생체적합성 키토산의 천연오일내 전기유변 특성

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Electrorheological Characteristics of Biocompatible Chitosan in Natural Oil

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Introduction

The electrorheological (ER) response produces an instantaneous, reversible change in rheological properties of a suspension when exposed to an electric field normal to the flow direction. The ER particles are polarized by the external electric field and the interaction among the resulting dipoles cause the particles to form fibrillated structures aligned with the electric field direction, and produce ER response. The reorientation of dispersed particles whose initial random distribution transforms into fibrillated structure result in the change of shear viscosity to a higher value (Tao et al., 2001). ER materials, which typically form semiconducting particle chains, are the intra- and intermolecular- structure of conducting polymers and the associated structural behavior are fundamental properties which strongly impact the physical properties manifested by this unique class of materials. Among these semiconducting polymeric particles possess polar groups such as amino ($-NH_2$), hydroxy (-OH) and amino-cyan (-NHCN), can be adopted. The polarizable and conductive polymers are anhydrous materials including polyaniline (Choi et al., 1999), poly(aniline-co-*o*-ethoxyaniline) (Block et al., 1990), poly(acequinone) radicals (Plocharski et al., 1997), and poly(p-phenylene) (PPP) (Trlica et al., 2000). The typical conducting polymers studied are based on a π-conjugated electron system constituting the polymer backbone (Kohlman et al., 1996). Polymers with conjugated π-electron systems display unusual electron properties, including high electron affinities and low ionization potentials. The local electron distribution of particles induces the ER effect under the applied electric field (Choi et al., 1998 and Cho et al. 2002). Chitosan is also used as ER materials including the branched amino polar group from these natural organic polymers resulting from the electronic donor group ($-NH_2$). Chitosan is a cheap, biocompatible, biodegradable, and non-toxic cationic polymer. As a series of different deacetylated chitinous materials derived from chitin by N-deacetylation, chitosan is a natural organic random copolymer primarily comprised of repeated sugar units with a structure of (1-4)-linked 2-amino-2-deoxy-β-D-glucopyranose, as well as some units with a structure of (1-4)-linked 2-acetic-amino-2-deoxy-β-D-glucopyranose (Chen et al., 2002). These chitosans have been previously modified and prepared to produce various chemical and biological properties (Muzzarelli 1990). Chitosan and chitin both are crystallizable (Ogawa et al., 1993) and possess excellent mechanical properties as well as being very attractive candidates for pharmaceutical applications. In this study, chitosan particles as anhydrous ER materials, suspended in a biocompatible corn oil were examined the electrical and rheological properties for an ER system.

Experimental

The chitosan used as anhydrous ER material was a powder supplied by Samchully Pharm. (Korea) with a deacetylation degree of 95 percent. Prior to use, the chitosan was put into a vacuum oven for approximately two days to remove any trace of moisture. The particle size of the chitosan was adjusted by using a 100 μm sieve. ER fluids were then prepared by dispersing chitosan particles in corn oil. The density of the corn oil was 0.916 g/m*l*, with a kinematic viscosity of 50 cS at 25°C. The conductivity of chitosan particles was measured using a 2-probe method. The pellets of dried chitosan particles were prepared with a 13 mm KBr pellet die. Pellet resistance was then measured using a picoammeter (Keithley model 487, Cleveland, U.S.A) with a conductivity cell. The conductivity (σ) was obtained from the relationship $\sigma = d/(A \cdot R)$, where d is the thickness, A is the surface area and R is the resistance of the pellet. Conductivity of the chitosan particles was measured to be 5.26×10^{-10} S/cm. Electrorheological properties of the chitosan based-ER fluids were measured using a rotational rheometer (Physica MC120, Stuttgart, Germany) with a Couette geometry equipped with a high-voltage generator (VG 5000, Stuttgart, Germany). The temperature was maintained at 25°C. Several DC electric field strengths (0.5 ~ 3.0 kV/mm) were applied to the insulated bob.

The flow curve was measured from a controlled shear rate (CSR) mode, in which a shear rate is applied to the ER fluid and the resulting shear stress is measured. A controlled shear stress (CSS) mode was also employed to obtain a yield stress. In the CSS mode, the ER fluid was stressed by an applied mechanical torque until the particle chain was broken to generate flow, and the stress at the onset of flow was reported as a static yield stress (Kim et al., 2000). The yield stress is greatly affected by the electric field strength and increases with particle concentration.

Results and Discussion

Chitosan is a cationic polyelectrolyte resulting from the amino group in the backbone of the molecule protonating in acidic solution. The chitosan particle shape was identified as irregular with rough surfaces. Fig. 1 shows the thermal gravimetric analysis (TGA) diagram for chitosan particles. The thermogram showed that the weight loss around 100 °C was due to water, and the decomposition of chitosan particles occurred above 300 °C. When the temperature was 400 °C, the weight loss of the chitosan particles was approximately 40%. The chitosan particles show a good thermal stability. Fig. 2 shows flow curves measured in the CSR mode for the 25 wt% chitosan-based ER fluid in the corn oil at various electric field strengths. Typical ER fluid behavior, from Newtonian fluid to solid-like, or Bingham behavior occurs as soon as the electric field is applied. These characteristics of ER fluids are known to be a consequence of the fibrillation of particles aligned along the electric field, and this structure formation is induced by the mismatch of the dielectric constants between suspended particles and the non-conducting medium. When a strain is applied perpendicular to the electric field, it distorts and destroys the fibril structures of particles aligned between the electrodes. The shear stress curve reveals a plateau region as the shear rate increased up to a critical value (*e.g*, 70 sec^{-1} for 0.5 kV/mm, 300 sec^{-1} for 1.0 kV/mm, and 600 sec^{-1} for 1.5 kV/mm). As the electric field strength increases the electrostatics become dominant over the hydrodynamic forces (See et al., 2002

and Cho et al., 1999).

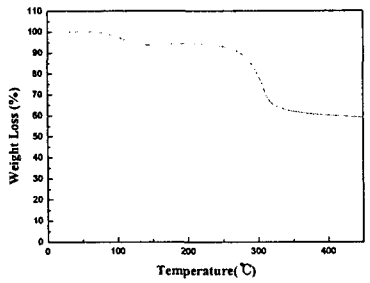

Fig. 1 TGA diagram of Chitosan

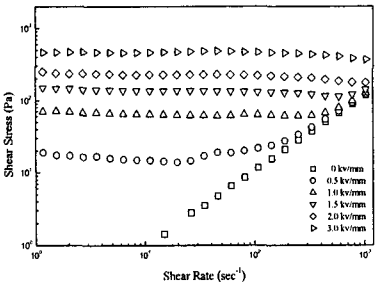

Fig. **2** Shear stress *vs.* shear rate for a 25 wt% chitosan-corn oil suspension for six different electric field strengths.

Fig. 3 (a) represents the dependence of static yield stress (τ_y) on electric field strength (E) for chitosan in corn oil obtained from the CSS mode. Generally, the correlation of τ_y on E is represented in power-law as follows:

$$\tau_y \propto E^{\alpha} \qquad (1)$$

The α values, in our study, were approximately 1.6 for both the corn oil and silicone oil suspensions. To explain the deviation from the polarization model behavior, which predicts $\alpha = 2$, Choi et al. (2001, and Sim et al., 2001) introduced the critical electric field strength, E_c into their universal scaling function. The slow polarization model contributed to the ER effect and the fibril structures were formed by particle rotation under an electric field. The proposed yield stress equation for a broad electric field strength range is:

$$\tau_y(E) = \kappa E^2 \left(\frac{\tanh \sqrt{E/E_c}}{\sqrt{E/E_c}} \right), \qquad (2)$$

where κ depends on the dielectric constant of the fluid and the particle volume fraction. Equation (1) clearly demonstrates the two regimes on the basis of E_c, showing different behavior at low and high electric field strengths, respectively.

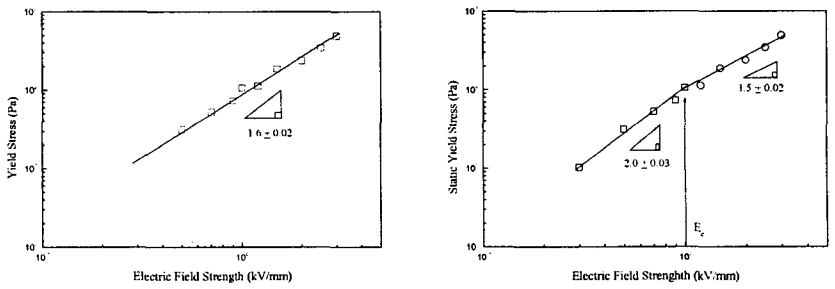

Fig. 3 (a) & (b) Yield stress *vs.* electric field strength for chitosan in corn oil.

The exponent in the power law expression varies with the electric field strength. In addition,

E_c appears to be proportional to the particle conductivity and is influenced by the conductivity mismatch between the suspended particle and liquid media. τ_y is proportional to E^2, that is $\alpha = 2$, for $E << E_c$, while $\alpha = 1.5$ for $E >> E_c$. E_c is measured as 1 kV/mm for corn oil suspensions in Fig. 3(b). The yield stress origins from the attractive forces between particles and explains two models such as polarization and conduction.

Conclusion

The ER response of this suspension system upon the application of the electric field was observed to behave as Bingham flow behavior. The shear stress and shear viscosity increased with electric field strength. Furthermore, it was found that the measured yield stress was proportional to E^2 for $E << E_c$ and $E^{1.5}$ for $E >> E_c$, where E_c is found to be 1 kV/mm for corn oil suspension, which obeys the nonlinear conduction model.

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