Electrorheological Properties of Chitin Suspensions

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SYNOPSIS

Electrorheological suspensions are suspensions of solid particles whose rheological behavior can be strongly modified by the application of an electric field. In this article, the electrorheological properties of suspensions containing chitin particles (and its derivative—carboxylmethyl chitosan particles) in silicone oil are reported for a range of suspension weight concentrations, applied field strengths, shear rates, etc. In these suspensions, glycerin was used as an activator. The adsorbed amount of glycerin, one of the electrorheological parameters, was also studied experimentally. The ER effect of the chitin suspension reaches the maximum at about 11% of weight concentration. The dependence of the experimentally determined dynamic yield stress on particle concentration and field strength is found to be similar to that reported for other systems. The dynamic yield stress is found to increase with the particle concentration and the applied electric field strength. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The electrorheological (ER) effect is noted for an essentially instantaneous reversible change in suspension viscosity upon the application of an electric field. This property comes from the transient aggregation of the solid phase due to the attractive forces between the dipolar moments induced on each particle by the external field. When the field is switched off, the aggregates disappear and the initial viscosity is recovered. This possibility of obtaining a rapid modulation of the viscosity with an electronic device has raised interest in those suspensions for practical applications in the field of hydraulics, robotics, and automotive applications. Electrorheology has recently been reviewed by Gast and Zukoski.[1]

ER suspensions usually consist of dielectric particles in insulating oil. The design of ER suspensions with optimal properties must combine a number of factors, namely, the parameters that can be varied to control ER effect, such as particle concentration and size and dielectric properties. Most of the reported ER suspensions are water-activated systems.

One of the primary disadvantages to the moist system is the limited temperature range. At higher temperature ($>70°C$), the moist system may be ineffective due to the loss of water. Solution of these problems and the development of better ER suspensions do depend on improving our understanding of how the phenomenon depends on the properties of the materials which make up ER suspension. In present study, water-free ER suspensions were made by using chitin and its derivative—carboxylmethyl chitosan—as the dispersed solid phase and glycerin as the activator. Glycerin film is adsorbed to the chitin and carboxylmethyl chitosan particles in the ER suspensions. These ER suspensions appear to be able to avoid the disadvantages of the moist ER systems since the polar liquid—glycerin—has a much higher boiling point than that of water, and they are stable even for long standing. Also, these glycerin-activated suspensions barely have any detectable current density, which will be favorable for practical utilization. On the other hand, they are good for environmental protection in future practical applications due to the biodegradable property of chitin and its derivative. The rheograms of the suspensions in the presence of or in the absence of an electric field are analyzed with the purpose of improving the understanding of the ER effect. More-

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over, the experimental relationship between the dynamic yield stress and the field strength or the suspension concentration is presented, which will give some information to the application of ER suspensions.

EXPERIMENTAL

Suspension Preparation

Chitin Suspensions

The chitin samples (Katakura Chikkarin Co., Tokyo, Japan) were grounded and immersed into the glycerin–methanol solutions at different concentrations, to make sure that the samples adsorb different amounts of glycerin. The fraction of the adsorbed glycerin M is defined as the following equation:

$$M = (W - W')/W' \times 100$$

where W is the weight of dispersed particles, and W', the weight of dry particles before the adsorbing of glycerin. After the removal of methanol, the samples were ball-milled, dispersed in silicone oil, and placed in a vacuum oven at room temperature until a constant weight was reached.

Carboxylmethyl Chitosan Suspension

The deacetylation of chitin was carried out according to the method of Roberts,[2] namely, the chitin samples were treated with 50 wt % NaOH at 100°C for 1 h to produce chitosan. The carboxylmethyl chitosan was then prepared by using the method of Hayes.[3] Also, the carboxylmethyl chitosan suspension was obtained by using the method similar to that of the above-mentioned chitin suspension. The deacetylation of chitin and the carboxylmethylation of chitosan are schematically shown in Figure 1.

The particle size of chitin and carboxylmethyl chitosan particles had a mean number average diameter of about 10 μm according to the microscopic examination. Particles were irregular in shape but without any tendency to anisometry.

Rheometry

In all the measurements discussed in this article, the electric field was applied transverse to the direction of shear. A concentric cylinder rheometer was used to examine the ER properties of the suspensions. To apply the large electric field strength across the concentric cylinders, each cylinder was insulated from the rest of the rheometer. The inner cylinder has an outer diameter of 14.6 mm and height of 30 mm. The outer cylinder has an inner diameter of 20 mm and height of 35 mm. The annual gap is 2.7 mm. The electric field strength was applied to the gap by grounding the outer cylinder and connecting the inner cylinder to a high-voltage source.

Steady shear rate rheological measurements were performed in the following manner: Voltages in the range of 100–2000 V were used at a frequency of 50 Hz. The suspension was loaded into the rheometer and the electric field was applied for at least 20 s before applying the shear. After the shear rate was applied, the suspension viscosity was then measured.

RESULTS AND DISCUSSION

Optimum Amount of Adsorbed Glycerin

In this study, glycerin was used as an activator instead of water in the suspensions, thus enhancing the suspensions' thermal stability greatly. The optimum amount of the adsorbed glycerin is presented in Figure 2. As shown in Figure 2, at different amounts of adsorbed glycerin, the apparent viscosity increases with increasing electric field strength. The suspension's ER effect is most significant when the adsorbed glycerin equals 5 wt %. For the adsorbed glycerin below 5 wt %, the apparent viscosity increases with the amount of glycerin. Above 5 wt %,
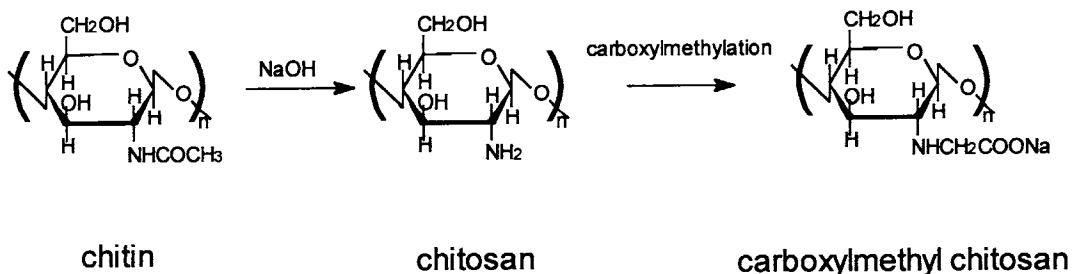

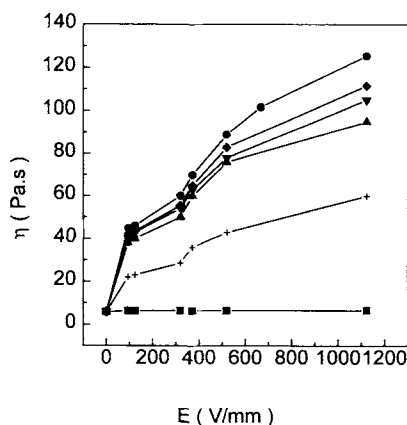**Figure 1** Scheme for the deacetylation of chitin and the carboxylmethylation of chitosan.

Figure 2 Viscosity vs. field strength curves at different glycerin amounts ($C = 11.8$ wt %, $\gamma = 17.03$ S^{-1}): (— ■ —) $M = 1$; (— ● —) $M = 5$; (— ▲ —) $M = 10$; (— ▼ —) $M = 15$; (— ◆ —) $M = 20$; (— + —) $M = 3$.

the viscosity decreases with the amount of glycerin. In the experiment, it is also found that, in the case of suspensions that involved particles without the adsorbing of glycerin, the ER effect is not observed at all. (All the suspensions used below are suspensions with 5 wt % of adsorbed glycerin.)

According to the above-mentioned phenomena, the adsorbed glycerin is considered to be adsorbed to the surface of particles to form the electric double layers, which, in turn, results in the increasing of the effective permittivity of the particles and the augmenting of the interparticle polarization forces. The decrease in the ER effect at sufficiently large glycerin concentrations is due to the drastic increase in the conductance of the suspension, which could screen the polarization of particles. Hence, the ER effect decreases. Also, excess glycerin would be detrimental to the overall performance of the ER suspension by creating an excessively conductive fluid. Conduction is accompanied by power consumption, heating, and electric breakdown; all are undesirable for practical ER fluids. When glycerin is not adsorbed to the dry particles, the electric double layers are not formed and the ER effect does not occur.

At the same time, the suspension's thermal stability was examined as well. The suspension was placed in an oven at 160°C for 3 days; then its ER effect was examined again and it shows no change at all.

Optimum Particle Concentration

Figure 3 shows the optimum weight concentration of particles. At a concentration below 11 wt %, the ratio of apparent viscosity to zero-field viscosity in-

creases with increasing concentration. This trend may be understood by considering the effects on polarization forces between particles. In very dilute suspensions (large distance between particles), the magnitude of this polarization force in the direction of the applied electric field is

$$F = (6\varepsilon_2 r^6 E^2)/\rho^4$$

where ε_2 is the dielectric constant of the particle; r, the radius of the particle; E, the field strength; and ρ, the distance between particles.[4] From this equation, it can be easily seen that with the decreased distance between particles, namely, the increased particle concentration, the polarization force between particles is greatly increased. Hence, the ER effect of the suspension increases with the increasing particle concentration.

When the particle concentration is above 11 wt %, the ratio of apparent viscosity to zero-field viscosity decreases with increasing particle concentration. Also, the ratio of apparent viscosity to zero-field viscosity reaches its maximum at about 11% of weight concentration. This is because, at higher concentration, particles are close to each other and the electric double layers around particles overlap. Therefore, the mutual action between particles increases, and the electric double layers may drop out of the particles. As a result, the suspensions' ER effect decreases.

Effects of Electric Field Strength and Shear Rate

Figure 4 shows the apparent viscosity of the suspension ($C = 11.8$ wt %) as a function of field strength at various shear rates. There are several
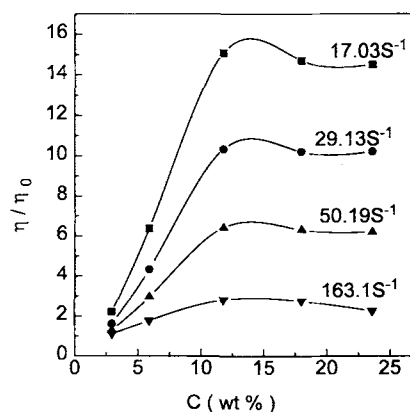

Figure 3 The ratio of apparent viscosity to zero-field viscosity as a function of particle concentration ($E = 500$ V/mm).
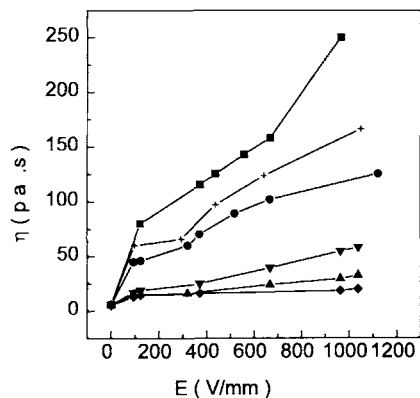
Figure 4   Experimental relationship between viscosity and electric field strength ($C = 11.8$ wt %): (— ■ —) 2.509 S^{-1}; (— ● —) 17.03 S^{-1}; (— ▲ —) 89.62 S^{-1}; (— ▼ —) 50.19 S^{-1}; (— ♦ —) 163.1 S^{-1}; (— + —) 4.481 S^{-1}.

important features seen in this figure which are almost common to all particle concentrations studied. First, the effect of the field strength is very significant at low shear rates and the increment of the ER effect is smaller at higher shear rates. Second, the suspension's ER effect increases with the increasing field strength. Third, the suspension's ER effect decreases with the increased shear rate.

According to the experimental facts, it is considered that, under the applied electric field, the interparticle interaction (polarization forces) leads to the aggregation of particles or even fibril formation between the electrodes. Such a structural skeleton is across the direction of the shear field and leads to an increased viscosity. In the presence of a shear field, the particles are also acted on by the viscous forces, which is modulated by hydrodynamic interactions with other particles in the suspension. These viscous forces scale as $6\pi\eta_s r^2\gamma$, where η_s is the viscosity of the suspending fluid; r, the radius of the particle; and γ, the shear rate. As γ is increased, the viscous forces increase, so that the tendency to breakdown the structural skeleton of the suspension is increased; therefore, the suspension structure formed due to the applied electric field is much easier to damage and the increment of the viscosity is much smaller, whereas at a high enough shear rate, the suspension viscosity almost becomes independent of the electric field. This suggests that, at high shear rate, the viscous forces are dominant, and the suspension structure does not vary appreciably with field strength.

Rheograms

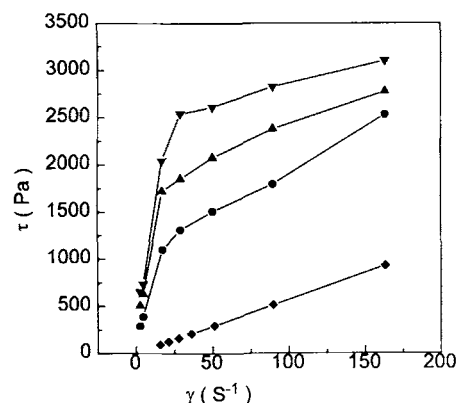The rheograms of the suspensions at different electric field strengths and concentrations are presented

Figure 5   Shear stress vs. shear rate curves at different field strengths ($C = 11.8$ wt %): (— ● —) $E = 400$ V/mm; (— ▲ —) $E = 700$ V/mm; (— ▼ —) $E = 1000$ V/mm; (— ♦ —) $E = 0$ V/mm.

in Figures 5 and 6, respectively. From the flow curves, namely, shear stress τ vs. shear rate γ curves in these figures, it can be seen that the dispersed phase concentration has influence on the suspension's behavior under continuous strain conditions. In the absence of or under an applied electric field, the higher the particle concentration, the greater is the suspension viscosity. When the particle concentration is below 5.9 wt %, the suspension viscosity (ER effect) barely increases with the electric field being applied.

In the absence of an electric field, the dependence of τ on γ is almost linear, while with the electric field being applied, there appears a yield limit τ_0, whose value increases with the electric field strength (see Fig. 7). This supports the inference about the growth of interparticle interaction forces and the
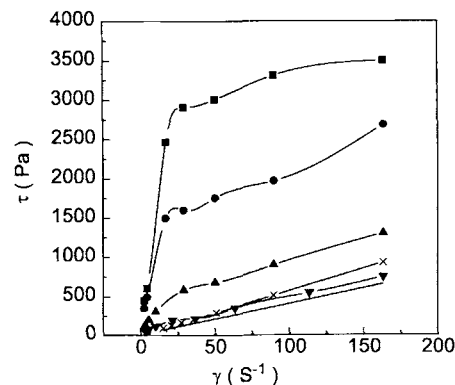

Figure 6   Shear stress vs. shear rate curves at different concentrations ($E = 500$ V/mm): (— ● —) $C = 11.8$ wt %; (— ▲ —) $C = 5.9$ wt %; (— ▼ —) $C = 2.95$ wt %; (— ■ —) $C = 23.6$ wt %; (——) $C = 2.59$ wt % ($E = 0$ V/mm); (— × —) $C = 11.8$ wt % ($E = 0$ V/mm).
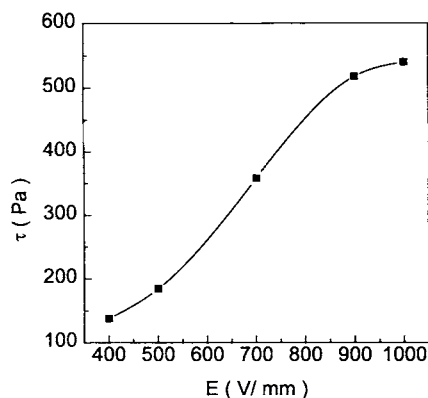
Figure 7 Dynamic yield stress as a function of field strength curve.

strengthening of the system structure with the increasing field strength. From Figure 5, it can be seen that the higher the particle concentration, the greater the anomaly of the viscoplastic behavior with the electric field being applied. The slope of the curve $\tau-\gamma$ within the range of small shear rates (the small shear rate region) increases with the field strength, which is equivalent to an increase of viscosity values. This can be explained by the increasing energy expended in the rupture of the system structure under the applied shear field. An analysis of the oblique region is important for the research of a transient process in the system structure under the applied electric field.

A transition from the small shear rate region to the high shear rate region on curves $\tau-\gamma$ corresponds to the transition from flow patterns with a nondestroyed structure to those with a strain-ruptured structure. This suggests that at low shear rates polarization forces control the suspension structure, but as the shear rate is increased, viscous forces become dominant. These experimental results suggest that under continuous shear the ER effect highly depends on the particle concentration and the balance between viscous and polarization forces.

We present the dynamic yield stress τ_0 vs. field strength and dynamic yield stress vs. particle concentration curves in Figures 7 and 8, respectively. The dynamic yield stress values, which represent the limiting values of the shear stress as the shear rate approaches a zero shear rate, were obtained by extrapolating the shear stress–shear rate data to the zero shear rate.

The phenomenon of the dynamic yield stress in the ER suspension has been commonly represented by the Bingham constitutive equation[5-7]:

$$\tau = \tau_0 + \eta_\infty \gamma$$

where τ_0 is the dynamic yield stress, and η_∞, the high shear stress viscosity in the absence of an electric field.

As shown in Figure 7, the dynamic yield stress increases with the applied electric field. This suggests that the system structure in ER suspensions is more stable in a strong electric field. At high field strength, the increase of the dynamic yield stress becomes less significant (see Fig. 7). This is due to the saturation of the particle structure with the electric field.

From Figure 8, it can be seen that the dynamic yield stress is a function of particle concentration. The dynamic yield stress increases with increasing particle concentration. This is because that, as the particle concentration increases, the polarization forces between particles increase and so does the suspension's ER effect. At larger concentrations, the dynamic yield stress reaches a plateau.

Carboxylmethyl Chitosan Suspension

Figure 9 shows the suspension viscosity vs. electric field strength curves of carboxylmethyl chitosan and chitin suspensions. The ER properties of the suspensions containing the carboxylmethyl chitosan particles are similar to those of the suspensions containing chitin particles, e.g., the ER effects increase with increasing concentration and the applied electric field strength, but decrease with increasing shear rate. It is found that the ER effect of the carboxylmethyl chitosan suspension is much more significant than that of the chitin suspension at a given shear rate. This phenomenon is due to the introduction of the carboxylmethyl group, which, in turn, results in the increase of the particle's permittivity. This increase in the particle dielectric constant causes the increase of the polarization forces be-
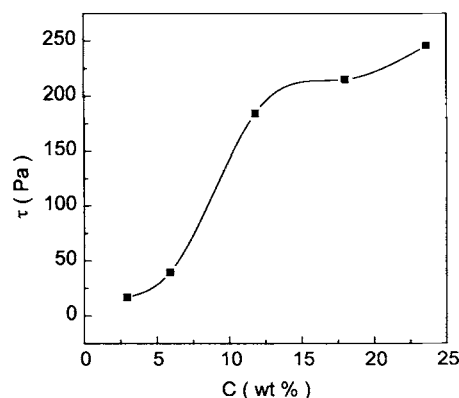

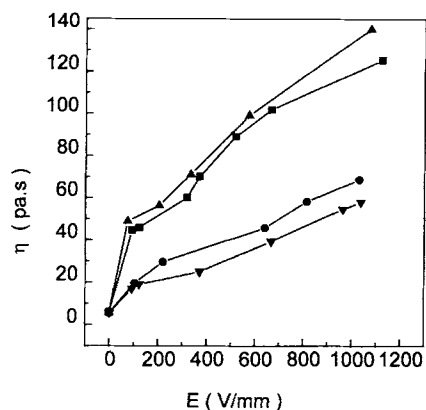**Figure 8** Dynamic yield stress as a function of concentration curve.

Figure 9 Suspension viscosity vs. field strength curves: (— ■ —) 17.03 S⁻¹ (chitin); (— ● —) 50.19 S⁻¹ (carboxylmethyl chitosan); (— ▲ —) 17.03 S⁻¹ (carboxylmethyl chitosan); (— ▼ —) 50.19 S⁻¹ (chitin).

tween particles and, as a result, the strengthening of the suspension structure.

The good adsorptive power of carboxylmethyl chitosan could possibly further enhance its permittivity. Also, the ability of chitosan to form complexes with metal ions makes this kind of material have a great potential to become excellent ER suspensions. Some of these works are well under way in our laboratory right now.

CONCLUSIONS

The continuous shear behavior of the ER suspension composed of chitin particles was studied as a function of concentration, shear rate, and field strength. Application of an external field induces polarization forces between the particles, resulting in strands of particles spanning the electrode gap, which, in turn, increases the suspension viscosity (makes the suspension display ER effect). The ER effect is found to depend on the particle concentration and the balance between viscous and polarization forces. The ER effect of the chitin suspension shows the maximum at about 11% of weight concentration.

With increasing shear rate, the transition from polarization force control to viscous force control of the structure occurs. When the shear rate is sufficiently high, the electric field almost ceases to have an effect on the suspension viscosity. The dynamic yield stress is found to increase with the particle concentration and the applied field strength.

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