

**MATERIALS CHARACTERIZATION AND DIELECTRIC STUDIES OF A NEWLY
SYNTHESIZED Na^+ ION CONDUCTING NANOCOMPOSITE POLYMER
ELECTROLYTES**

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ABSTRACT

Materials characterization and dielectric studies of a newly synthesized Na^+ ion conducting nanocomposite polymer electrolytes (NCPEs): $(1-x)[75\text{PEO}:25\text{NaPO}_3]+x\text{TiO}_2$, where $0 \leq x \leq 18$ wt.%. are reported. The composition: $[95(75\text{PEO}:25\text{NaPO}_3)+5 \text{TiO}_2]$ with ionic conductivity (σ) $\sim 2.3 \times 10^{-5} \text{ S.cm}^{-1}$ have been identified as optimum conducting composition (OCC). Material characterizations have been done with the help of X-ray diffraction (XRD), scanning electron micrograph (SEM), differential scanning calorimetric (DSC) and thermogravimetric (TGA) analysis. Dielectric constant (ϵ^*) and dielectric loss (ϵ_l) measurements have been carried out using different experimental techniques. The conductivity enhancements in the present NCPEs have been discussed on the basis of existing theories of dielectrics.

Keywords: Nanocomposite polymer electrolyte, XRD, SEM, DSC, TGA, Dielectric constant (ϵ^).*

INTRODUCTION

The ion conducting nanocomposite polymer electrolytes (NCPEs) is one of the important areas of research in the last 30 years. The NCPEs shows tremendous technological potential to develop flexible solid state polymeric batteries over the solid polymer electrolytes (SPEs) (Croce et al., 1998; Appetecchi et al., 2000; Ahn et al., 2003; Chandra et al., 2022). The main advantages of NCPEs are their mechanical properties, ease of fabrication of desirable shapes/ sizes and it is also important for improving the proper contact between electrode-electrolyte in polymeric

batteries (Bhide&Hariharan, 2006; Thakur, 2011). In the recent past, several PEO-based polymer electrolytes have been widely investigated because of their potential application in polymeric batteries. Polymer electrolyte films are formed, in general, via solution-cast and sol-gel routes. However, recently, an alternate hot-press technique has been developed for casting completely dry polymer electrolyte films (Appetecchi et al., 2003; Agrawal et al., 2008; Sharma et al., 2022). The sodium ion salt has several advantages over lithium. It is less reactive, much more abundant and less expensive over the lithium salts (Chandra et al., 2016; Chandra & Chandra, 2017).

In the present investigation, materials characterization and dielectric studies of a newly synthesized Na⁺ ion conducting nanocomposite polymer electrolytes (NCPEs): (1-x) [75PEO:25NaPO₃]+xTiO₂, where 0≤x≤18 wt.%. are reported. Materials characterization/polymer-salt complexations have been carried out with the help of XRD, SEM, DSC and TG analysis. Dielectric constant(ε*) and dielectric loss (ε_l) measurements have also been carried out using different experimental techniques.

MATERIALS AND METHODS

AR grade chemicals: poly (ethylene oxide) PEO (10⁵ MW, Aldrich, USA), NaPO₃ (purity > 98%, Merck, India) and TiO₂ (> 99.8%, particle size ~ 20nm, Sigma, USA) have been used for the synthesis of NCPEs: (1-x) [75PEO:25NaPO₃] + x TiO₂, where 0≤x≤18 in wt.%. The detail related to casting of SPE/ NCPEs by hot-press method has been discussed in detail in our earlier papers (Chandra et al., 2016; Chandra & Chandra, 2017; Chandra, 2017). Materials characterizations were carried out with the help of XRD [Shimadzu diffractometer] at Cu-Kα radiation, scanning electron micrograph [SEM: JEOL, JXA-8100, Japan], differential scanning calorimetric (DSC) analysis (model: Perkin Elmer) and TGA (model: SDT Universal) techniques.

The dielectric constant (ε*) and dielectric loss (ε_l) of NCPE has been determined with the help of following well-known equation:

$$\epsilon^* = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \quad (1)$$

$$\text{and } \epsilon_f = \frac{Z_r}{\omega C_o (Z_{r2} + Z_{i2})} \quad (2)$$

where $C_o = \epsilon_o A/l$, ϵ_o is the permittivity of the free space and $\omega = 2\pi f$, f is the frequency in Hz , l is the thickness of the polymeric film and A is the cross-sectional area of the film.

RESULTS AND DISCUSSION

A new sodium ion conducting nanocomposite polymer electrolytes (NCPEs): (1-x) [75PEO:25NaPO₃] + x TiO₂, where $0 \leq x \leq 18$ wt.% were synthesized by a novel hot-press method in our previous communication (Sharma et al., 2022a). Fig. 1 shows the ‘log σ -x’ plot of (1-x) [75PEO:25NaPO₃] + x TiO₂. As the filler concentration is increase ionic conductivity is also increases and the NCPE films beyond 15 wt.% were unstable and brittle. One can clearly note from the figure that the conductivity maxima ($\sigma \sim 2.3 \times 10^{-5}$ S.cm⁻¹) was obtained at 5 wt.% of TiO₂, then decreased on further addition of filler. Two orders of conductivity enhancement have been achieved at room temperature for NCPE film: 95 [75PEO:25NaPO₃] + 5 TiO₂ and this has been referred to as optimum conducting composition (OCC). Ion transport parameters viz. ionic mobility, mobile ion concentration, ionic transference number, activation energy values and ionic drift velocity of the present NCPEs were reported in our previous communication (Sharma et al., 2022b).

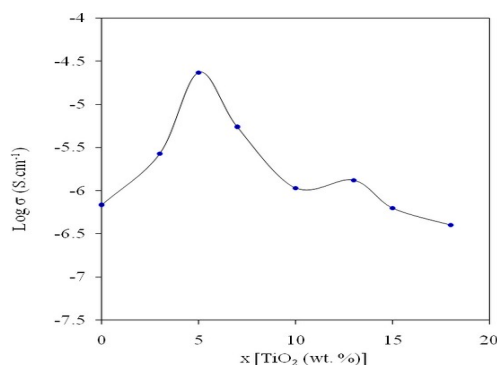


Fig. 1. ‘Log σ – x’ plot for the hot-pressed NCPEs: (1-x) (75PEO:25NaPO₃) + x TiO₂, $0 \leq x \leq 18$ in wt.%.

Fig. 2 shows the XRD patterns of NaPO₃, pure PEO, SPE host: [75PEO:25NaPO₃], nano filler TiO₂ and NCPE OCC: 95 [75PEO:25NaPO₃] + 5 TiO₂. It can be clearly noted from the figure that some of the peaks of pure PEO became relatively broader as well as less-prominent/ feeble

after salt complexation/ TiO_2 dispersal. This shows the increase in the degree of amorphicity after the dispersion of filler TiO_2 .

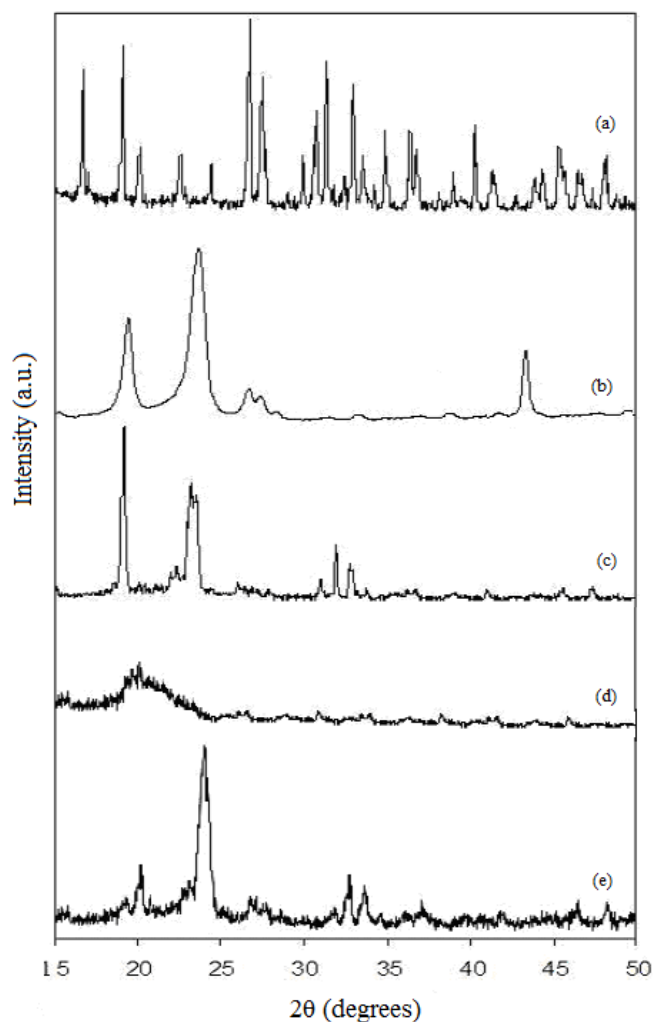


Fig. 2. XRD patterns: (a) NaPO_3 , (b) PEO, (c) polymer host:(75PEO:25 NaPO_3), (d) TiO_2 and (e) NCPE OCC: 95 (75PEO:25 NaPO_3) + 5 TiO_2 .

Fig. 3 shows the scanning electron micrograph (SEM) image of NCPE OCC: 95 [75PEO:25 NaPO_3] + 5 TiO_2 . The smooth surface morphology of NCPE OCC is clearly indication of uniform distribution of TiO_2 and reduction of degree of crystallinity while pure PEO shows rough surface morphology (Chu et al., 2003).

Fig. 4 shows the DSC thermograms for the pure PEO, SPE host and NCPE OCC. The broad endothermic peak was observed in polymeric films at $\sim 65\text{-}70^\circ\text{C}$ and it is corresponding to the melting point temperature of pure PEO. The slightly shifting in the melting point temperature towards higher side in SPE host is also indicative the confirmation of polymer-salt complexation

and the slightly shifting in the melting point towards lower side in NCPE OCC is due to the increase in the amorphicity, which is also indicative the formation of NCPE membrane. A possible mechanism for this behavior could be the creation of additional hopping sites and favorable conducting pathways for ionic migration(Chandra & Chandra, 2022).

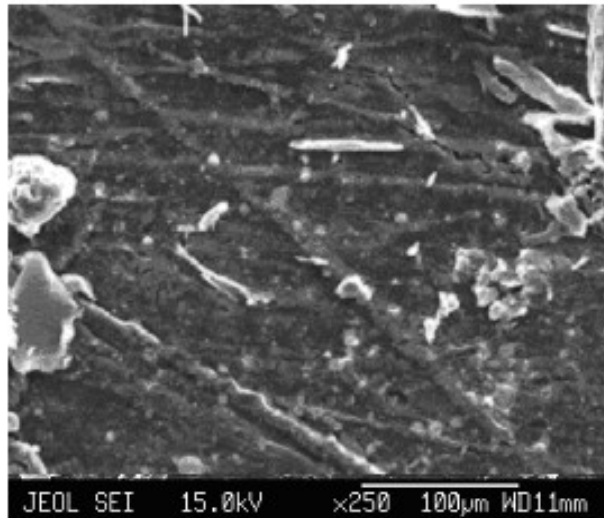


Fig. 3. SEM image of NCPE OCC: 95 (75PEO:25NaPO₃) + 5 TiO₂.

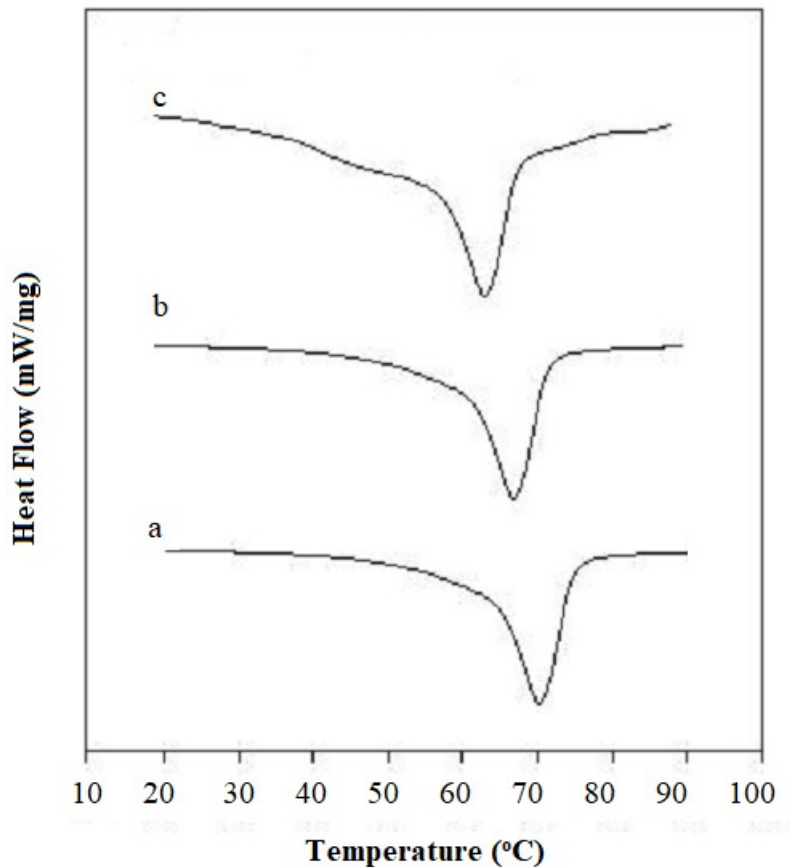


Fig. 4. DSC thermograms: (a) pure PEO, (b) SPE host: (75PEO:25NaPO₃), (c) NCPE OCC: 95 (75PEO:25NaPO₃) + 5 TiO₂.

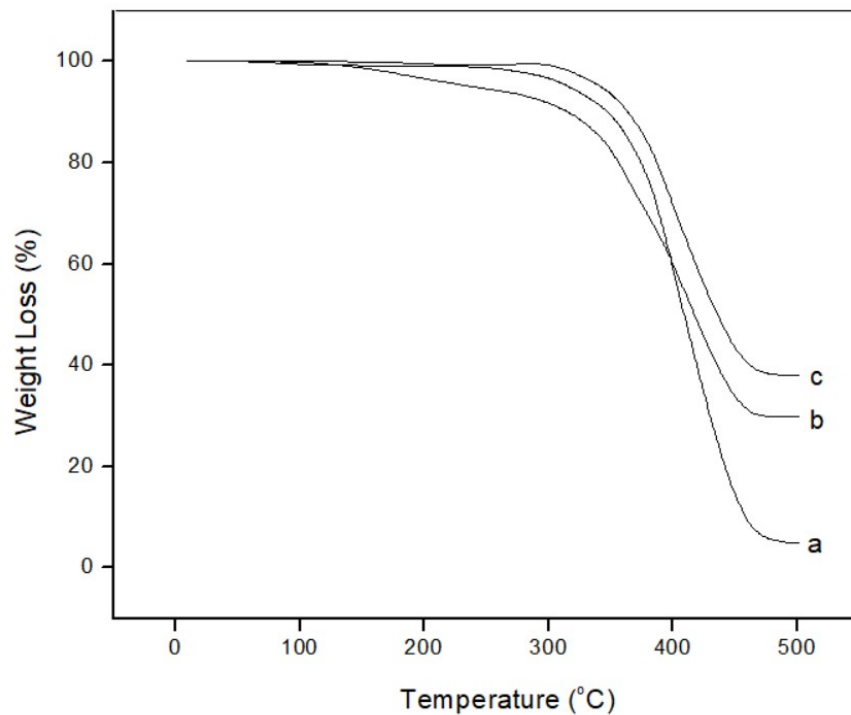


Fig. 5. TGA curves: (a) pure PEO, (b) SPE host: (75PEO:25NaPO₃), (c) NCPE OCC: 95 (75PEO:25NaPO₃) + 5 TiO₂.

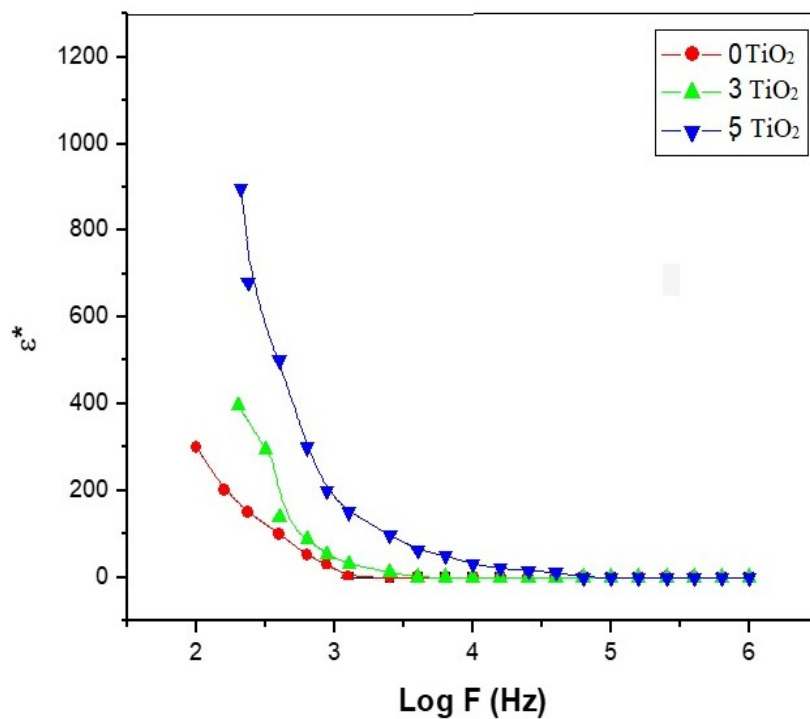


Fig. 6. Frequency dependence dielectric constants (ϵ^*) of hot-pressed NCPEs: $(1-x)$ $(75\text{PEO}:25\text{NaPO}_3)+ x \text{TiO}_2$ at different wet.%.

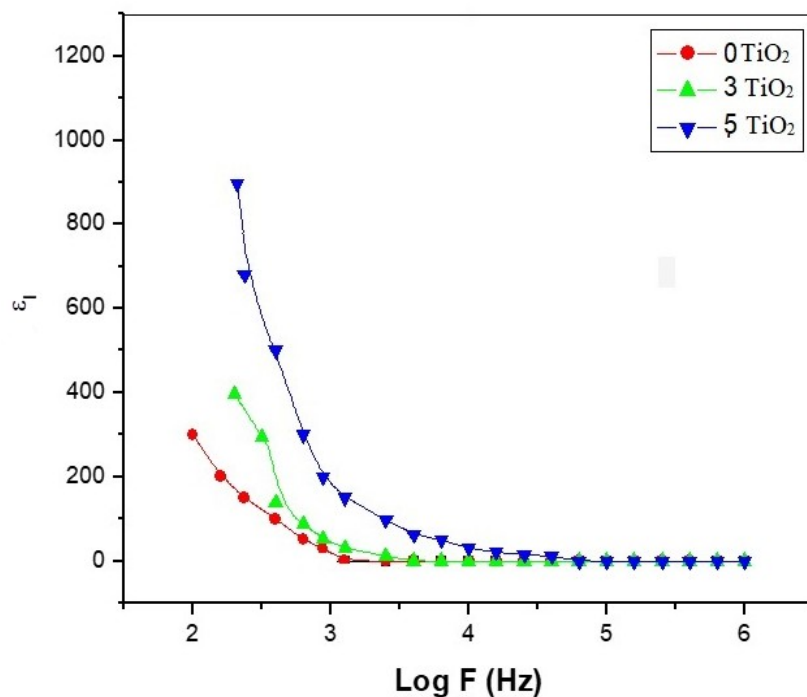


Fig. 7. Frequency dependence dielectric loss (ϵ'') of hot-pressed NCPEs: $(1-x)$ $(75\text{PEO}:25\text{NaPO}_3)+ x \text{TiO}_2$ at different wet.%.

The thermo-gravimetric analysis (TGA) curves for pure PEO, SPE host and NCPE OCC is shown in Fig. 5. It can be clearly shown from the figure that the total weight loss for pure PEO is larger as compared to both SPE host and NCPE OCC. The total weight loss for NCPE OCC is ~ 62 % and SPE host is ~ 70 % whereas for pure PEO is ~ 95 %. The thermal stability of pure polymer has been improved with addition of nano-filler SiO₂ and it is indicative of polymer-salt complexation as well as formation of NCPEs.

The increase in ionic conductivity of NCPEs can also be understood by dielectric studies. Figs. 6&7 shows the frequency dependence of dielectric constant (ϵ^*) and dielectric loss (ϵ_l) of NCPEs: (1-x) [75PEO:25NaPO₃]: x SiO₂. It can be clearly seen from the figures that at low frequency, both dielectric constant (ϵ^*) and dielectric loss (ϵ_l) rise sharply due to the electrode polarization as well as space charge effect, as reported by the several workers (Ramesh et al, 2002; Chandra et al., 2013). This is because at low frequency, there is time for charges to build-up at the electrode-electrolyte interface before applied field change direction. At higher frequency, rapid reversal of electric field causes no time for charges to build-up at the interface. After the addition of nano-filler TiO₂, the value of dielectric constant (ϵ^*) and dielectric loss (ϵ_l) start increasing. This is indicative of increase in the number of mobile ions in the polymeric electrolytes and this is responsible for overall increase in the conductivity of the present NCPEs.

CONCLUSIONS

Materials characterization and polymer-salt complexations of a new Na⁺ ion conducting nanocomposite polymer electrolyte (NCPE): (1-x) (75PEO:25NaPO₃) + x TiO₂, have been explained with the help of XRD, SEM, DSC and TGA studies. The conductivity enhancements in NCPEs have been explained by the dielectric studies. The present NCPE can be potentially used for the solid-state device fabrication viz. batteries, sensors, fuel cells etc.

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