Preparation and Electrorheological Characteristics of β-Cyclodextrin–Epichlorohydrin–Starch Polymer Suspensions

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ABSTRACT: Three environment friendly β-cyclodextrin polymer electrorheological (ER) particles (NS-β-CDP, WSS-β-CDP, and CLS-β-CDP) were synthesized by copolymerization through a mixture of β-cyclodextrin (β-CD) and epichlorohydrin in the absence of starch or in the presence of water-soluble and water-insoluble starch, respectively. The electrorheological properties of suspensions in silicone oil were then investigated under direct current (dc) electric fields. It was found that the yield stress of the typical WSS-β-CDP ER fluid was 6.2 kPa in 4 kV/mm, which is 35% higher than that of NS-β-CDP and similar to that of CLS-β-CDP. In the meantime, it can display a high ER performance even over a range of 65–95°C. The structures of these polymers were characterized by FT-IR and Raman spectrometry, respectively. The results demonstrated that all of these polymers keep the original structural character of β-CD and the copolymerizations between starch and β-CD indeed occur. Furthermore, it was found that there was some relationship between the characteristic strength of polymers and their dielectric properties. Hence, the improvement of copolymer dielectric properties resulted in the enhancement of ER effects. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1681–1686, 2004

Key words: electrorheological fluids; β-cyclodextrin; copolymerization; host–guest systems; synthesis

INTRODUCTION

Electrorheological (ER) fluids are smart materials, which involve rapid and revisable changes of fluid under an electric field of a few kilovolts per millimeter. Because this behavior could be exploited in hydraulic or robotic applications, such as electrical clutches or dampers in motor vehicles, ER materials have become an important research subject in soft-matter science.[1–4] In recent years, researchers have found that some common factors, including dielectric constant, conductivity, dielectric loss, and nontoxicity are considered as the basic reference factors in the design of ER materials.[5–8] According to this idea, in our previous work, we found that doping rare earth into anatase TiO_2 can improve the electrorheological effects of TiO_2 and broaden operational temperature range due to dielectric loss, and dielectric constant of TiO_2 at low frequency was improved by doping rare earth, but these kinds of materials still are far from practical use for easier sedimentation and lower shear stress. Similarly, we found that polyaniline-montrmorillonite clay nanocomposite materials display

notable ER effects and good suspension stability compared with the pure polyaniline particles, but these kinds of materials are far from use in the green process[9] because of their toxicity. Recently, some organic polymers that contain polysaccharide or consist of glucose units, such as chitosan,[10–13] phosphate cellulose,[14] kaolinite-carboxymethyl starch,[15] and polysaccharide/titanium oxide,[16] have attracted researchers. One of the advantages of these materials is lack of toxicity. Another is that they could overcome several shortcomings of hydrous systems, such as the temperature limitations, the density mismatch between the particle and the oil, and an insufficient yield stress.

In fact, the high performance ER materials are closely related to their molecular structures. With the development of ER materials, it is clear that those materials possess either branched polar groups such as amine (–NH_2), hydroxy (–OH), and amino-cyano (–NHCN) or semiconducting repeated groups. The polar groups may affect the ER behavior by playing the role of the electronic donor under the imposed electric field.[14] Therefore, the chemical structure of the materials is a primary factor in ER performance.

Cyclodextrin (CDs) are cyclic molecules that consist of six to eight glucose units: α-, β-, γ-cyclodextrins with six, seven, and eight glucose units, respectively. Their cylindrical structures with cavities of about 0.7 nm deep and 0.5–0.8 nm inside diameter yield various

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unique properties. According to its host structure, CDs can form supramolecular complexes in solution or in the solid state with organic molecules, especially aromatics, through host–guest interactions.[17–20] In addition, polymers containing CDs also have the capacity to form supramolecular complexes.[21,22] The main applications of these polymers are related to foods, drug release, chromatographic techniques, catalysts, and absorbents, and some potential application fields include molecular switches and molecular wires.[19,21–25] β-Cyclodextrin crosslinked polymer contains a 3D molecular chain structure. With a lot of hydroxy (–OH) on it, this chain structure can arrange regularly under an electric field, and thus can be used as potential high-performance and nontoxic ER materials.

Lately, the supramolecular complexes of β-cyclodextrin–epichlorohydrin crosslinking polymer/1-(2-pyridlazo)-2-naphthol (β-CDP-PAN) particles were synthesized and then mixed with silicon oil to prepare the ER fluids.[26,27] It was found that the β-CDP-PAN ER fluid showed a notable ER effect, due to the enhancement of dielectric properties by the structural change of β-CDP. However, it is also found that β-CDP synthesized only by β-cyclodextrin and epichlorohydrin can't endure a high electric field for a long time and is restricted to polarize in the electric field because it has a very rigid and dense CDs cavity in polymer molecules. Therefore, modification of β-CDP's polymer chains is worthwhile for the practical use of this material.

The ER effects of the starch/silicone oil system have been known since the pioneering work of Winslow.[28] This system has advantages in some aspects, such as antisedimentation, electric field endurance, nontoxicity, etc., but it almost loses ER effects when the particles have no water, thus preventing practical use. By proper modification of the β-CD polymer chain, this paper is an attempt to conquer some shortcomings and to prepare perfect electroherological materials by copolymerization of β-CD and epichlorohydrin in the presence of water-soluble and water-insoluble starch.

EXPERIMENTAL

Materials and instrumental

β-CD was provided by Shantou (China). Epichlorohydrin (EPi), water-soluble starch, and water-insoluble starch were purchased from Xi'an (China). All reagents were used without further purification.

IR spectra were recorded on a Bruker Equinox-55 using KBr pellets. Raman spectra were recorded on a JYU-1000 laser Raman spectra recorder. The shear stresses of the ER fluids were measured via a system consisting of a rotary rheometer (NXS-11A, China) and a high-voltage dc power source (GYW-010, China). The yield stress was measured on a parallel-plate force transducer. The dielectric properties of ER fluids were measured using an Automatic LCR Meter 4225 (Germany).

Synthesis of β-cyclodextrin–epichlorohydrin polymer and β-cyclodextrin–epichlorohydrin–starch polymer

A typical synthesis procedure is for a molar ratio EPi/CD = 10 and NaOH = 20% w/w is described below:[29] a mixture of 0 g starch (or 11.3 g water-soluble starch or 11.3 g crosslinked starch), 50 g β-CD, 25.4 g NaOH, and 102 mL water was stirred at 25°C for 24 h and 34 mL of epichlorohydrin was slowly added dropwise. The temperature was monitored during polymerization and kept at 50°C. The reaction was stopped after gel formation for 1 min by addition of acetone. After 30 min, acetone was removed and a pale yellow gel was obtained. The gel was washed liberally with distilled water until no chloride ion remained in aqueous solution and then was filtered and vacuum dried at 75°C for 12 h, and NS-β-CDP (46.5 g), WSS-β-CDP (47.0 g), and CLS-β-CDP (37.6 g) were obtained.

Preparation of ER material

The particles were ground by a mortar, passed through a 10-μm sieve to control the particle size and distribution. ER fluids were prepared by dispersing the dried NS-β-CDP, WSS-β-CDP, or CLS-β-CDP particles in silicone oil (ϵ_f = 2.60–2.80, σ_f = 10^{-12} to 10^{-13} S/m, ρ = 0.9–1.0 g/cm^3, $\eta \approx$ 500 mPa · s) dried at 150°C for 2 h before use with a 39% volume fraction, respectively, and then dried in a vacuum oven before use.

RESULTS AND DISCUSSION

Characterization and dielectric properties

Figure 1 shows FT-IR spectra of CLS-β-CDP, WSS-β-CDP, NS-β-CDP, and β-CD. The similar peak-shaped vibration of polymers and β-CD implies that polymers keep the original characteristic structure of β-CD. The characteristic bands of –OH strongly appear at nearly 3,440 cm^{-1} (O–H of stretching) and 1,640 cm^{-1} (O–H of plane bending). Also, the characteristic bands of CD are observed at 1,028–1,159 cm^{-1} (C–O and C–O–C of stretching). Compared with β-CD, the absorption of the polymers are wider and weaker, demonstrating that new ether bonds exist and resulted in the polarity decreasing. In addition, there are no peaks appearing at 1,265 cm^{-1} in the polymers, suggesting that all epichlorohydrin participate in the reaction and all chlorine are substituted thoroughly.
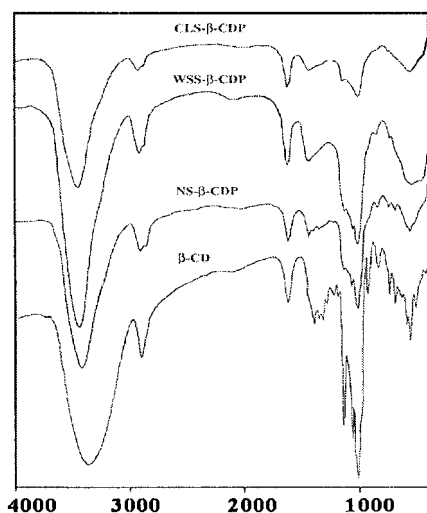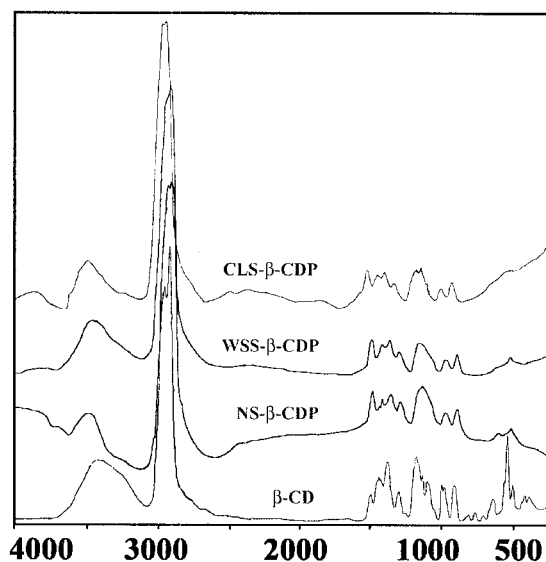
Figure 1   IR spectra of CLS-β-CDP, WSS-β-CDP, NS-β-CDP, and β-CD.

Figure 2 shows Raman spectra of CLS-β-CDP, WSS-β-CDP, NS-β-CDP, and β-CD. Similar to FT-IR spectra, Raman spectra of polymers and β-CD are mimetic; this further proved that the original host structure of β-CD is kept in NS-β-CDP, WSS-β-CDP, and CLS-β-CDP. As seen in Figure 2, the vibration band of the glucose ring of CDs appears at 933, 934, 944, and 947 cm^{-1} for WSS-β-CDP, CLS-β-CDP, NS-β-CDP, and β-CD, respectively. Obviously, comparing WSS-β-CDP with NS-β-CDP, the shift of 11 wavenumbers is positive for the copolymerization between β-CD and water-soluble starch. In the same case, the peak of CLS-β-CDP is shifted to a lower wavenumber, confirming the copolymerization of β-CD and water-insoluble starch occurs. Considering the inductive effect, the reason of the shift for nearly 10 wavenumbers is possibly that the starch tail of WSS-β-CDP or CLS-β-CDP is a stronger electron acceptor than the glycerol tail of NS-β-CDP, and in the meantime, the decline for around 14 wavenumbers from the pure β-CD is certainly understood. It is well known that the inductive effect is limited in a molecule. Thus, the peak of WSS-β-CDP at 933 cm^{-1} is similar to that of CLS-β-CDP. Also, the vibration bands of NS-β-CDP and β-CD have minor differences here. According to IR and Raman spectroscopy, we therefore conclude that, not only did the formation of polymers all keep the structure of β-CD, but also the WSS-β-CDP or CLS-β-CDP we obtained is really a copolymer of β-CD and starch, and not a simple mixture of them. The schematic structure of the synthesis of polymers is shown in Figure 3.

Our aim was to investigate polymers by IR and Raman spectroscopy and especially to find some relationships between the characteristic strength of polymers and their dielectric properties. It is well known that the strength in IR is related to the change of dipole

in the molecule, whereas the strength in Raman is in connection with the change of induced dipole in the molecule. Figure 4 gives the relative strength of some groups of polymers via NS-β-CDP, WSS-β-CDP, and CLS-β-CDP in a sequence. As seen in Figure 4, the ratio of the relative strength of v_s (C-O)/δ (O-H) in FT-IR increases from NS-β-CDP to WSS-β-CDP to CLS-β-CDP, of which CLS-β-CDP is 1.09 times than that of NS-β-CDP and 1.04 times than that of WSS-β-CDP. This result suggests that the polarity of the C–O bond in CLS-β-CDP is the strongest among the three polymers and increases with the formation of the copolymer between β-CD and starch. In Raman spectrometry, the ratio of the relative strength of v_s (C–H)/v_s (O–H) of WSS-β-CDP (5.07) and CLS-β-CDP (5.14) is nearly the same and that of NS-β-CDP (3.38) is the smallest, implying that the induced dipole of the C–H bond also increases when starch participates in the bonding. Although the dipole of C–H and C–O is smaller than that of O–H in the polymers, they are the greatest in number, thus the dipole of the polymer molecule increases in a sequence of NS-β-CDP to WSS-β-CDP to CLS-β-CDP.

To prove the above opinion and to give a reasonable explanation of ER effects, dielectric properties of the ER fluids were measured at room temperature through the frequency range 10^2 to 10^4 Hz. For the ER fluids of NS-β-CDP, WSS-β-CDP, and CLS-β-CDP, the dielectric constant (ϵ) and conductivity (σ) were measured as shown, respectively, in Figure 5. As shown in Figure 5, the dielectric constant of CLS-β-CDP ER fluid is 1.30 times than that of NS-β-CDP ER fluid and 1.08 times than that of WSS-β-CDP ER fluid (1000 Hz, 20°C). The conductivity is 1.55 times than that of NS-β-CDP ER fluid and 0.93 times than that of WSS-β-

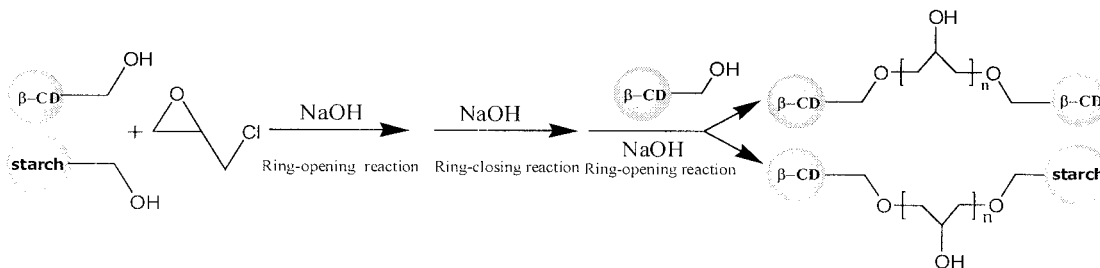**Figure 2**   Raman spectra of CLS-β-CDP, WSS-β-CDP, NS-β-CDP, and β-CD.

Figure 3　Scheme of the preparation of polymers.

CDP ER fluid (1,000 Hz, 20°C). These results show that the dielectric properties of CLS-β-CDP ER fluid are similar to that of WSS-β-CDP ER fluid and increased obviously compared with NS-β-CDP ER fluid. Apparently, this is in accordance with the results of IR and Raman spectroscopy. From the dielectric properties of these polymers' ER fluids, it can be seen that the dielectric constant decreased quickly but that the conductivity was increased rapidly with an increase in frequency. Due to interfacial polarization, the dielectric constant at low frequency is usually large, but with the emergence of loss peak at critical frequency, ϵ values at high frequency completely declined.[30] It is well known that, for a high dielectric constant and dielectric loss, proper conductivity is the physical base to obtain the critical optimum electrorheological effect.[6] In this paper, the dielectric constant of the copolymers' ER fluid was increased and the conductivity remained around 10^{-8} S/m. These properties are customary for the electrorheological effect.

Rheological properties

Generally, the yield stress and corresponding leaking current density are widely accepted as the most common standard to evaluate ER properties. Figure 6 shows the change of yield stress of NS-β-CDP, WSS-β-CDP, and CLS-β-CDP ER fluids, as well as leaking current density of their ER fluids (volume fractions of 39% in silicon oil) with the increase of dc field at 20°C, respectively. It can be seen from the curves that both WSS-β-CDP and CLS-β-CDP ER fluids display a good ER effect. The yield stress of WSS-β-CDP ER fluids is 6.2 kPa at 4 kV/mm, whereas it is 5.7 kPa for the CLS-β-CDP and 4.6 kPa for the NS-β-CDP at the same electric field, respectively. This value is 35% higher than that of the NS-β-CDP and 9% higher than that of CLS-β-CDP. It is noted that the β-CD suspension has no ER effect, even in the strong electric field. Hence, the glycerol tail or the glycerol bridge of NS-β-CDP, like a ligament connecting CDs, plays a significant role in the ER effect. The polymer formation results in the structural change of β-CD and further leads to the change of polarization properties, even though it is through bonding with starch. However, in the rheological measurements, we found that NS-β-CDP ER fluid cannot endure a strong electric field for a long time and it only remains a few minutes at 5 kV/mm. Based on this reason, we selected two types of starch to modify the structure of NS-β-CDP for obtaining the high performance ER materials. The experimental re-
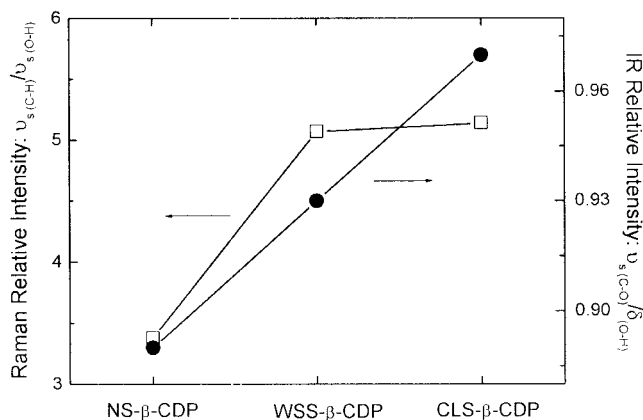

Figure 4　The curve of relative intensity ratio of groups of NS-β-CDP, WSS-β-CDP, and CLS-β-CDP in IR and Raman spectra.
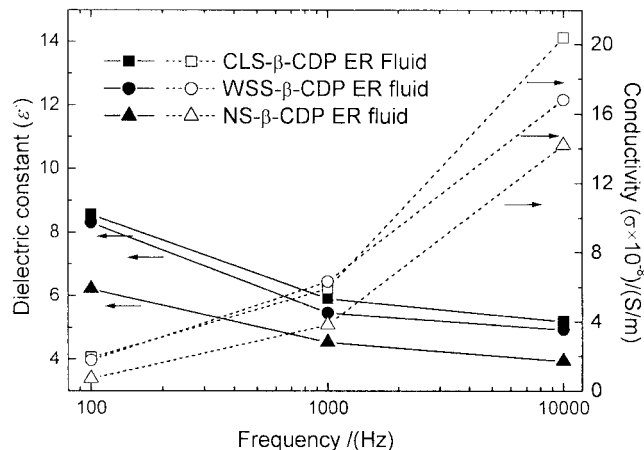
Figure 5　The curve of dielectric constant and conductivity of CLS-β-CDP-, WSS-β-CDP-, and NS-β-CDP-based ER fluids (φ = 39%) versus frequency at 20°C.
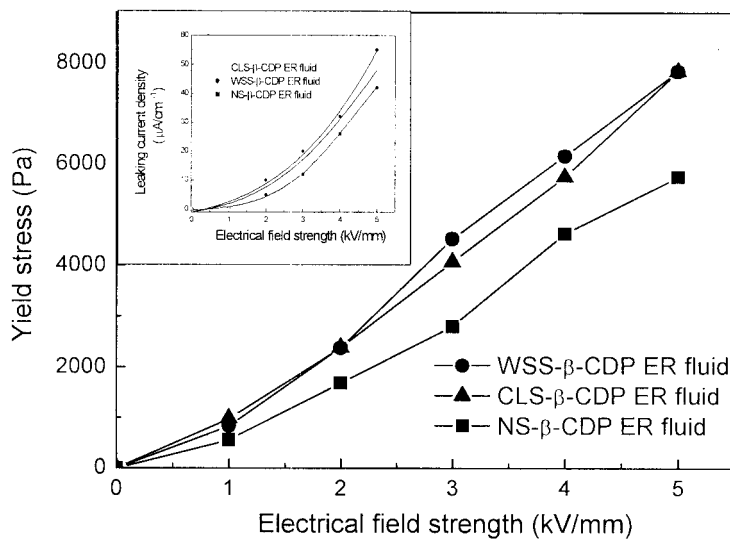
Figure 6 The yield stress of WSS-β-CDP-, CLS-β-CDP-, and NS-β-CDP-based ER fluids (φ = 39%) versus electric intensity (T = 20°C).

sults agreed well with our opinion. According to our structural characteristics, the reasonable explanation is that the copolymer formation between β-CD and starch (water-soluble or water-insoluble starch) results in the change of the structure as well as its properties. Compared with NS-β-CDP, the obvious difference is that CDs in copolymer are connected by the starch tail. It is well known that either water-soluble or water-insoluble starch certainly belongs to macromolecules. Thus, the polymer effect of starch and the dispersible action, which can disperse the gel network structure and tie CDs in order, are greatly contributed to ER effects, including the improvement of long duration in a strong electric field. In addition, the leaking current densities of ER fluids of polymers are around 30 μA/cm^2 at 5 kV/mm.

The shear stress of WSS-β-CDP ER fluid (39 vol %) versus the change in shear rate was measured using a rotary viscometer under an applied electric field (ca. 0–3 kv/mm, 20°C), and the results are plotted in Figure 7. It can be seen that the ER fluid behaves as a Newtonian fluid in the absence of an electric field and as a Bingham fluid when subjected to an electric field and shows significant ER effects. The shear stress of the ER fluid increases with increasing shear rate. Under the conditions 39 vol %, 20°C, E = 3 kv/mm (dc), γ = 75.36 s^{-1}, and the shear stress (τ) of the ER fluid is 3.58 KPa, whereas τ is only 0.59 KPa in the absence of the electric field. The former is 6.07 times the latter. Furthermore, the temperature dependence of WSS-β-CDP ER fluid, as shown in Figure 8, is obviously satisfactory. The operating temperature was measured over the range 22–95°C. The shear stress of WSS-β-CDP ER fluid increases with the enhancement of temperature, and nearly remains at the maximum stress over the range 65–95°C, which shows that WSS-β-CDP ER fluid demonstrates a significant ER effect.

CONCLUSION

To improve the ER properties of β-cyclodextrin–epichlorohydrin polymer particles, two copolymers of β-cyclodextrin–epichlorohydrin–starch (water-soluble and water-insoluble) were proposed to prepare electrorheological particles, the structures of which were characterized by FT-IR and Raman spectrometry, respectively. These corresponding polymer particles then were mixed with silicon oil to prepare the ER fluids, respectively. It was found that the typical WSS-β-CDP or CLS-β-CDP ER fluid showed a significant ER effect, due to the enhancement of dielectric properties by the structural change of β-CD polymer. The yield stress is 6.2 kPa for WSS-β-CDP and 5.7 kPa for CLS-β-CDP under 4 kV/mm dc, with leaking current
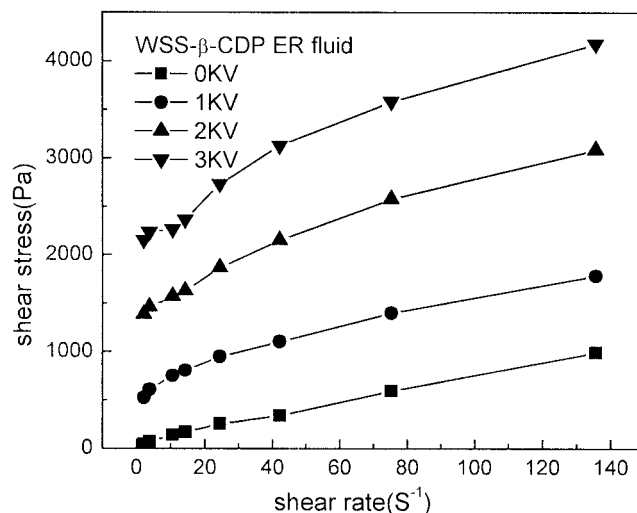
Figure 7 The curves of shear stress of WSS-β-CDP ER fluid (φ = 39%) versus shear rate (T = 20°C).
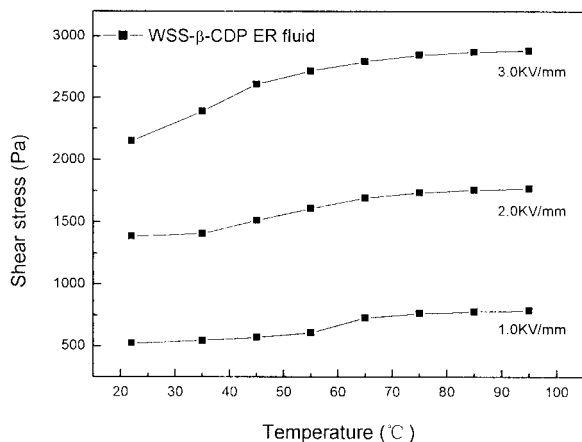
Figure 8 The temperature dependence of shear stress of WSS-β-CDP-based ER fluid ($\varphi = 39\%$) at different dc electrical fields and shear rate of 2.110S^{-1}.

density less than 35 μA/cm^2. The temperature dependence of the WSS-β-CDP ER fluid was also revealed to be a high performance ER candidate material in a high temperature range.

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