

Original article

Effects of ceramic filler in poly(vinyl chloride)/poly(ethyl methacrylate) based polymer blend electrolytes



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ABSTRACT

Effects of nano-ceramic filler titanium oxide (TiO_2) have been investigated on the ionic conductance of polymeric complexes consisting of poly(vinyl chloride) (PVC)/poly(ethyl methacrylate) (PEMA), and lithium perchlorate (LiClO_4). The composite polymer blend electrolytes were prepared by solvent casting technique. The TiO_2 nanofillers were homogeneously dispersed in the polymer electrolyte matrix and exhibited excellent interconnection with PVC/PEMA/PC/ LiClO_4 polymer electrolyte. The addition of TiO_2 nanofillers improved the ionic conductivity of the polymer electrolyte to some extent when the content of TiO_2 is 15 wt%. The addition of TiO_2 also enhanced the thermal stability of the electrolyte. The changes in the structural and complex formation properties of the materials are studied by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. The scanning electron microscope image of nano-composite polymer electrolyte membrane confirms that the TiO_2 nanoparticles were distributed uniformly in the polymer matrix.

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1. Introduction

The incorporation of inorganic filler into polymers is a common practice in polymer processing to enhance physical and mechanical properties. The high aspect ratio of the nanofiller gives rise to a high degree of polymer surface interaction resulting in much improved mechanical and barrier properties [1,2]. Polymers containing metal chloride have attracted much attention because of their useful technical applications. They may serve as optical components in a wide variety of opto-electronic devices. Therefore, the field of use of these polymeric materials, especially poly(ethyl methacrylate) (PEMA) as a polymer waveguide and as optical and/or electronic components, has become important, especially given that the properties and structure of the polymers can easily be tuned upon small additions of metal halide [3–6]. Nanoscale TiO_2 in the polymer electrolyte systems was confirmed to play some useful roles in forming particle networks within the polymer bulk (particle dispersion), inhibiting the crystallization and reorganization of polymer chains and interactions with lithium ion species. These features eventually resulted in the improvements of polymer electrolyte properties such as mechanical strength, ionic

conductivity, electrochemical stability, cation transference number, lowering of interfacial resistance, and so on [7]. TiO_2 may partially attach into the polymer chains or resides in the amorphous/crystalline boundaries and diffuse preferentially through the amorphous regions, forming charge transfer complexes, or it may exist in the form of molecule aggregates between the polymer chains. In the case of composite polymer electrolytes, the particle size and filler concentrations play an important role because the addition of a small amount of inert filler will collapse the chain organization of the polymers which in turn facilitates higher ionic conduction [8].

In this present work, to overcome the drawbacks of plasticized polymer blend electrolyte, PEMA/PVC based nanocomposite polymer electrolytes have been prepared with various weight ratios of TiO_2 ceramic filler to improve their ionic conductivity. PVC is commonly used as a general commodity plastic because of its excellent electrical and corrosion resistance, self extinguishing characteristics, low cost, and recoverability. However, its low impact strength and poor thermal stability limit its applications. The inherent problems of processing rigid PVC are also quite well known and are overcome by the use of certain plasticizers. Such cases run the risk of compromising the mechanical properties of rigid PVC. PEMA is chosen for blending with PVC because it has better miscibility and compatibility in low or high molecular weight and also offers good mechanical strength due to the lone

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electron pair in the chlorine atom, which in turn stiffens the backbone of the polymer [9]. Further, the problem of poor mechanical strength can be circumvented by blending PEMA with a polymer such as PVC, because of its poor solubility in the plasticizer medium results in a phase separated morphology that provides a rather rigid framework in the polymer electrolyte film.

2. Experimental

PVC (average $M_w \sim 534,000$) and PEMA (average $M_w \sim 515,000$) were purchased from Aldrich and dried under vacuum at 80°C for 24 h. Reagent grade anhydrous lithium perchlorate (LiClO_4) was used after drying in vacuum at 110°C for 24 h. The plasticizer propylene carbonate (PC) (from Aldrich) was used as supplied. The nanosized TiO_2 (<100 nm particle size) was purchased from Aldrich and used as a ceramic filler. All the electrolytes have been prepared by the solvent casting technique. Appropriate quantities of PVC, PEMA, and LiClO_4 are dissolved by adding them in sequence to tetrahydrofuran (THF) and stirred for 24 h. The resulting solution is poured onto a glass plate, and the THF is allowed to evaporate in air at room temperature for several hours. The films are further dried at 60°C for 24 h in vacuum to remove any traces of THF. Thin films thus obtained were subjected to XRD and FTIR studies to investigate the complexation behavior and the nature of crystallinity of the polymer electrolytes using a Bruker (D8 Advance) diffractometer and a Perkin-Elmer (Paragon 500 grating) IR spectrophotometer, respectively. Thermal stability of the film was also characterized by TG/DTA. TGA measurements were carried out under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 830°C . Nitrogen was used as the carrier gas with flow rate of $25\text{ mL}/\text{min}$. The electrical conductivity of polymer complexes was measured from impedance plots at different temperatures using a Keithley 3330 LCZ meter. The impedance measurement was recorded in the frequency range $40\text{ Hz}–100\text{ kHz}$ with signal amplitude of 10 mV . The SEM images were recorded using HITACHI S-3000 H Scanning electron microscope.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of pure PVC, PEMA, LiClO_4 , and $\text{PVC}(5)\text{-PEMA}(20)\text{-PC}(67)\text{-LiClO}_4(8)$ polymer electrolyte with $X\%$ of TiO_2 (where $X = 0, 5, 10, 15, 20$) are shown in Fig. 1. It is clear that both polymers are amorphous in nature because no sharp crystalline peaks are observed [10]. The diffraction peaks appearing at 2θ values 18° and 23° indicate the crystalline phase of LiClO_4 in Fig. 1(c). The peaks corresponding to LiClO_4 were not observed in Fig. 1(e)–(i), indicating that the LiClO_4 does not remain as a separate phase in the polymer electrolyte system which confirms the complete dissociation of LiClO_4 in the polymer matrix [11]. The characteristic peaks at $2\theta = 13^\circ$ for PVC and 18.6° for PEMA are revealed from Fig. 1(a) and (b), respectively. The diffraction peak of PEMA is markedly reduced in all the complexes. The shift and decrease in the relative intensity of the peaks suggest that complexation has occurred between the salt and the polymers. The analysis shows that the nature of diffraction patterns of pure samples significantly changed due to the disturbances in the ordered arrangement of polymer side chains when they are blended. This indicates that the salt, LiClO_4 , most likely blends with PVC/PEMA polymer blend at the molecular level and gives a clear indication of complexation of the salt in the polymer blend system. The obtained amorphous phase of polymer blend in the electrolyte membrane enhances higher ionic conduction, meanwhile the crystalline phase of the filler provides strong mechanical support

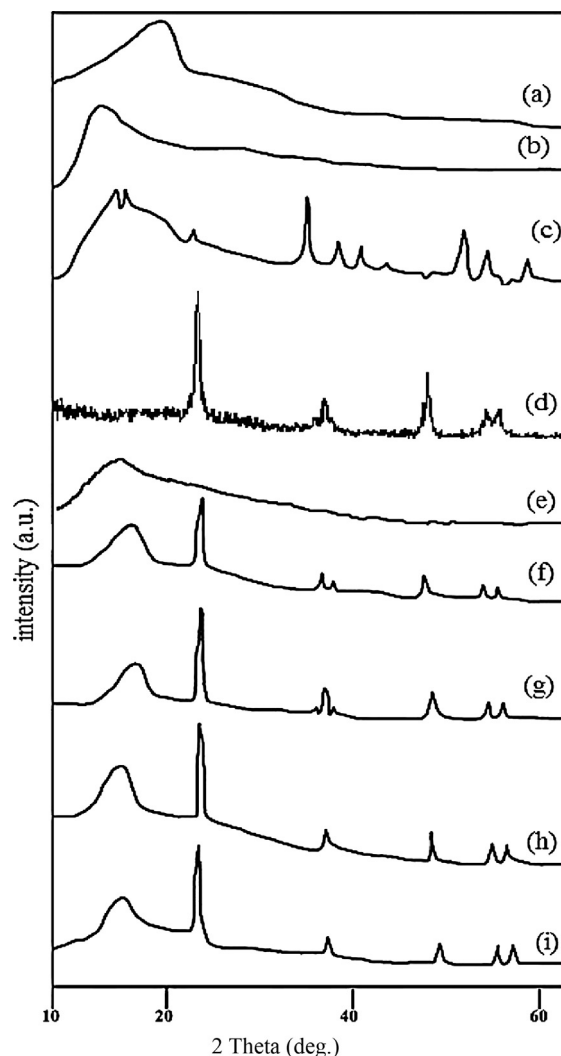


Fig. 1. X-ray diffraction patterns of (a) pure PEMA, (b) pure PVC, (c) pure LiClO_4 , (d) pure TiO_2 , (e) $\text{PVC}(5)\text{-PEMA}(20)\text{-LiClO}_4(8)\text{-PC}(67)\text{-TiO}_2(0)$, (f) $\text{PVC}(5)\text{-PEMA}(20)\text{-LiClO}_4(8)\text{-PC}(67)\text{-TiO}_2(5)$, (g) $\text{PVC}(5)\text{-PEMA}(20)\text{-LiClO}_4(8)\text{-PC}(67)\text{-TiO}_2(10)$, (h) $\text{PVC}(5)\text{-PEMA}(20)\text{-LiClO}_4(8)\text{-PC}(67)\text{-TiO}_2(15)$, and (i) $\text{PVC}(5)\text{-PEMA}(20)\text{-LiClO}_4(8)\text{-PC}(67)\text{-TiO}_2(20)$.

in the polymer electrolyte. We can observe that the position of the sharp peak coincided with a peak at $2\theta = 25.2^\circ$ and 48° from the X-ray scans of pure TiO_2 in Fig. 1(d). This confirms the presence of TiO_2 crystallites within the polymer matrix. On the other hand, the spectrum of PVC/PEMA films containing TiO_2 showed a sharp peak at $2\theta = 25.2^\circ$, showing $W \geq 5\text{ wt}\%$ can cause structural variations in the polymeric network. The nano-sized TiO_2 dispersed emulsion can penetrate the space between the polymer chains, and consequently the homogeneously dispersed ceramic filler in the matrix prevents or retards crystallization of the polymers due to its large surface area. The intensity of the peaks abruptly decreases in the composite electrolytes. No peaks appeared corresponding to the salt in the complexes, which confirms the amorphous nature of the electrolytes.

3.2. FTIR analysis

Polymer complexes with ionic salt and ceramic filler have been characterized by FTIR spectroscopy. This technique provides a powerful tool to characterize organic and inorganic components and their composition. FTIR spectra of composite polymer

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