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Rheological Study of Nickel Ferrite Ferrofluid

A. Amirimehr[a], E. Ghasemi[b]*, A. Fazlali[a]

[a]*Department of Chemical Engineering, Arak University, Arak, Iran*
[b]*Institute of Color Science and Technology , Tehran, Iran*

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ABSTRACT

In this work, a stable NiFe2O4 paraffin based ferrofluid was prepared via high energy milling. The rheological properties of ferrofluid were studied. Bingham plastic, Herschel–Bulkley and Casson models were used to evaluate the shear stress-shear rate dependency. The ferrofluid exhibited a shear thinning behaviour for all studied magnetic field. The magneto-viscous effect and thixotropy of ferrofluid were studied and the role of formation and destruction of magnetically induced structures and the interactions of nanoparticles and aggregates were discussed.

1. INTRODUCTION

Ferrofluids (FFs) are stable colloidal dispersions of nano-sized particles of Ferro or ferri-magnetic nanoparticles in a carrier liquid. Using of surfactant is a usual method for stabilization of magnetic nanoparticles [1].

Interest in these fluids is driven by both their growing importance for technical and medical applications and the wide variety of fascinating basic physics questions that can be addressed with their help, like the influence of dipolar interactions and magnetic fields on the structure and dynamics of fluids and phase transitions in such systems. Thus the rheology and magneto-viscous effect, i.e., the viscosity change due to an applied magnetic field, of these fluids have attracted considerable attention [2].

In most technological and biomedical applications of FFs, the magnetic material can be one of a MFe_2O_4 (M = Fe, Co, Cu, Ni, Zn, Mg, Mn, Ba) ferrites. Nano-ferrites are good candidates for biomedical purposes since they present a high magnetic moment, are chemically stable, and their surfaces are very reactive to attach biological molecules [3]. The most commonly used ferrites are magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Hence, most studies have focused on the rheological and magnetorheological properties of these ferrites [4-9] and other ones have been considered less. In this work, we have prepared nickel ferrite ($NiFe_2O_4$) FF via high energy milling in a planetary mill. The rheological and magneto-rheological properties of FF were investigated and discussed considering the effects of shear rate, magnetic field, interactions between nanoparticles and their aggregation.

2. MATERIALS AND METHODS

2.1. Materials $NiFe_2O_4$ magnetic nano-powder was purchased from Sigma-Aldrich Co. As specified by the vendor, the Physical form was nearly spherical, the particle sizes were <50 nm and the density was 5.368 g/cm^3. Pure liquid paraffin was provided locally (Dr. Mojallali Co.) and Oleic acid was purchased from Merck Co. All materials were from analytical grade without any purification.

2.2. FF preparation FF samples were prepared by milling method [8]. 20g of $NiFe_2O_4$ nano-powder was mixed with 50cc of oleic acid and milled in a Fritsch Co. Pulverisette model planetary mill in a ZrO_2 cup and balls for 2 h. The obtained suspension was centrifuged at 12,000 rpm to separate the extra and uncoated oleic acid. Then the obtained precipitate was dispersed in a suitable amount of paraffin using a mechanical mixer and ultrasonic bath (FRITSCH Ultrasonic, laborette 17, Frequency: 50–60 HZ), and the

*Corresponding Author's Email: eghasemi@icrc.ac.ir (E. Ghasemi)

concentration was adjusted to 40 wt%. Finally, a stable suspension was prepared.

2.3. Characterization

X-ray diffraction (XRD) peaks were obtained in continuous mode from 4-90 degree with a scanning rate of 0.04 deg/sec. The crystallite size was calculated from the X-ray line broadening using Scherrer's formula [10].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size in angstrom, K is the shape factor, λ is the x-ray wavelength, β is full width at half maximum (FWHM) of the diffracted peak in radians, and θ is the Bragg angle.

Magnetization measurements were carried out via an alternative gradient force magnetometer (AGFM) model 155 from a locally M. D. K. Co. at room temperature.

The size distributions of the particles/aggregates in the FF were measured with a Brookhaven 90plus Dynamic Light Scattering (DLS).

Rheological measurements were performed with a MCR300 Rheometer (Physica Anton Paar GmbH). A plate–plate spindle, PP25-MRD with a 1.95 cm diameter was employed for all of the measurements. To remove sample-loading effects, prior to each measurement, a shear rate of 1000 s^{-1} was applied for30s and after that the sample was kept at rest for another 30s without shear rate. A magnetic field was applied in the vertical direction to the sample during the tests. Using a Peltier and water circulation system, the temperature of the samples was controlled during the measurements with a precision of ±0.01 ℃.

3. RESULT AND DISCUSSION

The X-ray pattern of $NiFe_2O_4$ powder is shown in Figure 1. It can be observed that all of the peaks are related to $NiFe_2O_4$ phase. The relatively broad peaks are related to the small size of particles. The crystallite size, which was calculated using Scherrer's formula from the XRD line (311) broadening, is 10.6 nm, which is according to the size range reported in the mentioned Aldrich Co. data sheet (<50 nm). This size implies that the magnetic nanoparticles tend to be single domain [11].

Figure 2. shows the magnetic hysteresis curve of the FF, which was obtained from the magnetization cycle. Referring to the crystallite size of the nanoparticles (10.6 nm) and small remanent magnetization in the magnetic hysteresis curve, it could be claimed that the $NiFe_2O_4$ magnetic nanoparticles behave as the same as the super paramagnetic particles [11].

Lognormal size distribution of nanoparticles in FF is displayed in Figure 3. The mean particle size of the aggregates is 130 nm and the particle size varies in the range of 80 to 180 nm. This size distribution in FF is due to the formation of aggregates or clusters. Agglomeration processes in FF can be either derived by magnetic particle–particle interaction or by van der Waals interaction [11]. Also, according to the magnetic hysteresis curve, the magnetic interactions between the nanoparticles, which can lead to agglomeration, seems reasonable.

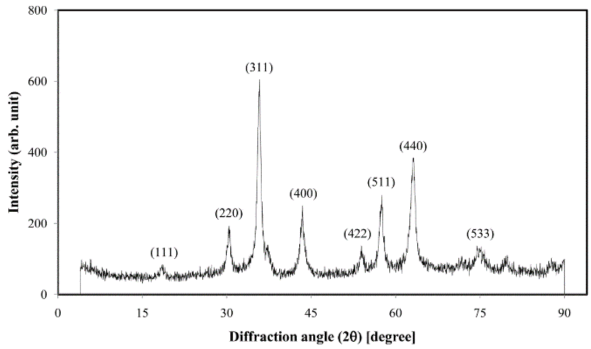

Figure 1. XRD pattern of $NiFe_2O_4$ nanopowder.

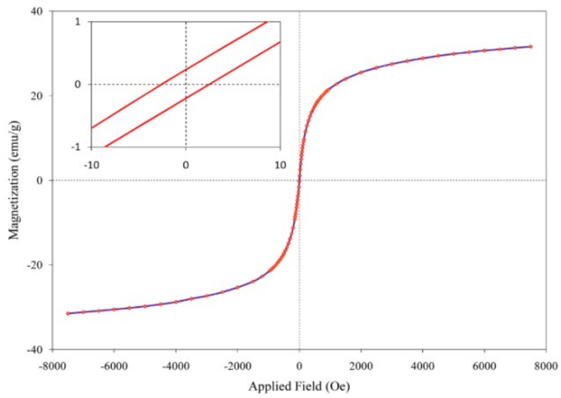

Figure 2. Magnetic hysteresis loop of $NiFe_2O_4$ nanopowder.

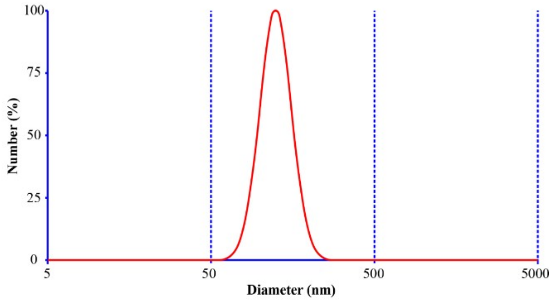

Figure 3. Lognormal size distribution of $NiFe_2O_4$ nanoparticles in FF.

Figure 4. shows the shear dependence of viscosity for FF and based fluid. It is obvious that this FF has shear thinning behaviour, this also reported for other FFs such as Fe_3O_4 and γ-Fe_2O_3 in different base fluids [6, 8, 12]. It can be seen that the based fluid, just at the narrow limit of low shear rates, has shear thinning and reveals Newtonian behaviour at a wide range of shear rate. The based fluid's behaviour is not the same as the FF. This indicates that the main portion of the rheological behaviour of FF depends on the nanoparticles interactions.

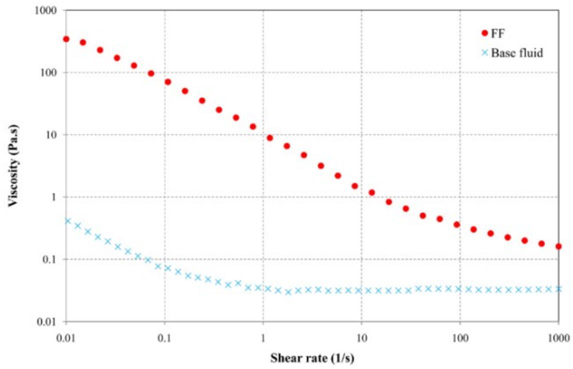

Figure 4. Variation of viscosity with shear rate for FF and Base fluid.

Figure 5. shows viscosity-shear rate variations at different magnetic fields. When the FF exposed to the magnetic field, the magnetic nanoparticles tend to arrange themselves along the direction of magnetic field (in this study, perpendicular to flow direction) and form the new structures with higher resistance under the magnetic field [11, 12]. By increasing magnetic field intensity, the interaction between the magnetic nanoparticles and their arrangement became stronger. Therefore, the viscosity of FF increases under an applied magnetic field.

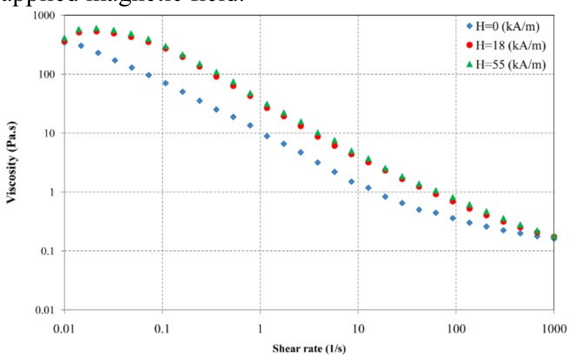

Figure 5. Shear-thinning behaviour of FF at different magnetic field strength at 25 ℃.

It is obvious that for all of different magnetic field in Figure 5. the behaviour of FF is shear-thinning. In absence of magnetic field, shear rate increase causes continuous viscosity decrease. However in presence of magnetic field, at shear rate of 0.01 s^{-1}, a small increase of viscosity is observed. The magnetic field leads to magnetization of nanoparticles and then they adhere to each other which leads to formation of aggregated structures, and these structures increase the viscosity. In spite of applying the shear rate, these structures don't break; in other word the shear force is not too strong to break down these structures. In fact it helps to rearrangement of particles and then to the formation of bigger aggregated structures. With more increase of shear rate the applied shear stress overcome to the strength of these structures and then the viscosity decreases gradually.

Figure 6. illustrates behaviour for shear stress-shear rate data of FF with and without the magnetic field. At low stress levels, the existences of three-dimensional structures (agglomerates) offer a very high resistance which is frequently interpreted in terms of a yield stress [13]. Above the yield value these structures break down and the FF starts to flow. Moreover it shows that when the magnetic field increases, the shear and yield stresses also increase. Similar behaviour have been observed and reported by Ghasemi et al. [6] for Fe_3O_4 kerosene based FF and Hosseini et al. [8] for γ-Fe_2O_3 paraffin based FF. They have related such behaviours to form magnetic induced structures. It should be considered that the formation of magnetic induced structures only changes the magnitude of viscosity and yield stress and has no effect on the shear-thinning yield behaviour of FF.

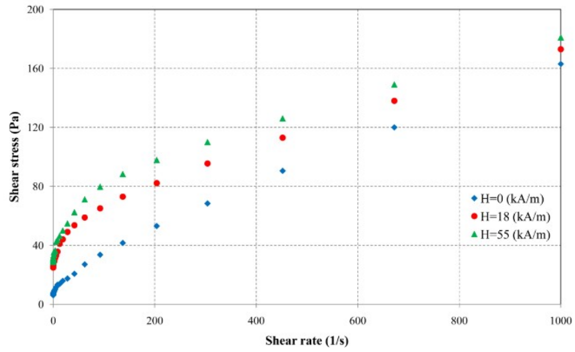

Figure 6. Effect of magnetic field on shear rate-shear stress variations at 25 ℃.

We have examined three empirical models for the relation of shear stress and shear rate with and without the magnetic field:

Bingham model: $$\tau = \tau_y + \eta\dot{\gamma} \qquad (2)$$

Casson model: $$\tau^{1/2} = \tau_y^{1/2} + \eta^{1/2}\dot{\gamma}^{1/2} \qquad (3)$$

Herschel–Bulkley (H. B.) model: $$\tau = \tau_y + K\dot{\gamma}^n \qquad (4)$$

where τ denotes the shear stress, τ_y the yield stress, η the viscosity and $\dot{\gamma}$ the shear rate. K is called the "consistency" and n is a dimensionless constant and both are structural-dependent parameters can be determined experimentally [14]. The values of yield stress and other related parameters to these models are tabulated in Table 1. For each model, the regression coefficient (R^2) is presented for comparison purposes.

In both absence and presence of the magnetic field, the results show that Bingham model present relatively higher yield stress (τ_y) and lower level of R^2) compared with the Casson and Herschel-Bulkley models. In the presence of magnetic field, formation of new structures and rearrangement of particles caused a change in particle's structures of FF. However, the Herschel–Bulkley (H.B.) model with two structural-dependent parameters, at various magnetic fields, presents the best fitness whit experimental data (Table 1).

TABLE 1. Yield stress of FF at different magnetic field strength obtained from model fitting of the experimental data (Figure 6).

Model	**0** (kA/m)		**18** (kA/m)		**55** (kA/m)	
	τ_y (Pa)	R^2	τ_y (Pa)	R^2	τ_y (Pa)	R^2
Bingham	10.55	0.9835	33.97	0.9299	40.47	0.8916
Casson	6.767	0.9997	27.86	0.9926	33.74	0.9801
H. B.	7.417	0.9995	25.89	0.9968	28.59	0.9978

For thixotropy assessment, the hysteresis loop test of FF has been evaluated by ascending and descending shear rate ramps, from 0.01 to 1000 s^{-1} (up ramp) and from 1000 to 0.01 s^{-1} (down ramp), respectively (Figure 7).

In the presence of magnetic field, for the range of 0.01 to 0.1, there is a hysteresis between up and down ramps. In the up ramp, at shear rate of 0.01 s^{-1}, the sample is exposed to both the magnetic field and the shear rate simultaneously. As mentioned before, at this point the formation rate of induced structures by the magnetic field is started and is faster than the destruction rate of structures by shear rate, therefore the viscosity increase. If the time is being enough, at certain shear rate, the effects of magnetic field and shear flow reach to equilibrium and after that the viscosity will be steady. Borin et al [15] have reported that this transient time last several minutes, but probably in our experiments the time step (3s) for each point was not enough and before achieving the equilibrium, the shear rate was increased. Over time, all possible induced structures by the magnetic field are formed and after that only the shear rate is an effective factor. Therefore in the range of 0.1 to 1000 the hysteresis loop was not be observed.

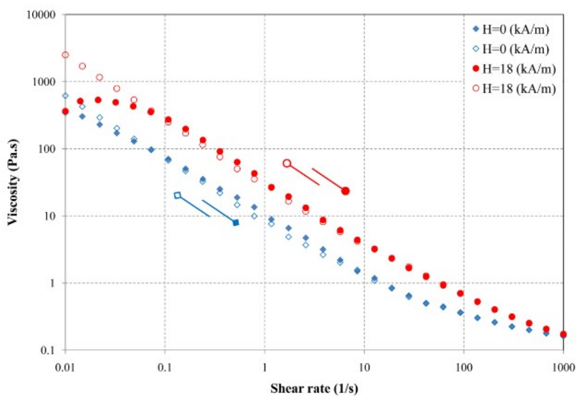

Figure 7. Thixotropic behaviour of FF at H = 0 and 18 (kA/m).

The hysteresis loops for magneto-viscous effect of FF under various shear rates are shown in Figure 8. The relative viscosity $(\eta-\eta_0)/\eta_0$ is considered as magneto-viscous effect [12, 16]. Where, η_0 and η are the viscosities of the FF before and after applying the magnetic field, respectively. As it was mentioned before, the viscosity increment by increasing magnetic field is the consequence of formation and rearrangement of new structures (chain-like or drop-like structures) and by increasing shear rate and destruction of these structures, a little increase in viscosity is observed. Zubareve and Iskakova [17] reported that poly-dispersity of FFs has a very important role in the formation of magneto-rheological properties. The large particles dominate the rheological properties of the fluids in the presence of magnetic fields [16, 17]. When the field is increased, the effects, determined by the biggest particles, tend to be saturate while the small particles form new structures result in further increase in viscosity of the system. The saturation of the total magneto-viscous effect, determined by particles of all sizes, must take place simultaneously with the saturation of the smallest particles effects. Thus, when the field is relatively weak, the magneto-viscous effect is provided by the biggest particles.

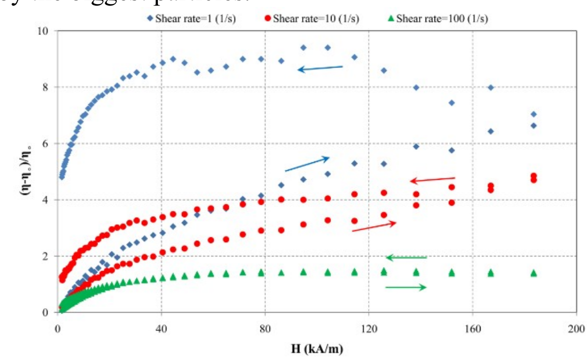

Figure 8. Hysteresis loop for magneto-viscous effect of FF at different shear rate.

Hosseini et al. [8] has reported similar behaviour for γ-Fe_2O_3 paraffin-based FF. They have observed the relative viscosity decreases above the magnetic field of 100 kA/m for low shear rates (1-10 s^{-1}). They ascribed this phenomenon to phase separation in the FF. It is well known that the magneto-viscous effect is directly related to the effective number of magnetic nanoparticles, which have a role in the formation of new structures [18]. The mean particle size of our sample is 130 nm which is appreciably smaller than 398 nm in their samples. It means that there is difference between the effective numbers of these two FF, which lead to different magneto-viscous behaviour of two FF.

The appeared hysteresis loop in every shear rate refers to the state of formation and destruction of new structures and also the arrangement of these structures. Probably, in descending magnetic field ramp i.e. from maximum value to zero, some of formed structures in ascending magnetic field ramp can't break down and caused increasing in viscosity. By increasing shear rate, there is less possibility for such structures to remain and the enclosed area of hysteresis loop is madesmall.

4. CONCLUSION

We have prepared a stable $NiFe_2O_4$ paraffin based FF via high energy milling method and investigated its rheological and magnetorheological properties. The results demonstrated that the corresponding FF is a non-Newtonian fluid with shear- thinning yield behaviour in either the absence or presence of a magnetic field. Good conformation between the rheological behaviour of the FF and the Herschel – Bulkley model was observed. In addition, any obvious thixotropy behaviour pertains to the non polar particles and medium was not experienced. The hydrodynamic size of particles showed that the aggregated structures can be formed. It was confirmed that under low shear rates, the magneto-viscous effect is irreversible under a magnetic field and is reversible at high shear rates. This was explained with magnetic field induced structures.

5. ACKNOWLEDGMENTS

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