

## Electrorheology of conducting polyaniline-BaTiO<sub>3</sub> composite

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### Abstract

Organic-inorganic composite of polyaniline and barium titanate (PANI-BaTiO<sub>3</sub>) was synthesized via an *in-situ* oxidative polymerization of aniline in the presence of barium titanate (BaTiO<sub>3</sub>) nanoparticles dispersed in an acidic medium. Barium titanate has large electric resistance and relatively high dielectric constant which is one of the essential properties for its electrorheological (ER) applications. The microstructure and composition of the obtained PANI/BaTiO<sub>3</sub> composite were characterized by SEM, FT-IR and XRD. In addition, we also employed a rotational rheometer to investigate the rheological performance of the ER fluids based on both pure PANI particle and PANI/BaTiO<sub>3</sub> composite. It was found that the composite materials possess much higher yield stresses than the pristine PANI due to unique dielectric properties of the inorganic BaTiO<sub>3</sub> particles. Finally, we also examined dynamic yield stress by analyzing its extrapolated yield stress data as a function of electric field strengths. Using the critical electric field strengths deduced, we further found that the universal yield stress equation collapses their data onto a single curve.

**Keywords** : polyaniline, composite, electrorheological fluid, yield stress, suspension

### 1. Introduction

Electrorheological (ER) fluid belongs to a class of colloidal suspensions, which presents rapid and reversible change of its shear viscosity under an electric field (Trlica *et al.*, 2000; Hao *et al.*, 2000). The ER fluid shows a Newtonian fluid behavior without an applied electric field. But when an electric field is applied to such an ER fluid, the particles are polarized and aligned along the direction of electric field, resulting an increased shear viscosity, and its rheological behavior can be expressed by a Bingham fluid equation with a yield stress. And, in order to obtain improved ER performance such as a large yield stress, the particles for the ER dispersing phase ought to possess high polarizability. The ER behavior is known to stem from the polarization of the particles and resulting structural change (Kim *et al.*, 1999; Kim *et al.*, 2002; Zhao *et al.*, 2002; Choi *et al.*, 1997).

Organic/inorganic composite takes advantages from the combination of their own individual unique properties. Recently, composites based on polyaniline (PANI) have gained great research interests as ER materials (Zhao and Yin, 2006). They include PANI/TiO<sub>2</sub> composite (Sung *et al.*, 2004a), PANI/V<sub>2</sub>O<sub>5</sub> composite (Mercouri *et al.*, 1989), and PANI/MCM41 composite (Cho *et al.*, 2004a). Concerning ER performance, the dielectric polarization theory

naturally appeared, because the ER behavior is closely related to the dielectric phenomena (Ikazakiy *et al.*, 1998).

In this study, we synthesized conducting PANI/BaTiO<sub>3</sub> composite by means of an organic-inorganic *in-situ* oxidative polymerization method (Gospodinova *et al.*, 1998). Advantages of utilizing PANI include its low cost, ease of preparation, excellent environmental stability, unique chemical and physical properties controlled by the oxidation and protonation state (Chin and Park, 2001). In addition, barium titanate has ferroelectric properties with high dielectric constant and good crystallinity (Kareive *et al.*, 1999) suitable for improvement of ER effect of pure PANI (Wei *et al.*, 2004; Patil *et al.*, 2001). These ER materials are known to be important for various electro-mechanical purposes, applicable as damping device, robotic controlled system, photo electrochemical devices, chemical sensors, electrochromic display, smart window and light emitting diode.

### 2. Experimental

PANI/BaTiO<sub>3</sub> composite was synthesized by an *in-situ* oxidative polymerization in the presence of barium titanate (Inframat Advanced Materials, LLC, USA) nanoparticles. Aniline (DC Chemical, Korea) and ammonium peroxydisulfate (APS) (Deajung, Korea) were used as monomer and initiator, respectively. BaTiO<sub>3</sub> nanoparticles with an average particle size of 100 nm were dispersed in 450 ml of 1 M HCl (Deajung, Korea) to get a homogenous phase by

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vigorous stirring (200 rpm) at 0°C, after then a 0.43 mole aniline was added to the reactor. The 0.55 mole of APS dissolved in 350 ml of 1 M HCl was dropped into the reactor within 4 hr. After dropping the initiator, the mixture was kept stirring with 200 rpm at 0 for 24 hr (Cho *et al.*, 2004b). The PANI/BaTiO<sub>3</sub> composite synthesized was centrifuged and filtered with distilled water, acetone and methanol sequentially to remove the excess initiator, monomer and oligomer. It was finally dried at 65°C in vacuum oven for 2 days. The density of PANI/BaTiO<sub>3</sub> composite was measured to be 1.57 g/ml using a pycnometer at room temperature.

FT-IR spectroscopy (Perkin Elmer System 2000) was used to identify the chemical structure of the composite prepared by grinding with KBr. Thermal properties of both PANI and PANI/BaTiO<sub>3</sub> composite were also examined by using a thermogravimetric analyzer (TGA, TA instrument Q50, USA). The XRD spectra was also performed using Rigaku DMAX 2500 ( $\lambda = 1.54 \text{ \AA}$ ) diffractometer. The morphology was observed using a scanning electron microscopy (SEM, S-4300, Hitachi). Electrical conductivity of the composite pellets was measured by a standard 2-probe method using a picoameter at room temperature (Choi *et al.*, 2005; Lee *et al.*, 2005). For the ER test, the composite has to possess appropriate value of conductivity. Thereby, we controlled the conductivity of composite particle by dedoping the synthesized both PANI and PANI/BaTiO<sub>3</sub> composite and monitored their pH to be 9 by using either 1 M NaOH or 1 M HCl solution (Strounina *et al.*, 2003). The final product was filtered, dried and sieved. Finally the obtained PANI/BaTiO<sub>3</sub> composite was dispersed in silicone oil (kinematic viscosity: 50 cS, density: 0.96 g/ml). Here, we used a sonicator for 1 hr to make the ER fluid well dispersed while preparing a 10 vol% ER fluid. ER behaviors were investigated by a rotational rheometer (Physica MC 120, Stuttgart) equipped with a DC high voltage generator. In order to get a reliable experiment result, we repeated each experiment for 3 times at 25°C (Kim *et al.*, 2006).

### 3. Results and discussion

Fig. 1 shows the FT-IR spectra of PANI, BaTiO<sub>3</sub> and PANI/BaTiO<sub>3</sub> composite. The characteristic peak of PANI showed the out of plane of aromatic C-H at 824 cm<sup>-1</sup>. In addition, those peaks appeared at 1595 cm<sup>-1</sup>, 1496 cm<sup>-1</sup> and 1302 cm<sup>-1</sup> attributed to the quinoid unit, benzoid unit, C-N stretch of aromatic amine, respectively. Distinctive peaks of BaTiO<sub>3</sub> appear in 568 cm<sup>-1</sup> and 438 cm<sup>-1</sup>.

The thermal property of both PANI and PANI/BaTiO<sub>3</sub> composite was characterized by TGA. The TGA test was carried out under air with a heating rate of 20°C/min. Onset decomposition temperature of the PANI/BaTiO<sub>3</sub> composite is higher than that of pure PANI. This behavior confirms

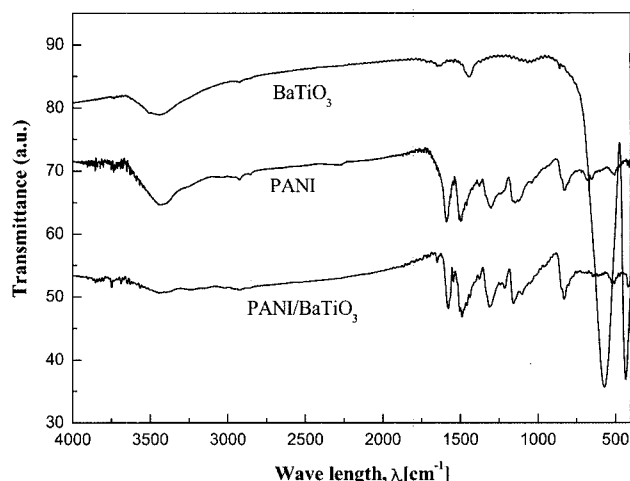


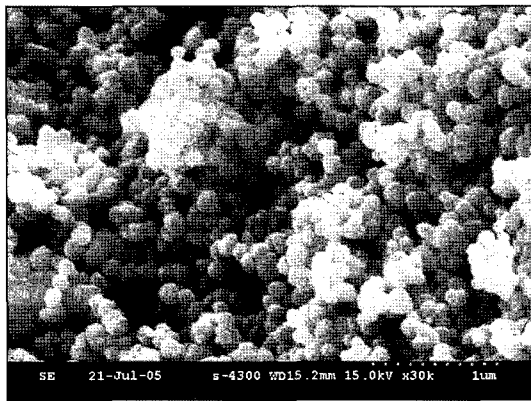
Fig. 1. FT-IR spectra of PANI, BaTiO<sub>3</sub> and PANI/BaTiO<sub>3</sub> composite.

the enhanced thermal stability due to the retardation effect of inorganic material on the decomposition of the composite. Residual weight of the PANI/BaTiO<sub>3</sub> composite was also found to be dependent on the content of BaTiO<sub>3</sub> nanoparticles. In this composite, BaTiO<sub>3</sub> content is fixed to be approximately 10 wt%.

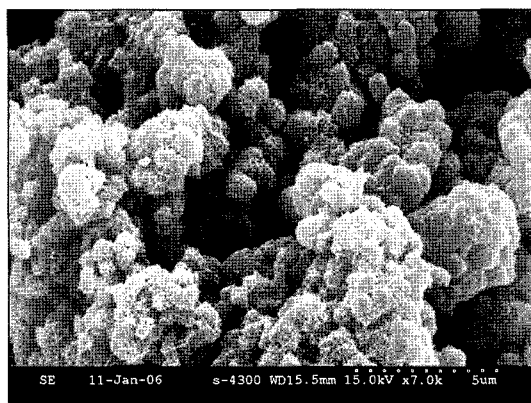
The SEM photographs of (a) BaTiO<sub>3</sub> and (b) PANI/BaTiO<sub>3</sub> composite are presented in Fig. 2. Fig. 2(a) shows that the BaTiO<sub>3</sub> nanoparticles seemed to be quite mono-dispersed spherical particles with an average size of 100~150 nm. As for the composite, we observed that there were also some spherical-like particles which showed much bigger size than that of pure BaTiO<sub>3</sub>. So, we attributed this to the embedding of BaTiO<sub>3</sub> nanoparticles into the PANI matrix.

X-ray diffraction patterns of the PANI, BaTiO<sub>3</sub> nanoparticles and PANI/BaTiO<sub>3</sub> composite were indicated in Fig. 3. PANI showed a wide amorphous peak at low  $2\theta$  region. Fig. 3(b) showed that the BaTiO<sub>3</sub> possessed good crystallinity. When BaTiO<sub>3</sub> nanoparticles were embedded into the polymer matrix, the interaction between PANI and BaTiO<sub>3</sub> restricts the growth of PANI chains around BaTiO<sub>3</sub> nanoparticles resulting a decreased crystallinity. The broad weak peaks of PANI disappears gradually. In addition, PANI/BaTiO<sub>3</sub> composite includes the similar main peaks as that of BaTiO<sub>3</sub> nanoparticles, evidently. This result reveals that PANI was deposited on the surface of the BaTiO<sub>3</sub> nanoparticles.

Fig. 4(a) and 4(b) present the characteristics of shear stress ( $\tau$ ) and shear viscosity ( $\eta$ ) as a function of the shear rate ( $\dot{\gamma}$ ) under various electric field strengths for the PANI/BaTiO<sub>3</sub> composite based ER fluid. The PANI/BaTiO<sub>3</sub> suspension behaved like a Newtonian fluid without an external electric field, in which shear stress increases linearly with shear rate. When under an electric field, the ER fluid



(a)



(b)

Fig. 2. SEM images of (a) BaTiO<sub>3</sub> (b) PANI/BaTiO<sub>3</sub> composite.

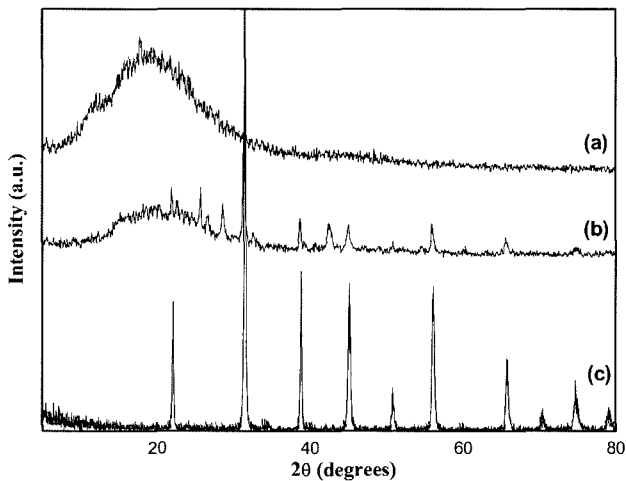
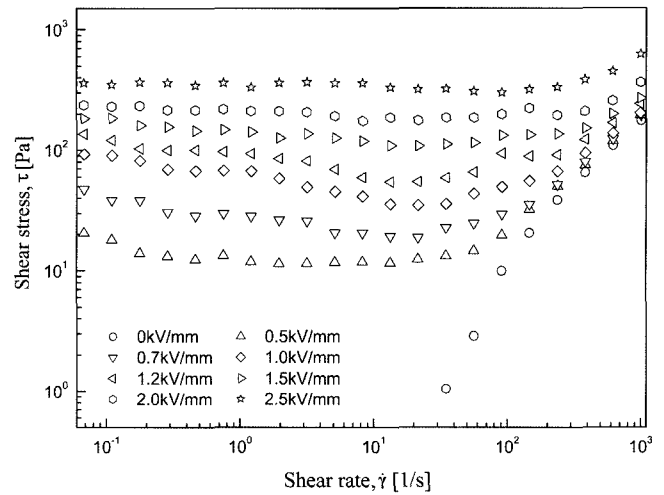
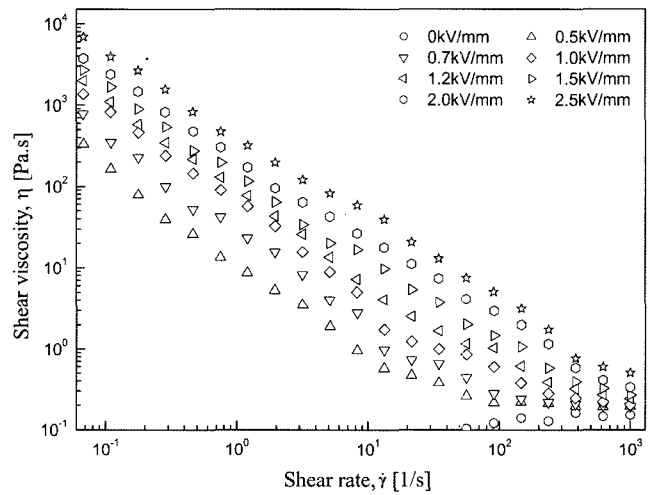


Fig. 3. XRD spectra of (a) PANI, (b) PANI/BaTiO<sub>3</sub> composite and (c) BaTiO<sub>3</sub>.

showed in general a Bingham-like behavior because the particles got polarized and formed chain-like structures. There was a plateau region of shear stress for a wide range of shear rates under an applied electric field. This could be explained by the reformation of the broken chain like



(a)



(b)

Fig. 4. (a) Shear stress vs. shear rate for 10 wt% PANI/BaTiO<sub>3</sub> composite based ER fluid (b) Shear viscosity vs. shear rate for 10 wt% PANI/BaTiO<sub>3</sub> composite based ER fluid.

structure. When increasing the electric field strength, the shear stresses abruptly increased over the entire shear rate range. This behavior has also been observed for various other semiconducting polymer-based ER fluids (Choi *et al.*, 1999; Sung *et al.*, 2004b). We obtained relative higher shear stress tested at 2.5 kV/mm compared with that of previous study (Sung *et al.*, 2004b). Furthermore it can be also noted that in the cases of 1.0 and 1.2 kV/mm, slight shear stress decreases were observed at the shear rate range of 10 1/s. Full description on this phenomenon can be found in the recent report (Cho *et al.*, 2005). Fig. 4(b) also shows the typical Newtonian fluid behavior without an electric field and a very severe shear thinning behavior when influenced by an electric field.

The dynamic yield stress from a controlled shear rate measurement (CSR) was estimated by extrapolating the

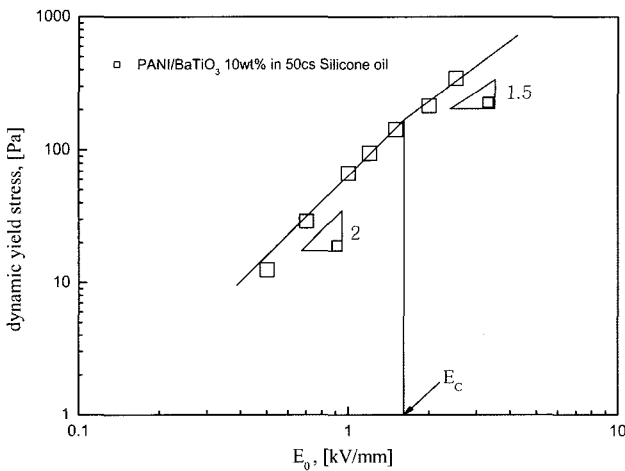
shear stress at shear rate =  $1 \text{ s}^{-1}$  (James and Blakey, 2004). Then, we plotted the dynamic yield stress as a function of various electric fields. It is well known that in general, the correlation of the dynamic yield stress and electric field was presented as follows:

$$\tau_y \propto E^m \quad (1)$$

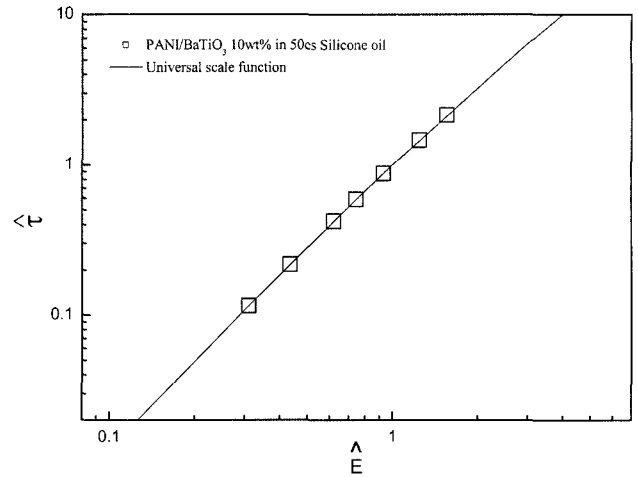
The dependency of the dynamic yield stress on the electric field strength differs from the  $E^2$  dependency suggested by the polarization model (Klingenberg *et al.*, 1991; See, 2004) depending on the particle concentration, particle shape and applied electric field strength. The applied electric field induces electrostatic polarized interactions among the particles and also between the particles and the electrodes. However, the polarization model does not describe the flow effect accurately; in that case, the ER response is influenced by the conductivity mismatch and the interaction between particles and medium. Various ER fluids show different exponents in Eq. (1). A correlation between yield stress and the electric field strength is represented in Figs. (5) and (6). To correlate the dynamic yield stress with the broad range of electric field strengths, Choi *et al.*, (2001) introduced the universal yield stress equation

$$\tau_y(E_o) = \alpha E_o^2 \left( \frac{\tanh \sqrt{E_o/E_c}}{\sqrt{E_o/E_c}} \right) \quad (2)$$

Here, the parameter  $\alpha$  depends on the dielectric property of the fluid, the particle volume fraction and the critical electric field,  $E_c$  originated from nonlinear conductivity effect can be obtained by the crossover point of the slopes for all ranges of the electric field strengths corresponding to the polarization model (slope = 2) and conductivity model (slope = 1.5), respectively (Sung and Choi, 2004c). As



**Fig. 5.** The replotted dynamic yield stress vs. electric field strength for ER fluid of 10 wt% PANI/BaTiO<sub>3</sub> dispersed in silicone oil.



**Fig. 6.**  $\hat{\tau}$  vs.  $\hat{E}$  for ER fluid of 10 wt% PANI/BaTiO<sub>3</sub> dispersed in silicone oil.

shown in Fig. 5, the estimated  $E_c$  was found to be 1.61 kV/mm for 10 wt% PANI/BaTiO<sub>3</sub> dispersed in silicone oil.

In order to collapse the data into a single curve, we normalized Eq. (2) using  $E_c$  and  $\hat{\tau}_y(E_c) = 0.762 \alpha E_c^2$

$$\hat{\tau} = 1.313 \hat{E}^{3/2} \tanh \sqrt{\hat{E}} \quad (3)$$

Here,  $\hat{E} \equiv E_o/E_c$  and  $\hat{\tau} \equiv \tau_y(E_o)/\tau_y(E_c)$ . We found that the data obtained from Fig. (5) collapsed onto to a single curve via normalized universal yield stress equation (Eq. (3)) as shown in Fig. 6.

#### 4. Conclusion

PANI/BaTiO<sub>3</sub> composite was synthesized via an *in-situ* oxidative polymerization. Thermal stability of the PANI/BaTiO<sub>3</sub> composite was increased compared with that of the PANI due to the embedding of inorganic particles in the polymer matrix. FT-IR spectra showed composite formation of PANI and inorganic components. PANI/BaTiO<sub>3</sub> composite based on ER fluid gave typical ER behaviors, showing higher shear stress than that of pure PANI which was attributed to the influence of BaTiO<sub>3</sub> nanoparticles on conducting polyaniline due to its high dielectric performance. We also analyzed the dynamic yield stress as a function of various electric fields by plotting the data in a log-log scale. We found the critical electric field for this ER fluid was 1.61 kV/mm. In addition, the extrapolated data was found to be collapsed in the single line after adopting our universal equation.

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## References

- Chin, B.D. and O.O. Park, 2001, Dispersion stability and electrorheological properties of polyaniline particle suspensions stabilized by poly (vinyl methyl ether), *J. Colloid Interf. Sci.* **234**, 334-350.
- Cho, M.S., H.J. Choi and W.S. Ahn, 2004a, Enhanced electrorheology of conducting polyaniline confined in MCM-41 channels, *Langmuir* **20**, 202-207.
- Cho, M.S., J.H. Lee, H.J. Choi, K.H. Ahn, S.J. Lee and D. Jeon, 2004b, Linear viscoelasticity of semiconducting polyaniline based electrorheological suspensions, *J. Mater. Sci.* **39**, 1377-1382.
- Cho, M.S., H.J. Choi and M.S. Jhon, 2005, Shear stress analysis of a semiconducting polymer based electrorheological fluid system, *Polymer* **46**, 11484-11488.
- 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., J.H. Lee, M.S. Cho and M.S. Jhon, 1999, Electrorheological characterization of semiconducting polyaniline suspension, *Polym. Eng. Sci.* **39**, 493-499.
- Choi, H.J., M.S. Cho, J.W. Kim, C.A. Kim and M.S. Jhon, 2001, A yield stress scaling function for electrorheological fluids, *Appl. Phys. Lett.* **78**, 3806-3808.
- Choi, K.C., E.K. Lee and S.Y. Choi, 2005, Preparation and characterization of conductive polyurethane films, *J. Ind. Eng. Chem.* **11**, 66-75.
- Gospodinova, N. and L. Terlemezyan, 1998, Conducting polymers prepared by oxidative polymerization: Polyaniline, *Prog. Polym. Sci.* **23**, 1443-1484.
- Hao, T., A. Kawai and F. Ikazaki, 2000, The yield stress equation for the electrorheological fluids, *Langmuir* **16**, 3058-3066.
- Ikazaki, F., A. Kawai, K. Uchiday, T. Kawakamiz and K. Edamurax, 1998, Mechanisms of electrorheology: The effect of the dielectric property, *J. Phys. D: Appl. Phys.* **31**, 336-347.
- James, D.F. and B.C. Blakey, 2004, Comparison of the rheologies of laterite and goethite suspensions, *Korea-Australia Rheol. J.* **16**, 109-115.
- 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-Australia Rheol. J.* **11**, 233-240.
- Kim, J.W., Y.H. Cho, H.J. Choi, H.G. Lee and S.B. Choi, 2002, Electrorheological semi-active damper: Polyaniline based ER system, *J. Intelligent Mater. Sys. Stru.* **13**, 509-513.
- Kim, J.W., C.A. Kim, H.J. Choi and S.B. Choi, 2006, Role of surfactant on damping performance of polyaniline based electrorheological suspension, *Korea-Australia Rheol. J.* **18**, 25-30.
- Kareive, A., S. Tautkus and R. Rapalaviciute, 1999, Sol-gel synthesis and characterization of barium titanate powders, *J. Mater. Sci.* **34**, 4853-4857.
- Klingerberg, D.J., F. van Swol and C.F. Zukoski, 1991, The small shear rate response of electrorheological suspensions. II. Extension beyond the point-dipole limit, *J. Chem. Phys.* **94**, 6170-6178.
- Lee, Y.H., Y.W. Ju, H.R. Jung, Y.I. Huh and W.J. Lee, 2005, Preparation of polypyrrole/sulfonated-SEBS conducting composites through an inverted emulsion pathway, *J. Ind. Eng. Chem.* **11**, 550-555.
- Mercouri, G.K., G.W. Chun, O.M. Henry and R.K. Carl, 1989, Conductive-polymer bronzes. Intercalated polyaniline in vanadium oxide xerogels, *J. Am. Chem. Soc.* **111**, 4139-4141.
- Patil, R.C. and S. Radhakrishnan, 2001, Piezoresistivity of conducting polyaniline/BaTiO<sub>3</sub> composite, *J. Mater. Res.* **16**, 1982-1988.
- See, H., 2004, Advances in electro-rheological fluids: materials, modeling and applications, *J. Ind. Eng. Chem.* **10**, 1132-1145.
- Strounina, E.V., R. Shepherd, L.A.P. Kane-Maguire and G.G. Wallace, 2003, Conformational changes in sulfonated polyaniline caused by metal salts and OH-, *Synth. Met.* **135-136**, 289-290.
- Sung, J.H., I. Lee and H.J. Choi, 2004a, Electrorheological response of polyaniline-TiO<sub>2</sub> composite suspensions *Int. J. Mod. Phys. B* **19**, 1128-1134.
- Sung, J.H., M.S. Cho, H.J. Choi and M.S. Jhon, 2004b, Electrorheology of semiconducting polymers, *J. Ind. Eng. Chem.* **7**, 1217-1229.
- Sung, J.H. and H.J. Choi, 2004c, Electrorheological characteristics of poly (o-ethoxy) aniline nanocomposite, *Korea-Australia Rheol. J.* **16**, 193-199.
- Trlica, J., P. Saha, O. Quadrat and J. Stejskal, 2000, Electrorheology of polyaniline-coated silica particles in silicone oil, *J. Phys. D: Appl. Phys.* **33**, 1773-1780.
- Wei, J.H., J. Shi, J.G. Guan and R.Z. Yuan, 2004, Synthesis and electrorheological effect of PAN-BaTiO<sub>3</sub> nanocomposite, *J. Mater. Sci.* **39**, 3457-3460.
- Zhao, X.P. and J.B. Yin, 2002, Preparation and electrorheological characteristics of rare-earth-doped TiO<sub>2</sub> suspensions, *Chem. Mater.* **14**, 2258-2263.
- Zhao, X.P. and J.B. Yin, 2006, Advances in electrorheological fluids based on inorganic dielectric materials, *J. Ind. Eng. Chem.* **12**, 184-198.