

# Molecular Composites Created by the Solution Blending of Polyaniline and Sulfonated Poly(Ether Sulfone)

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**ABSTRACT:** New conducting thermally stable blends of polyaniline (PANi) with sulfonated poly(ether sulfone) as a matrix were prepared by a solution-blending method. Camphorsulfonic acid (CSA) was used as a protonic agent for PANi. A sulfonyl group was introduced into the poly(ether sulfone) to enhance the coulomb interaction among the blends. The influence of the sulfonated group in poly(ether sulfone) was monitored with electrical property measurements. Ultraviolet-visible spectra of the blend compositions showed a well-developed polaron band. The compatibility of the blends, that is, hydrogen bonding and dispersion at the molecular level, was ascertained with X-ray diffraction

and Fourier transform infrared (FTIR) spectroscopy; these supported intermolecular interaction. A smooth and uniform morphology was observed in the blends. The electrical conductivity of the blends increased up to 14 S/cm with the protonation of the PANi complex with CSA, and the percolation threshold was found to be 2 wt % PANi. These new blends showed increases in conductivity and compatibility over other PANi-poly(ether sulfone) blends. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1138–1144, 2011

**Key words:** amorphous; blends; composites; conducting polymers; dispersions

## INTRODUCTION

Polyaniline (PANi) is used in many applications, including capacitors,<sup>1</sup> electrochromic displays,<sup>2</sup> batteries,<sup>3</sup> and field effect transistors.<sup>4</sup> The easy preparation and environmental stability of this electronically conducting material makes it a favorable candidate for these applications. Despite these interesting applications, the difficulty of processing conducting polymers by the usual methods of the polymer industry (extrusion, injection molding, lamination, etc.) restricts their large-scale use. Thus, several researchers have studied the possibility of synthesizing thermally processable conducting polymers.<sup>5,6</sup> Sulfonic acids, such as dodecyl benzene sulfonic acid and camphorsulfonic acid (CSA), have been used to obtain conductive PANi. Heeger et al.<sup>7</sup> reported the use of functionalized proton acid to dope PANi and to render the resulting PANi com-

plex soluble in common organic solvents in its conducting form. The functional group was judiciously chosen to be compatible with nonpolar or weakly polar organic solvents. The PANi conductivity properties are a function of not only of the degree of protonation and oxidation but also structural and conformational factors. The functionalized counter ions act as surfactants, which enable intimate mixing of PANi in a variety of bulk polymers in its conductive form. This means that one of the important tasks in PANi synthetic chemistry is the development of technological methods that lead to conducting blends containing doped PANi with the best combination of these parameters. These properties should match with other requirements for the end-use applications.

The technology of producing a polymer mixture has become a very important technique for obtaining new materials. Through the combination of conventional polymers with specialty polymers in recent decades, this mixing method has been more frequently used by the polymer industry than by those in research and development on new polymeric materials. The aim of making these blends, historically known as *polymer alloys*, is the synergistic combination of the properties. The field of producing conducting blends by the mixture of conducting and insulating polymers has been widely studied.<sup>8</sup> The main objective of our study was the preparation of polymeric materials with good thermal stability and

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processability with the retention of the electrically conductive properties of the PANi/dopant systems. The problems associated with these PANi materials are their intramolecular or intermolecular interactions, which lead to multiple aggregates. The resulting blend has no dispersion at a molecular scale, and the PANi remains aggregated; this prevents the dopant from being able to dope all regions of the PANi molecules uniformly. If these aggregates are disrupted by blending, the PANi molecules will be more effectively doped when they make contact with a dopant.

In this study, we developed a novel concept where dopants were directly linked to the rigid matrix polymer. We expected the motions of the PANi chains to be decoupled from each other, which would improve the aggregating problems and the interfacial segregation of the conducting chains from the matrix polymers. Thus, we decided to prepare molecular composites by introducing sulfonyl groups into the matrix polymer. In this fashion, the material was revealed to be more homogeneous, and it exhibited better conductive properties with thermal stability. To our knowledge, very few reports have been made on PANi blends with a sulfonated polymer matrix.<sup>9,10</sup> We used the solution-blending technique in this study. It has many advantages<sup>8</sup>: (1) it is very simple and easy to process, (2) dispersion at the molecular level can be achieved, (3) it needs much less time, and (4) it is economic. No reports have yet been made on this type of study.

## EXPERIMENTAL

### Materials

Ammonium per sulfate, hydrochloric acid, *m*-cresol, aniline, *N*-methyl-2-pyrrolidone, and CSA were commercial products and were purchased from Aldrich.

### Preparation of PANi [emeraldine base (EB)] and sulfonated poly(ether sulfone) (SPES)

SPES was synthesized in the laboratory.<sup>11</sup> PANi (EB) was prepared according to the procedure of Lee et al.<sup>12</sup>

### Preparation of the PANi (EB)–CSA/SPES blend

In a typical procedure, various amounts of SPES (between 0.98 to 0.75 g) were dissolved in 15 mL of *N*-methyl-2-pyrrolidone. The fine powder of an EB–CSA mixture (0.2–0.25 g) was stirred very well in 15 mL of *m*-cresol at room temperature for 24 h. Each EB–CSA solution was then transferred into a PES solution. These compositions were again agitated for 24 h. Each mixture was then homogenized at 13000

rpm with a homogenizer for 9 min. After homogenization, each composition was again agitated for another 24 h to maintain uniformity among the blends. Each composition was filtered through a Whatman 2.7- $\mu\text{m}$  filter. After filtration, we obtained free-standing films of the polyblends by casting the corresponding solutions on ultracleaned glass substrates. The solvent was evaporated at 50°C. Dark green blend films were formed with thicknesses of 25–45  $\mu\text{m}$ . *N*-Methyl-2-pyrrolidone–*m*-cresol (15/15 v/v) was maintained to form the aforementioned solution blends.

### Characterization

The ultraviolet–visible (UV–vis) absorption spectra [UV–vis/near-infrared (NIR) V-570 apparatus; Jasco] of the blend compositions were recorded in *m*-cresol. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 6700 spectrophotometer. Wide-angle X-ray scattering patterns were taken in the scattering-angle range 2–50° with  $2\theta$  varied at 5°/min with a Rigaku D/Max 2500V/PC instrument. Thermogravimetric analysis (TGA) was obtained on a TGA Q50 instrument under nitrogen at heating rate of 10°C/min from 25 to 800°C. We calculated the sulfonyl group substitution to poly(ether sulfone) through derivative thermogravimetric curves considering that the weight loss before 600°C of the SPES derivatives was related to the substituted groups; it was found to be 37% sulfonation.<sup>13</sup> Morphological aspects of the blend compositions film were evaluated by scanning electron microscopy (SEM; JEOL JSM-6380).

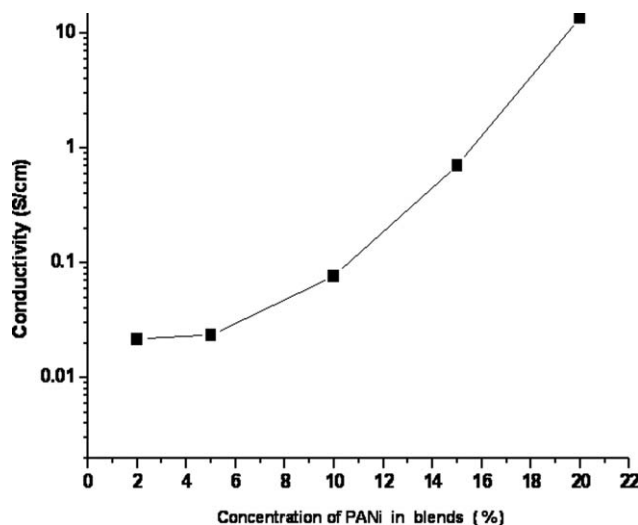
### Electrical properties (four-line probe)

The electrical conductivities of the blend films were measured with a four line probe<sup>14</sup> (Keithley 237 electrometer). The connectivity of the film with probe was maintained with four gold wires by carbon pasting. An electrical current was applied between the external terminals, and the voltage was measured between the two internal terminals. The measurements were performed at ambient temperature.

## RESULTS AND DISCUSSION

### Conductivity measurements

Figure 1 illustrates the conductivity versus the PANi compositions in the blend films. The conductivity was improved as the concentration of PANi in the blend increased. The highest conductivity was achieved in the blend with 20 wt % PANi (14S/cm). This higher conductivity was due to the SPES sulfonic groups interacting with the nitrogen atoms of



**Figure 1** Compositional variation of the conductivity under ambient conditions for the PANi/SPES solution blends.

PANi; this favored their partial protonation. The effect of partial protonation was further investigated in the blend films. In our previous study of PANi blends with poly(ether sulfone), we observed that 25 wt % PANi blends showed conductivities of up to 0.70 S/cm. A rise in the conductivity in this blend was due to partial protonation.

The percolation threshold was observed at 2 wt % PANi in the blends.<sup>15–16</sup> The conductor transition was very sharp. The uniform PANi dispersion was responsible for the sharp transition. This behavior revealed that a more homogeneous blend was obtained when we increased the energy input of stirring during the solution processing. The conductivity of the blends reached high values when the PANi concentration was increased in the blends. The PANi phase migrated preferentially to the SPES solution and above the percolation threshold. A low percolation threshold and a high conductivity at lower concentrations of PANi were the characteristic features of this system. The good homogeneity and the higher conductivity obtained by this method were attributed to effective protonation of the imine nitrogens. The processing methods, such as agitation and homogenization, played a crucial role in improving the conductivity and homogeneity and in obtaining a low percolation threshold.

### Thermal stability and conductivity

The electrical conductivity of the blend compositions was evaluated after we measured the resistance of the blend at room temperature. The thermal stability was also measured. The thermal resistance was also noted after heat treatment. We carried out these

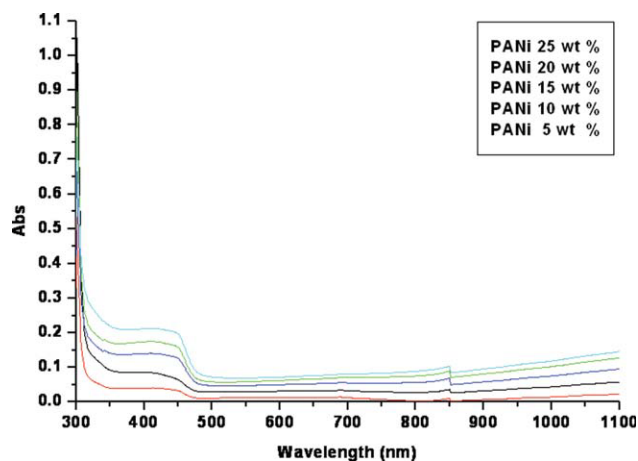
measurements by depositing each blend composition solution on a gold electrode fixed on a plastic substrate. It was dried thoroughly on hot plate at 50°C. We measured the resistance of the blend compositions by keeping the sample for 10 min at 50 and 120°C. The measurement of the resistance readings continued for up to nine cycles. The results indicate that the thermal stability increased with increasing concentration of PANi in the blends. This indicated intramolecular–intermolecular charge transport within the blend.

### UV–vis spectroscopy

UV–vis absorption spectra of the PANi/SPES blends were measured. All of the compositions were prepared in *m*-cresol. The spectrum of PANi/SPES is shown in Figure 2. Absorption peaks were observed in the range 250–1100 nm; these showed the increase in the concentration of PANi in the blends. Each blend composition showed a characteristic peak at 440 nm, which corresponded to the localized polaron to  $\pi^*$  band. Particularly, the band starting from 600 nm and extending into the NIR region was related to the doping level and formation of polarons of the conducting form, that is, a well-developed polaron band; the blending of PANi with SPES seemed to be involved in important modifications to expand the coil formation. No significant effects of the variation of the composition of the polymers, such as on the molecular weight or polydispersity, of the SPES on the spectra were observed. This was in good agreement with the results in previous reports.<sup>17,18</sup>

### FTIR spectroscopy

The results of the FTIR spectra of SPES and the blend compositions are shown in Figure 3. The



**Figure 2** UV–vis spectra of the PANi/SPES blends. The concentration of PANi (5–20%) was varied in the blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

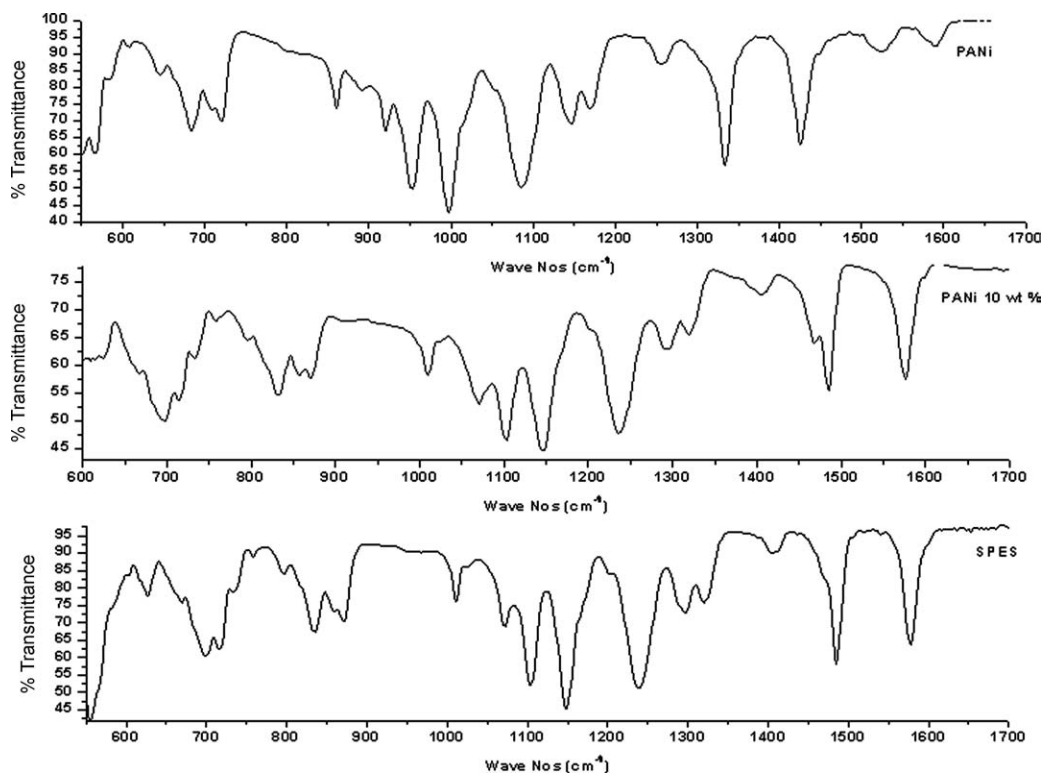


Figure 3 FTIR spectra of the PANi/SPES blends.

typical vibrational frequencies of SPES, such as for  $\text{SO}_3\text{H}$ ,<sup>9,10,19</sup> appeared at 1250–1150 and 1060–1030  $\text{cm}^{-1}$ . The strong band of the frequency, 1250–1150  $\text{cm}^{-1}$ , was ascribed to stretching vibration for  $\text{S}=\text{O}$ . The absorption band at 1060–1030  $\text{cm}^{-1}$  was assigned to the symmetric stretching band. All of the characteristic peaks of pristine PANi were observed in the PANi/SPES blends. The presence of two bands around 1580 and 1425  $\text{cm}^{-1}$  was assigned to the nonsymmetrical benzene ring stretching mode (ring stretching in the quinoid and benzenoid units, respectively). The peaks around 1252 and 1340  $\text{cm}^{-1}$  were due to the aromatic amine nitrogen ( $\text{C}-\text{N}$  stretching vibration) for doped PANi, associated with the oxidation or protonation states.<sup>20</sup> The peak around 1140  $\text{cm}^{-1}$  was assigned to the in-plane bending vibration of  $\text{C}-\text{H}$  ( $\text{N}-\text{Q}-\text{N}$ ,  $\text{Q}-\text{N}+\text{H}-\text{B}$ , and  $\text{B}-\text{N}+\text{H}-\text{B}$  modes, where Q is a quinoid ring and B is a benzenoid ring), which should have occurred during the protonation. The small shift in the peak position and the intensity were due to the different dopant levels of the resulting PANi. We observed that the  $\text{S}=\text{O}$  peak in the blends was slightly shifted, and the same was observed for  $\text{SO}_3\text{H}$ . This clearly indicated that hydrogen bonding<sup>21,22</sup> took place in the sulfonyl group of SPES and the amine groups of PANi, shown in Figure 4; intermolecular interaction was observed in the blends. This confirmed the fact that PANi was dispersed as an interpenetrating network in the SPES matrix.

### Thermal properties

The thermal stability of PANi, SPES, and the blend compositions were studied by TGA. Figure 5 shows

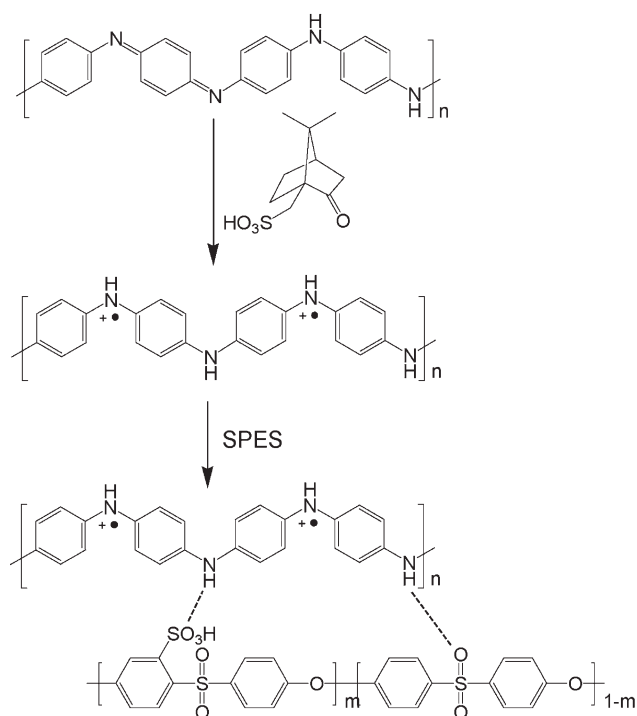
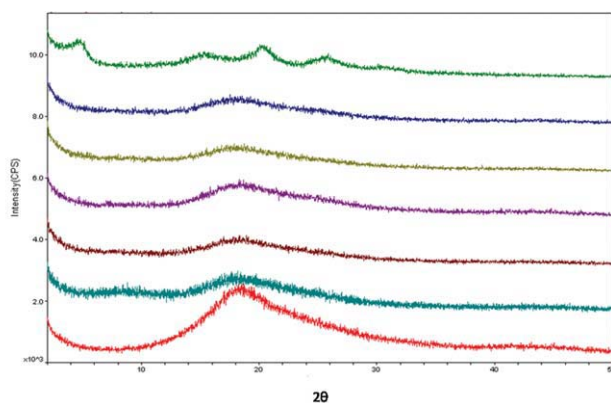


Figure 4 Hydrogen bonding in the PANi/SPES blends.





**Figure 5** XRD studies of the PANi/SPES blends: (a) SPES, (b) 5 wt % PANi, (c) 10 wt % PANi, (d) 15 wt % PANi, (e) 20 wt % PANi, (f) 25 wt % PANi, (g) 30 wt % PANi, and (h) PANi. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the weight loss and thermal stability in the blends. The interaction between the polymers was also noted from the degradation curves through the TGA studies. The TGA curve of pristine PANi showed a four-step weight loss. The first step in PANi at 100°C was due to the loss of water molecules. The second stage of decomposition started at 190°C and was assigned to the loss of solvent. The third weight loss, observed at 350°C, was assigned to dopant degradation, and further backbone degradation was observed. The TGA curve of SPES showed a three-step weight loss, and it well matched the reported data.<sup>11</sup>

The TGA curves of the blends (15 wt % and 25 wt % PANi) showed improvements in their thermal stability. The thermal stability of PANi and its blends can be altered by a protonating agent.<sup>23</sup>

Pristine PANi showed a 50% weight loss; after blending, the weight loss was reduced to 30%. As the concentration of PANi in the blend compositions increased, the weight loss decreased, and the thermal stability increased. A reduction in the weight loss indicated strong intramolecular and intermolecular interaction among the blend compositions. In these blends, the thermal stability was enhanced by the dopant CSA and SPES.

### X-ray diffraction (XRD)

The XRD patterns of the blend films are given in Figure 6. SPES showed an amorphous nature with amorphous peak at 19°. The crystalline peaks observed for pristine PANi were at 5, 15, 20, and 25°. As the concentration of PANi increased, there

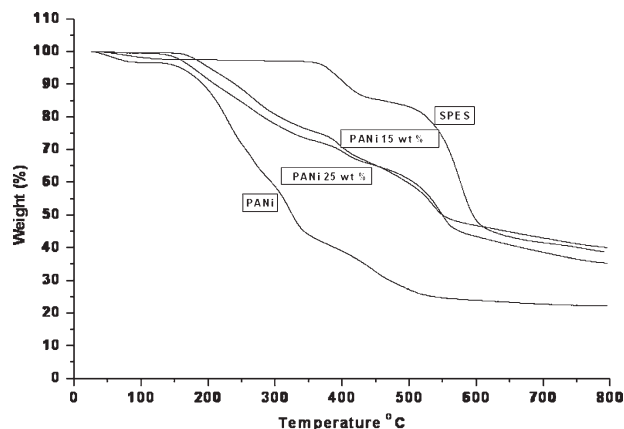
was a decrease in the intensity of the peaks. The relative intensity of certain diffraction pattern peaks changed significantly with the weight percentage of PANi when the compositions were compared with pure SPES at  $2\theta = 19^\circ$ . The crystallinity decreased with the addition of the PANi, and the peaks absolutely vanished (i.e., a nearly flat pattern was observed). Even 5 wt % PANi in the blends showed the same trend.

An interpenetrating network took place among the amorphous SPES and PANi.<sup>24</sup> This nature was a clear indication of the reduction in the crystalline phase in the polymer. No sharp peaks were observed, and the pattern clearly indicated a completely amorphous nature. These results clearly demonstrated the dominant presence of an amorphous phase in the blends.

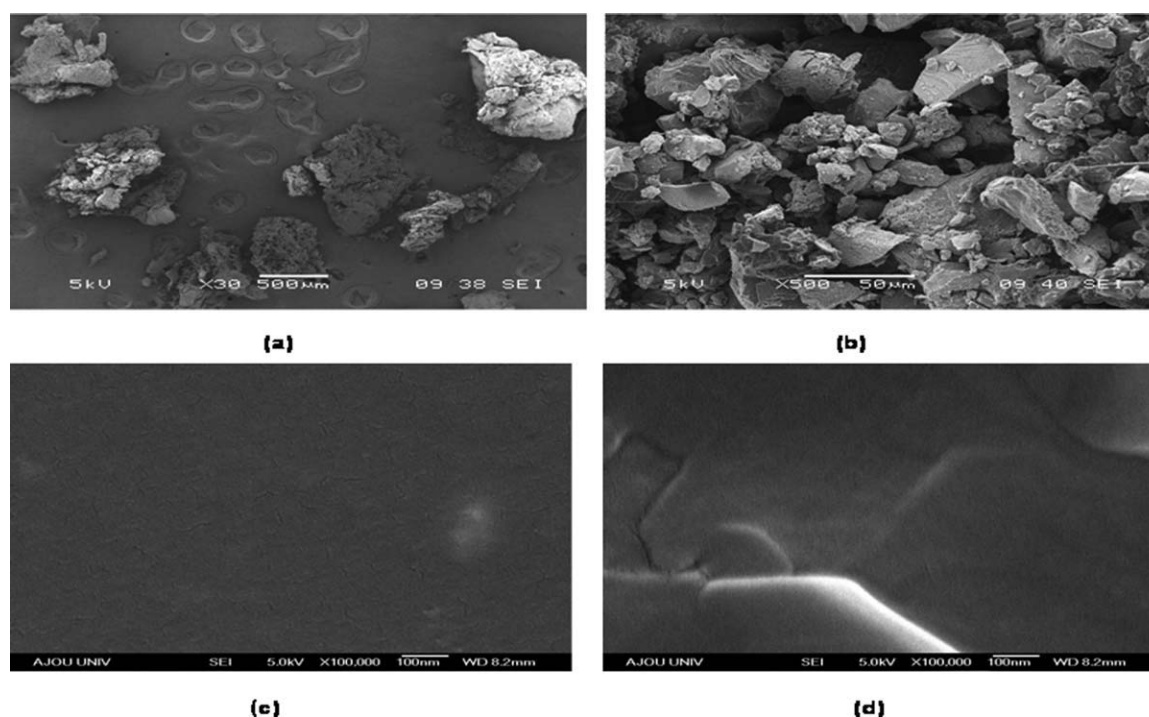
The crystallization process was also affected by the positive charge of PANi-doped macromolecules and their molecular mass, size, and nature of the doping agent.<sup>25</sup> Thus, the extent/absence of doping in PANi may have altered the degree of crystallinity in the blend and the size of the crystallites. This clearly showed that molecular composites, that is, dispersion at the molecular level, were achieved. This result also supports the interaction of PANi and SPES during the blend formation.

### Morphological features

The morphology of the SPES/PANi blends was studied. Micrographs of PANi, SPES, and blends with various percentages of PANi (10 and 25%) are shown in Figure 7. PANi and SPES showed various size granules, and semigranular structures were very apparent on the surface. However, the blend compositions exhibited a uniform morphology and indicated very intimate and uniform distribution of the two phases. Phase segregation was not observed. Some crystallites were observed in the 25% PANi micrograph; these may have been some traces of



**Figure 6** Thermograms of PANi, SPES, and the blends.



**Figure 7** SEM images showing the morphological properties of the PANi/SPES blends: (a) PANi, (b) SPES, (c) 10% PANi, and (d) 25% PANi.

CSA caused by the nonuniform crushing of EB-CSA or by resistive forces among the substituted sulfonyl groups and CSA. This highly uniform and smooth phase morphology of the PANi/SPES blends was a direct consequence of the mutual interaction between PANi and SPES in the solution blends, including the establishment of PANi/SPES hydrogen bonding.<sup>26</sup> Generally, PANi with insulating polymers shows two distinguished phases,<sup>27</sup> but the blends formed with this method showed a single phase and a continuous network structure.

### Blend studies

In these blends, the PANi and the SPES polymer played an important role in the structuring process. SPES dispersion did not affect the SPES/PANi interaction level or the associated electrical conductivity of the resulting blends. SPES as a matrix was chosen because it was thermally stable. The sulfonyl group substituted to the aromatic ring of poly(ether sulfone) acted as compatibilizer, coulomb interactions played crucial role in the blend films, and blends with very low weight percentages of PANi (2 and 5%) exhibited a dark green color. Most important was the hydrogen bonding occurring between the sulfonyl group and amine group in EB, which enhanced the compatibility and developed the conductivity in the blends. By proper selection of the functionalized doping acid, solvent, and insulating polymer, blends were made that possessed excellent

thermal and electrical properties. No reports have yet been made on this type of blend.

### CONCLUSIONS

This study addressed the development of novel blends of PANi mixed well in an SPES solution. The electrical conductivity of the blends was found to be 14 S/cm, and the percolation threshold was observed at as low as 2 wt % PANi. The blend compositions showed well-developed polaron bands with expanded coil formation, as determined by UV-vis spectra. The solution-cast blend films showed intermolecular-intramolecular interaction, as confirmed by FTIR spectra. Dispersion at the molecular level was investigated through XRD patterns. SEM micrographs confirmed a single-phase, homogeneous, uniform morphology. The addition of PANi to SPES made the system more polar and electrically conductive in nature and imparted thermal stability.

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