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Dielectric and structural modification of proton beam irradiated polymer composite

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Abstract

Polymer composite was prepared by doping different concentrations (from 10% to 40%) of Ni powder in polymethyl methacrylate (PMMA). These films were irradiated with 3 MeV proton beam at a fluence of 10^{13} ions/cm^2. AC electrical conductivity and dielectric response of the pristine and irradiated samples were studied in the frequency range 100 Hz to 30 MHz. A sharp increase in conductivity was observed beyond a frequency of 100 kHz for pure and dispersed PMMA. Dielectric permittivity remains almost constant for the wide frequency range and decreases at higher frequency. However, it increases with metal concentration as well as with fluence. The dielectric loss decreases exponentially as frequency increases. Structural study of the pristine and irradiated samples has been done using X-ray diffraction. The results show that the crystallinity and crystalline size decreases upon irradiation. FTIR spectra reveal the change in the intensity of functional groups of the polymer after irradiation. Average surface roughness observed to change with filler concentration and also with the irradiation as obtained from AFM analysis.

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Keywords: Polymer composites; Proton beam irradiation; Ac electrical properties; X-ray diffraction; FTIR spectroscopy; Atomic force microscopy

1. Introduction

Polymeric materials have a great potential in many important applications because of their versatile properties such as low density, ability to form intricate shapes and low manufacturing cost. However, the use of polymers is still limited because of their unexpected dielectric properties and inherent softness [1]. To overcome these tribulations, composite materials were prepared by incorporating active inclusions (such as metal powder, carbon black, graphite and conducting fibers) with passive polymer matrix. These composites, with enhanced physical and structural properties are important and relatively new class of material with variety of applications like electromagnetic shielding of electronic equipments [2], capacitors [3], sensors [4], switching devices [5], etc. The electrical characteristics of such composites are close to the properties of filler while the mechanical properties and processing methods are typical for plastics [6]. The achievement of metallic properties in such heterogeneous polymer-filler system depends on many factors and it is possible to control electrical and structural characteristics of the composites. The interfaces between filler and polymer play an important role on deciding the properties of the composites.

Metal–polymer composites have been subject of extensive research in last few decades and considerable work has been done for the investigation of structural and elec-

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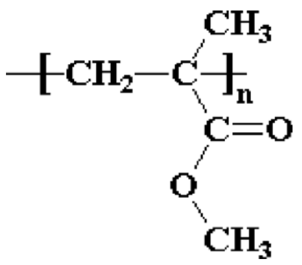
trical properties [3,7]. The electrical properties of insulating polymers can be improved greatly by doping metal particles like carbon [8], iron [9] or other conducting polymers [10]. Costa et al. [11] has reported the improvement in electrical, magnetic and structural properties of iron doped polymer. Similar result was also reported by Elimat [12] by doping carbon black in PMMA. AC conductivity and dielectric constant is observed to enhance inherently after doping. But the effect of ion irradiation on composites is yet to be explored in proper perspective.

Ion irradiation of polymer can induce irreversible change in their macroscopic properties such as electrical and optical properties and surface related mechanical property. These changes are responsible to fundamental events like electronic excitation, ionization, chain scission and cross links as well as mass loss, which take place due to ion beam irradiation [13]. Therefore the understanding of certain structural rearrangements influence on the properties of the polymeric materials/composites opens a way to design devices with required parameters. The radiation effect on the physical and structural properties of such material are required to study particularly, when such devices are being used in radiation environment. Irradiation makes the metal–polymer bonding more prominent and enhances the properties of the composites. The present study deals with synthesis of the polymer composite with different weight percent of Ni powder in PMMA and the effects of 3 MeV proton beam on electrical and structural properties of these composites. Pristine and irradiated samples have been characterized by means of Impedance gain/phase analyzer, X-ray diffraction and FTIR spectroscopy. The change in surface morphology of composites after irradiation has been studied using atomic force microscopy.

2. Experimental details

2.1. Sample preparation and irradiation

Polymethyl methacrylate (PMMA) is a well known thermoplastic polymer with versatile properties like excellent clarity, light weight, low cost, easy to process and resistant to most chemicals. Its structure is shown below. PMMA was synthesized by solution polymerization technique. 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 75 °C. PMMA was precipitated out in another beaker containing methanol. The precipitated PMMA was allowed to dry at room temperature for 2 h [14]. Nickel metal powder was purchased by Laborchemikalein Ltd., India and it was dissolved with PMMA in acetone. The composite films (thickness ~100 μm) of different concentrations of nickel powder (ranging from 10% to 40%) in PMMA were prepared by casting method. These films 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 samples were irradiated at a fluence of 1×10^{13} ions/cm^2. All irradiations were performed in vacuum (10^{-6} Torr) at ambient temperature



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2.2. Characterization

The dielectric properties of all samples were measured using an impedance phase analyzer (Solartron-1260) in the wide frequency range of 100 Hz–30 MHz. From the measured capacitance and dielectric loss, the conductivity of the material was calculated using equation

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

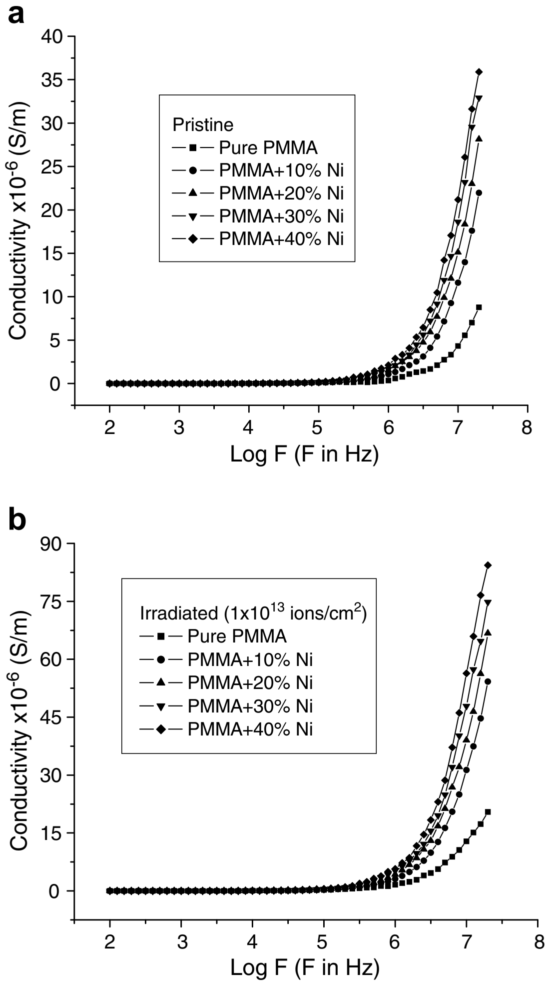

Fig. 1. Conductivity versus log frequency for (a) pristine and (b) irradiated composites.

and dielectric permittivity of the samples were calculated using relation

$$\epsilon = C_p/C_o$$

where C_p is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and vacuum capacitance $C_o = \varepsilon_o A/t$, A and t are the cross sectional area of the electrode and thickness of the sample respectively. ε_o: dielectric permittivity of air $= 8.85 \times 10^{-12}$ F/m.

The structural studies were carried out by X-ray powder diffractometer (model: Shimadzu, XRD-6000) with Cu Kα radiation (1.5418 Å) for a Bragg angle $35^\circ < 2\theta < 60^\circ$. All measurements were carried out at ambient temperature. FTIR spectra of pristine and irradiated PMMA films were recorded in the wave number range 4000–500 cm^{-1} using Thermo-Nicolet NEXUS 670 FT–IR spectrometer with a resolution of 4 cm^{-1}. Surface morphology of pristine and irradiated surface was studied using atomic force microscopy (Digital Nanoscope IIIa Instrument Inc.) in tapping mode. Topographical images were taken for 5×5 μm^2 surface area and average surface roughness has been determined.

3. Results and discussion

3.1. AC electrical conductivity

Fig. 1(a) and (b) shows the frequency dependent electrical conductivity of pristine and irradiated composites. The result states that the conductivity significantly changes with metal concentration and also with the fluence. Further almost all samples show similar results up to 10^5 Hz, typical for hoping conduction, means there is no much change in the conductivity with frequency in this range. The total conductivity of the composite depends on the microscopic and macroscopic conductivities. The microscopic conductivity depends upon the doping level, chain length etc. and the macroscopic conductivity depends upon the orderness and molecular orientations in the material [15]. The orderness increases with increasing metal concentration in the composite as revealed by XRD analysis, which is also responsible for increasing the conductivity. The increase

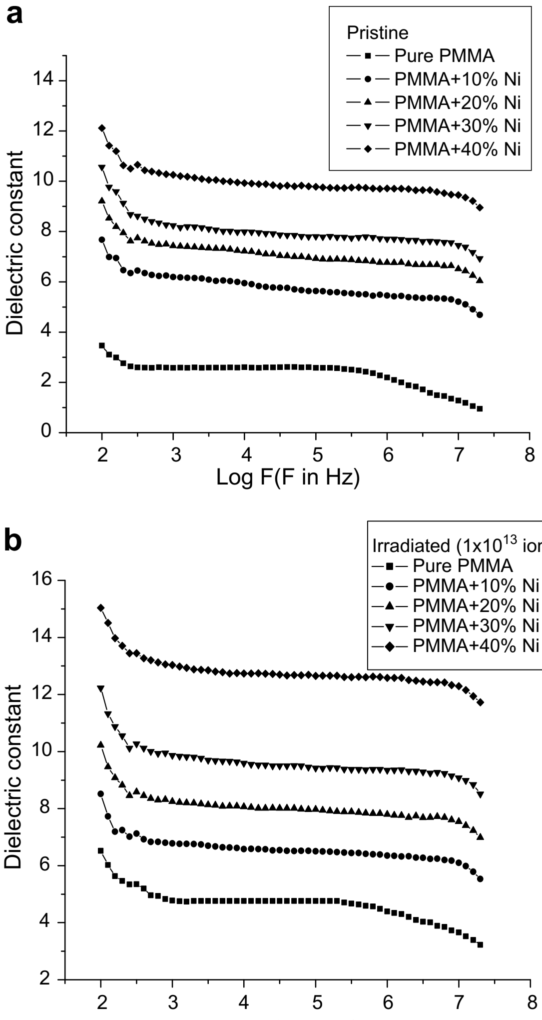

Fig. 2. Dielectric constant versus log frequency for (a) pristine and (b) irradiated composites.

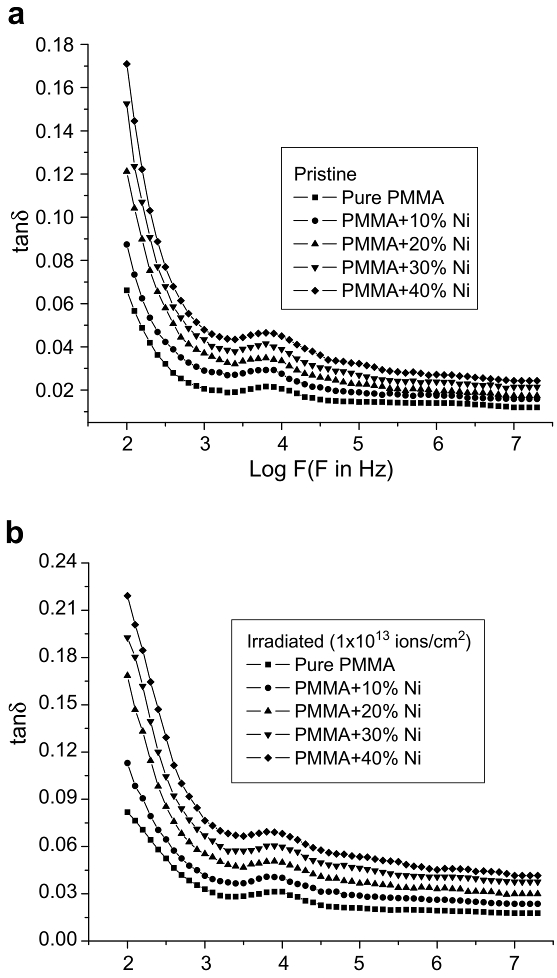

Fig. 3. Dielectric loss (tan δ) versus log frequency for (a) pristine and (b) irradiated composites.

in conductivity is related to a possible increase in the number of conduction paths created between the filler particles aggregates in the composite as a consequence electrical path is built in the polymer matrix in addition to a decrease in the width of potential barriers within the bulk regions of high conductivity. Therefore, more charge carriers may be

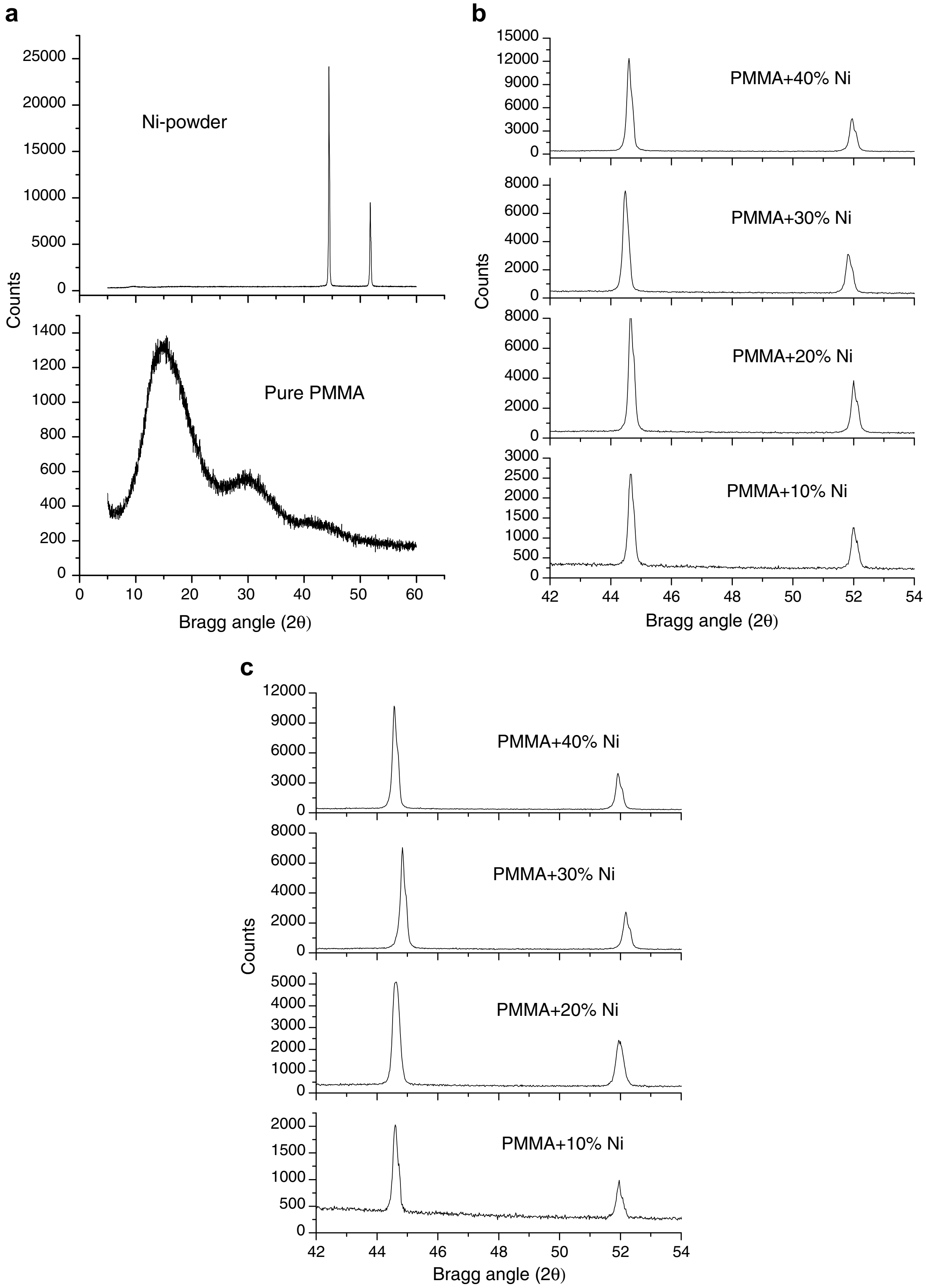

Fig. 4. XRD spectrum of (a) pure PMMA and filler (Ni powder), (b) pristine composites and (c) irradiated composites.

able to 'hop' by tunneling; resulting in the increase in the bulk conductivity and it also increases with increasing filler concentration [16]. Conductivity is further observed to increase after irradiation. Irradiation is expected to promote the metal to polymer bonding and convert polymeric structure into hydrogen depleted carbon network. It is this carbon network that is believed to make the polymer more conductive [17].

3.2. Dielectric properties

Fig. 2(a) and (b) and Fig. 3(a) and (b) shows the dependence of dielectric constant and loss tangent respectively on the frequency of the applied field, at different filler concentration and irradiation fluence. The dielectric permittivity as a function of frequency (100 Hz to 30 MHz) reflects the important effect of the filler concentration on the sample properties. The increase in dielectric permittivity with metal concentration is attributed to the increase in the volume fraction of the charges (electric dipoles) in the interfaces between polymer and metal particles. Ions under low frequency electric field can hop readily out of sites with low free energy barriers but tend to 'pile up' at sites with high free energy barriers. This leads to a net polarization of the dipoles and large value of dielectric permittivity. At higher frequencies, the polarization due to charge 'pile up' disappears and so permittivity decreases [18]. Thus the dielectric permittivity remains almost constant for wide frequency range. Similar results are also observed by Brosseau et al. [19] and Kuo and Chang [20]. In addition, the dependence of dielectric permittivity on frequency can be explained according to Jonscher's equation described as follows:

$$\varepsilon' - \varepsilon'_{\infty} \alpha \omega^{-b}$$

where ε'_{∞} is high frequency dielectric constant and ε', dielectric permittivity of the sample and $0<b<1$ [21]. Due to dispersion of organometallic compound, the quantity of the accumulated charges will increase because of the polarization of 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. High dielectric permittivity and dielectric loss at higher concentration of nickel in the polymer is attributed to the increase in crystallinity as revealed from XRD analysis. As a result the orderness increases the interfacial interactions between the polymer and metal and leads to maximum space charge polarization [22]. The observed nature of fluence dependent dielectric permittivity and dielectric loss can be explained by the prevailing influence of the enhanced free carriers due to irradiation [23].

3.3. X-ray diffraction

X-ray diffraction spectrum in Fig. 4(a) shows the amorphous nature of PMMA and the crystalline behavior of Ni powder. The average particle size of the Ni power was obtained 39.84 nm. From Fig. 4(b) and (c) the most prominent peaks are obtained at $2\theta \sim 51.9$ and 44.6 in all the cases. The appearance of sharp peak in composite indicates some degree of crystallinity, although the decrease in intensity of the diffraction peak and slightly broadening of the peak after irradiation gives evidence of decrease in crystallinity. However, no significant change in the peak position reveals that lattice parameters do not change significantly. The crystallite size has been calculated before and after irradiation using Scherrer's formula [24]

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

where b is FWHM in radians, λ is 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 of the cases it is close to 1. 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 [25]. The average crystallite size and % crystallinity of the pristine and irradiated samples is listed in Table 1. Irradiation induces large amount of energy deposition in the material leads to decrease in crystallite size which may be attributed to splitting of crystalline grains. The chain scissioning due to irradiation, which is also corroborated by FTIR spectra, assumed to be responsible for the reduction in crystallinity of the composite.

3.4. FTIR spectroscopy

FTIR spectra of pristine and irradiated pure PMMA and PMMA + 30% Ni are shown in Fig. 5(A–D), respec-

Table 1
% Crystallinity and crystalline size of the filler

Filler concentration (wt.%)	Crystalline size (nm)		% Crystallinity	
	Pristine	Irradiated	Pristine	Irradiated
10	34.73	27.78	12.42	6.76
20	36.82	28.35	19.53	16.79
30	37.25	34.92	23.78	16.13
40	38.18	36.64	25.37	22.36

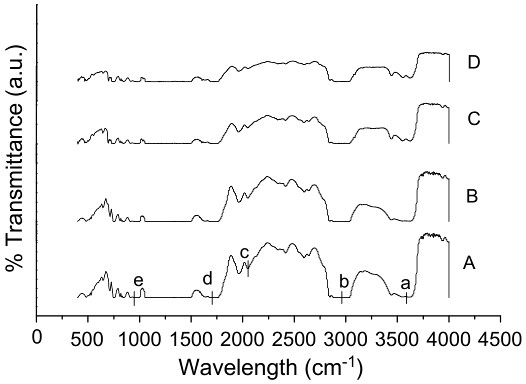

Fig. 5. FTIR spectra of (A) pristine pure PMMA, (B) irradiated pure PMMA, (C) pristine PMMA + 30% Ni and (D) irradiated PMMA + 30% Ni films.

tively. The absorption bands are obtained from the pristine spectrum which are identified as follows: (a) $-OH$ free stretching vibration: 3610 cm^{-1}, (b) $-CH_2$ group: 2835–2995 cm^{-1} [26], (c) $C{=}C$ stretching vibration: 2050 cm^{-1}, (d) nonconjugated $C{=}O$ ester stretching band in pendant group of PMMA ($-COOCH_3$): 1700 cm^{-1} and (e) $CH{=}CH$ (trans): 966 cm^{-1}. FTIR images show the interaction between macromolecule and filler particles. Small shift and alteration in the peak position is observed due to changes in the nearest surrounding of functional groups due to presence of metal particles. The peak corresponding to $-OH$ stretching vibration for pristine PMMA was observed at 3610 cm^{-1} and it shifted to 3620 cm^{-1} for 30% Ni doped polymer. The reduction in peak intensities after irradiation is attributed to the breakage of few chemical bonds and formation of free radicals, unsaturation, etc. due to emission of hydrogen and other volatile gases. However, metal and polymer are extremely different materials. The interaction between metal and polymer is generally very weak and the cohesive energy of polymer is typically two orders of magnitude lower than the cohesive energy of metals. It is observed that the hardness of the composite

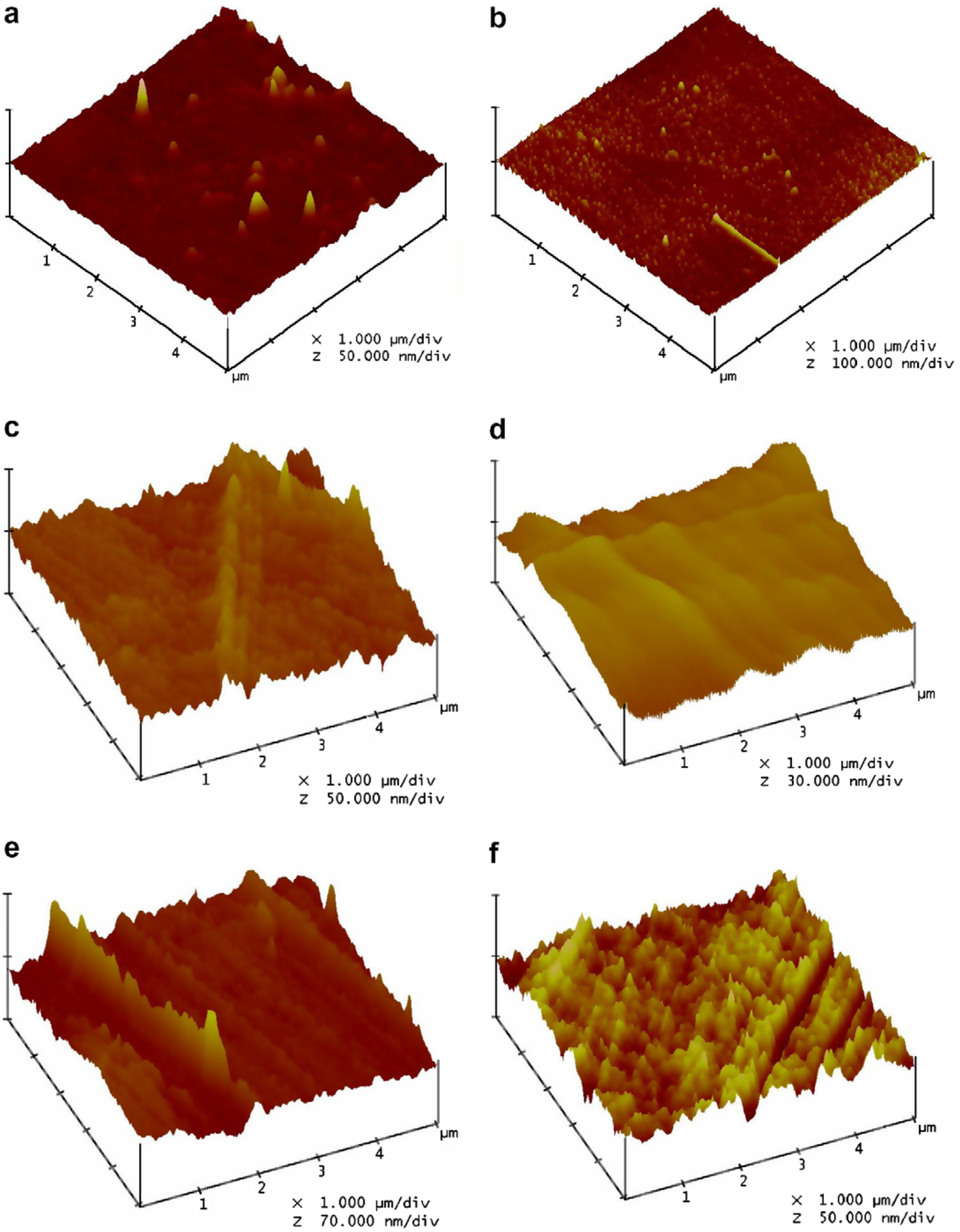

Fig. 6. AFM images of (a) pristine pure PMMA, (b) irradiated pure PMMA, (c) pristine PMMA + 20% Ni, (d) irradiated PMMA + 20% Ni, (e) pristine PMMA + 30% Ni and (f) irradiated PMMA + 30% Ni films.

increases after doping metal particle which indicates the cross linking phenomenon [14].

3.5. Atomic force microscopy

Surface morphology of pristine and irradiated composites was studied using atomic force microscopy in tapping mode. The images of the $5 \times 5\ \mu m^2$ surface area of pristine and irradiated (at a fluence of 1×10^{13} ions/cm^2) samples are shown in Fig. 6(a–f). The average surface roughness value observed for pristine and also for irradiated pure PMMA is 2.56 nm. However, it decreases from 6.23 nm and 9.39 nm to 4.75 nm and 5.09 nm, respectively for 20% and 30% nickel dispersed PMMA composites after irradiation. The relative smoothness is may be due to defect enhanced surface diffusion [14]. However the increase in roughness from 2.56 nm (pure PMMA) to 9.39 nm (PMMA + 30% Ni) is due to increase in density and size of metal particle on the surface of PMMA films [27].

4. Conclusions

Proton beam has significantly enhanced the electrical properties of the composite. This may be attributed to metal to polymer bonding and conversion of polymeric structure in to hydrogen depleted carbon network. Structural properties have observed to change due to irradiation. The crystallite size and crystallinity decreased after irradiation. The decrease in crystallinity reveals the formation of disorderness in the sample due to chain scissioning after irradiation. It is also corroborated with FTIR spectroscopy. The average surface roughness of the samples decreases upon irradiation.

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