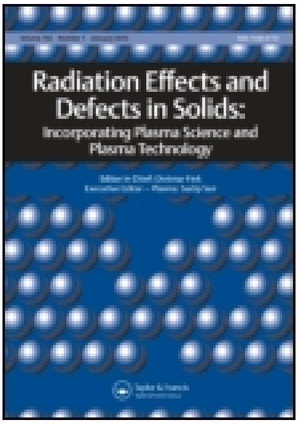

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Radiation-induced modification of organometallic compound dispersed polymer composites

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Radiation-induced modification of organometallic compound dispersed polymer composites

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Polymethyl methacrylate (PMMA) was synthesized by solution polymerization technique. Films of polymer composites were prepared by dispersion of different concentrations of nickel dimethylglyoxime in PMMA. These films were irradiated with 3 MeV proton beam at a dose of 1.48×10^5 Gy. The dielectric, structural properties and surface morphology of pristine and irradiated samples were studied by means of an LCR meter, X-ray diffraction (XRD) analysis and atomic force microscopy (AFM), respectively. The dielectric properties are observed to enhance with increase in metal compound concentration as well as with irradiation dose. This may be due to metal/polymer bonding and conversion of polymeric structure into hydrogen-depleted carbon network. AFM shows that the surface average roughness decreases after irradiation. Crystallite size of organometallic compound is observed to decrease after irradiation as revealed from XRD analysis.

Keywords: Polymethyl methacrylate; Organometallic compound; AC electric properties; Atomic force microsocpy; X-ray diffraction

1. Introduction

In recent years, technological devices at the nanometer scale are in demand. Therefore, there is a practical interest in the composites consisting of dielectrics with metal nanoparticles, which is encouraged by potential applications such as nonlinear optical switches, magnetic data storages, microelectronic devices, etc. [1, 2]. In such applications, a good adhesion between the polymer and the metal is required. 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 [3]. The preparation of composites with good dielectric property depends on loading filler homogeneously throughout polymer and effective microstructure in the composites [4]. With increasing metal concentration, metal clusters become larger,

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start to coalesce and continuous metal films are obtained with rather poor adhesion strength between two materials. When organometallic compound is irradiated with energetic ions, new adsorption sites are created resulting in an improved metal – polymer adhesion. High energy ion irradiation induces significant modification in the material by electronic excitation or ionization. The present work concentrates on the modification of organometallic compound dispersed polymeric films by proton beam irradiation. The dielectric response of a material provides information about the orientational and translational adjustment of mobile charges present in the dielectric medium in response to an applied electric field. The most important property of the material is its ability to polarize under the action of the field. Furthermore, interfaces among the different phases in the composites also play an important role on deciding the dielectric property [5].

Atomic force microscopy (AFM) gives surface morphology and the information about the change in surface average roughness of the sample before and after irradiation. X-ray diffraction has been done to determine crystallite size of the metallic compound in the polymer matrix. It also gives information about change in the crystalline behaviour of the composite due to irradiation.

2. Experimental details

Polymethyl methacrylate (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 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. The organometallic compound nickel dimethylglyoxime (Ni-DMG) was formed by dissolving 0.4 mole nickel chloride in 200 ml water and it was heated at 80 °C; a slight excess of the alcoholic dimethylglyoxime was added and then dilute ammonia solution was added dropwise with continuous stirring until precipitation takes place. The precipitate was then washed with cold water until free from Cl^- and dried at 110 °C for 1 h. Different concentrations of Ni-DMG compound (*i.e.* 5%, 10% and 15%) were dissolved with PMMA using toluene: acetone (solvent) in proportion of 60:40 and briz-35 surfactant (0.5 at % of polymer). The solution was mixed and stirred thoroughly for about an hour and then poured into a clean glass trough. The solvent was evaporated at room temperature to get films (thickness $\sim$150 μm) of dispersed PMMA with different concentrations of Ni-DMG compound [6, 7]. The films were irradiated with 3 MeV proton beam at a dose of 1.48×10^5 Gy at Physics Department, Punjab University, Chandigarh, India.

AC electrical response of all samples was measured in the frequency range 100 Hz–10 MHz at ambient temperature using variable frequency LCR meter (General Radio, USA, Model, 1689 /Hewlett Packard 4284 A). The conductivity was calculated using relation

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

and dielectric permittivity using relation

$$\varepsilon = \frac{C_p}{C_o}$$

where C_p is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and $C_o = \varepsilon_0 A/t$, A and t are the area of the electrode and thickness of the sample, respectively. ε_o: permittivity of vacuum $= 8.85 \times 10^{-12}$ F/m. Surface morphology of pristine and irradiated samples was studied using AFM in tapping mode (Digital Nanoscope IIIa Instrument Inc.). The structural studies were carried out by X-ray powder diffractometer (Bruker AXS D8 Advance) with Cu K_α radiation (1.5418 Å) for a wide range of Bragg angle ($5^\circ \leq 2\theta \leq 40^\circ$). All measurements were carried out at ambient temperature.

3. Results and discussions

3.1 *AC conductivity*

Figure 1 shows the variation of log conductivity with log frequency. It was observed that conductivity increases with increasing concentration of dispersed Ni-DMG compound (figure 1a) as well as with the dose (figure 1b).

The increase in conductivity with increase in concentrations of organometallic compound may be attributed to the conductive phase formed by dispersed organometallic compound in

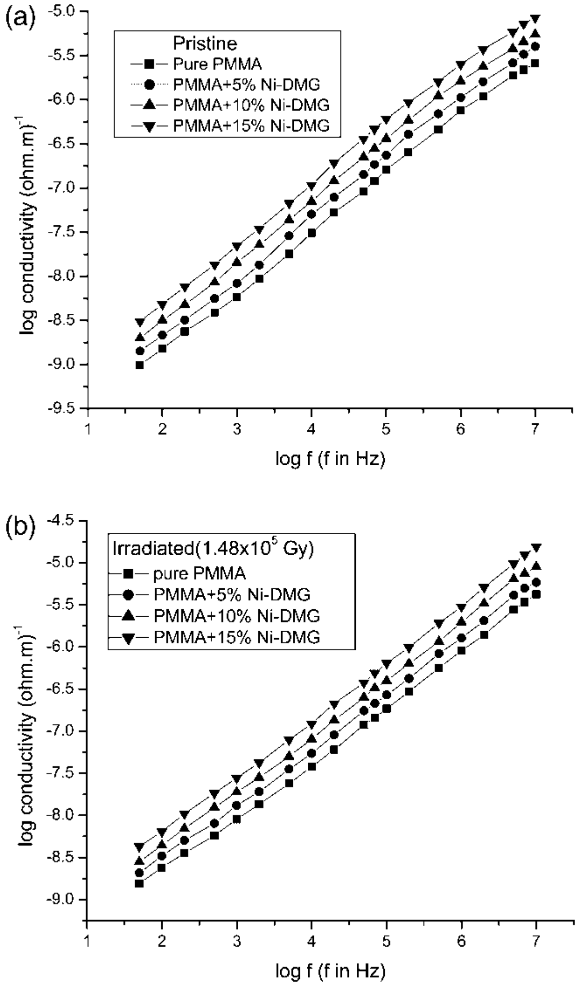

Figure 1. Log conductivity *vs.* log frequency for (a) pristine and (b) irradiated samples.

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 Ni-DMG compound in polymer matrix. The conductivity is also observed to increase after the irradiation. Irradiation is expected to promote the 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 polymer more conductive [8, 9].

3.2 *Dielectric permittivity*

Figure 2 shows the variation in dielectric permittivity with log frequency. It is observed that dielectric permittivity remains almost constant up to 100 kHz, because the motion of charge carriers is almost constant at these frequencies. Beyond this frequency, the dielectric constant decreases. As the frequency increases, the charge carriers migrate through the dielectric and get trapped against a defect site and they induced an opposite charge in its vicinity, as a result,

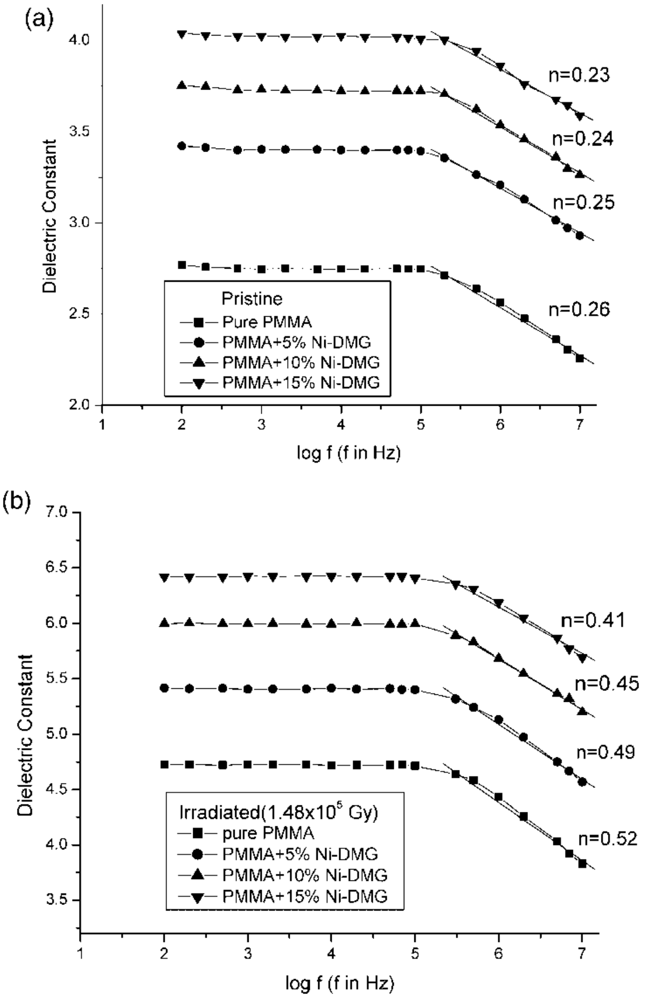

Figure 2. Dielectric constant *vs.* log frequency for (a) pristine and (b) irradiated samples.

motion of charge carriers is slowed down and the value of dielectric constant decreases. The decrease in dielectric constant at higher frequency can be explained by Jonscher's power law, *i.e.* $\varepsilon \alpha f^{n-1}$ where $0 < n < 1$[10]. The value of n increases on irradiation from 0.26 to 0.56 for pure PMMA. Similar results are also observed for dispersed PMMA. This may be due to the dominance of metal to polymer bonding due to irradiation, which reduces the dipole polarization and as a result, slop (n) increases.

According to Dissado and Hill [11] theory at high frequency, intra-cluster motions are dominant. In intra-cluster motions, the relaxation of a dipole will produce a 'chain' response in its neighboring dipoles and the reaction of the neighboring dipoles will, in turn, affect the first dipole, so the overall effect will be seen as a single cluster dipole moment relaxation [12]. This reduces the dielectric constant at these frequencies.

It is observed that the dielectric constant increases on increasing the concentration of Ni-DMG. Due to dispersion of organometallic compound, the quantity of accumulated charge 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 [13].The magnitude of the dielectric constant is higher for irradiated samples compared to those of pristine samples. The increase in dielectric constant may be attributed to chain scission, which results in an increase of free radicals, unsaturation, etc.

3.3 *Dielectric loss*

Figure 3 shows the behaviour of dielectric loss with frequency for pure and dispersed Ni-DMG samples at room temperature. The loss factor (tan δ) shows strong frequency dependence and decreases exponentially as frequency increases. The positive value of tan δ indicates the dominance of inductive behaviour. It is noticed that dielectric loss increases on increasing the concentration of filler and also with the irradiation dose. The increase in dielectric loss with increasing filler contents may be attributed to the interfacial polarization mechanism of the heterogeneous system.

3.4 *Atomic force microscopy*

Surface morphology of the pristine and irradiated metallized polymeric samples has been studied using AFM. The images of $2 \times 2\,\mu\text{m}$ areas were recorded in tapping mode as shown in figure 4.

Each AFM image was analyzed in terms of surface average roughness (R_a). The data shows that the surface average roughness (rms) increases with metal compound (Ni-DMG) concentrations but it decreases with the irradiation dose. The average surface roughness obtained are 8.6, 32.4 and 36.6 nm for pristine samples with metal concentrations of 5%, 10% and 15% and decreases to 6.5, 10.7 and 11.9 nm, respectively, after irradiation at a dose of 1.48×10^5 Gy. The increase in surface roughness (R_a) with increase in the concentration of metal compound may be due to the increase of density and size of metal particles on the surfaces of the polymeric films [14]. The decrease in surface roughness due to irradiation may be attributed to defect enhanced surface diffusion.

3.5 *X-ray diffraction*

Figure 5 (a and b) represents the diffraction pattern of the pristine and irradiated samples for the most prominent peak.

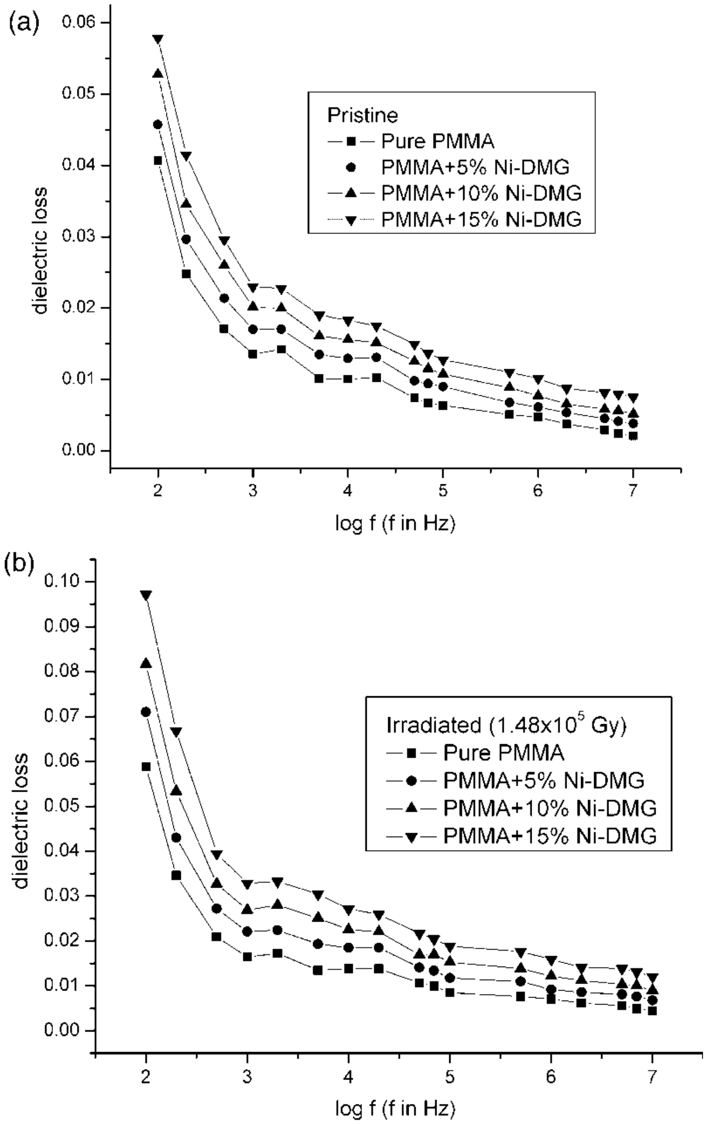

Figure 3. tan δ *vs*. log frequency for (a) pristine and (b) irradiated samples.

The peaks are obtained at $2\theta = 9.98$ and 10.61. The nature of the peak indicates the semi-crystalline nature of the sample. The crystallite size has been calculated before and after irradiation using Scherrer's equation [15]

$$b = \frac{K\lambda}{L\cos\theta}$$

where b is FWHM in radians, λ the wavelength of X-ray beam (1.5418 Å), L 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. The crystallite size obtained is listed in table 1.

Results show that crystallite size of the filler decreases slightly after irradiation. It is also observed that the intensity of the peak decreases after irradiation, but no significant changes

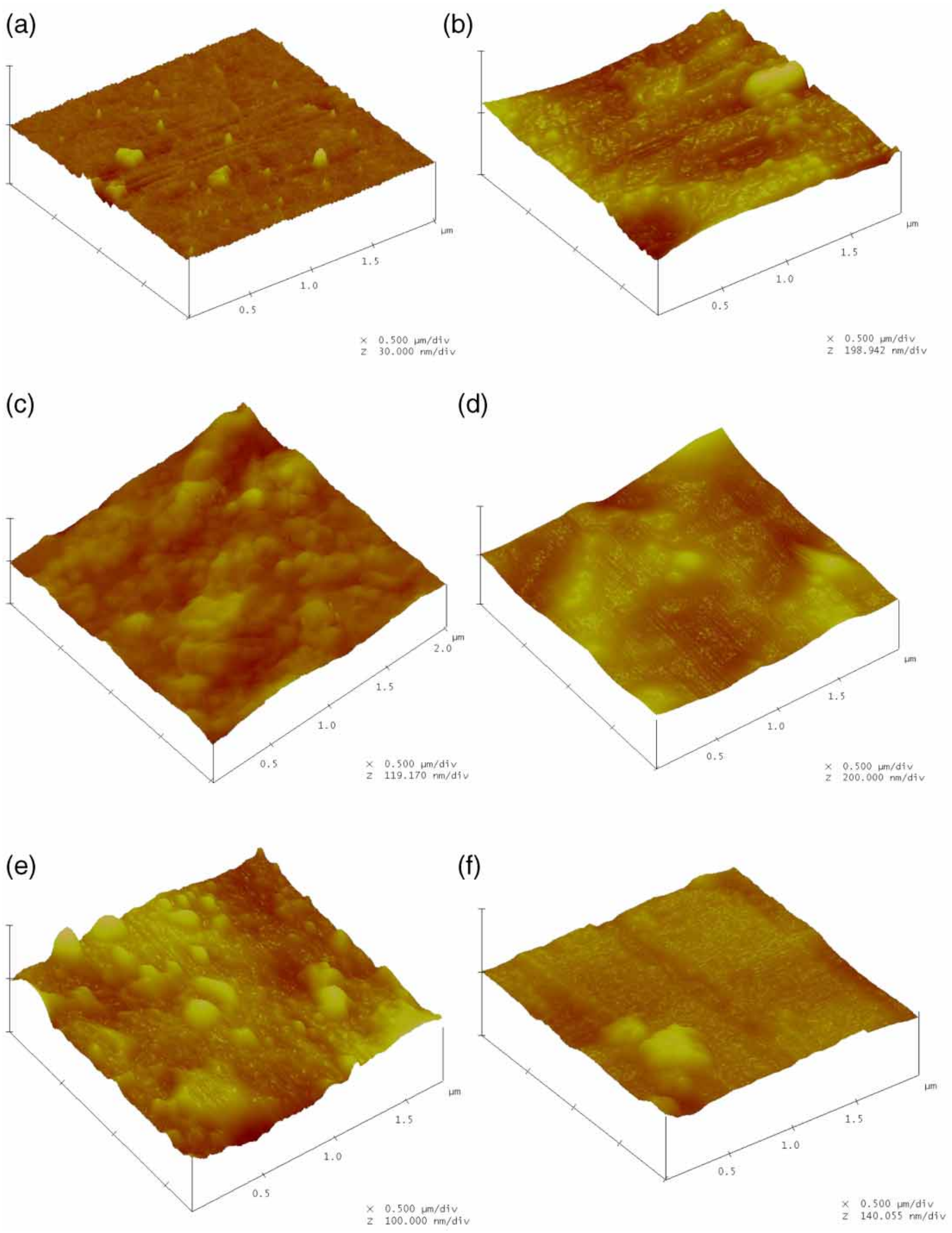

Figure 4. (a) AFM image of pristine PMMA+5%Ni-DMG. (b) AFM image of irradiated PMMA+5%Ni-DMG. (c) AFM image of pristine PMMA+10%Ni-DMG. (d) AFM image of irradiated PMMA+10%Ni-DMG. (e) AFM image of pristine PMMA+15%Ni-DMG. (f) AFM image of irradiated PMMA+15%Ni-DMG.

Table 1. Crystallite size of the pristine and irradiated samples by XRD.

	Crystallite size (nm)	
Sample	Pristine	Irradiated (1.48 × 10^5 Gy)
PMMA+5%Ni-DMG	45.6	44.6
PMMA+10% Ni-DMG	47.7	45.0
PMMA+15% Ni-DMG	48.5	45.7

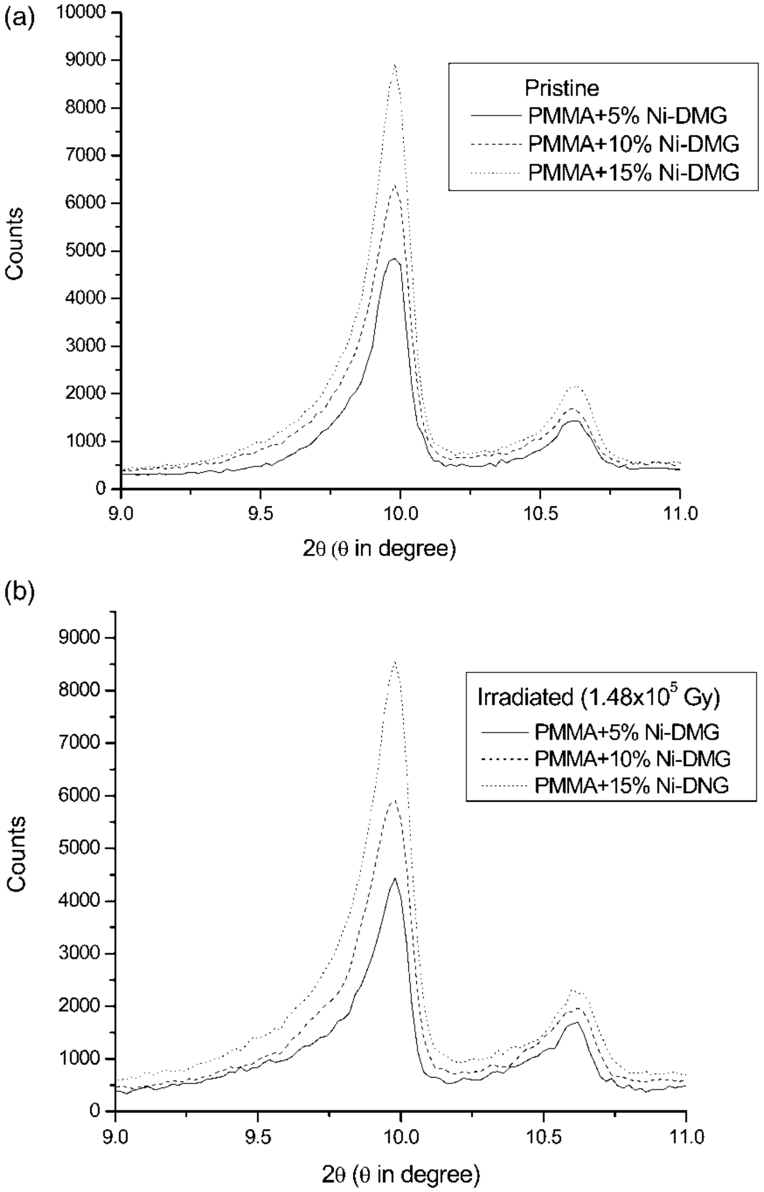

Figure 5. XRD pattern of (a) pristine and (b) irradiated samples.

in the peak position have been observed. This reveals that the lattice parameters do not change significantly but crystallinity of the sample decreases after irradiation [16].

4. Conclusion

Dispersion of organometallic compound (Ni-DMG) in PMMA films has enhanced the properties of the pure polymer significantly. The increase in dielectric properties with different concentrations may be attributed to the conductive phase formed by dispersed organometallic compound in polymer matrix. Proton irradiation has been shown to significantly enhance the dielectric properties. It may be due to the metal-to-polymer adhesion and conversion of the polymeric structure into a hydrogen-depleted carbon network. AFM analysis revealed that the irradiation makes the surface of the sample smoother. This relative smoothness is probably due to the sputtering effects and as a consequence surface diffusion occurs, which is responsible for the smoothness of the surface. An XRD analysis reveals that the crystallite size and degree of crystallinity of the sample decreased after ion beam irradiation.

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