Surface & Coatings Technology 203 (2009) 2595–2599

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Structural and chemical modification of polymer composite by proton irradiation

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ARTICLE INFO

Available online 3 March 2009

PACS:
72.80.Tm
61.10.Nz
68.37.Hk

Keywords:
Polymer composite
Proton irradiation
X-ray diffraction
FTIR
SEM

ABSTRACT

Polymethyl methacrylate (PMMA) was synthesized by solution polymerization technique. Different concentrations of organometallic compound/palladium (II) acetylacetonate [Pd(acac)] were dispersed in PMMA. The composite films were irradiated with 3 MeV proton beam at a fluence of 10^{13} ions/cm^2. The radiation induced changes in structural and chemical properties were studied by means of X-ray diffraction (XRD) and FTIR spectroscopy. The XRD results reveal that the crystalline size and crystallinity of the composite films decrease after irradiation, however crystallinity increases with filler concentration. This is due to the crystalline behavior of Pd(acac). Fourier transform infrared spectroscopy has been studied in transmittance mode. The decrement in the peak intensity is attributed to chain scissioning of the polymeric bonds. Chain scissioning is also responsible for the decrement in the crystallinity of the composites. The glass transition temperature was observed to decrease after irradiation as revealed from differential scanning calorimetry (DSC) thermograms. Scanning electron microscopy (SEM) reveals that the surface roughness increases due to irradiation.

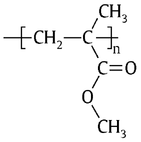
1. Introduction

The flexible properties of the polymers like high strength to weight ratio, low cost, ease of processing etc. is responsible for the vigorous development of polymer science and extensive utilization of polymeric materials in various fields of technology. Polymer composites have recently received a considerable amount of scientific and technological interest, because their properties can be properly controlled, by choosing the adequate doped particles, their size, concentrations and the synthesis conditions [1]. Organometallic compound can be combined with polymer to form hybrid materials. The metallic portion offers the potential for a wide range of electrical properties, substantial mechanical hardness and thermal stability, whereas the polymer part can provide high fluorescence efficiency, large polarisability, plastic mechanical properties, easy processing and structural diversity [2]. The study of physiochemical properties and the dynamics of polymeric composite system [3,4] are particularly important for the development of new materials for specific industrial applications. During the last few years some works have already been done on the effect of filler concentration on the properties of polymer composites. There are many reports on the enhancement in electrical properties and conductivity of the insulating material filled with metal particles [5–7]. But very few of them deal with the effect of ion beam on such composites. Ion beam irradiation of polymers can induce irreversible changes in their macroscopic properties. Electronic excitation, ionization, cross-links and chain scission as well as mass losses are accepted as fundamental events that give rise to the observed macroscopic changes [8,9]. Zhu et al. [10] has reported the chemical modification of different polymers by high energy ion beam and shown amorphization of polymeric structure after irradiation. Infrared spectroscopic study of 170 keV He^+ ions irradiated polymer has been studied by Gelamo et al. [11]. Fink et al. [12] studied the redistribution of Pd(acac) in PMMA using energetic ion beam. In this paper we have investigated the effect of proton beam irradiation on the composites prepared at different concentrations of Pd(acac) in PMMA and studied the dependence of structural and chemical properties of the composite on filler concentration and irradiation fluence. The glass transition temperature and surface morphology of the pristine and irradiated composites are also studied by means of the differential scanning calorimeters (DSC) and scanning electron microscopy (SEM) respectively.

2. Experimental detail

2.1. Sample preparation and irradiation

Polymethyl methacrylate (PMMA) is a well-known thermoplastic polymer. It was synthesized by solution polymerization technique. Its structure is shown below.



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doi:10.1016/j.surfcoat.2009.02.052

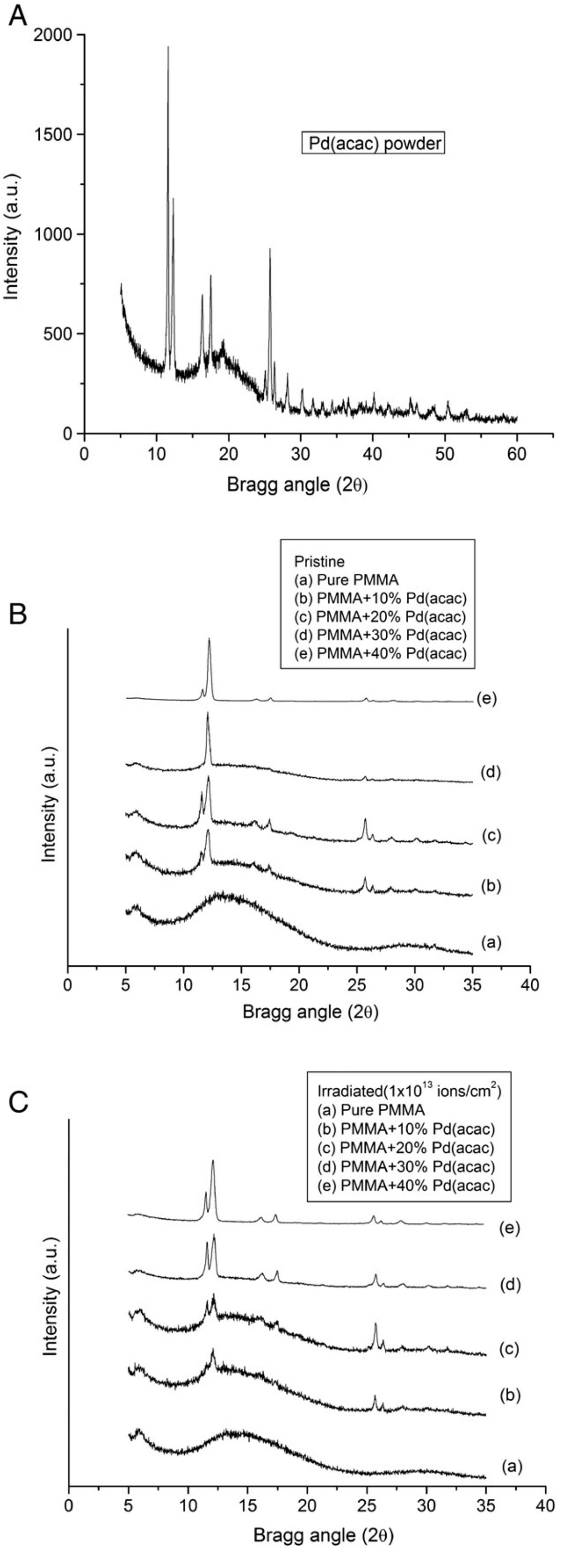

Fig. 1. XRD pattern of (A) Pd(acac) powder, (B)pristine and (C) irradiated composite films.

Table 1
Average crystallite size and % crystallinity by XRD analysis.

Sample	Average crystallite size (nm)		% crystallinity	
	Pristine	Irradiated	Pristine	Irradiated
PMMA+10%Pd(acac)	6.66	3.87	10.25	10.09
PMMA+20%Pd(acac)	15.59	11.34	15.64	11.23
PMMA+30%Pd(acac)	22.70	16.00	17.32	13.24
PMMA+40%Pd(acac)	23.39	22.28	38.79	25.53

Benzoyl peroxide (initiator) was 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 about 75 °C. PMMA was precipitated out in another beaker containing methanol. The precipitated PMMA was allowed to dry at room temperature for 2 h [13]. Organometallic compound/Pd(acac) [$Pd(C_5H_7O_2)_2$] was purchased from Sigma-Aldrich Chemie GmbH, Germany. Different concentrations of Pd(acac) were dissolved with PMMA in acetone. The mixture was properly stirred and self-supporting composite films (thickness ~150 µm) were prepared by casting method. These samples were irradiated with 3 MeV proton beam at a fluence of 1×10^{13} ions/cm^2 using the Cyclotron facility of the Physics Department, Punjab University, Chandigarh, India. The beam current density was of the order of 20 nA/cm^2. All irradiations were performed in vacuum (10^{-6} Torr) at ambient temperature.

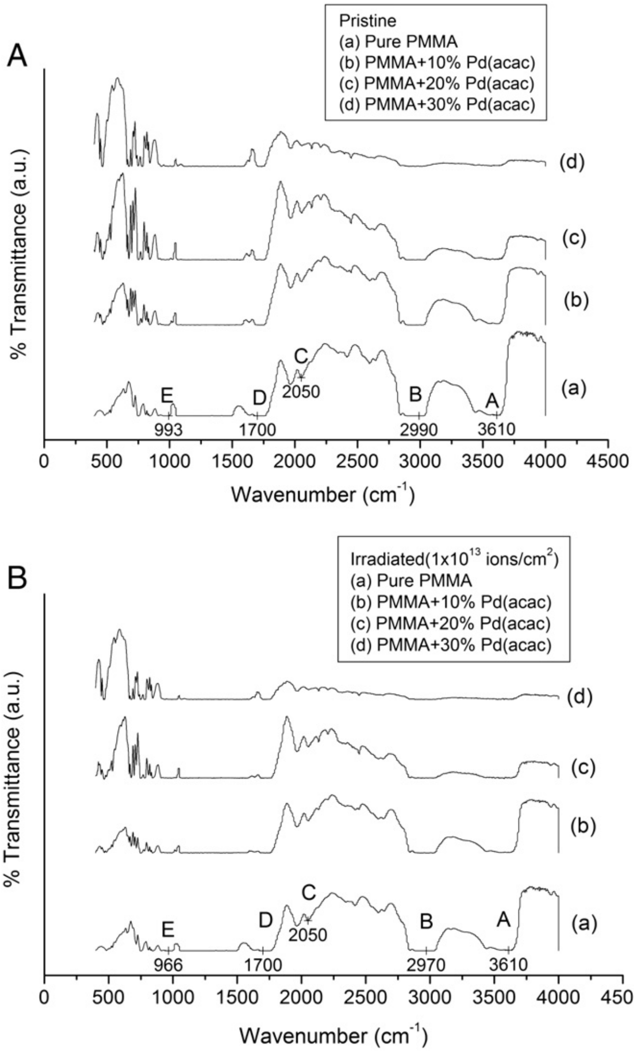

Fig. 2. FTIR spectra of (A) pristine and (B) irradiated films.

2.2. Characterization

The structural studies of pristine and irradiated samples were carried out using X-ray powder diffractometer (Bruker AXS D8 Advance) with Cu K_α radiation (1.5418 Å) for a Bragg angle range of ($5^o<2\theta<35^o$) at a scanning rate of 1°/min. The Fourier transform infrared (FTIR) spectroscopy of all samples was recorded in the wave number range 4000–500 cm^{-1} using Thermo-Nicolet NEXUS 670 FTIR spectrometer with a resolution of 4 cm^{-1}. Differential scanning calorimetry was studied using modulated DSC (TA Instr. Model, 2910) in the temperature range of 30 °C to 214 °C at a predetermined heating rate of 10 °C/min for pristine and irradiated (PMMA+40% Pd (acac)) samples. The Scanning electron micrographs of the composites were recorded using an Oxford_INCA energy dispersive X-ray spectrometer.

3. Results and discussions

3.1. X-ray diffraction

Fig. 1(A) shows the X-ray diffraction pattern for Pd(acac) powder. It shows the crystalline behavior of the organometallic compound. The most prominent peaks were obtained at 12.1°, 17.4 °, 25.7 ° and 28.0 °. Identical peaks were obtained for the polymer composites because of

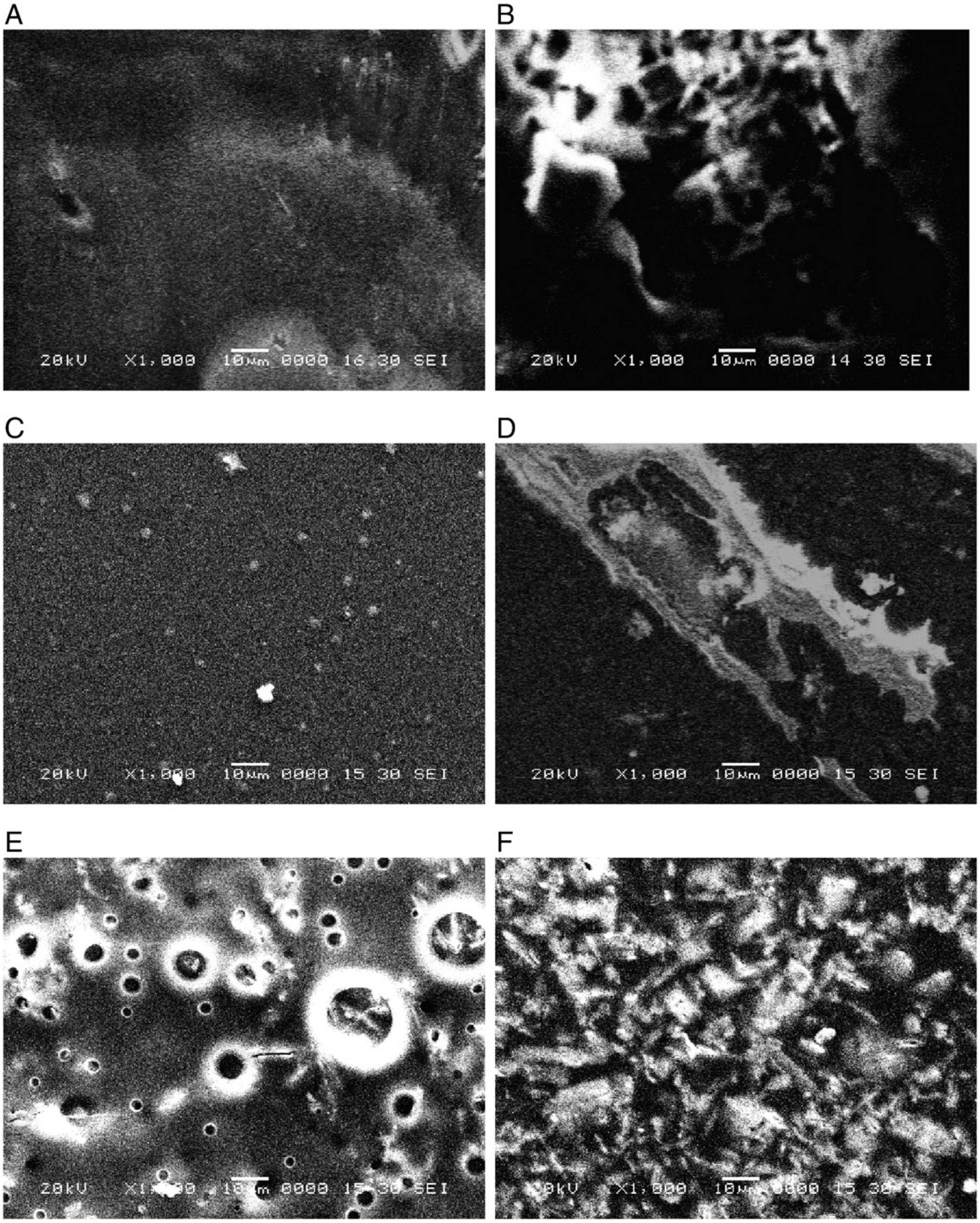

Fig. 3. SEM images of (A) Pure PMMA (pristine), (B) pure PMMA (irradiated), (C) PMMA+10%Pd(acac) (pristine), (D) PMMA+10%Pd(acac) (irradiated), (E) PMMA+30%Pd (acac) (pristine), and (F) PMMA+30%Pd (acac) (irradiated) films.

the presence of different concentrations of Pd(acac) in PMMA. Fig. 1 (B) and (C) shows the diffraction pattern of pristine and irradiated samples respectively at different filler concentrations. The spectrum represents the semi-crystalline nature of the composites. The crystallite size was calculated before and after irradiation using Scherrer's formula [14]

$$L = K\lambda / b\cos\theta$$

where b is FWHM in radians, λ the wavelength of X-ray beam (1.5418 Å), L is the crystallite size in Å, K is a constant which varies from 0.89 to 1.39, but for most cases it is close to 1 [15]. Irradiation deposits large amounts of energy in the material which leads to a decrease in crystallite size. This may be attributed to the splitting of crystalline grains. Percentage crystallinity of the composites was determined by area ratio method. In this method the areas of amorphous and crystalline parts of the pattern were calculated [16]. It has been observed that the percentage crystallinity of the composites increases with filler fraction. It reveals the crystalline nature of Pd(acac). However, it decreases after irradiation due to breakage of the polymeric bonds and emission of some volatile gases, which may form the disordered state in the composite structure. It is also corroborated with FTIR spectra. The decrease in crystallinity after irradiation can be further confirmed from DSC studies. The values of average crystallite size and % crystallinity of the pristine and irradiated samples are listed in Table 1.

3.2. Analysis of infrared spectra

Fig. 2 shows FTIR spectra of pristine and irradiated samples. The presence of different functional groups in the structure has been identified as follow: (a) the bond corresponds to –OH free stretching vibration has been obtained at 3610 cm^{-1}, (b) the broad band between 2835 and 2995 cm^{-1} assigned for $–CH_2$ group [17], (c) C═C stretching vibration is obtained at 2050 cm^{-1}, (d) nonconjugated C═O ester stretching band in pendant group of PMMA ($–COOCH_3$) observed at 1700 cm^{-1}, and (e) the bands at 966 cm^{-1} corresponds to CH═CH (trans). It has been observed that by doping filler, some new peaks have been formed at lower wavenumber range and these peak intensities increase with increasing filler concentration. However it decreases after irradiation. The reduction in peak intensities is attributed to the breakage of chemical bonds and formation of free radicals, unsaturation etc. due to the deposition of energy by ion beam. The main chain scission is chiefly caused by irradiation, due to the weak bond of the quaternary carbon atom in the main chain. The presence of tetrasubstituted carbon atom in the main chain of PMMA is responsible for its radiation sensitivity [18]. The absorption peaks at higher wavenumber decrease sharply as filler concentration increases. It might be due to the formation of a new bond of organometallic compound with polymeric chains by breaking traditional polymeric bond and this may be the reason for the formation of new peaks at lower wave number region. The overall reduction in intensity of the typical bands after irradiation signifies the chain scissioning phenomenon of the polymeric materials and conversion of polymeric structure into hydrogen depleted carbon network [19].

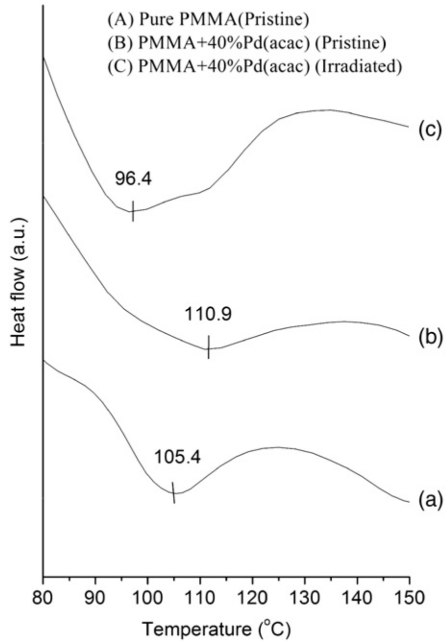

Fig. 4. DSC pattern for pure PMMA (pristine) and pristine and irradiated PMMA+40% Pd (acac) films.

3.3. Scanning electron microscopy

Fig. 3 (A, C, E) represents pristine and Fig. 3 (B, D, F) represents irradiated sample images of pure PMMA, PMMA+10% Pd(acac) and PMMA+30%Pd(acac) respectively. Surface morphology of composite shows appreciable change after proton beam irradiation. Partial agglomeration has been observed and surface roughness increases upon irradiation.

3.4. Differential scanning calorimetry (DSC)

Fig. 4 shows DSC thermograms of pristine PMMA, pristine and irradiated PMMA+40%Pd(acac) samples. The result reveals that the glass transition temperature (Tg) increases for the composite than the pure polymer but decreases after irradiation. Glass transition temperature is characteristic of a material and represents the transition from amorphous glassy state to rubbery state. The increase in Tg of composites may be due to interactions of Pd(acac) and PMMA in a more ordered state [20]. After irradiation Tg decreases, which reveals the amorphization of the composite after irradiation and it is also confirmed by XRD results.

4. Conclusion

Proton beam irradiation on polymer composite has significantly modified the structural properties as shown by X-ray diffraction analysis. The crystallite size and degree of crystallinity decreases after irradiation, however, it increases with increasing filler concentration. The chain scission by irradiation at higher fluence seems to be the dominant process as studied by FTIR spectroscopy. The results revealed that the polymeric structure get damaged after irradiation which is also corroborated by the XRD results. The surface morphology as studied from SEM images shows partial agglomeration on the composite surfaces after irradiation. Thermal property of the composite was studied by DSC analysis and it reveals that the Tg decreases after irradiation. It means that the composite system is moving towards a more disordered state after irradiation. XRD analysis also supports these results.

Acknowledgements

The authors are thankful to Dr. A.M. Avasthi, UGC-DAE-CSR, Indore, for providing the experimental facility. The laboratory facility and financial support given by IUAC, New Delhi is gratefully acknowledged.

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