

Crosslinked Chitosan Doped with $Y_2(CO_3)_3$ and Surface Energy and Electrorheological Properties

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ABSTRACT: Novel electrorheological materials based on crosslinked chitosan doped with $Y_2(CO_3)_3$ were synthesized with biocompatible chitosan as the substrate of the materials. The electrorheological performance, surface energy, and thermal decomposition behavior of the materials were investigated as functions of the composition change. The results show that doping $Y_2(CO_3)_3$ can improve effectively the electrorheological performance of

crosslinked chitosan with the formation of a metal-polymer complex when the doping degree is suitable. The surface energy plays an important role in influencing the electrorheological properties of the material. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2427–2432, 2007

Key words: crosslinking; metal-polymer complexes; rheology; synthesis; viscosity

INTRODUCTION

Electrorheological (ER) fluids can switch from a liquidlike material to a solidlike material within a millisecond under an external electric field. This rapid and reversible response has potential application in many electrically controlled mechanical devices that transform electrical energy into mechanical energy, such as clutches, valves, and damping devices.^{1–3} However, ER fluids have not been used largely because they do not have a high enough ER effect suitable for the requirements of most applications. To obtain highly active ER materials, various types of ER materials have been synthesized and studied, and the mechanism of the ER effect has been intensively discussed in many articles. Many researchers^{4,5} believe that the ER effect arises from polarization, especially the surface polarization of dispersed particles under an electric field. The conductive, dielectric, and surface properties of several water-free polymeric or inorganic material based ER fluids were investigated by Hao et al.;⁶ they found

that interfacial polarization could contribute to the ER effect and indicated that large interfacial polarization could result in the particle turning and forming a fibrillation structure along the electric field direction. The surface energy of a particle material should be a dominant factor in the interfacial polarization. Therefore, it is necessary to study the relationship between the ER properties and the surface energy of a material.

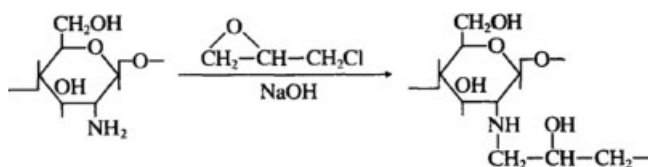
It is well known that the composition of particles, which influence the physical and chemical nature of a material, is essential to the polarization properties of the material. Therefore, it is possible to modify a material's polarization properties by the adjustment of the synthetic procedure so that an ER material having a desired composition is produced. The ER properties of biocompatible chitosan (CTS)^{7,8} and CTS derivatives^{9–14} as disperse phases have been investigated. Crosslinked CTS has better thermal stability and mechanical properties than CTS,^{15,16} and this is advantageous in practical applications. In previous studies, we have found that rare-earth complexes of phosphate cellulose [cellulose(–P–O)₃RE; RE = Ce, Gd, Er, or Y] have higher ER activity than phosphate cellulose, and the ER performance of the yttrium complex [cellulose(–P–O)₃Y] is the best among the cellulose(–P–O)₃RE complexes;¹⁷ in addition, we know that among the materials of SiO₂ adsorbing YF₃, Y₂(CO₃)₃, Y₂(C₂O₄)₃, and YPO₄, the SiO₂·Y₂(CO₃)₃ material reveals the best ER effect.¹⁸ Therefore, to find an ideal ER material that not only has better ER

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Scheme 1 Synthesis of crosslinked CTS.

performance but also is economical, facile, and non-toxic and to gain a better understanding of the mechanism of the ER effect and because $Y_2(CO_3)_3$ is a more economical and facile compound than other rare-earth compounds, we have synthesized a new type of organic polymer ER material, crosslinked CTS doped with rare-earth compound $Y_2(CO_3)_3$. Here we report our investigation on the ER properties of the polymer material and some novel results acquired therein.

EXPERIMENTAL

Materials

All reagents were provided by Beijing Chemistry Reagent Co. (Beijing, China) and used without further purification.

Synthesis of the crosslinked CTS material

Crosslinked CTS was synthesized with the following process (see Scheme 1). First, 4.3 g of CTS was dissolved in an acetic acid solution (2 mol/dm^3) and mixed with epichlorohydrin (ECH; 1 : 3 mass ratio), and the pH value of the mixture was adjusted to about 14 with a solution of NaOH. The mixture was then stirred for 24 h at room temperature. Afterwards, the product was washed with distilled water and acetone and baked at 70°C for 1 h. Finally, the particles were ground to 50–100 μm and dried at 50°C in a vacuum oven for 48 h. Sample 2 was thus obtained.

Syntheses of the $Y_2(CO_3)_3$ -doped crosslinked CTS materials

$Y(NO_3)_3$ was added to a solution containing both CTS and ECH (1 : 3 mass ratio) with a required $Y(NO_3)_3$ /CTS mass ratio. After adequate stirring, a solution of Na_2CO_3 was added to the mixture solution drop by drop to react with the Y^{3+} ions as fully as possible and to induce crosslinking between the

CTS molecules; a solution of NaOH was then added in drops until the pH value of the solution was about 14. Finally, following a procedure similar to that described previously, we obtained samples 3–5. The compositions of the samples are listed in Table II.

Characterization of the materials

The Fourier transform infrared spectra were recorded with KBr pellets with a Nicolet Magna-IR 750 spectrometer (Madison, WI) at 295 K.

The thermal decomposition properties of the materials were determined on a model STA449C+QMS403C simultaneous thermal analysis and mass spectrometry coupling system made by Netzsch-Gerätebau GmbH (Selb/Bavaria, Germany), and the samples were heated at a rate of $10^\circ\text{C}/\text{min}$ up to 700°C in argon gas.

The ER experiments were carried out with a Haake (Vreden, Germany) CV20 rotary viscometer. Various particle materials, after water removal, were mixed quickly with dimethyl silicone oil (density = 0.98 g/cm^3 and viscosity = 98 mPa s at 25°C) under stirring and ultrasonically dispersed for 5 min, yielding the ER fluid (25% weight fraction) samples. The suspensions were then put in the gap between the cylinders of the apparatus as soon as possible for ER measurements. In this study, the sample shear stresses and viscosities were determined at different electric field strengths (direct-current field) at a given temperature (20°C) in a shear rate range of $0\text{--}300 \text{ s}^{-1}$.

To obtain the materials' surface energy, the dried powders (0.3 g) of the samples were dry-pressed at 6 MPa for 5 min into pellets of 8 mm in diameter and 2 mm thick. The contact angles between the pellet and water drops were measured with a video-based contact-angle-measuring device (model OCA20), Dataphysics Instruments GmbH (Stuttgart, Germany). The surface energies of the materials were calculated with SCA21 software and the method equation of state (EOS).

RESULTS AND DISCUSSION

IR spectra of the materials

From Figure 1(A), we can find that the IR spectra of sample 1 (CTS) and sample 2 (crosslinked CTS) reveal

TABLE I
Thermal Decomposition Data of the Materials

Sample	Temperature range ($^\circ\text{C}$)	Weight loss (%)	Temperature range ($^\circ\text{C}$)	Weight loss (%)
Sample 1	110–212	2.3	247–700	63
Sample 2	90–190	1.7	227–700	58
Sample 3	90–185	2.1	225–700	57
Sample 4	95–188	2.1	229–700	55
Sample 5	80–180	2.0	235–700	57

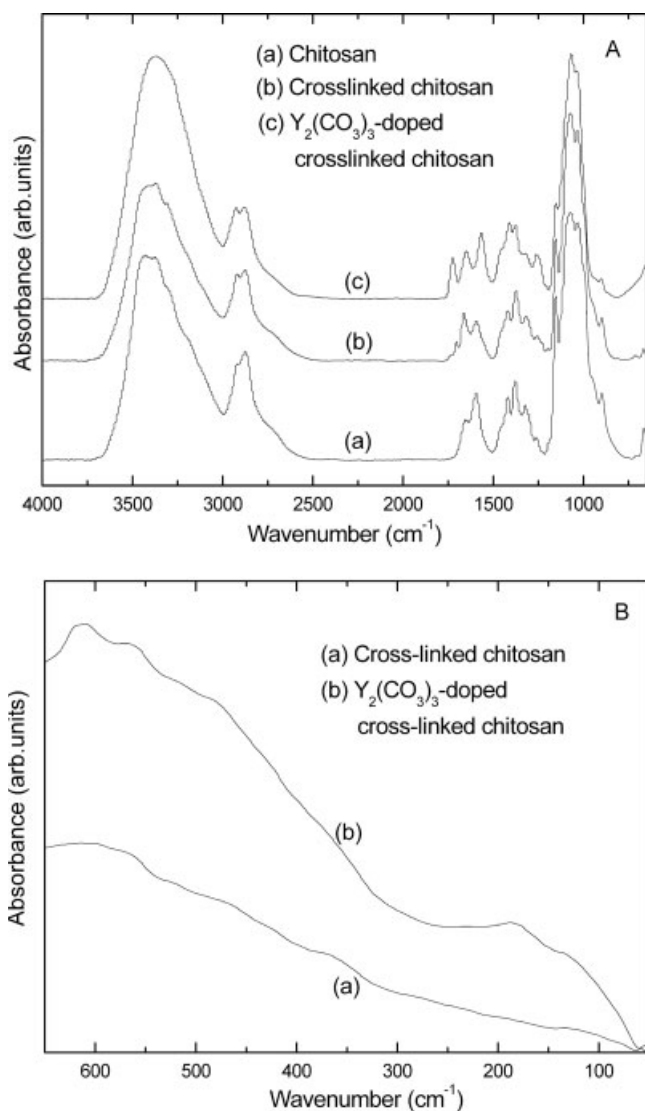


Figure 1 (A) IR spectra in the range of 650–4000 cm^{-1} for samples 1, 2, and 4 and (B) IR spectra in the range of 50–650 cm^{-1} for samples 2 and 4.

similar vibration peaks of $-OH$ and $-C-OH$ groups at 1256, 1032, and 1066 cm^{-1} , but the characteristic absorptions of the $-NH_2$ groups of both are different: a shoulder peak at 1657 cm^{-1} in the IR spectra of sample 1 is obviously strengthened and blueshifted to 1664 cm^{-1} in sample 2, and the peak at 1596 cm^{-1} is weaker in sample 2 than in sample 1. Moreover, a characteristic peak (3310 cm^{-1}) of the $-NH-$ group appears in the IR spectra of sample 2. These results from IR analysis show that the crosslinked CTS has been synthesized by the reaction between ECH and the $-NH_2$ groups in CTS molecules, and the $-OH$ groups do not participate in the reaction¹⁹ (see Scheme 1). A comparison with sample 2 [see Fig. 1(A)] shows that the characteristic absorption of the $-C-OH$ group is blueshifted from 1032 to 1039 cm^{-1} , and the characteristic absorption of the

$-NH_2$ group is redshifted from 1596 to 1567 cm^{-1} in sample 4 [for $Y_2(CO_3)_3$ -doped crosslinked CTS, the IR spectra of samples 3–5 are very similar, so sample 4 was selected as a representative]; this should be the result if the $-OH$ and $-NH_2$ groups in the CTS unit are coordinated to the Y^{3+} ions with the formation of the metal–polymer complexes. In addition, in Figure 1(B), we can see that the characteristic absorption of an $O-Y$ bond appears at 189 cm^{-1} in the IR spectra of sample 4, and this proves further the formation of the coordination bonds between the polymer and Y^{3+} ions.²⁰ The results from Figure 1(A,B) show that the coordination compounds have been obtained by the reaction between crosslinked CTS and Y^{3+} ions. The crosslinked CTS molecule is a multidentate ligand, so it can be coordinated to Y^{3+} ions with a bridge coordination mode and a chelate coordination mode.

Thermal decomposition properties of the materials

To gain a better understanding of the thermal decomposition properties of the materials, the thermal decomposition behaviors of samples 1–5 in the range of 30–700°C were studied with a simultaneous thermal analysis and mass spectrometry coupling system; relevant figures and data are shown in Figure 2 and Table I, respectively. The results from thermogravimetric analysis and mass spectroscopy indicate that these materials involve smaller weight losses (2–3%) with the release of a small number of OH^- fragments in the range of 90–200°C due to the loss of the water molecules adsorbed on the surface of the particles; afterwards, they are decomposed

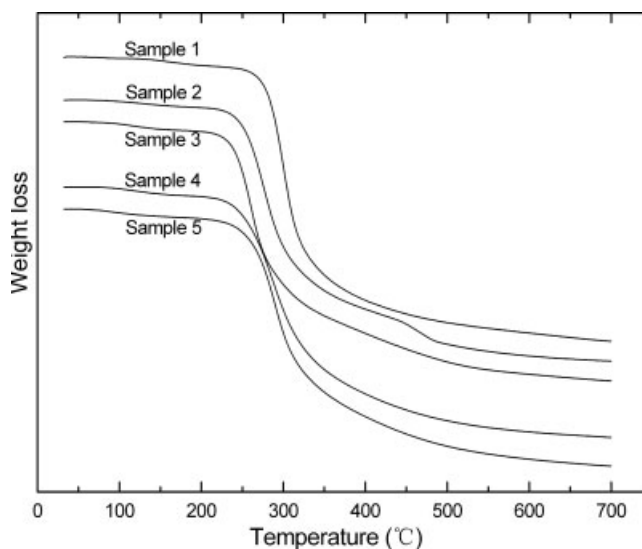


Figure 2 Thermal decomposition properties of the materials.

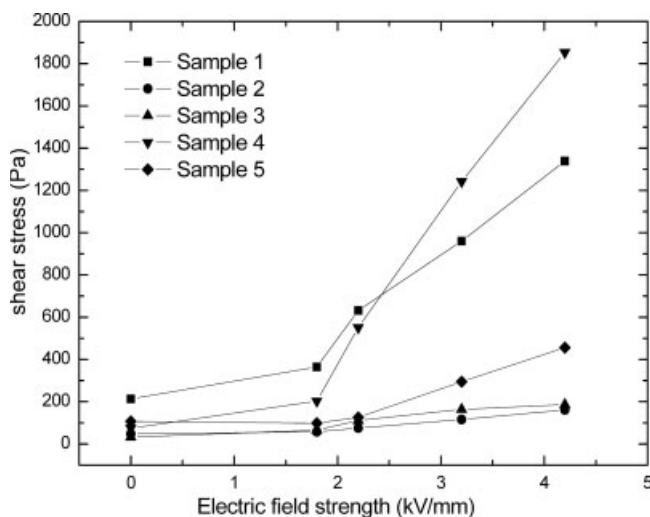


Figure 3 Electric field strength dependence of the shear stress of the suspensions at a shear rate of 150 s^{-1} .

with the release of a large number of the fragments of OH^- , CO , and CO_2 , in which the number of OH^- fragments is 10 times larger than those of CO and CO_2 (mass ratio), from 200 to 400°C ; only CO and CO_2 are found in the fragments when the temperature is beyond 400°C . These thermal decomposition behaviors show that the C—OH bonds in CTS and crosslinked CTS molecules are weaker than other bonds, and this leads to the breaking of the C—OH bonds and the appearance of more OH^- fragments, whereas the materials begin decomposition at a lower temperature. As is known, there are more C—OH groups in crosslinked CTS than in CTS (see Scheme 1), and this can be an important reason that the initial temperature of the destruction of samples 2–5 is slightly lower than that of sample 1. However, pure CTS shows the largest weight loss (63%) in the same temperature range ($200\text{--}700^\circ\text{C}$) among samples 1–5 (see Table I), and this indicates that the crosslinking decreases the rate of degradation and increases the stability of the polymer framework.¹⁵ The thermal decomposition behavior of samples 2–5 is similar; namely, the reaction between crosslinked CTS and Y^{3+} ions cannot influence the thermal stability of crosslinked CTS.

ER properties of the materials

Because the ER fluids in our investigation show similar shear rate dependences of the shear stress and apparent viscosity, we decided to use the ER behavior of the materials at a shear rate of 150 s^{-1} as an example in our discussions. Figure 3 illustrates the shear stresses of the suspensions as a function of the electric field strength at a shear rate of 150 s^{-1} for samples 1–5. In addition, to obtain a clear comparison between the ER performances of these materials, three types of shear stresses were employed: the shear stresses of the suspension with and without an applied electric field (τ_E and τ_0) and the relative shear stress (τ_r), which is defined in our work as the ratio of the shear stress at an electric field to the zero-field shear stress ($\tau_r = \tau_E/\tau_0$). τ_r was also used to represent the magnitude of the ER activity. The corresponding data at an electric field strength of 4.2 kV/mm and a shear rate of 150 s^{-1} are listed in Table II.

The results from Figure 3 and Table II show that the shear stresses of the suspensions of all materials increase under the applied electric field in comparison with the zero electric field strength case, exhibiting ER behavior. However, various ER activities can be observed for these materials. The zero-field shear stress of the suspension of pure CTS (sample 1) is much larger than those of the others. The high zero-field shear stress of the suspension is disadvantageous as an ER fluid. This fact indicates that forming crosslinked CTS and $\text{Y}_2(\text{CO}_3)_3$ -doped crosslinked CTS can effectively depress the zero-field shear stress of the CTS material. In the presence of an electric field, the shear stresses and τ_r values of sample 1 are larger than those of samples 2, 3, and 5 and smaller than those of sample 4 at an electric field strength greater than 2.5 kV/mm ; that is, the ER effect of samples 2, 3, and 5 is lower and that of sample 4 is higher than that of sample 1. These results show that forming crosslinked CTS does not heighten the ER activity of the CTS material; this may be imputed to the fact that after the crosslinking reaction, the composition and structure of the product (crosslinked CTS) are evidently different from those of CTS, and this leads to a fall in the ER effect. Never-

TABLE II
Compositions and Surface Energies of the Materials and Shear Stresses of the Suspensions

Sample	Composition (Y/CTS mass ratio)	τ_0 (Pa)	τ_E (Pa)	τ_E/τ_0	Surface energy (mN/m)
1	CTS	213	1339	6.3	18.4
2	Crosslinked CTS	47.65	160.9	3.4	35.88
3	$\text{Y}_2(\text{CO}_3)_3$ -doped crosslinked CTS (0.01)	32.21	186.2	5.8	38.54
4	$\text{Y}_2(\text{CO}_3)_3$ -doped crosslinked CTS (0.03)	74.88	1853	24.7	65.82
5	$\text{Y}_2(\text{CO}_3)_3$ -doped crosslinked CTS (0.05)	106.8	455.5	4.3	44.2

theless, doping $Y_2(CO_3)_3$ in crosslinked CTS can enhance the ER performance, especially when the doping degree is suitable, such as sample 4. The ER activity of sample 4 is the highest among the studied materials. The shear stress of the suspension is 1853 Pa and τ_r reaches 24.7 at an electric field strength of 4.2 kV/mm and a shear rate of 150 s^{-1} , and the zero-field shear stress is low (see Table II), so sample 4 is a better ER material. Samples 3 and 5 as $Y_2(CO_3)_3$ -doped materials have slightly higher ER performance than sample 2. Therefore, the impact of the doping degree on the ER properties of the crosslinked CTS material cannot be neglected. The ER behavior of the $Y_2(CO_3)_3$ -doped materials (samples 3–5) is related to the polarizability of the materials. The polarizability of the crosslinked CTS would increase with doping $Y_2(CO_3)_3$. However, the fact that the ER effect of sample 5 is smaller than that of sample 4 proves that superabundant $Y_2(CO_3)_3$ is unfavorable for improving the ER property, such as the case of sample 5. That is, there is an optimal value for the $Y_2(CO_3)_3$ -doping degree, and this value can be in close approximation to a ratio of Y to CTS (mass ratio) of 0.03. These ER behaviors can be apprehended by the actions of Y^{3+} ions and $Y_2(CO_3)_3$ in the materials. After the addition of $Y(NO_3)_3$ to the solution (see the Experimental section), the Y^{3+} ions are coordinated by $-NH_2$ or $-OH$ groups in CTS units, and subsequently entering CO_3^{2-} ions exist as counterions and ligands in the materials, sequentially, resulting in increasing interface polarization and ER effects of the particle suspension and enhancing with an augmented doping degree. However, when the content of Y^{3+} ions exceeds a saturation value, which is related to the potential number of atoms (oxygen and nitrogen atoms) coordinated with Y^{3+} ions in the crosslinked CTS, the superfluous $Y_2(CO_3)_3$ particles, in which the Y^{3+} ions are uncoordinated by a CTS unit, appear on the surface of the particles of the complex material. These $Y_2(CO_3)_3$ particles may affect the interface polarization in the suspension in an applied electric field and subsequently may decrease the ER activity of the material.^{21,22} The Y^{3+} -ion content in sample 4 may have reached the saturation value. The lower ER activity of sample 5 may be ascribed to it having superfluous $Y_2(CO_3)_3$ particles. The ER behavior of the materials can be related to their surface energy.

Effect of the surface energy on the ER properties of the materials

The surface energy data from Table II show that among the studied samples, the surface energy of sample 1 (pure CTS) is the lowest, and those of samples 2–5 are much larger than that of sample 1. That

is, forming crosslinked CTS can increase effectively the surface energy of the CTS material. In comparison with samples 3–5, the surface energy of sample 2 is lower, and this indicates that doping $Y_2(CO_3)_3$ is beneficial for elevating the surface energy. However, in a comparison of the materials doped with $Y_2(CO_3)_3$, sample 4 has the highest surface energy; the surface energy of sample 5 is lower, although it contains more $Y_2(CO_3)_3$ than sample 4. This may arise from existing $Y_2(CO_3)_3$ particles on the surface of the particles of the complex material, as mentioned previously.

Considering the ER properties of the materials, we can see that the influence of the surface energy on the ER performance of a material cannot be ignored. The low surface energy of the pure CTS material may lead to its stronger dissolving action in the dispersing medium (dimethyl silicone oil), which leads to high viscosity with and without an applied electric field.²³ The crosslinked CTS (sample 2), the surface energy of which is lower, has a lower ER activity than that of samples 3–5. The ER activity increases with the augmentation of the surface energy from sample 2 to sample 4; afterwards, the ER activity decreases with a fall of the surface energy, such as sample 5. These phenomena show that the material that has a larger surface energy, the suspension of which may have larger interface polarization under an electric field, should have a better ER performance. Here, some experimental results are noteworthy, such as the τ_r value of sample 1 being larger than those of samples 2, 3, and 5 and the τ_r value of sample 3 being larger than that of sample 5, although the surface energies of samples 1 and 3 are lower. The evident difference in the composition and structure between sample 1 and samples 2–5 should be responsible for their behaviors, such as a lower surface energy and higher τ_r value for sample 1. In other words, the rule that a material having a larger surface energy has a higher ER activity is only fitting for a comparison between those materials having similar compositions and structures. As for samples 3 and 5, the surface energies of both are in close approximation, so the τ_r value of sample 3 is only slightly larger than that of sample 5. That is, the magnitude of the ER activity for different materials cannot be confirmed by a comparison of their surface energies when their surface energies are in close approximation. It is necessary to study the relationship between the surface energy and interface polarization in detail.

CONCLUSIONS

Crosslinked CTS materials doped with $Y_2(CO_3)_3$ were synthesized, and their ER performance, surface energy, and thermal decomposition behavior were

investigated. The results show that doping $Y_2(CO_3)_3$ can improve effectively the ER performance of cross-linked CTS when the doping degree is suitable. The surface energy plays an important role in influencing the ER properties of the material. A material having larger surface energy may have better ER performance when the compositions and structures of different materials are similar.

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