Electrorheological Effects of Polyaniline-Type Electrorheological Fluids

Liucheng Zhang, Kai Su, Xiucuo Li

Chemical Engineering College, Hebei University of Technology, Tianjin, China

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ABSTRACT: Three kinds of particles—polyaniline (PANI), poly(*o*-toludine) (POT), and brominated polyaniline (Br-PANI)—were synthesized. With chlorinated paraffin as a disperse oil, their electrorheological (ER) effects were determined so that the influence of the phenyl substitute group on the ER effects could be considered. POT exhibited the strongest ER effect, whereas the Br-PANI ER effect was relatively poor. With the concept of polarization, this phenomenon was interpreted. The influence of the antidoping condition on the ER effects was also examined. An optimal antidoping condition was found for each kind of particle. Composite PANI/polyacrylamide (PAAm) and PANI/lithium polyacrylate (PAA-Li) particles were further prepared by emulsion polymerization. The testing results showed that the composite particles with certain amounts of PAAm or PAA-Li exhibited good ER effects. The dielectric and conductive behaviors were also determined so that the results could be explained. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 733–740, 2003

Key words: composites; emulsion polymerization; electrorheological fluid (ERF); polyaniline

INTRODUCTION

Electrorheological fluid (ERF) refers to a kind of smart material with rheological properties that make reversible changes drastically with changes in an external electric field. Generally, this kind of fluid is a suspension system consisting of fine, solid particles [electrorheological (ER) materials] suspended in an insulating, liquid medium. Although some applications have been developed,[1,2] the key factor for making an effective ERF is the choice or synthesis of a preferred ER material,[3] and many materials have been employed, with excellent properties obtained.[4–9] According to the chemical contents, they can be classified as inorganic, organic, or composite materials; according to the mechanism of polarization, they can be classified as intrinsically polarizable materials or extrinsically polarizable materials.[1] Because of their excellent properties, polyelectrolytes and polymer semiconductors have attracted much attention in this field. In earlier studies,[2–5] we prepared different types of ER materials based on polyelectrolytes or polymer semiconductors. In those studies, these two kinds of ERFs exhibited different ER behaviors. To find additional preferred materials and combine their merits, we prepared several types of semiconductor/polyelectrolyte particles and studied the ER effects of the ERFs based on them.

Correspondence to: L. C. Zhang.

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EXPERIMENTAL

Synthesis of polyaniline (PANI) and poly (*o*-toludine) (POT) and antidoped particles based on them

Vacuum-distilled aniline (or *ortho*-toludine) was dissolved in 2 mol/L hydrochloric acid and was then chemically oxidized by the titration of a solution of ammonium persulfate. The entire mixture was cooled with chilled salt water so that the temperature could be kept under 5°C for 4 h. The product particles were filtered and washed with excess deionized water and were then collected. The material was further antidoped with ammonia water with a very high pH value, about 12–13, for a few hours. The resultant particles were dried overnight in vacuo at 50°C.

Synthesis of partially brominated polyaniline (Br-PANI) particles

Excess bromine water was added to a suspension of PANI particles based on water. The system was heated, and the temperature was controlled within the range of 45–50°C, with reflux. The tail gas was treated with a solution of NaOH. The resultant particles were dried, sifted, and collected for later use.

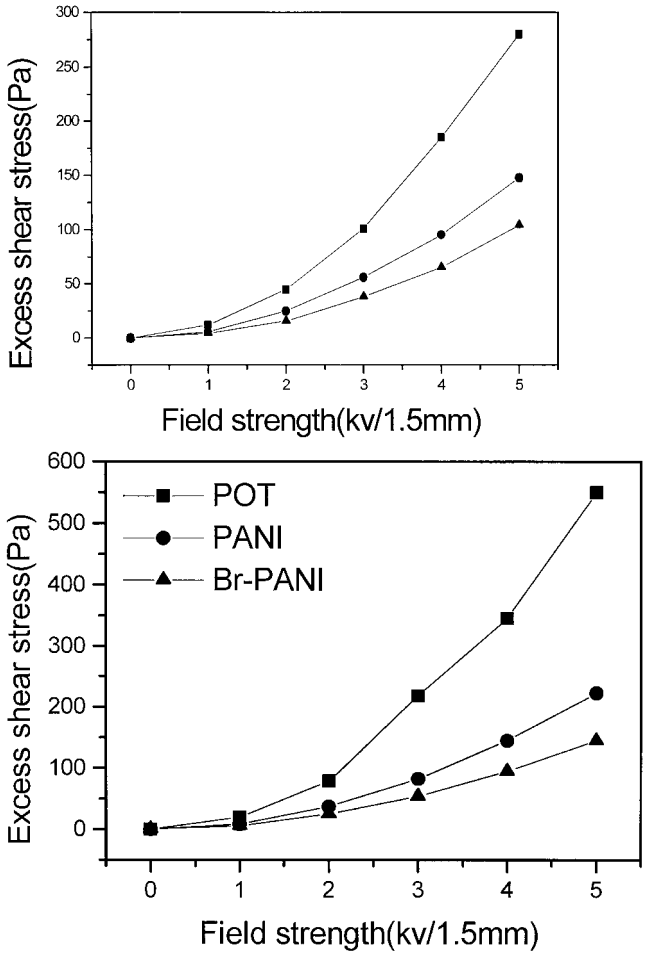


Figure 1 Influence of the substitutes of PANI on the excess shear stress of the ERFs.

Preparation of PANI/lithium polyacrylate (PAA-Li) or PANI/polyacrylamide (PAAm) composite particles

Antidoped PANI particles were sifted with a screen (300 mesh). The composite particles were synthesized by emulsion polymerization. The procedure is described next.

Cetyltrimethylammonium bromide and xylene were added to a flask equipped with a reflux condenser, a stirrer, and a thermometer and under nitrogen protection. The system was then heated to 70°C and was well stirred for 30 min. Lithium acrylate (or acrylamide), antidoped PANI particles, an initiator (ammonium persulfate), and a crosslinking agent (*N*,*N*′-methylene diacrylamide) were dissolved in a certain amount of water and then added to the flask. The emulsion polymerization was kept under 65°C for 8 h. The liquid phase was removed by reduced pressure distillation. The resultant composite particles were then collected and dried in vacuo at 100°C.

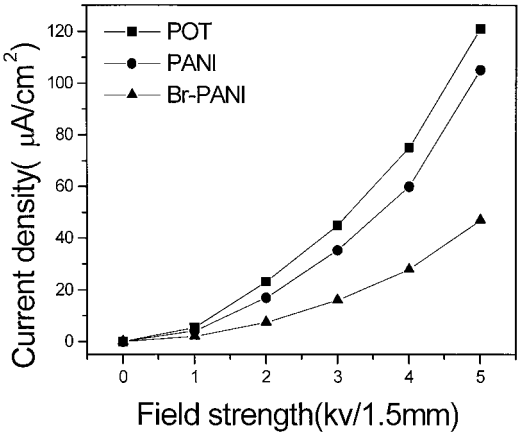


Figure 2 Influence of the substitutes of PANI on the current density.

The water content of these particles was controlled to less than 3%. With different insulating oils, many kinds of ERFs based on these particles were prepared.

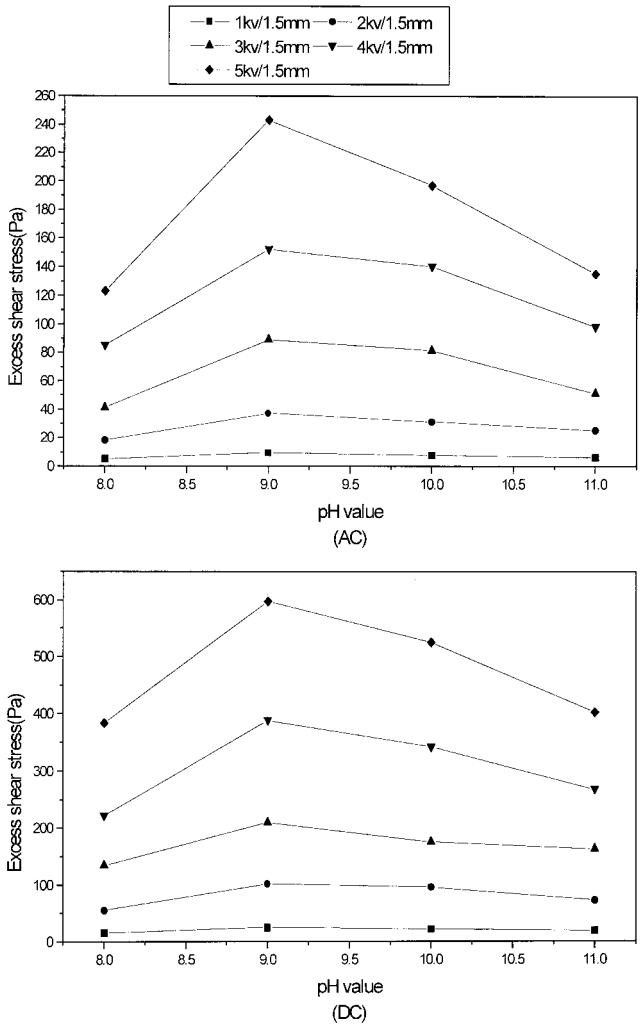


Figure 3 Influence of the antidoping condition of PANI on the excess shear stress.

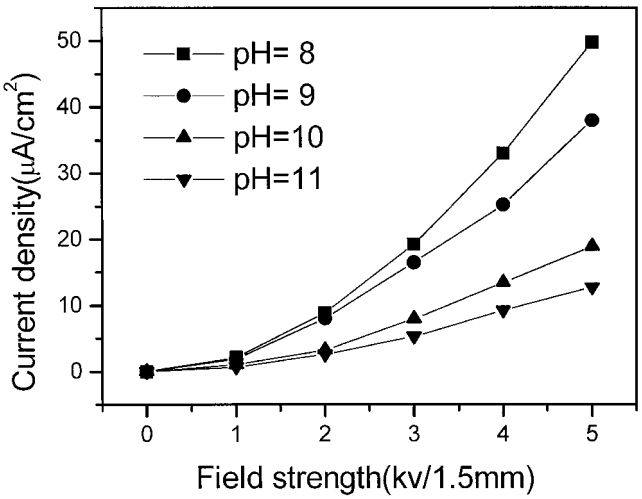


Figure 4 Influence of the antidoping condition of PANI on the current density.

The ER effects of these ERFs were measured with a modified coaxial cylinder-type rheometer (Rheotest II, HAAKE Mess-Technik Co., Karlsruhe, Germany).

RESULTS AND DISCUSSION

Influence of the substitute groups on the ER effect

To study the influence of the substitutes on the PANI backbone, we synthesized three kinds of dispersed particles: PANI, POT, and Br-PANI (the preparation of these particles is described in the Experimental section).

The ERFs, 30% solid and dispersed in chlorinated paraffin, were prepared with an oxidation polymerization method under the same polymerization conditions. The excess shear stress and current density were then tested so that their ER effects could be studied. Figures 1 and 2 show the ER properties of ERFs based on PANI, POT, and Br-PANI particles.

In principle, the conducting mechanism of PANI-type semiconductors is based on the flow of electrons or charge carriers along the conjugated PANI backbone.[6–9] With the adulteration of the dopant (Cl^-), the delocalization of those charge carriers and the electrons changes. Under an external field, the current carriers suffer two main kinds of interactions: (1) an attraction from the external field leading them to flow along the direction of the outer load and (2) a binding force from the conjugated backbone confining the flow of these charge carriers. With other conditions remaining the same, these two competitive actions result in an equilibrium state of the flow and, in the end, lead to ultimate polarization in the dispersed particle. Therefore, we may conclude that the structure of the backbone is a key factor, in addition to the doping condition, influencing the ER properties of this type of ERF.

However, there still exist many other influences that must be noted. These will be left for a later discussion.

Figures 1 and 2 show that the POT system exhibited the best ER effect, whereas the Br-PANI system effect was relatively poor. This phenomenon may be interpreted by the conducting mechanism of these polymeric conductors.

Doped PANI-type semiconductors transfer charges by the flow of electron-acceptor (protonic acid) current carriers (Cl^-). The introduction of substitutes in a benzene circle can vary the conductibility of the material. An electron-donating group can promote the conductivity of the semiconductor; whereas an elec-

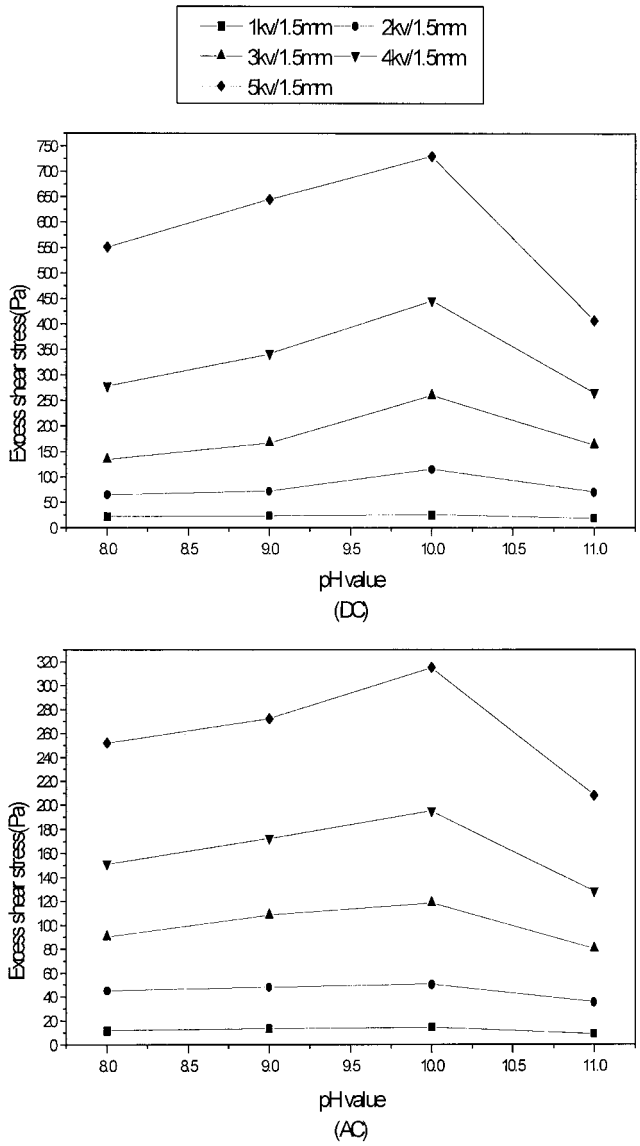


Figure 5 Influence of the antidoping condition of POT on the excess shear stress.

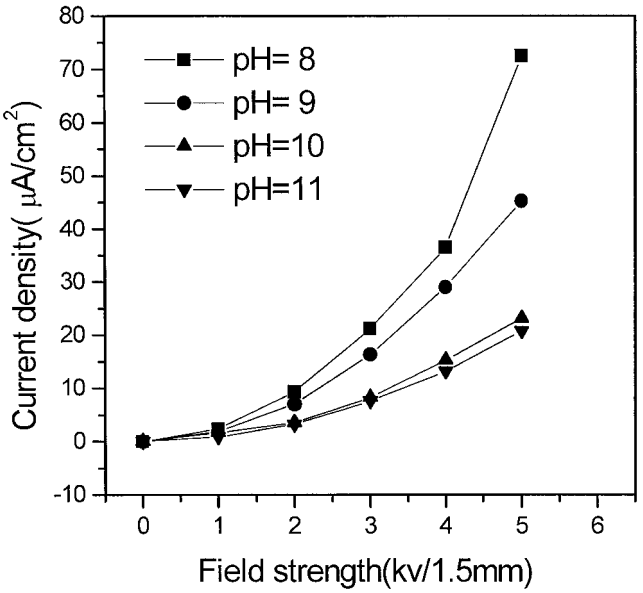


Figure 6 Influence of the antidoping condition of POT on the current density.

tron-withdrawing one can reduce the conductivity of the material.

The appearance of the ERFs, shown in Figures 1 and 2, demonstrated that the introduction of the methyl group really improved the conductivity of the ERFs and further improved their ER effects, whereas the introduction of Br reduced the ER effects of the corresponding ERFs.

Influence of the antidoping of PANI and POT particles

The conductivity of PANI-type conductors, a promising category of polymer conductors, can be controlled through doping with ammonia water of different pH values as an antidopant. Figures 3–6 indicate the influence of the antidoping condition on the ER effect. The testing results suggest that, for the ERFs based on PANI particles, the optimal antidoping condition was the use of ammonia water of pH 9, whereas the best pH value of ammonia water for ERFs based on POT was 10. However, as shown in Figures 4 and 6, the current density of each of these ER systems decreased as the pH value rose.

The ER effect is induced by the polarization of dispersed particles in an ER system. The polarization of these particles is basically caused by the delocalization state of the charge carriers along the PANI backbone. To improve the delocalization property of the charge carriers, we adopted the process of doping. However, this treatment enhanced the conductivity of not only the inner part of the particles but also their outer layers. With the promotion of the conductivity of the outer layers, the current flowing between the particles also increased.

This defect of doping was then compensated by the method of antidoping with ammonia water as an antidopant.

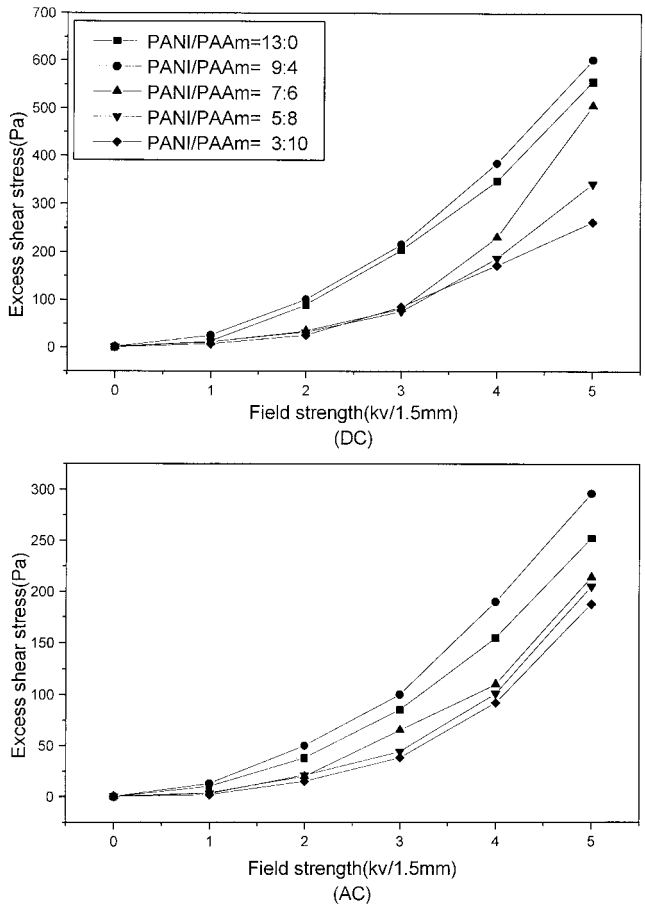


Figure 7 Influence of the PAAm content on the ER effect.

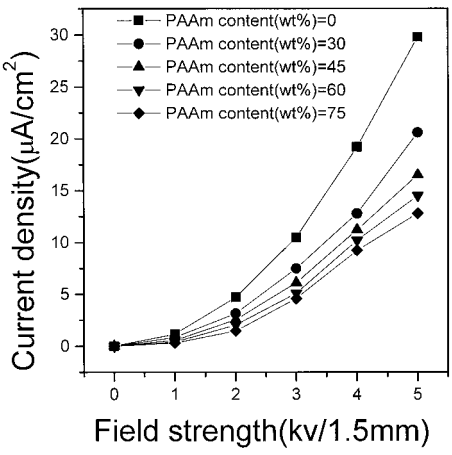


Figure 8 Influence of the PAAm content on the current density.

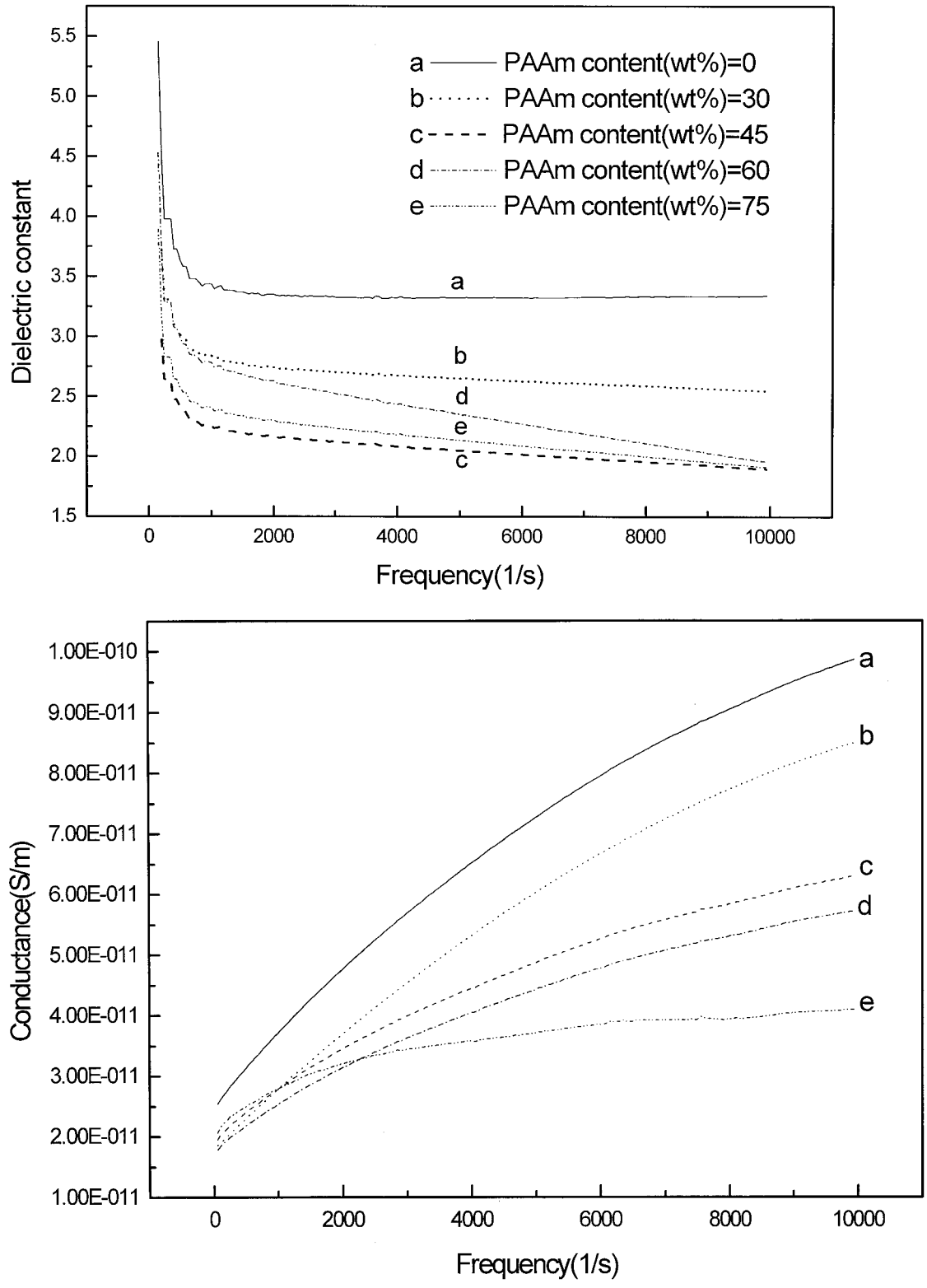


Figure 9 Influence of the frequency on the dielectric constant, conductance, and dielectric loss of PANI/PAAm particles.

The optimal antidoping condition was decided by the testing of the ER and conducting properties of the ERFs (as shown in Figs. 3–6). The optimal ER effect occurred under moderate current densities. These areas constituted ideal conditions for further studies on the ER effects.

In summary, the ER effects of the PANI system can be promoted by an antidoping process with ammonia

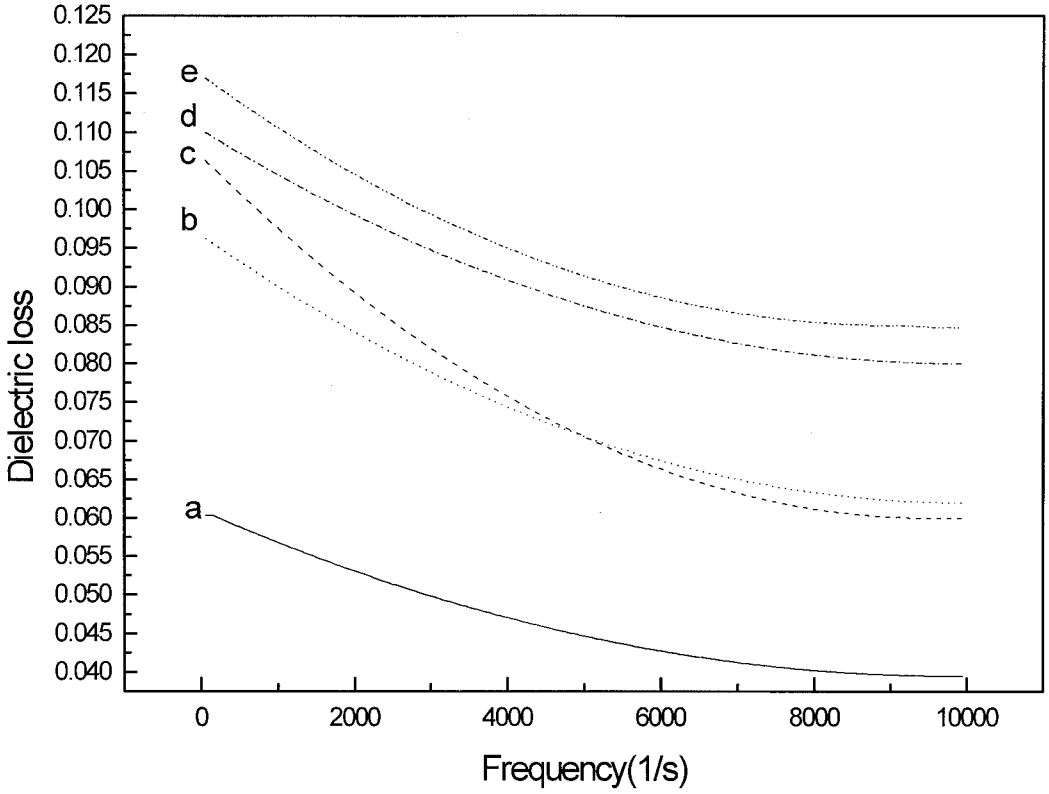


Figure 9 (*Continued from the previous page*)

water as an antidopant. The optimal pH value for PANI ERFs is 9, whereas the value for POT ERFs is 10.

ER effects of ERFs based on PANI/PAA-Li (or PAAm) composites

From this research, it was found that the leakage currents of PANI ERFs were relatively high. To solve this problem, we synthesized PANI/PAA-Li and PANI/PAAm composite particles by emulsion polymerization (as discussed in the Experimental section). Their ER effects are shown in Figures 7 and 8.

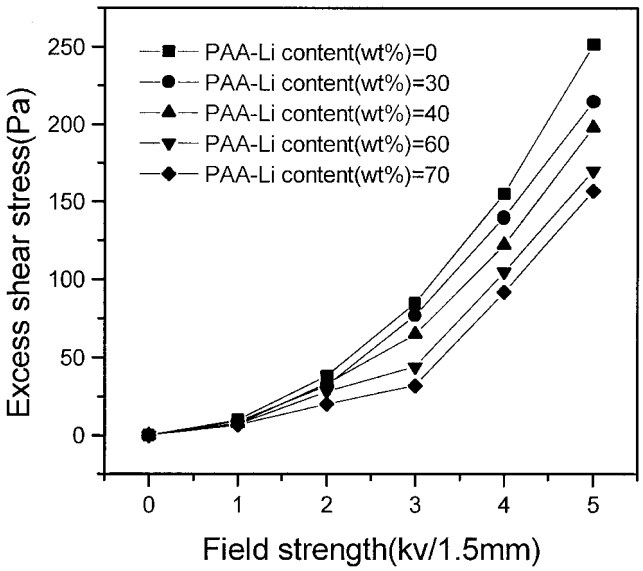
It was proved that, for all of these ERFs, the ER effects under a direct-current (dc) field were more pronounced than those under an alternating-current (ac) field. The testing results indicated that the ERF with a PAAm content of 30 wt % had the strongest ER effect.

According to the microscopic polarization of particles, the higher the polarization degree is, the more easily the particles form a cluster structure in a dispersion system. In fact, with an interfacial treatment of a composition, the polarization of particles becomes more complicated. First, the polarization of PANI-type semiconductors is achieved by the flow of charge carriers along (or sometimes across) the PANI backbones. The response time for this kind of conjugated, structured conduction is relatively short. Second, a polyelectrolyte coating introduces dipolar polarization. Finally, by the method of emulsion polymerization, interfacial polarization is also introduced. The latter two kinds of polarization are relatively slow. Under the ac field, these two kinds of slow polarization perhaps cannot follow the variation of an external load. Therefore, the ER effects of these ERFs under an ac field are relatively weak.

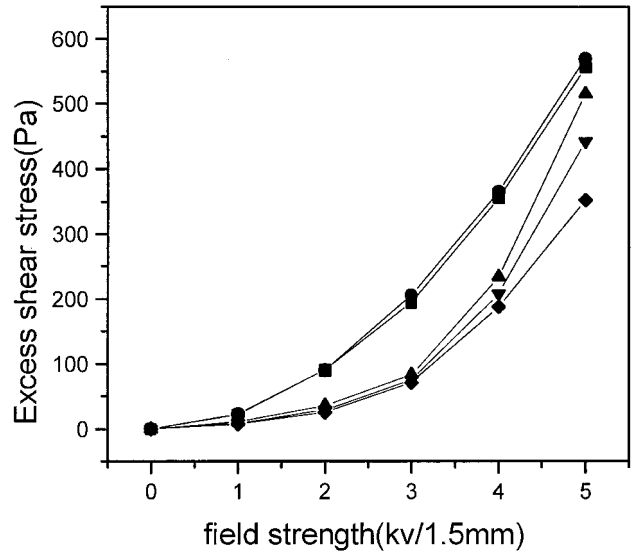
It can also be concluded from the experimental results that the sample with 75 wt % PAAm had a poor ER effect. This might have occurred because the conjugated, structured polarization in these particles was more important than dipole and interfacial polarizations.

For greater understanding of the polarization mechanism of the ERFs, the relationships of the dielectric constant, conductance, and dielectric loss for these ERFs and the frequency of the load were tested. The results are shown in Figure 9. The plots show that the system with 30% PAAm had the greatest dielectric constant. Furthermore, the introduction of PAAm and a surfactant resulted in increasing dielectric loss. The conductance of the composite particles was also smaller than that of pure PANI, as shown in Figure 9.

Using the same method, we further synthesized a series of composite particles of PANI/PAA-Li. Figure 10 shows the testing results of their ER effects. The



(AC)



(DC)

Figure 10 Influence of the PAA-Li content on the ER effect.

sample with 30% PAA-Li had the strongest ER effect under a dc field, whereas its ER effect under an ac field was second among those systems. The main reason is probably the introduction of dipole polarization and interfacial polarization with longer response times.

Figure 11 shows that the current density of the ERFs also decreased with an increasing amount of PAA-Li. The variations of the dielectric and conducting behaviors are shown in Figure 12 and 13. The sample with 30%

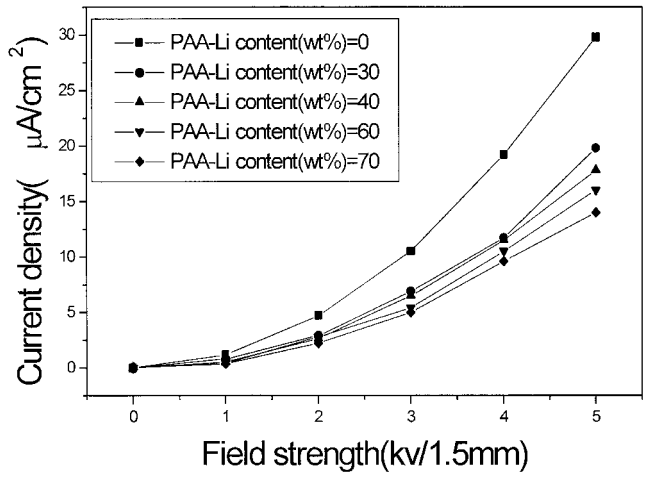


Figure 11 Influence of the PAA-Li content on the current density.

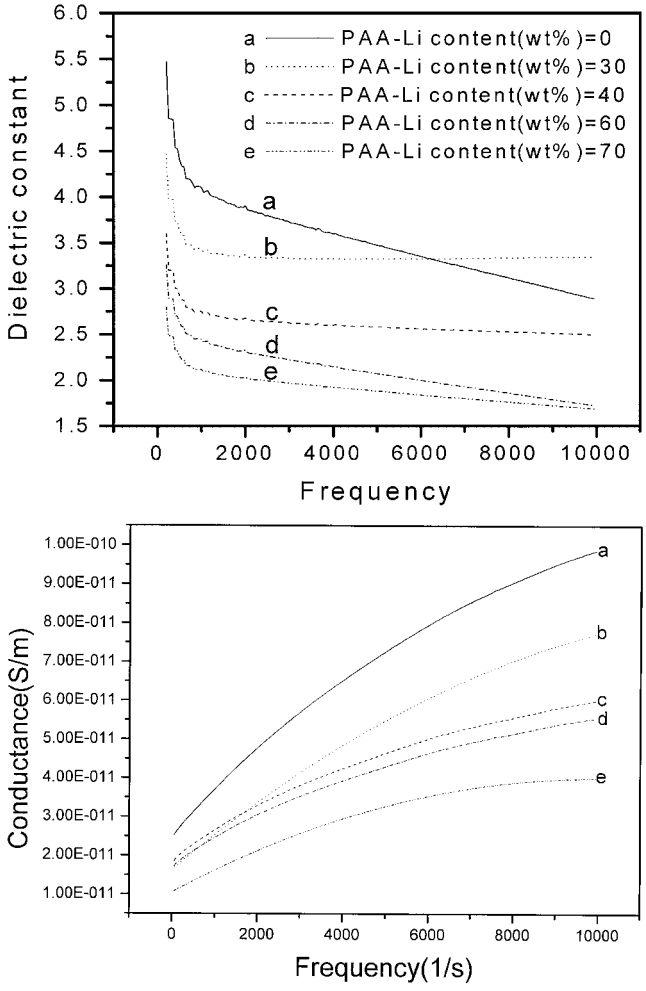


Figure 12 Influence of the frequency on the dielectric constant, conductance of PANI/PAA-Li particles.

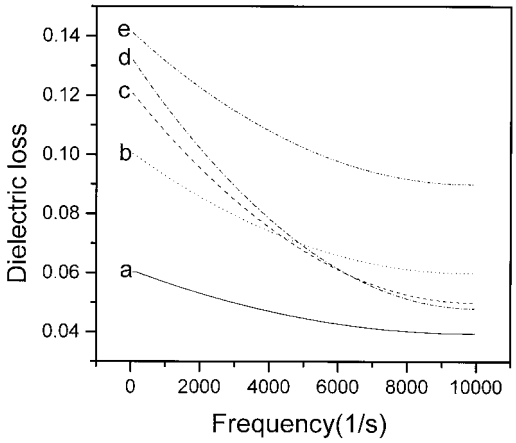


Figure 13 Influence of the frequency on the dielectric loss of PANI/PAA-Li particles.

PAA-Li had a relatively higher dielectric constant, a lower dielectric loss, and a moderate conductance value.

As described previously, composites consisting of PAAm or PAA-Li can improve the ER effect and reduce the current density of PANI-type ERFs. However, it should be noted that this method also introduces some relatively weaker polarization. Therefore, an excess amount of PAAm or PAA-Li is unfavorable. This conclusion requires further research into other organic conductors and polyelectrolytes.

CONCLUSIONS

1. The introduction of an electron-donating group on a benzene ring will enhance the ER effect of PANI-type ERFs, whereas the introduction of an electron-withdrawing group can reduce it.
2. The doping degree has a significant influence on the ER effect. The pH values for PANI and POT particles are 9 and 10, respectively.
3. Compounding a small amount of PAAm or PAA-Li with PANI produces favorable properties.
4. The ER effects of ERFs based on composites depend not only on the dielectric constant but also on the conductivity and dielectric loss of the system.

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