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Polymer 40 (1998) 261–265

polymer

Conductive polyaniline–SBS composites from in situ emulsion polymerization

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Received 4 March 1998

Abstract

The composites of polyaniline (PAn) and SBS were made by polymerization of aniline in the presence of SBS, using a direct, one-step in situ emulsion polymerization technique. The polymerization of aniline was carried out in an emulsion comprising water and xylene containing SBS in the presence of dodecylbenzene sulfonic acid, acting both as a surfactant and a dopant for PAn. The composites obtained can be processed by melt method (MP) or solution method (SP). Conductivity of the composites processed by different methods exhibits different percolation thresholds: 10 wt% for MP sample and 7 wt% for SP sample. At the same content of PAn, the conductivity of SP composite is higher than that of MP composite. The relationships between mechanical properties and PAn content, as well as morphological structure of the composites obtained by the two different processing methods were studied. When the PAn content is lower than 12 wt%, the composites behave like a thermoplastic elastomer with high elongation (~600%) and low permanent set (<50%). The conductivity of composite after secondary doping with *m*-cresol is about two orders of magnitude higher than the original.

Keywords: Polyaniline; Composite; Emulsion polymerization

1. Introduction

Conductive organic polymers have been studied extensively as a result of their wide application potential. However, most of them suffer from poor processibility. In recent years much research was concerned with their composites with conventional polymers. This approach has been successful in producing electrical conductive composites with a wide range of interesting mechanical and electrical properties. Rubber is also used as matrix for their unique mechanical properties. Up to now, there are several methods for preparing conductive polymer–rubber composites, such as, electrochemical [1–3], latex [4–6], absorption [7,8], inverse emulsion polymerization [9,10] and blending [11–13]. Polyaniline (PAn) has been of great interest to many researchers because of its high conductivity, environmental stability and redox properties. This polymer includes several species in different oxidative states such as perniganiline, emeraldine and leucoemeraldine. Only emeraldine salt from emeraldine base (EB) and a suitable strong acid shows high conductivity, but it cannot be dissolved. However, EB can be dissolved in *N*-methyl-pyrrolidone, concentrated sulfuric acid and other strong acids [14], which are difficult to apply commercially on account of their prohibitive price or strong corrosion. Recently, it was reported that EB doped with a functionalized protonic acid, for example, camphorsulfonic acid (CSA) and dodecylbenzene sulfonic acid (DBSA), can be dissolved in a non-polar or moderate polar organic solvent [15]. Composites of plastics and PAn doped with CSA or DBSA were prepared using a cosolvent method [16]. Österholm et al. [17] reported the emulsion polymerization of aniline in the presence of DBSA and the use of a solution blending method to prepare the composite.

This paper deals with in situ oxidative polymerization of aniline in an emulsion of (styrene–butadiene–styrene) triblock copolymer (SBS), using functionalized organic acid DBSA as emulsifier and dopant, in order to prepare conductive polyaniline composite in one step, instead of first polymerization of aniline in the presence of functionalized portonic acid, followed by washing, drying and dissolution of the product in organic solvent and then blending with solution of SBS to form the composite. The second aim is to obtain an electrical conductive thermoplastic elastomer. Secondary doping with *m*-cresol was also studied to improve the conductivity of the composite. Mechanical properties and morphological structure were also investigated.

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0032-3861/98/$ - see front matter
PII: S0032-3861(98)00224-9

2. Experimental

2.1. Materials

All chemicals used in this study were chemically pure. Aniline was distilled and stored in a refrigerator. SBS was supplied by Yue-Yang Petroleum Chemical Co. with a styrene content of about 30% and M_w of 1.2×10^5.

2.2. Polymerization and processing of the composite

93 g SBS was dissolved in 600 ml xylene with stirring, followed by adding 18.1 ml aniline dropwise. Then a 200 ml xylene solution of 97.6 g DBSA was added slowly. After mixing with 100 ml distilled water with vigorous stirring to form an emulsion, 100 ml aqueous solution of $(NH_4)_2S_2O_8$ was added dropwise into the emulsion with stirring at room temperature. The polymerization lasted for 12 h.

Melt processing method (MP): after polymerization the emulsion of PAn-DBSA–SBS was precipitated by pouring into acetone. The dark green sediment was filtered and washed with acetone and water, then vacuum dried for 48 h. The composites were pressed at 130°C for 7 min.

Solution processing method (SP): the resulting emulsion was de-emulsified 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–SBS composite in xylene was obtained, which was stable at room temperature during storage. 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 or pellet was fully immersed in *m*-cresol, becoming semi-swollen, and taken out and dried under infrared light and under vacuum at 40°C to constant weight.

2.3. Measurement

The conductivity was measured at room temperature by the four-point probe method for higher conductivity, and by the three electrode methods for lower conductivity. 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.

3. Results and discussion

3.1. Effect of SBS on the polymerization of aniline

Table 1 presents the effect of feeding ratio of An–SBS on the PAn content of composite and PAn yield, both of which were calculated on the basis of the elemental analysis. It was found that the PAn yield was increased from 40% to about 73% when the feeding weight ratio of An–SBS decreased from 2 to 0.11. It implies that SBS in the emulsion is beneficial to the aniline polymerization. The reason may be that the oxidation polymerization of An·DBSA occurs at the surface of emulsion particles, as the oxidant, $(NH_4)_2S_2O_8$, is present in the aqueous phase. PAn·DBSA formed at the surface moves to centre of the particles. The presence of SBS helps the uniform distribution of PAn·DBSA in the emulsion particles, since S and B segments in SBS, which are similar in structure to the dodecylbenzene group of DBSA, enhance the dissolution of PAn·DBSA in xylene.

3.2. Electrical and mechanical properties of composites obtained by MP method

Fig. 1 shows that the change of conductivity of PAn–SBS composite versus PAn content exhibits a percolation threshold. When the PAn content is lower than 4.6 wt%, the conductivity of composite changes slightly and approaches that of SBS. As the content of PAn increases from 4.6 to 17.2 wt%, conductivity of the composite increases rapidly from 10^{-9} to 2.4 S cm^{-1} and then slowly with increasing PAn content. The percolation threshold for the conductivity is about 10 wt% of PAn content in the composite.

The same figure indicates that PAn enhances the tensile strength of composite, as the PAn content is below 5 wt%, but the tensile strength of composite decreases seriously, when PAn content is over 6 wt%, probably because a certain

Table 1
Effect of SBS on the polymerization of aniline[a]

Feeding ratio of An/SBS (wt/wt)	PAn content[b] of the composite (wt%)	Yield of PAn[b] (%)
0.11	4.6	72.9
0.14	6.2	75.3
0.20	8.4	74.9
0.33	11.0	61.7
1.0	17.1	39.5
2.0	24.2	40.1

[a]Polymerization conditions: $(NH_4)S_2O_8$/An(molar ratio) = 0.5, DBSA/An (molar ratio) = 1.5, [An] = 0.2 mol l^{-1}, xylene–water (v/v) = 8/2
[b]Calculated on the basis of elemental analysis

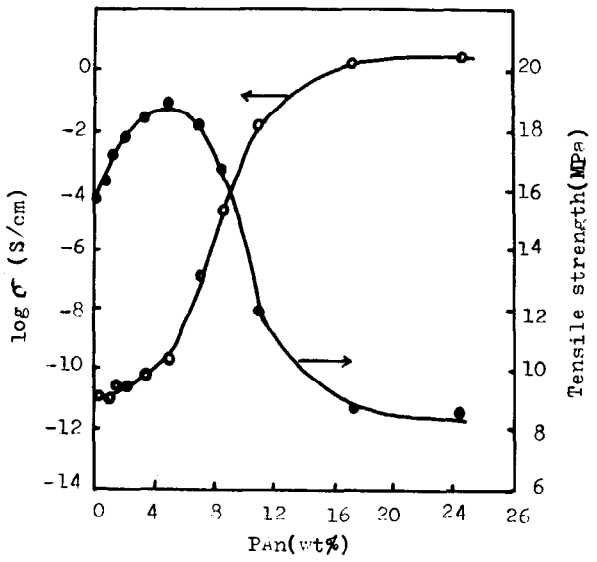

Fig. 1. Change of conductivity and tensile strength of the composites made from the MP method versus PAn content.

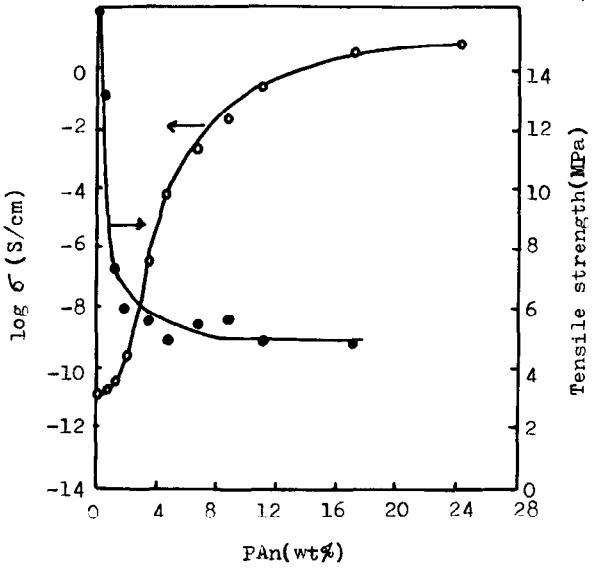

Fig. 3. Change of conductivity and tensile strength of the composites obtained by the SP method versus PAn content.

amount of PAn offer a reinforcing action, whereas excess PAn destroys the physically crosslinked network formed by PS segments of different SBS macromolecules.

From Fig. 2 it can be noted that the ultimate elongation of composite increases with PAn content of the composite up to 8 wt%, then falls down. The change trend of permanent set is similar to that of ultimate elongation. At PAn content higher than 16 wt% all the three mechanical properties became poor, but the composites with PAn content lower than 12 wt% behave like thermoplastic elastomer: the ultimate elongation is higher than 600%, whereas the permanent set is lower than 50%.

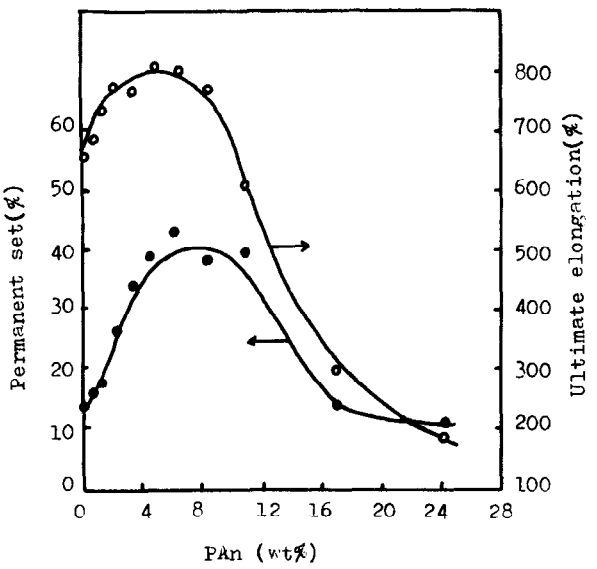

Fig. 2. Change of ultimate elongation and permanent set of the composites obtained by the MP method versus PAn content.

3.3. Electrical and mechanical properties of composites obtained by SP method

The conductivity of composites obtained by SP method (SP sample) is 10^5 times higher than that obtained by MP method (MP sample), when the PAn content of composite is 4.6 wt%, as shown in Figs 1, and 3. However, the conductivity of MP sample becomes near to that of SP sample, when the PAn content is above 16 wt%. These results indicate that processing method has a noticeable effect on the dispersion behaviour of the conductive component, which directly decides the formation of conductive path. Therefore, at a low content of conductive component, the conductivity of composite shows an obvious difference between the SP and MP samples, whereas no conductivity difference can be observed between MP and SP samples, as the conductive component content is high enough to form more complete conductive network. The percolation threshold of SP sample is about 7 wt%, which is apparently lower than that of MP sample.

The tensile strength of SP sample falls rapidly with increasing PAn content. The phenomenon may be explained by the uniformly dispersion of PAn in the matrix of the SP sample. During the solution process, PAn molecules can mix thoroughly with SBS, thus exerting influence on the formation of physically crosslinking glassy domains of PS, and the crosslink strength of PS domains is reduced by PAn molecules in the PS domains.

It is found from the effect of PAn content on ultimate elongation and permanent set of the SP samples (Fig. 4) that when PAn content is below 2 wt%, the composites have better elasticity than SBS. This is probably because the crosslink density of the composites with little PAn content is suitable for increasing elasticity, i.e. increasing ultimate elongation and decreasing permanent set. When the

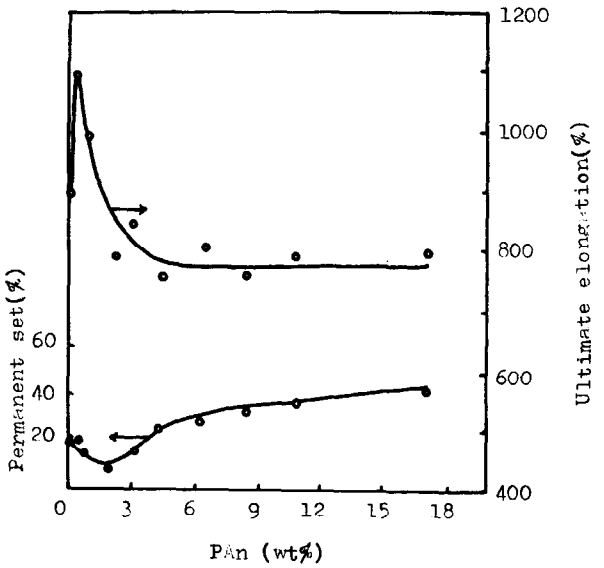

Fig. 4. Change of ultimate elongation and permanent set of the composites obtained by the SP method versus PAn content.

PAn content is near or higher than the percolation threshold, the ultimate elongation and permanent set show no change with increase of PAn content and the SP samples also behave like thermoplastic elastomer with ultimate elongation higher than 700% and with permanent set lower than 50%. But they exhibit lower tensile strength than the MP samples.

3.4. Morphological structure

Fig. 5a and b are the scanning electron micrographs of the broken sections of MP and SP samples, respectively. The PAn content of both samples used is 11.0 wt%. The MP sample presents a brittle fracture character (Fig. 5a) with microvoids of several micrometers size, whereas the SP sample displays a ductile fracture feature (Fig. 5b) with no holes. The difference may be ascribed to more destruction of the PS domain by the penetration of PAn molecules in the SP sample than that in the MP sample, resulting in lower strength and more ductile character of the SP sample. The microvoids in the MP sample may be due to the PAn aggregates.

Earlier analysis is further verified by the results of wide angle X-ray diffraction, as shown in Fig. 6. In the WAXD pattern, no difference exists between SP sample and pure SBS, which means that no crystal structure of PAn exists in the SP composite. In other words, a completely amorphous structure of PAn was obtained by the solution method. However, the WAXD pattern of MP sample shows a new narrow peak at small angle, which is attributed to long-range ordering crystallization. This phenomenon may be due to the self-assembly of PAn molecules into aggregates under processing temperature (130°C). The same phenomenon was found and discussed by Zheng et al. [18] in the study of thermal treatment of PAn-DBSA mixture. From the aforementioned results it is certain that the MP sample contains larger aggregates of PAn than the SP sample, which further supports the analysis for the electrical and mechanical properties of the composites.

3.5. Secondary doping of the composites

The concept of doping distinguishes the conducting polymers from other types of polymers. Two common forms of doping are presently well established in the conducting

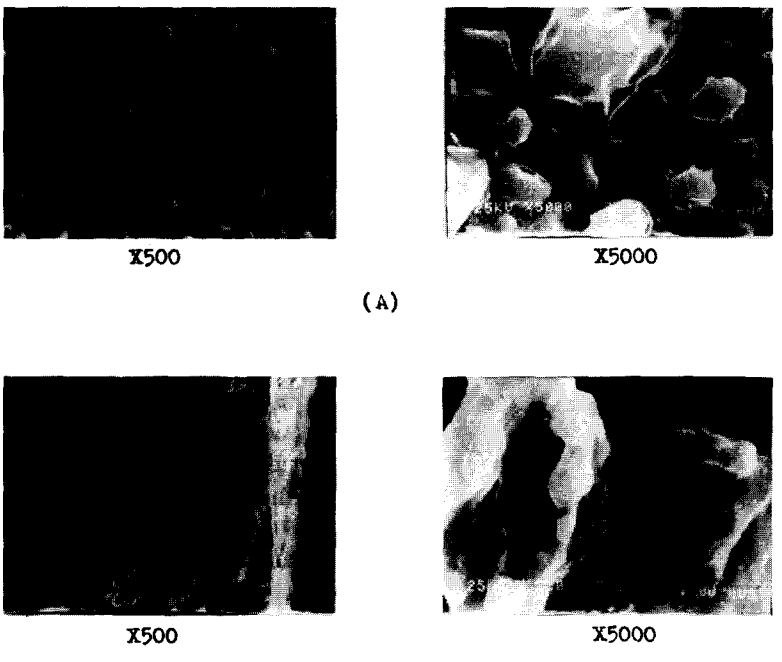

Fig. 5. SEM micrographs of the broken sections of PAn–SBS composites obtained by (a) the MP method; and (b) the SP method.

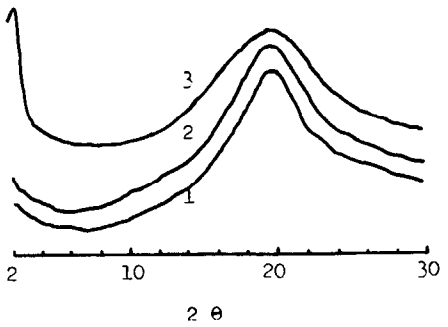

Fig. 6. WAXD patterns of SBS and PAn–SBS composites: 1-SBS; 2-PAn–SBS obtained by the SP method; 3-PAn–SBS obtained by the MP method.

polymer field, involving basically two different processes, viz., (1) 'redox doping', whereby oxidizing or reducing agents remove or add electrons from or to the polymer backbone, respectively; and (2) 'protonic acid doping', whereby the number of electrons associated with the polymer chain remain unchanged. The above dopings are named as 'primary doping'. Very recently, secondary doping has been recognized, which differs from the primary doping in that the newly enhanced properties may persist, albeit to a reduced extent, even upon complete removal of the secondary dopant.

Up to now, secondary doping was only reported for pure conductive polymers. In this study, the method of secondary doping was used to improve the conductivity of composite. The results are illustrated in Fig. 7. It can be seen from comparison of Fig. 7 with Figs 1 and 3 that the conductivity of SP and MP samples increases about two orders of magnitude after secondary doping with *m*-cresol. It verifies that secondary doping is also an effective way to increase the conductivity of primarily doped conductive composite. After secondary doping, the conductivity of SP sample increases more obviously than that of MP sample and the percolation threshold of SP sample decreased noticeably

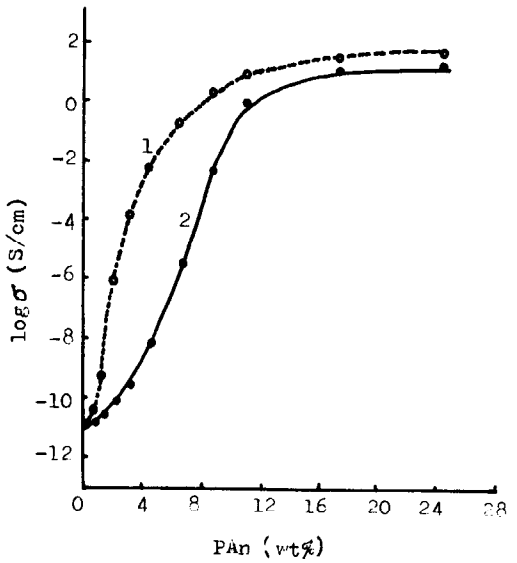

Fig. 7. Effect of secondary doping on the electrical conductivity of PAn–SBS composites: 1-SP sample; and 2-MP sample.

from 7 to 3 wt%, whereas the percolation threshold of MP sample shows very little change. This result demonstrates that the morphological structure of primarily doped conductive component in the composite affects markedly on the secondary doping. According to MacDiarmid [19], the main character of secondary doping is the change of molecular conformation from 'compact coil' to 'expanded coil' of the doped polymer. By secondary doping, the dispersion state of PAn in the composite can not be changed, but the connection of conductive component can be changed. There is more chance for the SP sample to increase the connection of the conductive component through expanding a conductive polymer backbone than for the MP sample, since there is more uniform dispersion of PAn in the SP sample than in the MP sample.

4. Conclusion

Electrically conductive composites have been prepared via a direct, one-step in situ emulsion polymerization technique. SBS present in the reaction system is beneficial to aniline polymerization. The processing method of the composite is an important factor that affects both the conductivity and the mechanical properties of the PAn-DBSA containing composites, which depend on the dispersion behaviour of conductive component in matrix. The above conclusion is consistent with the morpholigical structure of the composite based on the results of WAXD and SEM. Within a certain range of PAn content, the composites behave like a thermoplastic elastomer. Secondary doping was verified as an effective way to increase the conductivity of the composites.

References

[1] Mori K, Konno T, Oishi Y. Rubber Chem Technol 1993;66(5):806.
[2] Zoppi RA, De Paoli MA. Polymer 1992;33:4611.
[3] Tassi EL, De Paoli MA. Polymer 1994;35:565.
[4] Cooper EL, Vincent B. J Phys D Appl Phys 1989;22:1580.
[5] Liu CF, Maruyama T, Yamamoto I. Makromol Chem 1992;193:829.
[6] Xie HQ, Liu H, Liu ZH, Guo JS. Angew Makromol Chem 1996;243:117.
[7] Raddakrishuan S, Saini RD. Polym Int 1994;34:111.
[8] Zoppi RA, Felisberti MI, De Paoli MA. J Polym Sci, Part A Polym Chem 1994;32:1001.
[9] Ruckenstein E, Sun Y. Synth Meth 1995;74:107.
[10] Sun Y, Ruckenstein E. Synth Meth 1995;72:261.
[11] Olmedo L, Delueze C, Dufort M. Plast. Engng 1991;49:774.
[12] Zheng WY, Levon K. Polym Prepr 1994;35(2):759.
[13] Ruckenstein E, Chen JH. Polymer 1991;32:1230.
[14] Andreatta A, Cao Y, Chiang JC. Synth Meth 1988;26:383.
[15] Heeger AJ. Synth Meth 1993;3471.
[16] Cao Y, Smith P, Heeger AJ. Synth Meth 1993;3514.
[17] Österholm JE, Cao Y, Klavetter F, Smith P. Polymer 1994;35(13):2902.
[18] Zheng WY, Wang RW, Levon K. Macromol Chem Phys 1995;196:2443.
[19] MacDiarmid AG, Epstein AH. Synth Meth 1995;69:85.