

Short communication

Studies on an ionically conducting polymer nanocomposite

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Abstract

A nanocomposite electrolyte comprising a polymer–salt complex (PEO₂₅–NaClO₄) and an organically modified sodium montmorillonite (Na-MMT) has been prepared using tape casting technique. The effect of clay concentration on structural, microstructural and electrical properties has been investigated. X-ray diffraction (XRD) analysis confirmed the formation and structure of the nanocomposite. FTIR analysis suggested a clear evidence of polymer–ion–clay interaction indicated by the changes appearing in the $\nu(\text{ClO}_4^-)$ and $\nu(\text{C–O–C})$ bands as a function of the clay concentration. The surface properties and microstructure has been studied using atomic force microscopy (AFM) technique. Complex impedance spectrum (CIS) shows the existence of bulk and grain boundary effects in the nanocomposite films. The temperature dependence of electrical conductivity obeys VTF pattern of variation.

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1. Introduction

Development of ionically conducting solids based on polymer/polymer composites, better known as polymer electrolytes (i.e. PEs), appear to be a promising alternative over their liquid counterpart due to design flexibility, easier processability and possibility of miniaturization for device fabrication. However, PEs has some inherent problems such as simultaneous mobility of cation and anions, concentration polarization, higher interfacial resistance, etc. that impose restriction on their utility for applications in ionic devices. The challenge can be overcome if a PE having single ion conduction with high cationic transport is developed. The idea put forward, by Aranda and Ruiz-Hitzky [1] and subsequently popularized by Giannelis [2], to develop single ion conductors by intercalating an appropriate amount of polymer/polymer–salt complex in nanometric channels of inorganic clay came as a new approach. It also appears appealing because only cations of smaller dimensions can get entry into the clay channel with bulky anions remaining immobilized in the matrix. This new class of materials, in which intercalation of conducting polymer matrix into the nanoscale gallery of clay is achieved, is known as polymer nanocomposite electrolytes (PNCEs). Recently, studies on PNCEs have been reported in

literature [3–6] along with some excellent books and review articles [7,8].

In the present paper, we report a sodium ion conducting polymer nanocomposite electrolyte based on intercalation of PEO₂₅–NaClO₄ complex into the gallery of organically modified montmorillonite clay. The intercalation has been carried out for various clay concentration and its effect has been

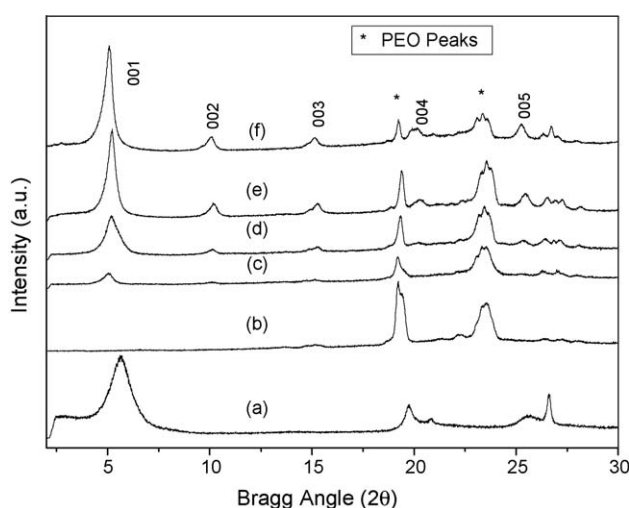


Fig. 1. X-ray diffraction (XRD) pattern of PNCE thin films with different concentration (x) of Na⁺ montmorillonite: (a) Na⁺ montmorillonite, (b) $x=0\%$, (c) $x=5\%$, (d) $x=10\%$, (e) $x=20\%$ and (f) $x=50\%$.

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investigated on sample structure/microstructure, and electrical properties.

2. Experimental

PNCE films were prepared by a tape cast technique using self-designed tape caster having thickness control down to 10 μm . AR grade precursors, i.e. polyethylene oxide, PEO

(M/S Aldrich, $M_w \sim 6 \times 10^5$), NaClO_4 (M/S Fluka) and Na montmorillonite clay (Na-MMT) were taken in an appropriate ratio. The clay was modified organically as reported elsewhere [9]. PNCEs with different clay ratio w.r.t. polymer (w/w) were prepared following the procedure reported by us [10]. The resulting freestanding thin films of PNCE have general formula: $(\text{PEO})_{25}\text{NaClO}_4 + x$ wt.% Na-MMT ($x=0-50$).

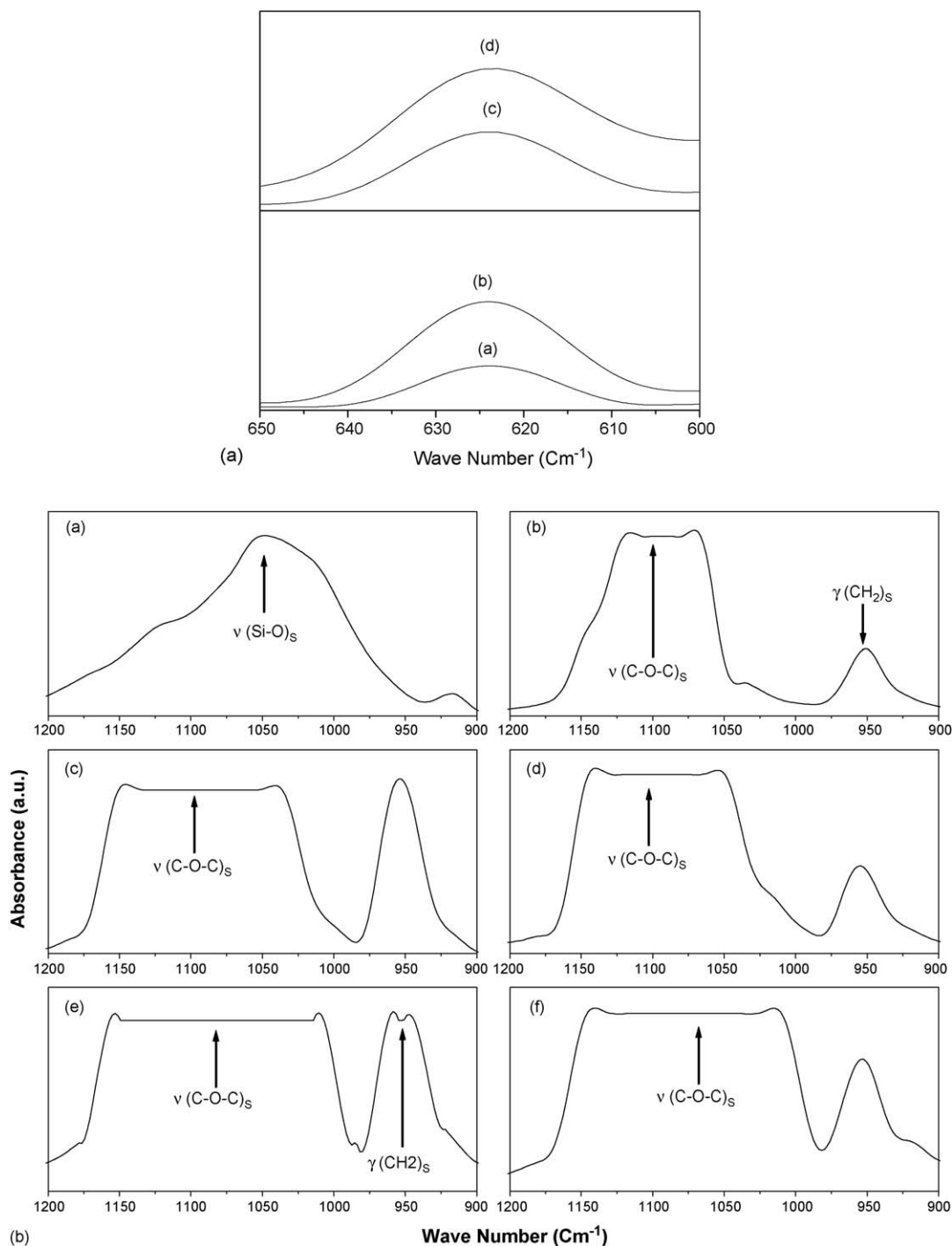


Fig. 2. (a) FTIR Spectrum showing changes in $\nu(\text{ClO}_4^-)$ band of PNCE thin films with different concentration (x) of Na^+ -MMT: (a) $x=0\%$, (b) $x=5\%$, (c) $x=10\%$ and (d) $x=50\%$. (b) FTIR Spectrum showing changes in $\nu(\text{C-O-C})$ band and $\gamma(\text{CH}_2)$ bands of PNCE thin films with different concentration (x) of Na^+ -MMT: (a) $x=0\%$, (b) $x=5\%$, (c) $x=10\%$, (e) $x=20\%$ and (f) $x=50\%$.

The sample testing and evaluation of its properties was carried out using standard techniques of XRD (Rigaku: Miniflex, Japan), FTIR (Thermo-Nicolet, NEXUS-870), AFM (Nanonics Imaging Ltd.), and impedance (HIOKI LCR Hi Tester: 3532) measurements over a range of temperature and frequency. The details are similar to that reported by us [10].

3. Results and discussion

3.1. X-ray diffraction (XRD) studies

The XRD patterns of the PNCE films under study are shown in Fig. 1. The pattern suggests relatively good crystalline organization along the *c*-axis, on intercalation as reflected from the 001 peak of Na-MMT. Clay addition has affected peak position, peak width and peak intensity suggesting an interaction between the polymer complex and clay networks. Further, an ion exchange between the clays (sodium cation) and the surfactant (ammonium ion) on clay modification causes an increase of the basal interlayer spacing in comparison to the Na⁺-MMT resulting in a

shift of diffraction peaks towards lower angle side in the diffractogram. The distance between the clay layers expressed by the d_{001} reflections increases with MMT concentration indicated by a shift in the position of 001 peak towards the lower angle side suggesting an increase in the gallery width due to successful intercalation of polymer complex in to the clay nanometric channels. It has also been observed that the d_{001} value increases for low concentration of clay followed by a decrease on higher clay concentration. A decrease in basal interlayer spacing with increase in the clay concentration may be related to decrease in polymer–salt intercalation into the clay gallery [11]. The two characteristics peaks of PEO (at 19° and 23°) are also affected indicated by an increase in their *d*-values (Fig. 1) on intercalation. It may be related to an interaction of PEO chains and the silicate layers. So, XRD analysis provides evidence for a very strong interaction of polymer chain with the clay network. Since ionic species are a part of the polymer–salt complex network intercalated in to the clay channel, an interaction of ionic species, with the clay layers is also a likely possibility. To corroborate this, we have carried out FTIR studies in order to probe

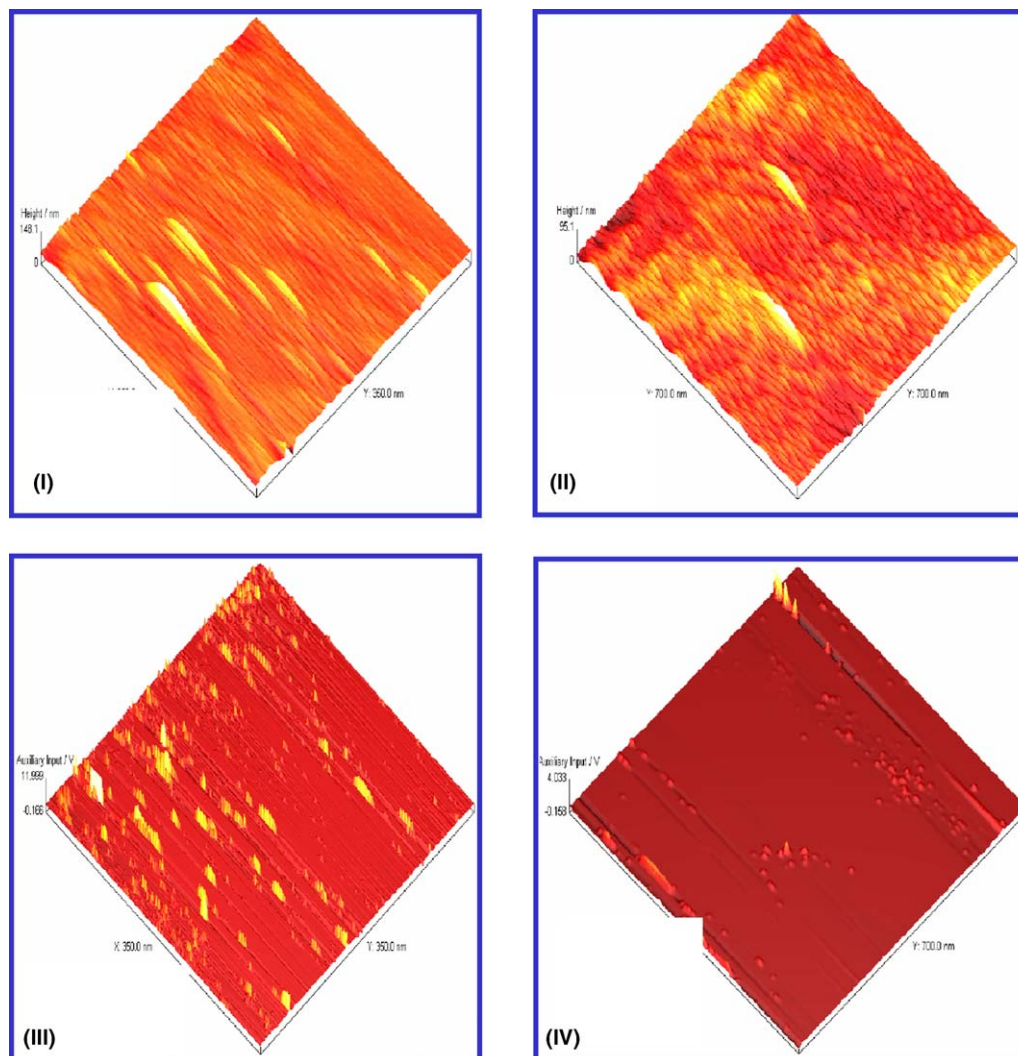


Fig. 3. AFM micrographs of PNCE films showing, topography for (i) $x=0\%$, (ii) $x=5\%$ clay concentration and phase image for (iii) $x=0\%$, (iv) $x=10\%$ clay concentration.

ion–polymer and ion–ion interaction in the nanocomposite electrolyte system.

3.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum recorded in the region of interest ($400\text{--}1200\text{ cm}^{-1}$) shows marked changes in the pattern shown in Fig. 2(a) and (b). Fig. 2(a) shows normalized spectrum of ClO_4^- band assigned to stretching of ClO_4^- ion. This band shows substantial changes in its pattern (i.e. intensity, width and symmetry) with rise in clay concentration providing a clear evidence of strong ion–clay interaction indicated by enhanced asymmetry of $\nu(\text{ClO}_4^-)$ band suggesting presence of two components at 624 cm^{-1} and another at 635 cm^{-1} attributed to “free anions” and the presence “ion-pair”, respectively [12]. The ion-pairs reduce the number of available free charge carrier in the matrix on clay addition. Fig. 2(b) shows FTIR spectrum in the wave number region $900\text{--}1200\text{ cm}^{-1}$. It has specific features of changes in the pattern of evolution of $\nu(\text{C-O-C})$ band and $\gamma(\text{CH}_2)$ bands noticed in terms of broadening of $\nu(\text{C-O-C})$ band and splitting in $\gamma(\text{CH}_2)$ bands (at 20 wt.% clay). These evidences

appear to be convincing to suggest a strong interaction between polymer–salt complex and clay layers on intercalation.

3.3. AFM studies

Fig. 3 shows AFM micrographs indicating changes in topography and phase in the PNCE films for various clay concentration. The AFM topographic (Fig. 3(i) and (ii)) and phase (Fig. 3(iii) and (iv)) images demonstrate formation of near surface nanostructure. The humps appearing in the three-dimensional topographic images suggest atomic corrugation at the nanoscale while color pattern confirms multiphase composite behavior of the polymer films on intercalation.

3.4. Electrical properties

Fig. 4(a) represent the complex impedance spectrum (CIS) of the PNCE films under study. The typical Nyquist plot of the samples comprises of a semicircular arc in the high frequency region followed by a tail in the low frequency region suggest-

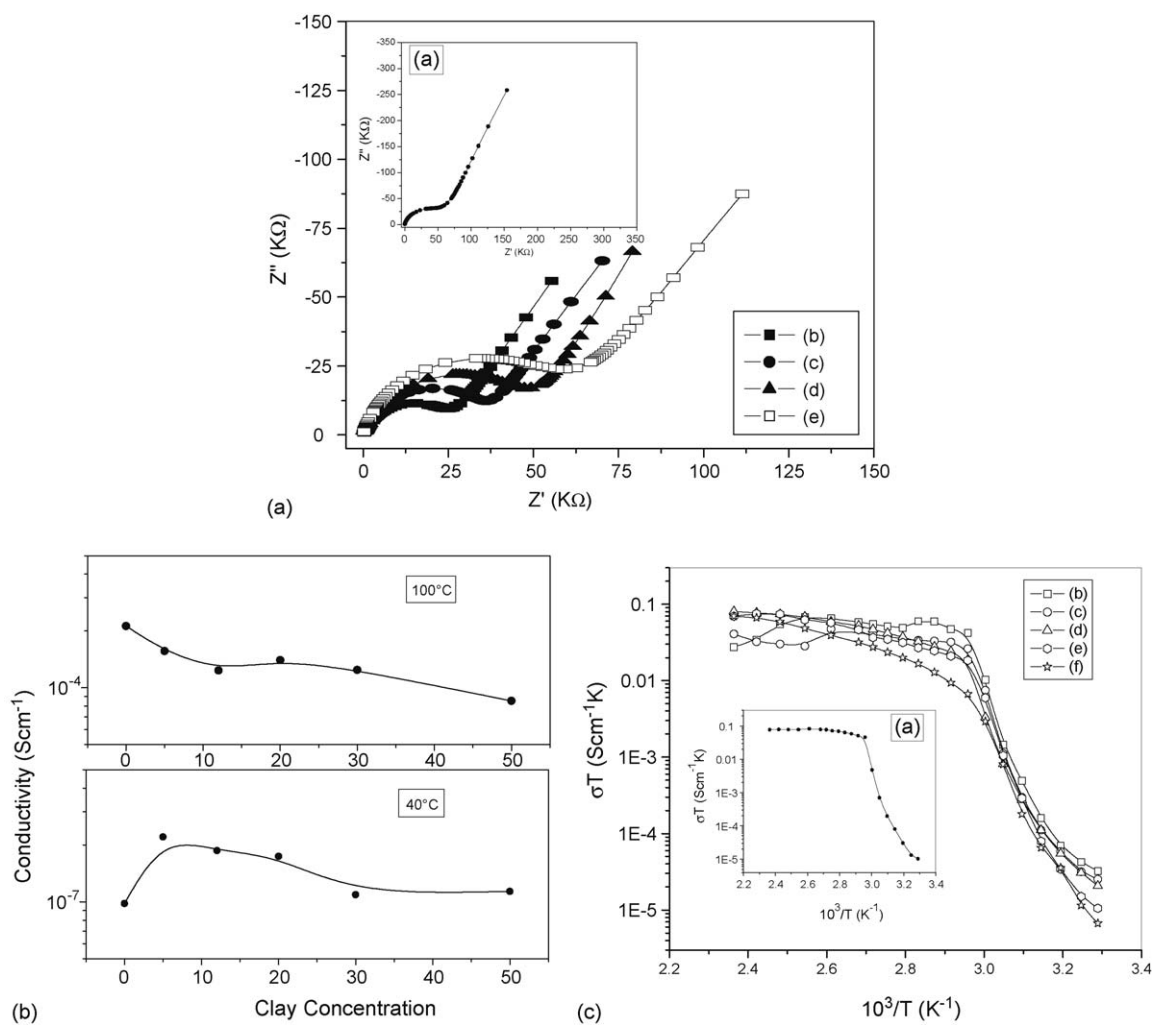


Fig. 4. (a) Complex impedance spectrum of PNCE with different concentration (x) of Na^+ -MMT: (a) $x=0\%$ (inserted), (b) $x=5\%$, (c) $x=10\%$, (d) $x=20\%$ and (e) $x=30\%$. (b) Variation of dc conductivity (σ_{dc}) of as a function of Na^+ montmorillonite concentration. (c) Variation of dc conductivity PNCE films (σ_{dc}) as a function of temperature with concentration of Na^+ -MMT: (a) $x=0\%$ (inserted), (b) $x=5\%$, (c) $x=10\%$, (d) $x=20\%$, (e) $x=30\%$ and (f) $x=50\%$.

ing a trend for another semicircular arc. The existence of more than one arc indicates the presence of multicomponent behavior of the system. The high frequency semicircle can be ascribed basically to the bulk properties of the PNCE films as expected. The intercept of this semicircle with the real axis (Z') gives an estimate of the bulk resistance (R_b) of the materials to be used subsequently for evaluation of electrical conductivity.

Fig. 4(b) shows the dc conductivity (σ_{dc}) of the PNCE films as a function of clay concentration of the materials at 40 and 100 °C. The value of σ_{dc} has been observed to increase initially on addition of clay (5 wt.%) 40 °C, which is followed by a monotonous decrease on further increase in clay concentration. It may be attributed to a possible interaction of the negative charges in the silicate layers with the Na^+ cation of polymer–salt complex on immediate clay addition. This may cause release of cations and a consequent concentration enhancement of the charge carrier. Hence conductivity may be expected to increase at lower concentration of clay. On further rise of clay concentration, there may be an increase in the system viscosity thereby causing restricted cation mobility possibly due to formation of “ion-pair” resulting in lowering of electrical conductivity [13]. This possibility has already been evidenced from the results of FTIR studies.

Fig. 4(c) shows σ_{dc} versus $10^3/T$ plot for different clay concentration. The pattern of variation indicates a monotonous increase in σ_{dc} with temperature up to crystalline melting (T_m) followed by saturation beyond which conductivity rises with rise in temperature. This behavior may be approximated to a typical VTF (Vogel–Tamman–Fulcher) pattern governed by the empirical relation:

$$\sigma T^{1/2} = \sigma_0 \exp \frac{-E_a}{k_B(T - T_0)} \quad (1)$$

where the symbols have their usual meaning. This behavior agrees well with a number of similar theoretically predicated patterns for PEO-based polymeric conductors reported earlier [14,15].

4. Conclusions

An ionically conductive polymer–clay nanocomposite electrolyte (PNCE) system is reported. Structural, microstructural

and electrical properties of the PNCE films have been analyzed for different clay concentration. XRD results suggest a strong interaction between polymer–salt complex and clay networks with definite evidence of the polymer–salt complex interaction with nanometric clay channels. The FTIR analysis have confirmed the existence of a strong “polymer–ion–clay interaction” in the composite network that governs and controls electrical properties in the PNCE films. A change in the surface morphology and topography with different clay concentration has also been observed in the micrographs and appear to be consistent with the changes in the electrical properties with clay concentration. The observed electrical conductivity is higher at 5% clay concentration at room temperature with a maximum value $\sim 2.20 \times 10^{-7} \text{ S cm}^{-1}$ at 40 °C. The temperature dependence of conductivity obeys VTF behavior.

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