Chapter V

Magnetorheological study of Gd_2O_3 nanorod based fluids

The control of properties and behavior of liquids is an important field both from the point of view of fundamental research and advanced applications. Two types of magnetic fluids are known since the middle of the 20th century: magneto-rheological (MR) fluid and ferrofluid (FF) [1−4]. In MR fluids micrometer sized particles are suspended in a liquid carrier. The MR fluid particles have zero magnetic moment in the absence of applied magnetic field and consequently, there is no magnetic interaction between them. However, when a magnetic field is applied, the MR fluid experiences a net magnetic moment due to strong magnetostatic interaction between the particles as a result of which they tend to align in the direction of the applied magnetic field. On the other hand, ideal FF contains magnetic particles smaller than 10 nm and coated with surfactant that are stabilizes against van der Waals attractive forces [1].

The magnetic fluids are capable of exhibiting magneto-viscous properties [5-7]. When a magnetic field is applied to FF, it undergoes noticeable changes in physical properties. The change in the fluid's viscosity due to an external magnetic fluid is termed as magneto-viscous effect (MV). The MV effect of FFs is established as one of the most challenging and vital property for ferrofluid application/ research [8, 9]. The viscosity of the FF is invariably sensitive to the applied magnetic field. Moreover, magnetoviscous response is one of the most fundamental and widely investigated property of the FFs. Based on this character; FFs have been widely used in many fields such as dynamic sealing [10], shock absorber [11], hyperthermia for cancer therapy [12] and so on. The variations of viscosity with respect to time, shear rate, temperature or other factor have been studied under the variation of magnetic field. McTague et al. have observed that the change of viscosity is a function of direction and strength of the magnetic field [13]. To explain McTague experiment, Shlimois et al. used single particle model and gave a relationship between the viscosity and applied magnetic field [14]. Odenbach et al. have reported that viscosity would increase in response to applied magnetic field [15]. Also, it was reported earlier that, field induced enhancement in viscosity is not generally valid for low shear rate region in case of concentrated fluids [15–19]. Essentially, large size particles and agglomerated particles have tremendous influence on the viscosity of the magnetic fluids and there could be clear relationship between the magnetoviscous effect and the agglomerated particles. The authors also explored the connection between the relative viscosity change with the varying intensities of applied magnetic field.

To understand the behavior of particular magnetic fluid, different authors employed different techniques and systems in presence of external magnetic field [20-25]. When the magnetic field is slowly increased to high values the FFs are capable of showing several fascinating structural transition [26, 21]. Initially, the randomly oriented particles undergo head-to-tail chainlike aggregation with chains aligned along the field direction. Owing to the lateral coalescence of the chains, they form columns by undergoing secondary aggregation [27, 28]. The presence of even topological defects in dipolar chains responsible for generating thermal fluctuation and perturbations in local lateral fields are mainly responsible for their lateral coalescence [29, 30].

This chapter describes rheological behavior of the pristine and γ-irradiated Gd_2O_3 nanorod based system fluids.

5.1.1 Gamma irradiation experiment on Gd_2O_3 nanorod based fluids

Ethanol is chosen as the carrier fluid. The Gd_2O_3 nanorods are dispersed in the carrier fluid (concentration of nanorods to ethanol 6.5 mg/mL) and then subjected to stirring (~200 rpm) for 8 h so that the particles are distributed homogeneously without clustering and aggregation. The MR fluid specimen is then divided into three equal parts for subsequent experimentation. The as-prepared MR fluids was irradiated by a γ-source (^{60}Co chamber available at UGC-DAE CSR, Kolkata) that is capable of emitting photons with an average energy of 1.25 MeV. Two doses of 1 kGy and 6 kGy have been selected for the irradiation experiment.

5.1.2 Magnetorheological property of Gd_2O_3 nanorod based MR fluids

Rheological behavior of the un-irradiated and γ-irradiated samples have been assessed at room temperature with the help of a rheometer (Phyica MCR 301, Anton Paar) working on parallel-plate geometry. A plate– plate spindle (with a gap thickness ~0.03 mm) has been employed and a typical sample volume of 210 µl is used for all the measurements.

The flow behavior of fluid can be immediately assessed by considering the dependency of shear stress on shear rate. When flow behavior shows a linear trend passing through the origin, the fluid under study is of Newtonian–type with slope recognized as apparent viscosity of the fluid. Conversely, any departures from the linear trend represent essentially characteristic property of only non-Newtonian fluids. Exhibiting a non-linear response, the non-Newtonian fluids characterize either a shear thinning or shear thickening behavior. In case of shear-thinning, the apparent viscosity of the fluid follows a decreasing trend with increasing shear rate [31]. On the other hand, if viscosity increases with increasing shear rate, then it is called shear thickening fluid [31]. The schematic representation of non-Newtonian behavior of colloidal particles shown in Figure 5.1. In the figure, (a), (b) and (c) signify equilibrium positions, shear thinning and shear thickening behaviour of colloidal particles.

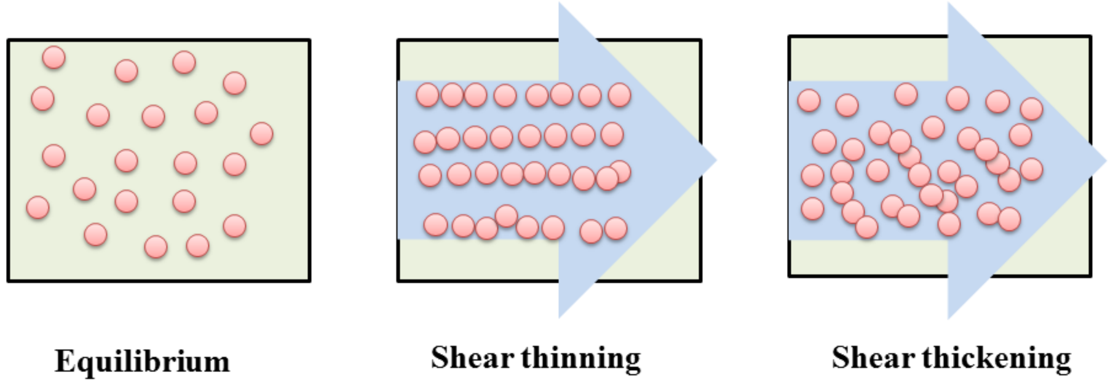

Figure 5.1: Distribution of colloidal particles (a) at equilibrium, (b) under shear, showing shear thinning and (c) shear thickening behaviour.

In order to investigate the influence of applied magnetic field on the apparent viscosity of Gd_2O_3 nanorod based nanofluids, the MV effect has been extensively studied. On performing the rheological measurements on pristine Gd_2O_3 nanorod based MR fluid with (sample concentration 0.5 mg/mL), we observed abrupt thickening and steady shear thinning behavior of the systems (Figure 5.2(a) and (b)). No significant change has been observed when the magnetic field was varied between 0-0.6 T. However substantial change is observed when the concentration is increased to 6.5 mg/mL. Figure 5.3 (a)-(c) shows the shear stress versus shear rate plots for unirradited and irradiated MR fluids subjected to different magnetic fields. These plots are fitted with the following power law equation [32]

$$\eta_v = K_v \dot{\gamma}^{m} \qquad (5.1)$$

where K_v is the constant which depend on the material under study and m is the power law index. The synthesized MR fluids followed the power law behavior with m-value 0.43–0.50 when magnetic field is varied in the range of 0–0.5T. As, m=1 would represent ideal Newtonian characteristics, in the present case, the very small m-value indicates the non-Newtonian response with higher shear thinning feature [1, 33]. The physical parameters related to rheological studies of the samples are shown in Table 5.1.

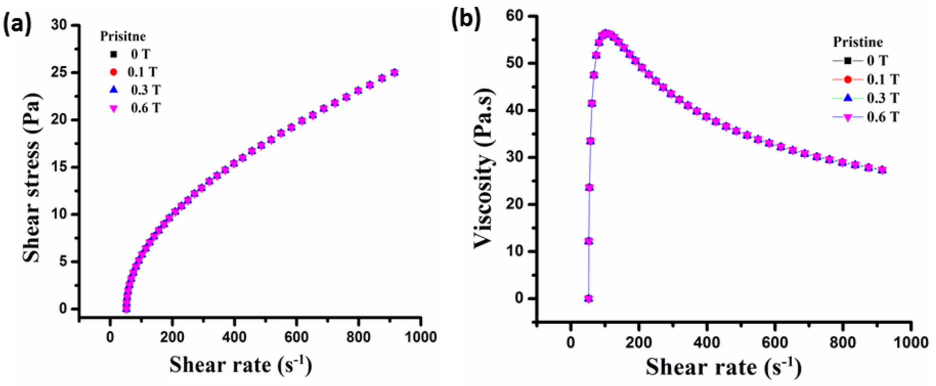

Figure 5.2:(a) Shear stress vs. shear rate of MR fluid containing pristine Gd_2O_3 (concentration 0.5 mg/mL) nanorods, (b) Apparent viscosity vs. shear rate curves for pristine MR fluid subjected to different magnetic fields.

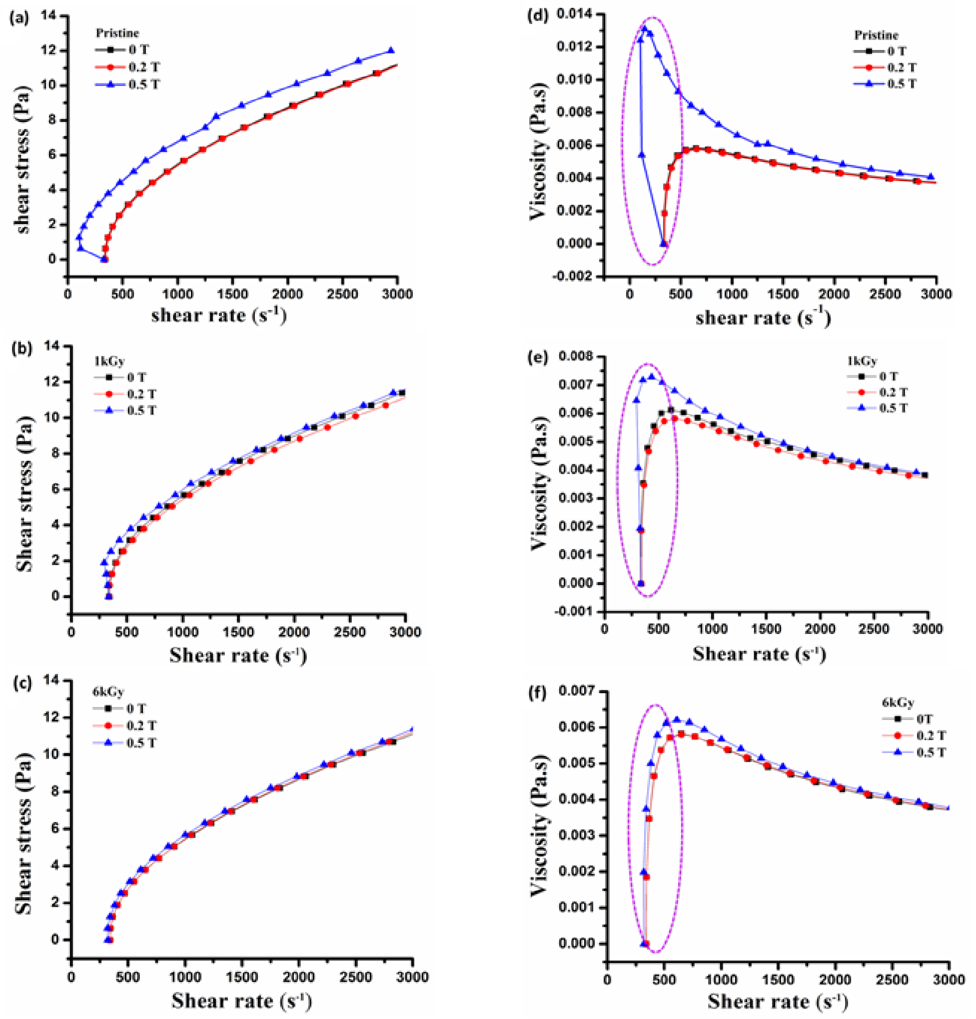

Figure 5.3: Variation of shear stress vs. shear rate for different sample (a) Pristine (b) 1kGy and (c) 6 kGy samples and the corresponding variation of shear rate with viscosity shown in (d) ,(e) and (f).

Figure 5.3 (d), (e) and (f) depict the magneto-viscous characteristics of pristine and γ-irradiated (1 kGy and 6 kGy) samples. Apparently, non-Newtonian behaviour can be observed for different samples in the presence of magnetic fields. The viscosity vs. shear rate curve under magnetic field variation have revealed abrupt shear thickening behavior of the fluids up to a critical shear rate ~510 s^{-1} for MR fluid irradiated with 1 kGy and 6 kGy γ-rays. The critical shear rate is much lower in case of pristine sample. Apparent viscosity follows a decreasing trend with increasing the shear rate afterwards thus illustrating a shear thinning response (Figure 5.3 (d), (e) and (f)). For 0.2 T field, viscosity decreases with increasing shear rate, similar to that in the absence of field. The schematic representation on shear thickening and shear thinning parts can be found in Figure 5.4. Randomly oriented nanorods under applied magnetic field would aggregate/align thus offering resistance to flow. But as the shear rate increases, nanorod assemblies break up as a result of which viscosity is lowered steadily giving rise to the shear thinning behaviour.

The shear thickening part of the experimental curves obey typical exponential associate curve fitting given by:

$$\eta_{vg} = \eta_o + \eta_1 \, (1 - e^{-(\frac{x}{\tau_g})}) \qquad (5.2)$$

where τ_g is the growth parameter in sec^{-1}. The parameter τ_g is nearly unchanged for pristine and irradiated samples (Table 5.1). It is known that, the rheological property has a strong dependency on the size distribution, deformability, internal viscosity, concentration, surface roughness, and volume fraction of the dispersed phase as well as on the nature of the particle-particle interaction [34, 35]. In an earlier work, Gd_2O_3 nanoparticle based fluids was shown to exhibit typical shear thinning behavior [36]. The different shape of the particles (like rod, disk or highly irregular particles) has been recognized as the key factor behind shear thickening response. Normally, anisotropic elongated structures respond to shear thickening at a lower volume fraction than the case of spherical particles [37]. According to Egres et al. elongated structures would show better shear thickening response at lower particle loading than the suspended spherical particles [38]. They have examined this with the help of an experiment that combines rheological measurements with small angle neutron scattering (SANS) and consequently prove that misalignment of rod-like structures is largely responsible for the shear thickening behaviour [38]. As an increased magnetic field is responsible for chain-like structure, which is capable of increasing in the viscosity, but disruption of chain-like structure could suppress apparent viscosity at higher shear rates [39]. The shear thickening of the elongated structures observed up to a certain shear rate may be due to randomly oriented nanorods. By introducing a small shear rate the nanorods will find a chance to move and rearrange to form stronger chains. However, at higher shear rates the shear force can disrupt the chains and therefore, the MV effect tend to decline [40]. The agglomeration of nanorods can also be also responsible for the increase of viscosity in low shear rate region.

The second part of the experimental curves essentially demonstrate shear thinning behavior exhibiting exponential decay curve fitting as given by the expression:

$$\eta_{vd} = \eta_0 + \eta_1 \, e^{-(\frac{x}{\tau_d})} \qquad (5.3)$$

where η_o is the initial viscosity, η_1 is the viscosity at zero shear rate for a particular trend, x is the shear rate and τ_d is the decay parameter in sec^{-1}. From the fitted curve, it is quite evident that the viscosity of the fluid is reduced and decay parameter (τ_d) follow a decreasing trend with increase in irradiation dose (Table 5.1). A reduction of the decay parameter indicates that the γ-irradiated nanorods exhibiting a longer relaxation characteristic as compared to the pristine one.

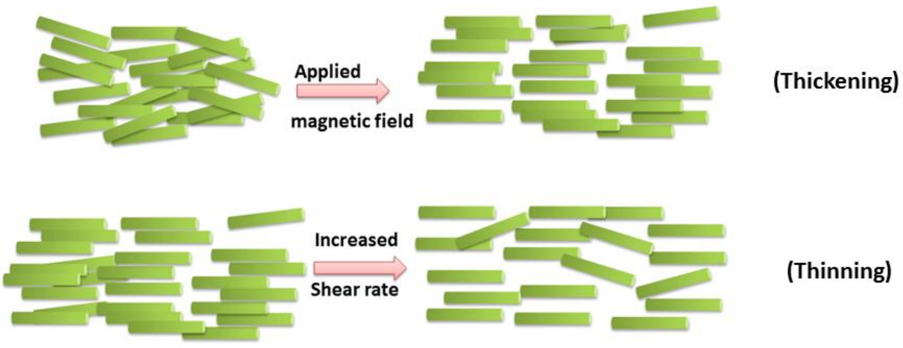

Figure 5.4: Schematic diagram of shear thickening and shear thinning feature

Table 5.1: Physical parameters related to rheological studies of Gd_2O_3 nanorods based system

Sample	τ_g			τ_d			m		
	0 T	0.2 T	0.5 T	0 T	0.2 T	0.5 T	0 T	0.2 T	0.5 T
Pristine	50.68	51.83	50.0	2260.06	2253.73	1070.46	0.50	0.49	0.50
1kGy	50.35	50.40	45.40	2214.30	2219.90	1459.00	0.50	0.50	0.50
6kGy	50.07	51.32	45.37	2153.87	2274.54	1875.29	0.49	0.43	0.48

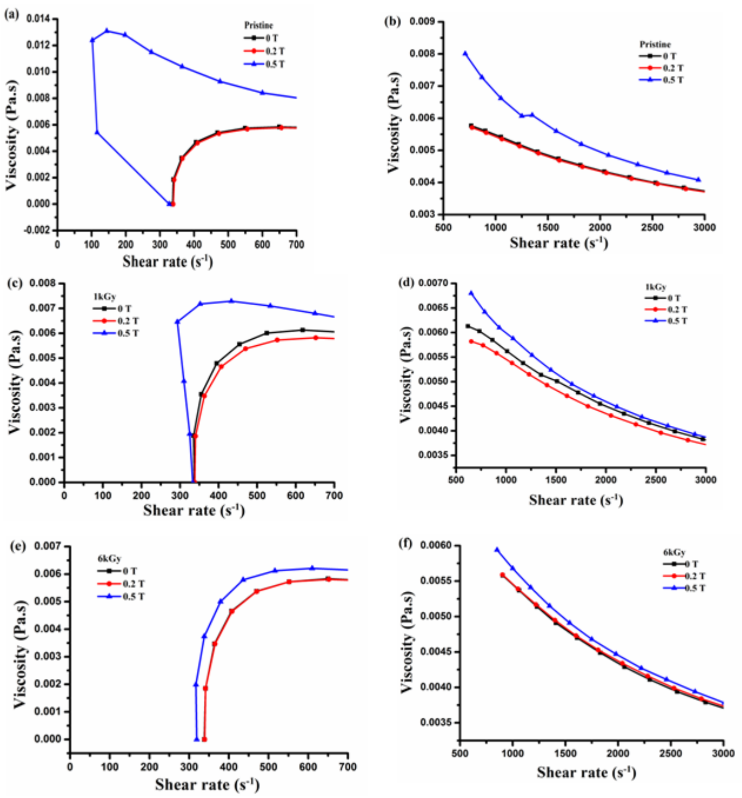

Figure 5.5: (a), (b), (c), (d), (e) and (f) represents both shear thickening and shear thinning part of pristine, 1kGy and 6kGy samples.

As an important observation, shear thickening response is found to be quite uniform for MR fluids irradiated with high does (6 kGy, Figure 5.5). The characteristic curves however become extremely random for pristine and low dose MR fluid samples.

5.2 Concluding remarks

The Gd_2O_3 nanorod based fluids has exhibited non-Newtonian behaviour. From the experimental data it was observed that the shear rate vs. viscosity plot showed shear thickening behavior up to a critical shear rate after which it displayed shear thinning features. The rheological plots displayed a non-Newtonian power law ($\eta_v=K_v\gamma^{\cdot m}$) behavior having power indices (m) varying in the range of 0.43–0.5. The apparent viscosity of the fluids increased with increasing the magnetic field. The present work reports an abrupt to smooth transitions of shear thickening- to- shear thinning jumps exhibited by fluids containing Gd_2O_3 nanorods. The shear thickening of the elongated structures may be due to presence of localized assemblies of the nanorods. A higher shear thickening response could also be due to aligned nanorods formed in presence of an external magnetic fluid. At a low shear rate, the nanorod chains are still available which move and rearrange to form stronger chains. However, at higher shear rates the shear force can lead to gradual disruption of the chains and consequently, shear thinning can be noticed. In the thesis we have discussed the observed phenomena. A plausible explanation considering theoretical treatment is still being considered by our group.

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