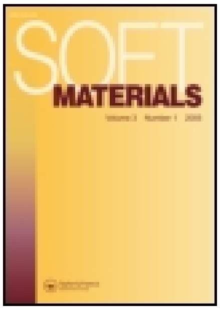

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MODIFICATION OF POLYMER COMPOSITE BY PROTON BEAM IRRADIATION

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□ *Composite films of the thermoplastic polymer (Polymethyl methacrylate) filled with different concentration of organometallic compound was prepared by chemical method. These films were irradiated with 3 MeV proton beam at the fluences of* 6×10^{12} *and* 1×10^{13} *ions/cm*^{2}*. The dependence of a.c. conductivity of pristine and irradiated films on frequency, fluence of proton beam, and filler concentration was studied. The result shows that the conductivity increases with increase in the concentration of the filler and also with fluence. Microhardness of the films was studied for the applied load ranging from 10–1000 mN. The hardness is observed to increase with the fluence. This may be due to the conversion of polymeric structure in to hydrogen depleted carbon network, which makes polymer more conductive and harder. Surface morphology was studied by means of atomic force microscopy (AFM). It reveals that the average surface roughness decreases after irradiation. Structural changes in the polymer structure due to irradiation have been studied using Fourier Transform Infrared (FTIR) spectroscopy.*

Keywords Electrical measurement, FTIR spectroscopy, Microhardness, Polymer composites, Surface morphology

INTRODUCTION

Composite materials, containing polymer matrix and organometallic compound as a filler, are a relatively new class of material with very interesting properties and verity of applications. The electrical characteristics of such composites are close to the properties of the filler, whereas their mechanical properties and processing methods are typical for polymers (1).

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These composites have several advantages over the conventional conductive materials, including processability, flexibility, light weight, and ability to absorb mechanical shock (2). The study of the structure, the properties, and the dynamics of the polymer composite systems (3–6) is particularly important for the development of new materials for specific industrial applications such as capacitor (7, 8). Some work has been done on the modification of the physical properties of the polymer by doping fillers like carbon fiber (9), iron (10–12), and nickel (9, 13, 14). Dielectric properties of these composites were observed to enhance with filler concentrations.

When polymeric materials are subjected to irradiation, a high number density of crosslinks is introduced and numerous double and triple bonds and free radicals are formed. As a consequence, such irradiation processed polymers become hard, electrically conductive, and optically dense, with improved resistance to chemicals and mechanical wear (15–19). The use of ion beam irradiation is getting high impetus as electrical and physical properties of the polymers can be modified in a controlled way by easy to control parameters like the energy and ion fluence. For instance, Fink et al. (20) has reported the formation of a ringed structure in PMMA after irradiation by 2.2 GeV Au ions and Ciesla and Starosta (21) have observed significant difference between pristine and ion irradiated samples. Balanzat et al. (22) and Zhu et al. (23) have studied the swift heavy ion modification of some physical properties of various polymers.

There are very few reports on the effects of irradiation on polymer composites. Polymer systems with organometallic compound can be tailored to exhibit novel electrical, mechanical, and surface properties after irradiation. In the present work we have reported the synthesis of polymer composites by doping different concentration of ferric oxalate in polymethyl methacrylate (PMMA) and effect of irradiation on some physical and chemical properties of this composite. Organometallic compound has been used as a filler to improve adhesion between filler and polymer because such compounds have a large number of functional groups, which makes more prominent bonding with the polymeric chain after irradiation (24). We have reported for the first time the effect of proton beam on the hardness of this composite. The dependence of the electrical and mechanical properties and surface morphology of the composite on the concentration of the filler and fluence has been reported.

EXPERIMENTAL DETAIL

Sample Preparation and Irradiation

PMMA $(C_5O_2H_8)_n$ was prepared by solution polymerization technique. The Benzoyl peroxide (BPO:0.8 g; an initiator for polymerization) was dissolved in fresh inhibitor-free 80 ml MMA(methyl methacrylate) monomer with ethyl acetate as a solvent (80 ml) in a round bottom flask. This solution was properly refluxed for about 5 h at 80°C temperature in the hot water bath. The resulting solution was precipitated out in another beaker containing methanol (100 ml). The precipitated PMMA was allowed to dry at room temperature for 2 h. Ferric Oxalate 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 (24). Ferric Oxalate (Fo) was then dissolved in PMMA using acetone and the solution was stirred thoroughly for about an hour and poured on a clean, uniform glass trough. The solvent was evaporated at room temperature to get film of thickness ~130 μm. The films of polymer with different concentration of ferric oxalate compound (viz. 5, 10, and 15 wt% of PMMA) were prepared. These samples were irradiated with 3 MeV proton beam using Cyclotron facility of Physics Department, Punjab University, Chandigarh, India. The beam current density was of the order of 20 nA/cm^2 and irradiated at the fluences of 6×10^{12} and 1×10^{13} $ions/cm^2$. All irradiations were performed in vacuum (10^{-6} torr) at ambient temperature.

Characterization

The a.c. electrical conductivity was measured using Impedance gain phase analyzer (Solartron-1260). Both the capacitance and dielectric loss were measured in the frequency range of 100 Hz to 10 MHz. Conductivity of the material was calculated using the equation

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

where C_p is the capacitance measured using an LCR meter, f is the frequency, D is the dielectric loss, and A and t are the cross-sectional area of the electrode and thickness of the sample, respectively.

The study of microhardness has been done by means of Vicker's microhardness tester (Future Tech. Corp., Japan; FM-700) in the load range of 10–1000 mN for 30-s indentation. Surface morphology was studied by Nanoscope-E (Digital Instrument from USA) in contact mode with silicon nitride tip. The length of cantilever was about 100 μm and having 0.5 N/m spring constant. To study the structural changes, including the alteration in position and intensity of the characteristic bands, the FTIR spectra of pristine and irradiated (1×10^{13} $ions/cm^2$) PMMA films were recorded in the wave number range 4000–500 cm^{-1} using a Thermo-Nicolet NEXUS 670 FT-IR spectrometer with the resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

When a energetic charged ion strikes a polymeric target, it loses its energy by two mechanisms known as electronic and nuclear stopping. The projected range of 3 MeV proton beam in PMMA was calculated to be 126 μm using SRIM-2003 code. The electronic stopping power of the beam is 1.418 eV/Å and nuclear stopping power of the beam is 8.879×10^{-4} eV/Å. The thickness of the polymer is slightly larger than the projected range of the beam in the polymer. Hence the beam was stopped in the polymer and maximum dissipation of heat took place at the end. The composite shows a lower projected range due to increase in density after doping filler.

Conductivity of the Composites

The a.c. conductivity of the composites as a function of the frequency, fluence, and filler concentration has been studied. Figs. 1(a–d) reveals that conductivity at low frequency (up to 10^4 Hz) for all the composites looks like a straight line, typical of hopping conduction (25). It is known that electrical conductivity of such composites depends on the type and concentration of the dispersed compound. The increase in conductivity is related to a possible increase in the number of conduction paths created between the filler particles aggregates in the composite in addition to a decrease in the width of potential barriers within the bulk regions of high conductivity. Therefore, more charge carriers may be able to "hop" by tunneling; resulting in the increase in the bulk conductivity and it also increases with increasing filler concentration (26–28). Generally, enhancement in a.c. electrical conductivity by increasing filler contents is attributed to the electronic interaction processes taking place in the composites. At low filler concentration the transport charge carriers are very low; conduction is only due to hopping and tunneling through a non-conducting medium between the neighboring particles. Therefore, the overall conductivity of such a composite is low. As concentration of the filler increases, the gap between the particles diminishes and conductivity slowly increases because charge transport becomes easier (29). From Fig. 1(e) it was observed that the conductivity is enhanced with the increase in concentration of filler and also with fluence.

Conductivity is further observed to increase upon irradiation. Irradiation is expected to promote the metal to polymer bonding and convert polymeric structure into a hydrogen-depleted carbon network. It is this carbon network that is believed to make the polymer more conductive (30).

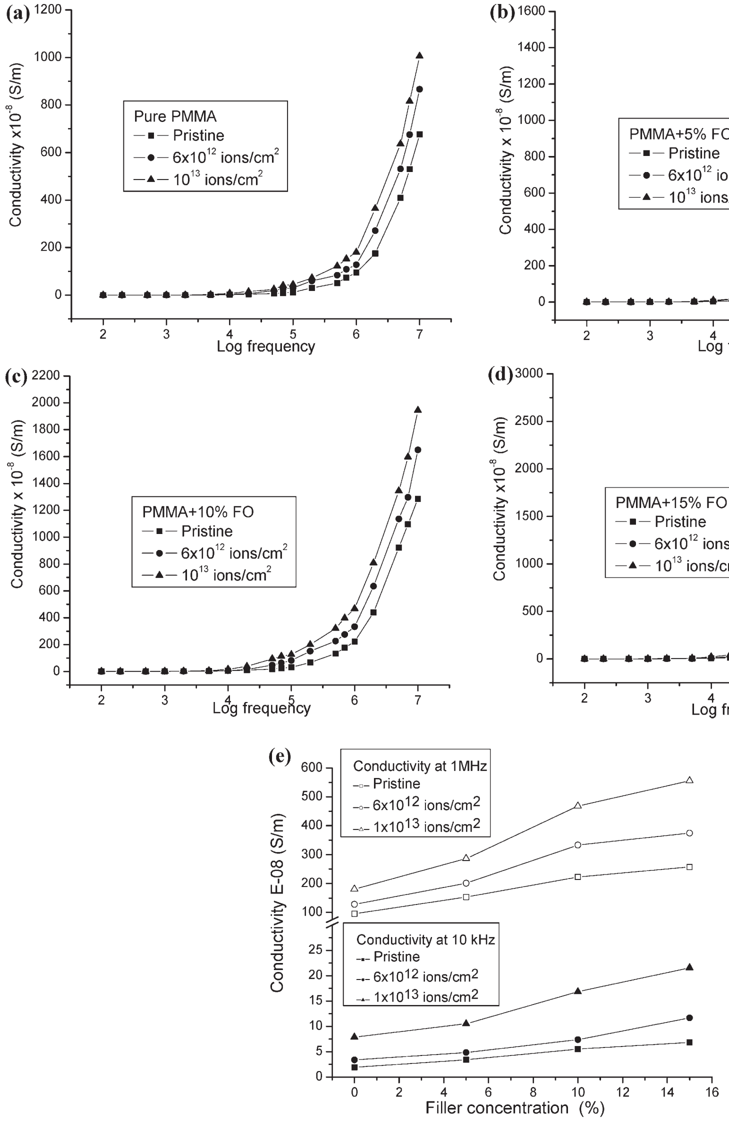

FIGURE 1 Conductivity versus log frequency for pristine and irradiated (a) Pure PMMA; (b) PMMA + 5%Fo; (c) PMMA + 10%Fo; (d) PMMA + 15%Fo; (e) Conductivity versus filler concentration for pristine and irradiated films.

Microhardness

Hardness can be defined as the ability of a material to resist penetration by another harder solid, calculated as a ratio of applied load to the surface area of indentation. 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. The hardness was calculated using the standard formula

$$Hv = 1.854xP/D^2$$

where P is applied load in mN obtained as the product of the load (in mN) and gravitational acceleration (g) = 9.8 ms^{-2} and D is the average diagonal length of indentation mark in microns. The microhardness indentations were carried out on the surface of the pristine and irradiated films at room temperature under different applied loads from 10–1000 mN and at a constant loading time of 30 s. Figure 2(a) shows the hardness values

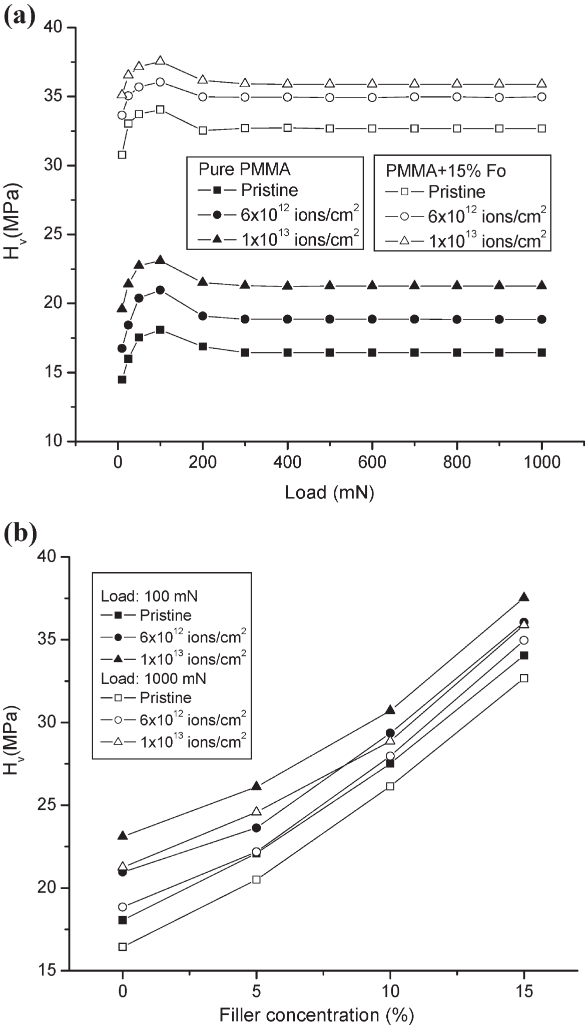

FIGURE 2 (a) Microhardness versus applied load for pristine and irradiated films of Pure PMMA and PMMA + 15% Fo; (b) Microhardness versus filler concentration for pristine and irradiated films.

of pristine and irradiated films of Pure PMMA and PMMA + 15% Fo. It has been observed that microhardness (Hv) value increases with the load up to 100 mN and then decreases and become saturated beyond the load of 300 mN. At higher loads, beyond 300 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. Figure 2(b) represents the variation in microhardness of the polymer composite as a function of filler concentration at different fluences for 100 mN and 1000 mN load. It is found that hardness increases for ferric oxalate dispersed PMMA films. It may be due to the improvement in bonding properties (31). The hardness also increases upon irradiation. This may be attributed to hydrogen depleted carbon network, which makes the polymer harder (30).

Atomic Force Microscopy

Surface morphology of pristine and irradiated composites was studied using atomic force microscopy in contact mode with silicon nitride (Si_3N_4) tip. The 3-dimension morphology of pristine and irradiated (at a fluence of 1×10^{13} ions/cm^2) samples are shown in Figs 3(a–h) in $2 \times 2\ \mu m^2$ area. The dips are obtained at some places, which might be due to inclusion of the oxalate. Average surface roughness was observed to decrease from 8.9 nm to 6.3 nm for Pure PMMA after irradiation and surface becomes relatively smoother. Similarly, it decreases from 27.8, 29.6, and 46.5 nm to 25.6, 22.0, and 32.5 nm, respectively, for 5, 10, and 15% ferric oxalate dispersed PMMA composites after irradiation. This decrease in roughness is attributed to defect-enhanced surface diffusion (24). However, the increase in roughness from 8.9 nm (pure PMMA) to 46.5 nm (PMMA + 15% Fo) is due to increase in density and size of metal particle on the surface of PMMA films (32).

FTIR Spectral Analysis

Figure 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) 1715 cm^{-1}: R-C=O (kepton of ester) (F) 3900–3000 cm^{-1}: C-H stretching (G) 3500 cm^{-1}: OH free stretching vibration (33). It is observed that there is no significant change in overall structure of the polymer but minor changes in peak intensities were observed upon irradiation. The reduction in peak intensities of the irradiated sample is ascribed to the breakage of chemical bonds and formation/emission of low molecule gases and/or free radicals due to irradiation.

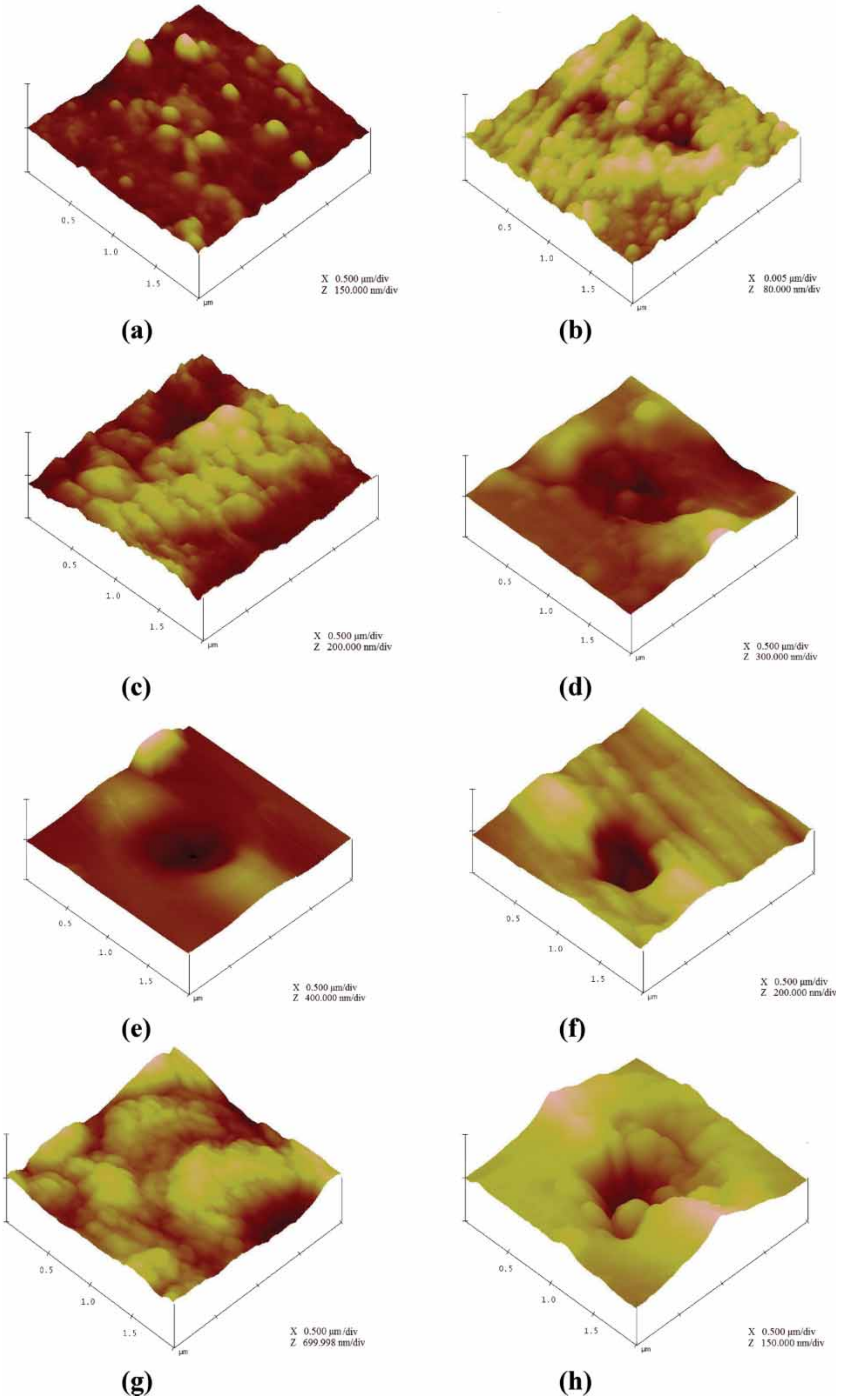

FIGURE 3 AFM image of (a) Pure PMMA (Pristine); (b) Pure PMMA (Irradiated); (c) PMMA + 5% Fo (Pristine); (d) PMMA + 5% Fo (Irradiated); (e) PMMA + 10% Fo (Pristine); (f) PMMA + 10% Fo (Irradiated); (g) PMMA + 15% Fo (Pristine); (h) PMMA + 15% Fo (Irradiated).

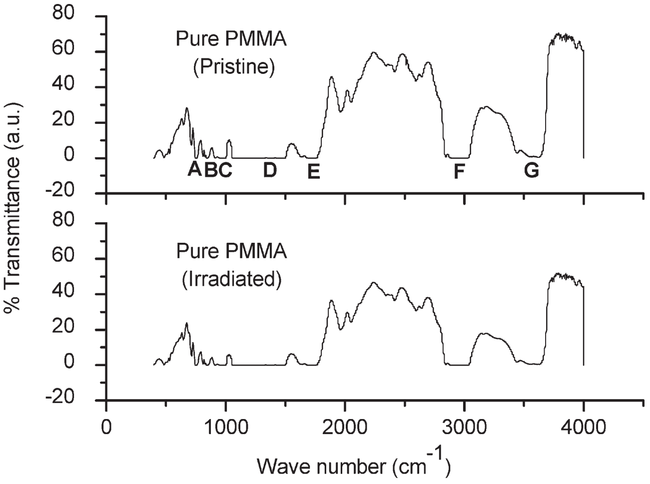

FIGURE 4 FTIR spectra of pristine and irradiated (1×10^{13} ions/cm^2) PMMA.

CONCLUSION

Proton irradiation has significantly enhanced the electrical and mechanical properties of the polymer composites. This is attributed to the fact that the radiation exposure on the polymeric composites converts the polymeric structure into hydrogen- depleted carbon network and promotes good bonding between metal and polymer. This makes the composite more conductive and harder. The surface of the sample becomes smoother after irradiation as observed from atomic force microscopy (AFM) study. This may be due to the defect- enhanced surface diffusion.

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