Volume 77 • Issue 2 • August 2016

Journal of Achievements in Materials and Manufacturing Engineering

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Effect of graphene as anti-settling agent for magnetorheological fluid

J. Thanikachalam *, P. Nagaraj, G.S. Hikku

Department of Mechanical Engineering, Mepco Schlenk Engineering College, Sivakasi, 626005, India

* Corresponding e-mail address: jthanik@gmail.com

ABSTRACT

Purpose: Magnetorheological fluids are field-responsive fluids containing magnetic particles suspended in a suitable medium. In this proposed work, the iron powder was dispersed in silicone oil to obtain magnetorheological fluid. These fluids can be transformed from liquid-like state to solid-like state within milliseconds by applying magnetic field and vice versa. The particles arrange as chain like pattern with the application of magnetic field, increasing the yield strength of the fluid. However, when the shear stress reaches the critical value, the chain like pattern breaks causing reduction in yield strength. One of the major limitations of these fluids is that the suspended particles settle down quickly forming cake like structure at the bottom, which is very difficult to re-disperse.

Design/methodology/approach: The present study focuses on increasing the Sedimentation time of the fluid by adding suitable Nano additives. For this purpose graphene nanoparticles with atomic thickness were introduced as an additive to decrease the sedimentation of the fluid. The added graphene sheets (gap-fillers) filled the interspaces of Iron particles and improved the sedimentation resistance. Different quantities of graphene were added (0.5 g, 1.5 g, 2.5 g and 3.5 g) and their normalized height was calculated with time. Interpolation method was also done to find the sedimentation values with Graphene addition which were not done experimentally.

Findings: The prepared samples were characterized using Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope, Optical Microscopy, Viscometer etc. Contour plot was interpreted to understand the effect of graphene addition towards the normalized height and viscosity of the fluid.

Keywords: Magnetorheological fluid; Normalized height; Graphene sheets; Ball mill; Interpolatio

Reference to this paper should be given in the following way:

J. Thanikachalam, P. Nagaraj, G.S. Hikku, Effect of graphene as anti-settling agent for magnetorheological fluid, Journal of Achievements in Materials and Manufacturing Engineering 77/2 (2016) 49-56.

MATERIALS

1. Introduction

The quick response time of MR fluids makes it a good choice for various applications, including damping device, pumps, anti-seismic protections, flexible fixture, clutches, etc. In all the application sedimentation of suspended particle becomes a major problem which restricts the commercial use of these fluids. Modesto T. Lopez et al., (2008) [1] reported the methods for the preparation of well dispersed suspensions of micron-sized iron particles in magneto-rheological (MR) fluids coated with different surfactants to reduce sedimentation rate. Jerome Claracq et al., (2004) [2] suggested that the MR fluids should be highly stable against settling and should have a high magnetic saturation. Y. Rong et al., (2000) [3] reported that after the application of magnetic field, if the MR fluid is compressed before the applied shear stress, then the obtained yield stress increases 10 times greater than those obtained from without compression. Stephen Samouhos, (2007) [4] developed MR fluids with carbon nanotube (CNT) –magnetite composite by non-covalent surface coating of magnetite particles over CNT. This increases the sedimentation stability and faster response to the magnetic field. Byung O. Park et al., (2011) [5] prepared MR fluid composed of soft magnetic carbonyl iron (CI) micro spherical particles, which is dispersed in a grease medium to reduce the sedimentation of the CI particles. Kiyohito Koyama et al., (1995) [6] reported that the electro-magneto-rheological (EMR) fluid shows higher yield strength when the applied magnetic field and electric field are superimposed in the same direction which is parallel to the stress. Wen Ling Zhang et al., (2012) [7] reported that MWNT/PS/CI composite was added as a magneto-responsive particles and can be used as an MR material which reduces the sedimentation problem. Ke Zhang et al., (2009) [8] reported the preparation of the polymer/CNT and magnetic particle/CNT composite using sono-chemical fabrication method. Functionalization or physical adsorption of dispersants onto the surface of CNT has been introduced to increase the dispersibility of the CNT in solvents. F. F. Fang et al., (2008) [9] reported the sedimentation problem of carbonyl iron (CI) particles in MR fluid. To overcome the problem the particles are treated with 4-aminobenzoic acid which acts as a grafting agent. The functionalized CNT is added to the surface treated CI particles and sonicated to give CI/CNT particles. Karemkarokoc et al., (2006) [10] developed a magneto-rheological brake (MRB) system which shows better performance advantages over the conventional hydraulic brake system. Yanwu Zhu et al., (2010) [11] reported that the average elastic modulus and the highest fracture strength of individual Graphene oxide platelets were ~32 Gpa and ~120 Mpa respectively. Z.J. Li et al., (2012) [12] prepared Few-Layer-Graphene (FLG) sheets from graphite by modification of the Hummers method. The steps involved are 1) intercalation, 2) re-intercalation, 3) pre-reduction, 4) reduction.

2. Material and method

2.1. Milling of iron powder

The iron powder was bought from Merck with 250-300 mesh. Particle size of 1-3 μm is required for various applications since it has a range of good mechanical property. In order to reduce the size of the iron powder, ball milling was performed. The size of the milled iron powder was checked at regular intervals with the help of Scanning Electron Microscopic (SEM) image to examine the size reduction. Also the additives and silicone oil were mixed along with the milled powder with the help of ball mill to ensure even distribution of additives in the fluid [13].

2.2. Preparation of graphene by modified hummer's method

2 g of graphite was sonicated in 200 ml water for 30 min to obtain expanded Graphene and filtered. 46 ml of H_2SO_4 was added to the expanded graphite. 6 g of potassium permanganate was crushed and added slowly to the above solution with continuous stirring with the temperature not exceeding 20°C. The stirring was continued for 2 hours at room temperature and 90 ml water was added. Stirring was done for another 1 hour and 280 ml of water was added to terminate the reaction. Add 5 ml of hydrogen peroxide to the above solution for ensuring complete reaction of potassium permanganate. The solution was filtered and washed with diluted hydrochloric acid with a ratio (10:1) to remove metal ions. Then the filtrate was washed several times with water until the pH value of the filtrate reaches to pH 7. The resultant filtrate was Graphene oxide. The Graphene oxide was refluxed for 2 hours with hydrazine hydrate with a ratio 1:2 in the presence of water. The hydrazine hydrate acts as reducing agent and reduces Graphene oxide to Graphene [14].

2.3. Preparation of MR fluid

Suspending medium

The suspending medium is a viscous fluid that does not allow the suspended particle to settle down. Silicone oil and mineral oil are most commonly used as a suspending medium [15-17]. Silicone oil is most preferably used in MR fluids because of its good temperature-stability and good heat-transfer characteristics, oxidation resistance, very low vapor pressure, and high flash points [18].

Suspending particles

The suspended particle should have a high magnetic behaviour; therefore they can be manipulated using magnetic fields. For this purpose Carbonyl iron powder, Iron powder and its alloy forms are commonly used. They are mostly used in micron sizes, since large size range makes the particle to sediment quickly and too small sized particles does not provide necessary yield strength for braking, the size of the powder selected will be in 1 to 3 μm. Iron powder is taken as the suspending particle since it is easily available and cheap compared to carbonyl iron forms [19].

Additives

The additives are used to reduce the sedimentation of the suspended particles. These additives help the particles to float on the medium to increase the stability of the fluid and also help to reduce the erosion of the suspended particles due to friction. Commonly used additive are grease, graphene oxide, etc. Here we use novel graphene nano sheets as the additive.

Preparation of MR fluid

20 g of iron powder and 100 ml of silicone oil were used as a precursor for preparing the MR fluid. The conventional MR fluids were prepared by suspending magnetic milled iron particles in silicone oil was considered as standard. Here the compositions of iron powder and silicone oil were kept constant (20 g and 100 ml respectively) and the concentration of Graphene was varied from 0.5 g to 3.5 g (0.5 g, 1.5 g, 2.5 g and 3.5 g). The mixing of MR fluid constituents was done using mechanical milling for even dispersion. The Table 1 shows the different compositions of MR fluid with the varied addition of additives.

Normalized height

The normalized height of prepared samples was calculated using the following formula [20],

$$Normalized\ height\ \% = \frac{height\ of\ the\ sediment}{total\ height\ of\ the\ fluid} * 100 \qquad (1)$$

Table 1.
Composition of sample preparation

Sample	Iron powder	Silicone oil	Graphene
Sample 1 (Standard)	20 g	100 ml	NIL
Sample 2	20 g	100 ml	0.5 g
Sample 3	20 g	100 ml	1.5 g
Sample 4	20 g	100 ml	2.5 g
Sample 5	20 g	100 ml	3.5 g

Fig. 1 shows the schematic to understand the parameters such as the height of the sediment and the total height of the fluid from which the normalized height can be calculated using the formula from the equation (1).

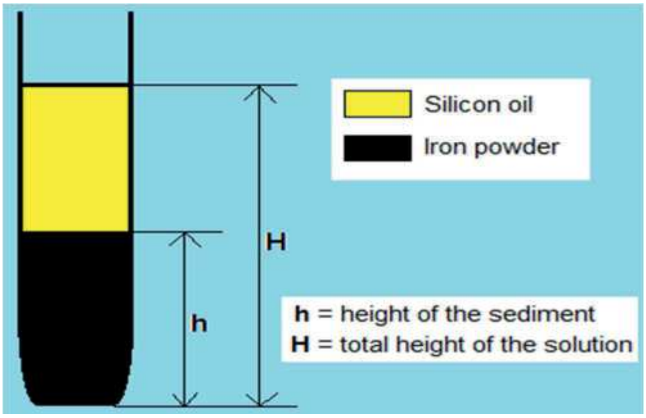

Fig. 1. Schematic to obtain the parameters for normalized height

3. Results and discussion

3.1. Scanning electron microscopic analysis

Scanning Electron Microscope (SEM) was used to determine the morphology of the synthesized nanoparticles. Figure 2 represents the SEM image of Graphene taken with secondary electron (SE) mode. This figure reveals the presence of sheet like structures which were exfoliated Graphene sheets. The image also shows the thickness of each sheet in atomic size. The image was taken with 8,000X magnification, with a working distance of 6.8 mm. The voltage given to the electron source was 10 kV.

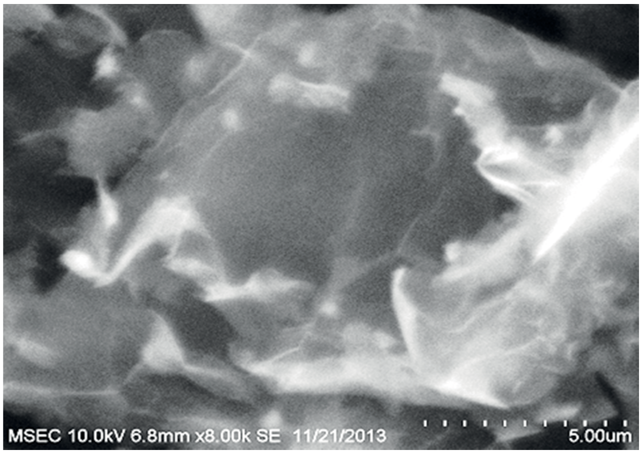

Fig. 2. SEM image of graphene sheets

Figures 3 and 4 shows the morphology and size of iron powder before and after milling respectively. Before milling the size of the iron particle was found to be approximately 50 µm. In Figure 4, SEM images corresponding to the samples drawn at different time intervals of the milling process were given.

The reduction in size of the particle with respect to different hours of milling can be visualized from the SEM analysis. Here wet milling was employed with toluene as a wetting agent for better grinding. From Fig. 4 it was observed that while milling the metallic iron particles, the particles get deformed to flake like structures due to the ductile property of iron. As time increases the size of the particle also gets reduced. After 9 hours of continuous milling uniform structure of iron particles with size 1~3 µm were obtained. Thus the time required to reduce the size of iron powder to desired range was optimized.

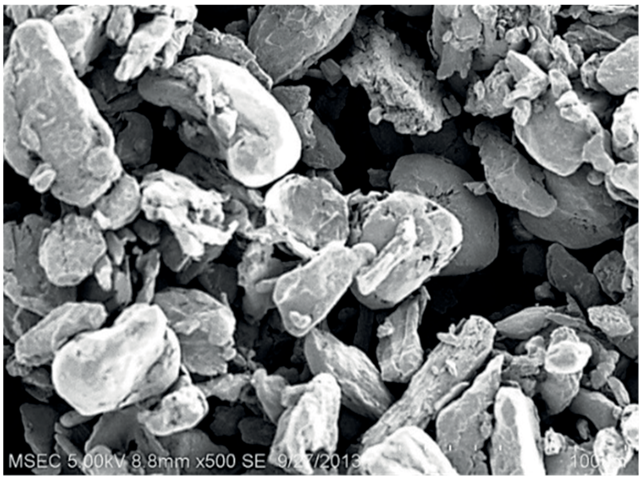

Fig. 3. SEM image of iron powder before milling

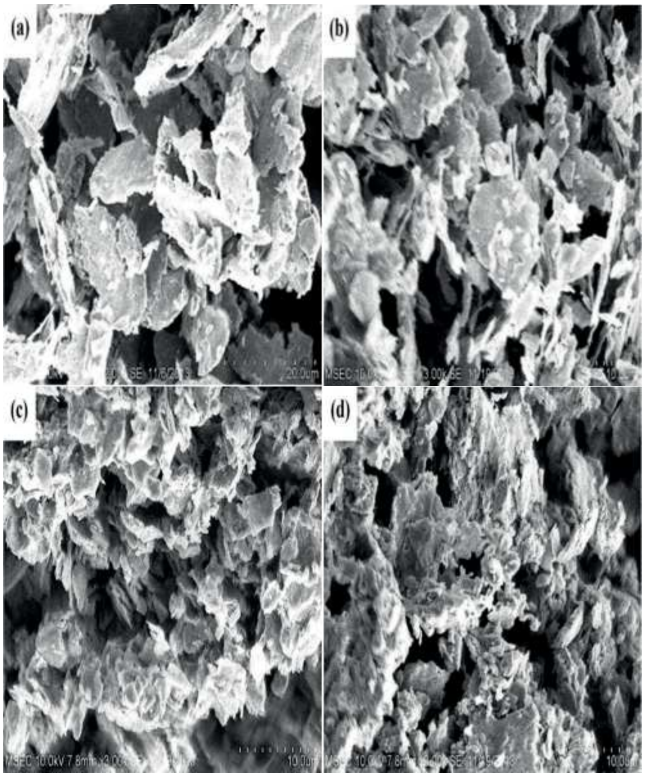

Fig. 4. SEM image of iron powder: (a) 2 hours, (b) 5 hours, (c) 9 hours and (d) 11 hours of ball milling

3.2. Optical macroscope

The alignment of the iron particles in the magnetic field direction was examined using compound optical microscope. The MR fluid was dispersed in a glass slide and the image was taken without magnetic field was given in the Figure 5 (a). When a magnetic field was applied the suspended particles in the MR fluid forms a chain like structure parallel to the direction of the magnetic field which was shown in Figure 5 (a).

These chains like structures were responsible for the change in viscosity of the fluid with the application of magnetic field.

3.3. Fourier transform infra-red (FTIR) analysis

Figure 6 shows the IR spectra of graphene sheets. The FTIR spectrum of the graphene sheets obtained confirms the successful reduction of the graphene oxide to graphene. The FTIR spectrum of graphene shows no peaks at C = O, C-OH, C-O-C, and C-O indicates the reduction of graphene oxide to graphene. Due to the absence of these groups the graphene was hydrophobic in nature. Therefore the prepared graphene gets easily dispersed in silicon oil. The peak at 1615 cm^{-1} arises due to the C=C characteristic vibrations from the graphene sheets [21]. Since there was no peak found at ~3500 cm^{-1} imply that atmospheric moisture was not absorbed on the graphene sheets.

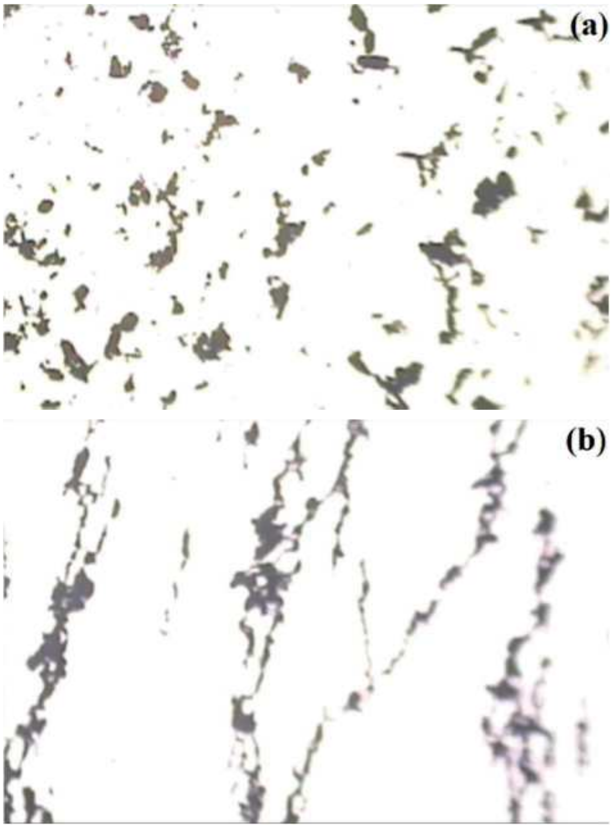

Fig. 5. Optical images of magneto-rheological fluid: (a) without magnetic field, (b) with magnetic field

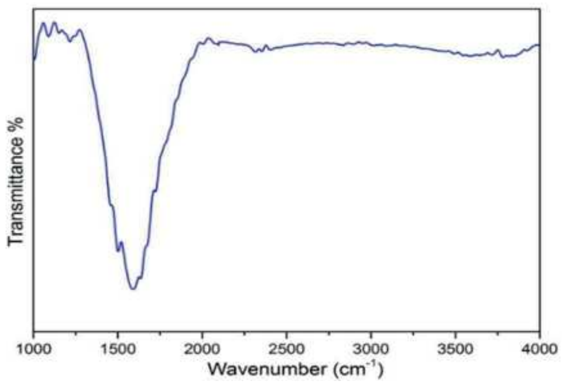

Fig. 6. FTIR spectrum of graphene

3.4. Normalized height

From the Fig. 7 the normalized height with varying time of sample 4 and sample 5 gives good result compared to other samples. This was due to the impact of graphene addition to the MR fluids. As the graphene addition increases the sedimentation decreases this explains the graphene can be used as anti-settling agent for such fluids. With the addition of 3.5 g of graphene to the standard the normalized height increases drastically from 22% to 81% i.e. lower sedimentation rate. The graphene sheets hold the iron particles from settling and also act as gap fillers for the fluid cause delayed and decreased sedimentation rate.

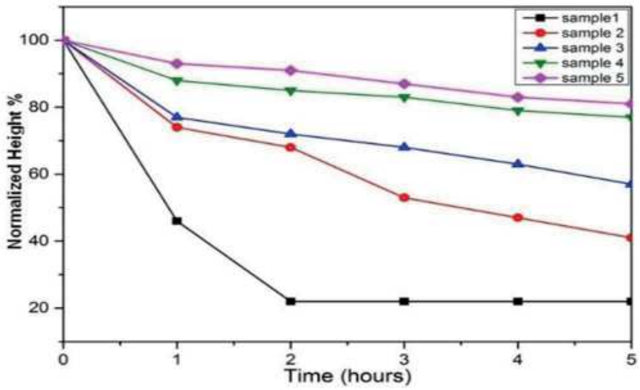

Fig. 7. Normalized heights of different MRF samples

In order to get clear information on the normalized height from the observed data, Interpolation has been carried out to interpret intermediate normalized height values for different quantities of graphene addition that were not done experimentally. Interpolation is very useful where the data surrounding the missing data are available and its trend, seasonality and longer term-cycles are known. Here different quantities of graphene addition from 0 to 3.5 g with an increment of 0.1 g was interpolated and the normalized height was plotted against time was shown in Figure 8.

From the Fig. 8 it was clear that the rate at which the sedimentation takes place is very rapid at first and it gradually declines.

3.5. Viscosity

Viscometer is an instrument used to measure the viscosity of a fluid. In general, either the fluid remains stationary and an object moves through it, or the object is stationary and the fluid moves past it. The drag caused by relative motion of the fluid and the surface is the measure of the viscosity. The viscosity of the prepared fluids was measured and tabulated below (Table 2).

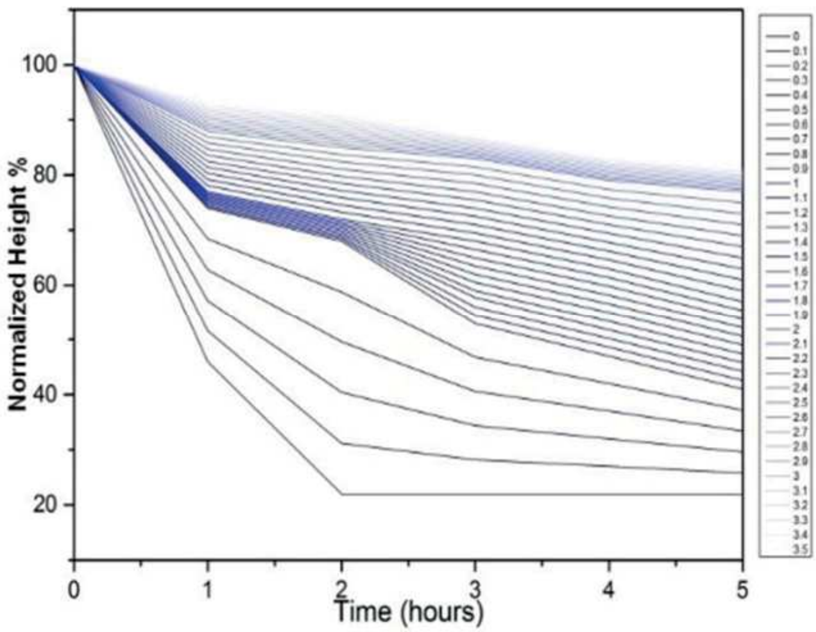

Fig. 8. Normalized height of different MR fluid samples using interpolation

Table 2.
Viscosity values for prepared MR fluids

SAMPLE	VISCOSITY
Sample 1	1216 cp
Sample 2	2056 cp
Sample 3	3113 cp
Sample 4	4203 cp
Sample 5	5407 cp

Table 2 shows the viscosity of different prepared samples. From the table it was understood that with the addition of graphene sheets the viscosity of the fluid also increases. Therefore the viscosity and normalized height of the fluid can be manipulated with the addition of graphene sheets.

3.6. Effect of graphene addition on viscosity and normalized height

The influence of graphene addition to the MR fluid with viscosity and normalized height is shown in Figure 9, in which normalized height was measured on an interval of one hour and the viscosity by means of varying percentage of graphene (0 g, 0.5 g, 1.5 g, 2.5 g and 3.5 g). The viscosity of the prepared MR fluid combinations was measured to be in the range of 1216-5407 cp. For each MR fluid sample, the viscosity appears to vary similarly as a function of the graphene addition. The normalized height values shown in Figure 9 increase rapidly throughout the graph at different time interval with graphene addition in which variations in obtained values were considerably smaller. This distinct feature shows the anti-settling ability of graphene nano sheets which withheld the sedimentation of iron particles to a certain extent. After the first hour of observation, the normalized value shows more or less equal values for graphene addition greater than 1 g but shows lower values for less than 1 g additions. With the increase in time interval the MR fluid without the addition of graphene, the iron particle settles completely showing poor results Fig. 9 (a-b). The graphene added MR fluids show better values for normalized height even after 5 hours Fig. 9 (a-e). With the increase in the addition of graphene, improved values for normalized height were obtained, i.e. for MR fluids with 3.5 g graphene addition the normalized height value was above 80 whereas the MR fluid without Graphene shows a value less than 30 after 5 hours Figure 9 (e). This is because with the increase in the addition of additives the gaps between the iron particles are filled with additives making graphene as gap fillers.

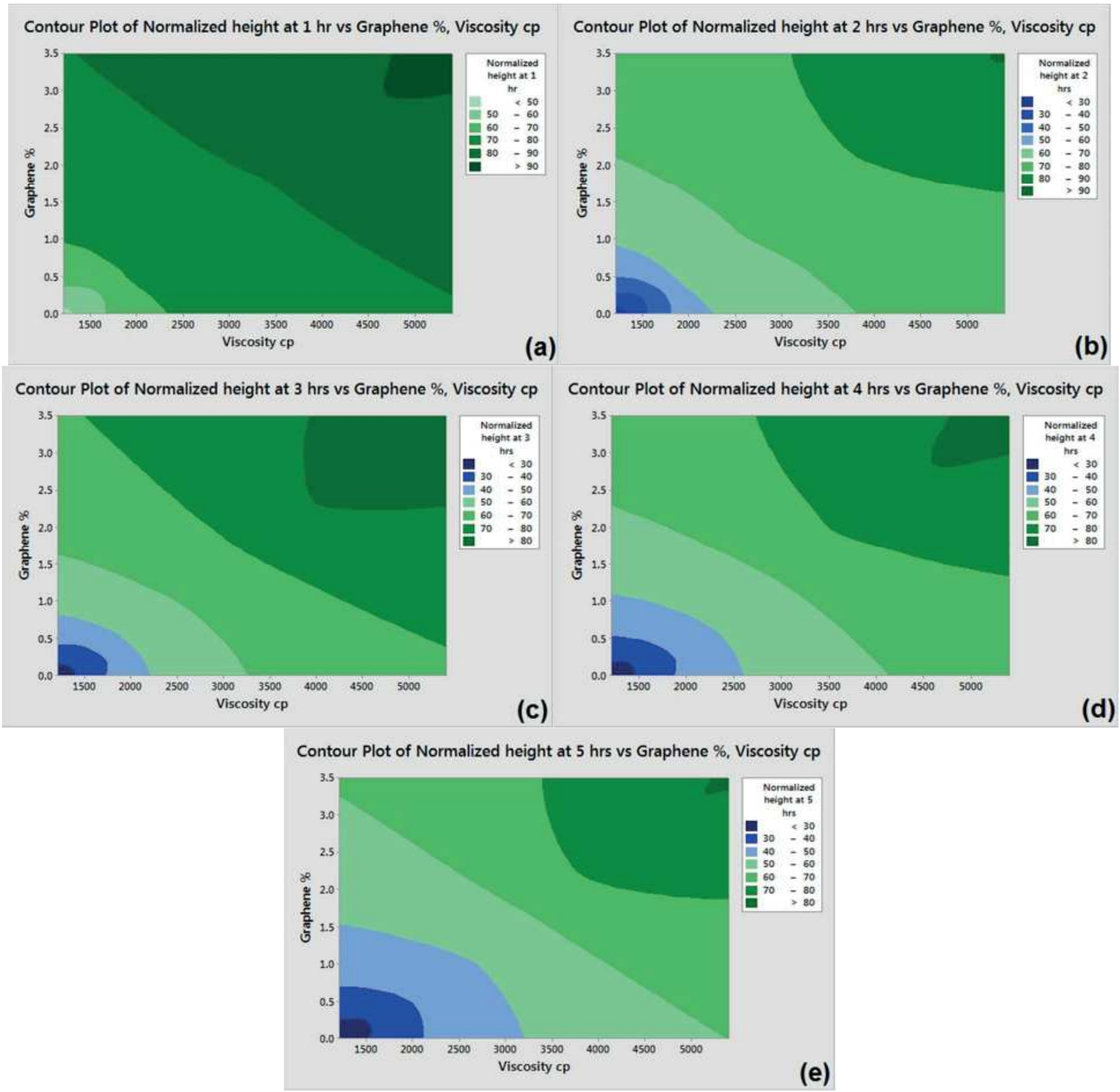

Fig. 9. Contour plot for normalized height at time (a) 1 hour, (b) 2 hours, (c) 3 hours, (d) 4 hours, (e) 5 hours vs. graphene% and viscosity

4. Conclusions

In this study, five systems of MR fluids were prepared and compared with respect to the sedimentation characteristics and viscosity. The successful addition of graphene sheets as anti-settling agent for magnetic iron particles was confirmed by the normalized height of these fluids. It was found that the addition of novel graphene additives improved the much needed normalized height significantly from 22% to 81%. Future studies may be done by adding different kind of additives to reduce the sedimentation of the suspended particle in MR fluid.

Acknowledgements

The authors would like to thank the management and the principal of Mepco Schlenk Engineering College for providing facilities and showing constant encouragement for successful completion of the project work.

List of abbreviations

MR fluid	Magnetorheological fluid
CI	Carbonyl Iron
MWNT	Multi Wall Nano Tube
PS	Polystyrene
CNT	Carbon Nano tube
SE mode	Secondary Electron mode

References

[1] T.M. Lopez-Lopez, P. Kuzhir, G. Bossis, P. Mingalyov, Preparation of well-dispersed Magneto-rheological fluids and effect of dispersion on their magnetorheological properties, Rheologica Acta 47 (2008) 787-796.

[2] J. Claracq, J. Sarrazin, J.P. Montfort Viscoelastic properties of magnetorheological fluids, Rheologica Acta 43 (2004) 38-49.

[3] Y. Rong, R. Tao, X. Tang, Flexible fixturing with phase-change Materials. Part 1. experimental study on magnetorheological fluids, The International Journal of Advanced Manufacturing Technology 16 (2000) 822-829.

[4] S. Samouhos, Carbon Nanotube-Magnetite composites, with applications to developing unique magnetorheological fluids, Journal of Fluids Engineering 129 (2007) 429-437.

[5] B.O. Park, B.J. Park, J.M. Hato, H.J. Choi, Soft magnetic carbonyl iron microsphere dispersed in grease and its rheological characteristics under magnetic field, Colloid and Polymer Scince 289 (2011) 381-386.

[6] Ki. Koyama, K. Minagawa, T. Watanabe, Y. Kumakura, J.I. Takimoto, Electro-magneto-rheological effects in parallel-field and cross-field systems. Journal of non-Newtonian Fluid Mechanics 58 (1995) 195-206.

[7] W.L. Zhang, Y.D. Liu, H.J. Choi, Field-responsive smart composite particle suspension: materials and rheology, Rheology Journal 24 (2012) 147-153

[8] K. Zhang, B.J. Park, F.F. Fang, H.J. Choi, Sonochemical Preparation of Polymer Nano-composites, Molecules 14 (2009) 2095-2110.

[9] F.F. Fang, H.J. Choi, Noncovalent self-assembly of carbon nanotube wrapped carbonyl iron particles and their magnetorheology, Journal of Applied Physics 103 (2008) 07A301.

[10] K. Karakoc, E.J. Park, A. Suleman, Design considerations for an automotive magnetorheological brake, Mechatronics 18 (2008) 434-447.

[11] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and Graphene Oxide: synthesis, properties, and application. Advanced Materials 20 (2010) 1-19.

[12] Z.J. Li, B.C. Yang, S.R. Zhang, C.M. Zhao, Graphene oxide with improved electrical conductivity for super capacitor electrode, Applied Surface Science 258 (2012) 3726-3731.

[13] H.B. Cheng, P. Hou, Q.J. Zhang, N.M. Wereley, Effect of storage and ball milling on the sedimentation and rheology of a novel magnetorheological fluid, Journal of Physics: Conference Series 149 (2009) 012043.

[14] L. Shahriary, A.A. Athawale, Graphene Oxide synthesized by using modified hummers approach, International Journal of Renewable Energy and Environmental Engineering 2 (2014) 58-63.

[15] H. Chiriac, G. Stoian, Influence of particle size distributions on magnetorheological fluid performances, Journal of Physics: Conference Series 200 (2010) 072095.

[16] M.R. Jolly, J.W. Bender, D.J. Carlson, Properties and applications of commercial magnetorheological fluids, Journal of Intelligent Material Systems and Structures 10 (1999) 5-13.

[17] E.S. Premalatha, R. Chokkalingam, M. Mahendran, Magneto mechanical properties of iron based MR fluids. American Journal of Polymer Science 2 (2012) 50-55.

[18] B.K. Kumbhar, S.R. Patil, A study on properties and selection criteria for magneto-rheological (MR) fluid components, International Journal of ChemTech Research 6 (2014) 3303-3306.

[19] R.V. Upadhyay, Z. Laherisheth, K. Shah, Rheological properties of soft magnetic flake shaped iron particle based magnetorheological fluid in dynamic mode, Smart Materials and Structures 23 (2014) 015002.

[20] A. Gomez-Ramirez, M.T. Lopez-Lopez, F. Gonzalez-Caballero, J.D.G. Duran, Stability of magneto-rheological fluids in ionic liquids, Smart Materials and Structures 20 (2011) 045001.

[21] S. Sun, Y. Cao, J. Feng, P. Wu, Click chemistry as a route for the immobilization of well-defined polystyrene onto graphene sheets, Journal of Materials Chemistry 20 (2010) 5605-5607.