

Controlling the Properties of Solvent-free Fe₃O₄ Nanofluids by Corona Structure

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Abstract: We studied the relationship between corona structure and properties of solvent-free Fe₃O₄ nanofluids. We proposed a series of corona structures with different branched chains and synthesize different solvent-free nanofluids in order to show the effect of corona structure on the phase behavior, dispersion, as well as rheology properties. Results demonstrate novel liquid-like behaviors without solvent at room temperature. Fe₃O₄ magnetic nanoparticles content is bigger than 8% and its size is about 2~3 nm. For the solvent-free nanofluids, the long chain corona has the internal plasticization, which can decrease the loss modulus of system, while the short chain of corona results in the high viscosity of nanofluids. Long alkyl chains of modifiers lead to lower viscosity and better flowability of nanofluids. The rheology and viscosity of the nanofluids are correlated to the microscopic structure of the corona, which provide an in-depth insight into the preparing nanofluids with promising applications based on their tunable and controllable physical properties.

Keywords: Corona structure; Fe₃O₄ nanoparticles; Liquid-like behavior; Solvent-free nanofluids

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Introduction

Recently, a novel family of nanofluids in the absence of solvents evolved from traditional nanofluids were developed, which are called solvent-free nanofluids that exhibit liquid-like behavior in the absence of solvents and preserve their nanostructure in the liquid state. These nanofluids are organic-inorganic hybrid particles comprising a charged oligomer corona attached to hard, inorganic nanoparticle cores. This new system possesses better dispersion, stability and can flow below 150°C. Since the thermal conductivity of nanoparticles is higher than those of other traditional liquids, nanofluids can be used potentially in microelectronics, fuel cells, and hybrid-powered engines, engine cooling, vehicle thermal management, domestic refrigerator, heat exchanger, and nuclear reactor. In addition, the nanofluids could be used as a lubricant on contact facings of solids minimizing wear.

Many kinds of solvent-free nanofluids had been synthesized such as SiO₂, TiO₂, DNA, γ -Fe₂O₃, C₆₀, protein, sepiolite, CaCO₃, Rh, ZnO and Si [1-17]. Our group had also synthesized several kinds of solvent-free nanofluids, including TiO₂, SiO₂, Fe₃O₄, Au and carbon nanotubes [18-26]. It was found that the flow properties of the solvent-free nanofluids were related to structures of surface modifiers. The nanofluids properties could be tuned based on variations in their structural components, including core shape, corona length, and molecular weight.

Praveen Agarwal and his co-workers reported a class of self-suspended nanoparticle liquids created by densely grafting charged organic telomers (short polymers) to the surface of inorganic nanoparticles [27]. The grafting density and molecular weight of the polyethyleneglycol (PEG) corona could be varied to produce a spectrum of liquids of controlled viscosity. Emmanuel et al. investigated the nuclear mag-

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netic resonance (NMR) relaxation and diffusion of silicabased Nano-scale ionic materials (NIMs) with a polymer canopy in order to determine the relationship between chemical structure and dynamics [28]. The results showed that the properties of the canopy related to the macroscopic properties. They also studied canopy diffusion and found that it was not restricted to the surface of the nanoparticles and showed unexpected behavior upon addition of excess canopy. The liquid-like behavior in NIMs was due to rapid exchange of the block copolymer canopy between the ionically modified nanoparticles [29]. Hsiu and his coworkers formulated a theory that estimated the equilibrium structure of homogeneous, liquid phase, solvent-free NOHMs without assuming a pairwise-additive inter-particle potential [31]. However, few reports have been concerned on the relationship between the properties and corona microscopic structures.

In this work, a series of experiments were designed to examine the relationship between structure of corona and properties of solvent-free nanofluids based on ferriferrous oxide nanoparticles. In the Fe_3O_4 solvent-free nanofluids system, the Fe_3O_4 nanoparticles formed the core, and the shell was the ionic liquid. We selected three kinds of surface modifiers $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)(\text{C}_{10}\text{H}_{21})_2\text{Cl}^-$, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ and $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3\text{Cl}^-$, which had same functional groups but different lengths and quantities of alkyl chains. The same counter anion $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{20}\text{O}(\text{CH}_2)_3\text{SO}_3^-$ was exchanged the Cl^- of the modifiers. The three kinds of nanofluids were synthesized in the same method during the whole experimentation and characterized in the same condition for obtaining the exact relationship between the corona microscopic structures and properties of nanofluids.

Experimental section

Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99%) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%) were from Tianli Chemical Reagents Co., Ltd.. Methanol (99.5%), ethanol (99.7%), ammonia (NH_4OH , 25% aqueous solution) and tetrahydrofuran were purchased as analytical grade reagents from Fuchen Chemical Ind., Ltd.. Acetone (98%) was from Fu Yu Chemical Ind., Ltd., and used without further purification. Deionized water was made in lab. 1-Decanaminium, N-decyl-N-methyl-N-[3-(trimethoxysilyl)propyl]-, chloride (1:1): $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)(\text{C}_{10}\text{H}_{21})_2\text{Cl}^-$ (3392, 40% methanol solution), 1-Octadecanaminium, N, N-dimethyl-N-[3-(trimethoxysilyl)propyl]-, chloride (1:1): $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ (6620, 40% methanol solution) and 1-Propanaminium, N,

N, N-trimethyl-3-(trimethoxysilyl)-, chloride (1:1): $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ (8415, 50% methanol solution) was from Gelest. Poly (oxy-1,2-ethanediyl), a-(4-nonylphenyl)-w-(3-sulfopropoxy)-, potassium-salt (1:1): $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{20}\text{O}(\text{CH}_2)_3\text{SO}_3^- \text{K}^+$ (PEGs) was from Sigma-Aldrich.

Synthesis of Fe_3O_4 nanoparticles

The Fe_3O_4 was prepared by chemical co-precipitation method [30-32]. 100 ml of 1 mol/l aqueous solution of FeCl_2 and 200 ml aqueous solution of 1 mol/l FeCl_3 were mixed and blanketed with nitrogen. 5% ammonia aqueous solution was trickled slowly to the mixture with stirring constantly in an ultrasonic wave apparatus. The insoluble black particles were washed several times with deionized water. The lump was grinded carefully after dried at 60°C.

Synthesis of solvent-free Fe_3O_4 nanofluids

Firstly disperse 0.5 g of Fe_3O_4 into 10 ml of ammonia (pH=10) and treat with ultrasound for 30 min at 30°C. 3 ml of ionic surface modifier was added into the mixture. The black precipitate formed immediately was aged for 24 h at room temperature by gently shaking it periodically. Washed the precipitate with deionized water and methanol 3~4 times. After dried at 70°C, the solid was dispersed in tetrahydrofuran. The insoluble solid particles were discarded and the solution was dried at 70°C to obtain the magnetic Fe_3O_4 chlorine salt. The nanofluids was prepared by treating 1 g of chlorine salt with 15 ml of an aqueous (16.5%) solution of potassium sulfonate salt (PEGs) in water at 70°C for 24 h. After dried at 70°C, the solid was dispersed in acetone and then centrifuged the solution. The insoluble particles were discarded and the solution was dried at 70°C again in order to obtain the solvent-free Fe_3O_4 nanofluids.

Characterizations

The structure of the Fe_3O_4 nanofluids was investigated by Fourier transform-infrared (FTIR) spectrometer analysis (WQF-310, Beijing Second Optical Instruments Factory) with KBr pellets. Transmission electron microscope (TEM) images were obtained on a Hitachi H-800 instrument. The thermogravimetric analysis (TGA) measurements were taken under N_2 flow by using TA TGAQ50 instrument. Differential scanning calorimetry (DSC) traces were recorded collected on a TA Q1000 Instruments with a heating rate of 10°C/min from -60°C to 60°C. Rheological properties were studied by using the rheometer of TA AR-G2 instrument with a heating rate of 5°C/min. Ultrasonic wave apparatus is from Kunshan Ultrasonic Instruments Co., Ltd. X-ray diffraction (XRD) analysis was carried out

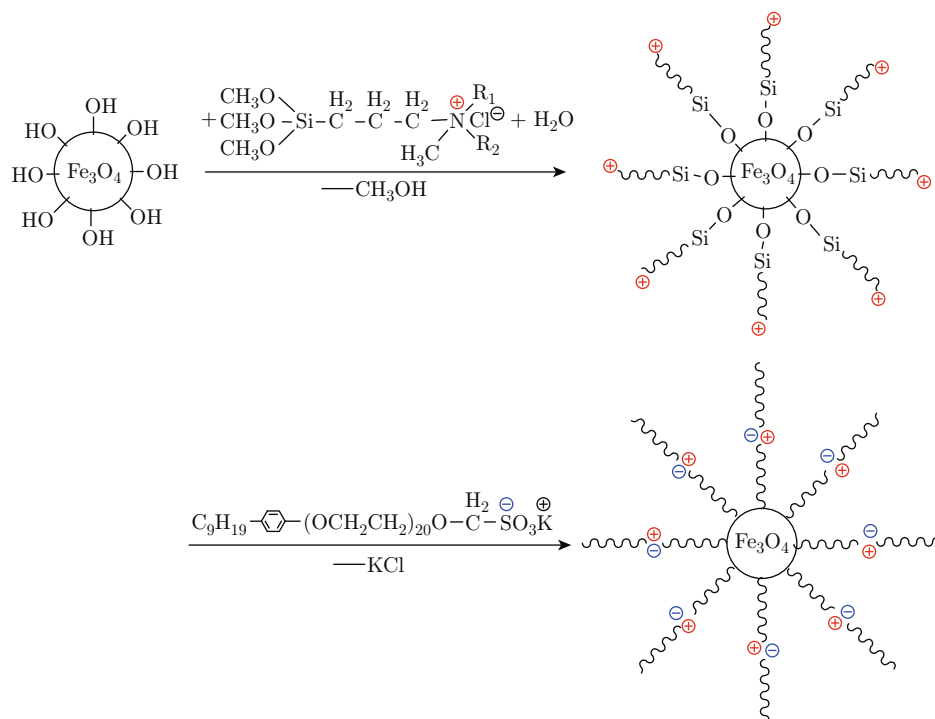


Fig. 1 The schematics of the reaction mechanisms.

on a Scintag D/MAX-3C using Cu K α radiation ($\lambda = 1.54\text{\AA}$).

Results and discussion

Comparison of corona structures

Solvent-free nanofluids are organic-inorganic hybrids, which are obtained through two steps. First, organic corona was grafted on an inorganic Fe_3O_4 core through covalent bond. Then bulky counter ion was ionically tethered with corona as the canopy (Fig. 1). In order to find the relationship between surface molecular structure and properties of nanofluids, we changed the molecular structure of organic corona and prepared different kinds of nanofluids. The molecular formulas of the three kinds of surface modifiers are shown in Fig. 2 and Table 1. Surface modifiers have different branched chains of R_1 and R_2 , which lead to different properties of nanofluids.

Table 1 The comparison of three kinds of corona structure

Modifier	R_1	M_1 :		M_2 :		Summation of M_1 and M_2
		Molecular Weight of R_1	R_2	Molecular Weight of R_2		
3392	$\text{C}_{10}\text{H}_{21}$	141	$\text{C}_{10}\text{H}_{21}$	141	282	
6620	$\text{C}_{18}\text{H}_{37}$	253	CH_3	15	268	
8415	CH_3	15	CH_3	15	30	

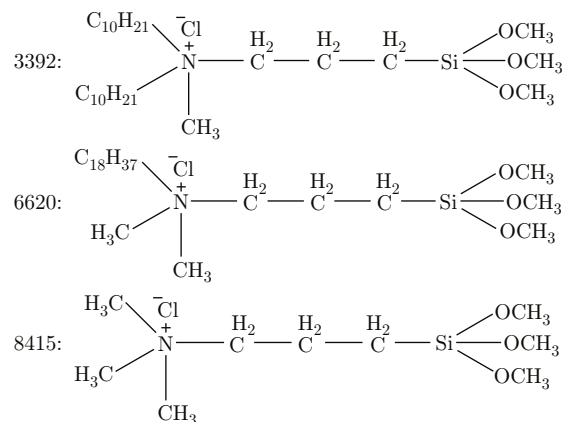


Fig. 2 The molecular formulas of three kinds of corona.

Characterization of Fe_3O_4 nanoparticles

The X-ray diffraction pattern of Fe_3O_4 nanoparticles is shown in Fig. 3. The diffraction peaks at $2\theta = 30.18^\circ$, 35.50° , 43.10° , 53.82° , 57.20° , 62.76° correspond to (220), (311), (400), (422), (511) and (440) crystal plane of Fe_3O_4 , respectively. This reveals that the magnetic particles are pure Fe_3O_4 with spinel structure.

Nanofluids chemical structures

In the FTIR spectrum of Fe_3O_4 solvent-free nanofluids (Fig. 4), the peak at 1647 cm^{-1} is attributed to the vibrations of benzene ring, which is a part of PEGs. The peak at 1105 cm^{-1} is attributed to the C-O bond stretching vibration of ether bond. The Fe_3O_4 solvent-

free nanofluids also possess absorption bands at 1036 cm^{-1} and 946 cm^{-1} due to Si-O-Si and Si-O-Fe bonds, respectively. The peaks at 2927 cm^{-1} and 2871 cm^{-1} are attributed to the stretching vibrations of $-\text{CH}_2-$ and $-\text{CH}_3$, respectively. The bending vibration peak of $-\text{CH}_2-$ appears at 1464 cm^{-1} . The peak at 3444 cm^{-1} is attributed to the stretching vibrations of $-\text{OH}$ from Fe_3O_4 nanoparticles. It indicates that three kinds of organ canopy surfactants are all grafted on the surface of Fe_3O_4 nanoparticles successfully.

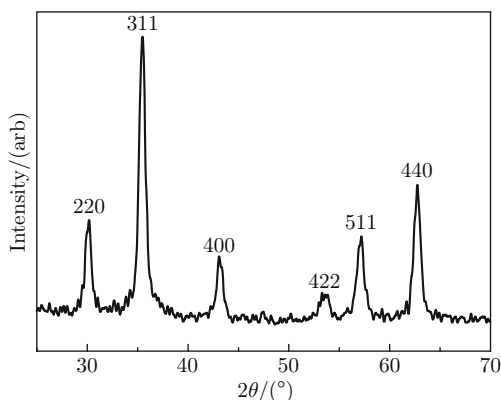


Fig. 3 X-ray diffractogram of Fe_3O_4 nanoparticles.

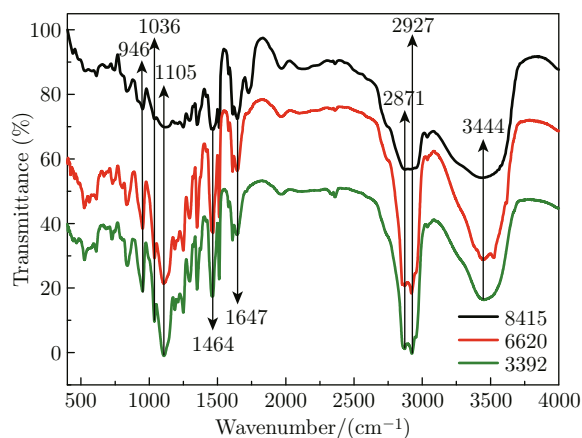


Fig. 4 FTIR spectrum of Fe_3O_4 solvent-free nanofluids.

Thermal analysis

TGA thermogram of the three kinds of Fe_3O_4 solvent-free nanofluids (Fig. 5) shows that there is little or no material loss when temperature is lower than 339.9°C which indicates that no solvent is present in Fe_3O_4 solvent-free nanofluids. The most weight loss takes place from 339.9°C to 425°C . The percentages of nanoparticles are as high as 8.28 wt% (3392 nanofluids), 9.80 wt% (6620 nanofluids) and 10.42 wt% (8415 nanofluids), respectively. The weight loss is probably due to the removal of the organic corona and canopy surfactant from the surface of Fe_3O_4 nanoparticles.

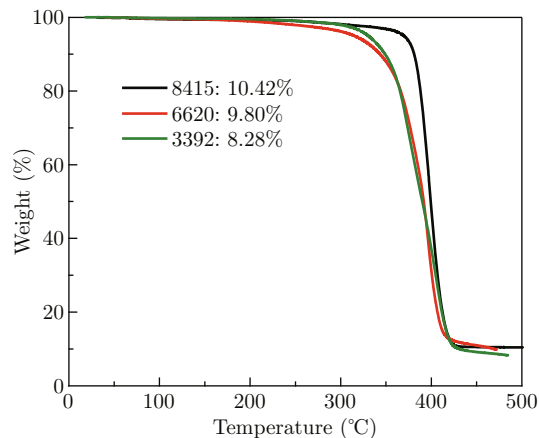


Fig. 5 The TGA curves of Fe_3O_4 solvent-free nanofluids.

DSC thermogram of the three kinds of nanofluids (Fig. 6) reveals that their melt temperatures (T_m) and crystallization temperatures (T_c) depend on the modifier's structure and the inset shows the magnified part of peaks of 6620 and 3392 from 20°C to 23°C . The T_c and T_m of PEGs salt are -12.44°C and 18.35°C , respectively. The crystallization temperatures of nanofluids 6620 and 3392 are lower than those of PEGs salt because ionic bonds restrict the movement of chain segments. Compared with modifier 6620, modifier 3392 has two chains of 10 carbon atoms, which is easy to be tangled and is difficult to arrange the chains in order. Modifier 6620 has only one chain of 18 carbon atoms. Hence, it is necessary for modifier 3392 to arrange chains in order at lower temperature. The T_c of modifier 3392 is lower than that of 6620.

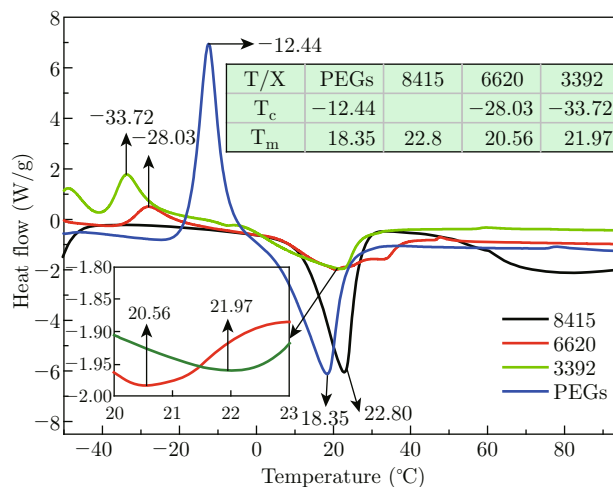


Fig. 6 The DSC curves of the Fe_3O_4 solvent-free nanofluids and PEGs. The inset shows the magnified part of peaks of 6620 and 3392 from 20°C to 23°C .

The peaks at 22.80°C , 20.56°C and 21.97°C are T_m of the nanofluids 8415, 6620 and 3392, respectively. T_m of the pure PEGs is 18.35°C . For the nanoparticles, modifier forms the corona, and PEGs form canopy. The

shell is composed of corona and canopy, whose molecular weight is higher than that of the pure PEGs. High molecular weight results in a high T_m for nanofluids.

Nanofluids physical characteristics

Figure 7 includes the TEM images and digital photographs of Fe_3O_4 solvent-free nanofluids at room temperature. It is clear that the three kinds of nanofluids are tan, transparent, and maintain good mobility at room temperature. The black spots in the TEM images are the mono-dispersed Fe_3O_4 particles, which are also regular spherical. The mean size is about 2~3 nm. It indicates that the dispersion of Fe_3O_4 nanoparticles is significantly improved after modified by organ canopy and corona surfactant.

Rheological analysis

Temperature tests were carried out with a constant strain value of 5% at angular frequency 628.3 rad/s. Figure 8(a) shows that values of loss modulus G'' are always greater than storage modulus G' over a temperature range of 21~80°C for the three kinds of nanoflu-

ids. When the loss modulus is greater than the storage modulus, the material has typical liquid-like behavior. Values of G'' decrease rapidly at 21~40°C, indicating that viscosity of systems change sharply. Then G'' decrease slowly from 40~80°C. With the chain length of modifier increasing, G'' decreased. Modifiers 6620 and 3392 have long chains, which have internal plasticization, therefore, they have lower G'' .

In the meantime, frequency sweep tests were carried out with angular frequency ranging from 628.3 to 0.06283 rad/s with a constant strain value of 5% at 25°C. The experimental data of storage modulus and loss modulus are shown in Fig. 8(b). The loss modulus is greater than the storage modulus, $G'' > G'$, and G' values are practically constant, indicating that a typical liquid-like behavior and the dominant viscous nature of the material exist under these conditions. When the modifier has long chain, the nanofluids have lower value of G'' . Modifier 8415 has short chain, and the nanofluids have the highest value of G'' among three modifiers. For the solvent-free nanofluids, long chain of modifier has the internal plasticization, which can decrease the loss modulus of system.

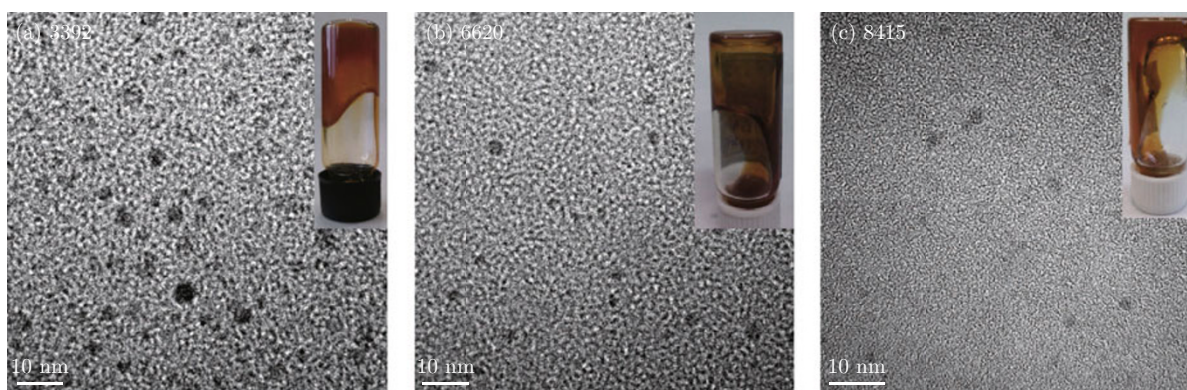


Fig. 7 The TEM images of Fe_3O_4 solvent-free nanofluids.

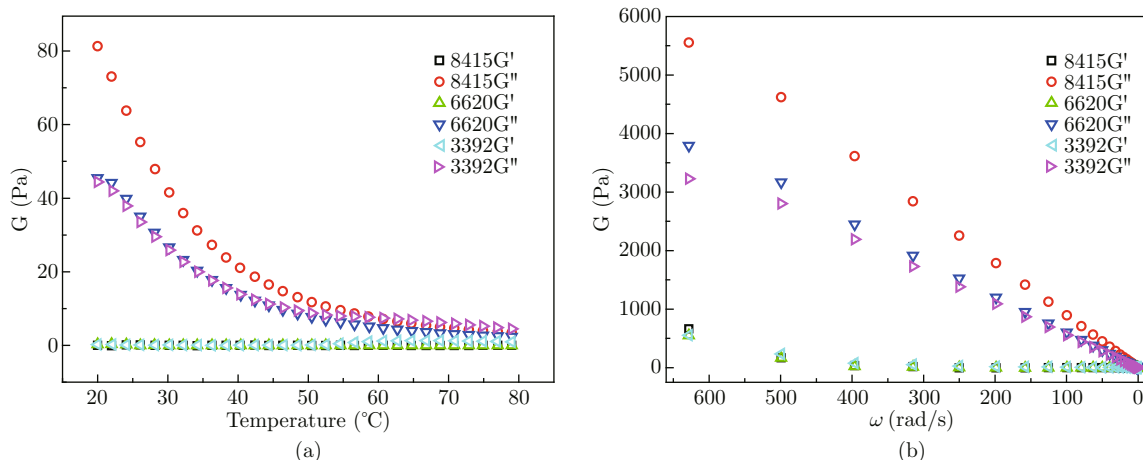


Fig. 8 (a) G'' and G' as a function of temperature for different nanofluids at 100 Hz. (b) G'' and G' as a function of angular frequency at 25°C.

Figure 9 shows the flow curves of the three kinds of Fe_3O_4 solvent-free nanofluids at room temperature. Shear stresses increase with shear rate increasing in all three systems, and they represent approximate linear relation. The slopes of three lines are differential viscosity of the three nanofluids which are related to molecular weights of three kinds of surface modifiers (Table 1). Summation of M_1 and M_2 of 8415 is the lowest and its differential viscosity is the highest. Summation of M_1 and M_2 of 6620 and 3392 equal to 268 and 282, respectively, therefore their differential viscosities are close to each other and much lower than 8415's differential viscosity at room temperature. It can be affirmed that these Fe_3O_4 solvent-free nanofluids are Newtonian liquid at lower shear rate.

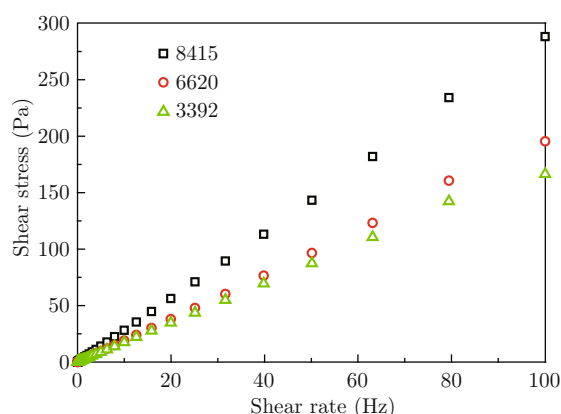


Fig. 9 Rheology of Fe_3O_4 solvent-free nanofluids.

The differential viscosities of the three nanofluids were measured over a temperature range of 21~80°C with an interval of 1°C (Fig. 10), and they decreased with temperature increasing. The inset shows double logarithmic plot of temperature versus differential viscosities of 6620 and 3392. The differential viscosity of 3392 nanofluids is lower than that of 6620 nanofluids at 21~45°C. After the two curves intersect at 45°C, the differential viscosity of 3392 nanofluids is gradually larger than that of 6620 nanofluids which is showed in the inset. This should be attributed to that the two long symmetric chains of 3392 have a stereochemical structure, which make the molecules farther apart from each other at low temperature and have better fluidity. It is easier for long chain to obtain good fluidity at higher temperature. In this case, the nanofluids 3392 and 6620 have lower viscosity than nanofluids 8415. There is no long chain in nanofluids 8415, whose viscosity is the highest at any temperature. The following major findings are: firstly, the longer chain has the better flowability; secondly, the stereochemical structure provides larger intermolecular distance and better flowability at lower temperature; lastly, it is the longer chain which contributes more to flowability at higher temperature.

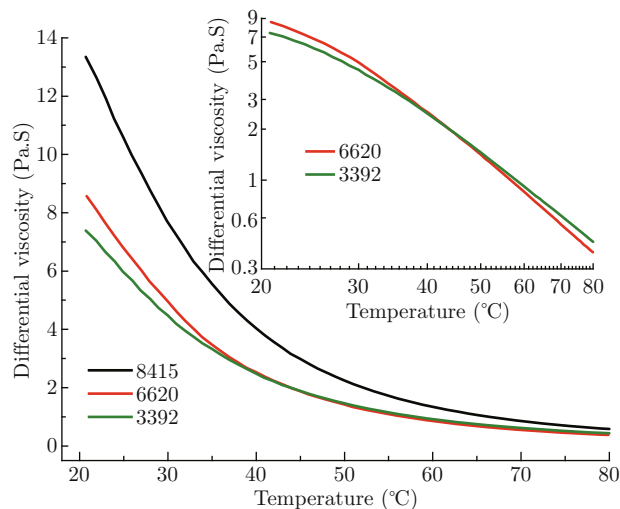


Fig. 10 High shear viscosity as a function of temperature for different nanofluids at 100 Hz. The inset shows double logarithmic plot of temperature versus differential viscosities of 6620 and 3392.

Conclusion

In summary, three kinds of Fe_3O_4 solvent-free nanofluids were prepared successfully by using the modifier 3392, 6620 and 8415, respectively. The percentages of nanoparticles are as high as 8.28%, 9.80% and 10.42%. The Fe_3O_4 particle with regular spherical shape has a size about 2~3 nm in diameter and monodisperses, and its dispersion and flowability are improved by the canopy surfactants. The synthesized nanofluids are tan transparent liquids and can flow well at room temperature in absence of solvent. The values of G'' are always greater than the values of G' , which are measured both with temperature and frequency. It indicates that solvent-free nanofluids have liquid-like behavior. Long alkyl chains of modifiers provide nanofluids lower viscosity and better flowability.

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References

- [1] A. B. Bourlinos, E. P. Giannelis, Q. Zhang, L. A. Archer, G. Floudas and G. Fytas, *Eur. Phys. J. E.* 20, 109 (2006). <http://dx.doi.org/10.1140/epje/i2006-10007-3>
- [2] Q. Li, X. Y. Wu, L. J. Dong, J. Huang, X. M. Shang, H. A. Xie and C. X. Xiong, *Wuhan. Univ. Technol.* 33,

- 22 (2011).
- [3] R. Rodriguez, R. Herrera, A. B. Bourlinos, R. Lic, A. Amassian, L. A. Archer and E. P. Giannelis, *Appl. Organometal Chem.* 24, 581 (2010). <http://dx.doi.org/10.1002/aoc.1625>
- [4] A. B. Bourlinos, S. R. Chowdhury, D. D. Jiang and Q. Zhang, *J. Mater. Sci.* 40, 5095, (2005). <http://dx.doi.org/10.1007/s10853-005-1301-8>
- [5] A. B. Bourlinos, R. Herrera, N. Chalkias, D. D. Jiang, Q. Zhang, L. A. Archer and E. P. Giannelis, *Adv. Funct. Mater.* 15, 1285 (2005). <http://dx.doi.org/10.1002/adfm.200500076>
- [6] A. B. Bourlinos, R. Herrera, N. Chalkias, D. D. Jiang, Q. Zhang, L. A. Archer and E. P. Giannelis, *Adv. Mater.* 17, 234 (2004). <http://dx.doi.org/10.1002/adma.200401060>
- [7] R. Rodriguez, R. Herrera, L. A. Archer and E. P. Giannelis, *Adv. Mater.* 20, 4353 (2008). <http://dx.doi.org/10.1002/adma.200801975>
- [8] T. Michinobu, T. Nakanishi, J. P. Hill, M. Funahashi and K. Ariga, *J. Am. Chem. Soc.* 128, 10384 (2006). <http://dx.doi.org/10.1021/ja063866z>
- [9] N. Fernandes, P. Dallas, R. Rodriguez, A. B. Bourlinos, V. Georgakilas and E. P. Giannelis, *Nanoscale* 2, 1653 (2010). <http://dx.doi.org/10.1039/c0nr00307g>
- [10] A. W. Perriman, H. Cölfen, R. W. Hughes, C. L. Barrie and S. Mann, *Angew. Chem. Int. Ed.* 48, 6242, (2009). <http://dx.doi.org/10.1002/anie.200903100>
- [11] Y. P. Zheng, J. X. Zhang, L. Lan and P. Y. Yu, *Appl. Surf. Sci.* 257, 6171 (2011). <http://dx.doi.org/10.1016/j.apsusc.2011.02.024>
- [12] Q. Li, L. J. Dong, W. Deng, Q. M. Zhu, Y. Liu and C. X. Xiong, *J. Am. Chem. Soc.* 131, 9148 (2009). <http://dx.doi.org/10.1021/ja902197v>
- [13] S. C. Warren, M. J. Banholzer, L. S. Slaughter, E. P. Giannelis, F. J. DiSalvo and U. B. Wiesner, *J. Am. Chem. Soc.* 128, 12074 (2006). <http://dx.doi.org/10.1021/ja064469r>
- [14] D. P. Liu, G. D. Li, Y. Su and J. S. Chen, *Angew. Chem. Int. Ed.* 45, 7370 (2006). <http://dx.doi.org/10.1002/anie.200602429>
- [15] A. B. Bourlions, S. K. Chowdhury, D. D. Jiang, Y. U. An, Q. Zhang, L. A. Archer and E. P. Giannelis, *Small* 11, 80 (2005). <http://dx.doi.org/10.1002/smll.200400027>
- [16] S. Raja, G. Devi and M. Karthikeyan, *Nano-Micro Lett.* 2, 306 (2010). <http://dx.doi.org/10.3786/nml.v2i4.p306-310>
- [17] V. Vasu and K. Manoj Kumar, *Nano-Micro Lett.* 3 (4), 209 (2011). <http://dx.doi.org/10.3786/nml.v3i4.p209-214>
- [18] P. Y. Yu, Y. P. Zheng and L. Lan, *Soft Nanoscience Lett.* 1, 46 (2011). <http://dx.doi.org/10.4236/sn1.2011.12008>
- [19] L. Lan, Y. P. Zheng, J. X. Zhang, P. Y. Yu, W. Shi, X. D. Yang and J. H. Li, *J. Funct. Mater. Devic.* 17, 279 (2011).
- [20] Y. M. Tan, Y. P. Zheng, A. B. Zhang and L. Lan, W. Chen, *Chinese J. Mater. Research* 25, 561 (2011).
- [21] Y. M. Tan, Y. P. Zheng and L. Lan, *Chem. J. Chinese Universities* 33, 206 (2012).
- [22] Y. P. Zheng, J. X. Zhang, L. Lan, P. Y. Yu, R. Rodriguez, R. Herrera, D. Y. Wang and E. P. Giannelis, *Chem. Phys. Chem.* 11, 61 (2009).
- [23] J. X. Zhang, Y. P. Zheng, P. Y. Yu, S. Mo and R. M. Wang, *Carbon* 47, 2776 (2009). <http://dx.doi.org/10.1016/j.carbon.2009.05.036>
- [24] J. X. Zhang, Y. P. Zheng, L. Lan, S. Mo, P. Y. Yu, W. Shi and R. M. Wang, *ACS Nano* 3, 2185 (2009). <http://dx.doi.org/10.1021/nn900557y>
- [25] L. Lan, Y. P. Zheng, A. B. Zhang, J. X. Zhang and N. Wang, *J. Nanopart. Res.* 14, 753 (2012). <http://dx.doi.org/10.1007/s11051-012-0753-4>
- [26] J. X. Zhang, Y. P. Zheng, P. Y. Yu, S. Mo and R. M. Wang, *Polymer* 50, 2953 (2009). <http://dx.doi.org/10.1016/j.polymer.2009.04.042>
- [27] P. Agarwal, H. B. Qi and L. A. Archer, *Nano Lett.* 10, 111 (2010). <http://dx.doi.org/10.1021/nl9029847>
- [28] M. L. Jespersen, P. A. Mirau, E. von Meerwall, R. A. Vaia, R. Rodriguez, N. J. Fernandes and E. P. Giannelis, *ACS Symposium Series* 1077, 149 (2011).
- [29] M. L. Jespersen, P. A. Mirau, E. von Meerwall, R. A. Vaia, R. Rodriguez and E. P. Giannelis, *ACS Nano* 4, 3735 (2010). <http://dx.doi.org/10.1021/nn100112h>
- [30] Y. Guo, Y. Li, X. L. Liu and H. Cai, *Inorg. Chem. Industry* 29, 21 (2007).
- [31] D. W. Hu and Y. M. Wang, *J. Chin. Ceram. Soc.* 36, 1488 (2008).
- [32] J. G. Zheng, Q. S. Chen and T. Yang, *Inorg. Chem. Industry* 40, 15 (2008).