
Ultra-high stability and magnetic response of magnetorheological fluids based on magnetic ionic liquids and carbonyl iron fibers

Xiaolin Li¹, Ruihua Guan¹, KangTai Ou¹, Qiang Fu^{1, 2}, Guiyan Yang¹, Youyi Sun^{1*}

1. Shanxi Province Key Laboratory of Functional Nanocomposites, North University of China, Taiyuan 030051, P.R. China.

2. School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo NSW 2007, Australia.

Abstract: A novel magnetic ionic liquid based on 1-methylethyl ether-3-butylimidazole (MBM) cation and $[\text{FeCl}_4]^-$ anion was synthesized for application in carrier of magnetorheological fluids (MRFs). Stability and magnetic response of the MRFs were investigated as function of anions chemical structure and content of carbonyl iron fibers. The MRFs based on the magnetic ionic liquids displayed better re-dispersibility, slower settling rates, as well as increased magnetic-induced stress comparing with conventional MRFs based on oils or ionic liquids. Furthermore, the mechanism of MRFs with good performance was investigated and proposed by molecular dynamic simulation. These results do not only confirm that the magnetic ionic liquids are potential carriers for MRFs, but also provide a new way to improve stability and magnetic response of MRFs for various applications.

Keywords: Magnetorheological fluids; Magnetic ionic liquids; Stability; Magnetic response; Molecular dynamic simulation.

Responding author: Fax: 86-351-3559669

E-mail address: syyi@pku.edu.cn (YY Sun)

1. Introduction

Magnetorheological fluids (MRFs) as an emerging “smart material” have attracted lots of attentions due to its unique ability to quickly change from liquid to a nearly solid state under external magnetic fields. Currently, MRFs have been applied shock absorbers, brakes, clutches, seismic vibration dampers, control valves, artificial joints and so on[1]. Generally, the MR performance, stability and yield stress of MRFs are three key parameters for its practical applications. These strongly depend on the structure and property of carriers and magnetic particles[2]. For example, MRFs based on aqueous or oil carriers exhibit high MR performance and large yield stress by incorporating metal alloy and carbonyl iron (CI). However, these magnetic particles easily form irreversible aggregations and precipitate due to their high density and magnetic interactions, restricting the practical applications of MRFs[3]. To overcome the above challenge, several strategies have been proposed and developed, such as adding thixotropic agents, surfactants, nanoparticles or polymeric core/shell-structured magnetic particles, and so on [4-6]. Although these strategies can effectively improve the stability of MRFs, yet these MRFs display low MR performance and low yield stress due to the low magnetic saturation of magnetic nanoparticles or the introduction of non-magnetic components [4-6]. Therefore, how to improve the stability, MR performance and yield stress of MRFs is still a great challenge.

Recently, ionic liquids (ILs) have been applied in carrier of MRFs due to their unique physicochemical properties, such as negligible vapor pressure, thermal stability, nonflammability, tenability and environment-friendly[7-10]. Furthermore, the ILs can be physically adsorbed on magnetic particles, enhancing the steric repulsion between the magnetic particles. For example, the effect of chemical structure of ILs on the stability of MRFs was firstly investigated in detail[7]. The IL (1-butyl-3-methylimidazolium hexafluorophosphate) based MRFs displayed a ultra-low sedimentation ratio (SR) of 0.05 within 1680 hours, indicating excellent stability. Contrarily, SR of MRFs based on 1-ethyl-3-methylimidazolium diethyl phosphate was about 0.4, indicating poor stability. The stability of MRFs based on IL and mineral oil (MO) was also investigated and compared [8]. The IL based MRFs exhibited better re-dispersibility and lower SR than oil based MRFs. The result was attributed to the large steric repulsion between magnetic particles, resulting from the

large volume of IL anions. The effect of a mixture of micro- and nano-sized particles on the sedimentation stability and rheological properties of the IL based MRFs was also investigated[9]. Although the viscosity of IL was six times higher than that of silicon oil, yet the sedimentation rate of IL based MRFs was faster. The result was attributed to that these magnetic particles were more easy aggregations in the silicon oil comparing to ILs. The effect of chemical structure of ILd on sedimentation stability and rheological properties of MRFs was also investigated and compared in detail [10]. The IL ([BMIM]⁺ [PF₆]⁻) based MRF displayed the lowest SR of 0.75 within 48 hours comparing to the MRFs based on [EMIM]⁺ or [BMIM]⁺ cations with different anions of [NTf₂]⁻, [CF₃SO₃]⁻, [SCN]⁻, [BF₄]⁻ and [CH₃COO]⁻. This result was due to the higher viscosity of IL [BMIM]⁺ [PF₆]⁻ comparing to other ILs. Although these IL based MRFs displayed good stability in previous works[7-10], yet they still showed low MR performance and yield stress. Therefore, it is still a high challenge to prepare MRFs with good comprehensive performance. The magnetic ionic liquids (MILs) are a new class of ILs with special paramagnetic behavior [11] and have been reported for various applications, such as catalyst, fluid-fluid separations and chemical reactions, etc [12-15]. This is an opportunity to develop a novel MRF with good comprehensive performance by employing MIL as carriers.

Herein, a novel MRF based on MIL was developed and prepared for the first time. Furthermore, the effect of ILs and MILs on stability, MR performance and yield stress of the MRFs were investigated and compared. A new mechanism about MIL based MRFs with good comprehensive performance was investigated and proposed by molecular dynamic simulation. It provides a new explanation for improving the performance of MRFs. This work will help to develop next-generation MRFs with high performance for various practical applications.

2. Experimental

2.1 Material

1-Butylimidazole (>98%) was purchased from Yanfeng Technology Co.Ltd., China. Chloromethyl ether (>95%) was purchased from Cheng du Aikeda Chemical Reagent Co. Ltd., China. 1-Chlorobutane (>98%) was purchased from Macklin Biochemical Co.Ltd., Shanghai, China. Carbonyl iron fibers (the diameter of the fibers is 0.1-0.4μm, and the aspect ratio is 100-500, >97.7%) were purchased from Jiangyou Hebao Nanomaterials Co.Ltd., China. FeCl₃·6H₂O (>99%) was purchased from Tianli

Chemical Reagent Co. Ltd., Tianjin, China. Deuterated dimethyl sulfoxide (DMSO- d_6 >99.9%) was purchased from Shanghai Tengzhun Biotechnology Co. Ltd., China. Dichloromethane and ethyl acetate were both purchased from the chemical market. All other chemicals (analytical grade) were obtained commercially and used without further purification.

2.2 Synthesis of IL and MIL

The IL of 1-chloromethyl ether 3-butylimidazole was synthesized as shown in following. 10.0g chloromethyl ether and 16.2g 1-butyl imidazole were dissolved in 20.0 mL dichloromethane under stirring at 9.0 °C. The mixture was reacted at 30.0°C for 3.0h under the protection of N₂, forming IL. The IL was purified by washing with dichloromethane and ethyl acetate for two times. 19.8g FeCl₃·6H₂O was added to 16.0g IL under stirring and reacted at 30.0°C for 3.0h under the protection of N₂, forming MIL of 1-methylethylether-3-butylimidazole iron tetrachloride. The MIL was purified by a rotary evaporator and dried under a vacuum.

2.3 Preparation of MRFs based on IL and MIL

MRFs (5-20 vol%) were prepared by mixing carbonyl iron fiber and IL (or MIL). The carbonyl iron fibers were firstly dispersed in acetone at room temperature under ultrasonic for 1.0h. Then the IL or MIL was dispersed in the above suspensions under ultrasonic for 1.0h. Finally, the mixture was heated to 80.0°C for 4.0h to remove the acetone, forming MRFs based on IL and MIL.

2.4 Characterization of Structure

The ¹H-NMR spectra were carried out on Avance III 400MHz NMR spectrometer at room temperature (DMSO- d_6).

FT-IR spectra were recorded on a Spectrum Nicolet spectrometer (Thermo Fisher, USA) from 500 to 4000.0cm⁻¹.

Raman spectrum was performed on InVia at a wavelength of 785.0nm at 298.0K.

The magnetic properties were measured by a vibrating sample magnetometer (Micro Sense, LLC, USA).

2.5 Characterization of sedimentation stability

The MRFs were poured into cylindrical polyethylene tubes with a diameter and length of 1.2mm×5.0mm. The tubes were placed vertically at room temperature. A supernatant layer was formed on the top of each sample due to the settlement of the magnetic particles under gravity. The sedimentation rate is used to evaluate the

stability of MRFs and obtained according to the following equation 1 [16]:

$$\text{Sedimentation rate} = H/H_0 \times 100\% \quad (1)$$

The H_0 (mm) and H (mm) are the initial height of the suspension in the tube and height of the supernatant layer as a function of time, respectively.

2.6 Characterization of re-dispersibility

The re-dispersibility of MRFs was measured on a rheometer (MCR-302, Anton Paar, Austria) as shown in the following: (i) the suspension was placed into the cell and a pre-shear of 300.0s^{-1} was applied for 2.0min; (ii) shear stress of suspension was measured as a function of time under a constant stress rate of 1.0s^{-1} . Generally, the sediment of magnetic particles in the suspension increased with increasing in hold time, leading to an increase of shear stress; Finally, the test results were presented in terms of shear stress growth rate to facilitate comparison of the re-dispersibility of MRs with different matrix. The growth rate of shear stress is obtained according to following equation 2 [17].

$$\text{Growth rate of shear stress} = \sigma/\sigma_0 \times 100\% \quad (2)$$

The σ_0 (kPa) and σ (kPa) are the initial shear stress of the suspension and shear stress of the sediment layer as a function of time, respectively.

2.7 Rheological measurements

Magnetorheological measurement was performed by using the same rheometer (MCR-302, Anton Paar, Austria). All rheological tests were subjected to shear pre-treatment of 300 s^{-1} for 2.0min. The shear stress was measured as a function of magnetic field strength from 0 to 800kA/m at a constant shear rate of 100 s^{-1} . The MR response of MRFs was measured under the magnetic fields of 0kA/m and 320kA/m, and this process was repeated for 10 times. The above tests were carried out at 25.0°C and a shear rate of 100 s^{-1} .

The static yield stress is defined as the minimum stress, corresponding to the value applied before the sample stops flowing [18]. The MRFs were placed into the cell and a pre-shear of 300s^{-1} was applied for 2.0min. Viscosity Vs shear stress was characterized as a function of magnetic field strength. The yield point was determined from the value corresponding to a sudden drop in viscosity (up to four or five orders of magnitude in viscosity reduction). And the associated shear stress was taken as static yield stress.

Dynamic yield stress was usually obtained by applying a set of reduced

steady-state shear rates[17], and then the relationship between shear rate and shear stress is obtained. Finally, the dynamic yield stress was calculated according to test results.

3. Results and discussion

3.1 Structure of MRFs based on IL/MIL and carbonyl iron fibers

The chemical structure of the IL and MIL was primarily confirmed by the ^1H -NMR spectra shown in Fig.1A, and the data are as follows: IL, $\delta=9.47$ (s, 1H, $-\text{N}=\text{CH}-\text{N}-$), 7.90 (dt, 2H, $J=8.2, 1.9\text{Hz}$, $-\text{N}-\text{CH}=\text{CH}-\text{N}-$), 5.53 (s, 2H, $-\text{N}-\text{CH}_2-\text{O}-$), 4.22 (t, 2H, $J=7.2\text{Hz}$, $-\text{N}-\text{CH}_2-\text{CH}_2-$), 4.04 (td, 2H, $J=7.2, 1.8\text{Hz}$, $\text{CH}_3-\text{CH}_2-\text{O}-$), 1.80(s, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.25 (td, 2H, $J=16.5, 15.8, 8.3\text{Hz}$, $-\text{CH}_2-\text{CH}_3$), 0.95-0.85 (m, 6H, $-\text{CH}_3$); MIL, $\delta=9.50$ (s, 1H, $-\text{N}=\text{CH}-\text{N}-$), 7.90 (s, 2H, $-\text{N}-\text{CH}=\text{CH}-\text{N}-$), 5.53 (s, 2H, $-\text{N}-\text{CH}_2-\text{O}-$), 4.23 (s, 2H $-\text{N}-\text{CH}_2-\text{CH}_2-$), 4.03 (s, 2H, $\text{CH}_3-\text{CH}_2-\text{O}-$), 1.81(t, 2H, $J=3.6\text{Hz}$, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.28 (s, 2H, $-\text{CH}_2-\text{CH}_3$), 0.92 (s, 6H, $-\text{CH}_3$). The approximate ratio of integral peak area was consistent with the ratio of the number of hydrogen atoms at different shifts within an allowable error range. At the same time, no additional peaks were observed in the ^1H -NMR spectra. This result indicated the formation of the IL and MIL. In addition, micro-structure of carbonyl iron fibers was also characterized by SEM images as shown in Fig.1B-C. It clearly showed fiber structure with a diameter and length of 182.0 nm and 18.6 μm , and the aspect ratio is about 102.2.

Fig.1.

Fig.2A shows the FT-IR spectra of IL and MIL. The two samples showed similar FT-IR absorption curves due to compose of the same cation of 1-methyl ether 3-butyylimidazole. The absorption peaks at 3059.0 cm^{-1} and 2958.0 cm^{-1} were assigned to C-H stretching modes of the imidazolium ring[19]. The absorption peaks around 1390.0 cm^{-1} and 1553.0 cm^{-1} were assigned to C-H bending modes and C=C stretching vibrations of the imidazolium ring, respectively[20]. The absorption peaks at 1158.0 cm^{-1} and 1107.0 cm^{-1} were assigned to C-N stretching modes and C-O stretching modes, respectively[20-21]. The absorption peaks below 1000.0 cm^{-1} were assigned to C-C and C-N bending vibration. The IR spectrum of MIL showed a wider absorption band around 3390.0 cm^{-1} comparing with IL, resulting from inter-molecular hydrogen bonding[20]. Fig.2B shows the Raman spectra of IL and MIL. For the IL sample, a strong absorption peak at 110.0 cm^{-1} was clearly observed,

which was assigned to Cl^- anion [22]. Other absorption peaks were assigned to the 1-methyl ether 3-butylimidazole. For MIL sample, similar absorption peaks were also observed. In addition, a new strong absorption peak at 331.0 cm^{-1} was observed, which was assigned to FeCl_4^- anion [23]. These results confirmed the formation of IL and MIL based on 1-methyl ether 3-butylimidazole. The M-H curve of MIL was characterized in magnetic field range of -11000 to 11000 Oe at 298K as shown in Fig.2C. It is found that the magnetization intensity of MIL linearly responded to the applied magnetic field, indicating the paramagnetic behavior [24]. The magnetic susceptibility of MIL was determined to be $1.82 \times 10^{-5} \text{ emu/g}$. These results indicated that the MIL had magnetic properties.

Fig.2.

The rheological behavior of IL and MIL was characterized and compared in Fig.3. The viscosity of IL was essentially independent of the shear rate between $0 \sim 400\text{ s}^{-1}$, indicating a Newtonian character in the range of shear rate [25]. The result was attributed to a partial break of cation-anion interactions under a low-shear rate. When the shear rate was further improved to $400 \sim 1000\text{ s}^{-1}$, the viscosity significantly dropped, indicating a shear-thinning behavior. The result was attributed to that the high-shear rate could decrease ion-pair interactions of IL. In contrast, the viscosity of MIL significantly dropped under a lower shear rate than 20.0 s^{-1} , which was also attributed to the decrease of cation-anion interactions of MIL. Then, when the shear rate was improved to higher than 20.0 s^{-1} , the viscosity slightly increased, indicating a non-Newtonian shear thickening behavior (Fig.3A). This phenomenon was attributed to the formation of hydrogen bonding between ion pairs at the high-shear rate [26]. In a comparison, the viscosity (250.0 mPa s^{-1}) of IL was greater than that (160.0 mPa s^{-1}) of MIL at zero shear rate. The viscosity of IL and MIL was also investigated as a function of temperature in Fig.3B. As expected, the viscosity of IL and MIL both decreased with increasing in temperature, which was consistent with previous work [27]. These results reveal that the MILs display different rheological behaviors with IL, in which the MILs with non-Newtonian shear thickening behavior are considered more suitable as a carrier for MRF because it can adsorb more energy at high viscosity.

Fig.3.

Fig.4 shows the sedimentation rate of the IL and MIL based MRFs. The carbonyl iron fibers could be well dispersed in IL or MIL, forming uniform MRFs as shown in Fig.4A. Furthermore, the IL and MIL based MRFs both displayed a low sedimentation ratio of 0.28 and 0.12 within 2160 h, respectively, indicating good stability. The average sedimentation rates of IL and MIL based MRFs were further calculated to be 0.000389 mm/h and 0.000167 mm/h, respectively. Comparing with present MRF based on IL and other MRFs reported in previous works, the MIL based MRF has better anti-sedimentation ability. The good anti-sedimentation ability of MIL based on MIL was attributed to following two reasons. Firstly, a strong hydrogen bond is formed between cations of MIL and magnetic particles. Compared with IL or other carries, MIL has low interaction between cation and anion and is easy to be adsorbed by magnetic particles. Secondly, the CI particles showed fiber structure, further improving the stability of MRF system.

Fig.4.

Generally, it is difficult to completely prevent the sedimentation of magnetic particles in the MRFs. Therefore, under shear force, the sedimented magnetic particles can be re-dispersed in carriers, which is also the key factor for the practical applications of MRFs[28]. The shear stress of MRFs was characterized to evaluate the re-dispersibility of MRFs as a function of hold time (Fig.5). The shear stress of IL based MRFs continuously increased with increasing in hold time. This result was attributed to the irreversible aggregation of CI fibers and the progressive separation of the solid and liquid phases[3]. In contrast, the shear stress of MIL based MRFs initially increased and then reached a plateau with increasing in hold time. The improvement of shear stress was attributed to the increase of the concentration of magnetic particles, resulting from their sedimentation[3]. While after 5 hours, the stable shear stress was due to slight change of concentration and reversible aggregation of CI fibers. For the MIL based MRF, its growth rate of shear stress was *ca.*10% after holding 168 hours. This result confirmed that the MIL based MRF exhibited better re-dispersibility comparing to the IL based MRFs. This also proves that the presented MIL based MRF is a highly attractive MRF material, and its irreversible aggregation has been significantly suppressed for a long period of time.

Fig.5.

3.3 MR performance of IL and MIL based MRFs

Fig.6 shows the shear stress of MRFs as a function of magnetic field strength. The shear stress of IL and MIL based MRFs both increased with increasing in the magnetic field strength. When a magnetic field is applied, the magnetic particles are magnetized, attract each other along the field lines, and resist external forces, resulting in a increase of shear stresses[29]. In a comparison, the MIL based MRF showed greater magnetic-induced shear stress than that of IL based MRFs at the same content of CI (Fig.6A). Generally, since the magneto-static interactions play a dominant function, the magnetic-induced shear stress is minimally affected by the carrier. However, in this study, the different result was observed, in which the anion of MIL could also effectively affect the MR performance of MRFs. The cycle stability of MRFs was further characterized as shown in Fig.6B. The consistent zero-field and field-induced stresses of IL and MIL based MRFs both slightly changed after 10 cycles. These results confirm that the present MRFs have good cycle stability, which is an important feature in the practical applications of MRFs.

Fig.6.

Fig.7 shows the shear stress of MRFs as a function of shear rate under external magnetic field. In the absence of a magnetic field, the shear stress of IL and MIL based MRFs was both proportional to the shear rate, indicating almost Newtonian characteristics as shown in Fig.7A-B[29]. In the presence of a magnetic field, the shear stress of IL and MIL based MRFs both firstly increased and then reached a plateau with increasing in shear rate. In addition, IL and MIL based MRFs both exhibited non-zero yield stress at an almost zero shear rate in the presence of magnetic field, revealing a Bingham plastic characteristic[30]. These results indicated that the IL and MIL based MRFs were typical viscoelastic materials[31]. In addition, the plateau stress was observed, which was defined as dynamic shear stress, resulting from the chain formation of CI particles[17]. When the shear stress was lower than the yield stress, it showed solid or gel state. Contrarily, when the shear stress was higher than yield stress, it showed a fluid state. Fig.7C shows the dynamic yield stress of IL and MIL based MRFs as a function of the magnetic field strength. As expected, the dynamic yield stress of the two MRFs both increased with increasing in magnetic field strength. Under a larger magnetic field strength, larger shear stress is required to break the column-like structure so that the fluid starts to flow, which can be attributed to the strong pull force between CI particles. The yield stress of MIL based MRF was

proportional to the magnetic field strength with a slope of 2.0. This corresponds to the magnetic polarization model based on magnetic interactions[32]. For the IL based MRF, the slope was about 1.0, indicating a deviation from the polarization model caused by the mass magnetization and connection of the particles[33]. Under the same volume fraction of CI particles (10.0 vol%), the MIL based MRF displayed larger dynamic yield stress than that of IL based MRF. These results demonstrate that the MIL as the carrier can effectively improve the dynamic yield stress of MRFs, which is a key parameter of MRF for practical applications.

Fig.7.

The viscosity of IL and MIL based MRFs was measured as a function of shear stress under various magnetic fields (Fig.8). The curves showed a sharp drop in shear stress associated with the static yield point of the MRFs [10, 18]. The static yield stress of IL based MRF was close to zero at zero magnetic fields, indicating nearly Newtonian fluid behavior (Fig.8A)[25]. In contrast, the static yield stress of MIL based MRF was *ca.* 100.0Pa at zero magnetic fields, indicating a non-Newtonian fluid behavior (Fig.8B). From Fig.8C, we found that the static yield stress of IL and MIL based MRFs both increased with increasing in the magnetic field strength. In a comparison, the static yield stress of MIL based MRF was significantly greater than that of IL based MRF under the magnetic field. These results further confirm that the MIL can effectively improve the yield stress of MRFs.

Fig.8.

The effect of content of CI fibers on rheological properties of MIL based MRF was also investigated as shown in Fig.9. As expected, the shear stress of MIL based MRF increased with increasing in the content and magnetic field strength (Fig.9A). Similar observations have been reported in previous works [34-36]. This result was attributed to larger magnetic dipole-dipole interaction at higher content of CI particles, leading to large stress [37]. It was found that the content had a slight effect on zero-field stress due to the low content and good dispersion of CI fibers in MIL. As seen from Fig.9B, all curves showed a similar trend. This result was attributed to larger magnetic interactions at higher content of CI particles. These interactions must be overcome until the yield stress reach, and once they are diminished, the rheological behavior of the MRF becomes Newtonian. For example, when the content of CI fiber increased to 20 vol%, the MRF displayed high yield stress of 80.0kPa under the

magnetic field of 800kA/m. In Table 1, we summarized the performance of MRFs based on different carries reported in present and previous works [7-10, 38, 39]. It was found that the present MIL based MRFs showed the best comprehensive performance (settling rate=0.000167 mm/h and yield stress=80 kPa) among all of the reported MRFs.

Fig.9.

Table 1.

The mechanism of present MRFs with excellent comprehensive performance was further investigated by molecular dynamics simulation (Fig.10 and 11). The molecular model of IL (or MIL) is established on the Materials Studio (sTable 1), and then the computational mode of CI fiber is simplified into iron atoms (sTable 2). Furthermore, the geometric structure of IL (or MIL) molecule and iron atoms was optimized by using Doml3 model as shown in Fig.10. It was found that the length (ca.1.914 Å) of bonds between the anion and cation of IL was shorter than that (ca.3.046 Å) of MIL (Fig.10A-B). As well-known, the radius of hydrogen bond between the two atoms is less than 2.95 Å [40]. The result indicated the formation of strong hydrogen bond between cations and anions of ILs. Contrarily, it was weak hydrogen bond between cations and anions of MILs. As shown in Fig.10C-D, the bond length between the cation of IL and iron atom was about 2.068 Å, while the bond length was about 2.057 Å for the cation of MIL and iron atom. These results indicated the formation of hydrogen bond between cation of IL (or MIL) and CI particles. In addition, the bond length between cation and anion in IL and MIL was 3.997Å and 3.827Å, respectively (Fig.10C-D) . This result indicated that there were few hydrogen bonds between the anions and cations of IL or MIL in the presence of CI particles.

In addition, the interaction energy (ΔE) is also used to evaluate the interaction between the IL (or MIL) molecule and CI particles and calculated by using density functional theory (DFT) as shown in the following equation 3.

$$\Delta E = E_{AB} - (E_A + E_B) \quad (3)$$

Where E_{AB} is defined as the total energy of the system composed of iron atom and IL (or MIL) molecule. E_A and E_B represent the energy of iron atom and IL (or MIL) molecule, respectively. The energy of the highest/lowest occupied molecular orbital (E_{HOMO}/E_{LUMO}) of IL and MIL was obtained through molecular orbital energy calculation. The energy gap value ΔE_{L-H} was then obtained, corresponding to the

stability of the IL molecule as shown in Table.2. The activation energy of anion and cation complexes of IL_{a-c} and MIL_{a-c} from the ground state required 249.91 kJ/mol and 141.02 kJ/mol, respectively. These results further indicated the formation of strong van der Waals interaction between cations and anions of ILs. In a comparison, there were few hydrogen bonds between cations and anions of MIL due to its greater steric hindrance. The binding energy of IL (or MIL) and iron atom was calculated to be ca. -4277.97 kJ/mol or -5271.31 kJ/mol, respectively. These results indicated the formation of stronger absorption between MILs and CI particles compared to IL and CI particles.

Table 2.

The MD simulation of MRFs (the molar fraction of CI particles and ionic liquid is 1:5) was further conducted as shown in Fig.11A-B. Here, the content of CI particles in MRFs is controlled by adjusting the molar ratio of molecules and iron atoms. The structure factor of IL and MIL based MRFs was obtained and compared through the MD simulation as shown in Fig.11C. The structure factors were plotted against reduced wavenumbers. We observed a similar peak at 3.0\AA^{-1} , indicating that the IL and MIL based MRFs had a similar chemical structure [41]. In addition, a new pre-peak at 1.0\AA^{-1} was observed for the MIL based MRF [41]. The pre-peak in the structure factor of MIL based MRF was attributed to the formation of network structure, resulting from the interaction between FeCl_4^- anions [41-42].

Fig.11.

The strong interaction between IL (or MIL) and CI particles was further confirmed by the IR spectra (Fig.12). As shown in Fig.12A, no IR absorption peaks were observed between 500.0cm^{-1} and 4000.0cm^{-1} for pure CI particles. In contrast, CI particles modified with IL or MIL showed some strong IR absorption peaks, which were assigned to the ILs or MILs (Fig.12A-D). However, the wide absorption bands around 3400.0 cm^{-1} and $2000\text{-}2200.0\text{ cm}^{-1}$ disappeared. In addition, a new absorption peak at 900.0 cm^{-1} was observed. These results indicated that the ILs or MILs were adsorbed on the surface of CI particles by the van der Waals interaction. The IR spectrum of CI particles modified with MIL slightly changed after washing under ultrasonication. In a comparison, the IR absorption peaks of CI particles modified with IL completely disappeared after the washing process. This result further suggested that there was a stronger interaction between MILs and CI particles compared to ILs and CI particles..

Fig.12.

Based on above simulation and experimental results, the excellent comprehensive performance of MIL based MRFs is attributed to the special structure of MIL as shown in Scheme 1. Firstly, the cation of MIL can form a strong physical interaction with CI particles, providing sufficient electrostatic repulsion between CI particles to prevent aggregation for a long period time. At the same time, it also provides good stability and re-dispersibility of MRFs based on MIL. Secondly, the FeCl_4^- anions easily form thixotropic gel network, further preventing the precipitation and aggregation of CI particles. These findings are expected to make MIL based MRF have long-term anti-settling properties. Moreover, the gel network can also restrict the movement of CI particles, resulting in greater shear stress. Finally, a MIL with magnetic properties may further enhance the magnetically induced shear stress under a magnetic field.

Scheme 1.**4. Conclusion**

In summary, a new class of magnetic ionic liquid (MIL) was synthesized and used as the carrier of MRFs. The MRFs exhibited excellent comprehensive performance, such as long-term stability and high magnetic response. These outstanding performance can be attributed to the following three reasons. Firstly, the cations of MIL can adsorb on the surface of CI particles, providing sufficient electrostatic repulsion. Secondly, the anions of MIL can promote the formation of network structure. Thirdly, the MILs have a magnetic properties. This work opens a new avenue for developing next-generation MRFs with superior performance for various practical applications.

Acknowledgement

The authors are grateful for the support of the National Natural Science Foundation of China under grants (51773184 and U1810114), and Shanxi Provincial Natural Science Foundation of China (201801D121104 and 201803D421081).

Conflict of Interest:

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted

References

-
- [1] J. de Vicente, D.J. Klingenberg, R. Hidalgo-Alvarez, Magnetorheological fluids: a review, *Soft Matter*, 2011,7, 3701.
- [2] B.J. Park, F.F. Fang, H.J. Choi, Magnetorheology: materials and application, *Soft Matter*, 2010,6, 5246.
- [3] M.T. López-López, A. Zugaldía, F. González-Caballero, J.D.G. Durán, Sedimentation and redispersion phenomena in iron-based magnetorheological fluids, *Journal of Rheology*, 2006,50, 543-560.
- [4] M.T. Manzoor, J.E. Kim, J.H. Jung, C. Han, S.B. Choi, I.K. Oh, Two-Dimensional rGO-MoS₂ Hybrid Additives for High-Performance Magnetorheological Fluid, *Scientific reports*, 2018,8, 12672.
- [5] D. Bica, L. Vékás, M.V. Avdeev, O. Marinică, V. Socoliuc, M. Bălăsoiu, V.M. Garamus, Sterically stabilized water based magnetic fluids: Synthesis, structure and properties, *Journal of Magnetism and Magnetic Materials*, 2007,311,17-21.
- [6] F.F. Fang, Y.D. Liu, H.J. Choi, Y. Seo, Core-shell structured carbonyl iron microspheres prepared via dual-step functionality coatings and their magnetorheological response, *ACS applied materials & interfaces*, 2011,3,3487-95.
- [7] C. Guerrero-Sanchez, T. Lara-Ceniceros, E. Jimenez-Regalado, M. Raşa, U.S. Schubert, Magnetorheological Fluids Based on Ionic Liquids, *Advanced Materials*, 2007,19,1740-1747.
- [8] A. Gómez-Ramírez, M.T. López-López, F. González-Caballero, J.D.G. Durán, Stability of magnetorheological fluids in ionic liquids, *Smart Materials and Structures*, 2011,20, 045001.
- [9] I. Jönkkäri, M. Isakov, S. Syrjälä, Sedimentation stability and rheological properties of ionic liquid-based bidisperse magnetorheological fluids, *Journal of Intelligent Material Systems and Structures*, 2014,26,2256-2265.
- [10] A.J.F. Bombard, F.R. Gonçalves, J. de Vicente, Magnetorheology of Carbonyl Iron Dispersions in 1-Alkyl-3-methylimidazolium Ionic Liquids, *Industrial & Engineering Chemistry Research*, 2015, 54,9956-9963.
- [11] S. Hayashi, H.O. Hamaguchi, Discovery of a Magnetic Ionic Liquid [bmim]FeCl₄, *ChemInform*, 2005,36,1590-1591..
- [12] M. H. Valkenberg , C. Decastro , W. F Hölderich. Friedel-Crafts acylation of aromatics catalysed by supported ionic liquids, *Applied Catalysis A General*, 2001,215,185-190..

-
- [13] N. Deng, M. Li, L. Zhao, C. Lu, S.L. de Rooy, I.M. Warner, Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation, *Journal of hazardous materials*, 2011,192, 1350-7.
- [14] N. Sahiner, S. Demir, S. Yildiz, Magnetic colloidal polymeric ionic liquid synthesis and use in hydrogen production, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2014,449 .87-95.
- [15] E. Kowsari, M. Mohammadi, Synthesis of reduced and functional graphene oxide with magnetic ionic liquid and its application as an electromagnetic-absorbing coating, *Composites Science and Technology*, 2016,126 ,106-114.
- [16] H.B. Cheng, J.M. Wang, Q.J. Zhang, N.M. Wereley, Preparation of composite magnetic particles and aqueous magnetorheological fluids, *Smart Materials and Structures*, 2009,18, 085009.
- [17] J.P. Rich, P.S. Doyle, G.H. McKinley, Magnetorheology in an aging, yield stress matrix fluid, *Rheologica Acta*, 2012, 51, 579-593.
- [18] M. Dinkgreve, J. Paredes, M. Denn, D. Bonn, On different ways of measuring "the" yield stress, *Journal of Non-Newtonian Fluid Mechanics*, 2016, 238,3841-3869.
- [19] L. Tao, J. Lu, B. Hu, J. Chen, S. Xu, F. Liu, D. He, Synthesis and characterisation of new polymeric ionic liquid poly(imidazolium chloride-4,6-dinitrobenzene-1,3-diyl), *Materials Research Innovations*, 2014, 19,65-68.
- [20] C. Chen, A functionalised ionic liquid: 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride, *Physics and Chemistry of Liquids*, 2010, 48, 298-306.
- [21] B. Haddad, D. Mokhtar, M. Gousseem, E.-h. Belarbi, D. Villemin, S. Bresson, M. Rahmouni, N.R. Dhumal, H.J. Kim, J. Kiefer, Influence of methyl and propyl groups on the vibrational spectra of two imidazolium ionic liquids and their non-ionic precursors, *Journal of Molecular Structure*, 2017,1134 582-590.
- [22] M. Ledinsky, P. Loper, B. Niesen, J. Holovsky, S.J. Moon, J.H. Yum, S. De Wolf, A. Fejfar, C. Ballif, Raman Spectroscopy of Organic-Inorganic Halide Perovskites, *The journal of physical chemistry letters*, 2015, 6, 401-6.
- [23] M. S. Sitze , E.R. Schreiter, E.V. Patterson, Ionic Liquids Based on FeCl₃ and FeCl₂. Raman Scattering and ab Initio Calculations, *Inorganic Chemistry*, 2001,40,2298-2304.
- [24] G. Wang, F. Zhou, Z. Lu, Y. Ma, X. Li, Y. Tong, X. Dong, Controlled synthesis of CoFe₂O₄/MoS₂ nanocomposites with excellent sedimentation stability for

magnetorheological fluid, *Journal of Industrial and Engineering Chemistry*, 2019,70, 439-446.

[25] H. Chen, Y. Ding, C. Tan, Rheological behaviour of nanofluids, *New Journal of Physics*, 2007, 9,367-367.

[26] J. Qin, G. Zhang, Z. Ma, J. Li, L. Zhou, X. Shi, Effects of ionic structures on shear thickening fluids composed of ionic liquids and silica nanoparticles, *RSC Advances*, 2016,6, 81913-81923.

[27] E. Altin, J. Gradl, W. Peukert, First Studies on the Rheological Behavior of Suspensions in Ionic Liquids, *Chemical Engineering & Technology*, 2006,29, 1347-1354.

[28] Phulé, P. Pradeep, J.M. Ginder, Synthesis and Properties of Novel Magnetorheological Fluids Having Improved Stability and Redispersibility, *International Journal of Modern Physics B*, 1999, 13,2019-2027.

[29] S.Y. Kim, S.H. Kwon, Y.D. Liu, J.-S. Lee, C.-Y. You, H.J. Choi, Core-shell-structured cross-linked poly(glycidyl methacrylate)-coated carbonyl iron microspheres and their magnetorheology, *Journal of Materials Science*, 2013,49,1345-1352.

[30] N.M. Wereley, A. Chaudhuri, J.H. Yoo, S. John, S. Kotha, A. Suggs, R. Radhakrishnan, B.J. Love, T.S. Sudarshan, Bidisperse Magnetorheological Fluids using Fe Particles at Nanometer and Micron Scale, *Journal of Intelligent Material Systems and Structures*, 2016,17, 393-401.

[31] S. Jha, V.K. Jain, Rheological characterization of magnetorheological polishing fluid for MRAFF, *The International Journal of Advanced Manufacturing Technology*, 2008,42, 656-668.

[32] C.M. Burba, H.C. Chang, The Nature of Cation-Anion Interactions in Magnetic Ionic Liquids as Revealed Using High-Pressure Fourier Transform Infrared (FT-IR) Spectroscopy, *Applied spectroscopy*, 2019,73, 511-519.

[33] A. Garcia-Saiz, P. Migowski, O. Vallcorba, J. Junquera, J.A. Blanco, J.A. Gonzalez, M.T. Fernandez-Diaz, J. Rius, J. Dupont, J. Rodriguez Fernandez, I. de Pedro, A magnetic ionic liquid based on tetrachloroferrate exhibits three-dimensional magnetic ordering: a combined experimental and theoretical study of the magnetic interaction mechanism, *Chemistry*, 2014, 20, 72-6.

[34] A.V. Anupama, V.B. Khopkar, V. Kumaran, B. Sahoo, Magnetic field dependent

steady-state shear response of Fe₃O₄ micro-octahedron based magnetorheological fluids, *Physical chemistry chemical physics : PCCP*, 2018,20, 20247-20256.

[35] A.M. Trendler , Holger Böse, Experimental studies on magnetorheological model suspensions, *Electrorheological Fluids and Magnetorheological Suspensions - 10th International Conference on ERMR*, 2006. 2007.

[36] V.G. Vasiliev, N.A. Sheremetyeva, M.I. Buzin, D.V. Turenko, V.S. Papkov, I.A. Klepikov, I.V. Razumovskaya, A.M. Muzafarov, E.Y. Kramarenko, Magnetorheological fluids based on a hyperbranched polycarbosilane matrix and iron microparticles, *Smart Materials and Structures*, 2016,25, 055016.

[37] E. Climent, M.R Maxey, G.E Karniadakis, Dynamics of Self-Assembled Chaining in Magnetorheological Fluids, *Langmuir*, 2004, 20,507-513.

[38] G. Dodbiba, H.S. Park, K. Okaya, T. Fujita, Investigating magnetorheological properties of a mixture of two types of carbonyl iron powders suspended in an ionic liquid, *Journal of Magnetism and Magnetic Materials*, 2008,320, 1322-1327.

[39] X. Liu, H. Lu, Q. Chen, Study on the Preparation and Properties of Silicone Oil-Based Magnetorheological Fluids, *Materials and Manufacturing Processes*, 2013, 28,631-636.

[40] H.Xu, W.X.Pan, R.X. Wang, D.J. Zhang, C.B. Liu, Understanding the mechanism of cellulose dissolution in 1-butyl-3-methylimidazolium chloride ionic liquid via quantum chemistry calculations and molecular dynamics simulations, *J Comput Aided Mol Des*, 2012, 26,329-337.

[41] T. Sakagami , K. Fuchizaki, Does a network structure exist in molecular liquid SnI₄ and GeI₄, *Journal of Physics Condensed Matter*, 2017,29, 145102.

[42] A. Garcia-Saiz, I. de Pedro, P. Migowski, O. Vallcorba, J. Junquera, J.A. Blanco, O. Fabelo, D. Sheptyakov, J.C. Waerenborgh, M.T. Fernandez-Diaz, J. Rius, J. Dupont, J.A. Gonzalez, J.R. Fernandez, Anion-pi and halide-halide nonbonding interactions in a new ionic liquid based on imidazolium cation with three-dimensional magnetic ordering in the solid state, *Inorganic chemistry*, 2014,53, 8384-96.

Table 1. Performance of MRFs based on various carriers and magnetic particles

Table 2. Frontier molecular orbital energy levels and energy gaps (kJ/mol) between anion and cation.

Scheme 1. Micro-structure of MRF based on (A) IL and (B)MIL.

Fig.1. (A) $^1\text{H-NMR}$ of IL and MIL, (B-C) SEM images of CI fibers.

Fig.2. (A) FT-IR and (B) Raman spectra of (a) IL and (b) MIL, (C) M-H curve of MIL as a function of magnetic field strength at 298.0K.

Fig.3. (A) Viscosity of (a) IL and (b) MIL as a function of shear rate at a temperature of 25°C, (B) Viscosity of (a) IL and (b) MIL as a function of temperature at a shear rate of 100S^{-1} .

Fig.4. (A) Optical photographs of MRFs based on (a) IL and (b) MIL as a function of hold time, (B) Sedimentation rate of MRFs based on (a) IL and (b) MIL as a function of hold time.

Fig.5. (A) Shear stress and (B) Shear stress growth rate of MRFs based on (a) IL and (b) MIL as a function of hold time.

Fig.6. (A) Shear stress of MRFs based on (a) IL and (b) MIL as a function of magnetic field strength, (B) Time dependence of shear stress for the MRFs based on (a) IL and (b) MIL under cyclic magnetic field of 0kA/m and 320kA/m.

Fig.7. Shear stress of the MRFs based on (A) IL and (B) MIL as a function of shear rate under various magnetic field strengths of 0kA/m, 160.0kA/m, 320.0kA/m, 480.0kA/m, 640.0kA/m and 800.0kA/m, (C) Dynamic yield stress of MRFs based on (a)IL and (b)MIL as a function of magnetic field strength.

Fig.8. Shear viscosity of MRFs based on (A) IL and (B) MIL as a function of shear stress under various magnetic field strengths of 0kA/m, 160.0kA/m, 320.0kA/m, 480.0kA/m, 640.0kA/m and 800.0kA/m, (C) Static yield stress of MRFs based on (a) IL and (b) MIL as a function of magnetic field strength.

Fig.9. (A) Shear stress and (B) Static yield stress of MIL based MRF with various contents of CI fibers, (a) 5.0vol%, (b)10.0vol%, (c)15.0vol% and (d)20.0vol% as a function of magnetic field strength.

Fig.10. Computational mode of (A)IL, (B)MIL, (C)mixture of IL and iron atom, (D) mixture of MIL and iron atom, (○ :H, ● :O, ● :C, ● :N, ● :Fe, ● :Cl).

Fig.11. Molecular dynamics simulation mode of the MRF based on (A) IL and (B) MIL, (C) The local structure factors of the MRF based on (a)IL and (b)MIL.

Fig.12. IR spectra of various samples, (A) CI particles modified with IL, (B) CI particles modified with MIL, (C) pure IL, (D) pure MIL, (E) CI particles modified with IL after washing with ethanol, (F) CI particles modified with MIL after washing

with ethanol, (G) pure CI particles.

Table 1.

Composition/content	Sedimentation rate	Re-dispersion	Yield stress	Ref
---------------------	--------------------	---------------	--------------	-----

MIL/CI(10vol%)	0.12	good	45kPa	present
MIL/CI(20vol%)	0.09	good	80 kPa	
trihexyltetradecylphosphonium chloride/Fe ₂ O ₃ (25wt%)	0.3	-----	2.1kPa	7
1-ethyl-3-methylimidazolium diethyl phosphate/Fe(10vol%)	0.7	good	-----	8
1-ethyl-3-methylimidazolium diethyl phosphate/CI (15vol%)	0.36	-----	16kPa	9
1-butyl-3-methylimidazolium hexafluorophosphate/CI (30vol%)	0.3	good	7kPa	10
Ammoniumn-diethyl-n-methyl-n-(2-Methoxyethyl)tetrafluoroborate/CI (80.6wt%)	-----	-----	4kPa	38
Silicon oil/CI (10vol%)	0.4	----	5.5 kPa	39

Table 2.

Complexes	E _{LUMO}	E _{HOMO}	ΔE _{L-H}
IL _{a-c}	-150.16	-400.06	249.91
MIL _{a-c}	-489.16	-630.19	141.02