구형 폴리아닐린 복합체의 전기유변특성

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Electrorheology of Spherical Polyaniline Composites

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Introduction

As one of smart materials which have controllable properties by an external energy, electrorheological (ER) fluid has been studied by many researchers with various kinds of materials. The ER fluid is a suspension of micron-sized semi-conducting or dielectric particles dispersed in a non-conducting fluid. The rheological properties of ER fluids are drastically altered by an applied electric field because the particles attract each other to form fibril structures parallel to the field direction (Hao T., 2001).

Despite their many potential applications such as active controllable dampers and torque transducers, the ER fluids are not widely commercialized yet due to their insufficient physical properties and limited understandings of mechanism for ER phenomena. In the theoretical development of electrorheology, ER fluids are assumed to be suspensions containing spherical and monodispersed particles. However, most of ER fluids studied possess particles of irregular granule and polydisperse size distribution. These irregularity of particles in ER fluids is one of the reasons that experimental results can not be directly compared with theoretical predictions. There were some studies using these sperical particles such as polystyrene containing anionic groups (Kuramoto et al, 1995) and PMMA having a double layered shell (Saito et al., 1999). ER characterizations in controlled experiments have not been performed completely in their reports.

In this study, monodisperse and spherical particles, which are only conductive at the surface, are used as the dispersed phase in ER fluids. Poly(methyl methacrylate) (PMMA)

microspheres with three different sizes were used as a core material and a polyaniline (PA) shell was made by *in-situ* polymerization through a consistent amount of aniline in the presence of core particles. Their ER and polarization properties were then investigated.

Experimental

At first, PMMA particles were synthesized via a dispersion polymerization method (Shen et al., 1994) which is one of most useful methods in making monodisperse polymer particles. The purified methyl methacrylate monomer and a radical initiator (azoisobutyronitrile) were dissolved in methanol containing poly(vinyl pyrrolidone) as a stabilizer at 25 °C. The particle size of PMMA was controlled by change of polymerization conditions such as stabilizer content and ratio of initiator to monomer. After removing oxygen by nitrogen purging, the reaction mixture was heated to 55 °C and then kept for 24 hours at that temperature. The synthesized monodispersed particles of 2, 4.5, and 9 μm were sufficiently washed by methanol and then dispersed in water prior to the PA polymerization.

The PMMA microspheres coated with PA were prepared by following the protocol of Barthet *et al.* (Barthet *et al.*, 1998). Aniline was added to this suspension by 4, 20, and 30 g per 100 g of PMMA. A small amount of hydroquinone was also added to the reaction system in order to minimize polymerization of aniline in water phase. The polymerization took place for 24 hours at 25 °C. Sample codes for composite microspheres were given as PAPMMA*X*-*Y* that is defined as follows: *X* is amount of aniline (by gram) per 100g of PMMA and *Y* represents to particle size of PMMA core *i.e.*, Y/10 μm. The PA-PMMA products were washed and their conductivities were controlled by same procedure as PA (Choi *et al.*, 1999) to the range between 10^{-9} and 10^{-10} S/cm, which is the desirable conductivity range for particle materials of ER fluids. After adjusting the conductivity, the products were dried in a vacuum oven at 25 °C. ER fluids were prepared by dispersing dried PA-PMMA particles in silicone oil at 10 vol%.

Electrorheological properties of ER fluids with PA-PMMAs and PA particles were measured via a rotational rheometer (MC120, Paar-Physica, Germany) with both stress and shear rate control, equipped a high DC voltage generator and concentric cylinder type measuring unit. The interfacial polarization which occurs in ER fluids under an external electric field, was also studied with dielectric spectrum of each ER fluid measured by an impedance analyzer equipped with a fixture for liquid samples.

Results and Discussion

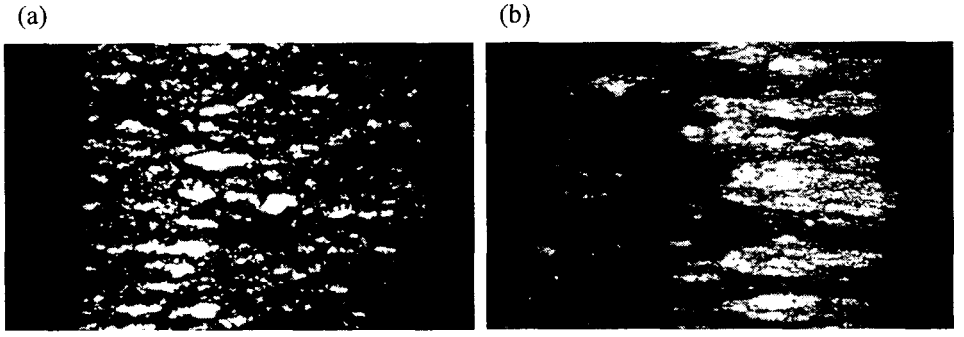

Fig. 1. Difference in particle chain formation for (a) PA based ER fluid and (b) PAPMMA20-20 based ER fluid at 3kV/mm. Black areas in both slides are electrodes.

Figure 1(a) and 1(b) are the fibrillations of particles under an applied electric field for ER fluids of PAPMMA20-20 and PA alone. It has been found that the PA system showed superior ER performance as compared to the core/shell PAPMMA systems due to the difference of interfacial polarization process between them, although PA exhibited weaker electrical properties than PAPMMAs (Cho et al., 2002). In addition to the analysis based on the interfacial polarization, electrodynamic variation provides another difference in ER behavior between PA and PAPMMA based ER fluids. The PA based ER fluid forms thin and dense particle chains under the electric field and particle moves slightly to form chain structures. However, the PAPMMA20-20 based ER fluid forms somewhat thick particle chains with low density, and PAPMMA20-20 particles are collected at the positive electrode, due to the dominant dielectrophoresis in PAPMMA20 based ER fluid, which is defined by the lateral migration of uncharged particles under an electric field. Although all ER fluids exhibit the dielectrophoresis phenomena, the fibrillation of particles is dominant in most cases because of the relatively high particle concentration (Schnelle T., Web page). However, for the PAPMMA based ER fluids in our study, both particle fibrillation and dielectrophoresis occur simultaneously under an applied electric field due to the insufficient electrostatic interaction among particles.

Figure 2 shows flow curves (shear rate *vs.* shear stress) under the electric field strengths of 3kV/mm of PAPMMA based ER fluids with particle sizes of 2, 4.5, and 9 μm. ER

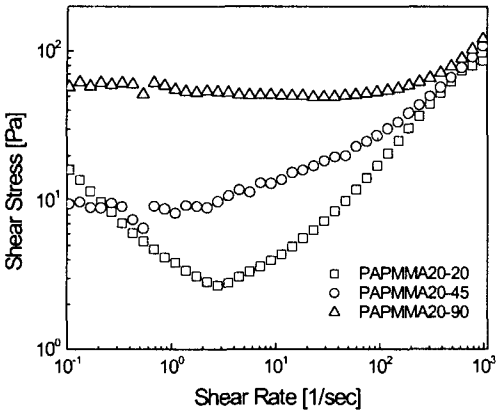

Figure 2. Particle size effect on flo curves for PAPMMA based ER fluid at 3kV/mm.

effects increased with particle size for the same ratio of PA and PMMA, suggesting different flow behaviors for different particle sizes. In addition, no stress decreases were observed at the low shear rate regime for PAPMMA20-45 and PAPMMA20-90, indicating that the interfacial polarization becomes larger as particle size increases. From dielectric spectrum, relaxation times of polarization under an applied electric field were obtained to be 10^{-2}, 10^{-3}, and 10^{-4} second for PAPMMA20-20, PAPMMA20-45, and PAPMMA20-90 ER fluids, respectively. It clearly shows that the PAPMMA20-90 system has the fastest response to the electric field, and this finding explains the flow behavior observed from Fig. 2.

Acknowledgement

This work was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea.

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