Studies on Composite Electrolytes Composed of Thermoplastic Polyurethane and Polyacrylonitrile

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ABSTRACT: Composite electrolytes comprised of thermoplastic polyurethane (TPU) with polyacrylonitrile (PAN) were investigated. Differential scanning calorimetry (DSC) and impedance spectroscopy were used to monitor the changes in the thermal characteristics and bulk conductivity of the composites due to the amounts of PAN in the composite. Fourier transform infrared spectroscopy (FTIR) was employed to identify the modifications in molecular interactions associated with TPU. The deconvolution of spectral bands associated with C═O and the NH group of TPU and the C≡N group of PAN was utilized to obtain such information. The bulk conductivity of the composites with different PAN content was determined, and the influence of PAN on that was brought out. The effects of temperature and lithium salt concentration on conductivity of the composites were analyzed with respect to TPU. The conductivity changes were correlated through DSC and FTIR results.

Introduction

Ever since the exciting discovery of poly(ethylene oxide) (PEO) electrolyte was first reported by Wright and Armand et al. in 1973,[1] the extended activities by many researchers have led to different solid-state polymer electrolytes (SPE). The researchers have focused their attention on the synthesis of novel polymeric materials possessing high ionic conductivity, mechanical strength, and thermal stability which could ultimately be used for practical applications.

Extensive research on the uses of PEO revealed that ionic conduction occurs in the amorphous region of the electrolyte.[1] In the search for producing amorphous, mechanically stable polyether host matrices for polymer electrolytes, different approaches such as synthesis of polymer blends,[2] composite polymer electrolytes,[3] and polymer network with physical and chemical cross-linking[4] have been made. Thermoplastic polyurethanes (TPU) have also been studied as a matrix for polymer electrolytes.[5]

TPUs are diblock, flexible elastomers consisting of a soft segment (polyether or polyester) reinforced by condensation with a hard segment (diisocyanate). The phase-segmented morphology, in which the hard and soft phases are thermodynamically incompatible, promotes hydrogen bonding within the hard domain involving urethane C═O and N−H moieties on adjacent polymer chain segments.[6] The elastomeric properties of the TPU vary with number of variables, including soft segment molecular weight and hard segment concentrations,[7] as a consequence of the alteration in hydrogen-bonding characteristics. Numerous studies have been attempted to elucidate the relationships between structure and properties of TPU. The uses of NMR,[8] FTIR,[9] SAXS,[10] and DSC[11] have revealed information related to structure and morphology of the TPUs at varying conditions. DSC has been essentially used to bring out the thermal characteristics of hard and soft segments in TPU. Several investigators used FTIR to examine the hydrogen-bonding characteristics of phase-segregated polyurethanes.[12−14] The extent and strength of hydrogen bonding as characterized by the band area and position of the corresponding free groups decide the morphology and the associated electrolyte properties in TPUs. The regions of main interest are the NH and C═O (amide 1) stretching vibration modes of hard segment of TPU.

Several factors contribute to the transformation of hydrogen-bonded NH band to free NH band.[15] The relative changes in concentration of free carbonyl group also can alter the morphology of the TPU and consequently affect the ionic conductivity. Hence, the presence of an external component, which can alter the hydrogen-bonding characteristics, has a definite role in altering the electrolyte characteristics. The presence of plasticizer[16] and added salt[17] have also shown significant effects in the state of intermolecular interactions in TPU. It will therefore be interesting to investigate the modifications in the molecular interactions between the groups present in the TPU in the presence of another polymer system.

Polyacrylonitrile (PAN) systems have shown a higher conductivity than PEO[18] or PPO,[19] and therefore investigations related to them received greater interest. Compared with PEO, the PAN−lithium salt system has many advantages. Abraham and Alagir[20] reported that ionic conductivity of PAN system could be as high as 10^{-3} S cm^{-1} in the presence of plasticizer at room temperature. The electrolyte films proved to have better mechanical strength than PEO at comparable ionic conductivity with PEO. In addition, PAN is more thermally stable than PEO.[21] Besides these advantages, the use of PAN-based electrolyte can inhibit the most disadvantageous dendrite growth in the charging process of Li batteries. Hence, it would be interesting to make a composite polymer electrolyte of TPU with PAN in it and analyze the modifications in morphology, thermal characteristics, and conductivity of TPU.

In the present study, composites of TPU with PAN were synthesized as simple and in the presence of $LiClO_4$. The influences of PAN on the morphology, thermal transition, and conductivity were studied. FTIR

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was used to investigate the modification in interaction between the hard and soft segment of TPU. We have examined the bulk impedance changes of solid and gelled electrolytes in the presence of $LiClO_4$ and correlated with FTIR and DSC results.

Experimental Section

Synthesis of Thermoplastic Polyurethane (TPU). TPU was synthesized in a batch reactor, comprised of four-necked round-bottomed flask with an anchor type stirrer, a nitrogen inlet, an outlet, and a thermocouple connected to a temperature controller. The soft segment, PEG-2000 (M_w = 2000 g mol^{-1}, Aldrich), and the chain extender, 1,4-BD (1,4-butanediol) (Aldrich), were kept in a vacuum oven at 80 °C for 24 h to remove the moisture. First, 0.05 mol of soft segment and 0.20 mol of chain extender were put into the reactor, and then 0.25 mol of the hard segment, MDI (4,4′-methylenebis(4-phenyl isocyanate)) was added stepwise. Dimethylformamide (DMF) was then used to control the viscosity of TPU during polymerization.

Molecular Weight Measurement. The average molecular weight, M_n and M_w, of the PU prepolymer were determined by GPC (Shimadzu R-7A data module; LC-10AS pump). Two linear columns in series were used for separation. The flow rate for DMF was 2 mL/min at 40 °C using polystyrene standards. The weight-average molecular weight (M_w) was found to be 1.95×10^3 g mol^{-1} and the PDI as 1.55.

Preparation of the Composite Electrolyte. Polyacrylonitrile (PAN) (Polyscience, PA) of molecular weight 1.5×10^5 was dried under vacuum at 50 °C for 48 h. TPU and PAN powder were blended physically in various compositions by solution casting. The mixture was dissolved in DMF and stirred vigorously for 1 h using a homomixer. Then, the solutions were coated on a polypropylene plate and dried under vacuum at 50 °C for 48 h. The films were then stored in an argon-filled drybox (Vacuum Atmosphere Co., USA). The thickness of the films was controlled between 50 and 100 μm. Compositions of TPU containing 10%, 20%, and 30% PAN were made and designed as S_1, S_2, and S_3, respectively. Composites of higher PAN content (>30%) did not give homogeneous films.

The desired lithium salt doped polymer film was prepared by dissolving the cast film in DMF with suitable $LiClO_4$/DMF solution. The film was made in the similar way as mentioned above.

DSC Thermograms. Thermal analysis of the TPU and composite were carried out using a differential scanning calorimeter, DSC (Du Pont TA 2010, USA), over the range −100 to +120 °C at a heating rate of 10 °C/min. Samples of film were taken and sealed in aluminum capsules for analysis.

Infrared Spectroscopy. FTIR spectra were recorded at room temperature using a Nicolet 550 FTIR system coupled to a computer. The spectra were collected over the range 400−4000 cm^{-1} by averaging 128 scans at a maximum resolution of 2 cm^{-1}.

Impedance Spectroscopy. Impedance measurements were performed by forming thin films of the composites of about 100 μm in thickness and 0.785 cm^2 in area. The ionic conductivity of the composite films sandwiched between two stainless steel electrodes was obtained under an oscillation potential of 10 mV from 100 kHz to 0.1 Hz by using Autolab PGSTAT 30 equipment (Eco Chemie B. V., Netherlands) together with the Frequency Response Analysis (FRA) system software. The temperature of the cell was controlled using a water thermostat (HAAKE D8 & G) and calibrated using a Pt resistance thermometer. The conductivity was calculated by

$$\sigma = \frac{1}{R_b}\frac{l}{A}$$

where R_b is the bulk resistance from ac impedance, l is the film thickness, and A is the surface area of the electrode.

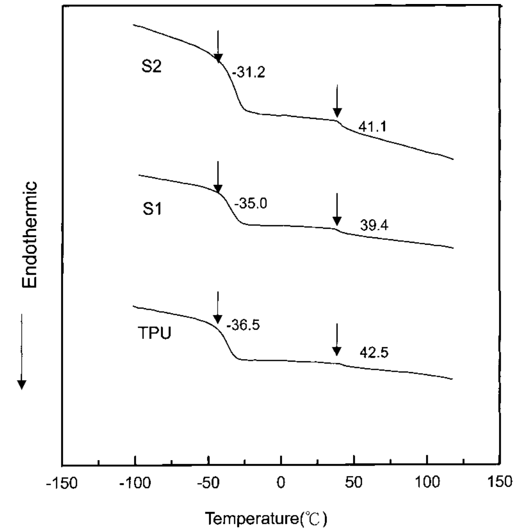

Figure 1. DSC thermograms of composite polymers and TPU. Composite of TPU: S_1 (TPU with 10% PAN) and S_2 (TPU with 20% PAN).

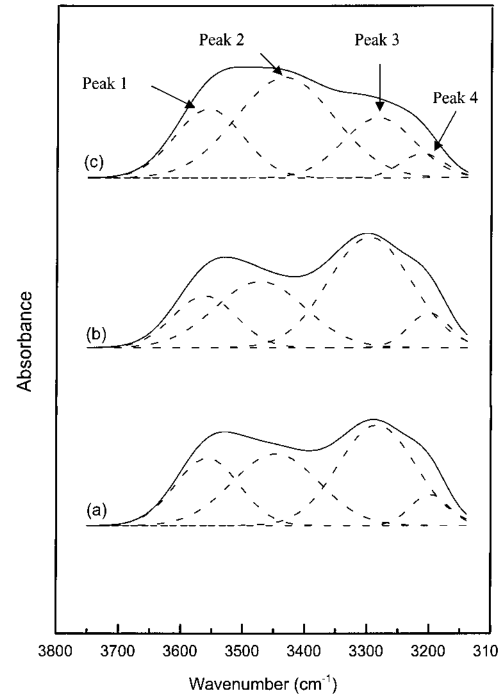

Figure 2. Deconvolution of N−H stretching region for composite polymers and TPU: (a) TPU, (b) S_1, and (c) S_2. Composite of TPU: S_1 (TPU with 10% PAN) and S_2 (TPU with 20% PAN).

Results and Discussion

Interaction between TPU and PAN. DSC and FTIR spectroscopy were used to identify the modifications in thermal and hydrogen-bonding characteristics in TPU when composites are made with PAN. DSC results were used to investigate the changes in the thermal transitions of polyether soft and urethane hard segments of TPU, which would arise due to the possible interactions between hard and soft segments of the TPU and C≡N group of PAN. DSC thermograms were recorded for pure TPU and composites of TPU with PAN. The composite polymer samples with 10%, 20%, and 30% PAN content are designated as S_1, S_2, and S_3, respectively. The DSC thermogram (Figure 1) revealed that there are variations in T_g's when the PAN content was changed. On making the composite with 10% PAN (S_1), the T_g of the PEG soft segment (SS) showed marginal increase from T_g of pure TPU, while the hard

Table 1. Deconvolution Data of the N−H Region for Various Composite Polymers and TPU

	peak position				peak area (%)[a]			
polymer	peak 1	peak 2	peak 3	peak 4	peak 1	peak 2	peak 3	peak 4
S_1	3563	3473	3297	3201	16.5	30.1	46.2	7.2
S_2	3558	3438	3289	3216	23.0	48.7	21.6	6.8
TPU	3557	3447	3284	3198	6.0	38.9	33.5	21.6

[a] The band areas are based on the total N−H stretching area. S_1, S_2: composites of TPU with PAN 10% (S_1) and 20% (S_2). Peak 1: free N−H bonding. Peak 2: overtone of C=O. Peak 3: hard−hard segment H-bonding (C=O and N−H). Peak 4: hard−soft segment H-bonding (−O− and N−H).

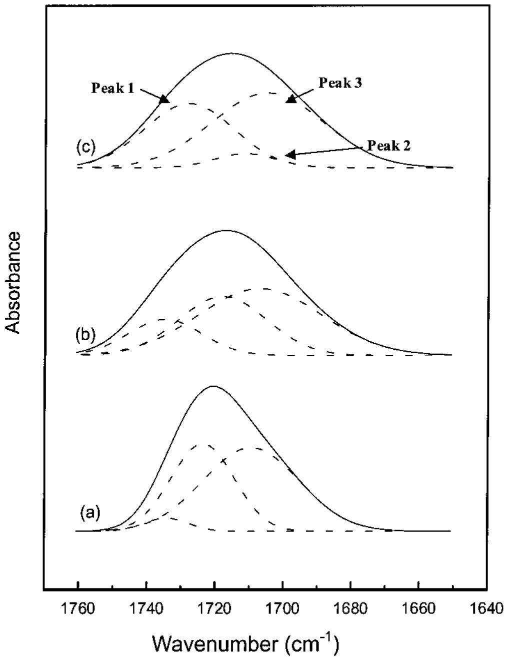

Figure 3. Deconvolution of C=O stretching region for composite polymers and TPU: (a) TPU, (b) S_1, and (c) S_2. Composite of TPU: S_1 (TPU with 10% PAN) and S_2 (TPU with 20% PAN).

segment (HS) T_g of TPU showed significant decrease. These changes in T_g inform that there might be interactions between the groups present in TPU and PAN. Several researchers reported on the phase-mixed state of TPU as a result of interactions between hard (C=O and N−H groups) and soft (C(O)−O−C) segments through hydrogen bonding.[6,22] To bring out this, IR spectral features associated with NH and C=O groups of TPU and the C≡N group of PAN were analyzed.

A comparison of FTIR spectra of S_1 and S_2 with different PAN content was made at the first instant to identify the changes in interactions between the groups of TPU and PAN. The deconvolution results of NH (Figure 2) and C=O (Figure 3) stretching regions (3100−3600 cm^{-1}) of TPU were used toward this purpose. Deconvolution of the NH stretching region was done by using the best fits of the Gaussian−Lorentizian sum. The maximum frequency and area of each band were determined by using the Nelder-Mead optimization procedure.[23] The band corresponding to hydrogen bonding between the NH and carbonyl (Figure 2) group of the hard segment showed a shift from 3297 cm^{-1} for S_1 to 3289 cm^{-1} for S_2. Table 1 indicates that the area associated with this band decreases from S_1 to S_2. The shift in lower frequency of the band corresponding to NH−carbonyl hydrogen bonding can be viewed as due to weakening of hydrogen-bonding strength. This is clearly evident from the lower value of the hydrogen-bonded N−H stretch band area. Also, an increase in the band area for free NH stretch was also observed (Table 1). The lowering of the extent of hydrogen bonding can cause the T_g to decrease for the hard segment, and this is consistent with the results from DSC measurements of S_1 and S_2 (Figure 1).

Table 2. Deconvolution Data of the C=O Region for Various Composite Polymers and TPU

	peak position			peak area (%)[a]		
polymer	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3
S_1	1732	1725	1709	14.0	29.4	56.6
S_2	1729	1718	1703	30.3	27.5	42.2
TPU	1734	1724	1709	4.1	39.1	56.8

[a] The band areas are based on total C=O stretching area. S_1, S_2: composites of TPU with PAN 10% (S_1) and 20% (S_2). Peak 1: free carbonyl. Peak 2: disordered H-bonded carbonyl. Peak 3: ordered H-bonded carbonyl.

The C=O stretch band of TPU is now considered for obtaining more information about the interaction between groups present in TPU and PAN. The bands corresponding to the stretching of the free urethane carbonyl group hydrogen bonded in ordered and disordered configurations are assigned here on the basis of the previous studies related to TPU (Table 2).[13−15,24] The deconvolution of the carbonyl region (1650−1760 cm^{-1}) was done by the Gaussian function (Figure 3). There are variations in band positions and band areas for S_1 and S_2 (Table 2). The three bands showed a shift to lower frequency with significant differences in the band areas. The band area of the free carbonyl stretch increase to a greater extent. These observations can be viewed in conjunction with the release of hydrogen bonds in the NH region (Table 1) and the marked decrease in the band area of the ordered H-bonded urethane carbonyl stretch region from S_1 and S_2. This ultimately resulted the lowering of T_g of HS, as noticed in the DSC results.

On the basis of the above discussions, it may be concluded that the presence of PAN in the composites modified hard−hard segment interactions of TPU, which consequently result a new morphology with an altered hydrogen-bonding characteristics between hard−hard segments. This can arise from the dipolar repulsive interaction between the C=O group of TPU and C≡N group of PAN.[25,26] Previous reports[27,28] on the interaction of C≡N group of PAN with C=O group of ethylene carbonate (EC) indicates that there can be strong interactions between the C≡N group of PAN and the C=O group of EC. An attempt was also made to find the changes in spectral characteristics of PAN as a result of this interaction by analyzing the peak position and intensity of the C≡N group. No obvious difference was noticed in this case, and this becomes reasonable. The C≡N stretch band is more stronger than C=O band, and hence the extent of interaction on C=O bond may not produce the same influence on the C≡N stretching band, especially when the PAN content in the composite

Table 3. DSC Data for the Composites with Different $LiClO_4$ Concentrations

film[a]	T_g (soft segment) (°C)	$\Delta T_g/\Delta C$ (°C/(mmol g))	T_g (hard segment) (°C)
S_1 (a)	−35.0		39.4
S_1 (b)	−25.8	27.9	37.1
S_1 (c)	−14.0	41.9	55.0
S_1 (d)	−9.1	27.6	35.2
S_2 (a)	−31.2		41.1
S_2 (b)	−23.6	23.0	42.2
S_2 (c)	−11.7	38.9	46.8
S_2 (d)	−2.2	30.9	36.7

[a] S_1, S_2: composites of TPU with PAN 10%(S_1), 20%(S_2). (a) 0 mmol/g; (b) 0.33 mmol/g; (c) 0.5 mmol/g; (d) 0.94 mmol/g.

Table 4. DSC Analysis Data for the Composites and TPU Doped with 0.5 mmol of $LiClO_4$/g[a]

polymer doped 0.5 mmol $LiClO_4$/g	T_g (soft segment) (°C)	$\Delta T_g/\Delta C$ (°C/(mmol g))	T_g (hard segment) (°C)	$\Delta T_g/\Delta C$ (°C/(mmol g))
TPU	−25.4	22.2	61.6	38.1
S_1	−14.0	41.9	55.0	31.3
S_2	−11.7	38.9	46.8	10.0

[a] S_1, S_2, and S_3: composites of TPU with PAN 10% (S_1), 20% (S_2), and 30% (S_3).

is low, as maintained in S_1 and S_2.

Interaction of Li^+ Ions with Composite Components. DSC measurements were made to examine the effect of $LiClO_4$ on the morphological based thermal transitions of the polyether soft and urethane hard segment of TPU. Different concentrations of $LiClO_4$ were added to the pure TPU, S_1, and S_2, and the results are presented in Table 3. Note that T_g of SS increases with increasing $LiClO_4$ concentration. The results are in line with observations made with $LiClO_4$-doped TPU containing either PEO[29] or poly(propylene oxide)[25] as SS and also in agreement with results on polyether complexes involving $LiCF_3SO_3$.[26] The increase in T_g arises from the formation of transient cross-link between Li^+ ion and ether oxygen of SS, leading to partial arrest of local motion of polymer segment. By taking T_g of the parent polymer, the data of each measurement were normalized with respect to concentration of $LiClO_4$, $\Delta T_g/\Delta C$, and presented in Table 3.

Few interesting observations were noticed from the analysis of the results obtained with S_1 and S_2. For both S_1 and S_2, as the salt concentration increases, $\Delta T_g/\Delta C$ of SS showed an increase up to the concentration of 0.5 mmol/g of $LiClO_4$ (Table 4) and thereafter started decreasing. At the initial conditions of $LiClO_4$ concentration, Li^+ ions interact to a greater extent with SS, causing an enhanced $\Delta T_g/\Delta C$ change in the SS. Beyond the concentration (0.5 mmol/g), the plasticizing effect generated from the formation of neutral contact ion pairs[30] and their inability to make ionic cross-links with Li^+ ions could result a decrease in $\Delta T_g/\Delta C$. Also, for the same concentrations of $LiClO_4$ (0.5 mmol/g of polymer) the $\Delta T_g/\Delta C$ value of SS of S_1 was much higher (Table 4) than that of pure TPU. This informs that the changed morphology in the presence of PAN as discussed previously provided a better environment for the Li^+ ion interaction with groups in TPU for S_1. However, $\Delta T_g/\Delta C$ of HS showed only a marginal decreasing trend with increasing $LiClO_4$ concentration. On the basis of these observations, it can be viewed that for S_1 the added Li^+ ion interacts more specifically with SS units of TPU than the urethane HS. A comparison of $\Delta T_g/\Delta C$ values of SS and HS of S_1 and S_2 with the same amount of added $LiClO_4$ (0.5 mmol/g) indicated that, with increasing PAN content, the effect of $\Delta T_g/\Delta C$ on the SS becomes less prominent while a dominant decrease in the value for HS was noticed. This can be taken as due to the involvement of Li^+ ion interaction with SS of TPU for S_1. However, the HS interaction becomes dominant when PAN content was increased to 20%. Thus, it is clear that changed morphology in TPU in the presence of PAN showed variations in interactions with $LiClO_4$.

To support this view, the infrared spectral absorption characteristics corresponding to HS and SS of TPU and also $C\equiv N$ group of PAN in the presence of different $LiClO_4$ concentrations were analyzed. The spectral bands of S_1 and S_2 with different addition of $LiClO_4$ concentrations were used toward this purpose. The bands corresponding to NH and $C{=}O$ stretching were deconvoluted and analyzed for the changes in peak frequencies and band areas. The increase in $-NH$ bond strength can be viewed due to the localization of the electron-rich oxygen as a result of coordination with Li^+ ions via hydrogen-bonded species. A weakening of hydrogen bonding also became evident from the observed lower band area for the hydrogen-bonded stretch of $-NH$. The band positions of hydrogen-bonded carbonyl (both ordered and disordered) were shifted to lower frequency. This indicates the weakening of the hydrogen-bonded $C{=}O$ bond strength. The observed increase in band area for free carbonyl justifies the above explanation.

An attempt was made to identify the possible interaction between the $C\equiv N$ group of PAN in the composites and the added Li^+ ion through IR spectral analysis. The $C\equiv N$ stretching band (2244 cm^{-1}) was analyzed for this purpose. Previous workers[27,28] observed a weak shoulder at around 2270 cm^{-1} as a result of interaction between the Li^+ ion and $C\equiv N$ group. This was attributed to the formation of an associate involving the pair of nonbonded electron on the nitrogen atom of the $C\equiv N$ group and the empty orbital of Li in Li^+ ions. Since the intensity of stretching band of $C\equiv N$ group was too strong, the weak shoulder at 2270 cm^{-1} became unidentifiable due to strong overlapping with the 2240 cm^{-1} band. Such an effect was dominantly noticed, especially when Li^+ ion concentration was low (Figure 4).[30] For both the composites S_1 and S_2, the addition of Li^+ ion did not make any significant changes in the band position of the $C\equiv N$ stretch band (Figure 4). It is known through earlier discussions from the analysis of IR bands of TPU groups of S_1 and S_2 that the $C{=}O$ and $N-H$ groups of TPU interacts with Li^+ ions specifically, and this can restrict the Li^+ interactions with $C\equiv N$. This fact may also be combined with the high intensity of the $C\equiv N$ group. As a result of these, no marked difference in $C\equiv N$ stretch band could be observed in the present study up to the added Li^+ ion concentration of 0.94 mmol/g of polymer. The above discussion related to the interaction of Li^+ ion with components of the composite clearly demonstrated that the added Li^+ ion interacts more with the $C{=}O$ and $N-H$ groups in TPU than with the $C\equiv N$ group of PAN. The indicated morphological changes in TPU in the presence of PAN makes a different extent of interaction of Li^+ ion with these groups in comparison with the parent TPU.

Composites as Electrolytes. The manifestation of the interactions between the components (TPU and PAN) in the composite and $LiClO_4$ will have reflections

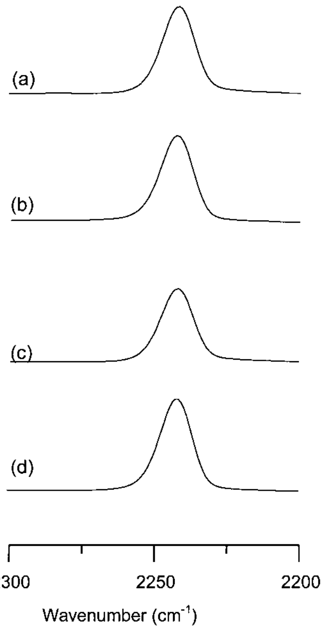

Figure 4. FTIR spectrum for $-C{\equiv}N$ group region of composite polymer S_2 (TPU with 20% PAN) with various $LiClO_4$ concentration: (a) 0.094, (b) 0.15, (c) 0.31, and (d) 0.94 mmol/g.

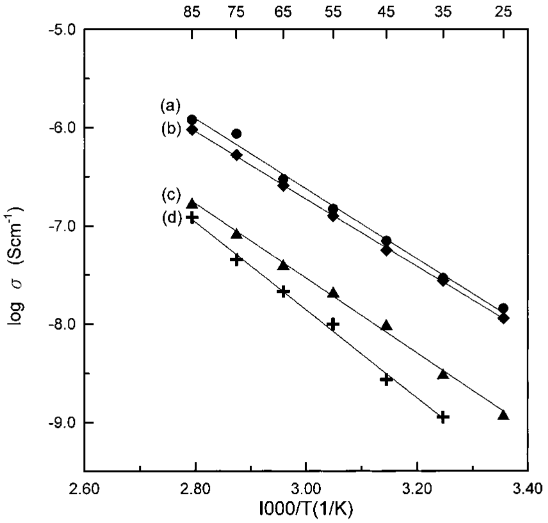

Figure 5. Arrhenius plot of conductivity for TPU and composite polymers doped with 0.5 mmol/g of $LiClO_4$: (a) TPU, (b) S_1 (TPU with 10% PAN), (c) S_2 (TPU with 20% PAN), and (d) S_3 (TPU with 30% PAN).

on the conductivity of the electrolyte. At the first instant, we have examined the changes in the conductivity with temperatures. Figure 5 gives the Arrhenius plot for TPU, S_1, S_2, and S_3 with a constant adding of Li salt concentration. At all temperatures, the conductivity of the composites was found to be lower in comparison with that of pure TPU. However, S_1 showed marginal conductivity changes from TPU while for S_2, a larger decrease in conductivity was noticed. This observation can easily be correlated with the results of DSC and FTIR studies. From FTIR and DSC results, it was found that the SS interaction gets altered dominantly in S_1. This caused changes in T_g of the soft segment. These interactions in soft segment did not cause much reduction in conductivity as observed here. On the contrary, for S_2, the hard−hard segment interactions in TPU changed much. This, however, can cause larger changes in conductivity as inferred from DSC and IR analysis.

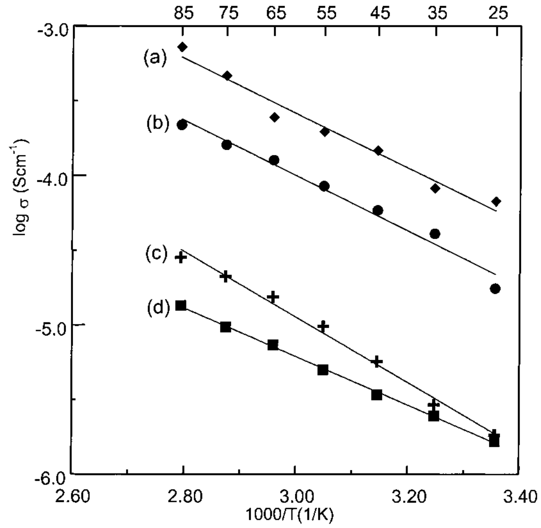

Figure 6. Arrhenius plot of conductivity for gelled TPU and composite polymers containing 50 wt % 1 M $LiClO_4$−PC: (a) TPU, (b) S_1, (c) S_2, and (d) S_3.

For making improved conductivity, plasticizers have been used to make gel electrolyte. The immobilization of liquid electrolyte in the region of polymer matrix produces conductive environment for ionic conductivity due to various associated factors. The temperature dependence of ionic conductivity was also determined for the composites gelled with PC in the presence of constant $LiClO_4$; Figure 6 gives the Arrhenius plot for the gelled composite (S_1, S_2, and S_3) and pure TPU. A marked increase in conductivity was observed for the gelled electrolytes in comparison with their corresponding solid electrolytes. Here also, increasing PAN content in the composite decreases the conductivity at all temperatures with a selected Li salt concentration. As noticed in dry films, the difference in conductivity between pure TPU and S_1 was marginal, but between S_1 and S_2, it was significant. The same reasoning as given for the dry films becomes valid here also. Additionally, in the presence of PC, Li^+ ion also starts interacting with the $C{\equiv}N$ group of PAN as evident from IR spectral analysis. This would make the units in polymer chains as rigid in comparison with dry films. Hence, a higher extent of the decrease in conductivity was observed between S_1 and S_2.

Conclusion

The presence of PAN to different extent in the TPU−PAN composites was found to influence the glass transition temperature of soft and hard segments of TPU. The T_g of ether soft segment showed a marginal increase with increasing PAN content in the composite while T_g of hard segment showed a significant decrease. These changes are well correlated with deconvolution results of infrared bands. A decrease in the hard−hard segment hydrogen-bonding interaction was evident arising from the dipolar repulsive interactions between the $C{=}O$ group of TPU and $C{\equiv}N$ group of PAN.

The addition of $LiClO_4$ to these composites resulted in the formation of transient cross-links between the Li^+ ion and ether oxygen of soft segment. FTIR results revealed that the changed morphology of TPU in the composite resulted in variations in interactions with soft and hard segment of TPU. The Li^+ ion interaction becomes dominant with hard segments when PAN content in the composite was increased from 10% to 20%. The added Li^+ ion interacts more with the C═O and NH group of TPU than with the C≡N group of PAN.

As dry films, the conductivity of these composites was found to be low in comparison with TPU. The composites with added of $LiClO_4$ possess higher conductivity than TPU itself at temperatures higher than the T_g of hard segment of TPU. Hence, the improved high-temperature conductivity and possibility of the PAN in the composite to inhibit dendrite formation can make these composites a suitable electrolyte in lithium batteries.

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References and Notes

(1) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polyme*r **1973**, *14*, 589.
(2) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3187.
(3) Wieczorek, W.; Such, K.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem.* **1994**, *98*, 6840.
(4) Scrosati, B. *Applications of Electroactive Polymers*; Chapman and Hall: London, 1993.
(5) Macallum, J. R.; Vincent, J. R. *Polymer Electrolyte Reviews* and *Polymer Electrolytes Reviews 2*; Elesvier: London, 1987 and 1989.
(6) Van Heumen, J.; Wieczorek, W.; Siekierski, M.; Stevens, J. R. *J. Phys. Chem.* **1995**, *99*, 15142.
(7) Seefried, C. G.; Koleske, J. V.; Critchfield, F. E. *J. Appl. Polym. Sci.* **1975**, *19*, 2493.
(8) Dickinson, L. C.; Shi, J. F.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1224.
(9) Li, Y. J.; Gao, T.; Chu, B. *Macromolecules* **1992**, *25*, 1737.
(10) Koberstein, J. T.; Galambos, A. F. *Macromolecules* **1992**, *25*, 5618.
(11) Van Heumen, J. D.; Stevens, J. R. *Macromolecules* **1995**, *28*, 4268.
(12) Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1985**, *18*, 1676.
(13) Skrovanek, D. J.; Coleman, M. M.; Painter, P. C. *Macromolecules* **1986**, *19*, 699.
(14) Wen, T. C.; Wu, M. S.; Yang, C. H. *Macromolecules* **1999**, *32*, 2712.
(15) Ferry, A.; Jacobsson, P.; Van Heuman, J. D.; Stevens, J. R. *Polymer* **1996**, *37*, 737.
(16) Wang, X. L.; Li, H.; Tang, X. Z.; Chang, F. C. *J. Polym. Sci., Part B* **1999**, *37*, 837.
(17) Mclennaghan, A. W.; Pethrick, R. A. *Eur. Polym. J.* **1988**, *24*, 1063.
(18) Armand, M. B. *Fast Ion Transport in Solid*; Elsevier: North Holland, 1979.
(19) Watanabe, M.; Oohashi, S.; Sanui, K.; Ogata, N.; Kobayashi, T.; Ohtaki, Z. *Macromolecules* **1985**, *18*, 1945.
(20) Abraham, K. M.; Alamgir, M. *J. Electrochem. Soc.* **1990**, *137*, 1657.
(21) Huang, H.; Chen, L. Q.; Huang, X. J.; Xue, R. J. *Electrochim. Acta* **1992**, *37*, 1671.
(22) Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *21*, 65.
(23) Lee, H. S.; Wang, Y. K.; Hsu, S. L. *Macromolecules* **1987**, *20*, 2089.
(24) Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C. *Macromolecules* **1986**, *19*, 2149.
(25) Watanabe, M.; Sanui, K.; Ogata, N. *Macromolecules* **1986**, *19*, 815.
(26) Albinson, I.; Mellander, B. E.; Stevens, J. R. *J. Chem. Phys* **1992**, *96*, 681.
(27) Wang, Z.; Huang, B.; Xue, R.; Huang, X.; Chen, L. *Solid State Ionics* **1999**, *121*, 141.
(28) Wang, Z. X.; Huang, B. Y.; Huang, H.; Xue, R. J.; Chen, L. Q.; Wang, F. S. *Spectrochim. Acta, Part A* **1996**, *52*, 691.
(29) Mclennaghan, A. W.; Hooper, A.; Pethrick, R. A. *Eur. Polym. J.* **1989**, *25*, 1297.
(30) Tatsuma, T.; Taguchi, M.; Iwakau, M.; Sotomura, T.; Oyama, N. *J. Electroanal. Chem.* **1999**, *472*, 142.

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