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Effect of X-ray Irradiation on Dielectric Properties of Polymer Electrolytes Complexed with $LiCF_3SO_3$

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Abstract: *Solid polymer electrolytes of polyethylene oxide (PEO) embedded with $LiCF_3SO_3$ was prepared and subjected to X-ray irradiation of different dosages (1.5 to 6 Gy). Ionic conductivity and dielectric studies were made over a frequency range of 100 Hz to 490 KHz. A little increase in ionic conductivity was noted for the sample irradiated for 1.5 Gy and the equivalent circuit remained unaltered for irradiated samples. Remarkable increase in dielectric constant was found for the irradiated samples. It was found that irradiation improved the dissolution of lithium salt and increased the polymer/Lithium interaction and thus improved the polarizability of the electrolyte. The frequency of hopping and liberation of free lithium ions were found altered by irradiation and hence the given dosage was found to have an optimum value in concern with the ionic conductivity of the electrolyte.*

Keywords: PEM fuel cell, polyethelene oxide, $LiCF_3SO_3$, dielectric properties

1. INTRODUCTION

Solid polymer electrolytes (SPE) are of great interest to many researchers due to its potential application in devices like rechargeable lithium ion batteries, electrochromic displays, fuel cells etc. It consists of salts dissolved in solid polymers. Among all polymers, Poly Ethylene Oxide (PEO) has been most extensively studied so far because of its efficiency in coordinating metal ions, due to the optimum distance and orientation of ether oxygen atoms in polymer chains [1]. But, it suffers from poor ionic conductivity of around 10^{-7} Scm^{-1} at room temperature in its pure form. Among various methods suggested to improve the conductivity, irradiation is found to be the best alternative. Irradiation of polymers result in the formation of gaseous products accompanied by polymer cross-linking or chain scission [2]. Cross-linking results in the formation of intermolecular bonds and chain scission results in the breaking of main and/or side chains of polymer backbone. X-ray irradiation was found to produce fruitful results in almost all areas wherever irradiation is suggested. X-ray irradiated polymers show loss of crystallinity, loss of mass or chemical modification [3, 4]. Hence, it is aimed to irradiate the polymer electrolyte with x-ray of different dosages in order to improve its performance electrically. PEO is semicrystalline in nature and hence the ionic conductivity is admitted to be happening by hopping through crystalline phase and by segmental motion through amorphous region. Thus, ionic conductivity in polymer electrolytes is very much coupled to the segmental motion of the host polymer. Therefore, more is the segmental mobility, higher is the ionic conductivity [5, 6]. Since, the polymer electrolytes have polar atoms (for solvating cations) in their backbone, one way to investigate their segmental mobility is using dielectric spectroscopy. Dielectric spectroscopy can also be used to study the ionic dynamics in the polymer electrolytes. The study of dielectric property of polymer electrolytes are important because it can be used as an indicator to prove that increase in ionic conduction is due to an increase in the number of free mobile ions in the polymer electrolyte.

In the present study, polymer electrolyte of polymer polyethylene oxide (PEO) embedded with lithium salt $LiCF_3SO_3$ (LiTf) have prepared and subjected to x-ray irradiation. The ionic conductivity of the electrolytes was studied using ac impedance spectroscopy and was analyzed using an equivalent circuit. The dielec-

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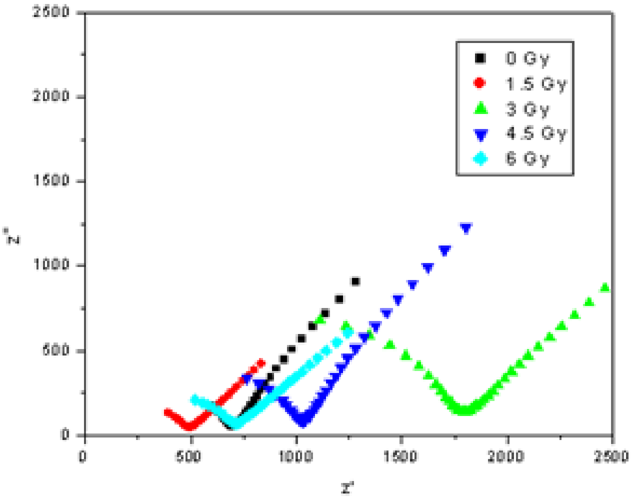

Figure 1. Cole-cole plot for the polymer electrolyte before and after irradiation.

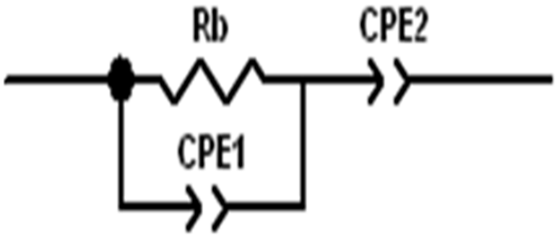

Figure 2. Equivalent circuit used to represent SPE.

tric constant and electric modulus have been obtained using electrochemical impedance spectroscopy. The conduction mechanism has been analyzed as a function of temperature and frequency for the samples obtained before and after irradiation.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Sample

PEO and LiTf (Sigma Aldrich) were dried under vacuum for 2 days at 40 and 60 °C respectively, to remove any moisture content in them. The PEO /$LiCF_3SO_3$ solid polymer electrolyte was prepared by dissolving 95 wt. % PEO and 5 wt. % lithium salt in acetonitrile and stirred overnight to get a homogeneous solution. The resulting solution was casted on a glass plate and the solvent was allowed to evaporate in the air at room temperature in dust free environment. Further, the films were pressed to thin membranes of 0.1 mm thickness using hot press apparatus. The temperature and pressure of the hot press were maintained at 90 °C and 5 torr, respectively. The temperature of hot press is sufficient enough to remove any traces present in the solvent. This process produced mechanically strong homogeneous membranes, which were dried under vacuum at 30 °C for 24 hours before subjected to characterization. The membranes were subjected to X-ray irradiation of four different dosages via; 1.5, 3, 4.5 and 6 Gy respectively. X-ray irradiation is given using c-arm Siemens clinical x-ray source with deliverance power of 5 radiance per exposure.

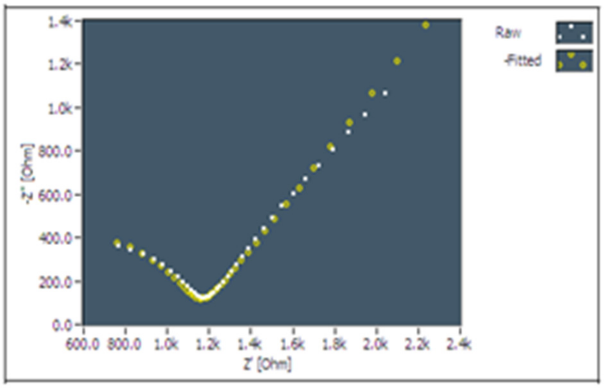

Figure 3. Fitted result before irradiation.

2.2. Material Characterization

The ac impedance spectroscopic analysis was carried out by ac impedance spectroscopic analyzer (ZAHNER IM6, Germany) with amplitude of 1 V in the frequency range between 100 Hz and 490 KHz. Dielectric spectroscopic data was obtained from the ac impedance data using the software IMSO. The equivalent circuit was analyzed using ZVIEW software.

3. RESULTS AND DISCUSSION

3.1. Ionic Conductivity

An electrochemical cell was formed using stainless steel as electrodes and the SPE as electrolyte. The cell impedance was measured in response to a small ac signal over a frequency range of 100 Hz and 490 KHz. The measured data is represented in terms of cole-cole plot for the samples obtained before and after irradiation, which is indicated in fig.1. By knowing the bulk resistance of the sample the ionic conductivity of the polymer electrolyte is calculated using the following equation [eq.(1) [7].

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where, t and A are thickness and area of the polymer electrolyte in contact with the electrodes respectively. The thickness of the film was measured by means of micrometer screw gauge. R_b represents the bulk resistance of the electrolyte film.

3.2. Electrical Circuit Modeling

The process of electrical circuit modeling is a very convenient method to analyze the impedance of thin film, corrosion, double layer etc. In this technique, an electrical circuit is modeled, which gives an impedance response identical to that of impedance obtained for the system studied. The electrical circuit is obtained by combining circuit elements called impedance elements. The impedance response of the SPE is best represented by an equivalent circuit, which is shown in fig.2. The impedance offered by this circuit element is similar to that of a resistor. CPE1 and CPE2 represent two constant phase elements. CPE is used to represent distorted capacitance. When an AC signal is applied, due to polarization effect internal capacitance is formed owing to dipole formation

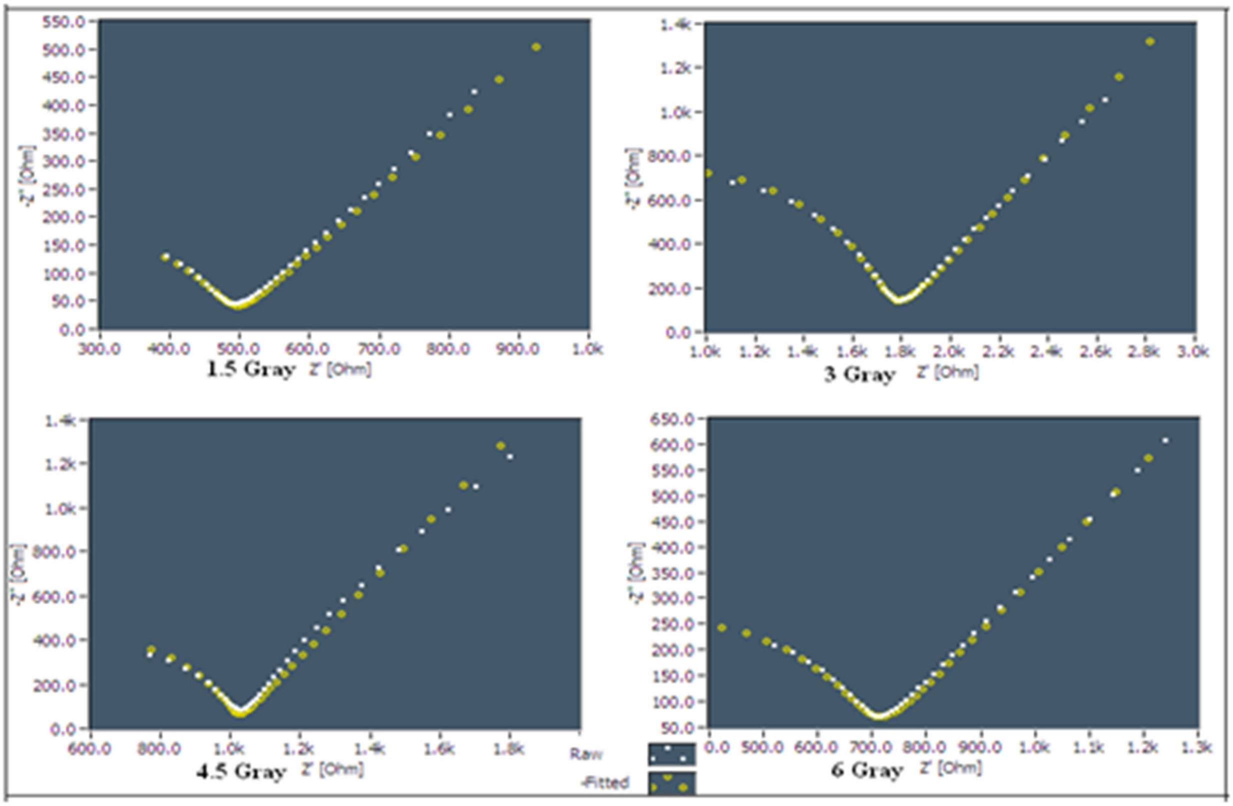

Figure 4. Fitted result after irradiation.

within the electrolyte. Non-uniformity in the polarization distorts the ideal capacitance and hence CPE 1 is used to represent this distorted capacitance. CPE 2 arises due to its inhomogeneity of the surface electrode. Figure 3 and figure 4 represents the fitted results before and after irradiation respectively.

The equivalent circuit shows the presence of constant phase element CPE1 in parallel with bulk resistance R_b , which is in series with another constant phase element CPE2. The constant phase element that is nothing but a distorted capacitor arises due to inhomogeneity of the surface of electrode. The deviation from the ideal behavior can be studied by analyzing the power value α in the mathematical equation representing the impedance value of CPE. The values of R_b, $C_{\alpha 1}$, α_1, $C_{\alpha 2}$ and α_2 are given in table (1) corresponding to different irradiation doses. The value of ionic conductivity is determined using the value of R_b given in table 1.The change in ionic conductivity with irradiation dosage is shown in fig.5.

Table 1. Values of Rb, C α1, α1, Cα2 and α2 for different irradiation doses.

Dosage / Gray	R_b / Ohms	$C_{\alpha 1}$ / Farads	α_1	$C_{\alpha 2}$ / Farads	α_2
0	1.1047k	2.942n	0.814	23.064μ	0.521
1.5	483	6.95n	0.779	45.5 μ	0.542
3	1.73k	895.4p	0.883	15.8 μ	0.56
4.5	1.009k	782.2p	0.894	6.65 μ	0.658
6	688.4	5.79n	0.785	42.56 μ	0.509

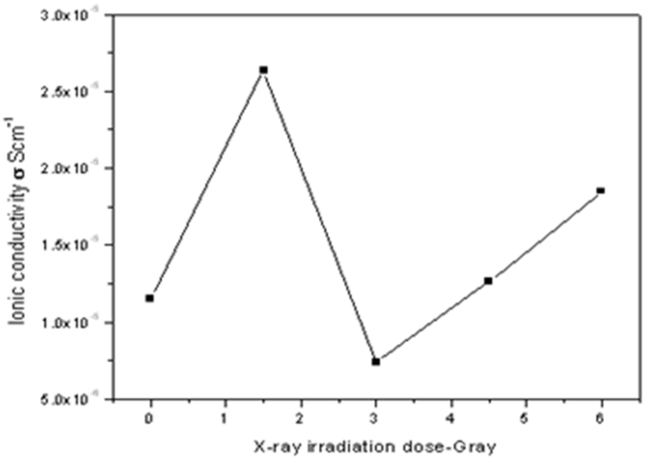

Figure 5. Ionic conductivity versus irradiation dose.

$$Z(j\omega)=\frac{1}{(j\omega)^{\alpha}C_{\alpha}} \tag{2}$$

3.3 Dielectric Permittivity

The study of dielectric property of polymer electrolytes is important since it can be used as an indicator to prove that the in-

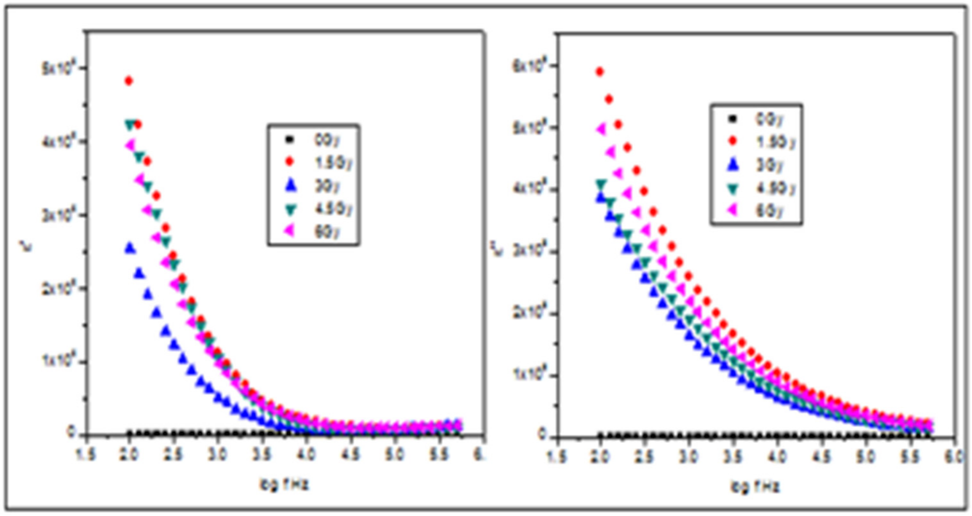

Figure 6. Variation of ε' and ε''as a function of x-ray irradiation.

crease in ionic conduction is due to an increase in the number of free mobile ions in the polymer electrolyte. The variation in the dielectric behavior of the polymer electrolytes as a function of irradiation, frequency and temperature were studied. The dielectric behavior of a system is characterized by the relative dielectric permittivity given by,

$$\varepsilon^{*} = \varepsilon' - j\varepsilon'' \tag{3}$$

The dielectric constant ε' is the real part of the complex permittivity. It is used to describe the storage capacity of the dielectric material. $\varepsilon''$is the imaginary part of the complex permittivity. The loss factor is related to the material's energy dissipation in each cycle of applied electric field.

3.3.1. Variation of Dielectric Characteristics as a Function of irradiation Dosage

Variation of dielectric characteristics as a function of irradiation dosage is shown in figure 6. It is observed that both dielectric constant and dielectric loss are found to increase for an irradiation of 1.5Gy. Further dosages decrease the dielectric permittivity, but not lower as for the sample without irradiation. The dielectric loss value is found to be quite higher which is common for ion conducting polymer electrolytes. The increase in the value of dielectric constant with irradiation may be due to enhanced dispersion of added lithium salt into the polymer matrix with irradiation. Due to enhanced dispersion, the quantity of accumulated charges will increase because of the polarization of polymer/metal at interfaces. This polarization additionally contributes to the quantity of charge and thus increases the dielectric constant of irradiated electrolytes. Similar results were discussed earlier by several authors [8, 9]. In dielectric analysis the loss factor corresponds to the conductivity of the material. Larger the dielectric loss greater will be the conductivity. The value of dielectric loss is found to increase with irradiation. It is an indication of enhanced relaxation.

3.3.2. Variation of ε' and ε''as a Fε''unction of Frequency and Temperature.

Figure 7 shows the variation in ε' and ε''as a function of frequency and temperature in the polymer electrolyte before and after irradiation (1.5 Gy alone is shown). It is evident that the dielectric constant and dielectric loss rise at low frequency and decrease at high frequency. The fall is rapid at lower frequencies and saturation appears at higher frequency range. Generally the polarization of a dielectric is contributed by ionic, electronic and dipole polarization. The electronic polarization occurs during a very short interval of time and it occurs at a higher rate of the order of 10^{-10} seconds. Ionic polarization occurs in a greater time interval of about 10^{-3} to 10^{-2} seconds and dipole polarization requires further longer time. In the case of polymer electrolytes the dielectric constant begins to drop after a certain frequency. The inability of the dipole molecules to orient themselves in the direction of electric field at a higher frequency may be the reason for this drop in dielectric constant value. Therefore, the raise at lower frequency may be due to polarization effect on the electrode surface. At lower frequencies, the ions get sufficient time to diffuse in the direction of the applied electric field resulting in higher value of polarization [10]. As frequency increases the ions do not get sufficient time to accumulate at the electrode due to the fast reversal of the electric field. Hence, the polarization gets decreased, which decreases the dielectric constant of the system. It is evident from the studies that the dielectric constant and dielectric loss increases with temperature invariably for all the samples. The polymer PEO exists in semicrystalline form at room temperature. Hence, it has a mixture of amorphous and crystalline phases. The amorphous regions are the area in which chains are irregular and entangled, whereas in crystalline region the chains are regularly arranged. Therefore, in the crystalline region the chains move with greater difficulty than through amorphous region. As temperature is increased the crystalline phase of polymer dissolves progressively into amorphous phase. This influences the polymer dynamics and thus the dielectric behavior. In addition to that flexibility introduced in the polymer

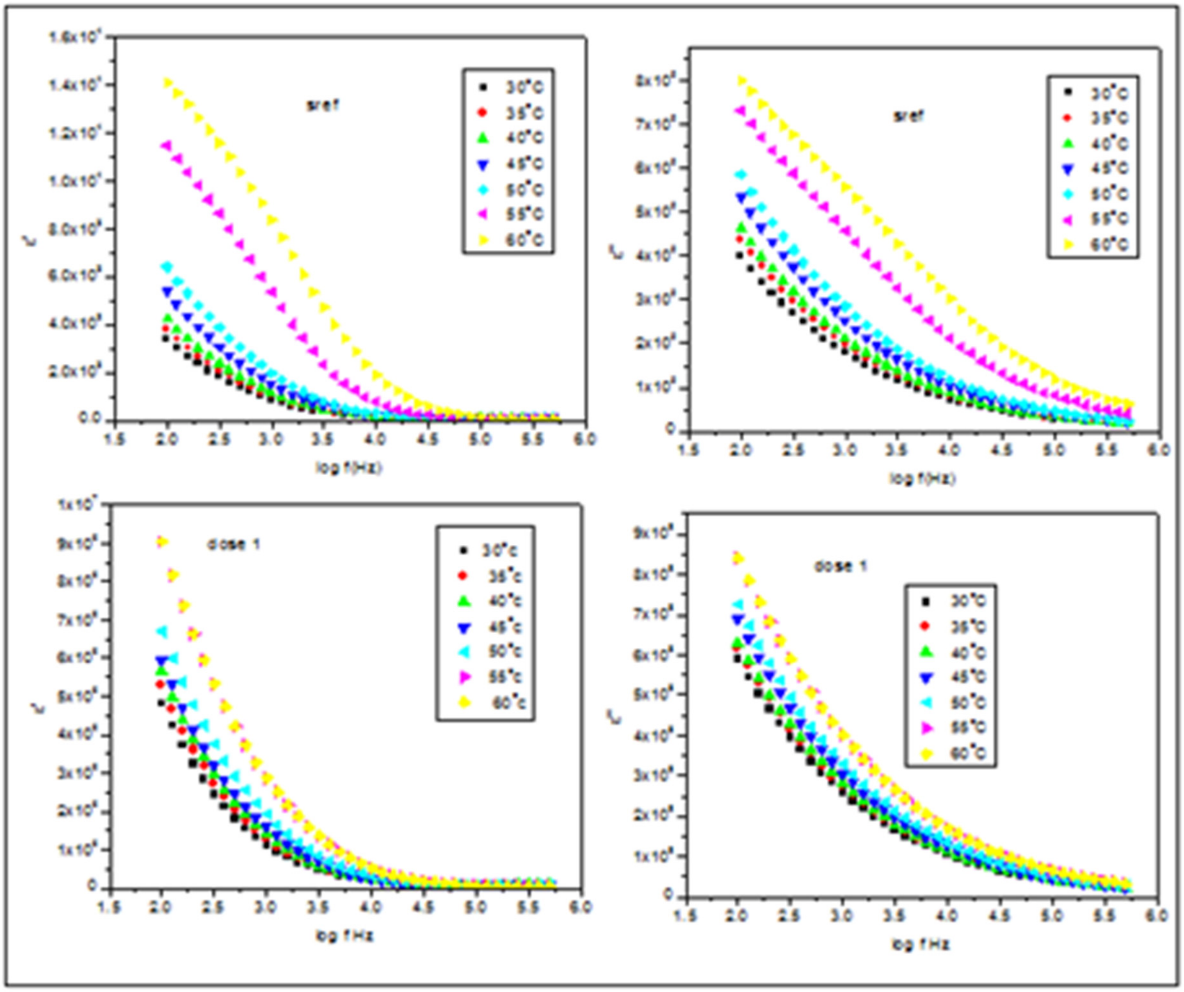

Figure 7. Variation of ε' and ε''as a function of frequency and temperature

backbone the motion of the charge carriers becomes easier on the enhancement of the temperature. This increases the value of dielectric loss even at higher frequencies [11]. The prepared samples before irradiation the dielectric permittivity value is found to increase steeply on the enhancement of temperature. But after irradiation the increase is no longer steeper, but varies exponentially. Moreover, the increase in dielectric constant and dielectric loss values with temperature are greater than the increase after irradiation. This observation is well pronounced in the polymer electrolyte irradiated by 1.5Gy.

3.4. Loss Tangent Spectra

The loss tangent is a parameter of a dielectric material that quantifies the inherent dissipation of the applied electric field. The dissipation (loss) factor tan δ is given by eq. (4)

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (4)$$

Figure 8 shows the variation in loss tangent as a function of frequency for different irradiation dosages. It is observed that the

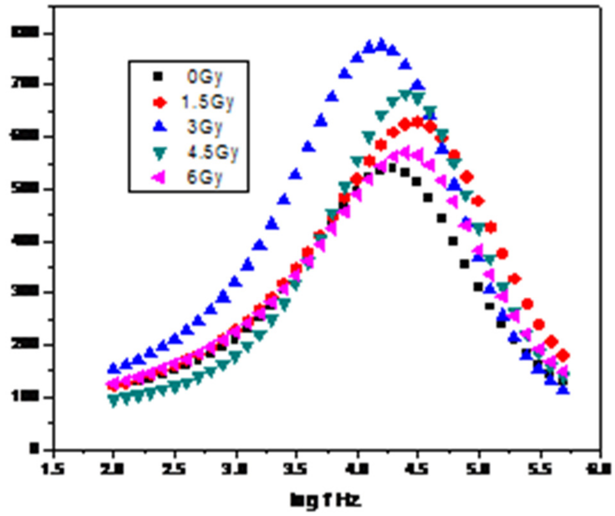

Figure 8. Variation in loss tangent as a function of frequency for different irradiation dosages.

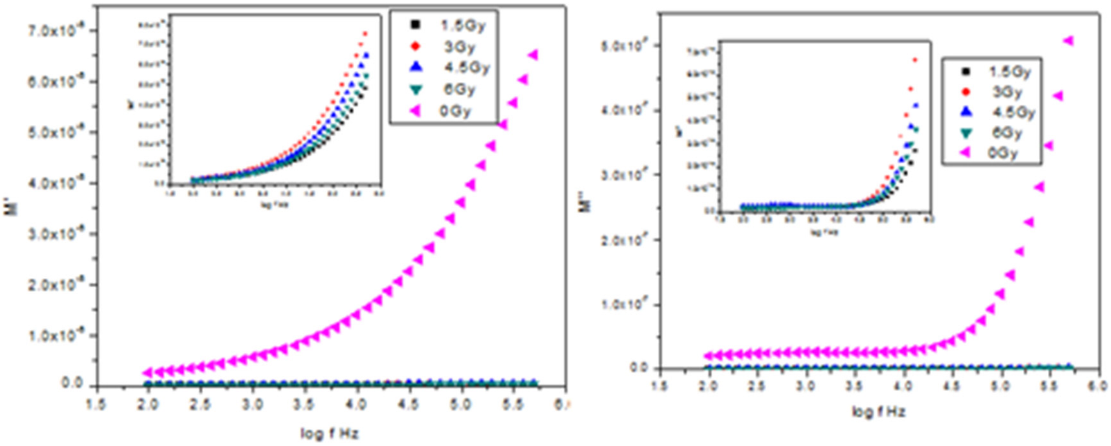

Figure 9. Variation in modulus spectra with irradiation at room temperature.

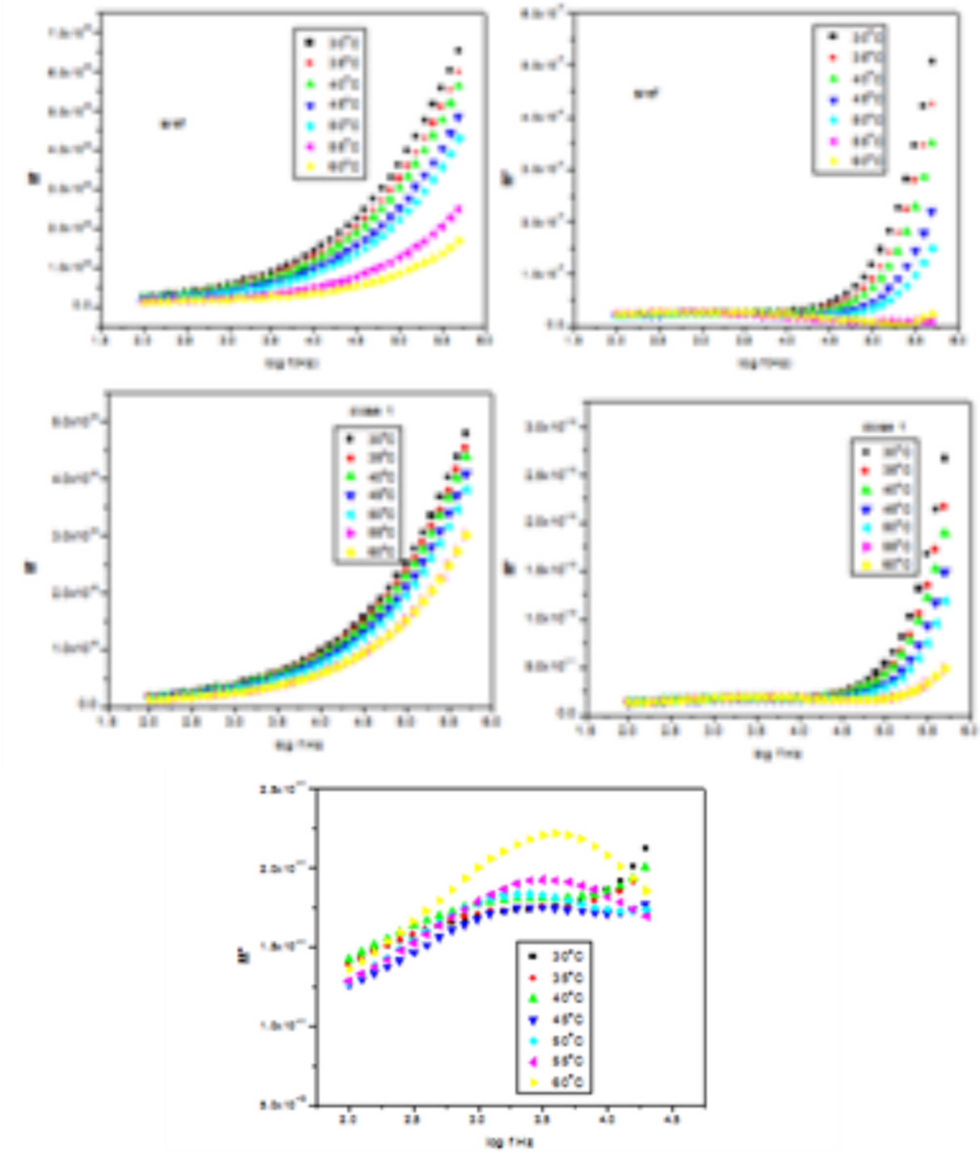

Figure 10. Dependency of temperature and frequency with moduli spectra.

increase in the magnitude of loss tangent suggests that there is increase in the number of free mobile charges [12]. But the relaxation peaks for different irradiation dosages fall on different position in the frequency domain. The peak at higher frequency indicates that the jumping probability of lithium ions per unit time increases and the peak at lower frequency indicates a lower jumping probability. [13] This may be the reason for reduced ionic conductivity obtained for the sample irradiated by 3Gy, which gives comparatively high value for the loss tangent magnitude.

3.5. Variation of Electric Moduli with Irradiation, Temperature and Frequency

The modulus spectra mainly reflect the bulk properties of the sample. The complex modulus is given by the inverse of complex dielectric permittivity [eq.(5)].

$$M^* = M' + jM'' \tag{5}$$

The main advantage of M* formalism is that the electrode effect can be suppressed [14]. M* representation is widely used to analyze the ionic conductivities by associating a conductivity relaxation time with the ionic process. It is also used to distinguish dielectric relaxation from ionic conductivity. For long range conductivity process the peak is obtained only at M'', but for relaxation process the peak is observed both in ε'' and M''. Figure 9 shows the variation in modulus spectra with irradiation at room temperature. The almost zero value for M' shows the removal of electrode polarization effect. The comparatively long tail observed for irradiated sample shows the larger value of capacitance associated with the electrodes [15]. The dependency of frequency and temperature with moduli spectra for samples obtained before and after irradiation is shown in figure 10 (1.5 Gy alone is shown). It is observed from this figure that the electrode polarization effect is almost reduced and hence a very low value, nearly zero is obtained in the modulus spectra for very lower frequencies. At lower frequency M'' exhibits a lower value, which might be due to the large value of capacitance associated with the electrode polarization effect as a result of accumulation of a large amount of charge carriers at the electrode/polymer interface. For irradiated sample the polarization was found higher than for non-irradiated sample. M'' represents the loss value similar to ε'' in dielectric spectra. Peak in M'' confirms that there is long-range conduction due to the presence of free mobile ions. In accordance with the conduction results the peak observed in M'' is well pronounced for the highest conducting sample *i.e.;* the sample irradiated by 1.5 Gy. Hence, it can be concluded that x-ray irradiation has favored the conductivity by enhancing the quantity and mobility of free ion in the polymer electrolyte.

4. CONCLUSIONS

Effect of x-ray irradiation on ionic conductivity was studied and equivalent circuit was modeled. The dielectric properties were analyzed with a view of understanding the cause for the change in ionic conductivity with irradiation. Dielectric constant was found to increase with irradiation and dielectric loss was found to be highest for the best conducting sample irradiated by 1.5Gy. From the loss tangent spectra it was found that irradiation altered the quantity and hopping frequency of the lithium ions. From the electric moduli spectra it was found that ionic conduction was enhanced for an irradiation dose of 1.5Gy.

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