Synthesis and Properties of Polyaniline/Sodium and Zinc Ionomer Composites

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ABSTRACT: Polymerization of aniline was carried out with stable poly(methyl methacrylate-butyl methacrylate-sodium acrylate) [P(MMA-BA-AANa)] and poly(methyl methacrylate-butyl methacrylate-zinc acrylate) [P(MMA-BA-$(AA)_2Zn$)] ionomer emulsions to improve the processability of polyaniline (PANI). The results indicated that the two ionomer emulsions not only improved the tensile strength of PANI but also maintained the conductivity of PANI at room temperature. Suitable polymerization conditions had been established for the synthesis of PANI/P(MMA-BA-AANa) and PANI/P(MMA-BA-$(AA)_2Zn$) composites. The obtained PANI composites had the conductivity of more than $10\,S\,cm^{-1}$ with tensile strength of more than 7.0 MPa at room temperature. The threshold values were proved to be 19 w/w% and 16 w/w% for PANI/P(MMA-BA-AANa) and PANI/P(MMA-BA-$(AA)_2Zn$) composites, respectively.

KEY WORDS   Polyaniline / Composite / Ionomer / Conductive Polymer /

Polyaniline (PANI) has emerged as one of the most promising conducting polymers for its potential applications in several technological areas, such as batteries,[1] electrochromic display,[2] electronic devices,[3] field effect transistors,[4] electrochemical sensors,[5] and the third order non-linear optical materials.[6] However, the processing difficulty of PANI has limited its utilization on an industrial scale although processed PANIs with the conductivity of $10^0\,S\,cm^{-1}$ have been obtained by research groups recently.[7-11] Attempts to improve the processability, flexibility and tensile strength of PANI film have met with some success. One of the effective ways is to synthesize PANI latex composite in emulsions, such as polyvinylpyridine, poly(vinylpyridine-*co*-methyl methacrylate), poly(vinyl aclcohol-*co*-vinyl acetate), and poly(ethylene oxide) emulsions.[6,12-15] The modified PANI latex composites have excellent tensile strength as well as electrical conductivity in the range of 10^{-2}—$10^0\,S\,cm^{-1}$.

It is well known that the tensile strength of the ionomer of poly(methyl methacrylate-*co*-butyl acrylate-*co*-sodium acrylate) [P(MMA-BA-AANa)] is higher than that of poly(methyl methacrylate-*co*-butyl acrylate-*co*-acrylic acid) [P(MMA-BA-AA)] because of the ionic domains in the ionomer. It thus seems reasonable to expect that the processability of PANI could be improved in ionomer emulsions. Here, we report a preparative route by which PANI composites with high conductivity and tensile strength could be obtained *versus* a polymerization of aniline (ANI) in the ionomer emulsions of P(MMA-BA-AANa) and poly(methyl methacrylate-butyl methacrylate-zinc acrylate [P(MMA-BA-$(AA)_2Zn$)]. Our results show that this method to obtain PANI latex composites is an effective way to improve the processability of electrical conductive PANI.

EXPERIMENTAL

Methyl methacrylate (MMA) and butyl acrylate (BA) were first washed by aqueous sodium hydroxide, followed by distilled water, dried with anhydrous sodium sulfate, and then distilled under vacuum. ANI and acrylic acid (AA) were purified by vacuum distillation. All the purified reagents were stored in the dark and sealed in ampoules at $-5°C$ until use. Sodium hydroxide, zinc oxide, potassium persulfate ($K_2S_2O_8$), ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium decylsulfonate were analytical regents and used without purification.

Sodium acrylate (AANa) and zinc acrylate ($(AA)_2Zn$) were prepared by reacting AA with sodium hydroxide and zinc oxide, respectively. The emulsion of P(MMA-BA-AANa) was prepared by reacting MMA, BA, and AANa in the presence of sodium dodecylsulfonate ($NaSO_3(CH_2)_{11}CH_3$) with $K_2S_2O_8$ as an initiator at 60°C for 2 h. The weight ratio of $H_2O : NaSO_3(CH_2)_{11}$-$CH_3 : MMA : BA : AA : K_2S_2O_8$ was $20 : 0.02 : 3 : 7 : 1.5 : 0.05$. P(MMA-BA-$(AA)_2Zn$) emulsion was obtained by the same method and the same weight ratio by replacing AANa with $(AA)_2Zn$. After 2 h of polymerization, the stable sodium and zinc ionomer emulsions were obtained. For both the sodium and zinc ionomer emulsions, the conversions of monomers were 90% and the solid contents of the emulsions were 30%.[16,17]

Triton X-100 (5—10 wt% of the ionomer emulsion) was added to the ionomer emulsion in a three-necked flask which was cooled to 0°C in an ice bath. Pure aniline was dissolved in 1.4 M (M = mol dm^{-3}) HCl aqueous solution to form a 0.5 M solution of ANI while solid $(NH_4)_2S_2O_8$ was dissolved in 1.4 M HCl to form a 0.25 M solution. The two solutions obtained were refrigerated to 0°C before they were separately added dropwise to the ionomer emulsion from different neck of the flask for a period of about 0.5—1 h. When aniline and $(NH_4)_2S_2O_8$ were dropped to the emulsions, the color of the emulsions was observed to change from milky to brown at the initial stage of the reaction and be-

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Table I. Elemental analysis of PANI/P(MMA-BA-AANa) and PANI/P(MMA-BA-$(AA)_2$Zn) ionomers

Aniline: emulsion (solid)	Experimental contents of C, H, N in the composites of AANa/$(AA)_2$Zn ionomer emulsions			Experimental contents of PANI in sodium/zinc ionomer of composites	Contents of PANI expected in sodium/zinc ionomer composites	Isolated yields of the composites
w/w	C %	H %	N %	%	%	%
1 : 0.55	58.7/56.1	6.43/4.17	5.15 /3.10	45.1/42.3	42.9/40.5	96.7/95.3
1 : 1.08	59.8/57.1	7.50/5.21	3.43 /2.05	30.0/27.6	27.7/25.1	96.9/95.7
1 : 3.30	61.5/58.7	8.02/5.42	1.80 /1.03	15.7/13.0	11.1/8.50	97.0/95.9
1 : 4.95	63.0/60.5	9.11/6.10	0.400/0.100	3.50/1.83	4.00/1.06	96.8/95.5
0 : 1	63.1/61.0	9.55/6.42	0 /0	0 /0	0 /0	97.0/95.2

came green finally. Upon complete addition of aniline and $(NH_4)_2S_2O_8$ solutions, the polymerization reaction was allowed to continue for another 6 h at room temperature. The polymerization was terminated by pouring the emulsion into an acetone solution, and the green powder of PANI/ionomer complex was precipitated. The green powder was filtered and washed until the pH of the washed water was neutral. The powder was then dried in a vacuum desiccator at 50°C for 4 h. The PANI composite films (0.1—2 mm) were obtained by hot pressing the dried powder at 120—140°C under the pressure of 7—10 kg cm².

The conductivity was measured by a four-probe method at room temperature. The content of PANI in the composites was analyzed by elemental analysis. The samples of sodium and zinc ionomer emulsions and PANI composites modified by sodium and zinc ionomers were investigated by transmission electron microscope (TEM) by staining with Os_3O_4 for 24 h.

RESULTS AND DISCUSSION

Stable emulsions of poly(MMA-BA-AANa) or poly-(MMA-BA-$(AA)_2$Zn) are obtained with the weight ratio of MMA : BA : AA of 3 : 7 : 1.5 (molar ratio is 1.0 : 1.8 : 0.69). The solid contents of the final emulsions of sodium and zinc ionomers are both 30%.[16,17]

Influence of PANI Content

Results from elemental analysis are presented in Table I. It can be seen that the PANI contents of PANI/sodium and PANI/zinc composites are all higher than those expected. Similar results have been reported for the PANI composites modified by Haloflex EP252 emulsion and polyvinylpyridine emulsion because of the presence of emulsions.[15] For the emulsion polymerization of aniline, adsorped aniline in the emulsion is polymerized on the surface of the emulsion particles. At the same time, some aniline is also polymerized in the aqueous solution. Hence, the obtained PANI composite contains mainly the PANI that is polymerized on the surfaces of the emulsion particles and the small amount of PANI in the aqueous phase. As there are some difficulties for the emulsion to be completely precipitated in an acetone solution, this has thus resulted in the PANI contents of the composites analyzed by elemental analysis being a little higher than those expected from full recovery.

Figure 1 shows the plots of electrical conductivity *versus* the PANI conent for the two ionomer composites synthesized. The curves of the two composites are fair-
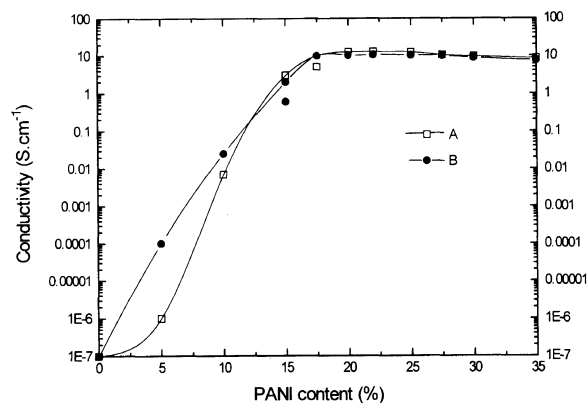

Figure 1. Influence of PANI content on the conductivity of sodium and zinc ionomer composites: □, sodium ionomer composite; ●, zinc ionomer composite. Polymerization condition: HCl 1.4 M; $(NH_4)_2S_2O_8$ 0.25 M; aniline 0.5 M; the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

ly similar. As the contents of PANI increase from 0 to 19 w/w% and 0 to 16 w/w% for PANI composites modified with sodium and zinc ionomers, respectively, both conductivities increase rapidly from 10^{-7} S cm^{-1} to 10^0 S cm^{-1}. However, the conductivity then levels off at about 10^1 S cm^{-1} as the PANI content increases further.

This phenomenon has also been noted for PANI composites modified by other emulsions and is turned as the percolation threshold.[12,15] PANI/P(MMA-BA) latex composite has the percolation threshold value at 5 w/w% and its conductivity at the percolation threshold value is 1 S cm^{-1}, and PANI/Haloflox EP 253 latex composite has the conductivity of 10^{-1} S cm^{-1} at the percolation threshold value of 5—10 w/w%.[12,15] From Figure 1, it is demonstrated that PANI/P(MMA-BA-AANa) and PANI/P(MMA-BA-$(AA)_2$Zn) composites have the conductivity in the range of 10^1 S cm^{-1} at percolation threshold values of 19 w/w% and 16 w/w%, respectively.

With increasing PANI contents, the tensile strengths of the two of ionomer composites increase while their elongations at break decrease as shown in Figure 2. The tensile strengths of the two composites reach their maxima at PANI contents of 25% and 13% for sodium and zinc ionomer composites, respectively. During the process of the polymerization of aniline in an emulsion, PANI particles are mainly formed on the surfaces of the emulsion particles. Compared with the ionomers, PANI is a hard filler in the composite and thus results in an increase in tensile strength as well as decreasing of
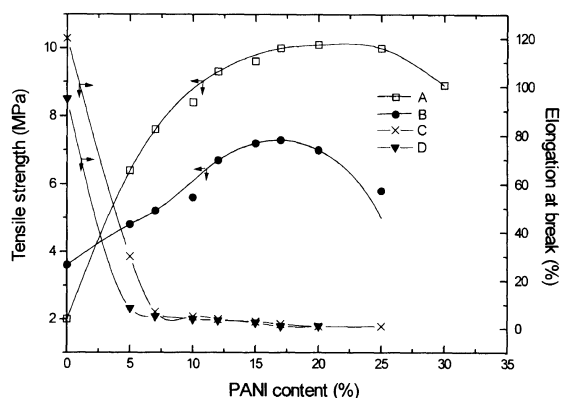
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Figure 2. Influence of PANI content on the tensile strength and elongation at break for the two composites: □ and ×, sodium ionomer composite; ▼ and ●, zinc ionomer composite. Polymerization condition: HCl 1.4 M; $(NH_4)_2S_2O_8$ 0.25 M; aniline 0.5 M; the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

Figure 3. Influence of molar ratio of $(NH_4)_2S_2O_8$ to aniline on the conductivity of the composites: □, sodium ionomer composite; ●, zinc ionomer composite. Polymerization condition (changing the amount of $(NH_4)_2S_2O_8$): HCl 1.4 M; aniline 0.5 M; $(NH_4)_2S_2O_8$ 0.25 M; PANI content 25% (wt).

elongation at break for the composites. As the contents of PANI in the composites increase, the amount of oxidant needed for the polymerization of aniline becomes larger, and the oxidative degradation of ionomers also becomes more severe. This results in yielding a more brittle composite.[12-15] The brittle characteristic of pure PANI will lower both the tensile strength and the elongation at break for the composites. Therefore, there is a maxima in each curve of the tensile strength *versus* PANI content for the two ionomer composites.

Influence of the Concentration and Amount of $(NH_4)_2S_2O_8$ as Oxidant

As shown in Figures 3 and 4, there is a maximum in each curve of conductivity *versus* molar ratio of $(NH_4)_2S_2O_8$ to aniline or conductivity *versus* concentration of $(NH_4)_2S_2O_8$ for the two ionomer composites. As the molar ratio of $(NH_4)_2S_2O_8$ to aniline is in the range of 0.32 to 2.0, the conductivities of both the composites are in the range of 10^0—10^1 S cm^{-1} and reach their maxima when the molar ratio of $(NH_4)_2S_2O_8$ to aniline is 0.5 for Zn^{2+} ionomer composite and 0.60 for Na$^+$ ionomer composite. After the maxima, the conductivity decreases with further increasing the molar ratio. The highest conductivities of PANI latex composite modified by sodium and zinc ionomer are 12.6 and 10.5 S cm^{-1}, respectively. Compared to that of the polymerization of pure aniline, larger amount of $(NH_4)_2S_2O_8$ is needed to achieve the similar results in the emulsion polymerization. The reason is that some $(NH_4)_2S_2O_8$ have been consumed in the oxidation of the ionomer chains.[20,21]

For both the composites, when the concentration of $(NH_4)_2S_2O_8$ is less than 0.25 M, the conductivity of two composites increases with increasing $(NH_4)_2S_2O_8$ concentration; when the concentration of $(NH_4)_2S_2O_8$ becomes larger than 0.25 M, the conductivity starts to decrease with the increase of $(NH_4)_2S_2O_8$ concentration.

The above results reveal that the maximum conductivity can be obtained in a suitable concentration of $(NH_4)_2S_2O_8$ and the molar ratio of $(NH_4)_2S_2O_8$ to aniline. Less $(NH_4)_2S_2O_8$ is not enough to oxidize aniline, as a result, the conductivity of the composite is
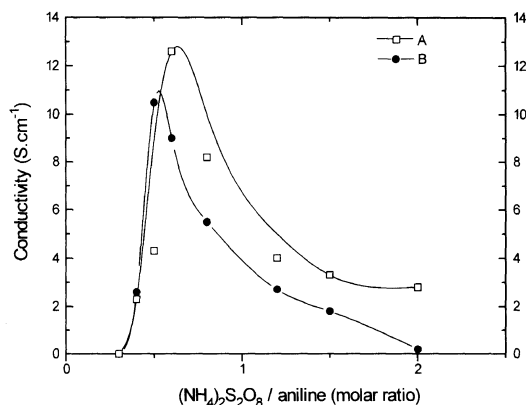

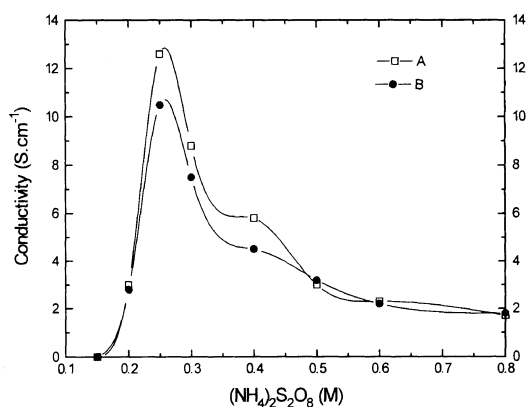**Figure 4.** Influence of the concentration of $(NH_4)_2S_2O_8$ on the conductivity of the composites: □, sodium ionomer composite; ●, zinc ionomer composite. Polymerization conditions: HCl 1.4 M; aniline 0.5 M; PANI content 25% (wt); the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

lower. Too much $(NH_4)_2S_2O_8$ leads aniline to be overoxidized to yield complicated structures, which affect the conductivity. Hence, the conductivity becomes lower. In addition, too much $(NH_4)_2S_2O_8$ can oxidize the emulsion, leading to lower both tensile strength and elongation at break.[13-15]

$(NH_4)_2S_2O_8$: aniline ratio and the concentration of $(NH_4)_2S_2O_8$ have great influence on the tensile strength of the composites. As shown in Figures 5 and 6, the tensile strength shows maximum value at $(NH_4)_2S_2O_8$: aniline of the molar ratio of 0.5 and at the concentration of $(NH_4)_2S_2O_8$ of 0.25 M.

Influence of the Concentration of Aniline

Figures 7 and 8 show that both composites reach the maximum conductivity, the lowest elongation and higher tensile strength at the aniline concentration of 0.5 M. This is attributed to the polymerization mechanism of aniline absorbed on the surfaces of the emulsion particles. When the concentration of aniline is low, the emulsion particles absorb little aniline. This will lead to a lower conductivity and tensile strength for the composites. With increasing aniline concentration, more aniline molecules are absorbed onto the emulsion particles
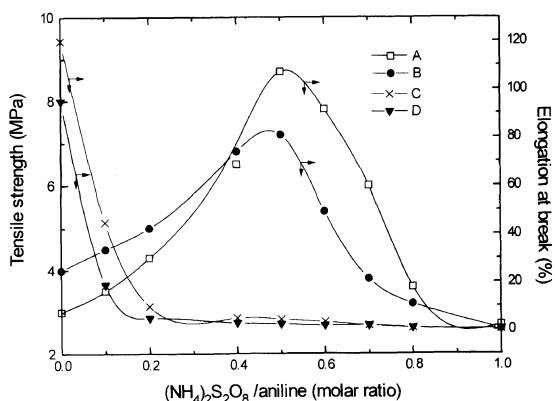
Figure 5. Influence of molar ratio of $(NH_4)_2S_2O_8$ to aniline on the tensile strength and elongation at break for the composites: □ and ×, sodium ionomer composite; ▼ and ●, zinc ionomer composite. Polymerization condition (changing the amount of $(NH_4)_2S_2O_8$): HCl 1.4 M; aniline 0.5 M; $(NH_4)_2S_2O_8$ 0.25 M; PANI content 25% (wt).

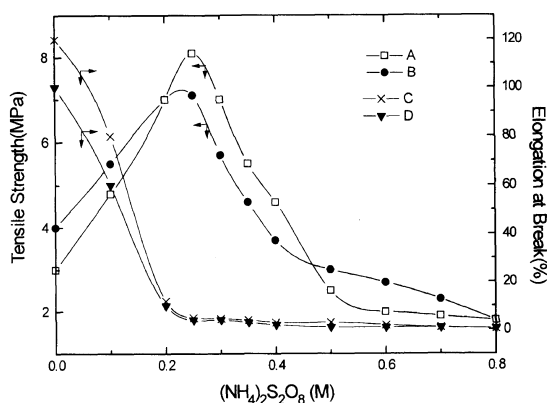**Figure 6.** Influence of the concentration of $(NH_4)_2S_2O_8$ on the tensile strength and elongation at break for the composites: □ and ×, sodium ionomer composite; ▼ and ●, zinc ionomer composite. Polymerization conditions: HCl 1.4 M; aniline 0.5 M; PANI content 25% (wt); the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

Figure 7. Influence of the concentration of aniline on the conductivity of the composites: □, sodium ionomer composite; ●, zinc ionomer composite. Polymerization condition: HCl 1.4 M; $(NH_4)_2S_2O_8$ 0.25 M; the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

Figure 8. Influence of the concentration of aniline on the tensile strength and elongation at break for the two composites: □ and ×, sodium ionomer composite; ▼ and ●, zinc ionomer composite. Polymerization condition: HCl 1.4 M; $(NH_4)_2S_2O_8$ 0.25 M; the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

Figure 9. Influence of the concentratio of HCl on the conductivity of the composites: □, sodium ionomer composite; ●, zinc ionomer composite. Polymerization condition: aniline 0.5 M; $(NH_4)_2S_2O_8$ 0.25 M; PANI content 25% (wt); the molar ratios of $(NH_4)_2S_2O_8$ to aniline are 0.5 and 0.6 for sodium and zinc ionomer composites, respectively.

and polymerized. That will increase the conductivities and the tensile strengths of the composites. However, too high concentration of aniline will also lead more free aniline in the aqueous phase. The free aniline polymerized in the aqueous phase will not mix well with the ionomer. Therefore, the tensile strengths of the composites suffer at high concentration of aniline.[18,19]

Influence of HCl Concentration

The effect of HCl on the conductivity is shown in Figure 9 curves of conductivity *versus* HCl concentration which reveal the optimum HCl concentration is in the range of 1.2—1.5 M. When the concentration of HCl changes from 0.8 to 1.2 M, the conductivities of the composites increase rather sharply. In the region of 1.2—1.5 M, the conductivities remain in the range of 10^1 S cm^{-1}. Further increase in the concentration of HCl results in decrease of conductivities of the composites.

The optimum concentration of HCl for the polymerization of pure aniline to yield the maximum conductivity is 0.5 M.[22] The results from the present study indicate higher HCl concentration is needed for synthesis of PANI/ionomer composites. In the polymerization of PANI composite, more HCl is absorbed onto ionomer
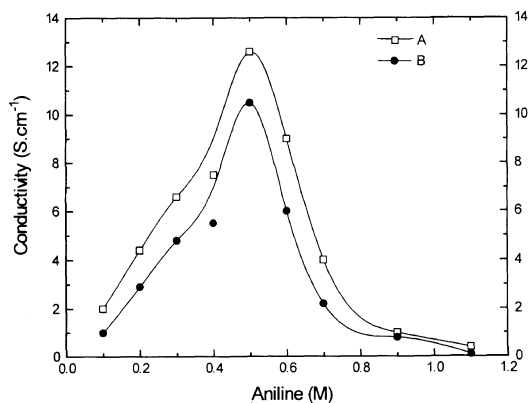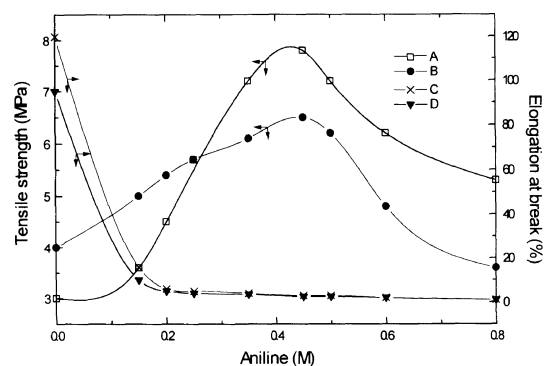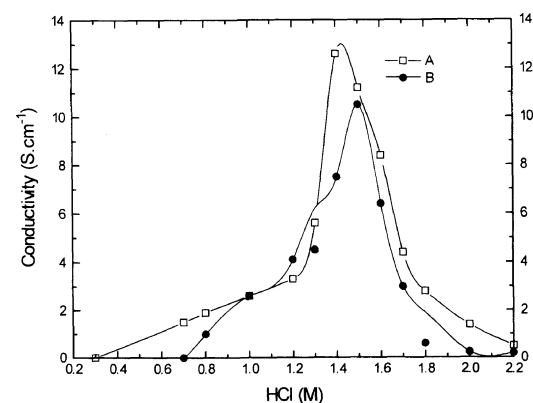
emulsion particles. Additionally, the high contents of –COONa or –COOZn groups in the ionomers (molar ratio of MMA : BA : AA is 1.0 : 1.8 : 0.69) could partially exchange with HCl. Therefore, the ionomers absorb more H$^+$ and result in more HCl exhausted during the polymerization of aniline in the ionomer emulsions
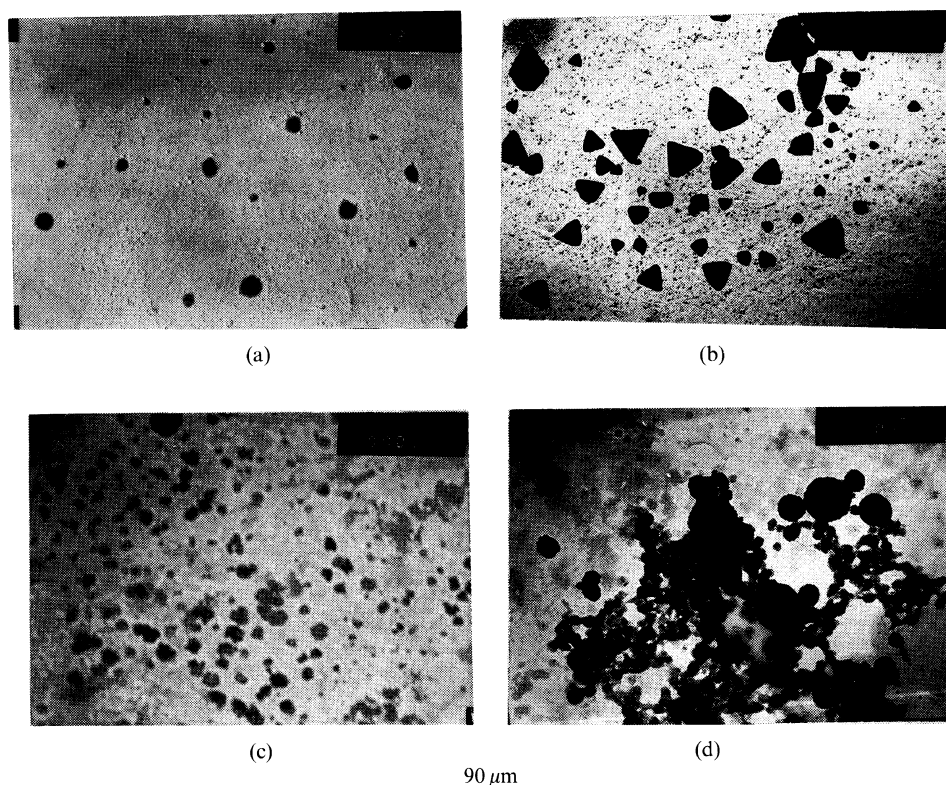
(a)   (b)

(c)   (d)

90 μm

Figure 10. TEM of the composites and the ionomers (Times 48 × 1000): (a) sodium ionomer; (b) sodium ionomer composite; (c) zinc ionomer; (d) zinc ionomer composite.

than that in pure aniline polymerization.

TEM of the Composites

Figure 10 shows the TEM micrographs of emulsions and composites. The TEM micrographs of ionomer emulsions show dark round particles, which are produced by the exchange Os_3O_4 with Na^+ or Zn^{2+}. That confirms that the emulsions are ionomers.[16,17]

In the TEM micrographs of the composites, the triangle particles of the composite produced by modifying sodium ionomer (Figure 10b) are larger than those of sodium ionomer emulsion (Figure 10a) because of the presence of PANI on the surfaces of the emulsion particles. Similarly, the net shapes in TEM of zinc ionomer composite (Figure 10d) are larger than those of zinc ionomer emulsion (Figure 10c) because of the absorbed PANI on the surfaces of the emulsion particles.[23,24]

CONCLUSION

The polymerization of aniline in poly(MMA-BA-AANa) and poly(MMA-BA-(AA)$_2$Zn) ionomer emulsions is investigated. The optimum polymerization conditions are established with respect to electrical conductivity, tensile strength, and elongation at break. It is found that the PANI composites with higher conductivity and larger tensile strength could be obtained under the following conditions: the molar ratios of $(NH_4)_2S_2O_8$/aniline are 0.5 and 0.6 for PANI composites produced by modifying sodium and zinc ionomer, respectively, and the concentration of $(NH_4)_2S_2O_8$ and aniline in 1.4 M aqueous HCl solutions are 0.25 and 0.5 M, respectively, and the optimum concentration of

HCl in the two polymerization systems is 1.2—1.5 M. The PANI composites prepared have the highest conductivity of $12.6\,S\,cm^{-1}$ for sodium ionomer composite and $10.5\,S\,cm^{-1}$ for zinc ionomer composite, both obtained composites have higher tensile strength of about 7 MPa. It is also found that the percolation threshold values of PANI/sodium ionomer and PANI/zinc ionomer composites are 19 w/w% and 16 w/w%, respectively. TEM studies confirm the existences of PANIs with larger triangle shapes in the sodium composite and larger net shapes in zinc ionomer composite, as compared with the corresponding ionomer emulsions.

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