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Two roles of guest and crosslinked degree on hydrosoluble β-cyclodextrin polymer electrorheological fluids

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Abstract

As a potential candidate for the development of well-controlled electrorheological (ER) materials, five hydrosoluble β-cyclodextrin polymer (**2**–**6**)/3-hydroxy-2-naphthoic acid particles (**2′**–**6′**) were synthesized. Fluorescence analysis conformed that all the polymers can form 1:1 type supramolecular complex with the guest. The ER properties of suspensions of these particles in silicon oil have been investigated under DC electric field. The yield stress of the typical supramolecular complex (**5′**) ER fluid was 9.23 kPa at 4 kV/mm. It was much higher than that of pure β-cyclodextrin polymer **5**, pure 3-hydroxy-2-naphthoic acid (guest) as well as the mixture of the host and the guest (**5** + guest). Just because of the formation of supramolecular complex, the improvement of dielectric constant, conductivity and loss tangent of **5** resulted in the enhancement of **5′** ER effect. Meanwhile, the measurement of **2′**–**6′** dielectric properties was given the evidence that the molar crosslinked degree (m) of the polymer has strong influence on the supramolecular complex ER behavior as well as the host. It was found that the yield stress of the supramolecular complex ER fluid increases initially with m, reaches the maximum at $m = 7.53$ and finally appears a decline at $m = 8.89$, while that of the host has an enhancement trend with the increase of m.

Keywords: Electrorheological fluid; β-Cyclodextrin; Supramolecular complex

1. Introduction

Electrorheological (ER) fluids have been regarded as a smart material, which display abrupt and reversible changes from a liquid-like material to a solid-like material within a millisecond under an applied external electric field [1–4]. The ER responses can be controlled by electrical properties of two contiguous phases, strength and frequency of electric field, pH, temperature, and contents of dispersed particles and additives [5–10]. Because the ER responses accompany changes in the variety of ER fluid properties, including rheological, electrical, optical, thermal, volumetric, and acoustic properties, the dependences of these properties have been attracted much attention [11–14]. However, larger-scale utilization of ER fluids has not yet been realized since the present ER materials possess some disadvantages such as low shear stress, toxicity, sedimentation and so on [1,11]. In recent years, researchers have found that good ER materials can be designed by dispersion of particles with large dielectric constant, suitable conductivity, proper loss tangent and non-toxicity [1,15,16]. Hence, research into ER fluids that are non-toxic and show useful properties and high performance is the key to ER technology.

Recently, some organic polymers that contain polysaccharide or consist of glucose units, such as chitosan [17–19], phosphate cellulose [20], kaolinite-carboxymethyl starch [21] and polysaccharide/titanium oxide [22], have been adopted as anhydrous ER fluids. One of the advantages of these materials is no toxicity. Another is that they could overcome several shortcomings of hydrous systems, such as the temperature limitation, the degree mismatch between the particle and the oil, and an insufficient yield stress. Note 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, which the polar groups may affect the ER behavior by playing the

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role of the electronic donor under the imposed electric field [20].Thus, the chemical structure of the materials is a primary factor in the ER performance.

Cyclodextrins (CDs) and their derivatives have been the subject of numerous investigations [23–27]. These compounds have been found a large number of applications in many areas, since they have become available in high quantities, e.g. chromatographic techniques [28,29], catalysts [30], absorbents [31], and some potential applications fields including molecular switches and molecular wires [32,33]. Cyclodextrins are cyclic oligosaccharides consisting of six to eight glucose units linking through α-1,4-glycosidic linkages, and are called α-, β-, and γ-cyclodextrin (CD), respectively. Due to their polar hydrophilic outer shell and relatively hydrophobic cavity, they are able to build up host-guest complexes by inclusion of suitable molecules. Specially, polymers containing CDs also have the capacity to form supramolecular complexes [34,35]. Because the polymeric form can increase the stability constant of these complexes and can enhance the properties of host as well as guest, much attention has been attracted by researches in recent years. Up to now, there have been no reports on applying CDs or their complexes to ER materials. More recently, we found that the supramolecular complexes of insoluble β-cyclodextrin crosslinked polymer/1-(2-pyridlazo)-2-naphthol particles ER materials showed a notable ER effect, due to the enhancement of dielectric properties. Furthermore, the properties of hydroinsoluble β-cyclodextrin polymer vary greatly with synthesis of the polymer [36,37]. However, the structure is quite difficult to characterize as well as its complex, and the dependence of ER behavior with the structure has been not yet clear.

In this paper, we focused primarily on using hydrosoluble β-cyclodextrin polymer as a host to build supramolecular complex. In order to understand the effects of structural and compositional factors that control ER behaviors, a series of hydrosoluble β-cyclodextrin polymer particles as well as their corresponding supramolecular complexes with the guest of 3-hydroxy-2-naphthoic acid were synthesized, and then these particles were dispersed in silicon oil to prepare the ER fluids. It was found that the polymer ER fluid showed a quite ER effect, and the enhancement of yield stress was observed when applied the supramolecular complex particles forming by the host and the guest, generally. As a compositional measurement for polymers, the crosslinked degree can be used as a key to link the microstructure and macro-property of the polymer. The experimental results show that the molar crosslinked degree of β-cyclodextrin polymer has strongly influenced on those properties of ER fluids and the dielectric properties. The preparation of supramolecular complex and β-cyclodextrin polymer is shown in Fig. 1.

2. Experimental

2.1. Synthesis of β-cyclodextrin polymer and supramolecular complexes *1′–6′*

β-CD was provided by Shantou (China). Epichlorohydrin (EP) and 3-hydroxy-2-naphthoic acid were purchased from Xi'an (China). All reagents were used without further purification.

Using the modified method [35], a typical synthesis procedure of hydrosoluble β-cyclodextrin polymer for a molar ratio EP/CD = 8:1 and NaOH = 20% w/w is described below: a mixture of 50 g β-CD, 25.4 g NaOH in 102 ml water was stirred for 24 h at 25 °C. The mixture was heated to 30 °C and 24 ml of epichlorohydrin was added rapidly, and stirred for 24 h at 30 °C and then quenched by addition of acetone, and a yellow sol was obtained. The sol was deposited with ethanol and H_2O, respectively. Then deposit with ethanol and H_2O again till no chloride ion remained in aqueous solution. The solvent was removed, and the white solid residue was dried in vacuum for 3–5 days at 75 °C, and the hydrosoluble β-cyclodextrin polymer was obtained. The polymer was ascertained to have retained the characteristic structure of β-CD by IR spectroscopy and the ratio of components (EP/β-CD) of the polymer was determined by element analysis method [34], which was calculated by the equation (Eq. (1)) as shown follows:

$$C = 12.01 \times (6 \times 7 + 3m)/(58.07m + 1135) \qquad (1)$$

Where m is the molar crosslinked degree of β-cyclodextrin polymer, and C is the content (anal. found) of carbon in β-cyclodextrin polymer. Sequentially, several polymers were obtained at various reaction ratios of EP/CD (EP/CD = 0, 2:1, 4:1, 6:1, 8:1 and 7:1) as well as their components, respectively. Here, the definition of the molar crosslinked degree (m) is one molar of β-CD contains molar numbers of epichlorohydrin in the polymer, so m of the polymers (0 (**1**), 1.01 (**2**), 2.86 (**3**), 6.13 (**4**), 7.53 (**5**) and 8.89 (**6**)) was determined, respectively.

Preparation of inclusion complex [37]: 4.0000 g β-CD and **2–6** mixed with 3-hydroxy-2-naphthoic acid at a mole ratio of CD/guest = 1:1, respectively. The mixture was ground for 3.5 h, respectively. After dried under vacuum, the supramolecular complexes (**1′–6′**, which are corresponded to β-CD and **2–6**.) were obtained.

2.2. 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 β-CD, polymer **2–6** and their supramolecular complex **2′–6′** particles in silicone oil ($\varepsilon_f = 2.60–2.80$, $\sigma_f = 10^{-12}–10^{-13}$ S/m, $\rho = 0.9–1.0$ 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.

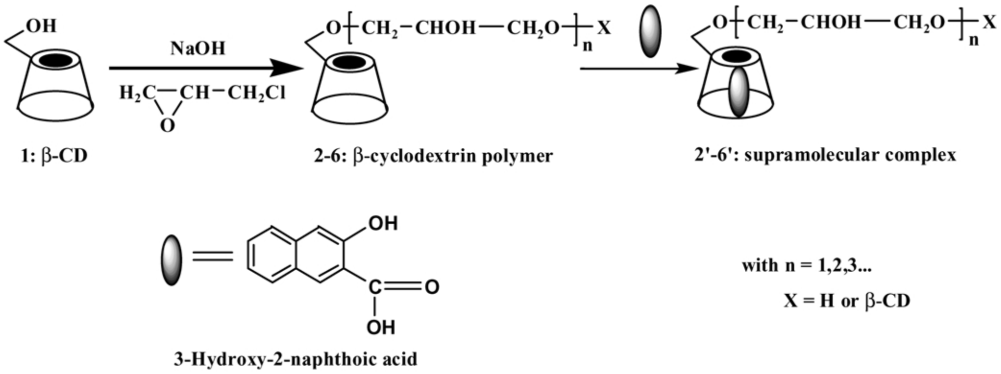

Fig. 1. Schematic structure of preparation of supramolecular complex and β-cyclodextrin polymer.

2.3. Measurement

IR spectra were recorded on a Bruker Equinox-55 using KBr pellets. Fluorescence emission spectra were measured with a PE LS50B fluorescence spectrophotometer ($\lambda_{ex} =$ 350 nm, $S_{em} = 10$ nm/$S_{ex} = 3.5$ nm (at 25 °C)). Ethanol aqueous solution (1 vol%) was used as a solvent for guest in the spectroscopic measurements and a guest concentration of 1×10^{-5} M was prepared. Five β-cyclodextrin polymer samples (5×10^{-3} and 5×10^{-2} M) of aqueous solutions were prepared, respectively. A controlled stress rheometer (the shear rate is $5.0\ s^{-1}$) with a polarizable cell and a DC high-voltage generator (GYW-010, CHINA) was used to determine the yield stress. The cell was of parallel plate geometry with a gap size of 1 mm. The dielectric properties of ER fluids were measured using an Automatic LCR Meter 4225 (GERMANY).

3. Results and discussion

3.1. Characterization of supramolecular complex

The structure of the polymers was characterized by FT-IR and element analysis. As shown in Table 1, the peaks of polymer **2–6** revealed the presence of characteristic absorption of CD in these polymers. The peaks at 3416–3432 cm^{-1} can be associated with the O–H stretching vibrations, peaks at 1644–1653 cm^{-1} with the plane bending of O–H, and between 1031 and 1159 cm^{-1} with CD ring stretching of the C–O or C–O–C. Compared with β-CD, the corresponding characteristic peaks of these polymers undergo blue shifts, which are 31–47 cm^{-1} for the O–H stretching vibrations, 6–15 cm^{-1} for the plane bending of O–H and 3–7 cm^{-1} for the CD ring stretching, indicating that CD cavities are indeed bond to one or more electric-donor groups such as the glycerol tail.

In order to further understand the polymeric structures, the composition of polymer **2–6** was examined by element analysis, respectively. Table 1 is only listed the *C* content (found, %) for each polymer. As shown in Table 1, the *C* content increases from polymer **2** to **6**, indicating the reaction ratio of EP/CD strongly influences on the polymeric composition. It is well known that the crosslinked degree is a characteristic measure, which gives the ratio of EP/CD for a polymer. Therefore, we can easily calculate the molar crosslinked degree of the polymer according to Eq. (1). The result shows that *m* increases with the increase of the *C* content; the higher *m* the higher content of *C*. In the meantime, the higher *m* shows the longer chain branches.

3-Hydroxy-2-naphthoic acid is a fluorescence reagent containing intramolecular hydrogen bond and the β-cyclodextrin polymers are soluble in water. We thereby can examine the formation of supramolecular complex between β-cyclodextrin polymer and guest—3-hydroxy-2-naphthoic acid in solution. Fig. 2 gives the fluorescence

Table 1
The main of IR spectra data, element analysis (*C* (%)) and molar crosslinked degree (*m*)

Sample	IR spectra data (cm^{-1})				Element analysis found (*C* (%))	*m*
	ν_s			δ(O–H)		
	(O–H)	(C–O)	(C–O–C)			
β-CD	3385 (s)	1156 (s)	1029 (s)	1638 (m)		0
2	3424 (s)	1159 (s)	1034 (s)	1645 (m)	45.30	1.01
3	3427 (s)	1159 (s)	1036 (s)	1647 (m)	46.69	2.86
4	3416 (s)	1153 (s)	1034 (s)	1653 (m)	48.64	6.13
5	3432 (s)	1159 (s)	1034 (s)	1644 (m)	49.34	7.53
6	3420 (s)	1159 (s)	1031 (s)	1645 (m)	49.94	8.89

spectra ($\lambda_{ex} = 350$ nm, $S_{em} = 10$ nm/$S_{ex} = 3.5$ nm) of guest in the presence and absence of **1**–**6**, which is of the same concentration in solution, respectively. As shown in Fig. 2, a strong increase in the fluorescence relative intensity is observed when β-CD or one of the β-cyclodextrin polymers presents in the guest solution. Meanwhile, the fluorescence relative intensity reaches the maximum and 5.1 times than that of guest in the presence of **6**, and even 2.6 times for **2** in the same case. Furthermore, a blue shift of about 8 nm is observed for these polymers, together with a broadening of the fluorescence band and enhancing of the quantum yield, indicating the lower polarity of species in the CD cavity. These results show that not only β-CD but also each polymer can form the supramolecular complex with guest. We also note that the enhancement of fluorescence relative intensity is quite different when the various polymer presents in the guest aqueous solution. The sequence of the enhancement is $\mathbf{6}' > \mathbf{5}' > \mathbf{4}' > \mathbf{3}' > \mathbf{2}' > \mathbf{1}'$ > guest, which increases with the increase of m, implying the polymer effect plays a significant role in this case. In addition, a well straight line of ΔI vs. m is obtained, where $\Delta I = I - I_0$, I is the fluorescence relative intensity of guest in different β-cyclodextrin polymer and I_0 is that of guest. This further demonstrates that the supramolecular complex is formed by the interaction of β-cyclodextrin polymer and guest, and the inclusive ratio of a CD cavity and guest is really the same for different β-cyclodextrin polymer.

Fig. 3 shows several double-reciprocal plots [38] for guest in polymer **2**–**6**, respectively. As shown in Fig. 3, each plot is well described as a single straight line. This leads to the conclusion that every polymer and guest can only form one type of supramolecular complex. The inclusive ratio of CD/guest is 1:1.

3.2. Dielectric properties and influence of molar crosslinked degree

The dielectric properties of the ER fluids were measured in the frequency of 10^2, 10^3 and 10^4 Hz at room temperature. For the ER fluids of **5**′, **5** and guest, the dielectric constant (ε), conductivity (σ) and dielectric loss (tg δ) were measured as shown, respectively, in Figs. 4 and 5. From the figures, it can be seen that ε, σ and tg δ were decreased by different degrees in **5**′, **5** and guest sequence. As shown in Fig. 4, the dielectric constant of **5**′ ER fluid is 1.6 times than that of the pure **5** ER fluid, 2.8 times than that of the pure guest ER fluid (100 Hz, 20 °C). The conductivity is 2.5 times than that of the pure **5** ER fluid, 98.5 times than that of the pure guest ER fluid (1000 Hz, 20 °C). In Fig. 5, the dielectric loss of the supramolecular complex ER fluid is 0.17 and 1.6 times than that of the pure **5** ER fluid (1000 Hz, 20 °C). These results show that the dielectric properties of the supramolecular complex ER fluid were improved obviously compared with the pure **5** or guest ER fluid. From the dielectric properties of **5**′ and **5** 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. [39,40]

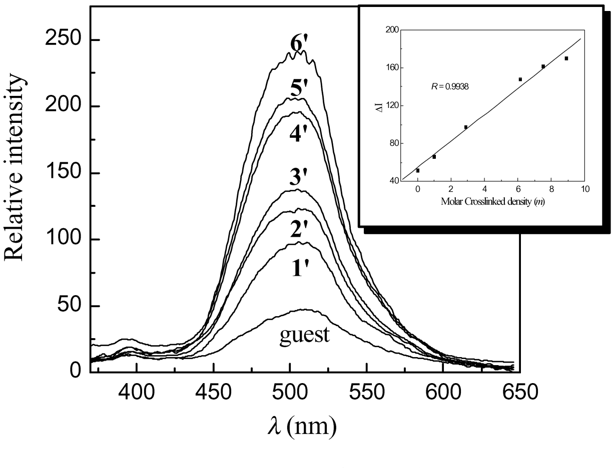

Fig. 2. Fluorescence spectrum ($\lambda_{ex} = 350$ nm) of 3-hydroxy-2-naphthoic acid (1.0×10^{-5} M) in the presence and absence of β-CD or various β-cyclodextrin polymer (7.0×10^{-4} M) in solution, and the plot of ΔI vs. m.

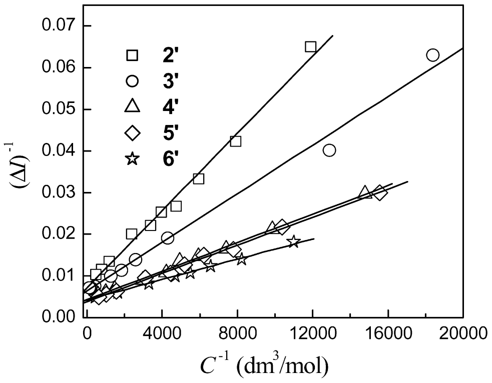

Fig. 3. Double reciprocal plots for complex **2**′–**6**′. The plots are linear, indicating 1:1 complexation only throughout the concentration range of β-cyclodextrin polymer used (0.0–0.05 M).

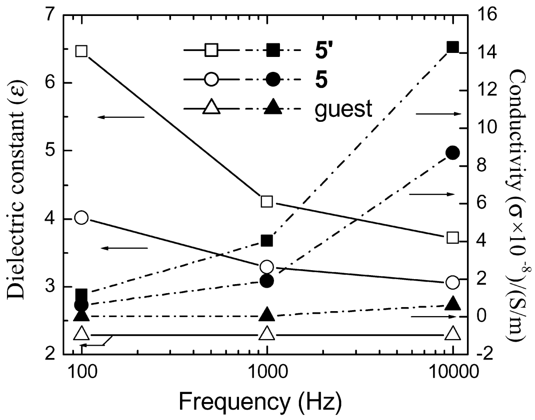

Fig. 4. Dielectric constant and conductivity vs. frequency for **5**′, **5** and guest ER fluids ($\Phi = 39\%$, $m = 7.53$).

In fact, the dielectric properties of ER fluids are closely

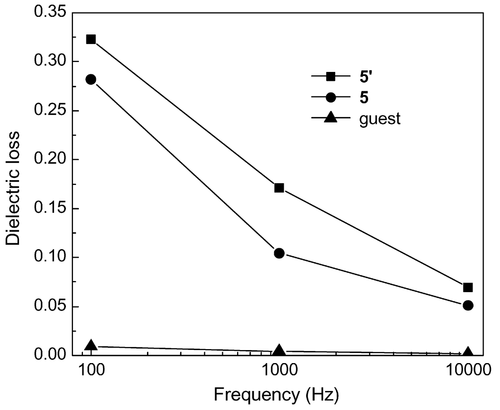

Fig. 5. Dielectric loss vs. frequency for **5′**, **5** and guest ER fluids ($\Phi = 39\%$, $m = 7.53$).

related to the structure of the particles. As the structural characterization, the supramolecular complex formation between β-cyclodextrin polymer and guest apparently means the structural change compared with the host or guest. Moreover, in this work, we provided the different polymer and thereby the structural difference is apparent. Fig. 6 gives the dielectric properties of supramolecular complex and host ER fluids vary with molar crosslinked degree (m) at 1000 Hz, 20 °C. It can been seen that both dielectric constant and conductivity of **2′**–**5′** ER fluids are improved than that of **2**–**5**, but that of **6′** ER fluid is lower than that of **6**. Note that the dielectric properties of supramolecular complex increase gradually with the enhancement of m, then reach the maximum at $m = 7.53$ and finally appear a decline at $m = 8.89$, while the dielectric properties of **2**–**6** ER fluids enhance with the increase of m. Since the m value is a measure to reveal the ratio of EP/CD for a polymer, the higher m value means the longer polymer tail leading to the stronger molecular debye and thereby the enhancement of the dielectric properties are caused. But the situation is changed when the supramolecular complex formation between the host and guest. Therefore, either for the supramolecular complex or β-cyclodextrin polymer ER fluids, the crosslinked degree of β-cyclodextrin polymer plays an important role and even can control the dielectric properties of ER particles to a certain degree.

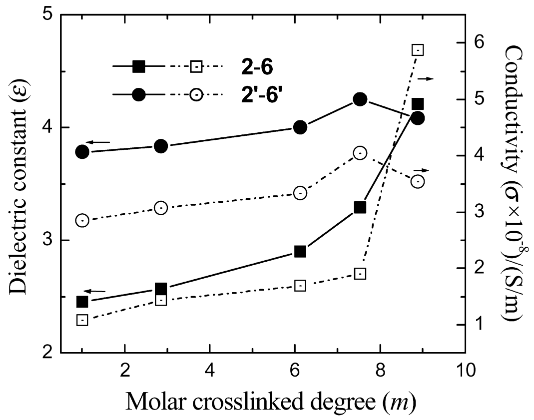

Fig. 6. Dielectric constant and conductivity vs. m for **2′**–**6′** and **2**–**6** ER fluids at 1000 Hz ($\Phi = 39\%$).

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]. The dielectric constant is connected to the polar strength whereas dielectric loss and conductivity are associated with the stability of the polar response between particles [21]. Davis [41] proposed that in DC and low frequency electric fields, the conductivity mismatch model, the static force between the particle is in direct proportion to the conductivity mismatch coefficient (Eq. (2))

$$\beta = (\sigma_p - \sigma_f)/(\sigma_p + 2\sigma_f) = (\Gamma - 1)/(\Gamma + 2) \tag{2}$$

Where $\Gamma = \sigma_p/\sigma_f$ (σ_p and σ_f are the bulk conductivity of the particles and the oil, respectively). Hence, the large Γ value is required to enhance the mechanical strength of the ER fluid. But if the Γ value and the conductivity of the particles are so large that the particles become conductors, the fluid will no longer show the ER effect. Block reported that ER fluids with a conductivity of around 10^{-7} S/m usually showed the largest ER effect because the strength of the interfacial polarization can reach a maximum in this case [42]. In this paper, the conductivity of the sepramolecular complex ER fluids remained around 10^{-8}–10^{-7} S/m and only 10^{-9}–10^{-8} S/m for that of host ER fluids except for that of **6′** and **6**. In the meantime, the dielectric constant and dielectric loss of the supramolecular complex ER fluid were both increased notably. These properties are customary for the ER effect. However, the dielectric constant of guest 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 [41], guest ER fluid has, therefore, no ER effect.

3.3. Yield stress and influence of molar crosslinked degree

The yield stress is generally used as a representative ER property [28]. Based on this, a serious of β-cyclodextrin polymer and its complex ER fluids were prepared, respectively. Fig. 7 shows the change of yield stress of **5′**, **5**, the mixture of **5** + guest and the pure guest ER fluids as well as leaking current degree of **5′** and **5** ER fluids with the increase of DC field at 20 °C, respectively. It can be seen from the curves that the **5′** ER fluid displays a notable ER effect, which the leaking current degree is less than 10 μA/cm^2 at 4 kV/mm. The yield stress of **5′** ER fluids is 9.23 kPa at 4 kV/mm, whereas it is only 3.25 kPa for the pure **5**, 0 kPa for the pure guest and 3.98 kPa for the **5** + guest at the same electric field, respectively. This value is about 2.8 times that of the pure β-cyclodextrin polymer and 2.3 times that of **5** + guest. It is note that the pure guest suspension has no ER effect even in the strong electric field, and the simple mixture **5** + guest suspension has slightly enhancement compared with **5** ER fluid, in the meantime, the **5′** ER

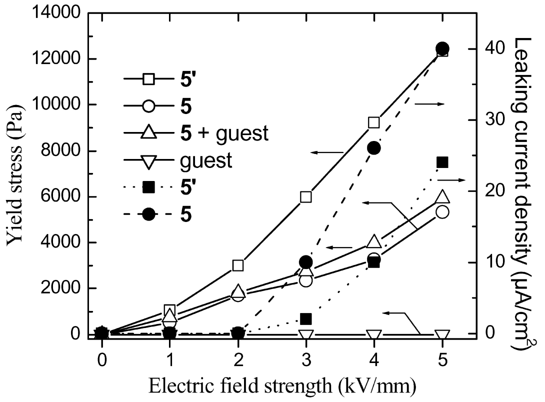

Fig. 7. The yield stress of **5′**, **5**, **5** + guest and guest ER fluids ($\Phi = 39\%$, $m = 7.53$) vs. electric intensity ($T = 20$ °C).

fluid is much stronger than that of the pure **5**. This is similar to our previous work [37] that guest is apparently not used as an additive. Thus, the strong enhancement of **5′** ER fluid is due to the supramoleular complex formation between **5** and guest resulting in the change of the host structure as well as its properties.

It is quite interesting that *m* has strongly influenced on the supramoleular complex or β-cyclodextrin polymer ER effect. The yield stresses of the supramoleular complex and β-cyclodextrin polymer under various *m* at 3 kV/mm are shown in Fig. 8, respectively. It can be seen from Fig. 8 that almost the supramoleular complexes show a higher ER activity than that of β-cyclodextrin polymer expect for **6′**. The yield stress of the supramoleular complex is 3.38–5.98 kPa at 3 kV/mm while that of β-cyclodextrin polyme is only 1.82–4.94 kPa in the same case, which of the average is decreased by 47.6% comparing with that of the supramoleular complex. As expected, the high enhancement of yield stress can be observed by the supramoleular complex formation. Moreover, the difference in viscosity between the different samples (**2′**–**6′**) in silicon oil is less than 26.0 Pa S, which was obtained by the measurement of ER properties of different sample at $E = 0$. Hence, such a tiny difference in viscosity does not play a dominant role in the increase of the yield stress. As seen in Fig. 8, the situation is different between the supramoleular complex and the host. For the supramoleular complex ER fluids, the yield stress increases with the increase of *m* firstly, then reaches the maximum at $m = 7.53$ but it decreases when $m = 8.89$, indicating that an appropriate *m* is necessary for the supramoleular complex. Contrarily, the enhancement of the yield stress with the increase of *m* is observed for β-cyclodextrin polymer, demonstrating the higher *m* in favor of its ER behavior in this case. This is well in agreement with the result of their dielectric properties.

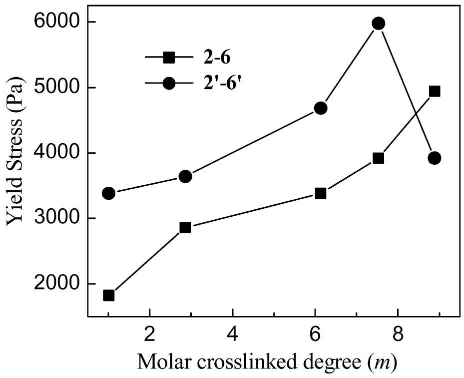

Fig. 8. The yield stress vs. *m* for **2′**–**6′** and **2**–**6** ER fluids at 3 kV/mm ($\Phi = 39\%$, $T = 20$ °C).

4. Conclusion

β-Cyclodextrin polymer has two advantages to be used as a based ER material. The one is that its structure can be easily modified by the formation of supramolecular complex with a guest. The other is that the structural composition itself can be controlled by selecting a suitable molar crosslinked degree. Based on this, five β-cyclodextrin supramolecular complexes (**2′**–**6′**) particles were synthesized and then dispersed in silicon oil to prepare the ER fluids, respectively. It was found that the typical **5′** ER fluid showed a notable ER effect, which was attributed to the enhancement of dielectric properties under the structural change. The yield stress was 9.23 kPa at 4 kV/mm DC, with leaking current degree less than 10 μA/cm^2. Moreover, it was found that the molar crosslinke degree plays a significant role to control the supramolecular complex ER behavior, which the maximum yield stress appeared at $m = 7.53$. Therefore, selecting an appropriate molar crosslinked degree is quite necessary for the supramolecular complex ER materials.

Acknowledgements

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References

[1] Hao T. Adv Mater 2001;13:1847.
[2] Cho MS, Cho YH, Choi HJ, Jhon MS. Langmuir 2003;19:5875.
[3] Block H, Kelly JP. J Phys D: Appl Phys 1988;21:1661.
[4] Krause S, Bohon K. Macromolecules 2001;34:7179.
[5] Kim YD. J Colloid Interface Sci 2001;236:225.
[6] Lee HJ, Chin BD, Yang SM, Park OO. J Colloid Interface Sci 1997;206:424.
[7] Gonon P, Foulc JL. J Appl Phys 2000;87:3563.
[8] Shchipunov YA, Dürrschmidt T, Hoffmann H. J Colloid Interface Sci 1999;212:390.
[9] Kim YD, Klingenberg DJ. J Colloid Interface Sci 1996;183:568.

[10] Kim JW, Noh MH, Choi HJ, Lee DC, Jhon MS. Polymer 2000;41: 1229.
[11] Hao T. Adv Colloid Interface Sci 2002;97:1.
[12] Tao R, Zhang X, Tang X, Anderson P. Phys Rev Lett 1999;83:5575.
[13] Zhao XP, Yin JB. Chem Mater 2002;14:2258.
[14] Kim JW, Liu F, Choi HJ, Hong SH, Joo J. Polymer 2003;44:289.
[15] Kim SG, Kim JW, Choi MS, Choi HJ, Jhon MS. J Appl Polym Sci 2001;79:108.
[16] Wang BX, Zhao XP. J Mater Chem 2002;12:1865.
[17] Choi US, Park YS, Lee SS. Colloids Surf A: Physicochem Engng Aspects 2002;211:85.
[18] Sung JH, Choi HJ, Jhon MS. Mater Chem Phys 2002;77:778.
[19] Choi US. Colloids Surf A: Physicochem Engng Aspects 1999;157: 193.
[20] Kim SG, Kim JW, Jang WH, Choi HJ, Jhon MS. Polymer 2001;42: 5005.
[21] Wang BX, Zhao XP. J Mater Chem 2002;12:2869.
[22] Liu Y, Li L, Fan Z, Zhang HY, Wu X, Guan XD, Liu SX. Nano Lett 2002;2(4):257.
[23] Jiao H, Goh SH, Valiyaveettil S. Macromolecules 2002;35(4):1399.
[24] Oana M, Tintaru A, Gavriliu D, Maior O, Hillebrand M. J Phys Chem B 2002;106:257.
[25] Zhang X, Gramlich G, Wang X, Nau WM. J Am Chem Soc 2002; 124(2):254.
[26] Schneiderman E, Stalcup AM. J Chromatogr B 2000;745:83.
[27] Harada A. Coord Chem Rev 1996;148:115.
[28] Cserhati T, Bojarski J, Fenyvesi E, Szejtli J. J Chromatogr 1986;351: 356.
[29] Crini G, Lekchiri Y, Morcellet M. Chromatographia 1995;40:296.
[30] Komiyama M, Hirai H. Polym J 1986;18(4):375.
[31] Komiyama M, Hirai H. Polym J 1987;19(6):773.
[32] Yoshida K, Shimomura T, Ito K, Hayakawa R. Langmuir 1999;15(4): 910.
[33] Shimomura T, Yoshida K, Ito K, Hayakawa R. Polym Adv Technol 2000;11:837.
[34] Su XD, Liu LZ, Shen HY. Anal Chem 1995;23(12):1361. in Chinese.
[35] Renard E, Deratani A, Volet G, Sebille B. Eur Polym J 1997;33:49.
[36] Gao ZW, Zhao XP. Mater Lett 2002;57:615.
[37] Gao ZW, Zhao XP. Polymer 2003;44:4519.
[38] Catena GC, Bright FV. Anal Chem 1989;61:905.
[39] Frost RL, Kristof J, Horvath E, Kloprogge KT. J Colloid Interface Sci 1999;214:318.
[40] Choi US. Colloids Surf A: Physicochem Engng Aspects 1999;157: 193.
[41] Davis LC. J Appl Phys 1992;72:1334.
[42] Block H, Kelly JP, Qin A, Waston T. Langmuir 1990;5:5.