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Electrical and Rheological Properties of Chitosan Malonate Suspension

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Abstract: The electrical and rheological properties of a chitosan malonate suspension in silicone oil was investigated by varying the electric fields, volume fractions of particles, and shear rates, respectively. The chitosan malonate susepnsion showed a typical electrorheological (ER) response caused by the polarizability of an amide polar group and shear yield stress due to the formation of multiple chains upon application of an electric field. The shear stress for the suspension exhibited a linear dependence on the volume fraction and an electric field power of 1.88. On the basis of the experimental results, the newly synthesized chitosan malonate suspension was found to be an anhydrous ER fluid.

Keywords: ER fluid, chitosan malonate, amide group, polarization model

Introduction

Electrorheological (ER) fluids are composed of electrically polarizables particles in a dielectric fluid and their ER performance are characterized by a rapid and reversible increase in apparent viscosity due to the formation of particle chains upon application of an electric field [1,2,3].

Since Winslow's discovery of the ER effect in 1947 [1], many researchers have investigated ER performance for hydrous and anhydrous ER fluids and demonstrated the polarization models based on the polarization particle chains which are formed by interactive force between the polarized particles in a dielectric fluid upon application field. The polarization model of ER fluids can be described by the equation mentioned below [3,4,5]

$$\tau_E \propto \phi K_f E^2 \beta^2 \quad (1)$$

where τ is the shear stress, ϕ the volume fraction of particles, K_f the dielectric permittivity of the base fluid, E the electric field and β is the relative polarization at dc or low frequency at ac fields given by [3,6]

$$\beta = (\sigma_p - \sigma_f) / (\sigma_p + \sigma_f) \quad (2)$$

where σ_p is the conductivity of particles and σ_f the conductivity of base fluid.

Generally, electrorheological (ER) fluids consist of highly polarizable particles in a dielectric fluid and they are classified by the hydrous ER fluids and anhydrous ER fluids. The hydrous ER fluids composed of cellulose [7] and corn starch [8] as the disperse phases have been widely used and studied for a long time. Their ER performance is dependent upon the activation of a low molecular solvent and mostly frequently water under an electric field. But they have lots of problems, including dispersion stability, durability, corrosion and a limited temperature in actual use. Recently, anhydrous ER fluids composed of polyaniline [9] and polyurethane [10] as the disperse phases, which do not contain water or polar solvent in the particles, have been introduced. However, they also have certain problems, such as dispersion stability and adhesion to the cell inspite of their high ER performance.

This study attempted to solve the basic problems of conventional ER fluids and introduced a chitosan derivative based on a natural biocompatible polymer, chitosan produced from chitin by N-deacetylation and composed of poly D-glucosamine as the disperse phase [11,12]. Chitosan malonate as the disperse phase were synthesized by chemical reactions between chitosan and malonic acid and the electrical and rheological properties of the synthesized chitosan malonate in silicone oil were investigated. The chitosan malonate suspension provided an ER performance under an electric field due to the polarizability of the branched amide group.

This study is to describe the ER behavior of the synthesized chitosan malonate suspension and to investigate the possibility of an anhydrous ER fluid.

Experimental

Materials

The base fluid used was silicone oil (Dow Corning Co.) with a specific gravity of 0.97, kinematic viscosity of 50cst at 40°C, and dielectric constant of 2.61 at 25°C. The chitosan as a raw material was a commercial powder (Jaekwang Co., Korea) with a nitrogen content of 4.8wt% and molecular weight of 100,000. As the dicarboxyl acid, malonic acid was provided by Sigma Aldrich. The chitosan malonate was synthesized by an amide reaction between chitosan and malonic acid of 0.5 mol ratio under the catalysis of TPP (Triphenyl phosphine) and DEAD (Diethyl azodicarboxylate). Their chemical reaction mechanism and chemical structure is shown in Scheme 1. The

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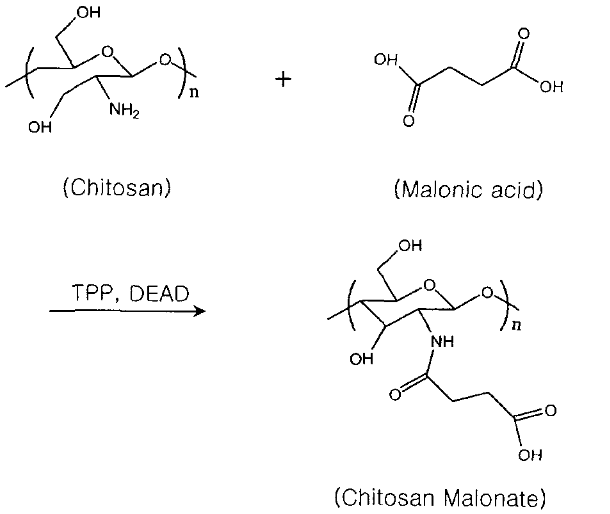

Scheme 1. Chemical reaction mechanism and chemical structure of chitosan malonate.

synthesized particle size was on average 25 μm in diameter. Prior to mixing in silicone oil, the chitosan malonate particles were dried for 5 h at 150°C and the silicone oil for 3 h at 130°C to remove any moisture in the vacuum oven. The chitosan malonate suspensions were then prepared at volume fraction of 0.1 to 0.3.

Tests

The dc current density of the chitosan malonate suspension was determined at room temperature by measuring the current passing through the fluid upon application of an electric field E_0 and then dividing the current by the area of the electrodes in contact with the fluid. The current was determined from the voltage drop across a 1 MΩ resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV. DC conductivity was taken to be ($\sigma = J/E_0$).

The rheological properties of the suspension were investigated in a dc field using a Physica Couette-type rheometer with a 1 mm gap between the bob and the cup. The resistance to shear produced by the suspension was measured as the torque on the drive shaft and then converted to shear stress and viscosity. The shear stress for the suspensions was measured under shear rate of 1 to 300 s^{-1}, electric fields of 0 to 3 kV/mm, and volume fractions of 0.1 to 0.3, respectively.

Results

The electrical properties of ER fluids are important for predicting the power requirements for the design of an ER device and also to identify the ER mechanism. The current density and conductivity of chitosan malonate suspension for the volume fraction ($\phi = 0.3$) with 0.5 mol ratio of malonic acid under the electric field are given in Fig. 1 and 2. In Fig. 1, the current density of the suspension showed an increasing trend with the electric field. As seen in Fig. 2, the conductivity of the chitosan malonate suspension increased with an increasing the electric field and moreover, the conductivity of the suspension is about 1 and 3 orders of magnitudes higher than those of the chitosan suspension and the silicone oil. This appeared to result from the polarizability of the polar group, an amide radical.

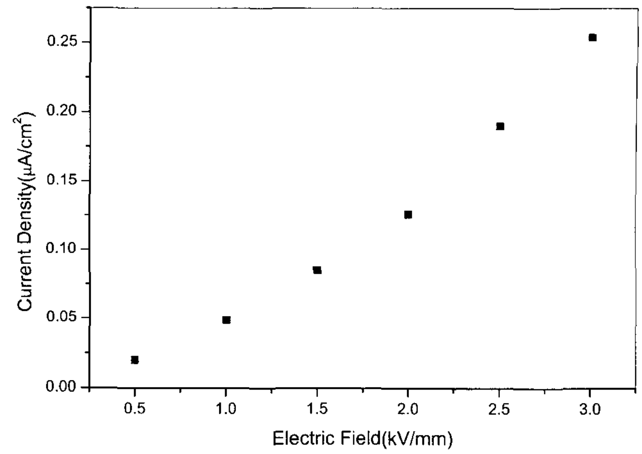

Fig. 1. Effect of electric field on current density for chitosan malonate suspension (ϕ=0.3).

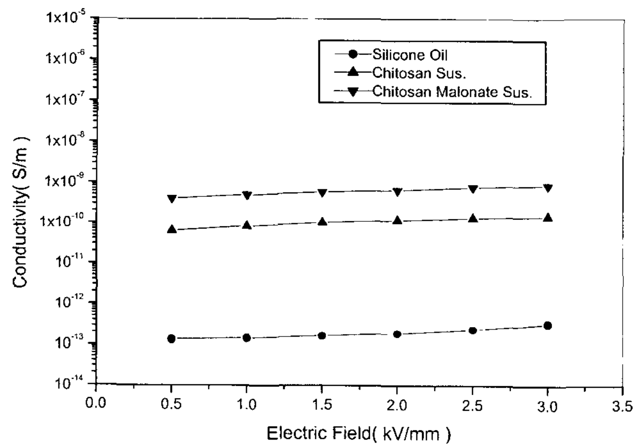

Fig. 2. Effect of electric field on conductivity for suspension.

To determine the effect of chitosan malonate suspension on the rheological properties, studies were conducted by varying the shear rates, electric fields, and volume fractions. The effect of the shear rate on the shear stress for the chitosan malonate suspension is illustrated in Fig. 3. The suspension exhibited a Bingham flow behavior upon application of the electric field (E = 3 kV/mm). Figure 4 shows a log-log plot of the shear stress versus the square of the electric field for the chitosan malonate suspension. The results in Fig. 4 indicate that the shear stress was proportional to an electric field power of 1.88, that is, $\tau \propto E^{1.88}$. This follows from the fact that the interaction force for the dipole in an electric field is proportional to the electric field intensity. The effect of the volume fraction of chitisan malonate particles in silicone oil on the shear stress is illustrated in Fig. 5. The results were obtained at a shear rate of 10 s^{-1}. The shear stress increases in a linear trend with the volume fraction of chitosan malonate particles. This was caused by the structure which mainly consisted of particle chains.

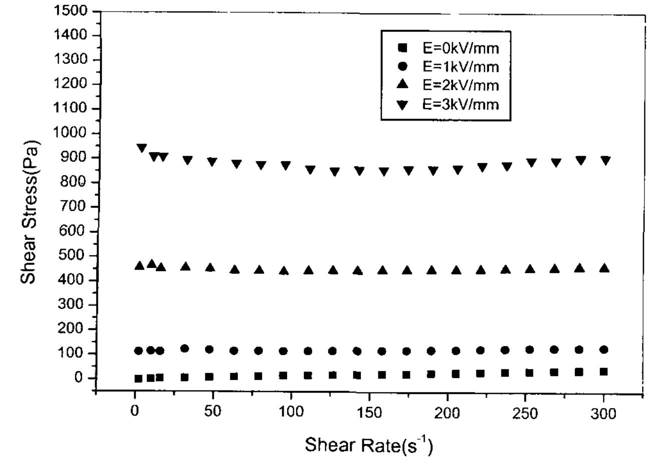

Fig. 3. Effect of shear rate on shear stress for chitosan malonate suspension (ϕ=0.3).

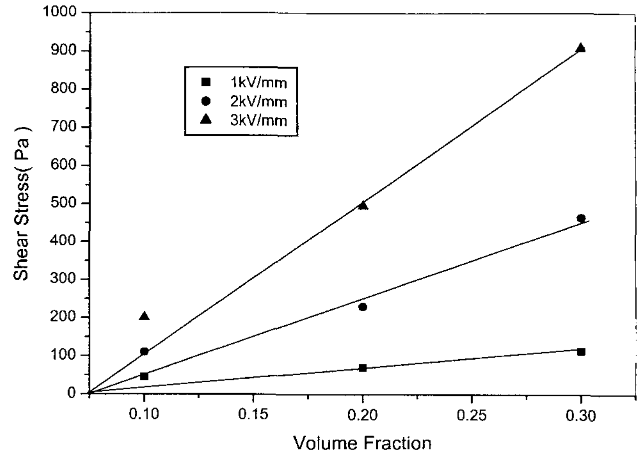

Fig. 5. Effect of volume fraction on shear stress for chitosan malonate suspension (γ=10 s^{-1}).

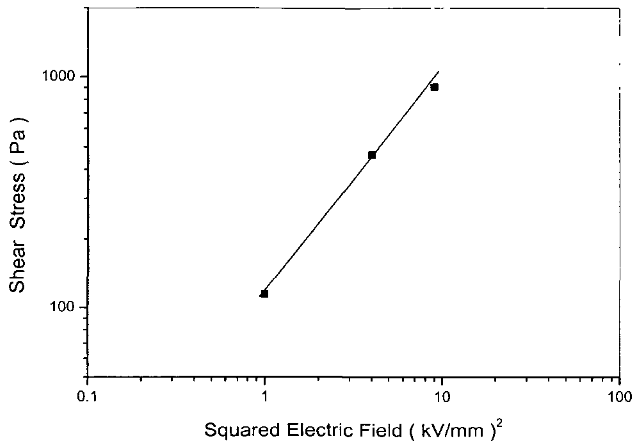

Fig. 4. Shear stress vs squared electric field for chitosan malonate suspension (ϕ=0.3, γ=10 s^{-1}).

Discussion

Polarization models based on a point-dipole approximation, with a focus on the mismatch between the real components of the dielectric permittivities of the particles and the based fluid, have been proposed to explain the behavior and can be described by Eq (1).

To explain the ER mechanism of the chitosan malonate suspension under an electric field, the results obtained with the suspension were examined based on the assumption that the base fluid and particles behaved as ideal dielectric materials, and the particles were aligned in chains or columns between electrodes. Using these assumptions, the theological analysis of Conrad *et al.* [3] for the polarization component of the shear yield stress gives

$$\tau_E = 44.1\ A_s\ \phi\ \varepsilon_o K_f (\beta E)^2 l \exp [(14.84 - 6.165(R/a))\beta^2]\} \\ x 1/(R/a)^8 (1 - 4/(R/a)^{10})^{1/2} l_{max} \quad (3)$$

where A_s is taken to be the structure factor pertaining to the alignment of the particles. This is equal to one for perfectly aligned single-row chains and can have a value of the order of ~10 for multi-chains or columns. K_f is the dielectric constant, β the relative polarizability ($\leqq$1), and R/a the ratio of the separation of the particle center to the radius ($\geq$2.05). The structure factor, A_s is obtained from the ratio value of the measured to the calculated shear stress using Eq. (3), that is, $A_s = \tau_{meas}/\tau_{calc}$. $A_s = 2$ was obtained for all the test conditions at a shear stress of 10 s^{-1}, electric fields of 1 to 3 kV/mm, and a volume fraction of 0.3, which may have been due to the formation of multi-chains aligned between the electrodes [13].

Conclusions

This study was conducted to deduce the ER behavior of a chitosan malonate suspension, estabilished the ER mechanism, and investigated their potential as an ER fluid. The following is a summary of the results:

(1) Chitosan malonate suspension in silicone oil showed an ER response upon the application of an electric field and the suspension exhibited a Bingham flow behavior. This was considered to result from the polarizability of the branched polar group, an amide radical.

(2) The shear stress of the chitosan malonate suspensions increased linearly with the volume fraction of particles and an electric field power of 1.88.

(3)The value of the structure factor, A_s was 2 and this may have been due to the formation of multi-chains aligned between the electrodes upon the application of an electric field.

Acknowledgments

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