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Enhancing electrorheological behaviors with formation of β-cyclodextrin supramolecular complex

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Abstract

According to the point that the host structure and the properties can be easily modified by the formation of host–guest complex, the supramolecular complexes of β-cyclodextrin cross-linking polymer/1-(2-pyridlazo)-2-naphthol (β-CDP-PAN) particles were synthesized. Then the electrorheological properties of the suspensions of β-CDP-PAN particles in silicone oil have been investigated under DC electric fields. It was found that the yield stress of the typical β-CDP-PAN ER fluid was 6.16 KPa in 5 kV/mm, which is much higher than that of pure β-cyclodextrin polymer (β-CDP), that of pure 1-(2-pyridlazo)-2-naphthol (PAN) as well as that of the mixture of the host with the guest (β-CDP + PAN). The structure of β-CDP-PAN was characterized by the fluorescence analysis and IR spectrometry, respectively. The results confirmed that the naphthalene ring of PAN is included in the cavity of β-CDP. Just as expected, the improvement of dielectric constant, conductivity and loss tangent of β-CDP resulted in good ER effect of β-CDP-PAN. Furthermore, it was found that the cross-linking degree (CLD) of the polymer strongly influences the ER behavior of β-CDP-PAN and β-CDP. When CLD remains in the range of 4-6, β-CDP-PAN exhibits much stronger ER effect, and for β-CDP, its suitable range is 5–8.

Keywords: Electrorheological fluid; β-Cyclodextrin; Supramolecular complex

1. Introduction

Electrorheological (ER) fluids are such smart materials whose rheological properties (viscosity, yield stress, shear modulus, etc.) can be readily controlled using an external electric field. Because ER fluids can switch from a liquid-like material to a solid-like material within a millisecond, they can be used as electrical and mechanical interfaces in various industries, including the automotive industry, robotics, and the military industry [1–3]. However, some of the shortcomings of these materials, such as low shear stress, narrow working temperature range, easy sedimentation, high leak current and toxicity, have greatly restricted their industrial development [2,4,5]. Hence, research into ER fluids that are nontoxic and show useful properties and high performance is the key to ER technology.

Initial studies on the ER fluids covered various wet-base suspensions, including cornstarch, silica gel, and cellulose as dispersed phases. In the wet-base systems, ER particles contained small amounts of water, typically adsorbed on the particle surface [6]. Many shortcomings are pertinent to these systems, for example, a narrow working temperature range due to water evaporation at high temperature and solidification at low temperature, a high current density due to the high conductivity of water, and device erosion caused by water [1]. Thus, it is quite nature that many kinds of water-free ER materials were developed, such as alumino-silicate [7,8], fullerene-type [9], high-T_C superconducting [10], micro-composite particles [6] and nanostrutural compounds [11,12]. Particularly, semiconducting polymers, including poly(acene quinone) radicals [13], polyaniline [14] copolypyrrole [15], and copolyaniline [16] have been widely adopted as materials for anhydrous ER fluids. But these materials also have some limitations such as toxicity, etc.

Recently, some organic polymers that contain polysaccharide or consist of glucose units, such as chitosan [17,18],

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phosphate cellulose [19], kaolinite-carboxymethyl starch [20] and polysaccharide/titanium oxide [21], have been adopted as anhydrous ER fluids. One of the advantages of these materials is no toxicity. Note that those wet-base materials including cellulose and starch have been converted into the dry-base materials that exhibit high performance ER effect by the modified structures. In fact, the high performance ER materials are closely related to their molecular structures. With the developing of ER materials, it is clear that those materials that possess either branched polar groups such as amine ($-NH_2$), hydroxy ($-OH$) and amino-cyano ($-NHCN$), or semi-conducting repeated groups. The polar groups may affect the ER behavior by playing the role of the electronic donor under the imposed electric field [19]. Therefore the chemical structure of the materials is a primary factor in the ER performance.

In recent years, much attention has been focused on molecular self-assembly. Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, regular and structurally well-defined aggregates joined by noncovalent interactions (hydrogen bonding, Van der Waals forces, electrostatic forces, $\pi-\pi$ interactions, size effect, etc.). Using molecular self-assembly to build supramolecular systems may give rise to many unique structural characteristics and novel physical/chemical properties [22–25]. Supramolecular chemistry, one of important branches in the self-assembly field, has taken a rapid progress in recent years. Cyclodextrins (CDs) are cyclic molecules which 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 unique properties [26]. In particular, CDs form supramolecular complexes in solution or in the solid state with organic molecules, especially aromatics, through host–guest interactions. In addition, polymers containing CDs also have the capacity to form supramolecular complexes [27–29]. The main applications of these complexes are related to chromatographic techniques [30, 31], catalysts [32], absorbents [33], and some potential applications fields including molecular switches and molecular wires [34,35]. Up to now, it has not been found to apply CDs complexes to ER materials.

In this paper, we use a kind of β-cyclodextrin polymer as the host to build supramolecular complex. There are two routes to affect the properties of β-CDP used as a basic ER material. One is that β-CDP can form supramolecular complex with a suitable guest, therefore, the intrinsical dielectric and polarization properties of β-CDP could be easily modified by different guest molecules into its cavity. The other is that β-CDP is one of polymers whose structure can be controlled by the cross-linking degree (CLD). The CLD decides the size of polymer arms and shows the monomer content in the polymer. Sequentially, it acts as a key to link the microstructure and macro-property of the polymer. Therefore, the supramolecular complex of β-cyclodextrin polymer with 1-(2-pyridlazo)-2-naphthol (PAN) has been prepared, and ER fluids have been presented by dispersion of β-CDP-PAN, β-CDP and PAN particles in dimethyl silicone with volume fractions of 27–31%, respectively [36]. The schematic structure of the preparation of β-CDP-PAN and β-CDP ER fluids is shown in Fig. 1. The experimental results showed that the supramolecular complex with notable dielectric properties really have a good ER effect. Furthermore, the influences of β-CDP-PAN and β-CDP, the CLD of the polymer on the ER effects, have been investigated.

2. Experimental

2.1. Synthesis of β-CDP-PAN, β-CDP particles and preparation of the ER fluids

β-CD was provided by Shantou (China). Epichlorohydrin and PAN (dark red powder) were purchased from Xi'an (China). All reagents were used without further purification.

A typical synthesis procedure [27,29] for a molar ratio EP/β-CD $= 10$ and NaOH $= 20\%$ w/w is described below: a mixture of 3.4 g soluble starch, 15 g β-cyclodextrin and an aqueous solution of 34 ml 20% NaOH was stirred at 50 °C and 12 ml of epichlorohydrin was slowly added with dropwise. The temperature was monitored during polymerization and kept at 50 °C. The reaction was stopped after 2 h 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, then filtered and dried at 110–120 °C for 12 h. A gray and insoluble product, β-CDP was obtained. The polymer was ascertained to have retained the characteristic structure of β-CD by IR spectroscopy [27] and the ratio of components (EP/β-CD) of the polymer was determined by the phenol-sulfuric acid method [37]: 25 mg dried polymer particle was immersed in a solution of 15 ml 0.5 mol. dm^{-3} H_2SO_4, hydrolyzed at 100 °C for 6–8 h, diluted in a volumetric flask by water, and then obtained a 250 ml hydrolytic solution. An aqueous solution of 3 ml 5% phenol was added to 1 ml the hydrolytic solution, mixed with 5 ml concentrated sulfuric acid and then recorded on a TU-1901 UV–Vis spectrophotometer at 490 nm after 20 min. Sequentially, several polymers were obtained at various reaction time ($T = 0$, 110, 120, 60 and 150 min) as well as their components, respectively. Here, the definition of the cross-linked degree (CLD) is one β-CD contains molecular numbers of epichlorohydrin in the polymer, so CLD of the polymers (0, 4.0, 4.6, 6.0 and 10.0) were determined, respectively.

The supramolecular complexes of β-CDP-PAN particles were prepared by self-assembly. 10 g β-CDP was ground into fine powder, immersed in water for 1–2 h, and then filtered. The mixture was added to a saturated alcohol

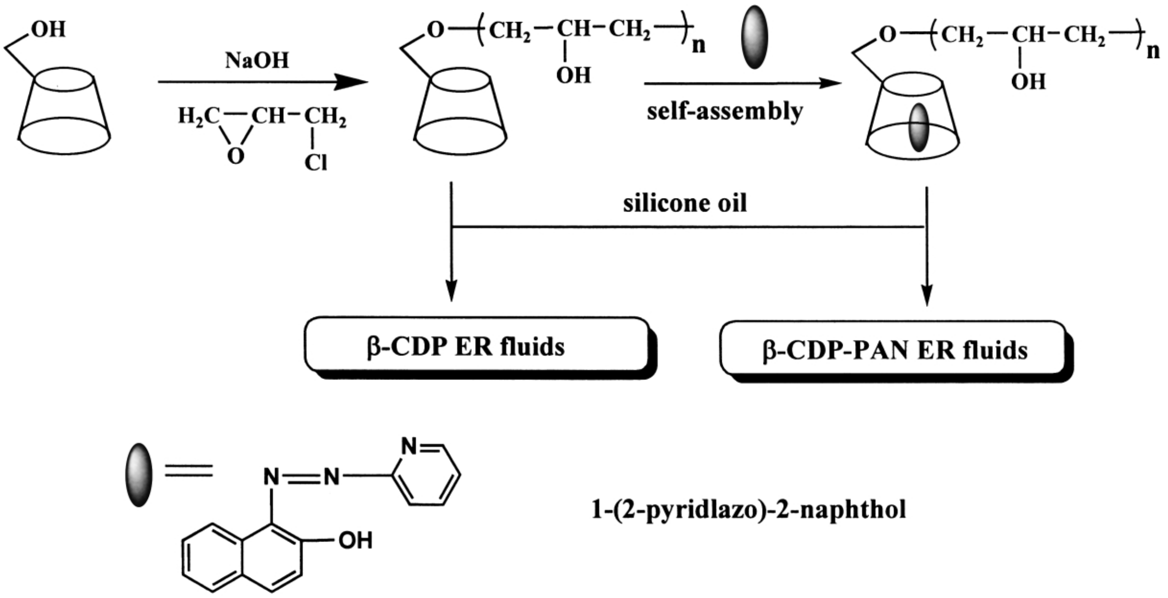

Fig. 1. Schematic structure of the preparation of β-CDP-PAN and β-CDP ER fluids.

solution of PAN, kept for 24 h, filtered and washed with distilled water until no color was found in aqueous solution. The filter residue was dried for 10 h at 110–120 °C and β-CDP-PAN particles were obtained. Similarly, the different CLD of β-CDP-PAN particles (CLD = 0, 4.0, 4.6, 6.0 and 10.0) were achieved with the different β-CDP.

ER fluids were prepared by dispersing the β-CDP-PAN (CLD = 0, 4.0, 4.6, 6.0 and 10.0), β-CDP (CLD = 0, 4.0, 4.6, 6.0 and 10.0), PAN, β-CDP + PAN (mixture of β-CDP with PAN, the molar ratio β-CD/PAN was 1:1, CLD = 4.6) particles in a nonconductive dielectric silicone oil ($\varepsilon_f = 2.60-2.80$, $\sigma_f = 10^{-12}-10^{-13}$ S/m, $\rho = 0.9-1.0 \times$ g/cm^3, $\eta \approx 500$ MPa S (25 °C)) in volume fractions of 27–31%, respectively, which were ground by a mortar, passed through a 10 μm sieve to control the particle size and distribution, and then dried in a vacuum oven before use.

2.2. Measurement

The chemical structure of β-CDP-PAN was characterized employing fluorescence spectra (Fig. 2) and IR (Fig. 3). Fluorescence emission spectra were recorded on a PE LS50B fluorescence spectrophotometer ($\lambda_{ex} = 400$ nm, ($S_{em} = 8$ nm)/($S_{ex} = 8$ nm)). IR spectra were recorded on a Bruker Equinox-55 using KBr pellets. Absorbency data were recorded on a TU-1901 UV–Vis spectrophotometer. 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 with a parallel-plate force transducer. The dielectric properties of ER fluids were measured using Automatic LCR Meter 4225 (Germany).

3. Results and discussion

3.1. Characterization of β-CDP-PAN

Fig. 2 gives the fluorescence spectra obtained at $\lambda_{ex} = 400$ nm of β-CDP-PAN, PAN, β-CDP and a simple mixture (β-CDP + PAN) of β-CDP with PAN (the molar ratio of PAN is the same as that in β-CDP-PAN). The spectrum of PAN shows that the peaks at 486, 545 and 600 nm in a solid sample. Also, for β-CDP-PAN, three peaks are observed at the same wavelength as PAN. Obviously, β-CDP-PAN causes strikingly larger increase in fluorescence than β-CDP and PAN in the wavelength range tested from 510 to 700 nm. In addition, β-CDP-PAN shows enhanced fluorescence with a ratio of the relative intensities at 545 and 600 nm, which I_{545}/I_{600} is 1.01 for β-CDP-PAN and 0.58 for PAN. However, no fluorescence enhancement is observed for the simple mixture and virtually nonfluorescent for β-CDP in this case. Therefore, it gives the evidence to the

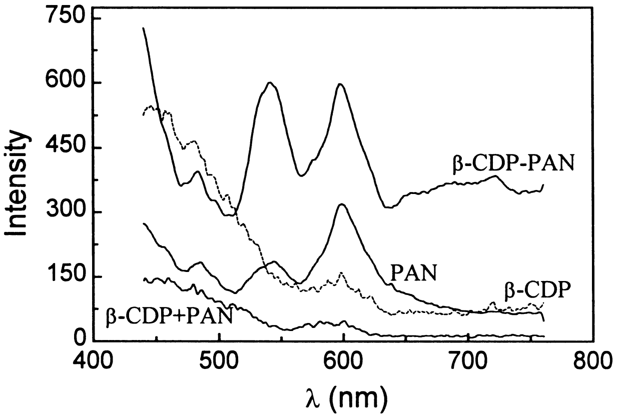

Fig. 2. Fluorescence spectra of β-CDP-PAN, PAN and β-CDP (CLD = 4.6).

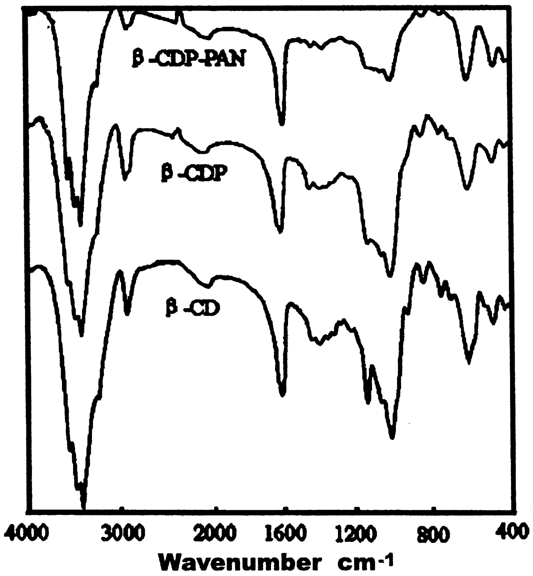

Fig. 3. IR spectra of β-CDP-PAN, β-CDP and β-CD (CLD = 4.6).

structural unit of PAN in the supramolecular complex, the fact indicating that the fluorescence change is caused by formation of a complex.

Fig. 3 shows IR spectra of β-CD, β-CDP and β-CDP-PAN. The similar peak-shaped variation of β-CDP and β-CD implies that β-CDP keeps the original structural character of β-CD. Also, the characteristic bands of CD are observed at 1028–1159 cm^{-1} (C–O and C–O–C of stretching, named Band A) and at 1624 cm^{-1} (O–H of plane bending, named Band B) for β-CDP-PAN. However, the relative intensities of β-CDP-PAN and β-CDP are very different from Band A and Band B. For β-CDP-PAN, the relative intensity of Band B is stronger than that of Band A, while they reverse for β-CDP. Obviously, the complex formation between β-CDP and PAN results in the change of polarity in or around CD cavity, and suggests that the polarity of CD cavity decreases and that of the hydroxyl group in CD entrance increases. When the internal cavity does not include any guest molecular, a few of water molecules exist in it according to the literature [26], the change of the relative intensity shows that PAN is included in CD cavity due to the polarity of PAN is less than that of water molecules. Hence, these results further indicate that the smallest polarity group among PAN molecule, naphthalene ring of PAN, is thought to be included in the cavity of β-CDP.

Su et al. reported [27] that the ratio of the complex between β-CDP and PAN is 1:1, but they thought that azo group of PAN is included in the cavity. In order to further prove our points, we used Chem3D to simulate the structure of the complex between β-CD and PAN. Examination of molecular models indicates that PAN is too large to be completely included in a single β-CD cavity, which can accommodate only one aromatic ring, either the naphthalene ring or the pyridine ring can enter the β-CD cavity. Since the naphthalene ring may be more hydrophobic than the pyridine ring, the first binding of PAN to CD could occur with the naphthalene ring, leaving the pyridine ring still exposed to the outside CD. Model studies further shows that PAN is not able to penetrate the β-CD cavity and the azo group of PAN in the cavity is difficult. Fig. 4 shows a proposed structure of the complex between β-CD and PAN.

3.2. Dielectric properties

The dielectric properties of the ER fluids were measured at room temperature in the range of 10^2 to 10^4 Hz. For the ER fluids of β-CDP-PAN, β-CDP and PAN, the dielectric constant (ε), conductivity (σ) and dielectric loss ($tg\delta$) were measured as shown, respectively, in Figs. 5 and 6. From the figures it can be seen that ε, σ and $tg\delta$ were increased by different degrees in PAN (except for ε), β-CDP and β-CDP-PAN sequence. As shown in Fig. 5, the dielectric constant of β-CDP-PAN ER fluid is 1.2 times than that of the pure β-CDP ER fluid, 2.1 times than that of the pure PAN ER fluid (100 Hz, 22 °C). The conductivity is 2.5 times than that of the pure β-CDP ER fluid, 20.3 times than that of the pure PAN ER fluid (1000 Hz, 22 °C). In Fig. 6, the dielectric loss of the supramolecular complex ER fluid is 1.9 times than that of the pure β-CDP ER fluid (1000 Hz, 22 °C). These results show that the dielectric properties of the supramolecular complex ER fluid were increased obviously compared with the pure β-CDP or PAN ER fluid. From the dielectric properties of β-CDP-PAN and β-CDP 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 interfacical 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 were completely declined [38,39]. It is well known that a high dielectric constant and dielectric loss, proper conductivity is the physical base to obtain the critical optimum ER effect [1]. In this paper, the dielectric

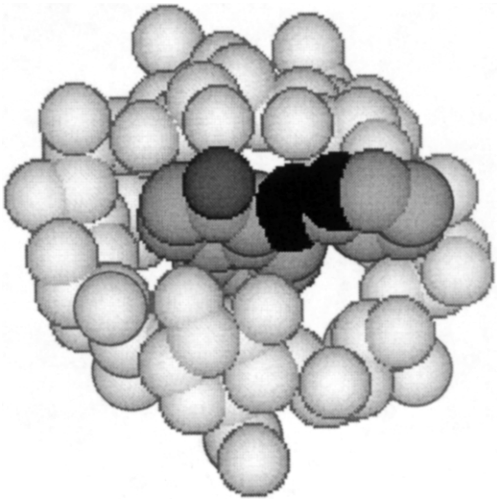

Fig. 4. The proposed structure of the complex between β-CD and PAN.

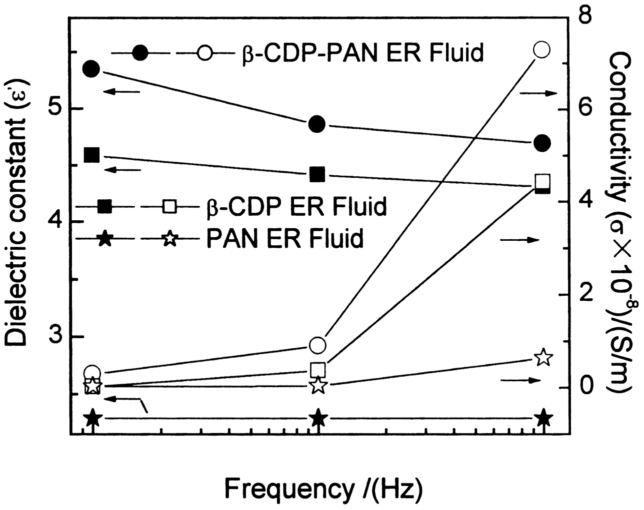

Fig. 5. Dielectric constant and conductivity vs. frequency for β-CDP-PAN, β-CDP and PAN ER fluids ($\Phi = 31\%$, CLD = 4.6).

constant and dielectric loss of the supramolecular complex ER fluid were both increased notably and the conductivity remained around 10^{-8} S/m. These properties are customary for the ER effect. However, the dielectric constant of PAN ER fluid has no change with the enhancement of the frequency and it is similar to that of silicone oil (2.60–2.80). According to the dielectric constant mismatch model [40], PAN ER fluid has, therefore, no ER effect.

3.3. Rheological properties

Generally, the yield stress and corresponding leaking current density are widely accepted as the most common standard to evaluate ER properties. Fig. 7 shows the change of yield stress of β-CDP, PAN, the mixture of β-CDP + PAN and β-CDP-PAN ER fluids, as well as leaking current density of β-CDP-PAN ER fluids (volume fractions of 31% in silicon oil, CLD = 4.6) with the increase of DC field at 22 °C, respectively. It can be seen from the curves that the β-CDP-PAN ER fluid displays a good ER effect. The yield stress of β-CDP-PAN ER fluids is 6.16 KPa at 5 kV/mm, whereas it is only 1.26 KPa for the pure β-CDP, 0 KPa for the pure PAN and 1.78 KPa for the β-CDP + PAN at the same electric field, respectively. This value is about 4.9 times that of the pure β-CDP and 3.5 times that of β-CDP + PAN. It is note that the pure PAN suspension has no ER effect even in the strong electric field, and the simple mixture β-CDP + PAN suspension has slightly enhancement compared with β-CDP ER fluid, in the meantime, the β-CDP-PAN ER fluid is much stronger than that of the pure β-CDP. Such observed ER phenomena are hard to explain if PAN would be regarded as an additive. Generally, additives can adsorb on the surface of the dispersed particles [41]. In fact, the surface effect of PAN is quite little in the β-CDP-PAN ER fluid as well as in the β-CDP + PAN suspension. According to our structural characteristics, the reasonable explanation is that the supramoleular complex formation between β-CDP and PAN results in the change of the host structure as well as its properties. In addition, the leaking current density of β-CDP-PAN ER fluids is less than 5 μA/cm^2 at 5 kV/mm. This shows that β-CDP-PAN ER fluids may be regarded as anhydrous ER materials.

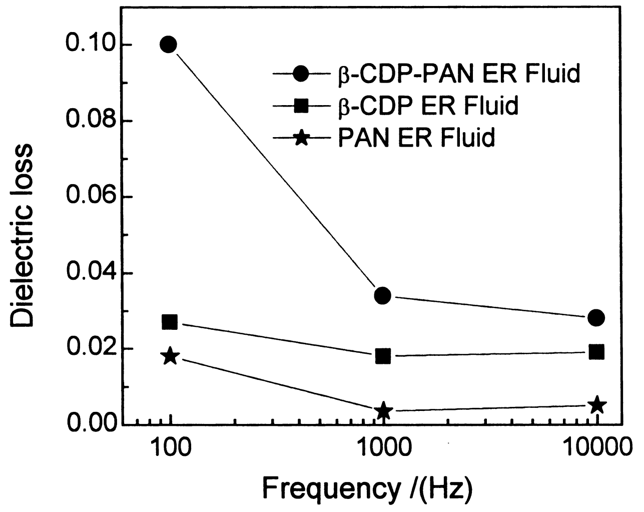

Fig. 6. Dielectric loss vs. frequency for β-CDP-PAN, β-CDP and PAN ER fluids ($\Phi = 31\%$, CLD = 4.6).

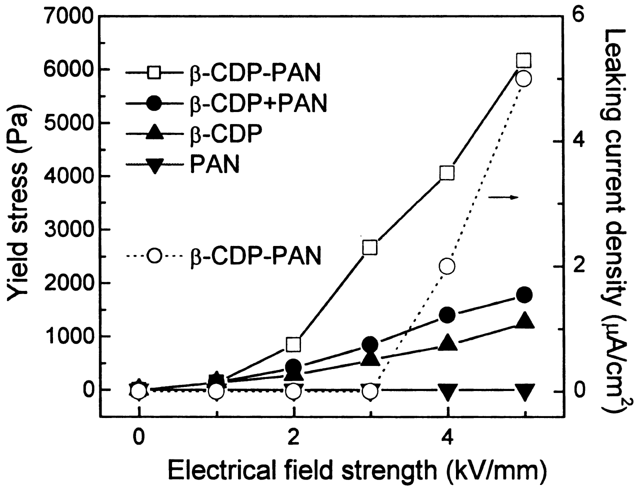

Fig. 7. The yield stress of β-CDP-PAN, β-CDP + PAN, β-CDP and PAN ER fluids ($\Phi = 31\%$, CLD = 4.6) vs. electric intensity ($T = 22$ °C).

Fig. 8 gives the relation of β-CDP-PAN and β-CDP ER fluids between shear stress and shear rate under an applied electric field (0–3.5 kv/mm, 22 °C). It can be seen that the β-CDP-PAN ER fluid behaves as Newtonian fluid in the absence of electric field and as Bingham fluid when subjected to an electric field. The widely accepted ER mechanisms suggest that particle polarization is responsible for the interaction forces between particles, which leads to rheological change in the ER fluids. The parameters in connection with particle polarization, such as high dielectric constant, suitable dielectric loss and conductivity, play an important role for high performance ER materials [1]. The dielectric properties of β-CDP-PAN ER fluid was improved

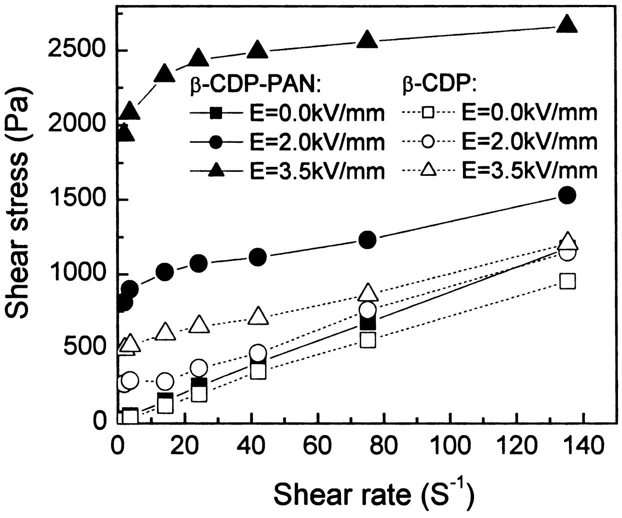

Fig. 8. The curves of shear stress of β-CDP-PAN and β-CDP ER fluids ($\Phi = 27\%$, CLD = 4.6) vs. shear rate ($T = 22$ °C).

by the supramolecular complex formation compared with the pure β-CDP ER fluid, so the shear stress of β-CDP-PAN ER fluid was increased notably.

Fig. 9 shows the variation of shear stress of β-CDP-PAN and β-CDP ER fluid with the increase of the temperature under 3 kV/mm (DC). It can be seen that the shear stress of β-CDP-PAN (1.9 KPa, 22 °C) increases gradually with the increase of the temperature, and it approaches to the max (2.9 KPa) when the temperature reached about 65 °C. After this temperature, however, the shear stress decreases gradually (2.8 KPa, 75 °C), and the leaking current density increases abruptly with the increase of temperature. In addition, the shear stress of β-CDP-PAN ER fluid is higher than that of β-CDP though it increases gradually with the increase of the temperature. The temperature range of ER fluid is one of the most important parameters to evaluate ER effect [36,37]. Generally, the temperature has two effects on the ER fluid: the effect on the polarization intensity of particle as well as Brownian motion. The increase of the temperature results in the decrease of activation energy polarized by electric field, but results in the increase of the polarization ability of the particle. On the other hand, Brownian motion does not contribute to the chain formation of the β-CDP-PAN particles. As a result, the ER effect decreases with the increase of the temperature while the leaking current density increases.

The sedimentation property of ER materials is one of the main criterion to evaluate whether the materials can be commercialized [5]. The property of the ER fluids decreases abruptly with the increase of the sedimentation of the particles, and this can be realized by controlling the size of the particles, preparing hollow particles or porous particles, selecting the base solution with close density and adding surfactant. The β-CDP-PAN ER fluid posses more long-term stability against sedimentation than the pure β-CDP ER fluid. For β-CDP-PAN, less than 3% oil of total volume fluid could be observed after standing the β-CDP-PAN fluid for 150 h and even longer period. As shown that in Fig. 10, the sedimentation ratio of β-CDP-PAN ER fluid is about 97% in 150 h and that of β-CDP is only about 80% indicating the stability of ER fluid can be changed due to the complex formation between β-CDP and PAN.

3.4. Influences of CLD on yield stress of β-CDP-PAN and β-CDP

The CLD plays an important role for a polymer. The higher CLD has the larger mechanical strength of the polymer. Also, it has greatly influences on β-CDP-PAN or β-CDP ER effect. The yield stress of β-CDP-PAN (left) and β-CDP (right) under various *E* and CLD are shown in Fig. 11, respectively. Obviously, the yield stress of them always increases with *E* but it appears a maximum when CLD

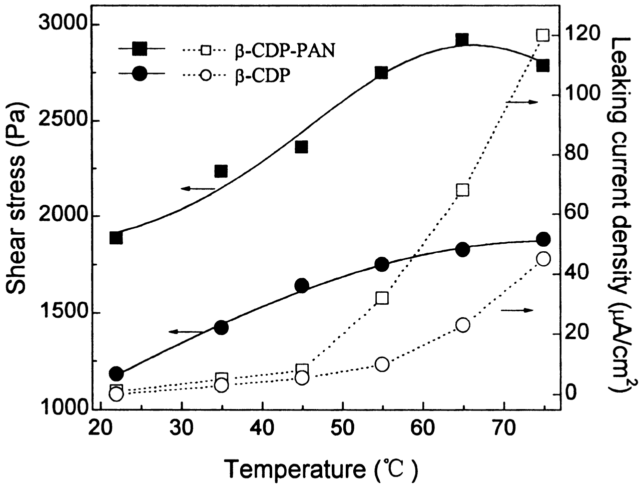

Fig. 9. The temperature dependence of shear stress of β-CDP-PAN and β-CDP ER fluids ($\Phi = 27\%$, CLD = 4.6) at different shear rate of 2.110 S^{-1} ($E = 3$ kV/mm).

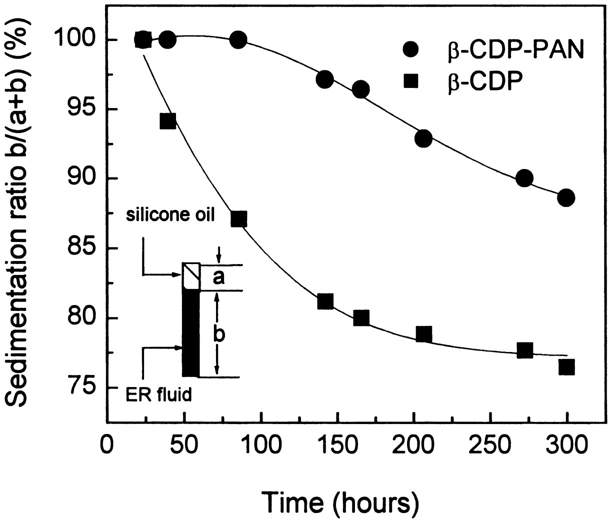

Fig. 10. The sedimentation ratio of β-CDP-PAN and β-CDP ER fluids ($\Phi = 27\%$, CLD = 4.6) at 22 °C.

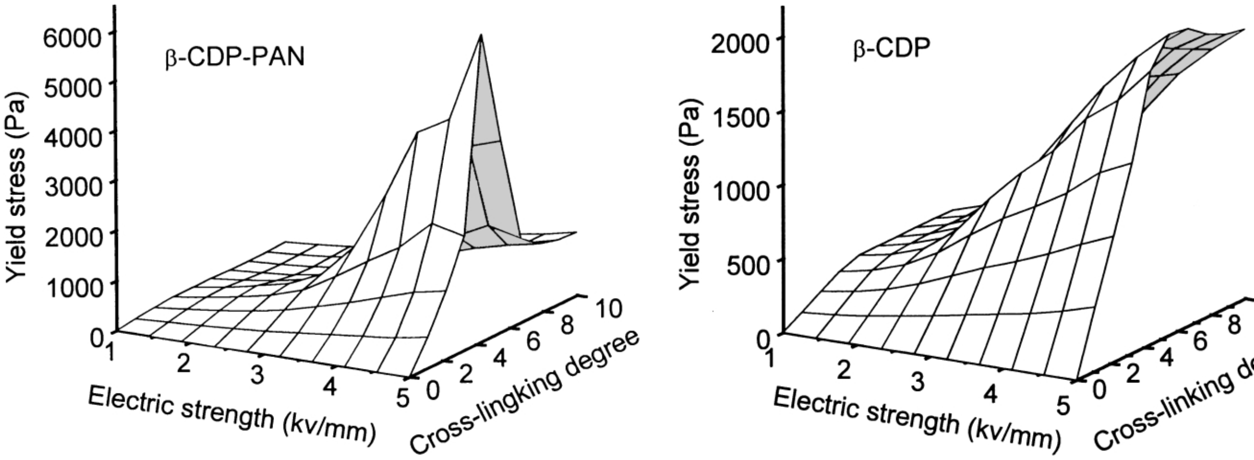

Fig. 11. The curves of yield stress of β-CDP-PAN (left) and β-CDP (right) ER fluids ($\Phi = 31\%$) under various E and CLD.

reaches a suitable value. When the electric field strength remains a certain value, the yield stress increases with CLD firstly, reaches the maximum and then decreases gradually. For example, the highest yield stress of β-CDP-PAN ER fluids is 6.2 KPa under a 5 kV/mm DC field when CLD is 4.6, and that of β-CDP is 2.7 KPa under the same electric field when CLD is 6. Thus, it is necessary to select a proprietary CLD range for β-CDP-PAN and β-CDP, respectively. The results indicate that the suitable CLD is in the range of 4–6 for β-CDP-PAN, 5–8 for β-CDP, respectively. Note that both β-CDP and its supramolecular complex have no ER effect when CLD is 0. Hence, CLD apparently influences the yield stress and makes it appear a maximum demonstrated the suitable CLD is quite important.

When CLD is 0, the dissociative β-CD is hard to get together regularly under an electric field. Once the cross-linking polymer forms, the polymer network is in favor of the formation of chainlike structure under the imposed electric field. However, the too high CLD means the reduction of their polarization strength due to the highly dense polymer network. Apparently, for β-CDP-PAN, the existence of the polarity group in PAN is very helpful in enhancing the polarization strength, and further makes its ER effect much stronger than β-CDP. Therefore, in this case, the CLD of the polymer plays an important role and like a bridge, which can combine the microstructure and the macro-property of the polymers. In the meantime, the supramolecular complex formation of cyclodextrin polymer is also an effective way to further change the microstructure and the macro-property of β-CDP.

4. Conclusion

A novel self-assembly technique was proposed to prepare the ER particles. The supramolecular complexes of β-cyclodextrin cross-linking polymer/PAN particles were synthesized and then mixed with silicon oil to prepare the ER fluids. It was found that the typical β-CDP-PAN ER fluid (CLD = 4.6) showed a good ER effect, due to the enhancement of dielectric properties by the structural change of β-CDP. The yield stress is 6.16 KPa (22 °C) under 5 kV/mm DC, with leaking current density less than 5 μA/cm^2. The temperature dependence and sedimentation stability were also improved simultaneously. Furthermore, the ER behaviors can be regularly affected by the CLD of the supramolecular complex. The results indicated that the suitable range of CLD was 4–6 for β-CDP-PAN. This technique provides a new route to design ER materials in chemical approach. The further study will be continued in the future.

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References

[1] Hao T. Adv Mater 2001;13:1847.
[2] Halsey TC. Science 1992;258:761.
[3] Block H, Kelly JP. J Phys D Appl Phys 1988;21:1661.
[4] Choi HJ, Lee YH, Kim CA, Jhon MS. J Mater Sci Lett 2000;19:533.
[5] Yin JB, Zhao XP. Mater Rev 2000;14(9):10. in Chinese.
[6] Kim SG, Kim JW, Choi MS, Choi HJ, Jhon MS. J Appl Polym Sci 2001;79:108.
[7] Filisko FE, Armstrong WF. European patent 0313351, 1989.
[8] Hao T, Xu Y, Xu Y. J Colloid Interface Sci 1997;190:334.
[9] Powell B. US Patent 5445759, 1995.
[10] Tao R, Zhang X, Tang X, Anderson P. Phys Rev Lett 1999;83:5575.
[11] Lu J, Zhao XP. J Mater Res 2002;17:1513.
[12] Choi HJ, Kim JW, Noh MH, Lee DC, Suh MS, Shin MJ, Jhon MS. J Mater Sci Lett 1999;18:1505.
[13] Choi HJ, Cho MS, Jhon MS. Polym Adv Technol 1997;8:697.
[14] Choi HJ, Kim TW, Cho MS, Kim SG, Jhon MS. Eur Polym J 1997;33:699.

[15] Goodwin JW, Markham GM, Vinent B. J Phys Chem B 1997;101:1961.
[16] Cho MS, Choi HJ, To K. Macromol Rapid Commun 1998;19:271.
[17] Choi US, Park YS, Lee SS. Colloid Surf A: Physicochem Engng Aspect 2002;211:85.
[18] Choi US. Colloid Surf A: Physicochem Engng Aspect 1999;157:193.
[19] Kim SG, Kim JW, Jang WH, Choi HJ, Jhon MS. Polymer 2001;42:5005.
[20] Wang BX, Zhao XP. J Mater Chem 2002;12:2869.
[21] Zhao XP, Duan X. J Colloid Interface Sci 2002;251:376.
[22] Fujita H, Ooya T, Yui N. Macromolecules 1999;32:2534.
[23] Maselko J. Mater Sci Engng 1996;C4(3):199.
[24] Whitesides GM, Mthias JP, Seto CT. Science 1991;254:1312.
[25] Pozuelo J, Mendicuti F, Mattice WL. Polym J 1998;30(4):479.
[26] Song LX, Zhou TY, Guo ZJ. Chin J Inorg Chem 2001;1:9. in Chinese.
[27] Su XD, Liu LZ, Shen HY. Anal Chem 1995;23(12):1361. in Chinese.
[28] Liu Y, Zhang DD. J Funct Polym 1995;8(1):3871.
[29] Renard E, Deratani A, Volet G, Sebille B. Eur Polym J 1997;33:49.
[30] Cserhati T, Bojarski J, Fenyvesi E, Szejtli J. J Chromatogr 1986;351:356.
[31] Crini G, Lekchiri Y, Morcellet M. Chromatographia 1995;40:296.
[32] Komiyama M, Hirai H. Polym J 1986;18(4):375.
[33] Komiyama M, Hirai H. Polym J 1987;19(6):773.
[34] Yoshida K, Shimomura T, Ito K, Hayakawa R. Langmuir 1999;15(4):910.
[35] Shimomura T, Yoshida K, Ito K, Hayakawa R. Polym Adv Technol 2000;11:837.
[36] Zhao XP, Gao ZW. Chinese Patent 011152028, 2001.
[37] Oubois M, Giller KA, Harmilton JK, Rebets PA, Smith F. Anal Chem 1956;28:350.
[38] Frost RL, Kristof J, Horvath E, Kloprogge KT. J Colloid Interface Sci 1999;214:318.
[39] Nakano M, Koyama K, editors. Proceeding of sixth international conference on ERF and MR suspensions. Singapore: World Scientific; 1998. p. 106.
[40] Davis LC. J Appl Phys 1992;72:1334.
[41] Duan X, Chen H, He Y, Luo W. J Phys D: Appl Phys 2000;33:696.