Variation in viscosity and ion conductivity of a polymer–salt complex exposed to gamma irradiation

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Abstract. We study changes in microstructure and resulting changes in the properties of $PEO(1-x)$–$NH_4ClO_4(x)$ samples where $x = 0.18$, when irradiated with gamma doses varying up to 50 kGy. Viscosities of aqueous solutions of the irradiated samples give an idea of the change in molecular weight and show correlation with ion conductivity. On the whole, there is a chain scission on irradiation, though there is evidence of some cross-linking at higher doses. The ion conductivity shows a strong increase for an irradiation of 35 kGy. DSC studies indicate a decrease in crystallinity with gamma dose.

1. Introduction

When polymers are exposed to high energy radiations such as γ-rays, there may be cross-linking and/or scission of the long polymer chains. Both processes may occur simultaneously, but usually one dominates [1,2]. This is manifested in the different physical and electrical properties of solid polymer electrolytes (SPE) as well [3]. Since polymer electrolytes are extensively used in practical devices and appliances [4], it is helpful to study the effect of irradiation on them. The risk of degradation on appliances exposed to radiation environment in nuclear reactors or outer space has to be considered as well as the possibility of improvement of properties on controlled irradiation. So identifying radiation-resistant materials as well as radiation-sensitive materials is necessary. We report a study on one such well-known polymer complex. Some preliminary results were reported in [5].

Polyethylene oxide complexed with x fraction by weight of ammonium perchlorate, $PEO(1-x)$–$NH_4ClO_4(x)$, is a well studied SPE [6–8]. We have irradiated the SPE films with gamma doses from 10 to 50 kGy. The changes produced on irradiation are studied using DSC, FTIR, viscosity in aqueous solution and impedance spectroscopy (IS). The change in average molecular weight produces a variation in viscosity of the aqueous solution [9]. The change in crystallinity shows up in DSC measurements. We try to correlate these results with the observed change in ion conductivity measured by impedance spectroscopy.

We also try to infer details about microstructure from the plots of conductivity vs. frequency in a double logarithmic scale. A power law is obtained at high frequencies, the exponent of which gives information about spatial and temporal disorders in the microstructure.

2. Experimental

2.1 *Sample preparation*

Polyethylene oxide from B.D.H., England (Mol Wt. = 6.105), methanol (99.9% pure) and ammonium perchlorate (Fluka, 99.5%) are used for sample preparation. The polymer films are prepared by the solution casting technique, with methanol as the solvent. Fraction x by weight of NH_4ClO_4 and $(1-x)$ fraction of PEO were dissolved in methanol. The suspension was stirred for 14–16 h at room temperature (33°C). Films were cast on a petri dish, dried in air for 4–5 days and then vacuum dried for 3–4 days. Thickness of the film was about 250 μm. We thus prepared films of total mass 2 g and composition: $PEO(1-x)$–$NH_4ClO_4(x)$, where $x = 0.18$.

2.2 *Gamma irradiation*

The samples were irradiated in a conventional gamma chamber, which uses a ^{60}Co source with a dose rate of 60 Gy/min or 6 krad/min. Samples were exposed to doses 10, 12, 15, 17, 20, 25, 30, 35, 40, 45 and 50 kGy. DSC has been done on all these samples, as well as on the unirradiated sample. Other measurements have been done on some of the samples.

2.3 *FTIR*

Fourier transform infrared spectroscopy (FTIR) was done on the pristine and irradiated samples on Shimodzu FTIR8400S, at the Physics Department, Jadavpur University, India.

2.4 *Viscosity measurement*

The unirradiated sample and samples irradiated with doses 10, 25, 35 and 45 kGy, were dissolved in distilled water to produce solutions of 7.65 g/l concentration.

Relative viscosity was measured by Ostwald viscometer at the Centre for Surface Sciences, Jadavpur University, India at room temperature ($33°C$).

2.5 *Impedance spectroscopy*

Impedance spectroscopy (IS) was done on an Agilent 4192A impedance analyzer, in the frequency range 5 Hz to 13 MHz. IS has been done on samples irradiated with 0, 10, 20, 30, 35 and 40 kGy gamma dose, at temperatures 20–50°C in air. Measurements were done in the cooling cycle. Heating cycle results are unreliable showing irregular variation. This is probably because surface irregularities prevent good contact between the sample and electrode. On heating to about 40–50°C the samples soften ensuring proper contact. Irradiation makes the samples brittle and they have to be handled carefully.

2.6 *DSC*

Differential scanning calorimetry (DSC) has been done on the unirradiated and irradiated samples using Pyris Diamond (Perkin Elmer) set-up for TG/DTA, at the Metallurgy Department, Jadavpur University, India. Heating was done at the rate of 10°C/min under nitrogen atmosphere.

3. Results

Viscosity and ion conductivity show correlated bahaviour, one being high when the other is low. Though the viscosity is measured for a dilute aqueous solution, it is seen that the change produced by irradiating the solid polymer electrolyte is retained in solution. DSC results are also consistent with these findings. We present the results below and discuss the implications.

3.1 *FTIR*

Figure 1 shows the results of infrared absorption frequencies for doses 0, 10, 35 and 50 kGy. Thicknesses are nearly equal and salt concentration is 18% for all the samples studied, and so intensities of the peaks in the graphs can be directly compared. There are evident changes with gamma irradiation. The most prominent change is in the peak at $1150\,\mathrm{cm}^{-1}$ (marked by an arrow), which has been attributed to C–C bond stretching and C–O–C asymmetric stretching [6]. This peak has an intensity of about 1.3 (in arbitrary units) in the unirradiated sample, it falls to about 1.1 at 10 and 35 kGy, rises again to 1.2 at a dose of 50 kGy. This can most obviously be correlated to main chain scission for low doses, where such bonds decrease in number. The subsequent increase at higher dose indicates cross-linking. So results from DSC, viscosity and FTIR are in agreement.
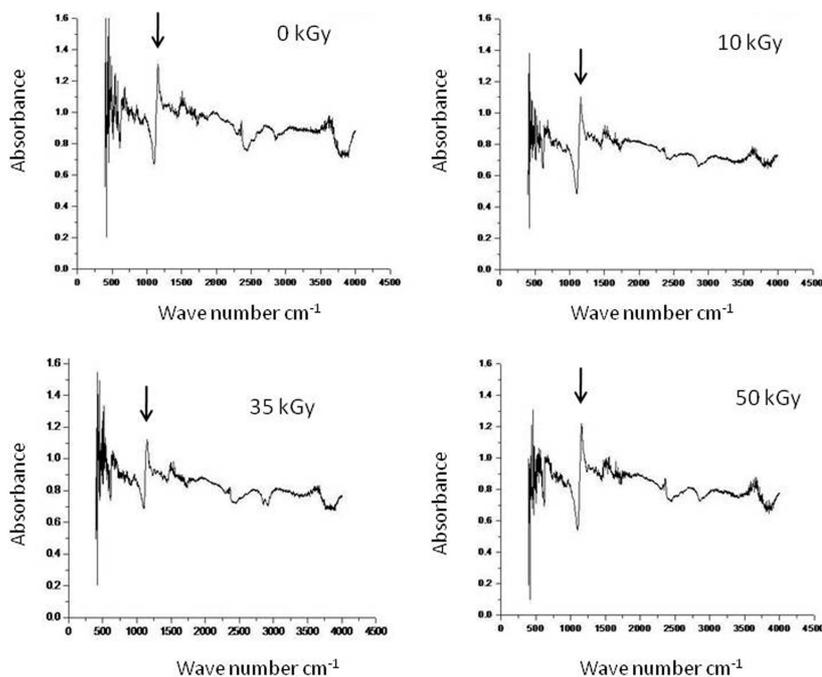
Figure 1. FTIR spectra for gamma doses of 0, 10, 35 and 50 kGy are shown. Intensity of the peak at 1150 cm^{-1}, marked by the arrow, is identified as C–C or C–O–C asymmetric stretching. It shows a decrease with irradiation up to 35 kGy, followed by an increase at 50 kGy.

3.2 *Viscosity in solution*

A simple way to probe the change in average molecular weight produced by ir-radiation, is to measure the viscosity of a solution in a suitable solvent [1]. It must be kept in mind however, that the viscosity is not simply proportional to the arithmetic mean of the molecular weights of all macromolecules. Higher molecu-lar weight chains contribute more to the viscosity. So a properly weighted mean is required [1]. Nevertheless, the viscosity of solutions of similar concentration in the same solvent for samples irradiated with different doses, does give an idea of whether the molecular weight is increasing or decreasing. Viscosity η measured relative to water at 33°C ($\eta_{\text{water}} = 0.7491$ cP) decreases from the unirradiated sam-ple, reaching a minimum around the dose 25 kGy, then increases somewhat up to 45 kGy.

The variation in viscosity of the polymer–salt complexes seems to indicate that initially chain scission is the dominating process with cross-linking catching up later. Polymer solutions are non-Newtonian at higher concentration, and so mea-surement at different shear rates and different concentrations will probably give more information.
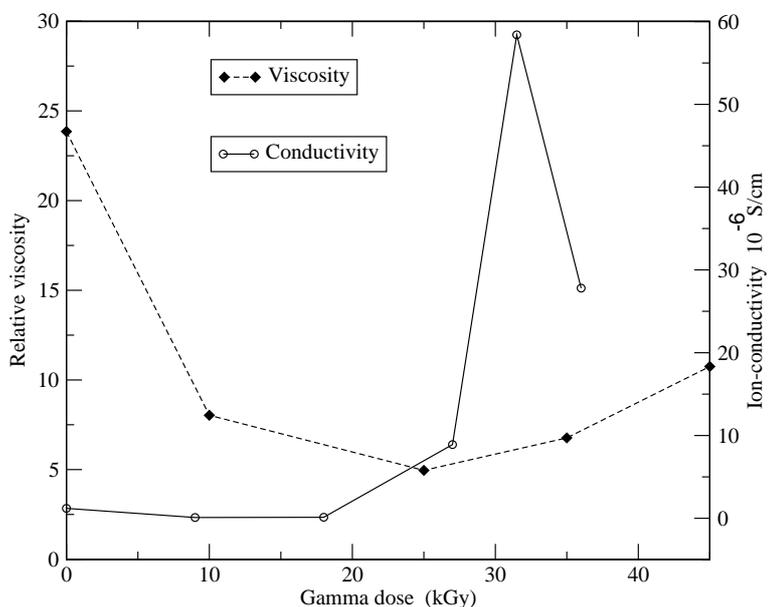
Figure 2. The relative viscosity in aqueous solution and the DC ion conductivity of the unirradiated sample and samples irradiated with 10, 25, 53 and 45 kGy gamma dose are shown. Conductivity is low, when viscosity is high.

3.3 *IS results*

The DC conductivity σ was extracted from the Cole–Cole plots. DC ion conductivity shows a non-monotonic variation like the viscosity. There is first a decrease at 10 kGy dose, followed by an increase with a maximum around 35–40 kGy. Compared to the unirradiated sample, there is an overall increase in σ on irradiation. Figure 2 compares the variation in ion conductivity and viscosity with gamma dose.

Frequency variation of the real part of the ion conductivity also shows that the initial doses of 10–20 kGy produces a decrease in σ at all frequencies, which is more than compensated by the subsequent increase in σ at still higher doses.

The frequency variation of the real part of σ is shown in figure 3 for different doses at 40°C. The change on irradiating the sample to 10–20 kGy is quite striking. Besides the magnitude being lower, the cross-over from the dispersionless variation to a power-law variation at higher frequencies occurs at a much lower frequency marked as A, compared to the cross-over marked B for the samples irradiated at higher doses. At gamma doses higher than 20 kGy, the cross-over points are again closer to the zero dose value. The details of the frequency dependence of the AC conductivity for disordered structures such as glasses and polymers, contains information about the microstructure and/or relaxation times of the sample [10–12]. The frequency range where the conductivity remains more or less constant, indicates that the charge carriers see an average structure, i.e. in the time corresponding to one cycle they cover distances on which the sample is homogeneous. At higher frequencies, there is usually a cross-over to a regime with a power-law
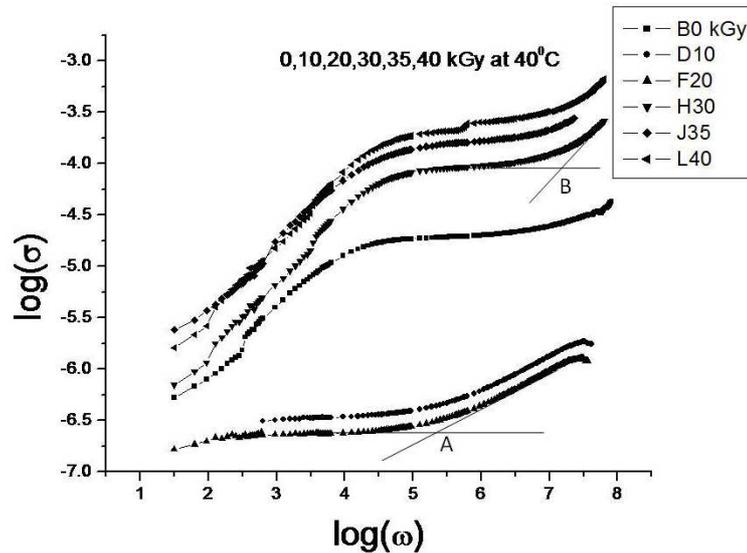
Figure 3. The real part of the AC conductivity at different frequencies shows an initial electrode-dependent regime, followed by a dispersionless DC regime. At still higher frequencies a power-law regime is observed. A and B indicate the cross-over frequencies for 20 and 30 kGy respectively.

frequency variation [13]. Here, the charge carriers remain confined in small units which may have a self-similar structure [12]. Such behaviour is attributed to a long-tailed distribution of relaxation times [10]. Since fractal morphology is observed in $PEO(1 - x)$–$NH_4ClO_4(x)$ [14], we assume in this case, spatial self-similarity at smaller length scales. So we infer that the microstructural units in the samples irradiated to 10–20 kGy are larger than in the unirradiated or higher irradiated samples, which is manifested in cross-over at a lower frequency. More measurements covering wider frequency ranges are necessary for a complete analysis of this aspect.

3.4 *DSC results*

DSC results show a systematic variation with irradiation dose, and an interesting observation is the presence of two minima for certain doses. Positions of the minima shift with irradiation dose, indicating a change in melting points. The results are shown in figure 4. More detailed results are to be found in [15]. The unirradiated DSC curve shows two minima, the deepest is at 71.5°C and there is a less prominent minimum at 60.5°C. This indicates the presence of two different crystalline species with different melting points. As dose increases, the deeper trough becomes less prominent, until at 17 kGy, the two minima are almost equal in depth. On further increase in dose, the higher temperature trough almost vanishes, now the only prominent minimum is at 58.5°C. So finally only one of the crystalline species survives the radiation, the other probably becomes amorphous.
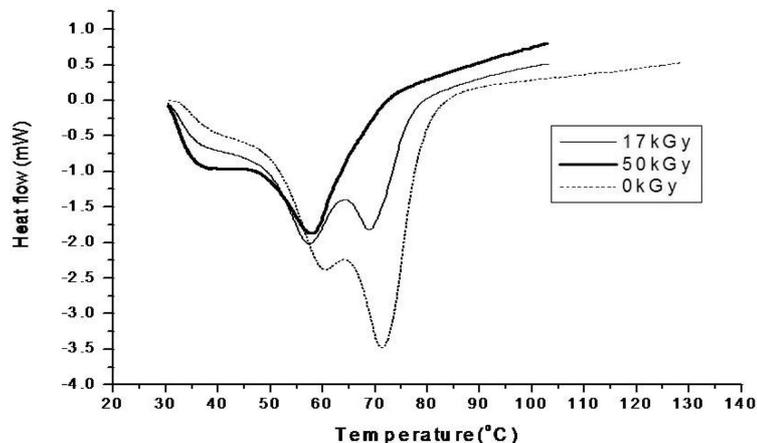
Figure 4. DSC traces for the unirradiated and gamma-irradiated samples. Only doses of 17 and 50 kGy are shown for clarity. Presence of two crystalline species with different melting point is clear. At 50 kGy irradiation, only one survives.
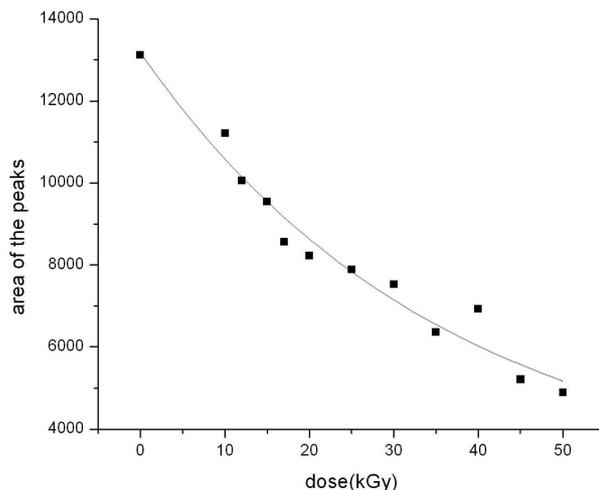

Figure 5. The total area enclosed by the troughs in the DSC traces decreases with gamma dose. The results follow an exponential curve quite well, as shown in the figure.

The area from baseline within the DSC curve has been calculated for all doses. A graph of the total area against radiation dose is shown in figure 5. As dose increases the area decreases monotonically, indicating a decrease in total crystallinity. The effect of gamma irradiation is found to be different from earlier results of ion beam irradiation on similar samples [16].

The overall observation is that the area within the dip in the absorbed heat vs. temperature curve, progressively decreases with increasing gamma dose. This

indicates a reduction in the total crystallinity [15]. Decrease in area of the DSC curve with temperature is shown in figure 5, with an exponential fit to the curve. Assuming that the area is proportional to the crystallinity χ, this variation can be understood as follows. If a dose dD produces a proportional change $d\chi$ in χ, we may write

$$d\chi = -c\chi \, dD, \tag{1}$$

where c is a constant. This leads to

$$\chi = A \exp(-cD), \tag{2}$$

A being determined by the initial crystallinity.

DSC results are consistent with viscosity results, since we normally expect scission of linear chains to lead to lower crystallinity [17].

4. Discussion and conclusions

A large number of reports on irradiation effects in polymers and particularly solid polymer electrolytes have appeared [3,18–21]. Ferloni *et al* [19] have irradiated aqueous solutions of PEO_{20}–$LiClO_4$. They found an improvement in ion conductivity without deterioration in mechanical strength, which occurs on irradiating dry samples [19]. Plasticizers and modifiers are added for further improvement [22]. Singh *et al* [17] found a large enhancement in σ on electron beam irradiation of low molecular weight $PEG(x)$–$LiClO_4$, which they attributed to chain scission and reduction in crystallinity. Song *et al* [18] considered cross-linking to be responsible for large enhancement in σ for $PEG(x)$–$LiClO_4$. So there are issues not yet resolved.

Earlier work on irradiation of the same polymer electrolyte, PEO–NH_4ClO_4 with $x = 12\%$, did not show significant improvement in conduction properties [8]. However at that salt concentration σ is very low for the pristine sample. The present work is done on samples where $x = 18\%$, and σ is the highest for the unirradiated sample. The overall finding is that ion conduction improves with gamma irradiation dose and this is related to the decrease in crystallinity observed in DSC studies. However, the improvement is not monotonic. The variation of viscosity and conductivity with gamma dose, show an inverse correlation which is realistic. The conductivity is minimum, when the viscosity is maximum. For maximum conductivity, the viscosity is not exactly minimum, but low over the range where σ is high. The DSC result of more or less monotonic decrease in total crystallinity, seems not perfectly in agreement with the arguments above, but the presence of multiple minima in DSC needs a closer scrutiny and analysis. Detailed study of the dynamic IS results promises to throw more light on changes in microstructure by irradiation.

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