Materials development and properties characterization of innovative magnetorheological (MR) fluids

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Materials Development and Properties

Characterization of Innovative Magnetorheological

(MR) Fluids

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List of Symbols

B	Magnetic induction
H	Magnetic field strength
I	Electric current
M_s	Magnetization Saturation
μ_0	Permeability of free space
m_d	Magnetic dipole
μ_p	Particle permeability
θ_{ij}	The angle between the joint line of the two dipoles and the field direction
μ_f	Carrier liquid permeability
U_{ij}^{dip}	Dipolar potential
F_{ij}	Magnetic force
F_i^{hydro}	Hydrodynamic force
$F_{ij}^{rep}(r_{ij})$	Repulsive force
γ	Shear strain
γ_0	Strain-amplitude
$\dot{\gamma}$	Shear strain rate
η_{app}	Apparent viscosity
η_{pl}	Plastic viscosity
η_m	Suspension viscosity in the absence of interactions
$\eta(\xi)$	Structural viscosity
η_0	Characteristic viscosity
η_∞	Viscosity for the destroyed structure
$\eta^*(\omega)$	Complex viscosity
$\tau_{yd}(H), \tau_{yd}$	Dynamic yield stress
τ_0	Shear stress amplitude
τ	Shear stress
τ_{ys}	Static yield stress

a	Particle radius
r	distance between particle centers
$\hat{e}_r$	The unit polar coordinate vector in r direction
$\hat{e}_\theta$	The unit polar coordinate vector perpendicular to r
$\phi(\Phi)$	Weight (volume) fraction
d	Average particle diameter
n	The flow index
K	Consistency parameter
ω	Oscillatory frequency
G	Material modulus
G'	Storage modulus
G''	Loss modulus
G_∞	Elastic modulus for the destroyed structure
G'_0	Storage modulus in plateau
$G(t)$	Relaxation modulus function
G_k	The k th weighting constant
γ_r	Recoverable strain in creep-recovery experiment
$R_\infty(\tau_0)$	Recoil function
$J(t, \tau_0)$	Creep compliance
σ	Shear stress
σ^e	Viscoelastic contribution of the shear stress
$\tan(\delta)$	Loss factor, $\tan(\delta) = G''/G'$
δ	Phase angle
ξ	Structural factor
θ	Characteristic time
χ	Kinetic function
$\delta/\delta t$	Upper convected derivative
$f(\xi)$	Empirical structural function
ν	Sedimentation ratio
λ_0	Relaxation characteristic time
λ_k	The k th relaxation time
α	Exponential factor

Δ_v	Horizontal shift factor
Δ_h	Vertical shift factor

Abbreviation

CTAB	CetylTrimethylAmmonium Bromide
SOS	Sodium Octyl Sulphate
DBSA	DodecylBenzeneSulphonic Acid
TEOS	TetraEthylOrthoSilicate
MR	MagnetoRheological
C-MR fluid (C-MRF)	Conventional MR Fluids
F-MR fluids (F-MRF)	Ferrofluids based MR fluids
Nano-MRF	MR Fluids of nano-sized particles
BP model	Bingham Plastic model
HB model	Herschel – Bulkley model
Ms	Magnetization saturation
SAOS	Small Amplitude Oscillatory shear
LAOS	Large Amplitude Oscillatory Shear
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
VSM	Vibrating Sample Magnetometer
TGA	ThermoGravitational Analyzer
C-M rule	Cox-Merz rule
R-D rule	Rutgers-Delaware rule

Summary

With the goal of developing innovative magnetorheological (MR) fluids, we performed the synthesis and characterization of new magnetic particles. With these particles, the properties of several new MR fluids were investigated.

In the material synthesis, Fe_3O_4 nanoparticles have been obtained using vesicle method, the magnetite particles were encapsulated in the vesicles formed from cetyltrimethylammonium bromide (CTAB) and sodium octyl sulphate (SOS). These small particles have no sedimentation issue, but their magnetization saturation is around 60 emu/g, which is not high enough for MR fluids. To obtain particles with higher magnetization saturation, iron based Fe-M-B (M can be Co, Cr or Ni) particles were synthesized using borohydride reduction method. A maximum M_s of 153 emu/g was achieved. And the particle size can be tailored from 40nm to 200nm by controlling the water/ethanol ratio of the solvent.

The mechanical behavior of the synthesized nano-MR fluids was investigated through rheological testing under magnetic fields. It was found that the Fe-Cr-B based nano-MR fluids have the merits of both ferrofluids and conventional MR (C-MR) fluids. They have moderate yield stress, and they have good anti-sedimentation property. Based on the rheological characteristic of the nano-MR fluids, a convected Jeffrey model was used to predict their dynamic behaviors.

The nano-MR fluids were obtained from a chemical method. While in a physical method, conventional MR fluids were mixed with ferrofluids. Experimentally it was

found these ferrofluids based MR fluids (F-MR fluids) had comparable yield stress with C-MR fluids, while the anti-sedimentation properties were greatly improved.

In addition to the magnetorheological study of nano-MR fluids and F-MR fluids, two more topics have been particularly investigated. One is the static yield stress measurement, where three different methods were used to get the static yield stress of F-MRF. The other is the interrelation between the apparent viscosity η_{app} in steady state shear flow and the complex viscosity η^* in oscillatory shear flow. Taking C-MR fluids as examples, the Cox-Merz rule and Rutgers-Delaware rule were analyzed and implemented. A general rule was summarized based on our experiences on suspensions with yield stress.

In the whole report, the MR properties of the new MR fluids were compared with commercial MR fluids MRF-132LD and other MR fluids. From these comparisons, we can have further understanding of new MR fluids and overall characteristics of different kinds of MR fluids.

Chapter 1

Introduction

Magnetorheology is a branch of rheology that deals with the flow and deformation of materials exposed to an external magnetic field. Many materials show magnetorheological properties such as magnetorheological (MR) fluids, ferrofluids, magnetic foam and magnetic elastomer [1-3]. The internal structure of these materials will change with an applied magnetic field, and accordingly the mechanical properties are changed.

Among all the MR products, MR fluids are the most representative to explain the characteristics of magnetorheology. They are suspensions of non-colloidal ($\sim 0.05\text{-}10\ \mu\text{m}$), multi-domain, and magnetically soft particles in organic or aqueous liquids [2, 4]. In the absence of magnetic fields, MR fluids behave mostly like typical non-colloidal suspensions such as ceramic suspensions [5, 6] or silica suspensions [7], they exhibit small apparent viscosity between 0.1 to 10 Pa-s at low shear rates. However, when MR fluids are exposed to strong external magnetic fields, their apparent viscosity will change dramatically within a few milliseconds. So the resistance of flow will be significantly increased. Once the magnetic field is removed, the MR fluids can return immediately to their original low viscosity status. So the change in the viscosity is completely reversible [8, 9].

Fig. 1.1 The applications of MR fluids, (a) washing machine shock absorber [10], (b) Seismic MR damper [11, 12], (c) MR clutch [13], (d) MR actuator [14].

By virtue of the excellent response characteristics of MR materials such as rapid response time, reversibility, and low energy consumption, many practical applications for MR materials were recognized immediately after the observation of this phenomenon. MR materials have been primarily considered as an ideal candidate for mechanical devices to achieve a real-time feedback control. Examples of some commercial applications include MR dampers (e.g., a washing machine shock absorber shown in Fig. 1.1 (a) and seismic MR damper Fig. 1.1(b)), MR clutches (Fig. 1.1(c)) and MR actuator (Fig. 1.1(d)) employed in hydraulics or robotics. Other potential applications for MR materials as “smart structures” are used for semi-active

vibration suppression in space structures [15, 16], robotic control systems such as superhuman joints that instantly lock or loosen with extremely high precision or manipulator grabs and positioning systems [17].

MR materials exhibit a very extensive diversity in their compositions [18], which caused a wide difference depending on the specific compositions. For instance, ferrofluids are colloidal suspensions of nano-sized magnetite (Fe_3O_4) [19], even under very strong magnetic field, the viscosity only increase several times of that without magnetic field. Phenomenally, we can only find that they change from totally fluids to gel-like material. However, the viscosity of commercial MR fluids under magnetic fields can increase several orders of magnitude of that without magnetic fields, they are composed of micro-sized iron (Fe) particles in mineral oil, synthetic oil or some polymers [2, 20]. In magnetic fields, they appear more like solid materials. There are also some other MR materials appearing in solid status such as magnetic elastomers and magnetic foams [1], which were obtained by adding micro-sized iron (Fe) particles into solid elastomers or foams.

The MR response is a very complicated phenomenon. The MR effect is affected by many factors including the applied magnetic field strength H , volume (weight) fraction of the particulate phase Φ (ϕ), the average particle diameter d , the permeability of the magnetic particles, the viscosity of the carrier liquid, etc. But generally, the flow ability of an MR fluid is qualitatively scaled by the apparent viscosity η_{app} [21], which is defined as

$$\eta_{app} = \tau / \dot{\gamma}, \quad (1.1)$$

where τ is the shear stress at the applied shear rate $\dot{\gamma}$. In this report, if no other special statement, the viscosity refers to the apparent viscosity η_{app} . To be more precisely, the performance of an MR fluid is primarily determined by the maximum yield stress it can be achieved, secondly the plastic viscosity, as expressed by the Bingham plastic model [1]:

$$\tau(\dot{\gamma}, H) = \tau_{yd}(H) + \eta_{pl}\dot{\gamma}, \quad \tau \geq \tau_{yd} \quad (1.2)$$

$$\tau = G\dot{\gamma}, \quad \tau < \tau_{yd}$$

Here $\tau(\dot{\gamma}, H)$ is the shear stress at the shear rate of $\dot{\gamma}$ under magnetic field H , G the material modulus. $\tau_{yd}(H)$ is the dynamic yield stress exhibited by the MR material at the magnetic field H . η_{pl} is the plastic viscosity, which is almost independent of the magnetic field H [1, 16]. It is found that an iron-based MR fluid at 40-50% volume fraction has a yield stress of about 100kPa under 1.0 Tesla [22]. If the magnetic field increases continuously, the yield stress can be further strengthened.

To improve the yield stress $\tau_{yd}(H)$, Tao employed a compression-assisted-aggregation system with MR fluids [23]. He used a suspension of carbonyl iron particles ($\approx 4.5\mu\text{m}$) in silicone oil with a volume fraction $\phi = 45\text{vol}\%$. After a magnetic field was applied, the MR suspension was compressed along the field direction. In this method he obtained a yield stress exceeding 800 kPa at a magnetic field of 458kA m^{-1} .

MR fluids also have their disadvantages. Because the density of those micro-sized iron particles is larger than that of the carrier media, the iron particles may sedimentate and cannot be easily re-distributed. If the particles were already tightly agglomerated, the

suspension is delaminated. The MR effect may disappear because only superficial carrier liquid got no reaction to external magnetic fields.

In this project, we targeted to develop new MR fluids of better performance than ferrofluids and C-MR fluids. Three factors are mainly considered for the new MR fluids, (a) anti-sedimentation property, (b) viscosity under magnetic fields, (c) viscosity at zero magnetic field. Associating with conventional MR fluids, several different kinds of MR fluids are produced. Their magnetorheological properties are systematically investigated and compared. And finally, the properties of these MR fluids are summarized so that we have clear understanding on the characteristics of different MR fluids.

In order to convey a clear picture about the understanding of magnetorheology, we present the fundamentals about MR fluids in Chapter 2. Firstly the mechanism for magnetorheological phenomenon is explained. Secondly the various compositions in MR fluids and their functions are introduced. Thirdly, the rheological properties of existing MR fluids are reviewed. Finally some mechanical models describing the MR dampers have been introduced.

In chapter 3, nanosized magnetite (Fe_3O_4) particles are synthesized via Cationic-Anionic Surfactant Vesicles. The magnetite (Fe_3O_4) particles in ferrofluids are very small, and the magnetization saturation is not high enough. So the MR effect of ferrofluids is very weak. To increase the MR effect, nano sized iron alloy has been selected for MR fluids because they have much higher magnetization saturation. The particles diameter can be controlled at 40-200nm, which can be shaped for different purpose accordingly. So in chapter 4, the synthesis of iron alloy particles is discussed and their chemical properties are investigated.

In chapter 5, the rheological properties of Fe-Cr-B based nano-MR fluids are investigated. Through the rheological study, the microstructural mechanism is proposed. Meanwhile a simple rheological model is developed to predict the properties in magnetic fields.

Although nano-MR fluids have good anti-sedimentation property, the yield stress is still not compatible with conventional MR(C-MR) fluids. To obtain MR fluids with higher yield stress, we developed ferrofluids based MR fluids (F-MR fluids) which were compounded by mirosized iron particles and ferrofluids. In chapter 6, the full rheological properties of F-MR fluids will be investigated.

Besides the exploration of new MR fluids, two particular topics were studied. One is the yield stress of MR fluids, the other is the interrelation between the steady shear properties and oscillatory properties. In chapter 7, the static yield stress of F-MR fluids will be measured with several different methods, the relationship between yield stress and the particle weight fractions/magnetic field strength is carefully discussed. In chapter 8, the interrelation between the steady shear properties and oscillatory properties was investigated. Based on the existing Cox-Merz rule used in polymers, and Rutgers-Delaware rules used in certain suspensions, we generalized the interrelation for more MR suspensions based on the experimental data.

Finally, an overall conclusion is given in Chapter 9, as well the future work is proposed.

Chapter 2

Literature Review on Magnetorheology

2.1 Introduction

In the past 60 years, electrorheological (ER) fluids are intensively investigated. They are suspensions of electrical field responsive particles suspended in non-conductive liquid media. The application of ER fluids is still very limited [24, 25]. However, MR fluids, as the analog of ER fluids, already have considerable industrial applications. MR fluids are magnetic field responsive fluids, when magnetic field is “on”, the magnetic particles are magnetized and formed chain structures like magnetic line. These chains act as backbone for the system. Their strength will change accordingly with the strength the magnetic fields, which changes the properties of MR fluids.

In this chapter, some fundamental background of MR fluids will be introduced. Firstly, the mechanism of chain structures is explained. Secondly, the material compositions and their effect on the properties of MR fluids are reviewed. Thirdly, some mechanical testing results are discussed. Finally, based on the current application of MR fluids in damping system, some viscoelastic models for MR fluids are introduced during the operation of MR fluids.

2.2 Mechanism of MR Fluids

The property of an MR fluid is strongly dependent on its microstructure. At zero magnetic field, the magnetic particles have no dipole moments and they are randomly moving in the media. When an external magnetic field is applied, a magnetic dipole moment will be induced in each particle. The particles aggregate and form chains of dipoles aligning in the direction of the applied magnetic field. As shown in Fig. 2.1, the structure of Fe_3O_4 particles were captured in emulsion using a CCD camera with/without magnetic fields [26].

(a)

(b)

Fig. 2.1 Nanosized Fe_3O_4 in emulsion, (a) zero field, (b) magnetic field $H = 1550\text{e}$ [26].

Under magnetic field, the particles were balanced by the following forces in a shear flow.

2.2.1 Magnetic force

Assuming that all the particles have an average diameter d and permeability μ_p , the permeability of the carrier liquid is μ_f , as illustrated in Fig.2.2. When an external magnetic field is applied, the particles acquire an induced dipole

moment $m_d = \frac{\pi d^3}{2} \left(\frac{\mu_p - \mu_f}{\mu_p + 2\mu_f} \right) H_0$, where H_0 is the magnetic field. The interaction

energy of two dipoles at r_i and r_j has the form $U = \frac{|m_d|^2 \mu_f}{4\pi r_{ij}^3} (1 - 3\cos^2 \theta_{ij})$, where

$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$ and θ_{ij} is the angle between the joint line of the

two dipoles and the field direction. If the expression for the dipolar moment was inserted into the interaction energy equation, we get the expression [27]:

$$U = \frac{\pi d^6 \mu_f \beta_m^2 H_0^2}{16 r_{ij}^3} (1 - 3\cos^2 \theta_{ij}), \quad (2.1)$$

where $\beta_m = \frac{\mu_p - \mu_f}{\mu_p + 2\mu_f}$. In a polar coordinate, the magnetic force is then given by (Fig.

2.2(a)):

$$\mathbf{F}_{ij} = \frac{\pi d^6 \mu_f \beta_m^2 H_0^2}{16 r_{ij}^4} [\hat{e}_r (1 - 3\cos^2 \theta_{ij}) - \hat{e}_\theta \sin 2\theta_{ij}], \quad (2.2)$$

where $\hat{e}_r$, $\hat{e}_\theta$ are the unit coordinate vectors. For a simplified model, two particles are in contact (Fig. 2.2(b)), the distance between two particles is $r_{ij} = d$, the magnetic force becomes

$$\mathbf{F}_{ij} = \frac{\pi d^2 \mu_f \beta_m^2 H_0^2}{16} [\hat{e}_r (1 - 3\cos^2 \theta_{ij}) - \hat{e}_\theta \sin 2\theta_{ij}]. \quad (2.3)$$

Fig. 2.2 Mechanical model of particles interaction in magnetic field H_0 , (a) two particles with distance $r_{ij} > d$, (b) two particles with distance $r_{ij} \leq d$.

2.2.2 Hydrodynamic force F_i^{hydro}

When a particle suspends in a fluid, it is subjected to hydrodynamic forces, which represents the force applied by the carrier media on the particle due to the viscosity. The force can be expressed by Stokes' formula for the hydrodynamic force on a sphere [28]. When Reynolds numbers $Re < 0.5$. The particle Reynolds number is usually small since the particles are sufficiently small, and the continuous phase sufficiently viscous. Even under the relatively extreme conditions, $\rho_f = 10^3 \text{ kgm}^{-3}$, $\eta_f = 0.001 \text{ Pa s}$, $d = 10^{-8} \text{ m}$, and $\dot{\gamma} = 10^3 \text{ s}^{-1}$, the Reynolds number $Re = \rho_f d^2 \dot{\gamma} / \eta_f \ll 1$. So the drag is assumed to be proportional to the difference between particle velocity and solvent velocity [28]. Hence, the force balance equation for the i th particle is [28]:

$$F_i^{hydro} = -3\pi\eta_f \left(\frac{dr_i}{dt} - v(r, t) \right) \quad (2.4)$$

Here, $\frac{dr_i}{dt}$ is the velocity of the particle moving in the fluid, $v(r, t)$ the imposed velocity

field of the solvent, and $\left(\frac{dr_i}{dt} - v(r, t) \right)$ the relative velocity of the particle.

2.2.3 Repulsive force

Short-range repulsive forces between magnetic particles arise from such phenomena as Born repulsion, solvation force, or steric interactions, they act over distances ranging from Angstroms to nanometers. These particles themselves, ranging in diameter from 0.5 to 100 μm , are considerably larger. Thus, magnetic particles are often perceived as hard spheres. With a short-range pair, the interaction potential of particles is [25],

$$V^{rep}(r_{ij}) = \begin{cases} \infty & r_{ij} \leq d \\ 0 & r_{ij} > d \end{cases} \quad (2.5)$$

This potential is easily employed in statistical mechanical models. Continuous short-range functions are often employed including exponential repulsion,

$$F_{ij}^{rep}(r_{ij}) = -F_0 \exp\left[-\kappa\left(\frac{r_{ij}}{d} - 1\right)\right] \hat{e}_r, \quad (2.6)$$

where $\kappa^{-1} \approx 0.01$ characterizes the range of the repulsive force, and the other form as a power-law repulsion

$$F_{ij}^{rep}(r_{ij}) = -F_0 \left(\frac{d}{r_{ij}}\right)^\varepsilon \hat{e}_r, \quad (2.7)$$

where typically $5 < \varepsilon < 37$. The prefactor F_0 is usually chosen as the magnetic force scale.

For microsized particles, the three above forces were balanced in the carrier media. While for nanosized particles, there may also exist Brownian force [29], Van der Waals force [25, 30].

2.3 Factors Affecting the Behavior of an MR Fluid

It could be seen from the above expression (2.3) - (2.7), the particle interaction energy is determined by the average particle diameter d , the viscosity η_f of the carrier media, the external magnetic field H_0 , the permeability of the particles μ_p and the carrier fluid μ_f .

Firstly, particles with high saturation magnetization (M_s) or permeability (μ_p) are the top priorities to be considered. With these properties, Strong interaction can be produced between two particles. They form fibril chains to maximize the MR effect under a moderate magnetic field. Iron particles have high permeability μ_p . They can be cheaply produced from iron pentacarbonyl by thermal decomposition [31]. Alloys of iron and cobalt have slightly higher magnetization saturation (up to $M_s = 2.4$ Tesla) and have also been used in MR fluids [31]. These micro-sized particles can give MR fluids high yield stress of 10–100 kPa in a strong magnetic field [31, 32].

Secondly, in the expression (2.3), we can see the relationship $F_{ij} \propto d^2$, so the particle diameter is a key factor contributing to the yield stress. If very high yield stress is expected, the simplest method is to increase the particle diameter.

But when increasing the particle size, serious sedimentation problem may happen because the density of metallic iron is much higher than that of the carrier media [33, 34]. The particles may settle and sometimes form a hard “cake” shape. When a magnetic field is applied, those particles cannot be chained any more. To reduce particle settling effect, thixotropic agents or surfactants are added into MR fluids to help stabilize the particles, such as carbon fibers, xanthan gum, silica gel or oleic acid, stearates, carboxylic acids, etc. These surfactants have a hydrophobic and a

hydrophilic end. One end will be attached on the particles and the other end floating around like whisker. These surfactants will prevent the particles come closer [31, 35]. On the other hand, these floating whiskers may slow down the velocity of the particles

$\frac{dr_i}{dt}$ in eq. (2.4), so that F^{hydro} is small.

Besides the addition of surfactant, some other methods to improve the anti-sedimentation property have also been implemented. For example, viscoelastic media or water-in-oil emulsions can be used as the carrier phases to increase the media viscosity η_f . Rankin et al. reported the use of viscoelastic media for MR fluids [36]. The sedimentation velocity of MR fluids using viscoelastic media was much slower than that using Newtonian media as media [36]. Fuchs et al. used polyurethane and silicone polymers as the MR fluid media [37], and they found the polymer gel based MR fluids (MR polymer gel) were quite stable [37, 38]. But the polymers or gels will greatly increase the zero-field viscosity, which results in the increase of on-off response time and degrade the MR effect [39, 40].

To improve the anti-sedimentation property of MR fluids, the decrease of the particle dimension also seems to be good method. For smaller particles, the ratio of thermal energy to gravitational energy is increased. The thermal motion may break off from the magnetic force or gravity. But inversely, the chain strength may not be as strong as those big particles in fields, which will decrease the yield stress as well. John et al. used nanosized iron particles of diameter 26.5nm for MR fluids [41], they found the yield stress of nano-MR fluids was much smaller .

According to the condition that MR fluids are used, the selection of carrier media also should be taken care. In LORD company, petroleum based oils, silicone, mineral oils,

polyesters, water, synthetic hydrocarbon oils have been used for different purposes [2]. Some polar liquids such as: triethylene glycol, diethylene glycol methyl ether, hexyls and cyclohexyl acetate, methyl propionate have also been tested for special usage [42]. All these organic liquids have almost the same μ_f . While in the formula $\beta_m = \frac{\mu_p - \mu_f}{\mu_p + 2\mu_f}$, if we increase the permeability μ_f of the carrier media, β_m is reduced. The magnetic force (eq.(2.3)) will be affected, so the agglomeration will be different. Ferrofluids have larger μ_f than the above listed oils [34]. And the carrier viscosity is also increased when using ferrofluids as carrier liquid, but not as serious as those gels [36]. As demonstrated, the anti-sedimentation was significantly improved comparing with conventional MR fluids using kerosene oil or silicone oil as liquid phase [34]. Meanwhile, nano-scale magnetic particle (Co-Fe₂O₃, CrO₂, Fe) have also been used as additives to MR fluids [43, 44].

2.4 Shear Flow Properties of MR Fluids

The mechanical properties such as the yield stress and the flow behavior of MR fluids are evaluated through rheological testing. Rheological study is a science of more experiences than theoretical works. It's defined as the study of flow and deformation in materials [45]. In a more apparent sense, rheology is the study of materials with interesting flow properties —typically those of viscoelastic nature, i.e. exhibiting a combination of viscous and elastic behavior. The rheological information can tell the equilibrium microstructure as well as the changes caused to the system when subjected to a flow field. Thus, in addition to providing fundamental (microstructural) information, rheology provides useful information related to the processing and handling of MR media. In fact, rheological data is routinely used in the

design of technological operation, even without an appreciation for its microstructural value [46].

Fig.2.3 Shear stress vs. magnetic induction at a shear rate $\dot{\gamma} = 26s^{-1}$ of conventional MR fluids with four different carrier liquids [2].

MR fluids are usually characterized by measuring the rheological properties under magnetic fields. If no magnetic field is applied, the viscosity is significantly dependent on the viscosity of the carrier media and the particle volume (weight) fraction. It means without magnetic fields, the rheological properties have no much difference comparing with other suspensions. The viscosity is very small between $0.1-10 Pa \cdot s$ in Newtonian flow. When a magnetic field is applied, the viscosity will be increased by several orders of magnitude. As shown in Fig. 2.3, the shear stress is continuously increased with the increasing magnetic induction B at a fixed shear rate $\dot{\gamma} = 26s^{-1}$ [2].

In a shear flow, the steady-state rheological response is usually described by Bingham Plastic (BP) model with a magnetic field-dependent dynamic yield stress $\tau_{yd}(H)$ [36],

$$\tau(\dot{\gamma}, H) = \tau_{yd}(H) + \eta_{pl}\dot{\gamma}, \quad \tau > \tau_{yd}, \quad (2.8)$$

$$\tau = G\gamma, \tau \leq \tau_{yd}. \quad (2.9)$$

Here G is the elastic modulus, $\tau(\dot{\gamma}, H)$ is the shear stress at the shear rate $\dot{\gamma}$ under a magnetic field H . The dynamic yield stress $\tau_{yd}(H)$ is an extrapolated stress at zero shear rate from eq. (2.8) during curve fitting [47]. And η_{pl} is the plastic viscosity, illustrated in Fig. 2.4(a). Meanwhile, the apparent viscosity η_{app} defined in the eq. (1.1) is also shown in the figure.

Fig.2.4 The flow curve illustration of MR fluids in magnetic fields, (a) Shear stress vs shear rate [48], (b) Shear stress vs strain [47].

It could be seen, the eq. (2.8) and (2.9) are separated by $\tau_{yd}(H)$. Eq. (2.8) means that the material microstructure is destroyed. It cannot bear the shear force and begins to flow along the shear, which is called the post-yield stage. The eq. (2.9) describes the stress-strain relation in pre-yield stage (Fig. 2. 4(b)) [47]. In this stage, MR fluids approximately show an elastic behavior under external shear stress. There is another shear stress which is even larger than τ_{yd} in this pre-yield stage, it's the minimum stress necessary for the unbounded strain or deformation of the material, defined as

static yield stress τ_{ys} [47]. Either the static yield stress τ_{ys} or the dynamic yield stress τ_{yd} has been used as an index to indicate the strength of an MR response.

In BP model, η_{pl} is a constant, but in different magnetic fields, the value may be different. This difference is considered in Herschel – Bulkley (HB) model,

$$\tau(\dot{\gamma}, H) = \tau_{yd}(H) + K\dot{\gamma}^n, \quad \tau \geq \tau_{yd}, \quad (2.10)$$

$$\tau = G\dot{\gamma}, \quad \tau < \tau_{yd}. \quad (2.11)$$

HB model has three parameters: the yield stress τ_{yd} , the consistency parameter K and the flow index n . The index n is an important parameter to classify the flow types, $n > 1$ indicates a shear thickening flow and $n < 1$ indicates a shear thinning flow [49].

Barnes et al. stated that a true yield stress didn't exist [50]. However, the measured yield stress is an important parameter to determine the capability of an MR fluid. For example, according to the value of τ_{yd} , they can be decided to be used in shock absorbers, clutches, engine mounts, control valves, and artificial joints [31]. To closely measure the static yield stress, Bossis and Lemaire designed a two-plate rheometer [51, 52]. They investigated two different systems, one is aqueous suspension of polystyrene spheres containing iron oxide with diameter about $0.8\mu\text{m}$, and the other is a ferrofluid with ordinary polystyrene inside (also called inverse ferrofluids) [53, 54]. They found that when the external field is larger than 300 Oersted, the yield stress is proportional to the square of the magnetic induction B [51, 52].

Fig. 2.5 Three particles in long chain under a magnetic induction B_{ave} .

Ginder and Co-workers analytically derived that the yield stress should increase linearly with the volume fraction [4, 55]. They predicted that the yield stress of an iron-based MR fluid of 50 vol% was able to reach 200 kPa. The result was based on single-chain structure with saturated magnetization [51]. As illustrated in Fig. 2.5, three particles in chain represent the particle interactions under magnetic induction B_{ave} . The force at a quarter of the particle was analyzed using Finite Element Method (FEM) [55]. It was found that at very low magnetic field, the static yield stress was proportional to B_{ave}^2 . When the particle magnetization is completely saturated, the yield stress becomes a function of saturation magnetization $\tau \propto M_s^2$. Bossis et al. predicted that the static yield stress was [51]

$$\sigma_{ys} = \sqrt{6} \phi \mu_0 M_s^{1/2} H^{3/2}. \quad (2.12)$$

Experimentally it showed that $\tau \propto H^{1.23}$, which is different from the expression (2.12) [56].

2.5 Oscillatory Shear Properties

The flow curves show how the material changes in response to continuous deformation. And how readily the material can be processed, or shaped into a useful product. While to explore the microstructures or the rates of structural rearrangement of MR fluids, oscillatory shear can be implemented for deep investigation. The measurement of G' and G'' is often the most useful way to characterize a complex material mechanically [49]. For example, through the log-log plotting of G' and G'' , the “liquid-like” and “solid-like” materials can be qualitatively measured. As shown in Fig.2.6, a material is defined as “liquid-like” if the storage modulus G' is much lower than the loss modulus G'' [49]. And usually G' is proportional to the square of frequency, $G' \propto \omega^2$, where the loss modulus is linear in frequency, $G'' \propto \omega$. For the solid-like suspension, $G' \gg G''$, and G' is nearly frequency-independent [49].

Fig.2.6 Illustrations of frequency-dependent storage and loss moduli G' and G'' for “liquid-like” and “solid-like” materials [49].

The flow curves show how the material changes in response to continuous deformation. And how readily the material can be processed, or shaped into a useful product. While to explore the microstructures or the rates of structural re-arrangement

of MR fluids, oscillatory shear can be implemented for deep investigation. The measurement of G' and G'' is often the most useful way to characterize a complex material mechanically [49].

2.5.1 Definition of dynamic moduli and their derivation

Assuming a viscoelastic fluid is subjected to an oscillatory strain with sufficiently small amplitude defined by:

$$\gamma(t) = \gamma_o \sin(\omega t) \quad (2.13)$$

where γ is the shear strain, t is time, γ_o ($\ll 1$) is the shear strain amplitude and ω is the frequency of oscillation. The shear rate is the time derivative of γ , which is in the form

$$\dot{\gamma}(t) = \gamma_o \omega \cos(\omega t) \quad (2.14)$$

The resulting shear stress response, $\tau(t)$ in the linear viscoelastic regime is also a sinusoidal wave with the same frequency ω , but shifted by an angle δ with respect to the shear strain wave,

$$\begin{aligned} \tau(t) &= \tau_o \sin(\omega t + \delta) = \tau_o (\sin \omega t \cos \delta + \cos \omega t \sin \delta) \\ &= (\tau_o \cos \delta) \sin \omega t + (\tau_o \sin \delta) \cos \omega t \end{aligned} \quad (2.15)$$

where τ_o is the shear stress amplitude. By splitting up the shear stress in this way, we see that there is a portion of the stress wave that is in phase with the imposed strain (i.e., proportional to $\sin(\omega t)$) and a portion of the stress wave that is out of phase with the imposed strain rate (proportional to $\cos(\omega t)$). The stress response in small amplitude oscillatory shear (SAOS) described by eq. (2.15) contains both, a part that is Newtonian-like which is proportional to $\dot{\gamma}$ and an elastic part which is proportional

to γ . Thus the SAOS experiment is ideal for probing viscoelastic materials, defined as materials that show both viscous and elastic properties.

The material functions for SAOS are the storage modulus $G'(\omega)$, and the loss modulus $G''(\omega)$. They are defined as follows

$$\text{SAOS material function } \frac{\tau}{\gamma_0} = G' \sin \omega t + G'' \cos \omega t \quad (2.16)$$

$$\text{Storage modulus } G'(\omega) = \frac{\tau_0}{\gamma_0} \cos \delta, \text{ Loss modulus } G''(\omega) = \frac{\tau_0}{\gamma_0} \sin \delta \quad (2.17)$$

G' is equal to the amplitude of the portion of the stress wave that is in phase with the strain wave divided by the amplitude of the strain wave. G'' is defined analogously as the amplitude of the portion of the stress wave that is out of phase with the strain wave, divided by the amplitude of the strain wave.

For a Newtonian fluid in SAOS, the response is completely in phase with the strain rate, $G' = 0$, $G''/\omega = \mu$. This can be shown by using the Newtonian constitutive equation and specifying the SAOS kinematics. For an elastic solid that follows Hooke's law (a Hookean solid), the shear response in SAOS is completely in phase with the strain, $G' = G$ and $G'' = 0$. For viscoelastic materials both $G'(\omega)$ and $G''(\omega)$ are nonzero and are generally functions of frequency [45].

In eq. (2.17), $\tan(\delta) = \frac{G''}{G'} = \frac{\sin(\delta)}{\cos(\delta)}$ is called loss factor, which is the ratio of the two

complex components. The two quantities, G'' and $\tan(\delta)$, are of interest for vibration damping. If they are small for a given frequency, the damping will be small; for large values of G'' and $\tan(\delta)$, the damping will be augmented [21].

2.5.2 Oscillatory properties of MR fluids

In an oscillatory shear experiment, a strain amplitude sweeping should be carried out to determine the linear viscoelastic range. In this range, the material is still in static status and $\tan(\delta) = \text{constant}$, the microstructure of build-up and destruction is balanced. After the linear range, there is more destruction than buildup, both G' and G'' will decrease, and $\tan(\delta)$ began to increase. The strain oscillation can be classified into two types, one is the Small Amplitude Oscillatory Shear (SAOS) characterizing linear viscoelastic properties, the other is Large Amplitude Oscillatory Shear (LAOS) characterizing non-linear viscoelastic properties [57].

In view of the limited studies on dynamic responses of MR fluids, Li et al. did a lot of fundamental research [58]. They found the linear viscoelastic region of an MR fluid was very small $\gamma_0 \leq 0.01\%$ [59]. As shown in Fig. 2.7 (a), in the linear range, G' keeps in plateau during the strain amplitude oscillation. After the linear range, it drops quickly which is several orders of magnitude less than that in the plateau range. Chin et al. also carried out the oscillatory shear using Fe_3O_4 as the magnetic particles [43]. With a volume fraction of $\Phi = 20\text{vol}\%$, the linear stage of G' and G'' were restricted to a very small strain. Both G' and G'' were rapidly decreased with increasing strain amplitude, causing the non-linearity [43].

In the linear strain range, frequency oscillation can be carried out. Fig. 2.7 (b) showed the frequency oscillation of an MR fluid, which was composed of carbonyl iron ($7\pm 1\mu\text{m}$) with many nanosized magnetic and non-magnetic particles [60]. It was found that G' and G'' are almost independent of the frequency ω under magnetic field. And G' was much larger than G'' showing gel-like behavior.

Fig. 2.7 Typical oscillatory shear curves, (a) determine the linear range of the MR fluids [59] , (b) frequency oscillation ($\gamma_0=10^{-4}$, $\Phi=15\text{vol\%}$, $H = 21350\text{A/m}$) [60].

It's already stated that the strain in SAOS was very small, any larger vibration may cause the fluids breakthrough the linear region. In particular, the understanding of MR fluids in LAOS is also crucial to the actual application of MR technology [61]. Since the LAOS is in the post-yield range, the moduli in large strain lose their mathematical meaning because G' and G'' are defined only in the linear viscoelastic regime. However, a good periodical LAOS test can also provide a lot information [57]. It can be carried out with controlled strain amplitude and time scale. Through Fourier transformation, several major phases can be retrieved [57, 62, 63]. Li et al. experimentally found during the frequency oscillation, the stress could reach to its

maximum value at transitional point from linear to nonlinear [64]. While in the whole frequency oscillation, the storage modulus G_1' will decrease to a minimum value and then increase forming a concave, the critical frequency of the minimum G_1'' is dependent on the strain [64].

2.6 Transient Shear

The above discussed shear flow curves and oscillatory shear are time-independent. But there are many different types of time-dependent shear flows, they can reveal MR fluids properties in the transient point from start to stop or inverse. The most frequently investigated transient shear about MR fluids includes shear start-up, stress creep and relaxation.

Fig. 2.8 Stress growth illustration, (a) stress response with overshoot in a stress growth experiment [65], (b) Shear start-up curves under fixed magnetic flux density of 0.57 T for different values of the shear rate [66].

2.6.1 Shear start-up

In the viscosity measurement, the stress starts from zero to steady status. At the stress growth stage, the microstructure will be changed. Under a very small shear

strain rate (slow stress increasing), the stress growth during the start-up stage can be generated clearly at time coordinate, as shown in Fig. 2.8(a) [47, 65]. See and Chen investigated the shear start-up of MR fluids under magnetic fields plotted in Fig. 2.8(b) [66]. The response resembles that of a solid-like material at the small strains, and there is clearly a transition region where yielding occurs, with the fluid reaching steady flow at large strains. It is seen that the strain dependence of the build-up of stress is nearly independent of shear rate for all rates investigated.

Fig.2.9 The creep-recovery illustrations of (a) solid block, (b) viscoelastic materials.

2.6.2 Creep –recovery behavior

In steady shear flow, a constant shear rate is applied to the material in order to investigate the stress behavior. In a creep test, a constant shear stress is applied to the system to investigate the changes of shear strain or shear rate. When a stress τ_0 is applied on an elastic block, the strain was suddenly increased to $\gamma_0 = \tau_0 / E$ according to Hookcan law. And when the stress is removed, the material returns to its original status without residual deformation (Fig. 2.9(a)). However, for a viscoelastic material,

it becomes more complex. As illustrated in Fig. 2.9(b), a stress is applied to the material, the creep compliance $J(t, \tau_0)$ keeps on growing by a fixed ratio $1/\eta(\dot{\gamma})$. At time t_2 , the stress is suddenly removed, the creep compliance doesn't drop to zero but gradually decreases until it's stabilized.

Although creep testing can help explain the particle interaction under shear within magnetic field, there were quite few related reports in the literature. Li et al have studied the creep behavior of a commercially available magnetorheological fluids under a fixed magnetic induction of 0.34T (Fig. 2.10(a)) [67]. They found that under a small stress the sample would initially show an elastic response and then undergo a transition to a viscous regime. See, Chen and Keentok also carried out the creep-recovery experiments for MR fluids (Fig. 2.11(b)) [66]. They increased the shear stress step by step with a constant magnetic induction of 0.57T. And they found that there was an initial jump in strain (the elastic response) followed by a very gradual transitional region, which can last for hundreds of seconds. When the stress was removed, the sample showed an immediate rebound, followed by a slow recovery. And finally a permanent strain was left.

(a)

(b)

Fig. 2.10 Creep-recovery curves for MR fluids, (a) a magnetic induction $B = 340\text{mT}$ [67], (b) magnetic induction $B = 570\text{mT}$ [66].

2.7 Numerical Models

In the previous part, we have reviewed the mechanical properties of some MR fluids, the BP model or B-H model have been used to characterize the flow behaviors. And it can be seen, the yield stress plays a significant role in their performance. In actual engineering application, the models must be more practical to suit functional requirement. Usually a viscoelastic material can be presented by a combination of mechanical elements such as springs and viscous dashpots [68]. The response of MR fluid devices can also expressed in this method. To better understand the application of viscosity, yield stress and so on, some engineering models introduced.

2.7.1 Bingham model

The simplest model to character MR fluids or MR devices is Bingham- Plastic (BP) model (Eq.(2.8)) or Herschel - Bulkley (HB) model (Eq.(2.10)). Fig. 2.11 shows the BP model, it's expressed as

$$F = f_c \cdot \text{sgn}(\dot{x}) + c_0 \dot{x} \tag{2.18}$$

Where x is the displacement, $\dot{x}$ is the speed of the damper movement. c_0 is equivalent to the viscosity η_{pl} , f_c is field dependent, equivalent to the yield stress τ_0 . Comparing with the BP model, $\dot{x}$ is equivalent to the shear rate $\dot{\gamma}$. This model accounts for the fluid behavior beyond the yield point, i.e. for fully developed fluid flow or sufficiently high shear rates. However, it assumes that the fluid remains rigid in the pre-yield region. Thus, Bingham model does not describe the material's elastic properties at small deformations, and according to experimental studies, it does not describe adequately the dynamic behavior of an MR-damper.

Fig. 2.11 Bingham model.

Fig. 2.12 Model illustration of the MR damper [71].

2.7.2 Li's model

In Bingham plastic model, the MR fluid is considered as rigid solid before the yield point, which is not true even for real solid material. Referring to the analysis of ER fluids in the pre-yield stage [48], Li et al. presented a model that the MR material was operated in two rheological domains: the pre-yield and the post-yield regions [71]. It is considered that, in the pre-yield region, deformations are viscoelastic and in the post-yield region, the deformations are viscoelastic, which is illustrated in Fig. 2.12.

The governing equations for the model proposed by Li et al. are [71]

$$F = F_{ve} + F_s, \quad |F| \leq F_c, \text{ pre-yield} \quad (2.19)$$

$$F = C_v \dot{x} + R\ddot{x} + F_c \operatorname{sgn}(\dot{x}), \quad |F| > F_c, \text{ post-yield.}$$

In which F is the damper force, F_{ve} the viscoelastic force, F_s the stiction effect F_c is the yield force, C_v is the viscous damping coefficient and R is the equivalent inertial mass. The viscoelastic force F_{ve} needs to be determined separately accordingly to viscoelastic theory. It was found through proper selection of the parameters, the model can well match the experimental data [71]. It separated the pre and post yield behavior of MR device, which is quite like the actual performance of MR fluids.

Besides the above models, there are some more models expected to better describe the performance of MR fluids. Oh and Onoda built a model for a variable MR damper to demonstrate vibration mitigation in a truss structure [72]. Choi et al. directly used a sixth-order polynomial model to describe the force-velocity relation in an MR damper [73]. Kamath and Wereley used a three-parameter Jeffrey's model to characterize the

pre-yield stage, and by combining the Newtonian flow in the post-yield stage, the two stages are both described [74].

2.8 Conclusions

In the above, we have reviewed the properties of MR fluids and they are summarized as follows,

- ◆ *Major factors affecting the performance of MR fluids.* The performance of an MR fluid is mainly determined by the particle diameter, the permeability of the particles and the carrier liquid, the viscosity of the carrier liquid and the particle volume fraction.
- ◆ *Shear flow properties.* Under magnetic fields, the behavior of MR fluids can be divided into two stages under shear. One is the pre-yield stage that the MR fluids behave like elastic solid materials having yield stress. The other is the post-yield stage where they behave like fluids.
- ◆ *Oscillatory shear.* Under magnetic fields, the linear range of G' and G'' is very small in strain amplitude oscillation. While G' and G'' are constant at small frequency stage, both of them will increase in large frequency.
- ◆ *Transient shear.* When very small shear strain is applied to MR fluids, the stress goes to an overshoot, then drops down and levels off quickly.
- ◆ *Numerical models.* To characterize the rheological properties, several models were proposed for MR fluids and MR devices, such as Bingham model, HB model and Li's model. All of them are semi-empirical and they can be used for control equations.

With the above review, we can see that all the mechanical properties were determined by the inherent property of MR fluids. For most conventional MR fluids, they can be

classified into two types: (1) they have large yield stress under magnetic field and small viscosity without magnetic field. But they have serious sedimentation problem. (2) They have large yield stress under magnetic field and there is little sedimentation, but the viscosity of the carrier media is large, so the MR effect is not very effective.

Trying to solve these problems, we aim to make some innovative MR fluids, so that the new MR fluids have some advantages over the conventional ones.

Chapter 3

Synthesis and Characterization of Magnetic Particles for Ferrofluids via Cationic-Anionic Surfactant Vesicles

3.1 Introduction

Magnetic nanoparticles are attractive materials because of their potential application in many areas such as magnetic targeting for drug delivery, cell separation & purification, DNA purification, magnetic storage, micro-control, etc [75-80]. Usually, magnetite (Fe_3O_4) is selected in these applications. Because it is a permanent soft magnetic material, biocompatible, and it has relative high magnetization saturation.

Fe_3O_4 can be achieved using physical method and chemical method. In the physical method, small particles can be obtained out of big ones by wet grinding for a long period of time (~ 1000 hours) [35]. The particle can be reduced from micro scale to nano-scale of about 10nm. The particle size distribution is quite large. But in this method, a large amount of particles can be produced continuously. In the chemical method, ultra fine Fe_3O_4 can be produced with slim size distribution. It's synthesized through chemical co-precipitation of Fe^{2+} and Fe^{3+} ions [35]. The molar ratio of $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$ is used and the reaction takes place in an alkaline solution as shown in equation (3.1) [35]:

The particle size of Fe_3O_4 obtained by this method is uniform. However, they will agglomerate even in an aqueous medium. To prevent agglomeration, they can be treated with surfactants [81, 82] or amphiphilic polymers [83].

In the first method, Fe_3O_4 particles can be coated with a layer of surfactant, so that two particles are separated by the surface surfactant. The most convenient method is through sol-gel hydrolysis. For example, magnetic particles can be stabilized by tetraethylorthosilicate (TEOS) [84]. The nano-sized magnetite particles in solution are diluted with certain amount of TEOS, Milli-Q water and 2-propanol. Hydrolysis will happen at room temperature for a few hours in an alkali environment [84]. At the low concentration, the TEOS can only grow in to a sol, and the sol attaches onto the surface of Fe_3O_4 forming a shell, as shown in Fig. 3.1 [84]. Due to the presence of negative charges on the surface of silica shells, these magnetic nanoparticles are repulsive between each other.

Fig. 3.1 (A-C) TEM images of Fe_3O_4 nanoparticles whose surfaces have been coated with silica shells of various thickness. In this case, the thickness of silica coating could be adjusted by controlling the amount of precursor added to the solution: (A) 10, (B) 60, and (C) 1000 mg of TEOS to 20 mL of 2-propanol. (D) A

HRTEM image of the iron oxide nanoparticle whose surface has been uniformly coated with 6 nm of amorphous silica shell [84].

Another approach is the vesicle method. It's proven that this method is adequate, versatile, and simple to synthesize nano-sized magnetic particles [85, 86]. In the vesicles, there are at least one cationic surfactant and one anionic surfactant [87]. Yaacob *et al* fabricated the magnetic nanoparticles inside the vesicles formed by the surfactants cetyltrimethylammonium bromide (CTAB) and decylbenzenesulphonic acid (DBSA) [85]. With an appropriate ratio of the CTAB/DBSA, they also obtained the magnetic nano-particles at room temperature [86].

In this chapter, the Fe_3O_4 particles are going to be stabilized by vesicles of cetyltrimethylammonium bromide (CTAB) and sodium octyl sulphate (SOS). The fabrication and properties of CTAB/SOS vesicles have been investigated in the literature [81, 88, 89]. Although the properties of CTAB/DBSA vesicles are similar to that of CTAB/SOS, no reports have been found in the literature, which used the CTAB/SOS vesicles to encapsulate magnetic nanoparticles.

The obtained magnetic particles were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM) and thermogravimetric analyzer (TGA). After the characterization, these particles were made into ferrofluids. Their rheological properties of these ferrofluids will be investigated.

3.2 Experiments on the Synthesis of Fe_3O_4

3.2.1 Materials

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) powder, ferric chloride tetrahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) powder, hydrochloric acid (HCl) solution (36.5%), sodium hydroxide (NaOH) beads, cetyltrimethylammonium bromide (CTAB) and sodium octyl sulphate (SOS) were obtained from Sigma Chemical Co. All the materials except for CTAB, were of analytical grade and used without any further purification. CTAB was recrystallized from a 2/1 mixture of ethanol and acetone. Water was deionized and deoxygenated prior to usage.

3.2.2 Nanosized Fe_3O_4 preparation

The CTAB/SOS vesicles were prepared following Yaacob's procedure [85, 86]. Three samples A, B and C were prepared, and all the procedures were similar except that the amount of iron ions was increased doubly from sample A to sample C. As an example for sample A, two stocks of 100ml diluted hydrochloride acid (HCl) with pH = 5.8 were prepared in advance, solid powder of CTAB (0.005 mol) and SOS (0.0065 mol) were mixed into the two acidic solutions respectively. 1.0g (0.005mol) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.7g (0.01mol) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the CTAB solution and the color became light green. The SOS solution was then injected into the CTAB solution using a syringe at a rate of 0.2ml/s with slight stirring using a magnetic stirrer. With the addition of SOS, all the chemicals were diluted. Thus the final concentrations of CTAB, SOS, Fe^{2+} and Fe^{3+} became 0.025M, 0.0325M, 0.025M and 0.05M respectively. The pH value of the mixture was increased to 5.9. Here the solution was acidic in order to prevent the precipitation of hydroxide $[\text{Fe}(\text{OH})_2]$. The compositions

for the three samples are listed in Table 3.1. The stirring was kept for 2 hours with nitrogen bubbling and then the solution was ultrasonicated for 15 minutes. The obtained vesicle solution was filtered through a $0.2\ \mu\text{m}$ filter to eliminate big agglomerated vesicles and then was sealed for future use.

Table 3.1 Sample compositions (before mixing with NaOH).

Sample	Fe^{3+} (M)	Fe^{2+} (M)	CTAB (M)	SOS (M)	pH
<i>A</i>	0.05	0.025	0.025	0.0325	5.9
<i>B</i>	0.1	0.05			5.9
<i>C</i>	0.2	0.1			6.1

The alkali NaOH solution of 100ml with $\text{pH} = 12.5$ was prepared and deoxidized by nitrogen bubbling for 30 minutes. Both the alkali and vesicle solutions were heated to 75°C for the coming synthesis of magnetite particles, because the best condition for making magnetite was reported to be above 65°C [90]. The hot alkali solution was poured into the heated vesicle solution with vigorous mechanical stirring and nitrogen bubbling. The color of the iron ion solution was turned from yellow to black immediately. After mixing, the stirring was kept for another 30 minutes. Finally the black colloid was neutralized by a 0.05M HCl solution, and then washed by DI water three times and ethanol one time.

3.3 Characterization of Nanosized Fe_3O_4

3.3.1 X-ray diffraction (XRD) for crystalline structure

All the samples (A, B, and C) were dried overnight under vacuum at 65°C . The crystalline structures of the samples were first determined using a powder X-ray diffractometry (XRD, Philips PW1830). The X-ray diffraction patterns were taken

from 20° to 70° ($= 2\theta$) with a scan rate of 1° per minute using a $\text{CuK}\alpha$ radiation source. The X-ray tube was operated at 40kV and 30mA.

3.3.2 TEM for particle morphology

The structures of the vesicles and magnetite particles were observed using Transmission Electron Microscopy (TEM, JEOL 2010) under an accelerated voltage of 200KeV. The TEM samples were prepared as follows. A small amount of the vesicle solution was diluted into a transparent solution by DI water, a drop of the diluted solution was titrated on a carbon-coated grid of 400 meshes by a syringe and it was allowed to air dry. The magnetite colloid samples for TEM were prepared in a similar procedure.

When observing the particles morphology using TEM, electron diffraction was also carried out to determine the crystalline structures.

3.3.3 VSM for magnetic properties

The magnetic properties of the dried samples were measured using a standard Vibrating Sample Magnetometer (VSM, 735 series Lakeshore). The hysteresis loop was obtained from the step increasing magnetic field with a maximum value of 10,000 Oe. The measurement sensitivity was 0.1emu. The magnetization unit was emu/g, which was normalized by the weight of the sample.

3.3.4 TGA for thermal stability

The thermal stability of the samples and the contents of the surfactants CTAB and SOS were investigated by measuring the deterioration temperature and weight loss using thermogravitational analysis (TA Instruments, Model 2090). About 20mg

of the dried sample was placed into a platinum TGA sample pan, and then heated in the TGA furnace from 40°C to 600°C with a heating rate of 10°C/min under nitrogen blowing. A curve of weight loss versus temperature was then obtained. The onset temperature of the weight loss after the moisture evaporation range was defined as the initial temperature of the decomposition of the sample.

3.4 Characterization Results and Discussion

(a)

(b)

Fig. 3.2 XRD patterns for the samples (A, B, and C) and the standard Fe_3O_4 , (a) X-ray diffraction pattern, and (b) electron diffraction in TEM for sample C.

3.4.1 Crystalline structures

Fig. 3.2(a) shows the magnetite crystalline structures of the three samples, which are compared with standard pure magnetite particles (Fe_3O_4). The characteristic peak positions for the three samples were superposed with the standard sample, indicating that it is magnetite particle in all the three samples. Comparing with the standard sample, the noise background was very strong for each sample during the scanning. And particularly the peak at the plane 422 was very weak, which are possibly due to the “impurity” of the surfactants used or some possible non-crystalline region.

The formation of Fe_3O_4 crystalline structures in the samples A, B, and C could be further confirmed using the electron diffraction attached on the TEM machine. An example is given in Fig. 3.2(b) for sample C. The clear rings at the planes of 220 and 311 are in good agreement with the XRD peaks at planes of 220 and 311.

Fig. 3.3 TEM micrograph for a mixture of CTAB and SOS solutions (CTAB:SOS = 0.025: 0.0325 in molar ratio) containing iron ions (0.05M Fe^{3+} and 0.025M Fe^{2+}) before adding NaOH.

3.4.2 Micrographics of vesicle and magnetic particles

The formation of the CTAB/SOS vesicular structures containing iron ions is shown in Fig. 3.3. Most of the vesicles were assembled into spherical sacs, and separated from each other. But still some of the vesicles were overlaid and aggregated. The vesicle diameter was ranged from 100nm to 200nm. Similar dimension range has also been obtained, such as CTAB : SOS = 80 : 20 [88], and CTAB: SOS = 3.0:7.0 in molar ratio [81].

(a)

(b)

(c)

Fig. 3.4 TEM micrographs of the magnetite particles in vesicles with different iron ion concentrations as indicated in Table 3.1, (a) sample A, (b) sample B, and (c) sample C. (In (b) and (c), the micrographs on the right side are the single vesicles with higher resolutions.)

Fig.3.4 shows the TEM micrographs for the three samples A, B, and C, which were prepared with different iron ion concentrations. In sample A of Fig. 3.4(a), it had the smallest amount of iron ions, vacancies or hollow structures could be observed inside the vesicles, it means that the vesicles were not fully filled with magnetite particles. The size variation of the magnetic vesicles was quite big. There is a thick layer shown in dark gray color, indicating magnetic particles in this area.

The TEM micrograph of the magnetic vesicles for sample B is shown in Fig. 3.4 (b). All the particles were presented spherical shape and they had relatively narrow size distribution. The particle diameter of sample B ranges from 100 nm to 200 nm, which is consistent to the vesicles size distribution. Being different from the hollow-like structure observed for sample A, sample B showed the solid dark color, indicating that the vesicles had been fully filled by the magnetite particles. When observing a selected single vesicle with a higher resolution, the smaller particles could be found

within the vesicle, as shown in the right picture in Fig. 3.4(b). In the picture, the particles were separated from each other, indicating that the packing density of the tiny particles was not high.

Fig.3.4(c) presents the magnetic vesicles for sample C. The big black vesicles, which were filled with magnetic particles, were observed. The vesicle surfaces were not as smooth as that of sample B. Outside the vesicles, some magnetic particles or their aggregates were scattered around the vesicles, as can be clearly seen at the right picture with higher magnification. The figure also shows that a lot of scattered particles forming a circle surrounding the vesicles, which may be caused by the static electro-magnetic repulsive force between the vesicle and the small Fe_3O_4 particles.

During the preparation of the three samples, only the content of iron ions is different. The generation mechanism of the magnetic particles is almost the same. In sample B, the content of magnetite particles would have just reached an optimal condition to pack all of the “rooms” of the surfactant vesicles. But in sample C, the amount of the produced magnetite particles had exceeded the vesicle capacity. Thus, the extra magnetite particles resided outside the vesicles.

3.4.3 Magnetic properties

The magnetic properties of the vesicle-stabilized magnetite particles were investigated through VSM analysis. The hysteresis loops were plotted in Fig. 3.5. The magnetization saturation (M_s) fall in 30-50 emu/g, about half of the saturation magnetization of the bulk material of Fe_3O_4 (89 emu/g magnetite) [91]. In Yaacob's experiments, only Fe^{2+} ions were used to make magnetic particles, the M_s is only 3.0

emu/g [85, 86]. When both Fe^{2+} and Fe^{3+} were used as described above, the M_s was dramatically increased.

Fig. 3.5 Magnetization hysteresis for the three samples A, B, and C.

Fig. 3.6 Thermogravimetry curve for the three samples.

3.4.4 Thermogravitational Properties

The dried samples of vesicle-stabilized magnetite particles were tested using the thermogravitational analysis to evaluate the decomposition temperature and the content of the surfactant in the samples. The result was shown in Fig.3.6. At lower temperatures (for example, $T < 200^\circ\text{C}$ for sample A), a nearly 5% weight loss was

observed due to the moisture restricted in the vesicles. After that, the rate of the curve suddenly increased. Around 420°C , the weight was leveled off. So the whole decomposition happened between 200 to 420°C . Under the nitrogen environment during heating, the decomposition residuals should be SOS and CTAB. Thus, the total weights of CTAB and SOS, determined from the TGA curves in Fig.3.6, were about 27%, 24% and 21% for sample A, B and C respectively.

Fig. 3.7 Schematic mechanism for the formation of vesicle-stabilized magnetic particles: (a) a vesicle formed from CTAB and SOS, and (b) the formation of magnetic particles inside and outside the vesicle.

3.4.5 Mechanism for formation of vesicle-stabilized magnetic particles

The significant effect of the magnetite loading on the morphological structure of the vesicle-stabilized magnetic particles has been shown in Fig.3.4. Although the mechanism of the such unique vesicle structures has not been reported somewhere else, we attempt to propose a schematic mechanism presented in Fig. 3.7 to explain the formation of vesicle-stabilized magnetic particles under different loadings of iron ions (Fe^{+3} and Fe^{+2}). Fig. 3.7(a) shows the vesicle structures of CTAB and SOS. Both CTAB and SOS have a hydrophobic end and a hydrophilic end, they can form a spherical ball with solution side. During the formation of vesicles, iron ions of Fe^{2+} and Fe^{3+} are encapsulated. When hydroxyl ions (OH^-) are added to the vesicular

solution, OH^- ions can penetrate into the vesicles by ionic exchange and react with iron ions to form the magnetic particles (Fig. 3.7(b)). In Fig.3.4 (b), the vesicles were packed with the magnetite particles, it seems that the inner wall of vesicles are more electrically negative, which could attract more Fe^{3+} and Fe^{2+} ions.

3.5 Magnetorheological Testing

The concentration of the Fe_3O_4 particles during synthesis is very dilute, which is not suitable for magnetorheological study. To get samples of different weight fractions, the dilute ferrofluid held in a small bottle without a cap was placed in an oven of 65°C , allowing water to vaporize slowly. The weight of each sample was monitored during drying and the drying was stopped when the weight reached the required value. In this way, the ferrofluids with magnetite (Fe_3O_4) weight fractions of 15% and 25% were prepared from sample B.

The rheological properties were investigated using a Paar Physica MCR300 parallel disk rheometer, which is introduced in Appendix A. A fixed volume of 0.4ml magnetic fluids was carefully dropped at the center of the disk. After loading, the circumference of the sample was sealed by silicon oil, a constant shear rate $\dot{\gamma} = 10\text{s}^{-1}$ was applied to the system for 2 minutes to stabilize the fluids.

The MR effect of ferrofluids was displayed in Fig 3.8 for the flow curves. Without magnetic fields, the stresses were linear to the shear rate. When the magnetic field was increased gradually, the stress was also increased. But it was no longer linear to the shear rate, but showing a non-Newtonian fluid behavior. It's shown in Fig. 3.8, at shear rate $\dot{\gamma} = 100\text{s}^{-1}$, the stress was almost doubled at the applied magnetic induction $B = 272\text{ mT}$ as compared with that at $B = 0.0\text{ mT}$.

Fig. 3.8 Flow curves of ferrofluids in different magnetic fields, (a) weight fraction $\phi = 15\text{wt\%}$, (b) $\phi = 25\text{wt\%}$.

Theoretically, it was regarded that the sedimentation can be avoided only when the particle diameter is below 20nm [35]. While in the above prepared ferrofluids, water was evaporated during the condensation, a lot of vesicles were left in the fluid. And from our observation, the ferrofluids were also quite stable with little sedimentation.

3.6 Conclusions

Conventionally, nanosized Fe_3O_4 particles were produced through mechanical grinding. But it takes very long hours (about 1000hours) [35]. In this work, they are intentionally made from chemical methods. The results are summarized as below.

Magnetite particles can be achieved through vesicle method. Here the CTAB/SOS vesicles were used to encapsulate the particles. Because the encapsulation is not fully filled by the magnetite particles, there is little sedimentation was found.

Previously, only Fe^{2+} was used to produce Fe_3O_4 particles in vesicles. The M_s was very small around 3emu/g. Here the particles were produced from Fe^{3+} and Fe^{2+} with M_s 30-50emu/g, which is much higher than 3emu/g.

Rheological testing showed that the ferrofluids were responsive to external magnetic fields. Without magnetic fields, they behave like Newtonian fluids, while under magnetic fields, they become in sol-gel status, behaving like non-Newtonian fluids.

In this chapter, we hope to find nanosized magnetic particles with high magnetization saturation. Although Fe_3O_4 in vesicles has no sedimentation issue, the M_s is not very satisfactory. And in rheological testing, the shear stress doesn't increase much even under the maximum magnetic field we can applied. So this kind of ferrofluids can only be used in small loading of damping system [79], or they are used in micro-control system [80].

This method also opens a window in biological application for magnetite particles. These particles can be encapsulated in some reagent or medicine, through magnetic control, they can be introduced to or focused in a certain positions for treatment.

Chapter 4

Synthesis and Characterization of Iron Alloy Based Nano-particles

4.1 Introduction

Microsized iron particles in magnetorheological fluids (MR fluids) have very high magnetization saturation M_s (about 200 emu/g) which favors the performance of MR fluids. However, conventional MR fluids containing microsized iron particles have a serious sedimentation issue due to the big sizes ($> 3 \mu\text{m}$ in diameter) of iron particles [92]. To solve the sedimentation issue, an alternative way is to use nanosized particles to replace microsized particles. For example, magnetic fluids fabricated from Fe_3O_4 nanoparticles have been commercialized and named ferrofluids [3, 93]. Comparing with micro-sized iron particles, Fe_3O_4 nanoparticles in ferrofluids almost never sedimentate in the absence of an external magnetic field. However, a new issue with Fe_3O_4 nanoparticles is the low magnetization saturation (about 89 emu/g) [94], which limits the use of ferrofluids for applications such as dampers that require high magnetization saturation.

Nevertheless, both MR suspensions and ferrofluids have their own advantages in applications. In-between these two kinds of fluids, a third kind of magnetic fluids can be developed from some other types of magnetic nanoparticles whose magnetization saturation is higher than that of Fe_3O_4 , and sedimentation is also better than conventional MR fluids. This work is dedicated to synthesis and characterization of stable iron-based alloy nanoparticles with high magnetization.

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A commonly used way to synthesize magnetic nanoparticles is the borohydride reduction method [95, 96]. In this method, metallic alloy nanoparticles can be produced from the following chemical reactions among their chlorides and sodium borohydride [97]:

Equation (4.1) shows that when NaBH_4 is dissolved in water to form BH_4^- , hydrogen bubbles are produced. Equation (4.2) explains that a black suspension is produced when metal ions (M^{2+}) from a metallic chloride are mixed into the NaBH_4 solution. Equation (4.3) shows the formation of boron, which can be verified by checking the composition of the solid nanoparticles in the black suspension. In fact, this method results in the formation of nanoparticles from M and B. Furthermore, when two different metallic chlorides (for example, FeCl_2 and CoCl_2) are used, alloy nanoparticles can be synthesized from two metals (for example, Fe and Co) and boron.

Using the borohydride reduction method, many kinds of metal or alloy nanoparticles have been fabricated [98-100]. For example, Yiping et al. synthesized Co-B nanoparticles by controlling the concentration of sodium borohydride [101]. They found that the particle size of Co-B decreased with increasing borohydride concentration. Manthiram et al. designed a T-form reactor for the synthesis of Fe-B and Fe-Co-B nanoparticles [96]. During the reaction, they applied an external

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magnetic field and observed that the magnetic field could improve the magnetization saturation [96]. The group also found that the molar ratio of $\text{Fe}^{2+}:\text{BH}_4^- = 1:5$ was optimal to achieve the highest magnetization saturation [96, 102].

Manthiram et al also found that the particle size was related to the solvent [103]. They varied the ethanol to water ratio in the reaction medium and observed that the particle diameter could be decreased by increasing the ethanol content in the aqueous medium [103].

The present work aims to develop stable and high-magnetization Fe-based alloy nanoparticles for MR fluids. The work is composed of two parts. In the first part, the Fe-Co-B nanoparticles ($\text{Fe}:\text{Co} = 4:1$) were synthesized using the borohydride reduction method [96, 101]. A mixture of water and ethanol was used as the solvent. The effect of ethanol content in the mixed solvent on particle size has been studied. In the second part, in order to study the effects of 3 selected metals (Co, Cr, Ni) on morphology, crystalline structures, and magnetic properties, we synthesized the Fe-B, Fe-Co-B, Fe-Cr-B, and Fe-Ni-B nanoparticles at a fixed molar ratio of $\text{Fe}:\text{M} = 4:1$, where $\text{M} = \text{Co}, \text{Cr}, \text{and Ni}$, both in the absence and in the presence of an external magnetic field of 3000 Oe. This also allows us to study the effect of an external magnetic field on the morphological and magnetic properties of the alloy nanoparticles. These synthesized magnetic nanoparticles are potentially useful for fabrication of MR fluids.

The microstructures of all the synthesized nanoparticles were characterized using transmission electron microscopy (TEM). The crystalline structures were characterized using XRD and the magnetic properties were measured using vibrating sample magnetometry (VSM).

4.2 Experimental

4.2.1 Materials

The following chemicals, purchased from Sigma-Aldrich, were reagent grade and used as received: iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$), sodium borohydride (NaBH_4 , $> 99\%$), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $> 99\%$), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $> 99\%$). Milli-Q water (resistivity $\geq 18.2\text{M}\Omega \text{ cm}$) was obtained from a Milli-Q water supplier.

4.2.2 Synthesis of Fe-Co-B nanoparticles with ethanol

The content of cobalt affects the magnetization saturation of a Fe-Co-B alloy. In order to obtain the highest magnetization saturation, the optimum ratio of Fe^{2+} : Co^{2+} was kept at 4:1 [96, 101]. Thus, the concentrations of BH_4^- , Fe^{2+} and Co^{2+} were taken as 0.5 M, 0.08 M and 0.02 M respectively. The synthesis was carried out in a rectangular jar as shown in Fig. 4.1. The jar was placed in a mixture of ice and water so that the temperature of the jar could be kept at 0°C . The borohydride and metallic ion solutions were separately stored in the two syringes with a maximum volume of 35 ml. They were dropped into the jar slowly at a rate of about 0.3 ml/s. Two parallel permanent magnets were placed at two sides of the jar, and the magnetic field was set at 1500 Oe by adjusting the distance between the two magnets. With adding the reagents, the mixture was stirred vigorously. The variation of the water to ethanol ratio in volume is shown in Table 4.1. At each ratio of water to ethanol, 200 ml of the BH_4^- solution and 200 ml of the metallic ion solution were mixed by syringe dropping. The mixing took about 12 minutes to complete.

Table 4.1 Formulation for synthesis of Fe-Co-B.

Sample Code	BH ₄ ⁻ solution (ml)		Metallic solution (ml)	
	Water	Ethanol	Water	Ethanol
A	200	0	200	0
B	195	5	195	5
C	185	15	185	15
D	170	30	170	30
E	150	50	150	50
F	120	80	120	80

During the mixing of the two solutions, some hydrogen bubbles were released. When no more bubbles came out at a time of about 30 minutes, the magnetic field was removed and stirring was kept for another 120 minutes. After stirring was stopped, the particles were washed three times with milli-Q water and once with ethanol through centrifugation, and then dried overnight in a glove box filled with nitrogen.

Fig. 4.1 A schematic graph for the experimental setup: ① mechanical stirrer, ② syringe with BH₄⁻ solution ③ syringe with metal ion solution, ④ rectangular jar, ⑤ ice-water mixture, ⑥ magnet.

Chapter 4 Synthesis and Characterization of Iron Alloy Based Nano-particles*4.2.3 Synthesis of Fe-B, Fe-Co-B, Fe-Cr-B and Fe-Ni-B nanoparticles without ethanol*

The content of cobalt, chromium or nickel incorporated in a Fe-based alloy is expected to affect the magnetization saturation M_s . In the present work, to obtain comparable results, the molar ratio of Fe:M was fixed at 4:1 for each alloy composition, where M was Co, Cr, or Ni. Furthermore, in order to examine the effect of a magnetic field on magnetization saturation, the synthesis for each formulation was carried with/without an external magnetic field applied. The experimental setup was the same to that shown in Fig. 4.1. The magnetic field was adjusted to 3000 Oe, which was stronger than that used for the synthesis of Fe-Co-B nanoparticles with ethanol in order to obtain a stronger effect on magnetization saturation. Similar to the synthesis of Fe-Co-B as described above, 200ml solution of 0.5 M NaBH_4 was used and no ethanol was added to the reaction medium (i.e. DI water). The details of the sample formulations are listed in Table 4.2.

Table 4.2 Sample formulations.

Iron-alloy particles	Sample code	$\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (g)	Metallic chloride (g)	Metallic solution (ml)	BH_4^- solution (ml)	Magnetic field (Oe)
Fe-B	<i>a</i>	4.7	0	200	200	0
	<i>b</i>					3000
Fe-Co-B	<i>c</i>	3.76	$(\text{CoCl}_2 \cdot 6\text{H}_2\text{O})$	200	200	0
	<i>d</i>		0.952			3000
Fe-Cr-B	<i>e</i>	3.76	$(\text{CrCl}_3 \cdot 6\text{H}_2\text{O})$	200	200	0
	<i>f</i>		1.066			3000
Fe-Ni-B	<i>g</i>	3.76	$(\text{NiCl}_2 \cdot 6\text{H}_2\text{O})$	200	200	0
	<i>h</i>		0.952			3000

The prepared two solutions were slowly injected into the jar with vigorous stirring. During the injection, a great amount of bubbles flowed out, and the solution became

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dark gradually. The injection took about 12 minutes. After the injection, the stirring was kept for another 120 minutes until no more bubbles came out. Then the samples were centrifuged and washed three times by milli-Q water and once by ethanol. When the magnetic field was applied during the reaction, the samples could be separated from the solutions by centrifugation.

4.2.4 Characterization

The particle size and morphology were characterized using transmission electron microscopy (TEM, Joel 2010). The samples for TEM were prepared as follows. Several drops of the washed nanoparticle sample (before drying) were diluted with ethanol and vibrated under ultrasonic for 20 minutes. A drop of the diluted sample was placed on a carbon coated Cu grid and dried naturally. The magnetic properties were measured using a vibrating sample magnetometer (VSM7300, lakeshore) at room temperature. Before the VSM measurements, the VSM machine was calibrated with a standard Ni sample. Finally, the thermal stability of the different particles was checked through TGA, they were heated in air flow from 40°C to 500-600 °C.

(i)

(ii)

Fig.4.2 TEM micrographs for Fe-Co-B synthesized in a mixed solvent of water and ethanol. The volume contents of ethanol in the aqueous solvent were (i) 0, (ii) 2.5%, (iii) 7.5%, (iv) 15%, (v) 25 %, and (vi) 40%.

4.3 Results and Discussion

4.3.1 *Effect of ethanol on particle size and morphology of Fe-Co-B nanoparticles*

The Fe-Co-B nanoparticles were synthesized in a mixed solvent of water and ethanol and the content of ethanol in the mixed solvent was varied from 0 to 40 vol%. The TEM micrographs of the Fe-Co-B nanoparticles are shown in Fig.4.2. The average particle diameters were calculated from 50 particles per graph and listed in Table 4.3. It is observed from the figure that the particle chains were formed and these chains were crossed over to form a network structure.

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Table 4.3 Average diameter of Fe-Co-B particles synthesized in a mixed solvent of water and ethanol.

Sample Code	A	B	C	D	E	F
Ethanol content (v %)	0	2.5	7.5	15	25	40
Particle diameter (nm)	170	120	90	75	60	35

It is known that in the presence of the magnetic field all the particles can be aligned in the direction of a magnetic field to form chains of particles. But when the magnetic field is removed and the suspension is stirred and/or vibrated under ultrasonic, the chain structures could be arranged into a network structure as shown in Fig.4.2.

Fig. 4.3 Effect of ethanol content in the reaction medium on the particle size of Fe-Co-B.

The effect of ethanol on particle size is further shown in Fig.4.3. From the figure as well as Table 4.3, it can be seen that by increasing the ethanol content in the reaction medium, the average particle diameter was decreased from 170 nm to 30 nm. That is, the particle size could be controlled over a broad range of ethanol content. This result is consistent well with those reported in the literature [12, 13]. However, the effect of ethanol on particle size is not a linear function of ethanol content in the reaction medium. The most significant effect of ethanol is observed for ethanol content ≤ 7.5

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vol%. Beyond 7.5 vol%, the particle sizes decreased approximately linearly with increasing ethanol content.

The effect of ethanol on water is interesting. When ethanol is added to water, a non-ideal mixture is produced. In such a non-ideal mixture of water and ethanol, ethanol has a stronger effect on water's structure and physical properties (such as boiling point) than it in an ideal mixture. In general, since ethanol is less polar than water, the addition of ethanol to water will result in a less polar solvent. Due to the chemical structure of ethanol molecules, the addition of even a few percent of ethanol to water can sharply reduce the surface tension of water, where ethanol behaves like a surfactant.

As verified above, the particle diameter could be controlled by the ethanol content. We explain this effect to be due to the reduced polarity of water by ethanol. When ethanol is mixed into water, the mixed solvent will have a polarity that is less than pure water. In such a less polar medium, the kinetic properties of metallic irons M^{2+} (or M^{3+}) and BH_4^- ions as well as the nucleation kinetics for the formation of alloy nanoparticles may be different from those in pure water. Although no suitable mechanisms have been found from the literature, the nucleation for particle formation is expected to be easier in a less polar medium than in a polar medium (water). This is because the interactions between irons (M^{2+} or M^{3+} , and BH_4^-) and water molecules are weaker in a less polar medium than in water so that the forward reactions (i.e. particle formation reactions) of equations (4.2) and (4.3) will be favored. As a result, smaller nanoparticles are formed in a less polar medium (i.e. water mixed with a higher content of ethanol).

Fig. 4.4 TEM micrographs for (i) Fe-B, (ii) Fe-Co-B, (iii) Fe-Ni-B, and (iv) Fe-Cr-B nanoparticles synthesized in the absence of an external magnetic field.

4.3.2 Effect of metal type on formation of Fe-based alloy nanoparticles and properties

Nanoparticles synthesized in the absence of an external magnetic field. Fig. 4.4 shows the TEM micrographs of Fe-B, Fe-Co-B, Fe-Ni-B, and Fe-Cr-B nanoparticles synthesized without applying a magnetic field. In the synthetic experiments, all the conditions were kept the same for obtaining comparable results. In Fig. 4.4(i), the Fe-B particles are almost spherical with an average diameter of 110 nm but they overlay each other. In Fig. 4.4(ii), the big Fe-Co-B particles seem to be composed of small

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crystallites or small particles. The similar results were observed by Dragieva et al who obtained the Co-B nanoparticles that were most likely formed by agglomeration of small particles [98].

Fig. 4.4(iii) and Fig 4.4(iv) show the nanoparticles of Fe-Ni-B and Fe-Cr-B respectively. Both of them are relatively well dispersed. Although all the reaction conditions for the synthesis of the four samples were the same, we observed the diameter difference among them [i.e. Fig. 4.4(i)] to 4.4(ii)]. The Fe-Ni-B particles have an average diameter of about 150 nm, while the diameter for Fe-Cr-B particles is only about 50 nm. The big difference in diameter in the particle size between Fe-Ni-B and Fe-Cr-B is related to the second metallic salts used.

In the chemical reactions for the synthesis of the samples in Fig.4.4, an external magnetic field was not applied. But we still can see that some particles were organized into chain-like structures. According to Manthiram and Zhang's presumption, the weak chain structures were probably resulted from the earth magnetic field. They synthesized many metal particles with or without a magnetic field [99] and observed that the chain structures were formed in the Fe-B particles but not in the Cu particles. Thus, it is suggested from the results that the earth magnetic field plays an important role in controlling the formation of chain structures of magnetic particles.

Nanoparticles synthesized in the presence of an external magnetic field. In the absence of a magnetic field in the reaction, all particles formed were spherical. When a magnetic field was applied, the particles were connected to form long chains. At the same time the particles were no longer in spherical shape, they formed 'cake-like' shape in the chains. As shown in Fig. 4.5, all the particles inside the chains were squeezed. This phenomenon indicates the nanosized iron alloy particles are elastic

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materials. In chapter 2, we explained the interaction between particles. In magnetic fields, the magnetic force F_{ij} must be larger than the repulsive force F_{ij}^{rep} , so that chain structures were formed. Because the particles were elastic, they were squeezed by the magnetic force.

Fig. 4.5 TEM micrographs for Fe-B particles synthesized under a magnetic field of 3000 Oe: (i) chain structures and (ii) squeezed particles in the chain.

Fig. 4.6 TEM micrographs for Fe-Cr-B chains synthesized under a magnetic field of 3000 Oe: (i) the long chains and (ii) the enlarged chain structures.

The similar chain structures were also observed for the Fe-Cr-B particles as shown in Fig.4.6. More interestingly, the long fibrous structures could be found (Fig. 4.6(i)) and

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the necklace-like structures were composed of the squeezed nanoparticles (Fig. 4.6(ii)).

Fig. 4.7 X-ray diffraction patterns for (i) Fe-Co-B particles (sample *d* in Table 4.2), (ii) Fe-Cr-B particles (sample *f* in Table 4.2), (iii) Fe-Ni-B particles (sample *h* in Table 4.2), and (iv) pure nickel particles for comparison.

Crystalline structures. Fig. 4.7 shows the X-ray diffraction (XRD) patterns for the alloy particles (i.e. the samples *d*, *f*, and *h* in Table 4.2) synthesized under a magnetic field of 3000 Oe. All the crystalline patterns for Fe-B, Fe-Co-B and Fe-Cr-B are shown over the range of 2θ from 20° to 100° . For comparison, the XRD patterns for

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pure nickel particles are included [Fig. 4.7(iv)]. It is observed that the patterns of Fe-Co-B and Fe-Cr-B are almost the same, except for the difference in the peak height. The 3 peaks between 35° and 70° are consistent with those found by other researches [96, 102, 104]. From Fig. 4.7(iii), it is noted that the Fe-Ni-B does not show the peak at the angle of 98° , while the positions of all other 5 peaks are the same to those of Fe-Co-B or Fe-Cr-B. It means that nickel in the alloy sample affected the crystal structure. To be consistent with pure nickel, the standard pure nickel sample, as shown in Fig. 4.7(iv), also does not exhibit the peak at 98° .

4.3.3 Magnetic properties

The magnetic properties were measured as a function of magnetic field up to 10 kOe at room temperature. Fig.4.8 shows the results for the Fe-Co-B nanoparticles synthesized in the aqueous medium with different contents of ethanol. The sample codes are given in Table 4.1. In the hysteresis loops (Fig. 4.8(i)), we can see that the magnetic loss is very small for all three samples, both with the small magnetic retentivity H_R and the low magnetic coercivity H_C . However, with decreasing particle size, the M_s also decreases. For these Fe-Co-B particles, the maximum M_s is 124 emu/g, which is higher than that of pure Fe_3O_4 (89 emu/g) [94]. The minimum M_s is 74 emu/g at the particle diameter of 35 nm, which is lower than that of pure Fe_3O_4 .

Fig. 4.8 Hysteresis loops and magnetization saturation M_s for the Fe-Co-B particles: (i) hysteresis loops of samples A, D and F (Table 4.1), and (ii) M_s vs the particle diameter d and (ii) M_s vs the particle diameter d .

Fig. 4.9 shows the hysteresis loops for the iron alloy nanoparticles: (i) samples a, e, and g; and (ii) samples b, d, f, and h, as given in Table 4.2, which were synthesized in the absence and the presence of an external magnetic field of 3000 Oe respectively. The values of magnetization saturation M_s are obtained from the hysteresis loops and listed in Table 4.4. Three findings can be attained from Table 4.4. Firstly, in each row

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in Table 4.4 (i.e. with or without a magnetic filed) Fe-B has the highest magnetization saturation, while M_s decreases in an order of Fe-B > Fe-Co-B > Fe-Cr-B > Fe-Ni-B. Fe-Ni-B has the lowest M_s . Secondly, the magnetic field is able to increase M_s by about 5-6% for each type of iron-based alloy. Thirdly, the magnetic losses for all samples are very small.

Fig. 4.9 Hysteresis loops for iron alloy nanoparticles: (i) samples a, e, and g; and (ii) samples b, d, f, and h, as given in Table 4.2.

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Table 4.4 Magnetization saturation of Fe-based alloy nanoparticles synthesized without and with an external magnetic field of 3000 Oe.

Magnetic field applied	Magnetization saturation Ms (emu/g)			
	Fe-B	Fe-Co-B	Fe-Cr-B	Fe-Ni-B
No	144	124	109	91
Yes	153	127	114	96

4.3.4 Thermal stability

Fig. 4.10 TGA curves of Fe-B and other alloy particles, (a) Fe-Co-B particles from the samples (A), (D) and (F), (b) The comparison of Fe-Ni-B, Fe-B and Fe-Cr-N.

To observe the thermal stability of anti-oxidization, thermogravimetric analysis was carried out. In the experiment, a sample about 20 mg was placed in a TGA tray in each experiment. The sample was heated with air flow so as to determine the capability to resist oxidization. Fig. 4.10(a) showed three samples of Fe-Co-B particles with different diameters. At the temperature $T < 300$ °C, the weights of the three samples were kept on decreasing. At this stage, the moisture inside the samples evaporated. Beyond this temperature, the weight of all three samples increased dramatically. It means at about 300 °C, the Fe-Co-B particles could be easily oxidized.

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And also we could see, the oxidization speed is independent of the particle size, because the three kinds of particles of different diameters have the similar oxidization curve.

Fig. 4.10 (b) presented the heating curves of Fe-B, Fe-Ni-B and Fe-Cr-B under air flow. The curves demonstrated the thermal stability of the three types of particles. It is evident that the Fe-Ni-B is the most unstable in air as the weight began to increase from near 200 °C. Its stability was even worse than that of Fe-B, whose weight began to increase from around 300 °C, similar to Fe-Co-B. In the Fe-Cr-B heating curve, the weight was kept on decreasing until 450 °C, which is totally different from the Fe-B, Fe-Co-B and Fe-Ni-B particles. So the nanosized Fe-Cr-B particles were quite stable at temperature below 400 °C.

4.4 Conclusions

In this part, the iron-based alloy nanoparticles have been synthesized using the borohydride reduction method. These magnetic nanoparticles are potentially useful for the fabrication of MR fluids. The effects of ethanol content in the aqueous reaction medium, metal type, and magnetic field on particle size & morphology, crystalline structure and magnetic properties of the magnetic nanoparticles have been systematically studied.

The particle sizes could be easily controlled by the ethanol content in the aqueous reaction medium. For example, by increasing the ethanol content from 0 to 40 vol%, the average diameter of Fe-Co-B particles could decrease from 170 to 35 nm, but the corresponding magnetization saturation M_s changed from 153 to 74 emu/g.

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When a magnetic field was not applied during the synthesis, the nanoparticles were loosely dispersed in the suspension while some short chains were formed for the Fe-B nanoparticles. Under a magnetic field, the particles were nicely aligned in the direction of magnetic field to form the particle chains. More interestingly, the spherical nanoparticles could be squeezed by a strong magnetic field (3000 Oe) into the flat-cake shapes.

The nanoparticles of Fe-B, Fe-Co-B, Fe-Cr-B, and Fe-Ni-B, synthesized in an aqueous solution without ethanol and at a fixed molar ratio of Fe:M = 4:1 where M is Co, Cr, and Ni, always had the following replaced by magnetization saturation M_s : Fe-B > Fe-Co-B > Fe-Cr-B > Fe-Ni-B. A magnetic field of 3000 Oe could enhance M_s by 5-6%. The magnetic losses for all the synthesized nanoparticles were very small. The thermal experiment showed that nanosized Fe-Cr-B particles were quite stable to avoid oxidization in air. They can resist oxidization at high temperature 400°C.

Chapter 5

Magnetorheological Properties of Nano-MR fluids

5.1 Introduction

It has been mentioned in chapter 2, nanosized magnetic particles have good anti-sedimentation property. Ferrofluids have no sedimentation problem, but they also don't show yield stress because of their ultrafine particle size and low magnetization saturation. In the magnetic force equation (2.3)

$$F_{ij} = \frac{\pi d^2 \mu_f \beta_m^2 H_0^2}{16} [\hat{e}_r (1 - 3 \cos^2 \theta) - \hat{e}_\theta \sin 2\theta], \text{ if the particle size } d \text{ is slightly increased}$$

and as well the particle permeability μ_p increased in $\beta_m = \frac{\mu_p - \mu_f}{\mu_p + 2\mu_f}$, F_{ij} may be possibly increased a lot.

It's seen in chapter 4, Fe-Cr-B particles have bigger particle size than magnetite (Fe_3O_4) in ferrofluids. And they also have higher magnetization saturation. Comparing with other Fe-M-B particles, they also have good thermal stability to resist oxidization. In this chapter, the property of MR fluids made from Fe-Cr-B particles will be investigated as follows.

MR properties Firstly the thixotropic property is carried out to confirm whether the flow curve is time related. After that, the shear flow curve and oscillatory properties are investigated.

Sedimentation properties The sedimentation property of nano-MRF will be tested and compared with C-MR fluids.

Rheological model To further understand the dynamic properties, a mathematical model will be constructed, so that the rheological properties are predictable.

5. 2 Experimental Setup

The Fe-Cr-B particles were fabricated following the procedure in Chapter 4 without the application of magnetic fields. The particles were centrifuged at 10000 rpm and then mixed with mineral oil. Here mineral oil was selected because it's thermally stable, has a high boiling point, low freezing point, and it is nontoxic. Also it's non-corrosive and anti-oxidant. Five samples of weight fractions 10wt%, 25wt%, 40wt%, 55wt% and 70wt% were produced. In all the samples, oleic acid was added in to help disperse the particles.

The conventional MR fluid is commercially on sale (MRF-132LD, Lord Co., Germany). This MRF-132LD has the advantage of high yield stress, wide temperature adaptability, low contamination and so on. Its rheological properties had been fully investigated by Dr. Li [58], for comparison usage, some data will be directly taken from his publications.

With the above samples, the rheological properties of nano-MRF were investigated using a controlled stress rheometer (Paar Physica, model MR200), as described in Appendix A.

5.3 Shear Flow Properties of Nano-MR Fluids

Most MR fluids have sedimentation problem, without proper treatment, they may delaminate or the distribution is not uniform. So every time the samples should be stirred sufficiently. To ensure the testing is repeatable, the flow curve of a sufficiently stirred sample is firstly tested as a benchmark. For example, Fig 5.1 plotted the flow curves of MRF-132LD stirred completely at three different times without magnetic fields. It could be seen, the three curves are not completely overlaid, but the gap between any two different testing is quite close. In this report, the flow curve benchmark of all samples at zero magnetic field is obtained first. In future for any experiment, the flow curve of the new sample is tested to compare with the benchmark, if the difference is $\pm 15\%$ of the benchmark, it will be regarded that the sample is uniform, all other experiments can be carried out. If the flow curve is far away from the three curves, the sample should be stirred again.

Fig. 5.1 Flow repeatability testing of MRF-132LD under zero magnetic field.

5.3.1 Thixotropic testing

Before the shear flow study, the thixotropic phenomenon was firstly observed. The purpose is to determine whether the shear stress changes significantly under a constant shear rate [105, 106]. If there is significant change, the viscosity will be a function of time. The thixotropic testing is illustrated in Fig.5.2, at time t_0 , a constant shear rate $\dot{\gamma}_1$ is applied to the system, and then at time t_1 , the shear rate is suddenly changed to $\dot{\gamma}_2$, similarly, $\dot{\gamma}_3$ is applied at time t_3 , then the process repeats the $\dot{\gamma}_2, \dot{\gamma}_1$. Correspondingly, the stress is recorded. As illustrated in Fig. 5.2(b), the stress is attenuated gradually at the same shear strain rate for thixotropic material.

(a)

(b)

Fig. 5.2 Thixotropic behavior illustration, (a) input shear rate $\dot{\gamma}$ vs. time t , (b) output shear stress τ vs. time t .

In our experiments, the above procedure was followed. The shear rates 10s^{-1} , 50s^{-1} , 100s^{-1} , 50s^{-1} and 10s^{-1} were added to the system for 100s in each step, the corresponding shear stress was plotted in Fig. 5.3. In the first case, the magnetic field effect was considered, as shown in Fig. 5.3(a), the sample of $\phi = 40\text{wt}\%$ was sheared with the above shear rate under different magnetic fields. In the second case, the weight fraction effect was considered, as shown in Fig. 5.3(b), all the samples were sheared under the magnetic induction $B = 181\text{mT}$.

In both of the figures, the stress keeps constant at each individual shear strain rate. When the shear rate is suddenly increased or decreased, the stress is also adjusted accordingly. And at the shear strain rate $\dot{\gamma}_1 = 10\text{s}^{-1}$ and $\dot{\gamma}_2 = 50\text{s}^{-1}$, the stresses kept almost the same in two different stage. This experiment confirmed that the shear flow behaviors are time independent, the thixotropic phenomenon doesn't apply to nano-MR fluids.

(a)

Fig. 5.3 Thixotropic experiments on nano-MR fluids, (a) Shear stress vs. time for $\phi = 40\text{wt}\%$ at different magnetic induction, (b) Shear stress vs. time for all samples at $B = 181\text{mT}$.

In Fig. 5.3(a), the MR effect is also displayed. As shown, with increasing magnetic field, the stress is also increased steadily. When the magnetic induction B is increased from 0.0mT , 91mT , 181mT to 272mT , the shear stress at $\dot{\gamma}_1 = 10\text{s}^{-1}$ was increased from 40Pa , 140Pa , 310Pa to 450Pa . Equivalent to magnetic field, the weight fraction effect is also displayed. At the same magnetic induction $B = 181\text{mT}$, the stress is also increased along the weight fraction ϕ .

5.3.2 Steady state shear flow

For all MR fluids, the flow property without magnetic fields is very important. When it's compared with the behavior under magnetic fields, the performance of a MR fluid can already be judged. The zero field shear flow curves of the 5 samples were plotted in Fig. 5.4. All the samples showed Newtonian flow without magnetic fields, even at the highest weight fraction $\phi = 70\text{wt}\%$.

Fig. 5.4 The flow curve of nano-MR fluids at zero magnetic field for the 5 samples.

Fig. 5.5 displays the shear stress of the smallest weight fraction $\phi = 10\text{wt}\%$ and the maximum $\phi = 70\text{wt}\%$ under different magnetic fields. The solid dots in the figures represent the experimental data, and the curves were fitted from H-B model (eq.(2.10)). At the small weight fraction $\phi = 10\text{wt}\%$ in Fig. 5.5 (a), all the stresses almost started from zero and linearly increased along the shear rate. So this behavior can be regarded as Newtonian flow:

$$\tau = \mu \dot{\gamma}, \tag{5.1}$$

where μ is the viscosity. So at very small weight fraction, the nano-MR fluids are not very sensitive to the magnetic field.

Fig.5.5 (b) shows the shear stress of the sample $\phi = 70\text{wt}\%$. With magnetic induction $B = 0.0\text{mT}$, the sample also shows Newtonian behavior. With the increasing magnetic field, the stress is evidently increased. And gradually, the behavior is changed from Newtonian flow to non-Newtonian flow. The stress is doubled at $B = 272\text{mT}$ than that without field at the highest shear rate. John et al. tested the flow properties of nanosized iron particles of 26.5nm with weight fraction $45\text{wt}\%$ [41], as shown in Fig.

5.5(c). This nano fluid has better MR performance than our nano-MR fluids because it has higher stress at the same shear rate, and also lower stress at zero magnetic field. The possible reason is that pure iron magnetic particles synthesized with Microwave Plasma Synthesis (MPS) technique has higher magnetization saturation [41]. But we know nanosized iron particles can be easily oxidized, so that the MR characteristics may disappear after long time of storage.

(a)

(b)

(c)

Fig. 5.5 The shear stress vs. shear rate curves of the samples in different magnetic fields. (a) $\phi = 10\text{wt}\%$, (b) $\phi = 70\text{wt}\%$, (c) iron based nano fluid [41]. The dots represent experimental data, the curves stand for the H-B model fitting in (a) & (b).

Using the H-B model (eq.(2.10)), all the yield stress τ_{yd} and the flow index n in different conditions are listed in Table 5.1. It shows that the yield stress is increased along the magnetic fields, as well the weight fractions. An exponent relation $\tau_{yd} = a\phi^b B^c$ was assumed to relate the yield stress τ_{yd} , the weight fraction ϕ and the magnetic induction B . Using the data listed in table 5.1, By least square method, the relation was found to be

$$\tau_{yd} = 966\phi^{1.3} B^{0.9}. \quad (5.2)$$

The results are shown in Fig. 5.6. All the solid dots represent the yield stress from the H-B model, the curves were the predicted results from formula (5.2). It shows that the formula fits well for the samples $\phi = 40\text{wt}\%$, $55\text{wt}\%$ and $70\text{wt}\%$. But for the lower weight fractions $\phi = 10\text{wt}\%$ and $25\text{wt}\%$, the predicted yield stress was much larger than the value from H-B model. In chapter 2, we have the yield stress $\tau_{yd} \propto H^{1.23}$ for conventional MR fluids [56]. Here for nano-MR fluids, the exponent 0.9 is less than

1.23, which means the magnetic fields have less influence on nano-MR fluids than on conventional MR.

Table 5.1 The fitting parameters using H-B model.

H-B Parameters	Weight fractions	Magnetic induction (Tesla)				
		0.00	0.068	0.136	0.204	0.272
Yield stress (τ_0)	10wt%	0.04	0.20	0.39	0.78	1.46
	25wt%	0.40	13.85	24.11	38.04	50.52
	40wt%	3.32	32.24	52.17	124.88	119.74
	55wt%	9.01	55.43	80.13	125.93	169.83
	70wt%	26.39	72.25	108.70	160.02	228.05
Index n	10wt%	0.99	0.98	0.94	0.88	0.83
	25wt%	0.98	0.80	0.75	0.64	0.55
	40wt%	0.99	0.91	0.69	0.56	0.51
	55wt%	0.98	0.90	0.68	0.48	0.42
	70wt%	0.92	0.81	0.65	0.54	0.46

Fig. 5.6 The yield stress for all the samples. All the solid dots represent the yield stress from the H-B model, the curves were the predicted results from formula (5.2).

5.3.3 Flow curve comparison with MR fluids

To investigate the difference between nano-MR fluids and C-MR fluids, the zero field flow curve is plotted in Fig. 5.7. It's shown that at the same shear rate, the

commercial MR fluids MRF-132LD have smaller shear stress than that of the nano-MR fluids of $\phi = 10\text{wt}\%$. It means nano-MR fluids have higher viscosity than C-MR fluids at zero field magnetic fields. While when the magnetic field is applied, as shown in Fig. 5.8(a), the shear stress of MRF-132LD is much larger than any nano-MR fluids [58]. And the yield stress of MRF-132LD is shown in Fig. 5.8(b), it is about two orders of magnitude higher than that of nano-MR fluids.

Fig. 5.7 Shear flow comparison between nano-MR fluids and MRF-132LD at zero magnetic field.

Fig. 5.8 The flow properties of MRF-132D under different magnetic fields, (a) Shear stress vs shear rate. (b) Dynamic yield stress obtained from H-B model [58].

Back to the table 5.1, the index n can indicate the curvilinear ratio of the flow. It's close to 1.0 for small weight fraction such as $\phi = 10.0\%$ or at low magnetic field. It means the shear flow behavior is closer to Newtonian flow. With the increase of the magnetic field or the weight fractions, n becomes smaller and smaller. For MRF-132LD, the index n can be indicated in Fig. 5.9(a), it should be smaller than the minimum value 0.42 as listed in Table 5.1. It means the shear stress in MRF-132LD is mainly contributed by the yield stress. After the yield stress, there is no significant stress increment. While for nano-MR fluids, after yield stress, the stress increment rate is larger than that of MRF-132LD.

5.4 Oscillatory Properties

Prior to the oscillatory test, a concentrated polymer is used to calibration the sample. As shown in Fig. 5.9, the dynamic moduli were tested both on a Haak rheometer and on the Physica rheometer. It showed both G'' and G' are matched. The figure indicates the Physica rheometer is well working.

Fig. 5.9 Rheometer oscillatory shear check using polymers xantham gum.

Before each oscillatory experiment, the sample was sheared at a constant shear rate $\dot{\gamma} = 10 \text{ s}^{-1}$ for 2 minutes. The oscillation was carried out at least 30 minutes after the completion of the constant shear. The pre-shearing ensures the samples uniformly distributed between the two plates, and 30 minutes was held to guarantee the sample was recovered from shearing. In all the strain amplitude sweeping, the frequency was fixed at $\omega = 2.0 \text{ Hz}$ all along.

5.4.1 Strain amplitude dependence

Firstly the strain amplitude oscillation was carried out to identify the strain over which the linear viscoelasticity holds. Fig. 5.10 shows the storage modulus of two samples under 5 different magnetic fields. At $\phi = 10\text{wt}\%$, the suspension is totally in fluidic status at $B = 0.0\text{mT}$, and although there is magnetic field, the strain amplitude cannot be started from a very small value such as $\gamma_0 = 0.1\%$. When increasing the magnetic field, the linear range can be displayed. The amplitude of the storage modulus was increased and the sample becomes more rigid. Under magnetic fields, the particles are chained up along the magnetic line, forming a gel-like system. With a larger weight fraction $\phi = 55\text{wt}\%$ as shown in Fig. 5.10(b), the linear range of the strain amplitude is exposed. There is a plateau for the G' under different magnetic fields. And with increasing the magnetic field, the linear strain range became smaller and smaller. From $B = 0.0\text{mT}$ to $B = 272\text{mT}$, the critical linear strain is decreased from 0.1% to 0.01% , which means the material is harder at higher magnetic field than that at lower magnetic field.

Fig.5.10 The storage module of nano-MRF under different magnetic fields (a) $\phi = 10\text{wt\%}$, (b) $\phi = 55\text{wt\%}$.

The above phenomenon can be explained in Fig. 5.11. When there is no magnetic field, the nanosized particles are randomly distributed in the carrier media, as illustrated in Fig. 5.11(a) and (b). Once the magnetic field is applied, the particles are polarized. In a uniform magnetic field, these particles adjust their position to the magnetic line, which are shown in Fig. 5.11(c) and (d).

Fig. 5.11 The structure of nanosized magnetic particles with/without the magnetic field, (a) the model of particles without magnetic field, (b) the actual structure of particles in fluids without magnetic fields, (c) the model of particles in magnetic field, (d) the actual structure of particles in magnetic fields.

Fig. 5.12 displays the loss moduli for the sample $\phi = 10\text{wt}\%$ and $\phi = 55\text{wt}\%$ under different magnetic fields, which are the counterparts of the storage moduli in Fig. 5.11. For the sample $\phi = 10\text{wt}\%$, the loss moduli keep on growing in higher magnetic fields before they suddenly dropped off. While for the sample $\phi = 55\text{wt}\%$, there is an overshoot between linear and nonlinear stage. It indicates that a higher energy is needed to destroy the structure.

Fig.5.12 The loss moduli of nano-MRF under different magnetic fields (a) $\phi = 10\text{wt}\%$, (b) $\phi = 55\text{wt}\%$.

Fig. 5.13 Strain amplitude sweeping for MRF-132LD [58].

Fig. 5.13 displayed the dynamic moduli of MRF-132LD at $B = 340\text{mT}$ [58]. The value of G' is so large which is close to the elastic modulus of a solid. While G'' is also quite large showing their viscous property. In the figure, the critical strain γ_{lin} is defined as the linear range. During this range, the loss modulus G'' is kept on increasing, and after the critical strain, it began to decrease. So there is an overshoot for G'' and it has no linear range.

As can be compared in Fig. 5.10, Fig. 5.12 and Fig. 5.13, the G' and G'' of nano-MR fluids are about 10^3 times smaller than that of MRF-132LD. Fig. 5.14 shows the ratio of G''/G'_0 for nano-MRF $\phi = 55\text{wt}\%$ (G'_0 is loss modulus at the beginning of the linear range γ_{lin}). Under lower magnetic fields, the ratio is kept at 1.0 until $\gamma_0 = 0.1\%$, afterward there is an overshoot. Under higher magnetic fields, the overshoot disappeared. Fig. 5.12(a) indicates that for $\phi = 10\text{wt}\%$, there are overshoots for G'' under all magnetic fields. Combining the behaviors of the samples $\phi = 10\text{wt}\%$ and $\phi = 55\text{wt}\%$, we can see that when G'' is less than 100Pa , the overshoot will happen.

According to the classification from Sim, Ahn and Lee, there are 4 types of oscillatory behavior for polymers, as shown in Fig. 5.15 [107]. In the figure, G'_0 and G''_0 are the

storage and loss moduli in the plateau stage. When $G'' < 100\text{Pa}$, the behavior of nano-MRF is quite similar to the type shown in Fig. 5.15(c)). While when $G'' > 100\text{Pa}$, the behavior is similar to that shown in Fig. 5.15(a).

Fig. 5.14 The ratio of G''/G' in strain amplitude sweeping for nano-MRF $\phi = 55\text{wt}\%$ under different magnetic fields.

Fig.5.15 The 4 types of LAOS behavior: (a) strain thinning; (b) strain hardening; (c) weak strain overshoot; (d) strong strain overshoot [107].

5.4.2 Frequency dependence

In the strain amplitude oscillation, the linear range of the sample $\phi = 10\text{wt}\%$ doesn't exist. While it can be easily detected for all the other samples, such as for $\phi =$

55wt% in Fig. 5.12(b). In frequency oscillation, the strain amplitude is set at the transitional point from linear to nonlinear. Fig. 5.16 displays the dynamic moduli for samples $\phi = 40\text{wt}\%$ and $\phi = 70\text{wt}\%$. In small frequencies, the storage modulus keeps constant, while it increases when the frequency continues to increase, as shown in Fig. 5.16(a) and (c). However, the loss modulus began to increase at the beginning of oscillation (Fig. 5.16(b) and (c)). The dynamic moduli for MRF-132LD are shown in Fig. 5.16. Contrary to nano-MR fluids, G' is increasing all the way along the frequency, while G'' keeps at constant.

Fig. 5.16 The frequency dependence for two samples under different magnetic fields, (a) storage modulus G' for $\phi = 40\text{wt}\%$, (b) loss modulus G'' for $\phi = 40\text{wt}\%$, (c) storage modulus G' for $\phi = 70\text{wt}\%$, (d) loss modulus G'' for $\phi = 70\text{wt}\%$.

Fig. 5.17 Frequency dependence of storage modulus G' , loss modulus G'' for MRF-132LD at $\gamma_0 = 0.05\%$, $B = 340\text{mT}$, $T = 20^0\text{C}$ [58].

Fig. 5.18 Loss factors of the nano-MR fluids in different magnetic fields, (a) $\phi = 40\text{wt}\%$, (b) $\phi = 70\text{wt}\%$, (c) the illustration of $\tan(\delta)$.

Fig. 5.18 shows the loss factor $\tan(\delta) = G''/G'$ along the frequency. This ratio represents the rigidness of a material. It is defined that the material is more solid-like when $\tan(\delta) < 1.0$, while it's more fluid-like when $\tan(\delta) \geq 1.0$ [49]. In the figures, $\tan(\delta) \geq 1.0$ happens only at the peak for sample $\phi = 40\text{wt}\%$ when there is no magnetic field. It means the material will behave more fluid-like during the corresponding frequency range. It's interesting to find that below 1.0Hz, $\tan(\delta)$ almost keeps constant under different magnetic fields. It starts to increase after 1.0Hz. Between 20 and 30Hz, it arrived to its peak position and dropped off afterward. We can expect at much higher frequency $\omega > 100\text{Hz}$, the $\tan(\delta)$ becomes even smaller.

The information of $\tan(\delta)$ is quite useful for the application of nano-MR fluids. As shown in the illustration of Fig. 5.18(c), there is an overshoot for $\tan(\delta)$ over the frequency range where it's several times larger than that at other positions. And at the overshoot stage, the fluids are softer. So when designing a nano-MR device, the range of the high loss factor should be taken into consideration.

5.5 Sedimentation Properties

The density of metallic particles is much larger than that of mineral oil or polymers. So the gravity will draw the heavier particles down to the bottom. The addition of filler or surfactant can help decrease the sedimentation speed, and even after sedimentation, the particles can be re-dispersed. In a fluid, all the small particles are randomly moving because of the Brownian motion, the smaller the particle size, the more active the particles move. Fig. 5.19(a) showed the samples of ferrofluids, nano-MRF ($\phi = 70\text{wt}\%$) and MRF-132LD. The testing method is illustrated in Fig. 5.20, a sample with volume V_0 was stirred sufficiently and placed on a desk. After

some hours, the superficial transparent solution V_I was sucked out using a syringe. So the sedimentation ratio ν is calculated by $\nu = V_I/V_0$ as plotted in Fig. 5.19(b). There is no sedimentation found from ferrofluids. While for nano-MRF and MRF-132LD, the sedimentation is mainly happened in the first 12 hours. That after 12 hours 10wt% carrier liquid was sucked out from the nano MR Fluids, and 14% from MRF-132LD. When the test was finished, more solution was separated from MRF-132LD.

Fig. 5.19 The sedimentation experiments, (a) ferrofluids, (b) nano-MR fluids, (c) MRF-132LD, (d) the sedimentation curve.

Fig. 5.20 The illustration of sedimentation testing.

Although both nano-MR fluids and MRF-132LD have sedimentation issue, we had to point out that the re-dispersive ability is quite different. We used a muddler to stir

these two fluids after 3 days, and found nano-MR fluids is easily stirred, while a certain force needed to stir MRF-132LD.

5.6 Oscillatory Modeling

An MR fluid has the common characteristics that a suspension has. Its distinguishing feature is the response under magnetic fields. During oscillation, there is competition between breakdown under shearing and build-up of the structure under magnetic fields. In this work, we use the modified upper convected Jeffreys model to describe the microstructure evolutions [108]. This idea is originated from structured network model for polymers [109]. They assumed that the total stress contains two items,

$$\sigma = \sigma^e + \eta_m \dot{\gamma}, \quad (5.3)$$

σ^e is the viscoelastic item from the interactions between the particles and the magnetic fields. $\eta_m \dot{\gamma}$ is the viscous item where η_m is the suspension viscosity in the absence of interactions. The viscoelastic item is described by a Maxwell type equation:

$$\frac{1}{G} \frac{\partial \sigma^e}{\partial t} + \frac{\sigma^e}{\eta(\xi)} = \dot{\gamma}, \quad (5.4)$$

where G is the elastic modulus of the structure and $\eta(\xi)$ is the viscous item that depends on the structural factor ξ . This factor is proportional to the total number of bonds and can be determined from the following kinetic equation:

$$\chi(\xi, \dot{\gamma}) \frac{\partial \xi}{\partial t} + \frac{1 - \xi}{\theta} = \xi \frac{\dot{\gamma}}{\gamma_c}, \quad (5.5)$$

where γ_c is the yield strain, θ is a characteristic time and χ is a kinetic function. The viscosity and the structural factor are related to the following empirical relation:

$$\eta(\xi) = \frac{\eta_p}{f(\xi)}. \quad (5.6)$$

with

$$f(\xi) = \frac{\xi^{1-n} - 1}{n}, \quad (5.7)$$

where n is an empirical parameter. For steady state conditions, $n = 0$, equations (5.4) to (5.5) reduce to the Bingham model. This model provides only a qualitative description of the dynamic behavior of colloidal suspensions as shown by Yziquel *et al* [108]. The model is shown to correctly predict decrease of the elastic modulus with increasing strain amplitude above a critical strain. However, the values of the loss modulus are considerably overestimated.

Based on the ideas of Marrucci *et al.* [110, 111] and Coussot *et al.* [112], the nonlinear behavior of concentrated suspensions is assumed to be the characteristics of the interactive particles, the flow properties are controlled by the simultaneous breakdown and the build-up of the suspension microstructure. The total stress contains a viscoelastic contribution due to interactions among particles and the shear stress from the carrier medium. The stress is expressed in a modified upper convected Jeffreys model with a single relaxation time:

$$\frac{\delta}{\delta t} \left[\frac{\sigma}{G(\xi)} \right] + \frac{\sigma}{\eta(\xi)} = \left(1 + \frac{\eta_\infty}{\eta(\xi)} \right) \dot{\gamma} + \eta_\infty \frac{\delta}{\delta t} \left(\frac{\dot{\gamma}}{G(\xi)} \right), \quad (5.8)$$

with

$$G(\xi) = G_0 \xi + G_\infty, \quad (5.9)$$

where η_∞ and G_∞ are the viscosity and the elastic modulus respectively for the destroyed structure and the solvent. $G_o + G_\infty$ is the equilibrium value of the elastic modulus of the structure. We assume that the modulus depends on the structural parameters as proposed by Marrucci et al. [113]. The modulus varies from $G_o + G_\infty$ for a completely structured network to G_∞ for a completely breakdown system, $\delta / \delta t$ is the upper convected derivative defined by

$$\frac{\delta \sigma}{\delta t} = \frac{d\sigma}{dt} - \nabla v \cdot \sigma - \sigma \cdot (\nabla v)^T, \quad (5.10)$$

$\eta(\xi)$ is the structural viscosity. But the viscosity is defined by the following relationship:

$$\eta(\xi) = \frac{\eta_0}{f(\xi)}, \quad (5.11)$$

where η_0 is the characteristic viscosity, and $f(\xi)$ is an empirical structural function given by the following relation,

$$f(\xi) = \left(\frac{1}{\xi} - 1 \right)^{\frac{(1-n)}{2}}. \quad (5.12)$$

The structural evolution parameter, ξ can be interpreted in terms of the second invariant of the rate-of-strain tensor, $II_{\dot{\gamma}}$. A kinetic equation is given assuming that the breakdown of the structure is controlled by $II_{\dot{\gamma}}$. The evolution of microstructure is given by the following equation [114],

$$\frac{\lambda_0}{k_1} \frac{\partial \xi}{\partial t} = (1 - \xi) - \frac{k_2}{k_1} \xi (\lambda_0 \dot{\gamma})^2. \quad (5.13)$$

Via the above equation, the structure breakdown is directly proportional to the dissipated power.

In the model, there are seven adjustable parameters G_0 , G_∞ , k_1 , k_2 , λ_0 (or η_0), η_∞ and n .

The parameter n , m , η_∞ can be obtained from a power law expression,

$$\eta = \eta_\infty + m\dot{\gamma}^{(n-1)} . \tag{5.14}$$

All the parameters in different weight fractions and magnetic fields were curve fitted and listed in Table 5.2. Those parameters can well express the shear thinning behavior of nano-MR fluids, as shown in Fig. 5.21. The model is deviated from the experimental results in the stage of large shear rate, which means the parameters η_∞ is not accurate all the time.

Table 5.2 The model $\eta = \eta_\infty + m\dot{\gamma}^{(n-1)}$ parameters for all the samples.

Weight fractions	Fitting parameter	Magnetic induction B (mT)				
		0	68	136	204	272
10wt%	η_∞	1.89	2.02	1.7	1.78	2.22
	m	2.88	3.15	7.75	13.39	15.38
	n	0	0.17	0.47	0.42	0.35
25wt%	η_∞	1.69	1.75	1.69	2.08	1.51
	m	2.43	15.45	33.63	60.28	105.39
	n	0	0.29	0.29	0.25	0.23
40wt%	η_∞	2.02	1.9	1.84	2.88	2.77
	m	5.37	12.89	48.31	122.81	225.17
	n	0	0.31	0.31	0.23	0.19
55wt%	η_∞	1.74	1.92	1.22	1.44	3.01
	m	5.88	46.56	122.76	240.1	351.26
	n	0.33	0.15	0.23	0.22	0.19
70wt%	η_∞	2.58	2.77	2.55	3.57	3.85
	m	28.6	69.07	117.58	186.89	329.32
	n	0	0.12	0.22	0.2	0.19

Fig. 5.21 The shear viscosity vs. shear rate at $B = 136\text{mT}$ for all the samples, the solid curves were fitted using the model $\eta = \eta_{\infty} + m\dot{\gamma}^{(n-1)}$.

Table 5.3 The experimental and curve fitted G'_0 comparison.

Magnetic field (mT)	Results	Weight fraction (%)				
		0.10	0.25	0.40	0.55	0.70
68.00	Experimental	17.40	104.30	235.20	429.80	825.00
	Curve fitting	64.00	122.20	233.20	445.10	849.70
136.00	Experimental	53.20	520.20	850.00	1410.00	2519.00
	Curve fitting	176.00	336.00	641.40	1224.40	2337.20
204.00	Experimental	83.10	850.00	2019.00	4102.00	5142.00
	Curve fitting	484.20	924.30	1764.40	3367.90	6428.80
272.00	Experimental	114.00	1609.00	5610.00	9415.00	17836.00
	Curve fitting	1331.90	2542.40	4853.10	9263.90	17683.30

The model is expected to predict the mechanical behaviors with limited parameters. Here the maximum storage modulus G'_0 was captured, its relation with the magnetic field and weight fractions is assumed to follow

$$G'_0 = a \exp(b\phi + cB). \tag{5.15}$$

Using the least square method, the parameters are $a = 15.12$, $b = 4.31$, $c = 14.88$. So finally the relation is $G'_0 = 15.12 \exp(4.31\phi + 14.88B)$. Table 5.3 listed the comparison between the experimental and curve fitted data. From the table, we can see the formula is good to predict the G'_0 for higher weight fractions. At low weight fractions, the value shows several times larger than the experimental results.

The equation (5.8) can be reduced to

$$\begin{aligned} \frac{\partial \sigma_{12}}{\partial t} + \left(G(\xi) \frac{f(\xi)}{\eta_0} - \frac{G_0}{G(\xi)} \frac{\partial \xi}{\partial t} \right) \sigma_{12} = \\ \left(G(\xi) \left(1 + \frac{\eta_\infty f(\xi)}{\eta_0} \right) - \eta_\infty \frac{G_0}{G(\xi)} \frac{\partial \xi}{\partial t} \right) \dot{\gamma} + \eta_\infty \frac{\partial \dot{\gamma}}{\partial t} \end{aligned} \quad (5.16)$$

For steady state shear flow, $\frac{\partial \sigma_{12}}{\partial t} = 0$, $\frac{\partial \dot{\gamma}}{\partial t} = 0$ and $\frac{\partial \xi}{\partial t} = 0$. Therefore, the eq. (5.16)

reduced to $\left(\frac{f(\xi)}{\eta_0} \right) \sigma_{12} = \left(1 + \frac{\eta_\infty f(\xi)}{\eta_0} \right) \dot{\gamma}$. Eq. (5.13) is reduced to $\frac{(1-\xi)}{\xi} = -\frac{k_2}{k_1} (\lambda_0 \dot{\gamma})^2$.

Together with eq. (5.12), the equation can be easily solved to obtain the steady shear viscosity by:

$$\eta(\dot{\gamma}) = \frac{\sigma_{12}}{\dot{\gamma}} = \eta_0 \left(\sqrt{\frac{k_2}{k_1}} \lambda_0 \dot{\gamma} \right)^{n-1} + \eta_\infty. \quad (5.17)$$

In the equation, $m = \eta_0 \left(\sqrt{\frac{k_2}{k_1}} \lambda_0 \right)^{n-1}$, and the parameters m , n , η_∞ can be obtained from the table 5.2.

Equation (5.13) and (5.16) can be numerically solved to predict the dynamic properties of suspensions using a fifth order Runge-Kutta method [108]. Above a critical strain, the output signal waveform is no longer sinusoidal. Therefore, the

elastic and viscous moduli are taken as the first harmonics of the output signal determined using a Fast Fourier Transform. In this study, all dynamic moduli are obtained from steady wave output signals corresponding to pseudo-steady structural states. Therefore, the value of k_I has no influence on the dynamic moduli predictions at low strain values. For the suspensions composed of interactive particles, the elastic modulus depends slightly on the frequency at small strain amplitude, then $G_0 + G_\infty$ is obtained from the experimental value at small frequencies. The ratio k_2/k_I was set at the critical strain from which the elastic modulus begins to decrease. $G_0/(G_0+G_\infty)$ controls the slopes of the elastic modulus after the critical strains. For the rate-dependent models, little influence of the parameter is noted and the viscous modulus is controlled by the characteristic time λ_0 .

Fig. 5.22 shows the stress vs. time in three strain amplitudes during oscillation for the sample $\phi = 40\text{wt}\%$ at $B = 136\text{mT}$ and $\omega = 2.0\text{ Hz}$. As the strain is increasing, the stress is effectively increased. Under any of the four strains, the stress shape showed deviation from standard sinusoidal function. It means under these strain amplitudes, the oscillation is large amplitude oscillatory shear (LAOS), the stress can be reduced to several trigonometric functions as

$$\tau = \tau_0 \sin(\omega t + \delta_1) + \tau_1 \sin(3\omega t + \delta_2) + \tau_3 \sin(5\omega t + \delta_3) + \dots \quad (5.18)$$

where τ_0, τ_1, τ_2 are the first, second and third primary stress. And $\delta_1, \delta_2, \delta_3$ the corresponding phase angles. As shown in Fig. 5.22, the waveform shifted more from the standard sinusoid when the strain was increased.

Fig. 5.22 The strain amplitude effect based on the sample $\phi = 40\text{wt}\%$ at $B = 136\text{mT}$ and $\omega = 2.0\text{Hz}$.

Fig. 5.23 The η_∞ effect based on the sample $\phi = 40\text{wt}\%$ at $B = 136\text{mT}$, $\omega = 2.0\text{Hz}$ and $\gamma_0 = 1.0\%$.

As previously mentioned, the curve fitting parameter η_∞ is deviated from the experiments. In the equation (5.21), different η_∞ is assumed, the sample $\phi = 40\text{wt}\%$ at $B = 136\text{mT}$ is selected as an example, which is shown in Fig. 5.23. Although η_∞ is varied from 0.5 to 3.0 shown in table 5.2, there is no difference found in the stress curve. Therefore, the value of η_∞ has no effect on the dynamic stress τ .

Fig. 5.24 The parameters k_2/k_1 effect for the sample $\phi = 40\text{wt}\%$ at $B = 136\text{mT}$ at different strain amplitude. (a) $\gamma_0 = 0.1\%$, (b) $\gamma_0 = 1.0\%$, (c) $\gamma_0 = 10\%$.

Fig. 5.24 displays the stress dependence on the adjustable parameter k_2/k_1 . Three strain amplitudes are compared. At very small strain $\gamma_0 = 0.1\%$, the sample $\phi = 40\text{wt}\%$ is in linear status, whatever the k_2/k_1 changed from 50 to 5000, the stress curves are all the same (Fig. 5.24(a)). At strain $\gamma_0 = 1.0\%$, the stress begins to show some difference from sinusoidal wave (Fig. 5.24(b)). It starts to change from linear to nonlinear stage. And in Fig. 5.24(c) at $\gamma_0 = 10\%$, the dynamic stress is definitely in nonlinear status, so the stress deviated accordingly along k_2/k_1 .

Fig. 5.25 shows the effect of the parameter λ_0 on the dynamic stress. First of all, we can see λ_0 has a deep effect on the amplitude of the stress. At two very small values $\lambda_0 = 9.4\text{E-}6$ and $\lambda_0 = 9.4\text{E-}5$, the dynamic stress is periodically repeated with irregular sinusoidal curves. When λ_0 increases, the waveform goes to regular, but the stress amplitude is quite different from each other.

Fig. 5.25 The effect of the parameter λ_0 on the dynamic stress.

Fig. 5.26 The stress dependence on the exponent n .

Table 5.4 The parameters of simulations at B = 136mT.

Weight fractions ϕ	n	G_0	η_∞	k_2/k_1	λ_0	m	η_0
10wt%	0.30	176.00	2.50	500.00	9.4E-4	7.75	0.76
40wt%	0.30	641.40	2.50	500.00	9.4E-4	48.31	4.76
70wt%	0.30	2,337.20	2.50	500.00	9.4E-4	117.58	11.58

According to the above factors study, all the parameters to be used in this project are listed in Table 5.4. The parameters k_2/k_1 , λ_0 are adjusted and taken from Fig. 5.23 and Fig. 5.24. Through those values including m , the value η_∞ can be resulted.

(a)

(b)

(c)

Fig. 5.27 Storage and loss moduli vs. strain amplitude at frequency $\omega = 2\text{Hz}$ with the magnetic induction $B = 136\text{mT}$. (.) the experimental storage modulus, (B) the experimental loss modulus, (□-□) simulated storage modulus, (□X□) simulated loss modulus. (a) $\phi = 10\text{wt}\%$, (b) $\phi = 40\text{wt}\%$, (c) $\phi = 70\text{wt}\%$.

Fig. 5.27 reported the simulated storage and loss moduli at 2.0Hz vs. the strain amplitude for three different samples at $B = 136\text{mT}$. The storage moduli, shown in the three figures, are constants up to a critical strain $\gamma_0 = 1.0\%$. These constants keep in the same level of the corresponding experimental data. After the critical strain, the storage modulus drops faster than the experimental G' . The loss modulus, is considerably smaller than the storage modulus in the model. But it's still larger than the experimental results. Same to the storage modulus, it also drops faster than the experimental G'' . However, the transitional point from linear to nonlinear is almost coincided with the experimental G'' .

5.7 Conclusions

In this chapter, the rheological properties of nano-MR fluids were carefully investigated and compared with MRF-132LD. The results are summarized as follows:

The flow of nano-MR fluids is not thixotropic, the shear stress is independent of time at a fixed shear rate. The flow curve under continuous shear rate can be characterized using H-B model, which is also applicable to MRF-132LD. However, the exponent index n of C-MR fluids is much smaller than that of nano-MR fluids, which means the shear stress increment ratio of nano-MRF is larger than that of MRF-132LD.

Without magnetic fields, nano-MR fluids don't show yield stress, as well as MRF-132LD. While under magnetic fields, their yield stress will be displayed. Although it is not very large, comparing with ferrofluids, the MR effect is much stronger. The yield stress of nano-MR fluids was also compared with that of MRF-132LD. it is about two orders of magnitude smaller than that of nano-MR fluids.

In strain amplitude oscillation, an overshoot was found in G'' when it's smaller than 100Pa. And in the linear range, there are plateau for both G'' and G' . While for MRF-132LD, the plateau only happened to G' . In frequency oscillation, G' kept constant and increased at higher frequency, while G'' kept on increasing from the start of oscillation. And it was found that in the scanned frequency range, there was an overshoot for $\tan(\delta) = G''/G'$. It means for different nano-MR fluids, there is a softening stage in the whole frequency, as shown in Fig. 5.17(c).

Both nano-MR fluids and conventional MR fluids have sedimentation issue, Comparing with micro-sized iron particles in MRF-132LD, nanosized iron particles settle slower. Even after sedimentation, nano-MR fluids are easier to be re-dispersed than conventional MR fluids.

The dynamic properties of nano-MR fluids have been simulated using the convected Jeffreys model. The results showed that the model cannot perfectly describe the dynamic behavior of nano-MR fluids, but it can tell the tendency of G' and G'' .

As a conclusion, nano-MR fluids have smaller yield stress than conventional MR fluids, but comparing with ferrofluids, it's a big improvement. And we also achieved our purpose that nano-MR fluids were more stable than C-MR fluids from anti-sedimentation. It can be seen, the produce of nano-MRF is compromised between the yield stress and the sedimentation.

Chapter 6

The Rheological Study of Ferrofluid Based MR Fluids

6.1. Introduction

In chapter 5, nanosized MR fluids have been investigated, they have good property to reduce sedimentation. But comparing with C-MR fluids, they have relative higher zero field viscosity, and under the same magnetic field, the yield stress of nano-MR fluids is far less than that of C-MR fluids. Ferrofluids have no sedimentation issue, but the MR sensitivity is very weak. Taking the advantage of both ferrofluids and C-MR fluids, these can be mixed to form ferrofluids based magnetorheological fluids (F-MRF). As demonstrated, the anti-sedimentation was significantly improved comparing with conventional MR fluids using kerosene oil or silicone oil as liquid phase [34]. Shimada et al. have obtained such kind of MR fluids, and named them as magnetic compound fluids (MCF) [115-117]. John et al. produced three different MR fluids using 30 μ m iron particles and 26nm iron particles [41]. They stated the hybrid MR fluids of 30 μ m and 26nm iron particles have much better anti-settling property than MR fluids from 30 μ m iron particles. Odenbach predicted that the ferrofluids based MR fluids or the hybrid of nanosized and micro-sized particles would be the trend of MR fluids [118]. Experiments have shown the yield stress of the hybrid magnetic fluids is compatible with conventional MR fluids [119]. These hybrid magnetic fluids are stable even after the removal of magnetic fields [41, 119].

In this chapter, the properties of ferrofluids based MR fluids (F-MRF) will be investigated,

- (1) The structures of these two difference systems are to be compared. When micro-sized iron particles are added into ferrofluids, under magnetic fields, there are interactions between small and big particles, so the interaction is studied.
- (2) The flow property may be different in the on/off status of magnetic fields. Under magnetic field, the yield stress and shear flow curves will be investigated and compared with MRF-132LD.
- (3) Oscillatory properties. Similar to chapter 5, the dynamic rheological properties of F-MRF will be studied and compared with MRF-132LD.
- (4) Creep-recovery properties. Under magnetic fields, F-MRF fluids become viscoelastic solid-like material. So similar to those materials, F-MRF will show elongation under constant shear stress, and will recovery when the stress was removed. All these unknown information will be studied.

6.2 Sample Preparation and Particle Structures

Micro-sized iron particles (Fe) and ferrofluids are the main sources for MR fluids. The iron particles were from Aldrich of spherical shape with average diameter $d = 4.5\mu\text{m}$. Ferrofluids were from Ferrotec used as carrier media. Four different samples of weight fractions $\phi = 20\text{wt}\%$, $\phi = 40\text{wt}\%$, $\phi = 60\text{wt}\%$ and $\phi = 80\text{wt}\%$ were prepared. Each sample was manually stirred for 30 minutes, and then it was vibrated under ultrasonic for 15 minutes. Similar to the method in chapter 5, a flow curve

benchmark at zero magnetic field was established for reference. The uniformity of the sample in each experiment is referred to the benchmark.

(a)

(b)

Fig.6.1 SEM photograph for F-MR fluids, (a) zero magnetic field, (b) under a medium magnetic field.

Fig. 6.1 showed the F-MRF particles observed in SEM. The micro-sized iron particles were clearly shown in the micrograph with an average diameter $4.5\mu\text{m}$. However, the nanosized Fe_3O_4 particles cannot be seen under SEM. Without magnetic field, the particles were randomly distributed (Fig. 6.1 (a)). Within magnetic fields, the particles aligned themselves in columns in the magnetic field direction (Fig. 6.1 (b)).

The interaction between micro-sized iron particles and nanosized particles has been studied by many people. López- López and Vicente took the particle picture without magnetic field using TEM [34]. As shown in Fig. 6.2(a), there are numerous ultrafine small particles attached on the big micro-sized iron particles. Shimada et al. proposed the model of particles interaction, as shown in Fig.6.2(b) [115]. The magnetite particles were attached on micro-sized iron particles, so that the micro-sized iron particles are separated by the ultrafine magnetite particles, which prevent them coming closer.

Fig. 6.2 Hybrid MR fluids, (a) micro-sized iron particles in ferrofluids $\phi = 40\text{wt}\%$ under magnetic fields [34], (b) Model of particles of MCF in magnetic fields [115].

In our research, the size of the iron particles is several hundreds of that of Fe_3O_4 in ferrofluids, it's impossible to clearly observe both of them using SEM or TEM. In order to mimic the particle interaction, we purposely use nanosized nickel particles to replace the micro-sized iron particles. Fig. 6.3 displayed the mixture of nickel and Fe_3O_4 particles in ferrofluids. It could be seen, the nickel particles are suspended in ferrofluids with diameter about 50-70nm. The hydrodynamic force stabilizes the nickel particles in ferrofluids. The small Fe_3O_4 particles have high surface energy, they were easily attached onto the surface of nickel particles. We found that the iron particles can be agglomerated with Fe_3O_4 particles, they can even form an agglomeration with a certain weight ratio of micro-sized iron particles and magnetite particles. But the agglomeration was suspended in ferrofluids, and they can be easily re-distributed after stirring.

Fig. 6.3 TEM photograph of nickel particles (nanosize) in ferrofluids.

Fig. 6.4 The sedimentation of F-MRF and MRF-132LD, (a) F-MRF, (b) MRF-132LD, (c) Sedimentation comparison between nano-MRF, F-MRF and MRF-132LD.

Fig. 6.4 (a) shows the sample of F-MRF, the iron particles are mixed in ferrofluids, there is no clear delamination between the micro-sized iron particles and ferrofluids. The sample of MRF-132LD is shown in Fig. 6.4(b) for comparison, the oil is totally segregated. Furthermore, the sedimentation comparison is shown in Fig. 6.4(c). It could be seen, the sample MRF-132LD settled faster than F-MRF and nano-MR fluids.

There are several possibilities for the better anti-sedimentation of F-MRF. The first reason is shown in the above Fig. 6.2 and Fig. 6.3, the ultrafine nano-sized magnetite particles are attached on the micro-sized iron particles. They keep these iron particles uniformly distributed with less agglomeration. Secondly, at zero magnetic field, the viscosity of ferrofluids is $\eta = 1 \text{ Pa S}$, while the viscosity of mineral oil for conventional MR fluids is less than 0.1 PaS . The force preventing particles from settling can be expressed by Stokes drag force mentioned in chapter 2 [110],

$$F^{hydro} = -3\pi\eta_f d_0 \left(\frac{dr_i}{dt} - v(r, t) \right) \quad (6.1)$$

The Stokes drag force can greatly decrease the sedimentation speed because the viscosity of ferrofluids is much higher than that of commercial mineral oil. Thirdly, in the expression $\beta_m = \frac{\mu_p - \mu_f}{\mu_p + 2\mu_f}$, the magnetic permeability of ferrofluids is $\mu_f = 1.1 - 8.0$ [120], which makes β_m smaller than other non-magnetic fluids. Therefore the particle interaction force F_{ij} (eq.(2.5)) will be weakened, the particles can be re-dispersed easily even after sedimentation. Besides, ferrofluids have higher density than those oils, the buoyancy of micro-sized iron particles in ferrofluids is also higher, which also contributes to the stability of MR fluids using ferrofluids as media.

6.3 Steady State Flow

Similar to those stated in chapter 5, the overall rheological properties of F-MRF were evaluated using the MR rheometer. In all the experiments, the temperature was controlled at around 25°C by the cooling system.

The fluids were initially sheared ($\dot{\gamma} = 10\text{s}^{-1}$) at zero magnetic field for 2 minutes to distribute the particles. The shear rate was started from 400s^{-1} to 0.1s^{-1} logarithmically in 2 minute. Before the shear rate was applied, the magnetic field was stabilized through adjusting the electric current. The dynamic yield stress was obtained by extrapolating the stress-shear rate data to zero shear rate [47].

Fig.6.5 displays the flow curves of F-MRF in different conditions. The continuous curves were fitted using the H-B model by least square method. Without magnetic field (Fig. 6.5(a)), the stress curves are almost straight lines starting from zero for the first three samples. When increasing the weight fraction to $\phi = 80\text{wt}\%$, the flow line is curved. As a comparison, the flow behavior of nano-MR fluids, F-MRF and MRF-132LD were shown in Fig. 6.5(b). We can see, the nano-MR fluids have larger zero field viscosity because the stress is larger than others. The stress of MRF-132LD is between the F-MR fluids of $\phi = 80\text{wt}\%$ and $\phi = 60\text{wt}\%$, which means under the same volume fraction, the viscosity of MRF-132LD is also smaller than that of F-MR fluids.

(a)

Fig. 6.5 The flow curve comparison at zero magnetic field, (a) F-MRF at zero field, (b) flow curves of nano-MR fluids, F-MRF and MRF-132LD.

Fig. 6.6 Flow curves for F-MRF, (a) Different weight fraction with $B = 254\text{mT}$, (b) $\phi = 60\text{wt}\%$ at stepped magnetic induction. The solid points represent the experimental data, and the continuous curves represent the H-B model.

At $B = 254\text{mT}$ shown in Fig. 6.6, the stress is bumped into a big value several hundreds times of that at $B = 0.0\text{ mT}$. The magnetic field has such a pronounced effect, which is much more influential than the weight fraction. Fig. 6.5(c) show the flow curves of sample $\phi = 60\text{wt}\%$ under different magnetic fields, it can be seen the magnetic field is very encouraging because whenever the magnetic induction B is increased 50mT , the stress is increased one or a half time of the previous value.

Similar to our experiments, Shimada et al. have produced a Magnetic Compound Fluid (MCF) composed of 10nm magnetite and $1.2\text{--}1.6\text{ }\mu\text{m}$ iron in a kerosene [117]. With the composition of $26.4\text{ vol}\% \text{Fe}_3\text{O}_4$ and $30.8\text{ vol}\%$ iron, the maximum shear stress was around 350 Pa at 44s^{-1} under magnetic field $B = 400\text{ Gauss}$, which is much less than ours. The possible reason is that the iron particle size is about 3 times smaller than our sample of $3.8\text{--}4.5\mu\text{m}$. While John et al. also tested the flow properties of suspensions of micron iron particles ($30\mu\text{m}$), nanometer iron particle (26.5nm) as well as the hybrid of nanometer and micron sized particles [41]. It is shown in Fig. 6.7, a maximum stress of 10kPa can be achieved from the hybrid fluid under a magnetic field of 600kA/m . The weight fraction of the hybrid fluid is $45\text{wt}\%$ with a $40:60$ weight ratio of nano and micron sized particles. And in their experiments, the MR fluids of $60\text{wt}\%$ micron sized particles had slightly larger shear stress than that of the hybrid fluids [41].

Fig. 6.7 The flow curves of hybrid fluid of 45wt% with 40:60 ratio of nano and micron sized powders under different magnetic fields [41].

Fig. 6.8 Flow curves for MRF-132LD under different magnetic fields [58].

Finally, the flow curve of MRF-132LD is taken for comparison, as shown in Fig. 6. Comparing with the weight fraction $\phi = 80\text{wt}\%$ under different magnetic field in F 6.6(a), the shear stress of F-MRF $\phi = 80\text{wt}\%$ and MRF-132LD under $B = 254\text{mT}$ quite close, and it's compatible with John's hybrid fluids. The above comparison indicate that both the F-MRF and hybrid fluids are compatible with MRF-132L while the anti-sedimentation property is greatly improved.

Table 6.1 listed the dynamic yield stress obtained from H-B model. We assume zero magnetic field, all the samples yield Newtonian flow without yield stress.

could be seen, with the increase of weight fraction, the yield stress is almost doubled when the weight fraction is increased by every 20wt%. The relation between the dynamic yield and the magnetic field is plotted in Fig. 6.9(a), as well the yield stress of MRF-132LD in Fig. 6.9(b). For both of them, the yield stress is exponential to the magnetic fields. In F-MR fluids, the μ_f of ferrofluids was larger than that of non-magnetic mineral oil, which caused smaller $\beta_m = \frac{\mu_p - \mu_f}{\mu_p + 2\mu_f}$ and correspondingly lower particle interaction energy $U = \frac{\pi d^6 \mu_f \beta_m^2 H_0^2}{16 r_{ij}^3} (1 - 3 \cos^2 \theta)$, so the yield stress of F-MR fluids are always slightly smaller than that of conventional MR fluids.

Table 6.1 The yield stress obtained from H-B model.

Weight fraction ϕ	Magnetic induction B (mT)						
	0.00	51.00	102.00	153.00	204.00	254.00	305.00
20wt%	0	26.40	73.24	197.31	455.36	736.71	1033.43
40wt%	0	48.06	128.06	311.51	753.68	1661.26	2565.84
60wt%	0	71.06	270.98	694.25	1480.30	2736.08	4274.25
80wt%	0	114.17	405.25	1144.76	2930.14	4332.45	6725.47

Fig. 6.9 The yield stress of MR fluids, (a) 4 F-MR fluids, (b) MRF-132LD [58].

6.4 Oscillatory Properties

6.4.1 Strain amplitude dependence

A series of strain oscillation were carried out for F-MRF. In this experiment, the sample was loaded onto the rheometer and sheared to ensure uniform particle distribution. The oscillatory frequency of 2Hz was performed in all the strain oscillations.

Fig. 6.10 shows the strain oscillatory behavior for F-MRF. Fig. 6.10(a) and (b) display the storage modulus G' and loss modulus G'' for sample $\phi = 40\text{wt}\%$. At zero magnetic field, both G' and G'' are very small, their linear range can be up to 1%. When magnetic field is applied, they are increased several orders of magnitude than that at zero magnetic field, and they become more rigid. As is shown in Fig. 6.10(a), the critical strain of the linear stage is decreased $\gamma_D < \gamma_C < \gamma_B < \gamma_A$ along the increasing magnetic field. Similar to nano-MR fluids, there is an overshoot for the loss modulus with applied magnetic field.

In Fig. 6.10(c), the dynamic moduli for all the samples at $B = 305\text{mT}$ are plotted. Both the G' and G'' are increasing step by step along the weight fraction. And it's found the rigidity is also increasing along the weight fraction. In the figure, the critical strain of the linear stage is $\gamma_4 < \gamma_3 < \gamma_2 < \gamma_1$ subsequently with the increasing weight fraction.

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Fig. 6.10 The oscillatory properties of sample $\phi = 40\text{wt}\%$ and $\phi = 80\text{wt}\%$. (a) G' for $\phi = 40\text{wt}\%$, (b) G'' for $\phi = 40\text{wt}\%$, (c) both G' and G'' for 4 samples at $B = 305\text{mT}$.

6.4.2 Frequency dependence

In the above strain amplitude oscillation, the linear viscoelastic range had been determined. The frequency sweeping was carried out from 0.1 to 100 Hz with very small strain amplitude γ_0 . Before each frequency oscillation, samples were sheared at a large amplitude strain ($\gamma_0 = 50\%$) of 10Hz for 120s. As a result of initial conditioning, the data were highly reproducible.

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Fig. 6.11 shows the typical frequency oscillatory results. Fig. 6.11(a) and (b) display the dynamic moduli for $\phi = 40\text{wt}\%$. Firstly we can see at zero magnetic field, both G' and G'' are very small. They keep constant at small frequency and both began to increase slowly from 1Hz. Under magnetic field, all the storage modulus G' is increased by at least two orders of magnitude than that at zero magnetic field. And it keeps constant all the way in the sweeping frequency range. As well the loss modulus G'' has a similar behavior.

Fig. 6.11 The dynamic properties under frequency oscillation at $\gamma_0 = 0.05\%$, (a) G' and G'' for sample $\phi = 40\text{wt}\%$ at different magnetic fields, (b) The loss factor $\tan(\delta)$ for sample $\phi = 40\text{wt}\%$, (c) G' and G'' for three samples at zero magnetic field, (d) the factor $\tan(\delta)$ for the three samples at zero magnetic field, (e) G' and G'' for all samples at $B = 254\text{mT}$.

Fig. 6.11(b) shows the ratio of loss factor $\tan(\delta) = G''/G'$, it indicates the rigidity of the material. At zero magnetic field, $\tan(\delta)$ is almost constant at small frequencies, it comes to an overshoot at $\omega_l = 20\text{Hz}$. And after that, it dramatically drops to a very small value. Under magnetic field, both G' and G'' almost keep constant (Fig. 6.11(a)). With the increasing magnetic field, $\tan(\delta)$ is reduced accordingly. It means with the increasing magnetic field, the sample becomes more solid-like.

Fig. 6.11(c) and (d) illustrate the dynamic properties of three samples at zero magnetic field. The phenomenon on sample $\phi = 40\text{wt}\%$ is also found on samples $\phi = 20\text{wt}\%$ and $\phi = 60\text{wt}\%$. All the G' started to increase at a certain frequency, then it suddenly increased after the constant stage. The comparison of the ratio G''/G' is shown in Fig.

6.10(d), there is an overshoot for all samples. While with the increasing weight fraction, the overshoot is slightly reduced.

Fig.6.11(e) shows the frequency oscillation behavior for all the samples at $B = 254\text{mT}$. Both G' and G'' keep constant in all the frequency range. The results indicate that if the material is quite rigid, the frequency has little effect on the dynamic properties in the scanned frequency range.

Table 6.2 Dynamic properties during frequency oscillation.

Weight fraction	Dynamic properties	Magnetic induction B (mT)			
		0	105	254	305
20wt%	G'	1.90E+02	5.51E+03	1.43E+04	4.31E+04
	G''	8.40E+01	1.92E+03	4.60E+03	8.79E+03
	$\tan(\delta)$	0.44	0.35	0.32	0.2
40wt%	G'	2.45E+02	1.91E+04	5.20E+04	2.00E+05
	G''	9.54E+01	5.43E+03	1.44E+04	4.85E+04
	$\tan(\delta)$	0.39	0.28	0.28	0.24
60wt%	G'	2.82E+02	3.77E+04	2.20E+05	4.64E+05
	G''	1.27E+02	7.67E+03	4.14E+04	7.62E+04
	$\tan(\delta)$	0.45	0.2	0.19	0.16
80wt%	G'	---	2.19E+05	1.06E+06	1.64E+06
	G''	---	3.78E+04	2.14E+05	2.06E+05
	$\tan(\delta)$	---	0.17	0.2	0.13

Table 6.2 listed all the G' , G'' in their linear stage, and corresponding $\tan(\delta)$. Both G' and G'' kept on increasing along the weight fractions and the magnetic fields. The rigidity of the samples in different condition was shown in $\tan(\delta)$. It was reduced steadily along the weight fractions and the magnetic fields. From the table, we can also see, at the highest magnetic field $B = 304\text{mT}$ and the highest weight fraction $\phi = 80\text{wt\%}$, the value of G' and G'' are still smaller than that of MRF-132LD.

6.4.3 Stress amplitude sweeping dependence

In addition to the above dynamic study, stress amplitude sweeping was also carried out. In the expression of the dynamic moduli, both G' and G'' are independent of the strain or stress in the linear status. So G' and G'' should be constant at the small stress. As the stress keeps on increasing, the elastic structure will be ruptured. And the structural rupture will be reflected in the dynamic moduli. So the stress oscillation is a good method to see the structural change [121]. Shih defined it as the static yield stress when the structure is suddenly changed, the point is the crossover of G' and G'' [122]. Unlike polymers, this method will over estimate the yield stress, as shown in Fig. 6.12, the cross point is far away from the linear stage. Usually, the G' curve is not always straight or it drops down dramatically. So how to define the linear stage is another issue. In this project, the static yield stress is defined at the cross point on the tangent of the linear section and the tangent of the dropping off section, as illustrated τ_{ys} in Fig. 6.12.

Fig. 6.12 shows the behaviors of F-MR fluids under stress amplitude oscillation. The linear portions are clearly displayed. After the linear portion, G' is dramatically dropped, which crossed over the loss modulus. Here we also found there is an overshoot for the G'' , it is not a constant but keeps on increasing before approaching to the overshoot. In the figures, the stress is started from different value because of initial setup, such as in Fig. 6.12(a), $\tau_1 = \tau_2 = 10\text{Pa} < \tau_3 < \tau_4$ at $B = 105\text{mT}$ for different samples.

(a)

(b)

Fig. 6.12 The dynamic moduli for F-MR fluids under stress amplitude oscillation at $\omega = 2.0\text{Hz}$, (a) $B = 105\text{mT}$ for all samples, (b) the sample $\phi = 40\text{wt}\%$ at different magnetic field.

Table 6.3 listed the dynamic moduli and $\tan(\delta) = G''/G'$ in their linear stage. It is found at zero magnetic field, $\tan(\delta)$ is around 0.2 for all samples. And when the magnetic field is applied, $\tan(\delta)$ is significantly dropped, it means the MR fluids were solidified under magnetic fields.

Table 6.3 The dynamic moduli in plateau from stress amplitude oscillation.

Weight fraction	Dynamic properties	Magnetic induction (mT)			
		0	105	254	305
20wt%	G'	6.20E+02	1.10E+04	3.60E+04	7.00E+04
	G''	1.45E+02	1.60E+03	2.30E+03	6.00E+03
	Tan (δ)	0.23	0.15	0.06	0.09
40wt%	G'	7.10E+02	4.00E+04	1.50E+05	3.20E+05
	G''	1.60E+02	3.92E+03	1.10E+04	2.90E+04
	Tan (δ)	0.23	0.1	0.07	0.09
60wt%	G'	9.00E+02	5.97E+04	2.70E+05	7.00E+05
	G''	1.80E+02	8.00E+03	1.80E+04	5.30E+04
	Tan (δ)	0.2	0.13	0.07	0.08
80wt%	G'	1.47E+03	3.10E+05	6.90E+05	1.90E+06
	G''	2.30E+02	1.98E+04	4.00E+04	7.05E+04
	Tan (δ)	0.16	0.06	0.06	0.04

6.5 Rheological Difference Between F-MRF and Conventional MR fluids

In the above description, we have seen that F-MRF and conventional MR fluids have similar properties. In order to find more difference between F-MRF and C-MRF, the MRF-132LD is diluted to 60wt% using mineral oil (C-MRF) so that its weight fraction is the same to F-MRF of 60wt%. In Fig. 6.13(a), a shear stress start-up was carried out for both F-MRF and C-MRF, and the strain was recorded. At the same weight fraction and the same magnetic field, both of them showed a changing point. From the definition of static yield stress (will be given in chapter 7), the static yield stress of C-MRF is larger than that of F-MRF because the changing stress of F-MR fluid is smaller. As the stress amplitude was increasing, the strain of F-MRF was increasing steadily. However, there was a discontinuity for the C-MRF. Fig. 6.13(b) shows the comparison of stress oscillation between the F-MRF and C-MRF. The pattern was quite similar to that of Fig. 6.13(a). Both G' and G'' were larger than their counterparts accordingly, and the changing stress of C-MRF was larger than F-MRF.

It's shown both G' and G'' of C-MRF were suddenly dropped which is not displayed in F-MR fluids.

Fig. 6.13 Magnetorheological properties comparison between F-MRF and M-MRF, with $\phi = 60\text{wt}\%$, (a) stress controlled yield stress measurements at $B = 97\text{mT}$, (b) Stress controlled oscillation at $B = 145\text{mT}$ and angular frequency $\omega = 2.0\text{ Hz}$.

6.6 Creep-Recovery

In previous section, a continuous increasing shear rate $\dot{\gamma}$ was applied to the samples to produce steady shear flow, it can be done by imposing a constant-pressure

driving stress or a constant-torque motor. In another method, a constant driving force can be produced by attaching a weight to drive the flow (Fig. 6.14(a)) [45]. This method had widespread use in the early days of rheological testing [45]. Since both the stress and the shear rate are constant at steady state, whether we drive the flow at a constant stress or at a constant shear rate, the same steady shear can be resulted.

Fig. 6.14 Creep behavior illustration, (a) Illustration of a constant driving stress (the mass) in the shear between two samples, (b) Relationships among the material functions in creep experiment.

The unsteady response to shear flow under a constant stress is different from the response under a constant strain rate. In the constant-strain-rate experiment, the buildup in stress is measured in the start-up experiment, whereas in the constant-stress experiment, the time-dependent deformation of the sample is measured during the transient flow. The unsteady shear experiment where the stress kept constant is called creep. And as the stress is released, the material may re-structure, which is the recovery. The creep-recovery experiment introduces the parameter of “response time” to the stress-dependency of both the viscous and the elastic behavior of solid and fluids. It is described as

$$\tau(t) = \begin{cases} 0 & t < t_0 = 0 \\ \tau = \tau_0(\text{constant}) & 0 \leq t \leq t_2 \\ 0 & t > t_2 \end{cases} \quad (6.2)$$

The creep-recovery is illustrated in Fig.6.14(b) [45, 67]. A constant stress τ_0 is applied instantaneously at time $t_0 = 0$ to the sample and maintained at that level to time t_2 , then the stress is suddenly removed. In creep experiments, because the stress is a preset value rather than measured, the material functions relate the measured sample deformation (strain) to the applied stress τ_0 . The material function defined for creep is called creep compliance $J(t, \tau_0)$:

$$J(t, \tau_0) = \frac{\gamma(0, t)}{-\tau_0} \quad (6.3)$$

$\gamma(0, t)$ is obtained from a measurement of shear rate $\dot{\gamma}$. At long enough times, the strain becomes linear with time, that is, the flow reaches steady state, and the slope of $J(t, \tau_0)$ is the steady-state shear rate, $d\gamma/dt = \dot{\gamma}_0 = \text{constant}$, divided by the imposed stress $-\tau_0$. The ratio $\dot{\gamma}_0/\tau_0$ is just the inverse of the steady shear viscosity. The steady-state compliance $J_s(\tau_0)$ can be calculated by extrapolating the linear portion of $J(t, \tau_0)$ at steady state back to time $t = 0$ (Fig. 6.14(b)).

$$J_s(\tau_0) = J(t, \tau_0) \Big|_{\text{Steady state}} - \frac{t}{\eta(\dot{\gamma}_0)} \quad (6.4)$$

After time t_2 , shown in Fig. 6.14(b), the stress τ_0 is removed, the strain will recoil. So a recoverable compliance is defined as

$$J_r(t', \tau_0) = \frac{\gamma_r(t')}{-\tau_0} \quad (6.5)$$

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The recoverable γ is the ultimate strain recovered after the recoiling sample has come to rest, and it's used to define the ultimate recoil function $R_\infty(\tau_0)$:

$$R_\infty(\tau_0) = \lim_{t' \rightarrow \infty} R(t', \tau_0) = \frac{\gamma_\infty}{-\tau_0} \quad (6.6)$$

For τ_0 not too large (linear viscoelastic limit), the strain at all times $\gamma(t)$ is just the sum of the strain that is recoverable γ_r . And the strain that is not recoverable is the strain due to steady viscous flow at $\dot{\gamma}_0$, in linear viscoelastic limit,

$$\gamma(t) = \gamma_r(t) + t\dot{\gamma}_0 \quad (6.7)$$

Dividing by $-\tau_0$, we obtain

$$J(t) = R(t) + \frac{t\dot{\gamma}_0}{\tau_0} = R(t) + \frac{t}{\eta_0(\dot{\gamma})} \quad (6.8)$$

By comparing this with eq. (6.4), the ultimate recoil is equal to the steady state compliance in the linear viscoelastic limit,

$$R(t)\Big|_{\text{steady state}} = R_\infty^0 = J_s^0. \quad (6.9)$$

In our experiments, a constant stress was applied and it was maintained for 100 seconds. After that, the stress was suddenly removed and another 100s was kept to the recovery behaviors. Fig. 6.15 plotted the creep-recovery curve of sample 40wt% at $B = 254\text{mT}$, by extrapolating the linear portion of $J(t, \tau_0)$ at $\tau_0 = 700\text{Pa}$, we got

$$J_s^0 = \frac{0.0733}{700}. \quad \text{In the experiment, } R_\infty^0 = \frac{0.782}{700}. \quad \text{The difference is}$$

$$\frac{R_\infty^0 - J_s^0}{J_s^0} = 6.67\% \text{ which is quite close to eq. (6.9) } R_\infty^0 = J_s^0.$$

Fig. 6.15 The creep-recovery behavior of $\phi = 40\text{wt}\%$, $B = 254\text{mT}$ at $\tau = 700\text{Pa}$.

Fig. 6.16 shows the creep-recovery behaviors of two samples under different stresses. In Fig. 6.16(a), the stress is increased from $\tau = 240\text{Pa}$ to $\tau = 420\text{Pa}$ by 60Pa step by step for sample $\phi = 20\text{wt}\%$ at $B = 305\text{mT}$. With the increasing stress, both J_s^0 and $R_\infty(\tau_0)$ were increased. Therefore, J_s^0 and $R_\infty(\tau_0)$ are function of the stress τ_0 although they may be equal $J_s^0 = R_\infty(\tau_0)$. Further more, the creep-recovery curves of the sample $\phi = 60\text{wt}\%$ under $B = 305\text{mT}$ were plotted in Fig. 16(b), and the trend of J_s^0 and $1/\eta_0$ in eq. (6.3) were listed in Table 6.4. It could be seen both J_s^0 and $1/\eta_0$ were kept on increasing along the increased stress. Ideally, $1/\eta_0$ should be a constant, but in our case, it's a function of stress τ_0 . The results are reasonable because MR fluids don't totally behave like most polymers which have the η_0 at very small shear rate.

(a)

(b)

Fig. 6.16 Creep-recovery behaviors of two samples, (a) $\phi = 20\text{wt}\%$ under $B = 305\text{mT}$, (b) $\phi = 60\text{wt}\%$ under $B = 305\text{mT}$.

Table 6.4 The coefficients J_s^0 and $1/\eta_0$ in eq. (6.9) at different stress τ_0 .

$\tau_0(\text{Pa})$	$J_s^0(\times 10^{-6})$	$1/\eta_0(\times 10^{-8})$
1600	4.1781	0.7864
1800	4.7252	0.8536
2000	5.3496	1.0737
2200	6.4646	1.5944
2400	8.3706	1.6294

6.7 Conclusions

In this work, the properties of ferrofluids based MR fluids were investigated. The results were summarized as follows:

In the ferrofluids based MR fluids, the nanosized Fe_3O_4 particles were attached on the big micro-sized iron particles. So the iron particles were separated by the surface attached Fe_3O_4 particles, which make the whole system easier to be re-dispersed.

For all the F-MRF samples, the flow curves can be well described by Herschel-Bulkley model. Comparing with nano-MRF, the yield stress has been improved greatly, and it's in the same order of magnitude of conventional MR fluids MRF-132LD.

In the oscillatory study, three different oscillation modes were carried out: strain amplitude oscillation, frequency oscillation and stress amplitude oscillation. In strain amplitude oscillation, it was found with the increase of magnetic field or weight fraction, the F-MRF became more rigid, it can be transformed from fluids, to sol-gel and then to solid depending on the strength of magnetic fields. There was an overshoot for the loss modulus when strain is exceeded its elastic limitation, which is during the transformation from linear (elastic) to nonlinear (plastic or fluidic). In frequency oscillation, both the storage modulus and loss modulus were kept almost constant in the whole frequency oscillation scope under magnetic fields. At zero magnetic field, there was also an overshoot for the ratio $\tan(\delta) = G''/G'$. In stress amplitude oscillation, the overshoot happened to loss modulus under all magnetic fields. In the pre-yield stage, the storage modulus kept in plateau. After that, both G' and G'' were dropped dramatically. In the linear range, F-MRF almost showed

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solidified property, all the $\tan(\delta)$ was so small that the loss modulus only took several percents of the storage modulus. Whilst in previous frequency oscillation, the $\tan(\delta)$ is much larger than that in the stress oscillation.

Some further experiments have confirmed that the yield stress of F-MRF is smaller than that of the conventional MR fluids with the same weight fraction and under the same magnetic fields. It was also found that the structural change of F-MRF was quite continuous under different loadings. On the contrary, the structure of conventional MR fluids will break down suddenly under a critical stress.

In creep-recovery experiments, we found at relative small stress, the samples can entirely recover after the creep stage. The steady state compliance can match the recoil, but both of them are also function of shear stress τ_0 .

Overall we found the rheological property of ferrofluids based MR fluids were quite close to that of conventional MR fluids. The yield stress of F-MRF is compatible with that of C-MRF in the same conditions, and the stability was improved a lot comparing with C-MRF. Although F-MRF also has sedimentation issue, its re-distribution property is much better than that of C-MRF.

Chapter 7

The Static Yield Stress of Ferrofluid-based Magnetorheological Fluids (F-MRF)

7.1 Introduction

In chapter 5 and chapter 6, we frequently mentioned the yield stress. In the characterization, we obtained the dynamic yield stress τ_{yd} through flow curves to extrapolate at zero shear rate. As mentioned in Chapter 2, the dynamic yield stress is obtained in the post-yield stage. While in the startup stage, MR fluids approximately show an elastic behavior under magnetic field. There is another shear stress which is the minimum stress necessary for the unbounded strain or deformation of the material, defined as static yield stress τ_{ys} [47], as shown in Fig. 2.4(b).

The measurement of τ_{ys} is not as easy as that of τ_{yd} . It can be regarded as the transition stress between elastic solid-like behavior and viscous liquid-like behavior. However, this transition usually occurs over a range of stresses, during which the material exhibits both elastic and viscous properties. For a meaningful measurement of the yield stress, the time frame of the experiment must be sufficiently long such that elastic stretching is appreciable and the viscous contribution is minimized. Many methods have been used to assess the yield stress by conventional rheometers, such as creep/recovery, stress relaxation and stress growth techniques [123]. In this project, we are trying to measure the yield stress by stress growth method. By controlling different parameters, three modes are used to measure the static yield stresses of the F-

MRF: (a) fixed shear rate mode, (b) strain sweep mode, and (c) stress sweep mode.

The relations among the yield stress, the magnetic field strength, and the weight fraction of micro-sized iron particles in the F-MRF have been studied and discussed.

7.2. Experimental

The following materials (as underlined) were purchased from commercial sources and used without further purification or any chemical treatments. Ferrofluids from Ferrotec USA: APG S10n, nanosized Fe_3O_4 (about 12nm), synthetic ester based, viscosity 300 mPa·s, magnetic saturation 400 Gauss/emu. Magnetorheological fluid from LORD Corporation: MRF-132LD, mineral oil based, carbonyl iron particles (4.5–5.2 μm), weight fraction 80 wt%. Carbonyl iron particles from Aldrich: particle size 4.5–5.2 μm , density 4.4 g/cm³. Mineral oil from Sigma: white, density 0.862 g/cm³, viscosity 0.1 Pas. Oleic oil from Sigma: 98% pure.

The F-MRF samples were prepared by mixing the iron particles into the ferrofluid. Oleic oil was used as the stabilizer. The samples were manually stirred for 30 minutes and then they were vibrated under ultrasonic for 15 minutes. The weight fractions of iron particles in the final F-MRF samples were adjusted to be 20, 40, 60, and 80 wt % respectively. The MR fluid (MRF-132LD) was diluted with mineral oil to a weight fraction of 60 wt % from the original weight fraction of 80 wt% and oleic oil was added as the stabilizer.

The static yield stress τ_{ys} is the minimum stress required to cause the material to flow [47]. The τ_{ys} values of F-MRF were measured using a MR rheometer (Paar Physica, Germany) with a parallel plate geometry [47]. A copper coil is built inside the rheometer, which can provide a magnetic field. To avoid sample slipping between

the two plates, the surface of the plates were treated by crude sandpaper to become rough.

Fig. 7.1 The static yield stress τ_{ys} measurements for MR fluids using three testing modes: (a) fixed shear rate mode (input: shear rate $\dot{\gamma} = \text{constant}$; output: shear stress τ); (b) strain sweep mode (input: logarithmically increasing shear strain γ , output: shear stress τ); and (c) stress sweep mode (input: logarithmically increasing shear stress τ , output: shear strain γ).

Three different testing modes were employed to measure the yield stress as shown in Fig. 7.1 [20, 37]. In Fig. 7.1(a), a constant shear rate $\dot{\gamma}$ is applied to the sample and the shear stress is measured as a function of time. This testing mode (Fig. 7.1(a)) is called “fixed shear rate mode”. In Fig. 7.1(b), a logarithmically increasing shear strain γ is applied to the sample. Similarly, the yield stress τ_{ys} is the maximum stress in the strain range. The testing mode illustrated in Fig. 7.1(b) is called “strain sweep mode”. In Fig. 7.1(c), the stress is increased logarithmically, and on the contrary to Fig. 7.1(b), the shear strain is taken. When the stress is beyond the yield stress, the increase in strain will accelerate, so that the slope of the strain-stress curve will be different before and after the yield stress and the transition point is defined as τ_{ys} . This is called

“stress sweep mode”. In this work, all experiments were conducted at room temperature (25 °C).

7.3 Results and Discussion

7.3.1 Shear stress at a fixed shear rate

The yield stresses of the F-MRF samples $\phi = 60\text{wt}\%$ with $\dot{\gamma} = 0.005\text{s}^{-1}$ was plotted in Fig. 7.2 under different magnetic fields. Before the yield stress, all the shear stress curves were converged in one straight line. It means the shear stress is independent of the magnetic fields before yielding. Beyond the yielding point, the shear stress is deviated from its original curve and leveled off. It can slightly show that for each curve, there is a small overshoot, this overshoot is the static yield stress τ_{ys} , and the leveling stress is the dynamic stress τ_{yd} .

Fig. 7.2 Shear stress of $\phi = 60\text{ wt}\%$ at $\dot{\gamma} = 0.005\text{s}^{-1}$ in different magnetic fields.

Fig. 7.3 compared the shear rate effect on the yield stress for sample $\phi = 40\text{wt}\%$ under $B = 145\text{ mT}$. In the stress vs time curve in Fig. 7.3(a), the maximum shear stress is increased from 800Pa to 1100Pa as the shear rate varied from 0.003s^{-1} to 0.05s^{-1} . At

shear rate 0.001s^{-1} , the stress didn't approach to its maximum value yet. There are overshoots at all shear rates, these overshoot stresses are the static yield stress τ_{yd} . And with larger shear rate, such as 0.05 s^{-1} , the overshoot became more evident. Fig. 7.3(b) plotted the same shear stress against shear strain. The overshoots are more clearly shown than they are in Fig. 7.3(a). And it's also found that even at different shear rates, the strains were overlapped before the overshoot point. It indicates that the strain increase is independent of the shear rate.

Fig. 7.3 Shear stresses of $\phi = 40\text{wt\%}$ under $B = 145\text{ mT}$ with different shear rate, (a) shear stress in terms of time, (b) Shear stress in terms of strain.

Fig. 7.4 Yield stress measurement for a lamellar gel-structured cream, (a) step-shear rate tests, (b) the stress behavior in terms of strain [124].

The overshoot occurs due to the finite viscoelastic response of the microstructure up to a critical level of strain, beyond which there is breakdown of the structure and corresponding stress decay. It was related to the limited elastic response and rapid break-up of the network structure [123, 124]. And very similar case occurred on a lamellar gel-structured cream [124], as shown in Fig. 7.4. The overshoot value is different in different shear rate, and before yielding, the stress curves are overlaid. However, in See and Chen's investigation for the stress start-up of MR fluids [66], the stress curves were overlaid before and after yielding, as shown in Fig. 7.5, at $\dot{\gamma} = 0.01s^{-1}$, $\dot{\gamma} = 0.1s^{-1}$, $\dot{\gamma} = 1.0s^{-1}$ and $\dot{\gamma} = 10s^{-1}$, the curves were well matched, and from here they concluded the strain dependence of the build-up of stress was nearly independent of shear rate for all rates [66]. The overlay phenomenon may be due to not enough recovery time after the first shear rate test, as Lidder and Boger pointed out when the recovery time was very short, there is no overshoot [123].

Fig. 7.5 The shear stress start-up at different shear rate for an MR fluids under 57mT [66].

7.3.2 Shear stress as a function of shear strain

Fig. 7.6 shows the shear stress measured using the strain sweep mode. In all the experiments, the strain γ was logarithmically increased from 0.1% to 10 %. Fig. 7.6(a) presents the shear stress curves for the F-MRF sample of $\phi = 60\text{wt}\%$ at different

magnetic induction of B . In a log-log scale, the stress at each B approaches to a maximum value or a plateau at very small strains ($< 2\%$), and then levels off. The stress plateau increases significantly with increasing B .

Fig. 7.6 Shear stress measured by the strain increase mode: (a) stress versus strain curves for the F-MRF of $\phi = 60\text{ wt } \%$ at different magnetic induction of B and (b) the stress-strain curve for the F-MRF of $\phi = 80\text{wt}\%$ at $B = 145\text{ mT}$.

Fig. 7.6(b) depicts the stress-strain relation for the F-MRF sample of $\phi = 80\text{ wt } \%$ at $B = 145\text{ mT}$. The stress first reaches a maximum value at a strain 0.85% to show a yield-like behavior. However, with increasing strain after the first maximum, the stress becomes unstable and fluctuates largely in the strain range from 3 to 20% . The stress tends to become stable at high strains ($\gamma > 30\%$). The fluctuation in stress after the first yield point would be due to destruction and re-construction of some chain clusters. Under a magnetic field, the chain-like clusters are well formed. When shear strain is applied, the chain clusters are shear-deformed and may be broken off if the strain is big enough. The observed stress reflects the resistant force of the test sample against the shear deformation. The initial monotonic increase in stress with strain means that the resistant force increases monotonically with strain. When the resistant force reaches a maximum, the yield point is shown. Usually, after the yield point, the

shear stress slightly decreases and then becomes relatively constant, meaning that a further increase in strain does not cause a further increase in stress as illustrated in Fig. 7.6(a). In Fig. 7.6(b), however, the fluctuation in stress may indicate an alternative change between the breaking-down of chain clusters and the reconstruction of some chain clusters during the deformation. As the F-MRF sample had the highest loading (80 wt%) of iron particles, the probability for the sample to reconstruct chain clusters would be higher than other less-loaded samples.

Fig. 7.7 Shear stress measured by stress sweep mode: (a) strain vs. stress curves for the F-MRF sample of $\phi = 40 \text{ wt}\%$ at different magnetic inductions of B as indicated; (b) strain vs. stress curves at $B = 97 \text{ mT}$ for four samples ($\phi = 20, 40, 60$, and $80 \text{ wt}\%$) of F-MRF.

7.3.3 Shear strain as a function of shear stress

Fig. 7.7 shows the yield stresses measured under the stress sweeping mode. Fig. 7.7(a) presents the strain versus stress curves for the F-MRF sample of $\phi = 40 \text{ wt}\%$ at various magnetic induction B as indicated. Fig. 7.7(b) gave the strain versus stress curves at $B = 97 \text{ mT}$ for four samples ($\phi = 20, 40, 60$, and $80 \text{ wt}\%$) of F-MRF. As originally described in Fig. 7.1(c), the yield stress is defined as the point before and

after which the slopes of the strain-stress curve are different. As marked in Fig.7.7, the transitional points for the curve slope change could be easily determined.

In Fig. 7.7(a), it is observed that the strain-stress curves for the sample $\phi = 40$ wt% are strongly dependent on the magnetic flux. With increasing the magnetic induction, the yield stress shifts to a greater value. Fig. 7.7(b) illustrates the effect of particle weight fraction on the yield stress at $B = 97$ mT. With increasing the weight fraction, the strain-stress curve shifts to the right and lower, resulting in a bigger yield stress but at a smaller strain. A common feature found from Fig.7.7(a) and (b) is that at a weaker magnetic field or a smaller weight fraction, the corresponding yield point is less sharper (or in other words, it is more difficult to define a yield point) than that at a stronger magnetic field or a bigger weight fraction. This is explained by a possible fact that at a weaker magnetic field or a smaller weight fraction, the structure formed from the chain clusters in an MR fluid is weaker or looser, and it can't withstand a bigger shear stress.

7.3.4 Yield stress as functions of magnetic strength and weight fraction

All the yield stresses obtained from Figs. 7.2-7.7 were listed in Table 7.1 and plotted against magnetic induction B in Fig. 7.5 for all the F-MRF samples studied in this work. At each weigh fraction and each test mode, the yield stress increases with B monotonically. On the other hand, at a given B , the yield stress increases steeply with weight fraction. At the very small magnetic induction, such as 0 and 48mT, the result is quite irregular, which means the yield stress under small magnetic field is not trustable. While under higher magnetic fields, it is noted that the testing modes of strain sweep and stress sweep result in the quite similar yield stress curves at a fixed weight fraction except the sample 60 wt%. The similarity between the strain sweep

mode and the stress sweep mode means that whether strain or stress is used as an input, the same yield stress can be obtained. However, the yield stress curve obtained under the fixed shear rate mode is higher than those under the other two modes for the same sample over the whole range of magnetic induction. In the fixed shear rate mode, the strain was increased linearly with very slow and small steps, so that the stress could follow the changes in strain. In the strain (or stress) sweep mode, however, the steps in increasing strain (or stress) were quite big, especially near the yield stress point because the strain (or stress) was logarithmically increased. Thus, the responding stress (or strain) might be unable to follow the strain (or stress) applied and a lower value of stress (or strain) was observed. As a result, a smaller yield stress was shown under both the strain and stress sweep modes.

Table 7.1 Static yield stresses (Pa) for F-MRF, which were measured using three testing modes at various magnetic induction B .

Weight fraction, wt%	Testing mode*	Magnetic induction B (mT)						
		0	48	97	145	193	241	290
20	I	0	26	65	197	350	581	792
	II	0	1.4	46	206	310	620	825
	III	2.3	22.1	115	208	400	630	860
40	I	0	20	211	475	810	1260	2380
	II	0	12	80	409	790	1200	2410
	III	2.1	19.5	391	720	1175	1625	2510
60	I	8.7	23	420	746	1550	2010	3220
	II	3.5	16	350	840	1600	2650	3950
	III	2.15	130	655	1120	2040	3000	4100
80	I	21.5	40	530	1430	3350	4400	6100
	II	20	58	440	1660	3250	4400	6100
	III	1.2	460	820	2340	3840	5700	8500

* Testing modes: I: strain sweep mode; II: stress sweep mode; III: fixed shear rate mode

under $\dot{\gamma} = 0.003s^{-1}$.

Fig. 7.8 Yield stress as a function of magnetic induction B measured using three different modes for the F-MRF samples with 20, 40, 60, 80 wt % of iron particles.

Fig.7.9 Yield stress as a function of magnetic induction B , which were measured under (a) the strain sweep mode, (b) the stress sweep mode, and (c) the fixed strain

rate mode for the F-MRF samples with 20, 40, 60, 80 wt % of iron particles as indicated with diamonds, circles, triangles, and squares respectively.

To further investigate the effects of the magnetic induction on the yield stress τ_{ys} , a function $\tau_{ys} = aB^b$, is assumed to correlate τ_{ys} with B , where a and b are constant. Since the scaling or power index b is the most interesting to know, in order to verify whether a constant b exists and how it depends on a test mode, the yield stresses shown in Fig.7.8 are plotted in a logarithmic scale in Fig.7.9 where the plots are shown separately based on the respective test mode. Under the three test modes (i.e. (a), (b) and (c) for strain sweep, stress sweep, and fixed shear rate modes respectively), the yield stresses at each weight fraction could be nicely expressed by a straight line with a slope of 2. The straight line shifts higher with increasing weight fraction, meaning that the coefficient a is dependent on weight fraction. Thus, we can conclude that the yield stress is proportional to the square of magnetic induction B , as expressed by $\tau_{ys} = aB^2$, which is not changed by the test modes. As can be seen from Fig.7.9, the coefficient a increases with weight fraction, meaning that the coefficient a is dependent on weight fraction. In this study, we did not intend to find an expression for the dependence of a on weight fraction as it is beyond the scope of this work. The scaling law $\tau_{ys} = aB^2$ is useful for one to predict the yield stress of a sample at any given B .

7.4 Conclusions

In this work, three test modes were used to measure the static yield stresses of F-MRF under magnetic fields. We found that the yield stresses measured with both the strain sweep mode and the stress sweep mode were very similar, while the yield stress

measured with the fixed rate mode was always higher than these measured with the other two modes for the same samples under the same magnetic field.

Finally, the scaling relation between the yield stress and magnetic induction was examined. The yield stress τ_{ys} was found to be proportional to the square of magnetic induction B . Thus the scaling law is expressed as $\tau_{ys} = aB^2$, which is independent of the testing modes. However, the coefficient a is a function of weight fraction.

Chapter 8

On the Extended Rutgers-Delaware Rule for

MR fluids Under Magnetic Fields

8.1 Introduction

In previous chapters, both steady shear flow and oscillatory shear properties of MR fluids have been studied. The steady flow property characterizes the mechanical behavior macroscopically, while the oscillatory property can present the microscopic structural behaviors. Their interrelation has been investigated on polymers and suspensions [125]. In this paper, the interrelation rule will be interpreted. Its extension to suspensions has been reviewed, and a general rule for either polymers or suspensions will be deduced from previous research. And finally this general rule is applied on MR fluids under different magnetic fields.

8.2 Interrelation Rules

8.2.1 Cox-Merz (C-M) rule

In 1958, Cox and Merz discovered a rule called by their names [125]:

$$|\eta^*(\omega)| = \eta_{app}(\dot{\gamma}) \quad \text{with } \omega = \dot{\gamma}. \quad (8.1)$$

This rule states that the magnitude of complex viscosity $|\eta^*(\omega)|$ equals the apparent viscosity $\eta_{app}(\dot{\gamma})$ when the oscillatory angular frequency ω is quantitatively equal to

the steady shear rate $\dot{\gamma}$. *Bird et al.* pointed out that this rule was generally true for linear and branched, monodisperse and polydisperse polymer systems [126].

The C-M rule is an empirical rule since it is found by experiments and not by rigorous theoretical derivation. However, the quantitative similarity reveals the interrelation between the two property parameters η_{app} and η^* , which characterize the rheological properties of a given material under two different working conditions. If a constitutive model under some reasonable assumptions can be constructed for the material, theoretical derivation based on the constitutive model supposes to be able to show the existence of the rule.

Let a relaxation modulus function $G(t)$ of a linear viscoelastic material be modeled as a discrete spectrum:

$$G(t) = \sum_{k=1}^{\infty} G_k e^{-\frac{t}{\lambda_k}}, \quad (8.2)$$

where G_k is the k th weighting constant for the k th relaxation time λ_k . Under some judicious assumptions, Renardy successfully derived [127]:

$$\eta_{app}(\dot{\gamma}) \approx \sum_{1 > \dot{\gamma}\lambda_k} G_k \lambda_k + \sum_{1 < \dot{\gamma}\lambda_k} \frac{G_k}{\lambda_k \dot{\gamma}^2}, \quad (8.3)$$

and

$$|\eta^*(\omega)| \approx \eta'(\omega) \approx \sum_{1 > \omega\lambda_k} G_k \lambda_k + \sum_{1 < \omega\lambda_k} \frac{G_k}{\lambda_k \omega^2}, \quad (8.4)$$

where $\eta'(\omega)$ is the dynamic viscosity. It is shown that when $\omega = \dot{\gamma}$ there is a quantitative similarity between the two viscosities. The relaxation modulus function

$G(t)$ serves as a link to relate the apparent viscosity $\eta_{app}(\dot{\gamma})$ to the complex viscosity $|\eta^*(\omega)|$. Thus, Renardy proved that for a category of materials obeying the empirical rule, the constitutive model equation (8.2) is valid, because based on the model there exists the interrelation rule. In other words, the interrelation rule may justify the approximate constitutive model proposed for the category of the materials.

8.2.2 Rutgers-Delaware(R-D) rule

If a constitutive model was proposed for a material, based on the constitutive model a theoretical derivation might be carried out to predict a new interrelation rule for the material properties. If the derived interrelation rule could be further verified by experiments, then the proposed constitutive model would be justified.

For example, based on the H-B power law constitutive model, Doraiswamy *et al.* successfully derived the interrelation between apparent viscosity and complex viscosity for concentrated suspensions with a yield stress [128]. In their assumptions, the material undergoes perfectly elastic deformation below the yield stress and exhibits shear thinning behavior after yielding. Their model consists of a Hookean elastic solid behavior below the yield stress σ_{yd} and an H-B power law behavior above σ_{yd} . When $\dot{\gamma}$ is high, the apparent viscosity can be approximately expressed as

$$\eta_{app}(\dot{\gamma}) = K \dot{\gamma}^{(n-1)}, \quad (8.5)$$

where K and n are constants. Based on this model, their theoretical derivations yield a new interrelation rule:

$$|\eta^*(\omega\gamma_0)| = \eta_{app}(\dot{\gamma}) \text{ with } \omega\gamma_0 = \dot{\gamma}, \quad (8.6)$$

which predicts the equality of the function of steady shear viscosity η_{app} at shear rate $\dot{\gamma}$ and the function of dynamic viscosity $|\eta^*|$ at an “effective shear rate” $\dot{\gamma}_{eff} = \omega\gamma_0$. Here γ_0 is the shear strain amplitude of the oscillatory shear flow, ω is the angular frequency, and $\dot{\gamma}_{eff}$ is indeed the shear strain rate amplitude. The new interrelation rule (8.6) is named Rutgers-Delaware rule firstly by Krieger [129], which is totally different from the Cox-Merz rule although it bears a superficial resemblance to equation (8.1). To validate the R-D rule, Doraiswamy *et al.* conducted an experiment on a suspension with 70 vol. % silicon particles in polyethylene [128]. The results indicated the agreement of the experimental data with the R-D rule.

8.2.3 Extended Cox-Merz rule

In the literature, various types of empirical rules (extended Cox-Merz rules) have been published by many researchers such as Yu and Gunasekaran [130], Yoon and Gunasekaran [131] for different categories of materials. If a material shows that the experimental η_{app} in a steady flow can be plotted as a straight line in the $\log \eta_{app}(\dot{\gamma})$ vs $\log \dot{\gamma}$ coordinate system, and the experimental $|\eta^*|$ in an oscillatory flow can also be plotted as a straight line in the $\log |\eta^*(\omega)|$ vs $\log \omega$ coordinate system, it is always possible to relate the two functions by the following relation,

$$\Delta_v |\eta^*(\omega \Delta_h)|^\alpha = \eta_{app}(\dot{\gamma}) \quad \text{with } \omega \Delta_h = \dot{\gamma} \quad (8.7)$$

where α is a power factor, which rotates the straight line of $\log |\eta^*(\omega)|$ vs $\log \omega$ to have the same slope of the straight line of the apparent viscosity $\eta_{app}(\dot{\gamma})$. Δ_v is non-dimensional vertical shift factor, and Δ_h is non-dimensional horizontal shift factor.

Setting $\Delta_v = 1$, which means no vertical shift is considered, we can determine α and Δ_h (see Appendix C). Thus the relation (8.7) reduces to

$$\left| \eta^* (\omega \Delta_h) \right|^\alpha = \eta_{app}(\dot{\gamma}) \quad \text{with } \omega \Delta_h = \dot{\gamma} \quad (8.8)$$

Similar to the R-D rule, the parameter $\omega \Delta_h$ can also be defined as “effective shear rate” $\dot{\gamma}_{eff} = \omega \Delta_h$. However, it is not necessary to be the maximum shear rate $\omega \gamma_0$ as defined in the R-D rule. In general, both α and Δ_h should be functions of γ_0 . If the two straight lines happen to be parallel to each other, we have $\alpha = 1$. Obviously, when $\alpha = 1$, and $\Delta_h = \gamma_0$, relation (8.8) reduces to the R-D rule (8.6). And when $\alpha = \Delta_h = 1$, relation (8.8) coincides with the C-M rule (8.1). So, relation (8.8) may be considered as a generalized form of the Extended C-M rules when log-log plots of $|\eta^*|$ vs ω and η_{app} vs $\dot{\gamma}$ are straight lines in the interested domains of $\dot{\gamma}$ and $\dot{\gamma}_{eff} = \omega \Delta_h$.

In this research, series of experiments on MR suspensions were designed and conducted; the experimental data were fully investigated to examine the validity of the three interrelation rules discussed above.

8.3 Experiments

Materials such as magnetorheological fluid (MRF-132LD, Lord Co., Germany), silicone oil (viscosity 0.1PaS, density 0.97g/cm³, Acer Chemical Industries, Singapore), carbonyl iron (particle size 4.5-5.2 μm , 4.4g/cm³, Aldrich Co.), oleic oil (Aldrich) were used.

Besides the available sample MRF-132LD, three homemade samples were prepared. The iron powders were mixed into silicone oil, and oleic acid was used as a stabilizer. The iron volume fractions of three samples were 0.10, 0.20 and 0.40 respectively.

The rheological properties of the four MR suspensions were measured using an MR rheometer (Paar Physica, Model: UDS 200, 1998) with parallel-plate geometry as explained in Appendix A. The required magnetic field was supplied from a built-in electromagnetic coil. The magnetic induction B in the MR sample is approximately proportional to the coil current I [132]:

$$B \approx pI \text{ (Tesla)}, \quad (8.9)$$

where p is a constant. It is convenient to use the coil current to indicate the different levels of magnetic field applied on the samples. All the experiments were conducted at room temperature (25°C). After a sample was loaded, a steady shear at $\dot{\gamma}=100\text{s}^{-1}$ was imposed for 2 min as an initial condition. The desired magnetic field was then applied by setting the current and waited for 2 minute, ensuring that the MR fluids formed into a stable structure.

In steady shear flow, the shear rate was varied from 100 to 0.01s^{-1} logarithmically in a time interval of 2 minutes. In oscillatory shear flow, the angular frequency ω was varied from 100 to 0.01 rad/s logarithmically at the strain amplitude $\gamma_0 \leq 100\%$, and from 10 to 0.01 rad/s logarithmically at $\gamma_0 > 100\%$.

8.4 Results and Discussion

8.4.1 Apparent viscosity vs strain rate

The relations of apparent viscosity versus strain rate for the MR samples with different volume fractions and/or under different magnetic fields were firstly investigated. In Fig. 8.1, the log-log plots of η_{app} vs $\dot{\gamma}$ for the samples of various volume fractions are presented at $I = 0.4A$. The plots appear to be parallel straight lines. This phenomenon is called shear thinning; and the relation between apparent viscosity and strain rate can be approximately written in the form of

$$\log \eta_{app} \propto (n-1) \log \dot{\gamma} \quad \text{with } 0 < n < 1. \tag{8.10}$$

Hence, the H-B power law model can be adopted for the MR fluids as indicated by Li [71].

Fig. 8.1 The apparent viscosity versus shear rate for MR samples of various volume fractions at coil current $I = 0.4A$.

In Fig. 8.2, the plots of apparent viscosity versus shear rate for MRF-132LD at various magnetic fields are presented. It has been testified that by either increasing the volume fraction or the magnetic field [71], the yield stress of MR suspensions can be evidently increased. Therefore, as shown in Fig. 8.1 or Fig. 8.2, the apparent viscosities increase as ϕ and/or I increase.

Fig. 8.2 The apparent viscosity versus shear rate for MRF-132LD at various magnetic fields.

8.4.2 Comparison between complex viscosity and apparent viscosity - The Extended Rutgers-Delaware rule

Two sets of the data (η_{app} versus $\dot{\gamma}$ and $|\eta^*|$ versus $\omega\gamma_0$ at different strain amplitude γ_0) are superimposed in one diagram to examine the validity of the R-D rule for MRF-132LD at different magnetic fields.

Fig. 8.3 Apparent viscosity and complex viscosity as a function of steady shear rate and effective shear rate, respectively (for MRF-132LD at different levels of magnetic field), at (a) $\gamma_0 = 100\%$, (b) $\gamma_0 = 10\%$.

By setting $\gamma_0 = 100\%$, the data obtained at four different levels of magnetic field are plotted in Fig. 8.3(a). It is interesting to find that the R-D rule is satisfied within a wide effective shear rate range for the samples at various magnetic fields. The valid ranges of shear rate under different level of magnetic fields are found to be different. The higher the magnetic field, the higher the upper limit of the valid range is. As the strain amplitude γ_0 equals 100%, i.e. $\dot{\gamma}_{eff} = \omega\gamma_0 = \omega$, equation (8.6) of the R-D rule

coincides with equation (8.1) of the C-M rule. However, it does not imply any meaningful relation between the two rules. Obviously, the R-D rule is γ_0 -dependent, but C-M rule is γ_0 -independent. The former represents the nonlinear viscoelastic behavior, but the latter the linear viscoelastic response.

By setting $\gamma_0 = 10\%$, the data obtained at different levels of magnetic field are plotted in Fig. 8.3(b). In these cases, the R-D rule (8.6) is violated. The two sets of lines are evidently deviated, keeping parallel to each other with $|\eta^*(\omega\gamma_0)| < \eta_{app}(\dot{\gamma})$ within a range of $\dot{\gamma}_{eff} = \omega\gamma_0 = 0.1\omega$. The upper limits of parallel ranges of effective shear rate are found to be lower than those subjected to $\gamma_0 = 100\%$. It is important to notice that although the H-B power law constitutive model (8.5) is valid for the MR suspensions under the given conditions, the R-D rule (8.6) is indeed not valid for the cases.

(a)

Fig. 8.4 Data of $|\eta^*|$ at various strain amplitudes are compared with $\eta_{app}(\dot{\gamma})$ for MRF-132LD at $I = 0.4A$ (a) $|\eta^*|$ vs ω with $\omega = \dot{\gamma}$, (b) $|\eta^*|$ vs $\omega\gamma_0$ with $\omega\gamma_0 = \dot{\gamma}$.

To investigate how the strain amplitude γ_0 imposed in oscillatory shear flow affects the interrelation between $|\eta^*|$ and η_{app} , a series of oscillatory shear flow experiments on MRF-132LD at coil current $I = 0.4A$ with various γ_0 were conducted. In Fig. 8.4(a) the data of $|\eta^*|$ are plotted against frequency ω for comparison with the C-M rule; and in Fig. 8.4(b) the data of $|\eta^*|$ are plotted against effective shear rate $\omega\gamma_0$ for comparison with the R-D rule. The solid lines in Fig. 8.4 (a) and (b) represent the function of η_{app} against $\dot{\gamma}$. They showed that neither the C-M rule nor the R-D rule is valid for the MR fluid under the given conditions.

Since the set of plots are all straight lines in the interested range of $\dot{\gamma}$, the general form of the Extended C-M rule (8.8) can be applied. Following the data process presented in Appendix C, the exponential factor α and horizontal shift factor Δ_h are

determined by shifting the lines of $|\eta^*|$ vs ω in Fig. 8.4(a) to coincide with the line of $\eta_{app}(\dot{\gamma})$, and shown in Table 8.1.

Table 8.1 Interrelation factors Δ_h and α as functions of γ_0 for MRF-132LD at $I = 0.4A$.

γ_0 (%)	1	10	50	100	300	1000
Δ_h	0.02	0.24	0.80	0.97	2.62	8.63
α	0.93	0.94	0.96	0.98	1.00	0.99

As all the straight lines are approximately parallel to the solid line of $\eta_{app}(\dot{\gamma})$, the power factor α is found to be close to 1.0 for all values of γ_0 . It is seen that when γ_0 increases, α approaches 1.0 asymptotically. It means that the higher the γ_0 , the more parallel of the line of $|\eta^*|$ vs ω to the solid line of η_{app} vs $\dot{\gamma}$. Since it is reasonable to set $\alpha = 1.0$, the Extended C-M rule (equation (8.8)) reduces to

$$|\eta^*(\omega\Delta_h)| = \eta_{app}(\dot{\gamma}) \quad \text{with } \omega\Delta_h = \dot{\gamma}, \tag{8.11}$$

which can be named as the Extended R-D rule with Δ_h as a function of γ_0 . Only when $\Delta_h = \gamma_0$, the Extended R-D rule reduces to the R-D rule.

Table 8.2 The interrelation factors Δ_h and α as function of γ_0 for MRF-132LD under different magnetic fields.

I	0.0A		0.4A		0.8A		1.2A	
γ_0 (%)	Δ_h	α	Δ_h	α	Δ_h	α	Δ_h	α
1	0.03	0.99	0.02	0.93	0.02	0.91	0.02	0.92
3	0.07	0.99	0.10	0.94	0.07	0.91	0.31	0.93
7	0.13	1.03	0.21	0.94	0.20	0.90	0.35	0.93
10	0.24	0.98	0.24	0.94	0.24	0.93	0.54	0.94
30	0.56	1.02	0.64	0.95	0.57	0.92	1.15	0.95
50	0.68	1.04	0.80	0.96	0.72	0.93	1.17	0.95
80	0.73	1.06	0.92	0.97	0.88	0.95	1.19	0.97
100	0.94	1.06	0.97	0.98	1.01	0.96	1.24	0.98
300	3.32	0.97	2.62	1.00	2.68	0.98	2.34	1.00
700	6.65	0.99	6.40	0.99	6.13	0.98	4.94	1.00
1000	8.91	1.00	8.63	0.99	8.50	0.98	7.16	1.00

The factor Δ_h increases as γ_0 is increasing, for the lines shifted to the left, $\Delta_h < 1.0$; and for the lines shifted to the right, $\Delta_h > 1.0$. There exists a line at $\gamma_0 = 100\%$, for which $\Delta_h = 0.97 \approx 1.0$, so almost no shift is needed. The factor Δ_h as a function of γ_0 is also plotted later in Fig. 8.5(b).

8.4.3 Effects of magnetic field and/or volume fraction

To further investigate the effects of magnetic field and/or volume fraction on the interrelation factors, two series of experiments were designed and conducted. The first series of experiments was carried out on MRF-132LD at different coil currents ($I = 0.0\text{A}, 0.4\text{A}, 0.8\text{A}$ and 1.2A). The obtained power factor α and horizontal shift factor Δ_h as functions of γ_0 are listed in Table 8.2.

The values of α are mostly close to 1.0, which implies that most of the lines of $|\eta^*|$ vs ω are approximately parallel to the lines of $\eta_{app}(\dot{\gamma})$. Therefore, it is reasonable to set $\alpha = 1.0$ for MRF-132LD at all levels of magnetic field; and the Extended R-D rule (8.11) is considered suitable. The data of Δ_h against γ_0 at four different magnetic fields are plotted in a log-log scale in Fig. 8.5(a)-(d), respectively. The two particular dash lines represent the lines for the C-M rule ($\Delta_h = 1.0$) and the R-D rule ($\Delta_h = \gamma_0$), respectively. The intersection point of the two lines is at $\gamma_0 = 100\%$. It is interesting to find that almost all the points ($\Delta_h, \gamma_0 < 100\%$) fall into the region between the two dashed lines, and all the points ($\Delta_h, \gamma_0 \geq 100\%$) approximately fall on the line of R-D rule, i.e.

$$\gamma_0 < \Delta_h(\gamma_0) \leq 1.0 \quad \text{with } \gamma_0 < 100\%, \quad (8.12a)$$

$$\Delta_h(\gamma_0) \approx \gamma_0 \quad \text{with } \gamma_0 \geq 100\%. \quad (8.12b)$$

Thus, the R-D rule is approximately obeyed when $\gamma_0 \geq 100\%$. For $\gamma_0 < 100\%$ all the curves of Δ_h vs γ_0 are similar in shape for different magnetic fields. It was found that at $I = 0\text{A}$, 0.4A and 0.8A , there is no much difference, so the function $\Delta_h(\gamma_0)$ can be approximately treated as independent of the magnetic field in the range of $0 < I < 0.8\text{A}$. A unified curve (the solid lines) is identified as shown in Fig. 8.5(a) – (c). The intersection point of the C-M rule and the R-D rule at $\gamma_0 = 100\%$ is found to be the critical point, at which the curve changes from a curvilinear curve to the straight line of the R-D rule. In the case when $I = 1.2\text{A}$, Fig. 8.5(d), the function $\Delta_h(\gamma_0)$ is found to be quite different from the other cases. It means that in general the function $\Delta_h(\gamma_0)$ is magnetic field dependent.

Fig. 8.5 Factor Δ_h vs strain amplitude γ_0 for MRF-132LD at (a) $I = 0A$, (b) $I = 0.4A$, (c) $I = 0.8A$, (d) $I = 1.2A$.

The second series of experiments were carried out on the homemade MR fluids of different volume fractions ($\phi = 0.1, 0.2$ and 0.4) at $I = 0.4A$ and $I = 0.8A$, respectively. The obtained exponent α and horizontal shift factor Δ_h as functions of γ_0 are listed in Table 8.3.

Table 8.3 The interrelation factors Δ_h and α as function of γ_0 for MR suspensions of different volume fractions at $I = 0.4A$ and $I = 0.8A$.

Magnetic field	0.4A						0.8A					
ϕ	0.1		0.2		0.4		0.1		0.2		0.4	
$\gamma_0(\%)$	Δ_h	α	Δ_h	α	Δ_h	α	Δ_h	α	Δ_h	α	Δ_h	α
1	0.05	0.96	0.07	0.95	0.06	0.93	0.04	0.95	0.06	0.97	0.08	0.92
5	0.23	0.98	0.21	0.97	0.36	0.91	0.24	0.97	0.3	0.95	0.36	0.88
10	0.41	0.97	0.51	0.98	0.61	0.92	0.38	0.98	0.47	0.95	0.52	0.92
50	0.75	0.99	0.92	0.99	0.8	0.95	0.75	0.99	0.83	0.97	0.93	0.96
100	1.05	1	1.17	0.99	1.02	0.95	1.09	0.99	1.12	0.98	1.2	0.97
300	2.79	0.99	2.71	0.99	3.1	0.96	2.73	0.99	2.88	0.98	3.04	0.97
700	6.36	0.99	5.98	0.99	7.16	0.97	5.84	0.99	6.46	0.98	6.68	0.97
1000	9.07	0.98	8.44	0.98	10.2	0.97	8.62	0.98	9.15	0.98	9.36	0.97

Similar to the data in Table 8.2, α in Table 8.3 is also close to 1.0 for most of them. It allows us to set $\alpha = 1$ for all the MR samples under different magnetic fields. Thus, the Extended R-D rule (8.11) is suitable for all the samples. The data of Δ_h against γ_0 for different samples at $I = 0.4\text{A}$ and $I = 0.8\text{A}$ are plotted in Figure 8.6(a) and (b), respectively.

The plots of Δ_h vs γ_0 in Fig. 8.6(a) and (b) are similar to the plot in Fig. 8.5. When $\gamma_0 \geq 100\%$ the R-D rule is approximately obeyed by all the samples of different volume fractions at different magnetic fields. When $\gamma_0 < 100\%$ the plots are not much different among the three samples. The similarity between Fig. 8.6(a) and (b) shows that the magnetic field effect on Δ_h is negligible in the range of $0.4\text{A} < I < 0.8\text{A}$. So, the function $\Delta_h(\gamma_0)$ for MR suspensions may be approximately treated as independent of both the volume fraction and the magnetic field in the range of I studied. Thus, a unified curve is identified in the Fig.8.6 (a) and (b).

Fig.8.6 Factor Δ_h vs strain amplitude γ_0 for MR suspensions with different volume fractions at (a) $I = 0.4\text{A}$ and (b) $I = 0.8\text{A}$.

Comparing Fig. 8.6(a) and (b) for MRF-132LD with Fig. 8.5 (b) and (c) for the homemade MR samples, the empirical unified curves at $\gamma_0 < 100\%$ are different. It says that the interrelation factor $\Delta_h(\gamma_0)$ of MR suspensions depends on the ingredients of materials (the particles, surfactants and matrix fluid used). The particles, surfactants and matrix fluid used in the three homemade MR fluids are different from that of the commercial available MRF-132LD.

8.5 Conclusions

Prior works regarding the theoretical links between the constitutive models and interrelation rules are reviewed. The validity of the rules may justify the constitutive models, and vice versa. In general, if both the log-log plots of $|\eta^*|$ vs ω and η_{app} vs $\dot{\gamma}$ are straight lines, the generalized form of Extended C-M rule is always available, in which the interrelation factors Δ_h and α are functions of γ_0 . For MR suspensions under magnetic fields, since the factor α is always very close to 1.0, the Extended C-M rule reduces to the Extended R-D rule, in which only one factor Δ_h as a function of γ_0 is concerned. The further experimental investigation on the MR samples of different volume fractions at different magnetic fields has shown that the function $\Delta_h(\gamma_0)$ is dependent on the ingredients of MR suspensions (particles, surfactants and matrix fluid). However, the shapes of the plots are all similar. At low strain amplitude $\gamma_0 < 100\%$, the curvilinear line lies in-between the straight lines of C-M rule and R-D rule. At high strain amplitude $\gamma_0 \geq 100\%$, the line coincides with the straight line of R-D rule. For samples with same ingredients, a unified curve of Δ_h can be identified in a range of magnetic field and/or for a range of volume fraction. Thus, the Extended R-D

rule equipped with the available function of $\Delta_k(\gamma_0)$ provides an empirical interrelation for the MR suspensions.

Chapter 9

Conclusions and Recommendations

9.1 Conclusions

In this project, the fundamentals of magnetorheological (MR) fluids were reviewed. Based on the limitation of existing MR fluids, we are stimulated to create new MR fluids to improve their performance. The important conclusions from our studies are listed below with four different categories:

9.1.1 Innovation of new MR fluids

Magnetite particles can be encapsulated in vesicles. A CTAB/SOS vesicle system had been used to encapsulate Fe^{2+} and Fe^{3+} ions, with adding in strong alkaline, magnetite (Fe_3O_4) particles can be formed and they are resided in the CTAB/SOS vesicles.

Nanosized iron particles were synthesized. By changing the water to ethanol ratio of the solution in the reaction, the particle diameter can be altered. As an example, Fe-Co-B particles have been achieved with diameter between 35nm and 170nm have been obtained. Using this method, some other nanosized iron alloy can also be produced, such as Fe-B, Fe-Cr-B, Fe-Ni-B, etc. From nano-sized Fe-Cr-B particles, nano-MR fluids were produced.

Ferrofluids based MR fluids were obtained. Different to conventional MR fluids that using oil as carrier media, ferrofluids based MR fluids (F-MRF) were made using ferrofluids as carrier media.

9.1.2 Investigation of Rheological Properties

MR fluids have the properties to change their rheological properties under magnetic fields. One of the critical criterions to decide the performance of an MR fluid is the magnetic field sensibility. In the whole project, a commercial MR fluid MRF-132LD was used as reference. The property of different MR fluids in this project were investigated and compared with that of this conventional MR fluid. The following results have been obtained.

Ferrofluids don't show strong response to external magnetic fields. Without magnetic fields, they behave like Newtonian fluids, while under magnetic fields, they become in sol-gel status, behave like non-Newtonian fluids.

The shear flow curves of nano-MR fluids can be characterized using H-B model. Without magnetic fields, nano-MR fluids don't show yield stress, while under magnetic fields, the yield stress will be displayed. Although the yield stress is not very large, it's about two orders of magnitude less than that of MRF-132LD. But comparing with ferrofluids, the MR effect of nano-MR fluids is much stronger.

In frequency oscillation for nano-MR fluids, G' kept constant and increased at higher frequency, while G'' kept on increasing from the start of oscillation. And it was found that in frequency sweeping range, there was an overshoot for $\tan(\delta) = G''/G'$, it means for different nano-MR fluids, there is a softening stage in the whole frequency range. The dynamic properties of nano-MR fluids have been simulated using the convected

Jeffreys model. The results showed that the model cannot perfectly describe the dynamic behavior of nano-MR fluids, however, it can show the tendency of G' and G'' .

For all the F-MRF samples, the shear flow curves can be well described by Herschel-Bulkley model. Comparing with nano-MRF, the yield stress has been improved greatly, and it's in the same order of magnitude of conventional MR fluids MRF-132LD. Some further experiments have confirmed that the yield stress of F-MRF is smaller than that of the conventional MR fluids with the same weight fraction and under the same magnetic fields. It was also found that the structural change of F-MRF is quite continuous under different loadings. On the contrary, the structure of conventional MR fluids will break down suddenly under a critical stress.

In strain amplitude sweeping, it was found with the increase of magnetic field or weight fraction, the F-MRF became more rigid, it can be transformed from fluids, to sol-gel and then to solid according to the strength of magnetic fields. There was an overshoot for the loss modulus when strain is exceeded its elastic limitation, which is during the transformation from linear (elastic) to nonlinear (plastic or fluidic). In frequency oscillation, both the storage modulus and loss modulus were kept almost constant in the whole frequency oscillation scope under magnetic fields. At zero magnetic field, there was also an overshoot for the ratio $\tan(\delta) = G''/G'$.

To study the yield stress of MR fluids, three methods have been used to measure the static yield stress of F-MR fluids. In shear rate method, the static yield stress is dependent on the shear rate. The larger the shear rate, the higher the yield stress will be obtained. In strain sweeping method, the stress becomes unstable after the pre-yield stage if the F-MRF has very high yield stress. Whist it's found the stress is vibrating

near the yield stress. The stress sweeping method is the most stable to achieve static yield stress. Through the comparison, it's found the yield stress measured in the last two methods is smaller than that measured in shear rate method.

The interrelation between the steady flow property and the oscillatory property has been studied on MR fluids. At low strain amplitude $\gamma_0 < 100\%$, the curvilinear line lies in-between the straight lines of C-M rule and R-D rule. At high strain amplitude $\gamma_0 \geq 100\%$, the line coincides with the straight line of R-D rule.

9.1.3 Study of sedimentation properties

As stated in the literature review, beside the magnetic field responding ability, the sedimentation property is also crucial to MR fluids. For all the MR fluids investigated in this project, their sedimentation property is summary as follows:

Ferrofluids have little sedimentation issue. The nano-sized Fe_3O_4 particles are very stable because of Brownian motion.

In Nano-MR fluids, the nanosized magnetic particles will sediment in long time run, while they settle slower than micro-sized iron particles in conventional MR fluids. After sedimentation, nano-MR fluids are easier to be re-dispersed.

For ferrofluids based MR fluids, the interaction mechanism between micro-sized particles and nanosized Fe_3O_4 particles were studied. In the fluids, the nanosized Fe_3O_4 particles were attached on the big micro-sized iron particles. So the iron particles were separated by the surface attached Fe_3O_4 particles, which make the whole system easier to be re-dispersed.

9.1.4 Significance of the nano particles and the innovative MR fluids

It's known that ferrofluids don't have strong response to magnetic fields, they can only be used in small loading in damping system, or they are used in micro-control system. The Fe_3O_4 particles were capable to be encapsulated in vesicles and there is no sedimentation issue. This property opens a window in biological application for Fe_3O_4 particles. These particles can be encapsulated in some reagent or medicine, through magnetic control, they can be introduced to or focused in a certain positions for treatment.

Nano-MR fluids have much smaller yield stress than conventional MR fluids, but comparing with ferrofluids, it's a big improvement. And we also achieved our purpose that nano-MR fluids were more stable than conventional MR fluids from anti-sedimentation. It can be seen, the produce of nano-MRF is a trade-off between the yield stress and the sedimentation.

Overall we found the property of ferrofluids based MR fluids were quite close to that of conventional MR fluids. Maybe the yield stress of F-MRF is smaller than that of C-MRF in the same conditions, but the stability was improved a lot comparing with C-MRF. And from the comparison between F-MR fluids and C-MRF, it's found from chapter 6, the mechanical property of F-MRF was more stable than that of C-MRF. This is an important significance for their applications.

9.2 Recommendation for Future Work

In this work, we have developed several different kinds of magnetic fluids for MR fluids. To overcome the sedimentation issue, nano-MR fluids and ferrofluids based MR fluids were presented, and their magnetorheological properties have been

deeply investigated. For better application of MR fluids, some further investigations can be carried out which are listed as follows.

1. Modeling of rheological properties

In chapter 5, we used upper convected Jeffrey model to characterize the rheological properties of nano-MR fluids. In the characterization, the model can only approximately elucidate the trend of dynamic moduli. Especially during the large shear strain stage, the modulus is far away from the experimental results. We still cannot approve whether the model is the best to characterize the behaviors or the parameters are not fully optimized. So some further investigation is necessary to polish the model. And in chapter 6, the rheological properties of ferrofluid based MR fluids have been investigated, but no proper model was given for this material. So it will also be good to characterize this kind of magnetic fluids.

2. The structure change of F-MRF

In chapter 6, we have compared the structure change of F-MRF and C-MRF during shear stress start-up and stress oscillation. And it's found the stress of F-MRF was changing continuously, however, the C-MRF is changed suddenly. But we didn't further investigate why they changed in different pattern. It's necessary to observe the structure change of the difference.

And In chapter 7, during the yield stress measurement in shear strain sweeping, It was found at higher magnetic field, the stress is fluctuating near the yield stress area, we have proposed this fluctuation is caused by structure construction and destroy in magnetic field. It is important to observe the structure change in magnetic fields. So in

future, the micro-structure change of the particles chains under magnetic fields should be investigated.

3. Hybrid MR fluids

In chapter 6, we have investigated the properties of ferrofluid based MR fluids. It's already approved that their yield stress is smaller than that of conventional MR fluids. The anti-sedimentation properties have been significantly improved. Following this approach, the nano sized Fe-Cr-B particles can also be mixed with ferrofluids or microsized iron particles. Definitely, the anti-sedimentation property will be further improved, and the yield stress can also be increased.

4. New application exploiting of nanoscale MR fluids

In this project, we have purposely produced and characterized some new magnetic fluids. And we only consider their traditional application in damping system. Using the magnetic responsive property and viscosity change characteristics, ferrofluids have been used for valves in microchannels [133] and for continuous pumping of water [80]. In all the applications, ferrofluids are used for testing and modeling. It is possible to use Fe-Cr-B based particles for these applications because the magnetic influence on the MR fluid of Fe-Cr-B particles is stronger so that such a MR system is possibly more robust and efficient.

Nanosized magnetic particles offer abundant and attractive potential applications in the field of biomedical engineering. First, nanosized magnetic particles carrying drugs or genes are able to penetrate target cells easily. Second, the nanoparticles are magnetic so that they can be manipulated by an external magnetic field gradient. Third, nanoparticles have a large surface that can be properly modified to attach

biological agents [134]. Contemporarily, only nanosized magnetite (Fe_3O_4) particles were selected for bio-technological experiments. However, because magnetite particles have very weak response to magnetic fields, their applications in such a field would be limited. As we have obtained good nanosized iron (Fe) based particles with tailorable dimensions and much higher magnetization saturation, they are possibly to be applied in the biomedical field [135]. Therefore, the application of nano-sized magnetic particles in biology is very challenging and meaningful.

As a summary, beside the application of mechanical damping system, nanoscale fluids have extensive prosperity for micro-controlling. They are also of great importance in biology, chemistry, physics and engineering.

Appendix A: Rheological Measuring System

The rheological measuring system is shown in Fig. A.1, it is composed of air sensor and motor, two parallel plates, electromagnet, USD and a computer. The MR sample is placed between two plates, as shown in Fig. A2. An electromagnet was embedded under the bottom disk so that a magnetic induction perpendicular to the disk can be produced. The top disk rotates while the bottom disk remains stationary. When the top disk rotates, a sensor measures the torque and feedbacks to computer. A fixed volume of 0.4ml sample was placed between two parallel plates. After loading, the gap of the two plates goes to 1.0mm controlled by the USD software, and the circumference of the sample was sealed by silicon oil.

Fig. A1 The MR rheometer (USD 200).

Fig. A2 The working part of the rheometer, (a) sample loading, (b) lower plate, and (c) upper plate.

The magnetic field is controlled by the DC current. The magnetic circuit runs through the metal body of the TEK 70MR, the hood and the measuring gap and measuring system. Inside the different materials, the field strength H is different. The magnetic induction is expressed by

$$\oint Hdl = N \cdot I = \frac{B}{\mu_0 \mu_{Fe}} \cdot l_{Fe} + \frac{B}{\mu_0 \mu_{Air}} \cdot l_{Air} + \frac{B}{\mu_0 \mu_{MS}} \cdot l_{MS} + \frac{B}{\mu_0 \mu_{MRF}} \cdot l_{MRF} \quad (A1)$$

- μ_{Fe}, l_{Fe} Effective length and relative permeability of the TEK 70MR
- μ_{Air}, l_{Air} Effective length and relative permeability of air
- μ_{MS}, l_{MS} Effective length and relative permeability of measuring geometry
- μ_{MRF}, l_{MRF} Effective length and relative permeability of the sample
- N Coil windings
- $\mu_0 = 1.2567E-06$ Vacuum permeability
- B Magnetic induction

Table A1 Magnetic induction density in mT (in dependence of the relative permeability of the MRF).

[A]	1	2	3	4	5	10	20	50	100
0.1	19	23	24	25	25	27	27	27	28
0.2	38	45	48	50	51	53	54	55	55
0.3	58	68	72	75	76	80	81	82	83
0.4	77	91	97	100	102	106	108	110	110
0.5	96	113	121	125	127	133	135	137	138
0.6	115	136	145	150	153	159	163	165	165
0.7	134	159	169	175	178	186	190	192	193
0.8	153	181	193	199	204	212	217	220	221
0.9	173	204	217	224	229	239	244	247	248
1	192	227	241	249	254	265	271	275	276
1.1	211	249	265	274	280	292	298	302	303
1.2	230	272	290	299	305	318	325	329	331
1.3	249	295	314	324	331	345	352	357	359
1.4	268	317	338	349	356	371	379	384	386
1.5	288	340	362	374	382	398	406	412	414
1.6	307	363	386	399	407	424	434	439	441
1.7	326	385	410	424	432	451	461	467	469
1.8	345	408	434	449	458	477	488	494	496
1.9	364	431	458	474	483	504	515	522	524
2	384	453	483	499	509	530	542	549	552
2.1	403	476	507	524	534	557	569	577	579
2.2	422	499	531	548	560	584	596	604	607
2.3	441	521	555	573	585	610	623	632	634
2.4	460	544	579	598	611	637	650	659	662
2.5	479	567	603	623	636	663	677	686	689

Table A2 Current in Ampere as a function of the relative permeability of the MRF.

[mT]	1	2	3	4	5	10	20	50	100
0	0	0	0	0	0	0	0	0	0
10	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
20	0.1	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.07
30	0.16	0.13	0.12	0.12	0.12	0.11	0.11	0.11	0.11
40	0.21	0.18	0.17	0.16	0.16	0.15	0.15	0.15	0.15
50	0.26	0.22	0.21	0.2	0.2	0.19	0.18	0.18	0.18
60	0.31	0.26	0.25	0.24	0.24	0.23	0.22	0.22	0.22
70	0.36	0.31	0.29	0.28	0.28	0.26	0.26	0.25	0.25
80	0.42	0.35	0.33	0.32	0.31	0.3	0.3	0.29	0.29
90	0.47	0.4	0.37	0.36	0.35	0.34	0.33	0.33	0.33
100	0.52	0.44	0.41	0.4	0.39	0.38	0.37	0.36	0.36
150	0.78	0.66	0.62	0.6	0.59	0.57	0.55	0.55	0.54
200	1.04	0.88	0.83	0.8	0.79	0.75	0.74	0.73	0.73
250	1.3	1.1	1.04	1	0.98	0.94	0.92	0.91	0.91
300	1.56	1.32	1.24	1.2	1.18	1.13	1.11	1.09	1.09
350	1.82	1.54	1.45	1.4	1.38	1.32	1.29	1.27	1.27
400	2.09	1.76	1.66	1.6	1.57	1.51	1.48	1.46	1.45
450	2.35	1.99	1.87	1.8	1.77	1.7	1.66	1.64	1.63

Appendix B: Parameter Identification Method

Assuming a function

$$\tau(t) = x_1 g_1(t) + x_2 g_2(t) + \cdots + x_n g_n(t). \quad (B1)$$

To data $(t_1, \tau_1), \dots, (t_m, \tau_m)$, *i.e.*, choose coefficients $x_1, \dots, x_n$ so that

$$\tau(t_1) \approx \tau_1, \tau(t_2) \approx \tau_2, \dots, \tau(t_m) \approx \tau_m.$$

In the above, $g_i(t)$ is given functions, $x_1, x_2, \dots, x_n$ are coefficients. The purpose is to develop simple, approximate model of observed data. The variables x can be computed by least-squares data fitting,

$$\text{minimize } \sum_{i=1}^m (\tau(t_i) - \tau_i)^2, \quad (B2)$$

or

$$\text{minimize } \sum_{i=1}^m \left(\frac{\tau(t_i) - \tau_i}{\tau_i} \right)^2. \quad (B3)$$

Formula (B2) is aimed to achieve the minimum value of the accumulative absolute error, while formula (B3) is to accumulate relative error. In a wide range of τ , the parameters are more accurate near the large value side if using formula (B2). On the contrary, they are more accurate near the small value side if using formula (B3).

Appendix C: Determination of factors in the Equation of Extended Cox-Merz Rule**Appendix C: Determination of Factors in the Equation of Extended Cox-Merz Rule**

Assume that the plot of $\log \eta_{app}$ against $\log \dot{\gamma}$ and the plot of $\log |\eta^*|$ against $\log \omega$ are straight lines, which can be expressed by linear equations respectively:

$$\log \eta_{app} = A + B (\log \dot{\gamma}), \quad (C1)$$

$$\text{and} \quad \log |\eta^*| = a + b (\log \omega). \quad (C2)$$

where a, b, A and B are known constants identified by curve fitting.

Denoting $Y = \log \eta_{app}$, $X = \log \dot{\gamma}$, $y = \log |\eta^*|$, $x = \log \omega$, we have

$$Y = A + BX, \quad (C3)$$

$$\text{and} \quad y = a + bx. \quad (C4)$$

Substituting $x = X - \log \Delta_h$, which implies $\omega \Delta_h = \dot{\gamma}$, into (C4), multiplying (C4) by α and adding $\log \Delta_v$ gives a new function

$$\Phi = \alpha y + \log \Delta_v = \alpha [a + b(X - \log \Delta_h)] + \log \Delta_v, \quad (C5)$$

where function $\Phi = \log(\Delta_v |\eta^*|^\alpha)$.

Matching the plot of Φ against X to the plot of Y against X requires

$$\alpha a + \alpha b(X - \log \Delta_h) + \log \Delta_v = A + BX. \quad (C6)$$

Setting $\Delta_v = 1$, we can determine

Appendix C: Determination of factors in the Equation of Extended Cox-Merz Rule

$$\alpha = \frac{B}{b} \quad \text{and} \quad \Delta_h = 10^{\left(\frac{a}{b} - \frac{A}{B}\right)} . \tag{C7}$$

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