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Conductivity enhancement in SiO_2 doped PVA:PVDF nanocomposite polymer electrolyte by gamma ray irradiation

M. Hema [a,*], P. Tamilselvi [a,b], P. Pandaram [c]

[a] Department of Physics, Kamaraj College of Engineering and Technology, Virudhunagar 626001, Tamilnadu, India
[b] Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam 638401, Tamilnadu, India
[c] Kudankulam Nuclear Power Project, Kudankulam, Tamilnadu, India

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ABSTRACT

Nanocomposite polymer electrolyte has been irradiated with 15 Gy Gamma rays. Exposure of gamma radiation caused scissoring and crosslinking of polymer chains thereby increasing amorphous phase of the polymer matrix because of which the ionic conductivity has been enhanced. Ionic conductivity of irradiated nanocomposite polymer electrolyte is enhanced to 9.4×10^{-4} Scm^{-1} at 303 K compared to un-irradiated system ($\sigma \sim 1.7 \times 10^{-4}$ Scm^{-1}). Temperature dependence of ionic conductivity of both un-irradiated and irradiated systems obeys VTF relation. Frequency and temperature dependence of dielectric and modulus of both systems have been analyzed. The ionic transference number of polymer electrolyte has been calculated by Wagner's polarization technique and it confirms that conducting species are predominantly due to ions in both systems.

1. Introduction

In recent years, solid polymer electrolyte attracts many researchers for its wide range of potential applications in lithium ion batteries, sensors, fuel cells, super capacitors, solar cells [1] because of its excellent properties of size flexibility, light weight, non-flammability, non-leakage [2,3]. For the past few decades, achieving the maximum ionic conductivity at room temperature is the one of the challenging criteria in polymer electrolyte [4]. Hence, different techniques such as blending, plasticization, addition of fillers and ionizing irradiation were used to enhance the properties. However, ionizing radiation is the one of the effective method to enhance the properties of polymer electrolytes. The ionizing radiation such as X-rays, alpha rays, beta rays and gamma rays causes chemical as well as physical changes in the exposed substance. Recently the researchers investigated that the effect of gamma radiation [5], electron beam radiation [6] and heavy ion radiation [7] on physical and chemical properties of polymer electrolyte. Among them, gamma radiation in polymer electrolyte causes chain scission and crosslinking simultaneously [8,9]. It increases the fraction of amorphous region in polymer electrolyte thereby enhancing the ionic conductivity. Literature review shows a very few work on gamma ray irradiation (15 Gy for 1 h) of nanocomposite polymer electrolyte based on PVA and PVDF.

The aim of the present work is to study the effect of gamma ray irradiation on the conductivity, dielectric properties of nanocomposite polymer electrolyte. Hence the optimized system of nanocomposite polymer electrolyte (80PVA:20PVDF:15$LiCF_3SO_3$:8SiO_2) from our earlier work [10] was taken for the present investigation and subjected to gamma ray irradiation.

2. Experimental

2.1. Preparation of nanocomposite polymer electrolyte

Poly(vinyl alcohol), PVA (M.w.: 1,25,000) and Poly(vinylidene fluoride), PVDF (M.w.: 5,30,000) were purchased from S. d.Fine, India, Lithium triflate, $LiCF_3SO_3$ from Alfa Aesar and N, N-Dimethyl formamide, DMF from Merck, SiO_2 (average particle size ~ 85 nm). The purchased raw materials were used without further purification.

Nanocomposite polymer electrolyte (80PVA:20PVDF:15$LiCF_3SO_3$:8SiO_2) has been prepared using solution casting technique. Appropriate quantities of each constituent were separately dissolved in DMF and stirred at the temperature of 60 °C. The dissolved polymers and the salt solutions were mixed together and stirred continuously at the same temperature, until homogeneous solution has been obtained. Thus, the obtained solution was casted

* Corresponding author.
E-mail address: mhemaphysics@gmail.com (M. Hema).

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in petri dishes. After vacuum dried for 24 h, the resulting films were flexible and free standing. Thickness of the prepared nanocomposite polymer electrolyte was in the range of 100 μm. Further, it has been irradiated with 15 Gy gamma ray radiation.

2.2. Irradiation source

Composite polymer electrolyte is irradiated by Cesium - 137 source of energy 0.662 MeV using the gamma auto irradiation system for the cumulative the dose of 15 Gy for 39 h (dose rate: 385 mGy/h) at ambient temperature (30 °C) with normal atmospheric pressure of 1012 mbar.

2.3. Characterization

2.3.1. XRD analysis

X-ray diffraction measurement was carried out in the X-ray diffractometer (D8 Advance ECO XRD systems with SSD160 1D detector, Bruker) using CuKα (λ = 1.54060A°) in the range of 10°–60° (40 kV, 25 mA) with the scan rate of 20°/m.

2.3.2. Differential scanning calorimetry (DSC)

DSC measurement was recorded using DSC-Q20 (Canada) over the temperature range of 40°–190 °C at a heating rate of 10 °C/min under nitrogen atmosphere that has been calibrated with the melting transition of aluminium.

2.3.3. AC impedance spectroscopy

AC impedance spectroscopy was studied using Biologic, SP-300 in the frequency window, 42 Hz–7 MHz at different temperatures from 303 K to 363 K by sandwiching the prepared polymer electrolyte film between stainless steel blocking electrodes.

2.3.4. Transference number measurement

Transference number was calculated using Wagner's Polarization technique [11] to confirm the ionic nature of prepared polymer electrolyte. In this measurement, polymer electrolyte was sandwiched between two stainless steel electrodes. A fixed dc voltage (1V) has been applied across the sample and the corresponding decay DC current is monitored as a function of time.

3. Results and discussion

3.1. XRD analysis

XRD pattern is used to examine the structural and crystalline phase of the polymer electrolytes. Fig. 1 shows the XRD pattern for un-irradiated and irradiated nanocomposite polymer electrolyte. Major broad peak observed at 20° in both un-irradiated and radiated nanocomposite polymer electrolyte corresponds to PVA:PVDF blend [12]. Influence of high surface area nano SiO_2 filler in both systems prevents the polymer chain reorganization and this prevention favors amorphous phase at ambient temperature [13]. After irradiation, intensity of the peak decreased and width of the peak increased in the irradiated system. It reveals that decrease in degree of crystallinity of polymer electrolyte. It is attributed to the degradation of polymer chains [14] that forms more number of polymer segments. Hence the exposure of gamma radiation enhances the amorphous phase of polymer electrolyte by the scissioning and crosslinking process.

3.2. DSC analysis

DSC thermogram is used to examine the glass transition (T_g) and melting temperature (T_m) of polymer electrolyte. Fig. 2 depicts the DSC thermogram of un-irradiated and irradiated nanocomposite polymer electrolyte. It is observed that, both glass transition and melting temperature of irradiated nanocomposite polymer electrolytes decreases (Table 1). Uniform dispersion of SiO_2 nanoparticles in polymer matrix confirmed from single T_g and T_m

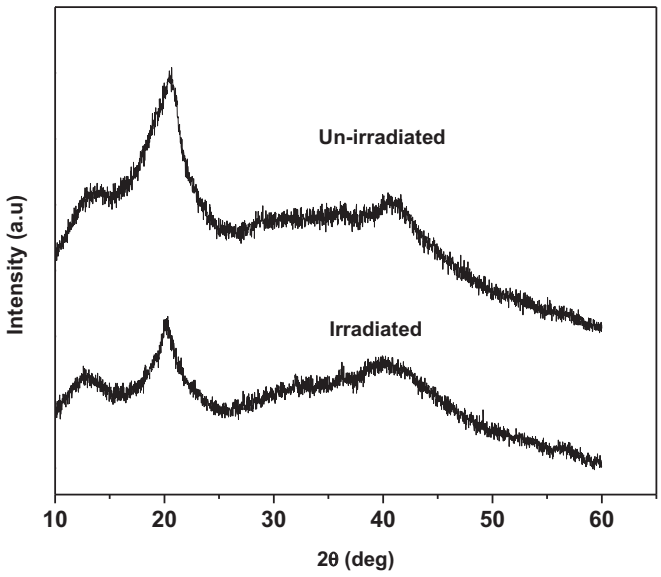

Fig. 1. XRD pattern for (i) un-irradiated and (ii) irradiated nanocomposite polymer electrolyte.

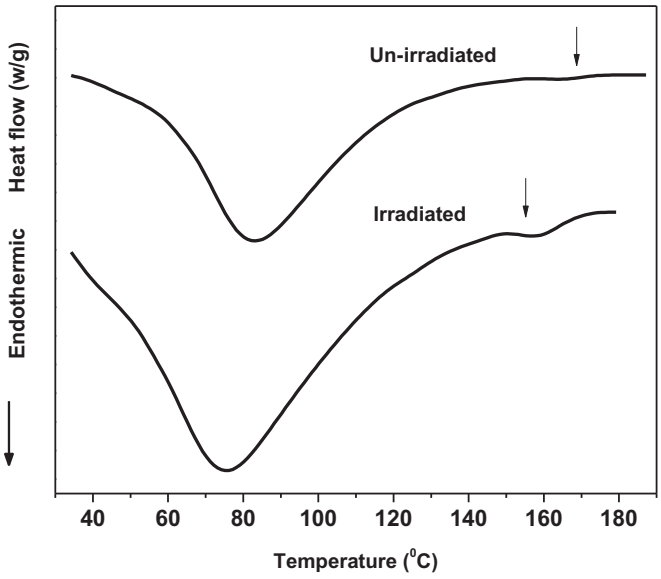

Fig. 2. DSC thermogram of un-irradiated and irradiated 80PVA:20PVDF:15LiCF$_3$SO$_3$:8SiO$_2$ nanocomposite polymer electrolyte.

Table 1
Glass transition and melting temperature of un-irradiated and irradiated nanocomposite polymer electrolyte.

80PVA:20PVDF: 15LiCF$_3$SO$_3$:8SiO$_2$ Nanocomposite polymer electrolyte	Glass transition temperature (°C)	Melting temperature (°C)	Degree of crystallinity (%)
Un-irradiated	81.2	162.5	40
Irradiated	75.3	157.7	33