

A Novel Soluble PANI/TPU Composite Doped with Inorganic and Organic Compound Acid

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ABSTRACT: A series of novel soluble and thermoplastic polyurethane/polyaniline (TPU/PANI) composites doped with a compound acid, which was composed of an organic acid (*p*-toluene sulfonic acid) and an inorganic acid (phosphoric acid), were successfully prepared by *in situ* polymerization. The effect of aniline (ANI) content, ratio of organic acid/inorganic acid, and different preparation methods on the conductivity of the TPU/PANI composites were investigated by using conductivity measurement. Lithium bisoxalato borate (LiBOB) was added to the prepared *in situ* TPU/PANI to coordinate with the ether oxygen groups originating from the soft molecular chains of TPU, and thus the conductivity of the composites was further enhanced. The molecular structure, thermal properties, and morphology of the TPU/PANI composites were studied by UV-visible spectroscopy, differential scanning calorimetry, and scanning electron microscopy, respectively. The results show that the *in situ* TPU/PANI composites

doped with the compound acid can be easily dissolved in normal solvents such as dimethylformamide (DMF) and 1,4-dioxane. The conductivity of the TPU/PANI composites increases with the increase of the ANI content, in the ANI content range of 0–20 wt %; however, the conductivity of the composites reduces with further increment of ANI content. The conductivity of the TPU/PANI composites prepared by *in situ* polymerization is about two orders of magnitude higher than that prepared by solution blending method. LiBOB can endow the *in situ* TPU/PANI composites with an ionic conductivity. The dependence of the conductivity on temperature is in good accordance with the Arrhenius equation in the temperature range of 20–80°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1886–1893, 2010

Key words: polyaniline; thermoplastic polyurethane; *in situ* polymerization; ionic conductivity

INTRODUCTION

Since Heeger and coworkers have discovered that polyacetylene¹ can be changed from an insulator to a high conducting polymer after doping, conducting polymers have aroused many interesting researches because of their large potential applications in energy storage systems,^{2–4} electronic devices,^{5–8} sensors for hazardous gases and toxic fumes,^{9–12} corrosion inhibitors for iron and mild steel,^{13,14} and the electromagnetic interference shielding materials.^{15–18}

Polyaniline (PANI) is one of the most promising conducting polymers. It has been widely studied over the past two decades because of their simple methods of preparation and good stability to environment. Unfortunately, the poor processability of PANI and its inadequate mechanical properties limit its large commercial applications.¹⁹ To overcome these problems, the following two methods are most commonly used:

1. Functionalized organic acid doping, such as dodecylbenzenesulfonic acid (DBSA) and camphor-sulfonic acid-doped PANIs. However, their conductivities are always lower than those of the inorganic acid-doped PANI composites. The processability of the resulting PANIs has also not been improved remarkably.
2. Techniques based on the dispersion of PANI into a polymeric matrix composed of conventional insulating polymers because it effectively combines the good processability and mechanical properties of common polymers with the conducting properties of PANI.

The use of a thermoplastic elastomer as insulating polymer matrix is very attractive because of the combination of its mechanical properties and processability. Vicentini and coworkers²⁰ have reported the properties of DBSA-doped thermoplastic polyurethane (TPU)/PANI composites prepared by the *in situ* as well as the solution blending method. However, it seems that the compound acid-, especially the inorganic and organic compound acid, doped TPU/PANI composites have not been

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previously reported. In this article, we report a compound acid, *p*-toluene sulfonic acid/phosphoric acid (*p*-TSA/PA), doped TPU/PANI composites. PA and *p*-TSA were selected due to the consideration of both the conductivity and processability (solubility) of the composites. Lithium bisoxalato borate (LiBOB) was added to TPU/PANI to endow the composites with an ionic conductivity. The composites would therefore have potential applications in the electrode materials, especially in the secondary Li-ion batteries. The influences of different preparation methods on the conductivity and morphology of the composites were investigated. The dependence of the conductivity on the aniline (ANI) content was found remarkably different from those reported in previous papers.^{20,21,22} TPU/PANI with the ANI content of 20 wt % had the best conductivity. LiBOB was able to further enhance the conductivity of the *in situ* TPU/PANI composites by about one order of magnitude. Thermal properties and morphology of the composites were also studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) measurements.

EXPERIMENTAL

Materials

ANI (analytical grade, Kelong Chemical Reagent, Chengdu, China) was distilled twice under reduced pressure and stored in a refrigerator. Ammonium peroxydisulfate (APS), also supplied by Kelong Chemical Reagent, was recrystallized twice in deionized water, and then located in a desiccator before use. Both *p*-TSA and PA were analytically pure and used without further purification. LiBOB was synthesized according to the method reported in the literature.²³ All the other chemicals used in this experiment were analytically pure.

Polyether (83A10) TPU was supplied by Bayer Company (Germany). It was dried under vacuum at 80°C for 4 h before use.

Synthesis of *in situ* TPU/PANI composites

A 10 wt % polyether TPU solution, named Solution A, was obtained from the procedure that the sets TPU and ANI were dissolved in anhydrous 1,4-dioxane under vigorous stirring for at least 1 h. *p*-TSA, PA, and sodium dodecylbenzenesulfonic acid (SDBS) [SDBS/(*p*-TSA + PA) = 0.1/0.9 (by wt), (*p*-TSA + PA)/ANI = 1/1 by mol] were dispersed into 1,4-dioxane at 5°C to obtain Solution B. Solution A was then slowly added into Solution B under stirring. After that, the APS (APS/ANI = 1/1 by mol) aqueous solution was added dropwise into the earlier mixture, and then the polymerization reaction

was maintained for 8 h at 5°C. The resulting dark green solution was precipitated in methanol. The precipitate was filtered, washed with deionized water several times, and dried under vacuum at 60°C for 24 h.

Preparation of TPU/PANI composites by solution blending

PANI, used in the preparation of the solution blending TPU/PANI composites, was synthesized by using a traditional emulsion polymerization,²¹ in which ANI was dispersed in an aqueous solution of *p*-TSA and PA (*p*-TSA/PA = 2/1 by mol) with SDBS as the emulsifier at 5°C. The APS aqueous solution was added into the mixture, and then the polymerization was maintained for 8 h. The final dark green emulsion was poured in methanol. The precipitate was filtered, washed with deionized water, and dried at 60°C for 24 h under vacuum. The resulting PANI powders were added into the TPU solution (1,4-dioxane as the solvent) under strong stirring for at least 1 h. The mixture was again precipitated in methanol, and then filtered, washed, and dried.

Preparation of TPU/PANI/LiBOB composites

The sets *in situ* TPU/PANI and LiBOB were dissolved in DMF. The LiBOB solution was then mixed with the *in situ* TPU/PANI solution under stirring for 1 h. The resulting mixture was poured into a specific polytetrafluoroethylene (PTFE) mold to form a thin film, which would be facilitated to the conductivity measurement later. All the prepared samples were located in ambient environment for 48 h, and then dried under vacuum at 60°C for 24 h before measurement.

Characterization

Conductivity measurement

All specimens (1-mm thickness and 25-mm diameter) used for the conductivity measurement were obtained by the casting technique as described in the earlier section. A four-probe conductivity equipment (SYD-2, Guangdong, China) was used for the conductivity tests. The conductivity was calculated according to the following equation:

$$\sigma = L/R_V S$$

where σ , L , R_V , and S are the conductivity, thickness, volume resistivity, and the surface area of the sample, respectively.

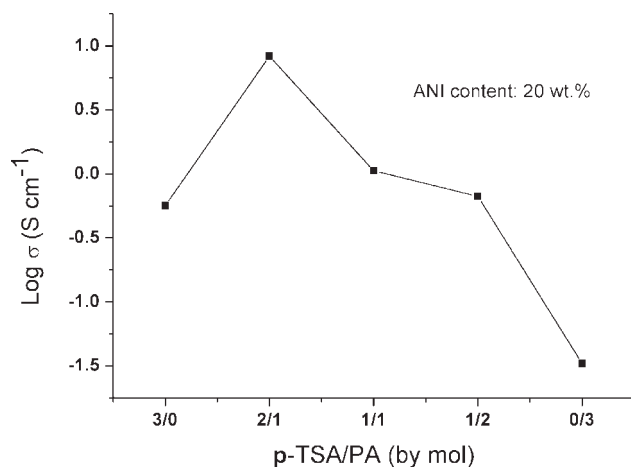


Figure 1 Effect of *p*-TSA/PA on the conductivity of the *in situ* TPU/PANI composites.

UV-vis spectroscopy

UV-vis spectra of the *in situ* TPU/PANI with different ANI contents were performed by using an UV-2100 (Shimadzu, Japan) UV-vis spectrometer.

DSC analysis

DSC measurements were carried out in a DSC204 (NETZSCH, Germany) analyzer from room temperature to 200°C with a heating rate of 10°C min⁻¹, under nitrogen protection using ca. 10 mg of each sample. The specimens were dried under vacuum at 80°C for 4 h prior to the measurement. Glass transition temperature (T_g) was calculated from the peak of the first derivative of the inflexion in the DSC curve.

SEM measurement

The liquid-nitrogen-frozen fractured surfaces of the *in situ* and solution blending TPU/PANI composites with different ANI and PANI contents, respectively, were observed using a JEOLJSM-5900LV SEM (Japan) setting with an accelerated voltage of 20 kV. The SEM samples were gold sputtered before the observation.

RESULTS AND DISCUSSION

Conductivity results

To obtain TPU/PANI composites with both high conductivity and good processability (solubility), *p*-TSA and PA were selected for doping, because the former was facilitated to the improvement of processability and the latter was benefited for the conductivity enhancement. Figure 1 shows that the conductivity of the *in situ* TPU/PANI composites increases to a maximum (8.3 S cm⁻¹) as the ratio of

p-TSA/PA reaches 2/1 by mol, and then it gradually decreases to 0.3 S cm⁻¹ with PA content, revealing the optimum ratio for the *in situ* polymerization.

As seen from Figure 2, the influence of the ANI content on the conductivity of the *in situ* TPU/PANI composites is not well fitted to the scaling law of traditional percolation theory.²⁰ The conductivity of the composites increases to 8.3 S cm⁻¹ as the ANI content reaches 20 wt %; however, the conductivity of the composites reduces to 0.4 S cm⁻¹ with further increment of the ANI content from 20 to 40 wt %. These results are consistent with other characterization features, which will be discussed later. The possible reason behind this is illustrated in Scheme 1. As we know that TPU is characterized by a two-phase morphology in which a soft phase containing either polyether or polyester is reinforced by condensation with a hard domain consisting of aromatic diisocyanate extended with a short-chain extender. In this article, the content of hard segments (CHS) of the polyether TPU can be calculated as follows:

$$\text{CHS} = (M_{\text{MDI}} + M_{\text{BD}}) / (M_{\text{MDI}} + M_{\text{BD}} + M_{\text{P}}) \times 100\%$$

where CHS is the content of hard segments, and M_{MDI} , M_{BD} , and M_{P} are the molecular weights of 4,4-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD), and polyether polyol, respectively. According to the above calculation, there are only about 14.5 wt % hard segments in the TPU molecular chains, in which the ANI monomers may have good interactions (compatibilities) with aromatic diisocyanate groups because of their similar molecular structures. In the soft segment domains, the ANI molecules (aromatic structure), having a bad miscibility with soft segments (ether oxygen groups), can

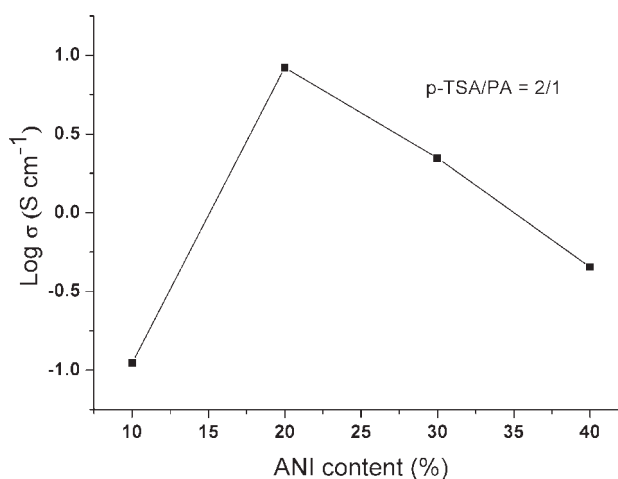
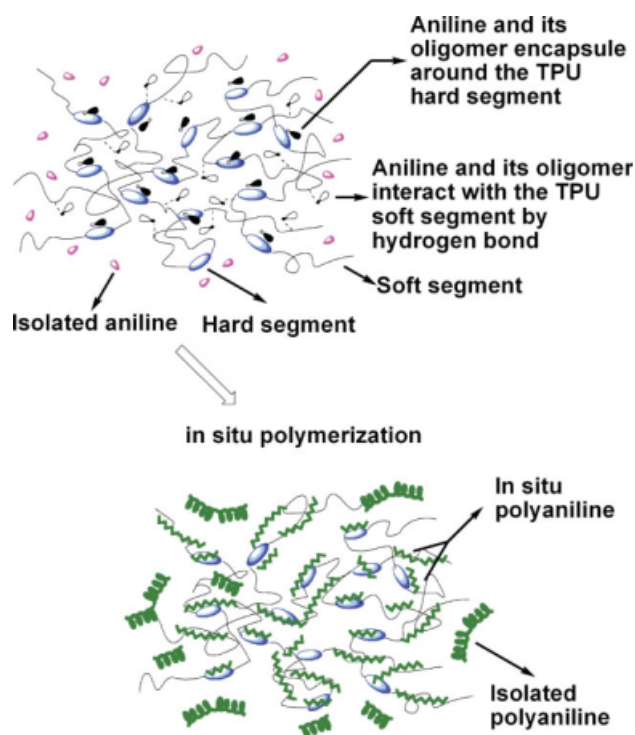


Figure 2 Effect of the ANI content on the conductivity of the *in situ* TPU/PANI composites.



Scheme 1 Schematic mechanism of the formation of the *in situ* TPU/PANI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

only interact with polyether by hydrogen bonds.^{24–26} However, such hydrogen bonds are restricted because their formations are originated from the interactions between the ether oxygen (EO) (or nitrogen) and hydrogen atoms.^{24–26} Based on the earlier discussion, the formation of the *in situ* PANI is probably derived from the following two factors:

1. ANI having a good miscibility with hard segments (about 14.5 wt %).
2. ANI interacting with the soft segments by hydrogen bonds.

With increasing ANI content, the increasing tendency of the interactions between ANI monomers or ANI oligomers is higher than that between ANI and TPU molecular chains when the ANI content changes from 20 to 40 wt %, revealing the increase of the isolated PANI (not the *in situ*) which will be filtered in the post-treatments.

Figure 3 demonstrates the effect of the PANI content on the conductivity of the TPU/PANI composites prepared by solution blending method. It reveals that the conductivity of the blending TPU/PANI composites increases from 1×10^{-3} to 1.4×10^{-2} S cm⁻¹ as the PANI content ranges from 10 to 40 wt %, which is in good agreement with the trend reported in the previous literature.^{20,22}

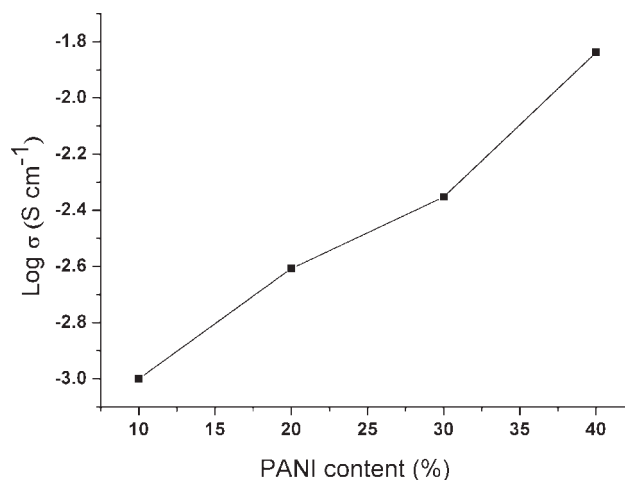


Figure 3 Influence of the PANI content on the conductivity of TPU/PANI prepared by solution blending method.

Figures 4 and 5 reveal the effects of the ratio of EO/Li and temperature on the conductivity of the *in situ* TPU/PANI/LiBOB composites. In Figure 4, the conductivity increases with Li/EO in the range of 1/10–1/6. However, the conductivity slightly increases with further increment of Li/EO, implying the fact that the introduction of LiBOB into TPU/PANI composites is helpful for enhancing the conductivity due to the coordination effects between Li⁺ ions and ether oxygen groups. Figure 5 shows that the conductivity of the TPU/PANI/LiBOB composites increases from 29 to 43 S cm⁻¹ when the ambient temperature ranges from 20 to 80°C, indicating the typical feature of the composites with ion-conductive ability. It is attributed to the fact that the temperature enhances both the mobility of the polymer chains to form more ion-conductive tunnels and the dissociation of LiBOB to obtain more free lithium cations.

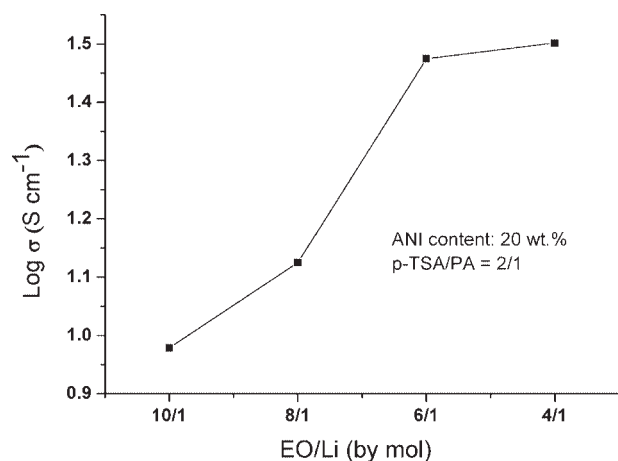


Figure 4 Influence of EO/Li on the conductivity of the *in situ* TPU/PANI composites.

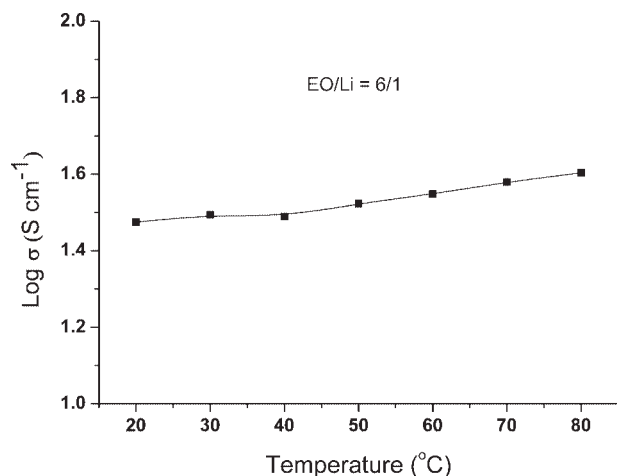


Figure 5 Effect of temperature on the conductivity of the TPU/PANI/LiBOB composites.

UV-vis spectra

Figure 6 shows the UV-vis spectra of the *in situ* TPU/PANI composites with different ANI contents. The characteristic peaks in the range of 300–800 nm are not observed for the pure TPU, indicating a poor conjugation in TPU molecular chains. In the case of the UV-vis spectra of the *in situ* TPU/PANI composites, the characteristic peaks of the traditional PANI in the scales of 300–400 and 500–700 nm corresponding to π - π^* (cis), π - π^* (trans), and polaron or bipolaron transitions are observed.^{27,28} Moreover, Figure 6 also reveals that the absorption strength of the peaks at both lower (\sim 400 nm) and higher (500–800 nm) wavelength regions increase with ANI content in the range of 0–20 wt %. However, the absorption strength of peaks reduces to some extent with further increment of the ANI content (\sim 40 wt %),

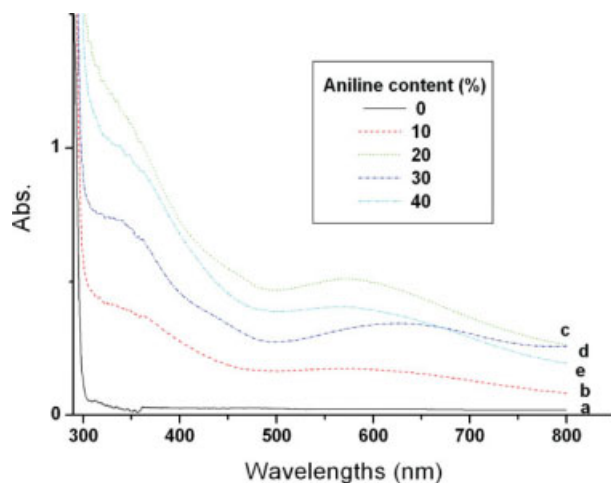


Figure 6 UV-vis spectra of the *in situ* TPU/PANI composites with different ANI contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

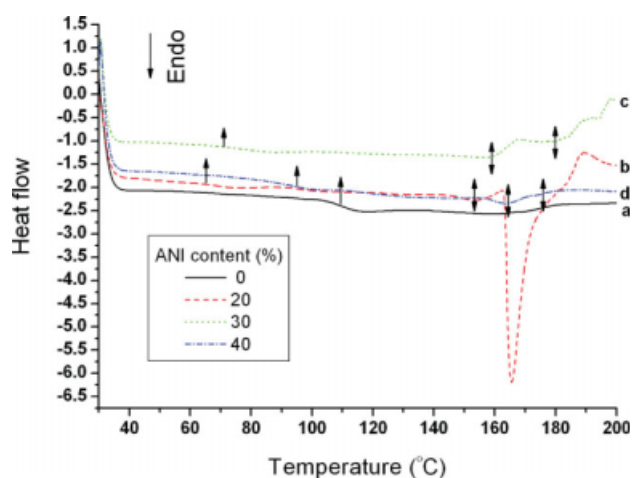


Figure 7 DSC curves of the *in situ* TPU/PANI composites with different ANI contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

illustrating that the TPU/PANI composites with the ANI content of 20 wt % is the best compounding of the *in situ* polymerization.

DSC analysis

DSC curves of the pure TPU and the *in situ* TPU/PANI with the ANI contents from 20 to 40 wt % are shown in Figure 7(a) and (b–d), respectively. In Figure 7(a), two DSC characteristic transitions at around 100 and 160°C are observed corresponding to the glass transition of the hard segments and the melting of TPU molecular chains, respectively.^{29–32} In comparison with the pure TPU, Figure 7(b–d) reveals that the DSC characteristic transitions at both lower (\sim 100°C) and higher (140–200°C) temperature regions change remarkably. At lower temperature region, two T_g transitions are observed. The former

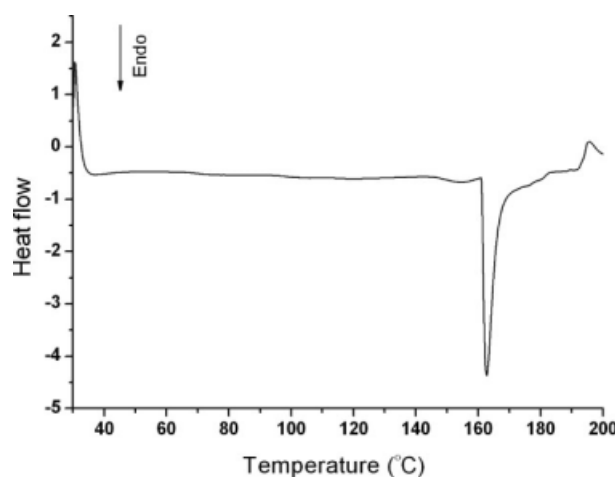


Figure 8 The second scanning DSC curve of the *in situ* TPU/PANI composite with the ANI content of 20 wt %.

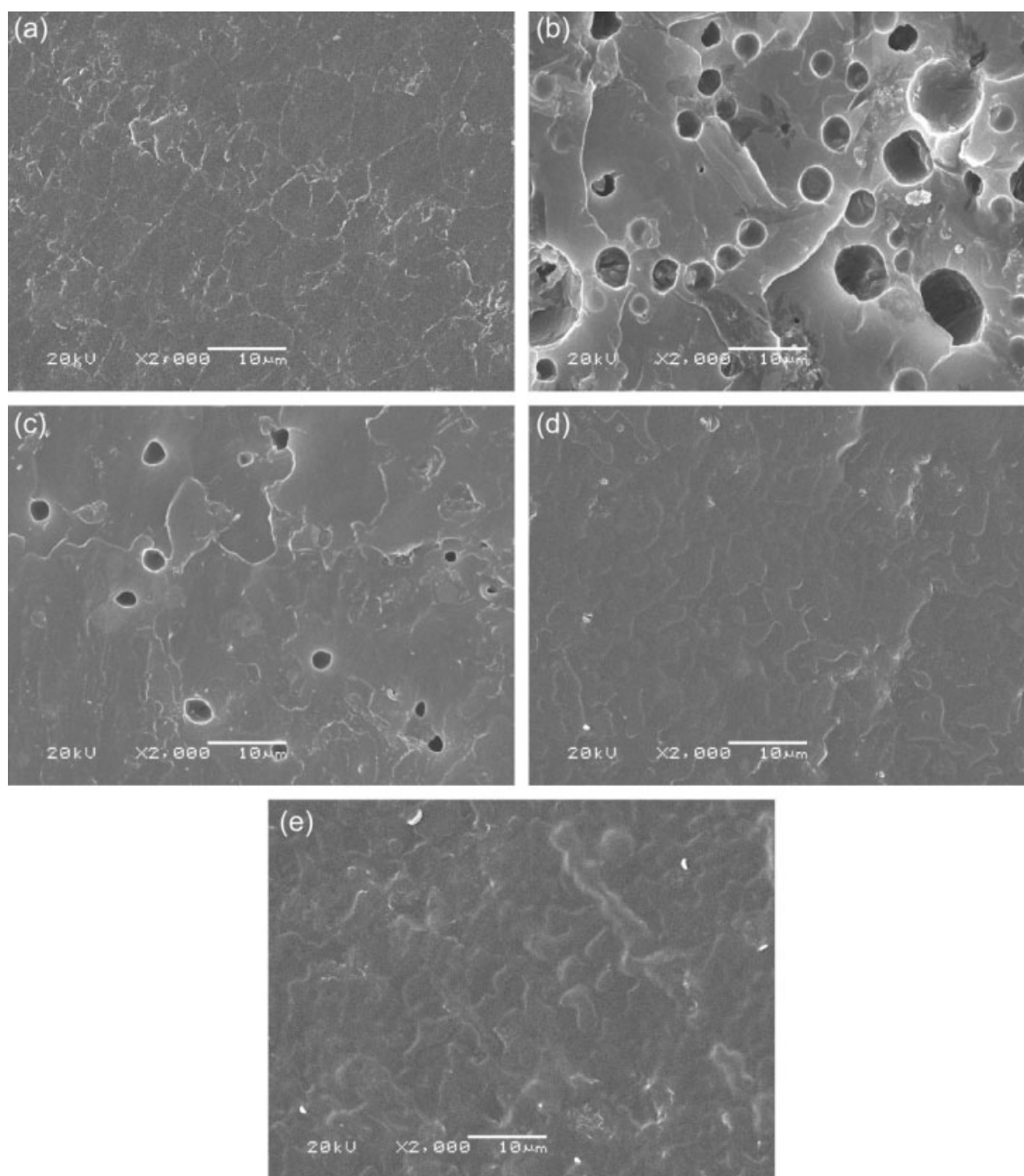


Figure 9 SEM micrographs of (a) pure TPU, the *in situ* TPU/PANI with ANI content of (b) 20 wt % and (c) 40 wt %, and the blending TPU/PANI with PANI content of (d) 20 wt % and (e) 40 wt %.

at around 60°C and the latter at about 100°C are attributed to the T_g transitions of the polyether molecular chains (soft segments) of TPU and the hard segments of both TPU and PANI, because the motion of the soft segments is evidently influenced by the interactions and hydrogen bonds between TPU and the *in situ* PANI whose molecular chains are relatively conjugate and rigid. In the case of the higher temperature range, two endothermic peaks are seen in all specimens. Especially, in Figure 7(b),

the second endothermic peak (at about 165°C) is obviously different from those of other samples. Both of its peak appearance and strength seem like the melting of polymer crystals instead of a typical amorphous TPU. This phenomenon maybe accounted for the following two reasons:

1. The *in situ* PANI, as a nucleating agent, easily leads the crystallization of the polyether molecular chains in TPU, and the second

endothermic peak is the melting of such crystals, because TPU is a typical amorphous or semicrystalline polymer.

2. The second endothermic peak is the melting of the *in situ* PANI oligomer crystals. If so, to the best of our knowledge, the PANI crystals with a melting temperature at about 165°C are synthesized for the first time, implying that PANI prepared by this method can be flexibly processed to be the shape of films, particles, sheets, etc., like a normal thermoplastic polymer produced by using a traditional processing equipment.

To confirm the repeatability of such interesting phenomenon, we have used another specimen cut from the same sample for repeating the DSC test. The repeated curve is shown in Figure 8. It is found that all the DSC endothermic and exothermic transitions and peaks are almost equal to those of the first scanning [Fig. 7(b)], indicating that such phenomenon is not stochastic but nearly related to both the microstructures of the *in situ* TPU/PANI composites and the interactions between TPU and the *in situ* PANI molecular chains.

Furthermore, we are endeavoring to further investigate such attractive phenomenon by using other measurements like hot-stage polarizing optical microscope, X-ray diffraction, thermal gravimetric analysis, elemental analysis, and molecular simulation. The characterization details and the molecular modeling results will be reported later as another full article.

SEM results

SEM micrographs of the pure TPU, TPU/PANI composites prepared by the *in situ* polymerization and solution blending method are shown in Figure 9(a–e). Figure 9(a) shows a relatively even and smooth topology of typical TPU. Many black PANI-like particles (300–2000 nm) are seen evenly dispersed in the *in situ* TPU/PANI composites [Fig. 9(b,c)]. Especially, some particles in the polymer matrix even contact each other [Fig. 9(b)], implying the formation of more electron conductive tunnels and the enhancement of the conductivity. As seen from Figure 9(c), with increasing ANI content from 20 to 40 wt %, the distance between adjacent PANI particles increases, indicating the reduction of the conductivity, which is in good accordance with the analysis in the earlier sections. Evident PANI particles such as those in the *in situ* TPU/PANI composites are not observed in the micrographs of the solution blending TPU/PANI [Fig. 9(d,e)]. Although the PANI microparticles are able to be effectively

blended into the TPU matrix by solution blending in an organic solvent, many PANI particles will be filtered by pouring the PANI/TPU blending solution into methanol due to the same post-treatment procedure as the *in situ* blends, which will result in the final reduction of the conductivity. That is the reason why the conductivity of the TPU/PANI blends prepared by solution blending method is two or three orders of magnitude lower in comparison with those prepared by the *in situ* polymerization.

CONCLUSIONS

The *p*-TSA/PA compound acid-doped TPU/PANI composites with both high conductivity and good processability are successfully prepared by the *in situ* polymerization. The conductivity of the *in situ* TPU/PANI is two orders of magnitude higher than those of the solution blending TPU/PANI. The *in situ* TPU/PANI with ANI content of 20 wt % has the best comprehensive properties. The prepared *in situ* TPU/PANI or TPU/PANI/LiBOB composites have potential applications in the processable conductive films, electronic devices, and lithium secondary batteries fields.

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