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Electrorheological characteristics of polyaniline and its copolymer suspensions with ionic and nonionic substituents

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Abstract Electrorheological (ER) characteristics of ER fluids, composed of suspensions of semiconducting polyaniline and two different copolyaniline particles in silicone oil, were determined experimentally. Ionic sodium diphenylamine sulfonate and nonionic *o*-ethoxyaniline were used to synthesize copolyanilines, i.e. N-substituted copolyaniline and poly(aniline-*co*-*o*-ethoxyaniline), respectively. ER fluids composed of these three different polymers were compared with respect to their rheological properties under an applied electric field. It was found that ER fluids containing a copolymer with an ionic group exhibited the highest ER performance among polyaniline and its copolymer systems in a shear-rate region above 1 s^{-1}.

Key words Electrorheological fluid · N-substituted copolyaniline · Polyaniline · Poly(aniline-*co*-*o*-ethoxyaniline)

Introduction

Most electrorheological (ER) fluids are suspensions of dielectric particles in nonconducting liquids [1, 2]. In the presence of an applied electric field, the suspended particles are polarized due to dielectric mismatch between the particles and the suspending fluid. The interaction among the polarized particles causes them to arrange themselves in the form of strings along the direction of the electric field. The fibrillation of the particles due to the electric field produces a large and reversible increase in the apparent viscosity [3, 4]. Clearly, the ER performance of an ER fluid crucially depends on the electrical properties of the suspended particles [5].

Polyaniline (PANI) has been generally recognized as an easily polymerized and thermally stable organic conducting polymer [6]. Furthermore, by varying the degree of doping, its conductivity can be continuously tuned.

PANI particles must be semiconductive to be used in an ER fluid [7, 8]. Compared to other ER fluids, those using PANI have relatively lower densities, better thermal stabilities, and a more controllable conductivity of the suspended particles. Hence, those fluids using PANI are considered to be among the most promising ER fluids, especially for anhydrous systems [9, 10].

Recently, an ER fluid composed of copolyaniline particles was investigated by Cho and coworkers [11, 12]. Copolyanilines containing a side group on their backbone were initially developed for better processibility and solubility compared to PANI. Thereby, the copolymerization of aniline with suitable substituted anilines has been one of the most frequently used techniques, and substituents are categorized by ionic and nonionic groups [13, 14, 15]. Some ionic side groups of PANI, for example, sulfonate groups, act as self-dopants [16]. For this semiconducting copolyaniline, the ionic groups in the polymer backbone influence the electrical properties.

In this study, PANI and its copolymers having ionic and nonionic substituents were synthesized, and the ER properties of dispersions containing these polymer particles were investigated.

Experimental

PANI was synthesized through oxidant polymerization using the modified method suggested by Leclerc et al. [15]. Sodium diphenylamine sulfonate (SDAS) and *o*-ethoxyaniline (EA) were used as comonomers for N-substituted copolyaniline (NCOPA) and poly(aniline-*co*-EA) (COPA), respectively. During the synthesis, the polymerization temperature was maintained at 0 °C for the three different experimental sets of PANI and the two different copolyanilines. The products were dedoped in aqueous basic solution in order to make the conductivity of the products suitable for ER fluids. The dedoping system was adjusted to pH 9.0. The particle size was controlled to be about 10 μm using a pearl mill. To prepare the ER fluid for rheological measurements, 10% (v/v) of the polymer particles was dispersed in silicone oil using a mechanical stirrer. In these ER fluids, silicone oil with a kinematic viscosity of 30 cS and a density of 0.96 g/cm^3 was used. The three different polymerization reactions were confirmed by Fourier transform (FT) IR spectra, and comonomer portions in the copolymers were determined by element analysis.

ER characterizations of each fluid were then carried out using a rotational rheometer (Physica; MC 120) with a high-voltage generator at 25 °C. Shear stress was measured as a function of shear rate up to 1000 s^{-1} at 3 kV/mm applied electric field. The measuring system was of a concentric cylindrical type.

For the conductivity measurements, a pellet of each sample of dried PANI was prepared, and then by applying the voltage, the resultant current was measured using a picoammeter (Keithley 487) with a custom-made cell (2 probe) for measuring the lower current (above 10^{-9} Ampere). The conductivity, σ, was calculated using the surface area (A), the thickness (d) and the resistance (R) of each pellet using the following equation.

$$\sigma = \frac{1}{R}\frac{d}{A}$$

In addition, before the conductivity test, the picoammeter was turned on for 2 h to achieve accurate measurements. The equilibrium measuring conditions such as constant pressure, smooth surface and the lowest resistance line were applied during measurement.

Results and discussion

The FT-IR spectrum of PANI and its copolymers obtained using KBr pellets are presented in Fig. 1. The peaks at 1586 and 1490 cm^{-1} originate from the aromatic C-C stretching vibrations, whereas those at 1309 cm^{-1} and 1144 cm^{-1} arise from aromatic amine stretching. The peak at 824 cm^{-1} is from the out-of-plane H deformation for aromatic rings, which occurs because of the homopolymer unit.

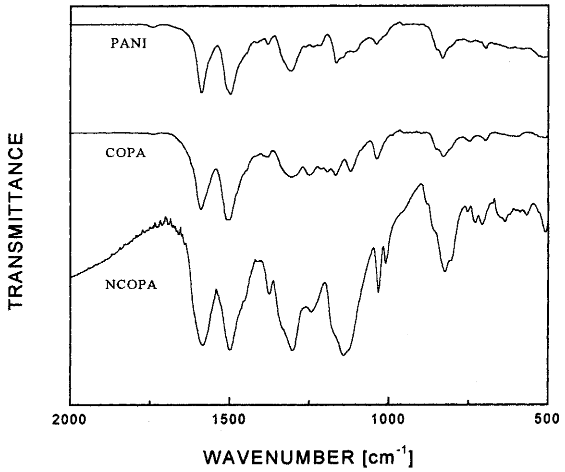

Fig. 1 Fourier transform spectra of polyaniline (*PANI*), (polyaniline-*co*-*o*-ethoxyaniline) (*COPA*) and N-substituted copolyaniline (*NCOPA*).

In addition, the characteristic peaks of the ionic NCOPA occur at 1029 and 1004 cm^{-1}, which are caused by the vibration of the sulfonate group. Nonionic COPA peaks due to the presence of an aromatic ether appear at 1000 and 1300 cm^{-1}.

The results of the elemental analysis are summarized in Table 1. The comonomer portions in the synthesized polymer become larger than those of the monomer feeding ratio for both COPA and NCOPA. Similar results have been observed [13], suggesting that both SDAS and EA are more reactive than aniline.

The flow curve in Fig. 2 shows the shear-stress behavior of PANI and the two different ionic and nonionic copolyaniline ER fluids under an applied electric field of 3 kV/mm. The shear rate was ramped up for this measurement.

In the low-shear-rate (below 1 s^{-1}) region, all three ER fluids show typical nonlinear behavior due to the fibril structures of the particles which is induced by the applied electric field. Since electrostatic interactions between particles are dominant under these conditions, most of the broken particle chains in this shear field are repeatedly reformed during shear.

Table 1 Results of the elemental analysis and calculated monomer portions in polyaniline (*PANI*), poly(aniline-*co*-*o*-ethoxyaniline) (*COPA*) and N-substituted copolyaniline (*NCOPA*)

	C (wt%)	H (wt%)	N (wt%)	Aniline (mol%)		Comonomer (mol%)	
				Feeding	In polymer	Feeding	In polymer
PANI	68.91	4.66	12.61	100.00	100.00	–	–
COPA	69.09	5.43	11.16	75.00	39.00	25.00	61.00
NCOPA	68.09	4.64	12.05	95.00	90.13	5.00	9.87

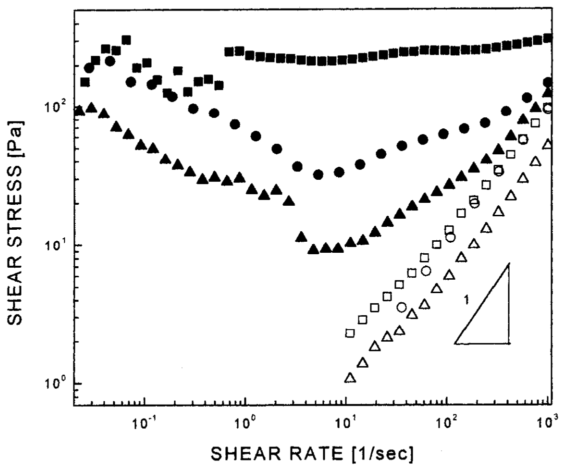

Fig. 2 Comparison of flow behaviors between the PANI, the COPA and the NCOPA systems of 10% particles (v/v) in silicone oil at 3 kV/mm: NCOPA (■, □); PANI (○, ●); COPA (▲, △). Open symbols represent values in the absence of an electric field

For the PANI and nonionic COPA ER systems, the shear stress as a function of shear rate initially decreases to a minimum value at a critical shear rate and then increases as the shear rate is increased. By increasing the shear rate, the chain-destruction rate becomes faster than the chain-reformation rate, and the number of particle chains passing through the gap between the measuring geometries decreases. Therefore, the rotating torque of the rheometer is reduced with increasing rotation speed in this shear-rate regime.

When the shear rate becomes high enough (above the minimum point), many of the particle chains which have been broken during shear do not have enough time to realign themselves with the electric field. The shear stress in this condition comes from hydrodynamic force rather than electrostatic interactions between the particles. Therefore electrostatic interaction between the particles is thought to be more important than hydrodynamic interaction below the critical shear rate and vice versa with a further increase in shear rates beyond the critical point. Thereby, the flow curve of the ER fluid should approach that of a Newtonian fluid whose shear stress linearly increases with shear rate. We can clearly see this in Fig. 2, in which the shear stresses under the electric field converge on the stress value in the absence of the electric field in the high-shear-rate regime. This phenomenon, which is related to flow instability, has already been observed by Sprecher et al. [17] in suspensions of ultrafine silica particles in silicone oil. Recently, for both styrene acrylonitrile copolymer-clay nanocomposite [18] and zeolite [19] ER suspensions, similar behavior has been also found. Note that a slope of 1 in Fig. 2 is representative of a Newtonian fluid. In addition, Choi et al. [10] also observed the drop in the shear stress at 10 s^{-1} shear rate for PANI synthesized under polymerization temperatures of 5 and −5 °C. They explained this phenomenon from the dielectric relaxation study by suggesting that the induced dipole moment of the rotating broken particles or clusters in this shear field cannot follow the external electric field, since the relaxation times of these particles are much larger than 10^{-1} s.

For the ionic NCOPA ER fluid, however, there is no stress decrease in the entire experimental shear-rate region; therefore, the particle chains are made continuously up to 1000 s^{-1}. The different flow curves between ionic and nonionic copolyaniline ER fluids must reflect the electrical properties of the particle itself.

First, the conductivities of PANI, COPA and NCOPA were found to be on the orders of 10^{-11}, 10^{-12} and 10^{-9} S/cm, respectively. Note that the conductivity of the COPA particle is comparatively low because of the presence of the nonionic side group along the main chain. It was found that in substituted copolyaniline, the conductivity decreases as the steric bulk of the substituent [20] increases. This occurs because the bulk substituent disrupts the coplanarity of the polymer chain and reduces the mobility of the charge carriers along the main chain. In addition, a bulky side group will increase the interchain distance and so the transport of charge carriers between chains will be reduced. In contrast with COPA, the ionic substituents in NCOPA contribute to higher conductivity because the sulfonate groups are self-dopants of copolyaniline

The apparent shear viscosities of the same ER fluids as in Fig. 2 are shown in Fig. 3. A shear-thinning behavior of these ER fluids is clearly observed. In addition, it can be found that for both PANI and COPA slope changes of the shear viscosities are observed at the critical shear rate (3 s^{-1}).

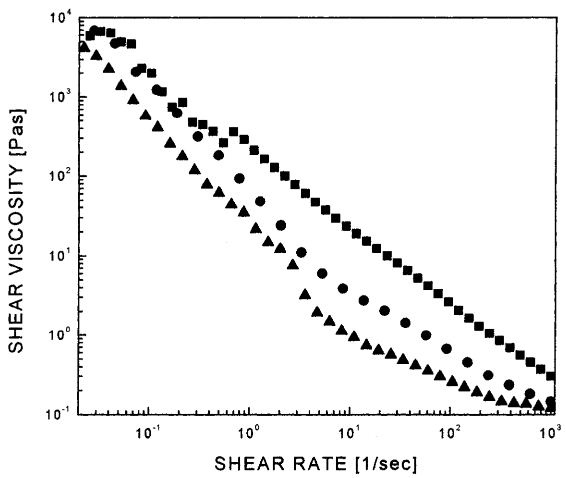

Fig. 3 Shear viscosity as a function of shear rate of 10% particles (v/v) in silicone oil at 3 kV/mm: NCOPA (■), PANI (●), COPA (▲)

Even though this difference in rheological properties occurs especially in the high-shear-rate regime, it cannot be explained solely in terms of the conductivity of the particle material. It can be concluded that the NCOPA ER fluid shows superior ER performance to PANI and COPA ER fluids at high deformation rates above shear rates of 1 s^{-1}.

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