

Thermo-stability of Conductive Blends of Polyaniline/ Poly(styrene-*co*-maleic anhydride)

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Abstract: Di-2-ethylhexylsulfosuccinate sodium salt (AOT) doped conducting polyaniline (PANI-AOT) was chemically polymerized. It was dissolved into a weakly polar solvent (toluene) and secondary doped with *m*-cresol. The conductivity of PANI-AOT was sharply increased from 30 S/cm to 400 S/cm after the secondary doping. Then the conducting polymer was firstly blended with a typical thermoplastic polymer, poly(styrene-*co*-maleic anhydride) (SMA) by solution blending method. The conductivity of PANI-AOT/SMA was relatively maintained even at 200 °C for several minutes. The TGA analysis also indicated that the thermostabilities of the blends were obviously improved compared with those of PANI-AOT.

Key words: Polyaniline; SMA; Blends; Conductivity; Thermostability

1. Introduction

Among intrinsically conducting polymers (ICPs), polyaniline (PANI) is known as a polymer having probably the best combination of stability, conductivity and low cost^[1,2]. As a consequence, its conducting composites are very close to applications on a large scale for the industrial applications, such as, electromagnetic shielding and microwave absorption, static electricity dissipation, heating elements (clothing, wall papers, etc.), conducting glues, conducting membrane materials, paint coatings for anticorrosion protection, and sensor materials^[3,4]. Nevertheless, the choice of the best method to produce composites with specified characteristics remains an unresolved problem. The problem arises because the processing method may significantly determine the properties of the manufactured composite materials. Known methods to produce PANI containing composites may be essentially reduced to two distinct groups: (1) synthetic methods based on aniline polymerization in the presence of or inside a matrix polymer, and (2) blending methods to mix a previously prepared PANI with a matrix polymer. Through blending PANI and matrix polymer, the specified characteristics will introduce into PANI. On the other hand, the conductivity and solubility of PANI were increased after doping with functionalized sulfonic acid, but the thermostability was decreased. Recently, J. Stejskal *et al.*^[5] reported that the conductivity of PANI doped with Di-2-ethylhexylsulfosuccinate sodium salt (AOT) was sharply decreased at 175 °C. Although the development of blends of PANI with common insulating polymers has been carried out and the thermostability was improved, the conductivity of the blends was drastically decreased. So it is a challenge to resolve these two problems in the blending of PANI with common insulating polymers. In this study, a typical thermoplastic polymer, styrene-*co*-maleic anhydride (SMA) was firstly used to blend with doped PANI-AOT by solution blending method and the thermostability was investigated.

2. Experimental

15 mmol of di-2-ethylhexylsulfosuccinate sodium salt (AOT) was dissolved in 80mL of toluene under constant stirring at 0°C for 30min. To the clear solution, 140mL of hydrochloric acid (HCl, 1M) was added and stirred for 1h and followed by addition of 15mmol of aniline and stirred for an extra hour at 0°C. Ammonium persulfate (APS, pre-cooled and dissolved in 20mL HCl) was added dropwise into the above milky mixture for 2h and the mixture was further reacted for 24h at constant temperature. The doped PANI (PANI-AOT) was filtered using Buchner funnel, washed with 100mL water and extracted into 200mL of toluene. The water-toluene mixture was allowed to standstill for at 2h and the water was removed later. The PANI-AOT/toluene is then concentrated to the specific weight percentage. The blends of PANI-AOT/SMA were prepared by mixing various amounts of SMA with PANI-AOT in acetone/toluene co-solvent according to the following procedure. Firstly, SMA was fully dissolved in acetone/toluene at room temperature. Then, various amounts of PANI-AOT secondary doped with m-cresol in the solution of acetone/toluene were added to SMA co-solvent and stirred until each solution was homogeneous. The obtained solution was used to cast film on the surface of glass slide. The films then dried on vacuum oven at 40°C for 24h. The conductivities of various amounts of PANI-AOT films were measured by four-probe method.

3. Results and Discussion:

The films of PANI-AOT/SMA blends were prepared and the conductivities were measured at various amount of PANI-AOT in the blends. Then the films were heat treated on oven at 80, 120, 160, 200°C. The conductivities of these films were changed with the time and the thermostabilities of the blends were improved with the increase of SMA content.

(1) The effect of the amount of PANI-AOT in the blends on the conductivity

To determine the effect of weight ratio PANI-AOT on the conductivity of PANI-AOT/SMA blend, a series of samples was prepared for measuring the conductivity of varying weight ratio of PANI-AOT in the blend of PANI-AOT/SMA between 0.1 and 0.8. The conductivity versus weight ratio of PANI-AOT for each sample is shown in Figure 1. It can be seen that the conductivity of PANI-AOT(3/1) is more than the change of PANI (1/1) at the same change range of weight ratio in the blends. AOT, it not only render the conductivity and solubility of PANI but also plasticize it, so more AOT content at the same weight ratio of PANI-AOT in the PANI-AOT/SMA blends results in the better blending between PANI and SMA in the blends. But, the excessive AOT content decreased the thermostability of PANI-AOT. Below 30% of PANI-AOT, the blends film is easy break, so the 40%, 80% of PANI-AOT films were select to compare with pure PANI-AOT when heat treated at different temperature.

(2) Conductivity degradation of the PANI-AOT, PANI-AOT/SMA blends

Before heat treatment, the conductivity of pure PANI-AOT (▲), 80% PANI-AOT(■) and 40% PANI-AOT (◆) in the blends are 400, 200 and 75S/cm, respectively. After heating at 80°C, the conductivities of PANI-AOT and the blends were slightly reduced with the increase of the heating time as shown in Figure 2 (a). After heating for 2h, the conductivities of 40%, 80% and pure PANI-AOT were reduced only about 17.5%, 22% and 30%, respectively. When heated at 120 and 160°C, the conductivity reduction of pure PANI-AOT was more rapid than that of the blends as shown in Figure 2

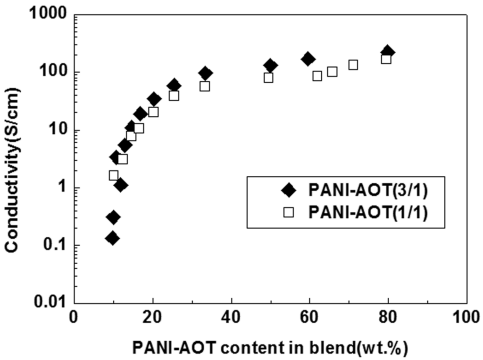


Figure 1 Conductivity versus weight fraction of PANI-AOT in the PANI-AOT/SMA blends

(b) and (c). The similar trend was observed when the PANI-AOT and the blends were heated treatment at 200℃. After heating for 2h at 200℃, the conductivities of pure PANI-AOT, 40%, 80% PANI-AOT blends were reduced and became 1/38, 1/14, 1/7 of the original conductivities, respectively as shown in Figure 2 (d). The effect of heating temperature on the conductivity of the PANI-AOT and the blends can be observed obviously from the Figure 2. All of the films were relatively stable at temperatures below 80℃. When the heating temperature is 200℃, the conductivity of pure PANI-AOT reduces dramatically.

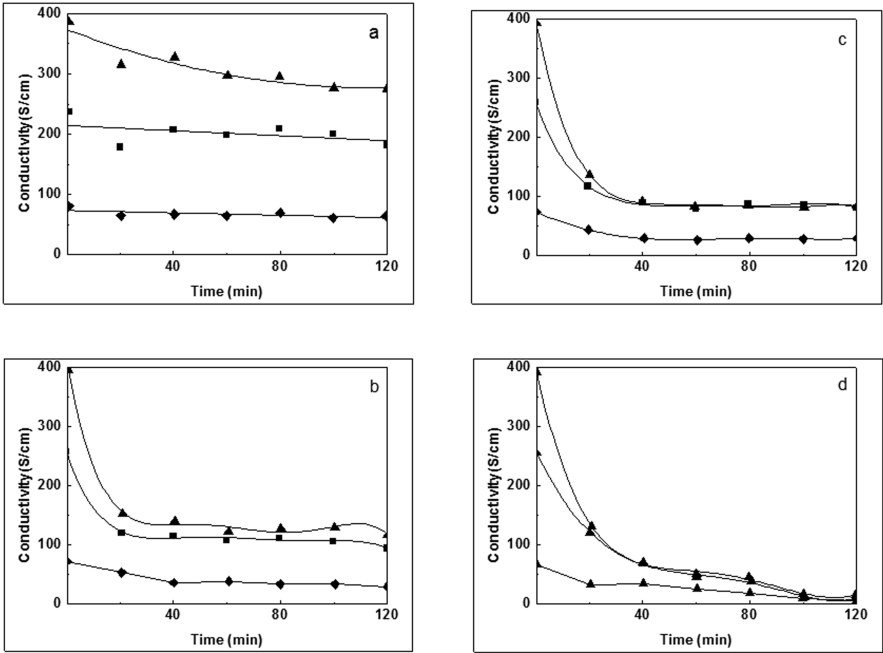


Figure 2 Relationship between the conductivity and heating time at several heating temperature (℃) of: 80, 120, 160, 200; (▲), (■) and (◆) are represent pure PANI-AOT, 80% PANI-AOT and 40% PANI-AOT, respectively.

The thermostabilities of the pure PANI-AOT and the blends were investigated using TGA analyzer. Figure 3 illustrates the weight (%) of PANI-AOT, SMA and the blends as a function of temperature. The SMA exhibited a high stability until 300℃ and showed a small weight loss, apparently caused by the loss of water and impurities. Pure PANI-AOT indicated the weight loss of about 60% in the temperature range of 100~300℃. This drastic weight loss should be associated with the degradation and evaporation of the dopant. The blends PANI-AOT/SMA tend to maintain the

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stability of the SMA at higher temperatures. The stability of the blends of PANI-AOT/SMA improved with increase of the blends of PANI-AOT/SMA improved with increase of the amount of SMA in the blends, compared with that of PANI-AOT.

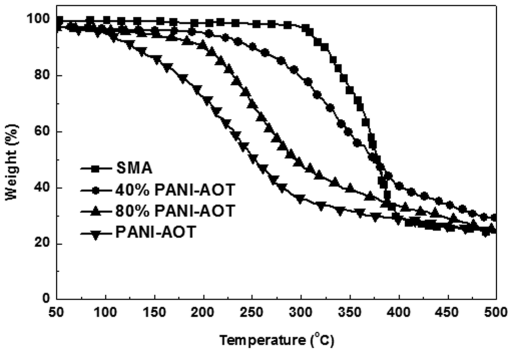


Figure 3 TGA analyses of pure PANI-AOT, PANI-AOT/SMA blends and SMA

In conclusion, the conductivities of the PANI/SMA blends was found to be relatively maintained even at 200°C for 2hrs, although the conductivity of the blends were slightly decreased, compared to pure doped PANI.

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