CHAPTER 4

Effect of 140 MeV Ag^{+11} ion irradiation on conductive additive filled in polyvinylchloride (PVC) polymer matrix

This chapter describes the characterization of three polymer composites prepared by dispersion of conductive fillers (carbon black (CB), Aluminum (Al), copper (Cu)) in polyvinylchloride (PVC) polymer matrix. These composites were irradiated with 140 MeV Ag^{+11} *ions at different fluences. The various results of experimentations before and after ion beam irradiation are presented. Scientific explanations of various properties e.g. electrical, structural, thermal and surface morphology of conductive composites are discussed.*

4.0 Introduction

Metal–polymer composites exhibit the properties of both metal and polymer and have been the subject of extensive research for the last two decades. They have a wide range of industrial applications because of their low density, high corrosion resistance, ease of fabrication, and low cost [1–5]. Polyvinyl chloride (PVC), as an important commercial polymer, has been studied and used widely in industrial fields for many years. However, due to its inherent disadvantages, such as low thermal stability and brittleness, PVC and its composites are subject to some limitations in certain applications [6, 7]. Therefore, it is necessary to develop new PVC products with high quality and good properties in order to yield high added values and broaden its applications.

Irradiation of materials by swift heavy ions (SHI) has attracted much attention as it induces large property variations. Ion beams have induced significant changes in structural, electrical and optical properties of polymers and polymers composites [8–11]. During irradiation of polymers by high-energy ions, their energy is transferred into the target material by electronic energy loss. This energy transfer leads to the formation of reactive species like radicals, gases and defects produce in the form of unsaturation, scissoning and cross-linking of the polymers.

This chapter describes the dependence of various properties of polymer composites on filler concentration and fluence of silver ion beam. The effect of 140MeV silver ion irradiation on following composites have been investigated in this chapter.

(1) Carbon black/PVC composites [12]

(2) Al/PVC composites [13,14]

(3) Cu/PVC composites [15,16]

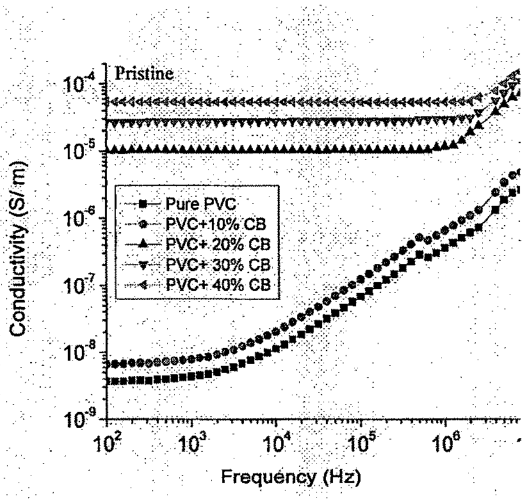
Properties and preparation method of composites have been discussed in chapter-2. The ac conductivity and dielectric constant were calculated using equation (2.4.25) and (2.4.12) respectively as discussed in chapter-2. AC electrical, structural, thermal properties and surface morphology of the conductor polymer composites are discussed. We would like to mention that the XRD results (patterns) could not observed in the case of carbon black (CB) and copper (Cu) composites, however we got XRD patterns in case of Al composite. Hence the XRD results are not discussed in case of CB and Cu composites.

4.1 Carbon black filled PVC composites

4.1.1 Electrical properties

(a) Frequency dependence ac conductivity

Figure 4.1(a-c) shows the variation of ac conductivity as a function of frequency for PVC/CB composites at different filler concentrations. It is observed that the pure PVC and 10% of carbon black composite show the insulating phase and after further doping at higher concentrations (i.e 20, 30 and 40 wt%), samples show conducting behavior [12]. As shown in figure, there are two trends, the ac conductivity remains constant up to 1M Hz and then increases steeply, which is a characteristics feature of disordered materials. At higher frequencies, ac conductivity increases because of the contribution of trapped charges, which are moving along smaller and smaller distances in a polymer chain [17]. The increase of ac conductivity at higher frequencies is due to the charge motion in the amorphous region and this supports the presence of trapped charges in this region. Figure 4.1d shows the variation of AC conductivity as a function of wt% of carbon black (CB) in polyvinyl chloride (PVC) at a fix frequency of 10 MHz and at an ambient temperature. It is observed that the ac conductivity of the composites increases with concentration of filler. It is assumed that an electrical conducting path and network of connections could be formed in the composites with increasing the content of the filler. It is known that electrical conductivity of such composites depends on the type and concentration of the filler [18]. It is also observed that the conductivity increases on increasing irradiation fluence. Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure in to a hydrogen depleted carbon network due to the emission of hydrogen and/or other volatile gases, that is believed to make polymer more conductive [19,20].



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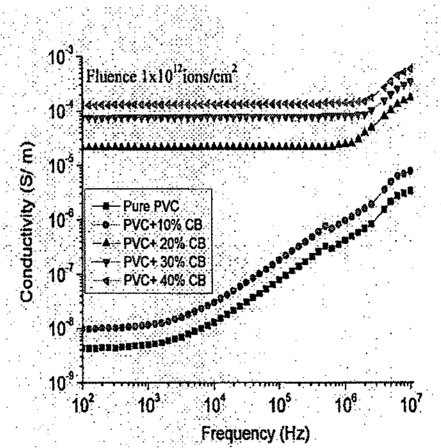

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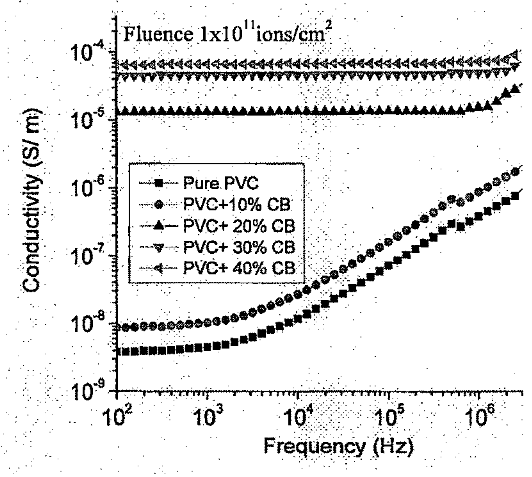

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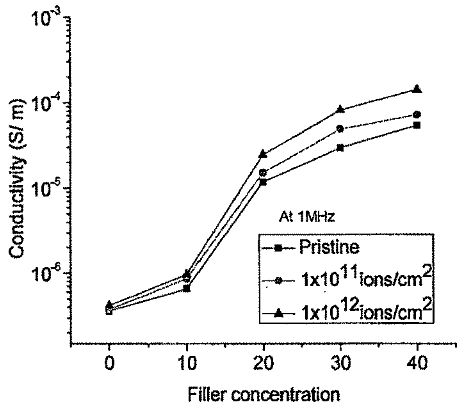


(d)

Fig.4.1 Conductivity vs. frequency for PVC/CB composites (a) Pristine and (b) Irradiated at a fluence of1×10^{11}ions/cm^2 (c) Irradiated at a fluence of 1×10^{12}ions/cm^2 (d) Conductivity vs. filler concentration of CB at 1MHz.

(b) Temperature dependence ac conductivity

Figure 4.2 shows the variation of conductivity of polymer composites with frequency of applied electric field, concentration and temperature for all pristine composites. Fig.4.3 shows the plot of ln (Ac-conductivity) with the inverse temperature for all pristine samples at two different freqüencies (10 KHz and 1 MHz). The increase in conductivity with increases of temperature is referred to as negative temperature coefficient. When the formation of new conducting paths dominates over the disruption of conducting paths, negative temperature coefficient (NTC) phenomenon is observed [21, 22]. Conductivity also increases with filler concentration and frequency of applied field.

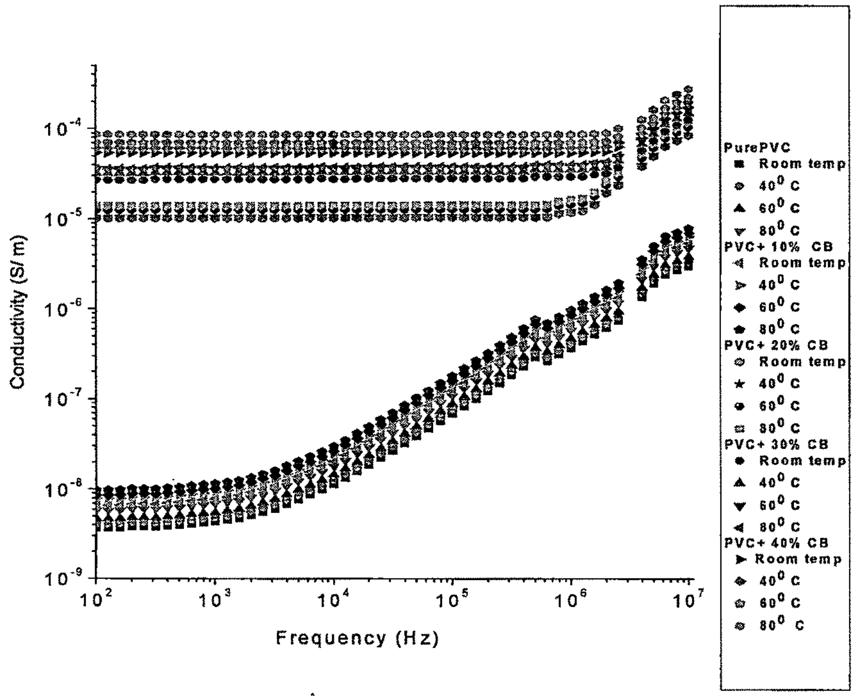


Fig. 4.2 Variation of conductivity of PVC/CB composites with frequency of applied electric field, concentration and temperature.

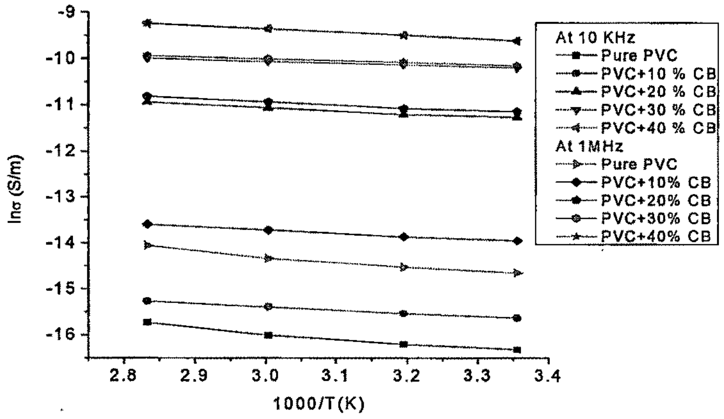
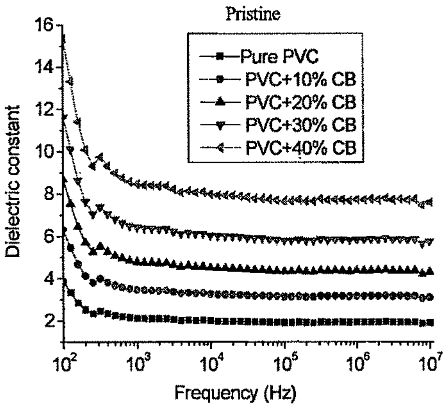


Fig. 4.3 Plot of natural log of conductivity (lnσ) versus inverse temperature, 1000/T [K] for PVC/CB composites.

(c) Frequency dependence dielectric constant

Figure 4.4 (a-c) shows the frequency dependent dielectric constant of polymer/carbon black composites at different filler concentration and ion fluence. For a pure PVC film, the dielectric constant is 1.9 at 1 MHz. After inserting 10% carbon black particles in polymer matrix, the dielectric constant increased to 3.1. In lower regions, dielectric constant increased rapidly which may be due to the free electrons in polymer composites, but at higher frequencies, the dielectric constant remains constant because motion of charge carriers is presumably constant at these frequencies. From Fig.4.4, it is also observed that the dielectric constant increases with the concentration of carbon black embedded in polymer matrix. The system under investigation is heterogeneous with different concentrations of carbon black dispersed in polymer matrix. It became more heterogeneous as filler concentration is increased to it, because of the formation of interfaces between the dispersed phase and the polymer matrix. The increase in the dielectric constant with filler content is a direct consequence of interfacial polarization effect between polymer and the filler particles. The quantity of the accumulated charges will increase in the composite after doping because of the polarization of the PMMA/filler at the interfaces. The polarization makes an additional contribution to the charge quantity [24]. From this point of view, the dielectric constant of the composites will be higher than the pure polymer [23, 24]. Our experimental results also support this explanation.

The dielectric constant was found to increase upon ion beam irradiation. The increase in dielectric constant due to ion beam irradiation may be correlated to the defects created along the ion tracks and structural modifications induced in the surrounding regions. The increase in dielectric constants for irradiated samples may be attributed to the disordering of the material by means of chain scission in polymer composites and as a result, the increase in the number of free radicals, unsaturation etc[25].



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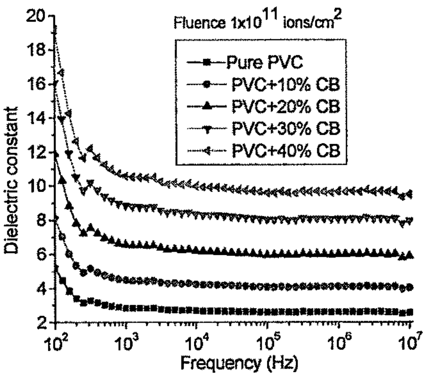

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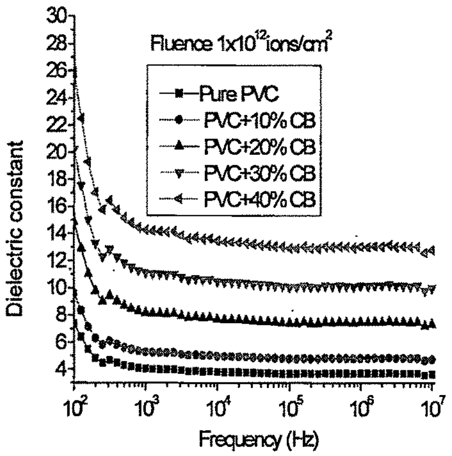


(c)

Fig.4.4 Dielectric constant vs. frequency for PVC/CB composites (a) Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm^2.

(d) Temperature dependence dielectric constant

Figure 4.5 shows the variation of dielectric permittivity of polymer composites with frequency of applied electric field, concentration and temperature for all pristine samples and Fig. 4.6 depict the dielectric constant as a function of temperature at fixed frequency for pure PVC and CB filled polymer composites with different concentrations of CB. For pure PVC and PVC/CB composite with lower concentration of CB (i.e.10wt%), the dielectric constant seems to be not much change with the increase in temperature. For higher concentrations of carbon black composites, increase in dielectric constant with increase in temperature is observed. The enhancement in dielectric constant with increasing temperature can be explained on the basis of two competing mechanisms: segmental mobility of polymer molecules and differential thermal expansion of PVC and carbon black [24].

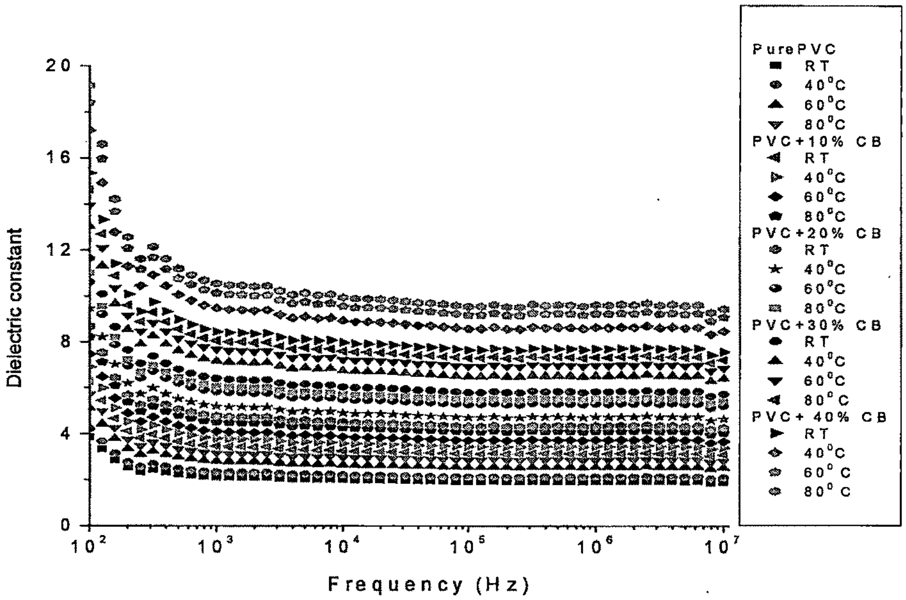


Fig.4.5 Variation of dielectric constant of PVC/CB composites with frequency of applied electric field, concentration and temperature.

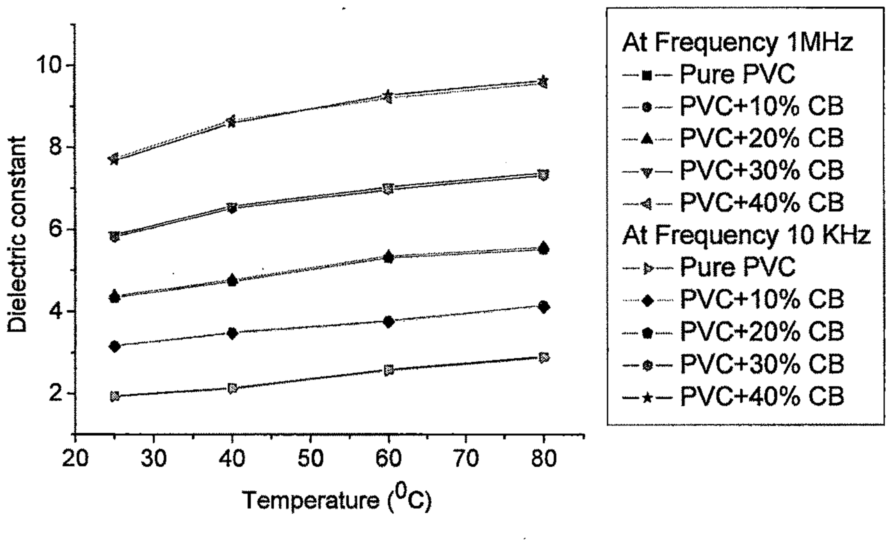
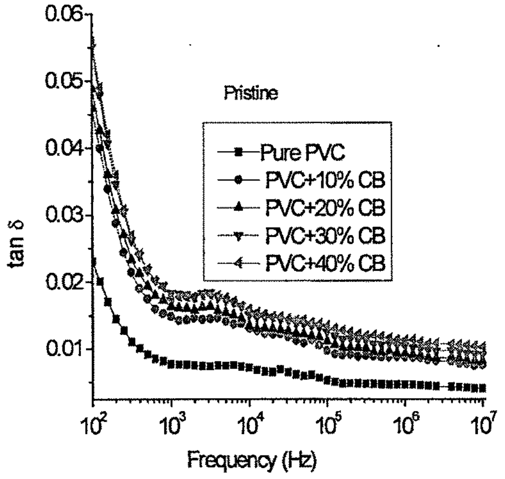


Fig.4.6 Variation of dielectric constant versus temperature at different concentration of PVC/CB composites at two different frequencies.

(e) Frequency dependence dielectric loss

Fig. 4.7 (a-d) shows the frequency dependence dielectric loss of the composite at different fluences. The dielectric loss decreases exponentially and then became less dependent on frequency. This is because the induced charges gradually fail to follow the reversing field causing a reduction in the electronic oscillations as the frequency is increased. In general, the dielectric loss values of PVC/CB composites are higher than that of pure PVC. The increase in dielectric loss with increasing filler content may be attributed to the interfacial polarization mechanism of the heterogeneous system [26]. Further, moderate increase in tanδ occurs due to the irradiation.



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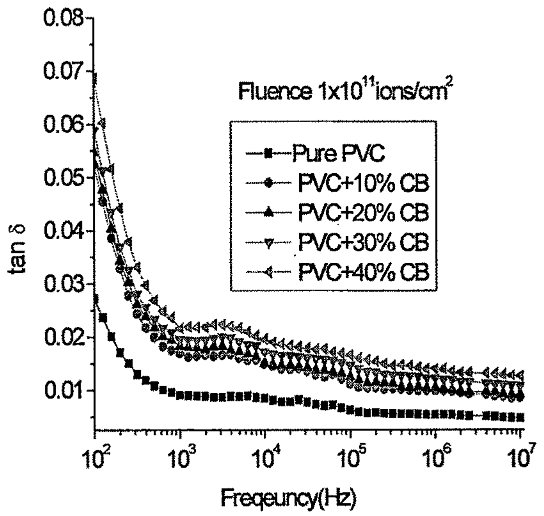

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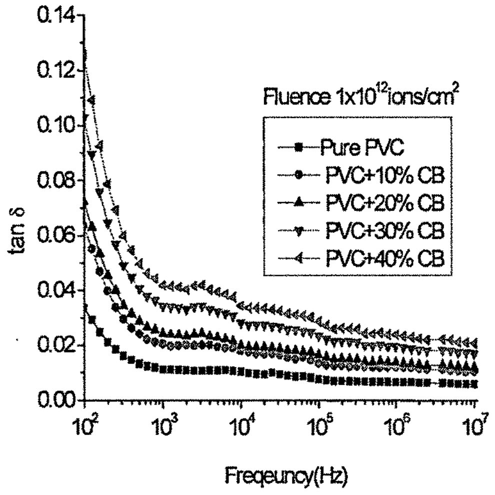

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Fig.4.7 Dielectric loss vs. frequency for PVC/CB composites (a) Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm^2.

(f) Temperature dependence dielectric loss

Figure 4.8 shows the variation of dielectric loss of PVC/CB composites with frequency of applied electric field, concentration and temperature for all pristine samples and Fig. 4.9 depicts the dielectric loss as a function of temperature at two different frequencies for pure PVC and CB filled polymer composites with different concentrations of CB. From fig.4.9 it can be seen that, dielectric loss factor increases moderately with increase in temperature [26].

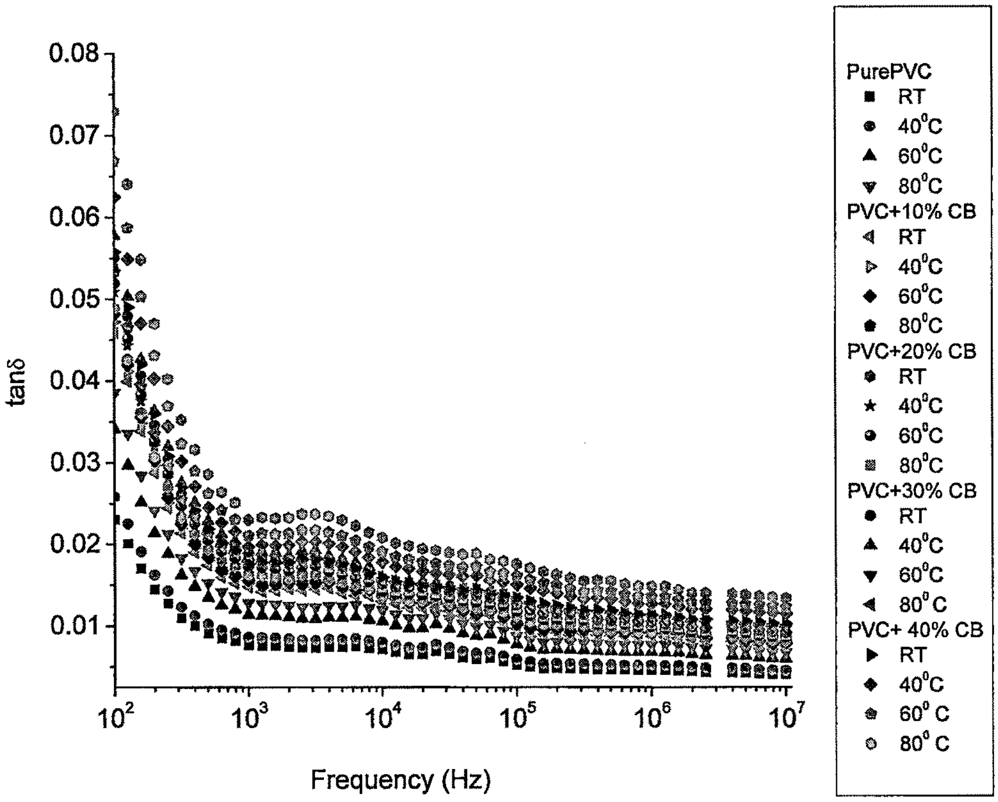


Fig. 4.8. Variation of dielectric loss of PVC/CB composites with frequency of applied electric field, concentration and temperature.

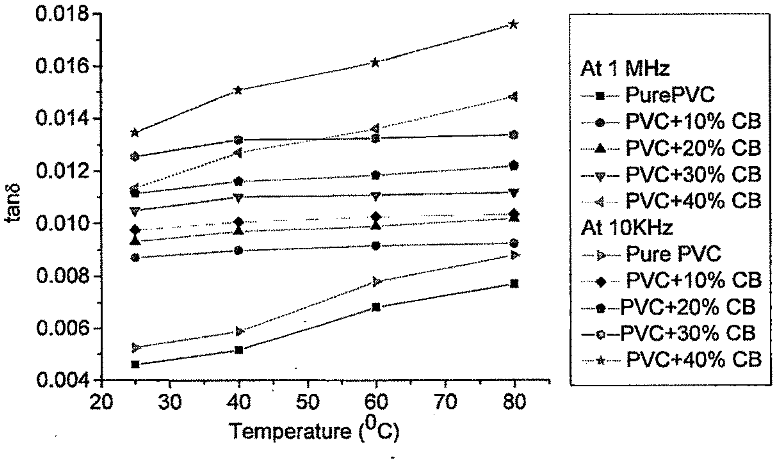


Fig. 4.9. Variation of dielectric loss versus temperature at different concentration of PVC/CB composites at two different frequencies.

4.1.2 Differential scanning calorimeteric (DSC) analysis

In DSC experiment one has a reference material, the sample to be probed, and a predetermined heating (or cooling) rate is imposed to the system for undergoing a given temperature excursion (40^0 to 150^0 C). A servo-system makes the sample to follow the temperature of the reference and the heating power difference between the sample and reference is recorded. That is, since dT/dt is fixed, one senses essentially dQ/dT, that is the heat flow in the samples.

It is well established that crystalline and amorphous phases in variable amount co-exist in most of the polymeric materials [27]. Polyvinyl chloride (PVC) is a well-known thermoplastic polymer exhibiting the glass transition temperature T_g supporting the above argument. DSC thermograms of pristine and irradiated PVC+40% CB were measured and shown in Fig. 4.10. For reference, the thermogram of Pure PVC is also shown. When the concentration of carbon black is increased in the polymer matrix, T_g is shifted to higher temperature, this may be attributed to the cross linking of polymer with CB particles. After irradiation, T_g is shifted to lower temperature, which reveals that the ion irradiation leads to chain scissioning and subsequently reduction in molecular weight. As a result, system moved towards the disordered state.

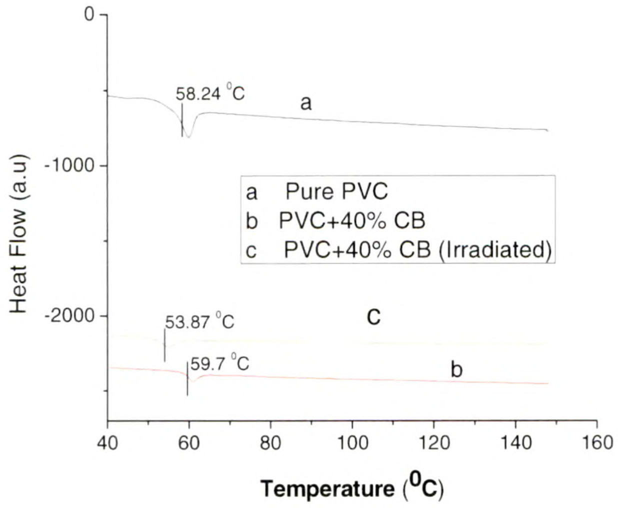
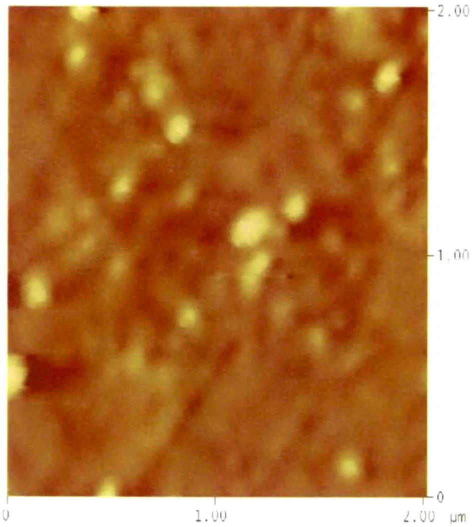


Fig. 4.10 DSC thermograms of (a) pure PVC pristine, (b) PVC + 40% CB(pristine) and (c) PVC + 40% CB (irradiated at a fluence of 1x 10^{12} ions/cm^2).

4.1.3 Surface morphology of the composites

(i) Atomic force microscopy (AFM) analysis

The surface morphology of pristine and irradiated PVC/CB composites was studied by AFM on 2x2 μm^2 area as shown in Figure 4.11(a-f). Each AFM image was analyzed in terms of surface average roughness (R_a). It is observed that roughness increases to 3.0 nm, 5.0 nm and 5.7 nm with carbon black concentration of 10%, 20% and 40% and decreases to 1.3 nm, 2.2 nm and 3.4 nm respectively after irradiation at a fluence of $1x10^{12}$ ions/cm^2. This relative smoothness is probably due to the defect enhanced surface diffusion [28]. However, the increase in roughness with filler concentration is attributed to increase in density and size of carbon black particles on the surface of PVC film [29].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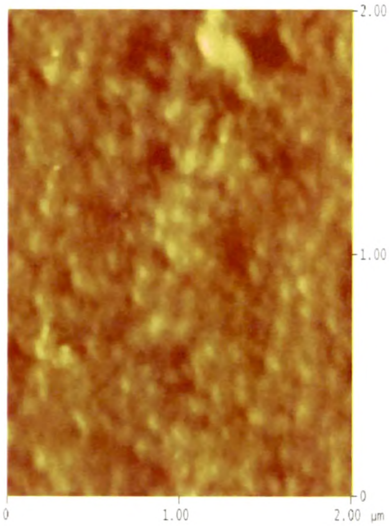
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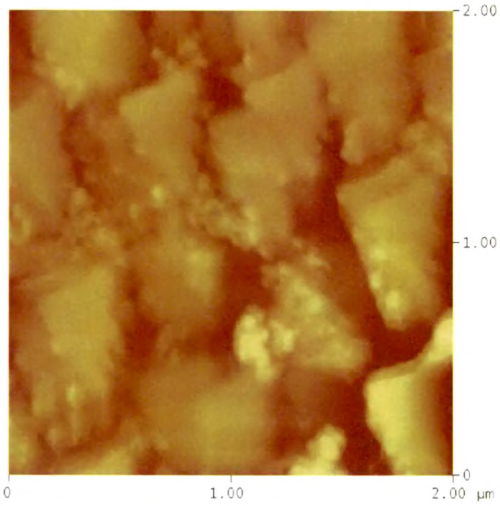
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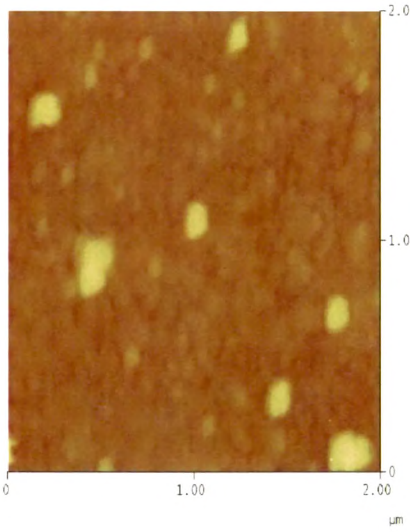
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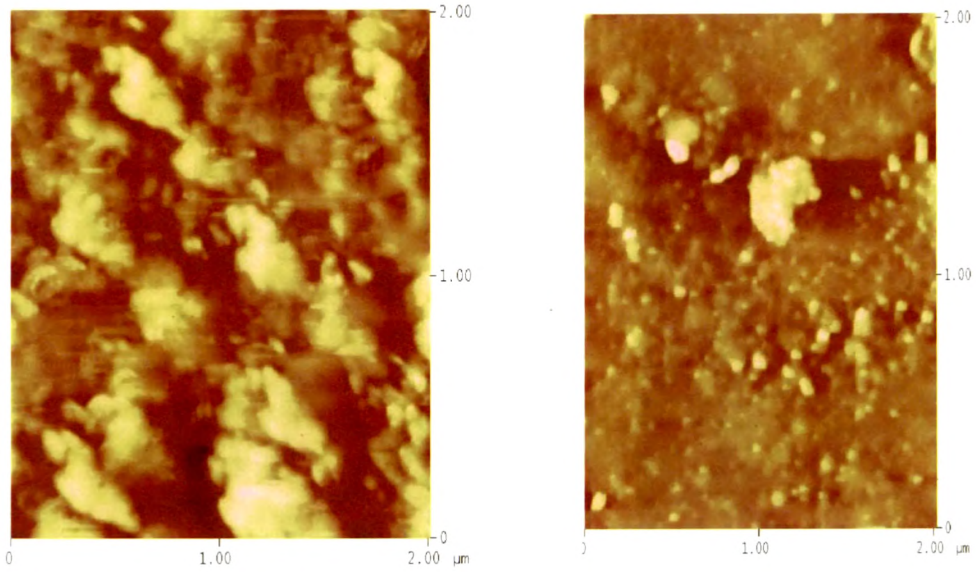


(e) (f)

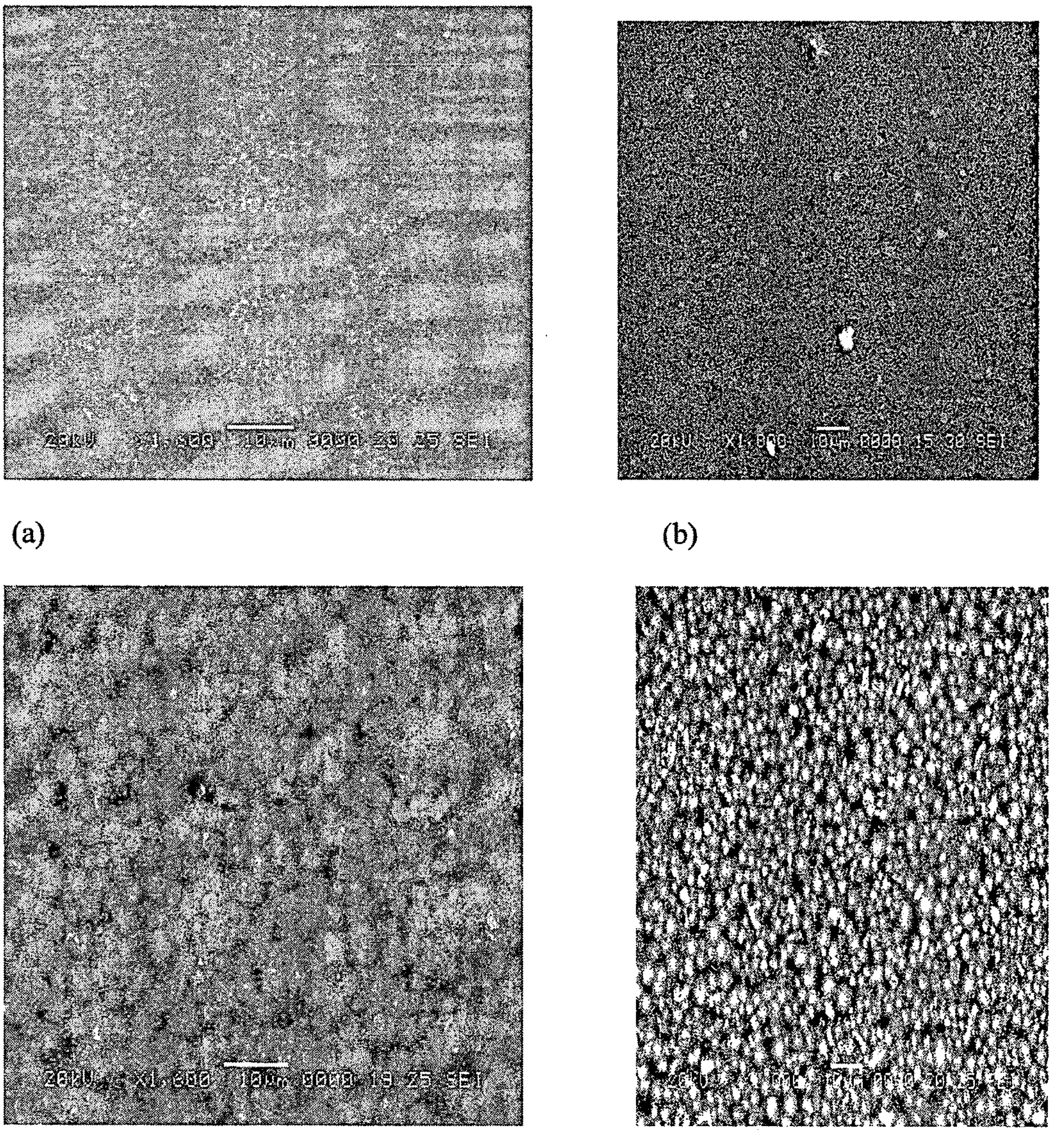
Fig.4.11 AFM images of (a) PVC+10% CB (pristine) (b) PVC+10% CB (irradiated~ 1x10^{12}ions/cm^2).

(c) PVC+20% CB (pristine) (d) PVC+20% CB (irradiated~ 1x10^{12}ions/cm^2)

(e) PVC+40% CB (pristine) (f) PVC+40% CB (irradiated~ 1x10^{12}ions/cm^2).

(ii) Scanning electron microscopy (SEM) analysis

The scanning electron microscopy (SEM) micrographs of the surfaces of PVC/CB (10, 40 wt%) composites are shown in figure 4.12 (a-d) before and after irradiation. It can be seen that connectivity of the polymer metal phase increases with increasing metal content in polymer matrix as would be expected from conductivity results. Aggregates of micro spherical voids are seen on the surface and its size reduces due to ion beam irradiation as shown in Fig. 4.12(b&d)



(a) (b)

(c) (d)

Fig. 4.12 SEM micrographs of (a) PVC+10% CB (pristine) (b) PVC+10% CB (irradiated~ $1x10^{12}$ions/cm^2).

(c) PVC+40% CB (pristine) (d) PVC+40% CB (irradiated~ $1x10^{12}$ions/cm^2)

4.1.4 Conclusions

The present results can be summarized as follows:

(1) The ac conductivity of the composites increases with increasing the frequency, concentration of filler and also with ion fluence.

(2) The ac conductivity also increases as temperature increases for all pristine PVC/CB composites. The phenomenon, that is, an increase of conductivity (or a decrease of resistivity) with an increase of temperature is termed as negative temperature coefficient (NTC) of resistivity.

(3) The increase in dielectric constant upon irradiation may be attributed to the disordering of the material by means of chain scission in polymer composites and as a result, the increase in the number of free radicals, unsaturation etc.

(4) The dielectric constant and dielectric loss of the PVC/CB composites increased with an increase in temperature, which is attributed to the segmental mobility of the polymer molecules.

(5) Thermal property of the composite was studied by DSC analysis and it reveals that the glass transitions temperature (Tg) decreases upon ion beam irradiation. It means that the composite system is shifted towards disordered state ie. amorphisation of the system.

(6) Atomic force microscopy (AFM) studies revealed that the average surface roughness of the composites increases with filler concentration and decreases upon irradiation. SEM micrographs indicate the connectivity of metal particles on increasing the concentration of filler and size of micro spherical voids is decreased upon irradiation.

4.2 Aluminum filled PVC composites: Results and discussion

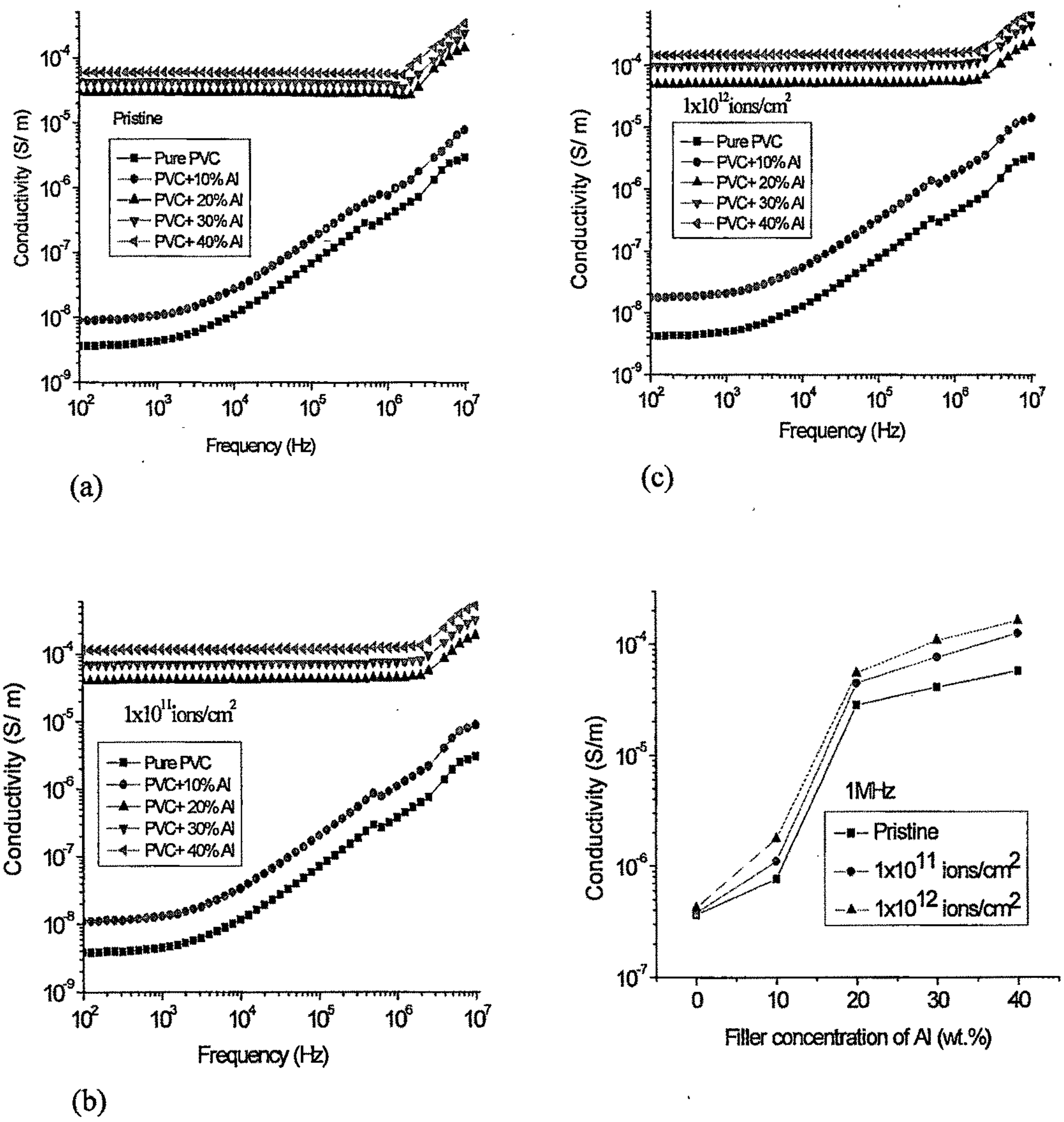
4.2.1 Electrical properties

(a)Frequency dependence ac conductivity

The variation of σ (AC conductivity) with frequency for different concentration of aluminum filler of composites and ion fluences is shown in Figs. 4.13(a-d) at ambient temperature. At low aluminum contents (10wt%), the electrical conductivity of the composites increases with increasing frequency. These specimens show a typical insulating behavior with a frequency-dependent conductivity. When the aluminum content reaches to 20 wt%, there is a transition from an insulator to semiconductor. The concentration of the filler, when composite changes the behavior from insulator to semiconductor is defined as percolation threshold which is associated with the formation of conducting network [30]. It is also observed that after the irradiation the conductivity increases with fluence (Fig.4.13(b-d). Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure in to a hydrogen depleted carbon network due to the emission of hydrogen and/or other volatile gases, which is believed to make polymer more conductive [19,20].

(b) Temperature dependence ac conductivity

One of the interesting features of conductivity is its temperature dependence, which allows one to understand conduction mechanisms in materials. Figure 4.14 shows the variation of conductivity of polymer composites with frequency of applied electric field, concentration of filler and temperature for all pristine composites. Fig.4.15 shows the variation of ln (Ac-conductivity) with the inverse temperature for all pristine samples at two different frequencies (10 KHz and 1 MHz). It is evident from figure that the conductivity (σ) of all composites increases with increasing the temperature from room temperature to 80 °C due to the increase of the mobility of free charges (i.e. polarons and free ions) that took place as a result of the excitation by heat. This characterizes semiconductor-like conduction in these composites [31].



(a)

(c)

(b)

(d)

Fig.4.13 Conductivity vs. frequency for PVC/Al composites (a) Pristine and (b) Irradiated at a fluence of $1\text{x}10^{11}$ions/cm^2 (c) Irradiated at a fluence of $1\text{x}10^{12}$ions/cm^2 (d) Conductivity vs. filler concentration at 1MHz.

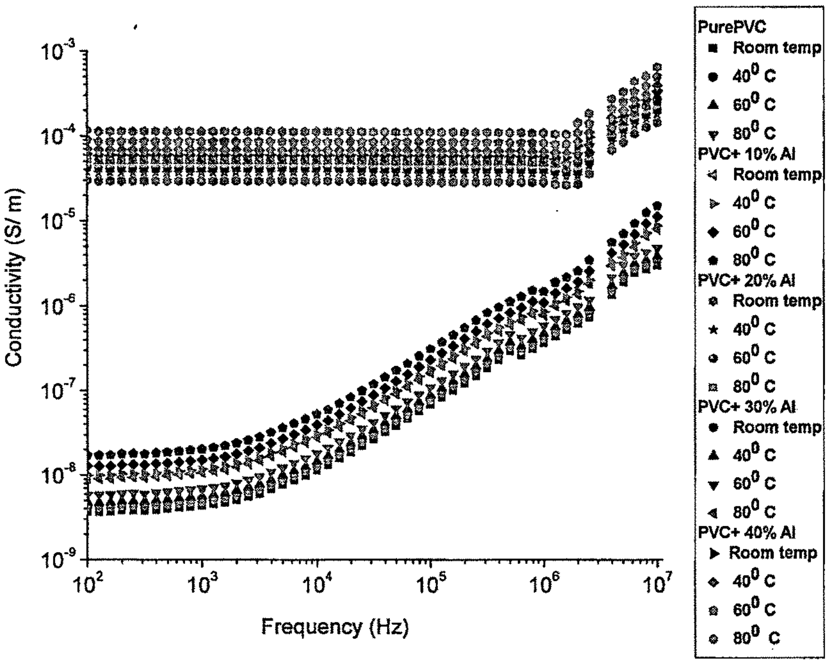


Fig.4.14 Variation of conductivity of PVC/Al composites with frequency of applied electric field, concentration and temperature.

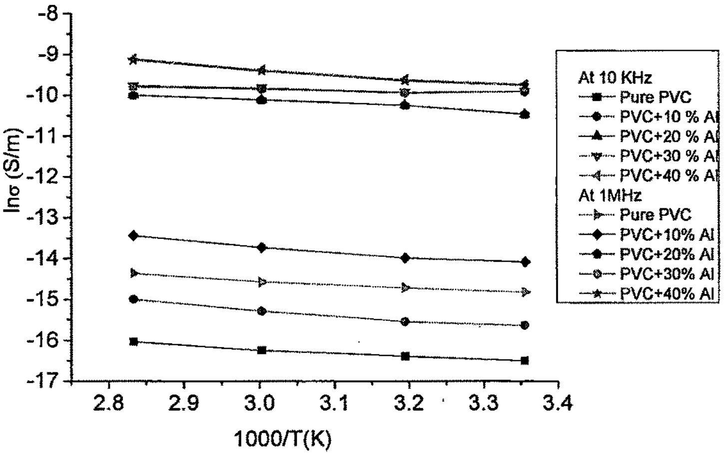


Figure. 4.15 Plot of natural log of conductivity (lnσ) versus inverse temperature, 1000/T [K] for PVC/Al composites.

(b) Frequency dependence dielectric constant

The variations of dielectric constant (the real part of the complex dielectric permittivity: $\varepsilon^* = \varepsilon' - j\varepsilon''$) of PVC/Al composites as a function of frequency, filler concentration and ion fluence at ambient temperature is shown in figure 4.16 (a-c). As expected, the variation tendency of dielectric constant with frequency is the reverse of electrical conductivity. The dielectric constant attains high value at low frequency and decreases moderately with increase in frequency. The decrease of dielectric constant is mainly attributed to the mis-match of interfacial polarization of composites to external electric field at elevated frequencies [32]. For a pure PVC film, the dielectric constant is 1.9 at a frequency of 1 MHz. After inserting 10% aluminum particles in polymer matrix, the dielectric constant increased to 4.6. The system under investigation is heterogeneous with different concentrations of aluminum particles filled in the polymer. It became more heterogeneous as filler concentration is increased to it, because of the formation of interfaces between the dispersed phase and the polymer matrix. For the composite film with 40 wt% of aluminum particles, the dielectric constant increased to 9.8 at a frequency of 1 MHz. Due to the dispersion of aluminum particles, the quantity of the accumulated charges will increase because of the polarization of the polymer/metal particles 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 [23, 24]. It is also observed that the enhancement of dielectric constant upon irradiation. This is attributed to the disordering of the material by means of chain scission in polymer composites and as a result, the increase in the number of free radicals, unsaturation etc.

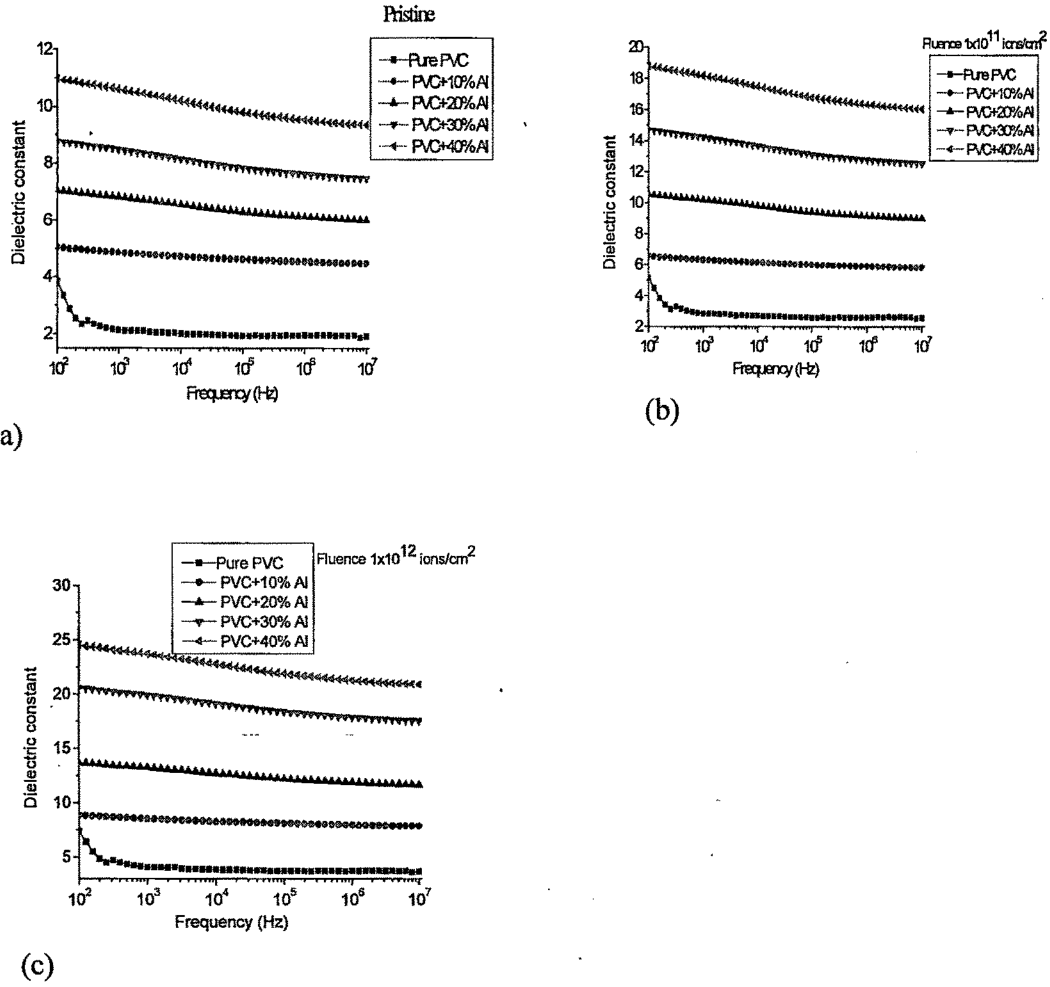


Fig.4.16 Dielectric constant vs. frequency for PVC/Al composites (a) Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm^2.

(c) Temperature dependence dielectric constant

Figure 4.17 shows the variation of dielectric constant of polymer composites with frequency of applied electric field, concentration and temperature for all pristine composites. Fig.4.18 shows the variation of dielectric constant with temperature from room temperature to 80^{0}C for all pristine samples at two different frequencies (i.e 10 KHz and 1 MHz).

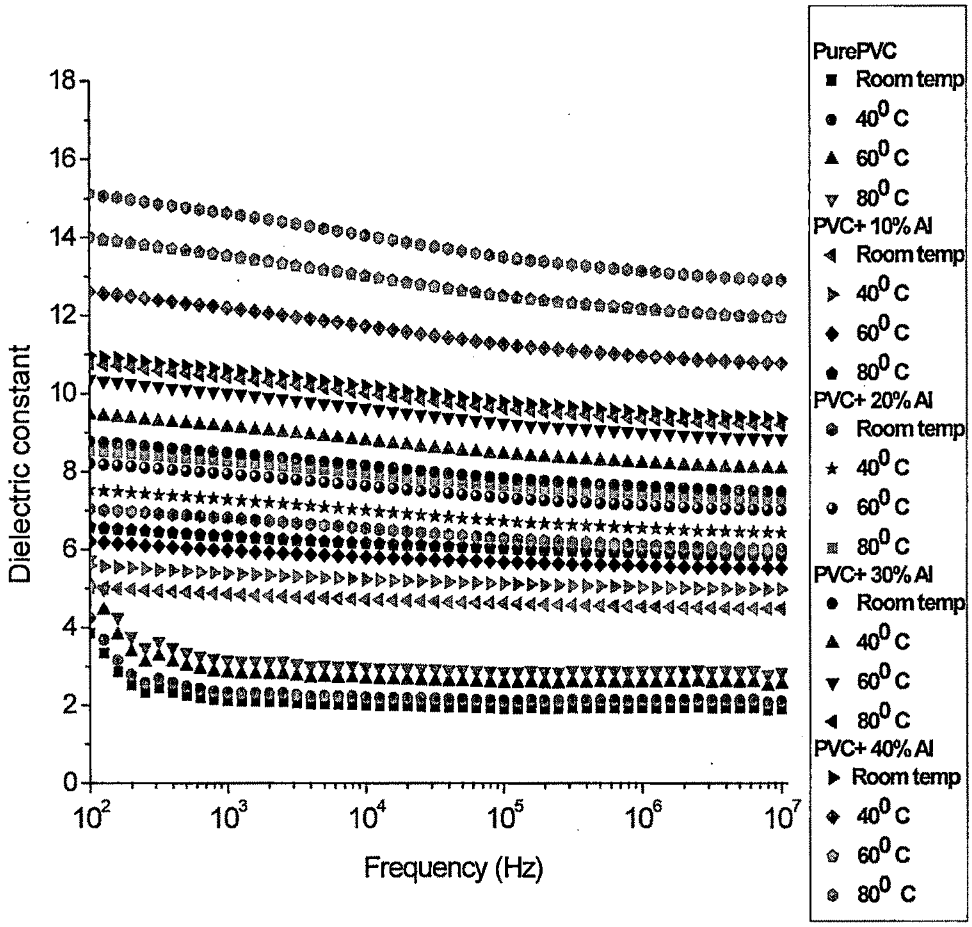


Fig. 4.17 Variation of dielectric constant of PVC/Al composites with frequency of applied electric filed, concentration and temperature.

From Fig. 4.18, it can be seen that dielectric constant increases as temperature increases. The increase of dielectric constant with temperature can be explained by the increase in the mobility of polar groups, and hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups [33].

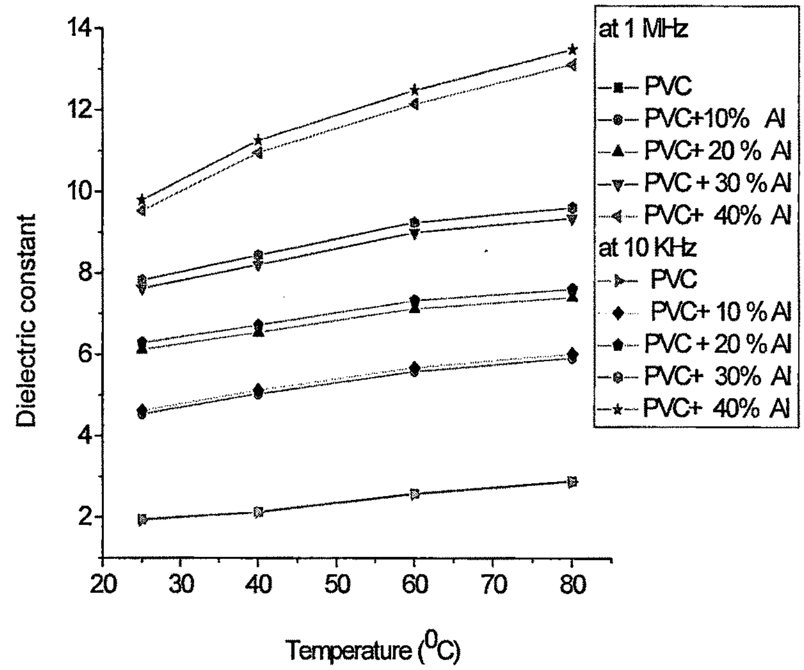
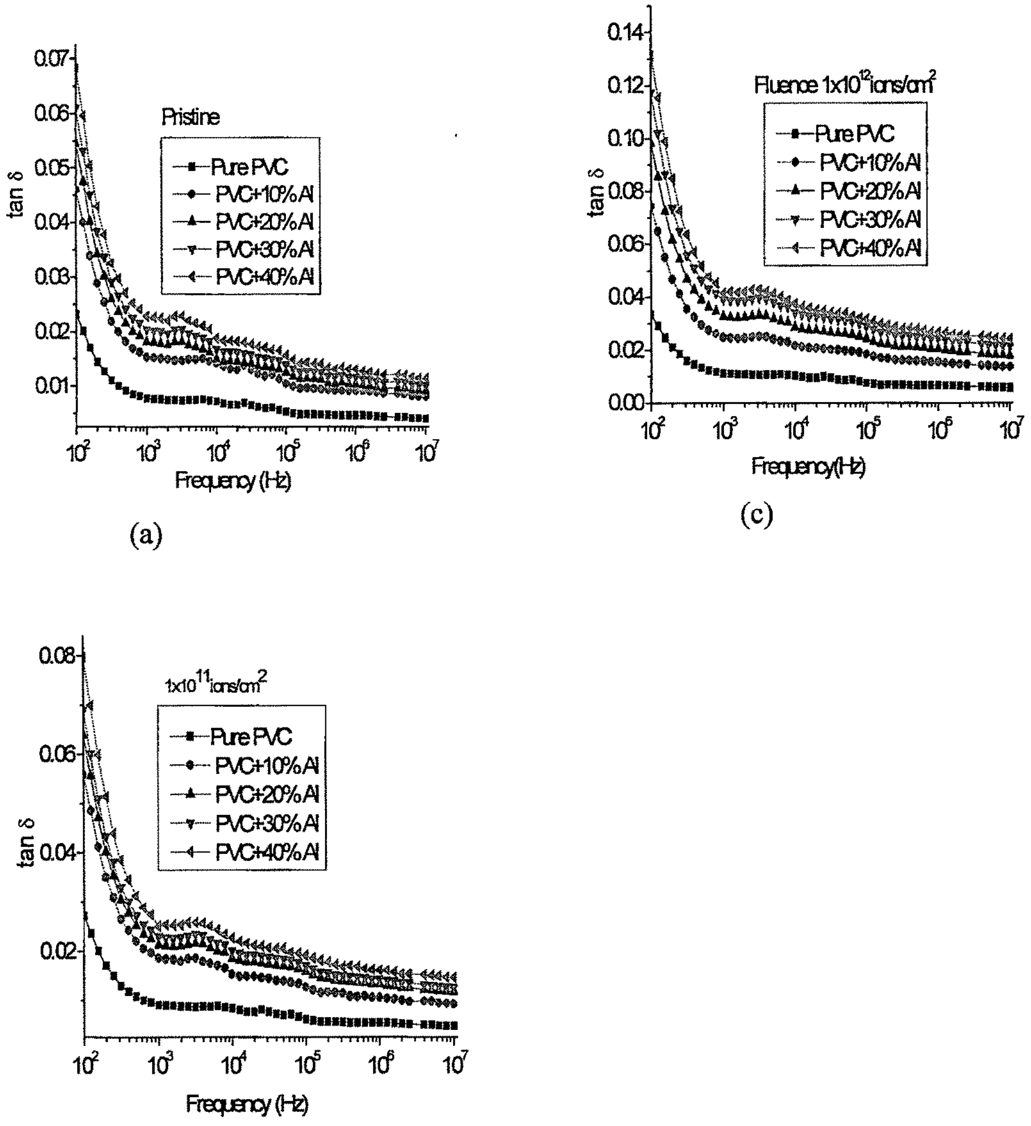


Fig.4.18 Variation of dielectric constant vs temperature at different concentrations of PVC/Al composites at two different frequencies.

(d) Frequency dependence dielectric loss

Fig. 4.19 (a-c) shows the frequency dependence dielectric loss of the composites as a function of aluminum (Al) and ion fluence. The dependence of tan δ of the PVC/Al composites on low frequency is shown in Fig. 4.19. The tanδ maintains a maximum value at low frequency and decreases exponentially with the increase of frequency. This is because the induced charge gradually fails to follow the reversing field causing a reduction in the electric oscillations as the frequency is increased. The increase in dielectric loss with increasing filler contents may be attributed to the interfacial polarization mechanism of the heterogeneous system [25]. Further, moderate increase in tanδ occurs due to the irradiation.



(a) (c) (b)

Fig.4.19 Dielectric loss vs. frequency for PVC/Al composites (a)Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm$^{2.}$

(c) Temperature dependence dielectric loss

Figure 4.20, represents the variation of dielectric loss with frequency at different temperatures ranging from room temperature to 80^{0}C for all pristine PVC/Al composites. The value of dielectric loss is increased moderately at higher temperatures, especially in low frequency region. The low frequency losses may be due to either the Maxwell-Wagner effect as a result of an alternating current (ac) in phase with the applied potential or the direct current (dc) conductivity [34, 35]. Fig. 4.21, represents the variation of dielectric loss with temperature at two different frequencies. The dielectric loss increases with increasing temperature but no loss peak was observed.

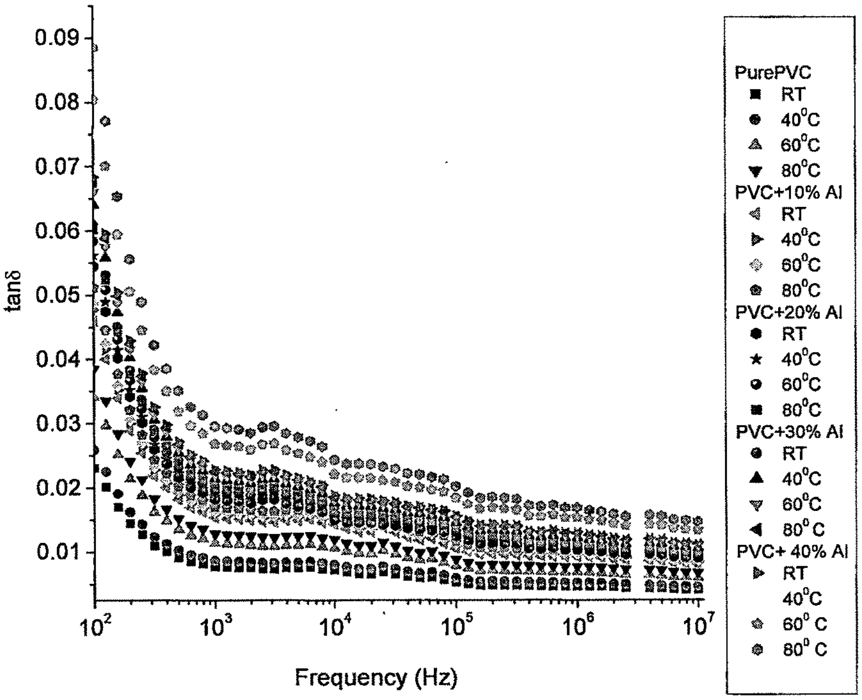


Fig. 4.20 Variation of dielectric loss of PVC/Al composites with frequency of applied electric field, concentration and temperature.

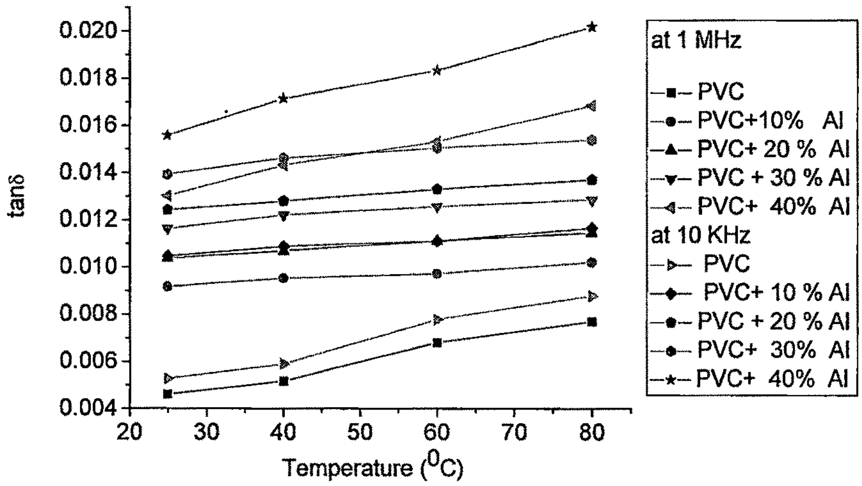


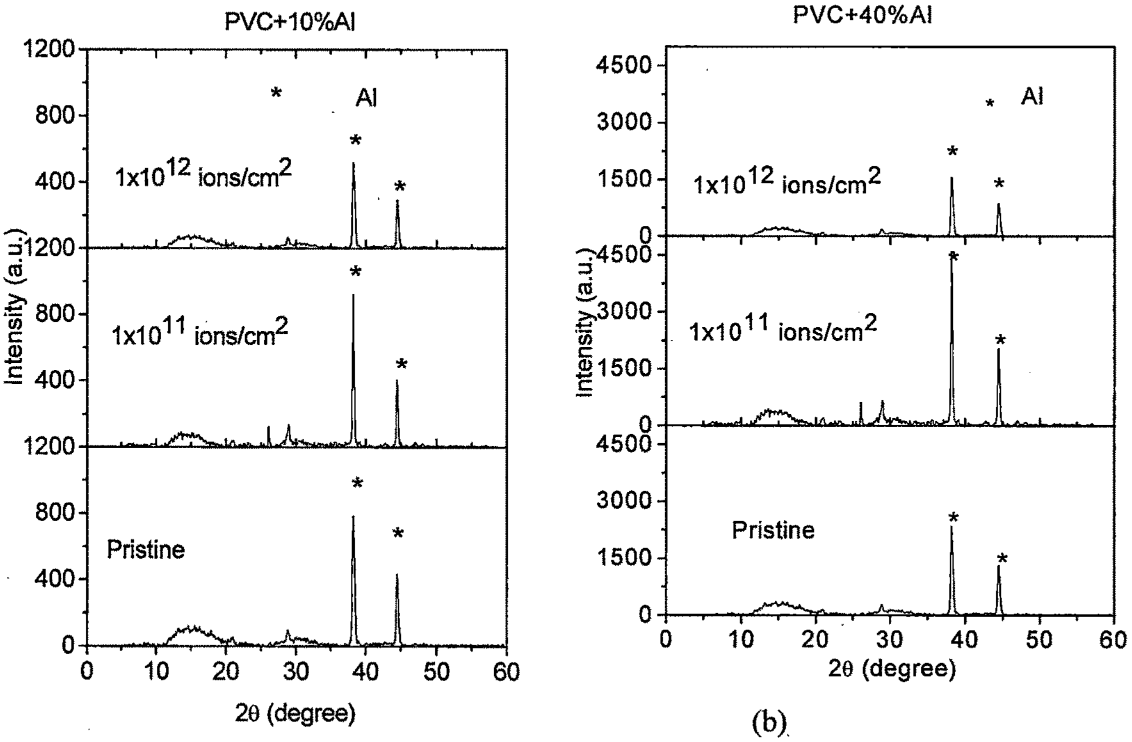
Fig.4.21 Variation of dielectric loss versus temperature at different concentrations of PVC/Al composites at two different frequencies.

4.2.2 X-ray diffraction analysis

The structural information about the PVC/Al composites (for 10% and 40% Al) has been investigated by XRD and the corresponding X-ray diffraction patterns of the polymer composites before and after SHI irradiation at the fluences of 1×10^{11} and $1\text{x}10^{12}$ ions/cm^2 are presented in Fig. 4.22 (a-b). The peaks are obtained at $2\theta = 38.20$ and 44.46. The nature of the peak indicates the semi-crystalline nature of the sample. The crystallite size has been calculated before and after the irradiation using Scherrer's equation [36]

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

where b is FWHM in radians, λ is the wavelength of X-ray beam (1.5418Å), 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. The percentage crystallanity of the composites was determined by area ratio method. In this method the areas of amorphous and crystalline parts of the patterns were calculated. The crystallite size and crystallinity (%) were listed in Table 4.1. From Fig 4.22 (a, b), the most prominent peaks are approximately obtained around 2θ ~ 38.20 and 44.46 in all the cases. These peaks are due to pure Al metal (JCPDS). From Fig.4.22, it can also seen one broadening hump around 2θ ~ 15^0 in all cases, this is due to PVC polymer matrix. It was observed that the degree of crystallinity increased upon the irradiation of PVC/Al composites at the fluence of $1x10^{11}$ ions/cm^2 (Table 4.1) for both composites (i.e 10%, 40%). The crystallinity of polymer composite was decreased on further increase of ion fluence i.e $1x10^{12}$ ions/cm^2 and the polymer composites tend to change into the amorphous phase (Figure 4.22 (a),(b)), Which is also observed in the case of PMMA/Al composites (Chapter-3 of section 3.2.2).



(a)

(b)

Fig. 4.22 XRD Spectra of (a) PVC+10%Al (pristine) and PVC+10%Al (irradiated at two different fluences $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2) (b)PVC+40%Al (pristine) and PVC+40%Al (irradiated at two different fluences $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2).

Table 4.1.

FWHM, crystallite size and % crystallinity of pristine and irradiated PVC/Al composites for 10% and 40% concentrations of filler.

Pristine (PVC +10%Al)				**Pristine (PVC +40%Al)**			
2 theta (deg.)	FWHM (B rad.)	Crystallite Size (nm)	Crystallinity (%)	2 theta (deg.)	FWHM (B rad.)	Crystallite Size (nm)	Crystallinity (%)
38.20	0.3655	27.07	7.283	38.30	0.3255	28.84	9.635
44.46	0.3504	27.22	4.10	44.56	0.3108	32.69	6.437
Average Crystallite Size = 27.14 nm				Average Crystallite Size = 30.76 nm			
Average Crystallinity = 5.70 %				Average Crystallinity = 8.03 %			

1x 10^{11}ions/cm^2 (PVC+10% Al)				**1x 10^{11}ions/cm^2 (PVC+40%Al)**			
2 theta (deg.)	FWHM (B rad.)	Crystallite Size (nm)	Crystallinity (%)	2 theta (deg.)	FWHM (B rad.)	Crystallite Size (nm)	Crystallinity (%)
38.25	0.2612	35.82	6.27	38.42	0.2109	44.30	22.12
44.50	0.2432	40.86	3.45	44.52	0.2014	45.40	18.968
Average Crystallite Size = 38.34 nm				Average Crystallite Size = 44. 85 nm			
Average Crystallinity = 4.85%				Average Crystallinity = 20.50 %			

1x 10^{12}ions/cm^2 (PVC+10%Al)				**1x 10^{12}ions/cm^2 (PVC+40%Al)**			
2 theta	FWHM	Crystallite Size	Crystallinity	2 theta	FWHM	Crystallite Size	Crystallinity

(deg.)	(B rad.)	(nm)	(%)	(deg.)	(B rad.)	(nm)	(%)
38.30	0.3542	27.22	3.53	38.32	0.2232	41.96	6.94
44.47	0.3344	28.84	2.29	44.42	0.2342	40.74	4.41
Average Crystallite Size = 33.59 nm				Average Crystallite Size =41.35 nm			
Average Crystallinity = 2.91 %				Average Crystallinity = 5.65 %			

4.2.3 Differential scanning calorimetric (DSC) analysis

DSC traces of the pure PVC and PVC+40% Al composites before and after irradiation at two different fluences are shown in figure 4.23. The pure PVC exhibits a heat flow change at approximately 58.24 °C, corresponding to the glass transition temperature (Tg) of PVC and glass transition of PVC +40% Al composite pristine and irradiated at different fluences of $1x10^{11}$ and $1x10^{12}$ ions/cm^2 at 64.17 °C, 65.30^{0}C and 60.55 °C respectively. It is also observed that the Tg of composite shifted towards higher temperature at a fluence of $1x10^{11}$ ions/cm^2, which reveals that the composite became more crystalline. The increase in glass transition has been observed with increasing filler, which is attributed to the confinement of intercalated PVC chains within the aluminum particles that prevents the segmental motions of the polymer chains. On further increase of the fluence (ie. $1x10^{12}$ions/cm^2) , Tg shifted to lower temperature, which reveals that the irradiation leads to chain scission and subsequently reduction in molecular weight. As a result, the system is changing towards disordered state. It is also corroborated with XRD results.

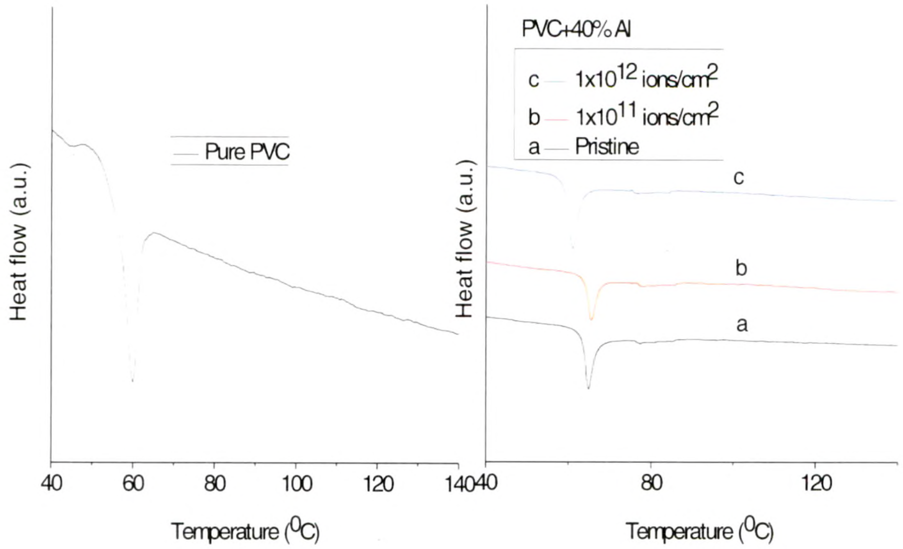


Fig.4.23 DSC patterns for pure PVC (pristine) and pristine and irradiated PVC+40% Al composites at two different fluences.

4.2.4 Surface morphology of the composites

(i) Atomic force microscopy(AFM) analysis

Surface morphology of the pristine and irradiated metalized polymeric samples has been studied using atomic force microscopy. The images of 5x5 μm^2 areas were recorded in tapping mode and shown in Fig. 4.24 (a-d). Each AFM image was analyzed in terms of surface average roughness (R_a). The average roughness values obtained for unirradiated films are 2.81 (for PVC+10% Al) and 15.2 (for PVC+40% Al) and for corresponding irradiated films at the fluence of $1x10^{12}$ ions/cm^2, the roughness was obtained as 4.71 nm and 22.3 nm respectively. The data shows that the surface average roughness (rms) increases with metal concentration and it is also increases after ion beam irradiation. This might be attributed to large sputtering effect due to high energy ion interaction with composite surface.

(ii) Scanning electron microscopy (SEM) analysis

The scanning electron microscopy (SEM) micrographs of the surfaces of PVC/Al (10, 40 wt%) composites are shown in Figure 4.25 (a-d) before and after irradiation. It can be seen that the particles are randomly distributed in polymer matrix. At low filler content (i.e.10 wt% Al), the particle are isolated. As the Al content is increased (i.e. 40% Al-filler), clusters of metal particles are formed (Fig. 4.25 c). A cluster may be considered as a region in the polymer matrix, where the conducting path is formed. Aggregates of micro cluster are clearly visible on the surface and metal/polymer phases increase due to ion beam irradiation as shown in Fig.4.25 (b, d).

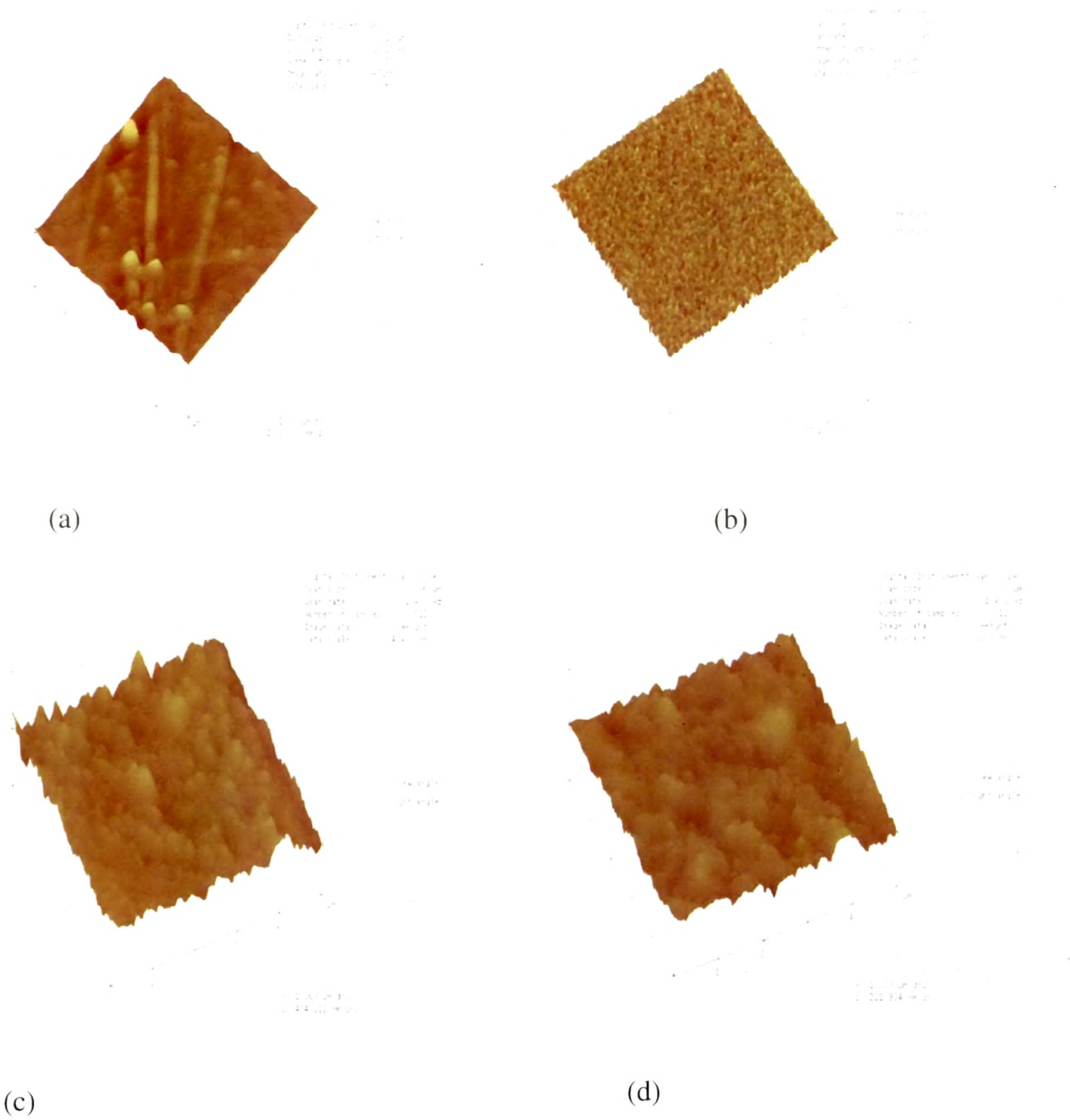
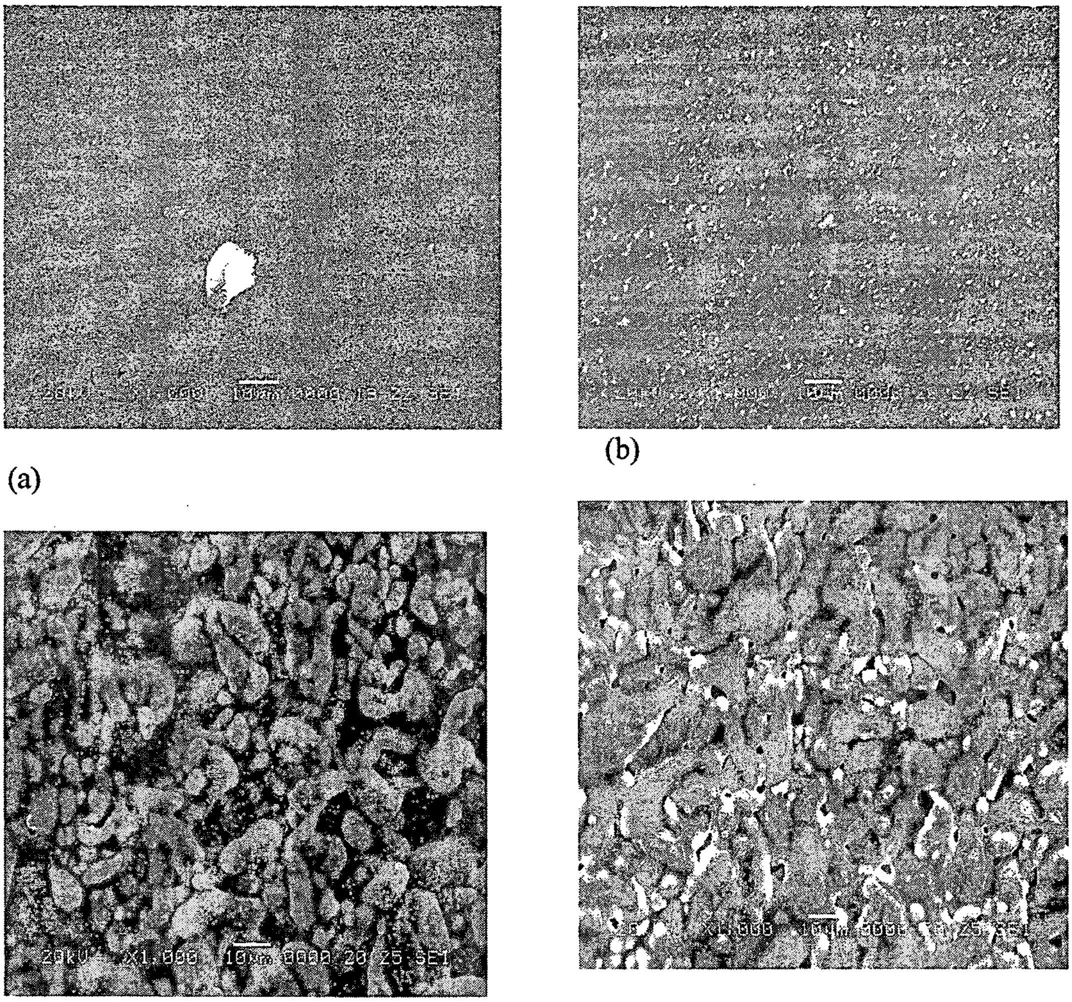


Fig.4.24 AFM images of a) PVC+10% Al (pristine) (b) PVC+10% Al (at a fluence of 1x10^{12}ions/cm^2).(c) PVC+40% Al (pristine) (d) PVC+40% Al (at a fluence of 1x10^{12}ions/cm^2).



(a) (b) (c) (d)

Fig. 4.25 SEM images of (a) PVC+10% Al (pristine) (b) PVC+10% Al (at a fluence of 1×10^{12}ions/cm^2). (c) PVC+40% Al (pristine) (d) PVC+40% Al (at a fluence of 1×10^{12}ions/cm^2).

4.2.5 Conclusions

Metal particles filled in Polyvinylchloride films changed the dielectric properties of pure polymer significantly. Dielectric properties are further modified by SHI irradiation. This may be attributed to the hydrogen depleted carbon network formed due to removal of hydrogen and/or other volatile gases from the polymer matrix. AC electrical conductivity increases with frequency, concentration of aluminum particles and also increases with ion fluence. At high frequency, conductivity obeys universal power law. The increase of dielectric constant with temperature can be explained by the increase in the mobility of polar groups. The ac conductivity also increases as temperature increases for all pristine PVC/Al composites. The phenomenon, that is, an increase of conductivity (or a decrease of resistivity) with an increase of temperature is termed as negative temperature coefficient (NTC). XRD analysis of the pristine and irradiated samples shows that the crystallanity improved upon irradiation at low fluence and deteriorated on further increase of the fluence, which could be attributed to cross linking of polymer chains at low fluence and degradation at higher fluence. The effect of ion beam irradiation causes both chain scission and cross-linking processes in PVC/Al composites depending upon irradiation fluence. The scanning electron microscope (SEM) micrographs indicate that the agglomeration of aluminum particles dispersed within the PVC at the higher aluminum concentration, yielding a conductive path through the composites. It is also corroborated with electrical conductivity result. The average surface roughness of the composites also changed as revealed from AFM studied.

4.3 Copper filled PVC composites: Results and discussion

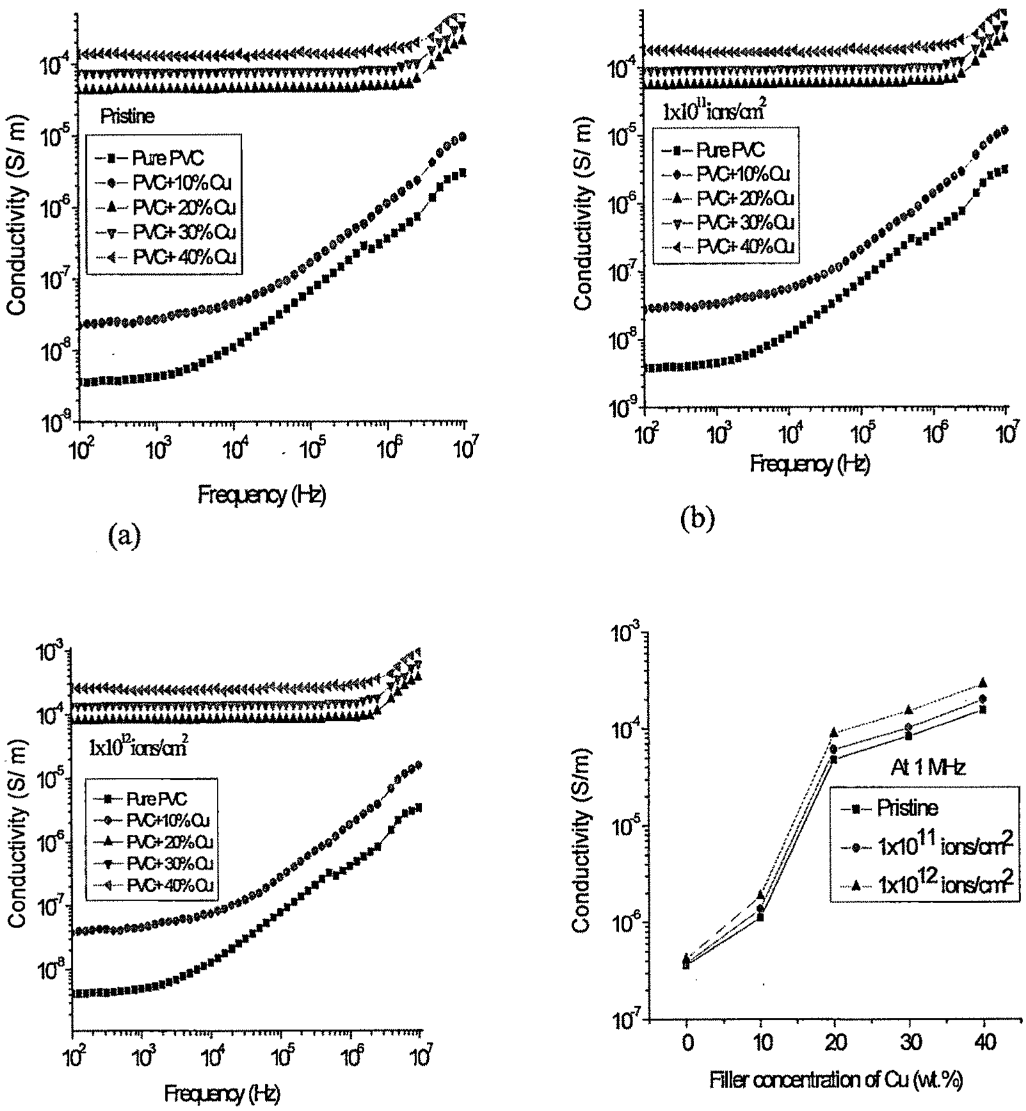
4.3.1 Electrical properties

(a) Frequency dependence ac conductivity

The variation of σ (AC conductivity) with frequency for different filler concentrations of copper (Cu) (i.e 0 to 40 wt%) and ion fluence is shown in Figure 4.26 (a-d) at ambient temperature. PVC is polar polymer with electrical conductivity in the order of 10^{-12} S/m and of the order of 10^{-8} S/m for pure copper metal at 20^0C [37,38]. Consequently, the electrical conductivity of Cu-filled composite is increased from that of pure polymer and hence a change in electrical conductivity with composition occurred. As shown in figure, 0 % and 10% composites behave as a insulating phase and after further doping at higher concentrations (20%, 30% and 40wt% Cu) samples show conductive behavior. At the percolation threshold, conductivity increased steeply as shown in Fig. 4.26 (d). A percolation threshold and drastic increase in electrical conductivity exists where the volume fraction of the filler becomes sufficient to provide continuous electrical paths through the polymer matrix [39]. The conducting elements of these paths are either making physical contact between themselves or separated by very small distances across which electrons can tunnel. It is also observed that the conductivity increases with increasing irradiation fluence. Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure into a hydrogen depleted carbon network due to emission of hydrogen and /or other volatile gases. It is this carbon network that is believed to make the polymer more conductive [19,20].

(a) Temperature dependence ac conductivity

Figs. 4.27 and 4.28 indicate that the conductivity increases many order of magnitude with increase in filler amount. It is also clear that the electrical conductivity increases by increasing temperature and showing the negative temperature coefficient of resistance.



(a)

(b)

(c)

(d)

Fig.4.26. Conductivity vs. frequency for PVC/Cu composites (a) Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm^2 (d) Conductivity vs. filler concentration at 1MHz.

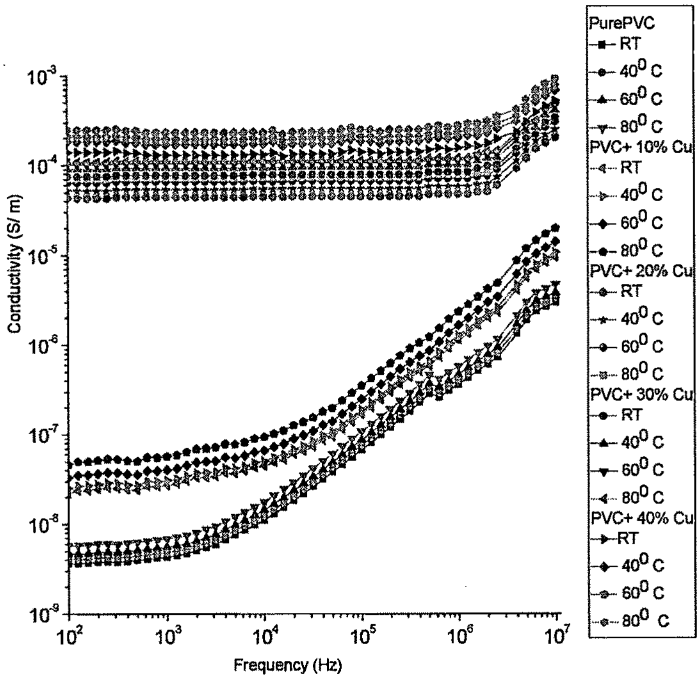


Fig.4.27 Variation of conductivity of PVC/Cu composites with frequency of applied electric field, concentration and temperature.

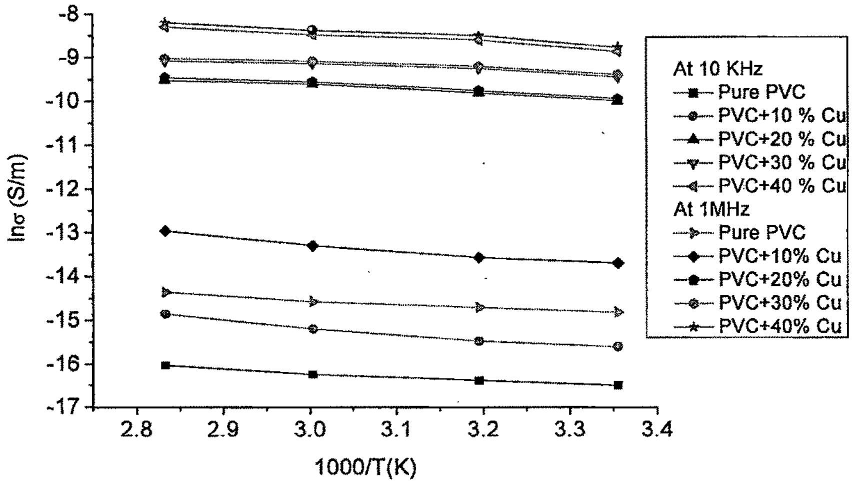


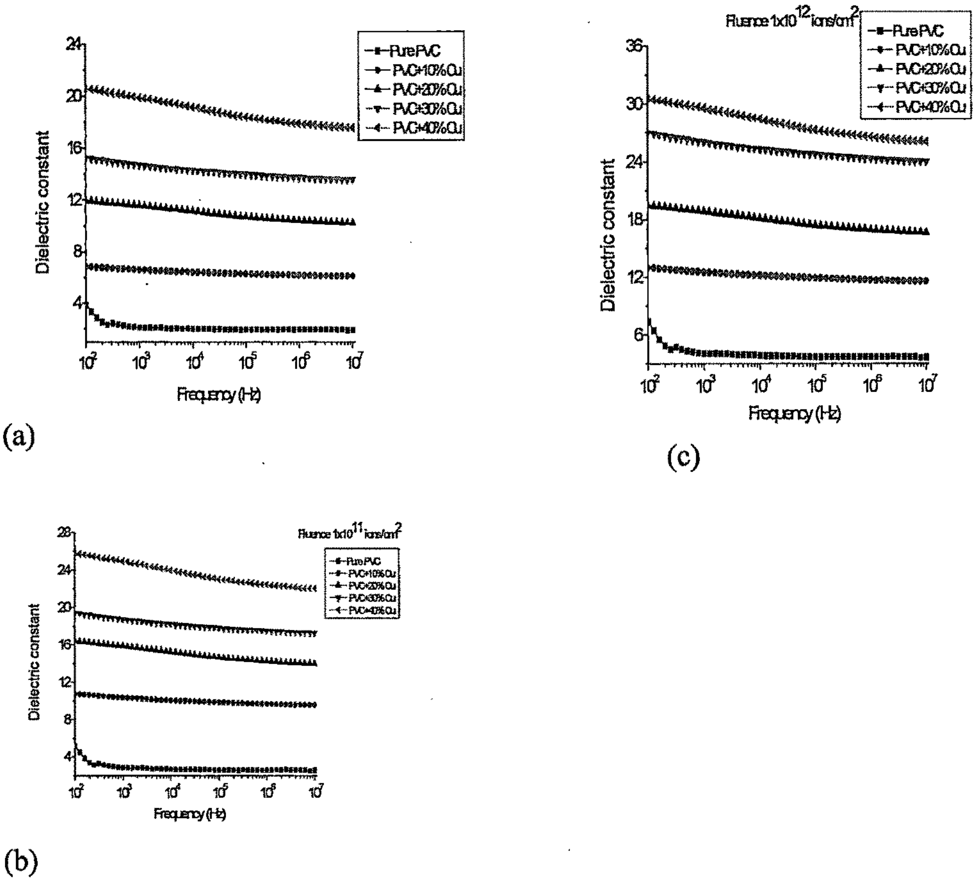
Figure. 4.28 Plot of natural log of conductivity (lnσ) versus inverse temperature, 1000/T [K] for PVC/Cu composites.

(b) Frequency dependence dielectric constant

Fig.4.29 (a-c) shows the variation of dielectric constant of PMMA/Cu composites as a function of frequency at different concentrations of Cu filler and at a different fluences. The increment in dielectric constant with filler content is a direct consequence of interfacial polarization effect between polymer and the filler particles. The polarization makes an additional contribution to the charge quantity. 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 [19].

(c) Temperature dependence dielectric constant

It is evident from Figure 4.30, which represents the variation of dielectric constant(ε') with frequency (f) at different applied temperatures for all pristine PVC/Cu composites. Fig.4.31 shows the variation of dielectric constant with applied frequency at two fixed frequencies. It is clear that the value of dielectric constant increases with increasing temperature because of two competing mechanisms occur in metal-polymer system when its temperature is raised : first, the increased mobility of segments of polymer molecules at elevated temperatures below the glass transition temperature; second, the differential thermal expansion of the polymer and metal (thermal expansion coefficient of PVC is greater than that of metal). The increased segmental mobility of polymer facilitates the orientation of dipoles, thereby leading to an increase in the dielectric constant [24].



(a)

(c)

(b)

Fig.4.29 Dielectric constant vs. frequency for PVC/Cu composites (a) Pristine and (b) Irradiated at a fluence of 1x10^{11}ions/cm^2 (c) Irradiated at a fluence of 1x10^{12}ions/cm^2.

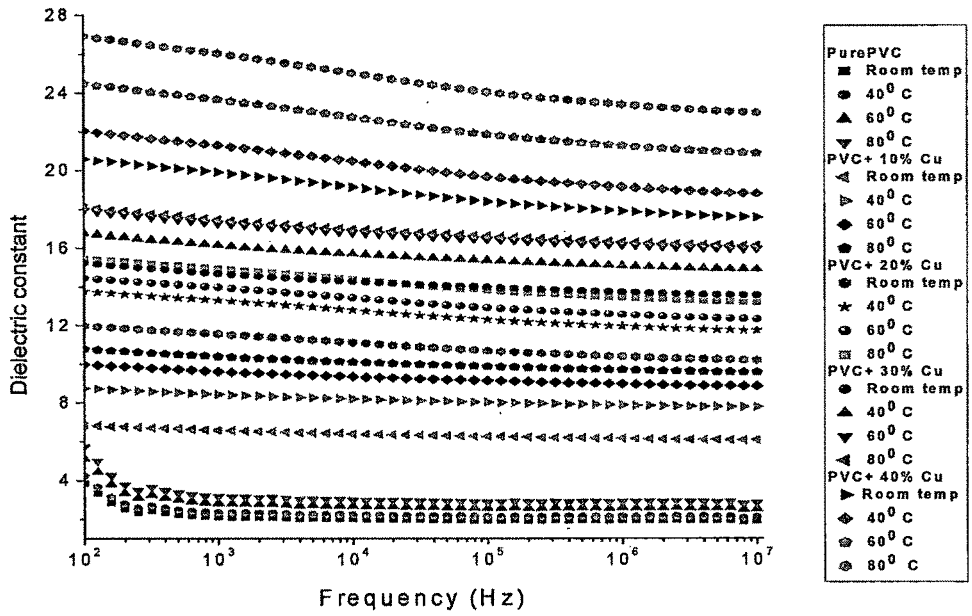


Fig.4.30 Variation of dielectric constant of PVC/Cu composites with frequency of applied electric field, concentration and temperature.

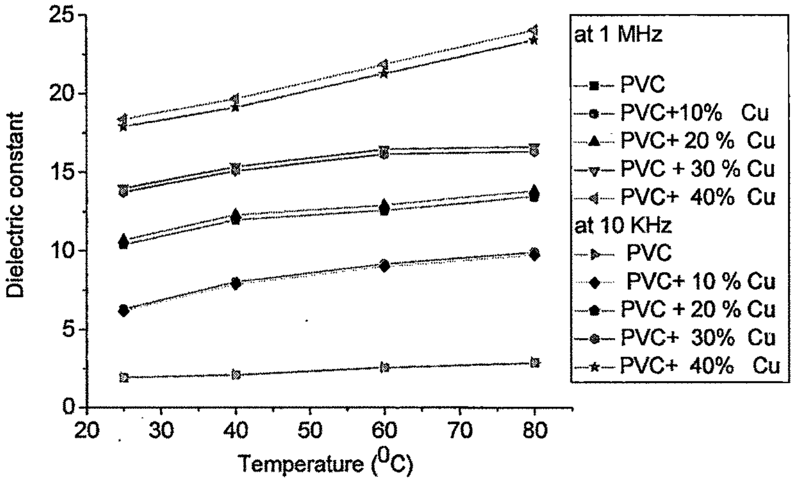


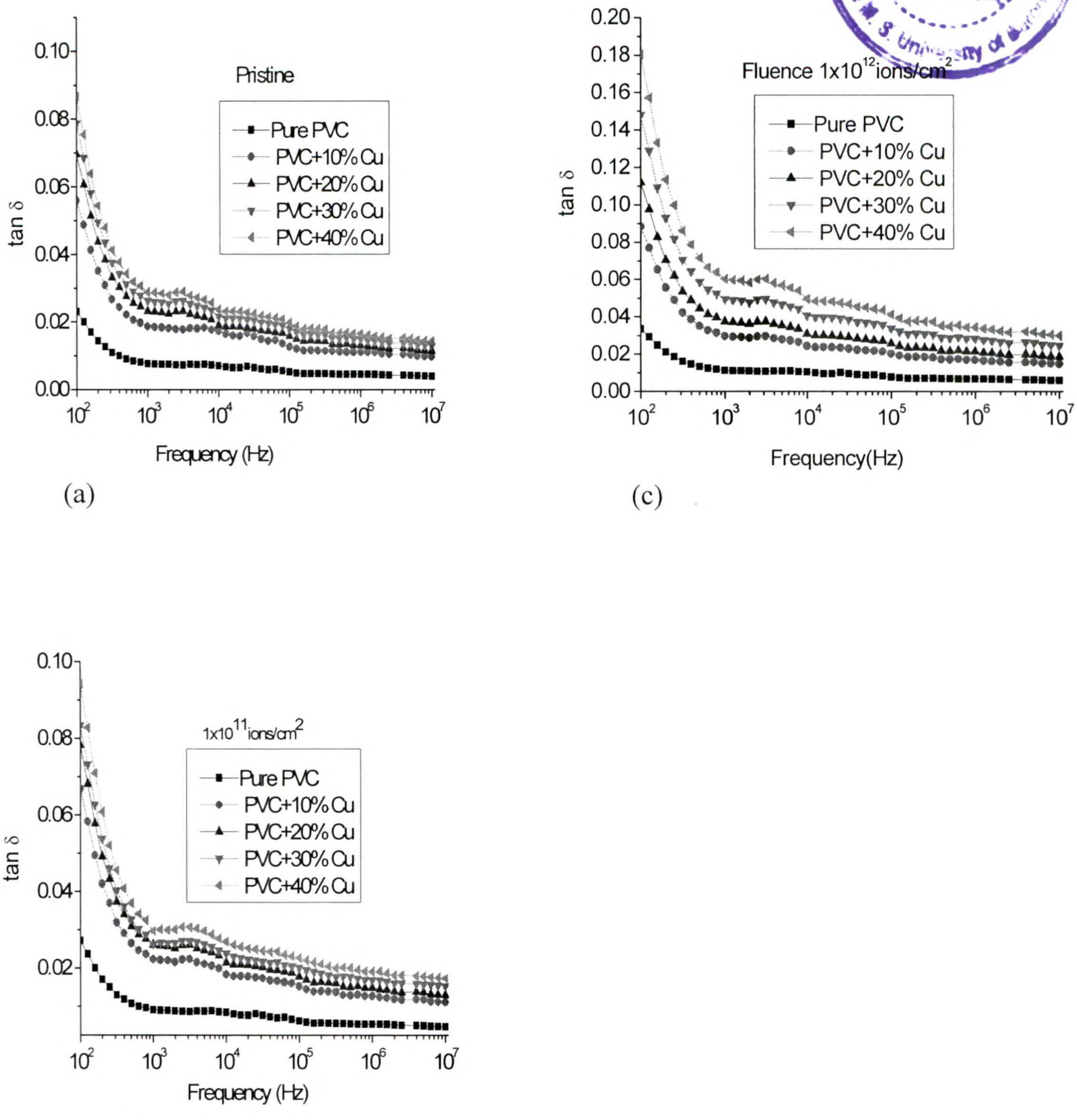
Fig. 4.31 Variation of dielectric constant versus temperature at different concentrations of PVC/Cu composites at two different frequencies.

(d) Frequency dependence dielectric loss

Fig 4.32(a-c) represents the dielectric loss versus frequency, filler concentration and ion fluence. It is observed that the value of dielectric loss is high at low frequency and decreases on increasing frequency. It is observed that loss factor increases with Cu concentration and also with the ion fluence. The growth in tan δ and thus increase in conductivity is brought about by an increase in the conduction of residual current and absorption current.

(e) Temperature dependence dielectric loss

Figure 4.33, which represents the variation of tanδ with frequency (f) at different applied temperatures for all pristine PVC/Cu composites. Fig.4.34 shows the variation of dielectric loss with temperature at two fixed frequencies. Dielectric loss value increases moderately with increasing temperature. The dielectric loss is due to the perturbation of phonon system by an electric field, the energy transferred to the phonon is dissipated in the form of heat.



(a)

(c)

(b)

Fig.4.32. Dielectric loss vs. frequency for PVC/Cu composites (a) Pristine and (b) Irradiated at a fluence of $1x10^{11}$ions/cm^2 (c) Irradiated at a fluence of $1x10^{12}$ions/cm^2

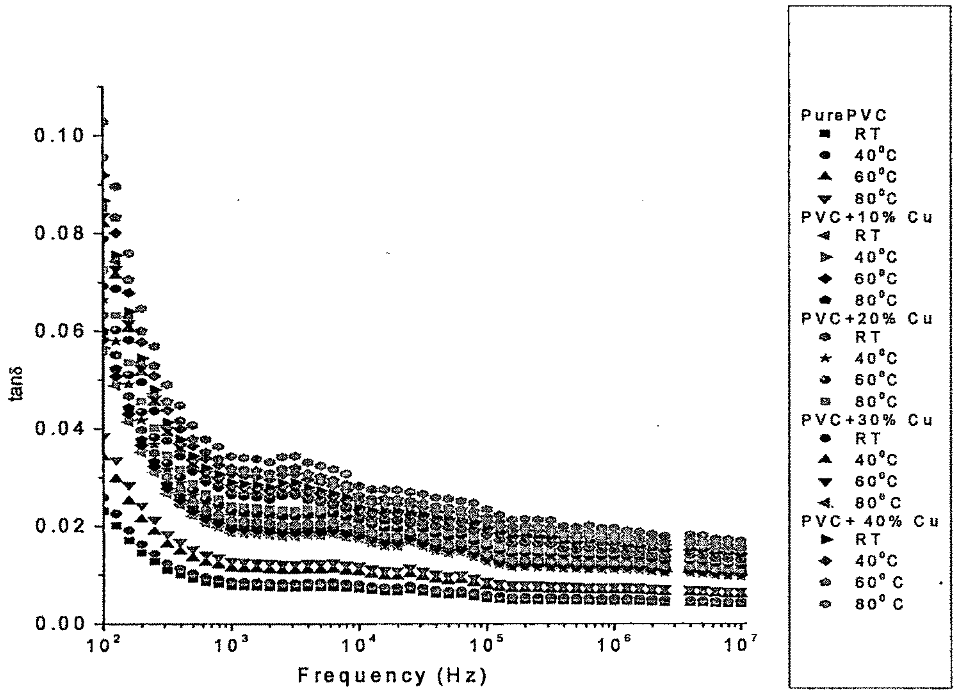


Fig.4.33 Variation of dielectric loss of PVC/Cu composites versus frequency of applied electric field, concentration and temperature.

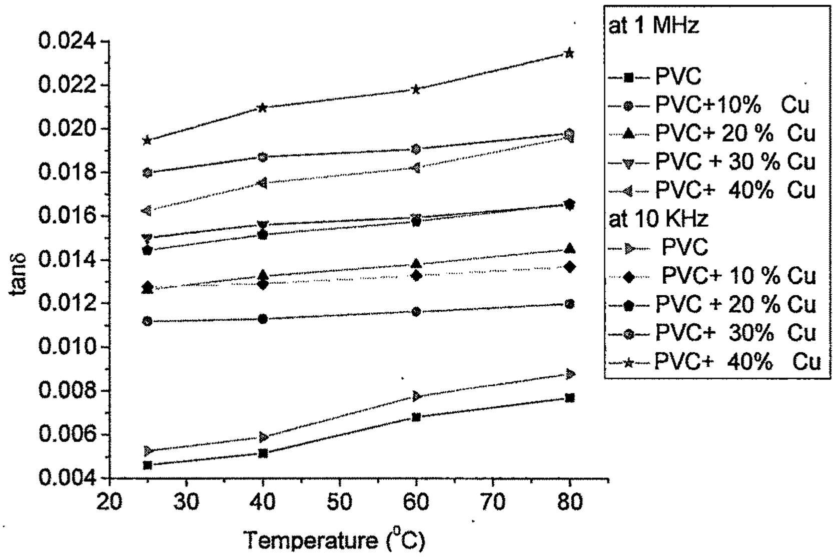


Fig. 4.34 Variation of dielectric loss versus temperature at different concentrations of PVC/Cu composites at two different frequencies.

4.3.2 Differential scanning calorimatric (DSC) analysis

Fig. 4. 35 shows DSC thermograms of pristine PVC and PVC+40% Cu composite pristine and irradiated at two different fluences. The results reveal that the glass transition temperature (Tg) increases for the composite as compared to pure PVC. The increase in Tg of composites may be due to the interactions of Cu metal particles and PVC in more ordered state [27]. It is also observed that Tg of composite shifted towards higher temperature at a fluence of $1x10^{11}$ ions/cm^2, which reveals that the composite became more crystalline. On further increase of the fluence (ie. $1x10^{12}$ions/cm^2) , Tg shifted to lower temperature, which reveals that the irradiation leads to chain scission and subsequently reduction in molecular weight. As a result, the system is changing towards disordered state.

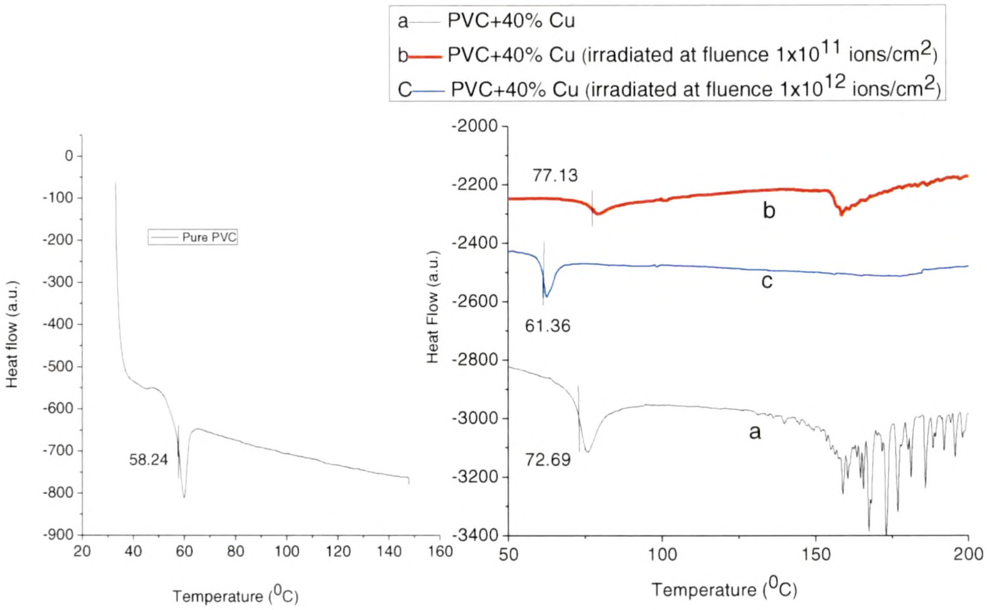


Fig.4.35 DSC patterns for pure PVC (pristine) and pristine and irradiated PVC+40% Cu composites at two different fluences.

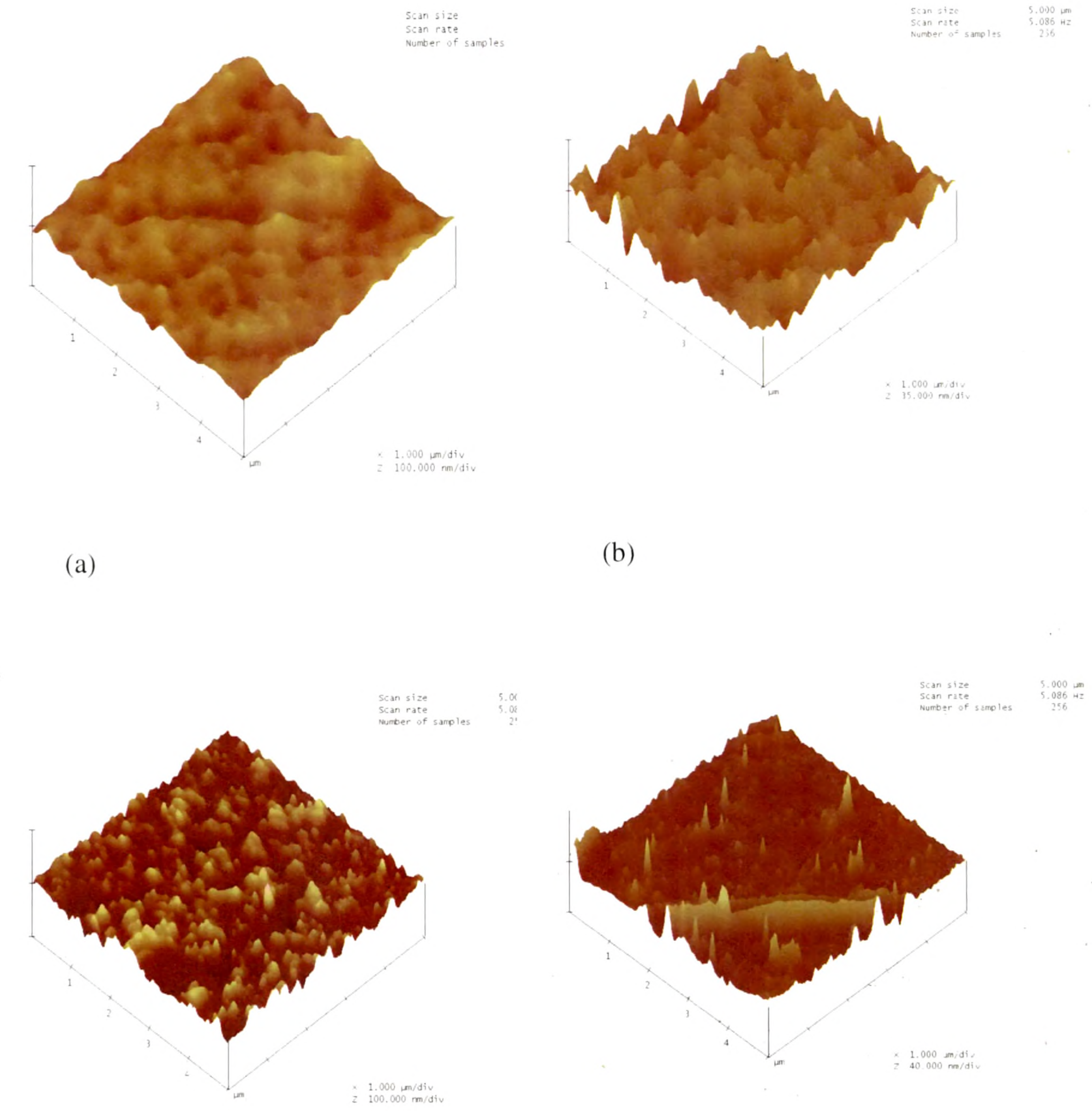
4.3.3 Surface morphology of composites

(i) Atomic force microscopy (AFM)

The surface morphology of pristine and irradiated films of PVC/Cu composites (10% and 40 %) was studied by AFM on 5x5 μm^2 area and shown in Fig. 4.36 (a-d). The average surface roughness values are increased from 12 nm to 16 nm and 24 nm to 38 nm respectively for 10 wt % and 40 wt % Cu dispersed PVC composites respectively after irradiation. The average surface roughness of the samples increased upon irradiation is attributed to the large sputtering effect due to the irradiation. However increase in roughness with filler concentration is attributed to increase in density and size of metal particles on the surface of PVC films.

(ii) Scanning electron microscopy (SEM)

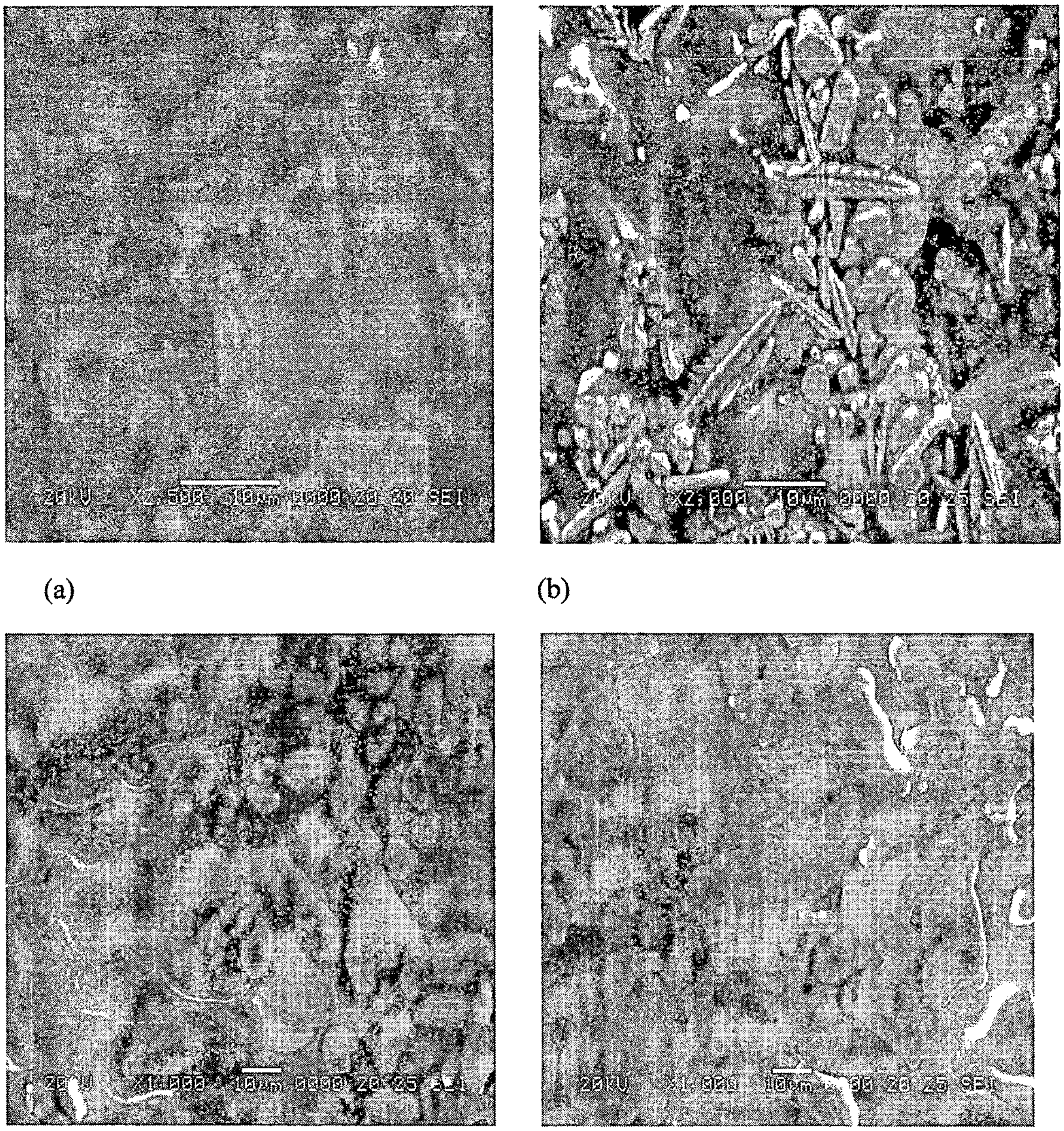
The morphologies of PVC containing different concentration of copper powder (10, and 40 wt.%) composites before and after irradiation are shown in Fig. 4.37 (a–d). It can be seen that at lower filler concentration (i.e.10 wt.%) Cu particles are discretely distributed (Fig 4.37 (a)) with relatively large inter-particles distances, such composite behaves as insulator. At the higher filler concentration (40 wt%), the SEM micrographs reveal large agglomerates of copper particles dispersed within the PVC, yielding a conductive network, as shown in (Fig 4.37 (b). Metal/polymer phases also increase due to ion beam irradiation as shown in Fig.4. 37(b,d).



(a) (b)

(c) (d)

Fig. 4.36 AFM images of (a) PVC+10%Cu (pristine) (b) PVC+10% Cu (fluence $1x10^{12}$ions/cm^2). (c) PVC+40%Cu (pristine) (d) PVC+40% Cu (fluence $1x10^{12}$ions/cm^2).



(a) (b)

(b) (d)

Fig. 4.37 SEM images of (a) PVC+10% Cu (pristine) (b) PVC+10% Cu (fluence $1x10^{12}$ions/cm^2). (c) PVC+40% Cu (pristine) (d) PVC+40% Cu (fluence $1x10^{12}$ions/cm^2).

4.3.4 Conclusions

The ion irradiation of polymer composites leads to the chain scission and cross-linking and as a result there are changes in the electrical, thermal properties and surface morphology of the composites. The conductivity of the composite systems exhibited a strong frequency dependence. Moreover, the dielectric constant tends to decrease moderately with increasing frequency while the conductivity displayed a reverse trend. It was observed that the dielectric properties and electrical conductivity gradually increased with filler concentration and also with ion fluence and was explained in terms of hopping conduction mechanism.

AC electrical conductivity increases by increasing temperature and showing the negative temperature coffiecent of resistance. Both dielectric constant and dielectric loss increased with increasing temperature. Thermal properties of PVC/Cu composites are analyzed by differential scanning calorimetry (DSC). An increase in glass transitions (Tg) was observed with increasing filler of copper particles and it also increases at lower irradiation fluence. Tg shifted to lower temperature on further increase of fluence. The microstructure was examined by means of SEM. The scanning electron microscope (SEM) micrographs indicate that the agglomeration of copper particles dispersed within the PVC at the higher copper concentration and yielding a conductive path through the composites. It is also corroborated with electrical conductivity result. The average surface roughness of the composites also changed as revealed from AFM studied.

4.4 Summary

The three types of composites containing CB/PVC, Al/PVC and Cu/PVC have been studied using 140 MeV silver ion irradiation. AC electrical, structural, thermal properties and surface morphology have been studied using different characterization techniques. The electrical properties of the three types of composites materials are compared over a wide range of frequency, filler concentration and ion fluence.

AC electrical conductivity of all pristine and irradiated composites at 40% filler concentration is shown in Fig. 4.38.

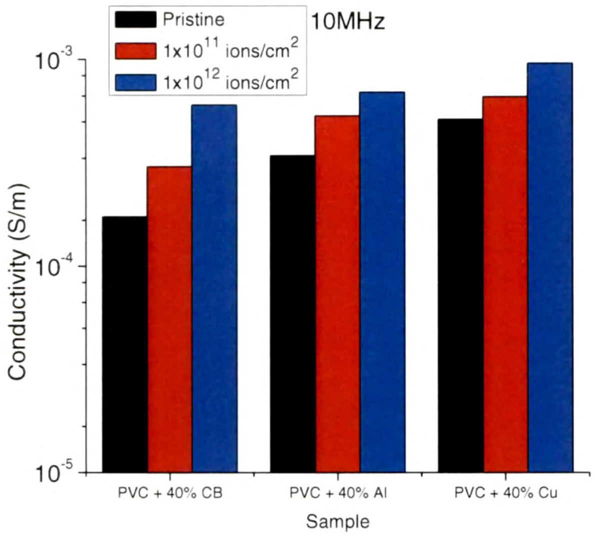


Fig.4.38 Comparison of conductivity of pristine and irradiated composites at two different fluences (i.e 1x10^{11} ions/cm^2 and 1x10^{12} ions/cm^2) keeping frequency constant (i.e. 10MHz).

The ac electrical conductivity of the samples was found to increase due to ion beam irradiation for all the three composites. It is assumed that an electrical conducting path and network of connections could be formed in the composites with increasing the content of the filler. It is known that electrical conductivity of such composites depends on the types and concentration of the fillers. Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure into a hydrogen depleted carbon network due to the emission of hydrogen and /or other volatile gases, which makes polymer more conductive.

The temperature dependence ac conductivity of pristine samples containing PVC/CB, PVC/Al and PVC/Cu composites have been studied over a wide temperature ranging from room temperature to 80^{0}C. The ac conductivity also increases as temperature increases in all cases. The phenomenon, that is, an increase of conductivity (or a decrease of resistivity) with an increase of temperature is termed as negative temperature coefficient (NTC).

Temperature dependence ac electrical conductivity of all pristine composites at 40% filler concentration and at a frequency of 10MHz is shown in Fig. 4.39.

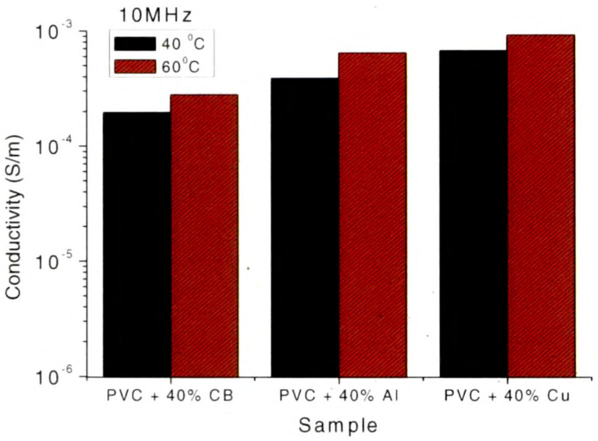


Fig.4.39 Comparison of conductivity of pristine samples for all composites at two different temperatures (40^{0}C and 80^{0}C) keeping frequency constant (i.e. 10MHz).

Both dielectric constant and dielectric loss of three different composites increased with an increase in concentration of filler, which has been attributed to interfacial polarization of heterogeneous system. The dielectric constant and dielectric loss were observed to increase upon irradiation. It is assumed that the system is moving towards disorder state.

For the interest of comparison, the composites with filler content (say 40 wt.%) are considered at two different fluences of ion beam irradiation (i.e. 1x10^{11} ions/cm^2 and 1x10^{12}ions/cm^2) keeping frequency constant i.e 10 MHz. The comparison for dielectric constant and dielectric loss is considered for all composites and shown in Fig. 4.40 and Fig. 4.41 respectively.

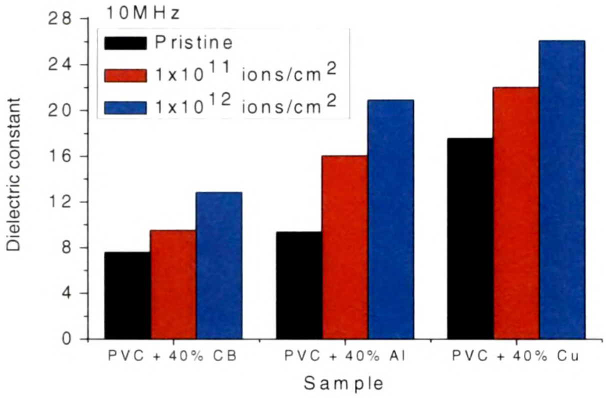


Fig.4.40 Comparison of dielectric constant of pristine and irradiated composites at two different fluences (i.e. 1x10^{11} ions/cm^2 and 1x10^{12} ions/cm^2) keeping frequency constant (i.e10MHz).

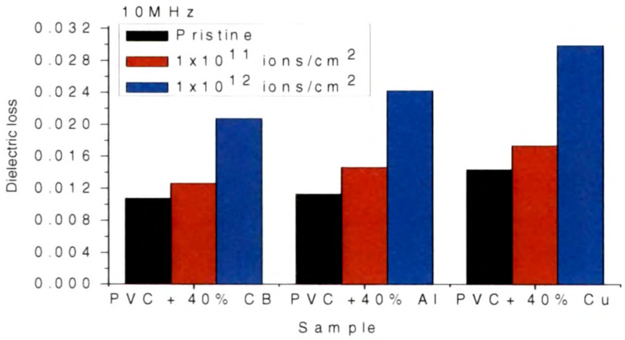


Fig.4.41 Comparison of dielectric loss of pristine and irradiated composites at two different fluences (i.e. 1x10^{11} ions/cm^2 and 1x10^{12} ions/cm^2) keeping frequency constant (i.e10MHz).

Temperature dependence dielectric constant and dielectric loss for all pristine composites at 40 wt % filler concentration and at a fixed frequency of 10MHz are shown in Fig. .4.42 and 4.43 respectively. The dielectric constant of the all conductor polymer composites system increased with an increase in temperature, which is attributed to the segmental mobility of the polymer molecules.

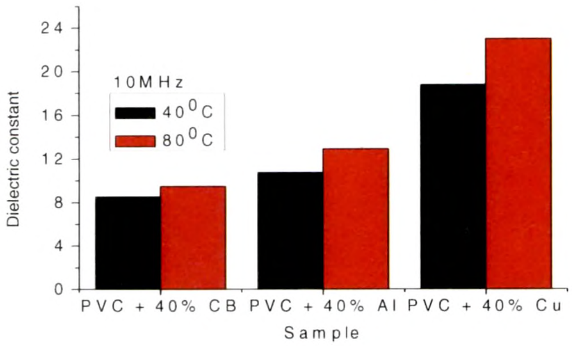


Fig.4.42 Comparison of dielectric constant of pristine samples for all composites at two different temperatures (40^{0}C and 80^{0}C) keeping frequency constant (i.e10MHz).

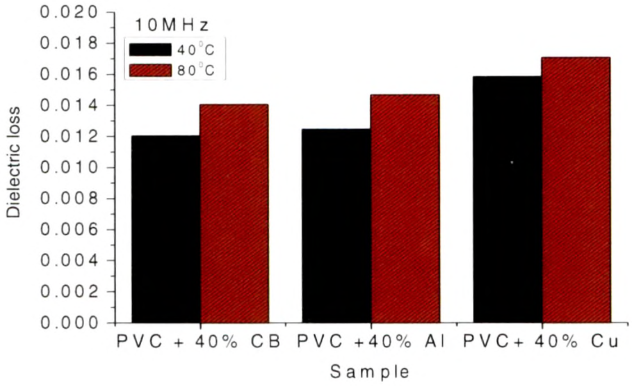


Fig.4.43 Comparisons of dielectric loss of pristine samples for all composites at two different temperatures (40^{0}C and 80^{0}C) keeping frequency constant (i.e10MHz).

Thermal analysis was carried out bsy means of DSC. The result reveals that the glass transition temperature (Tg) shifted towards higher temperature in comparison to the pure polymer, for the composites but decreases after irradiation in case of Carbon black composites. After irradiation Tg decreases, which reveals the amporphization of the composite after irradiation.

But in case of other two composites system i.e. PVC/Al and PVC/Cu, the glass transition temperature shifted towards higher temperature at a fluence of 1×10^{11} ions/cm^2, which reveals that the composite became more crystalline. On further increase of the fluence (ie. 1×10^{12}ions/cm^2) , Tg shifted to lower temperature, which reveals that the irradiation leads to chain scission and subsequently reduction in molecular weight. As a result, the system is changing towards more disordered state.

AFM study reveals that the average surface roughness decreases after irradiation in PVC/CB composites due to defect enhanced surface diffusion. But, in other two composites (i.e. PVC/Al and PVC/Cu), the average surface roughness increases after irradiation due to large sputtering effect from surface of the composites. In all cases, the average surface roughness increases with increasing filler concentration, which is attributed to increase in density and size of metal particles on the surface of composites. The microstructure was examined by means of SEM. The scanning electron microscope (SEM) micrographs indicate the agglomeration of conducting particles dispersed within the PVC at the higher filler concentration, yielding a conductive path through the composites. It is also corroborated with electrical conductivity result.

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