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Influence of particle size on shear behavior of amine-group-immobilized polyacrylonitrile dispersed suspension under electric field

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ABSTRACT

Different-sized particles dispersed electrorheological (ER) fluids were fabricated with poly(acryloamidino diethylenediamine) to observe the influence of the particle size on ER behaviors. The fine particles dispersed ER suspension showed stable shear stress under a DC electric field. On the other hand, the rough particles dispersed suspension showed trembling shear stress which is divided into four regions in a plot of shear stress against shear rate. Our suggested spring–damper model equation treated the wide range of shear rate and specific (trembling) behaviors of shear stress in ER fluids. In this study, we successfully obtained various ER fluids showing different behaviors just by changing the size of particles in the ER fluids. All of the curves of the shear stress plotted against shear rate were fitted well by our spring–damper model.

1. Introduction

Some intelligent (smart) materials can respond to an external environmental stimulus in a timely manner, producing a useful effect. The electrorheological (ER) fluids are such smart materials whose rheological properties are controllable through the application of an electric field, showing useful and special function with the effect of reversibility [1]. Three types of ER effects have been developed. When the rheological properties of an ER fluid increase with applied electric field, this termed the positive ER effect [2]. If the rheological properties decrease with applied electric field, this is called the negative ER effect [3]. Both the positive and negative ER effect can be enhanced by ultraviolet (UV) illumination is some ER systems. This phenomenon is defined the photo-electrorheological (PER) effect [4].

Due to their fast response time and controllable shear viscosity, ER fluid has been one of the most promising candidate as a new material for various industrial utilizations of such suspensions in active control devices such as dampers, shock absorbers, clutches, and brakes [5], and in new devices include gripping devices [6], seismic controlling frame structures [7], human muscle stimulators [8], and spacecraft development dampers [9]. Many efforts have been spent on developing high-performance ER materials including inorganics [10], polymers [11], and hybrids [12]. Among these materials, polymeric ER materials have been studied widely due to their advantages, such as low density, easy handling, and good dispersion-property [13].

Commercially available ER materials are directly used after the milling treatment in the range of 0.1 and 100 μm. Therefore, the suspending particles in ER fluids can have various sizes and shapes. Little attention has been paid to the particle shape and size, which, in addition to polarisability, could significantly influence the ER effectiveness of the fluid [14]. In this communication, we prepared two sizes of ER particles with amine-group-immobilized polyacrylonitrile (PAN) as an active particulate phase, and observed their behaviors under electric filed. The influence of the particle size was investigated. The suspensions showed good ER properties with interesting shear behaviors. The previously suggested spring–damper model was applied to fit the shear stress–strain curves of prepared ER fluids showing complex behaviors. Our suggested model equation treated the wide range ($0–1000\ s^{-1}$) of shear rates and specific behaviors of the shear stress in ER fluids.

2. Experimental

2.1. Preparation of poly(acryloamidino diethylenediamine) (PADD)

The preparation and analysis has been reported in detail earlier [15]. Briefly, PADD was obtained by heating PAN fiber (6 g, Hanil Synthetic Fiber Co. Ltd.) with diethylenetriamine (DETA) (500 g,

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Acros Organics Co.) and $AlCl_3 \cdot 6\,H_2O$ (20 g, Junsei Chemical Co.) at 120 °C for 3 h with stirring (degree of substitution: 97.2%). The DETA was used both as solvent and reactant. The modified PAN fiber thus obtained was washed with distilled water and ethanol, and then dried at 40 °C under vacuum.

^{13}C NMR (200 MHz, solid-state): δ = 32.33 (C1, —CH_2 backbone), 35.12 (C2, —CH backbone), 164.61 (C3, N—C=N), 39.41 (C4), 43.67 (C5), 48.10 (C6), 36.53 (C7).

2.2. Particles characterization

The synthesized PADD was ground to micro-particles using a ball mill. Particles of PADD (fine) and PADD (rough) were obtained by grinding for 24 h and 3 h, respectively. The particles of PADD (fine) and PADD (rough) were blended with KBr and then pressed into a disk for analysis. Fourier transform infrared (FT-IR) spectroscopy (GX FT-IR, Perkin-Elmer) was used to analyze these particles under nitrogen gas purging. ^{13}C NMR spectra were obtained on a Bruker MSL200 spectrometer in the solid state. The morphology studies of ER particles were observed by field-emission scanning-electron microscopy (FE-SEM, Hitachi S4200) instrument operating at 15 kV. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample-charging problems. The particle-size distribution was examined by dynamic light scattering (DLS, BI9000AT, Brook Heaven Co. Ltd.).

2.3. Suspension preparation and electro-rheological measurements

ER fluids were prepared by dispersing PADD (fine) and PADD (rough) particles into silicone oil, whose viscosity was 30 cS at 25 °C. The silicone oil was dried by molecular sieves before use, and the particle concentration was fixed at 30 vol.%. The rheological properties of the suspension were investigated in a static DC field using a Physica Couette-type rheometer (US200, Physica) with a high voltage generator. The measuring unit was of a concentric cylindrical type, with a 1-mm gap between the bob and the cup. The shear stress for the suspensions was measured under shear rate of between 1 and 1000 s^{-1} and electric fields of 0–3 kV/mm.

The DC current density J of PADD particles suspensions were determined at room temperature by measuring the current passing through the fluid upon application of the electric field E_0 and dividing the current by the area of the electrodes in contact with the fluid. The current was determined from the voltages drop across a 1-MΩ resistor in series with the metal cell containing the oil, using a voltmeter with a sensitivity of 0.01 mV. The DC conductivity was taken to be ($\sigma = J/E_0$).

3. Results and discussion

The particle size and shape have an impact on the ER effect. The ER effect is expected to be weak if the particles are too small, as Brownian motion tends to compete with particle fibrillation. Very large particles are also expected to display a weak ER effect, as sedimentation would prevent the particles form fibrillation bridges [1]. To observe the size effect of ER materials, poly(acryloamidino diethylenediamine) (PADD) was synthesized through the immobilization of DETA onto the PAN fiber. The spectra of the raw PAN and the synthesized PADD are shown in Fig. 1. After substitution of the nitrile group (C≡N, 2243 cm^{-1}) with an amine group, new peaks of N—C=N (amidine group, 1650 cm^{-1}), NH_2 (1600 cm^{-1}), NH (1580 cm^{-1}), and amine groups (3500–2000 cm^{-1}) appeared as shown in Fig. 1(b). CH_2 peaks of diethylenediamine also appeared at 1481 cm^{-1} with the CH_2 peak of the PAN backbone group (1454 cm^{-1}). The emergence of these peaks indicated that PADD was successfully synthesized from PAN fiber.

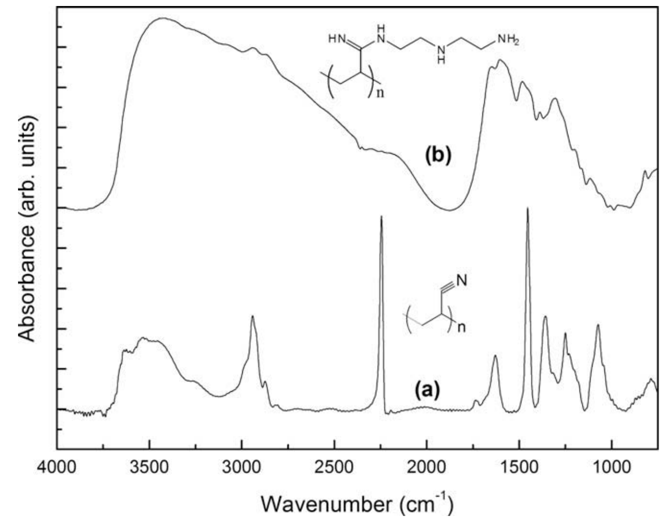

Fig. 1. FT-IR spectra of (a) raw PAN and (b) PADD.

The synthesized PADD was ground to micro-particles using a ball mill with different times (24 h and 3 h). The PADD fiber is very soft and flexible in the water or the high humidity environment. However, after drying under vacuum, it changes to be very hard and easily ground. The particles shape and size of two ER materials are shown in Fig. 2. One is PADD (fine) ground for 24 h, and the other is PADD (rough) ground for 3 h. PADD (fine) shows mono-dispersed size distribution (average particle sizes ca. 8 μm), and PADD (rough) shows bi-dispersed size distribution (average particle sizes ca. 9 and 20 μm). All particle shapes are similar and irregular.

Figs. 3–5 show the electro-rheological property of PADD (fine) and PADD (rough) dispersed ER fluids. Shear stress curves as a function of shear rate for PADD (fine) and PADD (rough) under 0–3 kV/mm electric field are shown in Fig. 3(a) and (b), respectively. PADD (fine) showed the typical Bingham plastic behavior although it showed some deviation. And it showed similar values of shear stress at shear rate of near 0 s^{-1} and 1000 s^{-1} under same electric field. However, PADD (rough) did not show typical Bingham plastic behavior. At a high DC electric field, it showed trembling behavior with Bingham behavior. In the low shear rate, this

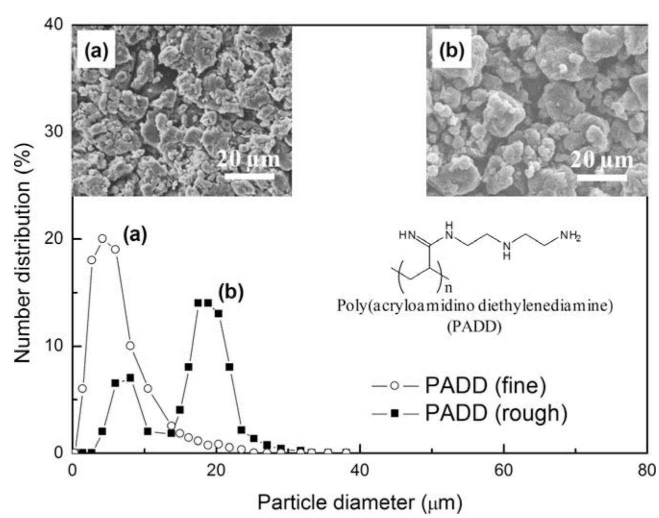

Fig. 2. FE-SEM images and the size distribution of (a) PADD (fine) and (b) PADD (rough).