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RESEARCH ARTICLE

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Preparation of PANI/PSF conductive composite films and their characteristic

Abstract Polyaniline (PANI)/polysulfone (PSF) composite films are successfully prepared by phase separation and one-step in-situ polymerization. It is found that the head-on face (in contact with solution) of the films is green while the back face is white. The chemical component and the surface morphology of both surfaces of the films are characterized by FT-IR spectra and SEM, respectively. The effect of the polymerization temperature, time and concentration of the reactants on the electrical properties of the films are discussed in details. The thermo-oxidative degradation of the films is studied by thermogravimetric analysis (TGA). The results indicate that the thermal stability of the PANI/PSF films is higher than that of the pure PSF film.

Keywords composite film, polyaniline/polysulfone, preparation, resistance

1 Introduction

In recent years, conductive polymers are being widely used in industries and experimental investigations due to their desirable properties. Among all kinds of the conductive polymers, polyaniline has attracted much attention due to its low cost, easy of fabrication, good environmental stability, chemical stability and good electrical conductivity [1–3]. However, its processability to make either films or coated layers is rather difficult because it is infusible and insoluble in common solvents, which is restricted to a practical application [4–5]. In order to improve its processability, much attention has been paid to feasible methods for preparing the composite of polyaniline and processable polymers. Solution processability of PANI has been performed by doping PANI with appropriately functional sulfonic and phosphonic acids as well as phosphoric acid diester [6–9]. Accordingly, many workers have prepared PAn composite films with polymethyl methacrylate (PMMA), cellulose acetate (CA) and so on by chemical oxidative polymerization. This article presents a new method for preparing PANI/PSF composite film with a typical asymmetric structure by phase separation and in situ polymerization. In comparison with the methods described in the literature, one of its advantages is that the film formation and the oxidation polymerization of aniline monomer occur simultaneously, so that the conductive layer of the composite films is thin, dense and its conductivity is high; furthermore, it adheres to the polysulfone substrates tightly. In addition, the influence of experimental conditions on the electrical properties of the films is discussed in detail.

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2 Experimental

2.1 Material

Aniline (99.5%, Beijing Chemical Reagent Company) was purified by distillation with zinc dust before use and stored in refrigerator at about 4°C. Polysulfone (PSF) was dried in vacuum at 60°C prior to use. All other chemicals used in this investigation were of analytical grade and were used as received. All the solutions were prepared with twice distilled water.

2.2 Preparation of film

Polysulfone (PSF) was dissolved in N,N-dimethyl acetamide, to give a final concentration of 0.08 g/mL at room temperature. Aniline monomer (2 mL) was mixed with the above PSF solution (10 mL) and stirred in nitrogen ambience. The mixture was coated directly on glass supports

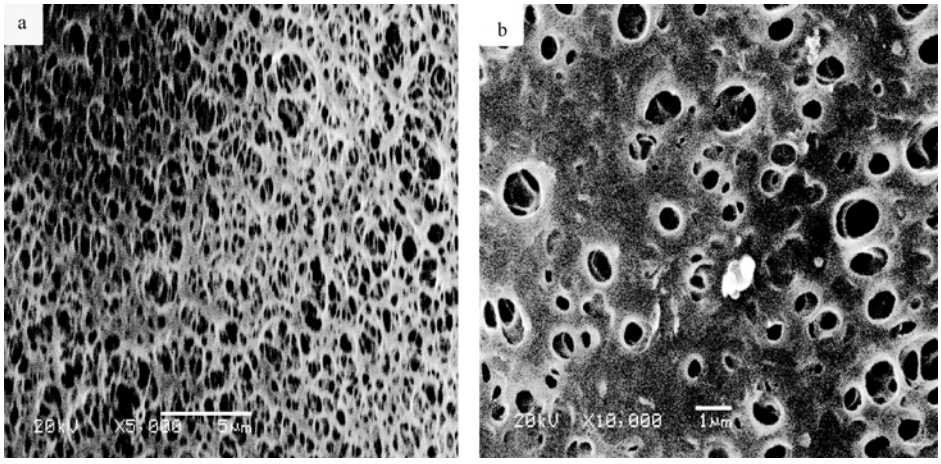

Fig. 1 Scanning electron micrographs of : (a) the outer face of the film and (b) the back face of the composite film

and then immersed them in the mixed solutions of dilute hydrochloric acid and ammonium persulfate (APS) at the given temperature. After 5–6 minutes, the film was peeled off the glass supports. Finally, the conductive films were rinsed with twice distilled water and dried at 60°C in the air.

2.3 Characterization of film

FTIR measurements of the films were performed in an ATR model on Nicolet NEXUS 670 spectrometer. The SEM (JSM-6500LV) was used to investigate the morphology of the composite film.

3 Result and discussion

3.1 Scanning electron micrographs (SEM) images

SEM was applied to observe the surface morphology of the composite film. The micrographs of the outer face and back faces are shown in Fig. 1 (a and b). As can be seen, the two surfaces of the composite film show sponge-like structures with different porosities. The back of the films had a very smooth surface with large and small grains, whereas the head-on face of the films was relatively rougher.

3.2 FTIR spectra

The FTIR spectra of the outer face of the film (a) and the back face of the film (b) are shown in Fig. 2. Part (a) and (b) are similar in contrast with these spectra. The bands corresponding to stretching vibrations of N–B–N and N=Q=N structures appear around 1475 cm^{-1} and 1574 cm^{-1}, respectively (where –B– and =Q= stand for benzenoid and quinoid moieties in the polyaniline backbone). The spectrum of part (b) reveals the bands at 1252 and 1305 cm^{-1} attributed to stretching vibrations of C-O and S=O bonds in the polysulfone backbone, respectively. It was also observed that features

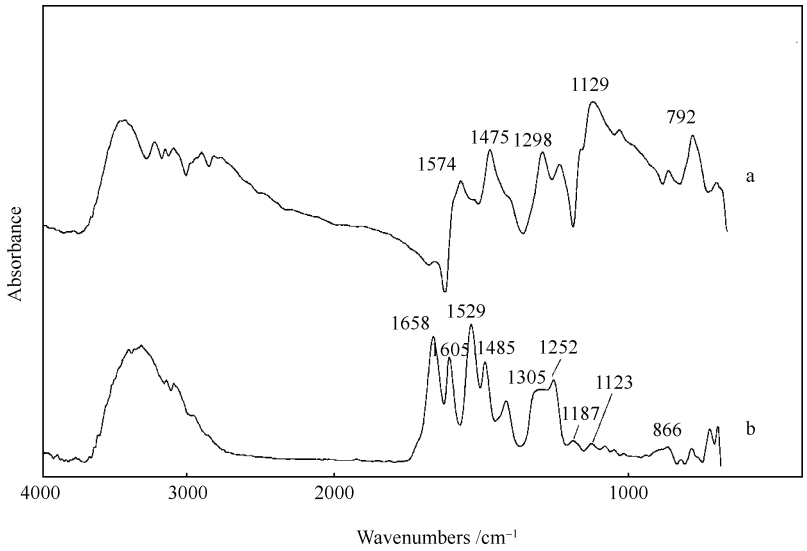

Fig. 2 FTIR spectra analysis (a) the head-on face of the film; (b) the back face of the film

of polysulfone remained partly in (a) although its characteristic bands (C-O and S-O) disappeared. This indicates that composite films are composed of two layers where the outer layer (head-on face) comprises polyaniline coated around the polysulfone and the inner layer (or back face) is composed of Polysulfone. This is in agreement with the SEM analysis.

3.3 Effect of molar ratio of APS to aniline

Fig. 3 shows the plots of film resistances against molar ratio of APS to aniline in N, N-dimethyl acetamide solvent . The HCl concentration in reaction mediums was 2.0 mol/L and the oxidation polymerization lasted about 5 minutes. It could be seen that there was minimum on curves of the film resistance versus the molar ratio of APS to aniline is the in range of 0.4. The resistance is about 104 Ω/cm. On the left side of the minimum point, the amount of APS was insufficient; it leads to the formation of oligomers. Contrarily, on the right side of the minimum point, APS was excessive, resulting in over-oxidation degradation of polyaniline. Therefore, the optimum molar ratio of APS to aniline is around 0.4.

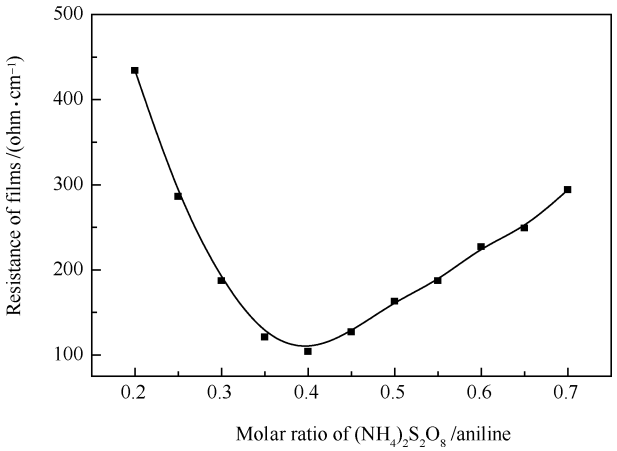

Fig. 3 Variety of the film resistance with molar ratio of APS to aniline

3.4 Effect of amount of dopants

The conductivity of polyaniline depends strongly on the properties and amount of dopants. In this experiment the HCl was used as the dopants. The effect of its concentration on the resistance of PANI/PSF film was investigated. In the experimental measurements, the molar ratio of APS to aniline was equal to 0.4 and temperature was maintained at 5°C. As shown in Fig. 4, the resistance of PANI/PSF film decreases rapidly, and then increases slightly, finally keeps approximately constant with the increase of acidic concentration. Minimum of the resistance achieve about at acidic concentration of 2.0mol/L and the resistance is about 110 Ω/cm. PANI exists in three different base forms. The only electrically conducting form is, however, the emeraldine salt form (ES). In contrast to other CPS, protons must thus be added to the PANI backbone in order to make it electrically conductive. The LEB form of PANI can be protonated with sufficiently strong acids to ES due to the presence of basic sites in the polymer structure. The protonation process is reversible, so increase of HCl concentrations will make more H^+ to dope into PANI chains and form a lot of polarons. When the concentration of HCl is up to 2.0 mol/L, the protonation will reach saturation, indicating that PANI chain is very favorable for the transport of electric charges. Therefore, the most suitable HCl concentration is about 2.0 mol/L for preparation of PANI/PSF film.

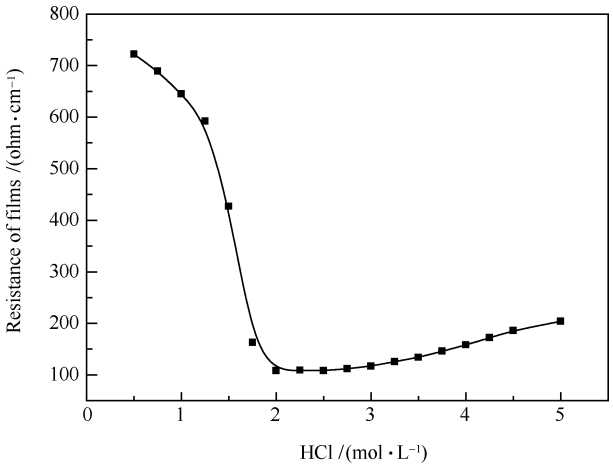

Fig. 4 Variety of the film resistance with the dopant concentration

3.5 Effects of polymerization time

The composite film resistance with polymerization time is shown in Fig. 5. When other conditions were maintained at the optimum value, the resistance of composite films decreases first, until it reaches the minimum, then it increases with polymerization time. Formation of PANI chains with high conductivity needs a suitable reaction time. Short time of oxidation polymerization is unfavorable for long chains

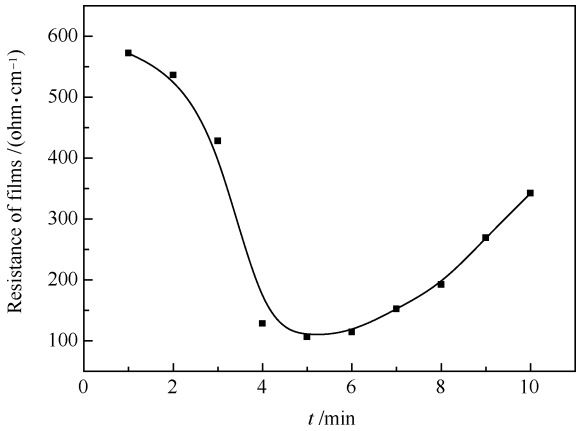

Fig. 5 Variety of the film resistance with polymerization time

of PANI. However, long time causes over-oxidation of PANI, resulting in low molecular weight. So 5–6 min is optimum for oxidation polymerization.

3.6 Effects of annealing temperature

The heat treatment for the composite films will change electrical and mechanical properties. After the composite films were annealed at different temperature for 30 minutes, the changes of film resistance were shown in Fig. 6. When treatment temperature was lower than 80°C, the film resistance was independent of temperature. When treatment temperature was in the range of 80–120°C, however, the film resistance increased with temperature. The decrease in conductivity is assumed to be due to the increased localization of the electronic wave function due to the loss of bound water molecules. This charge distribution due to the presence of moisture has been argued to reduce polarization effects of anion, and hence decrease scattering cross-section due to anion. When treatment temperature was above 120°C, the film resistance increased sharply. The rapid decrease in conductivity can be related to the decomposition of the PAIN/PSF composite film.

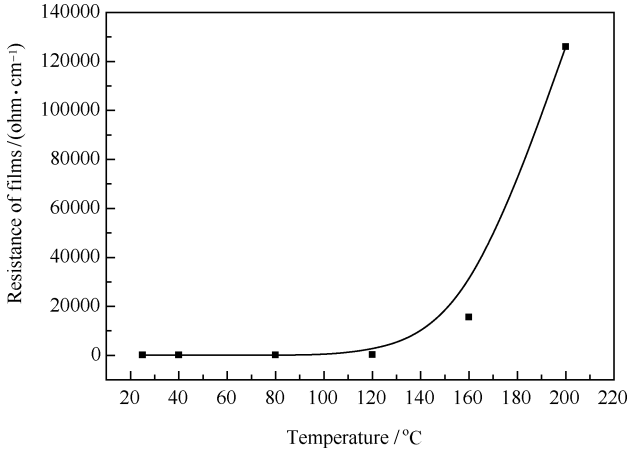

Fig. 6 Variety of the films resistance with annealing temperature

4 Conclusions

Polyaniline/polysulfone composite films were successfully prepared by one step in situ polymerization of aniline with APS as oxidant in dilute hydrochloric acid. An advantage of this method is that the film formation and the oxidation polymerization of aniline monomer occur simultaneously, which makes the conductive layer of the composite films compact and it also adheres to the PSF membrane tightly. The SEM observation showed that the composite film had an asymmetric structure. It can be reckoned from FTIR spectrum data that the head-on face of the composite film is composed of ployaniline layer, while the back face consists of PSF. The influences of the different conditions on the resistance of composite films were discussed.

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