ABSTRACT: A functional raspberry-like core−shell composite particle consisting of a conducting polyaniline (PANI) core and magnetic zinc ferrite shell is synthesized by Pickering emulsion polymerization. The morphology and chemical structure of the PANI/zinc-ferrite composite are evaluated by scanning electron microscopy, transmission electron microscopy, and Fourier-transform infrared spectroscopy. An electrorheological/magnetorheological fluid consisting of the PANI/zinc-ferrite composite dispersed in silicone oil with a particle concentration of 5 vol % is fabricated. Its rheological characteristics under external electric and magnetic fields are investigated by using a rotational rheometer. Under the electric or magnetic field, the PANI/zinc-ferrite particles form chain-like structures, demonstrating a solid-like state.

1. INTRODUCTION

Various emulsion polymerization synthesis routes have been employed for the fabrication of organic/inorganic hybrid magnetic particles having stimuli-responsive properties. However, in the typical emulsion polymerizations, organic surfactants are usually used as emulsifiers to stabilize the emulsion systems. In addition, they require an additional inconvenient step to remove the surfactants after the polymerization. Unlike the typical emulsion polymerization processes, Pickering emulsion polymerization utilizes solid particles as a stabilizer, and the fabricated polymer/solid particle composite after the polymerization does not require an additional process to remove the stabilizer. The characteristics of the Pickering emulsion rely on the kind of preferential wetting of the solid particles, by the oil phase or by the water phase. If the solid particles at the oil/water boundary are more hydrophilic, an oil-in-water emulsion is produced. Conversely, if the solid particles are more lipophilic, a water-in-oil structure is formed. In the studies on the fabrications of organic−inorganic composite materials by using the Pickering method, most of the obtained core−shell structures have been composed of polymer cores and inorganic shells. In the Pickering emulsion polymerization system, a hydrophilic inorganic material is usually employed as the stabilizer, and the hydrophobic monomer tends to be surrounded by solid particles in water to form a monomer-in-water emulsion with polymerized monomer droplets. Electrotheroeological (ER) and magnetorheological (MR) fluids are classes of smart fluids composed of electrically and magnetically responsive particles suspended in liquid media, such as silicone and mineral oils. More specifically, an MR fluid generally consists of soft magnetic particles and a nonmagnetic carrier medium, exhibiting liquid-like properties without a magnetic field. However, when a magnetic field is input, the magnetic particles in the medium build up a chain-like form along the magnetic field direction in a short time, and the MR fluid becomes solid-like. With the increase in magnetic field strength (H), the strength of the chain-like chains increases, and the solid-like properties of the MR fluid are enhanced (increased yield stress, viscosity, and dynamic modulus). When the applied external magnetic field is off, the chain-like structure disappears, and the MR suspension returns to a liquid-like state. Similarly to the MR fluid, ER fluids consist of semiconducting/polarizable particles suspended in a nonconducting liquid, in which the particles form chain-like structures owing to the electrostatic interactions under the stimuli by the external electric field. The ER fluid also has a reversible characteristic between the liquid- and solid-like state with/without an electrical field.

Received: February 10, 2020
Accepted: March 18, 2020
Published: March 26, 2020
be controlled by external electric or magnetic fields, and reversibly transform between solid- and liquid-like states, they are widely used in mechanical and industrial applications such as dampers, brakes, and clutches.\textsuperscript{12–14} Materials with dual stimuli-responsive characteristics under external electric and magnetic fields also attract increasing attention.\textsuperscript{15,16} Many magnetic particles including carbonyl iron (CI), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and cobalt ferrite (CoFe₂O₄) have been extensively used as MR materials.\textsuperscript{17} CI has a higher saturation magnetization than those of other materials, which can contribute to a higher MR performance. However, owing to the relatively high density of CI, the density mismatch between CI and carrier liquid is considerable, which usually leads to undesired sedimentation problems and thus hinders its engineering applications. On the other hand, Fe₃O₄ has been extensively studied as an MR material because of its magnetic characteristics, relatively low density, and simple synthesis. However, its saturation magnetization is relatively low, and thus MR fluids based on Fe₃O₄ do not exhibit high yield stresses, which limits their applications. In this regard, zinc ferrite has gradually attracted interest owing to its lower density than that of CI and higher saturation magnetization than that of Fe₃O₄.\textsuperscript{18} It is expected that zinc-ferrite-based MR fluids can exhibit not only high MR performances but also satisfactory sedimentation stabilities. Furthermore, nanosized zinc-ferrite particles could be effectively applied as a solid surfactant for the Pickering emulsion system for the first time.

In recent years, conductive polymers, as ER materials, have attracted considerable attention, particularly polyaniline (PANI), which has been widely investigated owing to its low density, controllable electrical conductivity, and simple synthesis. The conductivity is a significant factor determining the ER effect. When the electrical conductivity is too low, it is difficult to make a strong chain-like structure under an electric field, which leads to a low ER efficiency. On the other hand, if the electrical conductivity is too high, electrical breakdown is likely to occur at a low electric field strength, which leads to a reduced safety of the ER fluid during its application. Therefore, PANI is considered as one of the most promising particles for ER fluids because its electrical conductivity can be easily controlled by doping and dedoping with acid and alkali, respectively.\textsuperscript{19–21}

In addition, in recent years, core–shell composites have attracted considerable attention owing to their unique structural characteristics and uniform morphologies. Core–shell composites synthesized by Pickering emulsion polymerization also have been extensively tested as ER and MR suspensions. Kim et al.\textsuperscript{22} have fabricated a core–shell polystyrene (PS)/Fe₂O₃ composite by Pickering emulsion polymerization as an MR material. Liu et al.\textsuperscript{23} have synthesized a core–shell PANI@SiO₂ by Pickering emulsion polymerization and have studied its ER response. Ahn et al.\textsuperscript{24} fabricated a core–shell poly(methyl methacrylate) (PMMA)/Fe₂O₃ particle by Pickering emulsion polymerization and studied its stimuli-responsive characteristics under a magnetic field. The syntheses of core–shell composites as ER materials composed of graphene oxide (GO) shells and polymeric cores, such as PMMA/GO, poly(glycidyl methacrylate)/GO, and PS/GO,\textsuperscript{25–27} have been actively studied.

In this study, a raspberry-like core–shell PANI/zinc-ferrite composite particle is fabricated by Pickering emulsion polymerization with zinc ferrite as a solid stabilizer. As shown in Scheme 1, the aniline monomer is surrounded by the hydrophilic zinc-ferrite to form an aniline-in-water structure. After the addition of the initiator, the aniline is polymerized to form a PANI core coated by a zinc-ferrite shell. The ER and MR behaviors of the fabricated PANI/zinc-ferrite suspended in silicone oil are also investigated.

2. RESULTS AND DISCUSSION

Figures 1(a) and (b) show SEM images of both zinc-ferrite particles and the PANI/zinc-ferrite composite, respectively.

![Figure 1. SEM images of zinc-ferrite (a) and PANI/zinc-ferrite (b) and TEM images of zinc-ferrite (c) and PANI/zinc-ferrite (d).](https://dx.doi.org/10.1021/acsomega.0c00585)

The zinc-ferrite particles have sizes of approximately 100 nm, while the PANI/zinc-ferrite composite contains microparticles with nanoparticles on the surfaces. The TEM image (Figure 1(c)) presents that the zinc-ferrite particles have cubic morphologies. Their cubic shape is due to the application of oleic acid in the synthesis, where the oleic acid acts as a surfactant and controls the morphology of the particles.\textsuperscript{18} In addition, Figure 1(c) shows that the PANI/zinc-ferrite composite contains raspberry-like core–shell microparticles formed by the zinc-ferrite nanoparticle coatings on the PANI. Furthermore, the density of the PANI/zinc-ferrite composite of 5.4 g/cm³ measured was observed to be lower than that of zinc-ferrite of 5.9 g/cm³, indirectly indicating the formation of the PANI composite. On the other hand, as for the stability of the raspberry-like core–shell structure itself, it can be noted that it has been quite widely reported that core–shell structured polymer–inorganic particle composite particles from Pickering emulsion polymerization can be used as an effective filler for the polymer composites, enhancing their mechanical strength. This implies that the core–shell structured polymer–inorganic particle composite particles...
from the Pickering emulsion polymerization are considered to be mechanically stable.\textsuperscript{29}

Figures 2(a) and (b) show EDS results for the zinc-ferrite particles and PANI/zinc-ferrite composite, respectively. The atomic contents of C in the zinc-ferrite and PANI/zinc-ferrite composite are 17.14 and 60.95%, respectively. The increased C content in the PANI/zinc-ferrite composite is attributed to the PANI. The ratios of Fe to Zn in the zinc-ferrite and PANI/zinc-ferrite composite are similar. Thus, the zinc-ferrite and PANI components are combined in the composite.

The FTIR spectra demonstrate the successful synthesis of the PANI/zinc-ferrite composite (Figure 3). The peaks at 1608 (N–H scissoring vibration), 1485 (C–C stretching vibration), 1300 (C–N of secondary aromatic amine), 1235 (N–H bonding vibration) cm\textsuperscript{-1}, and at around 3400 cm\textsuperscript{-1} (weak vibration of N–H) represent the characteristics of pure PANI.\textsuperscript{30} The peaks at 3380 (O–H stretching vibration) and 542 (Fe–O functional group characteristic of the spinel ferrite) cm\textsuperscript{-1} are assigned to the zinc-ferrite.\textsuperscript{31} Thus, the FTIR spectra indicate that both PANI and zinc-ferrite are present in the PANI/zinc-ferrite composite.

Figure 4 shows magnetization behavior of both zinc-ferrite and PANI/zinc-ferrite composite particles as a function of the magnetic field. Saturation magnetization ($M_s$) is the maximum magnetization reached with the increased $H$. After this value is reached, the magnetization does not continue to increase with the input $H$. The $M_s$ values of the zinc-ferrite nanoparticles and PANI/zinc-ferrite composite are 91 and 73.7 emu/g, respectively. $M_s$ of the composite is lower than that of the zinc-ferrite because of the nonmagnetic PANI component. This indicates that the PANI/zinc-ferrite composite MR suspension may have a lower MR performance than that of the fluid based on the zinc-ferrite. In addition, both zinc-ferrite particles and PANI/zinc-ferrite composite have low coercivities ($H_c$) of 8 and 10 kA/m, respectively. This indicates that the two materials have soft magnetic properties. Thus, the MR fluids based on them are more sensitive in the return to the fluid-like state after the applied magnetic field is removed.
As PANI is an excellent electrically conducting material, while zinc ferrite is a soft-magnetic material, dual stimuli-responsive properties of the PANI/zinc-ferrite composite under electric and magnetic fields are expected. Scheme 2 shows a schematic of the resulting action of the PANI/zinc-ferrite-composite-based suspension under the electric and magnetic fields. Without H or electric field strength (E), the PANI/zinc-ferrite composite is freely dispersed in the carrier liquid. However, when a magnetic field or electric field is applied (H or E ≠ 0), the PANI/zinc-ferrite composite arranges in chain-like structures because of the induced magnetostatic or electrostatic interactions, respectively. To further investigate the MR and ER behaviors, the rheological properties of the PANI/zinc-ferrite composite dispersed in silicone oil under magnetic and electric fields are evaluated by using a rotational rheometer.

The MR properties are estimated by using a rotational parallel plate. Controlled shear rate tests are handled to measure shear stress (τ) (Figure 5(a)) and shear viscosity data (Figure 5(b)) as a function of shear rate (γ) under various H. According to the flow curve, the MR fluid exhibits rheological properties with a Newtonian-like behavior when the H is zero. However, when the H is applied, it exhibits a Bingham fluid-like property with a yield stress because the PANI/zinc-ferrite composite particles in the silicone oil build a chain-like form along the H. The τ increases with the H, indicating that the chain-like structure is enhanced. The Herschel–Bulkley (H–B) model is used to describe the flow curves

\[ \tau = \tau_y + K\gamma^n \quad \tau \geq \tau_y \]  

where \( \tau_y \) is the dynamic yield stress; \( K \) is a consistency index; and \( n \) is a flow index. The solid lines in Figure 5(a) are generated by using the H–B model. When the external H is applied, the shear stress curve is fitted with the H–B model.

Figure 5(b) demonstrates the shear viscosity as a function of the \( \gamma \) under various H. Under an applied H, the shear viscosity increases because of the formation of the solid-like phase, also exhibiting a shear-thinning behavior in the whole shear rate range.

The \( \tau_y \) of the PANI/zinc-ferrite-based MR fluid is obtained by using the flow curve at the zero shear rate limit. The relationship between the \( \tau_y \) and H is usually presented as

\[ \tau_y \propto H^\alpha \]  

where the index \( \alpha \) is usually 1.0–2.0. Figure 6 demonstrates the \( \tau_y \) of the PANI/zinc-ferrite-based fluid as a function of the H, where the slope of the fitted line generated by using eq 2 is 1.0. Generally, the \( \tau_y \) of an MR suspension is closely associated with the magnetic characteristics of the MR material. Results suggest that a larger saturation magnetization of the material could provide a larger \( \tau_y \) of the MR fluid. Moreover, with the
increase in the $H$, the magnetization of the material increases faster, which generally indicates that $\alpha$ in eq 2 is larger. In addition, $\alpha$ is also known to be related to the shape, size, and surface properties of the MR material and concentration of the MR fluid.33–35

Dynamic oscillation measurements are carried out to further study the viscoelastic properties of the PANI/zinc-ferrite-based fluid under a magnetic field. Amplitude sweep tests are performed in the strain range of 0.00001 to 1 at a fixed angular frequency ($\omega$) of 6.28 rad/s. Figure 7 represents the storage modulus ($G''$) as a function of the strain amplitude; $G''$ increases with the $H$. At strains smaller than 0.001, the MR fluid exhibits a linear viscoelastic (LVE) behavior. On the other hand, at strains larger than 0.001, the storage modulus is considerably decreased, and thus the chain-like structures in the MR suspension are destroyed owing to the excessive deformation. Therefore, a constant strain of 0.00007 within the LVE regime is selected for the frequency sweep tests.

An angular frequency sweep measurement is carried out from 1 to 200 rad/s with a constant strain of 0.00007. As shown in Figure 8(a), without magnetic field, $G''$ increases with the angular frequency ($\omega$), which indicates that the MR fluid shows a liquid-like property. However, under an external $H$, $G''$ is almost constant up to 100 rad/s, which indicates solid-like properties. This implies that under the stimulus by the external magnetic field the rheological behavior of the MR suspension changes from liquid- to solid-like due to the formation of a chain-like structure along the direction of the magnetic field.36,37

Further, to elucidate the transformation between the liquid- and solid-like behaviors of the MR fluid, the relaxation modulus ($G(t)$) is obtained through the angular frequency test and by using the well-known Schwarzl equation.

$$G(t) \cong G''(\omega) = 0.566G''(\omega/2) + 0.203G''(\omega)$$  \hspace{1cm} (3)

As shown in Figure 8(b), without a magnetic field, $G(t)$ rapidly decreases in a short time with fluid-like characteristics. However, under the magnetic field, $G(t)$ is almost constant or slightly decreases over a relatively long period of time with solid-like characteristics. With the increase in strength of the magnetic field, $G(t)$ is more stable, which indicates that the chain-like structures formed at the high $H$ are stronger.

The MR efficiency is calculated by using eq 4 based on the shear viscosity data in Figure 5(b):

$$\text{MR efficiency} = \frac{\eta - \eta_0}{\eta_0} \times 100\%$$  \hspace{1cm} (4)

where $\eta$ and $\eta_0$ are the shear viscosities under and without the $H$, respectively.

As shown in Figure 9, the MR efficiency increases with the $H$ and decreases with the increase in $\dot{\gamma}$. The decrease in MR efficiency occurs as the increase in shear rate destroys the chain-like structure formed along the direction of the $H$.

Furthermore, to evaluate the response of the PANI/zinc-ferrite-based ER suspension under the electric field strength ($E$), its flow curves are studied at different electric field strengths at shear rates of 0.1–200 L/s. The conductivity of the PANI/zinc-ferrite composite was measured to be 4.7–7682 Sc m m. As presented in Figure 10, without the $E$, the $\tau$ increases with the $\dot{\gamma}$. The shear viscosity slightly decreases at low shear rates and tends to be stable at high shear rates, similar to the Newtonian fluid behavior. However, under the electric field, significant shear thinning and yield stress appear, which indicate a Bingham-fluid behavior. The large change in rheological behavior of the fluid shows that the dispersed
PANI/zinc-ferrite particles are aligned in chain-like structures under the electric field. Nonetheless, despite showing its typical ER behavior of Figure 10, the rather higher electrical conductivity of the composite particles without the dedoping process of the PANI portion not only limited the $E$ applied up to only 1.0 kV/mm but also exhibited weak dependence of the $E$ on the increase of shear stress and shear viscosity. In addition, the density of the PANI/zinc-ferrite composite of 5.4 g/cm$^3$ measured was considered to be too high, especially for its ER test in an oscillatory mode, causing a sedimentation problem during the test.

The dynamic yield stress ($\tau_y$) of the PANI/zinc-ferrite-based ER fluid was obtained from the controlled shear rate tests by extrapolating the shear stress at a zero-shear rate limit and plotted as a function of electric field strength as shown in Figure 11. The relationship between the $\tau_y$ and $E$ can be presented as

$$\tau_y \propto E^{1.0}$$

The $\tau_y$ of the PANI/zinc-ferrite-based smart fluid under an electric field was observed to be lower than that under an applied magnetic field. This result might be due to the low content of PANI in the composite in addition to the fact that in general the $\tau_y$ of the ER fluids is lower than that of the MR fluids. However, it can be found that the relationship of dynamic yield stress with electric field strength is the same with its relationship with magnetic field strength, both of which are proportional to the first power of field strength. Note that this value is smaller than those from both the polarization and conduction mechanisms.\textsuperscript{40}

Furthermore, the ER efficiency was calculated from the shear viscosity curve using the following equation\textsuperscript{41}

$$\text{ER efficiency} = \left( \frac{\eta - \eta_0}{\eta_0} \right) \times 100\%$$

where $\eta$ and $\eta_0$ are the shear viscosities with and without the applied $E$, respectively. As given in Figure 12, the ER efficiency decreased with an increased shear rate and increased with an increase in the electric field strength. The value of ER efficiency was higher than $3 \times 10^4$ % at an electric field strength of 1.0 kV/mm, indicating that the PANI/zinc-ferrite particles formed chain-like structures under the application of the electric field.
3. CONCLUSION

The raspberry-like core–shell PANI/zinc-ferrite composite was synthesized by Pickering emulsion polymerization. Its morphology was observed by using SEM and TEM, which confirmed that the PANI was coated by zinc-ferrite particles and that the particle size of the composite was approximately 1 μm. The chemical structure and constituent elements of the composite were analyzed by FTIR spectroscopy and EDS, which demonstrated the successful synthesis of the PANI/zinc-ferrite composite. The PANI/zinc-ferrite-based ER/MR fluid was fabricated by suspending the composite particles in silicone oil (100 cSt) with a volume fraction of 5%. The responses of the fluid to the electric and magnetic fields were investigated. Without the electric or magnetic field, the PANI/zinc-ferrite-composite-based fluid exhibited a liquid-like state. However, under the electric or magnetic field, the composite particles arranged in chain-like structures, and the shear stress and shear viscosity largely increased, which reflected the solid-like behavior. In addition, dynamic oscillation tests of the PANI/zinc-ferrite-composite-based fluid were carried out at various $H$. The dynamic modulus increased with the $H$. The results also confirmed the transition from the liquid- to the solid-like phase.

4. EXPERIMENTAL SECTION

4.1. Materials. Iron(III) acetylacetonate and zinc(II) acetylacetonate hydrate both from Sigma-Aldrich, USA, are adopted as starting materials of the zinc-ferrite nanoparticle synthesis. Oleic acid (Sigma-Aldrich) is used as a surfactant, while benzyl ether (TCI, Japan) is used as a solvent to withstand the high reaction temperature. Hexane (Sigma-Aldrich, USA) and distilled water are used to wash residual materials.

4.2. Synthesis. Before the synthesis of the PANI/zinc-ferrite composite, zinc-ferrite is synthesized by thermal decomposition. First, 21.2 g of iron acetylacetonate and 10.5 g of zinc acetylacetate hydrate are added in benzyl ether (100 mL). Subsequently, 39.5 g of oleic acid is added in the above solution. The mixture is stirred for 30 min to well disperse the particles and heated to 120 °C for 30 min to remove the bound water. The mixture is then heated to 280 °C and reacted for 30 min with a reflux condenser. After the reaction, the mixture is cooled to room temperature and washed several times with hexane and distilled water. The product is finely dried by using a vacuum oven for 1 day.

The PANI/zinc-ferrite composite is synthesized by Pickering emulsion polymerization by using zinc-ferrite and aniline (Daejung, Korea) as starting materials. Ammonium persulfate (APS) is used as the initiator, while distilled water is used as the solvent. Distilled water and ethanol are used to wash the product after the reaction.

First, 1 g of zinc-ferrite particles is dispersed in 100 mL of distilled water under sonication for 30 min. Subsequently, 3 g of aniline monomer is added, and the sonication is continued for 1 h to obtain the Pickering emulsion. The emulsion is transferred to a reactor; 0.1 g of APS is added; and the reaction is proceeded for 12 h under stirring. The precipitate is washed by distilled water and ethyl alcohol several times and dried by using a vacuum oven for 12 h.

4.3. Preparation of the ER/MR Fluid. The PANI/zinc-ferrite composite particle (5 vol %) is dispersed in silicon oil (100 cSt, Shin-Etsu, Japan). Sufficient vibration and sonication are performed to obtain a uniform suspension.

4.4. Characterization. The morphological image of the PANI/zinc-ferrite composite is observed by using scanning electron microscopy (SEM) (SU 8010, Hitachi, Japan) and transmission electron microscopy (TEM) (CM200, Philips, Netherlands). Using a pycnometer (Accupyc 1330, Gas pycnometer, USA), the densities of the zinc-ferrite particle and PANI/zinc-ferrite composite were measured. The chemical composition is analyzed by using energy-dispersive X-ray spectroscopy (EDS, EX-250, HORIBA, Japan) and Fourier-transform infrared (FT-IR) spectroscopy (Bruker, VERTEX 80 V). As the magnetic characteristics of materials are closely associated with the MR behaviors, the relationship between the magnetization of the material and external magnetic field strength is analyzed by vibrating-sample magnetometry (VSM) (7407, Lake Shore, USA). The MR and ER properties of the PANI/zinc-ferrite-composite-based fluid are measured by using a rotation rheometer (MCR 302, Anton Paar, Austria) under various magnetic and electric field strengths, respectively.

■ AUTHOR INFORMATION

Corresponding Author

Hyoung Jin Choi — Department of Polymer Science and Engineering, Inha University, Incheon 22212, Korea; orcid.org/0000-0001-6915-4882; Email: hjchoi@inha.ac.kr

Authors

Joo Nyeon Kim — Department of Polymer Science and Engineering, Inha University, Incheon 22212, Korea
Yu Zhen Dong — Department of Polymer Science and Engineering, Inha University, Incheon 22212, Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00585

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (2018R1A4A1025169).
REFERENCES

(1) Yin, D.; Du, X.; Liu, H.; Zhang, Q.; Ma, L. Facile one-step fabrication of polymer microspheres with high magnetism and armored inorganic particles by Pickering emulsion polymerization. Colloids Surf., A 2012, 414, 289–295.
(2) Zhang, K.; Wu, W.; Meng, H.; Guo, K.; Chen, J.-F. Pickering emulsion polymerization: preparation of polystyrene/nano-SiO2 composite microspheres with core-shell structure. Powder Technol. 2009, 190, 393–400.
(3) Bon, S. A. F.; Colver, P. J. Pickering miniemulsion polymerization using laponite clay as a stabilizer. Langmuir 2007, 23, 8316–8322.
(4) Binks, B. P. Particles as surfactants—similarities and differences. Curr. Opin. Colloid Interface Sci. 2002, 7, 21–41.
(5) Weiss, K. D.; Carlson, J. D.; Nixon, D. A. Viscoelastic properties of magnet- and electro-rheological fluids. J. Intell. Mater. Syst. Struct. 1994, 5, 772–775.
(6) Felicia, L. J.; Philip, J. Magnetorheological properties of a magnetic nanofluid with dispersed carbon nanotubes. Phys. Rev. E 2014, 89, 022310.
(7) Samouhos, S.; Mckinley, G. Carbon nanotube-magnetite composites, with applications to developing unique magnetorheological fluids. J. Fluids Eng. 2007, 129, 429–437.
(8) Bombard, A. J. F.; Goncalves, F. R.; Morillas, J. R.; de Vicente, J. Magnetorheology of dimorphic magnetorheological fluids based on nanofibers. Smart Mater. Struct. 2014, 23, 125013.
(9) Sung Taek Lim; Hyong Jin Choi; Jhon, M.S. Magnetorheological characterization of carbonyl iron-ironorganoclay suspensions. IEEE Trans. Magn. 2005, 41, 3745–3747.
(10) Choi, H. J.; Jhon, M. S. Electrorheology of polymers and nanocomposites. Soft Matter 2009, 5, 1562–1567.
(11) Wu, J.; Zhang, L.; Xin, X.; Zhang, Y.; Wang, H.; Sun, A.; Cheng, Y.; Chen, X.; Xu, G. Electrorheological fluids with high shear stress based on wrinkly tin titanyl oxide. ACS Appl. Mater. Interfaces 2018, 10, 6785–6792.
(12) Ashour, O.; Rogers, C. A.; Kordonsky, W. Magnetorheological fluids: materials, characterization, and devices. J. Intell. Mater. Syst. Struct. 1996, 7, 123–130.
(13) Tao, R.; Xu, X. Reducing the viscosity of crude oil by pulsed electric or magnetic field. Energy Fuels 2006, 20, 2046–2051.
(14) Sun, S. S.; Yang, J.; Li, W. H.; Du, H.; Alici, G.; Yan, T. H.; Nakano, M. Development of an isolator working with magnetorheological elastomers and fluids. Mech. Sys. Signal Process. 2017, 83, 371–384.
(15) Wereley, N. M.; Pang, L. Nondimensional analysis of semiactive electrorheological and magnetorheological dampers using approximate parallel plate models. Smart Mater. Struct. 1998, 7, 773–742.
(16) Park, D. E.; Chae, H. S.; Choi, H. J.; Maity, A. Magnetite–poly(3,4-ethylenedioxythiophene) core–shell structured microspheres and their dual stimuliresponse under electric and magnetic fields. J. Mater. Chem. C 2015, 3, 3150–3158.
(17) Plachy, T.; Kutalkova, E.; Sedlack, M.; Vesel, A.; Masar, M.; Kuritka, I. Impact of corrosion process of carbonblack iron particles on magnetorheological behavior of their suspensions. J. Ind. Eng. Chem. 2018, 66, 362–369.
(18) Yang, Y.; Liu, X.; Yang, Y.; Xiao, W.; Li, Z.; Xue, D.; Li, F.; Ding, J. Synthesis of nonstoichiometric zinc ferrite nanoparticles with extraordinary room temperature magnetism and their diverse applications. J. Mater. Chem. C 2013, 1, 2875–2885.
(19) Marins, J. A.; Giuliani, F.; Soares, B. G.; Bossis, G. Hybrid polyaniline-coated sepiolite nanofibers for electrorheological fluid applications. Synth. Met. 2013, 185, 9–16.
(20) Lengalova, A.; Pavlik, V.; Saha, P.; Stejskal, J.; Quadrat, O. Electrorheology of polyaniline-coated inorganic particles in silicone oil. J. Colloid Interface Sci. 2003, 258, 174–178.
(21) Yin, J.; Zhao, X.; Xia, X.; Xiang, L.; Qiao, Y. Electrorheological fluids based on nano-fibrous polyaniline. Polymer 2008, 49, 4413–4419.
(22) Kim, Y. J.; Liu, Y. D.; Seo, Y.; Choi, H. J. Pickering-emulsion-polymerized polystyrene/Fe3O4 composite particles and their magnetoresponsive characteristics. Langmuir 2013, 29, 4959–4965.
(23) Liu, Y. D.; Zhang, W. L.; Choi, H. J. Pickering emulsion polymerization of core-shell-structured polyaniline@SiO2 nanoparticles and their electrorheological response. Colloid Polym. Sci. 2012, 290, 855–860.
(24) Ahn, W. J.; Jung, H. S.; Choi, H. J. Pickering emulsion polymerized smart magnetic poly(methyl methacrylate)/Fe3O4 composite particles and their stimulus-response. RSC Adv. 2015, 5, 23094–23100.
(25) Min, T. H.; Lee, C. J.; Choi, H. J. Pickering emulsion core-shell structured poly(methyl methacrylate)/ graphene oxide particles and their electrorheological characteristics. Polym. Test. 2018, 66, 195–202.
(26) Lee, C. J.; Choi, H. J. Graphene oxide as a Pickering emulsifier for poly(glycidyl methacrylate) composite particles and their suspension rheology under applied electric fields. Colloids Surf., A 2018, 550, 56–64.
(27) Kim, S. D.; Zhang, W. L.; Choi, H. J. Pickering emulsion-polymerized polystyrene–graphene oxide microspheres and their electrorheology. J. Mater. Chem. C 2014, 2, 7541–7546.
(28) Han, J. K.; Choi, H. J. Non-stoichiometric zinc-doped spinel ferrite nanoparticles with enhanced magnetic property and their magnetorheology. Colloid Polym. Sci. 2018, 296, 405–409.
(29) Zhang, X.; Guan, Y.; Zhao, Y.; Zhang, Z.; Qiu, D. Reinforcement of silicon rubber with raspberry-like SiO2@Polymer composite particles. Polym. Int. 2015, 64, 992–998.
(30) Trchova, M.; Stejskal, J. Polyaluminate: the infrared spectroscopy of conducting polymer nanotubes (IUPAC technical report). Pure Appl. Chem. 2011, 83, 1803–1817.
(31) Abbas, M.; Parvatheeswara Rao, B.; Kim, C. Shape and size-controlled synthesis of Ni Zn ferrite nanoparticles by two different routes. Mater. Chem. Phys. 2014, 147, 443–451.
(32) Zubieta, M.; Eceolaza, S.; Elejabarrieta, M. J.; Bou-Ali, M. M. Magnetorheological fluids: characterization and modeling of magnetization. Smart Mater. Struct. 2009, 18, 095019.
(33) Tsuda, K.; Takeda, Y.; Ogura, H.; Otsu, Y. Electrorheological behavior of whisker suspensions under oscillatory shear. Colloids Surf., A 2007, 299, 262–267.
(34) Lengalova, A.; PaviNvek, V.; Saha, P.; Quadrat, O.; Stejskal, J. The effect of dispersed particle size and shape on the electrorheological behaviour of suspensions. Colloids Surf., A 2003, 227, 1–8.
(35) Gow, C.; Zukoski, C. The electrorheological properties of polyaniline suspensions. J. Colloid Interface Sci. 1990, 136, 175–188.
(36) Barry, B. W.; Meyer, M. C. The rheological properties of Carbopol gels II. Oscillatory properties of Carbopol gels. Int. J. Pharm. 1979, 2, 27–40.
(37) Bica, I.; Choi, H. J. Preparation and electro-thermoconductive characteristics of magnetorheological suspensions. Int. J. Mod. Phys. B 2008, 22, 5041–5064.
(38) Schwarzl, F. R. Numerical calculation of stress relaxation modulus from dynamic data for linear viscoelastic materials. Rheol. Acta 1975, 14, 581–590.
(39) Lengalova, A.; Pavlik, V.; Saha, P.; Quadrat, O.; Kitano, T.; Stejskal, J. Influence of particle concentration on the electrorheological efficiency of polyaniline suspensions. Eur. Polym. J. 2003, 39, 641–645.
(40) Wang, B.; Tian, X.; He, K.; Ma, L.; Yu, S.; Hao, C.; Chen, K.; Lei, Q. Hollow PAQR nanostucture and its smart electrorheological activity. Polymer 2016, 83, 129–137.
(41) He, K.; Wen, Q.; Wang, C.; Wang, B.; Yu, S.; Hao, C.; Chen, K. A facile synthesis of hierarchical flower-like TiO2 wrapped with MoS2 sheets nanostructure for enhanced electrorheological activity. Chem. Eng. J. 2018, 349, 416–427.