

Preparation of Conductive Polyaniline-Sulfonated EPDM Ionomer Composites from *In Situ* Emulsion Polymerization and Study of Their Properties

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ABSTRACT: The composites of polyaniline (PAn) and zinc sulfonated ethylene-propylene-diene rubber (EPDM) ionomer were made by polymerization of aniline in the presence of the ionomer by using a direct, one-step *in situ* emulsion polymerization technique. The ionomers were prepared by sulfonation of EPDM rubber with acetyl sulfate in petroleum ether, followed by neutralization with zinc acetate solution. The ionomers with sulfonate contents of 10, 24, and 42 mmol SO₃H/100 g were used for preparation of PAn/ionomer composites. The *in situ* polymerization of aniline was carried out in an emulsion comprising water and xylene containing the ionomer in the presence of dodecyl benzene sulfonic acid, acting as both a surfactant and a dopant for PAn. The composite was characterized by IR and WAXD. The composite obtained can be processed by melt method. The conductivity of the composite with lower sul-

fonate content was higher than that with higher sulfonate content. Conductivity of the composites exhibits a percolation threshold at about 13 wt % PAn. When the sulfonated content is 10 or 24 mmol SO₃H/100 g and PAn content is 4–10 wt %, the composites behave as a thermoplastic elastomers with high ultimate elongation and low permanent set. The conductivity of the composite after secondary doping with *m*-cresol is higher than the composite before secondary doping by about one order. Addition of zinc stearate as an ionic plasticizer lowers both the conductivity and the mechanical strength of the composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2211–2217, 2004

Key words: polyaniline; composite; emulsion polymerization; ionomer; conductive polymer

INTRODUCTION

Over the last decade conductive polymers were studied extensively because of their wide application potential. However, most of them suffer from their poor processibility. Of all the conductive polymers, polyaniline (PAn) has been of great interest to many researchers because of its high conductivity, stability, easy preparation, affordability, and redox properties. Only emeraldine salt of PAn 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, which are almost impossible to use commercially because of either their high price or their strong corrosion. Thereafter, much research has been concerned with the composites of the conductive polymers with conventional polymers. There have appeared in the literature several methods for preparing conductive PAn/conventional polymer composites, for example, electrochemical,^{1,2} latex,^{3,4} emulsion po-

lymerization,^{5,6} and blending.⁷ Recently, Heeger⁸ indicated that EB doped with a functionalized protonic acid, for example, camphor sulfonic acid (CSA) and dodecyl benzene 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 by using a cosolvent method.⁹ Osterholm et al.¹⁰ reported the emulsion polymerization of aniline (An) in the presence of DBSA and the use of a solution blending method to prepare the composite. Several years ago, we reported the preparation of conductive PAn/(styrene-butadiene-styrene) triblock copolymer (SBS) composites¹¹ in one step via *in situ* emulsion polymerization. SBS is a thermoplastic elastomer containing polystyrene glassy domains as physical crosslinks and can be processed by plastics method without vulcanization. MackKnight and Lundberg¹² indicated that zinc sulfonated ethylene-propylene-diene rubber (EPDM) ionomer also behaves as a thermoplastic elastomer, in which ionic domains act as physical crosslinks and zinc stearate acts as ionic plasticizer.¹³

This article deals with *in situ* oxidative polymerization of aniline in an emulsion containing zinc sulfonated EPDM ionomer, using DBSA as emulsifier and

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dopant, so as to prepare conductive PAN/ionomer 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 ionomer to form the composite. The second aim was to obtain an electrical conductive thermoplastic elastomer from a thermoplastic elastomer-type ionomer. Secondary doping with *m*-cresol was also studied, to increase the conductivity of the composite. Mechanical properties and structure of the composites, as well as the effect of zinc stearate on the conductivity and mechanical properties of the composites, were also investigated.

EXPERIMENTAL

Materials

All reagents and solvents used were chemically pure. An was distilled under reduced pressure and stored in a refrigerator before use. EPDM 4045 was a Japanese product (Mitsui Co., Tokyo, Japan), containing 30% propylene units with a Mooney viscosity of 42 and iodine number of 24.

Preparation of zinc sulfonated EPDM ionomer

Eighty grams of EPDM was dissolved in 1 L petroleum ether with stirring. After addition of 5.5 mL acetic anhydride to the solution, 1.6 mL concentrated sulfuric acid (the amount of acetic anhydride and sulfuric acid may be changed according to the sulfonation degree and molar ratio of acetic anhydride/ $\text{H}_2\text{SO}_4 = 1.5$) was added dropwise with vigorous stirring at 3–5°C within 30 min. A small amount of ethanol was added to terminate the sulfonation. Zinc acetate equivalent to SO_3H content was dissolved in ethanol/water (1/1 v/v) solution, which was then added to the terminated sulfonated EPDM solution during stirring. The neutralization was carried out for 1.5 h at room temperature. The solution was flashed with boiling water to remove the solvent. The product was washed with water to remove acid and impurities. The ionomer was then dried under infrared lamp and vacuum oven at 60°C one after the another.

A sample of the sulfonated product was taken out before termination and precipitated with absolute ethanol. After decantation, the precipitate was dissolved in petroleum ether and precipitated again with ethanol. The dissolution-precipitation process was repeated until the upper liquid layer became neutral. Then, the precipitate was dissolved and titrated with 0.1 mol/L alcoholic solution of KOH by using phenolphthalein as indicator

$$\text{Sulfonation degree (mmol/100 g rubber)} = M \times (V_1 - V_0) \times 100/W$$

where M represents molar concentration of alcoholic KOH solution, V_1 and V_0 are the amounts of alcoholic KOH solution in milliliters used for titration of the sample and blank, respectively, and W is the weight of the sample.

In situ emulsion polymerization

46.5 g zinc sulfonated EPDM ionomer (EPDMI) was dissolved in 300 mL xylene with stirring, followed by adding 9 mL aniline dropwise. Then, a 100-mL xylene solution of 48.8 g DBSA was added slowly. After mixing with 50 mL distilled water with vigorous stirring to form an emulsion, 50 mL aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added dropwise into the emulsion with stirring at room temperature. The polymerization lasted for 12 h. After polymerization, the emulsion of PAN-DBSA ionomer was precipitated by pouring into acetone. The dark-green sediment was filtered and washed with acetone and water and then vacuum dried for 48 h.

The composites were pressed at 150°C for 10 min under 10–15 MPa.

Secondary doping

The film of the composite was fully immersed in *m*-cresol, becoming semi-swollen and then taken out and dried under infrared lamp and 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 conductivity the DDS-11 conductometer with copper disk electrodes was used. FTIR spectrum was taken via EQUINOX 55 spectrophotometer. Rigaku 3015 wide-angle X-ray diffraction apparatus was used to determine crystallinity. Elemental analysis was performed by using a Heracus CHN-Rapid apparatus for calculating the content of PAN. Mechanical properties were determined on a XL-2500 tensile tester at $25 \pm 5^\circ\text{C}$. Permanent set was measured as the percentage elongation 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

Effect of amount of the ionomer on the *in situ* polymerization of aniline

Table I shows that by increasing the feeding weight ratio of An/ionomer, the PAN content increases, whereas the PAN yield decreases. The higher the sulfonate content of the ionomer, the higher the PAN yield at the same feeding ratio. This implies that the

TABLE I
Effect of Amount and Sulfonate Content of the Zinc Sulfonated EPDM Ionomer on *In Situ* Polymerization^a of Aniline

Feeding ratio of An/ionomer(w/w)	PAn yield (wt %)		PAn content (wt %) ^b	
	Ionomer I ^c	Ionomer II	Ionomer I	Ionomer II
0.11	59.1	75.8	6.1	7.7
0.14	52.1	71.5	6.8	9.1
0.20	46.0	58.0	8.5	10.4
0.33	40.9	47.7	11.9	13.6
1.0	35.2	36.1	26.1	26.5
2.0	20.9	21.2	29.5	29.8

^a Polymerization conditions: molar ratios of $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{An} = 0.5$, $\text{DBSA}/\text{An} = 1.5$.

^b The PAn content was calculated on the basis of the elemental analysis of the composite, whereas the PAn yield was calculated from the PAn content.

^c Sulfonate contents of ionomer I and ionomer II are 10 and 40 mmol $\text{SO}_3\text{H}/100$ g, respectively.

presence of sulfonate groups in the ionomer favors the polymerization of aniline. This fact can be explained by the occurrence of An-DBSA polymerization on the surface of the emulsion particles, followed by penetration of PAn-DBSA into the center of the particles. The polarity of sulfonate group attract both An and PAn-DBSA molecules, causing more uniform distribution of PAn-DBSA in the emulsion particles, thus refreshing the surface of the emulsion particles. This offers a beneficial condition for the polymerization of An on the emulsion particles and retards the excess oxidation of PAn, resulting in a higher yield of PAn.

Characterization

Figure 1(a, b) shows the IR spectra of zinc sulfonated EPDM ionomer and its composite with PAn, respec-

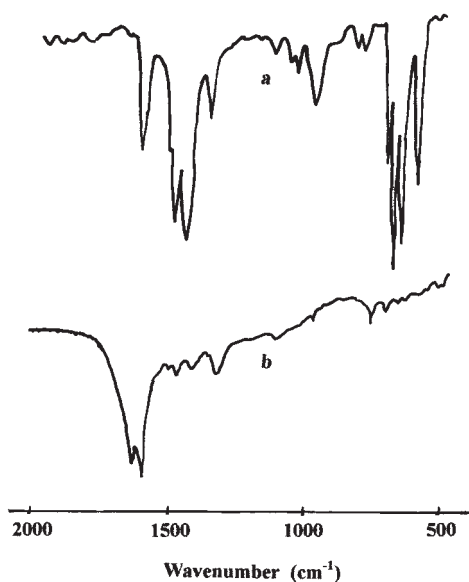


Figure 1 IR spectra for zinc sulfonated EPDM ionomer (a) and its composite with PAn (b).

tively. The former shows the absorption peaks at 1152 and 1039 cm^{-1} for the sulfonate groups of the ionomer, whereas the latter shows the absorption peak at 1599 and 778 cm^{-1} for the doped PAn besides those absorption peaks for the ionomer, although some absorption peaks for the ionomer are weakened because of the interaction between the ionomer and PAn.

Figure 2 illustrates WAXD spectra of (a) EPDMI with 10 mmol $\text{SO}_3\text{H}/100$ g; (b) PAn/EPDMI composite containing 10 mmol $\text{SO}_3\text{H}/100$ g and 13.2 wt % PAn; (c) PAn/EPDMI composite containing 40 mmol $\text{SO}_3\text{H}/100$ g and 13.6 wt % PAn; (d) composite (b) after secondary doping; (e) PAn/EPDMI composite containing 10 mmol $\text{SO}_3\text{H}/100$ g and 27 wt % PAn. It can be seen from Figure 2(a) that no crystalline peak of PAn exists and from Figure 2(b, c, d, e) that there occur crystalline peaks of PAn at $2\theta = 25^\circ$. The crystalline peak height increases with increasing PAn content, as

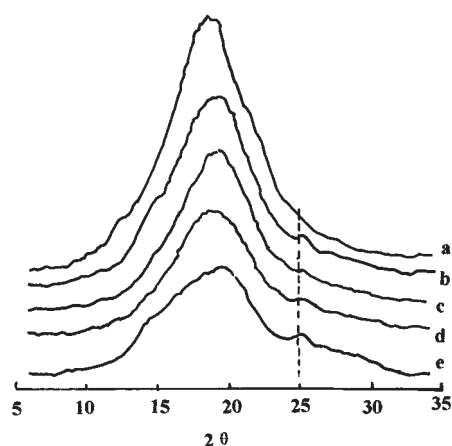


Figure 2 WAXD of (a) zinc sulfonated EPDM; (b) PAn/EPDMI composite containing 10 mmol $\text{SO}_3\text{H}/100$ g and 13.2 wt % PAn; (c) PAn/EPDMI composite containing 40 mmol $\text{SO}_3\text{H}/100$ g and 13.6 wt % PAn; (d) composite (b) after secondary doping; (e) PAn/EPDMI composite containing 10 mmol $\text{SO}_3\text{H}/100$ g and 27 wt % PAn.

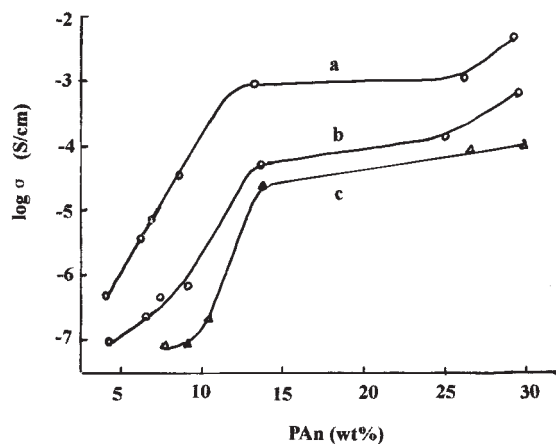


Figure 3 Conductivity of the PAN/ionomer composites versus PAN content (sulfonate content, mmol/100 g: a: 10; b: 24; c: 40).

compared in Figure 2(b, e). This fact indicates that PAN tends to aggregate together and self-assemble during the melt process, but due to the interaction between SO_3^- group of the ionomer and NH group of PAN, it is somewhat difficult to crystallize in long-range order to form crystalline domains. Thus, the higher the sulfonate content of the ionomer, the lower the crystallinity, as shown in Figure 2(c).

Secondary doping of the composite can increase the crystallinity of PAN, as shown in Figure 2(d).

Conductivity of the PAN/EPDMI composites

Figure 3(a–c) represents the conductivity of the composites containing the ionomers with sulfonate contents of 10, 24, and 40 mmol/100 g versus PAN content, respectively. The higher the sulfonate content of the ionomer, the lower the conductivity of the composite. For the composite containing ionomers with sulfonate content of 10 and 24 mmol/100 g, the conductivity increases with PAN content, until the PAN content reaches about 12–13 wt % and then changes slowly. The percolation threshold for the conductivity is about 12–13 wt % of PAN content in the composite. It seems that the lower the sulfonate content of the composite, the lower the percolation threshold. However, when the PAN content became higher than 25 wt %, the conductivity rises again. These phenomena can be interpreted as follows: A strong interaction occurs between the sulfonate groups of the ionomer and NH groups of the PAN molecules, thus enhancing the compatibility of PAN with the ionomer, resulting in more uniform distribution of PAN molecules in the ionomer. This prevents the formation of conductive routes of PAN. The conductivity of the PAN/ionomer composite is lower than that of the PAN/SBS composites¹¹ and

the percolation threshold of the former is higher than that of the latter. This fact is because SBS has no interaction with PAN, whereas the ionomer has interaction with PAN. However, excess PAN can form conductive routes itself, thus further increase of the conductivity occurs, as in the case of the composites containing 10 and 24 mmol $\text{SO}_3\text{H}/100$ g.

However, in the case of the composite with higher sulfonate content at 40 mmol $\text{SO}_3\text{H}/100$ g (c), the conductivity changes slightly below 9 wt % PAN content and then increases rapidly until the percolation threshold is reached at 13 wt % PAN. The conductivity of these composites is much lower than that of those composites with lower sulfonate contents and no second rise of conductivity occurs below 30 wt % PAN content, probably due to more interaction between NH groups of PAN and more sulfonate groups of the ionomer.

Mechanical properties of the composites

Figure 4 shows the tensile strength of the composites with different sulfonate contents versus PAN content. It is known that zinc sulfonated EPDM ionomer cannot be easily melt processed in the absence of ionic plasticizer, such as zinc stearate.¹³ Hence, the composite containing EPDM with higher sulfonate content and lower PAN content cannot be processed in the absence of zinc stearate. However, with increasing PAN–DBSA content, the composite can be melt processed in the absence of zinc stearate. The composite is easier to be melt processed than the ionomer with higher sulfonate content in the absence of zinc stearate. These facts indicated that DBSA seems to improve the melt processing of the sulfonated EPDM ionomer.

In the case of PAN/ionomer composite containing ionomer with 10 and 24 mmol $\text{SO}_3\text{H}/100$ g, the tensile strength of the composite increases quickly with PAN

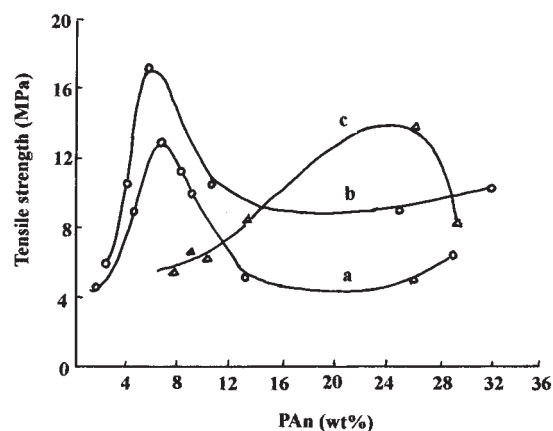


Figure 4 Tensile strength of the PAN/ionomer composites versus PAN content (sulfonate content, mmol/100 g: a: 10; b: 24; c: 40).

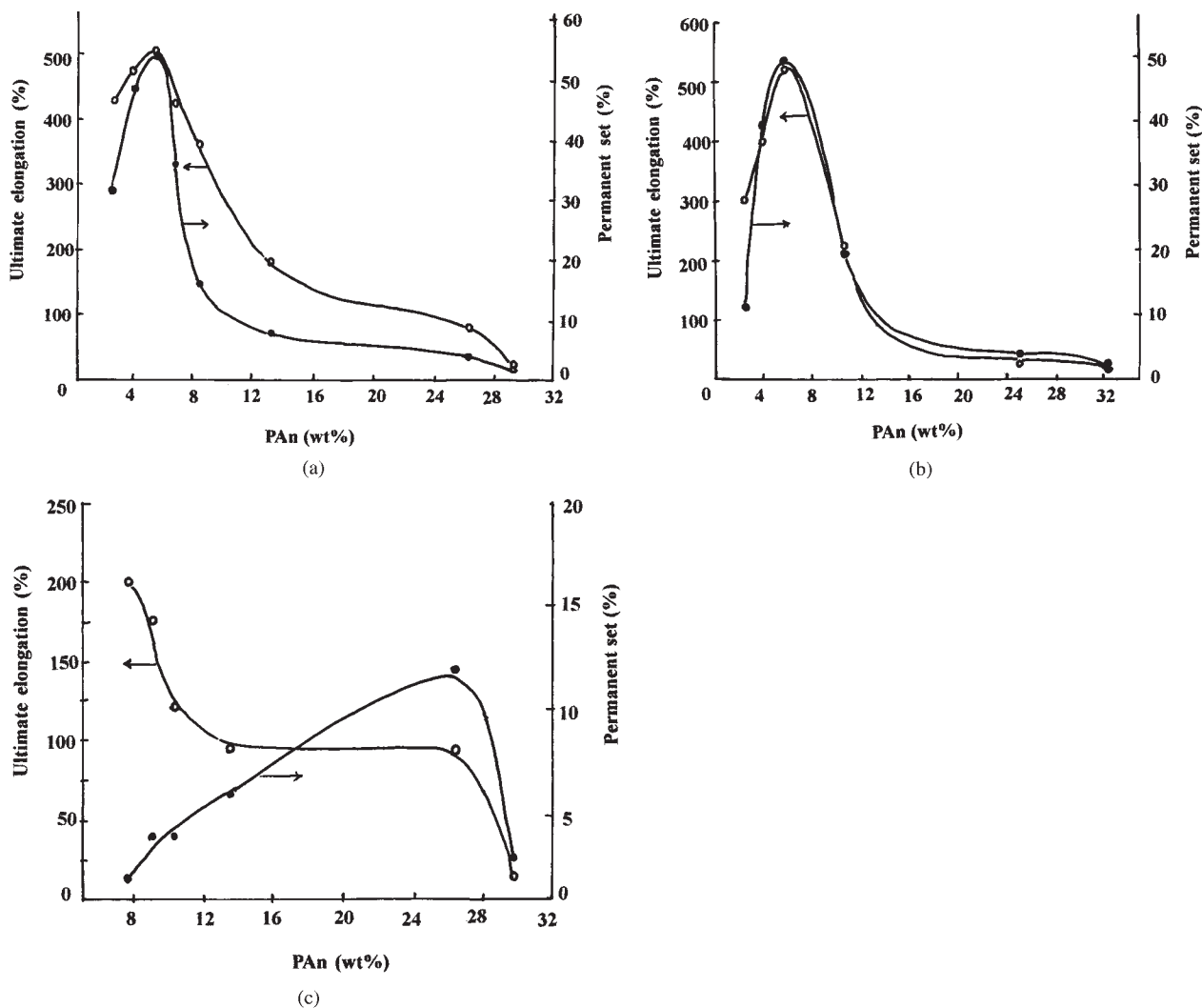


Figure 5 (a) Ultimate elongation and permanent set of the PAN/ionomer composites versus PAN content (sulfonate content, 10 mmol/100 g); (b) Ultimate elongation and permanent set of the PAN/ionomer composites versus PAN content (sulfonate content, 24 mmol/100 g); (c) Ultimate elongation and permanent set of the PAN/ionomer composites versus PAN content (sulfonate content, 40 mmol/100 g).

content at first until PAN content of about 7 wt % is reached and then decreases until 12 wt % PAN content is reached, probably because a certain amount of PAN-DBSA offers some reinforcing action, whereas excess PAN destroys the physically crosslinked network formed by ionic domains. A second rise of tensile strength begins at 26 wt % PAN, due to the rigidity of the PAN conductive routes.

In the case of composites containing the ionomer with 40 mmol $\text{SO}_3\text{H}/100$ g, the tensile strength of the composite rises relatively slowly and then falls. No second rise of tensile strength occurs within 28 wt % PAN content. This fact is due to more sulfonate groups which can interact with more PAN molecules. The PAN molecules distribute more uniformly in the ionomer matrix and prevent the formation of rigid conductive routes.

Figure 5(a, b, c) indicates that in the case of the composites containing the ionomer with 10 and 24

mmol $\text{SO}_3\text{H}/100$ g, with increasing PAN content, both ultimate elongation and a permanent set of the composites increase to maximum values about 500 and 50% at about 7 wt % of PAN, and then diminishes to 100 and 3%, respectively, at about 24 wt % PAN. In the range of the composites with 4 and 11 wt % PAN, the ultimate elongation is over 200% and the permanent set is <50%. This fact implies that these composites behave as thermoplastic elastomers. Beyond 12 wt % PAN, the composite behaves as plastics. However, in the case of the composites containing the ionomer with 40 mmol $\text{SO}_3\text{H}/100$ g, as shown in Figure 5(c), all the ultimate elongation is <200% and the permanent set is <10%. They behave as toughened plastics to rigid plastics.

The PAN/EPDMI composite is difficult to be dissolved in xylene; hence, it cannot be solution processed.

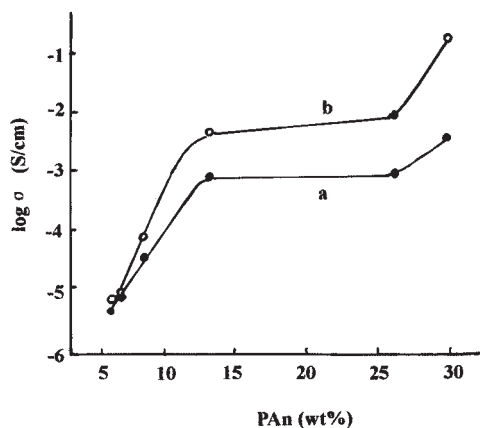


Figure 6 Conductivity of PAN/ionomer composite before secondary doping (a) and after secondary doping (b).

Effect of secondary doping on the conductivity of the composites

Secondary doping differs from the primary doping in that the enhanced conductivity persists even upon complete removal of the secondary dopant.¹⁴ In this study, the method of secondary doping was used to improve the conductivity of composite. It can be seen from Figure 6 that after the secondary doping the conductivity of the composite increases about one order and the percolation threshold changes somewhat from 13 to 11 wt % PAN. It verifies that the secondary doping is a way to enhance the conductivity of primarily doped composite of PAN/EPDMI. According to MacDiarmid and Epstein,¹⁴ the main character of secondary doping is the change of molecular conformation from "compact coil" to "expand chain" of the

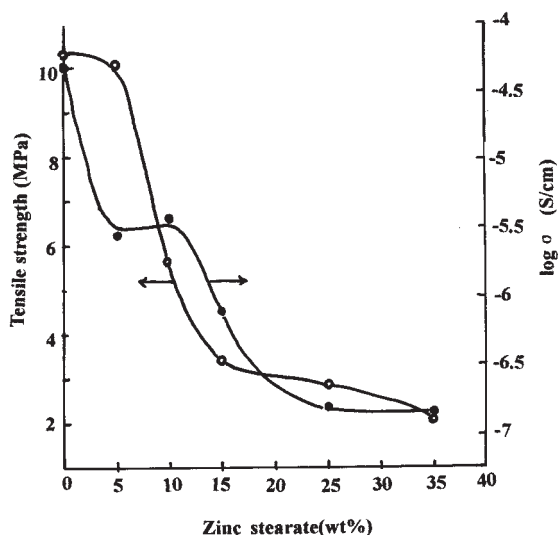


Figure 7 Effect of zinc stearate on the tensile strength and conductivity of the PAN/ionomer composites.

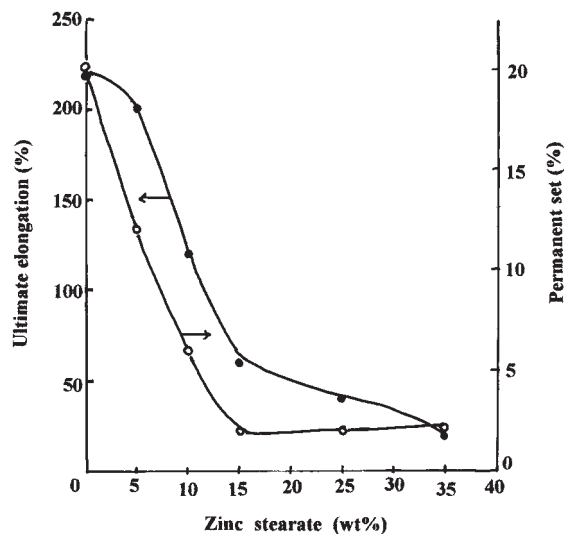


Figure 8 Effect of zinc stearate on the ultimate elongation and permanent set of the PAN/ionomer composites.

doped polymer. The above result implies that cresol weakens the interaction between PAN and the ionomer, expanding the PAN coils and enhancing the self-assembly of PAN chains to form conductive routes. WAXD analysis (Fig. 2) also demonstrates that secondary doping can enhance the crystallinity of PAN in the composite.

Effect of zinc stearate on the mechanical properties and conductivity of the composites

Makowski and Lundberg¹³ indicated that the zinc sulfonated EPDM ionomer can only be melt processed in the presence of zinc stearate and suggested that zinc stearate molecules enter into the ionic domains of the ionomer so that the interaction between the sulfonate groups of different ionomer molecules was replaced by the interaction between zinc stearate and sulfonate groups, resulting in the decrease of ionic domain size and more uniform distribution of ionic domains. These factors improve the mechanical properties of the ionomer. However, when the PAN/EPDMI composite is melt processed with zinc stearate, not only the conductivity of the composite diminishes, but also the tensile strength and the ultimate elongation decrease seriously, as shown in Figures 7 and 8. This phenomenon may be explained as follows: the interaction between the NH groups of PAN and the sulfonate groups of the ionomer tends to destroy the ionic domains and prevent the interaction between zinc sulfonate groups and zinc stearate, resulting in dispersion of zinc stearate as nonconductive fillers, thus lowering both the mechanical properties and the conductivity of the composites.

CONCLUSION

Electrically conductive composites of PAn with zinc sulfonated EPDM ionomer were prepared via a direct, one-step *in situ* emulsion polymerization technique. The zinc sulfonated EPDM ionomer present in the emulsion polymerization system is beneficial to aniline polymerization. The composites can be melt processed. DBSA seems to improve the melt processing of the composite. The conductivity of the composite increases with increasing PAn content, but decreases with increasing sulfonate content. Conductivity of the composites exhibits a percolation threshold at about 12–13 wt % PAn. Secondary doping can increase the conductivity of the composite about one order. Within a certain range of PAn content and lower sulfonate groups, the composites behave as conductive thermoplastic elastomers. Addition of zinc stearate as ionic plasticizer to the composite lowers both the conductivity and the mechanical properties of the composite.

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