



Characterization of Blended Polymer Electrolyte thin Films Based on PVDF+PEG Doped with Nano SiO₂

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ABSTRACT

Solution Casting Technique (SCT) is used to prepare the films of poly vinylidene difluoride (PVDF) + poly ethylene glycol (PEG)+Nano silicon dioxide (SiO₂). Modifications in structure, thermal stability and energy band gap values of all prepared thin films have been studied using XRD, SEM, DSC and UV-Vis. The disappearance of a small dip at higher concentrations of DSC plots of nano SiO₂ in PVDF+PEG indicates that the decrease in the crystallinity which also supported by XRD results. From the SEM results it is observed that, at 10 wt.% of Nano SiO₂ of concentration amorphous nature is more which leads increase in thermal stability of the material. FTIR results show strong growth in the CF₂ stretching with increasing concentration of Nano SiO₂ in PVDF+PEG and also the intensity of the aliphatic C-H scattering vibrational bands are observed in spectra of PVDF+PEG and PVDF+PEG+Nano SiO₂. The direct band gap values of PVDF+PEG+Nano SiO₂ polymer electrolyte indicates the influence of Nano SiO₂ on PVDF+PEG for better conducting properties.

Keywords: Poly vinylidene difluoride, Poly ethylene glycol, Silicon dioxide, Fourier transform infra-red spectrometer.

INTRODUCTION

The wide spread usage of polymers virtually all materials to made advances in science and technology. The nature of crystallinity and thermal stability of these polymer electrolytes for applications are of current interest¹⁻³. Blending of polymers is

outstanding method to get require properties such as increasing thermal stability, mechanical strength and conductivity, polymers have been doped with some salts (LiClO₄, NaClO₄, some nano fillers) and futher these are used in electrochemical devices such as batteries, Sensors, electric vechiles; Smartphone's and laptops . Characterization of PVDF solid polymer



electrolyte mixed with LiClO_4 using XRD, DSC, SEM, FTIR and UV was reported by us⁴. Some studies on polyvinylidene fluoride (PVDF) and polyethylene glycol (PEG) complexation of lithium perchlorate (LiClO_4) are recently reported⁵. In this paper, we present the preparation and characterization of a new solid polymer electrolyte system consisting of PVDF+PEG+Nano silicon dioxide (SiO_2). The prepared samples are characterized using the techniques DSC, XRD, SEM, FTIR and UV. The results are compared and discussed to explain the crystalline nature, thermal stability and optical absorption of the polymer electrolyte samples PVDF+PEG+Nano SiO_2 .

EXPERIMENTAL

Solid polymer blend films based on PVDF+PEG+Nano SiO_2 have been prepared by using solution casting procedure. Pure PVDF (320000MW from Merck), PEG(6000MW from Merck) and nano SiO_2 are added with various percentages i.e., (70:30), (70:30:2), (70:30:4), (70:30:6), (70:30:8), (70:30:10) by wt% ratio by Solution Casting Technique. The blend polymer electrolytes are dissolved in DMF by using ultrasonicator⁶ the homogeneous solutions are obtained by stirring the solutions about 10-12 hours. These solutions are allowed to get evaporated in dishes and after 48 h, thin films are obtained. These films are separated from the dish surface and are stored in Desiccators.

XRD patterns of the above polymers are recorded using PHILIPS PW 3710. Fourier Transform Infrared (FTIR) spectroscopic studies are carried out using JASCO FTIR-5300 Spectrometer. Surface properties of these polymers are studied using Scanning Electron Microscope (SEM). Optical absorption spectra are recorded at room temperature in the range of 200-1000nm using UV Optical Spectrometer. Thermal properties are studied using Differential Scanning Calorimetry (DSC) in the temperature range 50°C–250°C.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

As shown in Fig. 1, in DSC plots, there is a small endothermic dip at 174.34°C, for zero concentration of nano SiO_2 in PVDF+PEG [Fig.1

(A)]. As in Fig. 1(B) the endothermic peak is found at 188.40°C for 2% [Fig. 1 (B)]. For 4%, as in Fig. 1(C), the endothermic peak is found around 187°C. Increase of concentration of nano SiO_2 as in Figs. 1(C) to 1(F), the endothermic peak is not prominent.

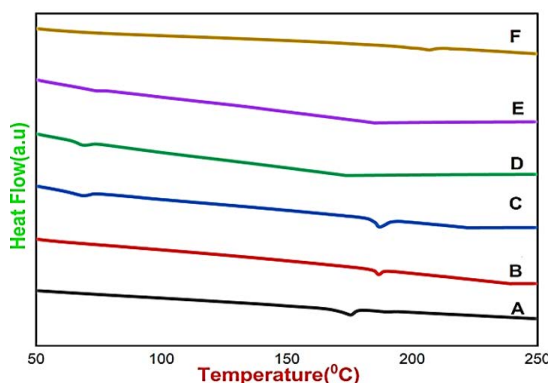


Fig. 1. DSC thermo grams (A) PVDF+PEG (70:30), (B) PVDF+PEG+Nano SiO_2 (70:30:2), (C) PVDF+PEG+Nano SiO_2 (70:30:4), (D) PVDF+PEG+Nano SiO_2 (70:30:6), (E) PVDF+PEG+Nano SiO_2 (70:30:8), (F) PVDF+PEG+Nano SiO_2 (70:30:10) electrolyte thin films

The disappearance of a small dip at higher concentrations of DSC plots indicates the decrease in the crystallinity. It is also observed in 1(D)&1(E) shifting of glass transition temperature (T_g) towards lower Temperature indicates Involved of PEG, nano SiO_2 ⁷.

X-Ray Diffraction Analysis

From Fig.2, it is clear that there is a sharp peak around $2\theta=20.20$ (110),(200) indicates β -phase PVDF^{8,9,10} with small peaks 18.590 (020) indicates α -Phase crystal of pvdf from the literature^{8,9} which is the Characteristic Peak of Pure PVDF, present in all the concentrations of nano SiO_2 in PVDF+PEG [Figs.2(A) to 2(F)] which represents a crystalline phase in the amorphous matrix of the samples. From Figs. 2(A) to 2(F), the sharp peak persists continuously where the small peaks disappear with increase of concentration. In Fig. 2, it is also clear that the magnitude of crystallinity decreases with increase the concentration of nano SiO_2 in PVDF+PEG. In the pure PVDF+PEG sample, the small peaks in addition to the sharp peak indicate the partial crystalline nature of the sample [Figure 2(A)].

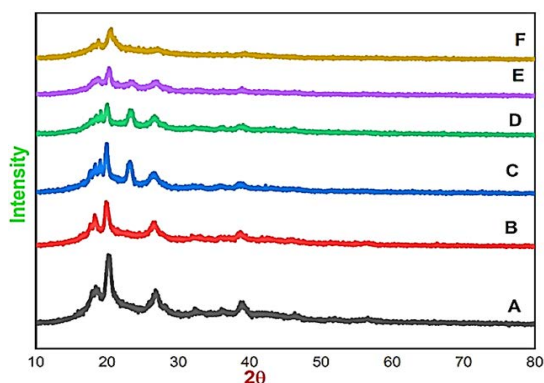


Fig. 2. XRD spectra of (A) PVDF+PEG(70:30), (B) PVDF+PEG+Nano SiO₂(70:30:2), (C) PVDF+PEG+Nano SiO₂(70:30:4), (D) PVDF+PEG+Nano SiO₂(70:30:6), (E) PVDF+PEG+Nano SiO₂(70:30:8), (F) PVDF+PEG+Nano SiO₂(70:30:10) electrolyte thin films

SEM

The surface morphology of PVDF+PEG and PVDF+PEG+Nano SiO₂ polymer systems is observed using SEM. Thus, Fig. 3 shows the surface structure of PVDF+PEG and PVDF+PEG+Nano SiO₂ polymer systems with different concentrations of nano SiO₂ in PVDF+PEG. From Fig. 3, it is clear that the surface of PVDF+PEG film appears to be crystalline for 0% nano SiO₂ which is also confirmed by XRD studies on these films. As the concentration increases, the crystalline nature decreases due to disappearance of crystalline phases and increase of amorphous nature. This occurs due to random positioning of molecules. For 10% concentration, the amorphous nature is more which also increases the thermal stability of the material. Fig. 3 shows the SEM pictures of PVDF+PEG membranes with increasing nano SiO₂ concentration representing the decrease crystallinity from Fig. 1(A) to Fig. (F). At lower nano SiO₂ concentration, nano SiO₂ particles homogeneously dispersed in PVDF+PEG matrix and led to an improvement of mechanical and thermal properties.

Figure 4 shows strong growth in the CF₂ stretching in FTIR with increasing concentration of nano SiO₂ in PVDF+PEG. In Fig. 4, the intensity of the aliphatic C-H scattering irrational bands are observed in FTIR spectra of PVDF+PEG and PVDF+PEG+Nano SiO₂. Using these polymer blend electrolytes electrochemical cells can be fabricated and their discharge characteristics can be studied. The FTIR pattern in Fig. 4 remains almost same with minor changes in the positions and widths of the peaks with increase of the concentration Nano SiO₂ in PVDF+PEG the peaks observed at 840 and 1174 cm⁻¹ are indicates β-phase crystals, similarly

the bands exist at 874, 960, 1074, and 1403 cm⁻¹ indicates the α-phase crystals of the PVDF^{8,9,10,11}.

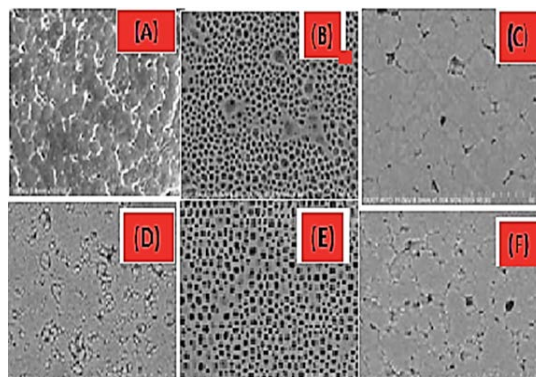


Fig. 3. SEM images of (A) PVDF+PEG (70:30), (B) PVDF+PEG+Nano SiO₂ (70:30:2), (C) PVDF+PEG+Nano SiO₂ (70:30:4), (D) PVDF+PEG+Nano SiO₂ (70:30:6), (E) PVDF+PEG+Nano SiO₂ (70:30:8), (F) PVDF+PEG+Nano SiO₂ (70:30:10) electrolyte thin films

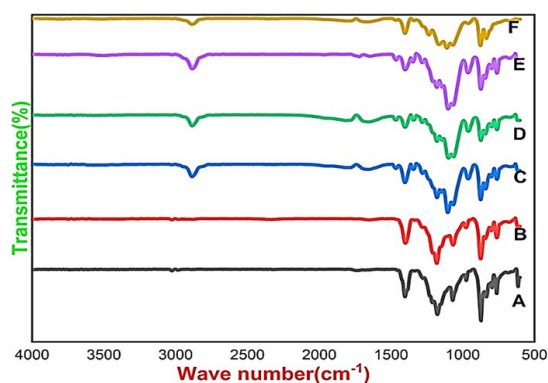


Fig. 4. FTIR spectra of (A) PVDF+PEG (70:30), (B) PVDF+PEG+Nano SiO₂ (70:30:2), (C) PVDF+PEG+Nano SiO₂ (70:30:4), (D) PVDF+PEG+Nano SiO₂ (70:30:6), (E) PVDF+PEG+Nano SiO₂ (70:30:8), (F) PVDF+PEG+Nano SiO₂ (70:30:10) electrolyte thin films

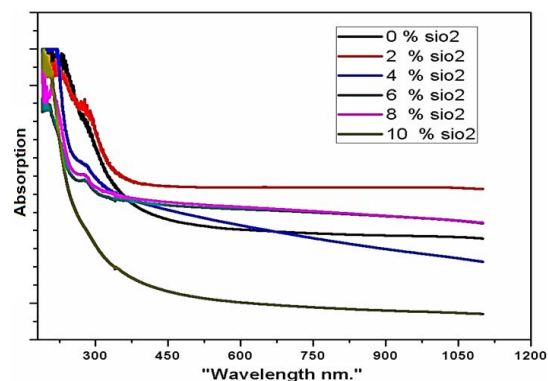


Fig. 5. UV absorption spectra of membranes of PVDF+PEG (70:30) with different concentrations of nano SiO₂

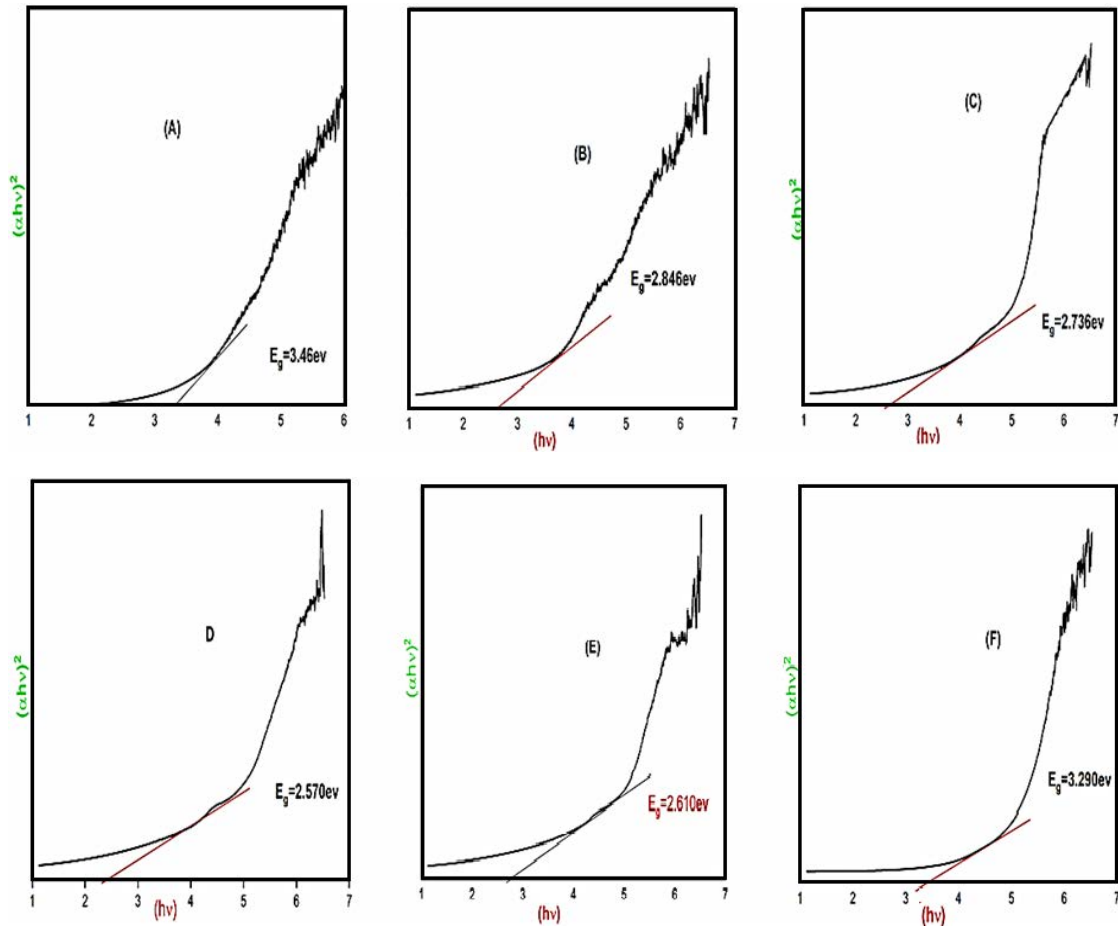


Fig. 6. UV spectra of (A) PVDF+PEG (70:30), (B) PVDF+PEG+Nano SiO₂ (70:30:2), (C) PVDF+PEG+Nano SiO₂ (70:30:4), (D) PVDF+PEG+Nano SiO₂ (70:30:6), (E) PVDF+PEG+Nano SiO₂ (70:30:8), (F) PVDF+PEG+Nano SiO₂ (70:30:10) electrolyte thin film

Table 1: The direct band gap values of PVDF+PEG+Nano SiO₂ electrolytes for different concentrations

Sample code	Wt%			Direct band gap(eV)
	PVDF	PEG	Nano SiO ₂ salt	
(a)	70	30	0	2.42
(b)	70	30	2	2.846
(c)	70	30	4	2.736
(d)	70	30	6	2.570
(e)	70	30	8	2.610
(f)	70	30	10	3.290

Figure 5 shows the optical absorption spectra recorded at room temperature in the range 150nm–1200nm using Optical Spectrometer. Near fundamental band edge, direct band transitions may occur^{12,13}. Thus, considering α as absorption coefficient, h as Planck's constant, ν as frequency of incident light and $h\nu$ as the photon energy, $(\alpha h\nu)^2$

versus $h\nu$ can be plotted as shown in Fig. 6. The direct band gap values of PVDF+PEG, PVDF+PEG +different concentrations of Nano SiO₂ are tabulated in Table 1. From Table 1, the band gap of pure PVDF+PEG polymer electrolyte is 2.420eV. The direct optical band gap values have been modified by the addition of nano SiO₂ to PVDF+PEG blend

thin film which supports the conductivity levels of PVDF+PEG+Nano SiO₂ thin films. Thus, the direct band gap values of PVDF+PEG+Nano SiO₂ polymer electrolyte indicates the influence of nano SiO₂ on PVDF+PEG for better conducting properties. Table 1 also shows that the direct band gap of 10% of Nano SiO₂ in PVDF+PEG is 3.290 eV.

CONCLUSION

DSC studies on nano SiO₂ doped on PVDF+PEG blend films revealed that the decrease in the crystallinity which leads good thermal stability and the same also supported with XRD and SEM results. FTIR results show strong growth in the CF₂ stretching with increasing concentration of nano SiO₂ in PVDF+PEG and also confirmed

that, intensity of the aliphatic C-H scattering vibrational bands decreases. The increase in direct band gap values of PVDF+PEG+Nano SiO₂ polymer electrolyte indicated that the influence of nano SiO₂ on PVDF+PEG for better conducting properties.

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Conflict of Interests

There is no conflict of interest

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