Molecule-based electrorheological material assembled using β-cyclodextrin as substrate

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Abstract

Molecule-based electrorheological (ER) materials as a novel type of ER materials, the inclusion compound \([H_2(β-CD-A)-PTA]\) between p-toluenesulfonyl acid (PTA, guest) and \(H_2(β-CD-A)\) (host) that is dicarboxylic acid of β-cyclodextrin (β-CD), and the rare earth (RE) complexes \([[(β-CD-A)-PTA],RE_2(\text{RE}=\text{La, Gd, Y})]\) of \(H_2(β-CD-A)-PTA\), were synthesized. The ER performance and dielectric property of the materials were studied. Our results show that the molecule-based ER materials assembled using β-cyclodextrin as a substrate, especially the inclusion compound and its rare earth (RE) complexes exhibit clear ER effect. The inclusion PTA can markedly enhance the ER performance of \(H_2(β-CD-A)\) material. The ER activity of the yttrium complex is the highest among these materials. The characteristic of the molecule in molecule-based ER materials is an important factor in influencing ER property.

Keywords: electrorheological material, chemical synthesis, electrorheological property

1. Introduction

An electrorheological (ER) fluid is made from an insulating liquid medium containing either a particulate material or a liquid material. The rheological properties of an ER fluid could reversibly change under an external electric field with the electric field strength (Wei, 2000; Hao, 2001). Because of their reversible and quick response to external electric fields, ER fluids have attracted much interest for their potential application in various mechanical devices, such as clutches, valves, damping devices, etc. (Coulter et al., 1993; Winslow, 1947; Block and Kelly, 1988). However, ER fluids have not been widely utilized because their ER effect is not strong enough to suit the requirements of most applications.

In order to obtain a material with a strong ER effect, a wide spectrum of ER materials have been synthesized and studied (Hao, 2002). However, molecule-based ER materials have not been reported previously except for research conducted in our lab (Jia et al., 2007; Jia et al., 2007; Jia et al., 2009). Unlike other inorganic materials, which are constructed with covalent bonds, ionic bonds or metal bonds between atoms or ions, molecule-based solid materials are assembled through weak interactions such as hydrogen bonds, π-π interactions, van der waals forces and/or coordination bonds. Therefore, molecule-based solid materials with any specific functionality can be synthesized by selecting suitable molecules and an appropriate assembly method. The research progress on molecule-based solid function materials with optical, electrical or magnetic properties has been reported (Becher and Schaubburg, 1995; Braga et al., 1999). Molecule-based magnetic materials have been studied extensively in the fields of chemistry, physics and material science (Kahn, 1993; Coronado et al., 1995; Miller and Drillon, 2002-2005). In previous studies (Jia et al., 2007), we have found that assembling PTA inside β-CD cavity, which induces the formation of an inclusion compound β-CD-PTA, can enhance obviously the ER performance of β-CD, the cooperation with a rare earth ion can heighten evidently the ER activity of β-CD-PTA. From the literature (Jia et al., 2009), we have seen that dicarboxylic acid \([H_2(β-CD-A)]\) of \(β-CD\) and its rare earth complexes showed a clear ER effect. In order to better understand the mechanism of the observed ER effect by assembling and studying novel molecule-based ER materials, and to find an ideal ER material with an enhanced ER performance and is economical and facile, we selected β-CD as a substrate of our ER materials, and synthesized a new series of molecule-based ER materials, the inclusion compound \(H_2(β-CD-A)-PTA\) and its rare earth complexes. The effects of the formations of the
inclusion compound and rare earth complexes on the ER performance have been investigated, and the relationship between the dielectric property and its ER effect for the materials is discussed in this paper.

2. Experimental

The dicarboxylic acid of β-CD, H₂β-CD (sample 2), was prepared and verified through the method described in the literatures (Jia et al., 2009; Huang et al., 2000). The inclusion compound H₂β-CD-PTA was synthesized by using following process: first, a mixture of H₂β-CD-A (1.50 g) and PTA (0.378 g) (12, molar ratio) and 5 cm³ of absolute alcohol was ground for 30 minutes, after the mixture was allowed to react at 50°C for 3 hours, and grinded further into fine powders, the white solid powders were finally dried in vacuum for 2 days at 50°C, the inclusion compound, H₂β-CD-PTA (sample 3), was thus obtained (Gao and Zhao, 2004). The schematic structure of the preparation of H₂β-CD-A and H₂β-CD-PTA is shown in Fig. 1.

The rare earth complexes of the inclusion compound were synthesized by mixing H₂β-CD-PTA (1.87 g) and 0.75 cm³ of LaCl₃ solution (0.992 mol/L), 1.0 cm³ of GdCl₃ solution (0.740 mol/L) or 0.67 cm³ of YCl₃ solution (1.10 mol/L), respectively (1.5:1, molar ratio), and 5 cm³ of absolute alcohol following a similar procedure as described above, the rare earth complexes [(β-CD-A)-PTA]·RE₂ (RE=La, Gd and Y) (samples 4–6) were established. The reaction scheme is as follows:

3[H₂β-CD-PTA]+2RECl₃→[(β-CD-A)-PTA]·RE₂+6HCl

The HCl in the product can be removed by a volatilization under heating.

The dried particle materials were mixed quickly with dimethyl silicone oil (density ρ=0.98 g·cm⁻³ and viscosity η=98 mPa·s at 25°C) under stirring, and ultrasonically dispersed for five minutes, yielding the ER fluid (25 wt%) samples. The suspensions were then put in the gap between the cylinders of the apparatus as soon as possible for ER measurements. The ER experiments were carried out using a German Rotary Viscometer (Type HAAKE CV20). In this study, the sample shear stresses and viscosities have been determined under different electric field strengths (E, dc field) at a given temperature (20°C) and a shear rate (γ) range of 0–200 s⁻¹.

Because of difficulties involved in direct measurements, the suspensions (45 wt%) of the materials were used to investigate their dielectric properties. The capacitance C and dielectric loss tangent (tanδ) at room temperature under various frequencies (f) were obtained on a HP4274A Multi-frequency LCR Meter. The dielectric constant (ε) was derived from the measured C according to the conventional relation, ε=C·d/(ε₀·S), where ε₀ is the dielectric constant of vacuum i.e. 8.85×10⁻¹² F·m⁻¹, and d is the thickness of the gap between the electrodes and S is the contact area of the electrodes.

IR spectra of the samples were recorded using KBr pellets with a Nicolet Magna-IR 750 spectrometer at 295 K. XRD analyses of the materials were carried out on a Bruker D8 ADVANCE X-ray diffractometer with Cu-Ka radiation at a wavelength 1.5406 nm in a range of 3°–50°.

The compositions and some ER data of the samples were listed in Table 1.

3. Results and discussion

3.1. Formation of inclusion compound and rare earth inclusion complex

The formations of the inclusion compound and rare earth inclusion complex were determined by IR and XRD analysis (Bratu et al., 2009; Nakanishi and Solomon, 1977; Nakamoto, 1986). The IR and XRD patterns of [(β-CD-A)-PTA]·RE₂ (RE=La, Gd and Y) (sample 4–6) are similar, so the IR and XRD pattern of [(β-CD-A)-PTA]·Y₂ were

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
<th>τ₀ (Pa)</th>
<th>τₑ (Pa)</th>
<th>τᵣ (τ₀/τₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>β-CD</td>
<td>44.33</td>
<td>158.1</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>H₂β-CD-A</td>
<td>53.91</td>
<td>275.3</td>
<td>5.1</td>
</tr>
<tr>
<td>3</td>
<td>H₂β-CD-PTA</td>
<td>75.95</td>
<td>1083</td>
<td>14.3</td>
</tr>
<tr>
<td>4</td>
<td>[(β-CD-A)-PTA]La₂</td>
<td>46.38</td>
<td>1086</td>
<td>23.4</td>
</tr>
<tr>
<td>5</td>
<td>[(β-CD-A)-PTA]Gd₂</td>
<td>50.31</td>
<td>1063</td>
<td>21.1</td>
</tr>
<tr>
<td>6</td>
<td>[(β-CD-A)-PTA]Y₂</td>
<td>53.07</td>
<td>1493</td>
<td>28.1</td>
</tr>
</tbody>
</table>
selected as a representative in following discussion.

Fig. 2 shows the XRD patterns of samples 2, 3, 6 and PTA. Comparing the XRD pattern of H$_2$(β-CD-A)-PTA (sample 3) to that of H$_2$(β-CD-A) (sample 2) and PTA, the characteristic peaks of sample 2 and PTA are not present in the XRD pattern of sample 3, indicating that sample 3 is not an aggregate composed of H$_2$(β-CD-A) and PTA, but an inclusion compound resulted from the inclusion reaction between H$_2$(β-CD-A) (host) and PTA (guest), thus not a mixture. The XRD pattern of sample 6 is different from that of sample 3, exhibiting a new phase in addition to the inclusion compound, and this new phase is the rare earth inclusion complex. Therefore, the XRD patterns of the materials can serve as evidence for the formation of the inclusion compound and the rare earth inclusion complex.

The IR spectra of the materials provide further proof for the formation of the inclusion compound and the complex (Nakanishi and Solomon, 1977; Nakamoto, 1986). Comparing with the IR spectra of H$_2$(β-CD-A) (host, sample 2) and PTA (guest) [see Fig. 3 (a)], the IR spectrum of sample 3 shows only characteristic absorptions of H$_2$(β-CD-A) and the characteristic absorptions of the sulfonic group anion (-SO$_3^-$) of PTA at 1124 cm$^{-1}$, the characteristic absorption of the -CH$_3$ group at 1455 cm$^{-1}$ and the characteristic absorption of the phenyl group at 1496 cm$^{-1}$, which are present in the IR spectra of the guest, have weakened to shoulder peaks, and the vibration peaks of the hydrogen bonds between the PTA molecules in the range of 1765–2735 cm$^{-1}$ have disappeared. These results can further confirm that sample 3 is an inclusion compound. Comparing with the IR spectrum of sample 3 [see Fig. 3 (b)], the characteristic absorption of an O-Y bond at 147 cm$^{-1}$ appears in the IR spectrum of sample 6, indicating that the rare earth ions have been coordinated to form the rare earth inclusion complex.

3.2. Electrorheological property of materials

Fig. 4 illustrates the shear stresses and static yield stress as a function of the electric field strength (E, dc field) at $\gamma$=150 s$^{-1}$ for samples 1-6. In order 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 applied electric field ($\tau_E$ and $\tau_0$), and relative shear stress ($\tau_r$), which is defined in our work as the ratio of the shear stress at an electric field to zero-field shear stress ($\tau_r = \tau_E/\tau_0$). Relative shear stress was also used to represent the magnitude of the ER activity. The corresponding data at E=4.2 kv/mm and $\gamma$=150 s$^{-1}$ are listed in Table 1.

From Fig. 4(a) and Table 1, we can see that: the change in the shear stress for sample 1 is small, and the shear stress of sample 2 clearly increases, with increasing electric field strength, therefore, sample 2 has better ER performance than sample 1, because the formation of The dicarboxylic acid of β-CD [H$_2$(β-CD-A)] has enhanced the ER activity of β-CD (Jia et al., 2009); the $\tau_r$ value (14.3) of H$_2$(β-CD-A)-PTA (sample 3) is much larger than that (5.1)
of \(H_2(\beta\text{-CD-A})\) (sample 2), namely the inclusion compound between \(H_2(\beta\text{-CD-A})\) and PTA has much higher ER activity than \(H_2(\beta\text{-CD-A})\), which shows that assembling PTA inside \(H_2(\beta\text{-CD-A})\) cavity can enhance obviously the ER performance of \(H_2(\beta\text{-CD-A})\). Comparing samples 3-5, we can see that the shear stresses of \([([\beta\text{-CD-A}]-\text{PTA})\text{-La}_2\] and \([([\beta\text{-CD-A}]-\text{PTA})\text{-Gd}_2\] (samples 4 and 5) are close to that of \(H_2(\beta\text{-CD-A})\)-PTA (sample 3) under an applied electric field, however, the shear stresses of sample 3 is larger than that of \([([\beta\text{-CD-A}]-\text{PTA})\text{-RE}_2\] (samples 4-6) without applied electric field [see Fig. 4(a)], therefore, samples 4 and 5 have higher ER activity than sample 3 (see Table 1). From Fig. 4(a), the shear stresses of \([([\beta\text{-CD-A}]-\text{PTA})\text{-Y}_2\] (sample 6) is the largest in an applied electric field among these materials. The data in Table 1 show that the \(\tau_r\) value of samples 4-6 are higher than that of sample 3, and the \(\tau_r\) value of sample 4 \([([\beta\text{-CD-A}]-\text{La}_2]\) is slightly larger than that of sample 5 \([([\beta\text{-CD-A}]-\text{Gd}_2]\). The \(\tau_r\) value of sample 6 is the highest among the complexes.

The results shown above indicate that PTA as a guest can improve the ER performance of \(H_2(\beta\text{-CD-A})\) as a host, this phenomenon can be related to the matches in the structure and polarity between PTA and \(H_2(\beta\text{-CD-A})\) molecules, the presence and polarization of PTA can enhance the polarizability of \(H_2(\beta\text{-CD-A})\) molecule in an electric field, which makes higher polarizability of the inclusion compound molecule, and sequentially larger interfacial polarization between the dispersed phase and the medium in the suspension of the inclusion compound than that of \(H_2(\beta\text{-CD-A})\) under an electric field (Hao et al., 1998). Considering the ER property of the materials, we can see that the suspension of \(H_2(\beta\text{-CD-A})\)-PTA material presents much higher zero-field shear stress than that of the rare earth complexes, which can be attributed to a change in the polarity of the molecule. The formation of the rare earth complex can increase the polarity of the molecule through the coordination bonds between the carboxyl and rare earth ions, the lower polarity of \(H_2(\beta\text{-CD-A})\)-PTA molecule 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 (Zhao, 2004), as a result of which the rare earth complexes exhibit higher ER activity than \(H_2(\beta\text{-CD-A})\)-PTA. Comparing the ER performance between complexes of different rare earth metal ions, the ER activity of \([([\beta\text{-CD-A}]-\text{PTA})\text{-Y}_2\] is the highest, this can be explained by the fact that the radius of the \(Y^{3+}\) ion is the smallest of the three. As is well known, the polarization of the metal ion with a smaller radius tends to be stronger in a complex. Therefore, it is not surprising that the ER fluid composed of \([([\beta\text{-CD-A}]-\text{PTA})\text{-La}_2\] which contains the rare earth ion with the smallest radius, \(Y^{3+}\), has the largest interfacial polarization and consequently the best ER performance. However, the suspension of the complex \([([\beta\text{-CD-A}]-\text{PTA})\text{-Gd}_2\] shows slightly lower ER effect than that of \([([\beta\text{-CD-A}]-\text{PTA})\text{-La}_2\], although \(Gd^{3+}\) has smaller ion radius than \(La^{3+}\), this is an unusual result. In previous studies (Jia et al., 2009), we have found that the ER activity of \([([\beta\text{-CD-A}]-\text{Gd}_2\text{)}\) is slightly higher than that of \([([\beta\text{-CD-A}]-\text{La}_2\text{)}\).

The results shown that, as molecule-based ER materials, the co-polarization between the cation and the anion within the molecule, which may play an important role in influencing the interfacial polarization under an electric field, has to be taken into account. Comparing the electron layer structures of the \(Y^{3+}\), \(La^{3+}\) and \(Gd^{3+}\) ions, \(La^{3+}\) and \(Gd^{3+}\) both have 5s\(^5\)5p\(^6\) electrons, whereas \(Y^{3+}\) does not. Thus, the polarization forces applied to the \([([\beta\text{-CD-A}]-\text{PTA})\text{-La}_2\] ion from \(La^{3+}\) and \(Gd^{3+}\) ions are comparable and the polarization forces from \(Y^{3+}\) are different. The \(Y^{3+}\) ion generates stronger polarization forces than \(La^{3+}\) and \(Gd^{3+}\) because of its smaller ion radius and particular electron layer structure. The weaker polarization force in \([([\beta\text{-CD-A}]-\text{PTA})\text{-La}_2\] and \([([\beta\text{-CD-A}]-\text{PTA})\text{-Gd}_2\] is critical, as it decreases the interfacial polarization in their suspensions under an electric field.
field. As a result, the ER activities of \([\beta-\text{CD-A})\text{-PTA}\]_La_2 and \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2 are weaker than that of \([\beta-\text{CD-A})\text{-PTA}\]_Y_2. Considering the ER performance of \([\beta-\text{CD-A})\text{-PTA}\]_La_2 and \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2, the electron layer structures of La\(^{3+}\) and Gd\(^{3+}\) are the same except for 4f orbit, and the radii of both are near, which can be the reason why the ER activities of their complexes are very similar when the ligand is the same. Therefore, the relative magnitude of both of the complexes in ER activity can change with a change of the ligand. The difference in the relative magnitude between the complexes of La\(^{3+}\) and Gd\(^{3+}\) in ER property for \([\beta-\text{CD-A})\text{-PTA}\]_La_2 and \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2 can be interpreted in terms of the difference in the polarization forces between the ligands. \([\beta-\text{CD-A})\text{-PTA}\]_La_2 is a more complex anion than \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2. As well known, the polarization force applied to a cation from a complex anion can not be neglected. The co-polarization between the cation and the anion within the molecule \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2 can be stronger than within the molecule \([\beta-\text{CD-A})\text{-PTA}\]_La_2, because the Gd\(^{3+}\) ion with 4f orbit may be polarized more easily than La\(^{3+}\) ion with 4f orbit. As a result, there are more covalent bond properties in Gd-O bond (coordination bond) for \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2 than in La-O bond (coordination bond) for \([\beta-\text{CD-A})\text{-PTA}\]_La_2, which may lead to weaker interfacial polarization in the suspension containing \([\beta-\text{CD-A})\text{-PTA}\]_Gd_2 particles than in the suspension containing \([\beta-\text{CD-A})\text{-PTA}\]_La_2 particles under an electric field. In other words, the property of the coordination bond can play an important role in influencing ER activity of a coordination compound material.

Fig. 4(b) shows the dependency of static yield stress (\(\tau_0\)) on electric field strength (E) for various material suspensions. Like many other ER fluids, samples 1-6 also possess the property that the yield stress increases as the electric field strength increases, as the result of an increase in the polarization interactions between particles. In order to understand a power law relationship between \(\tau_0\) and E (Choi et al., 2001; Kim et al., 2001), the \(\alpha\) values in equation \(\tau_0 \propto \mu E^\alpha\) were obtained from Fig. 4(b). For \(\beta-\text{CD-A})\text{-H}_2(\beta-\text{CD-A})\) (samples 1 and 2), both of them have given the observed \(\alpha\) (1.18 and 1.56) <2, but the \(\alpha\) values (2.42-2.68) of the samples 3-6 are all >2. The unusual results in this paper differ from the reports that the yield stress is proportional to the square of the electric field strength or \(\alpha<2\) (Choi et al., 2001; Kim et al., 2001; Park et al., 2009; Hong et al., 2009). The uncommon values of \(\alpha>2\) may be related to the characteristic of the molecule-based ER material. The molecule complex configuration that can dominate the polarity of a molecule play a dominant role in influencing the interaction between the molecules, sequentially it would influence the interface polarization and the interaction between the particles in the suspension under an applied electric field. Comparing with samples 1 and 2, there is a guest PTA inside the cavity of the molecule of samples 3-6. Therefore, the guest PTA may be responsible for making higher \(\alpha\) values of samples 3-6 because PTA's presence not only induces a change of the molecule composition but also induces a change of the molecule configuration.

The dependency of the shear stress on shear rate under different electric field strengths for the suspension of sample 6 was illustrated in Fig. 5(a). The change in shear stress is very small with increasing shear rate when no electric field is present. The dependency of shear stress on shear rate under an electric field is related to the applied electric field strength and the magnitude of the shear rate. Under an applied electric field, the shear stress clearly grows larger at \(\gamma>20\ s^{-1}\), thereafter decreases at \(\gamma>20\ s^{-1}\), the change in the shear stress is decreased gradually in a range of the shear rate of 30-200 \(s^{-1}\), with increased shear rate. These phenomena show that the interfacial polarization between the dispersed phase and the medium in the suspension is strongly affected by the electric field strength. Under high electric field strength, the electrostatic interaction force
between the particles, which originated from the induced dipole moment caused by the interfacial polarization, dominates the shear force; that is to say, the chain-like structure, which is established by the electrostatic interaction between the particles, is not fully broken even at high shear rates. Therefore, shear stress would increase with increasing shear rate, but the electrostatic interaction force between the particles is weaker under low electric field strength than under high electric field strength. However, with increasing shear rate, the shear force would increase, and the destruction rate of the particle chain structure would increase gradually. As a result, the increment in the shear stress would decrease gradually. Therefore, in order to achieve the best ER effect, the match between the electric field strength and shear rate is very important. In addition, Choi et al. (Cho et al., 2003) proposed an empirical rheological equation of state for many ER fluids with any complicated flow curves of shear stress as a function of shear rate, so the steady-state flow properties of our [(β-CD-A)-PTA],REβ-based ER fluids can be interpreted by using the equation.

According to an equation (Kim et al., 2001) describing the relationship between \( \tau_e \) and \( \delta_e \), the dynamic yield stress \( \tau_d \) of the suspension was obtained. Fig. 5(b) illustrates the dependency of \( \tau_d \) on shear rate under different electric field strengths for the suspension of sample 6. Comparing Fig. 5(b) with Fig. 5(a), we can see that the shear rate dependency of \( \tau_d \) is similar to that of \( \tau_e \).

### 3.3. Dielectric property of materials

The ER activity has been related to interfacial polarization, which is connected with the characteristics of dielectric spectra and conductivity (Cho et al., 2002; Cho et al., 2004). The dependence of dielectric constant \( (\varepsilon) \) and dielectric loss tangent \( (\tan\delta) \) on frequency, dielectric spectra of ER fluids can provide additional information on both analyzing their electrical polarization properties and interpreting the flow behavior of ER fluids.

The dielectric spectra in a range of the frequency (f) from 0.4 to 40 kHz for \( \beta-CD \), \( H_2(\beta-CD-A) \), \( H_2(\beta-CD-A)-PTA \) and \( [(\beta-CD-A)-PTA]_2 \) (samples 1, 2, 3, and 6, respectively) are illustrated in Fig. 6. The dielectric spectra of \( [(\beta-CD-A)-PTA]_2 \) are similar, so \( [(\beta-CD-A)-PTA]_2 \) is selected as a representative. The tanδ values of sample 1 with the lowest ER activity are the smallest, its ε values also are smallest at f=27 kHz, among these materials. The results from Fig. 6(a) show that: the ε values of \( \beta-CD \) are larger than those of samples 3 and 6 at f=27 and f=35 kHz, respectively; \( H_2(\beta-CD-A) \), of which the ER activity is lower than that of both \( H_2(\beta-CD-A)-PTA \) and \( [(\beta-CD-A)-PTA]_2 \), has the largest ε except for the ε value at f=400 Hz among the samples; the ε values of sample 3 having lower ER activity are slightly larger at f<4 kHz, then slightly lower than those of sample 6 having higher ER activity. From Fig. 6(b), we can see that: the tanδ values of both samples 3 and 6 decrease, whereas those of sample 2 increase with increased frequency; the tanδ values of sample 2 that has the lowest ER activity are the least at f<5 kHz, and at f>10 kHz are the largest among the samples 2, 3 and 6; the tanδ values of sample 3, which has lower ER activity, are slightly larger over the entire frequency range in the comparison with those sample 6.

Hao et al. (Hao et al., 1998) indicated that a large dielectric loss is required for a good ER material, because only a material having a large dielectric loss could give a large interfacial polarization once it is dispersed into a liquid, which can impel the particles to turn and form fibrillation chains along the electric field direction. Moreover, Hao and his co-workers (Hao et al., 1998) proposed an empirical criterion for selecting ER material: the particle dielectric loss tangent should be approximately 0.10 at 1000 Hz, and the larger the particle dielectric constant, the stronger the ER effect. However, the experimental results in regard to the dielectric property of a material and its ER effect, which are obtained in this study, do not accord entirely with Hao’s conclusions mentioned above. Here the behav-
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ior of sample 2 is noticeable, its ER activity is lower although its ε and tan δ are larger than that of samples 3 and 6 at higher frequency. Moreover, the behavior of sample 6 is also notable, it has higher ER activity, but its tan δ values are lower, the ε values are very close to those of sample 3. These infrequent results can be related to the characteristic of molecule-based ER material. Considering the molecule-based ER materials reported by us (Jia et al., 2007; Jia et al., 2009), β-CD, the inclusion compound of β-CD (β-CD-PTA), H₂(β-CD-A) and the rare earth complexes of both β-CD-PTA and H₂(β-CD-A), the correlation between the dielectric property and ER property is consistent with the conclusions obtained by Hao et al. (Hao et al., 1998; Hao et al., 1997). The molecule-based ER materials studied in this paper, (β-CD-A)-PTA, RE₃, and H₂(β-CD-A)-PTA, are more complicated molecule. For the type of molecule-based ER materials, the impact of the dielectric property on the ER property may be very small. Namely, the complexity of the molecule in a molecule-based ER material could even result in inconsistencies between the relative magnitude of the ER effects and the relative magnitude of the ε and tan δ. Therefore, it is difficult to infer the relative magnitude of the ER effects according to the dielectric properties of the materials, especially for different types of molecule-based ER materials. It is worthy to study the dielectric property of various types of molecule-based ER materials and its influence on the ER property in detail.

4. Conclusion

The inclusion compound [H₂(β-CD-A)-PTA] between H₂(β-CD-A) and p-toluensulfonic acid (PTA) and its rare earth complexes were assembled using β-CD as a substrate to construct the molecule-based ER materials. The characteristic of the molecule in molecule-based ER material is an important factor in determining ER property of the material. The inclusion PTA can enhance markedly the ER performance of H₂(β-CD-A) material. The ER activity of the yttrium complex is the highest among these materials, although its ε and tan δ values are not the largest.

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