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Solid polymer electrolytes of blends of polyurethane and polyether modified polysiloxane and their ionic conductivity

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ABSTRACT

Polymer electrolytes based on thermoplastic polyurethane (TPU) and polyether modified polysiloxane (PEMPS) blend with lithium salts were developed via an in-situ polymerization of TPU with the presence of PEMPS and salts. Morphological study of TPU/PEMPS electrolytes showed that TPU and PEMPS were immiscible and TPU/PEMPS electrolytes had a multiphase morphology. The lithium salt enhanced the interfacial compatibilization between TPU and PEMPS via the interaction of lithium ions with different phases. Three lithium salts with different interaction strengths with TPU and PEMPS were used to prepare TPU/PEMPS electrolytes with different levels of phase compatibilization: LiCl, $LiClO_4$, and $LiN(SO_2CF_3)_2$ (LiTFSI). The effect of PEMPS on ionic conductivity, dimensional stability and thermal stability of TPU/PEMPS electrolytes and their relationship with the blend morphology were investigated. TPU/PEMPS electrolytes showed good dimensional stability and thermal stability. The addition of PEMPS to TPU increased the ionic conductivity of TPU/PEMPS electrolytes. The room temperature ionic conductivity of TPU/PEMPS electrolytes with LiTFSI can reach up to 2.49×10^{-5} S/cm.

1. Introduction

The ionic conductive solid polymer electrolytes (SPEs) are composed of polymer and organic or inorganic salts. The polymeric property of polymer electrolyte gives it advantages over liquid electrolytes and rigid mineral electrolytes in terms of density, flexibility, processability and design possibility [1]. SPEs are substituted for the liquid electrolyte in new generation electronic devices like solid batteries, fuel cells, sensors, electrochromic devices [2].

Among many host polymers used in polymer electrolytes, polyethylene oxide (PEO) electrolyte is most well studied [2]. Its low ionic conductivity at room temperature due to its high crystallinity and its low dimension stability due to its low T_m impede the practical application of PEO electrolytes [3]. Various approaches have been conducted to develop high ionic conductive polymer electrolytes by tailoring the chemical structure of the host polymers, which include the development of polymer electrolytes based on linear polymers [4–6] comb-branched copolymers [7,8], block copolymers [9,10], cross-linked network polymers [11] and polymer blends [12,13].

Researchers [14–17] used thermoplastic polyurethane (TPU), especially polyether-based TPU, as a host polymer to improve the dimensional stability of electrolytes by utilizing its unique multiphase structure. TPU is linearly segmented block copolymer consisting of soft and hard segments. The hydrogen bonding between the carbonyl group and N–H group in the hard segments forms physically cross-linked hard domains distributed in the soft segment matrix [18]. The polyether-based soft segments act as polymer solvents to solvate the cations favoring the transportation of the ions and contribute to the conductivity of the polymer electrolyte. The hard segment is responsible for the dimensional stability acting as physical cross-link sites [17,19]. Generally, the polyurethane-based polymer electrolyte usually has a moderate conductivity at room temperature (below 10^{-5} S/cm) due to the presence of poor ionic conductive hard domains [17,20].

Blending is an effective method to obtain the desired properties [21]. Polymer electrolytes based on PEO/PPO [12], PEO/PAN [12], PEO/PMMA [22], TPU/PEO [13] have been reported. Blending TPU with another amorphous polymer having higher ionic conductivity than TPU is a useful approach to improve the performance of TPU electrolytes. However, whether incorporating the high ionic conductive component in TPU electrolyte can improve its ionic conductivity depends on the compatibilization and the interface between different phases. The interfacial adhesion between different phases could affect the ion transfer at the interface. For blend based polymer electrolytes, the blend phase morphology and the interfacial adhesion could have significant impact on the mechanical property, ionic conductivity and other properties of polymer electrolytes. But so far, few detailed studies on how the blend

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[1] Sadly, Dr Kyonsuku Min died during the preparation of this article.

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morphology and the phase interaction affect the properties of TPU blend electrolytes, especially ionic conductivity, have been reported.

In this work, a blend polymer electrolyte composed of a polytetramethylene glycol (PTMG) based TPU and an amorphous polyether modified polysiloxane (PEMPS) and lithium salt was prepared by an in-situ polymerization method and the effects of PEMPS on the ionic conductivity and the dimensional and thermal stability of PEMPS/TPU electrolytes and their relationship with morphology were investigated. The PEMPS was blended in polyurethane by in-situ polymerization of polyurethane with the presence of PEMPS and salts. The monomer of polyurethane, polyol, functioned as the common solvent to dissolve the salts and then became the soft segments of TPU after polymerization.

Polyether modified polysiloxanes can be prepared by either grafting or inserting the alkylene oxide containing segments into silicone [23]. A series of polyether modified polysiloxanes (PEMPS) electrolytes with diverse structures such as block copolymer, mono-comb or double-comb copolymer were synthesized and reported to have high ionic conductivity up to 10^{-5} S/cm at room temperature [24,25]. Their superior ionic conductivity is associated with their flexible and amorphous nature. This promotes high ionic conductivity, but gives poor dimensional stability. PEMPS electrolytes cannot function as separators in cell applications [26]. This study focuses on the investigation of the relationship between the blend phase morphology and the properties of blend electrolyte system composed of TPU and other polymer which has higher ionic conductivity than TPU. For this purpose, PEMPS electrolyte chosen in this study has higher ionic conductivity than TPU based polymer electrolyte. Three lithium salts with different interaction strength with TPU and PEMPS were used to prepare TPU/PEMPS electrolytes with different levels of phase compatibilization. Studies on PEO electrolytes reported that the order of the interaction strength between lithium salts and ether group is: LiTFSI > $LiClO_4$ > LiCl [2].

2. Experimental

2.1. Material

The thermoplastic polyurethane (TPU) used in this study was formulated with a low hard segment content and high soft segment content. The polyol used was polytetramethylene glycol (PTMG) with a molecular weight of 2000 g/mol purchased from Sigma–Aldrich chemical company. The chain extender, 1,4 butanediol, was purchased from ARCO and diisocyanate, 4,4′ diphenylmethane diisocyanate (MDI), was supplied by Bayer. Polyether modified polysiloxane (PEMPS) was purchased from Gelest, Inc. Three different lithium salts with various types of anions were used: lithium chloride LiCl, lithium perchlorate $LiClO_4$, lithium bistrifluoromethanesulfonimidate $LiN(SO_2CF_3)_2$ (LITFSI). They were supplied from Aldrich. The formulation of the polyurethane components in the electrolytes or in the blend contained 68.26% PTMG, 6.14% BDO and 25.60% MDI by mass when the stoichiometric ratio of hydroxyl to isocyanate functionality was maintained at unity. TPU component inside the polymer blend was synthesized via one-shot reaction. PTMG, PEMPS, salts or premixed monomer/salts mixture was dried under a vacuum at 80 °C for 1 day before polymerization of polyurethane. DBO was dried in a vacuum oven first and demoistured over 3 Å molecular sieves at room temperature for 2 weeks prior to polymerization. MDI was stored under vacuum at 0 °C before usages.

2.2. Preparation of TPU/PEMPS blend electrolytes

TPU/PEMPS electrolytes in this study were prepared by an in-situ polymerization method. In this method, TPUs were in-situ polymerized with the presence of PEMPS and lithium salt. Prior to polymerization, PTMG, PEMPS and salt were directly mixed together with a magnetic stirrer at 60 °C for 1 day to ensure the salts completely dissolved. Then the mixture was dried under vacuum at 80 °C for 1day. $LiClO_4$ and LiTFSI can be fully dissolved in PTMG and PEMPS. LiCl cannot completely be dissolved at high salt concentrations. The dried PTMG/PEMPS/salt mixture was poured into an aluminum pan on a hot stage and mixed with BDO and MDI at 80 °C using a stirrer, then the in-situ polymerization started. The reactive mixture was poured in a sheet and put into a vacuum oven for 24 h at 100 °C for further curing. The lithium salt concentration in the polymer electrolytes was represented by the stoichiometry ratio of the ether unit in the polymer to Lithium in the lithium salt, [O:Li]. The PEMPS concentration is represented by the weight ratio of TPU to PEMPS, W_{TPU}/W_{PEMPS}. The [O:Li] in this study is controlled as 16:1.

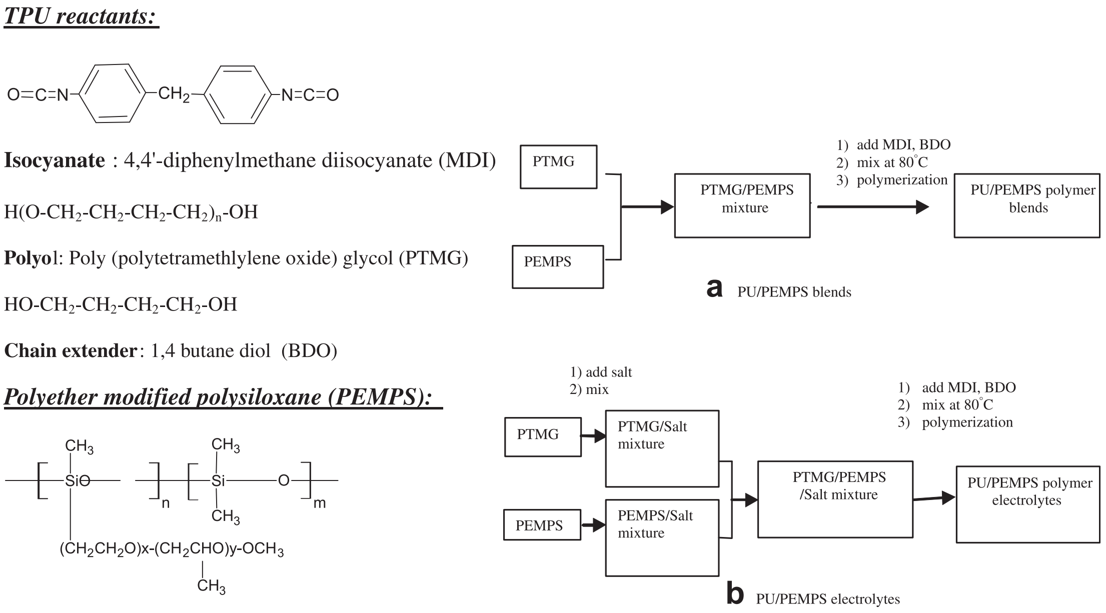

Fig. 1. Scheme of the preparation route of TPU/PEMPS blend and TPU/PEMPS electrolytes (lithium salts used in the above preparations are LiCl, $LiClO_4$ and $LiN(SO_2CF_3)_2$ respectively).

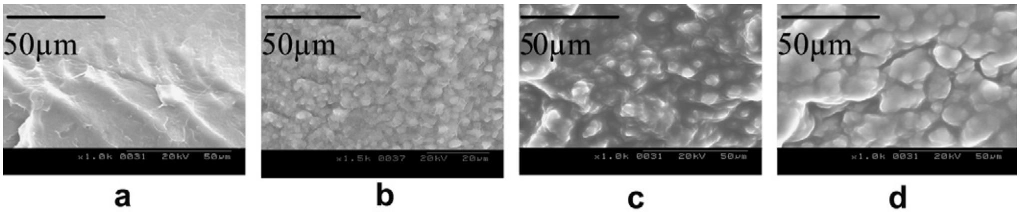

Fig. 2. SEM micrographs of fracture surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40.

TPU/PEMPS with $W_{\mathrm{TPU}}/W_{\mathrm{PEMPS}}$ equal to 100/10, 100/20, 100/40 respectively were prepared. TPU/PEMPS blend were prepared using the similar procedure but without adding lithium salts. The preparation route of polymer electrolytes is illustrated in Fig. 1.

2.3. Characterizations

The morphology of TPU/PEMPS electrolytes, especially the miscibility of PEMPS with TPU and the effect of lithium salts on their miscibility, were studied using Leitz Laborlux polarized optical microscope and Hitachi S-2150 SEM. The interaction of salt with PEMPS and soft segment/hard segment of polyurethane were studied by using Fourier Transform Infrared Spectroscopy (FTIR). Samples were scanned over the range of 4000–400 cm^{-1} by using Mattson Genesis Series FTIR. Samples were characterized by Differential Scanning Calorimeter (DSC) scanned in the range of -120 to 200 °C. All the DSC thermograms were recorded at a scan rate of 20 °C/min. The ionic conductivities of polymer electrolytes were measured by Multi-frequency LCR meter (Hewlett Packard 4274A). The electrolytes film samples were sandwiched between the stainless steel electrodes. The cell impedance was measured at various frequencies ranging from 100 Hz to 100 kHz. The tensile properties of polymer electrolyte films were tested by Instron 5567 tensile tester. The gauge length was controlled to be 2 cm. The films were cut into a 5 mm × 50 mm rectangular strip samples. The crosshead speed was 20 mm/min. The thermal stability of the TPU/PEMPS electrolytes was studied by Thermal Advantage Q500 modulated thermo gravimetric analyzer (TGA).

3. Results and discussion

3.1. Morphology of TPU/PEMPS electrolytes

The miscibility between TPU and PEMPS and the effect of lithium salts on their miscibility were investigated by optical microscopy and SEM. In optical microscopy, neat TPU film demonstrated phase separation with tiny domains less than 0.5 μm dispersed in the matrix. This was attributed to the phase separation of hard domain and soft domain of TPU. The blends of PEMPS and TPU without lithium salts were found immiscible at blend ratios from 10/100 to 40/100. The PEMPS formed droplets around 5 μm and dispersed in the TPU matrix. As the PEMPS concentration increased, the larger droplets of PEMPS domains were observed in the TPU matrix. However, the presence of lithium salts significantly changed the morphology of TPU/PEMPS blend. It was observed that after adding LiTFSI, the TPU/PEMPS became more homogenous.

Figs. 2 and 3 show the SEM morphology of TPU/PEMPS blend with and without LiTFSI, respectively. Neat TPU had a smooth homogenous morphology in SEM. TPU/PEMPS blends without LiTFSI exhibited a two-phase morphology at blend ratios from 100/10 to 100/40. The separated domain was around 10–30 μm in size and the size of the domain varied with the PEMPS concentration. The phase boundary is sharp. Comparing Fig. 2(b) with Fig. 2(d), it was observed that domain size of the two-phase morphology increased greatly when the composition of TPU/PEMPS reached 100/40. After adding the lithium salts, their morphology became homogenous as shown in Fig. 3. The observation agreed with optical microscopic results. It indicates that lithium salt promoted the compatibilization between PEMPS and TPU. This effect varied from the anion structure of lithium salts. Comparing the SEM of TPU/PEMPS electrolytes with different lithium salts, it was found that TPU/PEMPS with LiTFSI had better compatibilization between TPU and PEMPS than the one with $\mathrm{LiClO_4}$. TPU/PEMPS with LiCl had poor compatibilization. Wen et al. [19] reported that the interaction of salt with polyurethane caused the phase mixing between hard segments and soft segments in polyurethane electrolytes. Similar phase mixing behavior was also reported by Jeung in Ref. [17]. For TPU/PEMPS studied in this work, the polyether segment of PEMPS has similar chemical structure as soft segment of TPU. The interaction of salt with TPU and polyether segments of PEMPS improves the compatibilization between TPU and PEMPS.

The compatibilization effect of lithium salts makes it difficult to identify the PEMPS phase from the SEM images. The TPU/PEMPS electrolyte film was etched by methanol and then observed by SEM. PEMPS is soluble in methanol and TPU is insoluble in methanol. After etching by methanol, the cavities in the film surface occupied by PEMPS before etching were visible. The etched TPU/PEMPS/LiTFSI electrolyte film had a porous structure on the surface as shown in Fig. 4, which indicates the separated phase morphology. The domain size of PEMPS is around 1–10 μm. The morphological study of TPU/PEMPS electrolytes showed that TPU and PEMPS are not miscible with the presence of lithium salt and they have multiphase morphology, but the lithium salt improves the compatibilization between TPU and PEMPS.

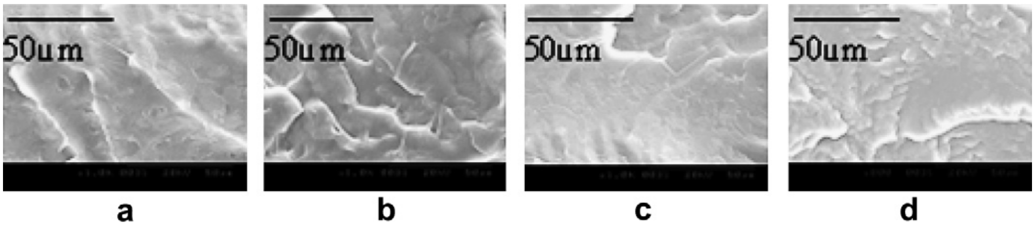

Fig. 3. SEM micrographs of TPU/LiTFSI electrolytes and TPU/PEMPS/LiTFSI electrolytes at [O:Li] = 16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40.

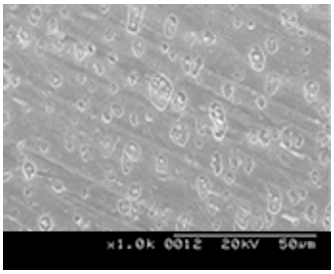

Fig. 4. SEM micrographs of the extracted film surfaces of TPU/PEMPS/LiTFSI electrolytes at [O:Li] = 16:1 and TPU/PEMPS = 100/40.

Fig. 5 shows the DSC thermograms of TPU/PEMPS blends with and without LiTFSI. Neat TPU has a glass transition temperature of soft segment around −62 °C and a melting temperature of soft segment around 14 °C. Due to the high soft segment content in the formula of TPU, the transition regions associated with hard segment were not apparent. The T_g of PEMPS was around −78 °C. All the TPU/PEMPS blends with various compositions showed only one glass transition shift as shown in Fig. 5(a). The T_g of TPU/PEMPS blend decreased as the PEMPS concentration increased. The T_m of the soft segment of TPU was increased slightly after adding PEMPS. Based on the multiphase morphology of TPU/PEMPS blends observed in previous section, the broad transition shifts are believed to be the results of the overlapping of T_g of soft segment of TPU and T_g of PEMPS and the shifting of each T_g caused by the interaction of the soft segment and PEMPS. The temperature resolution of T_g might be improved by cooling the sample at very slow rate to a temperature below T_g and then heating up at a high heating rate. The DSC thermograms of TPU/PEMPS electrolytes with LiTFSI at different blend ratios are shown in Fig. 5(b). The T_g of TPU with LiTFSI is −52 °C. The T_g of the soft segments of TPU/PEMPS electrolytes with different compositions was all in the range of −66 °C to −52 °C. After adding PEMPS, the T_ms of the soft segment of TPU increased and the T_g of the blend electrolytes decreased. It suggested the interaction between PEMPS and soft segment of TPU with the present of LiTFSI. Previous studies on PEO electrolytes reported that the ion movement was considered to be associated with the segmental micro motion of polymer [2] and the significant contribution to ionic conductivity came from the amorphous phase of the PEO electrolytes [27]. In this study, T_ms of the soft segment of TPU/PEMPS electrolytes were all below 25 °C, i.e., most of the soft segment was amorphous at room temperature. From the ionic conductivity point of view, it is beneficial for improving the ionic conductivity at room temperature.

The interactions of salts with TPU and PEMPS were investigated by the wave number shifts of the characteristic absorption peaks and their intensity changes in FITR. Three functional groups including ether group, carbonyl and N—H in TPU were examined: (1) the hydrogen-bonded N—H stretching mode and the free N—H stretch (3600–3100 cm^{-1}); (2) the carbonyl symmetric stretching vibration or amide band (1750–1650 cm^{-1}); and (3) the C—O—C stretch for the soft segment and C(O)—O—C stretch of the hard phase (1150–1000 cm^{-1}) [15,28]. In the FTIR of polysiloxane, the Si—O—Si asymmetric stretching [29] was in the range of 1100 cm^{-1}–1028 cm^{-1} and the C—O—C stretching of the ether group on the side chain of polysiloxane is around 1110 cm^{-1}, which was at the same location as the ether group in TPU. The frequency of the peak of ether group remains unchanged after adding PEMPS because the ether branch of PEMPS has a similar structure as the soft segment. The appearance of multiple peaks is attributed to the formation of the interaction between the ether oxygen in soft segments and the ether oxygen in PEMPS via their interactions with Li^+. In the C═O stretching region, no significant change of the relative intensity of the free hydrogen-bonded carbonyl peak at 1730 cm^{-1} to the hydrogen-bonded carbonyl peak at 1700 cm^{-1} was observed after the addition of PEMPS. In the N—H stretching reaction, the frequency of the center of the overlapped broad band of N—H group shifted to lower frequency as the concentration of PEMPS increased. These changes together with the DSC results indicated that the PEMPS not only interacted with soft segment but also the hard segment of TPU.

Based on the optical microscopy, SEM, DSC and FTIR results, it is found that the lithium salts have significant impact on the morphology of TPU/PEMPS. TPU is immiscible with PEMPS. The addition of lithium salts in TPU/PEMPS induced the compatibility enhancement between PEMPS phase and TPU phase. After adding LTFSI, the PEMPS dispersed in a much smaller domain in the blends, and the TPU phase and PEMPS phase are more fused together. The compatibility effect was attributed to the interaction of Li^+ with both TPU phase and PEMPS phase as illustrated in Fig. 6. Li^+ ions could act as anchors between the boundaries of different phases and improved the compatibility between PEMPS phase and TPU. Among three different lithium salts used in this study, LiTFSI has the strongest interaction with TPU and PEMPS; therefore TPU/PEMPS with LiTFSI has better phase compatibilization than other

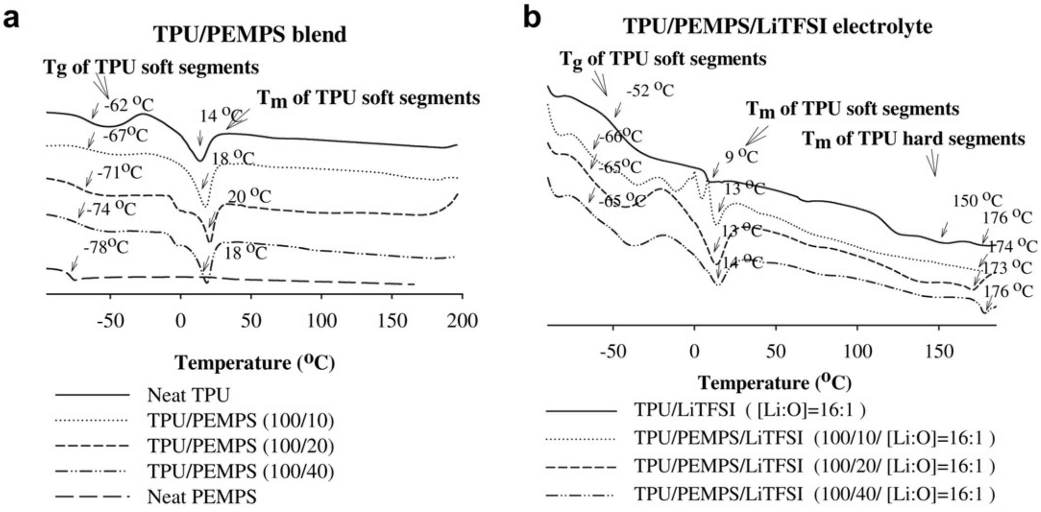

Fig. 5. DSC Thermograms of (a) TPU/PEMPS blends without salt and (b) TPU/PEMPS/$\text{LiN(SO}_2\text{CF}_3)_2$ electrolytes at [O:Li] = 16:1 with different blend compositions.

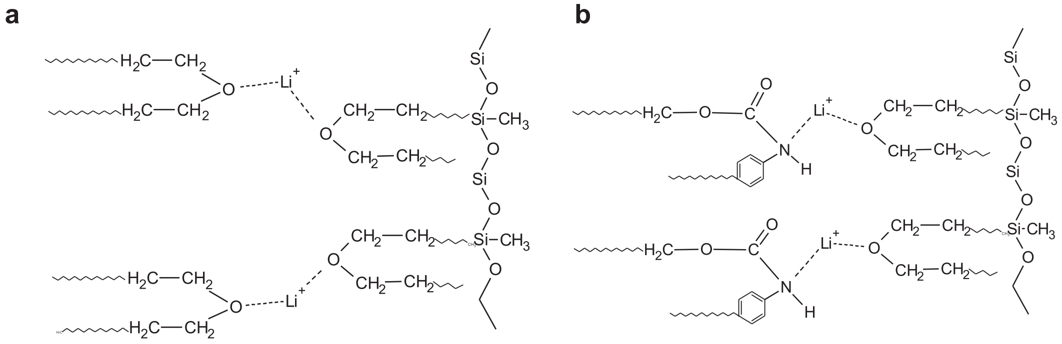

Fig. 6. Schematic representations of the possible interactions between (a) soft segments of TPU and PEMPS and between (b) the hard segment of TPU and PEMPS via lithium ions.

two. In Tandel's [30] study on PEO/PPO based electrolytes, the TEM results showed that the addition of the salt favored the miscibility of PEO and PPO blend. Kim et al. [31] reported simultaneous interaction of Li^+ with the oxygen atoms of the PEO and ether oxygen or ester oxygen of the PES.

3.2. Tensile property of TPU/PEMPS electrolytes

The important characteristics advantages of solid polymer electrolytes over liquid electrolytes are their solid nature, flexibility and easy processability for electrochemical device applications. The gel polymer electrolytes or plasticized polymer electrolytes can achieve very high ionic conductivity (10^{-2} S/cm) at high solvent content, but their dimensional stability is poor because of the inclusion of the large amount of volatile solvent or plasticizer [32]. The multiphase hard domain–soft domain morphology of TPU made TPU/PEMPS electrolytes would have good dimension stability. The stress–strain curves of neat TPU, TPU/PEMPS blend films and TPU/PEMPS electrolytes films are plotted in Fig. 7. Their tensile properties were summarized in Table 1. The TPU used in this study were formulated with high soft segments content and the neat TPU film exhibits large elongation up to 1100%.

Adding PEMPS to TPU without the presence of lithium salts significantly deteriorated the tensile properties of TPU as shown in Fig. 7(a). The TPU/PEMPS blend films were brittle regardless of the PEMPS concentration. This was attributed the immiscibility between TPU and PEMPS and their poor interfacial adhesion without lithium salts as discussed in morphological studies of TPU/PEMPS blend. On the contrary, TPU/PEMPS blend films with the presence of lithium salts were highly stretchable as shown in Fig. 7(b). Prior to adding lithium salts the TPU/PEMPS blend film could only be stretched to about 8–40%, but they could reach high up to 1200% after adding lithium salts in the blends. The dramatic change of tensile properties of TPU/PEMPS electrolytes after adding lithium salts was associated with the morphology change due to the interaction of lithium ions with each phase of the blend. These interactions enhanced the interfacial adhesion of the TPU/PEMPS electrolytes. TPU/PEMPS/LiTFSI electrolytes showed higher elongation at break than TPU/PEMPS/$LiClO_4$. It was because LiTFSI has better compatibilization on TPU/PEMPS than $LiClO_4$. It was also found that their modulus decreased as the PEMPS concentration increased. This was due to the contribution of the liquid nature of the PEMPS phase.

3.3. Thermal stability of TPU/PEMPS electrolytes

TGA of TPU/PEMPS blend and TPU/PEMPS/LiTFSI electrolytes were used to study the thermal stability of TPU/PEMPS electrolyte and the effect of the lithium salt on their thermal stability. Neat TPU had two steps of thermal degradation. The first step was attributed to the degradation of soft segments and the second step was associated with the degradation of hard segments. Neat PEMPS had only one-step thermal degradation. TPU/PEMPS blends had 5% weight loss temperatures between the value of neat TPU and PEMPS. Two-step thermal degradation was observed in the blends, in which the first one belonged to the degradation of the ether group in soft segments and PEMPS and the second one was due to

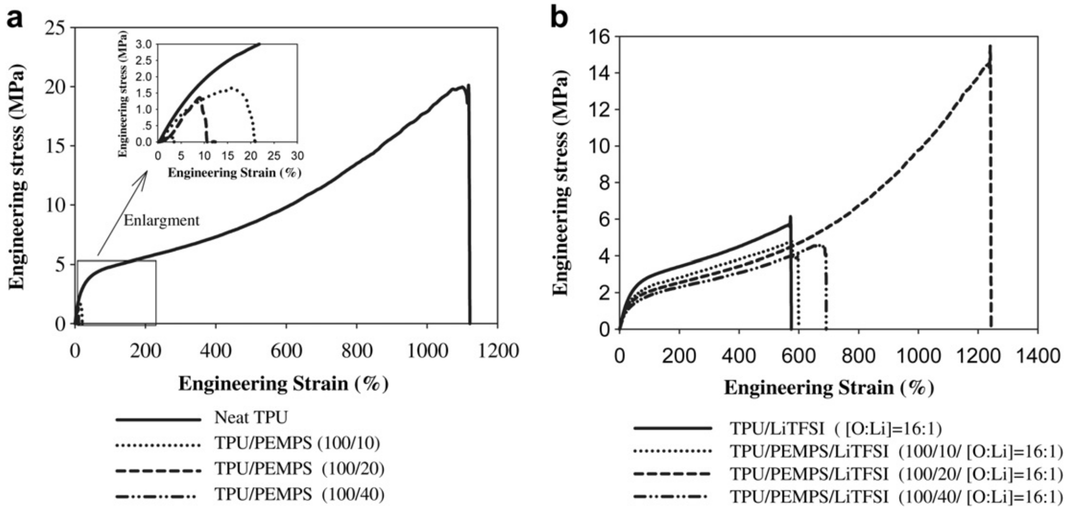

Fig. 7. Engineering tensile stress–strain curves of (a) TPU/PEMPS blend films and (b) TPU/PEMPS/LiTFSI electrolytes films with various compositions.

Table 1
Engineering tensile properties of TPU/PEMPS blends and TPU/PEMPS electrolytes with various blend compositions.

Materials	TPU/PEMPS	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat TPU	100/0	12.6	19.9	1100
TPU/PEMPS	100/10	18.0	2.1	38
	100/20	15.0	1.3	18
	100/40	11.4	0.1	8
TPU/PEMPS/$LiClO_4$	100/10	6.4	6.1	541
[O:Li] = 16:1	100/20	5.4	9.2	559
	100/40	3.5	2.1	330
TPU/PEMPS/LiTFSI	100/10	6.8	4.8	577
[O:Li] = 16:1	100/20	5.0	14.5	1237
	100/40	2.1	4.6	667

Table 2
TGA results of neat TPU, TPU/PEMPS blends and TPU/PEMPS electrolytes with different lithium salts at [O:Li] = 16:1.

Material	TPU/PEMPS	The temperature at 2% weight loss (oC)	The temperature at 5% weight loss (oC)
Neat TPU	100/0	296	314
Neat PEMPS	100/10	231	275
TPU/PEMPS	100/20	282	301
	100/40	292	310
	100/10	270	291
TPU/PEMPS/LiCl	100/10	265	282
[O:Li] = 16:1	100/20	258	278
	100/40	253	273
TPU/PEMPS/$LiClO_4$	100/10	253	274
[O:Li] = 16:1	100/20	245	271
	100/40	228	258
TPU/PEMPS/LiTFSI	100/10	175	257
[O:Li] = 16:1	100/20	172	241
	100/40	164	235

the degradation of the hard segments. The 2% and 5% weight loss temperatures of TPU/PEMPS blends and TPU/PEMPS electrolytes are summarized in Table 2. As the PEMPS concentration increased, the degradation temperature of blend electrolytes decreased. Polydimethysiloxane (PDMS) had better thermal stability than polyurethane [33]. In this study, PEMPS showed lower thermal stability than TPU because of the unstable ether branches on polysiloxane side chain. The —Si—O— was much stronger than —C—O—. The thermal stability of TPU/PEMPS electrolytes with LiTFSI decreased as the concentration of PEMPS increased. Similar trends were observed in TPU/PEMPS electrolytes with LiCl and $LiClO_4$. TPU/PEMPS/LiTFSI electrolytes had poor thermal stability. It is because the LiTFSI has the strongest interaction with polymers among the three salts and this interaction weakened the strength of ether group. The general operation temperature of devices using solid polymer electrolytes such as solid battery is under 100 °C, the thermal stability of TPU/PEMPS electrolytes prepared in this study was sufficient to meet the application requirement.

3.4. Ionic conductivity of TPU/PEMPS electrolytes

The A.C. ionic conductivity measurement method in this study was calculated from the bulk resistance obtained from the complex

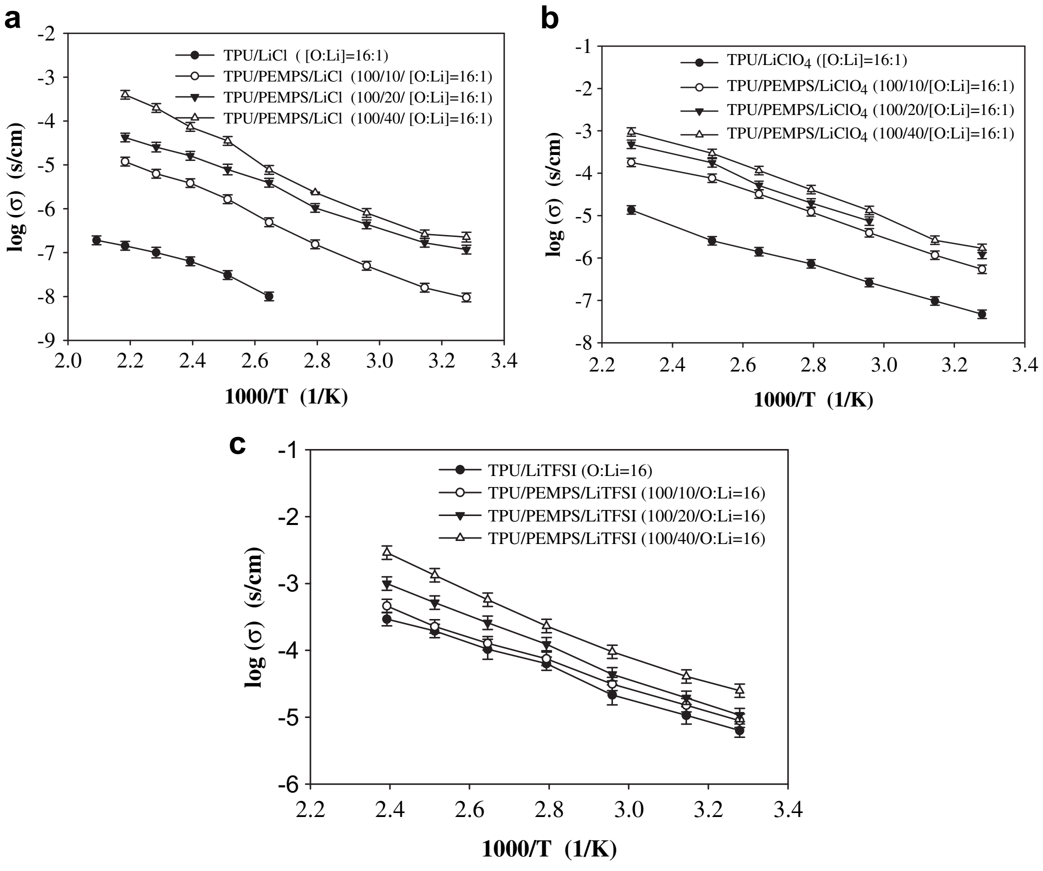

Fig. 8. The effect of temperature on the conductivity of (a)TPU/PEMPS/LiCl electrolytes, (b)TPU/PEMPS/$LiClO_4$ electrolytes and (c)TPU/PEMPS/LiTFSI electrolytes at [O:Li] = 16:1 with various blend compositions.

Table 3

The ionic conductivity at room temperature σ and activation energies E_a of TPU/PEMPS electrolytes with different types of salt and various blend compositions prepared by the in-situ process.

Materials	TPU/PEMPS	Conductivity at 300 K (S/cm)	E_a (eV)
TPU/PEMPS/LiCl	100/0	–	0.019
	100/10	9.51×10^{-9}	0.025
	100/20	2.34×10^{-7}	0.020
	100/40	2.25×10^{-7}	0.027
TPU/PEMPS/$LiClO_4$	100/0	7.51×10^{-8}	0.020
	100/10	5.43×10^{-7}	0.025
	100/20	1.22×10^{-7}	0.024
	100/40	1.69×10^{-6}	0.026
TPU/PEMPS/LITFSI	100/0	3.31×10^{-6}	0.023
	100/10	7.04×10^{-6}	0.020
	100/20	1.08×10^{-5}	0.019
	100/40	2.49×10^{-5}	0.020

impedance plot, which is a common practice in the measurement of polymer electrolyte [34]. Fig. 8 shows the ionic conductivity of TPU/PEMPS electrolytes with different PEMPS concentrations at various temperatures. The ionic conductivity of TPU/PEMPS electrolytes was temperature dependent and their conductivity temperature dependence followed Arrhenius law equation, $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ_0 is conductivity at the absolute temperature $T = 0$ K, E_a is the activation energies, and R is the gas constant. The ionic conductivity at 300 K and the E_a of TPU/PEMPS is summarized in Table 3. PEMPS improved the ionic conductivity of TPU electrolytes at given temperature, but nearly did not change E_a. The possible explanation for this is that the ionic conductivity contribution comes mainly from the soft segments of TPU and the ether segments of PEMPS and both of these two types of segments have similar ether structure. The temperature range in which the ionic conductivity measured in this study is above the T_m of the soft segment of TPU. In this temperature range both the soft segments of TPU and PEMPS are amorphous. The relationship of the ionic conductivity of TPU/PEMPS electrolytes versus PEMPS/TPU blend ratio at 300 K is shown in Fig. 9. It revealed that their ionic conductivity increased as the concentration of PEMPS increased and the increasing amount of ionic conductivity induced by adding PEMPS varies with the anion structure of lithium salt. For TPU/PEMPS/LiTFSI electrolytes and TPU/PEMPS/$LiClO_4$ electrolytes, the log σ almost changed linearly with the concentration of PEMPS. However, for TPU/PEMPS/LiCl electrolytes the log σ increased with the blend ratio first and then reaches to a plateau, i.e., the extra addition of PEMPS does not increase the ionic conductivity after TPU/PEMPS reaches up to 100/20.

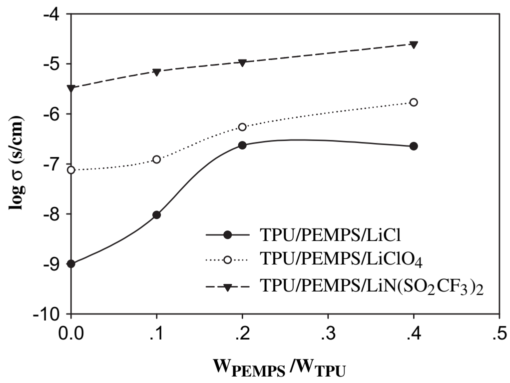

Fig. 9. The ionic conductivity at 300 K versus PEMPS/TPU ratio of TPU/PEMPS electrolytes with different lithium salts.

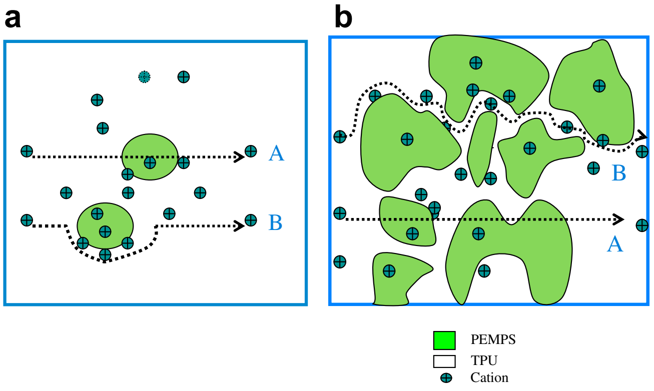

Fig. 10. Schematic representation of two possible lithium ions transferring routes. Path A: ion transfers through different phases, Path B: ions transfers around the interface between different phases. (a) TPU/PEMPS electrolyte with low PEMPS concentration, (b) with high PEMPS concentration.

The ionic conductivity of polymer blend electrolytes is strongly dependent on their compatibilization and the interfacial adhesion between different phases. In polymer electrolytes with poor phase interfacial adhesion, the sharp boundary could generate gaps and prevent the ions transfer from one phase into the other phase. Fig. 10 illustrates different possible ion transference routes at the interface between different phases. In the case of good interfacial adhesion, ions can transfer through the interface like Path A; and in the case of poor interfacial adhesion, ions could go around the interface like Path B. The latter route would significantly increase the path length of ion motion between electrodes and led to a high resistance at the interface. From the morphological study and the tensile test results of TPU/PEMPS electrolytes, it showed that TPU/PEMPS electrolytes have good interfacial adhesion due to the comptibilization effect of lithium salts. In this case, path A was dominant, so their ionic conductivity increased as the PEMPS concentration increased. The contribution of PEMPS phase on the ionic conductivity of TPU/PEMPS electrolytes came from two aspects: first, it increased the portion of high ionic conductivity components in the blend electrolyte because of the high ionic conductivity of PEMPS electrolyte itself; second, the lithium ions increased the phase compatibilization of TPU and PEMPS and enhanced the good interfacial adhesion, which made the Li^+ transfer from one phase to the other phase easily instead of circumventing the interface boundary. The exceptional behavior of TPU/PEMPS/LiCl electrolytes that the extra addition of PEMPS does not increase the ionic conductivity after TPU/PEMPS reaches up to 100/20, is due to the poor compatibilization effect of LiCl on TPU/PEMPS. When PEMPS reached certain loading, additional PEMPS in TPU worsen the interfacial adhesion at some locations and some ions cannot transfer through path A route and started to transfer through Path B route.

By adding PEMPS, the ionic conductivity of TPU/LiTFSI electrolytes with [O:Li] = 16:1 increased from 3.31×10^6 S/cm up to 2.49×10^{-5} S/cm. The higher ionic conductivity of TPU/PEMPS electrolytes could be obtained by increasing the salt concentration of LiTFSI and PEMPS. However, further increasing the PEMPS loading could significantly deteriorate the dimensional stability of TPU/PEMPS electrolytes because TPU is the only component providing high dimensional stability.

4. Conclusions

In this study, polymer electrolytes based on TPU and PEMPS blend with different lithium salts were developed via polymerization of TPU with the presence of PEMPS and lithium salts. TPU is immiscible with PEMPS. The interaction between lithium salts with TPU and PEMPS improved the compatibilization between TPU and PEMPS and their interfacial strength. Three lithium salts with different interaction strengths with TPU and PEMPS were used to prepare TPU/PEMPS electrolytes with different levels of phase compatibilization. It is found that the compatibilization and phase interfacial adhesion of TPU/PEMPS electrolytes have significant impact on their tensile, thermal and ionic conductivity properties. The tensile properties study of TPU/PEMPS electrolytes showed that TPU/PEMPS blends without lithium salts are brittle due to the immiscibility of TPU/PEMPS blends. But the addition of lithium salts to TPU/PEMPS blends improved the elongation significantly. The dramatic change of tensile properties of TPU/PEMPS electrolytes after adding lithium salts was associated with a morphology change due to the interaction of lithium ions with each phase of the blend. These interactions enhanced the interfacial adhesion of the TPU/PEMPS electrolytes. TPU/PEMPS/LiTFSI electrolytes showed higher elongation at break than TPU/PEMPS/$LiClO_4$. The loading of PEMPS had effects on the thermal stability and dimensional stability of TPU/PEMPS electrolytes. PEMPS lowered the thermal degradation temperature of TPU/PEMPS electrolytes, but they still meet the thermal stability requirement for electrochemical device applications.

The ionic conductivity of TPU/PEMPS electrolytes was temperature dependent and their conductivity temperature dependence followed Arrhenius law equation. Adding PEMPS to TPU increased the ionic conductivity of TPU/PEMPS electrolytes. The room temperature ionic conductivity of TPU/PEMPS electrolytes with LiTFSI can reach up to 2.49×10^{-5} S/cm, which is close to the application range. Based on the multiphase morphology of TPU/PEMPS electrolytes, it is believed that the contribution of PEMPS to the ionic conductivity improvement of TPU/PEMPS electrolytes includes: (1) PEMPS phase itself provides high ionic conductivity; (2) the interaction of lithium salts with PEMPS and soft segment/hard segment of TPU induced the phase compatibilization of TPU and PEMPS and enhanced the good interfacial adhesion, which made the Li^+ transfer from one phase to the other phase more easily instead of circumventing the interface boundary.

This work studied the relationship between the blend morphology and the tensile property, thermal stability and ionic conductivity of TPU blend electrolytes. The good phase compatibilization and interfacial adhesion are important to enhance the performance of the blend electrolytes. The TPU and polyether modified polysiloxane used in this study have moderate ionic conductivity. In a future study, a blend of polyurethane and modified polysiloxane or other polymer with much higher ionic conductivity and good phase compatiblilization can be used to further improve the ionic conductivity of polyurethane blend electrolytes.

References

[1] Liang W, Kuo P. Polymer 2004;45:1617.
[2] Gray FM. Polymer electrolytes. UK: The Royal Society of Chemistry; 1997.
[3] Cowie JMG. In: MacCallum JR, Vincent CA, editors. Polymer electrolyte reviews-1. , NY: Elsevier Applied Science; 1987.
[4] Watanabe M, Rikukawa M, Sanui K. Macromolecules 1984;17:2902.
[5] Harris CS, Shriver DF, Ratner MA. Macromolecules 1984;19:987.
[6] Clancy S, Shriver DF, Ochrymowycz LA. Macromolecules 1986;19:606.
[7] Bannister DJ, Davies GR, Ward IM, McIntyre JE. Polymer 1984;25:1600.
[8] Cowie JMG, Ferguson R. J Polym Sci Polym Phys Ed 1985;23:2181.
[9] Alloin F, Sanchez JY, and Armand M. Solid State Ionics 1003; 60:3.
[10] Alloin F, Sanchez JY, Armand M. Electrochem Acta 1992;37:1729.
[11] Meyer HW. Adv Mater 1998;10:439.
[12] Choi BK, Kim YW, Shin HK. Electrochim Acta 2000;45:1371.
[13] Wen T, Chen W. J Appl Polym Sci 2000;77:680.
[14] McLennaghan AW, Pethrick RA. Eur Polym J 1988;24:1063.
[15] VanHeumen JD, Stevens JR. Macromolecules 1995;28:4268.
[16] Ferry A, Jacobsson P, Heumen JD, Stevens JR. Polymer 1996;37:737.
[17] Jeung S. Doctoral dissertation. University of Akron; 2005.
[18] Parnell S. Doctoral dissertation. University of Akron; 2002.
[19] Wen T, Du Y, Digar M. Eur Polym J 2002;38:1039.
[20] Zhu W, Wang W, Yang B, Tang X. J Polym Sci: Polym Phys 2001;39:1246.
[21] Chiang W, Huang C. In: Shonaike GO, editor. Polymer blends and alloys. Marcel Dekker; 1999.
[22] Rajendran S, Kannan R, Mahendran O. J Power Sources 2001;96:406.
[23] Oh B, Vissers D, Zhang Z, West R, Tsukamoto H, Amine K. J Power Sources 2003;119–121:442.
[24] Nagaoka K, Naruse H, Shinohara I, Watanabe M. J Polym Sci Polym Lett Ed 1984;22:659.
[25] Fish D, Khan IM, Smid J. Br Polym J 1988;20:281.
[26] Kang Y, Lee W, Suh DH, Lee C. J Power Sources 2003;119–121:448.
[27] Berther C, Gorecki W, Minier M, Armand MB, Chabagno JM, Rigand P. Solid State Ionics 1983;11:91.
[28] VanHeumen JD, Wieczorek W, Siekierski M, Stevens JR. J Phys Chem 1995;99:15142.
[29] Fan Q, Fang J, Chen Q, Yu X. J Appl Polym Sci 1999;74:2552.
[30] Tandel PV. Master dissertation. University of Akron; 1994.
[31] Kim DW, Park JK, Rhee HW. Solid State Ionics 1996;83:49.
[32] Jacob MME, Hackett E, Giannelis EP. J Mater Chem 2003;13:1.
[33] Vlad S, Vlad A, Opea S. Europ Polym J 2002;38:829.
[34] Bruce PG. In: MacCallum JR, Vincent CA, editors. Polymer electrolyte reviews-1. NY: Elsvier Applied Science; 1987.