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Electron beam induced modifications in conductivity and dielectric property of polymer electrolyte film

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HIGHLIGHTS

- Film is exposed to 8 MeV Electron Beam with the doses of 25, 50, and 75 kGy.
- Morphology changes of the film conformed from Scanning Electronic Microscopy (SEM).
- AC conductivity shows increases with frequency as well as electron fluence.
- The dielectric constant was satisfying the universal law of dielectric constant.
- The dielectric relaxation time (τ) decreases with the increase of electron fluence.

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ABSTRACT

This paper describes the effect of 8 MeV of electron beam (EB) energy irradiation on the electrical conductivity and dielectric properties of sodium fluoride NaF-doped polyethylene oxide (PEO) film. The structural and chemical characterizations were employed using X-ray diffractometry (XRD) and Fourier Transform Infrared (FTIR) techniques respectively before and after irradiation. The morphology study carried out using Scanning Electronic Microscopy (SEM) analysis. The DC electrical conductivity showed increases with dose and temperature and was consistent with Arrhenius behavior. The maximum conductivity of 1.1×10^{-5} S/cm and minimum activation energy of 0.25 eV were obtained at 25 kGy, 338 K; further increases in the dose resulted in a reduction in conductivity. The real (ε') and imaginary (ε'') part of the dielectric constant suddenly decreased in a low frequency region (40–640 Hz), subsequently independent at higher frequency. The AC conductivity showed increases with frequency and temperature for all films. The dielectric constant and AC conductivity increased at the 25 kGy dose due to chain scission. Further increases in dose such as 50 and 75 kGy, resulted in a decrease in dielectric constant and AC conductivity due to cross-linking. The electric modulus approach was used to calculate the dielectric relaxation time (τ), which decreased at 25 kGy and then increased at 50 and 75 kGy doses. The modulus data were fitted using a non-exponential Kohlrausch–Williams–Watts (KWW) function $\phi(t)$, and the results indicate the existence of a non-Debye relaxation.

1. Introduction

The study of the electrical conduction of polymers under the influence of different parameters (ionizing radiation, temperature, thickness, etc.) has been the subject of considerable investigations. Thus, it is necessary to understand the influence of EB radiation on the physical properties of polymer electrolytes for exploiting their many potential applications in devices such as solid-state batteries, opto-electronic devices and electrochemical devices. Polyethylene oxide (PEO) is an exceptional polymer; it dissolves high concentrations of a wide variety of inorganic salts to form polymer electrolytes, and it exhibits ionic conductivity. In the present investigation, sodium fluoride was incorporated into PEO. As Na^+ is a fast conducting ion in a number of crystalline and amorphous materials, it may expected to enhance charge efficiency in a polymer system, thus improving electrical and dielectric performance. Solid polymer electrolytes (SPEs) have been widely studied for potential applications in solid-state batteries and other electrochemical devices (Meyer, 1998; Gray, 1997). SPEs are also of fundamental interest because of their unusual mechanism of ionic transport.

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Ionic transport in polymer electrolytes is affected by EB radiation, and there is significant alteration in the electrical and dielectric properties. The EB can also be used for various purposes such as the preparation of polymers (Chirinos et al., 2003) or for the modification of polymer properties (Sevil et al., 2003; El-Sayed et al., 2004; Walszczak et al., 1995; Abdel-Hamid et al., 2004). The induction of irradiation can affect structure or molecular (polymer unit) arrangement because of chemical changes such as the displacement of atoms, the creation of new double bonds (formation of unsaturation C═O), carbonization, chain scission (—C—C— bond scission), and radical—radical combination (cross-linking) (Ruck et al., 1997; Nouh, 2004; Bauffard et al., 1995). These modifications favor to promotion of charge transportation; hence, SEM has shown modifications in the electrical conductivity and dielectric properties of irradiated polymer electrolytes.

Therefore, the study of the electrical conductivity and dielectric property in EB-induced polymer electrolytes has become an interesting area of active research for understanding charge transportation. In this work, EB-induced modifications of the electrical conductivity and dielectric properties of polymer electrolyte films were reported. The conductivity and dielectric properties of polymer electrolytes have been investigated and reported over the past two decades (Tanaka et al., 1970; Srivastave and Srivastave, 1981) but the amount of reported work has been minimal. Pawde et al. studied the effect of EB irradiation on the mechanical and dielectric properties of polypropylene films (Pawde and Parab, 2011). Uchiyama et al. showed that chain scission and cross linking in PEO was a result of EB effect (Uchiyama et al., 2009). Singh N. L et al. observed that changes in the dielectric properties were due to chain scission and cross linking (Singh et al., 2004). In general, it is a well-known fact that conductivity in doped PEO is influenced by the concentration of defects and the volume of the amorphous region in the system. EB radiation has also been used to increase the amorphous volume and has been reported to enhance conductivity (Damle et al., 2008). EB-mediated degradation takes place in irradiated polymers (Singh et al., 2008; Vijayalakshmia et al., 2005). Based on these studies, a number of authors have recently investigated the effect of EB irradiation effect on the optical properties of doped polymer electrolyte films (Kilarkaje et al., 2011). In the present work, we studied the change in the electrical conductivity and dielectric property of EB-irradiated polymer electrolyte films over a dose range of 0–75 kGy. The obtained results reveal that electrical conductivity, dielectric constant (real and imaginary), and ac conductivity are all affected by EB irradiation.

2. Experimental methods

2.1. Polymer electrolyte film preparation

Polyethylene oxide (PEO, $M_w = 5 \times 10^6$) powder was procured from M/s. Shanghai Research Institute, Shanghai, China, Sodium fluoride (NaF) (M.W. 228.35) was obtained from M/s Loba chemicals, Mumbai, India, and methanol (acetone free) was obtained from the NICE laboratory. The film was prepared using the solution–cast technique. PEO:NaF (50:50 w/w) was dissolved in methanol (CH_3OH) and stirred for approximately about 6–8 h at room temperature to obtained a homogenous viscous mixture. The stirred mixture was cast onto polypropylene dishes and allowed to evaporate. The thickness of the film was measured using a Mitutoyo Dial thickness gauge and was determined to be 0.265 mm.

2.2. Electron beam irradiation

The polymer electrolytes were irradiated by an 8 MeV electron beam (EB) at the Variable Energy Microtron Center, Mangalore University, Mangalagangotri. The beam was controlled with the help a 20 mA current, pulse repetition rate of 50 Hz and pulse width 2.3 μs. The film (2 cm^2) sealed in thin transparent polyethylene bags, and was introduced perpendicularly to the beam direction; the electron beam doses were 25, 50, and 75 kGy. The required doses were controlled by adjusting the EB parameters and the conveyer speed.

2.3. Characterization

Before and after irradiation, the characterization of the films conducted by Fourier Transform Infrared spectroscopy, scanning electron micrographs and a PC based impedance analyzer.

2.3.1. Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectra of the irradiated and non-irradiated films were recorded in the transmission mode using a model AIM-8800 FTIR Spectroscopy in KBr medium. The spectra for polymer's transmittance were obtained for the polymer's transmittance obtained as a function of wave number in the 3500–500 cm^{-1} range. The variation in transmittance before and after irradiation was compared, and the peaks were analyzed to study the chemical changes.

2.3.2. Scanning electron micrograph (SEM) images

SEM images of the non-irradiated and irradiated films were obtained by a JEOL SEM (Model JSM, 6390 LV).

2.3.3. Conductivity and dielectric measurements

The DC electrical conductivity and dielectric properties were measured using a PC based Keithley Electrometer (model 6514) and a PC based Precision Impedance Analyzer (Model 6500B), with the PID and temperature controlled using a frequency range of 40 Hz–1 MHz and temperature range of 303–338 K, respectively.

The dielectric constant (ε') was calculated from the following equation:

$$\varepsilon' = C_p/C_o, \quad (1)$$

and

$$C_o = \varepsilon_o A/d \quad (2)$$

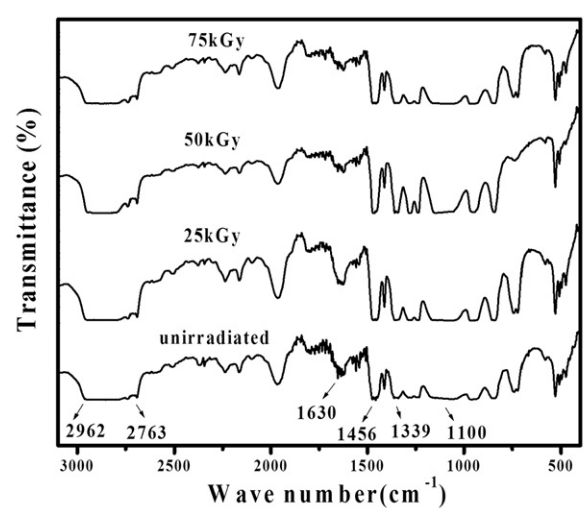

Fig. 1. FTIR spectra for unirradiated, 25, 50 and 75 kGy doses.

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