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Shear stress analysis of phosphorylated potato starch based electrorheological fluid

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Abstract

Electrorheological characteristics of a dispersed system of phosphorylated potato starch particles in silicone oil investigated via a rotational rheometer equipped with a high voltage generator is being reanalysized. Flow curves of these ER fluids both under several applied electric field strengths and with different degrees of phosphate substitution were mainly examined via three different rheological constitutive equations of Bingham model, De Kee-Turcotte model and our previously proposed CCJ model. Among these, the CCJ equation was found to fit the data of phosphorylated potato starch well.

Keywords : electrorheological fluid, potato starch phosphate, Bingham model, rheological equation of state

1. Introduction

Electrorheological (ER) fluids are suspensions of polarizable particles in a non-conducting liquid and exhibit drastic changes in rheological properties, *i.e.* solidifying, or becoming very viscous under an applied electric field along with magnetorheological fluid (Ekwebelam and See, 2007). Microstructural transition from a liquid-like to solid-like state is being obtained by controlled electric field strength (Shin and Cho, 2000; Chu *et al.*, 2000).

Particulate materials for most electroresponsive ER fluids include inorganic non-metallic, organic, polymers, polymeric semi-conducting materials, and polymer/inorganic composites (Kim *et al.*, 2006a; Kim *et al.*, 2006b; Sung and Choi, 2004). Various conducting polymeric particles have been used as ER materials such as polyaniline (PANI) (Lee *et al.*, 1998), polypyrrole (Goodwin *et al.*, 1997), poly(p-phenylene) (Plocharski *et al.*, 1997), and PANI nanocomposites with clay (Kim *et al.*, 2001) or MCM-41 (Cho *et al.*, 2004). These typical conducting polymers and modified particles are based on a ð-conjugated electron system in the polymer backbone. In addition, branched polar groups in several polymers including biopolymers of cellulose, chitosan and starch such as amine (-NH_2), hydroxyl (-OH) and amino-cyano (-NHCN) are known to induce electroresponsive behavior such that the polar groups may affect the ER behavior by playing the role of the electronic donor under the imposed electric field.

Starch, the most important energy source and abundant carbohydrate as common biopolymers, can be chemically, enzymatically or physically modified to obtain derivatives with different properties. Starch has been used as an ER material for wet-base hydrous system (Hao, 2001) and dry-base system with its modification (Sung *et al.*, 2005).

Starch consists of amylose and amylopectin, and phosphate groups in potato starch are known to be located in its amylopectin portion (Bergthaller *et al.*, 1999). The presence of phosphate group in starch increases the hydration capacity of starch pastes after gelatinization, and results in the correlation of the starch phosphate content to starch paste peak viscosity and gel-forming capacity (Viks-Nielsen *et al.*, 2001), in which chemical modification like phosphorylation of the starch prevents crystallization and affects viscosity of final products. And the only naturally occurring covalent modification of starch is known to be a phosphorylation process.

In this note, rheological property of the ER systems containing potato starch substituted with phosphate which was previously reported (Sung *et al.*, 2005) is being reexamined for several applied electric field strengths by a rotational rheometer equipped with a high-voltage generator, specifically by focusing on the degree of phosphate substitution in potato starch particles. Especially, the shear stress was reanalysized using three different shear stress models: Bingham, De Kee-Turcotte, and previously proposed Cho-Choi-Jhon (CCJ) model.

There have been extensive studies on quantitative analysis on both yield stress and shear stress behaviors (Duan *et al.*, 2000; Martin and Anderson, 1996; See, 2000; Tam *et al.*, 1997). However, a few reports on the constitutive equation can be found (Brunn and Abu-Jdayil, 2004; Eckart, 2000; See, 2000; Wang and Xiao, 2003). Recently, CCJ model (Cho *et al.*, 2005) was proposed as a model constitutive rheological equation of state for the ER fluids

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under an applied electric field, mainly considering their qualitative interpretation. Various ER systems have been reanalysized using this CCJ model such as polyaniline (Hong and Choi, 2007) and its derivatives (Fang *et al.*, 2006), and TiO_2 doped with chromium ion (Hong *et al.*, 2006).

2. Experimental

Highly substituted potato starch phosphate (HPSP) from potato starch was substituted with disodium hydrogen phosphate (Na_2HPO_4, Aldrich) and sodium hydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$, Aldrich) mixture with distilled water as previously described (Sung *et al.*, 2005). The pH of potato starch suspension in distilled water was initially adjusted at pH 6 with hydrochloric acid and sodium hydroxide via stirring for 20 min, and then mixed with solutions of three different molar ratios (0.5, 1.5, and 2.5) of phosphate (molar ratios ~ $Na_2HPO_4 : NaH_2PO_4 \cdot 2H_2O$) which were dissolved in distilled water at 35°C. This starch slurry was then filtered using a glass funnel and dried for 12 h. To enhance phosphorylation, this mixture was heated in a convectional oven at 150°C for 3 h, and then cooled in 50% methanol aqueous solution at 25°C. This product was filtered again and washed three times with ethanol. The final product of HPSP powder was sieved under 100 μm after drying it in the vacuum oven for 3 days.

Electrorheological properties of the HPSP-based ER fluids were examined via a rotational rheometer (Physica MC120, Stuttgart, Germany) in a Couette geometry (Z3-DIN) equipped with a high-voltage generator (HVG 5000, Stuttgart, Germany), and the operating temperature was controlled by circulating oil bath (Viscotherm VT 100). Five different DC electric field strengths (0 ~ 7 kV/mm) were applied to the measuring unit via the insulated bob. Using the controlled shear rate (CSR) mode, flow curves of the shear stress versus shear rate at several different electric field strengths were measured.

3. Results and discussion

Fig. 1 shows the SEM images of raw potato starch and HPSP (ratio = 1.5) (Sung *et al.*, 2005). Both potato starch and HPSP are oval-shaped and their sizes are in the range of 50 - 80 μm. The surface morphology of HPSP was observed to be rough compared with that of raw potato starch. The grafted phosphate groups might have affected this structure rendering it less rigid. Chemical modification of starch was found to increase the granular surface area and porosity.

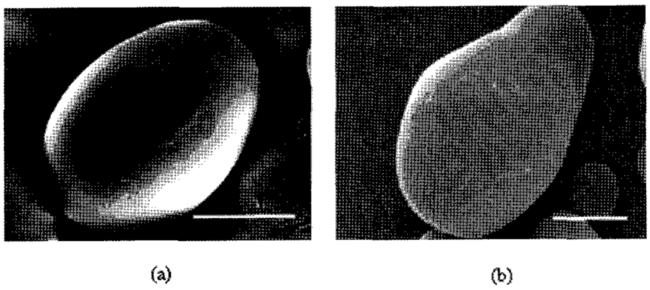

Fig. 1. SEM images photographs of raw potato starch (a) and HPSP with a molar ratio (1.5) of phosphate (b) [scale bar = 20 μm].

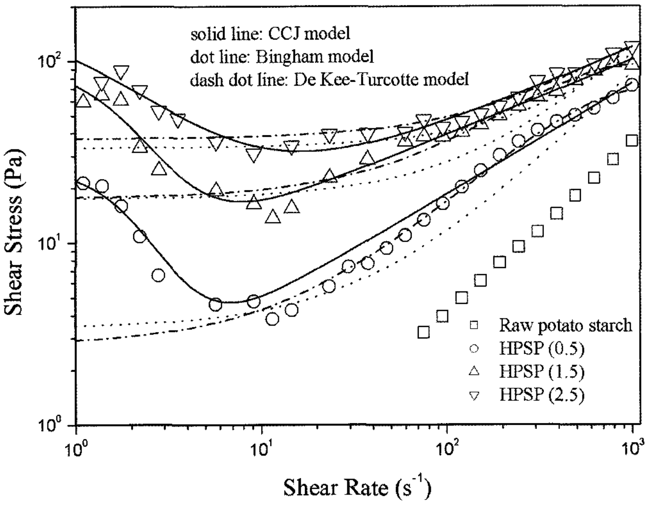

Fig. 2. Shear stress as a function of shear rate for unmodified potato starch and three different molar ratios (0.5, 1.5, and 2.5) of HPSP based-ER fluids (15 vol%) at the electric field strength of 2 kV/mm.

Fig. 2 describes the shear stress as a function of shear rate for three different molar ratios (0.5, 1.5, and 2.5) of degree of substitution with 15 vol% HPSP at 2 kV/mm. Note that the original potato starch without modification does not exhibit ER behavior showing a Newtonian fluid behavior with a linear relation between shear stress and shear rate. It might be possibly explained based on assumptions that either the ER effect it might possess is too small to detect or there exists a critical phosphorous content to give the ER behavior which is much higher than that of the original potato starch. Finding this clue might be also interesting for the further study. The fact that the higher the phosphate's substituent in potato starch the higher is the stress level due to the phosphorylation contribution indicates the higher content of polar functional groups.

However, the HPSP response exhibits a yield stress with non-Bingham fluid behavior. The shear stress reached minimum as the shear rate increased up to a critical value, where the electrostatic attractive force is supposed to be compensated with the hydrodynamic breaking force between chains formed. The shear stress decreases at low shear rate region, indicating the weakened electrostatic force contrast to the plateau shear stress behavior in the case of typical Bingham fluids.

The shear stress of HPSPs in the shear rate range 1 ~ 10 s^{-1} decreases since the fibrillar structures are decom-

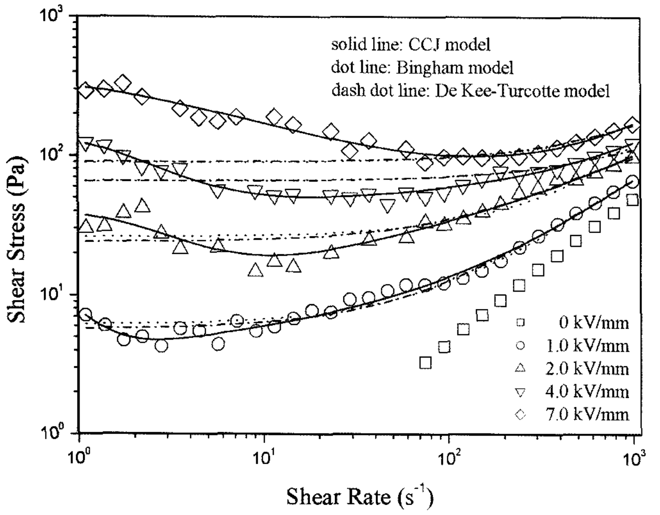

Fig. 3. Shear stress vs. shear rate for 15 vol% HPSP (2.5) at six different electric field strengths.

posed by shear deformation and regenerated by applied electric field. At high shear rates, the ER fluids exhibit liquid-like behavior as the chains are completely broken, however, ER fluids behave solid-like at the high electric field strengths since the particles chain resists under the shear deformation (Fig. 2).

Fig. 3 represents flow curves for shear stress vs. shear rate for HPSP (2.5) based ER fluid (15 vol%) at five different electric field strengths. The shear stress increases drastically as the electric field strength increases. Furthermore, Fig. 3 shows a shear stress plateau for a broad range of shear rates under an applied electric field. This represents a yield behavior in which particle chain structures, induced by electric field, break down via deformation.

The particle possesses net charges, arising from non-uniform polarization or electrostatic force under an applied electric field. The more polarized dipoles in the HPSP particles generate the better ER response via the formation of fibrillar structure under an external electric field. At a low shear rate region, the electrostatic interactions among particles are dominant compared to the hydrodynamic interactions induced by the external shear flow. The aligned particle chains or aggregate structures begin to break with a shear deformation, and these broken structures tend to reform the chains by the applied electric field, depending on the strength of the applied shear and particle-particle interaction in the fibrils. The shear viscosity increases under the electric field via the formation of chainlike or columnar structure of the particles. When a shear strain is applied to the aligned structures, it distorts, breaks and destroys the fibrillar chains, and results in a shear thinning behavior. On the other hand, such a decreasing flow curve phenomenon is regarded to be of great interest in general because, from a rheological viewpoint, most non-Newtonian fluids exhibit an increase in shear stress with shear rate due to the stability of the shear flow of a macroscopically uniform fluid (Coleman *et al.*, 1966; Walters, 1975; Moller *et al.*, 2006). Based on similar ideas of macroscopic non-uniformity such as layer formation, instability, slip or even shear bending in the sample, this abnormal behavior of decreasing flow curve predicted by the Doi-Edwards reputation model for concentrated polymer solutions under high shear rates has been explained in terms of the formation of stratified layers of low and high viscosity fluid (Doi and Edwards, 1979; Doi and Edwards, 1986; Cates *et al.*, 1993). In the case of ER fluid, the decreasing flow curve phenomena has been also analyzed based on the idea of macroscopic layer (Orihara *et al.*, 1999; See *et al.*, 2002). Nonetheless, despite all these plausible explanations, mechanism behind the decreasing flow curves for not only ER fluids but also other materials is on-going discussion area in rheology.

Meanwhile the structure in a concentrated suspension in the ER fluid is rigid enough to withstand a certain level of deforming stress without flowing (*i.e.*, yield stress). Three different models implying yield stress are used to analyze the shear stress distributions vs. shear rate of the HPSP dispersed ER fluids. The fitted lines in Figs. 2 and 3 are based on the values calculated from the model equations.

Bingham fluid model, shown in Eq. (1), is the simplest and most widely used one with two parameters originating from yield stress τ_o and Newtonian viscosity h_o, and is widely adopted as a model for the ER suspensions (first category).

$$\tau = \tau_o + \eta_o \dot{\gamma} \tag{1}$$

The Bingham model has two flow regimes; a rigid pre-yield behavior for shear stress less than the field-dependent yield stress and Newtonian flow characteristics beyond the yield stress τ_o (post-yield region). Dotted lines in Figs. 2 and 3 are from Eq. (1) and show deviation from the experimental data, especially for lower volume fractions of HPSP suspension.

The second category will assume $\tau(\dot{\gamma})$ to be independent of $\dot{\gamma}$ (*i.e.*, $\tau(\dot{\gamma}) = \tau_o = \text{constant}$) and adopt various expressions for $\eta(\dot{\gamma})$. Two commonly used forms are De Kee-Turcotte fluid model and CCJ model. The De Kee-Turcotte fluid model (Zhu *et al.*, 2005) given in Eq. (2) is accepted in various suspension systems including ER fluids.

$$\tau = \tau_o + \eta_1 \dot{\gamma} e^{-t_1 \dot{\gamma}} \tag{2}$$

where t_1 is a time constant having a unit of second.

Concurrently, as indicated in Fig. 2, deviations from the Bingham fluid model have been observed in several ER systems. The existence of a critical shear rate in the flow curve for various ER fluids was observed such that below the critical shear rate ($\dot{\gamma}_{crit}$) (a transition point of $\dot{\gamma}$), the shear stress decreases as a function of the shear rate, and above the critical shear rate, the fluid exhibits a pseudo-

Table 1. The optimal parameters in each model equation obtained from the flow curve of unmodified potato starch and three different molar ratios (0.5, 1.5, and 2.5) of HPSP based-ER fluids (15 vol%) at the electric field strength of 2 kV/mm

Model	Parameters	HPSP 0.5	HPSP 1.5	HPSP 2.5
Bingham	τ_o	3.42	17.42	33.20
	η_o	0.0826	0.1027	0.075
De Kee-Turcotte	τ_o	2.77	17.57	37.2571
	η_1	0.1537	0.2047	0.1216
	τ_1	0.00085	0.00098	0.00039
CCJ	τ_o	25	90	191
	t_2	0.5349	0.6155	1.0504
	α	2.5170	2.2163	1.0781
	η_∞	0.0067	0.0043	0.0150
	t_3	3.83E-6	5.72E-6	5.0E-5
	β	0.4169	0.6020	0.6336

Table 2. The optimal parameters in each model equation obtained from the flow curve of 15 vol% HPSP (2.5) at six different electric field strengths

Model	Parameters	1.0 kV/mm	2.0 kV/mm	4.0 kV/mm	7.0 kV/mm
Bingham	τ_o	6.09	25.99	65.85	89
	η_o	0.0627	0.079	0.05	0.08
De Kee-Turcotte	τ_o	5.66	23.95	65.40	90
	η_1	0.0717	0.1165	0.0552	0.0859
	t_1	0.0002	0.0005	0.0002	0.0001
CCJ	τ_o	15	37	130	375
	t_2	1.25	0.39	0.59	0.33
	α	3.69	1.56	1.54	0.72
	η_∞	0.06	0.04	0.06	0.098
	t_3	0.0067	0.0006	0.0009	0.0015
	β	0.8311	0.7018	0.9161	0.9728

Newtonian behavior. In order to fit such a complicated flow curve, Cho *et al.* (2005) recently proposed the constitutive rheological equation of state (CCJ model) of Eq. (3) for ER fluids under an applied electric field. The CCJ model is found to provide a better fitting of the HPSP based ER fluids;

$$\tau = \frac{\tau_o}{1+(t_2\dot{\gamma})^{\alpha}} + \eta_\infty\left(1+\frac{1}{(t_3\dot{\gamma})^{\beta}}\right)\dot{\gamma}. \qquad (3)$$

The above six-parameter model can cover the stress decrease phenomena at low shear rate region and provide an accurate value for the real yield stress in the case of PNQR based ER fluids (Cho *et al.*, 2005). The first term in Eq. (3) implies the shear stress behavior at a low shear rate region especially in the case of the decrease of shear rate and the second term describes well the shear stress behavior at a high shear rate region.

Here, τ_o is the dynamic yield stress defined as the extrapolated stress from low shear rate region, α is related to the decrease in the stress, t_2 and t_3 are time constants, and η_∞ is the viscosity at a high shear rate and is interpreted as the viscosity in the absence of an electric field. The exponent β has the range $0<\beta\leq 1$, since $d\tau/d\dot{\gamma}\geq 0$. The yield stresses and the optimal parameters for these three models are summarized in Tables 1 and 2.

The coefficient, a was observed to decrease with molar ratio. The β are 0.4169, 0.6020, and 0.6336 for HPSP 0.5, HPSP 1.5, and HPSP 0.5, respectively. From these results, 15 vol% HPSP series is found to become a Newtonian fluid in high shear rate region. Furthermore, it can be found that the yield stresses obtained from both Bingham and De Kee-Turcotte models for 15 vol% HPSP series are much lower than that from CCJ model. This can be explained from the fact that while CCJ model accurately fits the decrease of shear stress in the region of shear rate from 1 to 10 (1/s), other two models do not fit it well, so that as can be seen from Fig. 1, large deviation is observed at a very low shear rate from other two models.

As given in Table 2, α decreases with applied electric fields strength. The β are 0.8311, 0.7018, 0.9161, and 0.9728 for 1.0 kV/mm, 2.0 kV/mm, 4.0 kV/mm, and 7.0 kV/mm of electric field strength, respectively. From these results, 15 vol% HPSP was found to become a Newtonian fluid in high shear rate region with different electric fields strength. Besides, it can be found that the yield stresses obtained from both Bingham and De Kee-Turcotte models for 15 vol% HPSP with various electric fields strength are much lower than that from the CCJ model. This can be explained from the fact that while CCJ model accurately fits the decrease of shear stress in the region of shear rate from 1 to 3 (1/s), 1 to 10 (1/s), 1 to 20 (1/s), and 1 to 100 (1/s) with 1.0, 2.0, 4.0, and 7.0 kV/mm, respectively, the other two models do not fit them well as can be seen from Fig. 2, with large deviation at a very low shear rate region.

4. Conclusions

We modified the potato starches with highly substituted phosphate contents using disodium hydrogen phosphate and sodium hydrogen phosphate mixture and then observed the ER response of these suspended particles in an insulating oil. Steady state flow properties of the HPSP based ER fluids were interpreted by using three different yield stress models, such as Bingham, De Kee-Turcotte, and CCJ models. Among these models, the CCJ model was found to fit the decrease in shear stress at the low shear rate regime quite accurately.

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References

Bergthaller, W., W. Witt and H. P. Goldau, 1999, Potato starch technology, *Starch-Starke* **51**, 235-242.

Brunn, P. O. and B. Abu-Jdayil, 2004, A phenomenological model of electrorheological fluids, *Rheol. Acta* **43**, 62-67.

Cates, M.E., T.C.B. McLeish and G. Marrucci, 1993, The rheology of entangled polymers at very high shear rates, *Europhys Lett* **21**, 451-456.

Cho, M. S., H. J. Choi and W. S. Ahn, 2004, Enhanced electrorheology of conducting polyaniline confined in MCM-41 channels, *Langmuir* **20**, 202-207.

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.

Coleman, B. D., H. Markovitz and W. Noll, 1966, Viscometric flows of non-Newtonian fluids, Springer-Verlag, Berlin, p. 28.

Chu, S. H., S. J. Lee and K. H. Ahn, 2000, An experimental study on the squeezing flow of electrorheological suspensions, *J. Rheol.* **44**, 105-120.

Doi, M, S F. Edwards, 1979, Dynamics of concentrated polymer systems. Part 4. Rheological properties. *J. Chem. Soc. Faraday Trans. II* **75**, 38-54

Doi, M. and S. Edwards, 1986, The Theory of Polymer Dynamics, New York, pp. 268-269.

Duan, X. D., H. Chen, Y. J. He and W. L. Luo, 2000, Enhancing yield stress of electrorheological fluids with liquid crystal additive, *J. Phys. D-Appl. Phys.* **33**, 696-699.

Eckart, W., 2000, Phenomenological modeling of electrorheological fluids with an extended Casson-model, *Continuum Mech. Thermodyn.* **12**, 341-362.

Ekwebelam, C.C. and H. See, 2007, Using oscillatory shear to probe the effects of bidispersity in inverse ferrofluids, *Korea-Aust. Rheol. J.* **19**, 35-42.

Fang, F. F., J. H. Kim and H. J. Choi, 2006, Synthesis and electrorheological characterization of polyaniline/barium titanate hybrid suspension, *Macromol. Symp.* **242**, 49-54.

Goodwin, J. W., G. M. Markham and B. Vincent, 1997, Studies on model electrorheological fluids, *J. Phys. Chem. B* **101**, 1961-1967.

Hao, T., 2001, Electrorheological fluids, *Adv. Mater.* **13**, 1847-1857.

Hong, C. H. and H. J. Choi, 2007, Shear stress and dielectric analysis of H_3PO_4 doped polyaniline based electrorheological fluid, *J. Macromol. Sci. Part B-Phys.* **46**, 683-692.

Hong, C. H., H. J. Choi and M. S. Jhon, 2006, Comment on "Preparation and enhanced electrorheological activity of TiO_2 doped with chromium ion", *Chem. Mat.* **18**, 2771-2772.

Kim, J. H., F. F. Fang, K. H. Lee and H. J. Choi, 2006a, Electrorheology of conducting polyaniline-BaTiO3 composite, *Korea-Aust. Rheol. J.* **18**, 103-107.

Kim, J. W., C. A. Kim, H. J. Choi and S. B. Choi, 2006b, Role of surfactant on damping performance of polyaniline based electrorheological suspension, *Korea-Aust. Rheol. J.* **18**, 25-30.

Kim, J. W., S. G. Kim, H. J. Choi, M. S. Suh, M. J. Shin and M. S. Jhon, 2001, Synthesis and electrorheological characterization of polyaniline and Na^+-montmorillonite clay nanocomposite, *Int. J. Mod. Phys. B* **15**, 657-664.

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 Interface Sci.* **206**, 424-438.

Martin, J. E. and R. A. Anderson, 1996, Chain model of electrorheology, *J. Chem. Phys.* **104**, 4814-4827.

Moller, P. C. F., J. Mewis and D. Bonn, 2006, Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice, *Soft Matter.* **2**, 274-283.

Orihara, H., M. Doi and Y. Ishibashi, 1999, Two types of mechanism of electrorheological effect in polymer blends, *Int. J. Mod. Phys. B* **13**, 1949-1955.

Plocharski, J., H. Drabik, H. Wycislik and T. Ciach, 1997, Electrorheological properties of polyphenylene suspensions, *Synth. Met.* **88**, 139-145.

See, H., 2000, Constitutive equation for electrorheological fluids based on the chain model, *J. Phys. D-Appl. Phys.* **33**, 1625-1633.

See, H., A. Kawai and F. Ikazaki, 2002, Differences in the electrorheological response of a particle suspension under direct current and alternating current electric fields, *Colloid Polym. Sci.* **280**, 24-29.

Shin, S. and Y.I. Cho, 2000, A new scanning slit rheometer for electrorheological fluids, *Rev. Sci. Instrum.* **71**, 4665-4669.

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

Sung, J. H., D. P. Park, B. J. Park, H. J. Choi and M. S. Jhon, 2005, Phosphorylation of potato starch and its electrorheological suspension, *Biomacromolecules* **6**, 2182-2188.

Tam, W. Y., G. H. Yi, W. J. Wen, H. R. Ma, M. M. T. Loy and P. Sheng, 1997, New electrorheological fluid: Theory and experiment, *Phys. Rev. Lett.* **78**, 2987-2990.

Vikso-Nielsen, A., A. Blennow, K. Jorgensen, K. H. Kristensen, A. Jensen and B. L. Moller, 2001, Structural, physicochemical, and pasting properties of starches from potato plants with repressed r1-gene, *Biomacromolecules* **2**, 836-843.

Walters, K., 1975, Rheometry, Chapman and Hall, London, p. 24.

Wang, B. and Z. Xiao, 2003, A general constitutive equation of an ER suspension based on the internal variable theory, *Acta. Mech.* **163**, 99-120.

Zhu, H., Y. Kim and D. De Kee, 2005, Non-Newtonian fluids with a yield stress, *J. Non-Newton. Fluid. Mech.* **129**, 177-181.