

# Three Ways To Improve Electrorheological Properties of Polyaniline-Based Suspensions

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**ABSTRACT:** In order to improve further the electrorheological (ER) properties of polyaniline (PAn)-based suspensions, i.e., to enhance the static yield stress and to reduce the current density, three methods, namely, coating of the PAn particles with polymer, grafting on the particles with acrylamide, and nonequilibrium dedoping of the PAn particles with concentrated ammonia water, were tried. The results showed that PAn particles coated with poly(vinyl alcohol) or grafted with polyacrylamide can increase the static yield stress and decrease the current density of the ER suspension, whereas coating with poly(methyl methacrylate) or polystyrene reduced both the current density and the static yield stress. Nonequilibrium dedoping of the dried, protonated PAn particles with concentrated ammonia water showed the best effect on the ER properties of the suspension, exhibiting a static yield stress of 16 kPa with a current density of  $2.7 \mu\text{A}/\text{cm}^2$  under a 2.8 kV/mm dc electric field. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1641–1647, 1997

**Key words:** electrorheological suspension; polyaniline; grafting; coating; doping

## INTRODUCTION

Electrorheological (ER) fluids or suspensions are typically suspensions of particles dispersed in an insulative fluid that undergo a rapid increase in apparent viscosity when exposed to a high voltage electric field. Anhydrous ER suspensions containing particles of semiconductive polymers are a dramatic improvement over earlier ER fluids that required water or polar additives to demonstrate ER activity and lost the activity at higher working temperature.

Block et al.<sup>1</sup> indicated the use of low dielectric constant liquid containing dedoped or deprotonated polyaniline (PAn) particles as an ER suspension. Gow and Zukoski<sup>2</sup> studied the ER behavior of a suspension composed of PAn particles dedoped with aqueous sodium hydroxide at pH 6–9. Weber<sup>3</sup> reported the effect of the protonation

degree of PAn on the static yield stress, current density, etc., of the ER suspension composed of polydimethylsiloxane and PAn particles reprotonated by equilibrium with aqueous HCl solution at different pH values. Blackwood et al.<sup>4</sup> studied the ER properties of silicon oil containing PAn particles dedoped with phosphate or borate buffers. Pollack<sup>5</sup> improved the ER properties of PAn suspension in silicon oil by coating the PAn particles with higher molecular weight polysaccharide and indicated that the current density was reduced. PAn-based suspensions are attractive, because PAn particles are easy to prepare, are soft, and do not abrade the device. Their conductivity can be easily controlled by protonation and deprotonation with acid and base. The PAn-based suspensions also reach appreciable yield stress over a wide temperature range.

We have recently reported the effects of various factors on the ER properties of the PAn-based suspensions and showed that the PAn particles dedoped with diluted ammonia water at certain pH

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values dispersed in chlorinated paraffin oil exhibited a static yield stress of about 10 kPa and a current density of about  $40 \mu\text{A}/\text{cm}^2$  under a 2.8 kV/mm dc electric field.<sup>6</sup> However, the current density seems still higher than that required for ER fluid and will produce negative effects, such as consumption of power and electric discharge.

This article deals with the coating of PAN particles with poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), or polystyrene (PSt), grafting on PAN particles with acrylamide (AM), and nonequilibrium dedoping of thoroughly dried, HCl-protonated PAN particles with concentrated ammonia water, in order to improve further the ER properties of the PAN-based suspensions.

## EXPERIMENTAL

### Materials

PVA-12 with a polymerization degree of 2,400–2,500 was from Japan. PMMA and PSt were made with molecular weight of about  $20 \times 10^4$  and  $25 \times 10^4$ , respectively, by a suspension polymerization process. Polydiethylsiloxane (PDES), made by the Wuhan Institute of Chemical Technology, was vacuum dried at 100°C for 4 h before use. Chlorinated paraffin oil (CPO) with 52% chlorine content, produced by Gedian Chemical Factory, was dried with 4A molecular sieve overnight before use. All of the other reagents were chemically pure. AM was recrystallized with distilled water. Aniline (An) was purified by distillation under reduced pressure and stored in a refrigerator before use.

### Preparation of PAN Particles

PAN was synthesized by the oxidative polymerization of An by two different methods. In method 1 the oxidant,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , was added dropwise into a hydrochloric acid solution of An during stirring. The concentration of hydrochloric acid is 2 mol/L, and the molar ratio of An/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is 1. The HCl-doped PAN particles, obtained after washing with distilled water and 95% ethanol successively and drying under vacuum, were ground and passed through a 100-mesh sieve. In method 2, only the addition order is reversed, i.e., An was added dropwise into a hydrochloric acid solution of the oxidant during stirring.

### Dedoping of PAN Particles

Two dedoping methods were used. One is an equilibrium method, i.e., the ground PAN particles were immersed in diluted ammonia water with a certain pH value and stirred for 24 h. Then, the dedoped PAN particles were filtered, washed, and dried. The other method is the nonequilibrium dedoping method. The ground particles were vacuum dried at 100°C and then immersed in concentrated ammonia water (density =  $0.88 \text{ g}/\text{cm}^3$ ) for different times, so as to reach different dedoping degrees; then, the particles were filtered, washed, and dried.

### Coating of the PAN Particles with Different Polymers

A weighed amount of PAN particles ( $W_1$ ) prepared by method 1 and dedoped by the equilibrium method were well dispersed during stirring in a hot aqueous solution of PVA, an acetone solution of PMMA, or a toluene solution of PSt (each containing a certain weight of polymer  $W_2$ ). Then, an excess precipitating agent, namely, ethanol, water, or ethanol, respectively, was added during stirring. The precipitate was filtered out and put into distilled water. Because the density of PAN is larger than that of PVA, PMMA, or PSt, a concentrated aqueous solution of  $\text{Na}_2\text{SO}_4$  was dropped in until some solid floated up. After settling for 30 min, the floating solid was decanted. The remaining precipitate was filtered, washed with water, dried, and weighed ( $W_3$ ). The content of the coating polymer ( $Q$ ) and the coating efficiency ( $Ef$ ) were calculated as follows:

$$Q(\%) = (W_3 - W_1) \times 100/W_3 \quad (1)$$

$$Ef(\%) = (W_3 - W_1) \times 100/W_2 \quad (2)$$

### Grafting of PAN Particles with AM

The PAN particles obtained by method 1 and dedoped by the equilibrium method were dispersed in a certain amount of an aqueous solution of AM. Grafting copolymerization was carried out under nitrogen at 80°C for 4 h. The product was filtered and washed with water several times in order to remove the homopolymer of AM. The purified product was vacuum dried.

### Characterization and Testing

Elemental analysis of PAN was carried out with a CHN-600 apparatus and by an oxygen combustion

flask method. The doping increment of Cl/6C (atom ratio) was calculated as follows:

$$\text{Cl}/6\text{C} = (\text{wt } \%_{\text{Cl}}/M_{\text{Cl}})/(\text{wt } \%_{\text{C}}/6M_{\text{C}}) \quad (3)$$

$$\Delta\text{Cl}/6\text{C} = \text{Cl}/6\text{C} - (\text{Cl}/6\text{C})_0 \quad (4)$$

where  $\text{wt } \%_{\text{Cl}}$  and  $\text{wt } \%_{\text{C}}$  are the weight percentages of Cl and C obtained by elemental analysis;  $M_{\text{Cl}}$  and  $M_{\text{C}}$  are atomic weights of Cl and C.  $(\text{Cl}/6\text{C})_0$  denotes the ratio for the emeraldine base of PAN.

Wide-angle X-ray diffraction spectra (WAXD) were obtained with a Rigaku 3015 apparatus. Crystallinity ( $X_c$ ) was calculated according to the literature.<sup>7</sup>

The conductivity of the PAN particles ( $\sigma_p$ ) was measured by a four-probe method with a SZ 85 apparatus or a DDS-11A conductometer. The samples were made by pressing the PAN particles into plates under 30 MPa and were coated with a conductive adhesive.

The contact angle ( $\theta$ ) with water was determined with a JY-82 apparatus using a 0.05 mL droplet of deionized water. The contact angle was calculated by the equation

$$\cos \theta = 1 - \rho g h_m / 2\sigma_{gl} \quad (5)$$

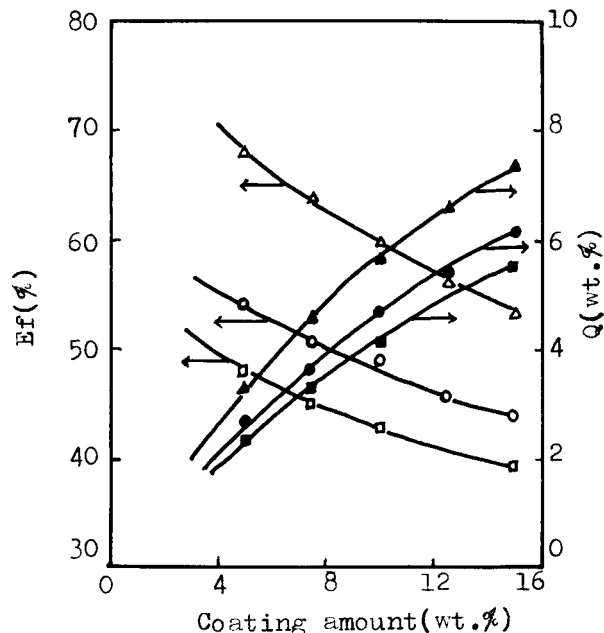
where  $g$  is the acceleration of gravity,  $\rho$  is the density of water,  $h_m$  is the height of the water droplet, and  $\sigma_{gl}$  is the surface tension of water in air. The samples were made by pressing the PAN particles into plates under 30 MPa.

### Preparation and Properties of ER Suspensions

The ER suspension was prepared by mixing a weighed amount of the PAN particles with a weighed amount of PDES or CPO in a mortar. Static yield stress was determined with a static yield stress apparatus made according to the literature<sup>8</sup> and calculated by the following equation:

$$\tau_s = (mg - m_0g)/S \quad (6)$$

where  $mg$  is the load needed to cause the suspension to flow under an electric field,  $m_0g$  is the load needed to cause the suspension to flow under zero field strength, and  $S$  is the electrode area (15 cm<sup>2</sup>). The distance between the two electrodes is 1.0 mm. High dc voltage was supplied by a high-voltage test transformer. Electric current was measured with a microampere meter.



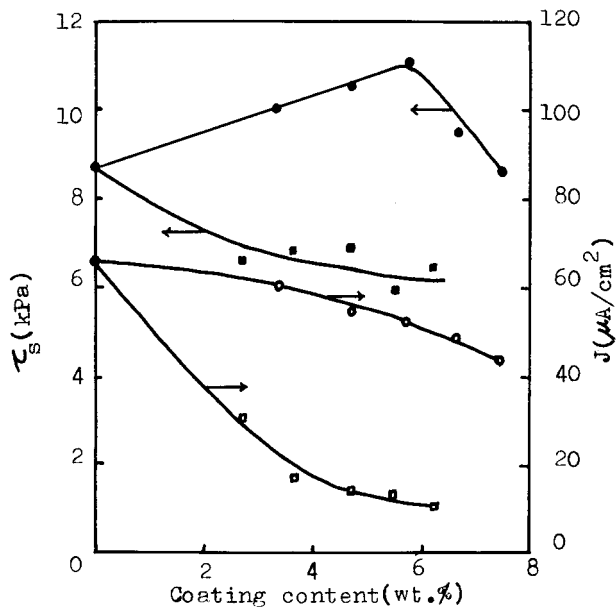
**Figure 1** Effect of polymer amount used on the coating content of PAN particles and the coating efficiency for different polymers: ( $\blacktriangle$ ,  $\triangle$ ) PVA, ( $\bullet$ ,  $\circ$ ) PMMA, and ( $\blacksquare$ ,  $\square$ ) PSt.

## RESULTS AND DISCUSSION

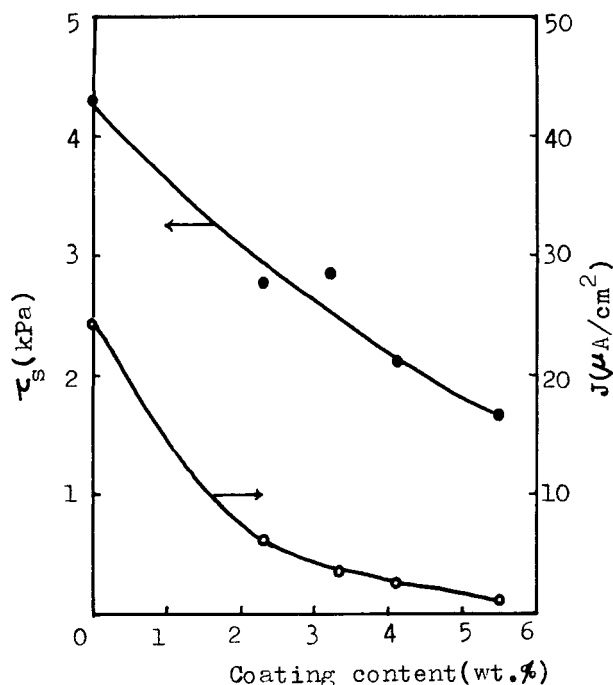
### ER Properties of the Suspensions Containing PAN Particles Coated with Insulative Polymers

Figure 1 illustrates the influence of the amount of PVA, PMMA, or PSt used for coating on the insulative coating content of the PAN particles and on the coating efficiency. It can be seen that with an increase of the polymer amount used, the coating content increases, whereas the coating efficiency decreases. This implies that the probability of the coagulation of the polymer, rather than the coating on the PAN particles, increases with the polymer amount used. PVA seems to be the best polymer for coating on the PAN particles, and PMMA is better than PSt. This phenomenon may be attributed to the interaction between the insulative polymer and the PAN particles. The OH groups of PVA can form strong hydrogen bonds with the N atoms of PAN, whereas the C=O groups of PMMA may form weak hydrogen bonds with the H atoms of the NH groups of PAN.

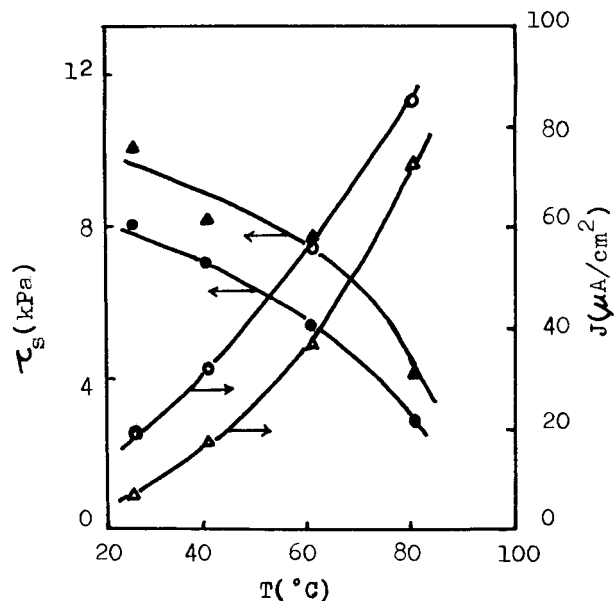
Figures 2 and 3 show the effect of insulative coating content on the static yield stress ( $\tau_s$ ) and current density ( $J$ ) of the ER suspension.  $\phi$  is the volume fraction of PAN in the suspension. PVA coating can improve the ER properties of the sus-



**Figure 2** Effect of the insulative coating content on yield stress and current density of the ER suspensions containing PAN particles coated with (●, ○) PVA and (■, □) PMMA in chlorinated paraffin oil ( $\phi = 0.25$ ,  $E = 2.8$  kV/mm).



**Figure 3** Effect of insulative coating content on yield stress and current density of the ER suspensions containing PAN particles coated with PSt in PSED ( $\phi = 0.25$ ,  $E = 2.1$  kV/mm).



**Figure 4** Comparison of the effect of working temperature ( $T$ ) on  $\tau_s$  ( $E = 2.8$  kV/mm) and  $J$  ( $E = 1.4$  kV/mm) of ER suspensions containing PAN particles (●, ○) uncoated and (▲, △) coated with PVA with 5.8 wt % coating content in chlorinated paraffin oil ( $\phi = 0.25$ ).

pension, enhancing the yield stress and reducing the current density. The maximum yield stress occurs at the suspension containing PAN particles with 5.8 wt % PVA coating. PMMA coating reduces both the yield stress and the current density, but the current density is reduced more obviously than the yield stress. Because the ER efficiency is proportional to  $\tau_s/J$ , PMMA coating can thus also improve the ER properties of the PAN-based suspension. However, the coating of PAN particles with PSt reduces both the yield stress and the current density almost at the same rate. These phenomena indicate that the improvement of ER properties by insulative coating is also related to the interaction or adherence of the coating polymer with the PAN particles. The more adherent the coating is, the larger is the yield stress and the less is the reduction of current density. The former may be attributed to the less repulsive force and shorter distance between the PAN particles with the more adherent coating, resulting in stronger dipole-dipole interaction and a stronger local field. The latter is probably due to less retardation of electron hopping between the particles.

Figure 4 compares the effect of working temperature on the ER properties of the suspensions containing the PAN particles coated with 6 wt % of PVA or not. In both cases, with increasing work-

ing temperature, the yield stress decreases, while the current density increases. The tendency is more evident above 60°C. This fact may be explained by the easier hopping of electrons at higher temperature, resulting in weakening the local field and increasing the current density. At each working temperature, the yield stress of the ER suspension containing PAn coated with PVA is higher than that without coating, whereas the current density of the former is lower.

### ER Properties of the Suspensions Containing PAn Particles Grafted with Polyacrylamide

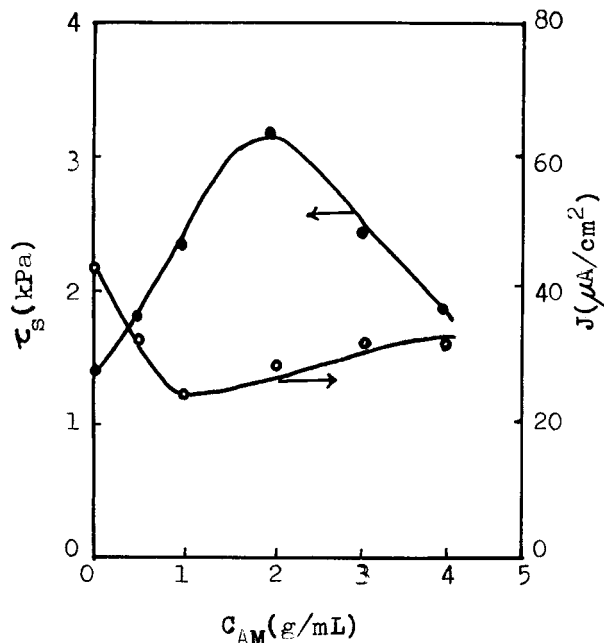
The PAn particles can be graft copolymerized with AM in water with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as the initiator under nitrogen at 80°C. The product was purified by repeated water extractions in order to remove the homopolymer of AM. The purified product was characterized by an FTIR spectrum, which showed that an absorption peak at  $1,650\text{ cm}^{-1}$  for C=O and NH of PAM appeared in addition to the absorption peaks of PAn.

Table I lists the effect of AM concentration ( $C_{\text{AM}}$ ) used in the graft copolymerization on the contact angle ( $\theta$ ) of the purified PAn-g-polyacrylamide (PAM). With increasing  $C_{\text{AM}}$ , the  $\theta$  decreases at first and then increases. A minimum  $\theta$  value exists at a  $C_{\text{AM}}$  of 1.0 g/100 mL. The contact angle can be related to the grafting degree on the PAn, because PAM is hydrophilic. Excess  $C_{\text{AM}}$  is not favorable to the grafting, because more homopolymerization of AM may occur at a higher concentration of AM without increasing the initiator concentration.

The relationship between  $C_{\text{AM}}$  used in graft copolymerization and the ER properties of the PAn-based suspension is shown in Figure 5. A maximum value of yield stress occurs at a  $C_{\text{AM}}$  of 2.0 g/mL, and a minimum value of current density occurs at a  $C_{\text{AM}}$  of 1.0 g/mL. The latter was coinci-

**Table I** Dependence of Contact Angle of the Grafted PAn Particles on the  $C_{\text{AM}}$  Used in the Graft Copolymerization

$C_{\text{AM}}$ (g/100 mL)	$\theta$ (°)
0	51.8
0.5	45.2
1.0	43.9
2.0	44.4
4.0	45.3



**Figure 5** Effect of  $C_{\text{AM}}$  used in graft copolymerization on the  $\tau_s$  and  $J$  of the ER suspension containing PAn particles in PDES ( $\phi = 0.20$ ,  $E = 2.8\text{ kV/mm}$ ).

dent with the minimum value of  $\theta$ . This fact demonstrates that minimum current density occurs at the maximum grafting of AM on PAn particles. The maximum yield stress value is more than twice the yield stress of the suspension containing PAn particles without grafting with AM. Hence, the insulative PAM grafted on the PAn particles also improves the ER properties of the PAn-based suspension.

### ER Properties of the Suspensions Containing PAn Particles Dedoped by the Nonequilibrium Method

Table II indicates the difference in structure and properties of PAn-1 and PAn-2 prepared by two different methods. PAn-1 was obtained by adding the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution dropwise to the hydrochloric acid solution of An, whereas PAn-2 was synthesized by adding An to a hydrochloric acid solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . PAn-1B and PAn-2B are the emeraldine base forms of PAn-1 and PAn-2, respectively, dedoped by excess 3% ammonia water. Elemental analysis shows the differences between the four products. The Cl contents of PAn-2 and PAn-2B are higher than those of PAn-1 and PAn-1B, respectively, probably because there is more substitution of the H atoms of the benzene rings of PAn-2 by Cl. The four products

**Table II** Effect of Polymerization Methods on Structure and Properties of PAN

Sample	Elemental Content (%)				$X_c$ (%)	$\sigma_p$ (S/cm)	Color
	C	H	N	Cl			
PAn-1	67.39	4.39	13.16	14.66	25.4	0.475	Dark green
PAn-1B	73.75	4.84	13.89	6.64	0	$1.30 \times 10^{-9}$	Brown
PAn-2	59.70	4.84	10.22	18.07	22.4	0.158	Green
PAn-2B	69.79	4.18	12.97	12.14	21.8	$1.29 \times 10^{-9}$	Black

also differ in color, which indicates that they exist in different oxidized states.

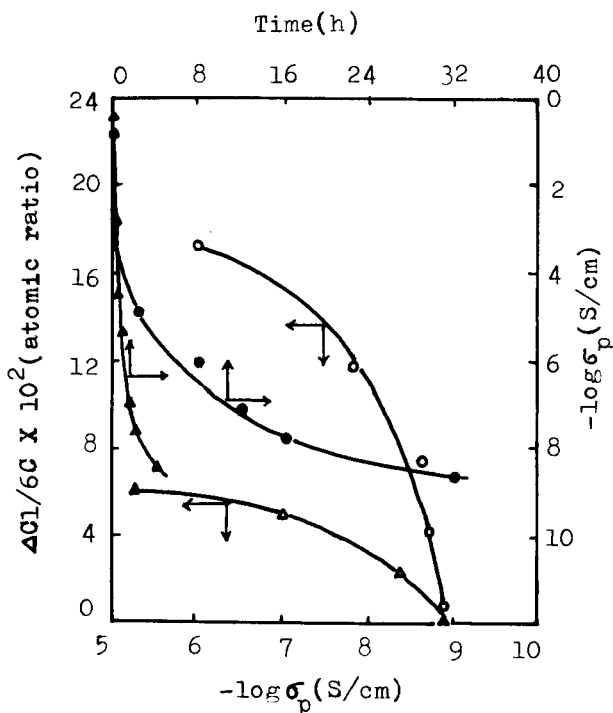
The crystallinities of different PAN samples were measured by WAXD spectra and are listed in Table II. The crystallinity of PAN-1 is higher than that of PAN-2. However, the crystallinity of PAN-1 diminished to zero, when it was completely dedoped, while the crystallinity of PAN-2 changed only a little, when completely dedoped. According to the different crystalline forms of doped PAN reported by Pouget et al.,<sup>7</sup> it is reasonable to suggest that the dedoping of PAN-1 occurs between PAN chains of the doped PAN-1 crystals, whereas the dedoping of PAN-2 occurs in the amorphous

regions at first and then slowly into the crystalline regions of PAN-2.

Figure 6 illustrates the influence of the nonequilibrium dedoping time of PAN particles on the conductivity of PAN. With increasing dedoping time, the conductivity ( $\sigma_p$ ) of both kinds of PAN particles decreases, but the  $\sigma_p$  of PAN-1 decreases more quickly than that of PAN-2. The doping increment  $\Delta Cl/6C$  of PAN-2 is higher than that of PAN-1 for the same conductivity. It seems more difficult to dedope PAN-2 than to dedope PAN-1 by the nonequilibrium method with concentrated ammonia water. Because the large diameter of  $NH_4^+$  ions can retard their penetration into the interior of PAN-2 particles, PAN particles with "core-shell structure" according to the dedoping degree may be formed. It is reasonable to expect that the dedoping degree of the shell should be higher than that of the core and that the conductivity of the shell should be lower than that of the core.

Figure 7 shows that with decreasing  $\sigma_p$  of PAN, the current density of the PAN-based suspension decreases obviously along the same curve for both PAN-1 and PAN-2. This fact demonstrates that the current density of the ER suspension chiefly depends on the  $\sigma_p$  of the PAN particles.

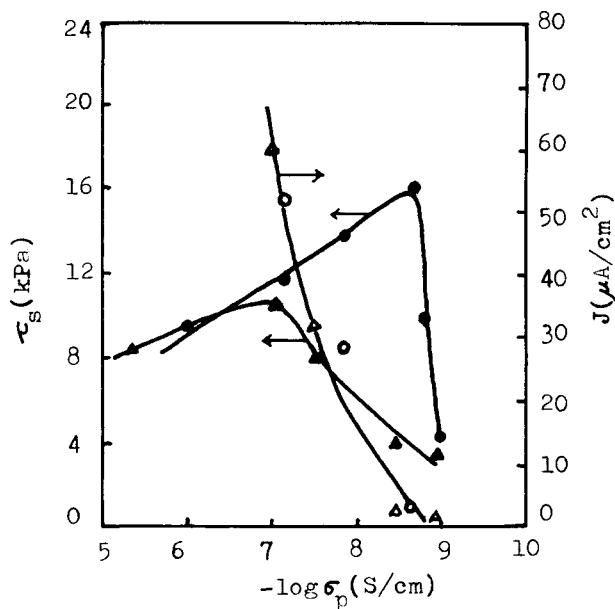
Maximum yield stress exists at different  $\sigma_p$  for PAN-1 and PAN-2. The occurrence of maximum yield stress may be attributed to the surface polarization, which is determined by the electron movement within the PAN particles and electron hopping between the PAN particles under a high-voltage electric field. When the electron movement within the PAN particles plays the important role in the surface polarization, then the yield stress increases with  $\sigma_p$ . However, when the electron hopping between the PAN particles determines the surface polarization of the PAN particles, the yield stress decreases with increasing  $\sigma_p$ . The maximum yield stress value is higher and occurs at a lower  $\sigma_p$  in the case of PAN-2 than in the case



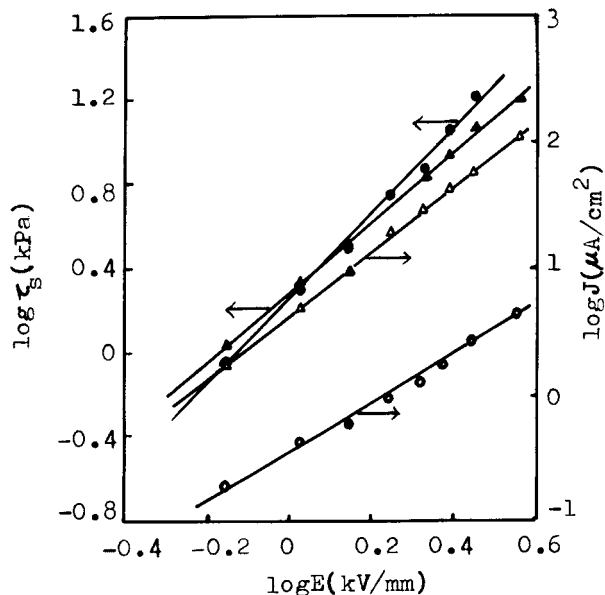
**Figure 6** Influence of nonequilibrium dedoping time on conductivity and doping increment of Cl/6C of the PAN particles, synthesized by two different methods: (▲, △) PAN-1 and (●, ○) PAN-2.

of PAN-1. Because the nonequilibrium dedoping of PAN-2 particles can form a “shell–core structure” of the particles, where the more insulative shell functions as an insulative coating on the PAN particles, electron hopping between particles is much less than the electron movement within the particles. Hence, the local field is enhanced and more electron movement within the PAN particles induces stronger surface polarization at a lower  $\sigma_p$ . Under optimal conditions, the PAN-2-based suspension can show a high ER activity with a yield stress of about 16 kPa and a current density of about  $2.7 \mu\text{A}$  under a dc electrical field of 2.8 kV/mm.

Figure 8 illustrates the linear relationships between  $\log \tau_s$  and  $\log E$  as well as between  $\log J$  and  $\log E$  for the ER suspensions containing PAN-1 or PAN-2 and also exhibiting the maximum  $\tau_s$  value. It can be noted that the change of  $\tau_s$  with  $E$  is greater in the suspensions containing PAN-2 than in the suspensions containing PAN-1, whereas the change of  $J$  with  $E$  is vice versa. This is because the PAN-1-based suspension exhibits



**Figure 7** Dependence of  $\tau_s$  and  $J$  for PAN-based suspensions on  $\sigma_p$  of the PAN particles, synthesized by two different methods: ( $\blacktriangle$ ,  $\triangle$ ) PAN-1 and ( $\bullet$ ,  $\circ$ ) PAN-2 ( $E = 2.8 \text{ kV/mm}$ ,  $\phi = 0.30$ , in CPO).



**Figure 8** Relationships between  $E$  and  $\tau_s$  and between  $E$  and  $J$  for ER suspensions containing ( $\blacktriangle$ ,  $\triangle$ ) PAN-1 or ( $\bullet$ ,  $\circ$ ) PAN-2.

larger  $\sigma_p$  and  $J$ , which lower the local field and the ER activity. For the PAN-2-based suspension, because  $J$  is quite small,  $\tau_s$  is proportional to  $E^{2.0}$ , which is in agreement with the polarization model prediction for electric field induced particle–particle interaction in the ER suspension.<sup>9</sup>

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