

## Analysis of organometallics dispersed polymer composite irradiated with oxygen ions

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**Abstract.** Thin films of polymethyl methacrylate (PMMA) were synthesized. Ferric oxalate was dispersed in PMMA films. These films were irradiated with 80 MeV O<sup>6+</sup> ions at a fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup>. The radiation induced changes in electrical conductivity, Mössbauer parameter, microhardness and surface roughness were investigated. It is observed that hardness and electrical conductivity of the film increases with the concentration of dispersed ferric oxalate and also with the fluence. It indicates that ion beam irradiation promotes (i) the metal to polymer bonding and (ii) convert the polymeric structure into hydrogen depleted carbon network. Thus irradiation makes the polymer harder and more conductive. Before irradiation, no Mössbauer absorption was observed. The irradiated sample showed Mössbauer absorption, which seems to indicate that there is significant interaction between the metal ion and polymer matrix. Atomic force microscopy shows that the average roughness ( $R_a$ ) of the irradiated film is lower than the unirradiated one.

**Keywords.** Polymethyl methacrylate (PMMA); ion irradiation; dielectric properties; microhardness; Mössbauer spectroscopy; AFM.

### 1. Introduction

In recent years, there is an increasing interest in polymer matrix composites prepared by mixing two or more constituents to make up some disadvantages in single material (Chen *et al* 2000; Etienne *et al* 2000; Pan *et al* 2000). For instance by combining different fillers with polymer, polymer composites with special physical properties applied in areas such as capacitor (Bai *et al* 2000; Dang *et al* 2002, 2003), can be fabricated. To prepare the composites with excellent dielectric property, therefore, the effective utilization of filled polymers depends strongly on loading fillers being homogeneous throughout polymer (Xiao *et al* 2001) and effective microstructure in the composites. Furthermore, interfaces among the different phases in the composites play also an important role on deciding the dielectric property. During the last few years much work has been done to study different aspects of metal/polymer interface formation using various microscopic and surface sensitive techniques. It is known that good adhesion between polymer and metal is crucial to device performance and reliability by the use of ion beam (Wang *et al* 2004; Zaporozhchenko *et al* 2000). The chemical changes brought about by ion beam in polymers underline that the physical modifications are limited to a few basic processes: gas evolution, cross linking and degradation. The chemical changes are more dramatic in polymers because of the macromolecular structure of these materials. The kind of changes, which predominate, depends on the polymer type

and radiation dosage. The ion irradiated polymers exhibited improved oxidation resistance and increased electrical conductivity. In this work, we show a new way to insert metal atoms into a polymer matrix. Organometallic compound (ferric oxalate) is in complex form and will give more functional groups after ion beam irradiation compared to inorganic fillers. There is a possibility to form oxides, hydroxides and other compounds by irradiation of organometallic dispersed polymer films. The ferric oxalate dispersed PMMA films were irradiated with 80 MeV O<sup>6+</sup> ions at a fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup>, and radiation induced changes in mechanical (microhardness), electrical properties, Mössbauer spectroscopy and surface roughness of the PMMA/organometallics composite films were investigated.

### 2. Experimental

As an organometallic compound, we used ferric oxalate. It 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 of ethanol was then distilled out and the substance was dried at 75°C for 3 h in an oven. PMMA was prepared by solution polymerization method. In this method, benzoyl peroxide (BPO, 0.8 g; an initiator for polymerization) was dissolved in freshly inhibitor free MMA (80 ml methyl methacrylate) monomer and ethyl acetate as a solvent (80 ml) in a round bottom flask and the solution was then refluxed for 5 h at 80°C temperature in hot water bath. The resulting solution was then precipitated out in another beaker con-

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taining methanol (100 ml). The PMMA, precipitated out in methanol, was dried at room temperature for 2 h. The polymerized PMMA and ferric oxalate compound of 10% was dissolved using acetone 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 ( $25 \pm 1^\circ\text{C}$ ) to get thin films (thickness,  $\sim 50 \mu\text{m}$ ) of dispersed PMMA with 10% concentration of ferric oxalate compound. The films were used for irradiation. Films were irradiated with 80 MeV  $\text{O}^{6+}$  ions at a fluence of  $1 \times 10^{11}$  ions/ $\text{cm}^2$  from the pelletron at the Nuclear Science Centre, New Delhi. A Carl Zeiss microscope and its accessories were used to investigate Vickers microhardness and surface morphology of pristine and irradiated surfaces were obtained using an atomic force microscopy (AFM) in the contact mode. AC electrical properties of all samples were measured in the frequency range 0.1–100 kHz at room temperature using variable frequency LCR meter (General Radio, USA; model-1689). The conductivity was calculated using the relation

$$\sigma = t/RA(\Omega^{-1} \text{ cm}^{-1}),$$

where  $R$  is the resistance measured,  $A$  the cross-sectional area of the electrode and  $t$  the thickness of the polymeric film. Mössbauer spectra were recorded at room temperature using  $\text{Co}^{57}$  (Rh) source in the constant acceleration mode. The line width of the spectrometer was 0.27 mm/s. Spectra were recorded before and after irradiation.

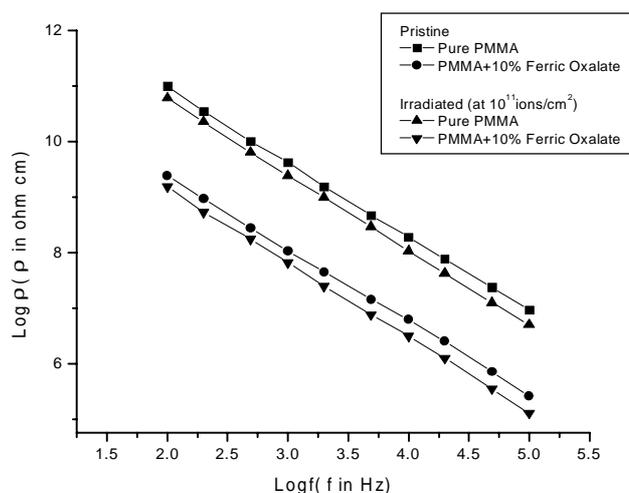
### 3. Results and discussion

#### 3.1 AC electrical frequency response

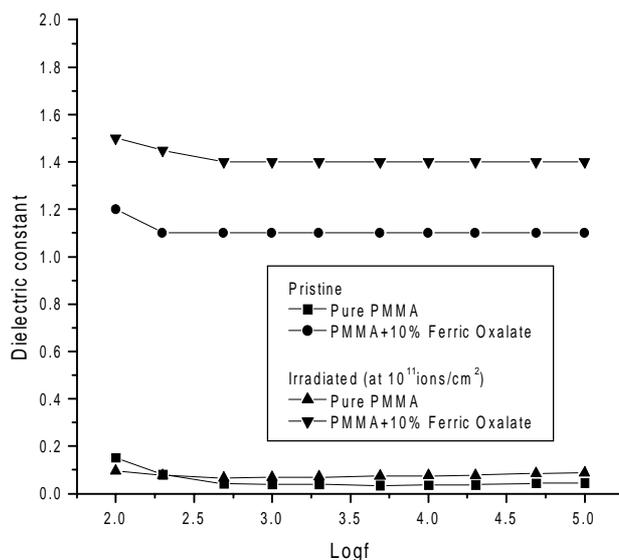
AC electrical measurement was performed for pristine and irradiated samples. Figure 1 shows the variation of log resistivity with log of frequency for the pristine and irradiated samples of pure PMMA and at 10% ferric oxalate concentration dispersed PMMA films. It is seen that the resistivity decreases rapidly in proportion to  $f^{-1}$ . It is also observed that resistivity decreases with increasing concentration of dispersed ferric oxalate compound in pure PMMA. For irradiated samples at a fluence of  $1 \times 10^{11}$  ions/ $\text{cm}^2$ , further decrease in resistivity is observed. The decrease in resistivity or increase in conductivity with ferric oxalate concentration 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 (Abu-Abdeen *et al* 2002; Mamunya *et al* 2002). As a result, the resistivity of dispersed films decreases on dispersion of ferric oxalate compound in the polymer matrix. It is also observed that after irradiation the resistivity of dispersed organometallic compound decreases. It is expected to promote metal-to-polymer adhesion 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 (Wang *et al* 2004).

Figure 2 shows the plot of dielectric constant vs log frequency for pristine and irradiated samples of pure PMMA and ferric oxalate dispersed PMMA films. As evident from the graph, the dielectric constant remains almost constant up to 100 kHz. At these frequencies, the motion of the free charge carriers is constant and hence there is no change in dielectric constant. It is also revealed that dielectric constant increases for ferric oxalate dispersed for pristine and irradiated samples.



**Figure 1.** Plot of log resistivity vs log frequency for pristine and irradiated pure and 10% dispersed ferric oxalate in PMMA films.



**Figure 2.** Plot of dielectric constant vs log frequency for pristine and irradiated pure and 10% dispersed ferric oxalate in PMMA films.

### 3.2 Microhardness

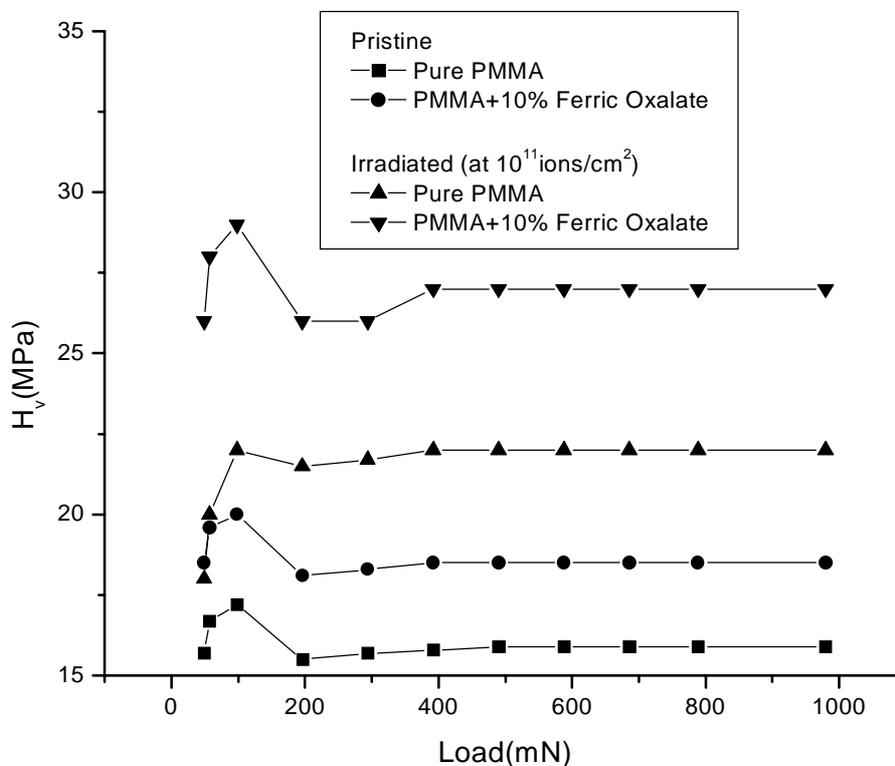
Figure 3 shows the plot of the Vickers microhardness ( $H_v$ ) vs applied load ( $P$ ) for pristine and irradiated films of pure PMMA, and dispersed ferric oxalate compound of 10% in PMMA films. The microhardness indentations were carried out on the surface of the pristine and irradiated films at room temperature under different applied loads from 50–1000 mN and at a constant loading time of 30 s.

It has been observed that microhardness ( $H_v$ ) value increases with the load up to 100 mN and then decreases and become saturated beyond the load of 400 mN. 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 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 for ferric oxalate dispersed PMMA films. It may be due to the improvement in bonding properties (Bowyer *et al* 1972). The hardness also increases on

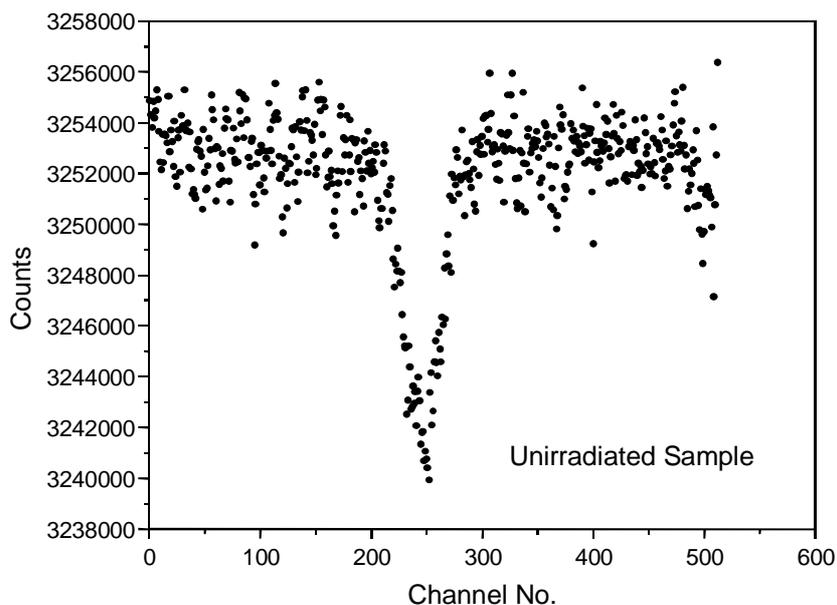
irradiation of the samples. This may be attributed to hydrogen depleted carbon network which makes the polymer harder (Wang *et al* 2004).

### 3.3 Mössbauer studies

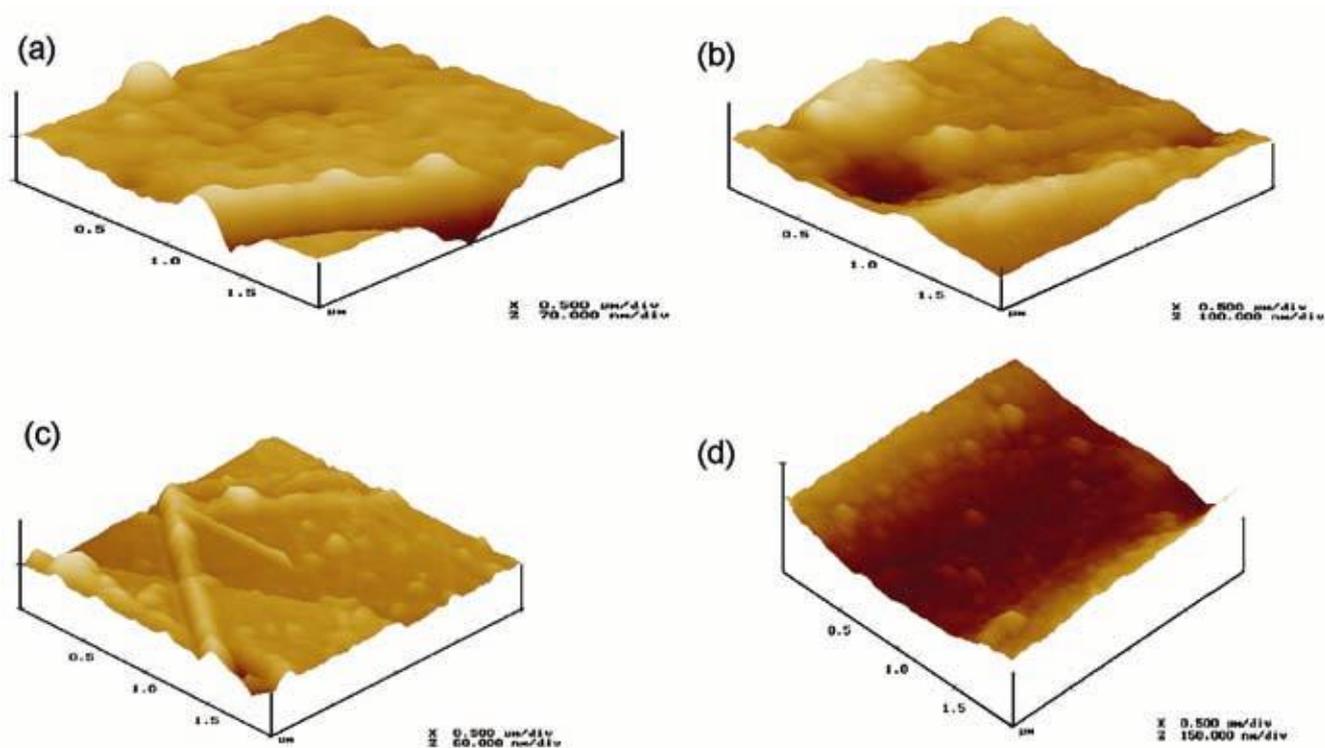
Mössbauer spectra were recorded for the samples before and after irradiation. The least square fitted values of unirradiated sample are listed in table 1 and spectrum is shown in figure 4. The fitted values indicate quadrupole splitting (QS) of  $\sim 0.45$  mm/s which corresponds to the Fe–C complex as reported earlier (Somayajulu *et al* 2001). Thus in unirradiated sample there is only Fe–C non-magnetic complexes formed. It is possible that Fe ions were either residing in the voids between the chains or got attached to the  $-\text{COOCH}_3$  group in the side chain without cross linking before irradiation. PMMA is known to undergo chain scissioning even at low (keV) ion energies. Therefore, high energy of the ion transferred energy per atom to the polymer chains makes scissioning more intense which may result in the amorphization of the sample. In the present case, after high energy irradiation of ferric oxalate dispersed PMMA films, it is expected that there is a possibility of the formation of cluster of Fe with oxygen, giving rise to magnetic interaction. However, the



**Figure 3.** Plot of hardness ( $H_v$ ) vs applied load ( $P$ ) for pristine and irradiated pure and 10% dispersed ferric oxalate in PMMA films.



**Figure 4.** Mössbauer spectra of dispersed ferric oxalate (10%) in PMMA film (pristine).



**Figure 5.** (a) AFM image of pure PMMA film (pristine), (b) AFM image of dispersed ferric oxalate (10%) in PMMA film (pristine), (c) AFM image of pure PMMA film (irradiated) and (d) AFM image of dispersed ferric oxalate (10%) in PMMA film (irradiated).

irradiated sample showed magnetic site with field values of  $\sim 510$  kOe. This indicates that there is a formation of Fe–O (could be  $\text{Fe}_2\text{O}_3$  phase) complex into the polymer matrix, by consequent breakage of Fe–C bonds which were observed in unirradiated sample. From Mössbauer

spectra, the value of QS and isomer shift (IS) for the irradiated samples showed that Fe is in the state 3+ or more. The spectra indicate the formation of magnetic sextet (Fe–O) with a doublet (Fe–C). The absorption % was low due to less quantity of irradiated material.

**Table 1.** Mössbauer parameter of dispersed ferric oxalate (10%) in PMMA film.

Quadrupole splitting (mm/s)	Isomer shift (mm/s)	Fractional area
0.45	-0.29	1

### 3.4 Atomic force microscopy

The surface morphology of pristine and irradiated films of pure PMMA, and dispersed ferric oxalate compound of 10% in PMMA was measured by AFM on  $2 \times 2 \mu\text{m}^2$  area are shown in figure 5. Each AFM image is analysed in terms of surface average roughness ( $R_a$ ). The roughness values are 13 nm and 21 nm for pristine and 6 nm and 19.2 nm for irradiated (at the fluences of  $10^{11}$  ions/cm<sup>2</sup>) samples, respectively. It is found that roughness increases for dispersed ferric oxalate polymeric film. The increase in roughness may be due to the increase of density and size of metal particles on the surfaces of PMMA films (Yan *et al* 2004). It is also observed that after irradiation the roughness of the surface decreases and the surface becomes significantly smoother. This relative smoothness is probably due to the sputtering effects (Qureshi *et al* 2006).

## 4. Conclusions

Ion irradiation has been shown to significantly enhance electrical, Mössbauer absorption and microhardness of organometallic compound dispersed PMMA films. It may be attributed to (i) metal to polymer adhesion and (ii) conversion of the polymeric structure to hydrogen depleted carbon network. Thus irradiation makes the polymer harder and more conductive. Mössbauer studies indicate that there is a formation of Fe–O (could be Fe<sub>2</sub>O<sub>3</sub> phase) complex into the polymer matrix due to irradiation. The surface roughness increases for dispersed ferric oxalate

PMMA film and decreases on irradiation as observed from AFM studies.

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