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Mechanism for improvement in mechanical and thermal stability in dispersed phase polymer composites

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Abstract We report substantial improvement in the mechanical stability, thermal stability, and conductivity of four series of ion-conducting dispersed phase composite polymer electrolytes (CPEs). Tensile strength of filler-dispersed composite films was ≥2 MPa in contrast to ~1 MPa for undispersed polymer–salt complex. Similarly, elongation at break has shown an increase by ~200–300% in the composite films. Filler-induced enhancement in thermal and mechanical stability has clearly been noticed. The improvement in the mechanical stability is also accompanied by a corresponding increase in electrical conductivity in the composite films by 1–2 orders of magnitude at lower (2 wt.%) of the filler loading. A mechanism for the improvement in mechanical stability has been proposed. The strength of the mechanism lies in evidenced polymer–filler interaction among the composite components. Suppression of thermal degradation and increased mechanical strength of the CPEs on filler addition has been explained on the basis of transient cross-linking of the polymeric segments and filler–polymer bridging effect.

Keywords Polymer composites · Ionic conductivity · Thermal stability · Tensile strength · FTIR

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Introduction

Ionically conducting polymer composites are important materials both from fundamental studies as well as practical applications in energy storage/conversion devices such as high energy density batteries, supercapacitors, etc. The polymer–salt complexes prepared by complexing polar polymers having electron-rich heteroatoms in its backbone [e.g., polyethylene oxide (PEO), polypropylene oxide, etc.] with alkali metal salts/acids ($LiClO_4$, $NaClO_4$, NH_4ClO_4, H_3PO_4, etc.) offer electrical (ionic) conductivity in the range of 10^{-4} to 10^{-7} S cm^{-1} at room temperature [1–5]. Almost all the solid polymer electrolytes (SPEs) are endowed with some inherent drawbacks that impose limitations on their applicability in devices. These are: (1) their semi-crystalline nature that hinders mobility of ions thereby lowering their conductivity, (2) poor thermo-mechanical stability, (3) slow kinetics, and (4) poor interfacial properties, etc. [1–8]. In order to overcome these chronic problems of ion-conducting polymers, various modifications such as co-polymerization, plasticization, ceramic dispersion, etc. have been suggested. However, these modifications have their own strength and weaknesses. Plasticization improves electrical conductivity of polymer electrolytes at the cost of mechanical strength/dimensional stability. Co-polymerization, on the other hand, is a cumbersome chemical process. The idea of dispersing inert ceramic fillers into the matrix of polymer–salt complexes was proposed originally by Weston and Steele [9] as an attractive approach with an aim to improve mechanical properties of the polymeric films. Subsequently, this approach resulted in additional improvement in thermal, electrical and electrochemical properties of the solid polymer electrolytes [10–16].

The enhancement in electrical conductivity on dispersion of inert filler particles has generally been explained in terms of the disruption of crystallization in the polymer host matrix [6]. The improvement in mechanical properties is normally explained on the basis that the filler particles act as a supporting matrix for the conductive polymer electrolytes and impart its dimensional stability without compromising its solid structure even at higher temperatures. However, the actual mechanism involved in the phenomena leading to lowering of thermal degradation behavior and enhancement in the mechanical (tensile/elongation) properties on ceramic filler dispersion in polymer–salt complexes is yet to be understood completely.

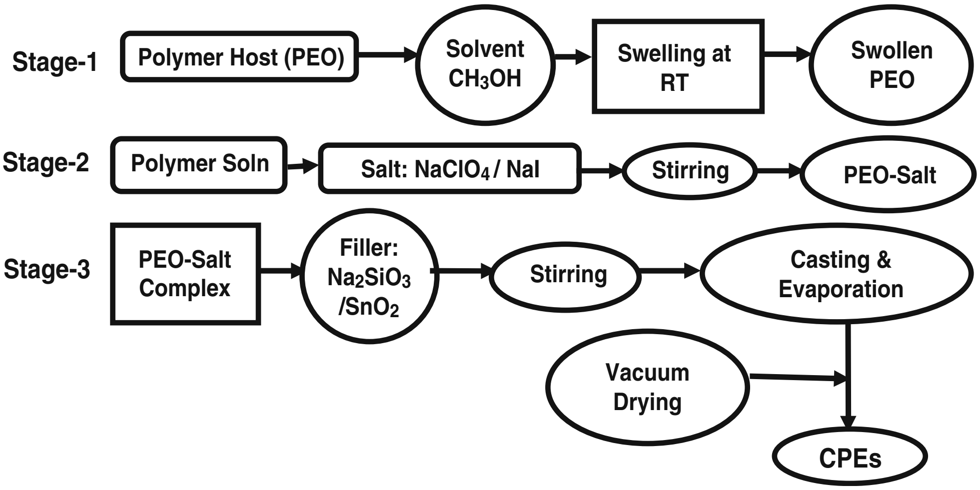
The central idea of this paper has been to understand and explain the enhancement in stability (mechanical and thermal) properties of the four series of dispersed phase polymer composites. The filler concentration-dependent changes in mechanical properties in an ion-conducting polymer composites are very important from device applications point of view. However, an understanding of the mechanism causing such a change has hardly been reported in literature. Secondly, an improvement in mechanical properties of the polymer composites with potential utility as an "electrolyte-cum-separator" film in energy storage/conversion devices is highly desirable to prevent separator rupture causing short circuit of the device during fabrication stages. Thirdly, changes in mechanical properties of a polymer-based ion-conducting film has a direct effect on its chain flexibility/structural behavior, motion of polymer chains/segments, and ion transport properties. In view of these factors that control and determine the suitability of an ion-conducting polymer composite electrolyte (CPE) film for device applications, an understanding of the role played by the filler component in improving mechanical properties in the composite phase becomes more significant and relevant.

In the present work, we aim to investigate the role played by the inert ceramic filler particles in the improvement of mechanical and thermal stability. The effect of filler concentration on enhancement in thermal and dimensional stability of the films has been investigated at the microscopic level using fourier transform infra-red (FTIR) spectroscopy technique. The FTIR results have been interpreted to propose an explanation for improvement in stability properties of the dispersed phase ion-conducting polymer composites (CPEs). A mechanism has been proposed in terms of polymer–ion–filler interactions arising due to: (1) polar/acidic nature of the filler particles and (2) transient cross-linking of polymer segments. The origin of such an effect appears to be consistent and convincing in the light of evidenced feasibility of polymer–ion–filler interaction among the composite components investigated at the microscopic level with FTIR spectroscopy.

Experimental procedure

Materials' preparation

Four series of CPEs based on PEO (Aldrich, M.W.~6×10^5) as the host matrix, complexed with the salts $NaClO_4$ and NaI (Fluka) and dispersed with inert ceramic fillers Na_2SiO_3 and SnO_2 (Fluka), have been prepared using the standard "solution-cast" technique. The particle sizes of the ceramic fillers were ~5 μm. The various steps involved in the sample preparation process may be represented schematically as below:



The details of the preparation method are described by us elsewhere [17–19]. The composition of the four different series of CPEs may be represented as $(PEO)_{25}$−salt $(NaClO_4/NaI)+x$wt.% fillers (Na_2SiO_3/SnO_2). The total number of samples prepared and investigated in each of the four series has been 9.

Materials' characterization

Thermal properties of the four series of CPEs under investigation have been analyzed by differential scanning calorimetry (DSC) technique. The DSC studies on different composition of CPEs were performed with a PERKIN ELMER DSC-4 unit. About 12 mg of each sample was heated in nitrogen atmosphere in the temperature range from −100°C to 250°C at a rate of 10°C min^{-1}. The mechanical measurements (tensile test) on the CPE films were carried out to determine their mechanical properties (tensile strength and maximum elongation at break), using a computer-controlled micro-force tester (INSTRON, MODEL: 4465, USA). Each sample of the CPEs, taken in the shape of rectangular strip (20×10 mm), was clamped between the holders of the universal tensile testing system. The speed of the elongation test was maintained at 2 mm min^{-1} for each of the specimen under test at room temperature. Electrical measurements has been carried out using Hioki LCR Hi Tester (Model: 3520) over a range of temperature (30–150°C) over a range of frequency (100 Hz–100 kHz). FTIR spectrum of the polymer–salt complex (PS) and different composite polymer electrolyte (CPE) films were recorded using a computer-controlled THERMO NICOLET FTIR spectrophotometer (Model: Nexus-870) in the wave number range 4,000–400 cm^{-1} at room temperature (~25°C). The experiments were carried out in an inert argon atmosphere by averaging 32 scans with a speed of 2 s per scan. The optical resolution for the spectra was 4 cm^{-1}.

Results

Thermal studies

The effect of dispersion of inert ceramic fillers in the polymer–salt complex has been clearly reflected in the DSC studies in terms of the changes in the glass transition temperature (T_g) of the polymer host as a function of the filler concentration. The DSC thermograms of $(PEO)_{25}$−salt $(NaClO_4\backslash NaI)+x$wt.% filler $(Na_2SiO_3\backslash SnO_2)$ [17–19] indicate two step changes owing to two glass transition temperatures, T_{g1} between −60°C and −45°C and T_{g2} between −28°C and −15°C. These glass transition temperatures, T_{g1} and T_{g2}, are attributed to the amorphous phases of the uncomplexed polymer (PEO) host and polymer–salt complex, respectively. It has been observed that the dispersion of inorganic ceramic fillers $(Na_2SiO_3\backslash SnO_2)$ in the $(PEO)_{25}$–$NaClO_4$ and $(PEO)_{25}$–NaI complex matrix substantially influences the glass transition temperature, T_{g2} of the polymer–salt complex matrix in the present studies. A variation of T_{g2} as a function of the filler concentration is shown in the Fig. 1a–d. It appears from the pattern of variation of T_{g2} that a small addition of the ceramic fillers results in the immediate lowering of glass transition temperature followed by subsequent increase in its value. Another minima in theT_{g2} vs. filler concentration plot appear at an intermediate concentration of the filler particles. Subsequent addition of the filler causes a general increasing trend of the glass transition temperature (T_{g2}).

It is generally believed that the glass transition temperature (T_g) is directly associated with the stiffness/flexibility of the polymeric chains and hence its value plays a crucial role in governing the segmental motion of the polymeric chains in the amorphous phase of the composite polymeric electrolyte films. The higher the value of T_g, the higher is the stiffness (and hence lesser is the flexibility) of the polymeric chains/segments and vice versa. A lowering in the value of glass transition on addition of even a small quantity of the filler particle results in an enhancement in the flexibility of the polymeric chains because of a possible delinking of the polymeric segments due to filler interaction with the polymer network. The overall effect suggests an expected enhancement in the tensile properties of the films on filler addition. An improvement in the thermal stability of the composite polymer films has been noticed during a thermal cycle between room temperature (~30°C) and 200°C in the case of $PEO_{25}NaClO_4+x$wt.% Na_2SiO_3 system. It was observed that a filler-free polymer complex film ($x=0$) developed many cracks after cooling it from 200°C to room temperature (Fig. 2a). However, such cracks were not observed in the filler-dispersed composite polymer films throughout the compositional range (Fig. 2b). This experimental result provides a clear and convincing evidence of an improved thermal stability (lowering of thermal degradation) of the filler-dispersed composite polymer films in comparison to the undispersed films (i.e., films with $x=0$). It is because a homogeneous dispersal of the inorganic ceramic filler in the polymer–salt complex has the better ability to prevent quick expansion of heat into the matrix, thereby limiting thermal degradation of the material.

Electrical conductivity

The temperature dependence of electrical conductivity, i.e., σ vs. 1/T curves for all the polymer complexes and composites,

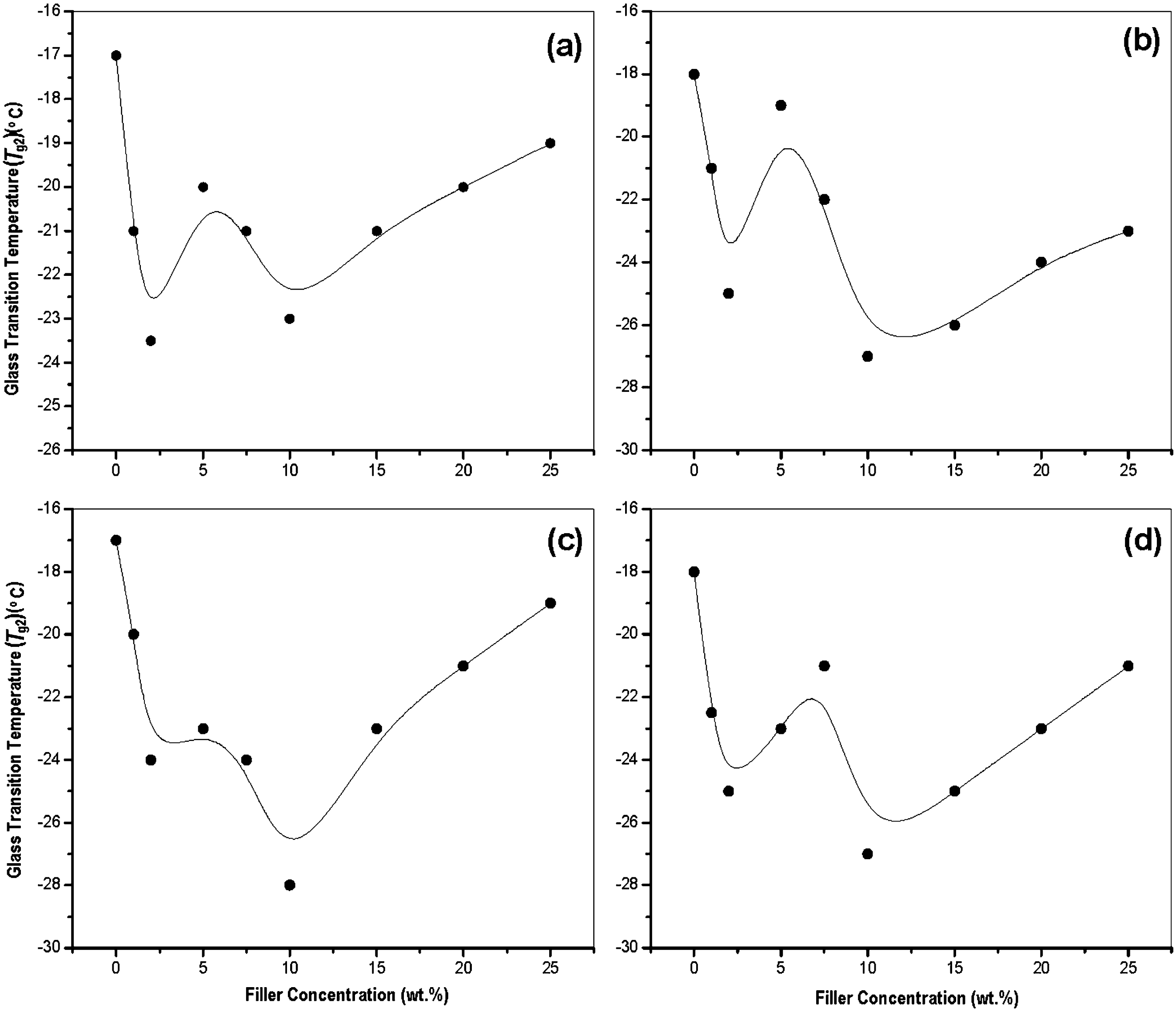


Fig. 1 DSC results (variation of glass transition temperature of the composite polymer electrolyte films as a function of filler concentration: **a** $PEO_{25}NaClO_4$+*x*wt.% Na_2SiO_3, **b** $PEO_{25}NaI$+*x*wt.%Na_2SiO_3, **c** $PEO_{25}NaClO_4$+*x*wt.% SnO_2, and **d** $PEO_{25}NaI$+*x*wt.% SnO_2

$(PEO)_{25}$ Na–salt ($NaClO_4$/NaI)+*x*wt.% fillers (Na_2SiO_3 and SnO_2) suggest an almost identical response observed in terms of two linear regions separated by a jump by varying degree depending on a particular combination of polymer–salt–filler components. Representative results for $(PEO)_{25}$−$NaClO_4$/NaI)+*x*wt.% Na_2SiO_3 are shown in the Fig. 3a, b. All the curves exhibits typical behavior of PEO-based polymer electrolytes. A sudden jump in conductivity has been observed for each composition. This jump temperature coincides with the crystalline melting temperature of PEO, T_m (~69–70°C as observed in DSC). This has been explained on the basis of semicrystalline to amorphous phase transition. The linear variation in conductivity as a function of temperature follows apparently an Arrhenius-type thermally activated process before and after T_m.

The conductivity σ obeys typical Arrhenius behavior before and after polymer phase transition (i.e., crystalline melting). It can be expressed as $\sigma=\sigma_0\ \exp(-E_a/kT)$ where, σ_0 is the pre-exponential factor, E_a is the activation energy, and k is the Boltzmann constant. The values of σ_0 and E_a, evaluated for different compositions of all the composite polymer electrolyte systems (CPEs), are given in Table 1. It provides clear distinction between the phenomena before and after the crystalline melting process (i.e., first-order thermodynamic phase transition) separately. It is a well-established fact that the high conductivity and low activation energy are complementary to each other. Both the properties appear to be optimum in solids with disordered open channels and layered structures in which the number of sites (vacancies) for ion jump outnumber the

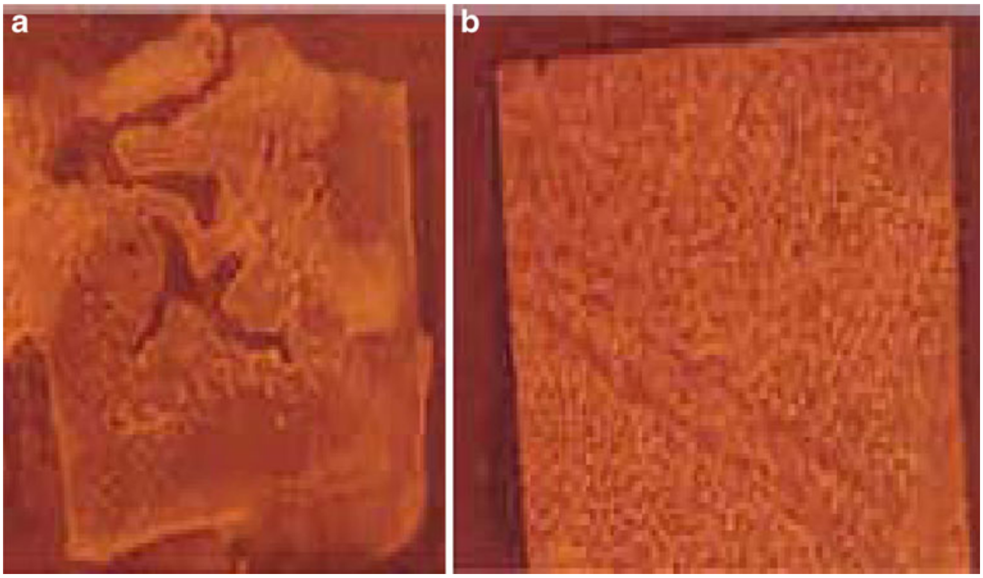


Fig. 2 Photograph showing thermal stability of the composite polymer film, ($PEO_{25}NaClO_4$+ *x*wt.%Na_2SiO_3) after thermal cycling at 150°C and subsequent cooling **a** x=0, **b** x=10%

available ions likely to occupy them. The polymer–ceramic grain boundaries (or interfaces) may provide similar structures. It can be deduced from the Arrhenius equation mentioned above that lower the values of activation energy, the higher is the ionic conductivity of the materials, provided that σ_0 remains constant. Further, comparative analysis of the activation energy values (Table 2) with the conductivity value for different filler composition at any specific temperature shows that for almost all the CPEs in the present studies, the minimum values of activation energy have been observed for the compositions which show maximum conductivity. Further, comparative analysis indicates that for all the CPEs, the conductivity starts increasing initially even after addition of 1–2 wt.% and attains a maximum for filler addition between 0 and 5 wt.% loading. Thereafter, another maxima has been observed at ~10 wt.% dispersion of the fillers. This increase is followed by monotonous conductivity drop on further addition of the fillers. A similar trend in the variation of conductivity has also been observed at a temperature of 100°C. This variation in the d.c. conductivity of the CPE films remains identical in profile in all the series irrespective of their composition, of course, with different degree of variation in their magnitude. Further, the filler concentration-dependent conductivity profile of the CPEs resembles that of the variation of polymer glass transition temperature (T_g) described in the Figs. 1a–d. The value of T_g is directly associated with the segmental motion of the polymeric chains in its amorphous phase. The exact correspondence of the conductivity and glass transition temperature variation as a function of the filler concentration suggests an active role of filler in tailoring the flexibility/stiffening of the polymer backbone. So, the higher the segmental motion of the polymer chains at a specific filler loading in the composite phase, the higher would be its ionic conductivity. It is this behavior that may also be responsible for an improvement in the mechanical properties of the CPEs. It is described below.

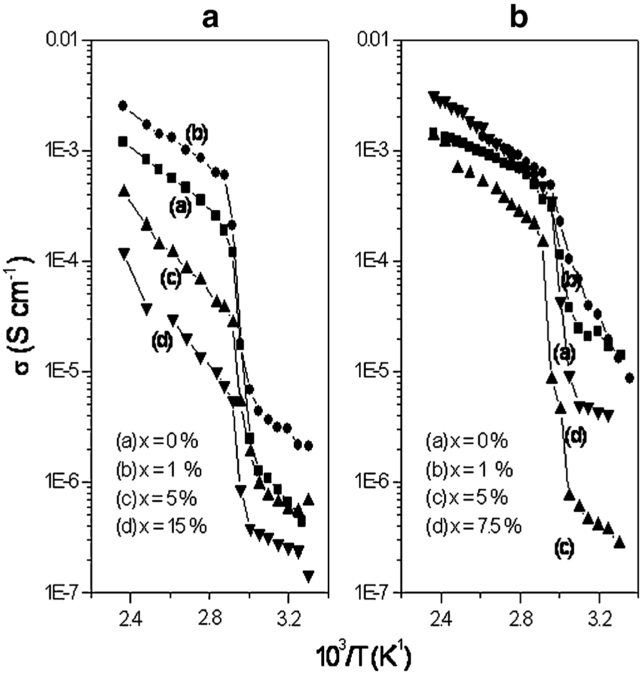


Fig. 3 Temperature dependence of electrical conductivity of **a** $(PEO)_{25}NaClO_4$+*x*wt.% Na_2SiO_3 and **b** $PEO)_{25}NaI$+*x*wt.% Na_2SiO_3

Mechanical properties

The mechanical properties of all the polymeric films have been observed in terms of their tensile strength (TS) and maximum percentage elongation (EL) at break. The

Table 1 Mechanical stability properties of different series of dispersed phase polymer composite films

Filler (wt.%)	Mechanical properties (tensile strength (TS) and elongation (EL) at break (%)) of dispersed phase polymer composite films							
	$PEO_{25}NaClO_4$+*x*wt.% Na_2SiO_3		$PEO_{25}NaI$+*x*wt.% Na_2SiO_3		$PEO_{25}NaClO_4$+*x*wt.% SnO_2		$PEO_{25}NaI$+*x*wt.% SnO_2	
	TS (MPa)	EL (%)	TS (MPa)	EL (%)	TS (MPa)	EL (%)	TS (MPa)	EL (%)
0	1.0	30	0.95	40	1.0	30	0.95	40
1	2.2	100	1.1	128	2.2	100	1.15	130
2	2.0	119	1.0	130	2.0	112	1.1	160
5	2.3	105	1.5	122	2.3	179	1.2	168
7.5	2.5	120	2.14	154	2.3	180	1.5	182
10	2.45	162	1.85	176	2.1	200	1.3	200
15	2.65	200	2.0	205	2.2	220	1.45	225
20	2.75	250	2.01	218	2.3	265	1.5	240
25	2.80	275	2.18	252	2.45	280	1.6	265

elongation produced in the polymeric films has been monitored as a function of applied load. The data so obtained for each CPE films has been used to evaluate applied stress and the corresponding strain produced in the material. The results have been expressed in the form of stress–strain plot. An analysis of the stress–strain diagram for different series of CPEs provide significant insight on various aspects of the mechanical properties of pure polymer–salt complex (undispersed PEs) and dispersed phase CPEs. A typical representative stress–strain plot is shown in Fig. 4a–d for $PEO_{25}NaClO_4$+*x*wt.% Na_2SiO_3.

The stress–strain curves (Fig. 4) have two distinct regions of elastic and plastic deformation. The linear portion of the stress–strain curve traces its origin to the

Table 2 Electrical conductivity of different series of dispersed phase polymer composite films

Filler (wt.%)	$PEO_{25}NaClO_4$+*x*wt.% Na_2SiO_3		$PEO_{25}NaI$+*x*wt.% Na_2SiO_3		$PEO_{25}NaClO_4$+*x*wt.% SnO_2		$PEO_{25}NaI$+*x*wt.% SnO_2	
	σ_0	E_a	σ_0	E_a	σ_0	E_a	σ_0	E_a
Pre-exponential factor (σ_0) and activation energy (E_a) of the of dispersed phase polymer composite (CPE) series before crystalline melting temperature (T_m)								
0	3.45×10^0	0.42	2.23×10^1	0.45	1.32×10^1	0.44	9.23×10^0	0.42
1	2.2×10^{-3}	0.18	1.56×10^5	0.67	2.857×10^5	0.68	4.2×10^0	0.41
2	–	–	4.03×10^4	0.65	1.617×10^5	0.68	1.8×10^5	0.66
5	9.6×10^{-4}	0.20	5.66×10^4	0.65	3.5×10^5	0.72	2.36×10^4	0.63
7.5	3.1×10^{-3}	0.22	5.93×10^{-1}	0.34	6.64×10^4	0.64	2.77×10^4	0.63
10	–	–	9.29×10^{-2}	0.28	9.47×10^4	0.65	4.19×10^2	0.50
15	1.6×10^{-4}	0.17	2.65×10^{-3}	0.20	2.071×10^6	0.76	3.14×10^7	0.81
20	1.8×10^{-4}	0.19	2.09×10^{-3}	0.20	4.75×10^6	0.78	1.154×10^7	0.80
25	–	–	1.18×10^1	0.43	4.48×10^6	0.78	9×10^7	0.86
Pre-exponential factor (σ_0) and activation energy (E_a) of the dispersed phase polymer composite (CPE) series after crystalline melting temperature (T_m)								
0	1.52×10^0	0.26	1.15×10^{-2}	0.12	1.588×10^{-1}	0.21	2.25×10^{-1}	0.22
1	1.4×10^0	0.23	3.65×10^{-3}	0.06	4.3×10^{-1}	0.19	2.75×10^{-1}	0.20
2	3.3×10^2	0.42	5.25×10^{-2}	0.16	1.58×10^0	0.35	2.74×10^{-1}	0.25
5	1.99×10^1	0.40	1.33×10^{-2}	0.16	1.7×10^0	0.40	3.83×10^0	0.34
7.5	1.67×10^3	0.53	1.64×10^{-2}	0.24	2.1×10^{-1}	0.25	1.02×10^{-1}	0.30
10	–	–	1.75×10^{-1}	0.23	4.6×10^{-1}	0.18	1.43×10^{-1}	0.23
15	3.3×10^1	0.46	1.33×10^{-2}	0.18	4.34×10^3	0.54	2.9×10^{-2}	0.26
20	3.9×10^1	0.49	4.51×10^{-2}	0.26	5.96×10^2	0.54	3.197×10^{-2}	0.29
25	–	–	3.06×10^{-1}	0.35	3.65×10^2	0.56	7.4×10^{-2}	0.30

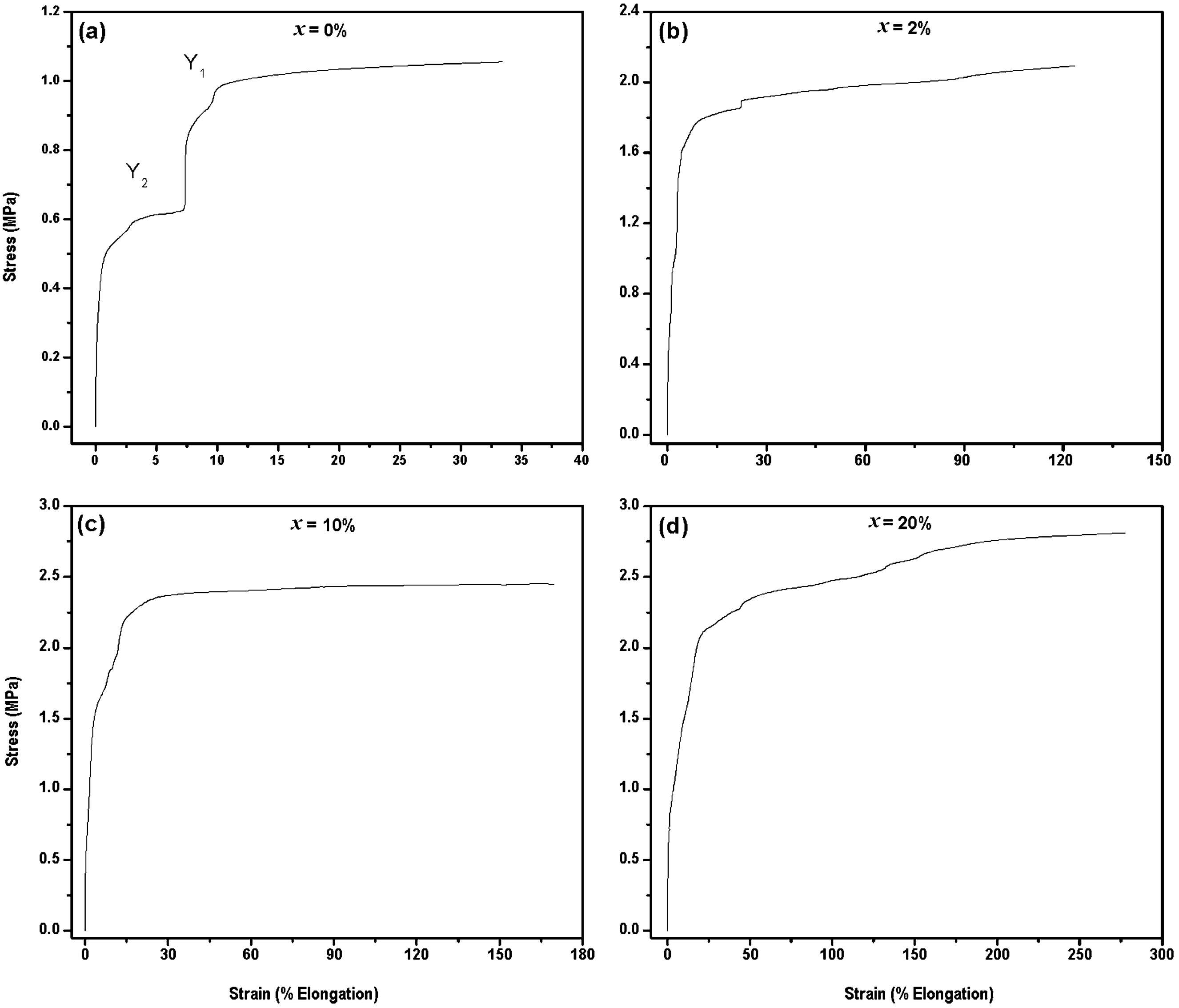


Fig. 4 Representative stress–strain plots for PEO_{25}–$NaClO_4$+$x$wt.%Na_2SiO_3 system **a** x=0%, **b** x=2%, **c** x=10%, and **d** x=20%

elastic region followed by the plastic deformation represented by the non-linear portion of the curves. This general feature has been observed in all the four series of composite polymeric films under study. Further, the undispersed polymer–salt complexes (PEs) show a distinct break (Fig. 4a) between elastic and plastic regions, representing upper and lower yield points namely Y_1 and Y_2, respectively. This indicates non-homogeneous character of pure polymer–salt complexes. These two yield points get suppressed on dispersion of even very low concentration (~2 wt.%) of fillers (Fig. 4b). These observations are almost of similar nature for all the four series of CPEs under investigation. This result is an indicative of the improvement in the mechanical properties of the composite polymeric films (CPEs) due to dispersion of the fillers Na_2SiO_3 and SnO_2.

The stress–strain plots enable us to evaluate mechanical parameters of interest, i.e., tensile strength (TS) and maximum percentage (%) elongation (EL) at break. Their estimated value for all the CPEs in the present study is shown in the Table 2. It appears that addition of even low concentration of fillers (~1–2 wt.%) enhances the tensile strength (maximum sustainable stress) ~2 times and maximum percentage (%) elongation at break by ~2–3 times for $NaClO_4$-based CPEs (Table 2). The NaI-based CPEs do not exhibit any substantial change, except for a minor improvement in tensile properties at low concentration of the fillers. This observed feature might possibly be related to the different anions present in the system. A substantial enhancement in the mechanical properties of the CPE films on further addition of the filler particles (up to 25 wt.%) has been observed. The normalized plots of tensile strength (TS/TS_{max}) as a function of filler concentration for all the four series of CPEs is shown in the Fig. 5a–d. The profile of the normalized plot indicates a general enhancement in tensile properties leading to dimensional stability of the CPE films on addition of filler particles when compared with undispersed PEs.

The pattern shows a gradual increase in the tensile properties at lower concentration of filler particles followed by almost a plateau region at higher filler concentration. A small dip in the profile of TS/TS_{max} as a function of filler concentration has been observed at ~2 and 10 wt.% of the filler particles for all the CPEs. This result is in close agreement with the minima observed, exactly at the same weight percent of the filler, in the variation pattern of glass transition temperature as a function of filler concentration (Fig. 1a–d). It suggests that the polymer backbone becomes slightly flexible at these concentrations of filler particles. The normalized tensile strength profile assumes a stable plateau beyond 10 wt.% of the filler concentration and remains almost unaffected throughout. It may possibly be attributed to a better affinity and compatibility of the fillers with the host polymer backbone at this concentration of the filler particles. However, such a possibility remains to be confirmed experimentally. It has, in fact, been studied at microscopic level using FTIR analysis described below in the next section.

FTIR spectroscopy studies

Fourier transform infra-red (FTIR) spectroscopy studies have been carried out with an aim to investigate the effect of filler particles, in the present studies, on the nature of interaction in composite polymeric (CPE) films. Figure 6a, b shows the FTIR spectra of $PEO_{25}NaClO_4+x$wt.% Na_2SiO_3 and $PEO_{25}NaClO_4+x$wt.%SnO_2, respectively in the wave number region of 600–1,200 cm^{-1}. The changes in the different spectral regions: (1) 600–650 cm^{-1}, (2) 800–900 cm^{-1}, and (3) 1,000–1,200 cm^{-1} have been observed due to the addition of filler particles in the

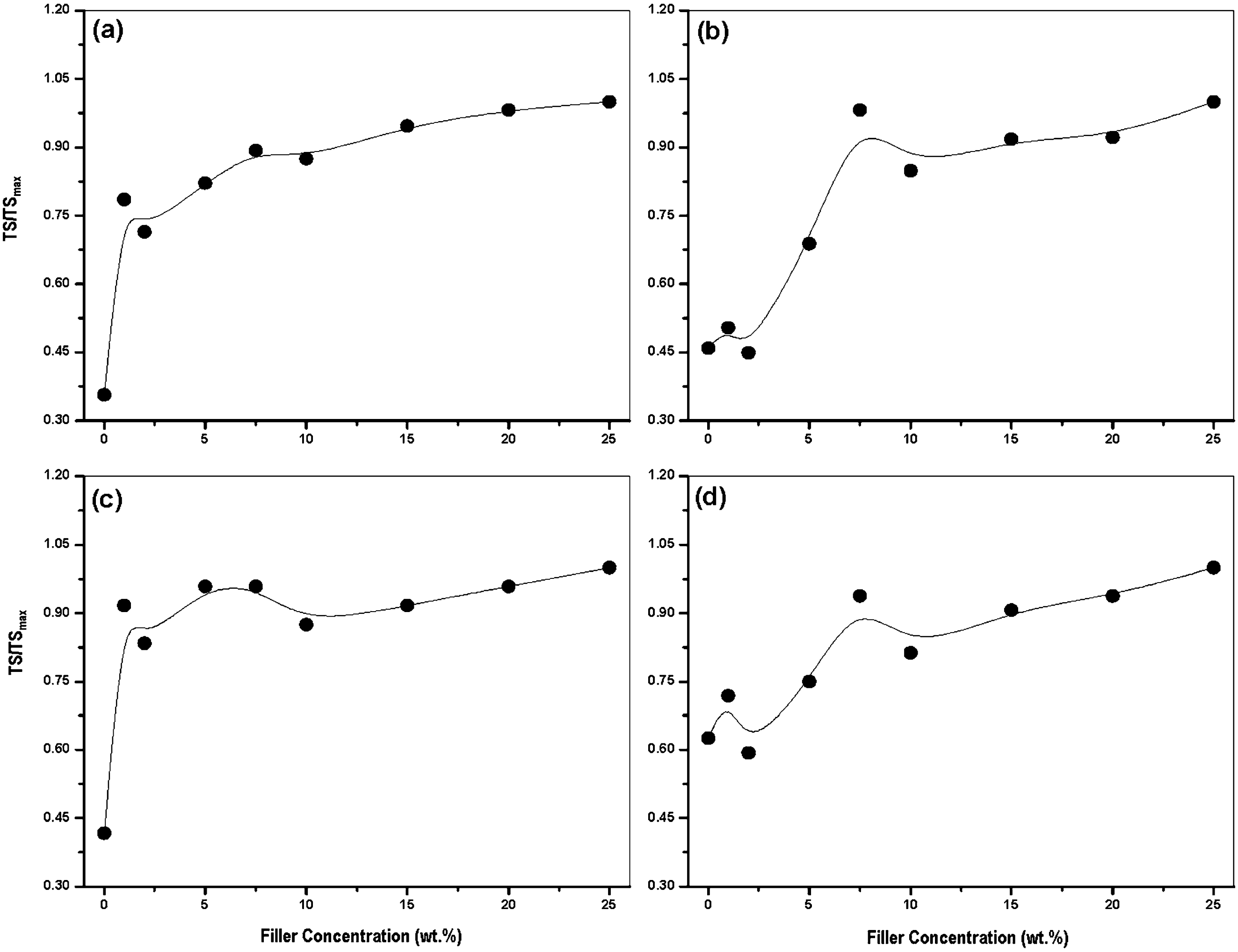


Fig. 5 Normalized tensile strength of composite polymer electrolyte films as a function of filler concentration **a** $PEO_{25}NaClO_4+x$wt.% Na_2SiO_3, **b** $PEO_{25}NaI+x$wt.% Na_2SiO_3, **c** $PEO_{25}NaClO_4+x$wt.% SnO_2, and **d** $PEO_{25}NaI+x$wt.% SnO_2

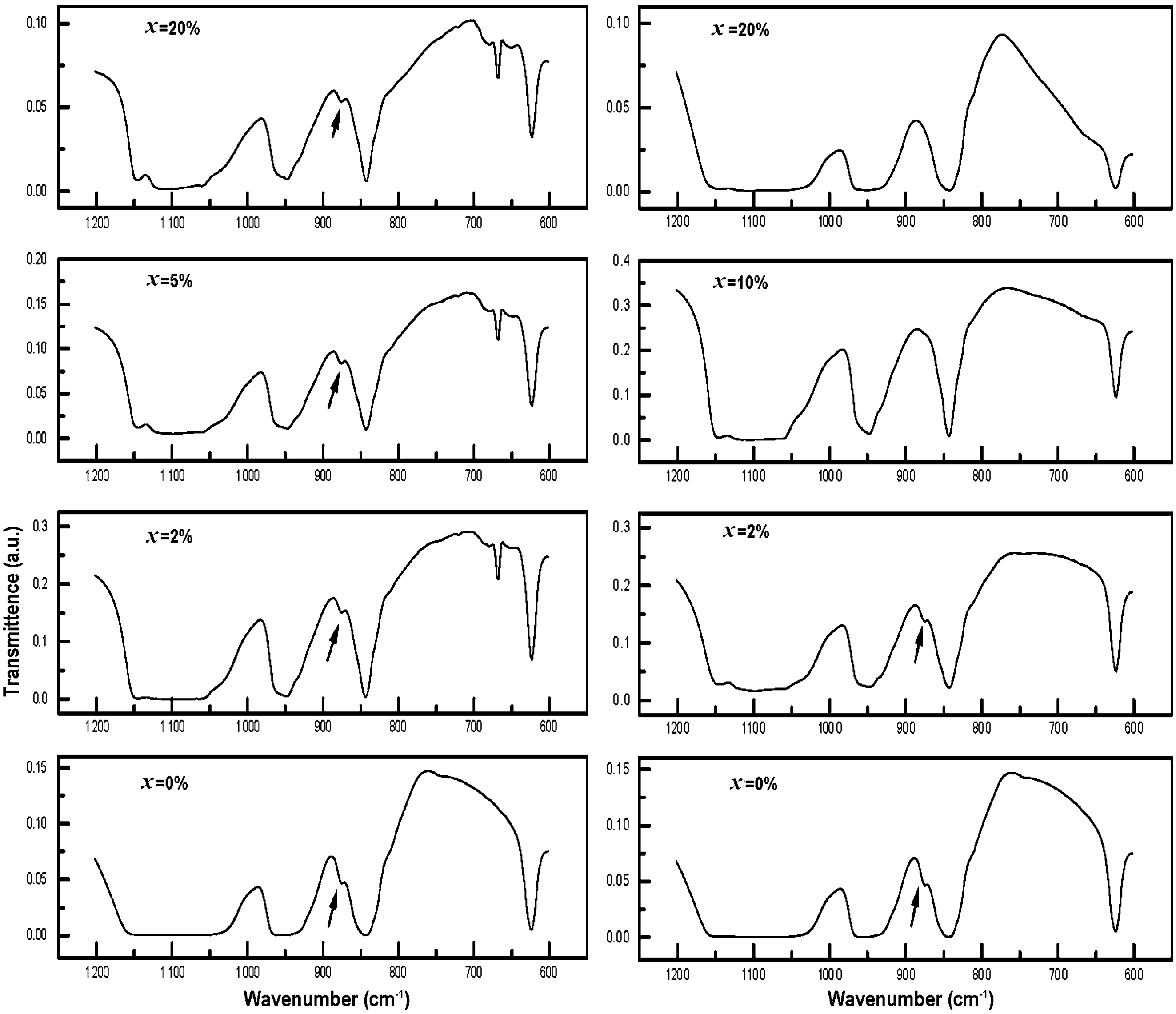


Fig. 6 FTIR spectrum of **a** $PEO_{25}NaClO_4$+xwt.% Na_2SiO_3 system and **b** $PEO_{25}NaClO_4$+xwt.% SnO_2 system in the spectral region 600–1,200 cm^{-1}

polymer–salt complex matrix. The details of these are described as follows:

The band in the spectral region 600–650 cm^{-1} has been attributed to $\nu_4(ClO_4^-)$ mode. It has been observed that this band gets affected substantially with dispersion of filler particles in the polymer host matrix. This may be due to changes in the chemical environment and ion–ion interactions associated with ClO_4^-, on addition of filler particles (Na_2SiO_3 and SnO_2) in the PEO–salt complexes. This interaction plays a crucial role in governing the conductivity behavior of the CPE films as a function of filler concentration. Some changes have also been observed in the spectral region 800–900 cm^{-1} due to filler dispersion, particularly with SnO_2. The vibrational modes in the region 800–900 cm^{-1} corresponds to the coupled CH_2 rocking and CO stretching modes [6] that are related with ion–polymer interactions in polymer–salt complexes and CPEs under investigation. The intensity of the peak observed at ~875 cm^{-1} starts decreasing and disappears completely on addition of 10 wt.% (or more) of SnO_2 fillers (Fig. 6b). This peak is not affected due to dispersion of Na_2SiO_3 fillers (Fig. 6a). The spectral features in this region are highly sensitive to any trans or gauche conformational changes in PEO chains. The disappearance of the peaks at ~875 cm^{-1} on addition of SnO_2 is indicative of the conformational changes which is not observed in Na_2SiO_3-based CPEs. More detailed studies are, however, required to confirm and analyze the conformational changes. The spectral region 1,000–1,200 cm^{-1} corresponding to C–O–C stretching mode has been found to be affected with the dispersion of filler particles. This spectral region consists basically of unresolved symmetric and antisymmetric C–O–C vibrations. Changes in the position, intensity and shape of these modes are associated with polymer–ion interactions. The variation in the peak position of the ν(C–O–C) band as a function of filler concentration for all the CPEs in the present study is shown in Fig. 7a–d. It has been observed that a significant change in the position of ν(C–O–C) band takes place for all the CPE systems, $PEO_{25}NaClO_4+x$wt.% Na_2SiO_3/SnO_2 and PEO_{25} NaI+$x$wt.% Na_2SiO_3/SnO_2. Initially, a downward shift in the wave number has been observed. A shift of the C–O–C stretch towards the lower frequency side, on addition of the filler particles, results in the weakening of the C–O–C bonds, thereby enhancing the flexibility of the polymeric chains. It is widely described in literature that the changes in the position of the C–O–C stretching mode are connected with the polymer–ion (cation) interactions and flexibility of the polymeric segments (chains) [20–23]. The pattern of variation in Fig. 6a–d indicates that stiffness of the polymer backbone gets affected substantially on addition of the filler particles. In other words, the pattern of Fig. 7a–d suggests that almost all the composite films (CPEs) are more flexible (having better tensile properties) than their parent undispersed polymer–salt complexes (PEs with x=0). The minima observed, therefore, at ~2 and 10 wt.% of the filler concentration (Fig. 7a–d) is indicative of the fact that the polymeric segments become more flexible preferentially at these filler concentrations in comparison to the pure PEs and CPEs with other filler combinations. The flexibility of the polymeric chains is

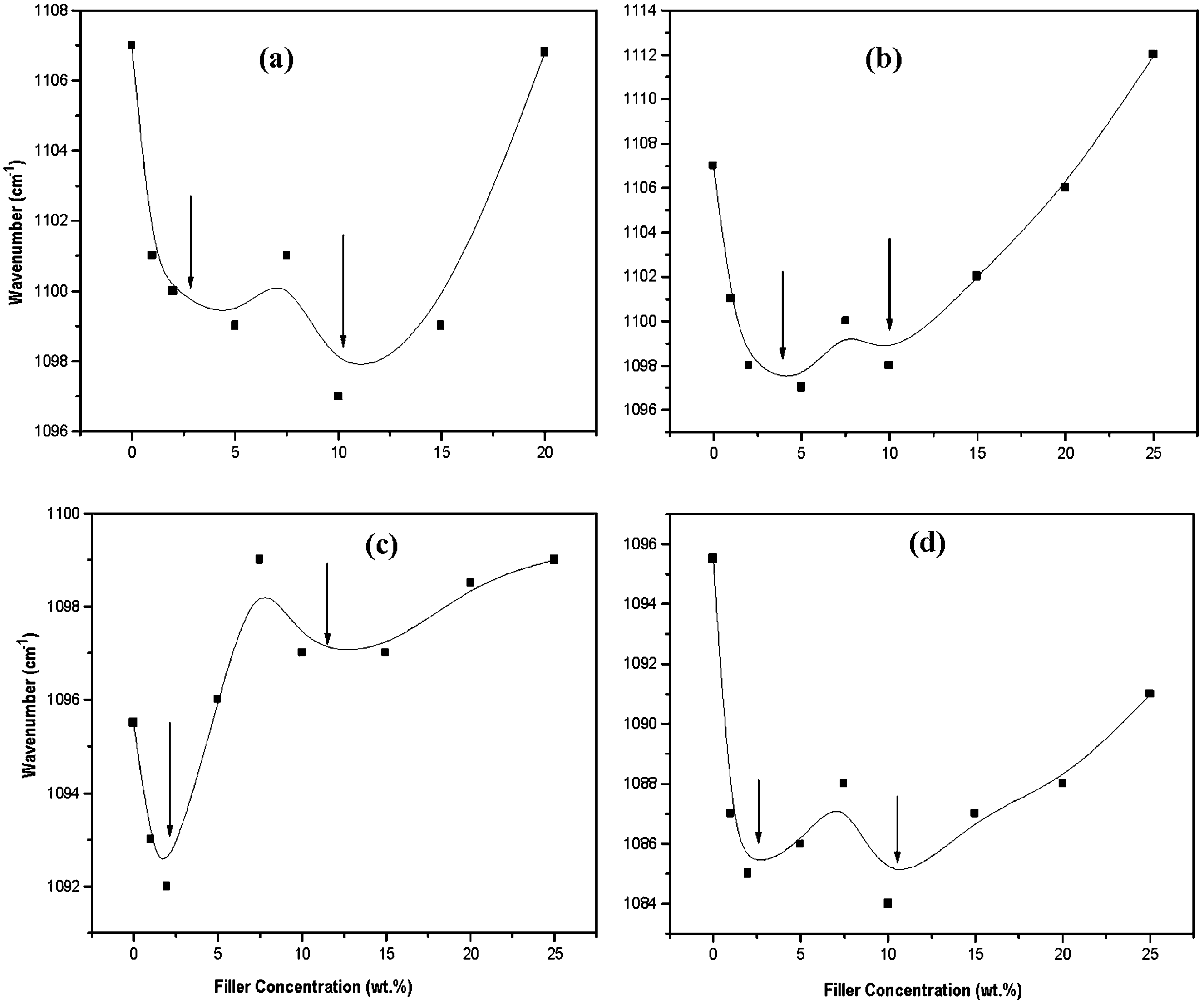


Fig. 7 Changes in the maximum of the C–O–C stretching mode as a function of filler concentration: **a** $PEO_{25}NaClO_4+x$wt.% Na_2SiO_3, **b** $PEO_{25}NaClO_4+x$wt.% SnO_2, **c** $PEO_{25}NaI+x$wt.% Na_2SiO_3, and **d** $PEO_{25}NaI+x$wt.% SnO_2 systems

directly related to the elastic (tensile) properties of the material films and glass transition temperature (T_g) of the polymer host. The lesser the value of T_g, the higher is the flexibility of the polymeric chains/segments [24]. Our DSC results on these CPEs have also shown minima in the plot of T_g vs. filler concentration at exactly the same concentration as in C–O–C shift confirming a microscopic level correlation with the present observations from the FTIR spectroscopy [25].

Discussion

On the basis of information obtained from FTIR spectroscopy studies as described above, it has been found that filler addition affects the polymeric host in a way that causes loosening/stiffening of the polymeric segments. The nature of the filler particles in a polyether type solvent having a low but finite permittivity (of the order of 4) plays a crucial role in determining the material properties. Further, it is generally believed that the cations coordinate with four ether oxygen in PEO–salt complexes [25, 26]. Such an ion–polymer interaction leads to the formation of inter- or intra-molecular transient cross-links of polyether chains [20]. This limits the flexibility (thereby increasing the viscosity) of the polymer host matrix [27]. Two types of cross-linking are possible in which the transient cross-linking between two nearby polymers may occur directly through the cation or through cation–anion interaction or a combination of both. These two possible cross-linking processes are illustrated in Fig. 8a, b.

The filler Na_2SiO_3 is basically an inert oxide having a net dipolar shift in the dielectric medium-like polymeric electrolyte matrix. The electropositive end of the dipoles may therefore interact with the electronegative ether oxygen and/or ClO_4^- ions. Another filler, SnO_2, is the oxide of basically acidic nature. It has a natural tendency to interact with the above-mentioned electronegative species. So the filler particles (Na_2SiO_3 and SnO_2) may possibly interact with the ether oxygen and/or ClO_4^- anions present in the polymer matrix as shown in Fig. 8a, b. In the case of composite polymer electrolytes, in the present studies, though the filler particles exist as a separate phase [22–24], a possibility of filler interaction with polymer host cannot be ruled out as evident from the FTIR spectroscopic observations on changes in the C-O-C mode as a function of filler concentration (Fig. 7a–d).

When the filler concentration is low, there is a possibility that the filler particles can either interact with the polymer or may compete with cations (Na^+) coordinated with ether oxygen and/or with anions (ClO_4^-). These interactions lead to the loss of transient cross-linking of polymeric chains indicated by the downshifting of C–O–C stretching band (Fig. 7a–d) resulting in an increase in the flexibility of the polymeric chains/segments. At higher concentration of filler particles, there is a possibility of bridging between the two nearby polymeric chains via acidic (or polar) filler particles (Fig. 7c). The bridging effect, arising due to a possible polymer–filler interaction, is expected to increase stiffening of the polymeric segments (i.e., enhance the tensile properties). An upward shifting of the maximum of C–O–C stretching band (Fig. 7a–d), as observed from FTIR results, at higher concentration of filler particles provides convincing evidence for this possibility. As a result, the polymeric backbone receives strength due to stiffening of the polymeric chains on filler addition. This, in turn, causes an enhancement in the mechanical strength of the compos-

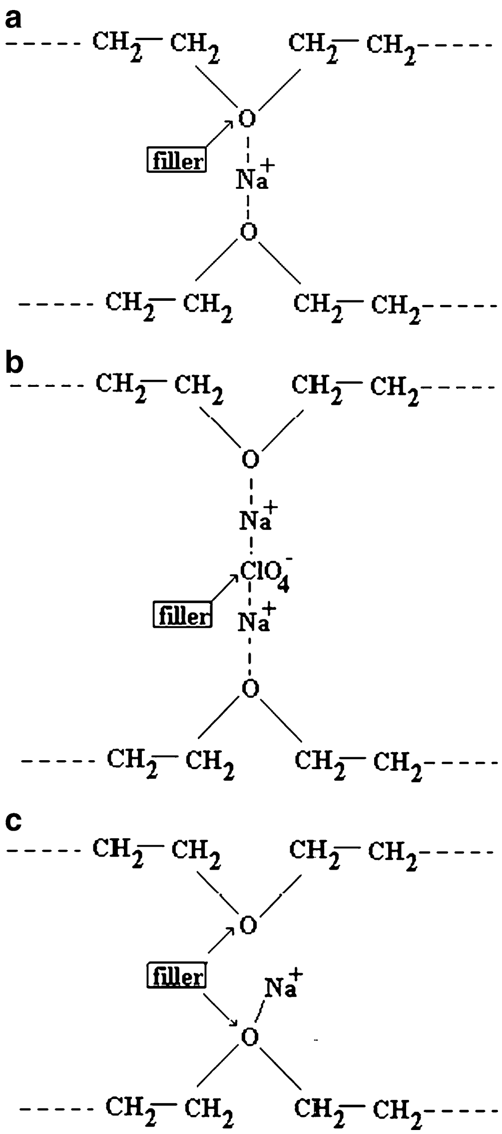


Fig. 8 Schematic illustration of polymer–filler interactions. **a** Transient cross-linking of polymer segments via cation interaction, **b** transient cross-linking of polymer segments via cation–anion interaction and **c** filler–polymer interaction (*bridging effect*)

ite polymeric electrolyte (CPE) films that becomes very high at a favoured filler concentration.

Conclusions

The role of inorganic ceramic fillers in improving the thermal and mechanical stability of the dispersed phase composite polymer electrolytes has been investigated. Thermal stability of the material has been observed to increase on filler addition due to an effective role played by ceramic fillers in preventing quicker distribution of heat into the material matrix. The variation in the glass transition temperature (T_g) as a function of filler concentration indicates an increase in the flexibility of the polymeric backbone on filler addition. Substantial improvement in the mechanical stability of the composite polymeric electrolyte (CPE) films in comparison to the pure polymer–salt complexes (PEs), on addition of ceramic fillers, has been noticed. The normalized plot of tensile strength as a function of filler concentration for all the CPEs in the present studies shows a progressive increase in the mechanical strength when compared with undispersed PEs (with $x=0$). The role of filler particles in the enhancement of mechanical properties of CPEs has been investigated using Fourier transform infra-red (FTIR) spectroscopy. FTIR results have indicated a possibility of flexibility/stiffening in the polymer backbone as a result of polymer–filler interaction. The enhancement in the thermal and mechanical stability of the CPEs under investigation on filler addition may be a result of an interaction of filler particles with the anions and polymer network in the composite phase. This has been evidenced from DSC and FTIR analysis. It has been attributed to a possible bridging of the filler particles between two nearby polymer chains via acidic or polar filler particles resulting in lowering of the polymer chain flexibility and consequent improvement in mechanical properties.

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