The Conductive Properties of the Electrorheological Suspensions Based on Dihydroxypropyl Chitosan Particles

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ABSTRACT: In this article, the electrorheological (ER) properties of the suspensions containing dihydroxypropyl chitosan particles in silicon oil with glycerin as activator are reported. In particular, the conductive property of these suspensions and its influencing factors, such as activator content, field strength, concentration, and shear rate, are investigated experimentally. The experimental results show that the suspension can display significant ER effects under the applied electric field strength. An optimum activator content exists, and the suspension's current density increases with particle concentration, activator content, and field strength, while it decreases with shear rate.
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Key words: dihydroxypropyl chitosan; electrorheological effect; conductive property; suspension; chitin

INTRODUCTION

Electrorheological (ER) suspensions are defined as suspensions whose rheological properties are strong functions of an electric field strength imposed on them. Since its discovery,[1,2] ER suspension has been recognized to have great potential engineering applications, thus attracting enormous interest in the research of electrorheology. However, there are many problems to be solved before ER systems find extensive commercial application. It has been long observed that wet particulates are most electrorheologically active, but these moist fluids are limited to a narrow temperature range (<70°C) and show undesirable levels of conductance arising from mobile ions.[3,4] Recent development of anhydrous suspensions based on conducting materials seems to have overcome some of these problems; however, they also show undesirable levels of conductance.[4,5] Solution of these problems and the development of better ER fluids do depend on improving our understanding of how the phenomenon depends upon the properties of the materials that make up ER fluids.

In present study, water-free ER suspensions were prepared by using dihydroxypropyl chitosan particles as the dispersed solid phase, silicone oil as the dispersing medium, and glycerin as the activator. Our experiments indicate that 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. Furthermore, the biodegradable feature of chitosan could be good for future applications in terms of environmental protection.

The conductance of ER fluid is believed to be an important parameter in ER effect, especially

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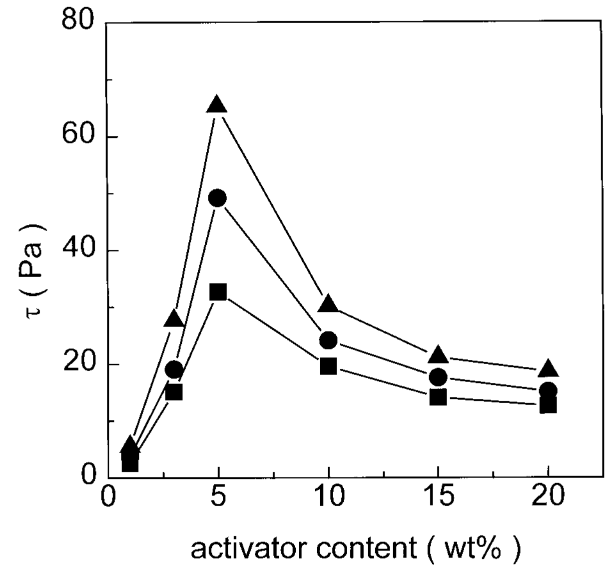

Figure 1 The suspension's shear stress versus activator content curve ($C = 15$ wt %, $\gamma = 2.5\ s^{-1}$): (▲) 1.0 kV/mm; (●) 0.8 kV/mm; (■) 0.5 kV/mm.

when it comes to actual applications. A large increase in the conductance of the fluid would result in excessive power demands with possible serious implications in terms of power supply and energy dissipation in the ER device. It could even cause dielectric breakdown.[6,7] For this reason, low conductance is an important goal for future ER fluids. Therefore, in this article, the influencing factors of the conductance of ER fluid are particularly studied, which might give some information on future applications of ER suspensions.

EXPERIMENTAL

Synthesis and Suspension Preparation

The deacetylation of chitin sample (Katakura Chikkarin Co., Tokyo, Japan) was carried out according to literature[8]; namely, the chitin samples were treated with 50 wt % NaOH solution at 100°C for 1 h to produce chitosan. The dihydroxypropyl chitosan was then prepared by the reaction of 3-chloropropan-1,2-diol with chitosan according to the method of Tokura et al.[9]

After drying, the dihydroxypropyl chitosan sample was grounded and immersed into the glycerin–methanol solutions at different concentrations for 72 h at room temperature. After the removal of methanol, the adsorbed glycerin content was measured by the weight method, and a certain amount of the dihydroxypropyl chitosan samples were dispersed in a given amount of silicon oil, then the mixture was ball-milled until microscopic examination indicated a mean particle size $<15\ \mu m$ and the absence of particles $>25\ \mu m$. Particles were irregular in shape but without any tendency to anisometry. The silicone oil used is a colorless oil with the following physical properties: density, 0.97 g/cm^3; viscosity, 100 mPa s^{-1} at 20°C; dielectric constant, 2.8; and boiling temperature, 300°C. There was little tendency for these dispersions to separate in the short term, and such dispersions that had separated after lengthy standing readily redispersed on agitation.

Methods of Measurement

For ER measurement, a concentric cylinder rheometer was used. To apply 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 a height of 30 mm. The outer cylinder has an inner diameter of 20 mm and a 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. The DC voltages in the range of 100–2500 V were used. The voltage was monitored using a multimeter attached to a

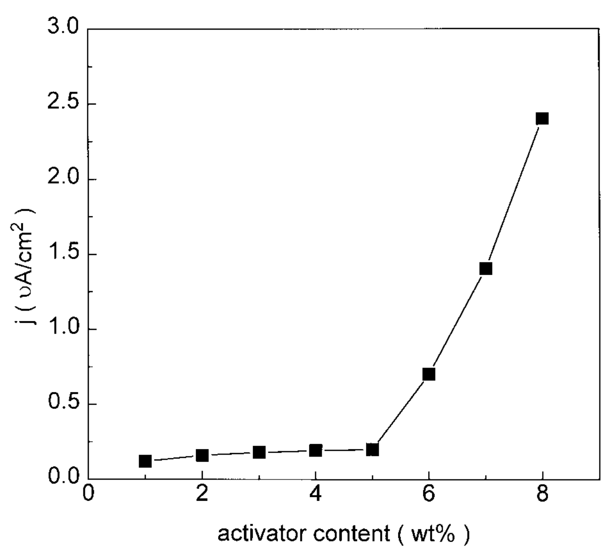

Figure 2 Suspension's current density versus activator content curve ($E = 1.0$ kV/min; $C = 15$ wt %).

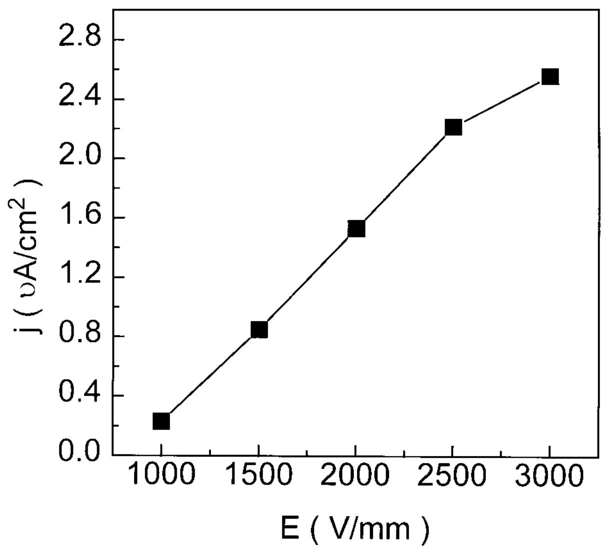

Figure 3 The suspension's current density as a function of field strength (C = 15 wt %; activator content = 5 wt %).

one-tenth voltage readout connection on the power supply. The current was monitored using a multimeter attached in series to the ground wire of the circuit. The current density was calculated through dividing the measured current by the surface area of the electrode. All experiments were carried out at room temperature, which varied between 18 and 22°C. No appreciable changes in rheological response were noted within this temperature range.

RESULTS AND DISCUSSION

Effects of Activator Content and Field Strength

In this study, glycerin instead of water was used as an activator in the suspensions, thus greatly enhancing the suspensions' thermal stability. The suspension's shear stress as a function of the activator content at different field strengths is shown in Figure 1. It can be easily seen that, at a given activator content, the suspension's shear stress increases with the increasing field strength; namely, the suspension's ER effect increases with field strength. There exists an optimum activator content at about 5 wt %. Under the optimum value, the suspension's ER effect increases with the increasing activator content, while over this value, the suspension's ER effect decreases with the activator content.

According to the fibrillation theory,[1,2,10] under the applied electric field, the interparticle forces (polarization forces) cause the dispersed particles to form chains or fibrils, which bridge the gap between the electrodes. This suspension structure leads to the field enhancement of shear stress or viscosity (ER effect). Therefore, the above-mentioned experimental phenomenon can be explained by considering the scale of the polarization forces between the dispersed particles. The polarization forces between dispersed particles scales as[10] $\pi\varepsilon_0\varepsilon_c(a\beta E)^2$, where ε_0 is the permittivity of free space, ε_c is the relative permittivity of the dispersing phase, a is the radius of the particle, and E is the applied field strength. β is the particle dipole coefficient given by $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$, where ε_p is the dielectric constant of the particles. It is obvious that the polarization forces increase with the increasing field strength, so the shear stress of the suspension increases with the field strength; namely, the suspension's ER effect enhances with the increasing field strength. 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 ER effect at a sufficiently large glycerin content is due to the drastic increase in the conductance of the suspension (see

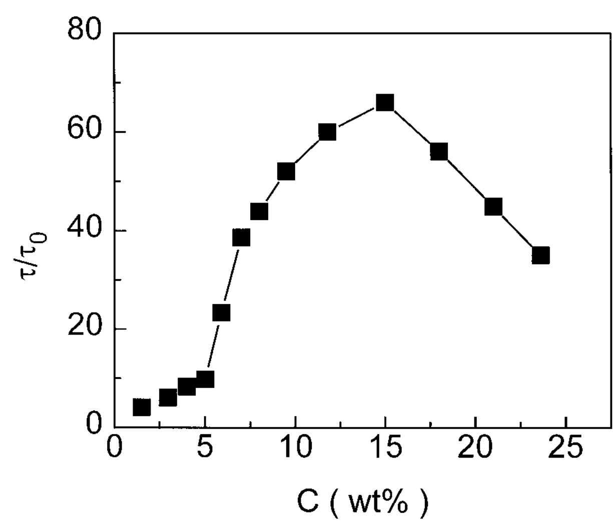

Figure 4 The relative shear stress as a function of particle concentration (E = 1.0 kV/mm; γ = 2.5 s^{-1}; activator content = 5 wt %).

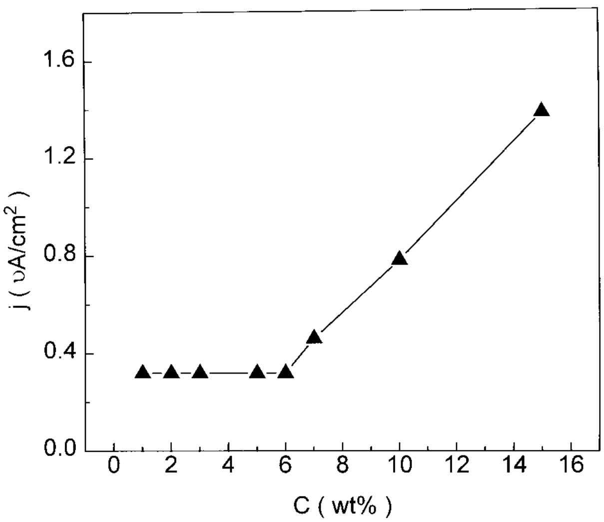

Figure 5 Suspension's current density versus concentration curve (E = 2.0 kV/mm; activator content = 5 wt %).

Fig. 2), which could screen the polarization of particles. Hence, the ER effect of the suspension 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 even electric breakdown; all are undesirable for practical applications.

In this experiment, the suspensions' thermal stability was examined as well. The suspensions were placed in an oven at 150°C for 48 h. Then, their ER effect was examined again, and it shows almost no change. For comparison, we also examined the thermal stability of the suspension using water as activator. After being placed in oven at 150°C for only half an hour, its ER effect was measured again, and it barely displays any ER effect. These results indicate that the suspensions with glycerin as activator have quite good thermal stability.

Under zero shear rate, the current density in the suspensions at different activator content and field strengths is shown in Figures 2 and 3, respectively. It can be noted that the suspension's current density first increases slowly with the increasing activator content; when the activator reaches a certain value, then the suspension's current density increases significantly with the increasing activator content. This activator content value coincides with the optimum activator content. As shown in Figure 3, the suspension's current density increases steadily with the increasing field strength.

The absorption of glycerin will enhance the surface conductance of dihydroxypropyl chitosan particles; on the other hand, glycerin as an impurity will also enhance the system's volume conductance; both these conductances increase with the increasing field strength, so the suspension's current density increases with the field strength. In addition, The field-induced particle chains or strands bridging the electrodes could provide conducting pathways as well.

Furthermore, under higher field strength, the space charge current could occur due to the electrons discharged into the fluid from the electrode. The space charge current is non-ohmic and proportional to the square of the field strength.[11] Under higher field strength, the space charge current could contribute to the current density of the suspension.

Effects of Particle Concentration

Figure 4 shows the relative shear stress of the suspension at different concentrations. The relative shear stress is the ratio of the suspension's shear stress to zero-field shear stress under the same shear rate, and the current density as a function of particle concentration under zero shear rate is shown in Figure 5.

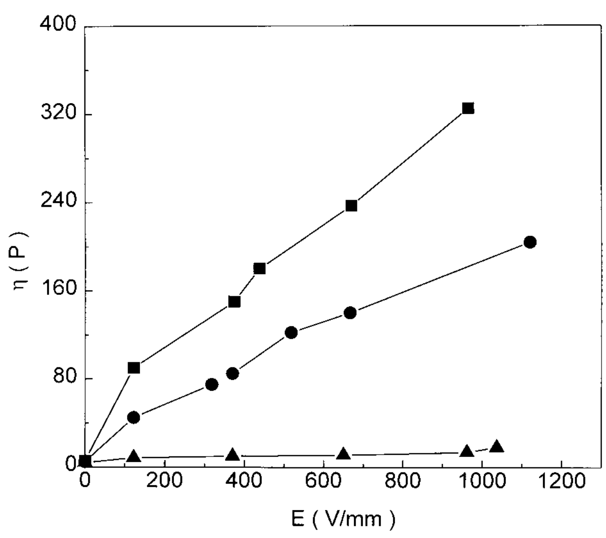

Figure 6 Experimental relationship between suspension viscosity and field strength (C = 15 wt %; activator content = 5 wt %); (■) 2.5 s^{-1}; (●) 17.0 s^{-1}; (▲) 163.1 s^{-1}.

It seems that there is a critical concentration and an optimum concentration, at about 5 and 15 wt %, respectively. Under the critical value, the suspension barely displays any ER effect. Over the critical concentration, the suspension's ER effect increases with the increasing concentration. The formation of particle chains or strands is a percolation process.[12] Only when there are enough particles in the dispersion should the particles strands or chains span the electrode gap. The shear field distorts the suspension structure (particle strands or chains), and the energy expended in this deformation results in the observed enhancement of shear stress or viscosity. This is why there exists a critical concentration. Over the critical concentration, the amount of particle strands bridging the electrodes increases with the increasing amount of particles (concentration), which in turn provides more conducting pathways. Hence, the current passing through the suspension increases with concentration. Under the critical concentration, the dispersed particles could only form short chains. There are less possible conducting pathways in the suspension; therefore, a small current passes the dispersion.

When particle concentration is above the optimum concentration value, the suspension's ER effect decreases with the increasing concentration. This is because, at a higher concentration, particles are close to each other, and the electric double layers may drop out of the particles, which, in turn, decreases the polarization forces between the suspended particles. As a result, the suspensions' ER effect decreases.

Effects of Shear Rate

The viscosity and current density of the suspension at different shear rates are shown in Figures 6 and 7, respectively. It can easily be seen that the suspension's ER effect decreases as the shear rate is increased; under lower shear rate range, the current density remains relatively high and barely changes with shear rate, while, at a higher shear rate, the suspension's current density decreases rapidly.

The polarization forces between the suspended particles induced by the applied electric field lead to the formation of particle strands or chains, which, in turn, results in the increased shear stress or viscosity (ER effect). In the presence of a shear field simultaneously, the dispersed particles are also acted on by the viscous forces, which will rupture the particle chains or strands. The viscous forces scale as $6\pi\eta a^2\gamma$, where η is the viscosity of the dispersing fluid, γ is the shear rate, and a is the radius of the particle.[10] It can be seen that as the shear rate is increased, the viscous forces acted upon the particles increase so that the tendency to breakdown the structural skeleton of the suspension is enhanced. Therefore, the suspension's ER effect decreases with the increasing shear rate.

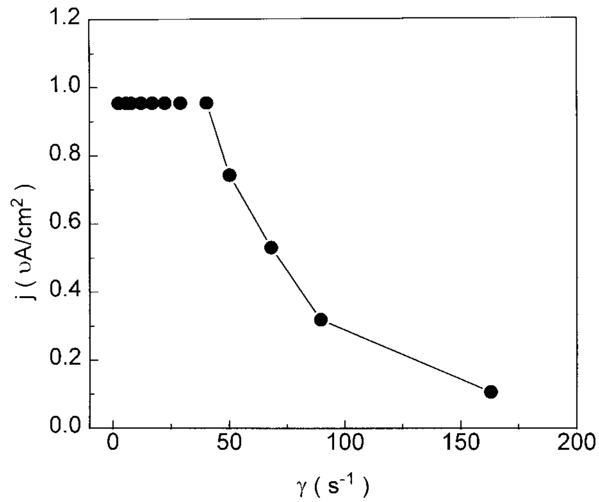

Figure 7 Suspension's current density versus shear rate curve (C = 15 wt %; E = 2.0 kV/mm; activator content = 5 wt %).

At a lower shear rate, the polarization forces remains dominant, and little damage is done to the suspension structure (particle strands or chains). Therefore, the suspension could display significant ER effect, and the current density remains relatively high. While with the enhancing shear rate, the viscous forces gradually take hold and finally become dominant, which results in more ruptured particle strands or chains, so the suspension's ER effect decreases, and the amount of the conducting pathways decreases; therefore, the current density of the suspension decreases. The higher shear rate could also decrease the conduction arising from the orientation movement of impurities.

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