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Electron beam and gamma ray irradiated polymer electrolyte films: Dielectric properties

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ABSTRACT

In this study, polymer electrolyte films were irradiated with electron beam (EB) and Gamma ray (GR) at 50 and 150 kGy. The induced chemical changes in films due to irradiations have been confirmed from the Fourier Transform Infra red (FT-IR) spectra. The X-ray Diffractometry (XRD) results show that crystallinity decreases by ~20% in EB and ~10% in GR irradiated films respectively compared to non-irradiated film. The micro structural arrangement was investigated by Scanning Electronic Microscopy (SEM) and the images reveal that there is a substantial improvement in the surface morphology in irradiated films. The real (ε') and imaginary (ε'') dielectric constant and AC conductivity are found to increase with increase in irradiation dose. Improved dielectric properties and conductivity (1.74×10^{-4} & 1.15×10^{-4} S/cm, respectively, for EB and GR irradiated films at room temperature) after irradiation and it confirm that EB and GR irradiation can be simple and effective route to obtaining highly conductive polymer electrolytes. From this study it is confirm that EB is more effectiveness than GR irradiation.

1. Introduction

In recent years, polymer electrolytes have been attracting scientific and technological importance because of their potential applications in many areas such as Li-ion polymer solid state batteries, super capacitor, electro-chromic devices, etc. Wright and Fenton first proposed the idea of preparation of polymer electrolytes in 1973, but its technological significances were achieved and appreciated by Armand et al. a few years later Armand, Chabango, and Duclot (1998). As advanced technology keeps on developing every day, the demand for polymers is raising continuously, in particularly polymer electrolyte because of its use in various promising applications Khan and Qureshi (1999). PEO based polymer electrolytes are still among the most extensively studied polymer ionic conductors due to fast ion transport, and they easily associate with other ions especially inorganic alkali and transition salts Chiu, Chen, Kuo, Huang, and Chang (2004). In particular to Cadmium chloride ($CdCl_2$)-doped PEO has attracted considerable attention because of fine tune their fundamental physical properties by simply varying the cluster size and composition makes them highly attractive for a variety of possible applications Liu et al. (2001). The main advantage of polymer electrolytes is the easy preparation of

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films of desired size and shape and its ability to form proper electrode/electrolyte contact in electro-chemical devices. These materials exhibit relatively complex multi-phase behavior in crystalline as well as amorphous phase. In the last few years, considerable efforts have been devoted to develop the volume of amorphous in polymeric materials, for which a number of different techniques such as doping, blending, plasticization, and ionizing radiation were used to reduce the crystallinity of polymer. In this case, EB and GR radiation methods were used for modify the material phase. Irradiation plays a prominent role in the modification of the physical properties of polymers because the radiation process directly provides the energy to the system. If ionizing radiation is passed through the matter, the energy deposit in the material causes irreversible changes in the macromolecular structure of the target material. Hence, the application of radiation in polymer technology has great importance to achieve desired modification in the physical properties polymeric materials.

Therefore, modification of polymer has become an important research area, mainly in industrial applications such as wire and cable, electronic devices, medical, and marine Drobny (2002), Chmielewski, Haji-Saeid, and Ahmed (2005) and Sperling (1992). On a large commercial scale, various radiation processing techniques such as EB, GR, UV, and X-rays or laser beams have demonstrated to be very effective means of improving the end-use properties of various polymers. In the present study, EB and GR irradiations with various dosages were used to expose the polymer electrolyte film, it interact with polymer chain could be undergo crosslink or chain scission leading to alteration in the macromolecular structure, which is most effective because no special additives are required. This structural modification in the irradiated polymer electrolyte is directly influence on physical properties; in this case the dielectric permittivity and electrical conductivity were observed increased with increasing the dose. The changes strongly depend on the physics and chemistry of the absorbed materials; as well as the chosen radiation energy and dose. The radiation effects may cause occurrence of ionization or excitation of the electrons in atoms, and displacement of atoms from their original site to adjacent lattice sites of the solid permit charges should be become free or loosely bonded to some trapping centers elsewhere in the material structure as a result cross-linking or chain scission Bouffard, Balanzat, Leroy, Busnel, and Guevelou (1997) and Mujahid et al. (2004). The presence of trapping charge within the material was influenced by the induced radiation, thus of the increase in the transport property Zahran, Kander, Hegazy, and Kassem (1993). Also, it is observed that alteration in the functional group of polymer causes a change in the physical properties of polymer films Fink (2004) and Dworecki, Hasegawa, Sudlitz, and Wasik (2001). In the past few years, the effects of EB and GR on polymers have been investigated individually and some of the results presented in the literature state that irradiation may reduce crystallinity, induce cross-linking, and produce a unsaturated carbonyl groups Cleland, Parks, and Cheng (2003), Mishra et al. (2001), Perloni, Magistris, Chiodelli, Faucitano, and Buttafava (1991), Nasef, Saidi, and Dahlan (2002) and Shah et al. (2008).

Dielectric measurements are performed to know the information about the molecular dynamics and the charge transportation mechanism in Polymer electrolytes films. Polymers with high dielectric permittivity have received increasing interest in recent years due to their potential applications in embedded capacitors, gate dielectrics and charge storage applications as they provide advantage in size and cost reduction. Literature survey reveals that, the dielectric studies on ionically conducting solids although important and valuable from scientific point of view, has not been studied extensively due to the limitations and complexity in data analysis.

Therefore, gaining a better understanding of the radiation influence on the ion dynamics and segmental motion of charges will facilitate to design new devices for required purposes. In addition, it is important to understand how the relaxation dynamics is affected by the dose. Thus, the effect of radiation on the physical and structural properties of such materials is required to be studied particularly, when such devices are being used in the radiation environment. The intention of this study is to investigate the effect of EB and GR on the dielectric properties of polymer electrolyte films.

2. Experimental

2.1. Materials

The Polyethylene oxide (PEO, Mw $= 5 \times 10^6$) powder was procured from M/s Sigma Aldrich Chemicals USA, Cadmium Chloride ($CdCl_2$) (M.W. 201.32) was obtained from SDFCL, Mumbai, India, and methanol (acetone free) was obtained from the NICE laboratory.

2.2. Methods

2.2.1. Polymer electrolyte film preparation

The film was prepared using the solution-cast technique. PEO: $CdCl_2$ (75:25%) was dissolved in methanol (CH_3OH) and stirred for approximately 6–8 hours at room temperature to obtain a homogenous viscous mixture. The stirred mixture was cast onto polypropylene dishes and allowed to evaporate at room temperature. The thickness of the film was measured using a Mitutoyo Dial thickness gauge and was determined to be 0.25 mm.

2.2.2. Irradiation source

The polymer electrolyte films were irradiated using electron beam accelerator with 8 MeV-20A current, pulse repetition rate of 50 Hz, pulse width 2.3 μs, and varying dose of 50, and 150 kGy in the air. They were also irradiated with gamma ray (^{60}Co source) at ambient temperature using a gamma cell at fixed dose rate of 9.5 kGy/hour and varying doses of 50 and 150 kGy.

2.2.3. FT-IR study

The FT-IR spectra of the non-irradiated and irradiated films were recorded in the transmission mode using model AIM-8800 FTIR Spectroscopy in the KBr medium. The spectrum of the transmittance as a function of wave number in the range