Korea-Australia Rheology Journal
Vol. 18, No. 1, March 2006 pp. 25-30

Role of surfactant on damping performance of polyaniline based electrorheological suspension

Ji Woo Kim, Chul Am Kim, Hyoung Jin Choi* and Seung Bok Choi[1]
Dept. of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea
[1]Dept. of Mechanical Engineering, Inha University, Incheon 402-751, Korea

(Received May 20, 2005; final revision received March 8, 2006)

Abstract

To enhance the stability of dispersed polyaniline (PANI) particles in a silicone oil system, a nonionic surfactant was adopted, and its effect on the electrorheological (ER) performance was investigated under an applied electric field. In the presence of a nonionic surfactant, the PANI based ER fluid exhibited not only an improved sedimentation stability based on the estimated sedimentation ratio but also an enhanced maximum yield stress behavior. Furthermore, the surfactant added ER suspension was applied to an ER damper system, and its damping performance was compared with the ER suspension without a surfactant.

Keywords **:** surfactant, electrorheological fluid, yield stress, polyaniline

1. Introduction

It is well known that as one of the most spectacular smart and intelligent materials, electrorheological (ER) fluids exhibit reversible changes in their rheological properties as a function of the electric field strength (Zhao and Yin, 2002; See, 2004). The ER fluids commonly consist of suspensions of micron-sized particles possessing a higher dielectric constant and/or conductivity than that of a non-conducting fluid. In the presence of a strong electric field, the suspended particles attract each other to form a solid-like network of fibers aligned in the field direction and the apparent viscosity can be enhanced tremendously (Kim *et al.*, 1999).

Furthermore, ER fluids have both a very fast response characteristic to an electric field in a few milliseconds and hence a wide control bandwidth (Jordan and Shaw, 1989). Consequently, they have been widely investigated for the purpose of various industrial applications, based on the rapid and reversible change in their rheological properties under an applied external electrical field transverse to the direction of the flow. Since their first discovery, this inherent feature has triggered tremendous research activities both in theory (Henley and Filisko, 2002; Gu *et al.*, 2002) and in the development of various engineering applications, such as shock absorbers (Kim *et al.*, 2001a), engine mounts (Williams *et al.*, 1993), clutch/brakes, and smart structures. Furthermore, recently, biodegradable polymers have been tested as a smart material in the feasibility of using ER fluids in a controllable drug delivery system. In the absence of an electric field, a base level of drug release will occur by diffusion across a mesh electrode. Upon the application of an electric field, it was envisioned that drug release may be controlled, either hindered or halted (Davis *et al.*, 1998). Nonetheless, these attractive and powerful materials have not yet been fully adopted for commercial products because of several unsolved problems, including their colloidal instability, low yield stress and high current density. Among a wide range of ER materials, the current study focuses on semiconducting polymer-based ER systems, because they possess many advantages. Various polarizable semiconducting polymers, including polyaniline (PANI) (Choi *et al.*, 1997; Hao *et al.*, 2000; Lengalova *et al.*, 2003), copolyaniline (Cho *et al.*, 1998; Choi *et al.*, 1999), polypyrrole (Kim *et al.*, 2002b; Kim *et al.*, 2002c), poly(acene quinine) radicals (Sohn *et al.*, 2002), phosphate cellulose (Kim *et al.*, 2001b), chitosan adipicate (Choi *et al.*, 2001) and polymer/clay nanocomposites (Kim *et al.*, 1999; Kim *et al.*, 2002a; Lu *et al.*, 2002) have been developed as dry-base ER materials. Polymer particles possessing polar groups such as amino, hydroxyl and amino-cyan can be also adopted. On the other hand, note that the wet-base systems including corn starch and mesoporous molecular sieve (Choi *et al.*, 2000) generally require active substrates such as water, surfactant and glycerin (Wu *et al.*, 1998). Actually, the above-mentioned dry-base anhydrous systems have been developed to overcome the shortcomings that wet-base systems possess. Concurrently, several researchers have reported that surfactant sys-

---

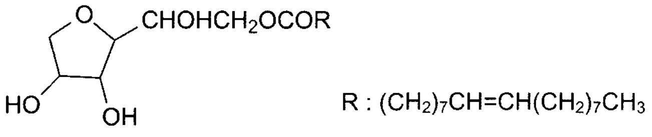
*Corresponding author: hjchoi@inha.ac.kr tems generally enhance the ER behavior. Kim (2001) reported on the nonlinear ER behavior using a surfactant bridge model, while Lee *et al.* (1998) demonstrated the effect of a surfactant on the properties of ER with different structures and surfactant concentrations.

Accordingly, the current study investigated the ER properties of a surfactant-added PANI-based ER fluid system, focusing on the effect of the surfactant on the colloidal stability of the PANI particles in the suspension. Not only the sedimentation stability of the ER particles was found to increase in medium oils, but also the yield stress of the ER fluid increased under an applied electric field. The ER fluids were further applied to an ER damper to investigate their damping characteristics.

2. Experimental

The PANI was synthesized through chemical oxidation polymerization, as previously reported (Choi *et al.*, 1997; Choi *et al.*, 1998). An ammonium peroxysulfate solution in 240 ml 1 M HCl was dropped into a well-stirred reactor containing an aniline (Junsei Chemical Co., Japan) monomer in 400 ml 1M HCl. During the synthesis, the mixtures were stirred at about 400~500°C rpm for 2 h and the temperature was kept at 0°C. The pH of the product was adjusted to 9.5 by adding either a NaOH or HCl solution. Thereafter, the particles for the ER fluid were obtained by dedoping, milling, washing, filtering, and drying, sequentially. The synthesized polymer particles were washed using distilled water to remove the initiator, unreacted monomer, and oligomer. They were then further washed with ethanol and cyclohexane to make the surface of the synthesized particles hydrophobic. Finally, the synthesized PANI particles were put into a vacuum oven for two days to eliminate any trace of water prior to their use as an ER material. The mean diameter of the particles was found to be ~1 μm using a particle size analyzer (Malvern), while the density of the PANI particles was measured to be 1.3±0.01 g/cm^3 using a pycnometer.

To prepare the ER fluids for rheological measurements, the PANI particles were dispersed in silicone oil (kinematic viscosity of 50 cS (centistoke) and density of 0.96 g/cm^3) by agitating the mixture at 1500~1800 rpm using a Pearl Mill (Shinil Co.). The concentration of dispersed particles was adjusted to 15 vol% in each sample. The nonionic surfactant used in the current study was Span80 (Sorbitan monooleate; Aldrich) with a density of 0.956 g/cm^3 and molecular weight of 956 g/mole. Its chemical structure is given as follows.



Scheme 1. Chemical structure of nonionic surfactant (Span80) used.

It was also oil-soluble and the HLB (hydrophile-lipophile balance) index was 4.2. The surfactant ratio to the weight of the particles was adjusted from 0 to 5 wt%. The PANI-based ER fluids with and without the surfactant were indexed as PANI-S and PANI, respectively. To examine the sedimentation stability, two mass cylinders (500 ml) were filled with 150 ml of the two ER fluids, PANI and PANI-S, respectively. To investigate the effect of the surfactant on the ER behavior, the desired amount of the surfactant was added in the case of PANI-S.

Rheological measurements were carried out using a rotational rheometer (Physica MC120, Stuttgart, Germany) with a Couette geometry (Z3-DIN and Z4-DIN), high voltage generator (HVG 5000, Stuttgart, Germany), and oil bath for temperature control. The gap sizes of the Z3-DIN and Z4-DIN were 1.06 mm and 0.59 mm, and the maximum attainable stresses 1.141 kPa and 6.501 kPa, respectively (Jhon *et al.*, 2001; Sung *et al.*, 2002). The HVG 5000 could supply a DC voltage of up to 10 kV. The suspensions were placed in the gap between the stationary outer measuring cup and the rotating inner bob. Various static DC electric fields perpendicular to the flow direction were applied to the cylindrical cup: the inner wall of the cup was a positive electrode, while the bob was grounded. The electric field was applied to the ER fluid for 3 min before the measurement in order to obtain an equilibrium internal structure for the ER fluid particles. The shear rate was varied from 10^{-2} to 10^3 s^{-1}. The shear stress at the transition point where the shear viscosity abruptly changed was interpreted based on the yield stress. Using both controlled shear rate (CSR) and controlled shear stress (CSS) modes, the shear stress versus the shear rate was measured at several applied electric field levels (Sung and Choi, 2004).

Fig. 1 shows a cylindrical flow-mode type ER damper adopted to study the damping characteristics (Choi *et al.*, 2003a; Hong *et al.*, 2002; Park *et al.*, 1999). The ER damper was divided into an upper and lower chamber by a piston, and fully filled with an ER fluid which flows through a duct between the inner and outer cylinders from one chamber to the other. The positive voltage was produced by a high voltage generator connected to the inner cylinder, whereas the negative voltage was connected to the outer cylinder. Meanwhile, the gas chamber positioned in the lower part acted as an accumulator of the ER fluid induced by the motion of the piston. The gas in the chamber was nitrogen with a gas pressure of 10 bar and the maximum piston velocity was 0.377 m/s with a shear rate about 7000 1/s in a flow mode. The electrode gap of the damper was 0.75 mm. The electric field was applied to the ER damper using a high voltage generator. The damping force was measured without applying an electric field prior

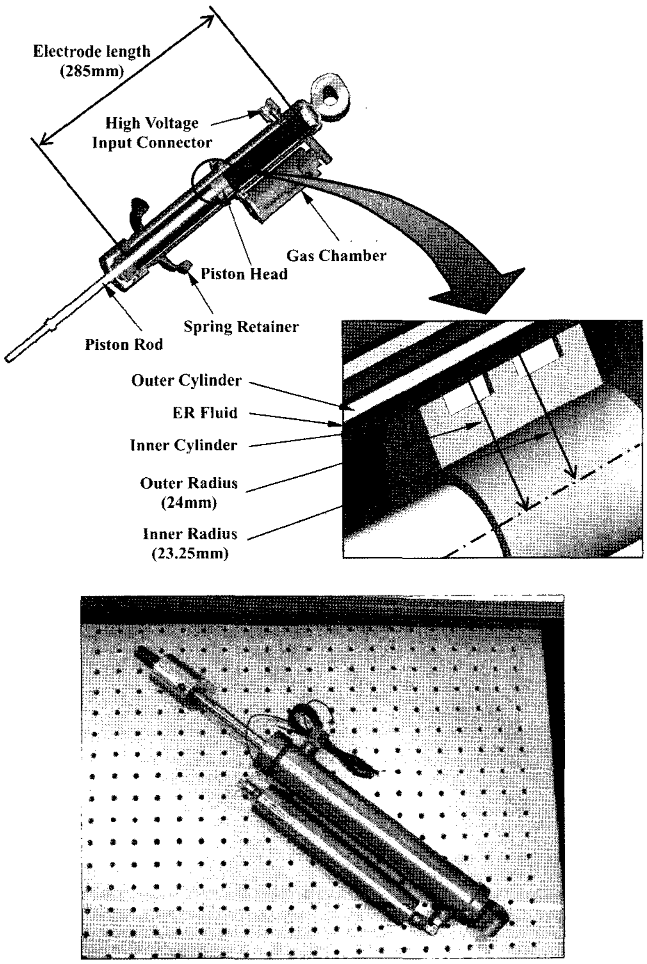


Fig. 1. Schematic diagram of a cylindrical flow-mode type ER damper.

to the test. The temperature of the ER damper was controlled by an electric heater surrounding the damper. The excitation magnitude and frequency on the ER damper were ± 20 mm and 1.89 Hz, respectively.

3. Results and discussion

Sedimentation of the dispersed particles in ER fluids has been regarded as one of main drawbacks in their industrial applications. The ER performance decreases with the increase of the sedimentation of the particles. The sedimentation is known to be mainly induced by a density mismatch between particles and suspending medium. This sedimentation problem, however, can be reduced by controlling the size of the particles, choosing the medium oil with close density and adding surfactant. To obtain the degree of sedimentation stability of the suspending PANI particles, we introduced the following Eq. (1).

$$\text{Sedimentation ratio (R)} = \frac{b}{a+b} \qquad (1)$$

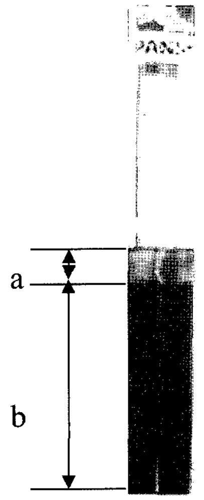


Fig. 2. The sedimentation ratio of PANI based ER fluid.

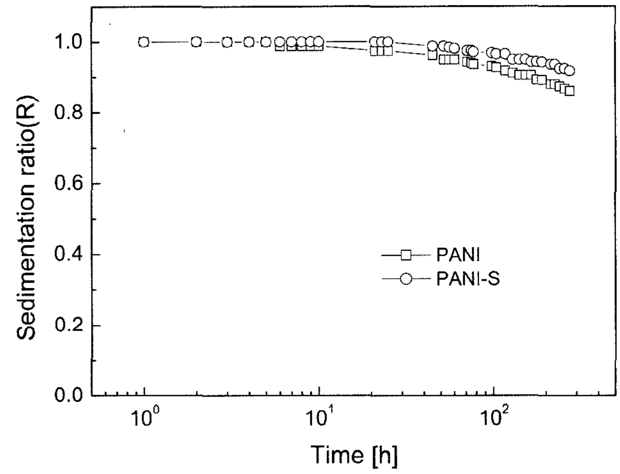


Fig. 3. The sedimentation ratio versus time for PANI and PANI-S.

Here, a and b can be obtained from the sedimentation test as given in Fig. 2. Concurrently, the colloidal stability of the ER fluids was studied via a sedimentation test. The change in height of the clear portion of the ER particles in the mass cylinder was observed as a function of time, and the sedimentation ratio obtained. The PANI particles dispersed in silicone oil without the surfactant exhibited drastic sedimentation compared with the case of PANI-S. Sedimentation was initiated after 20 h, and the sedimentation rate then accelerated through 40 h. In contrast, the surfactant (Span 80)-added system (PANI-S) was more stable than the PANI, as sedimentation started slowly only after 40 h as shown in Fig. 3.

Fig. 4 shows the flow curve of the surfactant added PANI based ER fluid. Without applied electric field strength, it shows Newtonian fluid behavior. As soon as the electric field is applied, Bingham fluid behavior appears with a yield stress and the shear stress increased with the applied

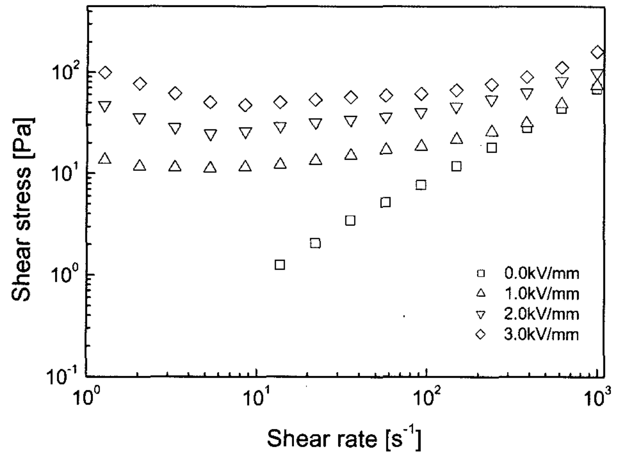


Fig. 4. Flow curve of surfactant added PANI ER fluid as a function of shear rate for different applied electric fields.

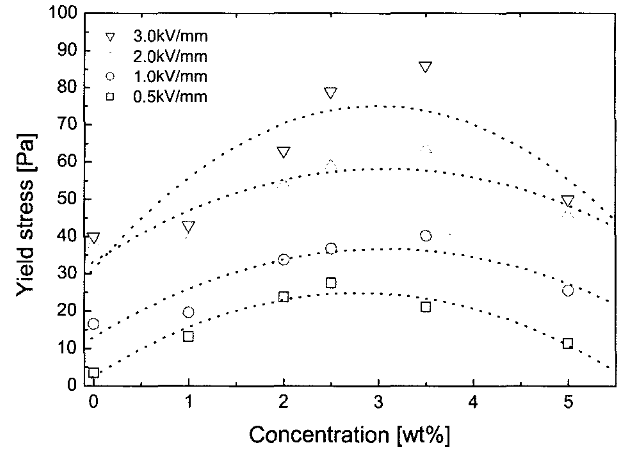


Fig. 5. ER behavior (yield stress) of surfactant added system as a function of surfactant concentration.

electric field strength. Especially in the case of 3.0 kV/mm, slight decrease of the shear stress was observed. In a low shear rate region, the electrostatic interactions among particles induced by external electric fields are dominant compared to the hydrodynamic interactions induced by the external flow field. The aligned particular structures begin to break with shear deformation, and the broken structures tend to reform the chains by the applied electric field, depending on the magnitude of the applied shear and particle-particle interaction in the fibrils. The decrease in shear stress is observed when increase in the reformed structures with shear rate is not as complete as those before applying shear flow. In other words, as the shear rate increases, the destruction rate of the fibrils becomes faster than the reformation rate. It is related to the rate of polarization under the shear by an applied electric field (Cho *et al.*, 2003).

Fig. 5 represents the maximum yield stress under applied electric fields as a function of the surfactant concentration in the PANI-S based ER fluids, in which the dynamic yield stress was obtained from the flow curves given in Fig. 4 at a zero shear rate limit for each sample. The particle concentration was fixed at 15 vol%. The results clearly showed that the maximum yield stress occurred at the middle point between 2 and 3 wt% surfactant concentration. Note that the dotted lines in Fig. 5 represent their best fit.

Fig. 6 shows the electric field dependent damping force relative to the piston velocity for both the PANI (filled symbol) and the PANI-S with 2 wt% surfactant (open symbol), when the piston velocity was changed by increasing the excitation frequency from 0.4 to 3.0 Hz, while maintaining a fixed excitation amplitude value. The damping force increased with an increase in both the electric field and the piston velocity, except at 5 kV/mm. It is evident that the damping force of the ER damper increases as the electric field increases. This is mainly attributed to the increment of the yield shear stress of the ER fluid (Park *et al.*, 1999). At a higher frequency region, the damping force decreased. This behavior was related to the chain structure of the ER fluid in a higher electric field, which was more linear compared to the system without the surfactant. In a higher electric field, the PANI-based ER fluid exhibited

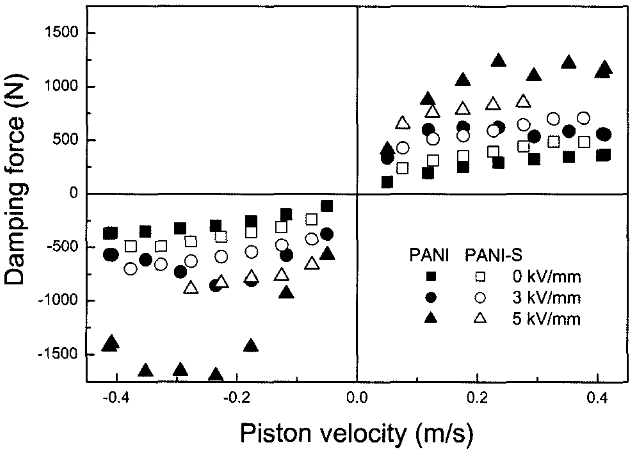


Fig. 6. Effect of electric field on damping force vs. piston velocity (a) PANI and (b) PANI-S.

Table 1. Composition of pristine and surfactant added ER fluids

Sample Index	pH	Medium viscosity	Particle conc. (%)	Medium oil	Additive
PANI	9.5	50cS	20 vol	silicone oil	
PANI-S	9.5	50cS	20 vol	silicone oil	Span80 (2wt%)

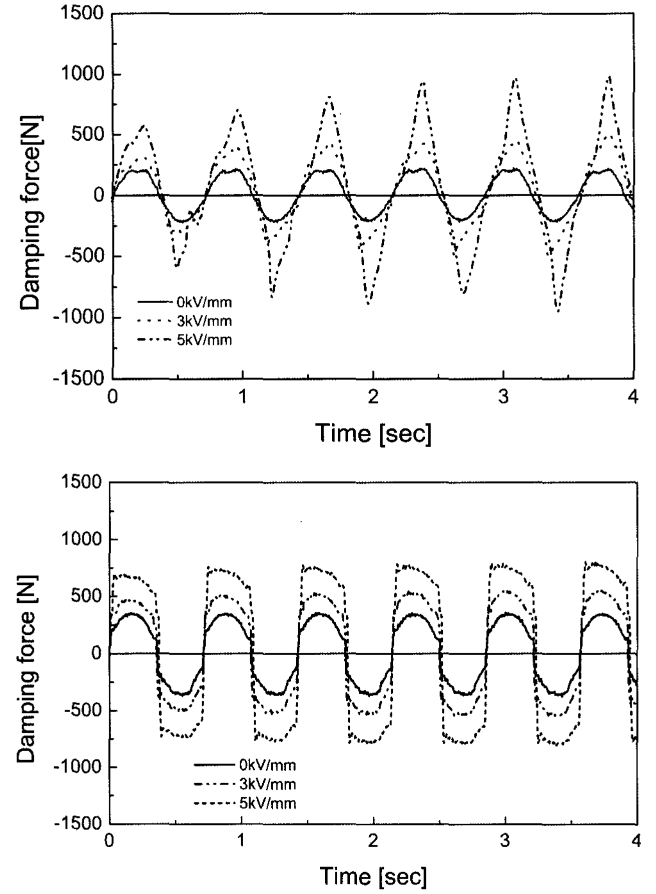


Fig. 7. Effect of electric field on damping force vs. time (a) PANI and (b) PANI-S.

this behavior. However, the amplitude of the damping force of the PANI-based ER fluid was higher than that of the PANI-S-based ER fluid.

Fig. 7(a) presents the damping forces as a function of time at an operating temperature of 25°C. As the electric field increased, the damping forces of the ER damper filled with the PANI-based ER fluid also increased. From this result, the damping force was determined as 210 N without an electric field. In contrast, the damping force at 5 kV/mm was 970 N, and thus the net increment of the damping force was 760 N. This result implies that a large range of the damping force of the ER damper could be continuously controlled by tuning the applied electric field. However, the curve shape of the PANI-based ER fluid for the damper was not well developed, as shown in Fig. 7(a), although it became a fully developed profile curve after 2~3 excitations. This behavior was caused by a mismatch of the response time (i.e. time lag between the output response time and input time) between the PANI-based ER fluid and the applied electric field. Detailed information regarding on the response time will be reported later. Fig. 7(b) shows that the curve shape of the PANI-S-based ER fluid for the damper was developed better than that in Fig. 7(a).

4. Conclusion

The current study adopted a surfactant-added system to investigate the role of a surfactant on the dispersion stability and properties of ER materials. Both the electrical responsibility based on the damping curves and the dispersion stability was found to be enhanced because the surfactant on the surface of the particles interacted well with the medium oil, thereby providing a good dispersion. Such finding by adding surfactant in PANI based ER fluid will be applied for various polymeric ER systems for future work.

Acknowledgement

This study was supported by research grants from both the Korea Science and Engineering Foundation through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University and the National Research Laboratory (NRL) Program (2005), Korea.

References

Cho, M.S., Y.H. Cho, H.J. Choi and M.S. Jhon, 2003, Synthesis and electrorheological characteristics of polyaniline-coated poly(methyl methacrylate) microsphere: size effect, *Langmuir* **19**, 5875-5881.

Cho, M.S., H.J. Choi and K. To, 1998, Effect of ionic pendent groups on a polyaniline-based electrorheological fluid, *Macromol. Rapid Commun.* **19**, 271-273.

Choi, H.J., J.W. Kim and K. To, 1999, Electrorheological characteristics of semiconducting poly(aniline-co-o-ethoxyaniline) suspension, *Polymer* **40**, 2163-2166.

Choi, H.J., M.S. Cho, K.K. Kang and W.S. Ahn, 2000, Electrorheological properties of a suspension of a mesoporous molecular sieve (MCM-41), *Micropor. Mesopor. Mater.* **39**, 19-24.

Choi, H.J., T.W. Kim, M.S. Cho, S.G. Kim and M.S. Jhon, 1997, Electrorheological characterization of polyaniline dispersions, *Eur. Polym. J.* **33**, 699-703.

Choi, H.J., M.S. Cho and K. To, 1998, Electrorheological and dielectric characteristics of semiconductive polyaniline-silicone oil suspensions, *Physica A* **254**, 272-279.

Choi, S.B. and S.S. Han, 2003, H-infinity control of electrorheological suspension system subjected to parameter uncertainties, *Mechatronics* **13**, 639-657.

Choi, S.B., J.H. Choi, Y.S. Lee and M.S. Han, 2003, Vibration control of an ER seat suspension for a commercial vehicle, *Trans. ASME*, **125**, 60-68.

Choi, U.S. and Y.S. Park, 2001, Electrorheological behavior of chitosan adipicate suspension as anhydrous ER fluid, *J. Ind. Eng. Chem.* **7**, 281-284.

Davies, J.L., I.S. Blagbrough and J.N. Staniforth, 1998, Electrorheological behaviour at low applied electric fields of microcrystalline cellulose in BP oils, *Chem. Commun.* 2157-2158.

Gu, G.Q., K.W. Yu and P.M. Hui, 2002, Relaxation theory for dynamic electrorheological effect, *Int. J. Mod. Phys. B* **16**, 2597-2602.

Hao, T., A. Kawai and F. Ikazaki, 2000, The yield stress equation for the electrorheological fluids, *Langmuir* **16**, 3058-3066.

Henley, S. and F.E. Filisko, 2002, Lamellar structures induced by coupled electromagnetic and shear fields: A defining character of ER/MR activity, *Int. J. Mod. Phys. B* **16**, 2286-2292.

Hong, S.R., S.B. Choi and M.S. Han, 2002, Vibration control of a frame structure using electro-rheological fluid mounts, *Int. J. Mech. Sci.* **44**, 2027-2045.

Jhon, M.S. and H.J. Choi, 2001, Lubricants in future data storage technology, *J. Ind. Eng. Chem.* **7**, 263-275.

Jordan, T.C. and M.T. Shaw, 1989, Electrorheology, *IEEE Trans. Electr. Insul.* **24**, 849-878.

Kim, D.H., S.H. Chu, K.H. Ahn and S.J. Lee, 1999, Dynamic simulation of squeezing flow of ER fluids using parallel processing, *Korea-Austalia Rheol. J.* **11**, 233-240.

Kim, J.W., H.J. Choi, H.G. Lee and S.B. Choi, 2001a, Damping characteristics of polyaniline-based electrorheological fluid, *J. Ind. Eng. Chem.* **7**, 218-222.

Kim, J.W., S.G. Kim, H.J. Choi and M.S. Jhon, 1999, Synthesis and electrorheological properties of polyaniline-Na$^+$-montmorillonite suspensions, *Macromol. Rapid Commun.* **20**, 450-452.

Kim, J.W., F. Liu and H.J. Choi, 2002a, Polypyrrole/clay nanocomposite and its electrorheological characteristics, *J. Ind. Eng. Chem.* **8**, 399-403.

Kim, S.G., H.J. Choi and M.S. Jhon, 2001b, Preparation and characterization of phosphate cellulose-based electrorheological fluids, *Macromol. Chem. Phys.* **202**, 521-526.

Kim, Y.D. and D.H. Park, 2002b, The electrorheological responses of suspensions of polypyrrole-coated polyethylene particles, *Colloid Polym. Sci.* **280**, 828-834.

Kim, Y.D. and I.C. Song, 2002c, Electrorheological and dielectric properties of polypyrrole dispersions, *J. Mater. Sci.* **37**, 5051-5055.

Kim, Y.D., 2001c, A surfactant bridge model for the nonlinear electrorheological effects of surfactant-activated ER suspensions, *J. Colloid Interf. Sci.* **236**, 225-232.

Lee, H.J., B.D. Chin, S.M. Yang and O.O. Park, 1998, Surfactant effect on the stability and electrorheological properties of polyaniline particle suspension, *J. Colloid Interf. Sci.* **206**, 424-438.

Lengalova, A., V. Pavlinek, P. Saha, J. Stejskal, T. Kitano, and O. Quadrat, 2003, The effect of dielectric properties on the electrorheology of suspensions of silica particles coated with polyaniline, *Physica A* **321**, 411-424.

Lu, J. and X.P. Zhao, 2002, Electrorheological properties of a polyaniline-montmorillonite clay nanocomposite suspension, *J. Mater. Chem.* **12**, 2603-2605.

Park, W.C., S.B. Choi and M.S. Suh, 1999, Material characteristics of an ER fluid and its influence on damping forces of an ER damper Part II: damping forces, *Mater. Design* **20**, 325-330.

See, H. 2004, Advances in electro-rheological fluids: materials, modeling and applications, *J. Ind. Eng. Chem.* **10**, 1132-1145.

Sohn, J.I., M.S. Cho, H.J. Choi and M.S. Jhon, 2002, Synthesis and electrorheology of semiconducting poly(naphthalene quinone) radical particles, *Macromol. Chem. Phys.* **203**, 1135-1141.

Sung, J.H., Y.H. Hyun, D.H. Kwon and H.J. Choi, 2002, Viscoelastic property of biodegradable polyester and polyethylene blends: Effect of molecular weight of polyethylene, *J. Ind. Eng. Chem.* **8**, 28-33.

Sung, J.H. and H.J. Choi, 2004, Electrorheological characteristics of poly(o-ethoxy)aniline nanocomposite, *Korea-Austalia Rheol. J.* **16**, 193-199.

Williams, E.W., S.G. Rigby, J.L. Sproston and R. Stanway, 1993, Electrorheological fluids applied to an automotive engine mount, *J. Non-Newtonian Fluid Mech.* **47**, 221-238.

Wu, S., F. Zeng and J. Shen, 1998, The conductive properties of the electrorheological suspensions based on dihydroxypropyl chitosan particles, *J. Appl. Polym. Sci.* **67**, 2077-2082.

Zhao, X.P. and J.B. Yin, 2002, Preparation and Electrorheological Characteristics of Rare-Earth-Doped TiO_2 Suspensions, *Chem. Mater.* **14**, 2258-2263.