Off-state viscosity and yield stress optimization of magnetorheological fluids: a mixture design of experiments approach

Rafael F Ierardi1 and Antonio J F Bombard2
1 Instituto de Engenharia Mecânica, 2 Instituto de Ciências Exatas
Universidade Federal de Itajubá – UNIFEI
Av BPS, 1303, Itajubá – MG, 37.500-903, BRAZIL
E-mail: bombard@unifei.edu.br

Abstract. The purpose of this paper was to optimize the blend ratio of ternary mixtures of carbonyl iron powders with different modes to get the minimum “off-state” viscosity as well as to maximize the yield stress under field in MRF. The Mixture Design of Experiments methodology was here employed considering the powders ‘A’ (coarse); ‘B’ (medium); and ‘C’ (fine) as mixture components and the viscosity and yield stress as mixture responses. The minimum viscosity was found over the A-C triangle edge of a response surface diagram. On the other hand, the maximum yield stress was found on the C corner (no blend). The results show the power and robustness of DOE methodology to optimize and to tailor MRF performance, according to the desired application.

1. Introduction
Magneto-Rheological Fluids (MRFs) are composite or multiphase materials. They are commonly prepared with some ferromagnetic phase dispersed in a chemically inert, non-volatile liquid. Typical materials include iron powders and mineral, silicone or synthetic oils. MRFs have the ability to change their rheological properties. When a magnetic field is applied, MRFs can change from a fluid to a near solid in a reversible way – with a relatively quick time of response (~10 milliseconds). The rheological properties are controlled by the magnetic field strength, which makes MRFs very promising for several technological devices, especially in mechatronics.

The magneto-rheological effect increases with the volume fraction of iron powder that is the active phase. However, one of the challenges in formulating good MRFs is to keep the so-called off state viscosity – the viscosity without magnetic field – as low as possible. Since the earlier works of Mooney [1], Krieger-Dougherty [2], Thomas [3], and Frankel and Acrivos [4] it is well established that the relative viscosity of any suspension increases exponentially with the volume fraction.

It is also well-known that mix powders with different particle sizes and/or size distribution can be advantageous. Chemical and food engineering processes, powder metallurgy and ceramics industries, etc. have used this approach with success [5]. Farris reported that there is substantial reduction on the relative viscosity in multimodal suspensions – when compared to unimodal suspensions – if the total volumetric fraction \( \Phi \) is above 55% v/v and depending both on the size ratio and volume fraction of large particles (\( \Phi_L/\Phi \)) [6].

The purpose of this paper was to optimize the blend ratio of ternary mixtures of spherical iron powders with different modes to get the minimum “off-state” viscosity as well as to maximize the yield stress under field in Magnetorheological Fluids. The Mixture Design of Experiments
methodology [7] was here utilized considering the powders ‘A’ (coarse), ‘B’ (medium), and ‘C’ (fine) as mixture components and the viscosity and yield stress as mixture responses.

2. Experimental
In order to evaluate the effect of mixing carbonyl iron powders with different particle sizes, we choose three carbonyl iron powders manufactured by BASF SE, Ludwigshafen, Germany. Table 1 summarizes some properties of these powders. The size distribution and chemical analysis, according to the manufacturer. The magnetic properties of dry, pure powders were measured with a SQUID magnetometer, Quantum Design MPMS-7. The saturation was measured at 50,000 Oe. The differential susceptibility was calculated at H = 3400 Oe, because the yield stress values of the MRF were measured at this field strength in the rheometer.

Table 1. Some properties of the BASF CIP used in the mixtures.

| CIP        | D_m | D_50 | D_10 | M_s (emu/g) | dM/dH @ 3400 Oe (emu/g.Oe) | Fe (%) |
|------------|-----|------|------|-------------|----------------------------|--------|
| A (coarse) | 25  | 9    | 5    | 248         | 0.018                      | > 99.5 |
| B (medium) | 18  | 6    | 3.5  | 227         | 0.014                      | > 99.5 |
| C (fine)   | 3.4 | 1.7  | 0.7  | 237         | 0.024                      | > 99.5 |

All the mixtures were prepared with a synthetic hydrocarbon oil (a polyalphaolefine). Dispersing additive as well as a thixotropic additive were used in all formulations, at the same concentrations. Each MRF was homogenized using a mechanical disperser Ika Turrax T-18, at 10,000 rpm, for 10 minutes. The total volume fraction of iron powder in all formulations is ~ 50% v/v.

The flow curve of each MRF sample was measured in a controlled stress rheometer (Anton Paar – Physica MCR 301) equipped with a magnetorheological device (Physica MRD-180) and using plate – plate geometry (20 mm diameter, 1 mm gap). The temperature was kept constant at 25°C. The profile to measure the viscosity was a shear rate ramp, increasing linearly from 1 to 1000 s^{-1}. The region between 200 – 1000 s^{-1}, visually considered linear was used to calculate the apparent viscosity, considered as the slope of the curve shear stress versus shear rate. Each experimental run was repeated three times.

The yield stress was measured through shear stress linear ramp, after applying the maximum field strength of MRD-180 (H_o ~ 3400 Oe) to the MRF sample. The shear stress value associated with a sharp drop in viscosity was taken as the yield value.

3. Results and Discussion
To obtain the data to feed the statistical analysis, apparent viscosity or yield stress values, each MRF blend was measured at least three times. Figures 1 and 2 are examples of flow curves used to measure off state viscosity and yield stress, respectively.

Table 2 resumes the proportions of each MRF blend; and the values for “off” plastic viscosity and/or yield stress values (mean and standard deviation, triple repetition, at least). Figure 3 and 4 show the mixture contour plots for apparent viscosity and yield stress, respectively.

To increase the maximum packing volume fraction and to reduce the viscosity for powders of uniform spheres with different size ratios, optimum blend ratio of binary, ternary, quaternary or quinary mixtures was well established by Lee: it should be the blend 73.5:26.5 of large/small powder, below 16:1 of size ratio. [8]. Besides, Dinger and Funk [9] – based on the seminal work of Andreasen and Andersen [10] – have shown that it is possible to reduce the viscosity of powder dispersions with mixtures. This, however, requires mixing at least two decades of particle size. Three or more decades are often used. The ideally infinite number of decades is obviously impossible. In such way the gross particles are the main components, and the amount of others decreases with size reduction.
Figure 1. Flow curve of a MRF blend. Apparent viscosity, as the slope above 200 s\(^{-1}\). No field.

Figure 2. Flow curves under applied field (\(H_0 = 3400\) Oe), used to measure the yield stress value.

Table 2. MRF blend proportions, apparent viscosity (no field) and yield stress @ \(H_0 = 3400\) Oe (mean values and standard deviation).

| Std Order | A  | B  | C  | Viscosity mean (mPa.s) | Viscosity sd | Yield mean (kPa) | Yield sd |
|-----------|----|----|----|------------------------|--------------|------------------|----------|
| 1         | 1  | 0  | 0  | -                      | -            | 33.7             | 0.497    |
| 2         | 0  | 1  | 0  | -                      | -            | 30.1             | 0.424    |
| 3         | 0  | 0  | 1  | 479                    | 47.23        | 55.0             | 4.92     |
| 4         | 0.5| 0  | 0  | 1757                   | 28.36        | 26.9             | 1.21     |
| 5         | 0  | 0.5| 0  | 410                    | 29.51        | 40.7             | 1.59     |
| 6         | 0  | 0.5| 0  | 476                    | 22.28        | 49.2             | 0.805    |
| 7         | 0.333| 0.333| 0.333| 454                    | 78.21        | 38.0             | 1.62     |
| 8         | 0.666| 0.167| 0.167| 955                    | 115.25       | 31.9             | 1.80     |
| 9         | 0.167| 0.666| 0.167| 1026                   | 42.12        | 34.6             | 1.14     |
| 10        | 0.167| 0.167| 0.666| 346                    | 2.89         | 44.7             | 0.702    |
| 11        | 0.90 | 0.05 | 0.05| 926                    | 97.69        | -                | -        |
| 12        | 0.05| 0.90 | 0.05| 1697                   | 174.32       | -                | -        |
| 13        | 0.25| 0.25 | 0.50| 363                    | 7.00         | 41.7             | 1.57     |
| 14        | 0.20| 0.20 | 0.60| 362                    | 13.12        | -                | -        |
| 15        | 0  | 0.25 | 0.75| 408                    | 11.27        | 48.5             | 1.63     |
| 16        | 0.25| 0  | 0.75| 379                    | 12.22        | 43.7             | 1.28     |
| 17        | 0.05| 0.15 | 0.80| 402                    | 5.03         | -                | -        |
| 18        | 0.10| 0.10 | 0.80| 340                    | 12.66        | 48.0             | 0.785    |
| 19        | 0.30| 0.10 | 0.60| 325                    | 21.45        | 42.5             | 1.89     |
| 20        | 0.10| 0.30 | 0.60| 386                    | 9.02         | 44.3             | 0.797    |
| 21        | 0.05| 0.05 | 0.90| 369                    | 18.25        | -                | -        |
| 22        | 0  | 0.30 | 0.70| 399                    | 15.52        | -                | -        |
| 23        | 0.207| 0.160| 0.633| 315                    | 5.00         | -                | -        |
| 24        | 0.323| 0  | 0.677| 269                    | 8.33         | 45.3             | 0.666    |
| 25        | 0.25| 0.75 | 0  | -                      | -            | 26.0             | 0.911    |
| 26        | 0.75| 0.25 | 0  | -                      | -            | 25.0             | 2.05     |
| 27        | 0  | 0.75 | 0.25| -                      | -            | 32.2             | 0.616    |
| 28        | 0  | 0.75 | 0.25| -                      | -            | 38.9             | 1.448    |

For powders with log-normal size distribution and mixing less than one size decade, the approach previously mentioned does not work. More recently, He and Ekere, through computer simulation, have suggested that for concentrated suspensions of non-colloidal particles with log-normal distribution, the viscosity decreases as the standard deviation of the particle diameters increases [11].
Two US patents report that to maximize “on-state” force of MRF, bimodal particle distribution is better than unimodal [12,13]. We confirmed this in a previous paper [14], but this work shows that question remains open.

As reported by Kordonski and co-workers [15], the magnetic properties, as saturation magnetization or magnetic susceptibility could be the reason for the higher yield stress of MRF with powder C. Thus, the figure 5 shows the magnetization curves for the three powders, until the range used to measure yield values in the rheometer. One can see, from figure 5, that powder C has the lower magnetization at the field strength used to measure yield stress. But susceptibility also has a role in the yield stress. Table 2 also shows susceptibility values. Perhaps, the susceptibility of powder C, even though slightly higher than powders A and B, could be the answer for this behaviour. However, the magnetic induction B was measured through a Hall probe in the magnetorheological cell, for the MRF with powders A, B or C (blends 1, 2 or 3 of table 2), and its value was the same: \( B = 433 \pm 2 \) mT. Thus, we think that the stronger structure of MRF with only powder C, under magnetic field, is due to particle size and or size distribution. Figure 6 shows the cumulative undersize curves for the powders A, B and C, measured by Low Angle Laser Light Scattering (LALLS), with a Malvern Microsizer Master.

**Figure 3.** Mixture contour plot of mean viscosity. No field, 25°C. Arrow indicates a region where viscosity is below 300 mPa.s

**Figure 4.** Mixture contour plot of mean yield stress, under applied field strength \( H_0 = 3400 \) Oe. Contour lines in kPa.

**Figure 5.** Magnetization curves for the pure powders used in this study. The arrow indicates the maximum field strength in the rheometer.

**Figure 6.** Cumulative undersize curves measured by LALLS, for powders A, B and C (right to left). Volume based size distribution.
According to the Lee [8], for a ternary blend to show reduced viscosity with relation to the pure components, the lowest size ratio between them should be 25:5:1. As the size ratio of A-B-C, taking in account the D_{50} values measured by LALLS is approximately 21:7:3, we did not find any ternary blend which minimized the viscosity.

4. Conclusions
The optimal solution for minimum off viscosity was obtained with binary blends, being the mixture of powders A-C 32:68 (MRF Blend 24th) correctly predicted as that of lower apparent viscosity. When it was prepared and measured – not by the chance, trial and error or serendipity – the apparent viscosity was ~ 270 mPa.s. Therefore, Mixture D.O.E. (Design of Experiments) was able to guide for viscosity optimization.

On the other hand, looking for maximum yield stress, the highest value (σ_y ~ 55 kPa @ 3400 Oe), was obtained with blend #3, using only ‘C’ powder, the finer CIP.

We found a blend which minimize the off viscosity, but not a unique MRF with the two ideal responses: minimum viscosity AND maximum yield stress. A priori, it seems that there is no advantage of ternary blends over binary ones.

References

[1] Mooney M 1951 J. Colloid Sci. 6 162–170
[2] Krieger I M and Dougherty T J 1959 Trans. Soc. Rheology 3 137-152
[3] Thomas D G 1965 J. Colloid Sci. 20 267
[4] Frankel N A and Acrivos A 1967 Chem. Eng. Sci. 22 847
[5] German R M 1989 Particle Packing Characteristics (Princeton: Metal Powder Industries Federation)
[6] Farris R J 1968 Trans. Soc. Rheol. 12 281 – 301
[7] Cornell J 2002; Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data – 3rd edition (New York, NY: Wiley)
[8] Lee D I 1970 J. Paint Technology 42 579 – 587
[9] Funk J E and Dinger D R 1993 Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing (Norwel, USA: Kluwer Academic Pub.)
[10] Andreasen A H M and Andersen J 1930 Koll. Zeitschr. 50 217 – 228
[11] He D and Ekere N N 2001 AIChe Journal 47 53 – 59
[12] Foister R T 1997, “Magnetorheological fluids”, US Patent 5,667,715
[13] Weiss K D, Carlson J D and Nixon D A 2000, US Patent 6,027,664
[14] Bombard A J F et al. 2005, Int. J. Modern Phys. B 19 1332-1338
[15] Kordonski W, Gorodkin S and Zhuravski N 2001, Int. J. Modern Phys. B 15 1078-1084

Acknowledgments
Bombard wishes to thank FAPEMIG for the Grant # CEX APQ-2676-5.02/07 as well as Grant CEX-213/08 to attend ERMR’08. Mr. Ierardi acknowledges CNPq (Brazilian Research Agency - Scientific Initiation Program). BASF SE help is gratefully appreciated.