Magnetorheological Performance of Nano Magnetorheological (MR) Fluid Based on NiFe$_2$O$_4$ Nanoparticles

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Abstract

The magnetorheological performance of nano magnetorheological (MR) fluids based on iron nickel oxide quasi spherical nanoparticles (NiFe$_2$O$_4$) was investigated. The field induced viscoelastic and rheological behavior of nano MR fluids were explored with varying strain amplitude and shear rates. The fluids were subjected to steady state flow conditions and oscillatory strain sweep test under an applied magnetic field. It was observed that the shear stress was proportionally increasing with respect to the applied field. The lower values of loss modulus ($G''$) indicates the formation of long bundles of thin and thick lengthened nano and micro cluster chains of nickel ferrite particles showing an enhanced magnetorheological response. The maximum shear stress was achieved at an optimum value of particle concentration, within 0 – 1.191 T magnetic flux density range. The study also reveals the increase in fluid sedimentation stability.

Keywords

Nanoparticles, Yield stress, Ferrography, Magnetorheology

Introduction

The magnetorheological fluids are the dispersion of micron sized magnetic particles in to the carrier medium such as hydrocarbon oil [1]. Whereas, the nano magnetorheological (MR) fluid is a colloidal suspensions of low coercivity and low remanence nano sized magnetizable particles. These suspensions are special class of smart fluids which reveal the rapid and reversible tendency to change its rheological behavior from free flowing type to semi-solid as subjected to magnetic field [2]. The nano magnetorheological (MR) fluid possess some of the important characteristics like quick response time, odorless, non-infectious, non-volatile, wide temperature range usage, good agglomerative stability and sedimentation stability.

The nano MR fluid consists of base oil, surfactant and magnetic particles. The common carrier media are a non-polar, non-volatile and non magnetizable organic solvent [3]. The sedimentation and agglomeration of particles is one of the most common issues in MR fluids [4]. One of the effective way to improve the fluid stability is to use nanoparticles for fluid preparation and coat them with a surfactant. An effective surfactant used should easily amalgamate with the carrier oil to form a molecular chain and provide a protective layer on particles to improve induced polarization on the suspended particles upon the application of magnetic field [5].

The nanoparticles used to prepare the nano MR fluid are a multi domain soft
magnetic material, where the coercivity (H_c) decreases due to the material transition from magnetic single domain to multidomain with in a crystallite [6]. The advantage of nano MR fluid with Low magnetic coercivity and low remanence will guarantee that the fluid can return to zero field status after the field is removed.

The nano MR fluid has a potential to be used in applications - such as dampers in various modes (valve, shear, squeeze and combination modes) brake, semi – active controlled suspended seat, clutches, hydraulic valves, polishing devices, seals, prosthetic leg etc and some of the potential applications include automotive clutches, earthquake dampers, engine mounts, MR elastomer dampers [7-9]. The recent progress of MR elastomer (MRE) was presented by Bastola et al [10]. The study investigated the magnetorheological effect and various parameters on which MRE’s are dependent. Ahmed et al. presented the use of magnetorheological materials for engineering applications such as MR fluids, MR foams, MR grease and MR plastomers [11].

The nano MR fluid when exposed to applied field the nanoparticles get magnetized and aligned along the magnetic flux direction forming fibrillar micro structure [12]. There by the change in steady shear rheological properties (increase in apparent viscosity) can be observed. Because of small sized particles the Brownian motion interrupts the formation of large fibrillar structure, resulting in the very small viscosity change when subjected to magnetic field. Under the application of strong magnetic fields the Brownian motion becomes negligible, chain formation will resists the magnetic and hydrodynamic forces thereby dictating the improved rheological behavior [13].

The rheological effects arise from the intermutual influences of the magnetic dipoles after magnetized. The physical property of the magnetic particles play a significant factor that influence the shear yield strength of the fluid. The size, shape, changing element composition (by varying precursor ratios), saturation magnetic strength and increase in volume concentration of magnetic particles are the main factors that describe the shear yield stress of the fluid [14-16]. The fibrillar microstructure also plays an important role in defining the shear yield stress of the fluid. Some of the theoretical models have been put forward to discuss the dipolar interaction of single chain, multi chain microstructure, and also to understand the dynamics of chain – chain interaction of straight and curved chains. These models state that a thick columnar structure was much stronger than a single chain structure, eventually when several chains aggregate together to form a 3D columnar structure, it was not easy to bend or fluctuate the microstructure [17, 18]. Researchers have employed some of the most powerful measuring techniques to characterize microstructure of the particle and fluid. Some of the techniques include small angle neutron scattering (SANS) [19], small angle X-ray scattering (SAXS) [20], Magnus MLX microscope (optical microscope) [21], Dynamic light scattering [22, 23] and other methods [24].

The researchers have reported the stress relaxation process on clustered iron nanoparticle based ferrofluid that can be ascribed to linear chain, dense and bulk aggregates [25]. The mathematical models have been developed to determine the viscoelastic properties of the magnetic nano fluids [26, 27]. These representations propose the rise in magnitude of stress and magnetoviscosity for multiple chain microstructure, and were responsible for amplified viscoelastic and magnetoviscous properties responses under the applied magnetic field.

Odenbach et al [28] has developed a relation between the influence of large size particles, Magnetoviscous effect and particle agglomerates in ferrofluids. The shear dependent Magnetoviscous effects were examined and the results indicate that the magnetoviscous effect was strong for high content of large size particle at low shear rates. A significant decrease in magneto viscosity was observed with decrease in the amount of larger size particles. It was also determined that the magnetic flux chains obtained were rigid and straight with small fraction of large size particles in the fluid [29].

The present study deals with the synthesis of NiFe$_2$O$_4$ based nano magnetorheological (MR) fluids prepared under probe sonication with varying carrier oils. To observe the flux line formations, the samples were tested for analytical ferrography. The study also explores the magnetoviscous, viscoelastic and rheological measurements to analyze the responses of the colloids. The sweep measurements were carried out with varying shear rates and magnetic fields. The present article can find significance in design and development of nano magnetorheological (MR) fluids.

Materials and Methods

Materials

The nickel ferrite (NiFe$_2$O$_4$) nanoparticles were used for preparation of nano MR fluid samples. The carrier oils silicone oil (C$_x$H$_{16}$ O Si$_x$, viscosity 100 cSt, density 0.965 g/Cm$^3$ at 25 °C) supplied by D.R.P. Silicone, Mumbai was used. The silicone oil possess higher flash points, oxidation resistance, good temperature stability and heat transfer characteristics [30]. The hydrocarbon oil (Grade.10 W 40, viscosity 0.749 Pa.s, density 0.856 g/m$^3$ at 30 °C) procured from Delta Auto life, Hyderabad was used. The hydrocarbon oil safeguards from corrosion resistance, oil thickening, enhances life and provides protection to the device. The stearic acid (CH$_3$(CH$_2$)$_{16}$ CO,H) procured from Hychem laboratories, Hyderabad was used as surfactant. This forms a continuous gelatin network by entrapping the particles and reducing the friction that enhances the sedimentation and agglomerative stability [31]. The schematic representation and components of nano MR fluid are presented in figure 1 and table 1.

![Figure 1: Schematic representation of components of NMRF.](image-url)
Ultra probe sonicator

A Probe Sonicator set up was used for preparation of nano MR fluid samples. It comprised of three major components Probe (also known as a horn), U/S Generator and Converter. During the operation, the probe’s tip expands longitudinally and the high frequency vibration of the tip causes cavitation and releases tremendous energy in the cavitation field making the dispersion of nanoparticles uniform. The Probe sonicator used was of Model PKS-500, Frequency 20 kHz and Power rating of 500W. It was supplied by M/S PCI Analytics Pvt ltd, Mumbai.

Preparation method

The commercially purchased surfactant was added to silicone oil. Then the dispersion medium was mixed with an ultra-probe sonicator at room temperature. Then the nickel ferrite nanoparticles with diameter ranging from 40 – 80 nm were dispersed in silicone oil under continuous sonication. The fluid prepared is named as NMRF S. The concentration of nanoparticles, carrier oil and surfactant used is as mentioned in table 1. The same procedure is repeated for next sample using hydrocarbon oil as carrier. The sample is named as NMRF H. The fixed volume concentration of nanoparticles, carrier oil and surfactant was used.

Ferrography

The Analex Rotary particle depositor (RPD) extracts the particles from the base oil by the action of gravitational, magnetic and centrifugal forces on the debris. The sample was deposited on a glass substrate in the form of three concentric rings, named inner, middle and outer ring. The sample collected on a glass substrate is viewed under the microscope to capture the chain alignment of magnetic nanoparticles. The ferrography testing results show the long chain formation of the nano and micro particles. These long chains provide resistance to the fluid flow resulting in rise of apparent viscosity of the fluid.

The samples were prepared using Analex (RPD) Rotary particle depositor (Rotary ferrography, Analex ferrography product manufactured by kittiwake). RPD was connected to D.C regulated power supply to adjust the rotor speed (RPM). The images were viewed under a bichromatic microscope set up which consists of camera, light source and digital LCD screen.

The figures 2 and 3 show the analytical ferrography pictures of silicone oil and hydrocarbon oil based nano MR fluids and MR fluids. The figures 2a, 2c, 3a and 3c show the particle dispersion without the application of magnetic field (i.e., H = 0).

Characterization of nano magnetorheological (MR) fluid

A parallel plate rheometer (Anton Paar, Modular compact rheometer (MCR) 501) was used to measure the rheological and viscoelastic properties of nano MR fluid samples. The special measuring plate, the plate–plate system 20/MRD/170/ Ti, D = 20mm with 5A power supply was employed for the measurements. The parallelism of measuring system was always maintained, i.e., 0.3mm for 95µL of fluid.[32] The Twin Gap system (immersion plate) of the magnetorheological device (MRD) allows a magnetic flux density of 1.3 T to be achieved during the characterization. The On state measurements data is recorded when the magnetic field is applied and the off state measurements data is taken when the applied magnetic field is zero.
ON state measurements

A parallel plate rheometer coupled with magnetorheological device (MRD) was used for nano MR fluid characterization. The MRD combines the lower plate and upper yoke (without yoke MRD functioning will be effected) for measuring the magnetic field during the fluid characterization. The upper yoke is required for maintaining and generating the magnetic field. Additionally H-PTD 200 peltier hood control and fluid circulator was used to control the temperature of lower plate and MRD. Water was used as counter cooling fluid when working from 5 to 70 °C temperatures. The magnetic flux density and other properties data was returned to the Rheoplus software to store in the measured rheological data. The rheometer was connected to computer to display the teslameter, temperature sensor and rheological data. Calibration and adjustment control was done before experiments were conducted. The normal force was set to 0.01N, temperature was maintained at 26 °C and gap between the plates was set as per the requirement. The measuring process was started only after the status shown as ‘O.K’ on rheometer.

Measuring procedure

The samples stored in the glass bottles were shaken well before use. Initially zero gap was set between the plates and reset normal force, when procedure was finished move the upper plate to the lift position. The elevation on to the lower and upper plate is made to form a gap of 0.3 mm. The specific quantity of sample was taken onto the lower plate using a microliter pipette. Do not over load the sample. The sample was pre sheared at 100 s⁻¹ by revolving the upper plate for 5 min to ensure the proper dispersion. Under no field and zero shear strain conditions the off state readings may be recorded. To begin with the readings, the field was applied to record viscoelastic, magnetoviscous data. After the measurements were recorded, the sample was degaussed to start the demagnetization with the inverse magnetic field. The procedure was repeated for other nano MR fluid sample.

Stability of nano magnetorheological (MR) fluid

The sedimentation of NMRF was measured by visual observation of the boundary between clear and turbid part of base oil. Prepared samples were placed in 40ml glass bottles for few days and were observed. As a result sedimentation ratio was calculated. Sedimentation ratio of the fluid is defined as shown in equation.

\[ R \% = \frac{x}{y} \times 100 \quad [33] \]

Where: R [%] – Sedimentation ratio

x – Length of the clear part

y – Length of the turbid part

Results and discussions

Microstructure of nano magnetorheological (MR) fluid

The Fig.2 shows the microstructure of silicone oil and hydrocarbon oil based nano MR fluids. It was noticed the dipolar interaction was much stronger in nano magnetic particles because of maximum areal coverage of particles. As a result the inter particle distance between the particles decreased and the areal coverage density increased. The dipolar interaction strength was increased, due to the formation of bulk dense linear chains. The interaction strength will enhance the magnetoviscous effect, shear stress and time of hydrodynamic relaxation. These fibrils grow with higher aspect ratio at maximum applied fields [34]. Reports have shown the simulations of fibrils formation from head to tail between the dipoles, orientational correlations inside dipolar chains and coil globule transitions [35]. The sample exhibits shear thinning behavior under shear. The microstructure of hydrocarbon oil based nano MR fluid show the strong Brownian motion between the particles and assistances the uniform dispersion. This helps in very less agglomerations and formation of thin columnar structures.

Microstructure of magnetorheological (MR) fluid

To understand the microstructure of nickel ferrite micro particles the magnetorheological (MR) fluids were prepared using 1 – 10 µm sized particles with a specific volume concentrations [36]. The formations of particle cluster was noticed from figure 3. The micro particles possess higher magnetization values, that causes the particles to saturate at lower magnetic fields strengths, showing the similar viscous response at lower and higher field strengths. The formation of too long magnetic chains can be destroyed by the visco hydrodynamic forces, where the particle and chain separation occurs at half the length of the chain with decreasing aspect ratios. The straight chains were formed due to weak Brownian force and strong dipolar interaction between the particles. Sometimes the weak Brownian forces can make the chain bent or fluctuate randomly.

The hydrocarbon oil based sample explains the quasi static shear process of the chain formations, where the chain relaxes into lowest energy state at a respective shearing step. Under such shearing process the deformations were observed to be no longer symmetric and eventually becomes unstable. During the initial deformation a gap emerges at one end of the chain, and then the gap widens as the strain increases. When the strain exceeds critical value the chain breaks at the end. This confirms the breaking point of the chain was at the ends, in other words the weak points of the MR Chain are at its ends.

Rheological measurements

Flow curves

Figures 4a and 4b show the variation of viscosity as a function of shear rate (0.1 – 100 s⁻¹) for NMRF samples in the presence of magnetic field. The measurements were carried out at room temperature. The shift from Newtonian regime to a shear thinning regime was clearly observed with the increase in shear rate. The viscosity decrease is due to the orientation of the particles in the direction of shear, leading to the
columnar formation. The thick and thin confined linear chain formations are dependent on the volume concentration and saturation magnetization of nanoparticles. With the increase in field strength the chains with increasing aspect ratios are observed [37]. The nano bridge formation due to dipole-dipole interaction of nanoparticles will rise to the supposition that under the influence of applied magnetic fields the occurrences of viscoelastic effects with low viscous responses were observed. This is one of the main reason why the inverse spinel ferrites show non-agglomerative chain formations even at lower magnetic fields [38] with low viscous levels of the non-Newtonian magnetic fluid.

Shear behaviour

The shear stress curves with respect to the shear rate ramp characterization of the NMRF samples is shown in figure 5. It is observed at lower shear rates the shear stress change is very small as compared to higher shear rates. The increase in shear stress was observed due to the formations of increasingly strong columnar fibril segments. The structure evolution of the samples at different shear rates under magnetic field were subjected to rheopectic effect in plate plate geometry. Where the chain aggregates tend to break and have an inclination to improve due to magnetostatic particle interaction after the static yield stress exceeds. This stress is called dynamic yield stress. The present NMRF samples confirm to the Bingham plastic model and partially confirm to the casson’s model and Herschel-Bulkley (H-B) model. It is expressed as [39, 40], i.e,

\[ \tau = \tau_y + \eta \dot{\gamma} \]  

(1)

Where \( \tau \) is the shear stress of fluid related to the yield stress (\( \tau_y \)), \( \eta \) is plastic viscosity of fluid and \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)).

\[ \sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_\infty \dot{\gamma}} \]  

(2)

Where \( \tau_0 \) is yield stress and \( \eta_\infty \) is the viscosity at higher shear rates.

\[ \tau = \tau_y + k \dot{\gamma}^n \]  

(3)

\( \tau \) is the shear stress, \( \tau_y \) is the on state and off state yield stress, \( \dot{\gamma} \) is the shear rate, \( n \) is the shear thinning factor and \( k \) is the consistency element. The values of shear thinning (n) exponent analyzed from this H-B model were 0.8 for NMRF S sample and 0.9 for NMRF H sample. It was achieved from the flow behavior of the fluid by extrapolating the linear regime of the shear stress curve with respect to the higher shear rates [41]. The studies show the quadratic increase in stress value with respect to the field strength.

Magnetoviscous effect

The magnetoviscous curves of the nano MR samples were shown in figures 6a and 6b to analyze the magnetoviscous effect from shear stress versus magnetic flux density graph. The transition of viscoelastic to viscoplastic fluid was observed from the plotted fittings. The increase in shear yield stress was observed with increasing shear rates. The high magnetic flux densities and high particle volume concentrations have facilitated the strong particle interactions by firming up the columnar segments [41]. This proves that the magnetorheological response of the fluid depends on the applied flux density and volumetric concentration of the particles. The nano MR sample with high and low particle volume concentration can form multiple strands columns, but with varying aspect ratios. The formed crystalline aggregates will obstruct the flow of the fluid. The aggregate formations was conflicted by erratic random dispersion, and such the aggregations can be expressed for a nano sized sphere in terms of coupling factor [42].

The figure 6b illustrates the magnetic sweep test results for NMRF samples. From the plotted fitting the enhancement in the viscosity is observed with increase in flux density and it saturates at higher fields. Beyond the yield point (post yield) due to transition from viscoelastic to plastic the change in apparent viscosity will stimulate the formation of fibrillar segments by enhancing the shear resistance. The magnetoviscous effect produced due to the magnetic polarization of the particles in the shear field will saturate post yield and no additional formation of fibril are observed [43]. The number of fibril segments appear before yield point will define the shear yield stress of the fluid.
Viscoelastic measurements

The strain amplitude and magneto sweep measurements were carried out to understand the viscoelastic behavior of the NMRF samples at a strain of 0.01% to 1% and at an angular frequency (ω) 10 rad s⁻¹. The figure 7 illustrates the elastic or storage modulus (G') and viscous or Loss modulus (G'') as a function of shear strain (%) of NMRF S and NMRF H samples at an applied magnetic field of 1.19T. The NMRF H samples exhibit linear viscoelastic nature with decrease in G' and G'' with respect to amplitude strain. G' is greater than G'' within the specified strain range at an applied magnetic field.

The NMRF S sample show a slight transition from linear to nonlinear regime. As the strain amplitude increases, the crossover was noticed and the viscous component overshoots the elastic component. This is because at small deformation rates, the redispersions of the columnar structures was opposed by the fibril ruptures that controls the transition from linear to nonlinear rheology. Further at higher strains, the nonlinear nature is exhibited that make the microstructure to breakdown due to loss of elasticity.

Stability of NMRF

Figure 8 shows the stability of nanoparticles for two different samples observed over a period of 35 days. Both the samples were stable during the observation period. No major sedimentation was noticed from day 1 to day 35. The high frequency ultrasonication has intensified the Brownian motion that has prevented nanoparticles from impact settling. The very low sedimentation of the particles in the fluid will enhance the shear yield strength of the fluid and increases the damping effect in the damping applications.

Conclusion

The nano MR fluid and MR fluid samples were synthesized and investigated for analytical ferrography testing to observe the chain formations of the nickel ferrite nano and micro particles. The magnetic field induced columnar structure formations were supported with the microscopic images showing more chains and subsequent chain growth into thick and thin bundles. The test results of nano MR fluid samples show the excellent chain formations. The agglomerated chain formations were noticed for MR fluid samples. The present article also discusses the magnetoviscous and viscoelastic behavior of nanoscale nickel ferrite based NMRF's. This article was intended at understanding the behaviour of nano magnetic ferrite particles based fluids. The nano MR fluid samples were prepared with fixed volume concentrations of nanoparticles and surfactants. The magneto rheometry studies reveal the silicone oil based NMRF show the highest yield stress. Both the samples exhibit rheopectic effect and the transition from Newtonian to non-Newtonian regime may be observed under the applied magnetic field and also fluids confirm the Bingham plastic model. The storage modulus (G') and loss modulus (G'') were measured as function of shear strain (%). The results show a slight crossover of G' over G'' for NMRF S sample and for NMRF H sample G' > G''. The surfactant used has enhanced the sedimentation stability of the fluids.

References

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