



Magnetorheological behavior of Pickering emulsions stabilized by surface-modified Fe₃O₄ nanoparticles

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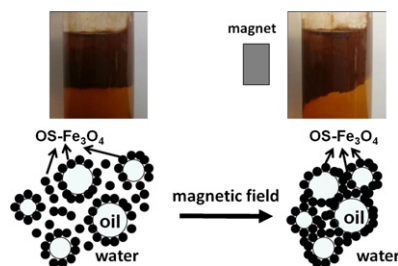
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HIGHLIGHTS

- ▶ Emulsions stabilized by modified Fe₃O₄ nanoparticles were prepared with various oils.
- ▶ Their rheological behavior was investigated with and without a magnetic field.
- ▶ All emulsions show dynamic elastic response and steady shear-thinning behavior.
- ▶ The presence of a magnetic field promotes particle attractions and associations.
- ▶ Modulus and viscosity increase with oil content and polarity and magnetic field intensity.

GRAPHICAL ABSTRACT

Silane-modified Fe₃O₄ nanoparticles can stabilize emulsions of both polar and non-polar oils, and the rheological behavior of these emulsions has been investigated as a function of oil volume fraction (ϕ_o), oil polarity and magnetic field intensity (ψ). All the emulsions show a similar elastic response with a modulus plateau at low frequency and a small phase angle ($<15^\circ$) in dynamic oscillatory shear, and shear-thinning behavior in steady shear measurements. This is independent of ϕ_o , oil polarity and ψ . The dynamic modulus (G') and complex viscosity (η^*) increase with an increase in ϕ_o and oil polarity, due to enhanced droplet packing and flocculation and particle aggregation on droplet surfaces. The presence of a magnetic field promotes particle attractions and associations and enhances the strength of the three-dimensional particle and droplet networks, thus remarkably increasing G' and η^* and raising the yield stress. The increase in modulus, viscosity and yield stress are beneficial for the elevation of the stability of these functional emulsions.



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1. Introduction

In recent years, super-paramagnetic Fe₃O₄ nanoparticles have attracted great attention in the biomedical field in relation to magnetic resonance imaging [1–3], hyperthermia therapy of cancers [4,5] and targeted drug delivery [6,7], due to their high magnetic saturation, negligible toxicity and easy surface modification. On application of a magnetic field, these particles carrying drugs or genes can be targeted to a specific site and/or held in the tumor. This kind of operation can reduce the harm to healthy organs, because the circulation of the drug throughout the body is limited and non-specific uptake by the reticular-endothelial system can be avoided. Taking advantage of Pickering emulsions [8], many kinds of functional materials based on Fe₃O₄ nanoparticles, such as magnetic hollow silica microspheres [9], Fe₃O₄/polystyrene/silica nanospheres [10], Fe₃O₄/polymer magnetic nanocomposites [11–13] and Fe₃O₄/poly(*N*-isopropylacrylamide-co-methacrylic acid) thermoresponsive composite latex [14] have been successfully prepared. The prediction, evaluation and improvement of the stability of magnetic Pickering emulsions play an important role in developing and expanding applications of the novel magnetic materials.

In an emulsion, one liquid is dispersed in another liquid in the form of droplets, and stabilization can be achieved by adding emulsifiers, such as amphiphilic surfactants and proteins or colloidal solid particles. Emulsifiers adsorb to the oil–water interface and form a protective film to resist droplet deformation and prevent droplet coalescence and macroscopic phase separation. However, unlike conventional surfactants, the free energy of adsorption for particles at an interface can be extremely large, so that the kinetic energy needed to detach the particles from the interface is not available from the thermal energy of the system [15]. For Pickering emulsions, the three phase contact angle at the oil–water interface (θ_{ow}) is a key parameter determining the type and stability of the resultant emulsions [16,17]. Hydrophilic particles with $\theta_{ow} < 90^\circ$ stabilize oil-in-water (o/w) emulsions, whilst hydrophobic particles with $\theta_{ow} > 90^\circ$ stabilize water-in-oil (w/o) emulsions [18]. A number of ways exist to change and optimize the wettability (θ_{ow}) of particles, such as *in situ* modification by using surfactants or adjusting pH or electrolyte concentration [19–23], and surface modification by chemical reactions prior to mixing them with oil and water [16,24–26].

Some groups have demonstrated that Pickering emulsions can be produced by both bare and modified Fe₃O₄ nanoparticles, such as trialkoxysilane-water emulsions stabilized by silane-modified Fe₃O₄ nanoparticles [27], dodecane-water and paraffin-water emulsions by oleic acid bilayer-coated Fe₃O₄ nanoparticles [28,29] and crude oil–water and hexane–water emulsions by Fe₃O₄ nanoparticles [30,31]. In our previous work [32,33], we systematically investigated unmodified and surface modified Fe₃O₄ nanoparticles as stabilizers of Pickering emulsions and the effects of particle concentration, oil volume fraction, oil polarity and surface modification on the type, stability, composition and morphology of these functional emulsions. All these emulsions are of the o/w type. The relatively hydrophilic unmodified Fe₃O₄ nanoparticles can stabilize emulsions of a non-polar oil like dodecane and a weakly polar oil such as PDMS, but cannot stabilize emulsions of highly polar oils such as butyl butyrate and decanol. However, due to an increase in particle hydrophobicity, the silane-modified Fe₃O₄ nanoparticles stabilize emulsions of both non-polar and highly polar oils. Similar to the case of unmodified Fe₃O₄ nanoparticles, the average droplet size and the volume fraction of stable emulsion in the presence of modified Fe₃O₄ nanoparticles increase with an increase in ϕ_o . Not all the particles are adsorbed to drop interfaces in the stable emulsions.

The occurrence of droplet coalescence is related to the thinning and rupture of the film formed by the continuous phase between the droplets when they approach each other, and the elastic, gel-like properties resulting from the interconnected particle network adsorbed at the oil–water interface can enhance the trapping of droplets in such emulsions, thus inhibiting film drainage and droplet coalescence [15,34]. It was demonstrated that using rheological characterization, the obtained viscoelastic response can provide much valuable information about the long term physical stability of the emulsions. In this study, Pickering emulsions stabilized by octyltriethoxysilane-modified Fe₃O₄ nanoparticles (OS-Fe₃O₄) were prepared with both polar and non-polar oils, and the rheological behavior was investigated both in the absence and presence of a magnetic field. The influences of oil volume fraction, oil polarity and magnetic field intensity were investigated in detail for both dynamic oscillatory shear and steady shear deformation.

2. Experimental

2.1. Materials

The water used was purified by an Aquapro ultra-pure water system (China), and its conductivity is 0.25 μ S/cm measured using an FE30/EL30 conductivity meter (Mettler-Toledo Instruments). FeSO₄·7H₂O (AR, 99%), FeCl₃·6H₂O (AR, 99%) and NaOH (AR, 95%) were purchased from Sinopharm Chemical Reagent Co. (China) and used as received. 36–38% HCl (AR) was obtained from Shanghai Lingfeng Chemical Reagent Co. (China) and was used as received. In preparing magnetic Pickering emulsions, two oils of different polarity were chosen and used without further purification. These were dodecane (AR, 99%) and butyl butyrate (AR, 99%) purchased from Aladdin Reagent Co. (China). Octyltriethoxysilane (AR, 98%) for particle surface modification was purchased from Sigma–Aldrich. Toluene (AR, 99%) and ethanol (AR, 99.7%) were purchased from Sinopharm (China).

2.2. Synthesis of octyltriethoxysilane-modified Fe₃O₄ magnetic nanoparticles

Fe₃O₄ magnetic nanoparticles were prepared by coprecipitation of aqueous ferrous and ferric ions. Before synthesis, aqueous phases of 0.5 M FeSO₄ with 0.2 M HCl, 1 M FeCl₃ solution with 0.2 M HCl and 1.5 M NaOH solution were prepared. During preparation, 100 mL NaOH solution was poured into a flask and heated to 80 °C, and then the mixture of 10 mL FeSO₄ solution and 10 mL FeCl₃ solution was added into the flask dropwise in a N₂ atmosphere and using an oil bath at 80 °C. After the above mixture turned black, it was allowed to cool with continuous stirring, and the particles obtained were washed three times with water and once with absolute ethanol.

Fe₃O₄ nanoparticles as prepared above were dispersed in 50 mL absolute ethanol by a KQ100 ultrasonic cleaning machine (Kunshan Ultrasonic Instrument Co., China) using a power of 100 W for 5 min and then poured into a flask. 100 mL toluene and an amount of octyltriethoxysilane (silane/Fe₃O₄ ratio is 0.01 mol/g) were added and the flask heated to 110 °C in a N₂ atmosphere. After holding the above mixture at 110 °C for 8 h, the black fluid was immediately poured into a beaker, and the modified particles were separated using a magnet. The solid black material was washed using absolute ethanol and water and then dried in a LGJ-10 common type freeze dryer (Beijing Huaxing Technology Development Co., China). As observed from the SEM images [32,33], the octyltriethoxysilane-modified Fe₃O₄ nanoparticles (OS-Fe₃O₄) have similar primary particle diameter in the range 15–35 nm to that of Fe₃O₄ particles,

and the aggregation extent of Fe₃O₄ particles is decreased after surface coating.

2.3. Preparation and characterization of magnetic Pickering emulsions

The hydrophobic OS-Fe₃O₄ nanoparticles were first dispersed at a concentration of 1 wt.% initially in oil (dodecane or butyl butyrate) by mixing for 1 h at a power of 100 W in a KQ100 ultrasonic cleaning machine. After the addition of deionized water, emulsions with different oil volume fractions (ϕ_o) of 0.3, 0.5 and 0.7 were prepared using an FM200 high shear dispersing emulsifier (Fluko Equipment Shanghai, China) at a speed of 14,000 rpm for 3 min.

After preparation, emulsions were immediately poured into cylindrical sample bottles and their stability was investigated by recording the change in height with time of the emulsion-aqueous phase interface and then evaluating the volume fraction changes of the stable emulsion and resolved water. An XPS-8C optical microscope (Yongheng Optical Instruments, China) was used to observe the emulsion droplet morphology, after appropriate dilution.

2.4. Magnetorheological measurements of magnetic Pickering emulsions

The magnetorheological behavior of Pickering emulsions stabilized by OS-Fe₃O₄ nanoparticles was examined at 25 °C with a Physica MCR 301 Rheometer (Anton Parr, Germany) possessing a magnetorheological device. The parallel plate geometry (of non-magnetic titanium) of 20 mm diameter was used with a gap of 0.5 mm. During the measurements, the electromagnetic coil was activated with a current from 0 A to 2.0 A, corresponding to magnetic flux densities (ψ) from 0 T to 0.22 T inside the gap. The direction of the external magnetic field is perpendicular to surface of the tested emulsions. To ensure the linear viscoelastic region, a dynamic strain sweep was conducted in the range $\gamma_0 = 0.00001-1$ (0.001–100%), where γ_0 is the setting strain, at a frequency $\omega = 1 \text{ rad s}^{-1}$. Dynamic frequency sweeps were performed from 100 to 0.1 rad s^{-1} with a strain of 0.06% in the linear régime, and the storage modulus G' , loss modulus G'' and complex viscosity η^* were recorded as a function of frequency. Steady shear measurements were carried out as a function of shear rate from 0.001 to 100 s^{-1} , and rheological parameters of shear stress τ and apparent viscosity η were obtained for each shear rate. All the emulsion samples are taken after creaming is complete, so the emulsion should be stable and homogeneous within the rheometer.

3. Results and discussion

3.1. Stability and morphology of emulsions stabilized by OS-Fe₃O₄ nanoparticles

The OS-Fe₃O₄ nanoparticles can stabilize emulsions of both dodecane and butyl butyrate. Microscope images of these emulsions taken 20 days after preparation and the change in the volume fraction of residual emulsion (*i.e.* volume of stable emulsion/total volume of oil and water) with time are given in Fig. 1, with relevant parameters listed in Table 1. All the emulsions reach a stable state before approx. 500 min following creaming but without coalescence, except for the butyl butyrate-in-water emulsion at $\phi_o = 0.7$ which shows a continual gradual decrease in the residual emulsion fraction. This particular emulsion was not evaluated further. The stable emulsion fraction increases with an increase in oil volume fraction and decrease in oil polarity, attaining a maximum of 83.9 vol.% for the dodecane-in-water emulsion of $\phi_o = 0.7$. The images reveal that the droplets of the OS-Fe₃O₄ nanoparticle-stabilized emulsions are spherical with their mean

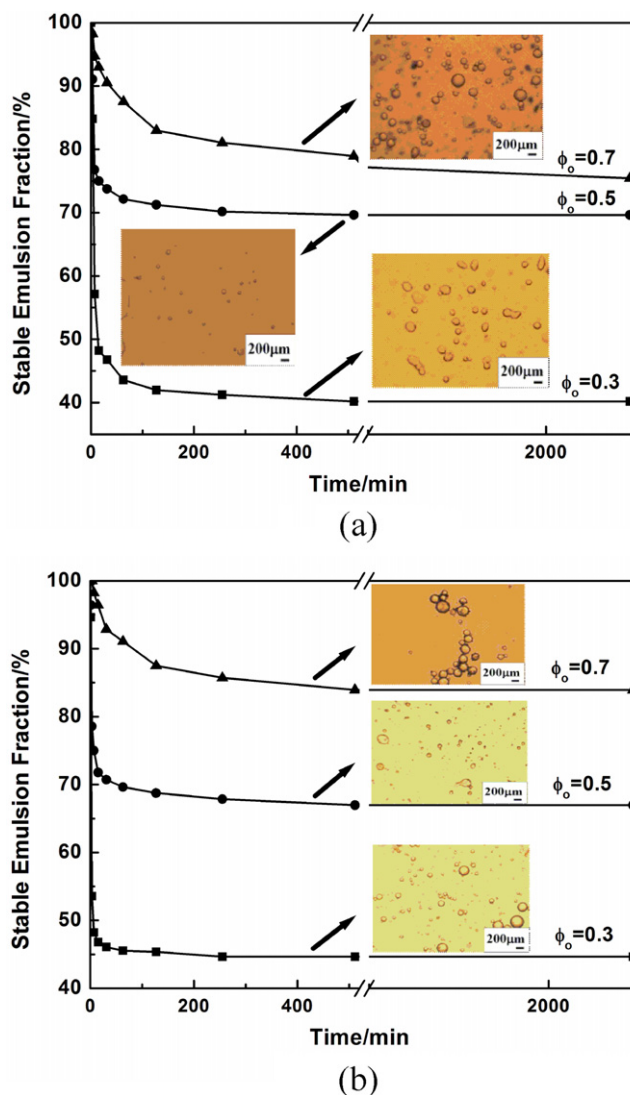


Fig. 1. Change in the volume fraction of residual emulsion versus time for o/w emulsions stabilized by OS-Fe₃O₄ nanoparticles at different ϕ_o for two oils: (a) butyl butyrate, and (b) dodecane. Microscope images of these emulsions were taken 20 days after preparation.

diameter varying from 40 to 150 μm , and the average droplet size increases with an increase in the oil volume fraction but hardly changes with the oil polarity.

3.2. Magnetorheological behavior of emulsions stabilized by OS-Fe₃O₄ nanoparticles

3.2.1. Dynamic oscillatory shear response

Dynamic oscillatory measurements yield the elastic and viscous responses of a viscoelastic system with the parameters of storage

Table 1
Parameters of o/w emulsions stabilized by 1 wt.% OS-Fe₃O₄ nanoparticles for different ϕ_o and oils, including the time for the emulsion to stabilize (t_E) and the stable emulsion fraction (V_e).

Oil	ϕ_o	t_E (min)	V_e (vol.%)
Butyl butyrate	0.3	511	40.2
Butyl butyrate	0.5	511	69.6
Dodecane	0.3	255	44.6
Dodecane	0.5	511	67.0
Dodecane	0.7	511	83.9

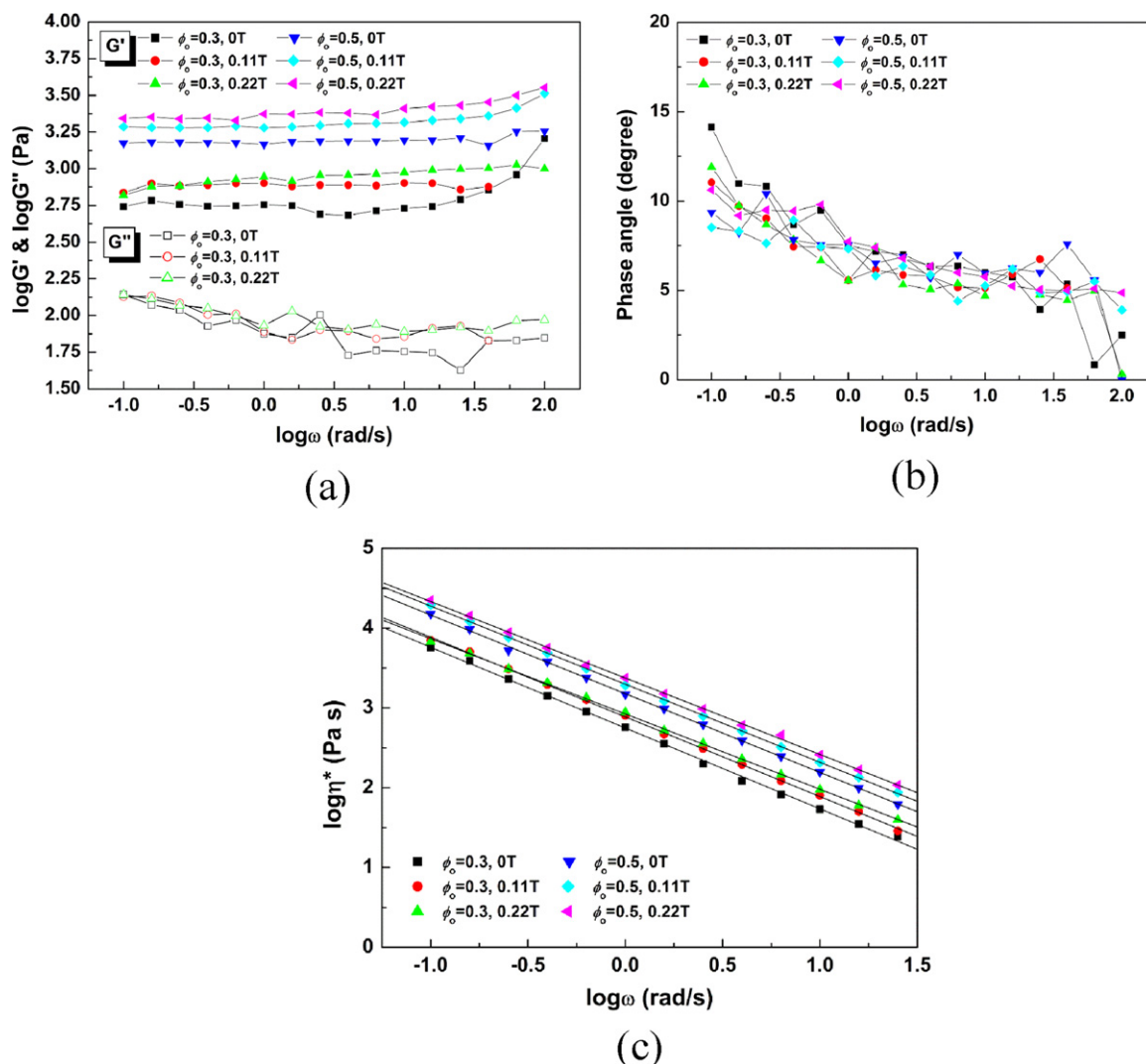


Fig. 2. Linear viscoelastic behavior of butyl butyrate-in-water emulsions stabilized by OS- Fe_3O_4 nanoparticles for different ϕ_o and magnetic field intensities at fixed oscillatory strain amplitude of $\gamma_0 = 0.06\%$ at room temperature: (a) double-logarithmic plots of storage and loss modulus versus frequency, (b) plots of phase angle versus frequency, and (c) double-logarithmic plots of complex viscosity versus frequency.

modulus (G'), loss modulus (G''), loss factor $\tan \delta (=G''/G')$ and complex viscosity (η^*). G' and G'' are generally utilized to determine if the emulsion is strongly or weakly flocculated, and if the former the emulsion presents solid-like behavior with frequency independent G' and $G' > G''$ [35]. δ is the phase angle, and in terms of a viscoelastic system, the stress and the strain are out of phase with each other. A phase angle of 0° means an elastic material, and a phase angle of 90° means a viscous liquid.

Dynamic strain sweep experiments were first conducted to determine the linear viscoelastic region of the emulsions stabilized by OS- Fe_3O_4 nanoparticles. The strain dependence of the storage modulus of these emulsions under different magnetic field intensities (data not shown here) indicates a régime of linear viscoelasticity below a strain of 0.1%, following which the elastic modulus exhibits a rapid decrease with the occurrence of the breakage in the droplet networks, *i.e.* the particle flocs surrounding the oil droplets [34,36]. The oil volume fraction and magnetic field intensity have no obvious influence on the linear régime of these magnetic Pickering emulsions, but the increase in oil polarity to butyl butyrate narrows the storage modulus plateau remarkably in the linear region and accelerates the decrease in the non-linear region, especially at high oil volume fraction and high magnetic field intensity. It seems that the droplet networks are tougher in

dodecane emulsions (non-polar oil) with higher deformation for yielding. The strain amplitude of 0.06% in the linear régime was selected for all the following frequency sweep tests.

The linear viscoelastic behavior of emulsions stabilized by OS- Fe_3O_4 nanoparticles under different magnetic field intensities is shown in Fig. 2 for butyl butyrate-in-water emulsions and in Fig. 3 for dodecane-in-water emulsions for different ϕ_o values. It is apparent that all the emulsions exhibit similar changes of G' , δ and η^* with frequency (ω) at different values of ψ . When ω varies from 0.1 to 100 rad s^{-1} , G' is always one order of magnitude greater than G'' (G'' data of butyl butyrate-in-water emulsions with $\phi_o = 0.3$ are shown as an example in Fig. 2a), and shows an elastic plateau at low ω either in the absence or presence of a magnetic field. This indicates the existence of an elastic network structure formed by the dispersed oil droplets in the emulsions. Thus it can be seen that the OS- Fe_3O_4 nanoparticle-stabilized emulsions exhibit a predominantly elastic response in the entire measured frequency range, and this soft gel-like structure endows the emulsions with high physical stability. The droplet associations responsible for the formation of a three-dimensional elastic network can be observed in the microscope images in Fig. 1, especially for the emulsions with higher ϕ_o , although the emulsion droplets have been diluted. In emulsions of both oils at high ϕ_o ($\phi_o = 0.7$), droplet aggregation can be seen as

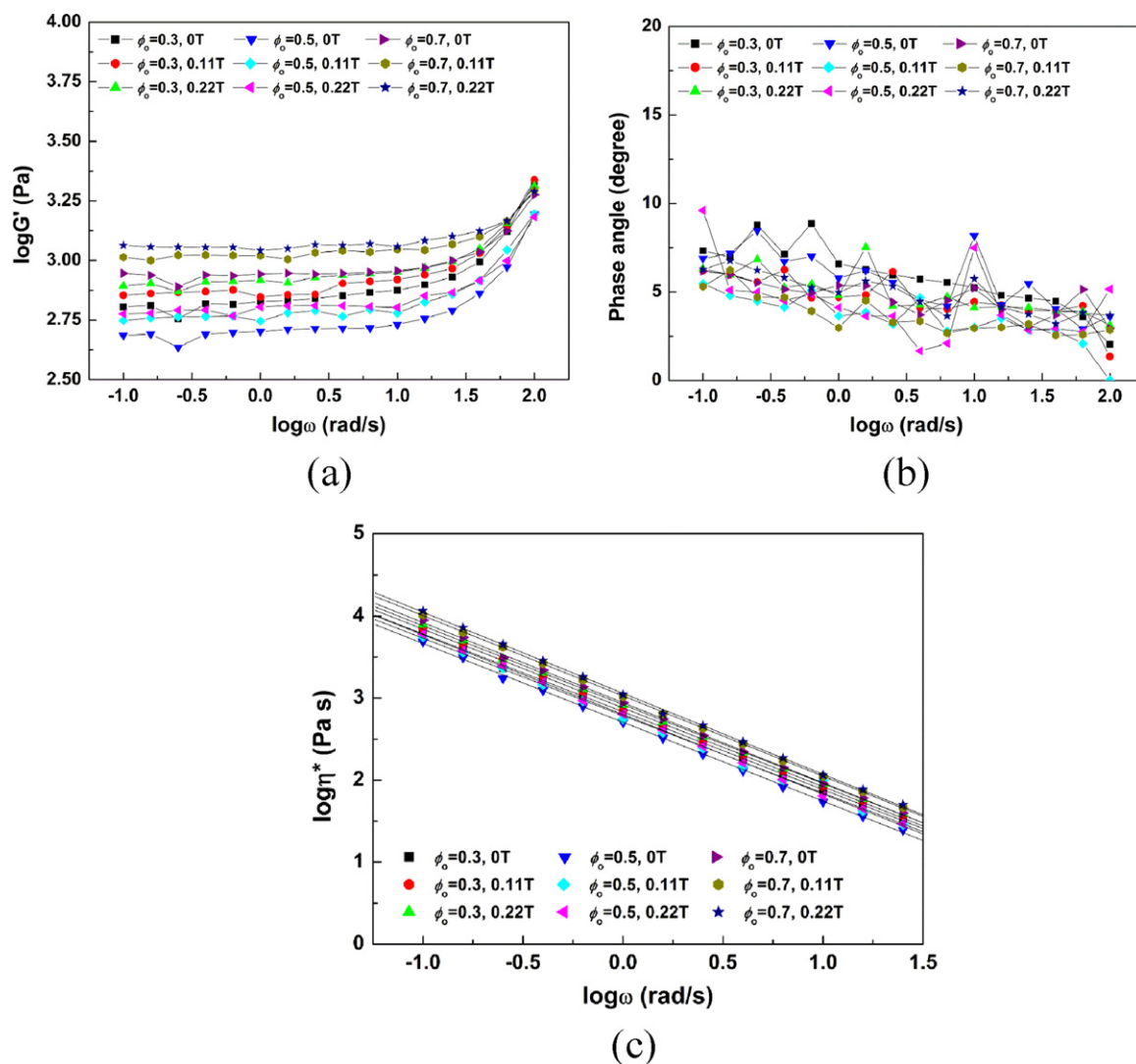


Fig. 3. Linear viscoelastic behavior of dodecane-in-water emulsions stabilized by OS-Fe₃O₄ nanoparticles for different ϕ_0 and magnetic field intensities at fixed oscillatory strain amplitude of $\gamma_0 = 0.06\%$ at room temperature: (a) double-logarithmic plots of storage modulus versus frequency, (b) plots of phase angle versus frequency, (c) double-logarithmic plots of complex viscosity versus frequency.

small clusters in the optical microscope images. High ϕ_0 enhances the droplet packing and flocculation [34], and the resultant increase in the strength of the interconnected droplet networks also leads to an increase in the elastic modulus and complex viscosity. The latter increase is more remarkable for the butyl butyrate emulsions, increasing by a factor of two when ϕ_0 increases from 0.3 to 0.5. In general, the phase angle is 0° for an elastic system and 90° for the purely viscous liquids. As for OS-Fe₃O₄-stabilized emulsions, the phase angle is lower than 15° for butyl butyrate (Fig. 2b) and lower than 10° for dodecane (Fig. 3b) over the whole frequency range, exhibiting an elastic response to the external shear stress and indicating the existence of well developed gel-like colloidal networks by the dispersed oil droplets, as revealed by the modulus data. Moreover, the viscosity of all the particle-stabilized emulsions decreases linearly with frequency following the power law $\eta^* \propto \omega^{0.9-1}$ (Figs. 2c and 3c), exhibiting a typical shear-thinning behavior of a non-Newtonian fluid.

Dodecane-in-water emulsions show similar modulus and viscosity to those of butyl butyrate-in-water emulsions when $\phi_0 = 0.3$, but lower modulus and viscosity than those of butyl butyrate-in-water emulsions when $\phi_0 = 0.5$, which suggests that the droplet

associations are stronger and more elastic in butyl butyrate emulsions of high ϕ_0 . In fact, in our previous work [33], we verified that the enhancement of the hydrophobicity of Fe₃O₄ nanoparticles leads to a decrease in the stability of dodecane-in-water emulsions but an increase in the stability of butyl butyrate-in-water emulsions. It should be noted that the emulsion stabilizer is colloidal OS-Fe₃O₄ nanoparticles; their state of dispersion greatly influences the strength of associated droplet networks. More particle aggregates adsorbed on the droplet surface will result in stronger elastic networks and higher modulus and viscosity of the emulsions. It seems that more OS-Fe₃O₄ nanoparticles are located at the polar oil-water interface forming stronger three-dimensional elastic networks due to the decreased affinity of the nanoparticles for both water and oil after surface modification. It is the viscoelastic particle network surrounding the droplets that helps to prevent droplet migration and coalescence, and strongly flocculated particles are beneficial for the long term stability of the emulsions [24]. The existence of viscoelastic networks has also been demonstrated for other Pickering emulsions, such as creosote-in-water and hexane-in-water emulsions stabilized by bentonite [15,34], carnation oil-in-water emulsions by silica [37] and corn

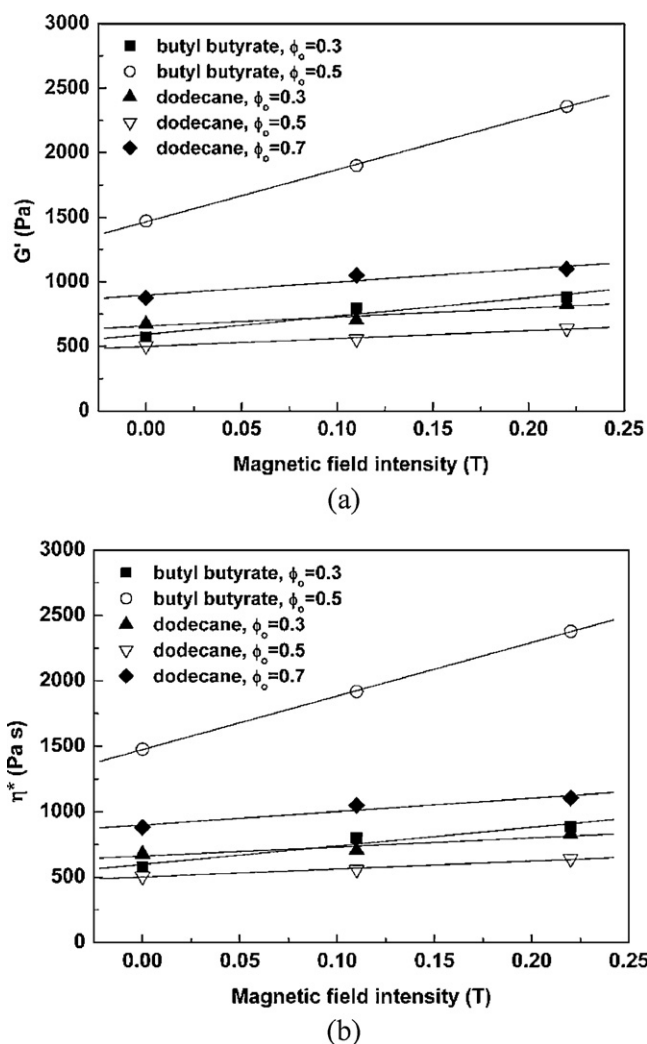


Fig. 4. Change of (a) the storage modulus and (b) complex viscosity at $\omega = 1 \text{ rad s}^{-1}$ with magnetic field intensity obtained from dynamic frequency sweep experiments for butyl butyrate-in-water and dodecane-in-water emulsions stabilized by OS- Fe_3O_4 nanoparticles at different ϕ_0 .

oil-in-water emulsions by chitin nanocrystals [38]. The exact composition plays an important role in dictating the physical stability of emulsions.

Beside oil volume fraction and oil polarity, the magnetic field intensity affects the modulus and viscosity of the emulsions stabilized by OS- Fe_3O_4 nanoparticles also, as reflected in Fig. 4. Both the elastic modulus G' and complex viscosity η^* increase linearly with magnetic field intensity (ψ), which can be described as:

$$G' = A + B\psi \quad (1)$$

$$\eta^* = A + B\psi \quad (2)$$

The constants of A and B obtained from the fits are listed in Table 2. It can be seen that the rate of increase of G' and η^* with ψ increases with an increase in ϕ_0 and oil polarity. Besides the accumulation of particles in the form of densely packed layers at the interface, the aggregation of particles in the form of an elastic network adsorbed at the interface due to attractive inter-particle forces is another mechanism responsible for preventing droplet coalescence in emulsions [38]. In our previous work, it was verified that not all the Fe_3O_4 nanoparticles were adsorbed at the interfaces in emulsions, with the weight fraction of particles (compared to the total amount) required for stable emulsions being below 0.70 and decreasing with an increase in ϕ_0 [32]. In the presence of a magnetic

Table 2

Parameters obtained from fitting the data in plots of G' and η^* as a function of magnetic field intensity for o/w emulsions stabilized by OS- Fe_3O_4 nanoparticles for two oils and different ϕ_0 .

Oil	ϕ_0	G'		η^*	
		A (Pa)	B (Pa/T)	A (Pa s)	B (Pa s/T)
Butyl butyrate	0.3	592.67	1418.18	597.50	1415.43
Butyl butyrate	0.5	1465.00	4045.45	1475.09	4092.86
Dodecane	0.3	657.33	700.00	661.43	692.85
Dodecane	0.5	499.33	609.09	501.27	607.91
Dodecane	0.7	896.67	1018.18	898.65	1023.11

field, the non-adsorbed magnetic particles will interact with the particle network adsorbed at the interface due to strong magnetic attractions, thus further enhancing the elastic particle networks surrounding the oil droplets and strengthening the modulus and viscosity of the emulsions. Meanwhile, the enhancement of the magnetic particle interactions also increases the interconnection of the dispersed oil droplets and the strength of the resultant elastic droplet networks. The existence of more excess magnetic particles with an increase in ϕ_0 and oil polarity further enhances this effect, and results in a more distinct elevation of the modulus and viscosity with magnetic field intensity.

Fig. 5 illustrates the influence of a magnetic field on the appearance of these emulsions. We placed a magnet close to the wall of the vessels containing the OS- Fe_3O_4 particle-stabilized emulsions. From the photographs, we see that after the magnet is put close to the emulsion, the emulsion droplets orient and aggregate toward the wall of the vessel in the direction of the magnetic field, and the butyl butyrate emulsions are more sensitive to the magnetic field than those of dodecane, as reflected in Fig. 4. In our previous work, polyethylene glycol-coated Fe_3O_4 nanoparticles can gradually move in a magnetic field to aggregate into string-like clusters oriented in the magnetic field direction due to the dipole-dipole interactions between the magnetic particles [39]. It should be mentioned that a critical magnetic field strength may exist for magnetic Pickering emulsions, at which emulsion droplets begin to coalesce and the emulsions destabilize to a fully phase-separated system [40]. In our experiments, when the magnetic field intensity increases to 0.33 T, the modulus and viscosity results fluctuate. The appearance of unreliable rheological data reveals the destabilization of these emulsions at high magnetic field intensity due to the extremely strong attractions and orientation of magnetic particles in the magnetic field direction. Indeed, at long time and high field intensity, coalescence of the emulsions occurred as reported by Melle et al. [40].

3.2.2. Steady shear flow response

According to Krynke and Sek [41], emulsions can be categorized into two main groups: dilute emulsions contain a low volume fraction of dispersed phase and display almost Newtonian behavior with a shear rate-independent viscosity, and concentrated emulsions contain a high dispersed phase volume fraction and exhibit non-Newtonian behavior in which the viscosity varies as a function of shear rate. The latter dependence can be described by a power law equation as [42]

$$\eta = K\dot{\gamma}^{n-1} \quad (3)$$

where η is the apparent viscosity, K is the consistency index, (essentially the viscosity of the system at a shear rate of 1 s^{-1}), $\dot{\gamma}$ is the shear rate and n is the power law index. From the values of n , we can evaluate the effect of shear on the system: shear-thinning occurs for $n < 1$, Newtonian behavior arises when $n = 1$ and shear-thickening occurs for $n > 1$.

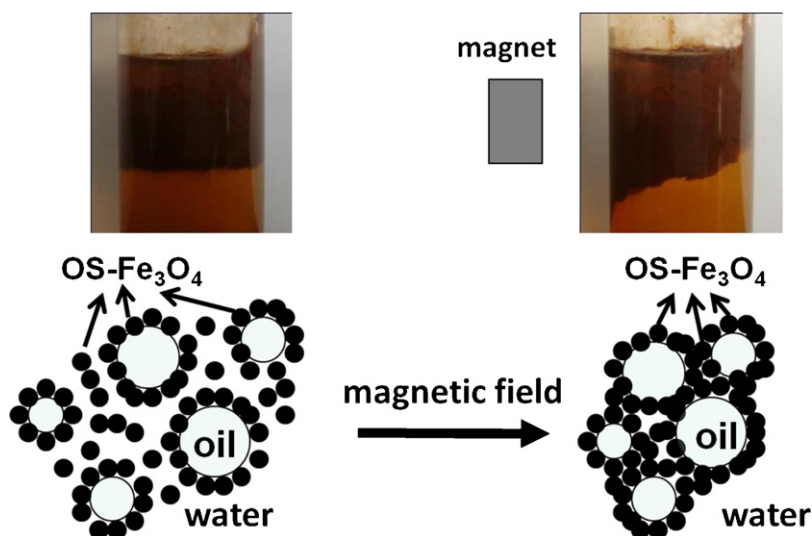


Fig. 5. Effect of a magnetic field on droplet and particle aggregation in OS-Fe₃O₄ particle-stabilized emulsions. Upper – photographs of the appearance of butyl butyrate-in-water emulsions ($\phi_o = 0.5$) without (left) and with (right) a magnet close to the vessel wall. Lower – schematic of the influence of a magnetic field on particle and drop aggregation.

Fig. 6 contains double-log plots of the shear viscosity as a function of shear rate for emulsions stabilized by OS-Fe₃O₄ nanoparticles under different magnetic field intensity, with (a) being for butyl butyrate and (b) being dodecane. All the emulsions show similar shear-thinning behavior, independent of ϕ_o , oil polarity and magnetic field intensity. In addition, at both low and high shear rate, there is a distinct deviation from the linear relationship, suggesting the existence of Newtonian viscosity plateaus: zero shear viscosity at low shear rate and equilibrium shear viscosity at high shear rate before and after structural breakage. As the shear rate increases, the hydrodynamic forces become large enough for droplet flocs to be deformed, elongated and aligned with the shear field, eventually being disrupted and leading to a rapid decrease in viscosity. Meanwhile, some trapped continuous phase between flocs can be released, further lowering the viscosity [43]. Similar to the dynamic viscosity, the shear viscosity increases with an increase in magnetic field intensity, due to the strengthening of interconnected particle and droplet networks. The magnetic field promotes particle flocculation, thus increasing the elasticity of adsorbed particle films and emulsion viscosity. The increase in emulsion viscosity results in a decrease in the probability of the

chances for droplet coalescence and the enhancement of emulsion stability.

The power law parameters of n and K obtained from fitting of the data in the shear-thinning region of Fig. 6 according to Eq. (3) are listed in Table 3. All of the Pickering emulsions are shear-thinning with $n < 1$ both in the absence or presence of a magnetic field, and this pseudoplastic behavior becomes more pronounced reflected by the decrease in n with the increase of oil polarity and the corresponding enhancement of the droplet flocculation. Other Pickering emulsion systems have been shown to exhibit shear-thinning behavior, including hexanol–water emulsions stabilized by bentonite particles [15,34] and chitin nanocrystals stabilizing corn oil–water emulsions [38]. The consistency index K , indicating the shear viscosity at 1 s^{-1} , increases progressively with an increase in ψ , similar to the dynamic viscosity. However, the K values do not increase with ϕ_o and oil polarity as the dynamic viscosity does. After shear-thinning and disruption of droplet flocculation, the viscosity decrease is more noticeable for the emulsions of polar oil at higher volume fraction.

The Herschel–Bulkley (HB) model can also be applied to describe the shear-thinning flow behavior of emulsions, occurring when the

Table 3
Power law parameters obtained from fitting the data of steady shear experiments according to Eq. (3) for o/w emulsions stabilized by OS-Fe₃O₄ nanoparticles with different ϕ_o and under different magnetic field intensity.

Oil	ϕ_o	$\psi = 0 \text{ T}$		$\psi = 0.11 \text{ T}$		$\psi = 0.22 \text{ T}$	
		$K (\text{Pa s}^n)$	n	$K (\text{Pa s}^n)$	n	$K (\text{Pa s}^n)$	n
butyl butyrate	0.3	9.0	−0.59	9.0	−0.56	13.9	−0.27
butyl butyrate	0.5	4.9	−0.36	5.6	−0.40	6.2	−0.36
dodecane	0.3	18.7	−0.06	26.7	−0.12	34.4	−0.20
dodecane	0.5	10.9	−0.33	18.1	−0.27	25.7	−0.29
dodecane	0.7	27.6	−0.14	26.6	−0.31	30.3	−0.31

Table 4
Herschel–Bulkley parameters obtained from fitting the data in the plots of shear stress as a function of shear rate under different magnetic field intensity for butyl butyrate-in-water emulsions stabilized by OS-Fe₃O₄ nanoparticles with different ϕ_o .

ϕ_o	$\psi = 0 \text{ T}$			$\psi = 0.11 \text{ T}$			$\psi = 0.22 \text{ T}$		
	$\tau_0 (\text{Pa})$	k_{HB}	α	$\tau_0 (\text{Pa})$	k_{HB}	α	$\tau_0 (\text{Pa})$	k_{HB}	α
0.3	2.53	0.038	1.01	4.60	0.009	1.24	9.74	0.041	0.98
0.5	2.43	0.002	1.56	3.09	5.92E−4	1.67	3.52	2.39E−4	1.89

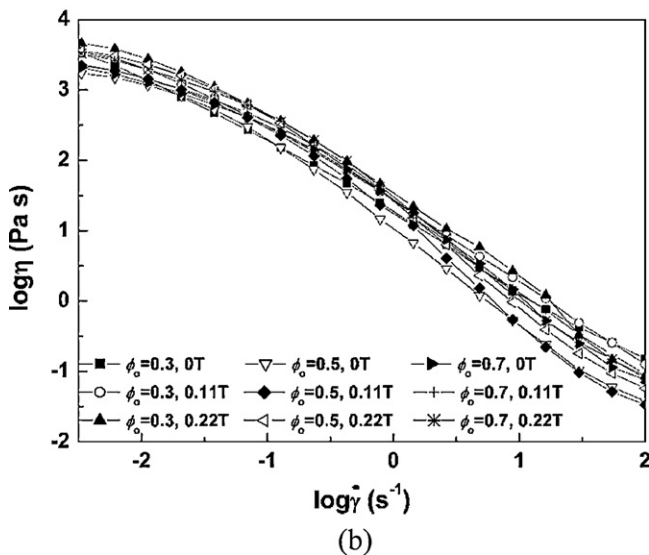
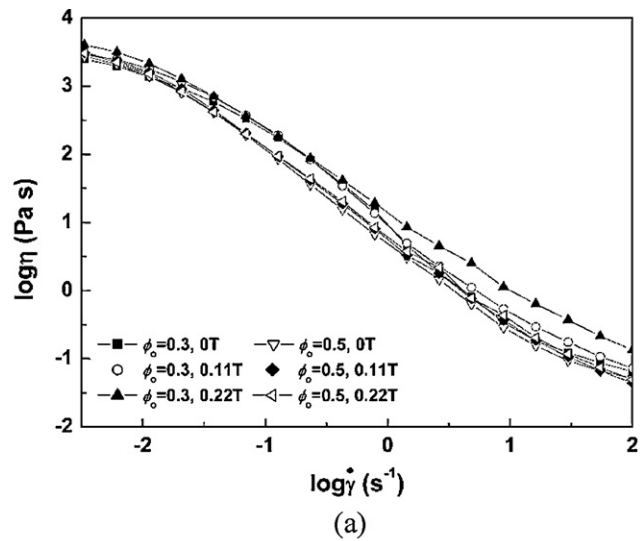


Fig. 6. Viscosity as a function of shear rate for o/w emulsions stabilized by OS-Fe₃O₄ nanoparticles with different ϕ_o and under different magnetic field intensity at room temperature: (a) butyl butyrate, and (b) dodecane.

network structure is destroyed once the loaded stress is greater than the yield stress [44], expressed as:

$$\tau = \tau_0 + k_{HB} \dot{\gamma}^\alpha \quad (4)$$

where τ is the shear stress, τ_0 the apparent yield stress and k_{HB} and α are model constants. As for the o/w emulsions stabilized by OS-Fe₃O₄ nanoparticles, this model is only applicable to the butyl butyrate-in-water emulsions, as reflected by the plots of shear stress as a function of shear rate in Fig. 7. The parameters obtained from fitting the data are displayed in Table 4. The failed fitting of the HB model for dodecane-in-water emulsions may be related to their relatively weaker shear-thinning behavior and yield sensitivity due to their tougher droplet networks. In general, the yield stress is considered as an indication of how well the emulsion can resist creaming or sedimentation. It is associated with the strength of the network formed in the emulsion, and the larger it is the more stable the emulsion [34,38]. From Table 4, it can be noted that the apparent yield stress of these emulsions is greater than that of bentonite-stabilized emulsions (0.48 Pa for 1 wt.% particles) [34], suggesting the higher stability of our magnetic Pickering emulsions to creaming. Moreover, the apparent yield stress values of our emulsions

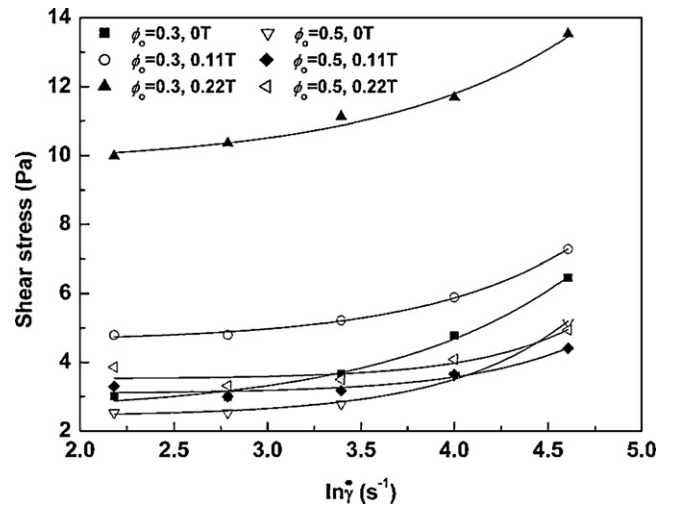


Fig. 7. Plot of shear stress as a function of shear rate for butyl butyrate-in-water emulsions stabilized by OS-Fe₃O₄ nanoparticles for two values of ϕ_o and different magnetic field intensities at room temperature.

increase with an increase in ψ and a decrease in ϕ_o , especially at high ψ .

4. Conclusions

Rheological measurements were utilized to characterize the linear and non-linear viscoelastic behavior of dodecane-in-water and butyl butyrate-in-water emulsions stabilized by silane-coated Fe₃O₄ nanoparticles in the absence and presence of a magnetic field. Similar to other Pickering emulsions, these emulsions exhibit solid-like behavior due to the existence of elastic particle and droplet networks, which are responsible for preventing droplet coalescence and retaining long term physical stability of the emulsions. The elastic modulus and viscosity are directly related to the elasticity of the network structure developed by particles and droplets, and stronger networks formed at higher oil volume fraction and higher magnetic field intensity lead to an increase in magnitude of both parameters. All the emulsions exhibit shear-thinning behavior in steady shear flow, with the apparent yield stress increasing with an increase in ψ and a decrease in ϕ_o , especially at high ψ .

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