Journal of Material Science and Mechanical Engineering (JMSME)
Print ISSN: 2393-9095; Online ISSN: 2393-9109; Volume 2, Number 3; April-June, 2015 pp. 254-259
© Krishi Sanskriti Publications
http://www.krishisanskriti.org/jmsme.html

Synthesis and Characterization of High Yield Stress Smart Fluids with No Sedimentation– A Review

Khandu L. Paval[1] and Santosh R. Patil[2]

[1]M. Tech. Design Student R.I.T. Sakhrale
[2]R.I.T. Sakhrale
E-mail: [1]khandupaval@gmail.com, [2]santosh.patil@ritindia.edu

Abstract—*Smart materials (also known as multifunctional materials) have been developed and studied over the past few decades. Their properties can be changed significantly during use and with very fast response of time. Both magnetorheological (MR) and electrorheological (ER) fluids are known to be smart materials. They can be rapidly and reversibly transformed from a fluid to solid state with very fast response time. ER and MR fluids show dramatic and tunable changes in their rheological properties under external magnetic or electric field strength respectively. These fluids can be effectively incorporated in various engineering applications like shock absorber, dampers, clutches, brakes etc. The major hurdle to use these fluids commercially is their low yield strength and problem associated with sedimentation. In this paper various smart fluids (ER & MR) have been studied. Special attention is given on development of stable, re-dispersible, durable, high yield stress smart fluids with less sedimentation rate. These fluids are briefly reviewed along with their rheological characteristics under external fields.*

1. INTRODUCTION

The lack of high performance materials, as well as the problem associated with no sedimentation, has inhibited broad engineering applications. Thus though these smart materials are seem to attractive, the future holds in development of the relationships between synthesis and processing of high yield strength smart materials with less or no sedimentation rate.

1.1 Objective of research work.

The overall objective of this research is to review high yield stress smart fluids which possess better ER/MR effect and less sedimentation. Although high yield stress smart 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 fluids having no sedimentation problem and characterization of high yield stress smart fluids by various methods. In this review we focused on the ER and MR fluids exhibiting high yield stress with less or no sedimentation. Our goal is to highlight the path of development of these fluids.

2. 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 Ferrofluids. Here in this review special attention is given on electrorheological fluids and magnetorheological fluids.

2.1 Electrorheological 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 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 and water free 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 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 μ = 4.6debye. 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 Fig. 1[5].

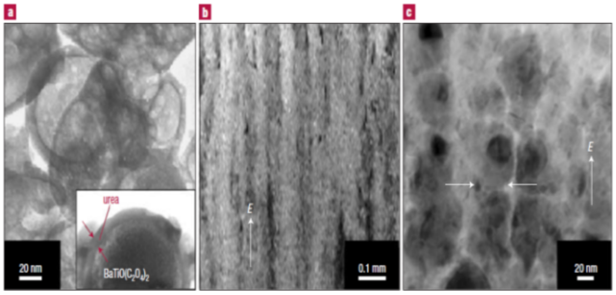

Fig. 1: a) Transmission electron microscope (TEM) image of urea coated nanoparticles. b) Optical microscope image of a sample, columns aligned along the field direction are visible. c) The arrows indicate one of the flattened interfaces.

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 fluid shows dramatically enhanced antisedimentation characteristics without scarifying the much yield stress [7]. Sedimentation phenomenon occurs due to the density mismatch of the 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 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 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 Fig. 2.

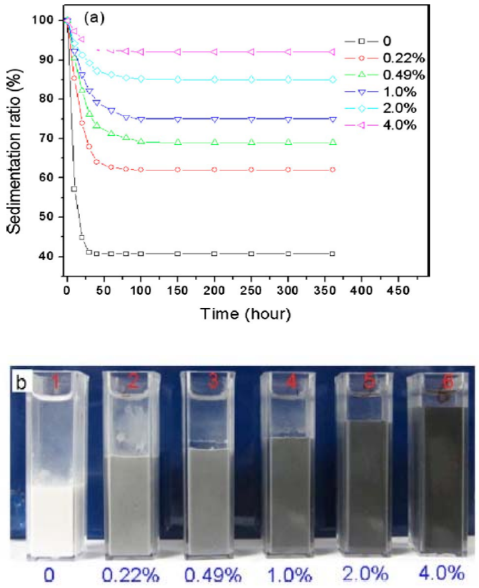

Fig. 2: a) Sedimentation ratio of BTRU and MWCNT-BTRU particles suspended in methyl terminated silicon oil (20cSt) with a concentration of 5.0. b) Sample images with different wt% after preparation.

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.. Fig. 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.

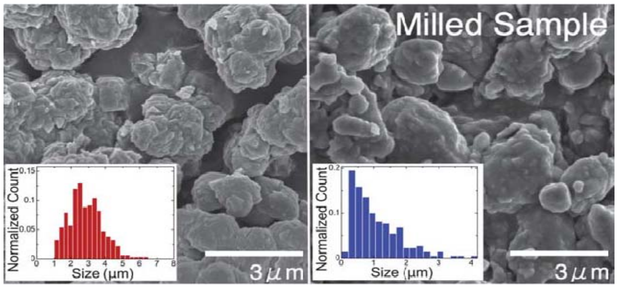

Fig. 3: Scanning electron microscope (SEM) images of STO particles before and after the milling process. Both insets show histograms of particle size.

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.

2.2 Closure

In the section of electrorheological fluids we have studied a different research papers (1996-2014) related to the development of ER fluids which exhibit high yield stress with less or no sedimentation. All the researchers, scientists have contributed in development of ER fluids and their remarkable work has achieved a milestone. Lot more work till has to be happen to replace the conventional fluids with smart fluids.

2.3 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 fluid, were first discovered by Rabinow in 1948 [12]. MRF exhibit a very fast reversible transition from liquid-like to solid-like state. In magnetic field each particle acquires an induced dipole. 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 [13] [14].

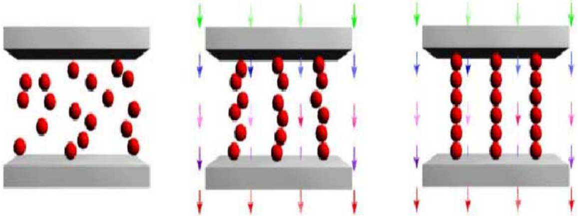

Fig. 4: Activation of MR fluid: (a) no magnetic field applied; (b)magnetic field applied; (c)suspended particle chains have formed (© 2005 Lord Corporation [4]. All rights reserved)

From the various research papers published on ER and MR fluids it can be concluded that MR fluids exhibit much higher yield stress as compared to the ER 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 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 fluid increases. Particles greater than 10 µm make it difficult to prepare MR suspension stable against the sedimentation [15] [16]. 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 fluids [17]. MR fluid must possess good stability and re-dispersibility for its practical applications. Most of the MR fluids suffered from irreversible aggregation of the suspended particles. Without special additives, most of the MR 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 fluids [18] [19]. Stability of MR fluids using visco-plastic medium against sedimentation and aggregation was satisfactory compared with that of ordinary MR fluids using Newtonian method [20]. Small amount of nano-sized ferromagnetic particles can beaded to enhance the dispersion stability of MR fluids without affecting the MR efficiency [21]. 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 Fig. 4.

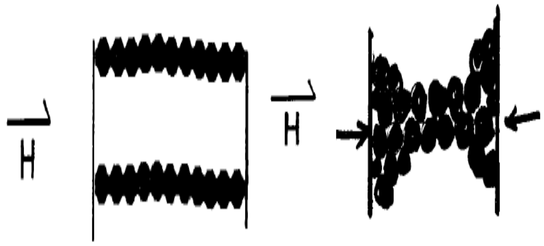

Fig. 5: Formation of the robust MR microstructure during compression–assisted aggregation. (a) Chains before the compression. (b) The compression forces the chains to aggregate into the thick columns.

With this approach an iron-based MR 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 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 fluids become super-strong [22]. In 2006 Wei Ping Wu have presented a novel approach for producing high yield stress MR fluids, with carbonyl iron powders coated with guar gum as magnetic particles in the MR fluids. Inducing a guar gum coating not only greatly improved the sedimentation stability but also strengthened the yield stress of the MR fluid. The morphology of carbonyl iron powders coated with different contents of guar gum is as shown in Fig. 6.

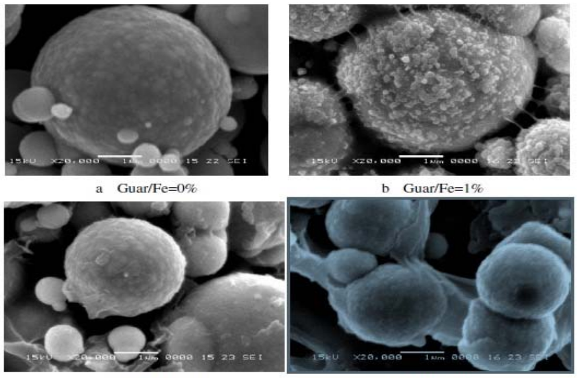
a Guar/Fe=0%
b Guar/Fe=1%
c Guar/Fe=3%
d Guar/Fe=14%

Fig. 6: Morphology evolution of composite iron particles with guar gum encapsulations (20000×).

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 fluids containing guar gum coated iron powders have excellent sedimentation stability and low zero-field viscosity. 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 fluid with yield stress of 52.5 kPa at 0.4 T and only 2-3% sedimentation after 3 months [23]. Another approach of using bidisperse 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. Fig. 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 fluid with 20% of the microparticles replaced with nanoparticles shows an increase in dynamic yield stress at the highest value of current (magnetic field) tested [24].

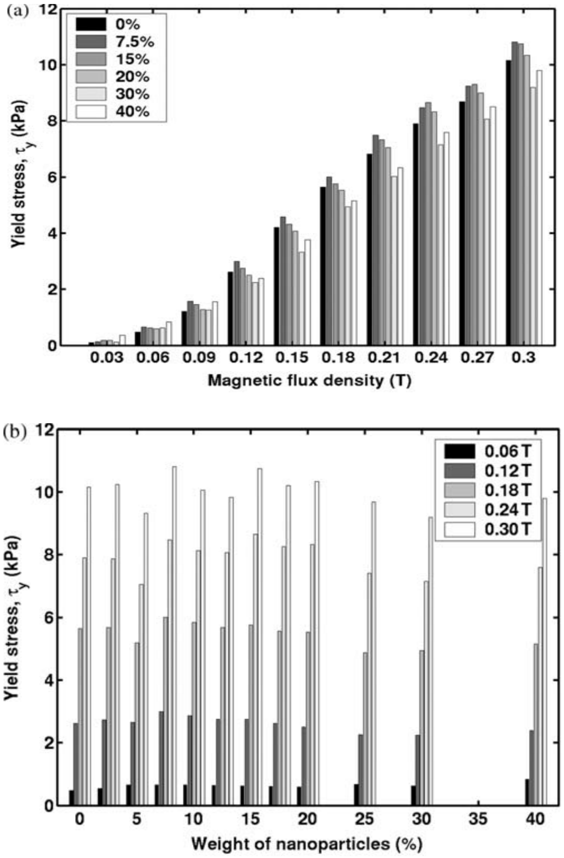

Fig. 7: (a) Yield stress vs. field and (b) yield stress vs. % nanoparticles.

Introduction of nanometer-scale Particles in small concentrations (< 15 wt %) can enhance the yield stress and reduce the sedimentation rate effectively [25][26]. 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 [27][28]. 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 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 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 fluids is the limit on particle loading to 10 vol. %, resulting in 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, 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" fluid was generated that contains both spherical and nanowire particles. These fluids not only display reduced sedimentation, but some formulations also display an increase in yield stress over conventional fluids [29] [30].

2.4 Closure

Many researchers have worked in the field of development of high performance magnetorheological fluids. Their theories and practices have made possible to develop MR fluids with yield stress as high as 800kPa with negligible sedimentation. Still lots more work have to be done in this field to replace the non-conventional MR fluids with smart MR fluids.

3. CONCLUDING REMARK

Both the electrorheological (ER) and magnetorheological (MR) fluids are very important fluids in the category of smart 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 fluids exhibiting high yield stress with less or no sedimentation. Our goal is to highlight the path of development of these fluids. Keeping this in mind we have studied the development progress of smart fluids which could replace the conventional fluids.

REFERENCES

[1] W.M. Winslow, Journal of applied physics 11, 319, 1949.

[2] X. W. Zhang, C. B. Zhang, T. X. Yu, "Characterization of electro-rheological fluids under high shear rate in parallel ducts", International journal of modern physics B Vol. 22, Nos. 31 & 32 6029-6036, 2008.

[3] Xianxiang Huang, Weijia Wen, Shihe Yang and Ping Sheng, "Mechanism of the giant electrorheological effect", Solid state communication 139 (2006) 581-588.

[4] Yuling Zhang, Jingkui Liang, "Electrorheological fluid with an extraordinary high yield stress", Applied physics letter, volume 80, number 5, 2002.

[5] Weijia Wen, Xianxiang Huang, Shihe Yang, Kunquan Lu, Ping Sheng, "The giant electrorheological effect in suspensions of nanoparticles",Nature materials Vol. 2, 2003.

[6] Weijia Wen, Xianxiang Huang, and Ping Sheng "Particle size scaling of the giant electrorheological effect", Applied physics letters volume 85, number 2, 2004.

[7] Jiaxing Li, Xiuqing Gong, Shuyu Chen, Weijia Wen, and Ping Sheng "Giant electrorheological fluid comprising nanoparticles: Carbon nanotube composite", Journal of applied physics 107, 093507, 2010.

[8] C.Shen, W. Wen, S. Yang and P. Sheng, "Wetting induced electrorheological effect", Journal of applied physics 99, 106104, 2006.

[9] X. Gong, J.Wu, X.Huang, Weijia Wen and Ping Shen, "Influence of liquid phase nanoparticles-based giant ER fluid", Nanotechnology 19, 165602,2008.

[10] Carlos S. Orellana, Jinbo He, Heinrich M. Jaeger "Electrorheological response of dense strontium titanyl oxalate suspensions". The royal society of chemistry, www.rsc.org/softmatter, 2011.

[11] R.Shen, X. Wang, Y. Lu, D. Wang, G. Sun, Z.Cao and K. Lu, Advanced matter, 2009, 21, 4631-4635.

[12] J. Rabinow, AIEE Translation. 67, 1308, 1948.

[13] Z. P. Shulman, W.I. Kodonsky, E.A. Zaltsgendler, I. V. Prokhorov, B. M. Khusid and S. A. Demchuk, International Journal of Multiphase Flow, 12, 935, 1986.

[14] Jong Hyeok Park, O. O. Park, Korea-Australia Rheology Journal Vol. 13, No. 1, March 2001 pp. 13-17.

[15] Y. Ma, Y. L. Zhang and K. Q. Lu, journal of applied physics 83(1998) 5522.

[16] J. David Carlson, "what makes a good MR fluid."Lord Corporation, 110 Lord Drive, Cary, North Carolina 27511, USA, 1993.

[17] P. P. Phule and J. M. Ginder, "Synthesis and properties of novel MR fluids having improved stability and redispersibility", International journal of modern physics B, 13:2019-2027, 1999.

[18] C. Shen, W. Wen, S. Yang and P. Sheng, "Wetting induced electrorheological effect", Journal of applied physics 99, 106104, 2006.

[19] Z. P. Shulman, E. V. Korobko and Y. G. Yanovskii, 1989, Journal of Non-Newtonian Fluid Mechanics, 33, 181.

[20] P. J. Rankin, A. T. Horvath and D. J. Klingenberg, "Magnetorheology in viscoplastic media", Rheological acta, 38:471-477, 1999.

[21] B. D. Chin, J. H. Park, M. H. Kwon & O. O. Park, (2001), "Rheological properties and dispersion stability of magnetorheological (MR) suspensions." Rheological Acta, Vol. 40, No. 3, (May, 2001) pp. 211–219, 0035-4511.

[22] R. Tao "Super strong magnetorheological fluids", Journal of physics: condensed matter, topical review, 2001.

[23] Wei Ping Wu, Bin Yuan Zhao, Qing Wu and Li Sheng Chen, "The strengthening effect of guar-gum on the yield stress of magnetorheological fluid", Smart mater Structure, 2006, 15, N94.

[24] N.M. Wereley, A. Chaudhuri and J.H. Yoo "Bidisperse magnetorheological fluids using Fe particles at nanometer and micron scale", Journal of intelligent material systems and structures, Vol. 17-May 2006.

[25] C. Kormann, H.M. Laun, N. Willenbacher Rheological acta, 1996-Springer.

[26] N. Rosenfeld, N. M. Wereley, R. Radakrishnan, T. S. Sudarshan, "Behavior of magnetorheological fluids utilizing Nanopowder iron", International Journal of Modern Physics B, Vol. 16, No. 17-18, (July, 2002) pp. 2392–2398, 0217-9792.

[27] R. C. Bell,E. D. Miller,J. O. Karli,A. N. Vavreck, D. T. Zimmerman, "Influence of particle shape on the properties of magnetorheological fluids", International Journal of Modern Physics B, Vol. 21, No. 28-29, (November 2007) pp. 5018–5025, 0217-9792.

[28] R. C. Bell,J. O. Karli,A. N. Vavreck, D. T. Zimmerman,G. T. Ngatu, N. M. Wereley," Magnetorheology of submicron diameter iron nanowires dispersed in silicone oil",Smart Materials and Structures, Vol. 17, No.1, (February 2008) pp. 015028-1–6, 0964-1726.

[29] G. T. Ngatu, N. M. Wereley, J. O. Karli, R. C. Bell, "Dimorphic magnetorheological fluids: exploiting partial substitution of microspheres by nanowires", Smart Materials and Structures, Vol. 17, No. 4, (August 2008) pp. 045022-1–8, 0964-1726.

[30] M. T. Lopez-Lopez, P. Kuzhir, G. Bossis, "Magnetorheology of fiber suspensions. I. Experimental", Journal of Rheology, Vol. 53, No. 1, (January/February 2009) pp. 115– 126, 0148-6055.