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ORIGINAL PAPER

Preparation of compatible polyaniline/polyethersulfone solution blends

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Abstract Thermally stable new conducting polymer blends of polyaniline/polyethersulfone were prepared by solution blending method in which *N*-methyl-2-pyrrolidone and *m*-cresol were used as solvent for polyaniline doped with camphorsulfonic acid, respectively. These blends show no phase separation with low percolation threshold (~ 2 wt% polyaniline) and well-developed polaron band. Scanning electron microscopy images of these blends exhibit uniform and smooth morphology. In these conducting blends electrical conductivity increased up to 0.7 S/cm.

Keywords Polyaniline-doped camphorsulfonic acid (PANi) · Polyethersulfone (PES) · Camphor sulfonic acid (CSA) · Solution blend

Introduction

Conducting polymers have attracted a great scientific and technological attention in the last years owing to their interesting electrical properties. These intrinsically conductive polymers (ICPs) find applications for their unique properties [1].

Polyaniline is considered as one of the unique member of conducting polymers because of its novel properties such as good stability and high conductivity. Doping is required for tailoring the electronic properties of conducting polymers. However, PANi has some limitations such as poor thermal stability, inherent brittleness, and does not have good mechanical properties [2]. To overcome this drawback it is often blended with a polymer having high thermal stability and mechanical properties. The proper selection of polymer matrix with a given doped PANi helps to create designed structuring in potentially useful blends.

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PANi blends are prepared by various techniques such as in situ [3], ex situ [4], and solution blending [5]. There are various types of blend methods [6] such as soluble matrix polymers and PANi doped by functionalized protonic acids (counter ion-induced processibility); undoped PANi with polymers soluble in amide or acidic solvents; soluble matrix polymers and substituted polyanilines; soluble ionic group substituted matrix polymers with undoped PANi. Naturally each of these methods has its own advantages and limitations. Specialty polymers mixed with PANi impart mechanical as well as thermal properties. Most importantly the processability is also developed in conducting polymers where as PANi imparts conductivity in it. Such blends found many applications in electronics [7–9].

In this study, intention behind selection of PES as matrix is because sulfonyl group of PES shows hydrogen bonding with amine group of PANi, thus compatibility can be achieved. Moreover, PES is thermally stable and possesses good mechanical properties. There were no reports available on solution blends of PANi/PES. This blend has found applications in semiconductor devices and in electromagnetic interference devices.

This article presents the studies in PANi/PES solution blends on the preferential interaction of PANi with one phase of PES (solvent–solvent interaction, dispersion at molecular level, good homogeneity, thermal stability, and conductivity in the blends with a low percolation threshold). Further FTIR and X-ray diffraction focuses on molecular composite formation.

Experimental

Materials

The PES used was purchased from Solvay Advanced Polymers, ammonium persulfate, hydrochloric acid, *m*-cresol, aniline, *N*-methyl-2-pyrrolidone (NMP), and camphor sulfonic acid were purchased from Aldrich.

Preparation of PANi (EB)

PANi (EB) is prepared by following the procedure of Lee et al. [10].

Doping procedure

CSA dopant was used for this experiment. Fine powder of EB–CSA mixture was taken in a 1:1.25 proportion and weighed (0.02–0.25 g) was stirred very well in 15 mL *m*-cresol at room temperature for 24 h. PANi in the emeraldine salt state was formed and further it was used in the blend preparation.

PANi (EB)–CSA/PES blend preparation

In a typical procedure various amounts of PES (between 0.98 and 0.75 g) were dissolved in 15 mL NMP.

Each EB–CSA solution was then transferred into PES solution. These compositions were agitated for 24 h. Each mixture was then homogenized at 13,000 rpm using 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 Whatman 2.7 μm filter. After filtration the free standing films of the polyblends were obtained by casting the corresponding solutions on ultra cleaned glass substrates. The solvent was evaporated at 50 °C. It was found that dark green color lustrous blend films were formed (with thickness of 25–45 μm).

Characterization

The UV–Vis absorption spectra (JASCO; V-570 UV/VIS/NIR) of the blend compositions were recorded in *m*-cresol. FTIR spectra were recorded by using NICOLET6700 spectrophotometer. Wide-angle X-ray scattering (WAXS) patterns in the range of scattering angles from 2° to 50° with the 2θ varied between 5°/min with a RiGaku D/MAX 2500V/PC. Morphological aspects of the blend films were evaluated by scanning electron microscopy (SEM) JEOL; JSM-6380.

Electrical conductivity (four line method)

The electrical conductivities of the blend films were measured by using a Keithley 237 electrometer four line probe technique [11]. The connectivity of the film with probe was maintained by using four gold wires by carbon pasting. An electrical current is applied between the external terminals and a voltage is measured between the two internal terminals. The measurements were performed at ambient temperature.

Results and discussion

To achieve more compatibility and conductivity in this solution blend, initially PES was tried to dissolve in *m*-cresol. As PES was not soluble in *m*-cresol it shows solubility in NMP.

These blend compositions have uniform dispersion, i.e., solvent molecules of NMP easily dispersed in *m*-cresol and showed no phase separation. PANi in the blend compositions were chosen up to 25 wt%. These blend films have better quality, flexibility, exhibit uniformity, and homogeneity. Further increase in PANi concentration is avoided because blend films develop brittleness [12].

Electrical conductivity of the blends

Figure 1 shows the influence of PANi contents on electrical conductivity of PANi/PES blends. The percolation curve profile of the blends was characterized by a sharp insulator–conductor transition which occurred at a relatively low amount of PANi inside the polymer matrix. The estimated percolation threshold was found to be in the range of 2 wt%. This threshold is similar to that found in the literature for other

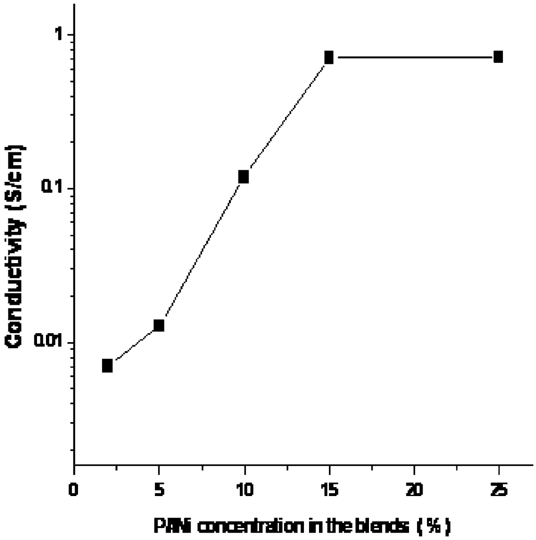

Fig. 1 Electrical conductivity at ambient condition for PANi/PES solution blends as a function of compositional variation

blends of PANi with common polymers [13–16]. Therefore, the relatively low percolation threshold indicated that the two classes of polymers (PANi and PES) had interactions and compatibility.

Percolation behavior depends upon blend preparation method. The low value of percolation threshold which was found for this blend suggested uniform dispersion and showed intermolecular interaction among the blends. It clearly appears that processing conditions dramatically influence on the percolation thresholds. The time of agitation of PANi before and after blending, rotating speed, and homogenization gives rise to an effective conducting pathway with lower amount of PANi over the film. This also suggests that EB–CSA dispersed in *m*-cresol and forms clear dark green solution with no traces of EB–CSA at the bottom. Leyva et al. [14] found that blends prepared in solution by magnetic stirring displayed a higher conductivity than those obtained by sonication. Conformation of PANi in the blend strongly influences the jumps distance needed for delocalization of the charge carriers and as a consequence the conductivity of the blend and that the chain conformation of doped PANi is influenced by several factors such as chemical nature of the dopant, host polymer, and solvents [17]. The conductivity of the films prepared using *m*-cresol/NMP smoothly increases with an increase in the relative PANi content to 0.7 S/cm at 25 wt%. Thus, we can conclude that the PANi content, the dopant used, the host polymer used, and compatibility in the blends are the main factors defining the blend conductivity.

Spectral analyses

UV–Vis spectroscopy

Figure 2 shows UV–Vis spectra of PANi/PES solution blends. The nature of the spectra were observed by making solution of each blend composition in *m*-cresol as

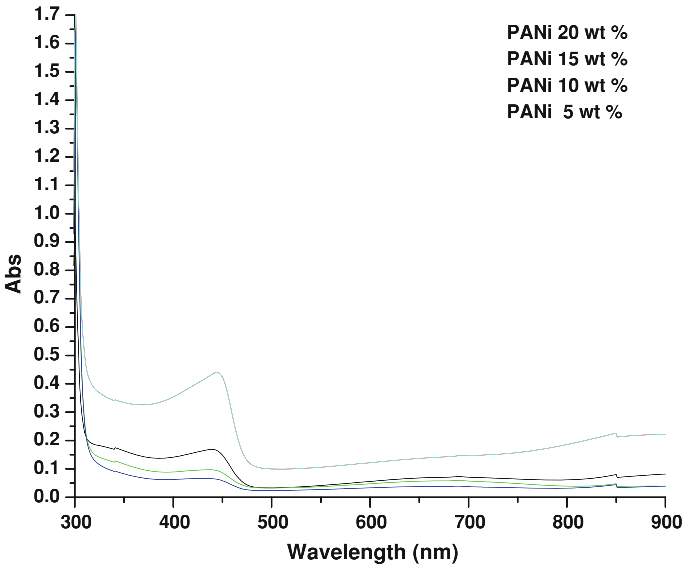

Fig. 2 UV–Vis spectra of PANi/PES blends with variation of PANi (5–20 wt%)

clear dark green solutions. This spectra show increasing concentration of PANi in the blends from the bottom to top (i.e., PANi 5–20 wt% PANi). The absorbance of blends increases with increasing concentration of PANi in the blends. All compositions show peak at 440 nm assigned, respectively, to π–$\pi*$ and polaron transitions show that blends are in conducting state [17]. All theses compositions show well-developed polaron band [18, 19]. The extended tail from 900-nm wavelength region indicates extended coil nature in the blend and may facilitate delocalization of electrons thus facilitate conductivity. The extended coil formation is observed mainly because of hydrogen bonding between sulfonyl group of PES and amine group of PANi. Ikkala [20] and Avlyanov et al. [21] explained the effect of EB–CSA in *m*-cresol extended conformation of PANi chains which leads to the improvement in solubility and conductivity. No significant effect of the ratio of the polymers on the spectra was observed.

FTIR spectroscopy

Figure 3 shows the typical FT-IR spectra of the blend films of PANi/PES ranging from 1,700 to 550 cm^{-1}. The characteristic bands derived from the conducting emeraldine salt state of PANi were observed in PANi/PES blends. The presence of the two bands around 1,580 and around 1,460 cm^{-1} is assigned to the non-symmetric benzene ring stretching mode (the ring stretching in quinoid and benzenoid units, respectively). The peaks observed at 1,240 and 1,300 cm^{-1} are due to the aromatic amine nitrogen (C–N stretching vibration) for doped PANi associated with the oxidation/protonation states [22]. According to Han and co-workers [23], a peak around 1,120 cm^{-1} can be assigned to in-plane-bending

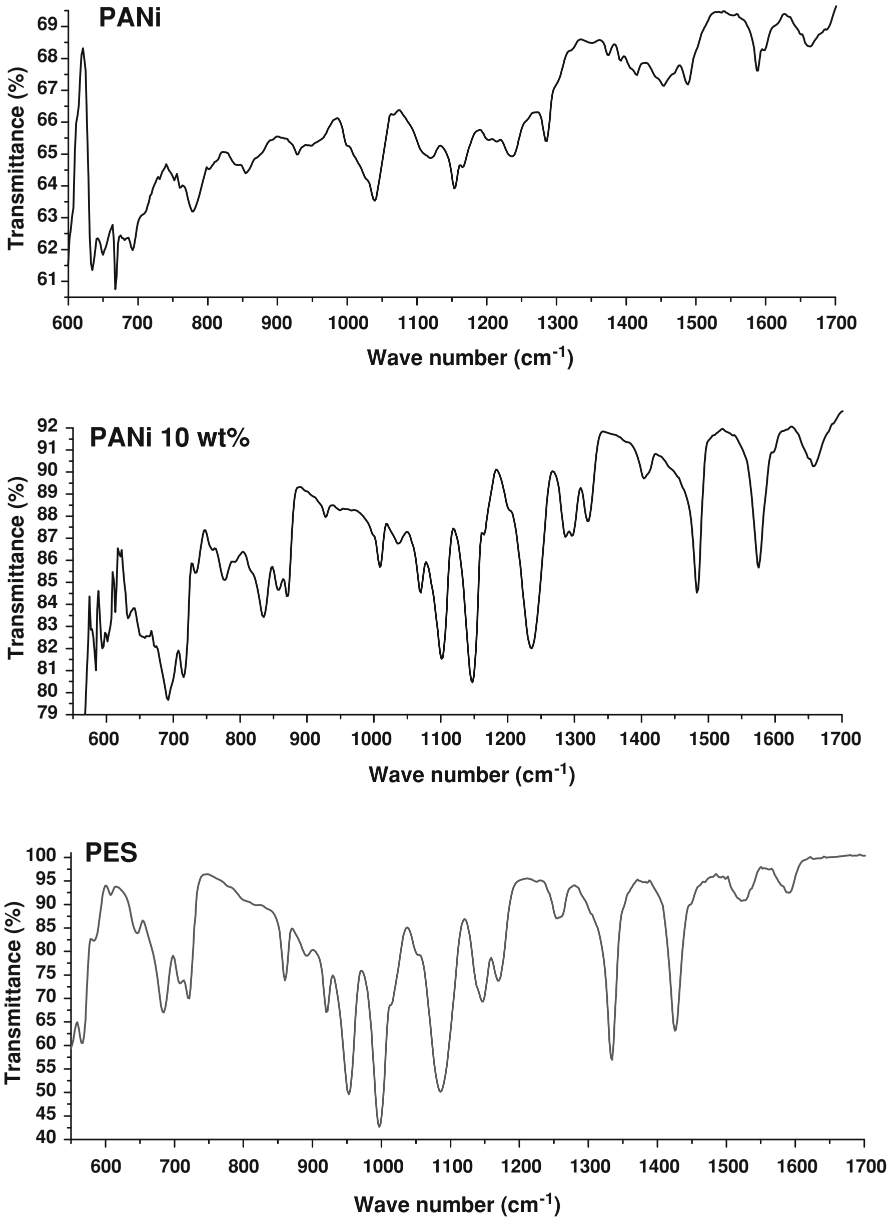

Fig. 3 FTIR spectra of PANi/PES blends

vibration of C–H (mode of N Q N, Q N+H–B and B–N+H–B; Q = quinoid ring, B = benzenoid ring) which should occur during the protonation. The small shift in the peak position and the intensity owing to the different dopant levels of the resulting PANi. Infrared absorption band at 1,150 cm^{-1} is attributed to the S=O stretch of PES. There is a slight shift observed for the peak position in the spectra of PANI/PES. This is because of intimate interaction among the PANi and PES. Yamada et al. [24] reported that such type of interaction observed in PANi blend with poly(methyl methacrylate-*co*-methacrylic acid) and poly(1-vinylpyrrolidone-*co*-acrylic acid). Also for PANI/PVA composites [25] benzenoid and quinoid absorption bands of PANi are significantly shifted to higher wave numbers for blends as a result of hydrogen bonding.

Therefore, there were obvious interactions between PANi and PES and those results support the fact that PANi and PES were compatible. The compatibility made the PANi/PES blends combine in a synergistic matter and so the mechanical properties of PANi increased via blending with PES.

X-Ray diffraction studies

The XRD of PANi

PES (Fig. 4) of various compositions of the blend films are presented in the range of 2°–50°. PES is amorphous polymer with aromatic and heterocyclic rings in its backbone and it is responsible for the low chain mobility and increases the polymer thermostability. Moreover, it develops compatibility with PANi. As the composition of PANi increases there is a decrease in the intensity of the peaks observed in

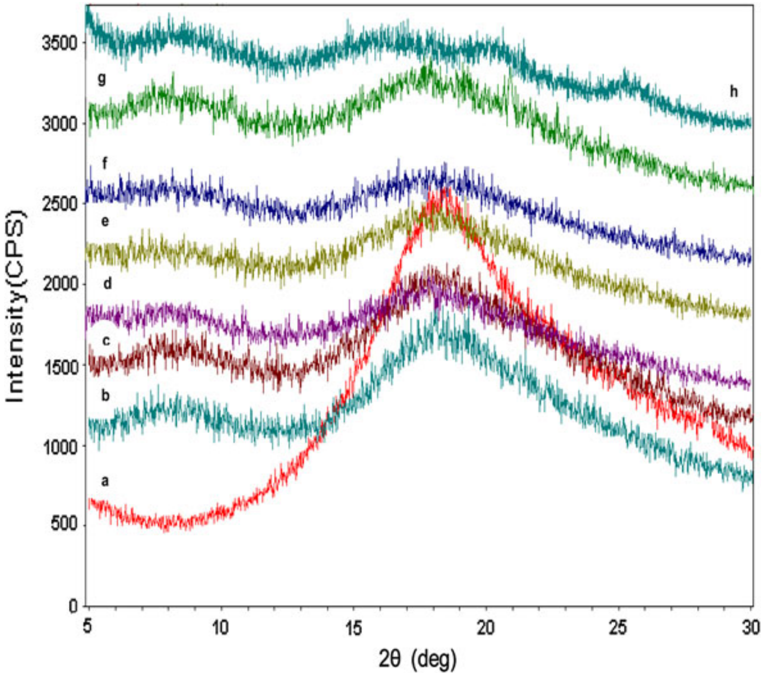

Fig. 4 X-Ray diffraction studies of PANi/PES blends (*a*) PES, (*b*) PANi 5 wt%, (*c*) PANi 10 wt%, (*d*) PANi 15 wt%, (*e*) PANi 20 wt%, (*f*) PANi 25 wt%, (*g*) PANi 30 wt% , and (*h*) PANi

pristine PANi at 15°, 20°, and 25° and is almost disappeared in blends and further it is almost flat. No sharp peaks were observed and the pattern clearly indicates a completely amorphous nature. It is a clear indication of physico-chemical interaction in the blends [26, 27] and there is no phase separation occurred. This shows that sulfonyl group of PES and amine group in PANi forms hydrogen bonding and ascertain molecular miscibility.

Morphological properties

Conductivity–morphology relationship

The blend morphology was studied to elucidate the structure responsible for the electrical conductivity behavior. Figure 5 shows SEM images of PANi, PES, and blend compositions. PANi shows granular and flake type morphology whereas PES shows thick layers. Uniform morphology is observed as the concentration of PANi increased in the blend. The phase morphology of PANI/PES content indicated a very intimate and uniform distribution of the two phases without any significant phase separation. This highly uniform phase morphology of the PANI/PES solution blends is a direct consequence of a mutual interaction between PANi and PES. Blend presents good homogeneity with more fine PANi molecules distributed throughout the PES matrix. Such compatibility promotes a better interaction between PES and EB–CSA. Pron et al. [28] reported that significant numbers of grain clusters or agglomeration led to an increase in the value of the percolation threshold and that the good dispersion of aggregated grains was a key factor in obtaining a low percolation threshold. In this study, the obtained percolation threshold value was ~2 wt% PANi and this result indicated that both the type of

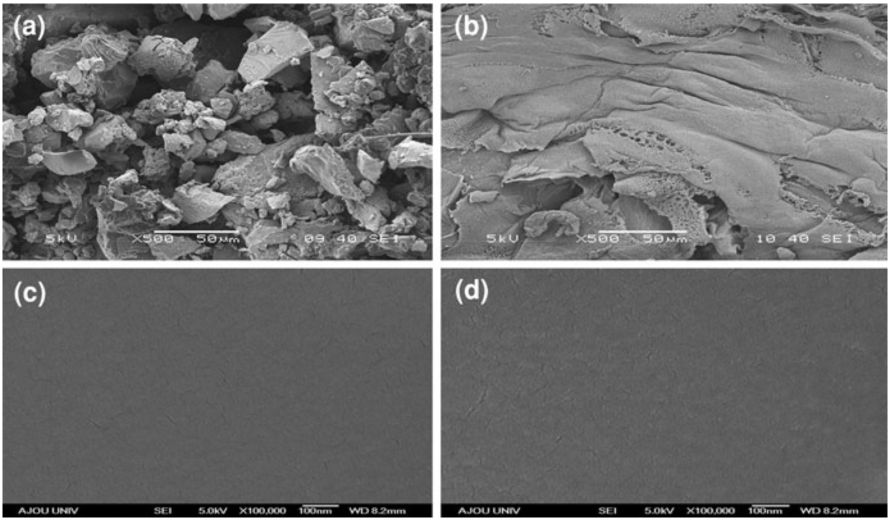

Fig. 5 SEM images of PANi/PES blends **a** PANi, **b** PES, **c** 10 wt% PANi, and **d** 25 wt% PANi

morphology and the sphere size of the polymer were decisive factors for high conductivity or low percolation thresholds because the smaller the spheres were the easier it was to make conducting paths of PANi [28].

The different electrical conductivity values observed for the blend formulations are directly related to the morphology and conductivity values of the doped PANi [15, 29].

Conclusions

PANi/PES solution blend was thoroughly characterized with various techniques and studied in detail using electrical conductivity measurements. Percolation threshold was observed at lower concentration of PANi (2 wt%) and blend compositions exhibit higher conductivity. UV–Vis spectra of the blends show well-developed polaron band. It shows the trend of molecular composite moreover these blends exhibit uniform morphology hence forming a conductivity phase in it. The above results aid an understanding of the extremely high interaction level, i.e., dispersion at molecular level in the blends confirmed by FTIR spectroscopy.

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