CHAPTER V

Rheological application of rare earth oxide nanoparticle-based ferrofluids
5.1 Principle of Rheology

Rheology is an independent natural phenomena and is based on the three fundamental concepts: kinematics, conservation laws, forces and stresses and consecutive relations [1]. Rheology is coined by Eugene C. Bingham, derived from the Greek words, ‘rheo’ means ‘flow’ and ‘logia’ means ‘study of’ and is the flow property of matter. Preparation and application in FFs in research and development sectors started nearly 50 years ago, in late sixties. The rheological properties are applicable to fluids, gels including dilute solutions of polymers and surfactants, concentrated protein formulations, semi-solids such as pastes and creams, molten or solid polymers and suspension of nanomaterials. The flow behaviour of the above mentioned material can be characterized by a dependency of shear stress (σ) on shear rate (\( \dot{\gamma} \)). The concept of rheology is mostly discussed to describe non-Newtonian, and non-Hookean systems. When the flow behaviour (shear stress vs. shear rate) shows a linear trend passing through the origin, the system represents a pure Newtonian fluid. A non-Newtonian fluid is the one whose flow curve is neither possess a linear trend nor passes through the origin. In otherwords, apparent viscosity is not constant at a given temperature and pressure but largely dependent on the flow geometry (dimension of the vessel where liquid flows) [2].

It may be noted that, the rheological properties of the dispersed solution is dependent on the nature of the particles, size distribution, deformability, internal viscosity, concentration, volume fraction of the dispersed phase as well as the nature of particle–particle interaction [3,4]. The suspensions (solid particles dispersed in a fluid) exhibit a wide range of rheological behaviour, including shear thinning, shear thickening, and finite normal stress difference. In a liquid suspension, three kinds of forces may work but to different degrees. Firstly, there
exist an interaction (attractive or repulsive) between the particles of colloidal origin. Secondly, the Brownian force (thermal) randomizes the colloidal particles a temperature. Finally, the viscous force of the carrier fluid acting on the particles of the colloidal solution [5]. So, rheology measurement, in a way is strongly dependent on the microstructural properties. The behaviour of suspensions, under shear has attracted a great deal of attention in recent years. The researchers have measured rheology in a number of ways; direct probes of the structure via light and neutron scattering under shear [6, 7] and computer simulations [8, 9] etc.

The non-Newtonian fluids exhibit either shear thinning or shear thickening behaviour. In case of shear-thinning, the viscosity of the fluid has a decreasing trend with the increase in shear rate, whereas shear thickening behaviour depicts increase of viscosity with shear rate [10]. The colloidal particles exhibiting non-Newtonian response can be found in a scheme in Fig. 5.1. In the figure, blue spheres represent colloidal particles in their respective equilibrium positions (a), shear thinning (b), and shear thickening behaviour (c). In equilibrium, random collisions among particles make them naturally resistant to flow. But as the shear stress (or, the shear rate) increases, particles arrange themselves in the flow direction, which lowers their viscosity, gives rise to the shear thinning behaviour. At yet higher shear rates, hydrodynamic interactions between particles dominate over stochastic ones, leading to the formation of hydroclusters of the colloidal particles. The difficulty of particles flowing around each other in a strong flow leads to a higher rate of energy dissipation and an abrupt increase in viscosity, which leads to the phenomenon called shear thickening. In both semi-dilute and mainly in concentrated dispersions, the strong hydrodynamic coupling between particles results in the formation of hydroclusters [11].
This chapter describes about the non-Newtonian rheological properties of the pristine and γ-irradiated undoped and Tb$^{3+}$ doped Gd$_2$O$_3$ based FFs.

5.2 Rheological behaviour of synthesized systems

In the past, the rheological behaviour of iron oxide nanoparticle based FF systems have been studied in great details and in most cases, pronounced shear thinning effect were observed [10, 12]. In an experimental result, it was shown that silica coated magnetic nanoparticle based FFs could represent strong magnetic field dependent changes in the rheological behaviour in FFs of low particle concentration [13]. A recent work, on the size dependent rheological response has revealed that the size of the plate-like iron particles could affect both the yield stress and the viscosity of the magneto-rheological fluid both in the absence and presence of the magnetic field [14].

In the present study, rheological measurements are performed using a rheometer (Malvern, Bohlin Gemini 200) working in the parallel plate geometry, which is surrounded by a thermal barrier in order to reduce the heat transfer from the sample area to the outside environment.
5.2.1 Flow properties of Gd$_2$O$_3$ nanoparticle based FFs

The flow behaviour (at a fixed shear stress of ~4.7 Pa and shear rate within 45 to 175 s$^{-1}$) of the pristine and $\gamma$-irradiated Gd$_2$O$_3$ based fluids are shown in Fig. 5.2. The terminal viscosities $\eta_{45}$ and $\eta_{175}$ can be obtained for different FFs. Whereas, $\eta_0$ which depicts viscosity corresponding to zero shear rate can be predicted by way of extrapolation. Basically, all the spectra show non-Newtonian characteristics with a shear thinning behaviour, to different extents. The experimental data points obeyed biexponential curve fitting as given by the expression:

$$y = y_0 + y_1e^{-(x/\tau_1)} + y_2e^{-(x/\tau_2)}$$ (6.1)

where $y_0$ is the initial viscosity, $y_1$ and $y_2$ are viscosities at a zero shear rate for a particular trend, $x$ is the shear rate and $\tau_1$ and $\tau_2$ are decay parameters in sec$^{-1}$. The intervening mechanism can be assimilated by two underlying mechanisms. From the fitted curve, it is quite evident that the viscosity of the fluid is reduced owing to two kinds of decay phenomena: the fast component that exhibits a higher magnitude of decay parameter and the slow component that has a smaller value of decay parameter. The overall viscous nature of the FFs is characterized by a competition between the formation and breakup of the nanoparticle based chains where van der Waal interaction plays a dominant role. A similar biexponential decay response was also observed in case of iron oxide nanoparticle based FFs [15]. In case of shear thinning the interparticle distance becomes adequately large and consequently, particles are well-separated from each other.
Fig. 5.2 Apparent viscosity vs. shear rate curves for different ferrofluids: (a) G0, (b) G1, and (c) G4 system.
When the FF is at rest the micro/nano-structural units are randomly oriented but they are not necessarily in isolation from each other. The high surface energy of the nanoparticles is capable of bringing them closer momentarily so that the system is stabilized by attaining minimum energy configuration. When subjected to a low shear rate, the fluid system resists any deformation and offers a high value of viscosity or a yield stress. The yield stress is generally applicable for Bingham type of fluid [16]. The fluid under study is recognized as non-Bingham type. When the magnitude of external shear rate is gradually increased, the structural units (in this case, surfactant coated Gd₂O₃ nanoparticles) act by aligning themselves along the direction of fluid flow, or leads to disintegration of aggregates into small flow units or into primary particles [17]. The interaction forces may then decrease and cause a lowering of the flow resistance and the apparent viscosity of the system. The behaviour of nanoparticles under shear stress is schematically shown in Fig. 5.3. It may be noted that, the nanoparticles of
the dispersed solution are agitated thermally and are always in a state of Brownian motion. The rate of particle movement can be related to a sphere equivalent hydrodynamic radius as calculated through the Stokes–Einstein equation [5]. All these changes in micro-structure facilitate flow response, i.e., lowering of their apparent viscosity ($\eta_0$) with the shear rate, resulting in a nanoparticle shear thinning behaviour. The shear thinning of well-dispersed suspensions can be described by the alteration in the structure and structural arrangement of the interacting particles [18].

The factors which influence the flow behaviour includes Brownian motion, velocity between the base fluid and the nanoparticles, temperature, mean nanoparticle diameter, nanoparticle volume fraction, nanoparticle density and base-fluid physical properties [19]. From the biexponentially fitted curves, both the fast ($\tau_1$) as well as slow ($\tau_2$) decay parameters follow a decreasing trend with increasing irradiation dose, but to varying extents. The fast decay parameter decreases from a value of 1107 s$^{-1}$ (G0) to 601.4 for G1, and 527.8 for G2 FF specimens. Also, the slow decay parameter has a decreasing trend: 23.8 s$^{-1}$ for G0, 21.2 s$^{-1}$ for G1, and 20 s$^{-1}$ for G2 systems. We correlate this behaviour with the defect manifestation mechanism on the nanoparticle surfaces as a result of $\gamma$ - irradiation. Since each of the spectra fits with the biexponential trace, we speculate that the rheological property is governed by two competitive mechanisms: one at the surfactant level and the other in particle level. The fast decay component can be associated with the rapid migration of excess surfactant molecules from the nanoparticle surfaces to the surrounding environment whereas, the slow decay component with large magnitudes account for a slower response of relatively heavy Gd$_2$O$_3$ nanoparticles. At an increased shear rate, the extra layers of the surfactants are believed to get detached away from the nanoparticle surface owing to disruption of weak van der Waal bonding. A rapid
decreasing trend of the fast decay parameter signifies that the irradiated nanoparticles in the FF would experience a stronger relaxation response as compared to the unirradiated one. As an analogy, the spherical balls having uneven surface would resist the flow behaviour more efficiently than the surfaces smoothened balls.

In the present case, the improvement of slow and fast (wrt time) component with radiation dose may account for this. It was evident from the HRTEM analysis (chapter IV, page no 109) that defects are actually formed on the nanoparticle surfaces and the whole phenomenon is attributed to the collective role of point defects. Defects like oxygen vacancies are very common in oxide compounds [20]. But, several Gd vacancies may also be produced during the synthesis step. In fact, the creation of a large number of free electrons by the energetic γ-rays (1.25 MeV) can take part actively in defect modification. It was reported earlier that γ-irradiation could result in particle growth of iron oxide nanoparticles in respective FFs [21]. On contrary, as Gd$_2$O$_3$ nanoparticles are stable against particle growth, the FF system can be regarded as an alternative candidate where flow property can be controlled by controlling defects created by energetic γ-irradiation.

Fig. 5.4 (a-c) depicts variation of shear stress with shear rate corresponding to the pristine and γ-irradiated, Gd$_2$O$_3$ nanoparticle based FFs. Essentially, the non-Newtonian behaviour is governed by a complex interaction between the particle and fluid and among the particles themselves. In this case, the shear stress and shear rate can be expressed by the relation:

$$\eta = \zeta \gamma^\delta$$

(5.2)
where $\zeta$ is a constant which depends on the system under study and $s$ is known as the power index which varies between $1/3$ and $1/2$ for shear thinning fluids [17]. For Gd$_2$O$_3$ nanoparticle based FF case, the $s$ value shows a decreasing trend with the irradiation dose, with respective values varying from 0.54 to 0.33 as for the un-irradiated specimen and the one irradiated with the highest dose (2.635 kGy). Even though the volume fraction of the nanoparticles in the carrier fluid is low (12.5 g-lit$^{-1}$), a modified non-Newtonian rheological behaviour is realized owing to the defect manifestation in nanoparticles suspended in a Newtonian type carrier fluid (ethanol). It is worth mentioning here, a high density material system is likely to dictate rheological feature differently with respect to the low density counterpart. In this context, noticeable rhological features can be witnessed even at a low volume fraction of the nanoparticles. As, $s=1$ would represent ideal Newtonian characteristics, in the present case, an increased value of $s$ due to irradiation suggests marginal transition of the studied FF towards Newtonian type. It is now apparent that, the nanoscale defect manifestation has played key-role in modifying the shear thinning aspect. In addition, rheology may provide a means to determine the degree of exfoliation/dispersion of the nanoparticles in the carrier fluid. The rheological properties change significantly with favorable particle-matrix interactions as compared to the non-interacting systems or strong particle-particle attraction. It is always difficult to extract independent contributions as they might work in a correlated manner. However, the contribution due to nanoscale defects can be featured at large, especially when induced by controlled irradiation.
Fig. 5.4 Shear stress vs. shear rate for different ferrofluids: (a) G0, (b) G1, and (c) G4 system
5.2.2 Flow properties of Tb$^{3+}$ doped Gd$_2$O$_3$ nanoparticle based FFs

The shear thinning behaviour as a measure of variation of apparent viscosity in response to the shear rate is shown in Fig. 5.5 (a-c). As can be found, the experimental data points obey bi-exponential decay curve fitting, described in the previous section (#5.2.1). Shear thinning accounts for large inter-particle separation of the nanoparticles of the FFs. The release of the surface tension during the relaxation stage, after stepwise surface deformation, may help characterizing surfactant adsorption (after expansion) and desorption (after compression) processes. The Brownian motion tends to randomize the particle movement, whereas the particle alignment along the flow direction (under a high shear stress) can be responsible for causing a apparently declined trend of viscosity. At a fixed shear rate, the amount of shear thinning is dependent on the interparticle separation of the structural units, which can be different for different FFs. Like undoped Gd$_2$O$_3$ NP based FFs, Tb$^{3+}$ doped Gd$_2$O$_3$ NP based FF also shows a non-Bingham type flow response. As the apparent viscosity decreases with the shear rate, it implies viscometric properties dominating over inter-particle interactions.

Since the nanoparticles of the dispersed solution are agitated thermally, they are in a state of continuous Brownian motion. All the changes in micro-structural units facilitate flow response, i.e., lowering of the apparent viscosity with the shear rate, leading to shear-thinning behaviour. From the bi-exponentially fitted curves (Fig. 5.3), the more rigid fast decay parameters as well as more flexible slow decay parameter were found to follow an increasing trend with increase in the irradiation dose. The fast decay parameter ($\eta_1$) has increased from a value of ~207 sec$^{-1}$ for GT0 to 1966.2 sec$^{-1}$ for GT1, and 2742.9 sec$^{-1}$ for GT2 FFs. Also, the slow decay parameter experienced a rising trend: 8.6 sec$^{-1}$ for GT0, 16.47 sec$^{-1}$ for
GT1, and 28.38 sec$^{-1}$ for GT2. The fast components of GT0 and GT2 have exhibited about $\sim$25 fold and 98 fold improvements with respect to their slow components. The relaxation process appeared to be slower when the interactions are more pronounced owing to the inclusion of Tb$^{3+}$ ions. We correlate the above mentioned behaviour with the presence of impurity ion (Tb$^{3+}$) and defect creation on the nanoparticle surfaces as a result of $\gamma$-irradiation. Since each of the spectra fits with the bi-exponential trace, we speculate that, the rheological property is governed by two competitive mechanisms: one at the surfactant level and the other is at the particle level. In chapter IV (section 4.3.1, page no. 108), the formation of defects on the surface of nanoparticle can be evident from the HRTEM analysis. In the cases of Tb$^{3+}$ doped Gd$_2$O$_3$ based FF system, the extent of variation of thinning behaviour with irradiation dose may be attributed to the role of point defects as the rest of the parameters are constant.
Fig. 5.5 Apparent viscosity vs. shear rate curves for different ferrofluids: (a) GT0, (b) GT1, and (c) GT4 system
Fig. 5.6 Shear stress vs. shear rate for different ferrofluids, (a) GT0, (b) GT1, and (c) GT4 system

Fig. 5.6 (a-c) depicts variation of the shear stress with the shear rate corresponding to the un-irradiated and $\gamma$-irradiated, Tb$^{3+}$ doped Gd$_2$O$_3$ nanoparticle based FFs. In this case also, the behaviour of the curves is described by a power law but with different power indices. The power index ($s$) shows an increasing trend from a value of 0.34 to 0.5, indicating thereby marginal transition from the non-Newtonian type to more or less Newtonian type.

5.3 A comparative account of rheological response of the studied FFs

It is known that, the irradiation (charged particles, photons etc.) processes lead to adequate surface passivation of the nanoparticles [8, 9]. Consequently, the overall nature/properties of the FFs get modified by creation of defects, which supersede the annihilation of pre-existing defects. The photon-matter interaction is specific to the reactive material surfaces. Doping, on the other hand, allows the modification of important properties by way of defect formation [22, 23]. Properties of the FF are also get influenced by the modification made to the doped nanoparticles that behave as an integral component of fluid. A dopant can
occupy either substitutional sites or interstitial sites. On several occasions, the dopant segregate along the grain boundaries [24, 25]. The creation of new energy states due to the incorporation of the dopant in the host alters overall properties including electronic structure, etc. Since the flow property is dependent on the nanoparticle morphology, the size, shape, as well as surface roughness can be linked to the doping aspect of the nanoparticles. It has been found that well-distributed dopants on the host matrix can inhibit the grain growth and yield along with improved mechanical properties [26, 27].

On comparing the shear thinning behaviour, it is observed that, both the FF systems (undoped and Tb$^{3+}$ doped Gd$_2$O$_3$) exhibit non-Newtonian shear thinning behaviour but to different degrees. The calculated decay parameters and power indices are presented in Table 5.1. In case of Tb$^{3+}$ doped Gd$_2$O$_3$ NP based FFs, the Tb related effect along with irradiation is clearly observable in the rheological response. In the earlier chapter, the dopant and irradiation induced changes, as regards Gd$_2$O$_3$ lattice structure has been demonstrated in detail [chapter IV, #4.2.1. page no. 109], where oxygen defects play major role.

<table>
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<th>Sample name</th>
<th>$\zeta$</th>
<th>$s$</th>
<th>$\eta_1$ (sec$^{-1}$)</th>
<th>$\eta_2$ (sec$^{-1}$)</th>
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<td>1107</td>
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<tr>
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<td>0.35</td>
<td>601.4</td>
<td>21.2</td>
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<tr>
<td>G2</td>
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<td>0.33</td>
<td>527</td>
<td>20</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.44</td>
<td>1966.2</td>
<td>16.47</td>
</tr>
<tr>
<td>GT2</td>
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<td>0.50</td>
<td>2742</td>
<td>28.38</td>
</tr>
</tbody>
</table>
5.4 **Concluding remarks**

The rheological feature of the FFs have exhibited non-Newtonian power law behaviour having power indices ($s$) varying in the range of 0.3-0.5. The typical flow behaviour i.e., variation of viscosity vs. shear rate displays a shear thinning behaviour with bi-exponential decay characteristics. The fast as well as slow decay parameters tend to decrease with the irradiation dose for undoped Gd$_2$O$_3$ based FF, whereas a reverse trend was observed for Tb$^{3+}$ doped Gd$_2$O$_3$ based FF. These novel FFs that comprise of advanced undoped and doped Gd$_2$O$_3$ nanoparticle system could serve as an alternative candidate in sealing, shielding, and servos applications in radiation sensitive zone.

**References**


