Preparation of Conductive Polyaniline/Chlorosulfonated Polyethylene Composites via *In Situ* Emulsion Polymerization and Study of Their Properties

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ABSTRACT: The conductive composites of polyaniline (PAn) and chlorosulfonated polyethylene (CSPE) were prepared by polymerization of aniline in the presence of CSPE, using a direct, one-step *in situ* emulsion polymerization method. The polymerization of aniline was performed in an emulsion comprising water and xylene containing CSPE in the presence of dodecylbenzene sulfonic acid, which acts both as a surfactant and a dopant for PAn. The composites can be processed by either melt method (MP) or solution method (SP). Conductivity of the composites obtained by different processing methods shows different percolation thresholds: 14 wt % for MP samples and 22 wt % for SP samples. At the same content of PAn, the conductivity of MP composites is higher than that of SP composites. The relationships between mechanical properties and PAn content obtained by the two different processing methods were also investigated. When PAn content of MP samples is between 12 and 18 wt %, the composites behave like a thermoplastic elastomer with tensile strength at 6–8 MPa, ultimate elongation > 400% and permanent set < 30%. The conductivity of composites obtained by SP method after secondary doping with *m*-cresol is about 6 orders of magnitude higher than the original at below 18 wt % PAn content and the percolation threshold for conductivity is lowered to 3 wt % PAn content. The composite shows no electrochromic activity in acidic solution of LiClO$_4$ in propylene carbonate, but after secondary doping exhibits electrochromic activity even in neutral electrolyte. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 845–850, 2000

Key words: polyaniline; emulsion polymerization; composite; chlorosulfonated polyethylene; conductive polymer; electrochromic property

INTRODUCTION

Over the last decade conductive polymers have been investigated extensively due to their wide application potentials. However, most of them suffer from their poor processibility. Recently much research has been concerned with the composites of the conductive polymers with conventional polymers. This results in producing conductive composites with a wide range of interesting mechanical and electrical properties. Of all the conducting polymers, polyaniline (PAn) has been of great interest to many researchers because of its high conductivity, stability, easy preparation, affordability, and redox properties. This polymer exists in different oxidative states, namely, perniganiline, emeraldine, and leucoemeraldine. Only emeraldine salt from emeraldine base (EB) and a strong acid shows high conductivity, but cannot be dissolved. However, EB can be dissolved in *N*-methylpyrrolidone, concentrated sulfuric acid, and other strong acids,[1] which are al-

most impossible to use commercially due to either their high price or strong corrosion. There have appeared in the literature several methods for preparing conductive PAn/conventional polymer composites, for examples, electrochemical,[2–4] latex,[5–7] emulsion polymerization,[8–11] and blending.[12–14] Recently, Heeger[15] indicated that EB doped with a functionalized protonic acid, for example, camphorsulfonic acid (CSA) and dodecylbenzene sulfonic acid (DBSA), can be dissolved in a nonpolar or moderate polar organic solvent. Composites of plastics and PAn doped with CSA or DBSA were made using a cosolvent method.[16] Osterholm et al.[17] reported the emulsion polymerization of aniline (An) in the presence of DBSA and the use of a solution blending method to prepare the composite. Last year we reported the preparation of conductive PAn/(styrene-butadiene-styrene)triblkock copolymer (SBS) composites in one-step via in situ emulsion polymerization.[18] Foot and Simon[19] first reported that PAn can be used in electrochromic device due to the change of colors during a voltammetric cycle at pH 0–1 media. Bernard and Hugot-LeGoff[20] showed that a weakly acidic electrolyte solution (at pH 3 but not pH 5) is best suitable for electrochromic purpose of PAn. Tassi and Paoli[21] prepared a electrochromic device based on a graft copolymer of PAn on nitrile rubber. The advantage of using an electrochromic material with rubber is the possibility in designing a flexible or curved electrochromic device.

This article deals with in situ oxidative polymerization of aniline in an emulsion of chlorosulfonated polyethylene (CSPE), an oil-resistant synthetic rubber, using DBSA as emulsifier and dopant, so as to prepare conductive PAn/CSPE composite in one step, instead of first polymerization of An in the presence of functionalized protonic acid, followed by washing, drying, and dissolution of the product in organic solvent and then blending with solution of CSPE to form the composite. The second goal is to obtain an electrical conductive thermoplastic elastomer from a synthetic rubber that needs vulcanization before use. Secondary doping with m-cresol was also investigated, in order to increase the conductivity of the composite. Mechanical properties and structure of the composites, as well as their electrochromic activity, were studied too.

EXPERIMENTAL

Materials

All reagents and solvents used were chemically pure. An was distilled under reduced pressure and stored in a refrigerator before use. Chlorosulfonated polyethylene of 40 type (CSPE) containing 33–37% Cl and 0.8–1.2% S was supplied by Jilin Chem. Ind. Co. (Jilin, China).

In Situ Emulsion Polymerization

Weighed amounts of CSPE, An, and DBSA according to An concentration of 0.2 mol/L, M ratio of An/CSPE = 0.33, M ratio of DBSA/An = 1.5 were dissolved in 800 mL xylene with stirring. After mixing with 100 mL distilled water with vigorous stirring to form an emulsion, 100 mL aqueous solution of ammonium persulfate (Ox) was added dropwise into the emulsion during stirring at room temperature. Concentration of Ox depends on the M ratio of Ox/An = 0.5. The *in situ* emulsion polymerization was carried out at 25°C for 12 h.

Processing of the Composites

Melting processing method (MP): after polymerization the emulsion of PAn-DBSA/CSPE was precipitated by pouring into acetone. The dried green precipitate was filtered and washed with acetone and water, then vacuum dried for 24 h at 40°C. The composite was hot-pressed at 130°C for 7 min.

Solution processing method (SP): the resulting emulsion was deemulsified and washed five times with acetone-water (1 : 1) mixture in a separating funnel to remove excess DBSA and ammonium sulfate. A green solution of PAn-DBSA/CSPE composite in xylene was obtained. The film of composite was obtained by casting the solution on glass, dried under infrared lamp and under vacuum at 40°C.

Method of secondary doping: the film of the composite was fully immersed in *m*-cresol, becoming semiswollen, and taken out and dried under infrared lamp and under vacuum at 40°C to constant weight.

Measurements

For higher conductivity the conductivity of the sample was measured at room temperature by the four-point probe method, whereas for lower
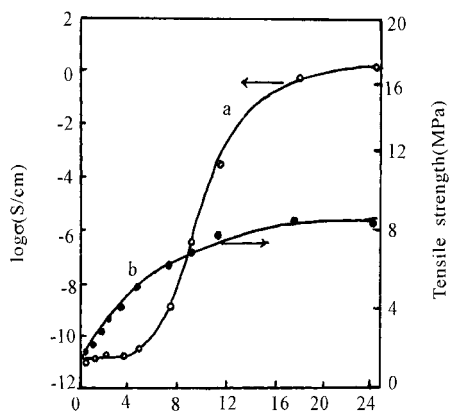
Figure 1 Conductivity (a) and tensile strength (b) of the MP samples of PAn/CSPE composites vs PAn content.

conductivity the three-electrode method was used. A JSM scanning electron microscope (SEM) was used to examine the morphology of the broken surface of the composite. Rigaku 3015 wide angle X-ray diffraction apparatus was used to observe crystallinity. Elemental analysis was performed using a Carlo Erba MOD 1106 apparatus for calculating the content of PAn. Mechanical properties were determined on a XL-2500 tensile tester at 25 ± 5 C. Permanent set was measured as the percentage elongation after the specimen was broken and reunited after 10 min.

Electrochromic Activity Measurement

Xylene solution of PAn/CSPE composite was coated on an indium-tin oxide (ITO) conducting glass plate, dried, and used as anode. 1.0 mol/L nonaqueous solution of $LiClO_4$ in propylene carbonate was used as electrolyte, platinum electrode as cathode, and Ag/AgCl as reference electrode. The electrochromic absorption spectra of the composite were recorded by ultraviolet (UV)-240 spectrophotometer.

RESULTS AND DISCUSSION

Electrical and Mechanical Properties of Composites Obtained by MP Method

Figure 1 shows that the change of conductivity of PAn/CSPE composite versus PAn content exhibits a percolation threshold. The PAn content of composite was calculated on the basis of the elemental analysis. When the PAn content is lower than 6 wt %, the conductivity of composite

changes slightly and approaches that of CSPE. As the content of PAn increases from 8 to 17 wt %, conductivity of the composite increases rapidly from 10^{-9} to 0.4 S/cm and then slightly with increasing PAn content. The percolation threshold for the conductivity is about 14 wt % of PAn content in the composite. The reason why the percolation threshold is higher than that of PAn/SBS composite[18] is probably due to the strong interaction between NH groups of PAn and —SO_2Cl groups of CSPE. The better compatibility between PAn and CSPE than that between PAn and SBS results in better dispersion of conductive component in the CSPE matrix, which inhibits the formation of conductive routes.

Figure 1 also shows that PAn enhances the tensile strength of the composite up to 16 wt % PAn, which denotes further the strong interaction between PAn and CSPE molecules or a reinforcing action offered by PAn on the matrix.

Figure 2 indicates that a maximum value of ultimate elongation and a minimum value of permanent set occur at about 6 wt % PAn. This implies that at this composition the composite possesses the best elasticity. However, the changes are not very large. The ultimate elongation varies between 400% and 550% and the permanent set varies between 12% and 33%. In combination with these three mechanical properties the composites with 12–18% PAn content behave like conductive thermoplastic elastomer with somewhat poorer tensile strength (about 8 MPa) than that of PAn/SBS.

Electrical and Mechanical Properties of Composites Obtained by SP Method

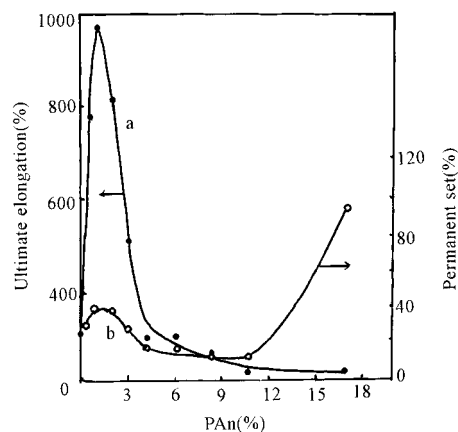The conductivity of composites obtained by SP method (SP sample) at the PAn content of 11 wt %
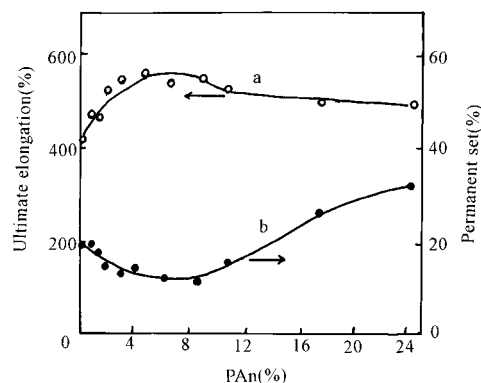
Figure 2 Ultimate elongation (a) and permanent set (b) of the MP samples of PAn/CSPE composites vs PAn content.
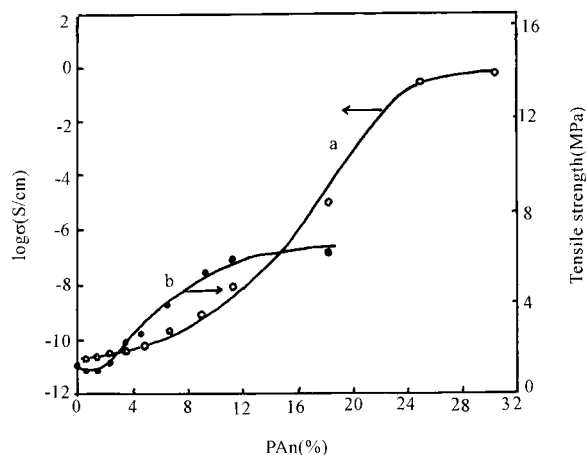
Figure 3 Conductivity (a) and tensile strength (b) of the SP samples of PAn/CSPE composites vs PAn content.

Figure 4 Ultimate elongation (a) and permanent set (b) of the SP samples of PAn/CSPE composites vs PAn content.

is almost 10^5 times lower than that obtained by MP method, as shown in Figure 3 and Figure 1. The percolation threshold for the conductivity is about 22 wt % PAn content. This is probably because the strong interaction between CSPE and PAn molecules favors the uniform dispersion of PAn in CSPE more thoroughly in solution casting than in melt processing of the composite, resulting in less probability of forming conductive routes in SP sample. This phenomenon is just the opposite from that of PAn/SBS composite.[18] In the latter case, the conductivity of SP composite is higher than that of MP composite, probably because no strong interaction occurs between SBS and PAn and glassy domains of polystyrene exist in SBS.

Figure 3 also illustrates that with increasing PAn content the tensile strength of SP sample decreases slightly at first and then increases up to about 6 MPa, which is lower than that of the MP sample. Figure 4 indicates that the ultimate elongation of SP samples increases with increasing PAn content abruptly to more than 1000% at first, falls abruptly to about 500% at 6 wt % PAn content and then decreases gradually. The change is somewhat similar to that of MP sample, but the extent is larger. The permanent set decreases at first to about 12% at 9–16 wt % PAn content and then increases to 40%. According to the mechanical properties and conductivity, SP method seems to be poorer than MP method in preparing conductive thermoplastic elastomer.

Structure

IR spectra of CSPE, SP sample of the composite, and the SP sample dedoped by NaOH solution are shown in Figure 5. Only very weak characteristic absorption peaks of doped PAn (1580, 1160, 800 cm^{-1}) and a weak characteristic absorption peak of CSPE (1400 cm^{-1}) can be seen in the spectrum of SP sample. This implies that a strong interaction occurs between —SO_2Cl groups of CSPE and —NH groups of PAn. However, after the SP sample of composite is dedoped with dilute NaOH solution, its IR spectrum shows the characteristic absorption peaks of emeraldine form of PAn (1600, 1160, 800 cm^{-1}). The reason may be attrib-
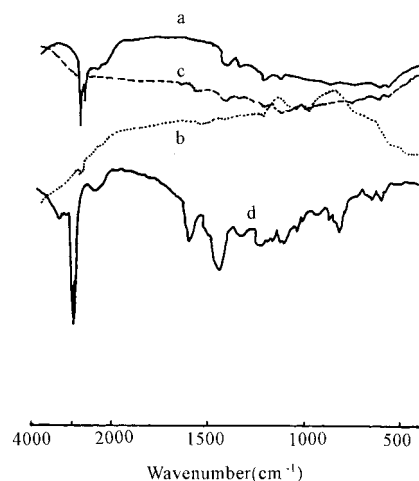
Figure 5 IR spectra of CSPE (a), MP (b), and SP (c) samples of PAn/CSPE composite and the SP sample dedoped with NaOH (d).
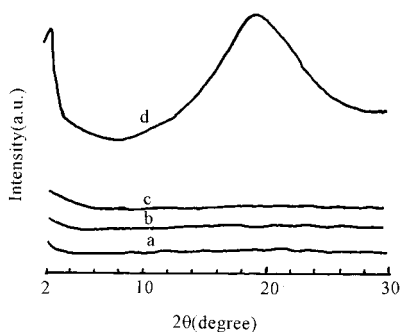
Figure 6 Wide-angle X-ray diffraction analysis of CSPE (a), MP (b), and SP (c) samples of PAn/CSPE composite and MP sample of PAn/SBS composite (d).

uted to the reaction of NaOH with —SO$_2$Cl groups of CSPE, resulting in elimination of the interaction between CSPE and PAn.

The morphology of SP sample of PAn/CSPE, as observed by SEM, exhibited a smooth broken surface, which is different from those of the samples of PAn/SBS.[18] The morphology of MP sample of PAn/SBS presents a brittle fracture character with microvoids, whereas the SP sample of PAn/SBS displays a ductile fracture.

Wide angle X-ray diffraction patterns (Fig. 6) indicate that neither CSPE nor MP and SP samples of the PAn/CSPE composites exhibit a crystalline peak, which indicates that no crystalline structure of PAn exists in the MP and SP samples of PAn/CSPE. This is different from the MP sample of PAn//SBS composite, which shows a narrow peak at a small angle,[18] as also shown in Figure 6. The latter phenomenon may be ascribed to the selfassembly of PAn molecules into aggregates in PAn/SBS under processing temperature. The reason why no PAn crystal formed in the PAn/CSPE composite is probably because in the latter case the interaction between CSPE and PAn is strong and no possibility for PAn molecules to aggregate into crystals.
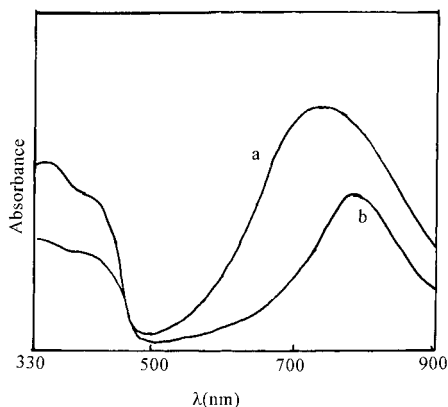
Secondary Doping of the Composites

Recently secondary doping has been recognized, which differs from the primary doping in that the newly enhanced conductivity persists, though to a reduced extent, even upon complete removal of the secondary dopant.[22] In this study the method of secondary doping was used to improve the conductivity of composite. It can be seen from comparison of Figure 7 with Figure 3 that the conductivity of SP samples increases obviously after

secondary doping with *m*-cresol and its percolation threshold decreases markedly to about 3 wt % PAn. It verifies that the secondary doping is also an effective way to enhance the conductivity of primarily doped composite of PAn/CSPE. According to MacDiarmid and Epstein,[22] the main character of secondary doping is the change of molecular conformation from "compact coil" to "expanded chain" of the doped polymer. The above result implies that *m*-cresol weakens the interaction between CSPE and PAn, expanding the PAn coils and enhancing the selfassembly of PAn chains to form conductive routes. However, the secondary doping almost does not affect the tensile strength and ultimate elongation of the composites; only the permanent set of SP sample with PAn content higher than 11 wt % increases sharply (e.g., to about 180% at 17 wt % of PAn). The latter phenomenon implies that more PAn molecules are expanded by secondary doping, resulting in diminishing elasticity of the composite.

Electrochromic experiment showed that before secondary doping the PAn/CSPE composite has no electrochromic activity. This is probably because no conductive route of PAn was formed in the composite, as mentioned above. However, after secondary doping, the composite possesses electrochromic activity not only in acidified solution of LiClO$_4$ in propylene carbonate but also in neutral solution of the electrolyte. Dark green color of the composite occurs at the coloring voltage of 0.9 V, whereas light yellow color appears at the bleaching voltage of -0.2 V, as shown in the absorption spectra of the composite at different
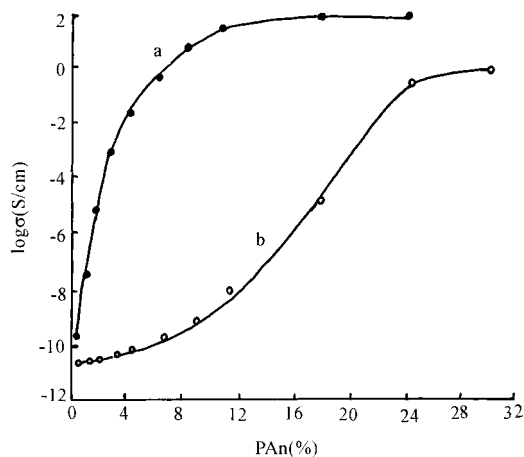
Figure 7 Conductivity of the SP sample of PAn/CSPE composite after secondary doping (a) and before secondary doping (b).

Figure 8   Electrochromic absorption spectra of the SP sample of PAn/CSPE composite after secondary doping at applied voltage of +0.9V (a) and −2.0V (b).

applied voltages (Fig. 8). The reduced leucoemeraldine state of PAn is yellow, whereas the oxidized and conductive emeraldine state of PAn is green. This phenomenon may be attributed to the existence of conductive PAn routes after secondary doping. The reason why the composite shows electrochromic activity in the neutral electrolyte is probably due to the fixation of the large functionalized protonic acid, DBSA, in the composite even after the secondary doping with *m*-cresol.

CONCLUSION

Electrically conductive PAn/CSPE composites have been obtained via a direct, one-step *in situ* emulsion polymerization. The processing method of the composite is an important factor that affects both the conductivity and mechanical properties of the composites. MP method is rather better than SP method. PAn/CSPE composites are quite different from PAn/SBS composites both in properties and in structure. Within a certain range of PAn content, the composites behave like a conductive thermoplastic elastomer. Secondary doping can improve the conductivity and the per-

colation threshold of the composite significantly without affecting the tensile strength. The composite shows no electrochromic activity before the secondary doping, but exhibits electrochromic activity after the secondary doping even in the neutral electrolyte condition.

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