NANOTECHNOLOGY IN HIGH YIELD STRESS SMART FLUIDS- A REVIEW.

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ABSTRACT

Electrorheological (ER) and Magnetorheological (MR) nano-fluids show dramatic and tunable changes in their rheological properties under external magnetic or electric field strength respectively. These nano-fluids can be effectively incorporated in various engineering applications like shock absorber, dampers, clutches etc. The major problem to use these nano-fluids practically is their low yield strength and problem of sedimentation. In this paper various smart nano-fluids (ER & MR) have been studied. Special attention is given on development of stable, re-dispersible, durable, high yield stress smart nano-fluids with low sedimentation rate. In this paper these nano-fluids are reviewed along with their rheological characteristics under external fields.

INTRODUCTION

The lack of high performance smart fluids, as well as the problem associated with sedimentation, has inhibited broad engineering applications. Thus though these smart fluids are seem to attractive, the future holds in development of the relationships between synthesis and processing of high yield strength smart nano-fluids with no sedimentation rate. The overall objective of this research is to review high yield stress smart nano-fluids which possess better ER/MR characteristics and less sedimentation rate. Although high yield stress smart nano-fluids have been investigated thoroughly since they were first discovered, very little research has been performed on the synthesis of stable, re-dispersible and durable smart nano-fluids having no sedimentation problem and characterization of high yield stress smart nano-fluids by various methods. In this review we focused on the ER and MR nano-fluids exhibiting high yield stress with less or no sedimentation. Our goal is to highlight the path of development of these nano-fluids.

SMART FLUIDS

A smart fluid is a fluid whose properties (for example viscosity, yield stress, surface tension etc.) can be changed by applying a magnetic field or an electric field. Popular examples of smart fluids are electrorheological (ER) fluids, magnetorheological (MR)

fluids and Ferro-fluids. Here in this review special attention is given on electrorheological fluids and magnetorheological fluids.

Electro rheological fluids

Electrorheological fluids (ER) are suspension of extremely fine non conducting polarizable particles (0.1-50 µm in diameter) in an electrically insulating fluid. An ER fluid undergoes increase in viscosity upon application of an electric field. This was first reported by Willis Winslow in 1949 and is termed as "Winslow effect" [1]. This discovery leads to development of ER based various engineering applications like breaks, clutches, damper, hydraulic valves, other applications such as bulletproof vests has been proposed for these fluids [2]. However, ER fluids have not found widespread commercial applications. This is mainly due to the fact that the maximum yield strength achieved by most of the conventional fluids is less than 15 kPa, much below 30 kPa required by many engineering devices and long term use is not possible because of sedimentation problem [3]. Since then lot of work have been done to overcome these hurdles.

Using a modified sol-gel technique surface modified complex strontium titanate (STO) micro particles are synthesized and resultant suspension of these particles immersed in silicone oil (No. 200, 0.5 St.). The nano-fluid shows excellent electrorheological properties having yield stress 27 kPa at a dc field of 3 kV/mm and 36% of volume fraction ø[4]. The used surfactant character of the particles plays significant role in improving the electrorheological properties of the suspension. But the yield stress based on sol-gel technique was not sufficient for commercial applications of ER fluids. This difficulty was overcome by discovery of giant electrorheological (GER) effect in 2003 by Weijia Wen. His remarkable works have achieved a milestone in development of high yield stress electrorheological nano-fluid with negligible sedimentation. He reported that fabrication of electrorheological suspensions of urea coated barium titanyl oxalate nanoparticles providing permanent dipoles can reach yield stress of 130 kPa at 5kV/mm, breaking the theoretical upper bound on conventional ER static yield stress. This GER suspensions shows low current density over a wide temperature range of 10-120 °C, with a reversible response time of <10 ms. An important feature of the GER suspension is its large dielectric constant around 50-60 (at 10 Hz). Urea is known to have a large molecular dipole moment of $\mu = 4.6$debye. Thus thin urea coatings having a significant dielectric response due to the existence of the interfaces plays a crucial role in the GER effect as shown in figure 1[5].
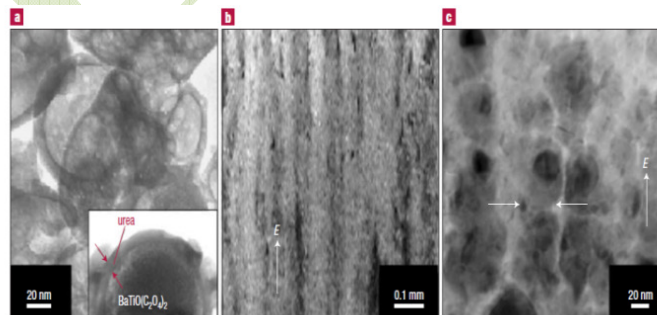

Figure1. a) Transmission electron microscope (TEM) image of urea coated nanoparticles. b) Optical microscope image of a sample, columns aligned along the field direction are visible. c) The arrows indicate one of the flattened interfaces.

Consequently in 2004 he reported that by decreasing the size of the barium titanyl oxalate nanoparticles coated with urea, using Rb doping, the GER effect can attain a yield stress of >250 kPa at 5kV/mm with reduced sedimentation. Half the particle sizes can double the maximum yield strength. However, at lower field range (below 2 kV/mm), the larger particle size ER fluid has a stronger ER effect than that for the smaller [6]. Jiaxing Li in 2010 proposed fabricated suspensions exhibiting the giant electrorheological effect (GER) effect comprising nanoparticles-multiwall carbon nanotubes (MWCNTs) composite particles dispersed in silicone oil. This type of GER nano-fluid shows dramatically enhanced antisedimentation characteristics without scarifying the much yield stress [7]. Sedimentation phenomenon occurs due to the density mismatch of the nano-fluid and solid phases as well as the aggregation of the nanoparticles. The resulting phase separation can cause a dramatic decrease in the ER effect. The antisedimentation property of ER nano-fluids can be enhanced by adding surfactant to the solvent phase or making the particle phase less dense that can either decrease the density mismatch or modify the surface or particle morphology [8]. Jiaxing Li and X. Gong developed a method in which MWCNTs are used to improve antisedimentation characteristics of ER nano-fluid. The non-conducting nanoparticles-nanotubes composites were fabricated by modifying the co-precipitation method with MWCNTs and urea coated barium titanyl oxalate (BTRU) nanoparticles as a components. Maintaining good dispersion and avoiding aggregation are important for both the antisedimentation characteristics as well as the ER effect. The presence of MWCNTs effectively prevents direct contact between the BTRU nanoparticles, thus minimizing their aggregation and sedimentation. Yield stress as high as 194 kPa was obtained in the MWCNT-BRTU suspensions. The yield stress of the sample, prepared by dispersing MWCNT-BTRU particles (with a MWCNTs mass fraction of 0.49%) in hydroxyl-terminated silicon oil at a concentration of 0.25, can reach 194 kPa at 5Kv/mm. This is only slightly smaller than that for similar sample comprising BTRU nanoparticles previously studied (215 kPa at the same conditions) [9]. The particles (MWCNT-BTRU), when dispersed in 20 cSt methyl-terminated silicon oil have been maintained for several months are shown to have enhanced antisedimentation property as shown in figure 2.
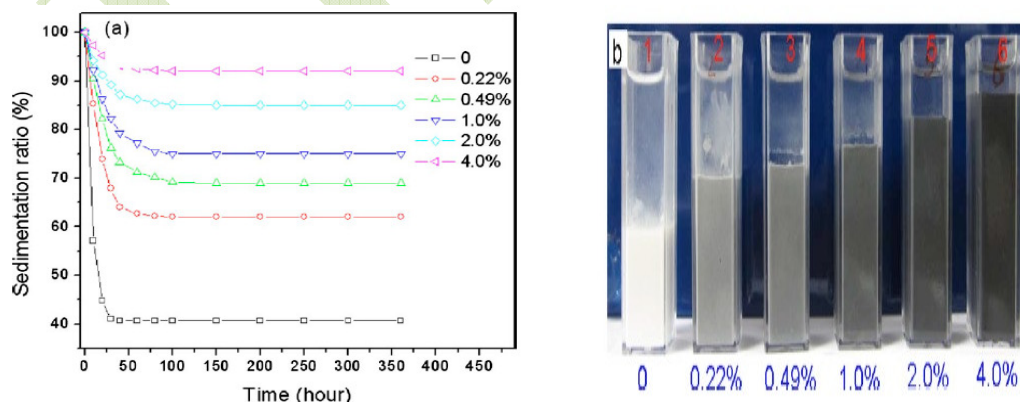

Figure2. a) Sedimentation ratio of BTRU and MWCNT-BTRU particles suspended in methyl terminated silicon oil (20cSt) with a concentration of 5.0. b) Sample images with different wt. % after preparation.

Another new approach is introduced by Carlos S. Orellana and co-workers showing that addition of polar molecules in suspensions of polarizable strontium titanyl oxalate (STO) particles in 10cSt silicone oil can dramatically increase the yield stress up to 200 kPa at 5kV/mm leading to a GER effect. The researchers has chosen the suspension of STO particles in 10cSt silicon oil   because it gives straightforward tuning of its performance under an electric field by simply varying the water content in the STO particles; no special coating with urea or other polar molecules is required as the water provides the dipoles. The magnitude of this yield stress directly correlates with the water content in the particles [10]. The combination of very large yield stresses and linear field dependence of the yield stress on the applied field was subsequently also observed in dense suspensions of calcium titanyl oxalate, titanium dioxide and strontium titanyl oxalate particles [11]. The sample of STO particles were mixed with 10cSt dry silicon oil (STO/oil- 4g/ml) using a high speed ball mill (spex sample prep, 8000D) in stainless steel vials for 1 hr.. Figure 3 shows The image of particle size before mixing was 3µm and after mixing there is significant decrease in particle size around 300-500 nm as shown in fig. 3. The sample found to be stable for several months. Stress and the current density are directly proportional and that both depend exponentially on the water content. As the sedimentation rate increases the GER effect decreases.
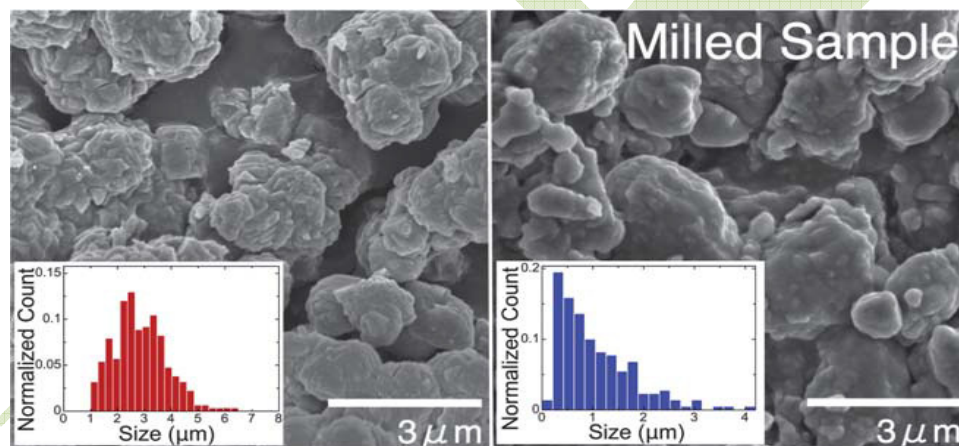

Figure3. Scanning electron microscope (SEM) images of STO particles before and after the milling process. Both insets show histograms of particle size.

A positive ER effect of nanofiber suspensions was reported by Jianbo Yin *et al.* by employing titanate nanofibers as dispersed phase Titanate nanofibers were uniform nanotube-like morphology with outer diameter of 10 nm and length about 100-200 nm after ultrasonic ER properties of suspension of titanate nanofibers in silicone oil were investigated by a steady shear viscosity.. in 2011, showed that Compared to the suspension of titania nanoparticles, the suspension of nanofibers showed higher yield stresses [12].
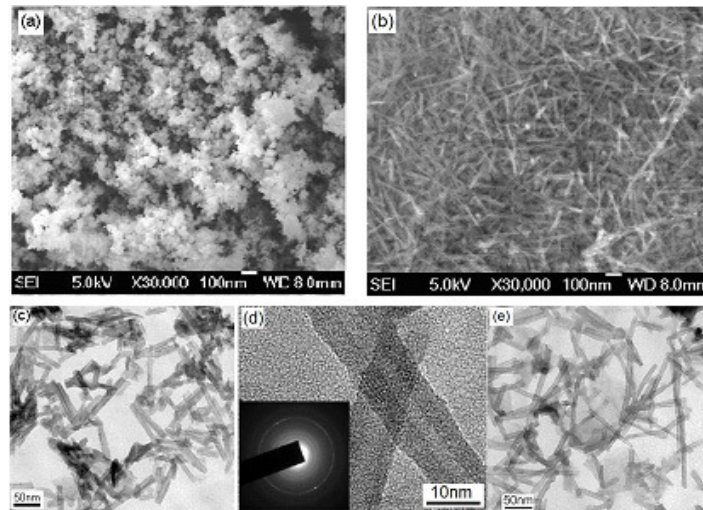
Figure4. SEM and TEM images. SEM images of raw material of titania nanoparticles (a) and formed Na-titanate nanofibers after hydrothermal treatment and 250°C-annealing (b); low-magnification TEM (c) and high-resolution TEM and corresponding ED pattern (d) of Na-titanate nanofibers; (e) TEM image of formed H-titanate nanofibers by washing Na-titanate nanofibers with HCl solution.

It is possible to reduce current density and hence sedimentation rate by more than one order of magnitude without compromising the yield stress by heating the mixed sample at 100°C for a couple of minutes. Carlos proved that addition of polar molecules in suspension of polarizable particles can increase the yield stress under an applied electric field. His experiments on dense suspensions of strontium titanyl oxalate in silicon oil gives yield stress of up to 200kPa at 5KV/mm.

Magnetorheological fluids

MR fluids an important class of smart material are suspension of soft fine magnetic particles (1-10μm) such as iron, nickel or cobalt in organic or aqueous (nonmagnetic) carrier nano-fluid, were first discovered by Rabinow in 1948 [13]. MRF exhibit a very fast reversible transition from liquid-like to solid-like state. In magnetic field each particle acquires an induced dipole.
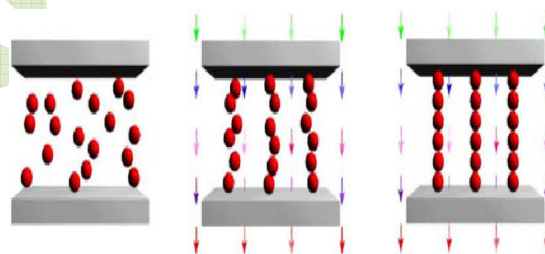

Figure5. Activation of MR nano-fluid: (a) no magnetic field applied; (b)magnetic field applied; (c)suspended particle chains have formed (© 2005 Lord Corporation [4]. All rights reserved)

When aligned along the field direction, the particle attracts each other, whereas the particles in the plane perpendicular to the field direction repel each other. The dipole-dipole interaction causes a chain formation in a direction parallel to field applied. This phenomenon is responsible for the development of yield stress in MRF as shown in fig 4 [14] [15]. From the various research papers published on ER and MR nano-fluids it can be concluded that MR nano-fluids exhibit much higher yield stress as compared to the ER nano-fluids. Practical applications like clutches and rotary brakes are possible with MRF that are not possible with existing ERF due to its relatively less yield strength. The size of the MR particles for preparation of magnetorheological nano-fluids in the range of 0.1 µm to 10 µm in diameter is considered. When the size of the particles becomes smaller, the destabilizing effect of Brownian motion becomes significant, leading to a decrease in the yield stress as the temperature of MR nano-fluid increases. Particles greater than 10 µm make it difficult to prepare MR suspension stable against the sedimentation [16] [17]. High saturation magnetization of the dispersed particles is required to produce maximum yield stress. Iron and carbonyl ion has high saturation magnetization of Fe element. Using Fe-Co alloys (composition of 50 wt% Fe, having the highest saturation magnetization about 2.4 Tesla), and Fe-Ni alloys gives much higher strength of MR nano-fluids [18]. MR nano-fluid must possess good stability and re-dispersibility for its practical applications. Most of the MR nanofluids suffered from irreversible aggregation of the suspended particles. Without special additives, most of the MR nano-fluids based on the micron-sized particles, suffers problems due to the settling and sedimentation. It is extremely hard to re-disperse the sediment, and the primary reason for this strong aggregation is the residual magnetization between the MR particles, which is not disappeared even without magnetic field. To overcome these problems additives such as polymeric surfactants and introducing a nano-structured composite with silica would be possible methods to enhance the stability of MR nano-fluids [19] [20]. Stability of MR nano-nano-fluids using visco-plastic medium against sedimentation and aggregation was satisfactory compared with that of ordinary MR fluids using Newtonian method [21]. Small amount of nano-sized ferromagnetic particles can beaded to enhance the dispersion stability of MR nano-nano-fluids without affecting the MR efficiency [22]. In 2001 R.Tao developed a general technique, a compression assisted-aggregation process to change the induced MR structure to a structure that consists of robust thick columns with strong ends as shown in figure 4.
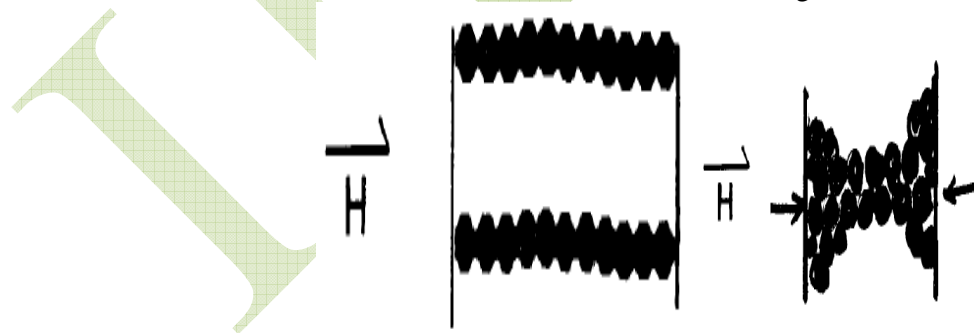

Figure6. Formation of the robust MR microstructure during compression–assisted aggregation. (a) Chains before the compression. (b) The compression forces the chains to aggregate into the thick columns.

With this approach an iron-based MR nano-fluid (suspension of carbonyl iron particles in silicon oil) becomes super strong having enhanced yield stress around 800 kPa at a

moderate magnetic field (B = 0.576 T). Immediately after a magnetic field is applied, compression of MR nano-fluid along the field direction before a shear force is applied produces chains in milliseconds. The compression pushes these chains to form thick columns with strong and robust ends. Once the weak points of MR microstructure are strengthened and the columns are very thick, the MR nano-fluids become super-strong [23]. In 2006 Wei Ping Wu have presented a novel approach for producing high yield stress MR nano-fluids, with carbonyl iron powders coated with guar gum as magnetic particles in the MR nano-fluids. Inducing a guar gum coating not only greatly improved the sedimentation stability but also strengthened the yield stress of the MR nano-fluid. The morphology of carbonyl iron powders coated with different contents of guar gum is as shown in figure 6. Obviously, with the increase of content of guar gum, the coating forms gradually and finally becomes smooth membrane-like coating surfaces. The thickness of the encapsulations significantly increases with the guar/Fe ratio, and finally the coating layers connected with each other, which made the particles bind to each other to form large conglomerations. The carbonyl iron powders were firstly coated with guar gum instead of ball milling, and then mixed with silicon oil. MR nano-fluids containing guar gum coated iron powders have excellent sedimentation stability and low zero-field viscosity.
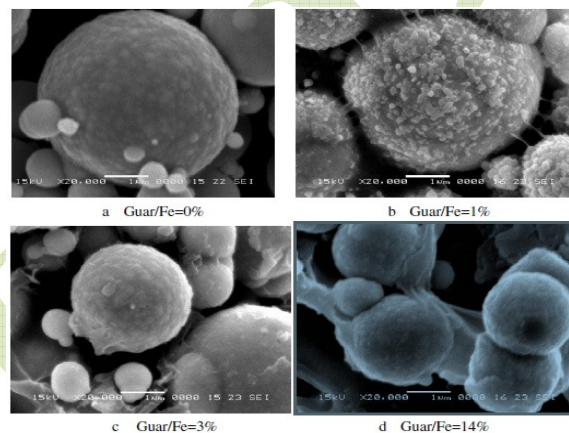

a   Guar/Fe=0%   b   Guar/Fe=1%

c   Guar/Fe=3%   d   Guar/Fe=14%

Figure7. Morphology evolution of composite iron particles with guar gum encapsulations (20000×).

The researchers have reported the best amount of guar gum induced is 3% to the amount of the iron powders, which leads to a MR nano-fluid with yield stress of 52.5 kPa at 0.4 T and only 2-3% sedimentation after 3 months [24]. Another approach of using bidisperse nano-fluids which are mixtures of two different powder sizes in the MR suspension reduces settling rate at the cost of reduction in the maximum yield stress. Figure 7 shows the Bingham-plastic yield stress as a function of magnetic field (Fig. a) and nanoparticles concentrations (Fig. b). From the graph it is clear that, the bidisperse MR nano-fluid with 20% of the micro particles replaced with nanoparticles shows an increase in dynamic yield stress at the highest value of current (magnetic field) tested [25].
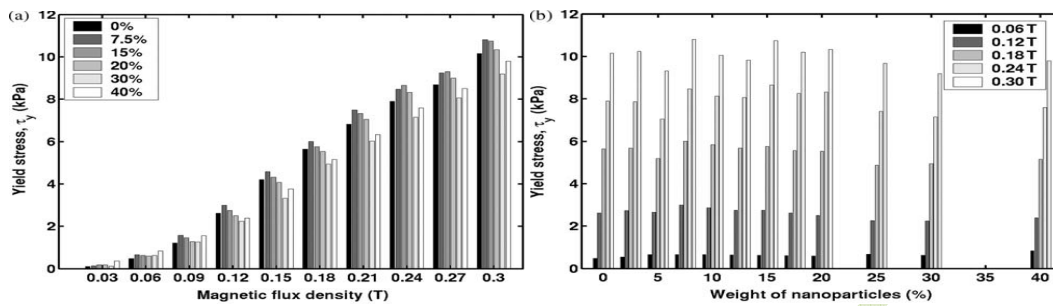
Figure8. (a) Yield stress vs. field and (b) yield stress vs. % nanoparticles.

Introduction of nanometre-scale Particles in small concentrations (< 15 wt %) can enhance the yield stress and reduce the sedimentation rate effectively [26][27]. More recent studies utilizing nanowires have shown promising results for not only reducing or preventing settling, but have also increased the apparent yield stress of the materials [28][29]. Unlike the ferromagnetic oxide particles used in previous studies done by Chin in 2001 and those formed from spherical particles adjoined in the presence of a magnetic field by Lopez *et al.* in 2009, nanowires have well defined structure and controllable length distributions. This facilitates systematic experimental and theoretical studies and will lead to increased understanding and design control. Nanowire-based MR nano-fluids have two distinct advantages over suspensions that contain only spherical particles. First, the maximum achievable yield stress can be twice that of conventional fluids (or greater, even at the same metal loading) and nanowire-based nano-fluids also provide more sensitive control over the yield stress at field strengths below magnetic saturation of the suspension. Second, sedimentation is greatly reduced, if not eliminated. However, one drawback to pure nanowire nano-fluids is the limit on particle loading to 10 vol. %, resulting in nano-fluids with a maximum yield stress much lower than most conventional MR fluids. The wires occupy a much larger effective volume compared to spheres, due to the excluded volume concept. Even so, nano-fluids using only nanowires display some very interesting and useful properties. For applications that require the highest yield stress (and thus maximum particle loading of 35-40 vol. %), a "dimorphic" nano-fluid was generated that contains both spherical and nanowire particles. These nano-fluids not only display reduced sedimentation, but some formulations also display an increase in yield stress over conventional fluids [31][32].

CONCLUSION

Both the electrorheological (ER) and magnetorheological (MR) nano-fluids are very important fluids in the category of smart nano-fluids. Conventional ER and MR fluids are not suitable for practical applications due to the lack of versatile performance like low yield stress, high sedimentation etc. To overcome these difficulties recent researches have lead to new interest in the development of non conventional ER and MR fluids with improved performance. In this review we focused on the ER and MR nano-fluids exhibiting high yield stress with less or no sedimentation. Our goal is to highlight the path of development of these nano-fluids. Keeping this in mind we have studied the development progress of smart nano-fluids which could replace the conventional fluids.

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