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Scaling analysis of electrorheological poly(naphthalene quinone) radical suspensions

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Abstract

A semiconducting poly(naphthalene quinone) radical (PNQR) was synthesized from Friedel-Craft acylation between naphthalene and phthalic anhydride and used as dispersing particles of a dry-base electrorheological (ER) material in silicone oil. Under an applied electric field (E), the dynamic yield stress (τ_{dyn}) of this ER fluid, obtained from a steady shear experiment with a controlled shear rate mode, was observed to increase with $E^{1.45}$. Based on this relationship, we propose a universal correlation curve for shear viscosity, which is independent of E using a scaling analysis.

Keywords : electrorheology, semiconducting polymer, poly(naphthalene quinone) radical, suspension, yield stress, scaling

1. Introduction

An electrorheological (ER) fluid is a suspension consisting of fine, electrically-polarizable semiconducting particles in a medium having a low dielectric constant and viscosity (Hwang and Lee, 1994; See, 1999). It exhibits dramatic reversible changes in rheological properties such as drastic increase of viscosity, yield stress, and viscoelasticity when exposed to an electric field. This change is known to be due to the migration of particles and formation of chainlike or columnar structures oriented in the electric field direction over the gap between electrodes (Halsey, 1992; Block and Kelly, 1988; Gow and Zukoski, 1989), induced by the mismatch of the dielectric constants between the suspended particles and the non-conducting oil (Gast and Zukoski, 1989). Thus, it is quite natural that dielectric polarization theory appeared, and among various polarizations, interfacial polarization is assumed to be responsible for ER phenomena (Hao *et al.*, 1999). In addition, due to the controllable viscosity and fast response, ER fluids are regarded as smart materials for active devices which transform electrical energy to mechanical energy, such as actuators, dampers and CD-ROM feeding system (Coulter *et al*, 1993; Kim *et al.*, 1999). Until recently, ER fluid characteristics due to a large dielectric or conductivity mismatch betweeen the particles and the suspending media were obtained as a result of either water or surfactant absorption in the particles. Corn starch (Thurston and Gaertner, 1991), silica (Otsubo *et al.*, 1992), and glass beads (Shih and Conrad, 1994) in insulating oils are typical representatives of hydrous systems.

On the other hand, dry-base ER fluids that have been recently developed are usually made with semiconducting polymers as the suspended particles, such as poly(acene quinone) radicals (Block *et al.*, 1990; Choi *et al.*, 1997a), polyaniline (Gow and Zukoski, 1989; Choi *et al.*, 1997b; Chin *et al.*, 1998), phosphate cellulose(Kim *et al.*, 2001), copolypyrrole (Good-win *et al.*, 1997), poly(p-phenylene) (Chin *et al.* 1999), and polyurethane (Bloodworth and Wendt, 1996). N-substituted copolyaniline synthesized from monomer mixtures of aniline and diphenylamine-4-sulfonic acid sodium salt (Cho *et al.*, 1998) and polymer-clay nanocomposites with styrene-acrylonitrile copolymer or polyaniline (Kim *et al.*, 1999) were also studied as potential dry-base ER materials. In these dry-base ER fluids, a polarization is induced by the electrons in the molecules of particles. Therefore, in contrast to the wet-base ER fluids, the dry-base ER fluids have advantages in the aspects of a density match between the particles and the oil, the control of conductivity (dielectric properties), thermal stability, and abrasion. ER fluids using poly (acene quinone) radicals (PAQRs) have been also studied as part of an anhydrous ER system (Block *et al.*, 1990; Choi *et al.*, 1997a), including poly (naphthalene quinone) radical (PNQR), poly(anthracene quinone) radical (PAnQR), and poly(pyrene quinone) radical (PPQR). Among these PAQRs, ER fluid using PNQR has been observed to show the best ER performance, regardless of the kind of anhydride used (Choi *et al.*, 1997a).

In this study, semiconducting PNQR, as a dry-base ER

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*Corresponding author: hjchoi@inha.ac.kr fluid, was synthesized and then mixed with silicone oil. Rheological properties of these ER fluids were measured and analyzed with a scaling law. We found that the shear viscosity of this ER fluid at different applied electric fields can be scaled into a universal curve by the dynamic yield stress, which is proportional to the electric field strength with a power index 1.45.

2. Experimental

PNQR was synthesized in a manner similar to the procedure reported by Phol and Engelhart (1962). Naphthalene and phthalic anhydride were monomers for the synthesis of PNQR, and zinc chloride was used as a catalyst for a Friedel-Craft acylation between monomers (Fig. 1). Polymerization occurred in a sealed reactor by maintaining a vacuum. The reaction temperature was about 250°C and the reaction time was 24 hours. Prior to use, the synthesized polymer was ball-milled with a dilute HCl aqueous solution in order to remove the catalyst and to control the particle size. After milling, the mixture was sieved with a 38 μm sieve to control the particle size of the synthesized polymer and then extracted into a Soxhlet apparatus, sequentially with water, ethanol and benzene, to purify the products. Finally, the polymer particle was dried in a vacuum oven at room temperature.

Observed conductivity of the PNQR was $3.33\times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ from a 2-probe method, and the density was 1.69 gcm^{-3} measured by a pycnometer at 25°C. The molecular structure of PNQR cannot be confirmed using a conventional method because of its insolubility and infusibility in most solvents. Thereby, the evidence of its polymerization was determined only from IR spectra (Fig. 2), thermal gravimetric analysis (TGA), density, and color change from monomer to polymer (Choi *et al.*, 1997a). Fig. 2 represents IR spectra of both the monomer mixture and the PNQR after polymerization. A peak at 1020 cm^{-1} indicating ether linkage of phthalic anhydride disappeared from the spectrum of PNQR, so that we can consider the polymerization reaction to be completed.

An ER fluid of silicone oil and polymer particles was prepared with a 0.05 polymer volume fraction. The kinematic viscosity of the silicone oil was 30 cS, and its density was 0.96 gcm^{-3}.

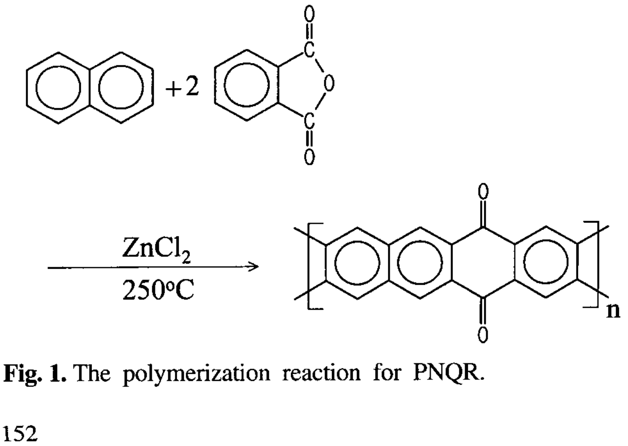

Fig. 1. The polymerization reaction for PNQR.

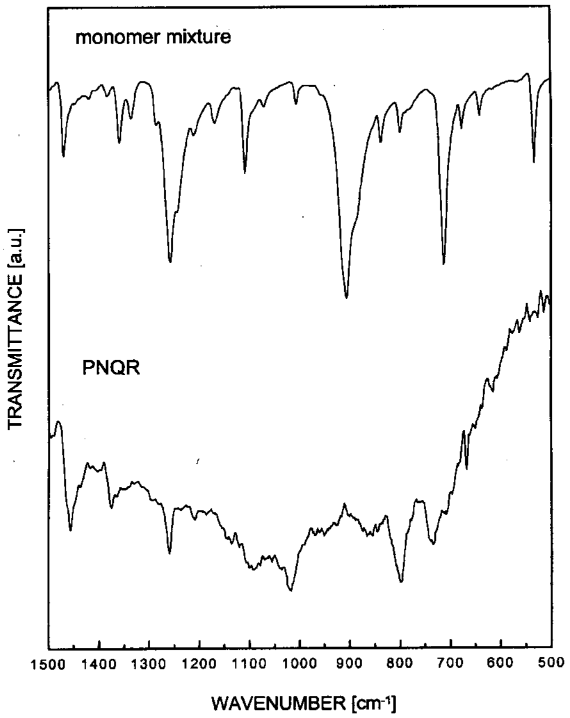

Fig. 2. IR spectrum of monomer mixture and PNQR after polymerization.

A rotational Physica rheometer (MC120) equipped with a high-voltage generator (HVG 5000) was used to determine the rheological properties of the ER fluids in this study. The concentric cylinder type (gap between bob and cup is 1.06 mm) measuring drive system was used for obtaining ER properties. The ER fluid (17 cm^3) under investigation was placed in the gap between the stationary outer cup and the inner rotating bob. An electric field was applied for five minutes in order to obtain an equilibrium structure before applying the shear. The applied electric field ranged from 0 to 3 kV/mm and all experiments were performed at 25°C.

3. Results and discussion

In general, the structure in a concentrated suspension can be sufficiently rigid such that it permits the material to sustain a certain level of deforming stress without flowing. The maximum stress that can be sustained without flow is called "the yield stress." For a simple shear flow, this type of behavior in ER fluids is described by the following Bingham model in general (Dealy *et al.*, 1990):

$$\begin{aligned} \tau(\gamma,E) &= \eta_{pl}\gamma+\tau_d(E) \quad && if\ \tau>\tau_d \\ \dot{\gamma} &= 0 && if\ \tau<\tau_d \end{aligned} \qquad (1)$$

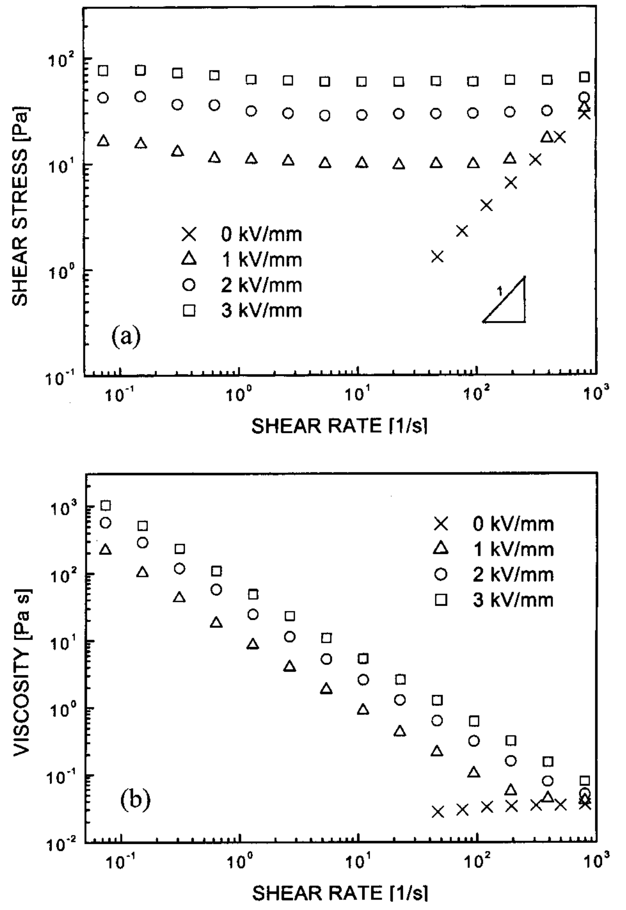

Fig. 3. Shear stress (a) and shear viscosity (b) as a function of shear rate at various electric fields.

Here, $\tau(\dot{\gamma},E)$ is the shear stress, τ_d is the dynamic yield stress, E is the applied electric field strength and η_{pl} is the plastic viscosity, which is independent of electric field strength *i.e.* approximately equal to the high shear rate suspension viscosity in the absence of an electric field (Parthasarathy and Klindenberg, 1996).

Figs. 3(a) and (b) show the typical ER behavior from the flow curve of shear stresses (τ) and shear viscosities (η) as a function of the shear rates ($\dot{\gamma}$) under various applied electric fields (E). The slope in Fig. 3(a) indicates Newtonian behavior, which corresponds to the case without an electric field. The level of shear stress considerably increased with increasing electric field. In this case, Bingam model is not suitable to the flow curves of PNQR ER fluid. The stress decrease is observed in the low shear rate region at all electric field, and Newtonian behavior is not developed up to 1000 sec^{-1}.

The characteristic feature of ER fluids is a sharp, sudden increase in the shear viscosity resulting from a imposed high electric field as shown in Fig. 3(b). A shear stress decline and plateau is observed in a wide range of shear rate under the applied electric field. These plateaus become larger as E increases and this behavior is though to arise from breakage of the particle chain structure (yield phenomenon).

The η as a function of $\dot{\gamma}$ shows shear-thinning behavior which is also from the yield process (Fig. 3(b)). At high $\dot{\gamma}$, η converges to the viscosity measured in the absence of an electric field. It means that particular fibril structures under the electric field are destroyed by the shear deformation. Similar shear thinning behavior has been also observed for various other ER fluids such as zeolite (Cho *et al.*, 1999b), mesoporous MCM-41 particle (Choi *et al.*, 2000), alumina particle (Parthasarathy and Kilngenberg, 1996), and polyaniline (Lee *et al.*, 1999).

In Fig. 3(a), the dynamic yield stress (τ_{dyn}) is determined by an extrapolation from the plateau region for each applied electric field (except 0 kV/mm). Since it is very difficult to obtain the true static yield stress from the controlled shear-rate mode, the τ_{dyn} is chosen as the yield stress for these systems. Fig. 4 shows that τ_{dyn} varies linearly with the imposed electric field in the logarithmic plot.

From Fig. 4, one can obtain:

$$\tau_{dyn} = 16.4\ E^{1.45}. \tag{2}$$

for the 5 vol% PNQR suspension under the various electric fields.

The stress, which develops as a result of an applied electric field, originates from the attractive force between particles. This attractive force can be explained by either the polarization model (Gast and Zukoski, 1989) or the conduction model (Felici *et al.*, 1994). Both models predict that this force is proportional to E^2. The conduction model does not, however, consider the effect of flow for ER fluids, because calculation of the ER effect is based on the conductivity between stationary adjacent particles. Thereby,

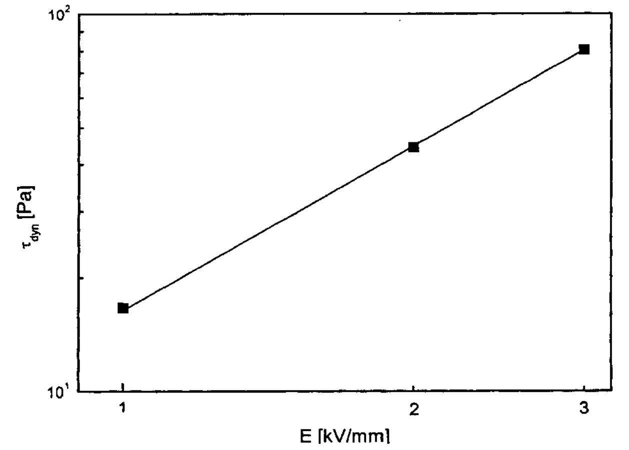

Fig. 4. The dynamic yield stress (τ_{dyn}) as a function of applied electric fields.

the conduction model is a static model rather than a dynamic one (Ikazaki *et al.,* 1998). Recently, Hao *et al.* (1998) proposed that the slow polarization (*i.e.,* the interfacial polarization) was the main contribution to the ER effect, and fibril structures in ER fluids under an electric field were formed by particle rotation.

Our system of PNQR 5 vol% does not follow the theory above-mentioned; τ_{dyn} is proportional to $E^{1.45}$ rather than E^2. This is mainly due to the theoretical assumption which regards dispersed particles as point-dipole spheres and suspensions as Brownian suspensions. PNQR used in this study is irregular granule and its suspension in silicone oil is non-Brownian. Chin *et al.*(1998) also observed that under strong electric field, dependence of the yield stress on the electric field strength was reduced to nearly unity for both semiconducting polyaniline and poly(p-phenylene) ER fluid systems, probably due to the complicated particle-to-particle interaction in the dense suspension.

As shown in Figs. 3(a) and (b), τ and η depend on the shear rate and the applied electric field. In addition, η curves at each electric field strength are shown to be parallel as given in Fig. 3(b). This means that η is nearly factorable into E- and $\dot{\gamma}$- dependent terms (Choi *et al.*, 1997b), as given in Eq. (2):

$$\eta(\dot{\gamma},E) = \Phi_1(E)\Phi_2(\dot{\gamma})$$

or

$$\eta(\dot{\gamma},E)/\Phi_1(E) = \Phi_2(\dot{\gamma})\,. \tag{3}$$

Because $\Phi_1(E)$ is the E-dependence of ER fluid properties, it can be considered from the relationship between τ_{dyn} and E. On construction of universal curve for the PNQRER fluid, $\Phi_1(E) = 16.4\ E^{1.45}$ of Eq. (2)

However, the above-mentioned scaling law concept, which generates a universal curve by shifting the data through the stress axis only, is not able to cover the whole shear rate regime. Thereby, we further adopt the following parameter λ (Klingenberg *et al.* (1991)) which makes shear rate dimensionless,

$$\lambda = \frac{16\eta_c}{\varepsilon_o\varepsilon_c\beta^2E^2}, \tag{4}$$

where $\eta_c = 0.029$ Pa · sec (viscosity of the suspension medium), $\varepsilon_o = 8.8542\times 10^{-12}$ F/m (permittivity of free space), $\varepsilon_c = 2.5$ (dielectric constant of the silicone oil at 50 Hz), $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$, and $\varepsilon_p = 31.5$ (dielectric constant of a PNQR particle at 50 Hz).

Universal curves obtained through this scaling analysis are given in Fig. 5(a) for the PNQR ER fluid and, in addition, Fig 5(b) shows another universal curve constructed by following the method of Parthasarathy and Klingenberg (1996).

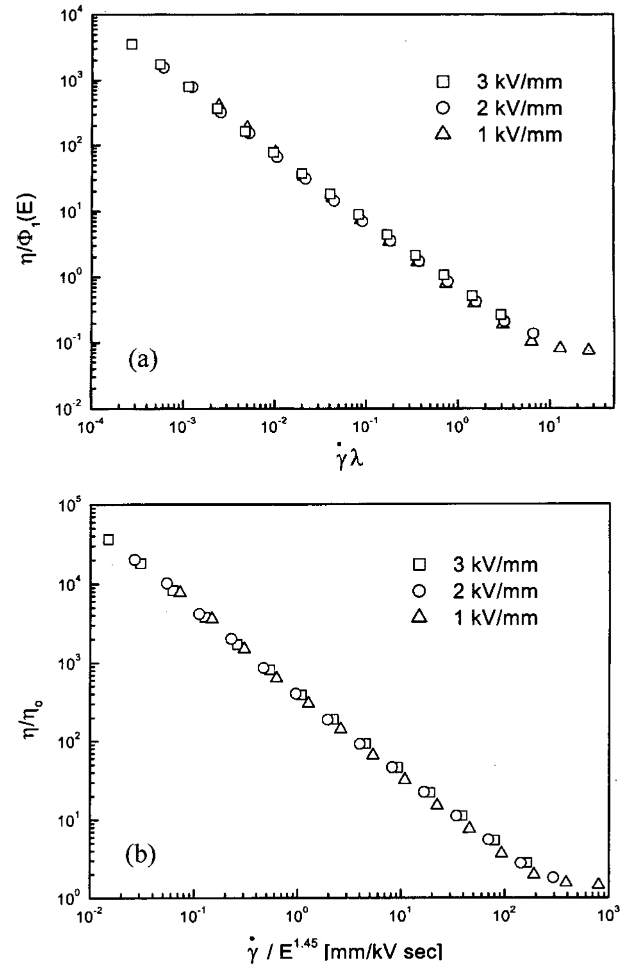

Fig. 5. Universal curves of viscosity obtained through the scaling analysis (a) and through a method suggested by Parthasarathy and Klingenberg (1996) (b).

This scaling law used for Fig. 5(a) was also applied to a semiconducting polyaniline ER fluid, and the results were acceptable (Choi *et al.,* 1998). In contrast to the scaling analysis on the steady shear stress presented in this paper, Tanaka *et al.* (1995) discussed the scaling behavior of the temporal response of ER suspensions with cation exchange resin particles as a function of Mason's number ($\equiv\lambda\dot{\gamma}/32 = \eta_c\dot{\gamma}/2\varepsilon_c\varepsilon_0(\beta E)^2$), which is a ratio of the viscous force to induced dipole interaction, and the response times of the ER effect of an exponential expression with plural modes were multiplied by the shear rate.

In conclusion, the semiconducting PNQR suspension in silicone oil showed typical ER effect under the applied electric field. The τ_{dyn} is observed to be proportional to $E^{1.45}$, which is slightly different from the theoretical prediction. By adopting a scaling law based on the factorable trend of shear viscosity with shear rate at different electric fields, a universal curve can be constructed using a time scale parameter, λ (Eq.4).

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References

Block, H. and J. P. Kelly, 1988, *J. Phys. D, Appl. Phys.* **21**, 1661.

Block, H., J. P. Kelly, A. Qin and T. Waston, 1990, *Langmuir* **6**, 6.

Bloodworth, R. and E. Wendt, 1996, *Int. J. Mod. Phys. B* **10**, 2951.

Chin, B. D., Y. S. Lee and O O. Park, 1999, *Int. J. Mod. Phys. B* **13**, 1852.

Chin, B. D., Y. S. Lee, H. J. Lee, S. M. Yang and O O. Park, 1998, *Korean J. Rheol.* **10**, 195.

Cho, M. S., H. J. Choi and K. To, 1998, *Macromol. Rapid Commun.* **19**, 271.

Cho, M. S., H. J. Choi, I. J. Chin and W. S. Ahn, 1999, *Micropor. Mesopor. Mater.* **32**, 233.

Choi, H. J., M. S. Cho, K. K. Kang and W. S. Ahn, 2000, *Micropor. Mesopor. Mater.* **39**, 19.

Choi, H. J., M. S. Cho and M. S. Jhon, 1997a, *Polym. Adv. Tech.* **8**, 697.

Choi, H. J., T. W. Kim, M. S. Cho, S. G. Kim and M. S. Jhon, 1997b, *Eur. Polym. J.* **35**, 699.

Coutler, J. P., K. D. Weiss and J. D. Carlson, 1993, *J. Intell. Mater. Sys. Struct.* **4**, 248.

Dealy, J. M. and K. F. Wissburn, 1990, In *Melt Rheology and its Role in Plastics Processing: Theory and Applications* Van Nostrand Reinhold, New York, p. 18.

Felici, N., J. N. Foulc and P. Atten, 1994, In *Electrorheological Fluids, Mechanisms, Properties, Technology and Applications* ed. by R. Tao and G. D. Roy, 1990, World Scientific, Singapore, p. 139.

Gast, A. P. and C. F. Zukoski, 1989, *Adv. Colloid Int. Sci.* **30**, 153.

Goodwin, J. W., G. M. Markham and B. Vinent, 1997, *J. Phys. Chem. B* **101**, 1961.

Gow, C. J. and C. F. Zukoski, 1989, *J. Colloid Interface Sci.* **136**, 175.

Halsey, T. C., 1992, *Science* **258**, 761.

Hao, T., A. Kawai and F. Ikazaki, 1998, *Langmuir* **14**, 1256.

Hao, T., A. Kawai and F. Ikazaki, 1999, *Int. J. Mod. Phys. B* **10**, 2885.

Hwang, I. and S. J. Lee, 1994, *Korean J. Rheol.* **6**, 83.

Ikazaki, F., A. Kawai, K. Uchida, T. Kawakami, K. Edmura, K. Sakurai, H. Anzai and Y. Asako, 1998, *J. Phys. D: Appl. Phys.* **31**, 336.

Jordan, T. C., M. T. Shaw and T. C. Mcleish, 1992, *J. Rheol.* **36**, 441.

Kim, H.K., S. C. Lim, S. B. Choi and Y. P. Park, 1999, *Korean J. Rheol.* **11**, 97.

Kim, J. W., S. G. Kim, H. J. Choi and M. S. Jhon, 1999, *Macromol. Rapid Commun.* **20**, 450

Kim, S. G, H. J. Choi and M. S. Jhon, 2001, *Macromol. Chem. Phys.* (in press).

Klingenberg, D. J., F. von Swol and C. F. Zukoski, 1991, *J. Chem. Phys.* **94**, 6170.

Lee, J. H., M. S. Cho, H. J. Choi and M. S. Jhon, 1999, *Colloid Polym. Sci.* **277**, 73.

Otsubo Y, M. Sekine and S. Katayama, 1992, *J. Rheol.* **36(3)**, 479.

Parthasarathy, M. and D. J. Klingenberg, 1996, *Mater. Sci. Eng.* **R17**, 57.

Phol, H. A. and E. H. Engelhardt, 1962, *J. Phys. Chem.* **66**, 2085.

See, H., 1999, *Korea-Australia Rheol. J.* **11**, 169.

Shih, Y. H. and H. Conrad, 1994, *Int. J. Mod. Phys. B* **8**, 2835.

Tanaka, K., A. Sahashi, R. Akiyama and K. Koyama, 1995, *Phys. Rev. E* **52**, R3325.

Thurston, G. B. and E. B. Gaertner, 1991, *J. Rheol.* **35(7)**, 1327.