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Conductive blends of dodecylbenzene sulfonic acid-doped polyaniline with poly (vinyl pyrrolidone)

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Conducting composites of Poly (vinyl pyrrolidone) (PVP) and dodecylbenzene sulfonic acid doped polyaniline (PANI-DBSA) were prepared by solution casting. Electrical properties of the blends were characterized by means of electrical conductivity measurements. Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were used to investigate the hydrogen bonding and miscibility behavior of the blend. It was found that the electrical conductivity of the composites was increased with the increase of PANI-DBSA content and the percolation threshold was around 10 wt %. The formation of the hydrogen bonding between PVP and PANI-DBSA was identified by the FTIR spectra.

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Keywords: Poly (vinyl pyrrolidone), Polyaniline, Blend, Conductivity

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1. Introduction

In recent years, intrinsic electrically conductive polymers (ICP) have been studied enthusiastically because of their potential application in light-emitting diodes, batteries, electromagnetic shielding, antistatic coating, gas sensors and activators. However, the major drawback of these polymers is the difficult in processibility, in the doped i.e., conducting state which frequently impedes their blending with industrial polymers. Such blends are of great technological importance because they combine good mechanical properties of the conventional insulating polymers with electrical properties of the conducting ones. “All polymers” conductive materials frequently offer better properties than conductive composites containing inorganic conductive phase like carbon black or metal particles, especially if their percolation threshold is considered.

Polyaniline (PANI) is one of the most intensively investigated ICPs due to its environmental stability, low cost of raw material and ease of synthesis [1]. However, as other ICPs, PANI is insoluble, infusible and non-processable, which retard its potential applications.

In order to improve the processability of PANI, numbers of methods have been studied, of which the most widely adopted strategy is to dope PANI with organic acids with long alkyl chain such as camphor sulfuric acid (CSA) or dodecylbenzene sulfonic acid (DBSA), with the bulk non-polar tail renders the polyanilines in conducting form to be soluble in some ordinary organic solvent such as m-cresol, chloroform and xylene [2.3]. Therefore, such doped PANI can be solution processed together with common insulating polymers in proper solvent. As a matter of fact, solution blending of PANI doped by camphor sulfonic acid (PANI-CSA) with polar polymer matrixes, such as PMMA [4-6], PA [7] and PANI doped by DBSA (PANI-DBSA) with PS [8], EPDM [9], PVC [10], PI [11] and SEBS [12, 13] have been report.

Poly (vinyl pyrrolidone) (PVP) because of its outstanding absorption and complexes abilities is very useful in pharmacy and medicine [14, 15], PVP is used for the preparation of synthetic plasmas, to creations of hydrogels by radiation methods and to creations of thromboresistion hydrophilic gels [16]. In our study, the conductive complex PANI-DBSA was prepared by a method known as “emulsion polymerization”, where the DBSA as a surfactant and a protonating agent for the resulting electrically conducting polyaniline. The composite films were obtained by casting the solution in which PANI-DBSA and PVP were dissolved in chloroform. The resultant films showed higher conductivity at low PANI-DBSA loading, compared with other blends. The structural characteristics and morphology of the PANI-DBSA/PVP composites were investigated.

2. Experimental

Synthesis of PANI-DBSA

The emulsion polymerization of aniline was performed by a procedure described in literature [17]. In a typical polymerization, a solution of 4.65ml (0.05mol) of aniline and 24.5g (0.075mol) of DBSA and chloroform was prepared in a 250ml Erlenmeyer flask under stirring. The medium was kept at 0°C and an aqueous solution containing 4.68g (0.02mol) ammonium peroxide sulfate (APS) in 20ml of water was slowly added .The total polymerization time was 24h. The polymerization was terminated by pouring the emulsion into acetone. The precipitate as a dark green powder was filtered, washed with acetone and dried under vacuum at room temperature.

Blend preparation

PANI-DBSA and PVP (supplied by from China Medicine (Group) Shanghai Chemical Reagent Corp) were dissolved in chloroform at room temperature until a homogeneous viscous solution was obtained, and PANI-DBSA/PVP blend films were prepared via the casting of blend solutions onto a glass substrate. The evaporation of chloroform was carried out at 40°C for about 72 h in a convection oven.

Characterization

Fourier transform infrared absorption spectra for the composite powder of the PANI-DBSA and PVP were taken with a Nicollet 20sx-B FT-IR spectrometer. The scanning ranged from 4000 cm^{-1} to 400 cm^{-1} with 16 times of scanning.

The glass transition temperatures of the blend was performed using a DSC from Du-Pont (DSC-9000) with scan rate of 20°C/min and temperature range 30-220 °C. The measurement was made using 5-10 mg sample on a DSC sample cell after the sample was quickly cooled to 30 °C from the melt of the first scan. The glass transition temperature was obtained as the inflection point of the jump heat capacity with scan rate of 20 °C/min and temperature range 30-220 °C.

Thermogravimetric analysis (TGA) thermograms were obtained by using a Perkin-Elmer TGA-7 in a dry nitrogen atmosphere. All the blends were heated at 20 /min form 25 to 550 . The temperature at which an abrupt decrease in sample weight occurred was designated as the decomposition temperature.

Electrical conductivity of the blends was measure by the usual four-probe method, doing five measurements in three different samples of each composition, the standard deviation being always less than 1%.

Optical micrographs of the prepared blend films were obtained at magnification of 500 using Olympus Bx61 microscope.

3. Results and discussion

Theoretically, PANI has the potential to form hydrogen bonds with carbonyl polymers. Because of H-donating in imine groups, PANI has been found to be compatible or partially compatible with some polymer counterparts [18, 19]. FTIR has been the method of choice to probe the nature and extent of interactions in polymer blends. The premise of using an IR to study polymer blends is that the mixing of two components at the molecular level will cause changes in the oscillating dipole of the molecules. This will manifest itself as changes in the frequency and bandwidth of interacting groups in the spectrum. If the PANI-DBSA and PVP interact, then the functional groups in the FTIR spectra will show band shifts compared to the spectra of the pure PANI-DBSA and PVP.

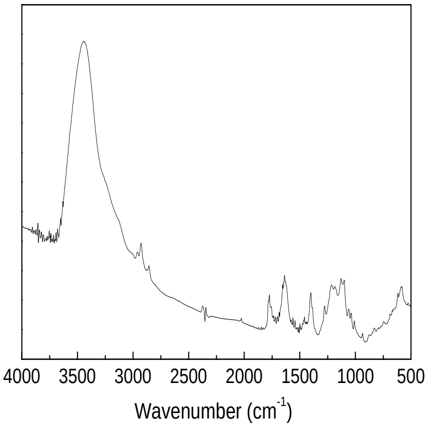


Fig. 1. FTIR spectrum of PANI-DBSA.

The infrared spectrum of pure PANI-DBSA is shown in Fig. 1. The spectrum of PANI-DBSA cast film has characteristic absorptions at 3447 cm^{-1} (=N-H stretching), 1559 cm-1 (N=quinoid=N), 1478 cm^{-1} (N=benzoid=N), 1295 cm^{-1} (quinoid=N-benzoid), 1240 cm-1 (C aromatic-N stretching) and 1030 cm $^{-1}$ (S=O stretching).

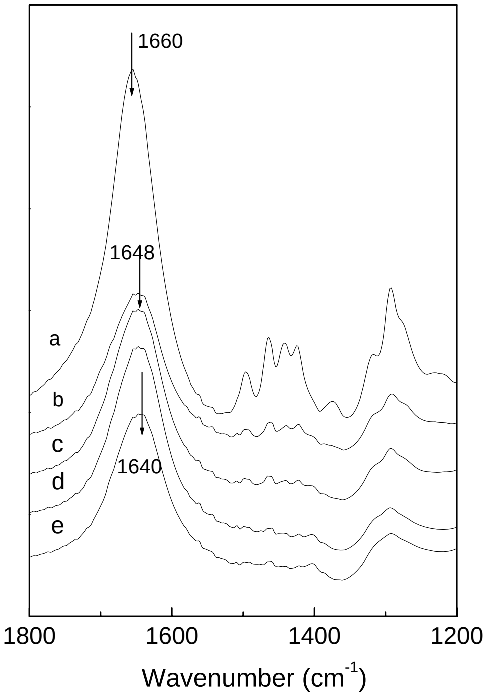


Fig. 2. FTIR spectrum of PANI-DBSA/PVP blends: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40 wt% of PANI-DBSA.

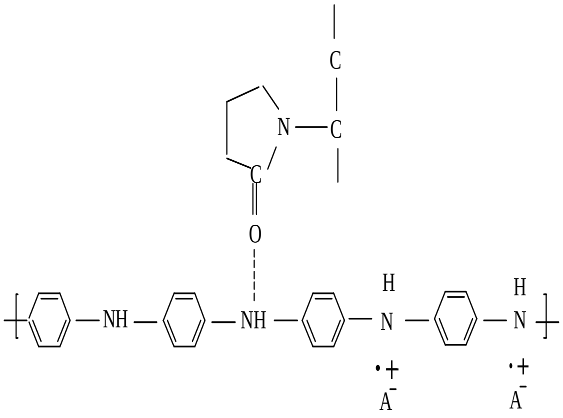


Fig. 3. Scheme of the hydrogen bonding between PANI-DBSA and PVP.

With respect to the nature of interaction between PANI-DBSA and PVP, it is assumed that the hydrogen bonding occurs due to the fact that the hydrogen atoms of PANI-DBSA possess acidity and the oxygen atoms of PVP offer electro negativity. A comparison FTIR spectrum of pristine PVP and PANI-DBSA/PVP blends clearly shows the occurrence of the hydrogen bonding (Fig. 2). The carbonyl stretching absorption band of PVP which locating at 1660 cm^{-1} shift to lower frequencies by up to 20 cm^{-1} with the increase in the content of PANI-DBSA. This observation can be interpreted by the effect of forming hydrogen bonding between the carbonyl group and the imines group (Fig. 3).

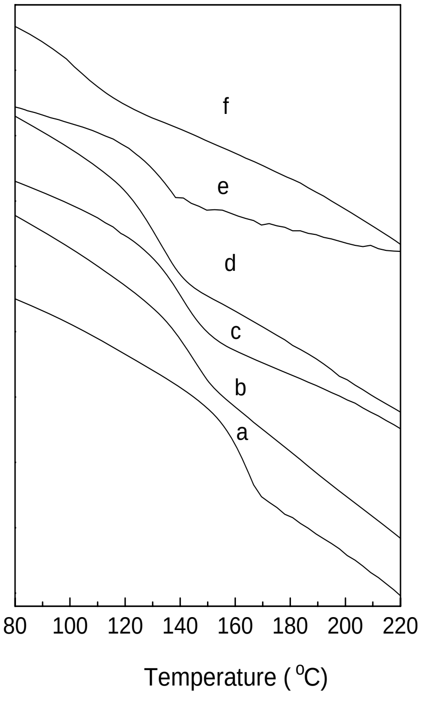


Fig. 4. DSC thermograms of PANI-DBSA/PVP blends: (a) 100, (b) 90, (c) 80, (d) 70, (e) 60, (f) 50 wt% PVP.

Doped PANI, such as PANI-HCl, does not show any glass transition temperature. However, when doped with a long alkyl chain acid, such as DBSA, CSA, the resultant doped PANI exhibits the T_g that could be detected at low temperature. Long alkyl chains suspended in the backbone of PANI act as plastisers and make PANI segment have motion at low temperature. So it should be easy to understand that the T_g of PANI-DBSA is dependent on the DBSA concentration. Ikkala et al [20] found that the Tg values of PANI-DBSA could vary from 65 ºC to 130 ºC as the long alkyl chain acid content decrease.

The DSC analysis is one of the convenient methods to determine the miscibility in polymer blends. Fig. 4 shows the DSC thermograms of the PANI-DBSA/PVP blend with various compositions, revealing that all PANI-DBSA/PVP blends have only a single glass transition temperature.

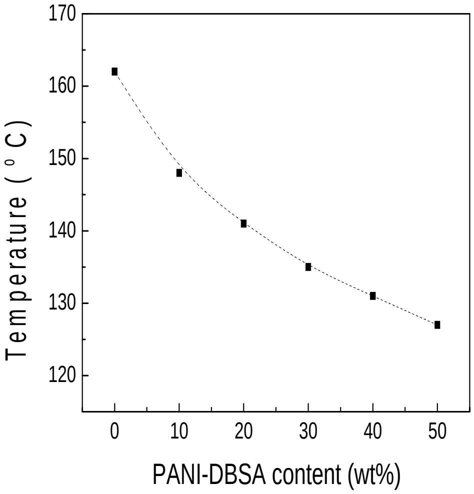
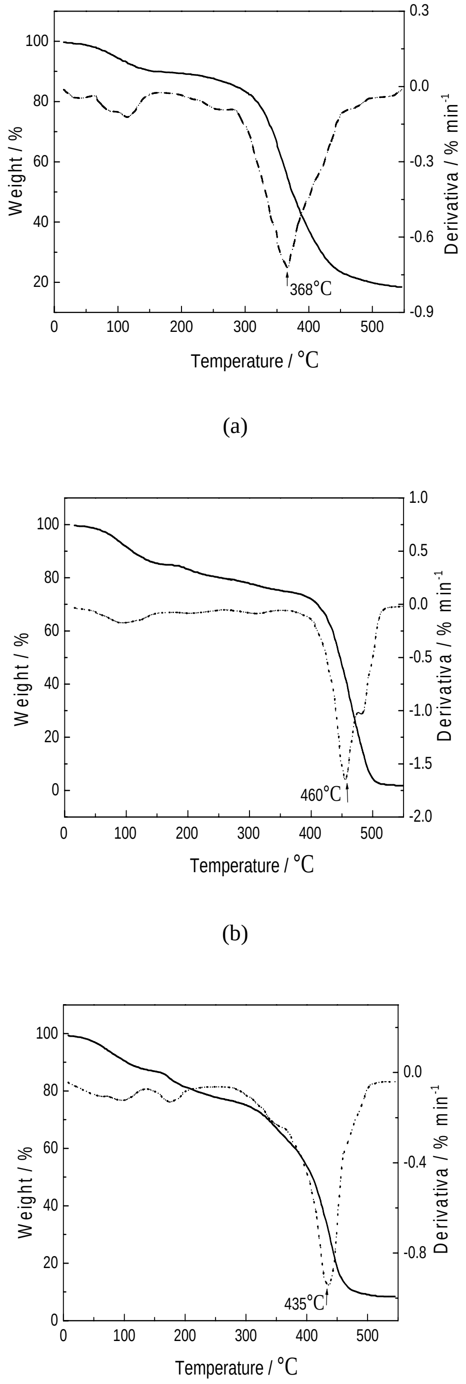


Fig. 5. Glass transition temperature of PVP and PANI-DBSA/PVP blends form DSC measurements.

The calculated mean T_g values for pure PVP and PANI-DBSA/PVP blends are shown in figure 5. The glass transition temperature of PVP is 162℃. PANI-DBSA/PVP blends have only a single glass transition temperature and gradually get low with increasement of PANI-DBSA content in the blends. Generally, the shift trend of Tg can be considered as the index of miscibility of polyblends. Thermodynamically speaking , hydrogen bonding among different components of polymer blends will make pronounced contribution to compatibilities, because it makes entropy change (H) negative, so leads to Gibbs free energy (G) lower upon mixing different components. Form this point of view it is now well understand that why there is only one T_g for PANI-DBSA/PVP blends. It is the hydrogen bonding that builds the interactions between the PANI-DBSA filler and the PVP matrix.



(a)

(b)

(c)

Fig. 6. TGA thermograms of (a) PANI-DBSA, (b) PVP, (c) PANI-DBSA/PVP blend with 50 wt% PANI-DBSA.

The TGA thermograms of PANI-DBSA, PVP, and PANI-DBSA/PVP blend with 50wt % PANI-DBSA are shown in Fig. 6. It is observed that the PANI-DBSA has much lower thermal stability than PVP. Therefore, the thermal stability of the PANI-DBSA/PVP blend with 50wt % PANI-DBSA is poor compared with PVP. Although decomposition temperature of the blend is lower than pure PVP but is much higher than PANI-DBSA. This indicates that hydrogen bonding between PANI-DBSA and PVP can stabilize PANI-DBSA. This suggests that the stronger interaction between polymers will increase the thermal stability.

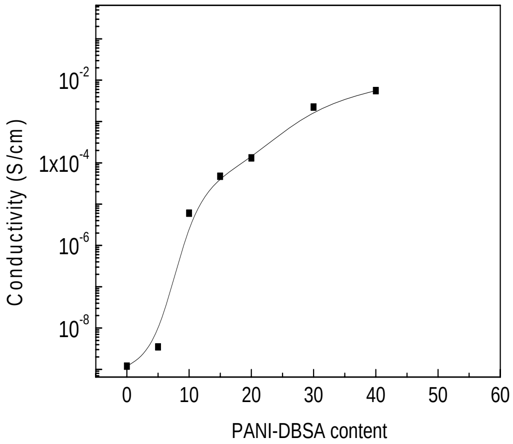


Fig. 7. Electrical conductivity of and PANI-DBSA/PVP as a function of PANI-DBSA content.

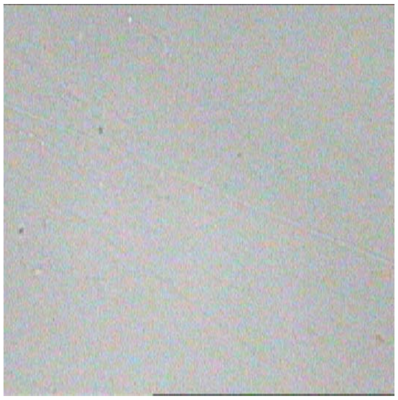
The composite films prepared by solution casting were from light green to dark green color with more introduction of PANI-DBSA. Conductivity values of various films are shown in Fig. 7. As we expected when the mass fraction of PANI-DBSA was 5% mass ratio, the conductivity increased from 10^{-9}S/cm of matrix polymer to 10^{-8}S/cm of the composites. If the PANI-DBSA was added to 5 % mass ratio, it was up to 10^{-4}S/cm .A sharp increase in conductivity expectedly takes place as the PANI-DBSA content initially increases from nearly 5 wt % to approximately 10wt%. Beyond 10 wt% PANI-DBSA, the conductivity slightly increased, reaching a value close to the values obtained for the pure conducting polymer.

This behavior can be divided into two regions. When the conductive PANI-DBSA phase is dispersed, the conductivity of the blend films is low. As the conductive PANI-DBSA phase is modified from dispersive to the continuous phase, the blend conductivity increases abruptly. This sharp increase in the conductivity of the PANI-DBSA/PVP blend films with the addition of PANI-DBSA may be due to the formation of more elongated and connected domains. Once the conductive component forms a continuous phase, the addition of more PANI-DBSA will has a small effect on the conductivity of the blend.

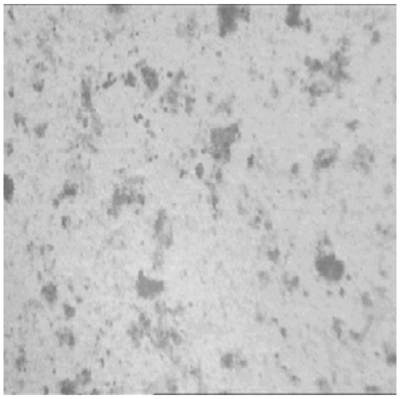
The low value of percolation threshold is an important factor in the preparation of the conductive blend of polyaniline and insulating polymer because the desired mechanical properties of the host polymer can be retained with a small weight of PANI. In general, the conductivity behavior of the blend films can be explained using the morphology of the conductive phase.

Fig. 8 show that optical micrographs of

PANI-DBSA/PVP blend films with different weight ratios of PANI-DBSA with a magnification of 200×. The bright region is related to PVP phase while the dark region to PANI-DBSA. The pure PVP image shows a regular smooth surface with granular structural. With the incorporation of PANI, the surface morphology is modified and the phase contrast is very distinct for the conductive PANI. With increasing the proportion of PANI-.DBSA, the area of the dark-colored region increases, as would be expected for a classical particulate composite with a metal or graphite filler rather than a polymer blend. There are also some large particles present even at fairly low loadings (e.g., 5 wt %). However, on the basis of the evidence as previously mentioned, we believe that there is significant miscibility between the polymers. The 5 wt% blends appear to contain isolated PANI-DBSA particles, and so should be well below the percolation threshold for conductivity; nevertheless it will be seen below that there is significant residual conductivity in these samples. As the loading is increased to 10 wt%, the PANI-DBSA clusters appear to be interconnected and form an interconnected network.



(a)



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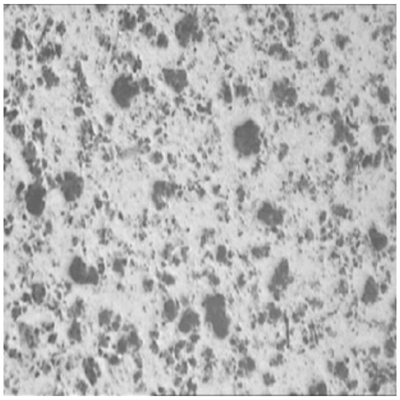

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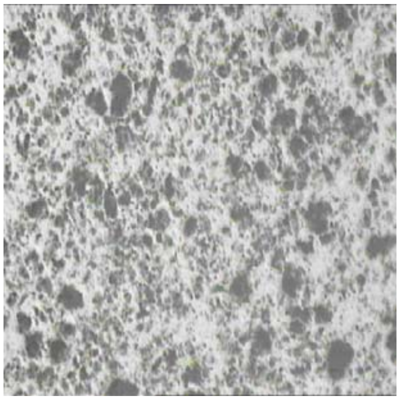

(d)

Fig. 8. Optical micrographs of PANI-DBSA/PVP blends including (a) 0 wt% PANI-DBSA, (b) 5 wt% PANI-DBSA,(c) 10 wt% PANI-DBSA, (d) 20 wt% PANI-DBSA (200×magnification).

4．Conclusions

Blends of polyaniline doped with dodecylbenzene sulfonic PVP were successfully prepared using cosolvent method. The percolation phenomenon was observed in the conductivity curves in these blend films. It was found that the electrical conductivity of the composites was increased with the increase of PANI-DBSA content and the percolation threshold was around 10wt %. DSC measurements showed that there was only one T_g for each blend and the values of T_g varied with the PANI-DBSA content. This implies that the PANI-DBSA/PVP blend is at least partially compatible. The formation of the hydrogen bonding between the carbonyl groups in PVP and the imines groups in PANI-DBSA was identified by the FTIR spectra.

Acknowledgements

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