# Experimental Studies on Magnetorheological Fluids

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## Nomenclature

| | | | |
|---|---|---|---|
| $\tau$ | Shear stress | $\tau_y$ | Magnetic field induced dynamic yield stress |
| $\eta$ | The plastic viscosity | $\dot{\gamma}$ | The shear rate |
| $\phi$ | Volume fraction of particles | $[\eta]$ | The intrinsic viscosity |
| $\eta_0$ | The viscosity of the carrier liquid | $\mu_0$ | Permeability of the vacuum, |
| $\phi_m$ | The maximum particle loading | $H$ | Applied magnetic field |
| | | $M_s$ | Saturation magnetization |

## Introduction

Smart materials are defined as the materials having properties that can be tuned or altered under externally applied fields. These materials are usually polycrystalline or single crystal in their solid state. These smart materials exhibit properties such as ferroelectricity, pyroelectricity, piezoelectricity, and magnetostriction. Another class of smart materials is known as the “field responsive fluids”. Magnetorheological (MR) fluids, electrorheological (ER) fluids, ferrofluids, and some gels belong to this group. A common property of these fluids is that they are all dispersions of particles in a carrier liquid and their properties are controlled by externally applied magnetic or electrical field.

MR fluid can be defined as ferromagnetic or ferrimagnetic particles dispersed in an organic or aqueous carrier liquid. MR fluid has reversible and tunable ability to transform from liquid to viscoelastic solid in fractions of a millisecond when subjected to a magnetic field. MR fluid has a consistency like paints in the “off-state” ($B = 0T$) regime. In the “on-state” ($B \neq 0T$) regime the magnetic particles line up, forming chain-like structure in the direction of the applied magnetic field in order to minimize the magnetic dipole interactions between the particles. This chain alignment causes a considerable increase in the yield stress. This increase is non-linear since the particles are ferro or ferrimagnetic. Depending on the composition, particle size, volume fraction, magnetic saturation, and flux density, the yield stress can go up to 100 kPa (Genç and Phulé, 2002).

The ferromagnetic or ferrimagnetic magnetic phase is multi-domain with low coercivity and high saturation magnetization. The diameters of the particles range from 0.01 to 20 μm. Due to its high saturation magnetization ($Ms = 203.7$ emu/gr), carbonyl iron (CI) produced by decomposition iron penta-carbonyl ($Fe(CO)_5$), is the most commonly used magnetic material (Cullity and Graham, 2010). Besides iron, cobalt, nickel, iron oxides ($Fe_3O_4$, $Fe_2O_3$), ferrites, and transition metal alloys are also used in the synthesis of the MR fluid. Silicone oils, synthetic or semi-synthetic oils, lubricating oils and mineral oils, many other polar organic liquid and water have all been reported to be used as carrier liquid (Genc and Derin, 2012).

Due to their field dependent rheology, MR fluid is used in automobile dampers, (Abu-Ein *et al.*, 2010; Zeinali *et al.*, 2016; Attia *et al.*, 2017), clutches (Hema Latha *et al.*, 2017), and brakes (Kumbhar *et al.*, 2015). They are also utilized in polishing devices (Jha and Jain, 2009), loud speakers, vacuum sealing, cancer therapy (Liu *et al.*, 2001).

Although iron having high saturation magnetization could be a good candidate for magnetic phase, its high density could be a disadvantage. Mismatch between the density of the magnetic particles and carrier liquid causes sedimentation which deteriorates the MR effect. To improve the sedimentation stability without sacrificing the MR effect is a challenge. One way to make a stable suspension is to coat the magnetic particles with a surfactant in order to create steric stabilization (Phulé *et al.*, 1999). The stability could also be improved by using nanoparticles such as magnetite ($Fe_3O_4$), because thermodynamic forces can overcome the gravitation settling when the particle size decreases to a critical value (Rosensweig, 2014). Microcrystalline cellulose, carbon nanotubes, silica, and graphene oxide, nano-hollow $Fe_3O_4$ spheres are other additives that are investigated by various scientists (Ashtiani *et al.*, 2015).

After the brief introduction of MR fluids, in the rest of the paper, the recent experimental studies of the MR fluids will be discussed. These studies will include the improvement of MR effect and sedimentation stability, as well as the experimental findings of the rheological and stability measurements.

## Magnetorheology

Rheology is the study of flow, especially the non-Newtonian flow of liquids, the plastic flow of solids, and deformation of materials under applied forces (Macosko, 1994). Magnetorheology is the science of investigation of the flow and deformation of MR fluids under magnetic field (Laun *et al.*, 1996). The rheological experiments involve the determination of on-state yield stress in steady shear mode under magnetic field, off-state and on-state shear viscosity, and rheological experiments in oscillatory mode.

Rheometer is an instrument that measures the stress and deformation of the material. Throughout the years researchers have developed variety of apparatus or customized commercial rheometers with special magnetic field inductors to measure the yield stress and viscosity of the MR fluids. A rotational parallel plate geometry inserted into a coil was used by Lemaire *et al.* (1993) whereas Laun *et al.* (1996) performed experiments with a concentric cylinder geometry. A cone and plate type rheometer was

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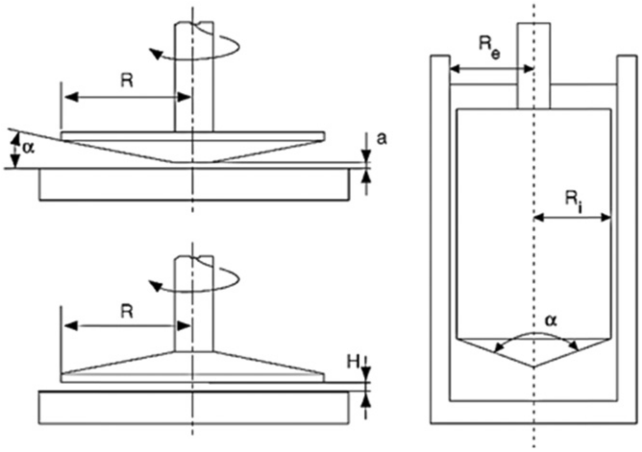

**Fig. 1** Measuring systems: cone-plate, plate-plate, and concentric cylinders. Available at: https://wiki.anton-paar.com/en/basics-of-rheology.

utilized by Gans *et al.* (1999) in order to measure the rheological behavior of ferrofluids. **Fig. 1** represents the different measuring systems of a rheometer.

Dang *et al.* (2000) and Jha and Jain (2009) used pressure driven capillary rheometer. Genc and Phule used a custom built rheometer with a double concentric cylinder geometry as seen in the **Fig. 2** (Phulé *et al.*, 1999; Genc, 2002).

In the beginning of 2000, the rheometers with magnetic field systems started to be manufactured by the pioneering companies such as Anton Paar, Physica, and Paar Physica. Schematic image in **Fig. 3** is given for Physica MCR301 rheometer.

## Experimental Studies on the Rheological Characterization of MR Fluids

Experimental studies are very significant for the analysis and validation of the theoretical models proposed by the scientists. These experimental studies reveal the rheological behavior including on-state yield stress, viscosity, viscoelastic properties, and sedimentation stability of MR fluids. In the following sections recent experimental studies on MR fluids will be discussed.

### Magnetorheological Models

Rheological properties of the MR fluids may show variation depending on the magnetic particles, concentration, carrier liquids, and additives. Thus, it is not possible to explain the MR behavior of all the samples by a simple model. MR fluids have been analyzed by fitting the experimental data to mainly three non-Newtonian models. Bingham plastic Model, Herschel Bulkley Model and Casson Model (Jha and Jain, 2009; Esmaeilnezhad *et al.*, 2017; Saha *et al.*, 2019). These models are given in **Fig. 4**.

In these models, yield stress and the viscosity are two parameters that describe the properties of the MR fluids. The experimental studies have confirmed that MR fluids exhibit two regimes which are known as pre-yield and post-yield regimes. Pre yield regime characterized by an elastic response whereas the post-yield regime characterized by a viscous response (Mohammadi *et al.*, 2010; Gao *et al.*, 2015). Although the fluids' behavior in the pre-yield regime is complex, their behavior in the post yield regime is simple.

In the post yield regime where the shear stress is proportional to the shear rate, that is when the viscosity is constant, the model is Bingham Plastic Model. Bingham Plastic Model is the simplest and most widely used model for MR fluids. The pre-yield and post-yield equations for Bingham Plastic model are given as in Eqs. (1a) and (1b), respectively (Macosko, 1994).

$$\dot{\gamma} = 0, \quad \tau < \tau_y \tag{1a}$$

$$\tau = \tau_y + \eta\dot{\gamma}, \quad \tau \geq \tau_y \tag{1b}$$

where $\tau$ and $\tau_y$ are shear stress and magnetic field induced dynamic yield stress, respectively; $\eta$ is the plastic viscosity and $\dot{\gamma}$ is the shear rate. The dynamic yield stress can be obtained by extrapolating the shear stress vs shear rate curve to zero shear rate. The yield stress of MR fluids is defined as the breaking of the chains of magnetic particles formed by dipolar interaction under magnetic field. According to this model, once the chains are broken, the fluid starts to flow.

In case the viscosity is not constant, i.e., showing post yield shear thinning and shear thickening, the Herschel Bulkley model is a better choice than Bingham Plastic Model. In this model, the constant post yield viscosity in the Bingham Plastic Model is replaced with a power model. Eqs. (2a) and (2b) define the pre-yield and post-yield regimes, respectively.

$$\dot{\gamma} = 0, \quad \tau \leq \tau_y \tag{2a}$$

$$\tau = \tau_y + K\dot{\gamma}^n, \quad \tau \geq \tau_y \tag{2b}$$

where $\tau$ and $\tau_y$ are shear stress and magnetic field induced dynamic yield stress, respectively; $\dot{\gamma}$ is the shear rate; K is the consistency

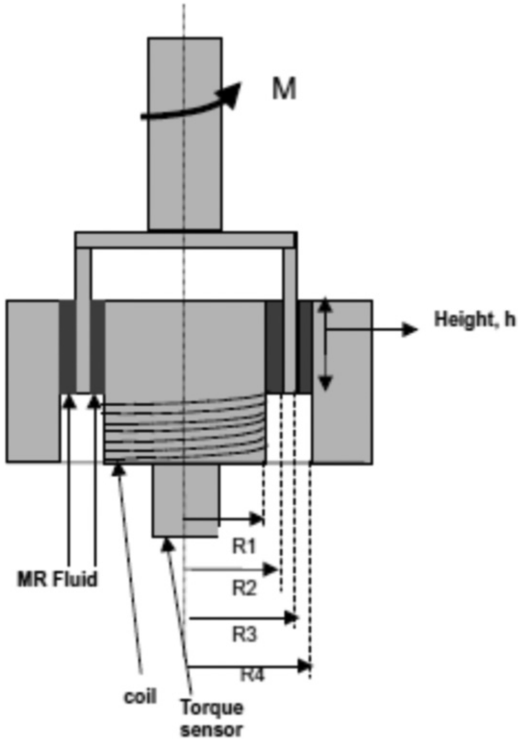

**Fig. 2** Schematic drawing of double concentric cylinder. Reproduced from Phulé, P.P., Mihalcin, M.P., Genc, S., 1999. Role of the dispersed-phase remnant magnetization on the redispersibility of magnetorheological fluids. J. Mater. Res. 14 (7), 3037–3041.

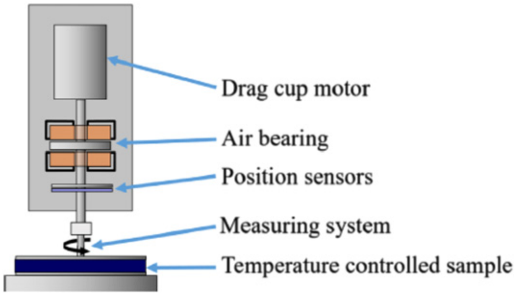

**Fig. 3** Schematic image of Physica MCR301 rheometer. Reproduced from Wang, G., *et al.*, 2017. Development of manganese ferrite/graphene oxide nanocomposites for magnetorheological fluid with enhanced sedimentation stability. J. Ind. Eng. Chem. 48, 142. Available at: wiki.anton-paar.com/en/basics-of-rheology.

coefficient and n is the flow behavior index. The flow behavior index, n, accounts for the pseudo-plastic, or shear thinning behavior when $n > 1$ and shear thickening behavior when $n < 1$. The equation simplifies down to Bingham model when $n = 1$.

Casson Model, which is assumed to have an infinite viscosity at zero rate of shear is given by Eq. (3).

$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta}\sqrt{\dot{\gamma}} \tag{3}$$

where $\tau$ and $\tau_y$ are shear stress and yield stress, respectively; $\dot{\gamma}$ is the shear rate.

The experimental studies conducted over the years by various scientists have shown that Bingham Plastic, Herschel Bulkley, and Casson models could be utilized to describe the flow properties of MR fluids for practical and industrial purposes. Genç and Phulé (2002) reported a yield stress of 100 kPa for 40% iron based MR fluid at a magnetic induction 0.8 T based on the Bingham Plastic Model. Mohammadi *et al.* (2010) showed that for their ferromagnetic nanoparticle fluid, Bingham Plastic model worked well in the post yield regime. However, Herschel Bulkley model described the fluid behavior adequately in both pre and post-yield regimes (Mohammadi *et al.*, 2010). They also concluded that Herschel Bulkley model was in good agreement with the experiment for all shear rates at low magnetic fields. Zhu *et al.* (2019) adopted Bingham Plastic Model for their MR fluids prepared using nano-sized iron and micron-sized iron particles. Esmaeilnezhad *et al.* (2017), analyzed pure carbonyl iron based MR fluids and magnetite added MR fluid using Bingham, Herschel Bulkley Model, and Casson Model. According to the statistical parameter $R^2$, the Herschel Bulkley and Casson

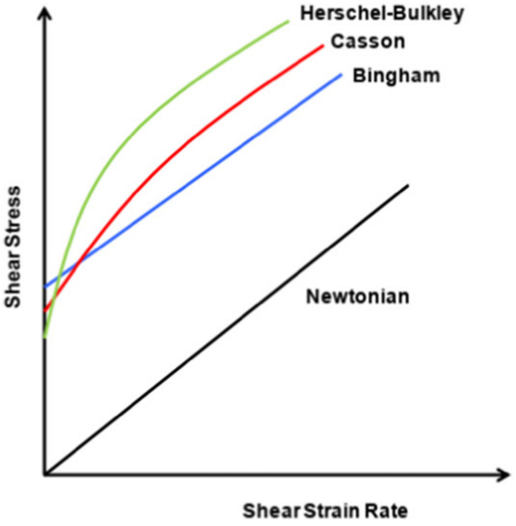

**Fig. 4** Schematic of rheological models. Reproduced from Zelelew, H.M., Papagiannakis, A.T., 2012. Interpreting asphalt concrete creep behaviour through non-Newtonian mastic rheology. Road Mater. Pavement 13 (2), 266–278.

Model had a better fit to the experimental data than the Bingham Model. Bingham Plastic Model showed better fit at higher magnetic fields and at higher shear rates (Barnes, 1989). Jha and Jain (2009) developed an MR fluid for optical polishing in which abrasive SiC (20 vol%) particles were dispersed. Their experimental results showed good agreement with Herschel Bulkley and Casson Model. According to their argument, Bingham Plastic Model was not a realistic model for MR Polishing Fluids with some abrasives in it. Li *et al.* (2007) and Choi and Lee both showed that their experimental results were in good accordance with the Bingham Model.

One of the most important requirements of the MR fluid is to have a high yield stress on which the magnetic phase has a significant impact. According to the analytical approach developed by Ginder (1998), the yield stress shows variation with the applied magnetic field, concentration, and the saturation magnetization of the magnetic particles. At low magnetic fields the yield stress is proportional with $H^2$ given by Eq. (4).

$$\tau_y = \phi\mu_0 H^2 \tag{4}$$

At intermediate levels of the magnetic field, the yield stress is predicted as Eq. (5).

$$\tau_y = \left(6^{0.5}\right)\phi\mu_0 (M_s)^{0.5} H^{3/2} \tag{5}$$

When the field is high enough the particles reach saturation and at this point the yield stress becomes independent of the applied magnetic field. In the high field regime, the yield stress is given by Eq. (6).

$$\tau_y^{sat} = \frac{4}{5^{\frac{5}{2}}}\xi(3)\phi\mu_0\, M_s^2 \tag{6}$$

In these equations $\tau_y$ is the yield stress, $\phi$ is the volume fraction of the suspended magnetic particles, $\mu_0$ is permeability of the vacuum, H is the applied magnetic field, and $M_s$ is the saturation magnetization. Verification of this model was examined by Genc (2002) and Genç and Phulé (2002). Phulé *et al.* (1999) reported that the saturation magnetization is responsible for the lower yield stress rather than the particle size.

Another factor influencing the maximum yield stress is the volume fraction. An increase in the volume fraction leads to the increase in the yield stress. Although the yield stress is linearly proportional to the volume fraction of the magnetic phase in these models, Bombard *et al.* showed that it was true only for concentrations smaller than 30 vol% (Bombard *et al.*, 2014). MR fluids with concentrations larger than approximately 30 vol% the yield stress increased faster than linear.

## Experimental Studies on the Enhancement of On-State Yield Stress of MR Fluids

The most frequently used magnetic material is carbonyl iron (CI) due to its high saturation magnetization. Recent works have suggested that the most promising MR fluids have been prepared by dispersing sterically stabilized magnetic nanoparticles, such as iron, cobalt, nickel transition alloys and their oxides in the MR fluid (Song *et al.*, 2009; Leong *et al.*, 2016; Zhu *et al.*, 2019). In those works, yield stresses increased to almost four times the yield stresses achieved using standard fluids. The magnetic nanoparticles, which could be spherical or needle-like in shape, are located between CI particles by filling their open spaces. Hajalilou *et al.* (2017) enhanced the MR effect of CI based MR fluids by dispersing a mixture of 1 wt% soft magnetic spherical $NiZn_{0.5}\,Fe_2O_4$ and $Fe_3O_4$ nanoparticles with saturation magnetization of 49.77 and 20.72 emu/g respectively. These nanoparticles have a tendency to fill out the cavities between micron-sized CI particles and reinforce the chain formation under magnetic field. **Fig. 5** depicts the behavior of MR fluids with and without nanoparticles under magnetic field.

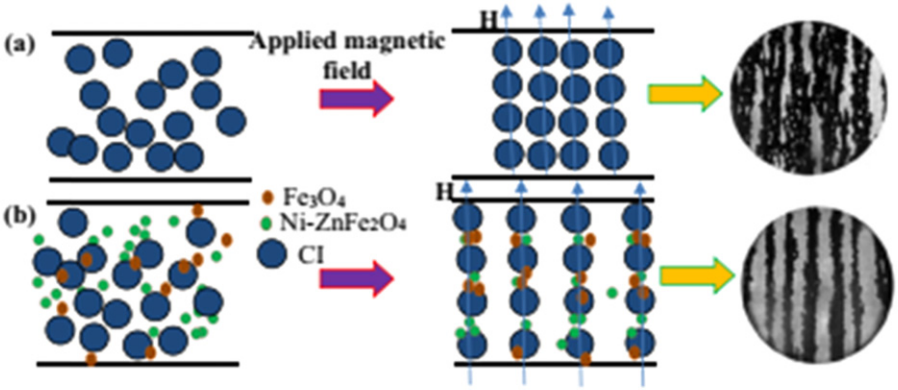

**Fig. 5** Schematic drawing of MR fluid. (a) No nanoparticle is added. (b) Nanoparticles are added. Reproduced from Hajalilou, A., *et al.*, 2017. Enhanced magnetorheology of soft magnetic carbonyl iron suspension with binary mixture of Ni-Zn ferrite and $Fe_3O_4$ nanoparticle additive. Colloid Polym. Sci. 295 (9), 1499–1510.

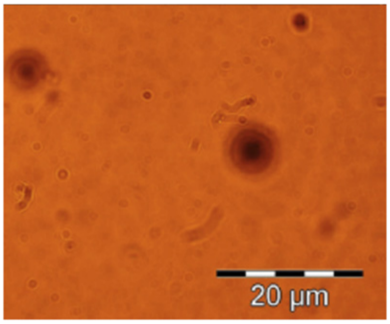

**Fig. 6** Halo formation around the micro-size ferromagnetic particle. Adapted from Iglesias, G.R., *et al.*, 2012. Dynamic characterization of extremely bidisperse magnetorheological fluids. J. Colloid Interf. Sci. 377 (1), 153–159.

These arrangements improve the MR effect. However, there may be a critical concentration of magnetic nanoparticles beyond which a slight decrease of yield stress could be observed. Iglesias *et al.* (2012) showed that 3% magnetite concentration is enough to achieve an MR response comparable to that obtained for an MR fluid without magnetic particles. As the magnetite nanoparticle concentration increased, slight decrease in the yield stress was observed and this could be due to the halo of nanoparticles around iron weakening the field induced structure (Iglesias *et al.*, 2012). In **Fig. 6**, the halo formation of nanoparticles can be observed.

Researchers have also added non-magnetic particles such as fumed silica, clays, carbon fibers and carbon nanotubes in the suspension (Hong *et al.*, 2013) to improve the suspension stability. However, those non-magnetic additives generally cause a reduction in the MR effect. Therefore, magnetic nanoparticles are more preferred in the synthesis of MR fluids. An interesting result was obtained by Bombard *et al.* (2014). They reported the enhancement of MR effect by dispersing magnetic chromium dioxide nanofibers up to 80%. When they compared the yield stress of spherical particles with the nano-fibers (magnetic or non-magnetic) they concluded that the main factor behind this MR enhancement was the particle shape anisotropy.

Yang *et al.* (2016) reported the effect of different surfactants on the MR effect. They showed that with an addition of proper dimer acid as surfactant provoked a significant increase in the on-state yield stress. On the other hand, the MR fluid prepared by the addition of oleic acid did not show any increase compared with the MR fluid without the surfactant. **Table 1** summarizes different types MR fluids and their yield stresses under magnetic field.

## Experimental Studies on the Viscosity of MR Fluids

Understanding and controlling the properties of suspensions in MR is essential for designing equipment, reducing production costs and tailoring products microstructure. In terms of MR fluids applications, a number of key issues should be taken into account. One issue is to enhance the field dependent shear stress of the MR fluids and the second important critical issue is the low viscosity of MR fluids in the absence of the magnetic field. The ratio between off-state viscosity and on-state yield stress may be expressed as the "turn-up" ratio. The general aim in designing controllable fluid actuators is generally to maximize the "turn-up" ratio under given operating conditions. For instance, in brake applications the vehicle will experience more drag with high off-state viscosity MR fluid compared to the low viscosity fluid.

**Table 1** Summary of recent studies on the enhancement of the yield stress of MR fluids

| *MR fluid* | *Additive* | *Highest B (T)* | *Yield stress (kPa)* | *References* |
|---|---|---|---|---|
| 80 wt% CI | – | 0.8 | 100 | Genç and Phulé (2002) |
| 30 wt% CI | – | 0.431 | 1 | Esmaeilnezhad *et al.* (2017) |
| 30 wt% CI | 0.5 wt% $Fe_3O_4$ | 0.431 | 1 | Esmaeilnezhad *et al.* (2017) |
| 40 wt% YIG | – | 1.2 | 25 | Anupama *et al.* (2019) |
| 72 wt% 3 μm CI | 10 wt% 8 μm CI | 0.115 | 80 | Guo *et al.* (2017) |
| 32 vol% CI | 3 vol% $Fe_3O_4$ | 0.431 | 20 | Iglesias *et al.* (2012) |
| 40 vol% CI | – | 0.544 | 20 | Zhu *et al.* (2019) |
| 70 wt% CI | – | 0.431 | 9 | Jang *et al.* (2015) |
| 70 wt% CI | 1% $\gamma$–$Fe_2O_3$ | 0.431 | 11 | Jang *et al.* (2015) |
| 70 wt% CI | 1 wt% halloysite | 0.431 | 8.7 | Hong *et al.* (2013) |
| 15 vol% CI | Oleic acid | 1000 | 50 | Yang *et al.*, 2016 |
| 15 vol% CI | – | 1000 | 50 | Yang *et al.* (2016) |
| 15 vol% CI | Dimer acid | 1000 | 80 | Yang *et al.* (2016) |

The MR fluid viscosity is mostly influenced by various factors: viscosity of the carrier liquid, particle loading, addition of surfactant, and nanoparticles (Genc, 2002; Yang *et al.*, 2016). Kumbhar *et al.* (2015) analyzed the off-state viscosity of silicone oil and synthetic oil based MR fluids with 45 vol% CI loading. They also synthesized 60 vol% CI based MR fluid in sunflower oil. The viscosity of the sunflower oil is much less than the synthetic and silicone oil and as a result in order to reach to the off-state viscosity values of synthetic and silicone oil based MR fluids, the volume fraction of magnetic phase was increased from 45% to 60% (Kumbhar *et al.*, 2015).

Yang *et al.* (2016) investigated the effect of surfactants, oleic acid and dimer acid, on the off-state viscosity. The rheological experiments showed that the addition of the surfactant had a significant effect on the off-state viscosity of the MR fluids. The experimental data were compared with two commonly used theoretical predictions: Krieger-Dougherty and Mooney Equation (Macosko, 1994). They are given in Eqs. (7) and (8), respectively.

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{7}$$

$$\eta = \eta_0 \exp\left(\frac{[\eta]\phi}{1 - \frac{\phi}{\phi_m}}\right) \tag{8}$$

In these equations $\phi$ is the volume fraction of particles, $\phi_{\mathrm{m}}$ is the maximum particle loading, $[\eta]$ is the intrinsic viscosity and $\eta_0$ is the viscosity of the carrier liquid. The viscosity of MR fluid without any surfactant was in good agreement with Mooney prediction. As the amount of surfactants increased the deviation from the theory become more pronounced. The reason for this deviation was attributed to the resistance of the adsorbed surfactant layer acting on the particle (Yang *et al.*, 2016).

The overall suspension properties of MR fluids show non-Newtonian behavior, exhibiting shear thinning behavior. The shear-thinning behavior can be explained as a perturbation of the suspension structure by applied shear. At low shear rates, the suspension structure is close to equilibrium, since thermal motion dominates over the viscous forces. The shear thinning is strong for highly filled dispersions and at very low concentrations of magnetic particles the viscosity vs shear rate curves gets closer to the Newtonian behavior. Genc investigated the viscosity of MR fluids with different volume fractions ($\phi = 5, 10, 20, 30, 40$ vol%) of magnetic powder dispersed in silicone oil (Genç, 2019). **Fig. 7** presents the change of viscosity of MR fluids with shear rate. The suspension showed shear thinning behavior at volume fractions larger than 5 vol%.

The particle concentration dependence of suspension off-state viscosity was analyzed using the relationship between relative viscosity ($\eta_{\mathrm{r}}$) and volume fraction ($\phi$). The $\eta_{\mathrm{r}}$ - $\phi$ dependence was in good agreement with Mooney over the whole range of solid loading measured experimentally (Genç, 2019). Mooney equation is given in Eq. (8).

The addition of nanoparticles into the MR fluid affects the viscosity as well. Esmaeilnezhad *et al.* (2017) reported a slight increase in the off-state and on-state viscosity of MR fluids with magnetite nanoparticle additive. Same kind of increase also observed in the study by Iglesias *et al.* (2012).

## Rheological Properties in Oscillatory Mode

Oscillatory dynamic tests are performed to examine the linear viscoelastic (LVE) behavior of MR fluids. The measurements can be performed in two different modes: frequency sweep mode and amplitude sweep mode. The amplitude sweep test carried out at fixed frequency identifies LVE region. The amplitude sweep mode enables the measurement of storage and loss moduli versus shear rate at constant frequency. Frequency sweep test is used to measure storage and loss moduli versus frequency. The frequency sweep test includes two modes: constant shear stress and constant shear rate.

Ginder (1998) predicted the shear storage modulus G′, by analytical models at intermediate and high magnetic field. The relation has been described as

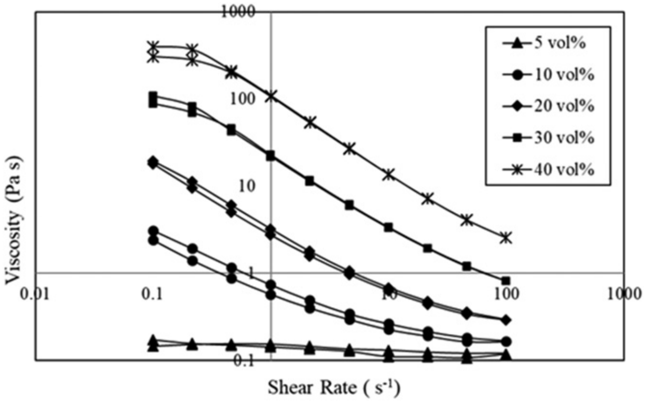

**Fig. 7** Off-state viscosity of MR fluids prepared with 5, 10, 20, 30, and 40 vol% of CI particles.

$$G' = 3\phi\mu_0 M_s H \tag{9}$$

At low magnetic fields, where $M_s$ is linearly related to H, Eq. (10) is expressed as

$$G' \propto \phi\mu_0 H^2 \tag{10}$$

In these equations, $\phi$ is the volume fraction of the suspended magnetic particles, $\mu_0$ is permeability of the vacuum, H is the applied magnetic field, and $M_s$ is the saturation magnetization.

Bombard *et al.* (2014), Esmaeilnezhad *et al.* (2017), and Mohammadi *et al.* (2010) investigated the non-linear yielding behavior of MR fluids in oscillatory shear tests under magnetic field for constant frequency. In their studies they observed that the values of G″ was higher than G′ in a large range of strain amplitude in absence of magnetic field, which presented a liquid-like behavior of MR fluids. When the magnetic field was applied, both G′ and G″ increased with the increasing magnetic field strengths, in which G′ had a much higher value than G″ ($G' \gg G''$). This indicated that the MR fluids have a solid-like behavior due to the formation of chain-like structures.

## Stability and Redispersibility of MR Fluids

Magnetorheological fluids should earn certain characteristics to survive in the market of engineering applications. Stability against sedimentation is one of the most important characteristics of MR fluids that has to be considered and yet it has been a challenge of MR fluid technology. The stability of fluids against sedimentation and centrifugation still remains a central problem.

The stability and redispersibility of MR fluids depend on particle size, viscosity of the carrier liquid, density difference between the dispersed magnetic phase and the carrier liquid, and the interaction energies of the magnetic particles. Magnetic particulates used in the most typical MR-fluid compositions settle out over a period of time (a few hours to a few days). The settling behavior is not surprising given the high density (~5.2 g/cc for ferrites, ~7.8 g/cc for iron) of the particulates compared to most organic liquids. Most MR fluid compositions reported in the earlier literature also show poor redispersibility, i.e., once the particles settle out, they form a very tightly bound network or "cake like structure" and it is extremely difficult to "remix" the MR fluids. Thus, the lack of redispersibility has been a serious problem which deteriorates the MR effect.

Phule *et al.* studied the reasons underlying the lack of redispersibility. Following their calculations of *short range* van der Waals and *long range* magnetic interaction energies they concluded that the magnetic interactions originating from the remnant magnetization are strong and hence, their influence on the formation of a cake or agglomeration of magnetic particles used in MR fluids was quite significant (Phulé *et al.*, 1999). And they suggested that in order to prepare redispersible MR fluids, surfactants that could provide a steric or electro-steric repulsion must be used.

The agglomeration of powders suspended in a liquid can be prevented by creating a mutually repelling charged double layers or physically preventing the close approach of particles due to steric hindrance of the molecule adsorbed on the particle surface. The surfactants could be long chain molecules with a functional group at the end of the tail. These groups could be cationic, anionic, or nonionic. The functional group is attached to the outer surface of the magnetic particle by either chemical, physical bonding or the combination of both, providing steric repulsion increasing the hydrodynamic radius (**Fig. 8**). As the thickness of the adsorbed polymer increases and the size of the magnetic particle decreases, the stability of the magnetic dispersion increases.

In MR fluids, one procedure to prevent sedimentation is the introduction of thixotropic agents and surfactants. The most popular surfactant is oleic acid which is an unsaturated fatty acid. Although it is widely used in the synthesis of ferrofluids and in some MR fluids, the double bond in oleic acid makes it unstable and ready to react with iron particles. To overcome this problem, Morillas *et al.* (2015) used 1-octanol as the additive in their poly-alpha-olefin (PAO) based MR fluid. It is very similar to octanoic acid which is a saturated fatty acid. The only difference between 1-octanol and octanoic acid being the alcohol group present in the last carbon instead of a carboxylic group. Besides carboxylic acids, alcohols could be good candidates due to hydrogen bonding

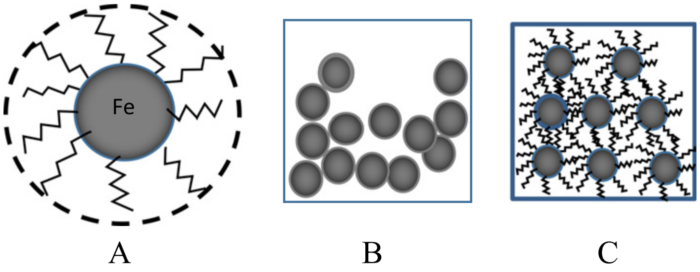

**Fig. 8** (A) Schematic drawing of the adsorption of the surfactant onto the iron particle, (B) the agglomeration or iron particles without surfactant, (C) sterically stabilized iron particles.

capabilities. In their study, they concluded that the stability of MR fluid strongly depended on 1-octanol concentration. Their experiments showed that 1-octanol concentration ranging between 0.1 and 1 wt% provided a good sterically stabilized suspension. However, 5 wt% 1-octanol concentration developed micelles which resulted in the destabilization of the MR fluid (Morillas *et al.*, 2015).

In another study Yang *et al.* (2016), synthesized MR fluids using dimer acid (DA), which is a dimeric fatty acid. It has carboxylic acid groups at two ends of the chains which helped to improve hydrophilic property of materials. CI/DA exhibited enhanced stability compared to the pristine CI particles. Yang *et al.* (2016) investigated the relation between the sedimentation ratio with the concentration of oleic acid and dimer acid as well. As the concentration of the oleic acid increased, the sedimentation ratio also increased. On the other hand, as the concentration of the dimer acid increased, the sedimentation ratio decreased. MR fluid with 2% oleic acid showed the best sedimentation stability. Bica *et al.* (2013) investigated the effect of lauric acid and/or myristic acid on the stability of MR fluids. They saw that coating a double layer of magnetite nanoparticles lead to an appropriate stability of MR fluids. Lopez–Lopez *et al.*, added aluminum stearate to kerosene based MR fluid and observed that the surfactant improved the redispersibility of the suspension.

Ashtiani *et al.* (2014), Ashtiani and Hashemabadi (2015), and Ashtiani *et al.* (2015) investigated the effect of stearic acid and the chain length on the sedimentation stability of MR fluids. They utilized stearic acid, palmitic acid, myristic acid, and lauric acid with 18, 16, 14, 12 carbon atom chain, respectively. Their observation revealed that stearic acid had made the suspension more stable. Stearic acid with a longer chain built a stronger gel-like network that trapped CI particles in silicone oil and this enhanced the stability. **Fig. 9** shows the entrapment of the iron particles in the polymer.

Cheng *et al.* (2018) investigated the effect of changing the organic molecule coating structure on MR fluid sedimentation. They prepared four different MR fluids with 4 different types of surface modifiers in which the length of the carbon atom chain varied. The experiments showed that the sedimentation stability of the coated magnetic particles greatly improved as the carbon chain got longer.

High viscosity grease or other thixotropic materials are used by various scientists. Premalatha *et al.* (2012) and Rankin *et al.* (1999) used grease as additives in their MR fluids and all of them concluded an improvement in the stabilization of MR fluids. Premalatha *et al.* (2012) also investigated the effect of grease fraction on the stability and saw that the sedimentation of the fluid was less significant at higher percentages of grease. Genc and Phule used PDMS-OH (polydimethyl siloxane–hydroxy terminated) as surfactant in PDMS based MR fluids. MR fluids synthesized with smaller CI particles (3–5 μm) showed a much better stability than MR fluids with coarser CI particles (7–9 μm) (Genc, 2002).

Besides using surfactants, the utilization of submicron magnetic particles produced by a variety of processes may improve stability. Coating magnetic particles, nanoparticles additives, combining MR fluids with ferrofluids could be considered as stabilization methods.

The nanoparticles dispersed into the MR fluid could be magnetic or non-magnetic. Fumed silica, organo-clay, and carbon nanotubes are non-magnetic nanoparticles applied to MR fluids to improve dispersion stability of heavy magnetic particles. Addition of nonmagnetic submicron size fillers is an effective method by providing physical layer that improves the stability. Hong et.al reported the effect of nano-sized halloysite clay mineral on CI based MR fluid. Mixing 1% rod like halloysite clay particles with the 70% CI based MR fluid reduced the particle density, resulting in a better stability than pristine CI particles. They saw that the sedimentation rate decreased significantly.

Carbon nanotube is a gap-filling submicron-sized additive in MR fluids. Fang *et al.* (2007) prepared 70 wt% CI based MR fluid with 0.5 wt% single walled carbon nanotube. The rheological and sedimentation experiments were conducted on these materials and also pristine CI based MR fluid. It was found out that the added SWNT not only sustained the MR properties but also improved the sedimentation stability significantly (Fang *et al.*, 2007). At the end of 800 h, the sedimentation ratio was 0.84 and 0.90 for CI based MR fluid and CI/SWNT based MR fluid, respectively.

Although non-magnetic nanoparticles enhance the stability of MR fluids, they generally decrease the MR effect. Therefore, application of magnetic nanoparticles such as iron, its oxides ($Fe_3O_4$, $\gamma$-$Fe_2O_3$), magnetic ferrites, and mixture of magnetic ferrites is suggested (Leong *et al.*, 2016).

In another study to reduce the density mismatch of the between the magnetic phase and the carrier liquid, Saha *et al.* (2019) synthesized hollow sub-micron magnetite spheres which made the particles lighter keeping the magnetization unchanged. They investigated the sedimentation on 3 different MR fluids synthesized with 100 nm magnetite nanoparticles (NP100), 250 nm (NHP250) and 700 nm (NHP700) hollow magnetite nanoparticles whose densities are 5.655 gr/cm$^3$, 5.208 gr/cm$^3$, and 5.214 gr/cm$^3$, respectively. The MR fluids with nano-hollow spheres showed better stability than the nano particles due to lighter densities. The sedimentation ratio for NP100, NHP250, and NHP700 were 25%, 50%, and 40%, respectively. Fang *et al.* used 11 vol% core–shell structured polystyrene (PS)/Fe3O4 microbeads in the synthesis of MR fluids in silicone oil. The density of (PS)/Fe3O4 microbeads was reduced to be 1.90 g/cm$^3$ which was nearly two-fifth of pristine $Fe_3O_4$ particles They observed that the reduction of the density mismatch between the carrier liquid and the magnetic phase improved the sedimentation stability. However, the MR effect decreased due to the decrease in the saturation magnetization.

Jang *et al.* (2015) focused on another magnetic ferrite, $\gamma$-$Fe_2O_3$, in the synthesis of composite MR fluid. They compared traditional CI based MR fluid and CI/$\gamma$-$Fe_2O_3$ based MR fluid, $\gamma$-$Fe_2O_3$ particles had rod-like shape with a density of 4.7 gr/cm$^3$. The CI and, $\gamma$-$Fe_2O_3$ concentrations were 70 wt% and 1 wt%, respectively. Addition of the nano-ferrite showed a slight improvement on the sedimentation stability.

Recent works have suggested highly stable MR fluids could be synthesized by using ferrofluids as dispersion media for micron size CI particles (Susan-Resiga and Vékás, 2014). The ferrofluids are composed of sterically stabilized magnetic nanoparticles less than 10 nm. The concentration of the magnetic nanoparticles in the ferrofluid can vary from 1% to 24% while the concentration of CI particles ranges up to 40 vol%.

Patel (2011) synthesized MR fluids by dispersing micron-sized magnetite particles in nano-sized magnetite based ferrofluid. They observed that the nanofluid based MR fluid was more stable than the conventional MR fluids. Magnetic nanoparticles filled out the micro-cavities between the micron size magnetic particles which restricts the aggregation of larger particles (**Fig. 10**). This caused a field induced separation in MR fluids providing a better stability.

Iglesias *et al.* (2012) synthesized magnetite (8 nm in average diameter) based ferrofluid in mineral oil at different concentration and then added 32 vol% CI particles. The nanoparticles in the ferrofluid form a protective layer around the micron-size ferromagnetic particles. This layer appears as "halo" which contributes to a better stability by avoiding the short range attraction between them. Besides stability, a better redispersibility of the lose sediment in the suspension was also achieved.

Although magnetic oxidized nanoparticles have been used to prepare MR fluids with good sedimentation stability, the field induced yield stress of those MR fluids was low due to their low saturation magnetization. This could be disadvantage in many applications. Improving the sedimentation stability without sacrificing the MR effect is a challenge. Instead of using magnetic oxides, elemental magnetic materials could be suitable to increase MR effect since they have higher saturation magnetization. High purity iron nanoparticles could be good candidate in the production of composite MR fluids. Zhu *et al.* (2019) prepared MR fluids with 10 vol% nano-sized iron particles and micron-sized iron particles. Although the sedimentation stability showed an improvement, the yield stress was almost one fifth of the micron-sized MR fluid. Summary of the sedimentation ratio of different MR fluids is given in **Table 2**.

Many techniques to determine the sedimentation in MR fluids have been developed including visual observation, thermal conductivity, inductance monitorıng, magnetic flux density monitoring, optical approaches (Cheng *et al.*, 2018). The most commonly used technique is the observation of the rate of the sedimentation. The fluid is placed in graduated cylinder and boundary between clear and turbid part of the carrier liquid is recorded over time until it reaches the steady state. The schematic drawing of the experimental set up is given in **Fig. 11**, where A is the supernatant, B is the MR fluid that has settled. A + B is the total height of the fluid. The sedimentation ratio can be defined as a proportion between the height of sediment and the MR fluid. The ratio is given in Eq. (11).

$$\textit{Sedimentation ratio } (X\%) = \frac{B}{A+B} \times 100 \tag{11}$$

**Table 2** Summary of sedimentation stability of MR fluids

| *Magnetic phase* | *Carrier fluid* | *Additive* | *Time (h)* | *Sedimentation ratio* | *References* |
|---|---|---|---|---|---|
| 70 wt% CI | Mineral oil | 0.5% SWNT | 800 h | 0.9 | Fang *et al.* (2007) |
| 70 wt% CI | Mineral oil | 0 | 800 h | 0.9 | |
| 25 wt% CI | Silicone oil | 0 | 15 days | 0.64 | Wang *et al.* (2017) |
| 25 wt% $MgFe_2O_4$/graphene oxide | Silicone oil | | 15 days | 0.82 | |
| 10 vol% CI | Silicone oil | $Fe_3O_4$ | 10 days | 0.6 | Zhu *et al.* (2019) |
| 10 vol% CI | Silicone oil | $Fe_3O_4$ | 10 days | 0.6 | |
| 80 wt% CI | Mineral oil | 3 wt% graphite | 800 h | 0.95 | Lim *et al.* (2004) |
| 80 wt% CI | Mineral oil | 0 | 800 h | 0.75 | |
| 20 vol% CI | Mineral oil | 2% OA | 30 days | 0.95 | |
| 20 vol% CI | Mineral oil | 0.5% DA | 30 days | 0.75 | Yang *et al.* (2016) |
| 20 vol% CI | Mineral oil | 0 | 30 days | 0.6 | |

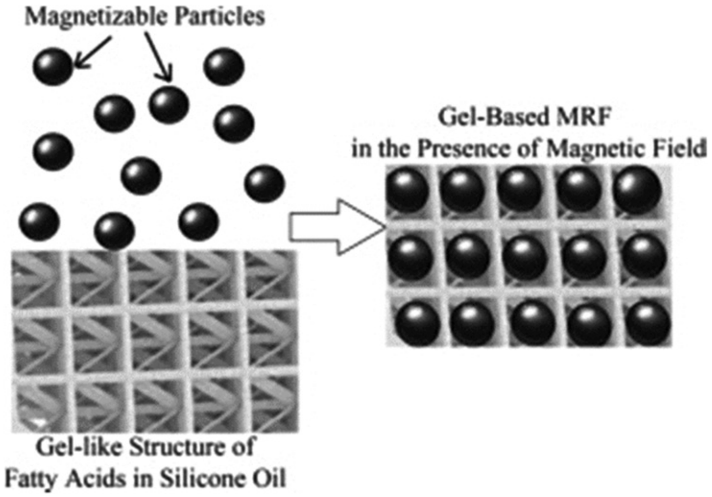

**Fig. 9** Entrapment of iron particles in the gel-like structure. Reproduced from Ashtiani, M., Hashemabadi, S.H., 2015. An experimental study on the effect of fatty acid chain length on the magnetorheological fluid stabilization and rheological properties. Colloids Surf. A. Physicochem. Eng. Asp. 469, 29–35.

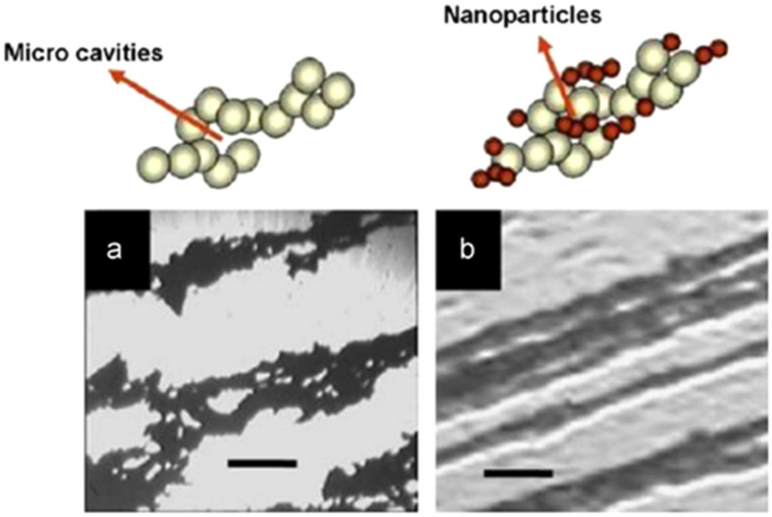

**Fig. 10** Schematic and microscopic image of the nanoparticles filling the cavities. Reproduced from Patel, R., 2011. Mechanism of chain formation in nanofluid based MR fluids. J. Magn. Magn. Mater. 323 (10), 1360–1363.

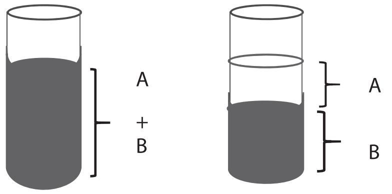

**Fig. 11** Experimental set-up for determining the sedimentation rate.

## Summary

MR fluids are suspensions of magnetic particles in a carrier liquid. Being responsive to the magnetic field and being able to control the properties make them very attractive in many industrial applications. MR fluids when exposed the magnetic field, their viscosity and yield stress increases significantly. Increased yield stress and reduced particle sedimentation due to gravity are two factors that make a good MR fluid. However, reducing the sedimentation stability without sacrificing the MR effect have been an important challenge since the discovery of the MR fluids. These problems mostly arise from the type, shape, size, and volume fraction of the magnetic particles.

In order to improve the yield stress and stability, many researches have been conducted. Among these studies are selecting the appropriate magnetic phase and carrier liquid, decreasing the mismatch between the density of the particles and the carrier liquid by coating the magnetic particles, and introducing magnetic or non-magnetic nanoparticles into the suspension. Carbonyl iron is the most commonly used magnetic particle due to its high saturation magnetization, low coercivity, and relatively low cost. Highest yield stresses have been obtained by using carbonyl iron based MR fluids. However, due to its much higher density than the carrier liquid, the sedimentation has been a big problem.

Coating the magnetic particles with polymeric materials is one of the methods to reduce the sedimentation. Although the sedimentation stability is enhanced considerably, the MR effect is decreased. Another promising stabilization method which enhances the MR effect is the suspending micron-sized magnetic particles in a ferrofluid. Existence of the nanoparticles in the base fluid increases the viscosity and fills out the cavities of the between the micron size particles and thus, enhances the sedimentation stability.

Among all the discussed methods in the previous sections, combining of ferrofluids with carbonyl iron particles, adding stabilizers, and using nanowires can be considered as the most effective methods to improve stability and MR effect. However, these problems still remain a challenge which have to be investigated.

*See also*: Introduction to Magnetorheological Fluids. Key Elements of Magnetorheological Fluids. Physics of Magnetorheological Fluids

## References

Abu-Ein, S.Q., *et al.*, 2010. Experimental investigation of using MR – Fluids in automobiles suspension systems. Res. J. Appl. Sci. Eng. Technol. 2 (2), 159–163.
Anupama, A.V., *et al.*, 2019. Steady-shear response of magnetorheological fluid containing coral-shaped yttrium-iron-garnet particles. Mater. Res. Bull. 113, 45–50.
Ashtiani, M., Hashemabadi, S.H., 2015. An experimental study on the effect of fatty acid chain length on the magnetorheological fluid stabilization and rheological properties. Colloids Surf. A. Physicochem. Eng. Asp. 469, 29–35.
Ashtiani, M., Hashemabadi, S.H., Ghaffari, A., 2015. A review on the magnetorheological fluid preparation and stabilization. J. Magn. Magn. Mater. 374, 711–715.
Ashtiani, M., Hashemabadi, S.H., Shirvani, M., 2014. Experimental study of stearic acid effect on stabilization of magnetorheological fluids (MRFs). In: Proceedings of the 8th International Chemical Engineering Congress & Exhibition, p. 4.
Attia, E.M., *et al.*, 2017. Theoretical and experimental study of magneto-rheological fluid disc brake. Alex. Eng. J. 56 (2), 189–200.
Barnes, H.A., 1989. Shear-thickening (“dilatancy”) in suspensions of nonaggregating solid particles dispersed in Newtonian liquids. J. Rheol. 33 (2), 329.
Bica, I., Liu, Y.D., Choi, H.J., 2013. Physical characteristics of magnetorheological suspensions and their applications. J. Ind. Eng. Chem. 19 (2), 394–406.
Bombard, A.J.F., *et al.*, 2014. Magnetorheology of dimorphic magnetorheological fluids based on nanofibers. Smart Mater. Struct. 23 (12), 125013.
Cheng, H., *et al.*, 2018. Improving sedimentation stability of magnetorheological fluids using an organic molecular particle coating. Smart Mater. Struct. 27 (7), 075030.
Cullity, B.D., Graham, C.D., 2010. Introduction to Magnetic Materials, second ed. Wiley-IEEE Press.
Dang, A., Ooi, L., Fales, J., Stroeve, P., 2000. Yield stress measurements of magnetorheological fluids in tubes. Ind. Eng. Chem. Res. 39 (7), 2269–2274.
de Gans, B.J., Blom, C., Mellema, J., 1999. The development of a magnetorheometer and its use in investigating ferrofluids. In: Nakano, M., Koyama, K. (Eds.), Proceedings of the 6th International Conference on Electrorheological Fluids, Magnetorheological Suspensions and their Applications, pp. 462–469.
Esmaeilnezhad, E., *et al.*, 2017. Rheological analysis of magnetite added carbonyl iron based magnetorheological fluid. J. Magn. Magn. Mater. 444, 161–167.
Fang, F.F., Jang, I.B., Choi, H.J., 2007. Single-walled carbon nanotube added carbonyl iron suspension and its magnetorheology. Diam. Relat. Mater. 16, 1167–1169.
Gao, H.K., Yang, F., Qu, D.S., 2015. Flow analysis and modeling of magneto-rheological fluids. In: Chan, K., Yeh, J. (Eds.), International Conference on Electrical, Automation and Mechanical Engineering. Atlantis Press, pp. 716–719.
Genc, S., 2002. Synthesis and Properties of Magnetorheological (MR) Fluids (PhD Dissertation). University of Pittsburgh.
Genç, S., 2019. Investigation of off-state viscosity of magnetorheological fluids. Int. J. Adv. Eng. Pure Sci. 3, 232–237.
Genc, S., Derin, B., 2012. Field responsive fluids – A review. Key Eng. Mater. 521, 87–99.
Genç, S., Phulé, P.P., 2002. Rheological properties of magnetorheological fluids. Smart Mater. Struct. 11 (1), 140–146.
Ginder, J.M., 1998. Behavior of magnetorheological fluids. MRS Bull. 23 (8), 26–29.
Guo, Y.Q., *et al.*, 2017. Preparation and experimental study of magnetorheological fluids for vibration control. Int. J. Acoust. Vib. 22 (2), 194–200.
Hajalilou, A., *et al.*, 2017. Enhanced magnetorheology of soft magnetic carbonyl iron suspension with binary mixture of Ni-Zn ferrite and $Fe_3O_4$ nanoparticle additive. Colloid Polym. Sci. 295 (9), 1499–1510.
Hema Latha, K., Usha Sri, P., Seetharamaiah, N., 2017. Design and manufacturing aspects of magnetorheological fluid (MRF) Clutch. Mater. Today Proc. 4 (2), 1525–1534.
Hong, C.H., Liu, Y.D., Choi, H.J., 2013. Carbonyl iron suspension with halloysite additive and its magnetorheology. Appl. Clay Sci. 80–81, 366–371.
Iglesias, G.R., *et al.*, 2012. Dynamic characterization of extremely bidisperse magnetorheological fluids. J. Colloid Interf. Sci. 377 (1), 153–159.
Jang, D.S., *et al.*, 2015. Enhanced magnetorheology of soft magnetic carbonyl iron suspension with hard magnetic gamma-$Fe_2O_3$ nanoparticle additive. Colloid Polym. Sci. 292 (2), 641–647.
Jha, S., Jain, V.K., 2009. Rheological characterization of magnetorheological polishing fluid for MRAFF. Int. J. Adv. Manuf. Tech. 42 (7–8), 656–668.
Kumbhar, B.K., Patil, S.R., Sawant, S.M., 2015. Synthesis and characterization of magnetorheological (MR) fluids for MR brake application. Eng. Sci. Technol. Int. J. 18 (3), 432–438.
Laun, H.M., Kormann, C., Willenbacher, N., 1996. Rheometry on magnetorheological (MR) fluids: I. Steady shear flow in stationary magnetic fields. Rheol. Acta 35 (5), 417–432.
Lemaire, E., Bossis, G., Graselli, Y., 1993. Yield stress and structuration of magnetorheological suspensions. J. Magn. Magn. Mater. 122 (1–3), 51–52.
Leong, S.A.N., *et al.*, 2016. Synthesis, characterization and magnetorheological properties of carbonyl iron suspension with superparamagnetic nanoparticles as an additive. Smart Mater. Struct. 25 (2), 025025.
Li, W.H., *et al.*, 2007. Magnetorheology of single-walled nanotube dispersions. Mater. Lett. 61 (14–15), 3116–3118.
Lim, S.T., *et al.*, 2004. Magnetorheology of carbonyl-iron suspensions with submicron-sized filler. IEEE Trans. Magn. 40 (4), 3033–3035.
Liu, J., Flores, G.A., Sheng, R., 2001. In-vitro investigation of blood embolization in cancer treatment using magnetorheological fluids. J. Magn. Magn. Mater. 225 (1–2), 209–217.

Macosko, C.W., 1994. Rheology: Principles Measurements and Applications. Wiley-VCH Inc.

Mohammadi, N., *et al*., 2010. An experimental evaluation of pre-yield and post-yield rheological models of magnetic field dependent smart materials. J. Mech. Sci. Technol. 24 (9), 1829–1837.

Morillas, J.R., Bombard, A.J.F., de Vicente, J., 2015. Preparation and characterization of magnetorheological fluids by dispersion of carbonyl iron microparticles in PAO/1-octanol. Smart Mater. Struct. 25 (1), 015023.

Patel, R., 2011. Mechanism of chain formation in nanofluid based MR fluids. J. Magn. Magn. Mater. 323 (10), 1360–1363.

Phulé, P.P., Mihalcin, M.P., Genc, S., 1999. Role of the dispersed-phase remnant magnetization on the redispersibility of magnetorheological fluids. J. Mater. Res. 14 (7), 3037–3041.

Premalatha, S.E., Ramalingam, C., Mahendran, M., 2012. Magneto mechanical properties of iron based MR fluids. J. Polym. Sci. Pol. Chem. 2 (4), 50–55.

Rankin, P.J., Horvath, A.T., Klingenberg, D.J., 1999. Magnetsignificant at higher percentages of greaseorheology in viscoplastic media. Rheol. Acta. 38 (5), 471–477.

Rosensweig, R.E., 2014. Ferrohydrodynamics. Dover Publications.

Saha, P., Mukherjee, S., Mandal, K., 2019. Rheological response of magnetic fluid containing $Fe_3O_4$ nano structures. J. Magn. Magn. Mater. 484, 324–328.

Song, K.H., Park, B.J., Choi, H.J., 2009. Effect of magnetic nanoparticle additive on characteristics of magnetorheological fluid. IEEE Trans. Magn. 45 (10), 4045–4048.

Susan-Resiga, D., Vékás, L., 2014. Yield stress and flow behavior of concentrated ferrofluid-based magnetorheological fluids: The influence of composition. Rheol. Acta 53 (8), 645–653.

Wang, G., *et al*., 2017. Development of manganese ferrite/graphene oxide nanocomposites for magnetorheological fluid with enhanced sedimentation stability. J. Ind. Eng. Chem. 48, 142. Available at: wiki.anton-paar.com/en/basics-of-rheology.

Yang, J., *et al*., 2016. Viscosity and sedimentation behaviors of the magnetorheological suspensions with oleic acid/dimer acid as surfactants. J. Magn. Magn. Mater. 417, 214–221.

Zeinali, M., *et al*., 2016. Magnetorheological fluid characterization and applications. In: Reference Module in Materials Science and Materials Engineering. Elsevier Ltd, pp. 1–12.

Zhu, W., *et al*., 2019. Iron nanoparticles-based magnetorheological fluids: A balance between MR effect and sedimentation stability. J. Magn. Magn. Mater. 491 (May), 165556.