Synthesis and Characterization of Processable Conducting Polyaniline/Polystyrene Composite

Abdolreza Mirmohseni*, Ali Oladegaragoze, and Maryam Farbodi

Polymer Research Technology Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Received 22 September 2007; accepted 4 February 2008

ABSTRACT

The preparation and characterization of polyaniline/polystyrene (PANI-PS) composite are described. The polyaniline composite was synthesized by chemical polymerization of aniline in polystyrene emulsion matrix. The effects of dioctyl phthalate (DOP), N-methyl-pyrrolidone (NMP) and mineral oil as plasticizer on improving the processability of PANI-PS composite are investigated by melt flow index (MFI) determination. It has been found that, among three tested plasticizers, DOP is more compatible with the composite. Using 35% (w/w) DOP, the MFI value of 0.093 g/10 min was recorded at 170°C. The DSC measurements of PANI-PS composite show a softening point at 106°C indicating that the obtained composite is melt processable above this temperature. Based on solubility studies, the composite is soluble in conventional organic solvents. The conductivity of about 0.013 S/cm is obtained for a free standing film of composite. Also the composite has shown excellent adhesion properties onto the steel plate. Cyclic voltammetric studies have revealed that the synthesized composite is electroactive, too.

INTRODUCTION

Since the successful synthesis of conducting polyacetylene by Shirakawa et al. in 1971 [1] conducting polymers have received considerable attention due to their interesting physicochemical and electrical properties. Intrinsically conducting polymers (ICPs) are a novel class of synthetic materials that have both the electrical and optical properties of semiconductors and metals together with mechanical properties and processability of polymers. These polymers have become a popular basic material for advanced applications including separation membranes [2,3] electrochromic displays [4,5],
polymeric batteries [6,7], sensors [8,9], and corrosion protection coatings [10,11].

Although, a variety of ICPs have been synthesized and investigated, polyaniline (PANI), polypyrrole, polythiophene and their derivatives are most often studied due to their stability compared with other conducting polymers. Among these, PANI has emerged as the most promising conducting polymer due to its straightforward polymerization, environment stability, and relatively high conductivity properties. However, PANI is considered as one of the intractable polymers because of its weak mechanical properties and poor processability. There are many ways to improve the processability and mechanical properties of PANI. Introduction of various functional groups or long alkyl chains on the aromatic ring of aniline can lead to PANI derivatives with higher solubility in organic solvents and even in water, but the conductivity of such PANI derivatives is much lower than the PANI itself. Blending of PANI with other conventional polymers is another way to promote PANI applicability and processability specifications. There are many reports on the blending of PANI with conventional polymers such as polyvinyl alcohol (PVA) [12], polymethyl methacrylate [13] polyurethane [14], and PVC [15].

Also, there are some published reports about preparation and characterization of PANI-PS blends in which polystyrene is selected as a matrix polymer because of its high processability and satisfactory mechanical behaviour [16-18]. Sathyanarayana et al. [16] have used an inverted emulsion method for the synthesis of PANI-PS blend. They showed that the thermal stability of PANI decreases by increasing the polystyrene content of the blend. The thermal stability of free standing PANI-PS blend and its electrical properties has been described by other researchers [17]. In another study, the effect of PANI-PS blending method on its morphology and electrical properties has been investigated by Bae et al. [18]. However, the processability properties of the PANI-PS composite have not been studied in details.

In this work, preparation of a melt and solution processable PANI-PS composite was followed by applying a simple chemical in-situ polymerization method in presence of para-toluene sulphonic acid (p-TSA) as counterion. Emulsion polymerization was used to prepare PS and the chemical polymerization of aniline was carried out in the presence of PS. Characterization tests such as DSC were performed to evaluate the processability of PANI-PS composite against pure PANI. As a new idea, the effect of various plasticizers to improve the processability of PANI-PS composite was investigated. For the first time, the MFI test was carried out on a conducting polymer (PANI) composite. Recorded MFI values were considered as a criterion for PANI composite processability. Solution processability of composite was determined in a number of common solvents. Finally, the adhesion, electrical, and electrochemical properties of the synthesized composite were tested.

**EXPERIMENTAL**

**Materials and Reagents**

Ammonium persulphate, p-TSA, aniline, styrene, potassium persulphate, sodium lauryl sulphate, NMP, DOP, sodium hydrogen phosphate, hydrochloric acid, dimethylforamide (DMF), 1,2-dichloroethane, butyl acetate, tolune, xylene, dichloromethane, tetrahydrofuran, and chloroform were all purchased from Merck, Germany.

Aniline and styrene monomers were distilled prior to use. Other reagents were used as received without further purification.

**Instrumentation**

A model 101 cyclic voltameter (Sahand Pardazan, Tabriz, Iran), a Wenking TG97 galvanostat/potentio-stat (Bank Electronic Co., Niedersachsen) and a model 5MPCA MFI equipment (Ray-Ran Co. England) were all employed for characterization of the composite.

DSC test was performed with a Perkin-Elmer DSC7 differential scanning calorimeter at a heating rate of 10°C/min in air.

Cyclic voltammetry studies were carried out with a conventional three-electrode electrochemical cell including gold film coated by PANI-PS composite as working electrode (area=0.25 cm²) in combination with platinum counter and Ag/AgCl reference electrodes. The composite was coated on the gold film electrode with a thickness of 25 μm.

The electrical conductivity of the films was measured at room temperature by the four-probe technique.
Table 1. Recipe for the polymerization of styrene.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mass (g)</th>
<th>Content (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>100</td>
<td>66.18</td>
</tr>
<tr>
<td>Styrene</td>
<td>50</td>
<td>33.09</td>
</tr>
<tr>
<td>Sodium lauryl sulphate</td>
<td>1</td>
<td>0.66</td>
</tr>
<tr>
<td>Potassium persulphate</td>
<td>0.05</td>
<td>0.033</td>
</tr>
<tr>
<td>Sodium hydrogen phosphate</td>
<td>0.05</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Procedures

**Polystyrene Preparation**
Polymerization of styrene was carried out by emulsion method with recipe given in Table 1. In a glass reactor equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet tube were placed 100 g of distilled water together with 0.05 g potassium persulphate (initiator), 0.05 g sodium hydrogen phosphate (pH regulator) and 0.1 g sodium lauryl sulphate (emulsifier). After dissolving the mixture, 50 g styrene was added. The system was purged with nitrogen to remove dissolved air. Polymerization was carried out at 70°C under stirring rate of 100 rpm for a period of 2 h. The polymerization process continued at 95°C for 2 h until a homogenous milky suspension was obtained.

The polymer was precipitated by adding 70 mL methanol as non-solvent to 10 g emulsion followed by stirring the mixture. Polystyrene was filtered and dried at 100°C and weighed. The concentration of the polystyrene in the emulsion was calculated to be approximately 27.5 wt%.

**Preparation of the PANI-PS Composite**
The PANI composite (with 3/1 weight ratio of PS to aniline) was synthesized by the chemical oxidation of aniline in polystyrene emulsion matrix (27.5 wt%). For this reason, 65 mL emulsion was diluted with 65 mL of distilled water and loaded into the reactor. p-TSA was used either as a dopant or protonic acid to dissolve aniline in water. Six gram aniline dissolved in 50 mL of 0.5 M. p-TSA was added to polystyrene emulsion cooled to 4°C. Then, ammonium persulphate as an oxidant in the same molar ratio with aniline was added dropwise under vigorous stirring. After 30 min, the solution became green in colour which indicates the formation of PANI. The reaction mixture was stirred for 5 h at temperature range of -3 to 0°C. Finally a green suspension was formed.

**Purification of PANI-PS Composite**
In order to remove the unreacted monomers and oxidants the final product was washed strongly with deionized water followed by centrifugation at 2400 rpm for 15 min. This washing process was repeated three times.

**Film Preparation**
A solution casting method was used to prepare the free standing films of PANI-PS composite. Purified composite was dissolved in NMP and cast on glass surface. Evaporation of solvent was completed in an oven of 60°C for 6 h.

**Conductivity Studies**
Prepared PANI-PS composite films were doped by immersing in a 1 M solution of p-TSA for 24 h. The film was dried under high vacuum for 48 h. After this period, the conductivity reached a constant value.

**Adhesion Measurement by Tape Testing**
An X-cut was made on the film prepared on the substrate (a steel plate) according to ASTM standard D 3359-95a. The cuts (six in all) were 20 mm long and 2 mm apart from each other. A pressure-sensitive tape was applied over the cut and then removed. The adhesion was assessed qualitatively on a 0-5 scale based on the percentage of removed area (Table 2). According to this classification, from 0B to 5B the removed area is decreased and the subsequent adhesion is increased.

Table 2. Adhesion classification according to ASTM standard D 3359-95a.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Removed area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>none</td>
</tr>
<tr>
<td>4B</td>
<td>~5%</td>
</tr>
<tr>
<td>3B</td>
<td>5-15%</td>
</tr>
<tr>
<td>2B</td>
<td>15-35%</td>
</tr>
<tr>
<td>1B</td>
<td>36-65%</td>
</tr>
<tr>
<td>0B</td>
<td>&gt;65%</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Characterization of the Composite

Electroactivity
The film cast from the composite was subjected to cyclic voltammetry (CV) studies (Figure 1). As it is expected for the PANI, the prepared film undergoes two separate oxidation and reduction processes. The well defined oxidation-reduction responses indicate that the composite is electroactive. The first response (1 and 1’ curves) are due to oxidation-reduction of leucoemeraldine to emeraldine and vice-versa. The second responses (2 and 2’ curves) are due to oxidation of emeraldine to pernigraniline and vice-versa.

Adhesion Testing
The adhesion of the PANI-PS composite was determined after a film cast onto a steel plate according to ASTM standard D 3359-95a. The results showed that the composite was classified as 5B with 0% of the area removed during the adhesion test.

Conductivity
Free-standing films of PANI-PS composite were prepared by casting the solution onto a glass slide. The conductivity of the films was measured at room temperature and a conductivity of about 0.013 S/cm was obtained. The conductivity value obtained is comparable with the previously reported value for PANI–PS composite with similar 3/1 weight ratio of PS to aniline [19]. However, it is expected that the value can be improved by optimizing the ratio of PANI/PS and polymerization temperature. It should be noted that with the current value of conductivity there are many applications including antistatic and anticorrosion coatings.

Processability Studies
The mould-processability of the prepared composite was investigated. For this, the PANI-PS composite was poured into a glass moulding and heated. The results showed that at temperatures above 105ºC, the composite takes the shape of the mould. These results are compatible with the result of DSC test (Figure 2). According to DSC curve of the PANI-PS composite there is an apparent change in 106ºC that can be considered as softening point.

The effect of various plasticizers on improving the processability of PANI-PS composite was investigated. Three compounds of DOP, NMP, and mineral oil were used as plasticizers. The PANI-PS composite was mixed with each of plasticizers in various percentages by a mechanical mixer for 1 h. The MFI of PANI-PS composite with different percentages of each of the above mentioned plasticizers were measured at three different temperatures 150, 170, and 190ºC.

Using NMP and mineral oil as plasticizer, no MFI data were obtained for PANI-PS composite at three
Table 3. MFI Data obtained for PANI-PS composite with various DOP contents at different temperatures.

<table>
<thead>
<tr>
<th>DOP content (w/w%)</th>
<th>MFI at 150°C (g/10 min)</th>
<th>MFI at 170°C (g/10 min)</th>
<th>MFI at 190°C (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>-</td>
<td>0.093</td>
<td>0.294</td>
</tr>
<tr>
<td>40</td>
<td>0.152</td>
<td>0.274</td>
<td>0.376</td>
</tr>
</tbody>
</table>

tested temperature conditions. The MFI data obtained for PANI-PS composite with various DOP contents are given in Table 3. According to the results, no MFI data were obtained for samples containing DOP content of less than 35% (w/w). When the DOP content reached 35% (w/w) the MFI value of 0.093 g/10min was obtained at 170°C. It is evident from Table 3 that the MFI data of the PANI-PS composite is dependent on DOP content and temperature. Higher MFI values were obtained for the composites at higher temperatures or when more DOP was used in PANI-PS system. Therefore, DOP with optimum weight percent of 35-40% (w/w) can be used to plasticize and improve the processability of PANI-PS composite.

Solubility Studies
Solubility of PANI-PS composite was determined in a number of organic solvents (Table 4). The PANI-PS composite in powder form was added to 100 mL of each solvent including: NMP, DMF, 1,2-dichloroethane, butyl acetate, toluene, xylene, dichloromethane, tetrahydrofuran, and chloroform and stirred for 1 h before filtering. The dry weight of the filter paper was used to calculate the solubility of the PANI-PS composite. It was found that, PANI-PS composite is relatively soluble in all above mentioned solvents. The best solvents for PANI-PS composite are determined to be NMP and DMF.

CONCLUSION

PANI as a conducting polymer suffers from lack of mechanical and processability properties. With the aim of preparing a melt and solution processable PANI composite, PS was selected as a matrix polymer.

Polystyrene synthesis was carried out by emulsion method and then preparation of polyaniline-polystyrene composite was carried out through the chemical polymerization of aniline in an emulsion containing polystyrene. The cyclic voltammetric studies showed that the composite is electroactive similar to pure polyaniline and the conductivity value of about 0.013 S/cm was obtained for a free standing cast film. The composite showed excellent adhesion properties onto the steel plate. This is an important characteristic in which various coating applications such as anticorrosion and antistatic properties can be introduced. DSC and mould-processability tests showed that the PANI-PS composite has a softening point at 106°C which can be moulded above this temperature.

The effect of various plasticizers (DOP, NMP, and mineral oil) on improving the processability of PANI-PS composite was investigated in the temperature range of 150-190°C. Using NMP and mineral oil as plasticizers, no MFI data were obtained. The MFI value of 0.093 g/10 min was measured for the composite with DOP content of 35% (w/w) at 170°C. This value was further improved by increasing the temperature and DOP content of the composite. Solubility studies of PANI-PS composite in NMP, DMF, 1,2-dichloroethane, butyl acetate, toluene, xylene, dichloromethane, tetrahydrofuran, and chloroform revealed that the composite is relatively soluble in most common solvents. However, the best solubility was obtained in NMP and DMF.

It can be concluded the prepared PANI-PS composite has an acceptable conductivity, electroactivity, and adhesion properties as well as good melt and solution processability ones. Besides, this composite can be used as coating or moulding material in many
uses such as in anticorrosion protections and antistatic applications.

ACKNOWLEDGEMENTS

We are most grateful of the continuous financial support of this research project by the University of Tabriz.

REFERENCES