Rapid Communication

The influence of intercalation rate and degree of substitution on the electrorheological activity of a novel ternary intercalated nanocomposite

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Abstract

Kaolinite/dimethylsulfoxide (DMSO)/carboxymethyl starch (CMS) ternary nanocomposites were prepared according to the combination of intercalation and solution reaction. The results show that the intercalation rate (IR) of kaolinite in the ternary composite is adjusted by changing the mass rate, and the basal spacing of kaolinite was swelled from 0.715 to 1.120 nm. At the suitable component ratio of ternary nanocomposite, the optimum electrorheological (ER) effect can be attained. It is apparent that the notable ER effect of ternary ER fluid was attributed to the prominent dielectric property of the ternary nanocomposite electrorheological fluids (ERF), which is closely associated with the IR. With the increase of degree of substitution, the ER effect of ternary composite ERF is enhanced.
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1. Introduction

Kaolinite ($Al_2Si_2O_5(OH)_4$) is a dioctahedral 1:1 layered aluminosilicate with two kinds of interlayer surfaces [1,2]. Kaolinite is one of the host materials for forming layered silicate–organic intercalation compounds [3,4]. Intercalation reaction has been well known as a method for forming inorganic–organic nanocomposites. The kind of guest species intercalated between the layers of kaolinite is limited due to hydrogen bonding between hydroxyl groups of $AlO_2(OH)_4$ octahedral sheets and SiO_4 tetrahedral sheets. Kaolinite has been described as nonexpendable clay [5]. One reason is that kaolinite does not possess an exchangeable ion in the layer. The other is that the *d*-spacing is just 0.714 nm. Only a limited number of polar guest species, such as *N*-methylformamide (NMF) and dimethylsulfoxide (DMSO), can be directly intercalated [6]. Hydrogen bonding plays a significant role for enhancing blend miscibility between host (components) and guest

(clay particles). The choice of intercalation kaolinite with DMSO (dielectric constant is about 47) is aimed at modifying the dielectric and polarization properties of kaolinite, so as to improve its electrorheological (ER) activity, reduce cost and attain the goal-high cost performance.

Electrorheological fluids (ERF) are typical suspensions composed of micrometer size particles and dielectric liquids [7–9]. The ER response produces an instantaneous, reversible change in rheological properties of a suspension when exposed to an electric field in the flow direction. The material parameters of ERFs such as viscosity, yield stress, and shear modulus can change obviously and reversibly upon the application of an external electric field. Such changes are caused by the formation of an internal chain-like structure that is formed by the rearranging of dispersed particles within the fluid [10–12]. Physically, ER effect originates from the dielectric polarization of particles dispersed in the oil medium. It is accepted that the origin of the ER response is due to the aggregation (fibrous structure) of the particles in the suspensions. The formation of these aggregates is ascribed to polarization of the

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materials due to the permittivity mismatch between suspending liquid and solid particle [13,14].

The parameters in connection with particle polarization such as dielectric constant, dielectric loss, or conductivity have been considered as the basic factor dominating ER effect [15,16]. It is well-known that the chemical natures, including molecular and crystal structures of materials, are critically important to the dielectric and polarization properties, thus it is possible to modify the dielectric and polarization properties to increase ER activity by designing the molecular and crystal structure of ER materials. Further, polymeric particles possessing polar groups of the hydroxyl groups as the natural organic polymers provide a source of the disperse phases. These polar groups may affect the ER behavior by playing the role of electronic donor so that the chemical structure of the organic materials becomes an important factor in the ER performance [17–22]. Carboxymethyl starch (CMS) (possessing polar group –OH and –COONa) is aimed at modifying the dielectric and polarization properties. Firstly, starch can only dissolve in cold water partly. However, due to the carboxymethylating modification, CMS is cold water-soluble starch ether. Its hydrophilic properties are enhanced enormously and can contribute to the improvement of the affinity between hydrophilic clay (kaolinite) and CMS [23]. Furthermore, CMS is coated on the surface of kaolinite/DMSO intercalate, which is also aimed at prohibiting the deintercalation and ensuring the high intercalation rate (IR) for enhancing the ER effect.

The solvent medium method is used to prepare CMS. Ethanol used as the solvent medium and sodium monochloroacetate used as the carboxymethylating agent are provided. The reaction is through alkalization and etherealization to form CMS. Firstly, sodium hydroxide reacts with the hydroxyl group of the starch to give alkoxide groups; then the carboxymethyl groups are formed between the starch alkoxide and the sodium monochloroacetate. The reaction is simply shown in Fig. 1.

In this study, we synthesize the kaolinite/DMSO/CMS ternary nanocomposite particles, and characterize their physical and chemical properties. Kaolinite/DMSO/CMS ternary nanocomposites are prepared according to the combination of intercalation and solution reaction. Firstly kaolinite/DMSO intercalating nanocomposites with different IR are synthesized by the direct intercalation method. Then CMS is coated on the surface of kaolinite/DMSO intercalate by the solution method. We also prepare an ER fluid using synthesized nanocomposite, and measure its rheological properties under high electric field.

2. Experimental

The kaolinite sample employed in this work was from Wu Han, China. It was received as a finely divided white powder of high purity, and its chemical composition in wt% as oxides is SiO_2, 48.97; Al_2O_3, 34.22; Fe_2O_3, 0.6; TiO_2, 0.27. The specific surface area is $26 \, m^2 \, g^{-1}$. The kaolinite used to prepare the nanocomposites was used without further purification.

Cornstarch was purchased from Tan Jin Chem. Third Co., China. DMSO (Bei Jing Yatai Co., China), sodium hydroxide (Xi'an Chem. Factory, China), chloroacetic acid (Cheng Du associated with Chem. Institute, China) were used as received.

2.1. Preparation of kaolinite/DMSO/CMS ternary nanocomposites

First, 20 g cornstarch and 150 ml ethanol were placed in a 1000 ml vessel and stirred with a magnetic stirrer for 1 h. Then 25 g sodium hydroxide was added at 30 °C and reacted for 0.5 h to activate corn starch. After that, the mixture of 25 g sodium hydroxide and 70 g chloroacetic acid were added to the vessel at 50 °C and the mixture stirred for 5 h. The product was filtered off and washed several times with ethanol, then dried under vacuum at 50 °C for 3 h. The resulting CMS was crushed in a mortar. The degree of substitution in CMS was measured by the acid pickling method.

Kaolinite (3 g) were dispersed in 40 ml ethanol and stirred for 3 h. Then 2.25 g DMSO (mass ratio kao: DMSO = 1:0.75) were added drop by drop into the kaolinite suspension. When it was dropped, the temperature was increased to 45 °C with the purpose of evaporating the ethanol. The sample was sealed in a weighing bottle and placed in an oven for 14 h at 80 °C, and the resulting material (kaolinite–DMSO intercalate) was altered.

In a 100 ml vessel, 1.8 g CMS and 50 ml of distilled water were mixed and stirred for 10 h, then the appropriate amount of kaolinite-DMSO intercalation was added slowly into the vessel at room temperature. After the addition was completed, the mixture was stirred for 14 h. The product was frozen and dried for 10 h in a freeze drier at −50 °C. Then the sample was crushed and dried under vacuum at
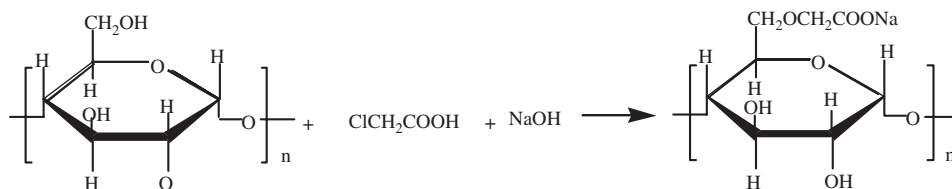

Fig. 1. The schematic illustration for the reaction mechanism of CMS.

60 °C for 5 h, and at 80 °C for 2 h. The obtained kaolinite/DMSO/CMS ternary nanocomposite was then crushed in a mortar.

2.2. Preparation of kaolinite/DMSO/CMS ternary nanocomposites ERF

The silicone oil was first dried at 100 °C for 2 h, and then the ternary composite particles, pure kaolinite, and pure CMS were further dehydrated in vacuum for 3 h at 100 °C for the preparation of ER fluids, and then were mixed quickly with silicone oil at volume percent $30\phi\%$ and $15\phi\%$, respectively ($\varepsilon_f = 2.60-2.80$, $\sigma_f = 10^{-12}-10^{-13}\,\mathrm{S\,m^{-1}}$, $\rho = 0.9-1.0\,\mathrm{g\,cm^{-3}}$, $\eta = 500\,\mathrm{mPa\,s}$). The suspensions were ground using a carnelian mortar for 1 h in order to thoroughly disperse the particles in the silicone oil [24].

2.3. Analyses

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer (D/III-γA, Japan) using Cu$K\alpha$ radiation with a scanning rate of $1°\,\mathrm{min^{-1}}$. All measurements were taken using a generator voltage of 40 kV and a current of 20 mA.

Furthermore, the dielectric relaxation spectra of all prepared ER fluids were examined using the HP 4284A Precision LCR meter. Frequency of alternating current (AC) electric fields ranged from 20 Hz to 1 MHz. All these experiments were performed at 25 °C. The shear stress of ER fluids was measured by a parallel plate force transducer (China, shear rate is fixed at $5\,\mathrm{s^{-1}}$). A rotary viscometer (NXS-11A; China; the gap between the outer cup and the inner bob is 2 mm) and a high-voltage DC power source (GYW-0/0; China, 0–10 kV) were used to research the rheological properties of the ER fluids (shear rate range is from 0 to $105\,\mathrm{s^{-1}}$).

3. Results and discussion

3.1. X-ray characterization

Fig. 2 shows the X-ray diffraction patterns of the kaolinite (a), kaolinite/0.75DMSO hybrids (b), kaolinite/0.60DMSO hybrids (c), kaolinite/0.75DMSO/0.60CMS (d), kaolinite/0.60DMSO/0.60CMS (e), respectively. The result shows that the peak of 7.15 Å (d_{001}) of kaolinite decreases after kaolinite reacts with DMSO, and that a new peak at 11.20 Å is observed. This result indicates that DMSO is intercalated into the interlayer space of kaolinite, and the kaolinite–DMSO composite is formed [25]. In the meantime, according to the change of d_{001} peak intensity to before and after intercalation, the IR can be calculated:

$$\mathrm{IR} = I_{001\mathrm{composite}}/(I_{001\mathrm{composite}} + I_{001\mathrm{kaolinite}}), \qquad (1)$$

where $I_{001\mathrm{composite}}$ is the new d_{001} peak intensity of intercalate, and $I_{001\mathrm{kaolinite}}$ is the d_{001} peak intensity of residue kaolinite in the intercalates. In order to get the
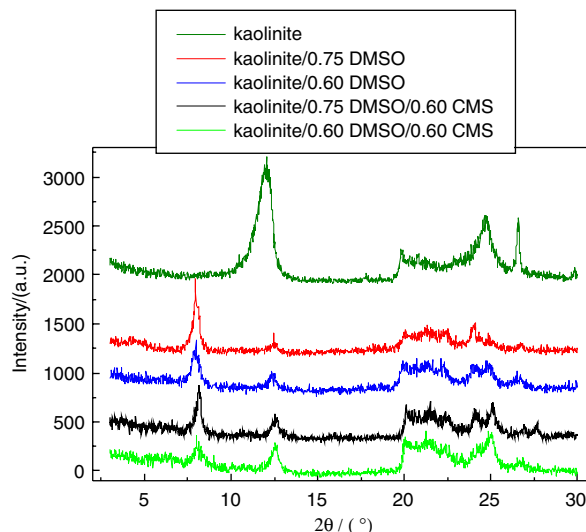

Fig. 2. XRD patterns (a) kaolinite; (b) kaolinite/0.75 DMSO; (c) kaolinite/0.60 DMSO; (d) kaolinite/0.75DMSO/0.60CMS; (e) kaolinite/0.60 DMSO/0.60CMS.

kaolinite/DMSO composite with different IR, the different amounts of DMSO should be added into the reaction system. As shown in Fig. 2(b) (mass rate of kaolinite/DMSO is 1:0.75) and (c) (mass rate of kaolinite/DMSO is 1:0.60), the value of IR for kaolinite/DMSO composite is 81.1% and 63.5%, respectively. The content of CMS is then fixed and the relevant ternary composite is got. As shown in Fig. 2(d) (ternary mass rate is 1:0.75:0.6) and (e) (ternary mass rate is 1:0.6:0.6), the value of IR for kaolinite/DMSO/CMS is measured as 61.5% and 46.9%, respectively. So when the mass rate of ternary composite is adjusted, the ternary composite possessing different IR should be got. When DMSO intercalated the layer of kaolinite (the basal spacing swell 0.405 nm), kaolinite can be seen as an open nano-container under one-dimensional scale. However, under the condition of thermal treatment and grinding, etc., kaolinite/DMSO composite would be deintercalated [26]. When kaolinite/DMSO composite is coated by the CMS, the "open nano-container" (kaolinite) is changed to the "sealed nano-container". So it enhances the stability of intercalation that is beneficial for the enhancement of ER effect.

3.2. Dielectric properties of ER fluid

For the different kaolinite/DMSO/CMS ERFs, kaolinite/DMSO ERF, kaolinite/CMS ERF, CMS ERF, and kaolinite ERF (volume fraction is fixed at 15% simultaneously), the dielectric constant (ε), conductivity (σ) and dielectric loss (tg δ) were measured as shown, respectively in Fig. 3. ε, σ and tan δ play an important role in high performance ER materials. The dielectric constant is connected to the polar strength, and dielectric loss, and conductivity are associated with the stability of polar response and effect between particles. It is well known that
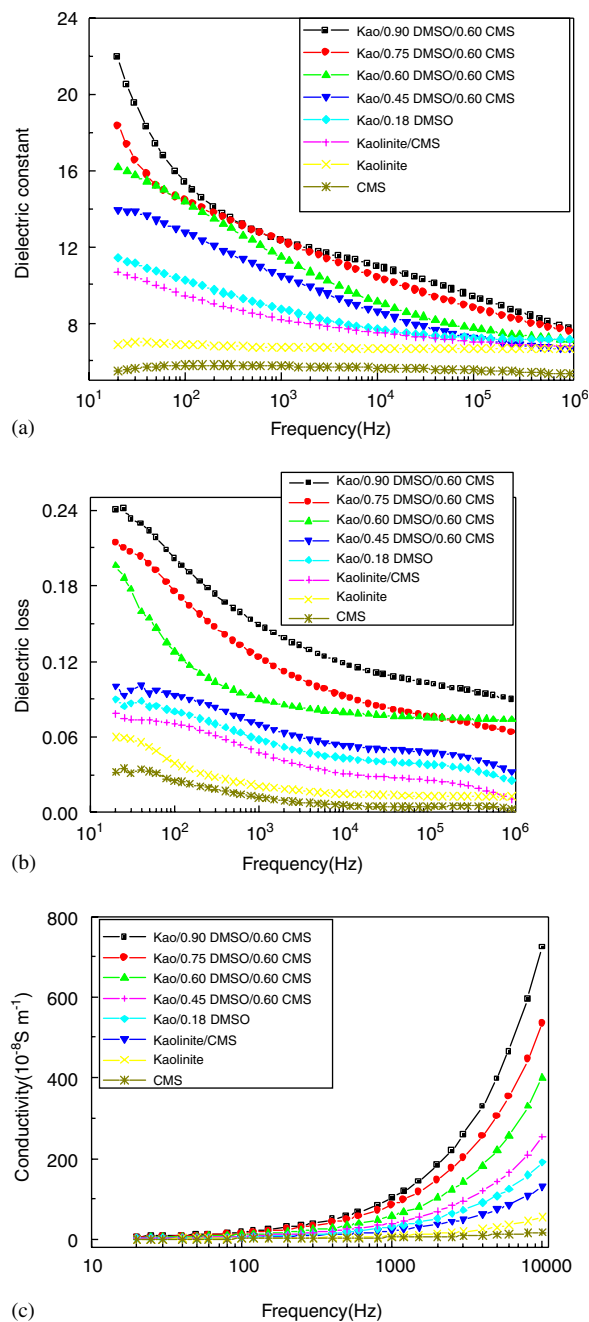
Fig. 3. Dielectric spectra as a function of electric field frequency (a) dielectric constant of ERFs; (b) dielectric loss of ERFs; (c) conductivity of ERFs.

the serials of kaolinite/DMSO/CMS ternary composite accompanying the increase of DMSO content, the conductivity of ternary composite ERF is increased. But excessive DMSO (e.g., 0.90 DMSO) may impel the conductivity to increase rapidly; the leaking current density of ERF is high enough to break the internal chain-like structure of ERF, and the mechanical properties will decrease. Suitable conductivity plays as an important role in the high ER effect. As high conductivity can lead to large leaking current density, even breakdown can occur under the high electric field. Meanwhile, the low conductivity leads to low conductivity mismatch and the weak polarization of particle, so the ER effect is also weak. The dielectric constant and dielectric loss of ternary nanocomposite ERF are both increased notably and the conductivity remains at the suitable range by controlling the mass rate (1:0.75:0.60). These properties are favorable to increase the ER effect. In Fig. 3, the conductivity of this composition is adjusting to an optimum point that is beneficial to ER activity. In addition, Block et al. reported that ERF with a conductivity of around $10^{-7}\,\mathrm{S\,m^{-1}}$ usually show the largest ER effect, because in this case, the strength of interfacial polarization can reach a maximum [31]. So the suitable component ratio of ternary nanocomposite possessing the optimum ER effect is correlated with the dielectric properties of ERF.

3.3. The rheological properties of ER fluids

Fig. 4 (a) shows the shear stress of kaolinite/DMSO/CMS (mass rate 1:0.75:0.60) ternary composite ER fluid with an increase of DC electric field under a fixed shear rate ($5\,\mathrm{s^{-1}}$, with a parallel-plate force transducer). At the same time, in order to contrast the mechanical properties, the binary ERF (such as kaolinite/CMS (mass rate 1:0.6), and kaolinite/DMSO (mass rate 1:0.18, much higher DMSO content should lead ERF to break under DC strong field)), and single component ERF (such as pure kaolinite and pure CMS) are prepared at the same volume fraction $\Phi 30\%$. It can be seen from the curves that the shear stress of ternary composite ERFs are much higher than that of a pure kaolinite ERF. Under the electric fields of $5\,\mathrm{kV\,mm^{-1}}$ and volume fraction $30\Phi\%$, the shear stress of kaolinite/DMSO/CMS ternary ERFs can be $17\,\mathrm{kPa}$, which is 14 times and 4.25 times higher than that of pure kaolinite ERF and kaolinite/CMS ERF. The shear stresses of kaolinite/DMSO/CMS ternary ERF (15 vol% in silicone oil) as a function of shear rate under various electric fields are shown in Fig. 4(b). In the range of shear rate, the shear stress of the suspension increases with the shear rate. In the presence of the electric field, we can observe a Bingham plastic behavior in ternary composite suspension, which is the typical rheological characteristic of ERFs under electric field.

The Fig. 5 shows that the shear stress of kaolinite/DMSO/CMS ternary ERF connects with the content of DMSO and CMS under different DC field strengths. Along

a high dielectric constant and dielectric loss, and proper conductivity are the physical bases to obtain the critical optimum ER effect [27–30]. The results show that the dielectric constant of ternary composite is increased by the intercalation of DMSO at the low-frequency region due to the interfacial polarization, shown as Fig. 3(a) (the result of tg δ is similar to this). As shown in Fig. 3(c), the σ of ternary composite ERF remarkably increased at 10 kHz compared with that of single component ERF and binary composite (kao/CMS or kao/DMSO) ERF. Moreover, in
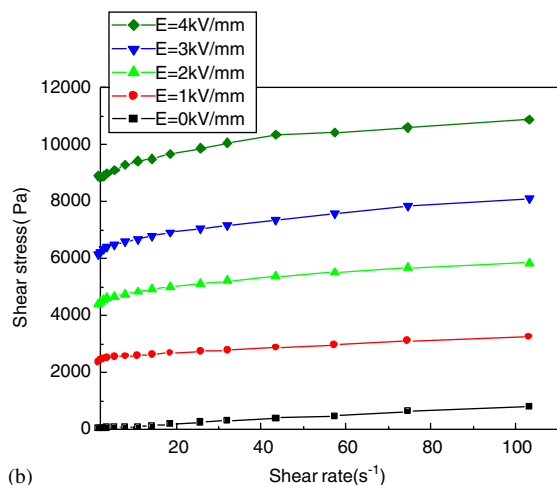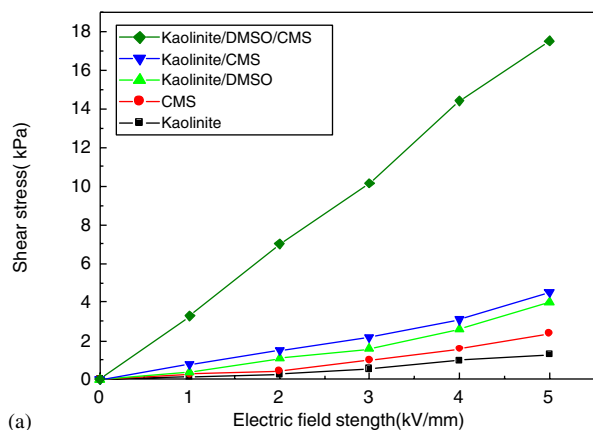
(a)

(b)

Fig. 4. (a) Shear stress as a function of DC electric field for ERF of pure kaolinite, CMS, kaolinite/DMSO, kaolinite/CMS, kaolinite/DMSO/CMS, respectively; (b) the shear stress of kaolinite/DMSO/CMS (15 vol% in silicone oil) ERF as a function of shear rate under various electric fields.
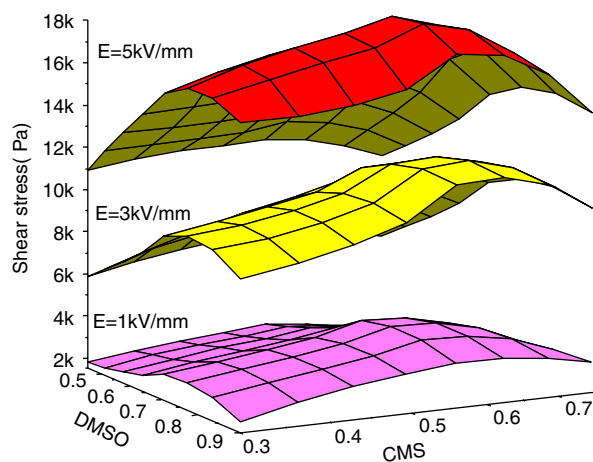

Fig. 5. Shear stress of kaolinite/DMSO/CMS ERF as a function of different components at different electric field.

with the increase of DMSO and CMS the ER effect is increased, and when the mass rate of kaolinite/DMSO/CMS come to 1:0.75:0.60, the mechanical activity will
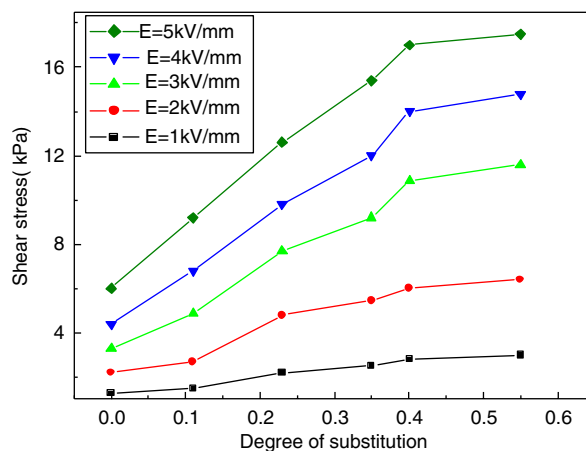

Fig. 6. The shear stress of ternary nanocomposite ERF as a function of the degree of substitution for CMS.

reach the peak. The content of DMSO or CMS then continuously increases, and the shear stress of ternary composite ERF will decrease. So there should be an optimum point (mass rate 1:0.75:0.60) and this may let the ER effect achieve the optimization due to the synergetic effect of the ternary composite.

The amount of carboxymethyl groups formed in the CMS is indicated by the degree of substitution, DS. The DS is defined as the average number of substitutes per anhydro glucose unit, AGU, and the monomer unit of starch. The CMS having different DS can be attained by changing the concentration of alkali and acid, the temperature and duration of the reaction, solvent system etc. Settling the mass rate of ternary system as 1:0.75:0.6, the influence of DS on the ER effect is researched, shown as Fig. 6. Accompanying the increase of DS, the ER effect of ternary composite ERF is enhanced. High DS means that more hydroxyl (–OH) groups are substituted by carboxymethyl sodium ($-CH_2COONa$), so the numbers of Na^+ is increased and charge carrier of particle is enriched, and then the polarization ability of particle is improved; however, when the DS of CMS is greater than 0.4, the increasing trend of ER effect becomes slow. If we want to get better mechanical properties by increasing the DS of CMS, the cost for preparing the ERF will be more and that will be against the goal of high cost performance for ERF. So in our work, the DS of CMS is adopted as 0.4 to prepare the ternary composite.

4. Conclusions

According to the physical and chemical design, kaolinite/DMSO/CMS ternary nanocomposites were prepared. The result shows that DMSO moderately intercalated the interlayer of kaolinite, and the basal spacing of kaolinite was swelled from 0.715 to 1.120 nm. By adjusting the intercalation rate and component ratio of ternary nanocomposite, the dielectric properties of the ternary composite is notable increased, which can be considered as the intrinsic reason

for the enhancement of the rheological properties of ternary ERF. Under the electric fields of $5\,kV\,mm^{-1}$ and volume fraction $30\Phi\%$, the shear stress of kaolinite/DMSO/CMS ternary ERFs can be 17 kPa, which is 14 times and 4.25 times higher than that of pure kaolinite ERF and kaolinite/CMS ERF. With the increase of degree of substitution, the electrorheological effect of ternary composite ERF is enhanced.

Acknowledgments

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