



# Structural and dielectric properties of (PEO–PMMA)–SnO<sub>2</sub> nanocomposites



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## ABSTRACT

Polymer nanocomposite (PNC) films based on poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blend as host polymer matrix dispersed with tin dioxide (SnO<sub>2</sub>) nanoparticles have been prepared by the solution-cast method. X-ray diffraction measurements confirm that these films are semicrystalline and the degree of crystalline phase reduces with increase of SnO<sub>2</sub> contents in the polymer blend. The scanning electron microscopy reveals that the surface morphology of the PNC films is smooth with homogeneous distribution of the SnO<sub>2</sub> particles. Complex dielectric permittivity, electrical conductivity, electric modulus and impedance spectra of the PNC films have been investigated in the frequency range from 20 Hz to 1 MHz. The real part of the dielectric permittivity of these films has non-linear increase with the increase of SnO<sub>2</sub> nanoparticles contents in the PEO–PMMA blend over the audio frequency range, whereas it is found tunable with nanofiller concentration in the range from 2 to 3 at the radio frequencies. Dielectric loss tangent and the loss part of electric modulus spectra exhibit relaxation peaks which are ascribed to cooperative chain segmental dynamics of the PEO and PMMA macromolecules. It is observed that the polymers chain segmental dynamics becomes much faster when only 1 wt% SnO<sub>2</sub> nanoparticles are dispersed in the polymer blend matrix, which further enhances moderately with the increase of SnO<sub>2</sub> concentration up to 5 wt%. The dielectric relaxation time and electrical conductivity values of the PNC film are found Arrhenius in temperature of activation energies 0.15 eV and 0.43 eV, respectively.

## 1. Introduction

Instead of new polymers synthesis, the blending of different polymers has become simple, effective, inexpensive and green chemistry technique for the preparation of advanced polymeric materials with tailored physico-chemical properties in order to fulfill the technological requirements of industries [1–4]. For the better performance of polymers blend, miscibility of each component is one of the most important factors governing the various properties of the blend matrix. Although, the polymer blend miscibility is strongly dependent on the method of its preparation, but it is also quite dependent on the blend constituents composition and the difference in glass transition temperatures of the blended polymers.

So far, numerous polymer blends based on the synthetic polymers had been prepared and characterized for the physical, chemical and structural properties [1–3]. Among the synthetic polymers, linear chain poly(ethylene oxide) (PEO) is a semicrystalline, whereas the bigger side-groups containing poly(methyl methacrylate) (PMMA) is an amorphous material. The glass transition temperature  $T_g$  of PEO ( $T_g \sim 221$  K) and PMMA ( $T_g \sim 402$  K) represent an extreme case of

dissimilarity which is around 181 K [5,6]. Further, the solution cast film of PEO is highly flexible-type, whereas PMMA film has high optical transparency but is brittle under loaded force. As compared to polar PEO film, the PMMA film has good thermal stability, weather resistance, chemical inertness and relatively low value of dielectric permittivity which make the PMMA a crucial dielectric material as an insulator in the fabrication of organic thin film transistors. Because of the above-mentioned properties of the PEO and PMMA, the characterization of miscibility, thermal properties, structural phases, chain dynamics and other properties of PEO–PMMA blend with varying composition had been the intensive topic of the investigators [5–17]. From a thermodynamic point of view, minimal heterogeneous chains interactions are present in the PEO–PMMA blend as revealed from their Flory-Huggins interaction parameter value, which is close to zero [7]. In regards to the polymers miscibility, it has been established that the PEO–PMMA blend exists as a single amorphous phase for concentrations of PEO in the blend which are  $\leq 30\%$  by weight [8,10,12,13]. The dynamical behaviour of the PEO–PMMA blend structures had been explored by different experimental and molecular simulation techniques over the broad ranges of time and temperature scales which is

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found strongly PEO and PMMA composition dependent in the blend [5,9,13,14,16].

The structural dynamics of most of the polymeric systems are complex in nature, the slower motion involved with the glass transition and associated with relaxation of main-chain backbone (segmental motion) is denoted by  $\alpha$ -relaxation, whereas the faster dynamics including side-group motion and the local dipolar arrangements in addition to the rotation and vibration is referred to secondary or  $\beta$ -relaxation process [18]. In a single amorphous phase PEO–PMMA blend, it has been observed that there is merged  $\alpha\beta$ -process due to changes in dynamics with relaxation times which are Arrhenius in temperature [9,10]. As compared to the dynamics of bulky chain segments of PMMA, the dynamics of lighter chain segments of PEO is much faster. But in the blend of these polymers, the dynamics of PMMA significantly enhances owing to plasticizing nature of the PEO for the PMMA matrix, and therefore, the PMMA coupled chain dynamics with PEO exhibits the merged  $\alpha\beta$ -process [9]. Such coupled chain segmental dynamics in the blend play an important role in ions transportation when PEO–PMMA blend matrix is used as a host for the preparation of solid polymers electrolytes (SPEs) [19–22].

Although several physico-chemical properties of the polymer blend can be tailored by their composition variation, but to achieve more rigidity and the higher thermal and chemical stability of such materials, there is enormous work in progress on the inorganic nanofiller dispersed polymer nanocomposites (PNCs) [23–32]. The PNC materials possess various useful and tunable properties of inorganic nanofiller as well as the organic polymer. The formation of interfacial interactions (physical or electrostatic) between the nanofiller and the dipolar group/s (functional group/s) of the polymer chain is the most decisive factor which establishes the various useful properties of the PNC materials.

Keeping all the above-mentioned facts in mind, in the present manuscript, the PNC films based on PEO–PMMA blend matrix dispersed with nanoparticles of tin oxide (Stannic oxide;  $\text{SnO}_2$ ) have been prepared, and the study concentrates on their structural, morphological, dielectric and electrical characterizations. The PEO–PMMA blend of 50/50 wt% amounts was used because this blend composition is of the semicrystalline nature and exhibits a variety of morphologies (dendrites, dense-branched, stacked needles, needles, feather-like) [17,33]. The choice of  $\text{SnO}_2$  nanoparticles in the preparation of the PNC films is owing to its high chemical and mechanical stabilities. This ceramic material can be synthesized in form of nanocrystals, nanorods, nanowires, nanoribbons, nanotubes, nanosheets, and porous and hollow microspheres [34]. Further,  $\text{SnO}_2$  is a wide band-gap ( $\sim 4$  eV) n-type semiconductor of tetragonal rutile structure which exhibits excellent optical transparency [34,35]. It is the most suitable inorganic material for photocatalysis and electrocatalysis application and commonly used in the performance enhancement of the polymeric membranes [36,37], and also for the transparent organic resistive memory devices [38]. Furthermore, it has been recognized as the high-performance material for the gas sensor [34], the dye-sensitized solar cell [39], electrode material for the lithium-ion batteries and supercapacitors [40].

The aim of this study is to explore the suitability of varying filler concentration (PEO–PMMA)– $\text{SnO}_2$  films as nanodielectric materials and their uses in the preparation of SPE materials. Currently, there is a huge industrial demand for the flexible-type polymeric nanodielectric materials having inter-balanced dielectric and physico-chemical properties in order to replace the traditional electrical insulators in various kinds of advanced microelectronic devices namely high energy density capacitors, polymer field-effect transistors, polymer-based logic circuits, electrochromic devices etc. [41–46]. The dielectric properties of the polymeric nanodielectric are usually tuned by properly selecting the identity, shape and dielectric permittivity of the inorganic fillers, and also engineering the interfaces between fillers and the flexible-type polar/non-polar polymeric matrix at their various compositions [24,27,41]. In the PEO–PMMA blend, the flexibility of the film is owing to the presence of PEO which acts as a plasticizer for PMMA, whereas

PMMA increases the mechanical stability and reduces the crystalline phase of PEO in the blend. Further, PMMA has low values of dielectric permittivity [47,48] as compared to that of the PEO [49], and therefore, the inter-balanced dielectric properties of this blend are expected as per simple mixing rule. Further, the tuning of these dielectric properties by dispersing  $\text{SnO}_2$  into the PEO–PMMA blend has also been focused in this manuscript, because the  $\text{SnO}_2$  dispersed polymers matrices have confirmed their suitability in the enhancement of ionic conductivity of the gel and solid polymer electrolytes [50–55]. The characterization of detailed dielectric and electrical properties and the polymer segmental dynamics of  $\text{SnO}_2$  dispersed PEO–PMMA blend based PNC films are required for selection of their suitable composition in the preparation of new SPEs for the energy storage devices and also for several other ultimate applications which are governed by the dielectric properties.

## 2. Experimental

### 2.1. Sample preparation

PEO ( $M_w = 6 \times 10^5 \text{ g mol}^{-1}$ ), PMMA ( $M_w = 3.5 \times 10^5 \text{ g mol}^{-1}$ ) and  $\text{SnO}_2$  (nano powder of particle sizes  $< 100 \text{ nm}$ ) were obtained from Sigma-Aldrich, USA. Anhydrous acetonitrile and tetrahydrofuran were obtained from Loba Chemie, India. The nanocomposites of PEO–PMMA blend dispersed with  $x$  wt%  $\text{SnO}_2$  ( $x = 0, 1, 3$  and  $5$  wt% amount of  $\text{SnO}_2$  to the weight of PEO–PMMA blend) were prepared by solution casting method. For the preparation of (PEO–PMMA)– $x$  wt%  $\text{SnO}_2$  films, 50/50 wt% blend of PEO and PMMA was used. Initially, PEO and PMMA each of  $0.5 \text{ g}$  was dissolved in acetonitrile and tetrahydrofuran, respectively, in separate glass bottles and then these were mixed to obtain the PEO–PMMA blend solution. The required amount of  $\text{SnO}_2$  for a particular sample was firstly suspended into acetonitrile under magnetic stirring. After that this  $\text{SnO}_2$  suspended solution was mixed slowly with the polymer blend solution, and under continuous magnetic stirring the homogeneously  $\text{SnO}_2$  dispersed (PEO–PMMA)– $x$  wt%  $\text{SnO}_2$  solution was obtained. This solution was cast onto a poly propylene dish and it was kept to dry slowly at room temperature which finally resulted in flexible-type freestanding PNC film. The PNC films of various  $\text{SnO}_2$  concentrations were prepared by following the same steps as mentioned above. These PNC films were dried in the vacuum oven prior to their characterizations.

### 2.2. Characterizations

The X-ray diffraction (XRD) patterns of the PNC films were recorded in reflection mode at a scan rate of  $0.05 \text{ degree s}^{-1}$  using a PANalytical X'pert Pro MPD diffractometer of Cu  $K\alpha$  radiation ( $\lambda = 0.1540 \text{ nm}$ ) for their structural characterization. The XRD patterns of all the PNC films were recorded with continuous operation of the diffractometer in order to maintain identical experimental condition. The morphology of these PNC films was examined by Carl ZEISS EVO 18 scanning electron microscope (SEM).

Dielectric and electrical measurements of the PNC films were carried out by employing dielectric relaxation spectroscopy (DRS) using an Agilent Technologies 4284A precision LCR meter equipped with 16451B solid dielectric test fixture in the frequency range from  $20 \text{ Hz}$  to  $1 \text{ MHz}$ , at  $30 \text{ }^\circ\text{C}$ . The temperature dependent DRS measurements were also made for the  $3 \text{ wt}\%$   $\text{SnO}_2$  containing PNC film. Frequency dependent values of capacitance  $C_p$ , resistance  $R_p$  and loss tangent ( $\tan \delta = \epsilon''/\epsilon'$ ) of the each PNC film sandwiched between the circular electrodes of dielectric test fixture were measured in the parallel circuit operation for determination of their dielectric and electrical spectra. A micro-processor-controlled oven was used for temperature dependent measurements by putting the dielectric test fixture in the cavity of the oven. Prior to sample measurements, the open circuit calibration of the cell was performed in order to eliminate the effect of stray capacitance of

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