Electroresponsive Polymer–Inorganic Semiconducting Composite (MCTP–Fe₃O₄) Particles and Their Electrorheology

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ABSTRACT: Polymer–inorganic semiconducting composite (MCTP–Fe₃O₄) particles were fabricated by loading nanosized Fe₃O₄ on the microporous covalent triazine-based polymer (MCTP) through a chemical coprecipitation method and then applied to an electrorheological (ER) material. The structural and morphological images of MCTP–Fe₃O₄ composite were examined by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. Their magnetic property was also investigated by vibrating sample magnetometry. The chain structure formation of MCTP–Fe₃O₄ dispersed in silicone oil under an external electric field was confirmed using an optical microscope. The ER fluid based on MCTP–Fe₃O₄ was processed by dispersing the composite particles in an oil medium, and for comparison, an ER fluid based on pure MCTP was also prepared by the same process. The ER performance of two different ER fluids was scrutinized by a rotational rheometer, which demonstrated that MCTP–Fe₃O₄ showed better ER characteristics than MCTP-based ER suspension.

INTRODUCTION

Electrorheological (ER) fluids are constituted by suspending electrically polarizable/semiconducting particles in a liquid medium with a relatively low permittivity, and the phase change between fluid-like and solid-like states of ER fluids is tunable by the application and revocation of an electric field.1−4 When there is no electric field, the ER suspensions demonstrate a fluid-like phase, where the particles are freely dispersed in a liquid medium. Under an external electric field, the originally suspended particles aggregate together to organize into columnar-like structures in the medium, which stiffens the structure of ER suspensions, thus presenting solid-like properties. After the electric field is removed, the ER fluids can be restored to their original fluid-like state. This tunable phase transition makes ER fluids to have great potential for applications in various engineering fields.5−10

As for actively electroresponsive ER materials, conjugated semiconducting polymers have been widely researched as ER materials and have shown worthy ER properties, which were generally derived from their advantages of controllable electric conductivity, low density, and fine dispersion stability.11−14 Furthermore, composites based on conjugated semiconductive polymers have also been introduced as ER materials.15−19 Especially, polymer–inorganic composites can not only improve the disadvantages of high density and low interfacial polarization of inorganic particles but also demonstrate the synergistic effect of inorganic–organic components.

Very recently, the ER behaviors of semiconducting microporous covalent triazine-based polymer (MCTP)-based ER fluid have been reported, showing that the MCTP could be a potential ER material with its proper particle size, low density, and suitable electrical conductivity.10 Concurrently, magnetic Fe₃O₄ particles have also been widely applied in many areas because of their high saturation magnetization (Mₛ), biological compatibility, low cost, and easy synthesis process.16−18 In addition, their unusual electrochemical properties induced by the transfer of electrons between Fe²⁺ and Fe³⁺ cause electrical conductivity of the Fe₃O₄, drawing interest from their electrorheological (ER) performance along with their magneto-rheological (MR) characteristics.19 However, as with most inorganic materials, its high density and unsuitable particle size on the nanoscale may limit its application in ER fluids.

Therefore, in this study, we fabricated polymer–inorganic (MCTP–Fe₃O₄) composite particles by synthesizing nanosized Fe₃O₄ particles on the MCTP microspheres via a chemical coprecipitation method. ER properties of MCTP–Fe₃O₄-based ER fluid were then investigated and compared with those of MCTP-based ER suspension, finding that the MCTP–Fe₃O₄-based ER suspension showed better ER properties than MCTP alone, judging by the shear stress curves, shear viscosity curves, and ER efficiency.

RESULTS AND DISCUSSION

Morphological and structural characteristics of MCTP–Fe₃O₄ were observed by both SEM and TEM measurements. The SEM image (Figure 1a) showed that the nanosized Fe₃O₄ particles were generated on the surface of the MCTP microsphere, whereas the TEM image (Figure 1b) revealed that the shape and size of the Fe₃O₄ nanoparticles were

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spherical and about 10 nm, respectively. However, the uneven distribution of Fe₃O₄ nanoparticles makes the morphology and properties of MCTP–Fe₃O₄ heterogeneous, which is very likely to have an extra effect on its ER characteristics.

The structural formation of the MCTP–Fe₃O₄ was investigated by FTIR. Similar to the FTIR spectrum of MCTP (Figure 2b), MCTP–Fe₃O₄ (Figure 2a) also shows a series of peaks in the region between 1000 and 1700 cm⁻¹, indicating the characteristic peaks of the s-triazine-based groups, and the slight shift of some peaks results from the combination with Fe₃O₄. Furthermore, there is a significant new absorption peak at 586 cm⁻¹ in the MCTP–Fe₃O₄ corresponding to the Fe—O bond in Fe₃O₄ (Figure 2c).

The MCTP–Fe₃O₄ particles were also examined using XRD, and results are shown in Figure 3c, in which the broad peak below and above 20° (2θ) corresponded to the stacking of aromatic sheets in the amorphous MCTP (Figure 3a). The XRD spectrum of the MCTP–Fe₃O₄ also revealed relatively sharp peak points at 2θ angles of 30.2, 35.6, 43.1, 53.7, 57.4, and 62.9°, which matched to the (220), (311), (400), (422), (511), and (440) crystalline planes of the Fe₃O₄ nanoparticles (Figure 3b), respectively.

MCTP–Fe₃O₄ composite particles were expected to be magnetic because of the presence of the Fe₃O₄ component in the composite. The magnetization curve (Figure 4) of MCTP–Fe₃O₄ showed a superparamagnetic behavior, being consistent qualitatively with that of pure Fe₃O₄ fabricated via a chemical coprecipitation process with ferrous and ferric ions. The Mₛ of MCTP–Fe₃O₄ was 3.3 emu/g, and this very low value compared with that of Fe₃O₄ might be ascribed to the very low content of magnetite in the composite. Because of the extremely low Mₛ value, even though the MCTP–Fe₃O₄ could be magnetized, it was not strong enough to be used as an MR material.

Before the rheological tests of the MCTP–Fe₃O₄-based ER suspension by a rotational rheometer, the buildup of the chain structure of the MCTP–Fe₃O₄ suspended in an oil medium (Figure 5b) after the application of an electric field was virtually detected using optical microscopy (OM) compared to that of the randomly dispersed state without an electric field (Figure 5a). As shown, without an electric field applied, the MCTP–Fe₃O₄ particles exhibited a freely dispersed state in the silicone oil. However, when the electric field is applied, electrostatic interactions between neighboring particles drive the originally randomly dispersed particles to form chain-like structures along the direction of the electric field, indicating the suspension turned into a solid-like state.

The ER properties of both MCTP and MCTP–Fe₃O₄-based ER suspensions were then measured using a rotational rheometer with concentric-type cylinder geometry (CC17/E). The steady shear flow tests were performed in controlled shear rate mode for several electric field strengths for the shear rate covering from 0.1 to 1000 s⁻¹. Figure 6 shows shear-rate-dependent shear stresses (Figure 6a) and shear viscosities.
(Figure 6b) for MCTP (lines) and MCTP–Fe₃O₄ (symbols)-based ER suspensions for different electric field strengths. As presented in Figure 6a, without an electric field strength applied, they exhibited Newtonian fluid behaviors with similar shear stresses. However, they exhibited Bingham fluid behaviors with a distinct increment of the shear stresses with increased electric field strengths. In addition, the ER fluid based on MCTP–Fe₃O₄ showed higher shear stress values than those based on the MCTP under external electric field strengths. However, compared to the MCTP, the shear stress curve of the MCTP–Fe₃O₄-based ER fluid showed some fluctuations, which could also be found in many other studies. For the competition between hydrodynamic and electrostatic forces in ER fluids in general, if the electrostatic forces prevail, the chain structure destroyed by the hydrodynamic force can be reorganized immediately, and the shear stress remains constant. Thus, the fluctuations in the shear stress curves can be understood that the electrostatic interaction force does not always prevail; in other words, the hydrodynamic and electrostatic forces are alternately dominant. In addition, the fluctuations could also come from various physical conditions of the ER fluid and dispersed particles. As observed in the SEM and TEM images from Figure 1, the Fe₃O₄ nanoparticles were not uniformly distributed on the surface of the MCTP, resulting in quite different morphologies from typical ER materials. This fact would induce nonuniform electric field responses for each part of the material. The fluctuation of shear stress may be partly related to this heterogeneity of the ER material. At the same time, without an electric field, the shear viscosities presented an almost constant value in the entire shear rate regime, indicating a Newtonian fluid state. With an external electric
field, they exhibited typical shear-thinning behaviors. The shear viscosities of MCTP–Fe$_3$O$_4$-based ER suspension were also larger than those of MCTP-based ER suspension.

To examine the ER effects of two ER suspensions more intuitively, we calculated the ER efficiency according to eq 1

$$ER\ efficiency = \frac{\eta_f - \eta_0}{\eta_0} \times 100\%$$

where $\eta_f$ and $\eta_0$ are the shear viscosity with and without an electric field, respectively. As presented in Figure 7, we plotted shear-rate-dependent ER efficiency for MCTP–Fe$_3$O$_4$ (symbols)- and MCTP (line)-based ER suspensions for different electric field strengths.

![Figure 7. Shear-rate-dependent ER efficiency for MCTP–Fe$_3$O$_4$ (symbols)- and MCTP (line)-based ER suspensions for different electric field strengths.](image)

Figure 7. Shear-rate-dependent ER efficiency for MCTP–Fe$_3$O$_4$ (symbols)- and MCTP (line)-based ER suspensions for different electric field strengths.

Note that the Bingham model has been extensively employed to explain shear stresses of the ER suspensions under electric field strengths applied, which can be expressed as follows:

$$\tau_f = \tau_{dy} + \eta_0 \dot{\gamma}, \ \tau_f \geq \tau_{dy}$$

$$\dot{\gamma} = 0, \ \tau_f < \tau_{dy}$$

Here, $\tau_f$ is the shear stress under an electric field, $\dot{\gamma}$ is the shear rate, and parameters $\tau_{dy}$ and $\eta_0$ represent dynamic yield stress and shear viscosity at an infinite shear rate, respectively. The fitting results of the Bingham model are shown as dotted lines in Figure 8. Generally, the Bingham model shows two regions. In a low shear rate range, the shear stress shows a stable value with a plateau behavior; at a high shear rate area, the shear stresses increase with shear rate. However, under the electric fields in this study, specifically at a high electric field strength region, the shear stress values for MCTP–Fe$_3$O$_4$-based ER suspension showed a trend of decline and then rise, in which the Bingham model could not properly fit the experimental data. Therefore, a more complex model named Cho–Choi–Jhon (CCJ) model with six parameters was developed as shown in eq 4:

$$\tau_f = \frac{\tau_{dy}}{1 + (\dot{\gamma}^2)^{\alpha}} + \eta_0 \left[1 + \frac{1}{(t_2)^{\beta}}\right] \dot{\gamma}, \ 0 < \beta \leq 1$$

Here, $t_1$ and $t_2$ are time parameters; $\eta_0$ is usually viewed as the shear viscosity at an infinitely high shear rate when there is no electric field; an index $\alpha$ is responsible for the control of the decreased area of the shear stress; $\beta$ is for governing the increase of shear stress in a high shear rate area. Fitting results of the CCJ model are also shown as solid lines in Figure 8. It can be seen that the CCJ model matched the experimental data better than the Bingham model. Furthermore, Table 1 shows the fitted parameters of CCJ equation for MCTP–Fe$_3$O$_4$-based ER suspension, where the coefficient of determination $R^2$ is a measure of goodness of fit. The closer $R^2$ is to 1.0, the better the model fits the experimental data. As shown in this table, the $R^2$ are very close to 1.0 when the electric field strengths are 0.5, 1.0, and 1.5 kV/mm, which means that the CCJ model can explain well the experimental data. However, at an electric field strength of 2.0 kV/mm, the value of $R^2$ is relatively lower. This may be because the high electric field intensity is close to a critical value for the occurrence of electrical breakdown, which leads to a special change in the behavior of the ER suspension; therefore, the CCJ model does not match it well. The fitting value of $\eta_0$ is independent of the electric field strength, similar to the case of the Bingham fluid model for ER fluids. Even though it is defined to be the shear viscosity at an infinite shear rate in the absence of an electric field, under a limited maximum shear rate ($10^3$ s$^{-1}$) of our experimental condition, it varied randomly for different electric fields. This is because, even in the presence of an electric field, when the shear rate is very high, the chain structure is considered to be almost completely destroyed and the shear viscosity becomes close to the viscosity without the electric field, similar to previously reported studies.

From its dynamic oscillation test, Figure 9 presents storage ($G'$) and loss moduli ($G''$) as a function of strain. Without an external electric field strength, $G''$ was larger than $G'$, indicating the fluid-like state of the ER fluid. However, with an electric field, $G''$ became higher than $G'$, being increased with an increased electric field strength. This means that the ER suspension transformed to a solid-like state and the chain-like structure caused by the electric field became more and more rigid as the electric field strength increased. In addition,
showed stable values in a low strain range (i.e., linear viscoelastic region $\gamma_{LVE}$), and it drastically declined when the strain exceeded a certain value (critical strain $\gamma_c$), indicating that at this moment the breakdown of chain-like structures began to occur.\textsuperscript{44} As shown in Figure 9, the critical strain for MCTP$^{-}\text{Fe}_3\text{O}_4$-based ER suspension was about 0.05%.

Elastic stresses were evaluated on the basis of the relationship of $\tau_e = G'\times\gamma$, in which $\tau_e$ is the elastic stress and $\gamma$ is the strain. Figure 10 shows elastic stresses as a function of strain, where the red circles marked the elastic yield stresses, which were presented as a function of applied electric field strength in Figure 11.

Dynamic yield stresses plotted in Figure 11 were deduced from Table 1. As shown in Figure 10, both elastic and dynamic yield stresses were observed to be dependent on the electric field strength applied for MCTP–Fe$_3$O$_4$-based ER suspension with the following power-law relationship of eq 5

$$\tau_y \propto E^{1.5}$$  \hspace{1cm} (5)

where $\tau_y$ represents either elastic or dynamic yield stress and $E$ is the electric field strength. In this work, the exponent equal to 1.5 is matched with a well-known conduction model.\textsuperscript{45,46} Therefore, it can be concluded that the behavior of MCTP–Fe$_3$O$_4$ particles in ER fluid was governed by the mismatch of conductivity between the particles and carrier liquid rather than the mismatch of dielectric constant.\textsuperscript{47}

Furthermore, the dependence of angular frequency on $G'$ and $G''$ for MCTP–Fe$_3$O$_4$-based ER suspension was investigated in a fixed strain of 0.02%, in which the electric field strength induced columnar formation will not be destroyed by excessive strains. Without an electric field applied, both $G'$ and $G''$ showed distinct increments with angular frequency (Figure 12). However, under an external electric field, both $G'$ and $G''$ showed mostly stable values in the whole frequency window, implying that the MCTP–Fe$_3$O$_4$-based ER suspension transformed from a fluid-like state to a solid-like form by an application of electric field.\textsuperscript{48}

To further investigate the phase transition of the MCTP–Fe$_3$O$_4$-based ER suspension from a fluid-like state to a solid-like state, we evaluated shear relaxation moduli $[G(t)]$ through angular-frequency-dependent storage [$G'(\omega)$] and loss modulus [$G''(\omega)$] using the Schwarzl equation\textsuperscript{49} as shown in eq 6:

$$G(t) \approx G'(\omega) - 0.560 G''(\omega/2) + 0.200 G''(\omega)$$  \hspace{1cm} (6)

The value of $G(t)$ was presented as a function of time in Figure 13, where $G(t)$ dropped sharply when there was no electric field, showing a liquid-like state. However, it remained relatively stable in the entire timescale under an external electric field, meaning a phase change to a solid-like phase.

In addition, to verify the stability of the ER fluid, the shear stress curves of the initial test (closed symbols) and the shear

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Table 1. Fitted Parameters of CCJ Model for MCTP–Fe$_3$O$_4$-Based ER Fluid

| Electric field strength (kV/mm) | $\tau_{dy}$ | $t_1$ | $\alpha$ | $\eta_{\infty}$ | $t_2$ | $\beta$ | $R^2$ |
|-------------------------------|------------|-------|----------|----------------|-------|--------|--------|
| 0.5                           | 15.2       | 0.8636| 0.55     | 0.19           | 0.0122| 0.87   | 0.99   |
| 1.0                           | 44.6       | 0.0097| 0.64     | 0.14           | 0.0036| 0.42   | 0.99   |
| 1.5                           | 52.5       | 0.0743| 2.79     | 0.16           | 0.0015| 0.86   | 0.99   |
| 2.0                           | 94.2       | 0.035 | 89.41    | 0.03           | 0.000033| 0.79   | 0.86   |

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Figure 9. Strain amplitude sweep tests: storage (closed) and loss moduli (open) vs shear strain for different electric field strengths.

Figure 10. Strain-dependent elastic stress under different electric field strengths.

Figure 11. Electric-field-dependent elastic (closed) and dynamic yield stresses (open).
stress curves remeasured after the steady shear and dynamic oscillation tests (open symbols) without and with an electric field (0.5 kV/mm) are shown in Figure 14. Obviously, there is no significant difference between the two experimental results, indicating that the MCTP–Fe₃O₄-based ER fluid has good stability and the ER performance is not easily reduced because of the ER tests.

As known, the dielectric characteristics of ER suspension were closely linked with the ER properties, and Figure 15 shows the dielectric characteristics of the MCTP–Fe₃O₄-based ER suspension, where the curves were fitted from the following Cole–Cole equation:

\[
\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon_0 + \frac{\Delta\varepsilon}{1 + (i\omega\lambda)^{1-\alpha}}; \quad 0 \leq \alpha < 1
\]  

Here, \(\varepsilon^*\) is the complex dielectric constant, \(\varepsilon'\) is the dielectric constant, and \(\varepsilon''\) is the loss factor. \(\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty\) represents the polarizability of ER suspension, and \(\varepsilon_0\) and \(\varepsilon_\infty\) are dielectric constant values at frequencies reaching 0 and \(\infty\), respectively. \(\omega\) is the angular frequency of applied electric field; \(\lambda = 1/2\pi f_{\text{max}}\) is the relaxation time of interfacial polarization between the particles and carrier liquid in ER suspension with the electric field, where \(f_{\text{max}}\) is the frequency of where the loss factor is maximal. The exponent \((1 - \alpha)\) reflects the distribution broadness of the \(\lambda\), when the \(\alpha\) equals 0, meaning a single relaxation time. Table 2 shows the fitted results of the Cole–Cole equation. It should be noted that small \(\lambda\) and \(\Delta\varepsilon\) usually can contribute to high enhancement of shear stresses of

![Figure 12](image_url). Angular frequency sweep tests: storage (closed) and loss moduli (open) vs. frequency for different electric field strengths.

![Figure 13](image_url). Time-dependent shear relaxation moduli for different electric field strengths.

![Figure 14](image_url). Shear stress curves of an initial test (closed) and after the steady shear and dynamic oscillation tests (open) for MCTP–Fe₃O₄-based ER fluid.

![Figure 15](image_url). Dielectric properties: (a) dielectric constant (cubic) and loss factor (trigonal) vs frequency and (b) loss factor vs dielectric constant. Solid lines drew from Cole–Cole equation.

| parameter | \(\varepsilon_0\) | \(\varepsilon_\infty\) | \(\Delta\varepsilon\) | \(\alpha\) | \(\lambda\) (s) |
|-----------|-----------------|-----------------|-----------------|---------|-------------|
| value     | 5.7             | 2.85            | 2.85            | 0.625   | 0.135       |
ER suspension under an electric field. As shown, the $\Delta \lambda$ of MCTP$-\text{Fe}_3\text{O}_4$-based ER suspension was 2.85, which is a relatively higher value. However, the $\lambda$ was 0.135 s, indicating a sluggish polarization under an electric field, which is most likely the evidence that MCTP$-\text{Fe}_3\text{O}_4$-based ER suspension obeys the conduction model rather than the polarization model.

**CONCLUSIONS**

MCTP$-\text{Fe}_3\text{O}_4$ composite was prepared and characterized by SEM, TEM, FTIR, and XRD. The chain-like structure of the MCTP$-\text{Fe}_3\text{O}_4$ composite dispersed in silicone oil in the presence of electric field strengths was directly observed by OM. ER characteristics of MCTP$-\text{Fe}_3\text{O}_4$-based and MCTP-based ER suspensions were tested by a rotational rheometer, and the ER performance of the former conformed to the conduction model, which was closely related to its electrical conductivity. In addition, the MCTP$-\text{Fe}_3\text{O}_4$-based ER fluid showed better ER properties than pure MCTP-based one, being attributed to the excellent association of $\text{Fe}_3\text{O}_4$ nanoparticles and the synergistic effect between the two components in the composite.

**EXPERIMENTAL**

**Characterization.** The morphological and structural characteristics of MCTP$-\text{Fe}_3\text{O}_4$ composite particles were investigated using both high-resolution scanning electron microscopy (HR-SEM, SU-8010, Hitachi, Japan), transmission electron microscopy (TEM, CM200, Philips), and Fourier transform infrared vacuum spectrometry (FTIR, Bruker VERTEX 80V, Germany). Their crystalline characteristics were observed by a multipurpose X-ray diffractometer (MP-XRD, Pro MRD, Netherlands). The magnetization curve was observed by vibrating sample magnetometry (7407, USA). The ER tests of the MCTP$-\text{Fe}_3\text{O}_4$-based ER suspension were carried out using a rotational rheometer with a Couette geometry cell (MCR 300, Anton Parr, Austria) attached by a high-voltage dc generator.

**Synthesis of MCTP$-\text{Fe}_3\text{O}_4$ Composite.** MCTP was prepared as previously reported. First, cyanuric chloride and 1,3,5-triphenylbenzene were mixed in dichloromethane (100 mL). Once anhydrous AlCl$_3$ was added into the mixture under a nitrogen environment, it was refluxed for 16 h using a condenser at 70 °C. Finally, the temperature of the reacted solution mixture was lowered down to room temperature, and brownish black product particles were obtained through sequential processes of filtration, cleaning, and drying under vacuum.

The MCTP$-\text{Fe}_3\text{O}_4$ composite particles were prepared by introducing $\text{Fe}_3\text{O}_4$ onto MCTP by a chemical coprecipitation method. One gram of MCTP was dispersed in 100 mL of a solution containing ferric chloride hexahydrate (Sigma Aldrich, USA) and ferrous chloride tetrahydrate (Sigma Aldrich, USA) in concentrations of 0.02 and 0.01 M, respectively. The mixture was transferred to a reactor and stirred for 1 h, followed by adding 1 M NaOH (Sigma Aldrich). The reaction mixture was heated up to 60 °C and remained for 3 h. The precipitated particle products were collected by a magnet, cleaned using water and acetone, and dried.

**Preparation of ER Fluids.** For ER measurements, MCTP$-\text{Fe}_3\text{O}_4$-based ER suspension was fabricated by suspending MCTP$-\text{Fe}_3\text{O}_4$ in a silicone oil (shear viscosity = 9.65 × 10$^{-2}$ Pa s) with a sample volume concentration of 5 vol. % For a uniform and better dispersion of the particles, it was shaken (Vortex Genius 3, IKA, Germany) and sonicated (Power Sonic 410, Hwashin Tech. Co., Korea). For comparison, MCTP-based ER suspension (5 vol %) with the same concentration was also prepared similarly.

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