

Preparation and Characterization of Conducting Poly(diphenylamine) Entrapped Polyurethane Network Electrolyte

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ABSTRACT: Composites of thermoplastic polyurethane (TPU) with poly(diphenylamine) (PDPA) were prepared by entrapping diphenylamine (DPA) molecules into the matrix of TPU and polymerizing DPA within the TPU matrix. Swelling rate of the parent TPU and the composites in 1M LiClO₄ in propylene carbonate solution were compared to understand the influence of the presence of PDPA in the composite in altering the morphology, conductivity, and electrolyte behavior. The nitrogen atoms in the PDPA interact and are likely to form hydrogen bonding with the carbonyl and ether groups in TPU. As a result, different morphology, thermal, and impedance behavior were witnessed for the composites in comparison to TPU. Results from differential scanning calorimetry, scanning electron micros-

copy (SEM), thermogravimetric analysis, and ac impedance measurements were obtained as supporting evidences. An increase in glass transition temperature for the composite in comparison to TPU infers the increase in phase mixing of soft and hard segment of TPU. The SEM micrograph shows the presence of fibrillar morphology of PDPA molecules in the composite. The ionic conductivity of the swelled composite was 1-fold higher than that of pure TPU. A schematic representation showing the interaction of PDPA molecules with TPU is presented. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 611–617, 2006

Key words: polyurethane; poly(diphenylamine); composites; hydrogen bonding; polymer electrolyte

INTRODUCTION

Electro-active polymers have been the objects of increasing academic and industrial interest in the last two decades. Subsequently, significant progress had been achieved in the development and the characterization of new class of materials comprising of conducting polymers.

The polyaniline class of materials received interest because of the environmental stability, processability, and its electrical, optical, electrochemical properties,¹ electrochromism,² ease of doping,³ and ease of preparation. Among the polyaniline class, poly(diphenylamine) (PDPA) has attracted much attention recently. Many properties of PDPA^{4–9} that include electrochemistry, conductivity, luminescence, and electrochromism are found to be different from polyaniline and polymers of other N-substituted aniline derivatives. In recent studies,^{8,9} attempts have been made to incorporate newer properties into PDPA by grafting nonconducting polymer onto the backbone. In fact, this opens up the possibilities of the creation of new polymeric materials with interesting characteris-

tics. We envisage that on making composites of PDPA with polyurethanes loaded with lithium salts, the electrolyte forming properties of polyurethanes could be improved. The functional groups in PDPA can have interaction with lithium ions and polyurethane groups and provide scope for different electrolyte characteristics.

Various methods are being followed for making composites of conducting polymers with convectional polymers. Blends of HCl-doped PANI nanoparticles with poly(vinyl alcohol) (PVA) were prepared by suspending PANI/HCl particles in PVA.¹⁰ Polyacrylamide film, impregnated with ammonium persulfate, was exposed to HCl vapor, and then to aniline vapor for making the blend.¹¹ Bi and Pei¹² have prepared the composites of polyurethane and polypyrrole and characterized. Self-assembled polyaniline micro/nanotubes were solution blended with polyurethane to get a highly dispersed fractal network composite.¹³ By combining the high-dielectric copper phthalocyanine oligomer and conductive PANI within polyurethane matrix, preparation of an all-organic three-component dielectric percolative composite with high dielectric constant has been demonstrated.¹⁴ Properties of waterborne polyurethane/polyaniline codoped with dodecyl benzene sulfonic acid and hydrochloric acid blends were presented and compared

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with the ultrasonically treated blends.¹⁵ The combination of the conducting properties of PANI with the mechanical performance of polyurethanes was accomplished through the preparation of networks of PANI and polyurethane.¹⁶ The two polymers were interconnected to form the network via condensation of a NCO-terminated PU prepolymer and the amine groups of PANI.¹⁶ A series of urethane–aniline block copolymers based on a polyurethane prepolymer and oligomer of amine-terminated polyaniline were prepared for a conductive material and characterized by ¹³C NMR and FTIR spectroscopy.¹⁷ The chain mobility and the domain size of the soft segment (SS) in the urethane units gradually decreased as the content of amine groups was increased.¹⁷ Polymer blends of polyaniline complexes and water-based polyurethane were studied in the nanometer scale.¹⁸ Recently, characterization and applications of polyurethane-based conducting blends/composites with PANI, polythiophene, or polypyrrole were reviewed.¹⁹

In this work, composites of PDPA and thermoplastic polyurethane (TPU) containing poly(ethylene glycol) (PEG) and 2,6-toluene diisocyanate (TDI) as soft and hard segments were prepared and doped with lithium perchlorate. For evaluating the electrolyte characteristics, the composites were characterized for structure, morphology, and electrochemical behavior.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG; Mw 400) was dried under reduced pressure at 80°C for 24 h before use. 2,6-Toluene diisocyanate (TDI) was used as received. LiClO₄ was dehydrated at 120°C under reduced pressure for 72 h. Propylene carbonate (PC) (E.Merck), diphenylamine (DPA; E.Merck), and potassium peroxydisulphate (PDS) (E.Merck) were used as received.

Synthesis of TPU

The TPUs were synthesized in a batch reactor consisting of a 2000 mL, four-necked, round-bottom flask with an anchor stirrer, a nitrogen inlet and outlet, and a thermocouple connected to the temperature controller. The polyols, PEG-400 (weight-average molecular weight (Mw) = 400 g/mol), and the chain extender, 1,4-butanediol, were kept in a vacuum oven at 80°C for 1 day. The polyols (0.05 mol) and 0.20 mol of the chain extender were put in the reactor first and mixed well at 50°C. After 30 min, the temperature was increased to 85°C, and two drops of the catalyst, dibutyl tin dilaurate, were added to the reactor. Then, 0.25 mol of the hard segment, TDI, was added stepwise to the reaction mixture. Dimethylformamide was used to

control the viscosity of the TPUs during the polymerization.

Preparation of PDPA-TPU composite

A typical procedure is outlined. TPU film of 175 μm was dried under vacuum oven at 75°C for 2 days. PDS was dissolved in PC to make 0.2M PDS/PC solution. TPU film was immersed into PDS/PC solution for 2 h. The film was taken out from the solution and the excess solution present on the surface of the film is removed by soaking with filter paper. The film was then immersed into 20 mM DPA/PC solution at room temperature for 5 h. The color of the film changed to green. In this process, the composite comprising of PDPA and TPU was formed. The composite film was then withdrawn and washed with water to remove the unreacted components. TPU (parent) film and the composite films were dried under vacuum at 85°C and used for further characterization.

Swelling study and method of making PDPA-TPU–LiClO₄/PC electrolytes

LiClO₄ was dissolved in PC to make 1M LiClO₄/PC solution. Swelling experiments of the polymer electrolytes were carried out inside the glove box by dipping a preweighed (500 mg) PDPA-TPU in 1M LiClO₄/PC. Films were kept immersed for different time intervals. After which, the films were withdrawn and the surface electrolytes were removed by soaking with a filter paper. The weight of the swelled film was noted. Percent swelling (S_w) was determined from

$$S_w = 100(w - w_0)/w_0$$

where w_0 is the initial weight of the film and w is the weight of the film after swelling.

The swelled composite film (PDPA-TPU –LiClO₄/PC) was used for electrolyte characteristics.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out using a DSC 2010 Differential Scanning Calorimeter (TA Instruments, USA) over a temperature range of –150 to 150°C at a scan rate of 10°C/min. The samples were sealed in Al crucibles inside the glove box. The sealed samples were taken out of the glove box only at the time of DSC experiments. The samples were first annealed at 150°C for 10 min, cooled down to –150°C, and then scanned. All the thermograms are base line corrected and calibrated against Indium metal. Glass transition temperature (T_g) was reported as the midpoint of the transition process and melting temperature was the peak temperature.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the prepared polymer electrolyte samples was performed under nitrogen atmosphere using a PerkinElmer TGA 7/DX Thermal Analyzer with a scan rate of 20°C/min until 650°C.

Scanning electron microscopy

Scanning electron microscopy (SEM) observations were carried out with Au-coated vacuum ion sputter by liquid hydrogen method (JOEL 840 A). The rotating system was attached in the instrument, utilized for accurate measurements for various magnifications.

Impedance measurements

Impedance measurements of the TPU (parent) and composite electrolytes were performed using thin films. Film thickness was maintained in the range of 175 μm and the area of contact was 1.0 cm^2 . For measurement of ionic conductivity, the samples were sandwiched between two stainless steel electrodes. The electrodes were then fixed in an airtight double wall glass cell, through the outer jacket of which thermostated water was circulated for measurements at different temperatures. Cell assembly was carried out in dry argon atmosphere inside a glove box. Conductivity measurements were performed using the EG and G PAR 6310 Potentiostat/Galvanostat controlled by the frequency response analysis system software under an oscillation potential of 25 mV. The conductivity was calculated with the relation,

$$\sigma = \frac{1}{R_b} \times \frac{\lambda}{A}$$

where R_b is the bulk resistance from alternating current impedance, λ is the film thickness, and A is the surface area of the electrode.

RESULTS AND DISCUSSION

Swelling study

The swelling behavior of TPU and PDPA-TPU composite were studied. Both the electrolytes were dipped in 1M LiClO_4 in PC (the thickness of both the films were about 175 μm). The swollen weight (S_w) was determined versus various immersion times and the results are represented in Figure 1.

In the case of PDPA-TPU composite, the percentage of S_w in 1M LiClO_4 /PC was found to be higher than the parent TPU. It implies that the composite can uptake more liquid electrolyte than TPU. Interestingly, the dimensional stability of both the composite

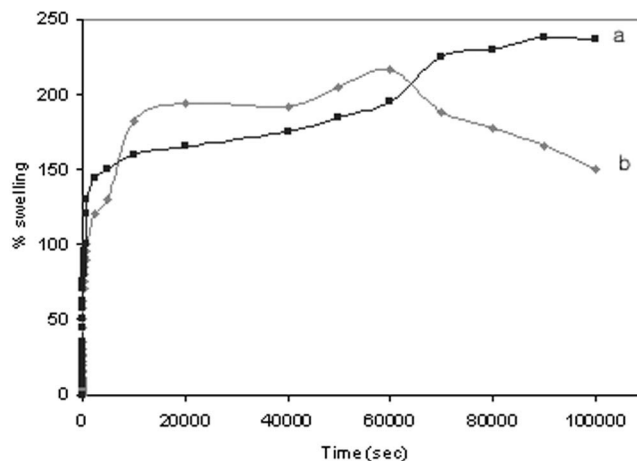


Figure 1 Swelling behavior of (a) PDPA-TPU composite and (b) TPU in 1M LiClO_4 /PC.

electrolytes was not affected by the incorporation of PC.

TPU film could be swelled for more than 200% by soaking in 1M LiClO_4 /PC for 16 h and thereafter showed a decreasing trend. This may be due to the decomposition of the backbone groups of TPU molecule by the presence of LiClO_4 /PC or the removal of soluble portions of the components from the TPU. However, interestingly, the PDPA-TPU composite did not show such a decreasing trend. This indicates that the backbone structure of TPU becomes stabilized by the presence of PDPA. TPU-PDPA has a more pronounced swelling rate than the parent TPU. The composite was found to swell to the maximum value of swelling of about 290% in about 6 days. This indicates that PDPA-TPU composite has better stability than its parent TPU on doping with LiClO_4 /PC. The presence of PDPA molecules inside the TPU matrix may be the reason for the increase in the chemical stability. PDPA, being insoluble in PC, acts as the reinforcing filler to the TPU matrix and increases the stability of the composite.

Differential scanning calorimetry

DSC thermograms of pure TPU and TPU-PDPA composite are presented in Figure 2. TPU consists of thermodynamically incompatible hard and soft segments (HS and SS) and shows separate thermal transitions for the individual segments. In the parent TPU, the SS T_g is observed in the negative temperature region, whereas, depending upon the amount of hard segment, multiple thermal transitions are observed in the region of 70°C to >200°C for the hard segments. These multiple transitions may be associated with short-range ordering of the hard-segment domains, long-range ordering and microcrystallinity in the hard domain, etc.

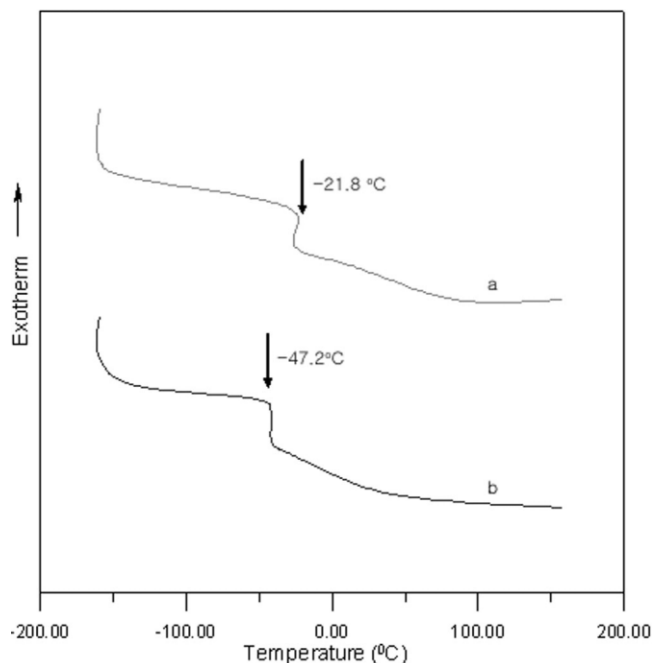


Figure 2 DSC thermograms of (a) PDPA-TPU composite and (b) TPU.

DSC thermogram of pure TPU shows a SS T_g at about -42.7°C . Addition of PDPA alters the SS T_g of the parent TPU. An increase in T_g of the SS was observed from -42.7°C to -21.8°C . The increase in T_g may be due to the hydrogen bonding interactions between ether or carbonyl groups in TPU with $-\text{NH}$ molecule of PDPA. This is envisaged based on the literature.^{20–25} Hydrogen bonding interactions in TPU and its composites have been well documented by us and others through FTIR spectroscopy. Intermolecular hydrogen bonding interactions between $-\text{NH}$ groups and carbonyl or ether groups in TPU have been described. In the case of composites of TPU,²⁵ intermolecular hydrogen bonding interactions were attributed between groups like $-\text{CN}$ (in the case of TPU-PAN) and carbonyl or ether groups in TPU. However, in the present study, PDPA also has $-\text{NH}$ groups. Hence, we believe that FTIR spectroscopy would not bring useful information about hydrogen bonding interactions between $-\text{NH}$ groups in PDPA and TPU groups, specifically. As a possibility, we anticipate that the change in the SS T_g may arise from the additional hydrogen bonding interactions between $-\text{NH}$ groups in PDPA and TPU groups.

Thermogravimetric analysis

Thermograms of the TPU-PDPA composite, parent TPU, and PDPA are shown in Figure 3. TPU has a two-stage weight loss starting at about 290°C with 10% residual mass at 420°C . The presence of PDPA in

TPU-PDPA composite is evident from the difference in thermal behavior of the composite. The first weight loss of composite (TPU-PDPA) was noticed at 282°C . A residual weight of about 20% was found at 420°C . The weight loss at the lower temperature is expected to arise from PDPA. Oligomeric portions of PDPA decompose at this temperature range.^{26,27} The chemically prepared PDPA started losing weight at 190°C and continues up to 350°C , which may be due to the weight loss of the counter anions. The second stage weight loss corresponds to the decomposition of the PDPA backbone.¹⁹

SEM topography

Figure 4 shows the SEM images of TPU film and composite films. A difference in morphology could be seen for the composite in comparison to the parent TPU, under the same magnification. The composite has a fibrillar structure due to PDPA in contrast to smooth morphology of TPU.

Impedance measurement

To understand the conductive behavior of TPU-PDPA- LiClO_4 complex electrolyte, the ac impedance analysis of the composite film, sandwiched between two stainless steel blocking electrodes, was performed. The impedance spectrum of the composite film at room temperature under potential amplitude of 25 mV from 100 kHz to 0.1 Hz was obtained. A typical Nyquist plot of the composite is shown in Figure 5. A straight line starting from the real axis in

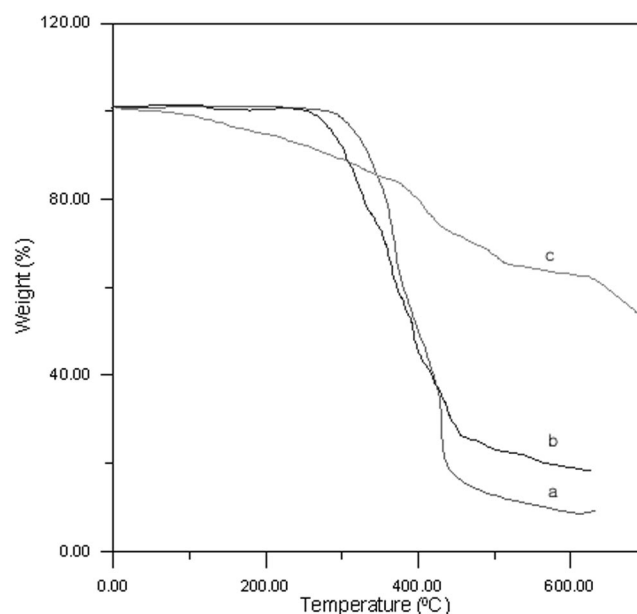


Figure 3 Thermograms of (a) TPU, (b) PDPA-TPU composite, and (c) PDPA.

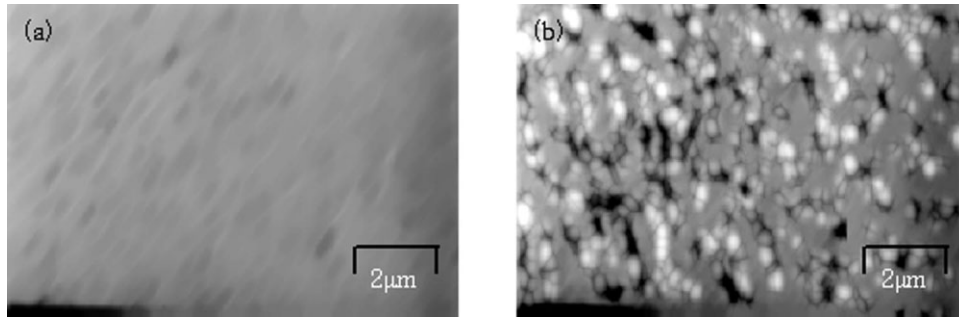


Figure 4 SEM micrographs of (a) TPU and (b) PDPA-TPU composite.

the high frequency region could be seen, and an equivalent circuit representing the impedance behavior is presented in Figure 5. The equivalent circuit consists of bulk resistance (R_b) in series with a parallel circuit of the double layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}). On the basis of the simulation, impedance (Z) can be expressed as:

$$Z = \left(R_b + \frac{R_{ct}}{1 + (R_{ct}\omega C_{dl})^2} \right) - \left(\frac{R_{ct}^2\omega C_{dl}}{1 + (R_{ct}\omega C_{dl})^2} \right)j$$

where ω is the angular frequency and j represents the imaginary part of Z .

The order of magnitude of the dimensionless parameters, ($R_{ct}\omega C_{dl}$), in comparison to unity signifies the analysis.

In general, two extreme possibilities can be visualized like,

if $R_{ct}\omega C_{dl} \gg 1$, then $Z \rightarrow R_b$ and

if $R_{ct}\omega C_{dl} \ll 1$, then $Z \rightarrow R_b + R_{ct}$

Usually, the larger $R_{ct}C_{dl}$ system needs the lower frequency to obtain the value of $R_b + R_{ct}$. However, in the case of composite electrolyte, the frequency is not

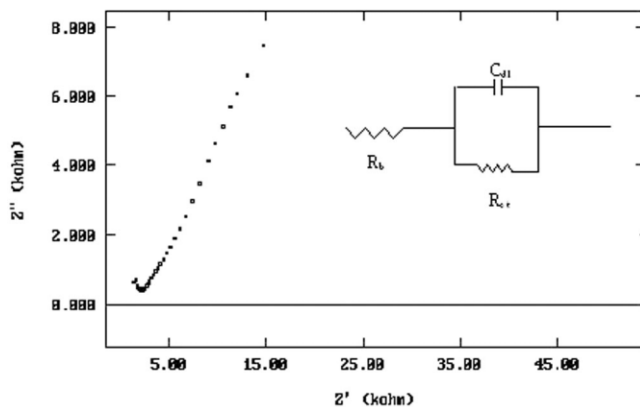


Figure 5 Nyquist plot of PDPA-TPU composite. (Inset: equivalent circuit for PDPA-TPU composite).

enough to satisfy $R_{ct}\omega C_{dl} \ll 1$. It is apparent from the impedance plot of the composite electrolyte that the arc has not bended toward the real axis to obtain $R_b + R_{ct}$. It may be due to the fact that the use of SS electrodes restricts the charge-transfer reaction to occur under the small oscillation potential. $R_{ct} C_{dl}$ is too large to produce the arc for obtaining $R_b + R_{ct}$. The straight line response of the film represents the response if C_{dl} parallel to the large R_{ct} .

The conductivity (σ) of the composite electrolyte and the parent TPU were determined from the bulk resistance (R_b), which was obtained from the value of Z' at the minimum of jZ'' in the complex impedance plot (Z' and Z'' are the real and imaginary part of the impedance, and j is a constant) by the relationship

$$\sigma = \frac{1}{R_b} \times \frac{\lambda}{A}$$

where λ is the thickness of the electrolyte films and A is the area of cross section. Figure 6 shows the temperature dependence of conductivity of TPU/PC-LiClO₄ and the composite electrolyte as a function of reciprocal temperature. It is evident from Figure 6 that the variation of conductivity with reciprocal temper-

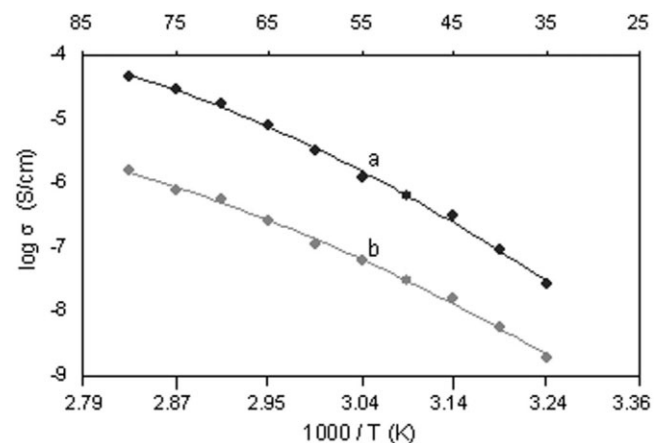
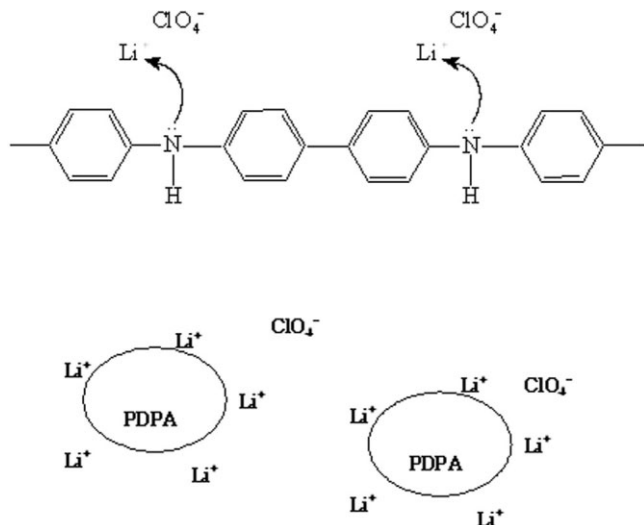


Figure 6 Temperature dependence of ionic conductivity of (a) PDPA-TPU composite and (b) TPU.



Scheme 1 Interaction of Li^+ ions with PDPA.

ature follows Vogel-Tamman-Fulcher relationship, and suggests that the ion transport is coupled with the polymer segmental motion.

$$\sigma(T) = AT^{-1/2} \exp[-B/k_B(T - T_0)]$$

where A is a constant proportional to the number of charge carriers, B is the pseudoactivation energy related to polymer segmental motion, k_B is the Boltzmann constant, and T_0 is a reference temperature usually associated with the ideal T_g at which free volume disappears or the temperature at which the configurational entropy becomes 0. It is to be noted that the relationship of conductivity with salt concentration is a complex one.

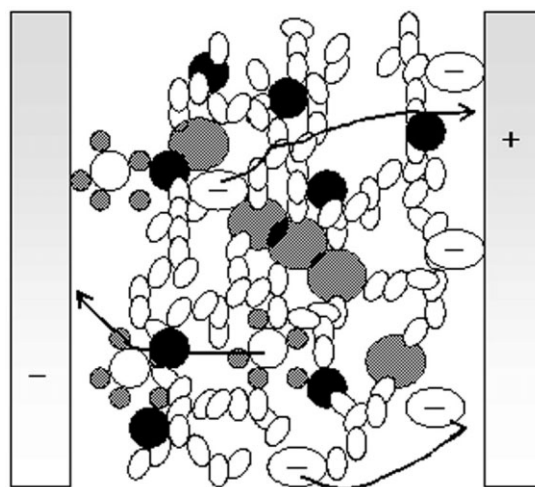
It is apparent from the figure that the conductivity of both the electrolytes increases while increasing the temperature from 35 to 80°C. This is quite reasonable that the increase in the temperature would increase the number of free charge carriers and hence the conductivity is improved. Another obvious observation from Figure 6 is that the composite electrolyte shows enhanced conductivity than the parent TPU for all the temperature studied. The conductivity of the composite electrolyte is about 2.7×10^{-8} S/cm at 35°C. Conductivity of the composite is an order of magnitude higher than the parent TPU containing the same concentration of lithium salts. Such an increase in the conductivity on the addition of the conducting polymers has been observed by many researchers. Yamasaki et al. observed an increase in conductivity of 1-fold by the addition of polyaniline into the PEO matrix.²⁸ Li and Khan²⁹ have observed the same trend on addition of poly(vinyl pyridines). Addition of polypyrrole onto the TPU matrix has enhanced the conductivity.³⁰

The enhancement of conductivity may be due to the fact that the presence of PDPA moieties in the TPU matrix has facilitated the Li^+ ion transport. Scheme 1 represents the possible interaction of Li^+ ions with PDPA molecules. It can be inferred that Li^+ ions get coordinated with nitrogen atom of the PDPA backbone. The addition of Li^+ ions may create a positive charge over nitrogen atom, which will be electronically stabilized by delocalization of electrons in the PDPA matrix. This makes the free movement of ClO_4^- along the polymer matrix, leading to the consequent increase in the conductivity.

Scheme 2 explains the ionic movements in the composite film. It can be noted that the change in the electrostatic environment in the composite with PDPA in it not only holds the lithium ion but also attracts the extra lithium ion that solvated. From the swelling studies, it is noted that the swelling rate of composite film is higher than that of its parent TPU (Fig. 1). More swelling rate implies more solvation of the lithium ions. The addition of PDPA molecules may weaken the hydrogen bonding between $\text{C}=\text{O}$ and $-\text{NH}$, causing an increase in the flexibility and free volume. This fact is in consistent with the observation of an increase in $SS T_g$ on addition of PDPA molecules to the TPU matrix (Fig. 2). When the potential is applied, a lithium ion might hop between various $\text{PDPA}^{\delta+}$ moieties and contribute for the ionic conductivity.

CONCLUSIONS

Polymerization of DPA in the matrix of TPU results in the formation of the composite that consists of PDPA and TPU. The composite can be doped with LiClO_4 and swelled in PC to obtain dimensionally stable electrolyte film. The composite can be swelled in 1M LiClO_4/PC to a higher percentage than the parent TPU.



Scheme 2 Ionic motions in the PDPA-TPU composite film.

The presence of PDPA in the composite increases the phase mixing of soft and hard segment of TPU. The SEM micrographs of the composites were found to have fibrillar morphology of PDPA. A 1-fold increase in conductivity was observed for the composite in comparison to the parent TPU. This enhanced conductivity arises from the probable hydrogen bonding interactions between the groups in TPU and PDPA.

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