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SHORT COMMUNICATION

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Effect of polymerization temperature on polyaniline based electrorheological suspensions

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Abstract As one of the intrinsically polarizable materials used in electrorheological (ER) fluid, polyaniline was synthesized by the chemical oxidation of aniline with ammonium peroxysulfate. ER fluids were prepared by dispersing polyaniline particles in silicone oil, and their rheological properties were measured. The effect of the polymerization temperature of polyaniline on its ER characteristics was investigated. ER fluids with polyaniline particles synthesized at −10°C (PA-10) showed the best ER performance (yield stress) compared with those synthesized at higher temperatures. A difference in the flow behavior of the ER fluids was also investigated through the dielectric spectra of ER fluids.

Key words Electrorheological fluid – Polyaniline – Dielectric spectrum

Introduction

Electrorheological (ER) fluids are those whose rheological properties can be changed by an imposed electric field. Commonly they are composed of a suspension of micron sized particles in a non-conducting fluid. When an electric field is imposed, the rheological properties of the fluid vary, showing a characteristic fibrillation; the strings of the particles are oriented along the direction of the electric field. This structure is known to be induced by a mismatch of the dielectric constants of the suspended particles and the non-conducting oil [1, 2]. In the absence of an electric field, the fluid exhibits either a Newtonian or non-Newtonian fluidlike behavior, depending on the particle concentration. Under the influence of an electric field, ER fluids suddenly change from a fluidlike state to a solidlike state, due to the fibril structures of the particles, and stress is required to break the chainlike or columnar structure and make it flow. This stress, referred to as yield stress, is field-dependent and is the main characteristic of an ER fluid. ER fluids also show increases in their shear viscosities of several orders of magnitude at low shear rates. Recently, polymer semi-conductors have been adopted as dry-base, nearly anhydrous ER fluids. Examples include polyurethane containing metal ions [3], acene quinone radical polymers [4, 5], polyaniline [2, 3, 6, 7] and copolyaniline [8, 9]. By comparison with other ER fluids, polyaniline has advantages with respect to density, conductivity control, and thermal stability. Polyaniline is also easy to polymerize by oxidation polymerization at relatively low temperatures (near 0°C); it can also be doped from a conducting state to an insulating state using simple protonic acids. This allows for a change in the particle dielectric constant and conductivity, while all other particle properties and suspension characteristics remain identical for the study.

In this study, we report experimental results for the ER and dielectric properties of an ER fluid made of silicone oil suspensions of semi-conducting polyaniline particles, synthesized at four different polymerization temperatures. The ER properties of the system were investigated as a function of the electric field, shear rate, and polymerization temperature of polyaniline.

Experimental

Polyaniline was synthesized by oxidation polymerization using the modified method suggested by Leclerc et al.

[10]. An amount of 0.6 mol of aniline was added to 400 ml of 1M HCl, and was chilled and stirred. A prechilled solution of ammonium peroxysulfate (0.36 mol in 200 ml of 1M HCl) was then added dropwise to the reaction system, with continuous stirring, for 1 h. The reaction proceeds very quickly; the solution color becomes dark-green within a few minutes of addition. After adding drops for 2 h, the reaction conditions were maintained for a further 2 h, to allow completion at the four different polymerization temperatures of 5 (PA5), 0 (PA0), −5 (PA-5) and −10°C (PA-10), using a constant temperature bath. All temperatures were maintained to within 0.1°C. After the reaction, polyaniline particles were ground using a ball mill and passed through a 38 μm sieve. To obtain semi-conducting polyaniline, we dedoped the polyaniline particles by reducing the pH of the aqueous medium which contained the particles to pH 9.0 using aqueous NaOH and HCl solutions . The pH of the aqueous polyaniline suspension remained constant for 1 day. The pH-controlled particles were filtered and washed using distilled water, ethanol, and cyclohexane, thus removing oligomer and excess monomer and making the particle surface hydrophobic. Finally, the products were dried in a vacuum oven at room temperature. The synthesized polyaniline was identified from characteristic IR peaks, obtained by a Fourier transform infrared (FT-IR) spectrometer. The shape of the polyaniline particles was irregular and laminar, as observed from a scanning electron microscope (SEM) photograph. The density of polyaniline was also measured, using a pycnometer at 25°C, as 1.30 g cm^3. The average particle size of the polyaniline particles, as obtained using a Fisher sub-sieve sizer, was 1.8 μm.

The conductivities of the polyanilines were measured using the two-probe method with compressed disks. The conductivities of PA-10, PA-5, PA0, and PA5 were found to be 2.2×10^{-10} S cm^{-1}, 5.0×10^{-11} S cm^{-1}, 9.0×10^{-12} S cm^{-1}, and 5.0×10^{-12} S cm^{-1}, respectively. Therefore, PA-10 had the highest conductivity among the polyanilines used in this study.

The ER fluid was prepared by dispersing the synthesized polyaniline particles in silicone oil. Silicone oil was dried in a vacuum oven and stored with molecular sieves before use. The density and kinematic viscosity of the silicone oil are 0.95 g ml^{-1} and 30cS at 25°C, respectively. All ER fluids were prepared by dispersing the particles with an ultrasonicator for 30 min at room temperature. The prepared ER fluids were then stored in a desiccator prior to use.

Rheological properties were determined using a rotational Physica rheometer (MC120) with Couette type geometry, a high-voltage generator, and an oil bath for temperature control. An electric field was applied for 5 min to give an equilibrium chain-like, or columnar structure, before applying the shear. All measurements were performed at (25 ± 0.1)°C. We also measured the dielectric spectra of the ER fluids using an impedance analyzer (HP 4284A) with a liquid test fixture in the frequency range of 10–10^6 Hz.

Results and discussion

Figure 1 shows the FT-IR spectrum of polyaniline. The peak at 825 cm^{-1} indicates aromatic C—H, at 1145 and 1310 cm^{-1} aromatic amine, and at 1490 and 1590 cm^{-1} C—C stretching and vibration. FT-IR spectra show that the polyaniline synthesized for this study is similar to that of an emeraldine base [11].

The effect of the polymerization temperature of the polyaniline on the flow behavior of ER fluids, which have a 10% (v/v) particle content, with an applied electric fluid (3 kV mm^{-1})is given in Fig. 2. The ER fluid (ER-10) consisting of PA-10, which was synthesized at −10°C, gives the largest dynamic yield stress, which is calculated by extrapolation from the constant stress regions. This result might be due to the fact that PA-10 has the largest conductivity. It is known that a higher molecular weight polymer can be obtained by polymerization at a lower temperature [12]. In addition, higher molecular weight polymers usually have higher polymer conductivity. For particles of the same size, those made of higher molecular weight polyaniline will have higher conductivities, because the total number of polymer molecules in a particle will be less, so that the overall contact resistance between different polyaniline molecules will be smaller. Therefore, it can be assumed that the ER properties exhibited by PA-10 were due to enhanced electrical characteristics resulting from an increased molecular weight. Unfortunately, we cannot measure the molecular weight of polyanilines because they are insoluble in general organic solvents.

Furthermore, a different flow behavior for ER-10 at 3 kV mm^{-1} is observed and compared with other ER fluids, as shown in Fig. 2a. The shear stress developed at

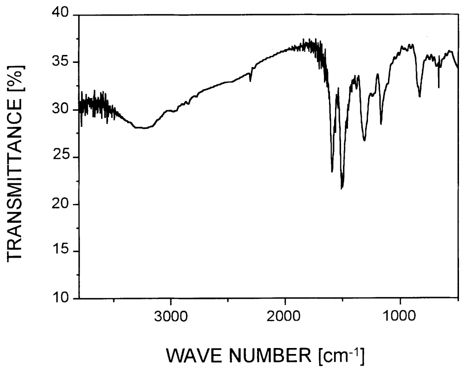

Fig. 1 Fourier transform infrared spectrum of polyaniline

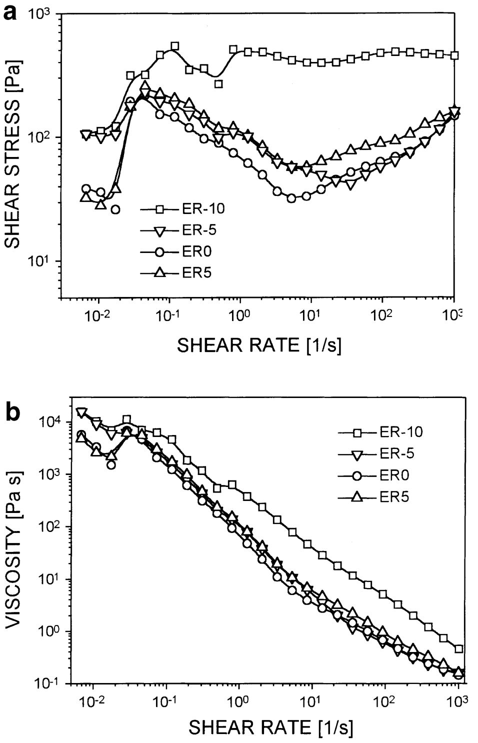

Fig. 2a,b Shear stress (**a**) and viscosity (**b**) versus shear rate for electrorheological (ER) fluids [10% (v/v) particles in silicone oil] at 3 kV mm^{-1}

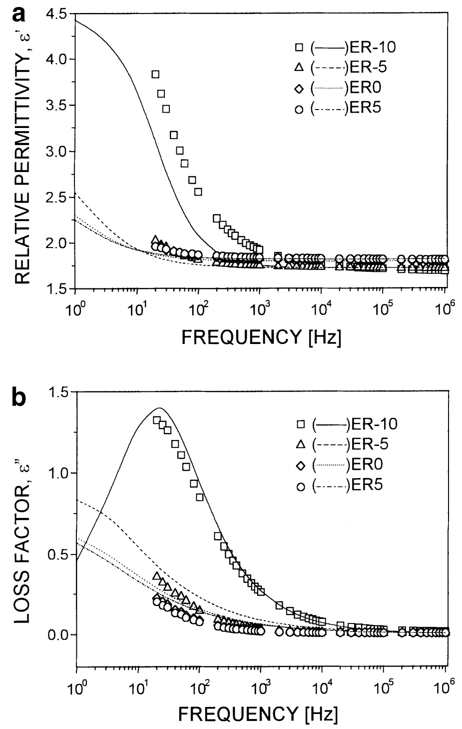

Fig. 3a,b Dielectric spectra of ER fluids; (**a**) relative permittivity and (**b**) loss factor as a function of frequency

a lower shear rate according to the electric field and remained constant through the whole shear rate region for ER-10. For the other ER fluids, shear stress decreases with increasing shear rate after a maximum stress, and then increases with shear rate in the high shear rate (> 10 s^{-1}) region. Thus ER-10 is a much better ER fluid than the other systems, especially in the high shear rate region. This result for ER-10 in the high shear rate region cannot be explained simply by the conductivity difference of the particles. However, rapid shear-thinning behaviors are given for all ER fluids (Fig. 2b). The viscosity of ER-10 is higher than that of the others for the whole shear rate range. The unique behavior of shear stress and viscosity for ER-10 is due to the reformation of particle chain structures, even in the region of the high shear field.

To explore the differences in flow properties, as shown in Fig. 2, we also investigated the polarization properties of ER fluids. We obtained dielectric spectra of these ER fluids in the frequency range 10–10^6 Hz, using an impedance analyzer. Figure 3a and b shows the variations of the permittivity (ε′) and loss factor (ε″), respectively, for our samples. We observed dielectric relaxation of ER-10, as shown by the shape of ε′ and ε″ in Fig. 3, indicating its characteristics of interfacial polarization [13, 14]. These dielectric spectra are fit with the Cole-Cole formula [15],

$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon'_\infty + \frac{\varepsilon'_0 - \varepsilon'_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (0 \le \alpha < 1) \ , \qquad (1)$$

where ε'_0 is ε′ as $\omega \to 0$, and ε'_∞ is ε′ as $\omega \to \infty$. τ is the relaxation time for the interfacial polarization, and the exponent (1-α) determines the broadness of the relaxation time distribution. If $\alpha = 0$, this equation represents Debye dielectrics which have a single relaxation time.

Fits of Eq. (1) to dielectric data are shown in Fig. 3 as dashed and solid lines, and we can obtain τ for each ER fluid from the fitting results, that is 0.05, 1, 1.5, and 2 s for ER-10, ER-5, ER0, and ER5, respectively. The α value of ER-10, which is 0.4, is the smallest among these ER fluids and it shows that ER-10 has the narrowest distribution of polarization relaxation time. It is thought that the relaxation time distribution becomes narrow as a function of the particle conductivity, and it is consistent with the results of Webber [13], and Conrad and Chen [16].

It is thought that the difference in the dielectric spectra of our samples is due to the varying degrees of polarization. PA-10 has a higher molecular weight and conductivity than the other polyaniline particles synthesized at higher temperatures. Therefore, it also has a longer backbone, which is the electron path, and this contributes to the polarity and polarization process of ER-10. As a result, ER-10 can polarize at higher electrical frequency than the other ER fluids.

This may explain the different rheological behaviors shown in Fig. 2, especially in the shear rate region from 10^{-1} to 10^{3} s^{-1}. The drop in shear stress at 10^{-1} s^{-1} shear rate for ER-5, ER0 and ER5 suggests that the induced dipole moment of the rotating particles or clusters in this shear field cannot follow the external electric field. Hence shear stress decreases as shear rate increases. In addition, because the relaxation time of ER-10 (0.05 s) is much smaller than that of the others (1–2 s), the polarization of ER-10 can stay in phase with the external electric field so that the shear stress of ER-10 remains unchanged. In conclusion, the better ER performance of ER-10 can also be explained through the electrical relaxation analysis calculated from a dielectric spectrum.

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