

Rapid communication

Electrorheological properties and structure of $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$

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Abstract

The core-shell structural $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ samples of giant electrorheological (ER) activity have been synthesized by a sol–gel method and studied by TEM, X-ray diffraction and IR spectroscopy. From the analysis of the X-ray diffraction, it is found that the component of samples is $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ with a different content of urea. The observations of the TEM morphology show that $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ particles are spherical with a size of around 80 nm and a surface coating with 5–10 nm thickness consisting of urea. The samples show an increasing trend of ER effect as the addition of urea increasing. Moreover, by IR spectroscopy study, it is revealed that some peaks of C=O band and C–O band vibrations of $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ are split into two peaks after urea added. The extent of the splits increase with the increase of urea content, which is resulted by the interaction between the chemical bonds of urea and oxalate of $\text{BaTiO}(\text{C}_2\text{O}_4)_2$. It is evident that the giant ER activity of the sample has a close relationship with the interfacial polarization between the core and the shell of $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$.

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1. Introduction

In recent years, there has been considerable interest in the effect of the electrorheological (ER) fluid both for its fundamental scientific issues in mechanism of ER effect and various applications as electrical and mechanical interfaces, including various mechanical devices, display, ink jet printer, muscle stimulator, optical or microwave apparatus [1–4]. Most of these applications need a high yield stress ER fluid, but the ER fluid which has been reported in the last decades is low in yield stress [5–11].

Not long ago, Wen et al. have reported that an ER suspension of urea coated $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ particles can increase the static yield stress up to about 20 times [12]. It is well-known that the $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ materials have a common ER activity and urea scarcely has any ER activity. It is an intense interest in the great enhancement of the ER effect of the material. In most of the investigations, the

mechanism of this giant ER fluid is discussed by the model of the particle polarization, which is suggested that the solid particles are polarized under DC electric field, dispersed in a non-conducting medium, formed chains or columns aligned by the polarization force along the electric-field direction. But the effect of dynamic conditions on the formation of chains or columns is ignored in this mechanism. The common polarization and conduction models [13–14] are independently related to dielectric constant and conductivity difference between the particle and the continuous phase. Recently, researchers further suggested that the slow polarization, in particular the strong interfacial polarization, is a key to ER effect [15–18]. This mechanism treats particle polarization by using complex dielectric constant, $\epsilon = \epsilon' - i\epsilon''$, where the real part ϵ' is related to polarizability and the image part ϵ'' (also expressed by $\sigma/2\pi f$, where σ is the conductivity and f is frequency [19]) is related to polarization time and stability of interaction between particles. Thus, two parameters in polarization are accepted to be key to high ER activity. However, it is not all the materials with a core-shell structure have the same giant ER activity as $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/$

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NH₂CONH₂) material does. As yet, the reported mechanisms, including the particle polarization and slow interfacial polarization, cannot interpret it well.

In this paper, we report the synthesis of (BaTiO(C₂O₄)₂/NH₂CONH₂) material with a giant ER activity by a sol–gel method and the study of its microcosmic mechanism by XRD, TEM and IR spectroscopy. It is found that the ER effect of the samples increases as the increase of urea content. By IR spectroscopy study, it is revealed that some peaks of C=O band and C–O band vibrations of BaTiO(C₂O₄)₂ are split into two peaks after urea added. Meanwhile, the extent of wavenumbers of these split peaks increases as the addition of urea increasing. It is suggested that the idiographic and microcosmic interfacial polarization between core and the shell of the urea-coated particles is the key to the giant ER activity of the core-shell structure (BaTiO(C₂O₄)₂/NH₂CONH₂) sample.

2. Experimental

2.1. Preparation of (BaTiO(C₂O₄)₂/NH₂CONH₂) particles and its ER fluid

(BaTiO(C₂O₄)₂/NH₂CONH₂) particles with different concentration of urea addition were prepared by the reported methods [20]. All reagents were of analytical grade and used without further purification. In total, 5.0 g barium chloride (BaCl₂·2H₂O) was dissolved in distilled water at about 60–70 °C. Separately, 5.4 g oxalic acid (C₂H₂O₄·2H₂O) was dissolved in water at about 65 °C in an ultrasonic tank, with about 3 mL titanium tetrachloride ($\rho \sim 1.73$ g/mL) slowly added. The above two solutions were mixed in an ultrasonic bath at about 65 °C. The molar ratio of the components in the mixed solution was [Ti⁴⁺] : [Ba²⁺] : [C₂O₄²⁻] = 1.0 : 1.05 : 2.2.

After that, the mixed solution was divided into three parts. Urea was added, respectively, into two of the three parts of the mixed solutions in a weight ratio of 2:3. The products in the solutions became a white colloid, which was cooled to room temperature. The precipitate was washed with distilled water, filtered, and vacuum-dried at 75 °C for more than 24 h to remove all trace water. The sample without urea addition is called sample 1, and the remain two samples with the weight ratio 2:3 of urea are called samples 2 and 3, respectively.

For the static microstrain measurement of ER effect, the dried white powder was mixed with methyl silicone oil fluid (H-201) quickly and homogenized it by grinding. In the mixed liquid, solid concentration is 20%. After putting on the shelf for a few days, a stable final suspension with no observable sedimentation was obtained.

2.2. Measurements of the ER activity and the structure characterization

The ER effect was characterized by the static microstrain under DC electric field. The experimental data was

collected by a static microstrain measurement system. The system used for measuring the dynamic yield stress of ER fluids is designed and assembled in the light of the principle of simple shearing stream. This equipment is driven by a screw gearing which precise location and velocity modulation are controlled. The yield stress is measured by a force sensor and a strain tester.

The crystalline phase of the products was identified by X-ray powder diffraction (XRD) using an MXP18AHF X-ray diffractometer (MAC Science Co. Ltd., Japan) with graphite monochromatized CuK α radiation ($\lambda = 1.54018$ Å). Morphology and size information of the (BaTiO(C₂O₄)₂/NH₂CONH₂) particles were obtained on a Hitachi Model H-800 transmission electron microscope (TEM). Infrared absorption spectrum was recorded on a Magna-IR 750 Fourier transform infrared (FT-IR) spectrometer scanning in the range of 4000–400 cm⁻¹.

3. Results and discussion

Fig. 1 shows the results of the static microstrain measurement that the ER activity of the urea-coated samples increases more remarkably than the bare one, which coincide with the results reported by Wen et al. [12], and the ER effect of the samples increases with the increase of urea content.

The XRD patterns of the dried white powder are shown in Fig. 2, which shows that the major phase is monoclinic BaTiO(C₂O₄)₂ (JCPDS File No. 47-0801) with lattice parameters $a = 14.954$ Å, $b = 19.332$ Å, $c = 13.947$ Å, $\beta = 106.43^\circ$ and the minor phase is urea (JCPDS file no. 89-6731). From the XRD patterns, it can be found that most peaks of urea and BaTiO(C₂O₄)₂ are congruent except for (101) peak of urea at $d = 3.5947$ Å ($2\theta = 24.77^\circ$). The intensity of the XRD peak at $2\theta = 24.77^\circ$ enhances with the increasing of urea addition.

Fig. 3(a) is the TEM image of the BaTiO(C₂O₄)₂/NH₂CONH₂ particles, which shows that the size of the particles is around 80 nm, and each one of BaTiO(C₂O₄)₂/NH₂CONH₂ particles has a surface coating with about 5–10 nm thickness. Fig. 3(b)–(d), are the TEM images of amplificatory single particle of samples 1, 2 and 3, respectively. It can be observed that the thickness of the

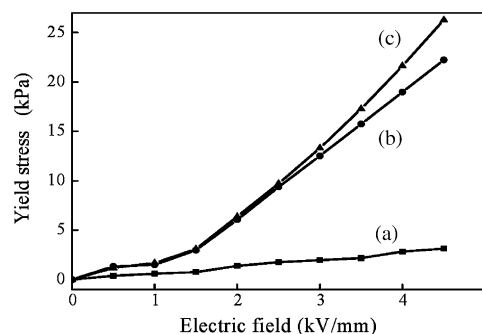


Fig. 1. Plots of static yield stress against the intensity of applied electric field of (a) sample 1, (b) sample 2, and (c) sample 3.

surface coating increase as the addition of urea increasing. Combination with the above XRD results, it is suggested that the surface coating is consisted by urea.

Fig. 4 shows the IR spectra of the uncoated $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ particles and the core/shell structure ($\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2$)

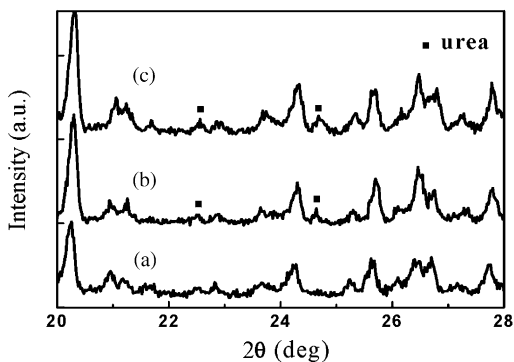


Fig. 2. X-ray diffraction patterns of the uncoated $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ particles of (a) sample 1 and the core/shell structure ($\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2$) particles of (b) sample 2 and (c) sample 3.

(C_2O_4) $_2/\text{NH}_2\text{CONH}_2$) particles which were fabricated with two different contents of urea addition. It can be found that 9 peaks ($3536, 1712, 1658, 1415, 1273, 813, 530 \text{ cm}^{-1}$) appear in the IR spectrum of sample 1 (without urea). It is known that the presence of absorption peaks at $1712, 1658 \text{ cm}^{-1}$ can be assigned to vibrational frequencies of $\text{C}=\text{O}$ band vibration, while the broad peak absorption at 3436 cm^{-1} is assigned to the ones of the absorbed water. Two absorption peaks at $1418, 1273 \text{ cm}^{-1}$ are attributed to the ones of $\text{C}-\text{O}$ band vibration. The absorption peak at 812.7 cm^{-1} can be assigned to the frequencies of $\text{C}-\text{C}$ band vibration. Corresponding to the ones of sample 1, the same absorption peaks are observed in the IR spectra of samples 2 and 3, respectively. By further analysis, it is revealed that some peaks of samples 2 and 3 were split. The selected IR absorption peaks and their split peaks are listed in Table 1, which are determined by a Lorentz function simulation. The IR results show that all the information of $\text{C}=\text{O}$ band vibration in IR spectra can be assigned to $\text{BaTiO}(\text{C}_2\text{O}_4)_2$. In Fig. 4 and Table 1, it is worth to note that the peaks of $\text{C}=\text{O}$, $\text{C}-\text{O}$ and $\text{C}-\text{C}$ band vibrations of

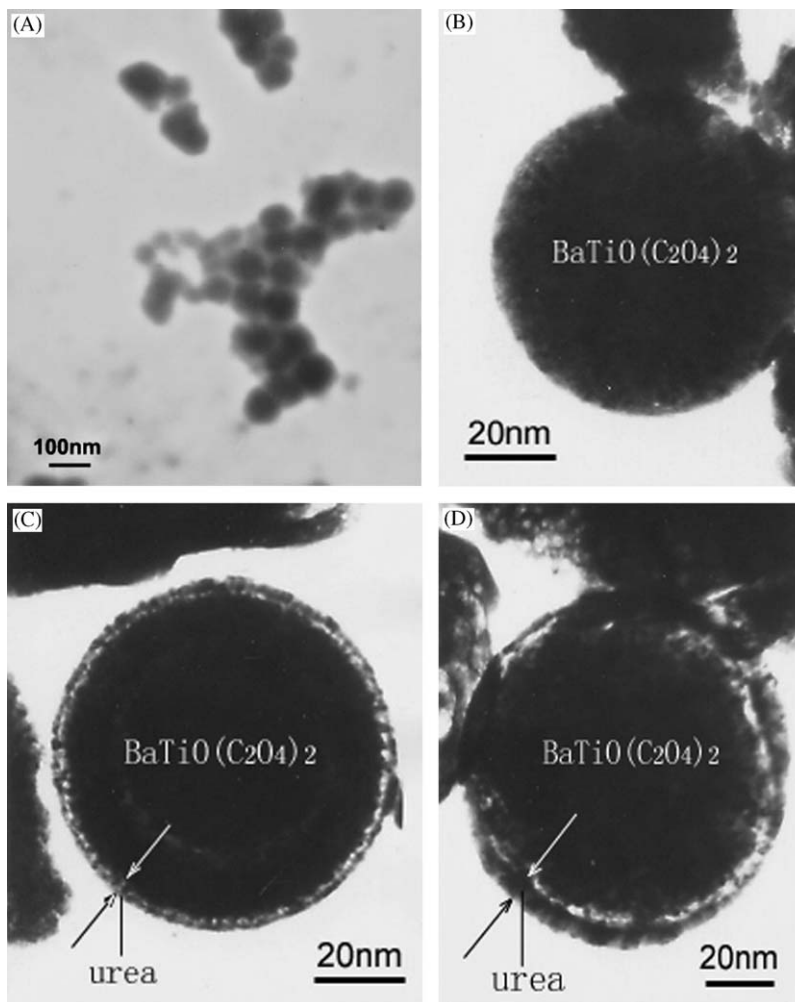


Fig. 3. TEM images of ($\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2$) particles of (A) sample 3 and amplificatory single particles of (B) sample 1, (C) sample 2, and (D) sample 3, respectively.

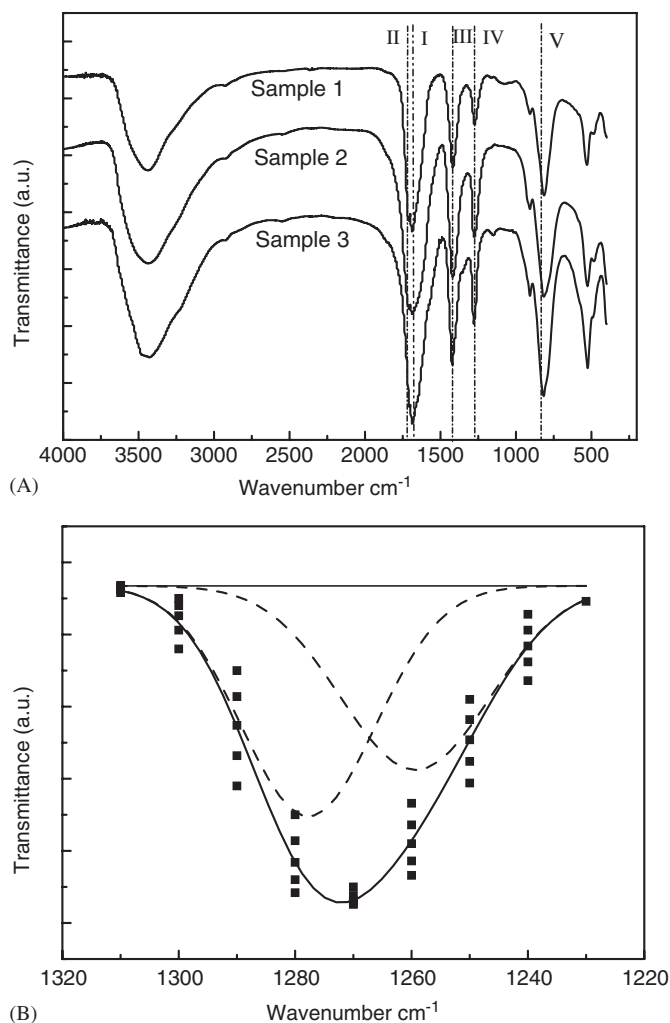


Fig. 4. (A) IR spectra of the uncoated $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ particles (sample 1) and the core/shell structure $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ particles (samples 2 and 3). (B) Peak IV of sample 2 and its two split peaks, which were determined by a Lorentz function simulation.

Table 1
Wavenumbers of split absorption peaks of samples with different urea addition

Peak	Sample 1 (cm^{-1})	Sample 2 (cm^{-1})	Sample 3 (cm^{-1})
I	1658.4	1621.0 1707.4	1636.8 1702.8
II	1712.4	1631.5 1710.9	1659.5 1725.9
III	1415.4	1404.9 1429.0	1403.8 1426.2
IV	1271.2	1259.3 1277.7	1268.5 1282.5
V	812.7	780.8 821.0	766.1 814.9

$\text{BaTiO}(\text{C}_2\text{O}_4)_2$ are split into two peaks while urea added. One is corresponding to the peak (main peak) of sample 1 without urea addition. Another one (shoulder peak) appears at a related low wavenumber place comparing

with the main peak, and its wavenumber is decreased as urea addition increasing.

Combining the results of static microstrain measurement and the IR spectra of $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ with different concentration of urea addition, it can be found that the ER activity of the samples increases under direct current electric field, and the wavenumber of the shoulder peak decreases, as the concentration of additional urea increasing. By the complement of information of Fig. 3, it is suggested that the main peaks are assigned to $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ of the main body inside the microspheres of sample, and the shoulder peaks are assigned to $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ of the interlayer between the core and the shell of the particles. From this point, it is revealed that the giant increase of ER effect of the core-shell samples has a very close relationship with the structural change of the $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ of the interlayer. Furthermore, the main change of the $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ of the interlayer is the decrease of wavenumbers of the C=O, C–O, and C–C band vibrations, which can be contributed to the increase of the lengths of the C=O band and the C–O band. It is suggested that the effect of urea addition on the bare $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ is the dipole polarization between the strong polare C–N–H bonds of urea and the C=O, C–O bonds of oxalate. As a result, the lengths of the C=O band and the C–O band increase, and the vibration frequencies of the C=O band and the C–O bond reduce, while the vibration frequency of C–C bond decreases. Meanwhile, the ER effect increases. There is a very close relationship between the change of the chemical bonds of urea-coated samples and the change of their ER effect.

Particle polarization is now widely thought to be responsible for the interaction forces that lead to the rheological change of ER fluid. The parameters in connection with particle polarization, such as high dielectric constant and dielectric loss and suitable conductivity, have been accepted as the basic factors that dominate the ER effects. Furthermore, the dielectric and conduction properties are closely related to the molecular or crystal structures of the materials [21]. Thus, it is possible to modify dielectric properties to increase ER activity by altering the molecular and crystal structures of ER materials. For the above results, it is suggested that the dipole polarization between C–N–H bonds of urea and C=O and C–O bonds of oxalate increases the dipole moment of the interlayer of the particles, while ER activity increases enormously. It is reported that urea of the $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ material could be replaced with other chemicals, such as acrylamide. Comparing acrylamide and urea having same C–N–H chemical bonds and unsaturated part, acrylamide can have a similar effect on the $\text{BaTiO}(\text{C}_2\text{O}_4)_2$. It can be seen that the model of interlayer polarization coincides well with the experimental results.

In summary, we synthesized the core-shell structure $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ samples with a giant ER activity by a sol–gel method and studied by IR spectroscopy,

TEM and X-ray diffraction. The size of the particles is around 80 nm, and each one of $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$ particles has a surface coating with 5–10 nm thickness consisting of urea. It is found that the ER effect of the samples increases as the doping concentration of urea increasing. Moreover, by the IR spectroscopy study, it is found that the C=O, C–O and C–C band lengths of $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ decrease with the increase of urea content, which is resulted by the interaction between the chemical bonds of urea and oxalate of $\text{BaTiO}(\text{C}_2\text{O}_4)_2$. It is evident that the giant ER activity of the sample have a close relationship with the interfacial interaction between the core and the shell of $(\text{BaTiO}(\text{C}_2\text{O}_4)_2/\text{NH}_2\text{CONH}_2)$.

Acknowledgments

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