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International Journal of Current Research
Vol. 5, Issue, 10, pp.2840-2849, October, 2013

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

FAST NEUTRONS EFFECT ON THE DIELECTRIC PROPERTIES OF POLY (VINYL ALCOHOL)/HYDROXYPROPYL CELLULOSE BLENDS

[1]Mimouna M. Abutalib and *[2]Osiris W. Guirguis

[1]Physics Department, College of Science (Girls Branch), King Abdulaziz University, Jeddah, Saudi Arabia
[2]Biophysics Department, Faculty of Science, Cairo University, Giza 12613, Egypt

ARTICLE INFO

Article History:
Received 08th July, 2013
Received in revised form
10th August, 2013
Accepted 14th September 2013
Published online 10th October, 2013

Key words:
Poly (vinyl alcohol),
Hydroxypropyl cellulose,
PVA/HPC blends,
Fast neutrons irradiation,
Dielectric properties.

ABSTRACT

Thin transparent films of poly (vinyl alcohol)/hydroxypropyl cellulose (PVA/HPC) (100/0, 96/4, 92/8, 88/12, 84/16 and 0/100 wt/wt%) blends were prepared by using solution-cast technique. In the present study, the temperature-dependent (in the range 295-390 K) dielectric dispersion was used to probe the molecular mobility of the amorphous phase of the blend systems near the glass transition temperature (T_g). The dielectric properties on certain chosen blends (100/0, 92/8 and 88/12 wt/wt%) before and after irradiation with different fast neutron fluencies within the range from 10^5 to 10^8 n/cm^2 were investigated. The results noticed that all the samples face to changes in the values of the dielectric permittivity (ε'), dielectric loss tangent ($\tan\delta$) and a.c. electrical conductivity (σ_{ac}). The data also indicated that the measurable changes in the glass transition temperature (T_g) may be due to the fact that the position of T_g is strongly dependent on the molecular weight, purity and water content of the sample. These changes may be attributed to degradation process and/or to cross-linking process either by the presence of HPC with different concentrations or by irradiation with different fast neutron fluencies or both of them. This suggests that, the observed dispersion and the correlated barrier hopping mechanism depend on composition and temperature of blend matrix.

INTRODUCTION

The categories of materials that are used as biomaterials include metals, ceramics, carbons, glasses, modified natural biomolecules, synthetic polymers and composites consisting of various combinations of these material types (Dumitriu, 1996). The physical properties of polymers may be affected by doping. A graft copolymer is a type of branched copolymer with the side chain being different and separate from the main chain. Detailed studies of doped polymer with different dopant concentrations allow the possibility of choice of the desired properties (Abdullah and Hussen, 2010; Kulkarni and Sa, 2009). Blending is an especially important process for developing industrial applications of polymeric materials (Çaykara and Demirci, 2006). Blending, natural polymer with synthetic polymer seems to be an interesting way of polymeric composites. The selection and use of polymers can potentially form hydrogen bonds when two polymers mixed, as well as the study of blends properties, are of importance to find further applications of the resulting blend materials for biomedical and pharmaceutical devices (Kulkarni and Sa, 2009). Cellulose was blended with poly (N-vinyl-2-pyrrolidone) (Masson and Manley, 1991), poly (methyl methacrylate) (Nishioka *et al.*, 1993) and poly (2-hydroxy ethyl methacrylate) (Nisko and Hirose, 1992). Poly (vinyl alcohol) can be blended with poly (N-vinyl-2-pyrrolidone) (Nisko *et al.*, 1994), hydroxypropyl cellulose and hydroxypropyl methyl cellulose (Sakellariou *et al.*, 1993). Here, hydrogen bonding interaction is an important aspect of miscibility since intermolecular interactions regulate the compatibility among the component polymer molecules (Folkes and Hope, 1993). Poly (vinyl alcohol) (PVA) is a promising semi-crystalline material for biomedical applications (Ebru Oral *et al.*, 2007). PVA is a vinyl polymer with a semi-crystalline structure (Assender and Windle, 1998), and high tensile strength (Bodugoz-Senturka *et al.*, 2008). Because of its non-toxicity, it has been proposed in medical applications as a drug delivery vehicle (Peppas *et al.*, 2008; Sintzel *et al.*, 1996), sensor devices and as a substitute for cartilaginous tissue by itself (Swieszkowski *et al.*, 2006; Kobayashi and Oka, 2004; Kobayashi *et al.*, 2005; 2003; Oka *et al.*, 2000; Bray and Merrill, 1973) or as a blend with other polymers (Joshi *et al.*, 2006). Furthermore, PVA, a colorless, water-soluble synthetic resin employed principally in the treating of textiles and paper. PVA is used in sizing agents that give greater strength to textile yarns and make paper more resistant to oils and greases. It is also employed as a component of adhesives and emulsifiers, as a water-soluble protective film, and as a starting material for the preparation of other resins (Abdullah and Hussen, 2010). The hydroxyl side groups in PVA allow strong hydrogen bonding and render it highly crystallizable (Ricciardi *et al.*, 2004). PVA is a candidate hydrogel material for an interpositional spacer. It can be made into a hydrogel by either chemical or physical crosslinking. Chemical crosslinking can be achieved using functional crosslinking agents, such as gluteraldehyde, or by using ionizing radiation (Bodugoz-Senturka *et al.*, 2008). Ionizing radiation such as gamma or electron-beam produces two types of free radicals on PVA chains. The reaction of free radicals with diffused oxygen or hydroxyl free radicals in water causes eventual chain scission, whereas the combination of free radicals causes cross-linking. Although radiation causes predominantly chain scission in dry PVA (Bhat *et al.*, 2005), cross-linking prevails in aqueous solutions (Wang *et al.*, 1998). In addition, chemically crosslinked PVA hydrogel has been gaining increasing attention in the field of biomedics (Kim *et al.*, 2003). It is used in surgical devices, sutures, hybrid islet transplantation, implantation,

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***Corresponding author: Osiris W. Guirguis,**
Biophysics Department, Faculty of Science, Cairo University, Giza 12613, Egypt.

blend membrane (Saxena *et al.,* 1999), in synthetic cartilage in reconstructive joint surgery (Peppas and Merril, 1977), as a new type of soft contact lens (Eaga *et al.,* 2009), as sheets to make bags for premeasured soap, for washing machines, or to make longer bags used in hospitals (Dumoulin *et al.,* 1987).

The amalgamation of polymer and pharmaceutical sciences led to the introduction of polymer in the design and development of drug delivery systems. Polysaccharides fabricated into hydrophilic matrices remain popular biomaterials for controlled-release dosage forms and the most abundant naturally occurring biopolymer is cellulose (Kamel *et al.,* 2008). Hydroxypropyl cellulose (HPC) belongs to the group of cellulose ethers which has been used already for a year by paper of conservators as glue and sizing material. The material is soluble in water as well as in polar organic solvents (makes it possible to combine aqueous and non aqueous conservation methods) (Hofenk-de Graaff, 1981). HPC is used as a topical ophthalmic protectant and lubricant; as a food additive; a thickener and as an emulsion stabilizer with E number E463. In pharmaceuticals, HPC is used as a disintegrant and is a commonly used binder for the wet granulation method of making tablets (Ishikawa *et al.,* 2001). The aim of the present work is to enhance the dielectric properties of the poly (vinyl alcohol) (PVA) by preparing and characterizing thin transparent films of poly (vinyl alcohol)/hydroxypropyl cellulose (PVA/HPC) (100/0, 96/4, 92/8, 88/12, 84/16 and 0/100 wt/wt%) to be used in the field of bioequivalent materials. The study is carried out to explore the role of addition of HPC on the irradiation response of PVA films. The induced changes in dielectric permittivity (ε'), dielectric loss tangent (tan δ) and a.c. electrical conductivity (σ_{ac}) caused by both different concentrations of HPC and low-level fast neutron fluencies (10^5-10^8 n/cm^2) as functions of temperature in the range 295-390 K at three different frequencies (1, 10 and 100 kHz) are investigated on the prepared blends.

EXPERIMENTAL WORK

Materials and Sample Preparation

Poly(vinyl alcohol) (PVA) granules with molecular weight of 125 kg/mole was supplied from El-Nasr Company, Cairo, Egypt. Hydroxypropyl cellulose (HPC; Pharmacoat 606) with molecular weight of 95 kg/mole was supplied by Shin Etsu Chemical Co., Tokyo, Japan. Thin transparent films of poly (vinyl alcohol)/ hydroxypropyl cellulose (PVA/HPC) blend (100/0, 96/4, 92/8, 88/12, 84/16 and 0/100 wt/wt%) were prepared by using solution-cast technique (Osiris and Manal, 2011;2012;2013; Abutalib *et al.,* 2013; Suhas Nalle *et al.,* 2010; El-Zaher and Osiris, 2005). This method depends on the dissolution, separately, the weighted amounts of the poly (vinyl alcohol) (PVA) granules and hydroxypropyl cellulose (HPC) powder in double distilled water. Complete dissolution was obtained using a magnetic stirrer in a 50 ^{o}C water bath. To prepare thin films of the homopolymers (PVA and HPC) and the blend of their samples (PVA/HPC) with different weight percentages 100/0, 92/8, 88/12, and 0/100 wt/wt%, the solutions were mixed together at 50 ^{o}C with a magnetic stirrer. Thin films of appropriate thickness (about 0.01 cm) were cast onto stainless steel Petri dishes (10 cm diameter). The prepared films were kept at room temperature (ca. 25 ^{o}C) for 7 days until the solvent completely evaporated and then kept in desiccators containing fused calcium chloride to avoid moisture. The samples were measured at room temperature (about 25 ^{o}C) as solid films (slabs) of dimensions 1 x 4 cm. The prepare thin films of the blend of PVA/HPC were irradiated with fission neutrons with mean energy of approximately 4.2 MeV from Americium-Beryllium (241Am-Be) neutron source of activity 5 Ci (185 GBq) and with emission rate 0.87 x 107 n/s at the Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt. During irradiation the prepared samples were fixed in positions that neutrons were incident approximately normal. The irradiation temperature was adjusted to be about 25 ^{o}C. The films were exposed to four different fast neutron fluencies covers the range from 1 x 10^5 to 1 x 10^8 n/cm^2 (Abutalib *et al.,* 2013). The fast neutron fluence was measured using a calibrated TLD-700 Thermoluminescence detector at the location of the sample.

Dielectric measurements

For measuring the dielectric properties [the dielectric permittivity (ε′), dielectric loss tangent (tan δ) and a.c. electrical conductivity (σa.c.)] in three different frequencies (1, 10 and 100 kHz) and at different temperatures covering the range 295-390 K; the PVA/HPC blended samples were prepared in the form of discs of dimensions 1.2 cm in diameter and 0.01 cm in thickness. Good contacts were accomplished through painting both surfaces of the sample with air drying electrically conducting silver paste. The sample holder consists of two parallel plates of copper 1.2 cm diameter, the upper one being supported by a light pressure spring. Heating of the films during measurements was carried out using a locally manufactured double wound furnace with a copper tube inserted in it to ensure the uniformity of temperature. The temperature recorded by means of copper-constantan thermocouple placed near the sample. All the dielectric data were collected while heating at a rate of 1 ^{o}C/minute. The accuracy of the temperature measurements was within ± 1%. The dielectric parameters of the samples before and after irradiation with different fast neutron fluencies were carried out using a Hioki 3531Z Hiester Programmable Automatic RLC Meter (Japan). The dielectric permittivity (ε′) of the samples was calculated by measuring the capacitance C of the sample and can be given from the relation (El-Bassyouni *et al.,* 2013):

$$\varepsilon' = C/C_o$$

where

C_o is the capacitance of the vacuum capacitor which is given by:

$$C_o = \varepsilon_o \, A/d$$

ε_o is the dielectric permittivity of vacuum (= 8.85 x 1012 F/m), A is the sample area (in m^2) and d is the sample thickness (in m). The dielectric loss tangent (tan δ) is recorded directly from the RCL meter. The a.c. electrical conductivity (σ_{ac}) of the samples was obtained by measuring the resistance (R) of the sample and using its dimensions to calculate σ_{ac} using the relation:

$$\sigma_{ac} = (1/R)\,(d/A)$$

where A is the area of the sample, d is the thickness of the sample and f is the frequency in Hz. The accuracy of the dielectric measurements was within ± 1%.

RESULTS AND DISCUSSION

The investigation of dielectric properties of polymeric materials is one of the most methods of unravelling the origin of dielectric dispersion and relevant phenomena (El-Falaky *et al.,* 2012; Frübing, 2001; Fanggao *et al.,* 1996).

Dielectric permittivity

Figures (1a,b) represent the temperature dependence of the dielectric permittivity (ε') at three different frequencies (1, 10 and 100 kHz) for pure poly(vinyl alcohol) (PVA) and pure hydroxypropyl cellulose (HPC), respectively. It is clear from Fig. (1a) that, each **ε′**(T) curve reveals one pronounced peak appeared at about 342 K (about 69 ^{o}C) which is in agreement with that previously reported in the literatures (El-Zaher and Osiris, 2005; Garrett and Grubb, 1988; Tager, 1972). As the frequency increased, ε' of the PVA film at T_g showed a decreasing trend varying from 74 to 36 for frequency change from 1 to 100 kHz. The increase in ε' with temperature below T_g is explained in terms of facilitation in the orientation of dipoles present in the polymer. Above T_g the decrease in ε' with temperature is attributed to

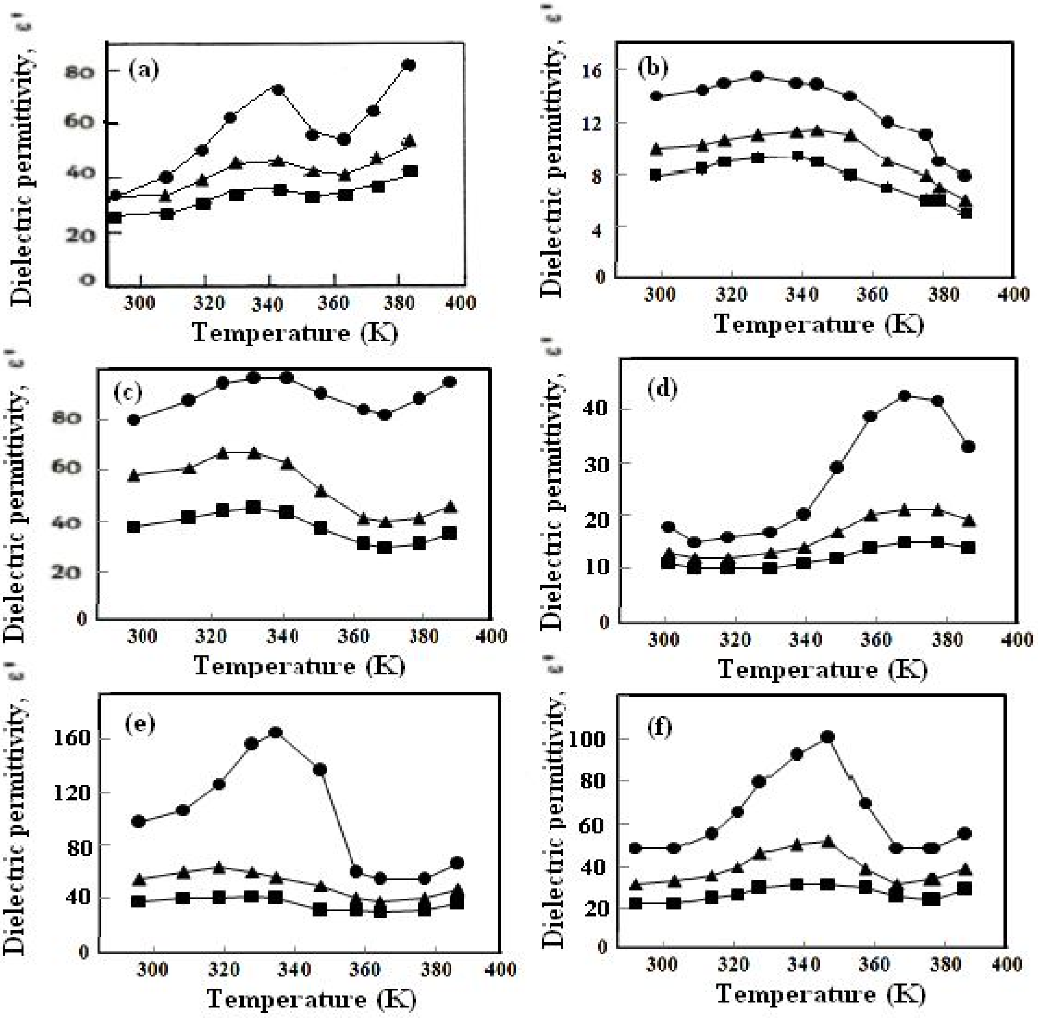

Figure 1: Dependence of dielectric permittivity (ε′) on temperature at different frequencies for PVA/HPC blended samples: (a) 100/0, (b) 0/100, (c) 96/4, (d) 92/8, (e) 88/12 and (f) 84/16 wt/wt%. (●) 1 kHz, (▲) 10 kHz and (■) 100 kHz.

the increase in chaotic thermal oscillations of the molecules and the diminishing degree of order of the orientation of the dipoles. The remarkable increase of ε' with temperature after the end of the glass transition temperature peak is indicating the effective role of the segmental movement associated with orientational rotation of the polar units of the macromolecular chain in the high elastic state (Eaga *et al.,* 2009). Besides, the peaks observed in **ε′**(T) curves, T_g were found to shift towards lower temperature (about 338 K) with increasing frequency. This can be explained as at low frequencies, the polar molecules have sufficient time to reorient themselves in the direction of the applied electric field even at low temperatures when the viscosity is high, while as the frequency increases, the dipoles do not have sufficient time for orientation along the filed direction at the same temperature (Frübing, 2001). If the temperature is increased the viscosity of the medium decreases and the dipoles acquire sufficient mobility for orientation, hence, as the frequency of the applied field increases, the peak in the **ε′**(T) curves shift towards lower temperatures. On other hand, it is noticed from Fig. (1b) for pure HPC that, **ε′**(T) values for HPC are slightly changes by both temperature and frequency over the whole investigated ranges. The general variation of ε' is conformity with that already reported previously for many polymers (Tager, 1972). The temperature dependence of the dielectric permittivity at different frequencies for PVA/HPC blended samples is shown in Figs. (1d-f). It can be seen that there is one peak characterizing the glass transition temperature of the composite samples. Also, it is clear from the figures that, the dielectric analysis of the blends yields broadness in the peak corresponding to T_g for pure PVA and appears as a shoulder.

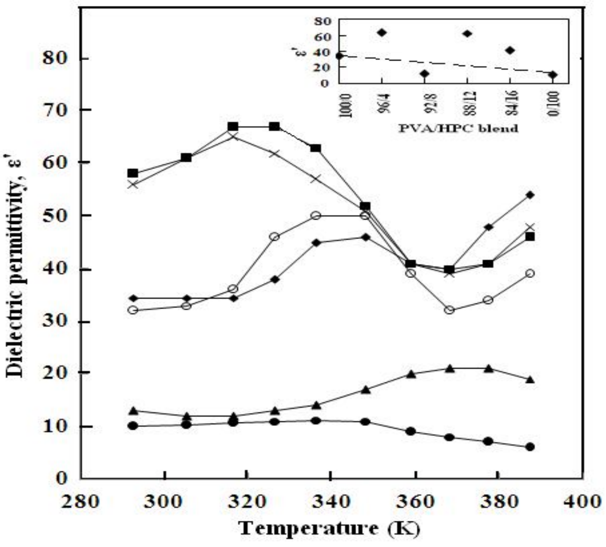

Figure 2: Temperature dependence of the dielectric permittivity (ε′) for PVA/HPC blended samples at 10 kHz: (♦) 100/0, (■) 96/4, (▲) 92/8, (x) 88/12, (o) 84/16 and (●) 0/100 wt/wt%. The inset of the figure shows the variation of ε′ as a function of HPC concentration at 10 kHz and 310 K.

Figure 2 shows the temperature dependence of the dielectric permittivity (**ε′**) for PVA/HPC blend samples at 10 kHz. It can be seen that as the temperature increases the values of ε' for each particular blend increase. In addition, ε' values of the blend sample of

92/8 wt/wt% are lower than that of the pure PVA sample in the range of temperature under study. On the other hand, 96/4, 88/12 and 84/16 wt/wt% blended samples show higher values of ε' in comparison with the pure PVA sample over the whole temperature range. Accordingly, mixing of PVA and HPC biopolymers are expected to increase the number of charge carriers considerably in the polymer network. It is possible to consider the effect of interfacial polarization or Maxwell-Wagner effect which exists only in multiphase systems of inhomogeneous polymeric materials in which the phases present possess different permittivities and conductivities (El-Falaky *et al.,* 2012; Garrett and Grubb, 1988; Tager, 1972). At higher percentage of HPC, it acts predominantly as an intermolecular plasticizer where the HPC molecules are distributed in the inner-aggregate space. This will hinder the polymer chain elongation and consequently may result in the decrease of the dielectric permittivity (Tager, 1972). Considerable change in the position of T_g in PVA/HPC blends was detected and represented in Table 1. The data observed indicated that the measurable changes in T_g may be due to the fact that the position of T_g is strongly dependent on the molecular weight, purity and water content of the sample.

Figures (3a-c) illustrate the temperature dependence of dielectric permittivity (ε') for 100/0, 92/8 and 88/12 wt/wt% blended samples, respectively, before and after irradiation with different fast neutron fluencies in the range 10^5-10^8 n/cm^2 at 10 kHz. It is clear from Fig. (3a) for pure PVA that, the ε'(T) curve at neutron fluence 106 n/cm^2 shows an increase in the magnitude of ε' over the whole temperature range from 295 to 390 K in comparison with unirradiated one. This may be attributed to the increase in the degree of ordering inside the PVA molecules and/or the induced dipoles due to irradiation (Salama *et al.,* 1988). This radiation induced degradation on the polymer network. The other neutron fluencies (10^5, 10^7 and 10^8 n/cm^2) show a decrease in the magnitude of ε' over the whole temperature range than that of the unirradiated one. This observation may be due to the process of cross-linking that occurs as a result of the reaction between the polymeric free radicals that occur as results of irradiation to change the chemical structure of the polymer and hence alter its dielectric properties (Garrett and Grubb, 1988; Salama *et al.,* 1988). Besides, cross-linking and degradation, evolution of hydrogen may also take place due to irradiation of the polymer material. The inset of the figure shows the behavior mentioned above for unirradiated and irradiated pure PVA at 10 kHz and 310 K. It is observed that the value of ε' at neutron fluence 10^6 n/cm^2 is higher than that for the unirradiated sample and the values of ε' at fluencies 10^5, 10^7 and 10^8 n/cm^2 are smaller than that for the unirradiated one. Furthermore, it is clear from the figure that, by irradiating PVA samples with fast neutrons, the values of T_g at the peak (ε'_{max}) show a dramatic variation (Table 2). The position of T_g is dependent on the degree of crystallinity, the microstructure and molecular weight of the polymer. It is noticed from Table 2 that, the observed shift of T_g towards lower temperature side may be attributed to the predominance of the degradation process. While the shift of T_g towards higher temperature side indicates the predominance of the cross-linking process. From Fig. (3b) for 92/8 wt/wt% blend, the curves show that ε' of irradiated samples with neutron fluencies 10^5 and 10^8 n/cm^2 have higher values than the unirradiated one over the whole temperature range. Increasing the neutron fluencies (10^6 and 10^7 n/cm^2), shows unremarkable change in the values of the dielectric permittivity up to the glass transition point. The above variation indicates that the radiation induced changes in the chemical structure as well as physical properties of the polymer and alteration in its chemical bonds through degradation and/or cross-linking process (Garrett and Grubb, 1988; Salama *et al.,* 1988). The inset of the figure shows the behavior mentioned above for unirradiated and irradiated PVA/PHC blend at 10 kHz and 310 K. From Table 2, it is observed that the position of T_g peak is largely shifted to low temperature values by irradiation with fast neutrons fluencies up to 10^8 n/cm^2. It is noticed from Fig. (3c) for 88/12 wt/wt% blended sample that, the ε' of irradiated samples with neutron fluence 10^8 n/cm^2 has higher value over the whole temperature range while neutron fluencies 10^5, 10^6 and 10^7 n/cm^2 have lower values than that of the unirradiated one (see the inset of the figure). As previously discussed irradiation with fast neutrons causes induced changes in the chemical structure as well as alters the physical properties of the polymer. Cross-linking process is the predominant process for samples irradiated with fluencies 10^5, 10^6

Table 1. Values of the glass transition temperature (T_g) for PVA/HPC blended samples at 10 kHz

Blended samples PVA/HPC (wt/wt%)	100/0	96/4	92/8	88/12	84/16	0/100
Glass transition temperature, T_g (K)	340	322	373	317	342	336

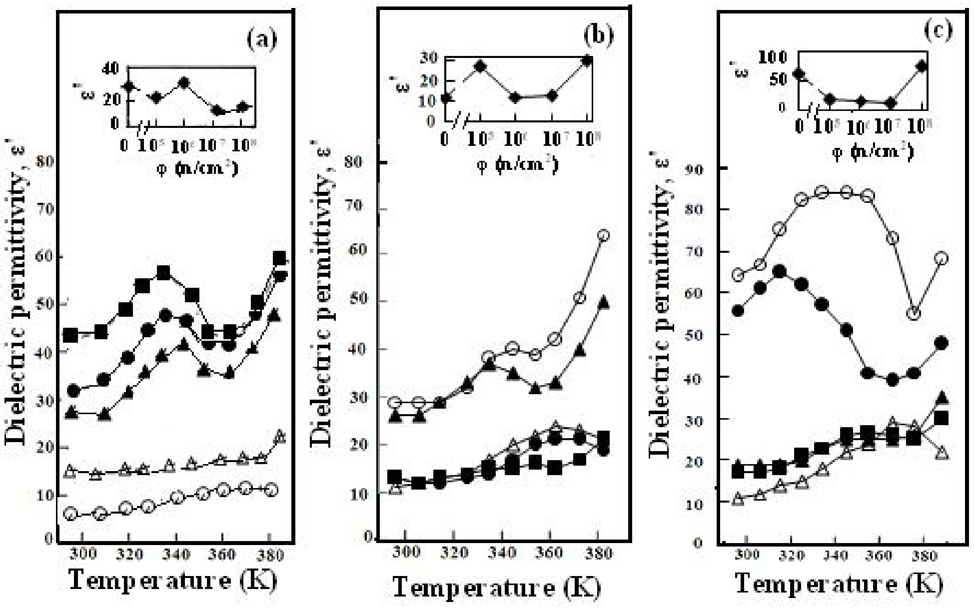

Figure 3: Temperature dependence of the dielectric permittivity (ε′) for unirradiated and irradiated 100/0 (a), 92/8 (b) and 88/12 wt/wt% (c), PVA/HPC blended samples with different fast neutron fluencies at 10 kHz: (●) unirradiated, (▲) 1 x 10^5, (■) 1 x 10^6, (Δ) 1 x 10^7 and (○) 1 x 10^8 n/cm^2. The inset of the figure shows the variation of ε′ as a function of neutron fluencies (φ) at 10 kHz and 310 K.

and 10^7 n/cm^2 followed by degradation by increasing the neutron fluence up to 10^8 n/cm^2. The position of the glass transition temperature (T_g) is largely shifted toward higher temperature values (Table 2).

Table 2. Values of the glass transition temperature (T_g) for unirradiated and irradiated with neutron fluencies for 100/0, 92/8 and 88/12 wt/wt% PVA/HPC blended samples

Neutron fluence (φ) (n/cm^2)	Glass transition temperature, T_g (K), for the blended samples (wt/wt%)		
	100/0	92/8	88/12
Unirradiated	342	371	314
1 x 10^5	343	347	354
1 x 10^6	334	356	354
1 x 10^7	357	366	365
1 x 10^8	370	347	339

Dielectric loss tangent (tan δ)

For polymers, two types of dielectric losses have been identified. The first type, called dipole segmental loss, which is associated with orientation rotation of polar units of the macromolecules under conditions, where segmental movement is possible which occurred in the vicinity of glass transition temperature (T_g). The second type, called the dipole-group loss, is due to orientation of polar groups themselves which occurred at a temperature lower than T_g of the material. The variations of the dielectric loss tangent (tan δ) with temperature at various frequencies for PVA/HPC blended samples are represented in Figs. (4a-f). It can be seen from Fig. (4a) for pure PVA that, tan δ curves exhibit one pronounced relaxation peak represents the glass transition relaxation (α-relaxation) of the amorphous region at about 66, 63 and 55 °C at 1, 10 and 100 kHz, respectively. In addition, tan δ values decreases with increasing the frequency over the whole temperature range. Moreover, tan δ_{max} values at T_g varies from about 3.8 to 1.3 for a frequency range from 1 to 100 kHz, as well as the peak positions were found to shift towards lower temperature with increasing frequency which is in agreement with the previously mentioned. The dielectric loss tangent peak is attributed to dipole-segmental loss which is to the rotation of the chain in segments. Moreover, it is clear from Fig. (4b) for the pure HPC that, tan δ values decrease by increasing frequency and exhibits independent behavior on temperature at frequency 100 kHz. From the obtained results (Figs. 4c-f), it is observed that on each tan δ spectrum, the usual shape of dielectric relaxation appears around the glass transition temperature (T_g) of amorphous regions. When the frequency is increased the temperature corresponding to the maximum of tan δ shifted towards higher temperature. However, the magnitudes of the loss peak decreased with increasing the frequency of measurement. It is also seen that there is a slight up turn in the loss factor at high temperature as a result of increased ionic mobility Huo and Cebe, 1992). Appearance of dielectric loss peaks has been reported in both polar as well as non-polar polymers (Sharma and Ramu, 1991). The variation of the dielectric loss tangent (tan δ) with temperature for PVA/HPC blended samples at constant frequency (10 kHz) is represented in Fig. (5). It is noticed that, tan δ shows different variations over the whole temperature range for the different concentrations of HPC. The inset of the figure at 10 kHz and 310 K indicates that addition of HPC with 4 and 12 wt% causes maximum increase in the magnitude of tan δ compared with the pure PVA and a decrease in tan δ values with HPC percentage weights 8 and 16 wt%. It is also clear from the figure that, the relaxation peak for blend sample 92/8 wt/wt% appears as a shoulder-like transition and

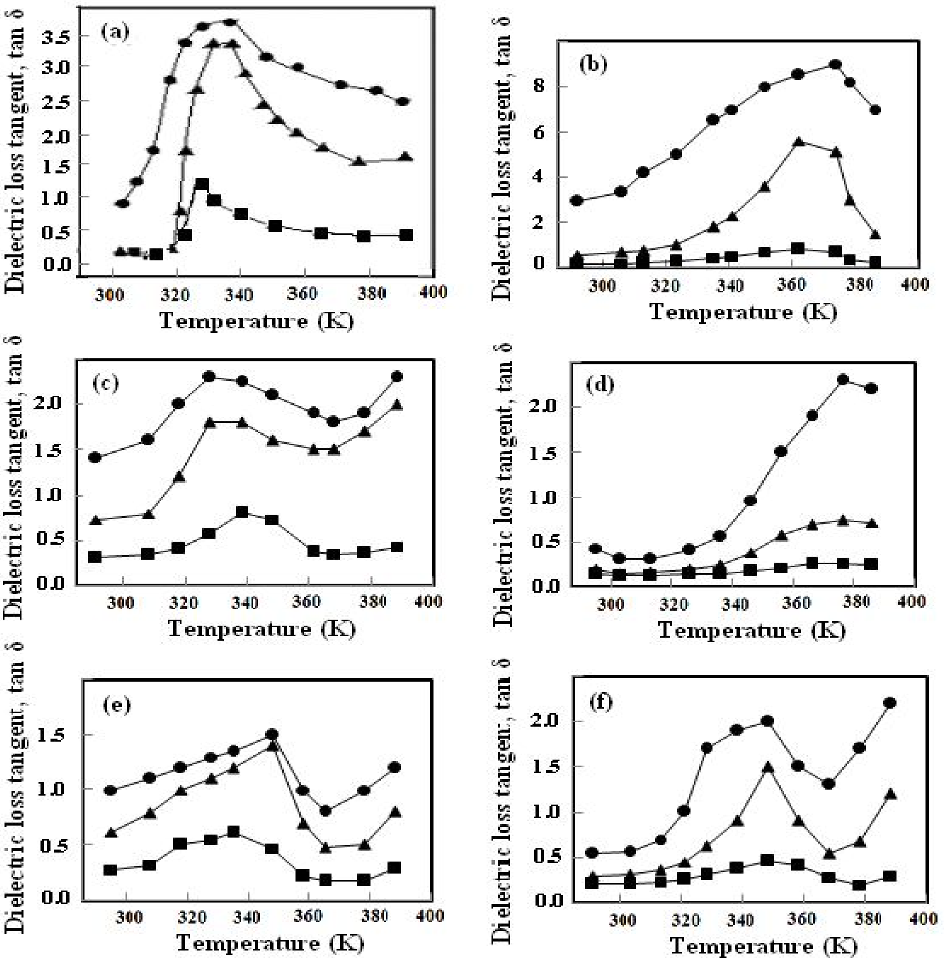

Figure 4: Dependence of the dielectric loss tangent (tan δ) on temperature at different frequencies for PVA/HPC blended samples: (a) 100/0, (b) 0/100, (c) 92/8 and (d) 88/12 wt/wt%. (●) 1 kHz, (▲) 10 kHz and (■) 100 kHz.

reappears as a peak at about 75 °C for 88/12 and 84/16 wt/wt% PVA/HPC blended samples. In the current case, the occurrence of the peak on each tan δ spectrum may be attributed to the dipole segmental loss where the rotation of the polar units is facilitated due to segmental motion. The temperature at which this occurs corresponds to the glass transition temperature (T_g). The tan δ spectra of 88/12 and 84/16 wt/wt% PVA/HPC blended samples show the same transition, but they are shifted towards higher temperature compared with pure PVA. One can expect that this peak appearing in the heterogeneous blends is clearly due to an interfacial polarization since its position and magnitude are dependent on the composition of the blend (Hedvig, 1977).

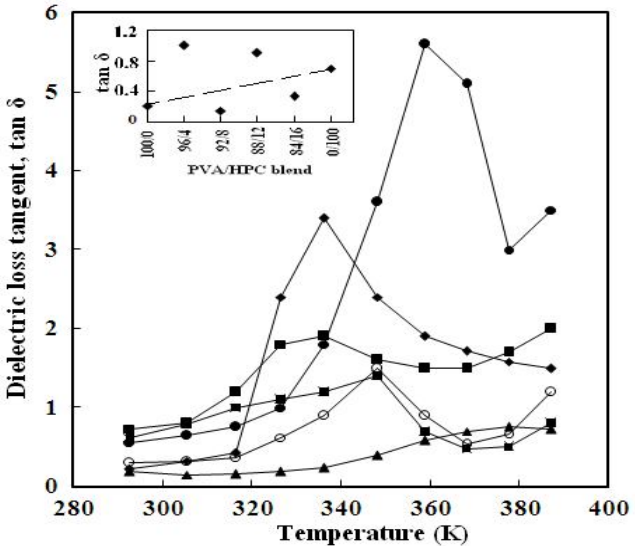

Figure 5: Temperature dependence of the dielectric loss tangent (tan δ) for PVA/HPC blended samples at 10 kHz: (♦) 100/0, (■) 96/4, (▲) 92/8, (x) 88/12, (o) 84/16 and (●) 0/100 wt/wt%. The inset of the figure shows the variation of tan δ as a function of HPC concentration at 10 kHz and 310 K.

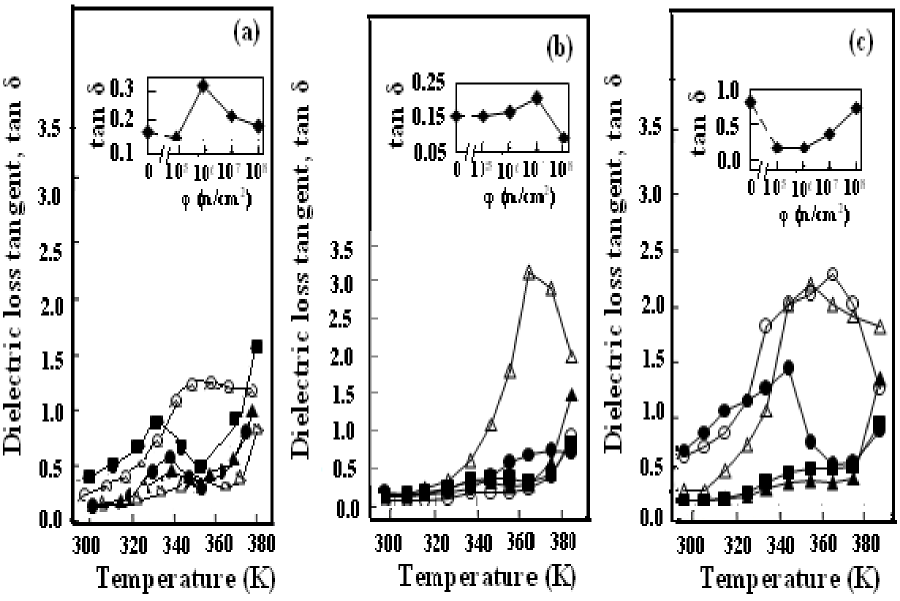

Figure 6: Temperature dependence of the dielectric loss tangent (tan δ) for unirradiated and irradiated 100/0 (a), 92/8 (b) and 88/12 wt/wt% (c), PVA/HPC blended samples with different fast neutron fluencies at 10 kHz: (●) unirradiated, (▲) 1 x 10^5, (■) 1 x 10^6, (Δ) 1 x 10^7 and (○) 1 x 10^8 n/cm². The inset of the figure shows the variation of tan δ as a function of neutron fluencies (φ) at 10 kHz and 310 K.

As known water can influence the dielectric relaxation of polymers in various ways (Suzuki *et al.,* 1981). It usually enhances the local relaxation process by dipole-dipole coupling and it can act as an effective plasticizer in polar polymers. If water can form a hydrogen bonded super-structure, it produces a very specific dielectric response, often termed, "anomalous low frequency dispersion" (Dissado and Hill, 1983). The essence of this kind of response is that both ε' and tan δ decrease with increasing frequencies as noticed from the obtained results. On the other hand, the arrangement of the polar groups is considered as a very important factor affecting the polymeric units' mobility. So that, if the electric field of this polar groups compensate one another, the polar bonds will be symmetrically arranged and consequently the polymeric chains will posses sufficient flexibility which increases the segmental movement of the polymer (Osiris *et al.,* 1999; Tager, 1972). This could be interpreted the increase in the value of tan δ with the increasing HPC contents.

Figures (6a-c) show the variation of dielectric loss tangent (tan δ) with temperature at frequency 10 kHz for 100/0, 92/8 and 88/12 wt/wt% PVA/HPC blended samples, respectively, before and after irradiation with fast neutron fluencies in the range 10^5-10^8 n/cm². As shown in Fig. (6a) for pure PVA sample, the values of tan δ increase with increasing the neutron fluencies up to 10^6 n/cm². This accompanied by shifts in the peak position of tan δ toward lower temperature (about 62 °C). For samples irradiated with neutron fluencies of 10^5 and 10^7 n/cm², the behaviors are very close to that of the unirradiated one. In addition, the inset of the figure shows a sharp increase in tan δ for fluence 10^6 n/cm² irradiated sample followed by a decrease with increasing the neutron fluences up to 10^8 n/cm², but still higher than the value of the unirradiated one. From Fig. (6b) for unirradiated and irradiated PVA/HPC blends, it is clear that the values of tan δ increase are nearly similar to that of the unirradiated one below the glass temperature points. Moreover, a sharp increase in tan δ values for fluence 10^7 n/cm² irradiated sample is detected. On the other hand, it is observed from Fig. (6c) for 88/12 wt/wt% PVA/HPC blended sample that the values of tan δ of unirradiated sample are higher than those of the irradiated values with different neutron fluencies below the glass temperature positions. As shown, the curves of 10^5 and 10^6 n/cm² irradiated samples indicate that tan δ are smaller than the unirradiated values over the whole temperature range. With increasing the neutron fluencies, the values of tan δ increase. Also, shift in the peak positions is observed for different neutron fluencies which indicate the presence of chemical changes in the polymeric repeating units. Moreover, the trend of the glass transition temperature (T_g) can be attributed to cross-linking process is predominant which it supposed to give a more rigid structure in which the movement of individual segments of the polymer chain is inhibited. It is recognized that HPC concentration and neutron irradiation plays a predominant role in both morphological and microstructure change occurring in the polymer matrix (Garrett and Grubb, 1988). Such blended sample behaves as a system in which one phase relaxes like the amorphous one while the existence of crystalline phase restrict the general long-range segmental motions in the amorphous phase characterizing a glass transition. Therefore, the variation of magnitude, peak position and broadening of the glass transition peak may be attributed to the change in the microstructure induced by the addition of HPC and fast neutron fluencies.

a.c. electrical conductivity (σ_{ac})

The reciprocal temperature dependences of a.c. conductivity ($\ell n\ \sigma_{ac}$) for PVA/HPC blended samples measured at different frequencies (1, 10 and 100 kHz) are shown in Figs. (7a-f). It is clear from Fig. (7a) for pure PVA (100/0 wt/wt%) that, the plots can be divided into segments and the values of σ_{ac} increase with increasing the temperature and frequency. It is also observed from Fig. (7b) for pure HPC (0/100 wt/wt%) that, the high temperature region for pure HPC sample obeys the normal Arrhenius equation (Perepechko, 1981): [$\sigma = \sigma_o \exp(-\Delta E/KT)$, where σ_o is a constant, ΔE is the thermal activation energy and K is the Boltzmann's constant]. Moreover, it is noticed that, the value of σ_{ac} increases by increasing the temperature in the high temperature region which may be due to the greater mobility through the amorphous region of HPC. It is noticed from Figs. (7c-f) for PVA/HPC blended samples that, σ_{ac} strongly dependent on frequency and HPC concentration. In addition, σ_{ac} increases by increasing the temperatures in the low temperature region (up to 80 °C), which may be accounted as liberation of more charge carriers or the greater mobility though the amorphous region of the sample. On other hand the decrease in σ_{ac} values above 80 °C with temperature for both pure PVA and its blended samples may be attributed to the decrease in mobility due to molecular aggregates while are formed by the inhomogeneous distribution produced above the glass transition temperature.

Figure 8 shows the reciprocal temperature dependence of a.c. electrical conductivity ($\ell n\ \sigma_{ac}$) for PVA/HPC blended samples at 10 kHz. It is seen that, the plots can be divided into two regions nearly obeying the normal Arrhenius equation (Perepechko, 1981). From the figure and its inset at 10 kHz and 310 K, it is noticed that 92/8 wt/wt% blended sample exhibits a minimum conductivity at all temperature points of measurements. As the concentration of HPC increases, the conductivity increases but still lower than that of the pure PVA sample. The increase in conductivity with temperature may be accounted by liberation of electrons or ions from traps or the greater ease of electrons or ions through the amorphous region of the blended samples. At concentration of HPC (4 and 12 wt%), the system formation is facilitated and delocalization of conduction electrons and/or ions carriers takes place, giving rise to higher conductivity (Ibrahim *et al.*, 1997). However, the relatively higher HPC concentration the mobility of charge carrier decreases, mostly due to scattering of ionized molecular aggregates. These molecular aggregates may be formed due to the inhomogeneous distribution of HPC as well as its non-bonding parts and hence the conductivity decreases. The obtained results may indicate morphological structure changes in the polymer matrix (Reddy, 1993).

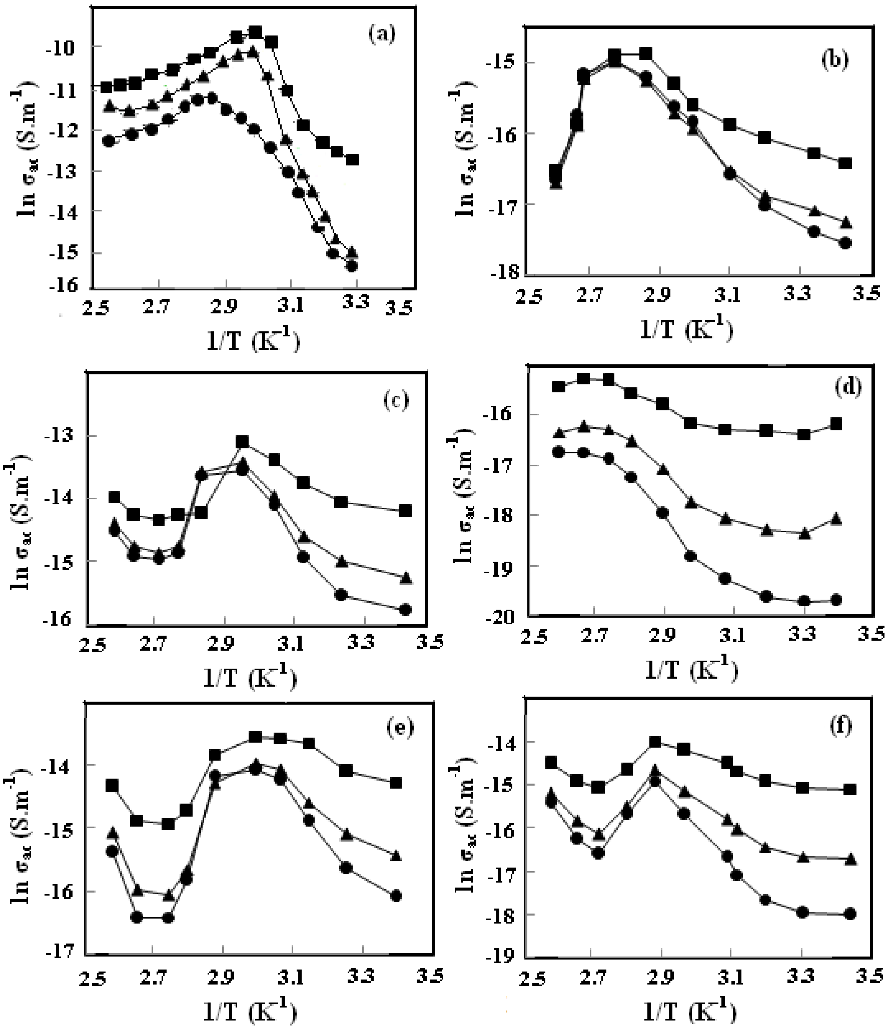

Figure 7: Reciprocal temperature dependence of the a.c. conductivity ($\ell n\ \sigma_{ac}$) for PVA/HPC blended samples at different frequencies: (a) 100/0, (b) 0/100, (c) 96/4, (d) 92/8, (e) 88/12 and (f) 84/16 wt/wt%. (●) 1 kHz, (▲) 10 kHz and (■) 100 kHz.

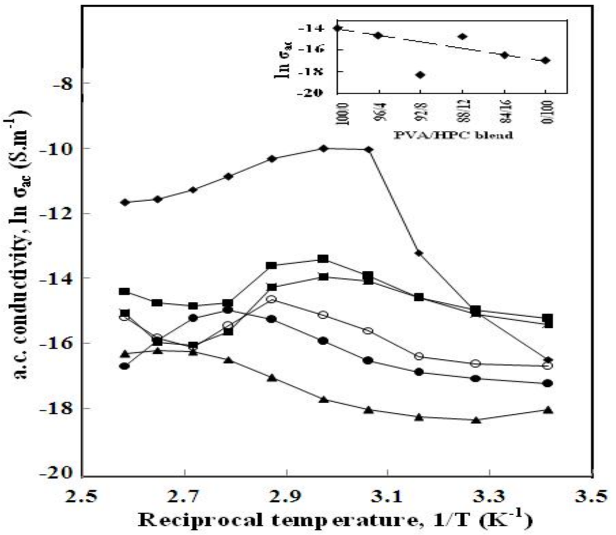

Figure 8: Reciprocal temperature (1/T) dependence of the a.c. conductivity ($\ell n\ \sigma_{ac}$) for PVA/HPC blended samples at 10 kHz: (♦) 100/0, (■) 96/4, (▲) 92/8, (x) 88/12, (o) 84/16 and (●) 0/100 wt/wt%. The inset of the figure shows the variation of $\ell n\ \sigma_{ac}$ as a function of HPC concentration at 10 kHz and 310 K.

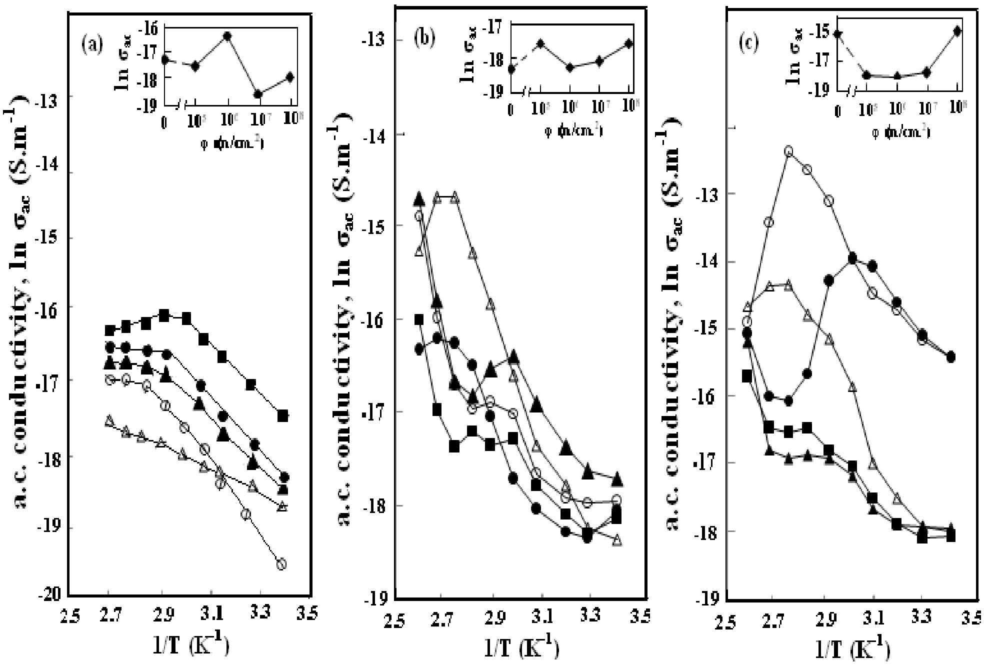

Figure 9: Reciprocal temperature dependence of the a.c. conductivity ($\ell n\ \sigma_{ac}$) for unirradiated and irradiated 100/0 (a), 92/8 (b) and 88/12 wt/wt% (c), blended samples with different fast neutron fluencies at 10 kHz: (●) unirradiated, (▲) 1 x 10^5, (■) 1 x 10^6, (Δ) 1 x 10^7 and (○) 1 x 10^8 n/cm^2. The inset of the figure shows the variation of $\ell n\ \sigma_{ac}$ as a function of neutron fluencies (φ) at 10 kHz and 310 K.

Figures (9a-c) show the reciprocal temperature dependence of a.c. electrical conductivity ($\ell n\ \sigma_{ac}$) for PVA/HPC blended samples at 10 kHz for unirradiated and irradiated samples, respectively. From Fig. (9a) for pure PVA samples, it is shown that at low temperature region (below 330 K) the neutron fluence 10^6 n/cm^2 exhibits maximum conductivity while by increasing the neutron fluencies up to 10^8 n/cm^2, a decrease in σ_{ac} is occurred. The increase in conductivity at low temperature may be attributed to degradation which occurs by the effect of neutron irradiation as well as by oxygen which produces oxidative degradation (Cygan and Laghari, 1989). On the other hand, the decrease in conductivity with increasing fast neutron fluences may be due to cross-links that formed inside the polymer matrix. The inset of the figure confirms the previously mentioned which means that degradation process predominate at neutron fluence irradiation 10^6 n/cm^2 (increase in σ_{ac}), while higher neutron fluencies caused cross-linking process predominate (decrease in σ_{ac}).It is clear from Fig. (9b) for 92/8 wt/wt% blended sample that with respect to the unirradiated value, irradiated sample with fluencies 10^5 and 10^7 n/cm^2 undergo maximum increase in the values of σ_{ac} with temperature below the glass temperature positions. At higher temperature region irregular trends can be observed. In addition from Fig. (9c) for 88/12 wt/wt% blended sample, sharp decrease in σ_{ac} due to neutron fluencies of 10^5, 10^6 and 10^7 n/cm^2 was followed by sharp increase in σ_{ac} with increasing the neutron fluence up to 10^8 n/cm^2. The inset of the figures show the dependence of σ_{ac} on neutron fluence (φ) for PVA/HPC blended samples at 10 kHz and 310 K. It is noticed that, the decrease of σ_{ac} with fast neutron is expected to be due to cross-linking formation inside the polymer matrix. On the other hand, the increase in σ_{ac} for samples irradiated with neutron fluencies may be expected to be due to the degradation which occurs by the effect of neutron irradiation as well as oxygen which produces oxidative degradation (Cygan and Laghari, 1989). Moreover, the decrease in σ_{ac} may be due to that the addition of HPC causes a decrease in the mobility of charge carriers due to scattering of ionized molecular aggregates which may be formed due to inhomogeneous distribution as well as the non-bonding parts of the blend. Furthermore, this behavior is well defined experimentally for a wide range of materials, the conduction of which occurs by hopping mechanism (Sharma *et al.*, 1991).

Acknowledgement

The authors are very grateful to Prof. Dr. Nabawia A. Abdel Zaher, Professor, National Institute for Standard, Giza, Egypt for her kind help to bring this work.

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