Radiation Physics and Chemistry 98 (2014) 124–131

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Effect of electron beam irradiation on polymer electrolytes: Change in morphology, crystallinity, dielectric constant and AC conductivity with dose

S. Raghu [a], Subramanya Kilarkaje [a], Ganesh Sanjeev [b], G.K. Nagaraja [c], H. Devendrappa [a,*]

[a] Department of Physics, Mangalore University, Mangalagangothri- 574199, India
[b] Microtron Centre, Department of Physics, Mangalore University, Mangalagangotri- 574199, India
[c] Department of Chemistry, Mangalore University, Mangalagangothri- 574199, India

HIGHLIGHTS

- 8 MeV EB irradiation effect on dielectric constant and AC conductivity of polymer electrolyte films was observed.
- Occurrence of chain scission due to breaking of bonds was confirmed by FT-IR analysis.
- AC conductivity increases with dose due to more number of free charges involved in conduction.

ARTICLE INFO

Article history:
Received 8 April 2013
Accepted 29 January 2014
Available online 5 February 2014

Keywords:
Electron irradiation
Polymer electrolyte
DSC
FT-IR
Dielectric properties

ABSTRACT

Polymer electrolyte (PEO:Li_2SO_4) films were exposed to 8 MeV electron beam (EB) with various doses to investigate the radiation effect on dielectric permittivity (real and imaginary) and AC conductivity by using PC based Impedance Analyzer in the frequency range of 40–1 MHz at different temperatures. The change in chemical interaction, morphology, and thermal properties was analyzed with the help of Fourier Transform InfraRed (FT-IR), Scanning Electron Micrographs (SEM) and Differential Scanning Calorimeter (DSC) techniques respectively for before and after irradiation. The chemical change was confirmed from the FT-IR result which showed that peak intensities corresponding to C–H, C=C, and –C–O–C– bonds decrease with increase in EB dose clearly indicating that the degradation of polymer chain or segments (i.e., $–CH_2–CH_2–$). The DSC result showed that the melting temperature of unirradiated film is 69.42 °C which reduced to 67.55 °C for 30 kGy dose suggesting an exothermic behaviour. The SEM images give that surface roughness and crack depths increase with increasing dose. The XRD result reveals a decreased ~30% crystallite size for 30 kGy dose compared with unirradiated film. Further, it is seen that dielectric permittivity and frequency dependent conductivity were found to increase with increasing irradiation dose. The maximum AC conductivity was observed to be 1.88×10^{-4} s/cm for 30 kGy and the estimated change in charge carrier concentration also showed high for 30 kGy dose. The AC conductivity obeys Power's law. The frequency exponent (s) parameter shows temperature dependent behaviour which decreases after irradiation.

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1. Introduction

In recent years electron beam (EB) irradiation technique is becoming an advanced approach to optimize the physical properties of polymer materials such as dielectric, electrical, structural, and thermal properties (Cleland et al., 2003). However, the modification depends upon the irradiation dose rate and material characteristics. Modified polymer electrolytes are prominent materials for a wide range of potential applications like polymer light-emitting diode (Santos et al., 2004), solid state battery, optical display (Sevil et al., 2003), and electronic device (Fink et al., 2005; Suzuki, 2003). Whenever EB energy interacts with polymer material it induces change in the molecular structural arrangement such as ionization, displacing atoms, carbonization, and production of free radicals; as a result chain scission and cross linking leading to degradation occur. The radiation not only alters the chemical structure of the polymer, but it can also enhance the presence of trapped charges or creates defects in the polymer

* Corresponding author. Tel.: +91 824 2287363; fax: +91 824 2287289.
E-mail address: dehu2010@gmail.com (H. Devendrappa).

http://dx.doi.org/10.1016/j.radphyschem.2014.01.024
0969-806X © 2014 Published by Elsevier Ltd.

matrix (Chen et al., 1996). Thus, these alterations are responsible for the change in the dielectric, electrical and thermal properties of irradiated polymers (Wielunski et al., 1997; Kumar et al., 2003; Virk et al., 1998; Randall et al., 1983).

In other words, irradiated polymers can convert them from insulators to good electrical conductivity materials which is a good sign and these materials can be used in various electronic applications (Clough, 2001). Generally polymer electrolytes are found in solid or viscoelastic state; the molecular structure plays a significant role in determining the dielectric behaviour (Leyla et al., 1984). Therefore, in this work, dielectric constant and AC conductivity of modified polymer are examined to understand charge transportation (Hazarika et al., 2012). These phenomena are powerful means to know the charge relaxation and mobility in polymer electrolytes (Karmakar and Ghosh, 2011).

Electrical conduction by ions is believed to take place only in the amorphous and free volume regions and chain motions are supposed to aid the ions to move. However, dielectric parameters of polymer electrolyte are a much more complex system because of the competition between intra–inter chain process in the transport mechanism, the radiation modification being still more complex. However, in this paper the dielectric, AC conductivity and thermal behaviour of modified polymers will be studied. Lower EB doses such as 10, 20, and 30 kGy have been used because obtained results are more consistent than with high doses. It was observed from FT-IR that carbonyl group (C=O), C–O–C, C=C and CH_2 peaks intensity changes with increasing the dose suggesting the occurrence of chain scission, which gives evidence that the melting point and crystallite size results were well correlated. This in turn increases the volume of the amorphous region in the polymer system; hence the AC conductivity increases. Joykumar Singh et al. (2004) reported the enhanced ionic conductivity of EB irradiated PEG:$LiClO_4$ polymer electrolyte films, i.e. 7.27×10^{-7} S/cm for an unirradiated sample and 1.31×10^{-5} S/cm for 15 kGy irradiated sample and Kronfli et al. (1988) reported that the conductivity enhancement of gamma rays irradiated PEO-LiX films was found to be 10^{-5}–10^{-4} S/cm at 60 °C and 10^{-6}–10^{-5} S/cm at 30 °C. These values are well comparable and consistent with the observed result.

The literature review revealed that very little work has been reported on EB induced effect on dielectric and AC conductivity of polymer films. Thus, in the present investigation (PEO:Li_2SO_4) polymer electrolyte films were prepared using solution cast method and were exposed to 8 MeV EB with different doses to study the effect of EB irradiation on dielectric permittivity, AC conductivity, morphology, and thermal behaviour of the polymer electrolyte films.

2. Experimental methods

25% Li_2SO_4 doped PEO film was prepared by using the solution-cast technique. PEO ($M_w=5\times10^6$) powder was procured from M/s. Sigma-Aldrich, USA, lithium sulfate (Li_2SO_4) from M/s Loba Chemicals (M.W.127.96), and methanol (acetone free) from NICE Chemical. The PEO:Li_2SO_4 of 75:25 weight percentage was dissolved in methanol (CH_3OH) and the mixture was stirred for about 6–8h at room temperature. The stirred homogeneous mixture was then cast onto a polypropylene dish and allowed to evaporate at room temperature. The thickness of the film was measured using Mitutoyo Dial Gauge and was found to be 0.265 mm. An 8 MeV EB was used to irradiate the film in the free air environment at the Variable Energy Microtron Centre, Mangalore University, Mangalagangotri. The dose rate was adjusted with a current of 20 mA, pulse repetition rate of 50 Hz, and pulse width of 2.3 μs. The irradiation experiment was conducted in a fixed set-up and the dose was measured using the chemical dosimeter. The doped film (2 cm^2) was sealed in thin transparent polyethylene bags and irradiated with 10, 20, and 30 kGy doses. The FT-IR was done using AIM-8800 FT-IR Spectroscopy in KBr medium. The DSC study was performed using Universal V4.5A TA Instrument in the temperature range of −80 to 80 °C with a scanning rate of 1 °C/min. The SEM images of unirradiated and irradiated films were obtained by SEM; JEOL Model JSM, 6390LV model. The dielectric permittivity and AC conductivity were evaluated by measuring the capacitance and loss tangent using PC based Precision Impedance Analyzer (Model 6500B) with PID temperature controller in the frequency range of 40 Hz–1 MHz and temperature range of 303–338 K.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 illustrates the FT-IR spectra of unirradiated and irradiated polymer films. The chemical changes due to EB irradiation are identified from the variation in FT-IR peaks intensity and frequency shifts compared with that of the unirradiated film. The lists of peak assignments are cited in Table 1. The peak observed in the range of 2800–3000 cm^{-1} corresponds to C–H stretching vibration; the intensity of the peak decreases and widens slightly with increasing dose signifying the degradation of polymer chain or segments as a result of breaking the bond. The C–O–C stretching band appears at 1100 cm^{-1} in unirradiated film and this peak intensity decreases with the dose suggesting that radiation affects the polymer chains. The peak observed at 1656 cm^{-1} indicates the

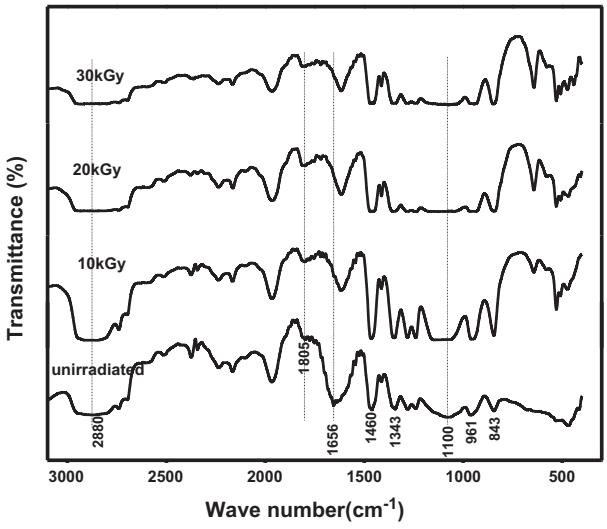

Fig. 1. FT-IR spectra of pristine and irradiated polymer electrolyte films.

Table 1
Relevant data of FT-IR spectra of unirradiated and EB irradiated films.

Unirradiated (ν/cm)	10 kGy (ν/cm)	30 kGy (ν/cm)	Peak assignment
–	646	646	–
843	846	848	–
961	955	956	C−H in-plane bending
1100	1100	–	C−O−C stretching
1343	1343	1343	CH_2 asymmetric bending
1460	1460	1459	CH_2 symmetric bending
1656	1618	1618	C=O stretching
–	1805	1805	C=O stretching
2880–3000	–	–	CH stretching vibration

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