similar trend, with the microhardness increasing for both pristine and dispersed ferric oxalate films. These results suggest that the increased microhardness is due to the irradiation process, which enhances the crystallinity and stiffness of the PVC films.

3.3 Atomic Force Microscopy

The AFM images provide a detailed view of the film surfaces, revealing the topographical changes caused by the irradiation. The images show an increase in the roughness and a decrease in the surface area, indicating a denser and more compact structure in the irradiated films.
evident from Fig. 3, the dielectric constant remains almost constant up to 100 kHz. At these frequencies, the motion of the free charge carriers is constant, hence, there is no change in dielectric constant. It is also revealed that dielectric constant increases as ferric oxalate concentration increases for pristine and irradiated samples. The magnitude of dielectric constant is higher for irradiated films compared to pristine one. The increase in dielectric constant may be attributed to the chain scission and as a result, the increase in the free radicals, unsaturation, etc.

3.2 Microhardness

Fig. 4 shows the plot of the Vickers’ microhardness ($H_v$) versus applied load ($P$) for pristine [Fig.4(a)] and irradiated [Fig.4(b)] films of pure PVC, and dispersed ferric oxalate compound of 5, 10 and 15% in PVC films. The microhardness indentations were carried out on the surface of the pristine and irradiated films at room temperature under the different applied loads from 50 to 1000 mN and at a constant loading time of 30 s.

It has been observed that $H_v$ value increases with the load up to 100mN and then decreases and becomes saturated beyond the load of 300mN. The hardness can be defined as resistance to indenter penetration, or as the average pressure under the indenter, calculated as the applied load divided by the projected area of contact incorporating the plastic component of displacement. The hardness is known to be influenced by surface effects. Particularly at low penetration depths, the strain hardening modifies the true hardness of the material. At the higher loads, beyond 400 mN, the interior of the bulk specimen is devoid of surface effects. Hence, the hardness value at higher loads represents the true value of the bulk and it is consequently independent of the load. It is found that hardness increases as ferric oxalate concentration increases. It may be due to the improvement in bonding properties. The hardness also increases on irradiation of the samples. This may be attributed to the growth of a hydrogen depleted carbon network which makes the polymer harder.

3.3 Atomic Force Microscopy

The surface morphology of pristine and irradiated films of pure PVC, and dispersed ferric oxalate compound of 5 and 15% in PVC was measured by AFM on 5x5μm² area as shown in Fig. 5. Each AFM image is analyzed in terms of surface average roughness ($R_a$). The roughness values are 5.7, 9.3, and 22 nm for pristine and 2.7, 6.7, and 19.3 nm for irradiated (at the fluences of $10^{11}$ ions/cm²) samples, respectively. It is found that roughness increases as ferric oxalate concentration increases. The increase in roughness may be due to the increase of density and size of metal particles on the surfaces of the PVC films. It is also observed that after irradiation the roughness of the surface decreases and the surface becomes significantly smoother. This relative smoothness may be attributable to defect enhanced surface diffusion.

4 Conclusions

Ions irradiation has been shown to significantly enhance both electrical and microhardness of organometallic compound dispersed PVC films. It may be attributed to the metal to polymer adhesion and to convert the polymeric structure in to hydrogen depleted carbon network. This carbon network is believed to make the polymer harder, more conductive. The surface roughness increases as concentration of ferric oxalate increases, but decreases on irradiation, as observed from AFM studies.

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