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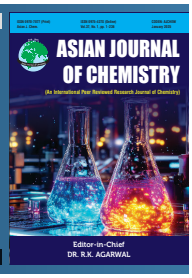

Irradiation Effects on Structural, Microstructural and Electrochemical Properties of PEO-NH_4ClO_4 Polymer Electrolytes

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This study investigates the effects of γ-irradiation on the structural and electrochemical properties of polymer electrolytes composed of PEO(1-x)-NH_4ClO_4(x) with x = 0.16, 0.20, 0.24 and 0.26. Studying the effects of different γ doses (up to 60 kGy) on the thermal transitions, microstructure, molecular weight and ion conductivity of the system is the main objective. Differential scanning calorimetry (DSC) was used to evaluate changes in crystallinity and thermal transitions, while viscosity measurements of aqueous solutions were employed to assess the molecular weight variations. The γ-irradiation caused both crosslinking and chain scission in the polymer matrix, with scission being the dominant effect. A significant increase in the ion conductivity was observed at 35 kGy, indicating improved ion transport due to enhance the amorphous character. DSC results showed a clear, exponential decrease in crystallinity with increasing dose. Viscosity data supported the occurrence of molecular weight reduction, correlating well with conductivity trends. This study provides a comprehensive analysis linking γ-induced structural modifications–particularly microstructural disorder and molecular weight changes–to enhanced ion transport in PEO-NH_4ClO_4 polymer electrolytes. The observed exponential decline in crystallinity with dose reinforces the mechanism of γ-induced crosslinking and scission.

Keywords: γ-Irradiation, Polymer electrolyte, Viscosity, Ion conductivity.

INTRODUCTION

Ionizing radiations, such as γ-rays and electron beams, have been extensively utilized to modify the structural, microstructural and electrochemical properties of polymers [1]. Irradiation of solid polymer electrolytes (SPEs) has emerged as a pivotal method for enhancing their ionic conductivity and electrochemical performance, offering significant advancements in the energy storage applications [2,3]. Exposure to γ-rays, the electron beams or heavy ions induces permanent modifications in the polymer matrix, leading to changes in conductivity that are both dose-dependent and influenced by ambient conditions. These irradiation processes can result in either crosslinking or scission of polymer chains, thereby altering the molecular weight distribution and affecting the electrical and mechanical properties of the SPEs [4,5].

Recent studies have demonstrated that γ-irradiation can effectively increase the ionic conductivity of polyethylene oxide (PEO)-based electrolytes by reducing crystallinity and enhancing amorphous regions, which facilitate the ion transport [6-8]. For instance, research has shown that γ-irradiation leads to significant improvements in ion diffusion within PEO-NH_4I based SPEs [8]. Similarly, electron beam irradiation has been reported to modify the optical, thermal and electrical properties of polymer electrolytes, offering potential for tailored applications [9]. However, despite these advancements, there remains a lack of consensus on the optimal irradiation doses and conditions that maximize conductivity enhancements without compromising the structural integrity of the polymers. Variations in the irradiation parameters can lead to the inconsistent results, underscoring the need for standardized protocols. Moreover, the underlying mechanisms governing the irradiation-induced modifications are not fully understood, particularly concerning the interplay between crosslinking and chain scission effects.

Despite the extensive body of literature on polymer electrolyte systems, particularly polyethylene oxide (PEO)-based composites with various inorganic salts, several critical gaps remain unaddressed. Previous studies have primarily focused

on the ionic conductivity, mechanical properties and thermal stability of these systems [10-12]. However, there is a lack of systematic investigation into the microstructural evolution and its correlation with salt concentration–especially in the medium to high doping range. Furthermore, the limitations of existing solution-casting methods in ensuring homogeneous dispersion and reproducible film morphology have not been sufficiently addressed [13]. Most existing works have reported conductivity enhancement with salt doping but have not thoroughly examined the role of ammonium-based salts like NH_4ClO_4, which offer potential advantages due to their high ionic mobility and compatibility with the PEO matrix. In particular, the influence of varying salt concentrations (*e.g.*, beyond the standard 0.1-0.2 wt. fraction) on film uniformity, crystallinity reduction and potential ionic conductivity improvements remains under explored. Lack of critical analysis of the limitations in existing solution casting methodologies for polymer–salt composite films. Insufficient exploration of ammonium perchlorate as a dopant in PEO matrices in terms of film homogeneity, microstructural stability and phase distribution. Absence of a comprehensive study linking salt concentration to morphological and conductive performance beyond traditional doping limits (*i.e.* $x > 0.20$) [14,15].

Addressing these gaps, this study explores the impact of γ-irradiation on the structural, microstructural and electrochemical characteristics of polyethylene oxide (PEO)-based solid polymer electrolytes (SPEs). By systematically varying the salt concentrations and irradiation doses, we aim to identify the optimal conditions that enhance ionic conductivity while preserving or improving mechanical stability. This research seeks to provide a deeper understanding of the irradiation induced modifications in polymer electrolytes, paving the way for their improved performance in energy storage applications.

EXPERIMENTAL

Sample preparation: Poly(ethylene oxide) (PEO) with a molecular weight of 6×10^5 g/mol, procured from B.D.H., England, was used as host polymer. Analytical-grade methanol (99.9%) as solvent and ammonium perchlorate (NH_4ClO_4) with 99.5% purity (Fluka) was used as salt dopant. The polymer films were synthesized using a solution casting technique. Specifically, NH_4ClO_4 and PEO were weighed in appropriate fractions–x (for salt) and (1–x) (for polymer)–and dissolved in methanol. The solution was stirred continuously for 14-16 h at room temperature (~305 K) to ensure thorough mixing and homogeneity. The resulting mixture was cast into Petri dishes and air-dried for 4-5 days. Subsequently, the films were vacuum-dried for an additional 3-4 days to eliminate the residual solvent. The average film thickness obtained was approximately 250 μm. The total mass of each film was maintained at 2 g. The compositions prepared were PEO(1–x)–NH_4ClO_4(x), with x values of 0.16, 0.20, 0.24 and 0.26.

γ-Irradiation: The samples were irradiated in a conventional γ chamber, which uses a ^{60}Co source with a dose rate of 60 Gy/min or 6 Krad/min. We report results for samples with doses 10 to 60 kGy for varying x and compare their properties.

Differential scanning calorimetry (DSC): DSC was performed on the un-irradiated and irradiated samples for $x = 0.24$ and 0.26, using Pyris Diamond (Perkin-Elmer) instrument. Heating was done at the rate of 10 ºC/min under nitrogen atmosphere.

X-ray diffraction (XRD): The XRD analysis of samples with $x = 0.16$ and 0.20 were conducted on Bruker AXS (Germany) model no. D8 ADVANCE XRD (powder) instrument.

FTIR: FTIR analysis was conducted on the pristine and irradiated samples with $x = 0.24$ and 0.26 on spectrum RX-1 Perkin Elmer, instrument.

Impedance spectroscopy: Impedance spectroscopy was carried out on a Hioki LCR Hi Tester (model:3520) in the frequency range 1 to 105 Hz. The temperature range of measurement was 35 ºC to 55 ºC. The literature indicates a consistent interest in enhancing the performance of PEO-based polymer electrolytes through various salt dopants and fabrication techniques [8]. However, few studies also systematically explore the influence of ammonium salts like NH_4ClO_4 over a broader concentration range [16,17]. Moreover, the correlation between film fabrication techniques and resulting structural integrity is often overlooked. This work addresses these deficiencies by focusing on the reproducibility, compositional variation and film morphology under controlled solution-casting conditions.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC): Differential scanning calorimetry (DSC) measurements were performed on polymer electrolyte samples with NH_4ClO_4 concentrations $x = 0.24$ and 0.26 to investigate the influence of γ-irradiation on the crystallinity of the PEO matrix. A clear and systematic decrease in the area under the DSC curve was observed with increasing irradiation dose (Figs. 1 and 2). The calculated area from the baseline, which correlates directly with the degree of crystallinity, decreased exponentially with dose.

$$\chi = A \exp(-cD)$$

where χ is the crystallinity; D is the radiation dose; c is a material dependent constant and A is the initial crystallinity of the non-irradiated sample. This exponential decay indicates that chain scission becomes the dominant effect under irradiation, reducing crystalline domains in the PEO matrix. This trend has been similarly reported by Sunitha & Radhakrishnan [18] in their study on γ-irradiated PEO–$LiClO_4$ systems.

The reduction in crystallinity with increasing dose is consistent with the findings of Kumar *et al.* [4], who reported that γ-irradiation introduces the free radicals that enhance chain scission and hinder recrystallization, resulting in more amorphous phases. However, unlike Li-based systems, ammonium salts may introduce additional protonic mobility due to NH_4^+ dissociation, which may further contribute to enhanced segmental motion post-irradiation–this synergistic effect is unique to the present study and has not been extensively discussed earlier. In contrast, Raghu *et al.* [5] observed a mild increase in crystallinity at low doses (~10 kGy) in PEO–$NaNO_3$ samples, attributing it to initial cross-linking effects that briefly dominate over scission. This slight contradiction emphasizes the salt-dependent response of polymer electrolytes to irradiation. In

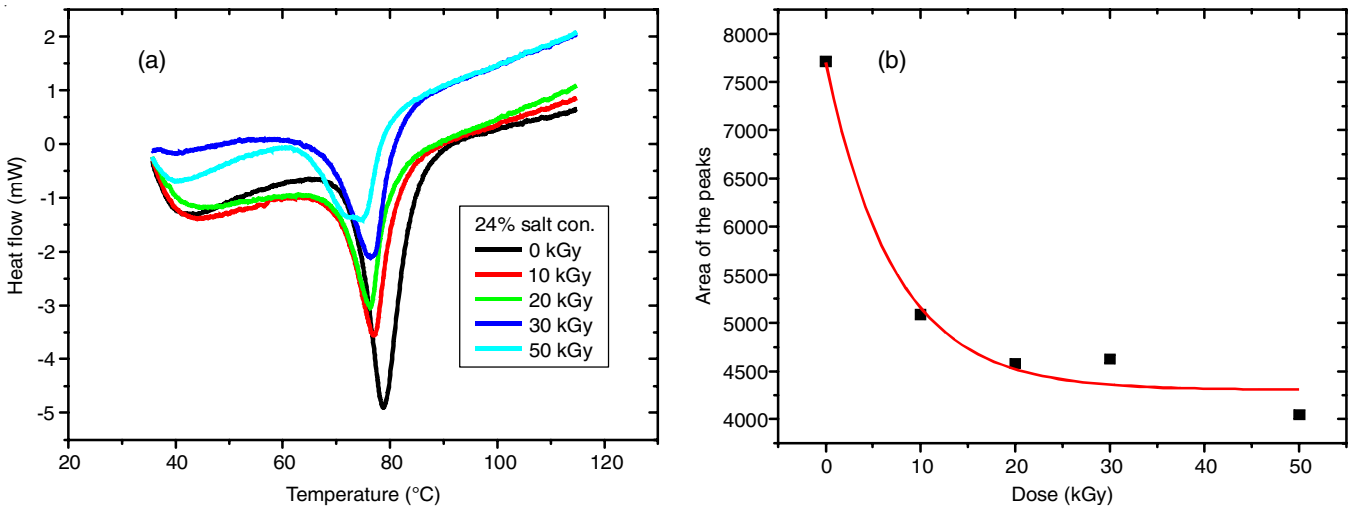

Fig. 1. DSC curves for unirradiated and irradiated samples (x = 0.24) for various radiation doses (a) and area *vs*. dose for DSC curves at heat flow 10 ºC per min (solid line represents an exponential fit to the curve) (b)

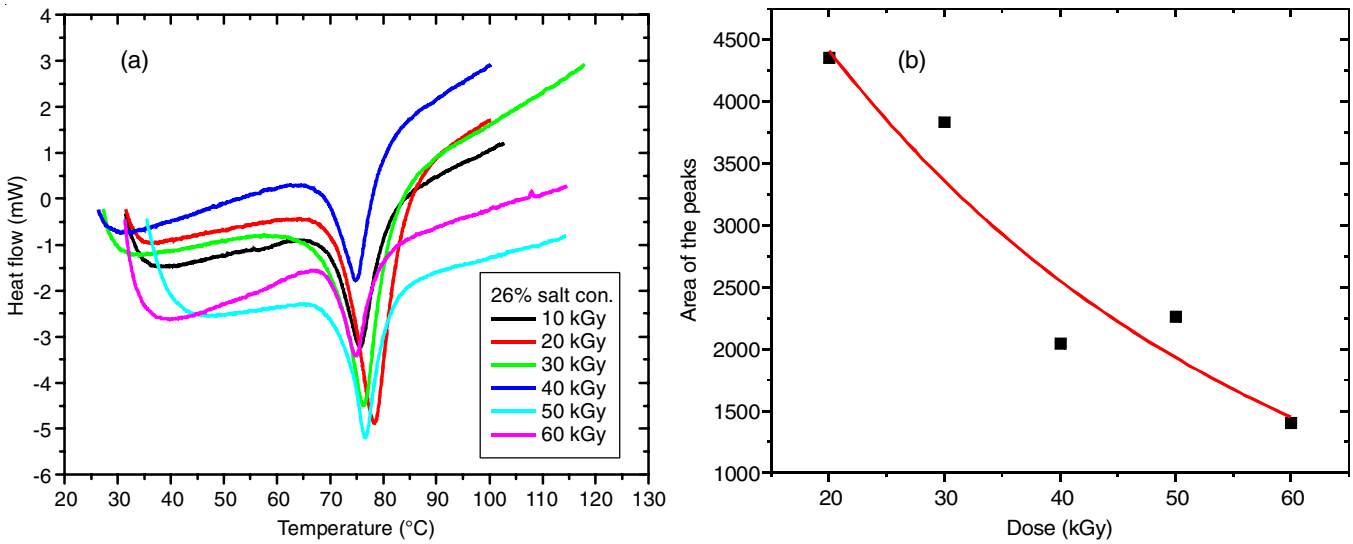

Fig. 2. DSC curves for unirradiated and irradiated samples (x = 0.26) for various radiation doses (a) and area *vs*. dose for DSC curves at heat flow 10 ºC per min (solid line represents an exponential fit to the curve) (b)

present case, the consistently decreasing trend in crystallinity even at lower doses suggests that NH_4ClO_4 leads to more aggressive scission-driven amorphization, possibly due to its hygroscopic nature or lower decomposition threshold under γ exposure.

X-ray diffraction (XRD): The XRD results for the unirradiated sample and at various doses of irradiation for x = 0.16 and 0.20 samples are shown in Figs. 3 and 4. The major XRD peak positions at 2θ = 14.2º,16.5º,19.3º, 22.1º, 22.6º, 23.8º and 25.7º do not change appreciably on irradiation in both the cases, indicating that the primary crystalline phase retains its structural integrity across the dose range investigated. However, a noticeable broadening and reduction in intensity of these peaks, particularly in the higher dose regions, suggest an increase in amorphous content with irradiation [19,20].

However, the consistency of the trend and its reproducibility across two distinct concentrations (x = 0.24 and 0.26) reinforce the reliability of the observed phenomenon (Figs. 5 and 6).

These findings are consistent with previously reported studies [4], where γ or ion irradiation has been shown to induce partial amorphization without significantly altering the crystal lattice parameters. For instance, Raghu *et al*. [21] reported the similar stability in peak positions alongside increasing amorphicity in material, validating the observed behaviour in the present study. On the other hand, a few studies have also indicated possible peak shifts or the formation of new phases under high-dose irradiation [13], which contrasts with the present results. The absence of such transformations here could be attributed to the relatively moderate irradiation doses used, or to the intrinsic radiation resistance of the material matrix for the specific dopant concentrations studied. Therefore, the XRD analysis confirms that while irradiation enhances structural disorder (*i.e.*, amorphicity), it does not significantly disturb the long-range order of the crystalline domains, in agreement with existing models and reinforcing the validity of the current experimental observations.

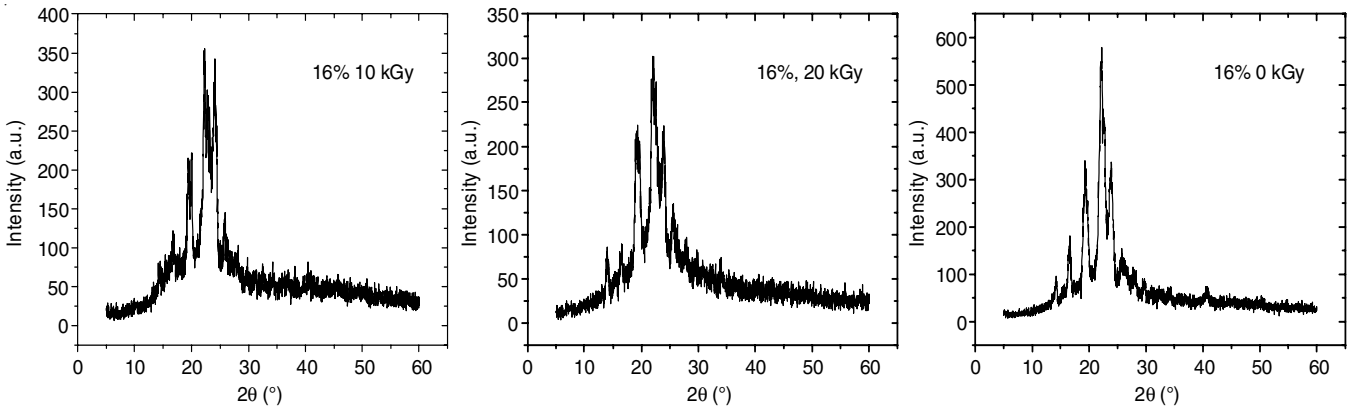

Fig. 3. XRD spectra for sample with x = 0.16 at different radiation doses (0, 10, 20 kGy)

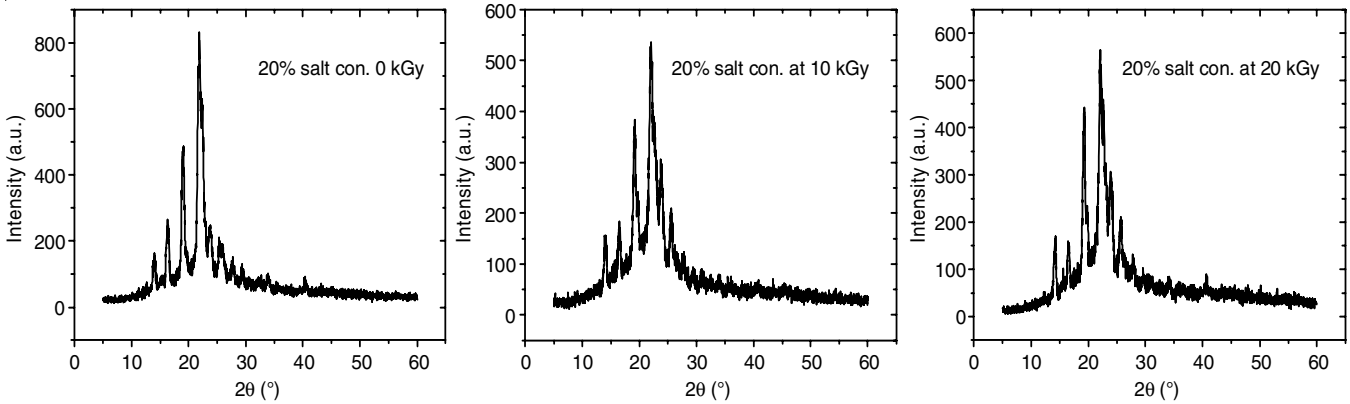

Fig. 4. XRD spectra for sample with x = 0.20 for various radiation doses (0, 10, 20 kGy)

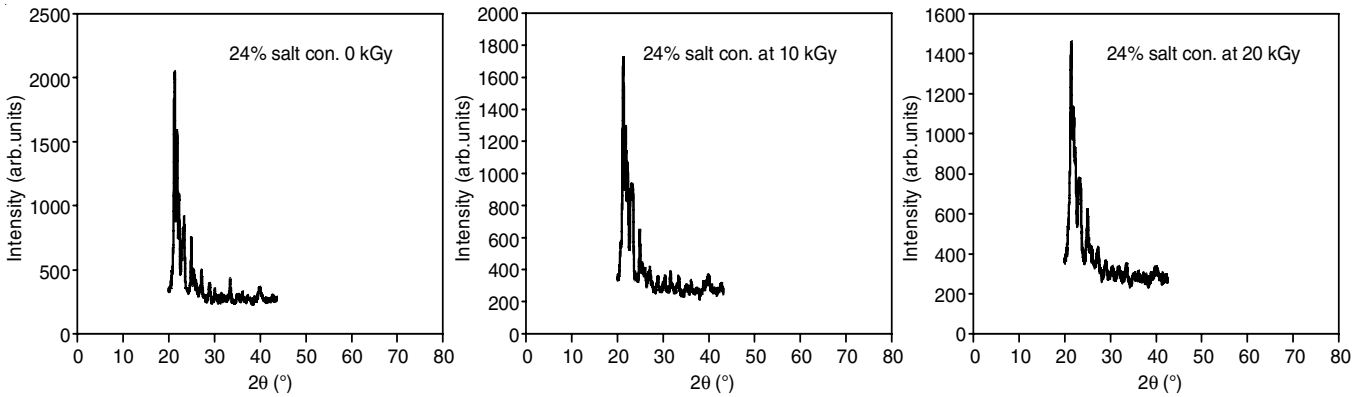

Fig. 5. XRD spectra for sample with x = 0.24 for various radiation doses (0, 10, 20 kGy)

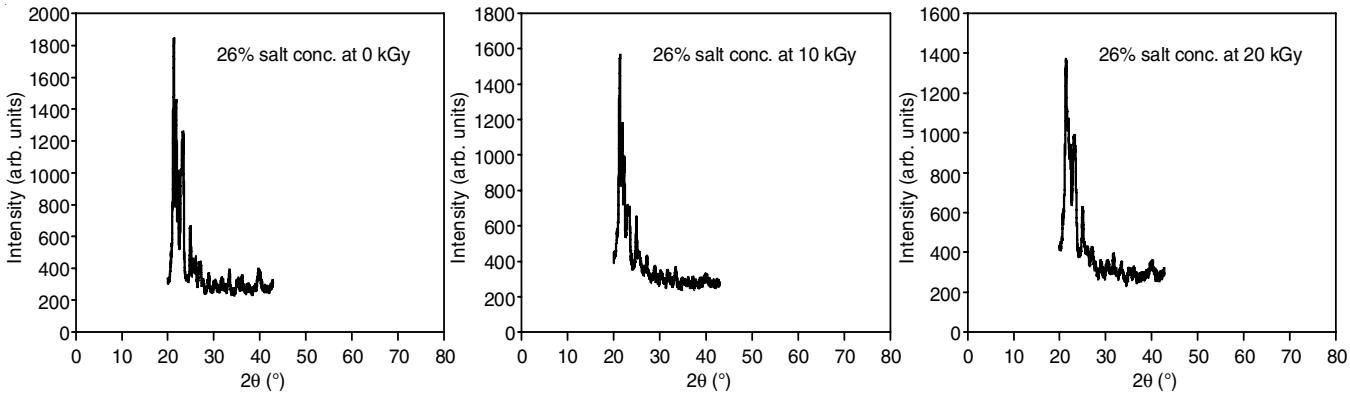

Fig. 6. XRD spectra for sample with x = 0.26 for various radiation doses (0, 10, 20 kGy)

FTIR: Infrared absorption frequencies were measured over the irradiation dose range of 0–60 kGy for samples with x = 0.26, as shown in Figs. 7 and 8, respectively. Given the nearly identical thicknesses of the samples, direct comparisons of absorbance intensities were made between the two concentrations. The FTIR spectra reveal the significant modifications in absorbance profiles with increasing γ-irradiation dose, highlighting structural transformations at the molecular level [22-24].

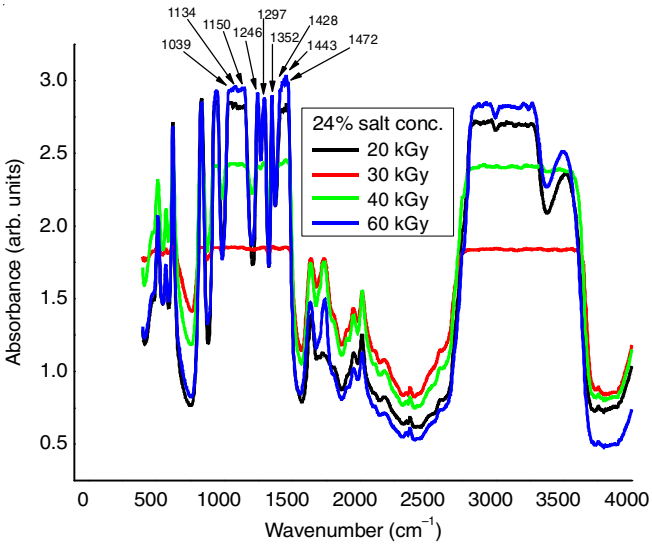

Fig. 7. Absorbance *vs.* wave number plot for sample with x = 0.24 at different radiation doses

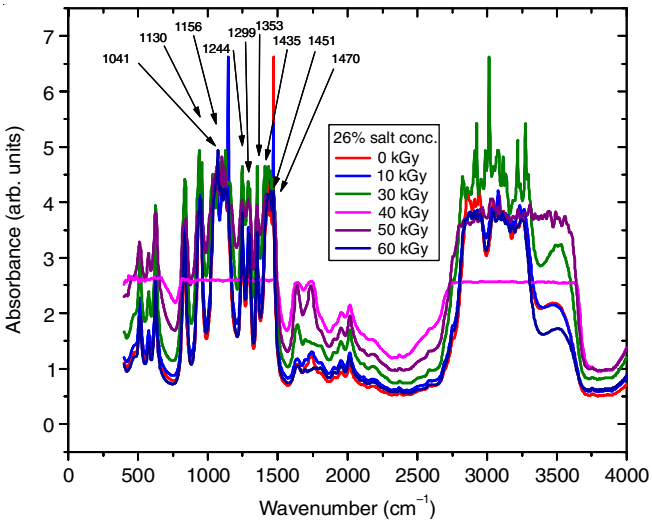

Fig. 8. Absorbance *vs.* wave number plot for sample with x = 0.26 at different radiation doses

The presence of the crystalline phase of polyethylene oxide (PEO) is confirmed by the characteristic C–O–C stretching vibration peaks, observed at 1150, 1134 and 1039 cm^{1} for x = 0.26. The slight shifts in these peak positions suggest interactions between PEO and the embedded electrolyte, consistent with the previously reported findings on polymer-salt complexation effects [4]. Peaks corresponding to CH scissoring are observed at 1428, 1443 and 1472 cm^{1} for x = 0.24 and at 1435, 1451 and 1470 cm^{1} for x = 0.26. A sharp decrease in peak intensity at 30 kGy for$x$ = 0.24 and 40 kGy for x = 0.26 suggests significant chain scission events, which disrupt polymer order and enhance amorphous content [25,26].

Impedance spectroscopic studies: The impedance spectroscopy results for different concentrations and γ doses have been analyzed for the samples. A detailed study of the complete Cole-Cole plot reveals features which may give important information about the sample. The Cole-Cole plots at a specific radiation dose but at different temperatures for samples with x = 0.16 is shown in Fig. 9. The DC conductivity can be obtained from a Cole-Cole plot by locating the points on the real Z axis. A plot of the dc conductivity *vs* γ-radiation dose for the different samples at 35 ºC is shown in Fig. 10. The samples with both x = 0.16 and x = 0.20 show an increase in conductivity at 30 kGy irradiation and a subsequent drop at 40 kGy. However, samples with x = 0.24 shows a maximum conductivity at around 20 kGy dose with a fall at higher doses while samples with x = 0.26 shows a steady rise in conductivity with increase in radiation dose. A close comparison of the dc conductivity plots for x = 0.16, 0.20, 0.24 with x = 0.26 reveals that there can be an enhancement in conductivity at around 30 kGy dose for x = 0.26 which has not been experimentally detected. Samples with x =0.20, 0.24 and 0.26 salt concentrations shows a slight decrease in conductivity at 10 kGy followed by appreciable increase in conductivity at higher doses. These results are consistent with the earlier study on samples with x = 0.18, where similar behaviour was observed [14]. Nonetheless, for x = 0.18, the configuration for impedance spectroscopy varied, and the measurements were conducted during the cooling cycle. Therefore, a quantitative comparison of conductivity results for x = 0.18 with those for x = 0.16, 0.20, 0.24 and 0.26 will lack significance.

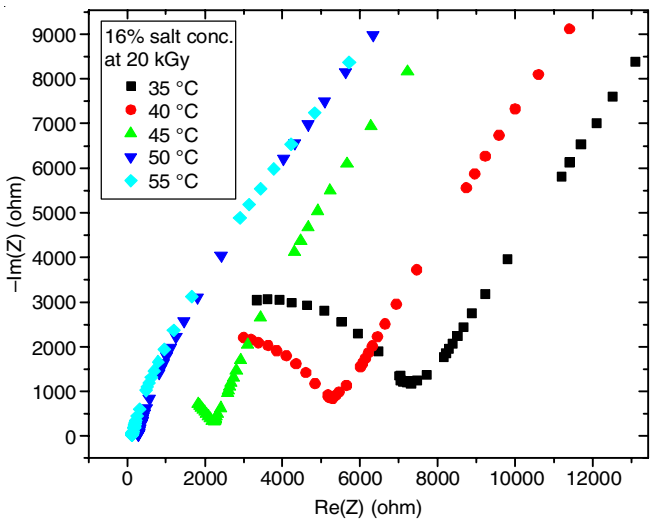

Fig. 9. Zoomed high frequency regime of the Cole-Cole plot for the sample with x = 0.16 irradiated with 20 kGy γ dose at different temperature

The significant new finding is that when x = 0.16, the increase in conductivity is substantially greater than in previous cases. In the Cole-Cole plot, the low frequency regime is attributed to impedance of the electrodes with two semicircles

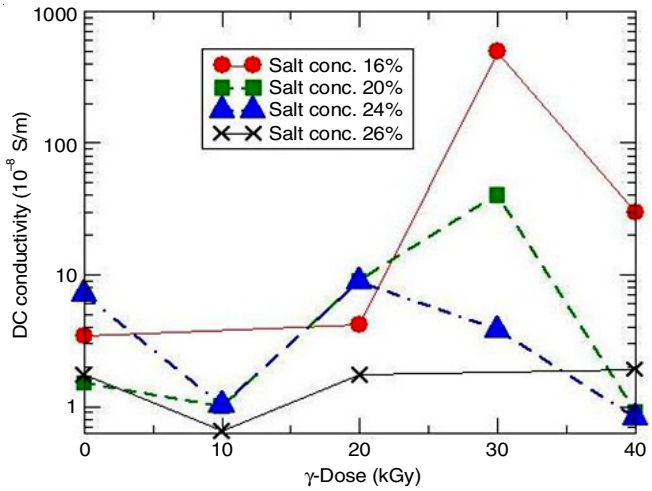

Fig. 10. DC conductivity (on logarithmic scale) *versus* radiation dose for samples with x = 0.16, 0.20, 0.24 and 0.26 at 35 ºC

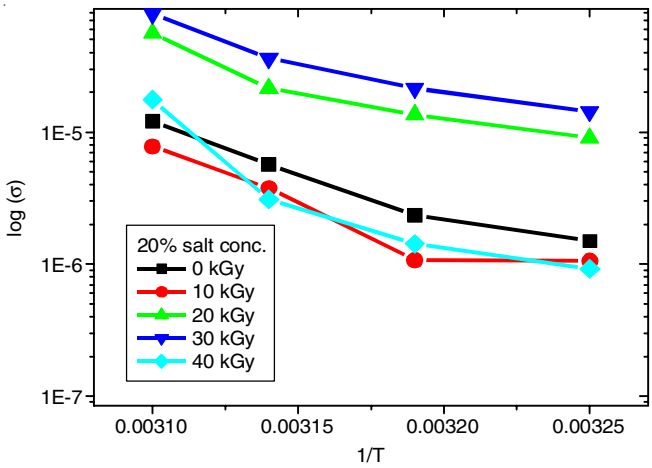

Fig. 11. Log(σ) *vs.* 1/T for samples with x = 0.20 irradiated with different γ doses

representing the sample impedance. These two semicircles arise due to the presence of two different conducting phases or due to existence of a phase boundary between the amorphous crystalline phases in the samples.

Equivalent circuits consisting of combination of resistors, inductors and capacitors can be employed with suitably chosen parameters to give a best fit with the Cole-Cole plots explain the presence of inductive loops at high frequency in samples [15]. While we cannot rule out the possibility of the inductive feature being due to peculiarities of the set-up or to transient effects [18,27] it may possibly reflect the peculiarities in the salt-polymer microstructure with helically coiled polymer molecules [19]. The helical structure of PEO chains is well established and it is known that the ions of the electrolyte occupy positions within the polymer coil structures [20,22]. Spirally coiled or zigzag polymer molecules [23,24] may affect the path of charge carriers and induce a winding motion.

These observations align with the earlier reports indicating that γ-irradiation initially leads to polymer chain scission, reducing crystallinity and increasing segmental disorder [13-15]. Moreover, the subsequent increase in peak intensity at higher doses supports the notion of radiation-induced crosslinking, which has been shown to stabilize the molecular networks and partially restore absorption features [28].

Temperature variation of conductivity: The temperature variation of conductivity for sample with x = 0.20 for different radiation doses is shown in Log (σ) *vs.* 1/T plots in Fig. 11. The plot is almost linear for the unirradiated sample, but becomes rather non-linear on irradiation. The average slope for dose (D) = 30 kGy is less than that of the unirradiated sample, indicating that the activation energy is lower in this case.

However, some contrasting studies have reported continuous degradation without a significant recovery in peak intensity at higher doses, particularly for less radiation-resistant polymer systems [4]. The divergence may be due to differences in the polymer composition, irradiation conditions or the nature of the dopant. In summary, the observed shifts in vibrational modes, variations in peak intensities and dose-dependent behaviour validate the structural interpretations derived from the current model. The results demonstrate a consistent pattern with previously reported effects of γ-irradiation on polymer electrolytes, thereby confirming the reliability and relevance of the present experimental framework.

Conclusion

The present findings, particularly the dose-dependent conductivity behaviour and the interpretation of impedance features, are largely in agreement with previous literature. However, the distinct responses observed for different salt concentrations, especially the anomalous enhancement in x = 0.16, provide new insights and extend existing understanding of γ-irradiation effects on polymer electrolytes. The γ-irradiation significantly influences the properties of solid polymer electrolytes (SPEs) by inducing changes in their microstructure, molecular weight and also enhances the ion conductivity of SPEs, with a notable increase observed around a dose of 30-35 kGy. This enhancement is attributed to radiation-induced scission, which increases the segmental motion of polymer chains, facilitating ion transport. Irradiation leads to a decrease in crystallinity, as evidenced by X-ray diffraction (XRD) studies. A significant enhancement, nearly two orders of magnitude, is observed for a salt concentration of x = 0.16 at a radiation dose of 30 kGy. This suggests that optimizing salt concentration and radiation dose is crucial for maximizing conductivity. The study highlights the intricate balance between scission and crosslinking processes under γ-irradiation, offering insights into tailoring SPE properties for specific applications. However, advanced analysis methods to delve deeper into the microstructural alterations caused by γ-irradiation, linking these alterations to overall properties to inform the development of superior SPEs.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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