

Compressible Magnetorheological Fluids

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ABSTRACT: A novel compressible magnetorheological fluid (CMRF) has been synthesized with additives that provide compressibility to the fluid. This CMRF has been designed to provide an elastic component to a magnetorheological fluid (MRF) that can be used as a springless damper. CMRF provides controllable compressibility to the MRF. The controllability of the fluid is achieved by the use of magnetic particles and an external magnetic field, and the fluid is made compressible by the addition of suspended compressible polymer particles. The compressibility of the fluid has been characterized with force–

displacement measurements. This CMRF has controllable off-state viscosity and high shear yield stress. The incorporation of polymeric particles into the MRF also decreases the settling of iron particles and improves the redispersion of the fluid. To make the fluid more redispersible, the surface of the iron particles is coated with a high-temperature fluorinated polymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3348–3356, 2010

Key words: atom transfer radical polymerization (ATRP); living polymerization; shear; viscosity

INTRODUCTION

Magnetorheological fluids (MRFs) have the ability to convert from a liquid state to a nearly solid state under the influence of a magnetic field. These fluids are suspensions of magnetizable particles (carbonyl iron particles or magnetizable alloys of iron, nickel, and cobalt) in a carrier fluid.¹ Intelligent fluids may change properties, including flow, stiffness, damping, and other characteristics, in response to changes in the applied temperature and electric and magnetic fields. MRFs are field-controllable, and their rheological properties can be changed by the application of a magnetic field. In the absence of a magnetic field, these fluids are free-flowing liquids. Under a strong magnetic field, the tangent viscosity of these fluids is increased within milliseconds, and they exhibit solidlike characteristics.² Under a magnetic field, the magnetic particles align themselves along the path of the field and create chainlike structures. These structures restrict the motion of the fluids, increase their tangent viscosity, and cause an increase in the yield stress. Typically, MRFs contain a 0.3–0.5 volume fraction of pure iron particles with a nearly

spherical shape. The size typically ranges from 1 to 8 μm , and the density ranges from 7 to 8 g/cm^3 . This leads to a reasonable shear yield stress and a reasonable off-state viscosity range.³ The main applications of MRFs are semiactive vibration control and torque transfer, which includes brakes and clutches.⁴ Lord Corporation MRF (Cary, NC) has commercialized several MRFs and a variety of MRF-based systems. The applications include dampers for vehicle vibration control, rotary brakes for aerobic exercise equipment, and special purpose devices for medical rehabilitation, seismic damping, and virtual surgery. Recently, the most likely applications for MRFs have been in automotive-suspension technology. Delphi Corp. supplies the Magne Ride system to General Motors, using materials supplied by Lord Corp.⁵

A compressible magnetorheological fluid (CMRF) provides controllable compressibility beyond conventional MRFs. The controllability of the fluid rheology is achieved by the use of magnetic particles with an external magnetic field and compressibility from suspended polymeric particles. Hong et al.⁶ described a liquid spring having a body of compressible liquid enclosed within a piston system.

A highly compressible MRF can be used to develop a compact automotive strut with a spring rate and controllable damping without the integration of a conventional steel spring. Such a springless damper is useful for various suspension systems because of the light weight of the working fluid and the high energy absorption associated with the device. Carrier fluids for CMRFs can be used,

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including silicone oil, poly(α -olefin), or any other hydraulic oil. Silicone fluid is a highly compressible material with compressibility as high as 18% at high external pressures (up to 414 MPa).⁷ With a silicone fluid or any other hydrocarbon carrier fluid and the addition of compressible polymeric particles, very high compressibility can be attained for a wide range of applied pressures. The typical compressibility data for Dow Corning silicone fluids show that a silicone fluid compresses about 1.5% by volume at 13.8 MPa, about 3% at 34 MPa, and about 6% at 69 MPa.⁸ Above 13.8 MPa, the fluid has greater compressibility than conventional hydraulic oil. Among silicone fluids, the lowest viscosity fluid provides the highest compressibility, and thus a silicone oil with a viscosity of 10 mm²/s and the hydrocarbon oil poly(α -olefin) with a viscosity of 10 mm²/s were selected as carrier fluids to synthesize CMRFs.

To increase the compressibility of typical MRFs, several compressible polymeric additives are included in the fluids, including microspheres. There are different kinds of microspheres available with different functionalities. Highly crosslinked polymeric microspheres are used for heat resistance and solvent resistance. They are synthesized by emulsion polymerization.⁹ Porous polymeric microspheres, which include ion-exchange and related resins, are in widespread use in applications in synthetic chemistry, metal extraction, catalysis, and medicine.¹⁰ Also, glass microspheres are used as low-density fillers in many high-shear processes. They can withstand pressures up to 10,000 psi.

Microspheres are small, spherical, gas-filled plastic particles. They were first developed by Paul and Jones in 1953 and were prepared in silicone.¹¹ These microspheres have been commercially available for more than 30 years. Microspheres with an inorganic shell are used as fillers for cement and latex dispersions and for insulation.

Microspheres contain two major components. One is the shell, and the other is the blowing agent. The microspheres used in these experiments contain a shell that is a copolymer of vinylidene chloride, acrylonitrile, and methyl methacrylate. Isobutane and isopentane are the blowing agents inside the shell.¹² When the encapsulating hydrocarbon inside the thermoplastic shell is heated, its pressure increases, and the thermoplastic shell softens; this results in a dramatic increase in the volume of the microspheres. After full expansion, its volume becomes more than 40 times greater than the original volume. Because of the expanded gas inside the shell, the microspheres are easy to compress, and after the removal of the applied pressure, they come back to their original volume. The microspheres are highly resilient.¹² Because of this resiliency, they can withstand thousands of cycles of loading and unloading with-

TABLE I
Physical Properties of Various Microspheres

	Particle size (μm)	Density (kg/m^3)
Dry expanded	60–90 ^a	30
	100–140 ^b	30
Dry unexpanded	35–45 ^c	14
	28–38 ^d	14

The data were taken from Macintyre et al.¹²

^a Grade 091 DE 80 d30 (Expancel, Inc., Duluth, GA).

^b Grade 092 DET 120 d30 (Expancel).

^c Grade 091 DU 140 (Expancel).

^d Grade 092 DU 120 (Expancel).

out collapsing or breaking under normal circumstances, and they can be used in shock-absorbent materials. They are also highly chemically resistant.¹² There are many sizes of microspheres available in both expanded and unexpanded forms. Table I shows the physical properties of microspheres that are used as additives to make the fluids more compressible.

The incorporation of microspheres improves the redispersion of the iron particles. Furthermore, the redispersion is improved when the iron particles are coated with a polymer. There are several approaches to preparing inorganic particles coated with polymers. These include atom transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), reversible addition fragmentation chain transfer, and click chemistry. Researchers have investigated different polymerization processes. Polymers have been grafted onto inorganic particles treated with silane coupling agents,^{13,14} surface-initiated ROMP on Si/SiO₂ particles has been examined by Kim et al.¹⁵ Choi et al.¹⁶ have synthesized TiO₂ nanoparticles coated with polystyrene via admicellar polymerization, and they have found that dispersion in oil is better than uncoated particles. The improved redispersion of iron particles has been achieved with supramolecular polymers used to coat iron particles with zinc terpyridine coordination polymers.¹⁷ In our previous work,¹⁸ the surface of iron particles was modified with poly(butyl acrylate) by surface-initiated ATRP to reduce the settling of iron particles in MRFs.

In this research, the surface polymerization of iron particles has been performed by ATRP with 2,3,4,5,6-pentafluorostyrene, which is thermally stable at temperatures higher than 140°C. Polymer chains are grown from the particle surface and are chemically bonded to the surface of the particle. This approach also provides greater flexibility and control of the molecular structure of polymers.¹⁹ To provide better redispersion and reduce settling of CMRF, the iron particle surface is covalently grafted with 2,3,4,5,6-pentafluorostyrene. Grafting not only

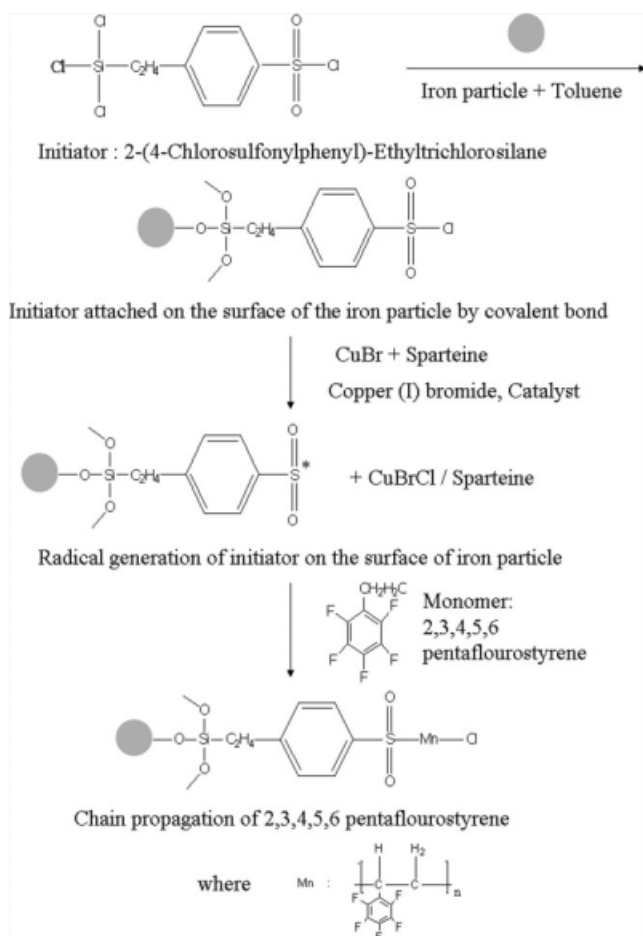


Figure 1 Surface coating of iron particles by ATRP with the monomer 2,3,4,5,6-pentafluorostyrene.^{16,19}

improves the stability of the iron particles in suspension but also increases the compatibility of the particles with the carrier fluid.

ATRP has the following features: the polymerization can be performed under very mild conditions (room temperature) with a high yield and with a broad range of monomers. Figure 1 shows a schematic diagram of the surface coating of iron particles.

EXPERIMENTAL

Materials

Compressible particles were suspended in two different carrier fluids to compare their compressibility. One was a silicone oil with a viscosity of 10 mm²/s (GE Silicone-Dow Corning, Bensalem, PA), and the other was poly(α -olefin) with a viscosity of 10 mm²/s (Corena Fluid poly alpha olefin (PAO) 32, Shell Oil). PAO is produced through the hydrogenation of oligomers (such as dimers, trimers, and tetramers). The oligomers are highly uniform and provide a low volatility fluid that performs at both high and low temperatures without forming gum or deposits in

machinery. Another advantage of PAO is its lower cost than any other fluids. Carbonyl iron particles (1–8 μm carbonyl iron powder; CN 6.6, BASF) were used as the magnetizable particles. Microspheres [both expanded (DE [dry expanded] and DET [dry expanded thermally]) and unexpanded (DU [dry unexpanded])] are supplied by Expancel, Inc. (Duluth, GA). Methanol (Aldrich), ethanol (AAPER), octyl pyrrolidone (Aldrich), CuBr (Aldrich), CuBr₂ (Aldrich), sparteine (Aldrich), toluene (Aldrich), 2,4-(chlorosulfonylphenyl) ethyltrichlorosilane (CTCS; Gelest, Inc.), and 2,3,4,5,6-pentafluorostyrene (Aldrich) were used as received without further purification.

Synthesis of CMRFs

A silicone oil with a viscosity 10 mm²/s was used at a concentration of 20 wt %. Micrometer-size carbonyl iron particles (1–8 μm ; 79.75 wt %) were added to the carrier fluid, which was stirred thoroughly for 10 min at 1000 rpm with a mechanical mixer. Then, expanded microspheres (0.25 wt %) were added to the carrier fluid, which was stirred thoroughly for 10 min.

Surface polymerization of iron particles by ATRP

CTCS (an excellent initiating group for ATRP) was immobilized on the surface of the iron particles by a self-assembled monolayer-deposition method. For polymerization on the surface of the iron particles, the monomer 2,3,4,5,6-pentafluorostyrene was used. This monomer has high thermal stability and oil and water repellency and good chemical resistance.

The iron particles (290 g) were washed with distilled water and then ethanol. After filtration, the particles were dried in a vacuum oven at 50°C. The dried particles were dispersed in 100 g of the nonpolar solvent toluene with 1 g of CTCS and reacted at room temperature for 24 h. The particles, treated with an initiator, were washed with tetrahydrofuran several times and dried in a vacuum oven at a low temperature for 24 h. The CTCS-functionalized iron particles were then grafted with the monomer 2,3,4,5,6-pentafluorostyrene. For polymerization, a reactor was charged with 0.1 g of CuBr, 0.1 g of sparteine, 0.05 g of CuBr₂, 290 g of initiator-treated iron particles, 4 g of 2,3,4,5,6-pentafluorostyrene, and 68 g of the solvent *N*-octyl pyrrolidone. The system was sealed with nitrogen and reacted for 24 h at 80°C. Finally, the mixture was filtered, washed several times with methanol, and dried in a vacuum oven at a low temperature.

Mechanical compressibility

Compressibility tests were performed with an Instron 8821S hydraulic shaker to determine the bulk modulus of the fluids. A cylinder with a 2-in. bore

and a 4-in. maximum stroke was used. The top end of the cylinder damper was fixed to the Instron load cell, whereas the bottom was attached to the actuator of the Instron instrument. During each test, the cylinder was filled with 150 mL of a sample.

Magnetorheological (MR) rheometer

An Anton Paar Physica MER300 MR rheometer (Ashland, VA) was used. It was operated in either the stress- or strain-controllable mode. To measure the off-state tangent viscosity and shear yield stress of CMRFs, this instrument was used under a controlled magnetic field.

Scanning electron microscopy (SEM)

SEM provides information related to the crystal structure, crystal orientation, phase distribution, compositional differences, and presence and location of electrical defects. To observe and characterize the 2,3,4,5,6-pentafluorostyrene-coated iron particles by the ATRP method, SEM was used.

Settling analysis: visual observation

Sedimentation is a significant problem in the development of CMRFs. It causes severe problems in devices in the presence of a magnetic field. If any micrometer-size particles are suspended in a fluid and the densities of the particles and the fluid are different, then the particles settle quickly. For small particles, the settling rate is low, but the yield stress is also low. The settling behavior of CMRFs can be characterized by visual observation.²⁰ By this method, the settling rate can be determined by the measurement of clear fluid formation as a function of time when the particles settle through the fluid, leaving a clear fluid layer at the top. This layer is measured as a clear fluid volume fraction in a graduated glass cylinder. The fluids are placed in graduated glass cylinders and left to settle for up to several days at room temperature and at 100°C. The change in the clear fluid volume is measured as a function of time. The settling rate on day i is determined as follows:

$$\text{Volume}(\%) = \Delta H_i / H_0 \times 100\%$$

where H_0 is the total height of the fluid column and ΔH_i is the height of the clear oil layer on day i .

Accelerated settling test

This method was described by Gorodkin et al.²¹ With this method, the settling velocity of iron particles is characterized by a sedimentation constant parameter (S). It is the ratio of the sedimentation velocity (u) to the acceleration of gravity (g):

$$S = \frac{u}{g}$$

CMRFs contain a magnetically dispersed phase; for this reason, the magnetic permeability of these fluids depends strongly on the volume fraction of the particles. The sedimentation of the magnetic particles due to gravitational forces leads to a lower iron particle concentration and therefore lower permeability in the upper layer. Thus, the sedimentation velocity of the particles can be estimated via the change in the magnetic permeability. With this approach, it is assumed that all the particles settle at a constant velocity. To measure the sedimentation velocity, a centrifugal instrument specifically designed for this purpose is used.²¹

Two test tubes filled with CMRFs are held to the centrifuge rotor, which is attached to a casing. The open ends of the test tubes are plugged to prevent the evaporation of the carrier medium during the experiment. Measuring solenoids are tightly pressed against the walls of the test tubes that are fastened to the casings. Solenoid coils are connected to an inductance meter through a rotating current collector, and continuous inductance measurements are collected while the sample is in rotation. Both test tubes are filled with CMRFs. Data are collected from one test tube, and the other is filled with a CMRF for balancing. The sedimentation constant is a function of the rotation rate, time, and inductance values.

Redispersibility

When iron particles settle, they agglomerate and form a cake. However, it is not a major issue if the particles can be redispersed easily after agglomeration, and these fluids can be used effectively in devices such as dampers. A method has been developed to measure the redispersibility of MRFs.²² To settle the iron particles and produce cake formation, a CMRF is stored for several days at room temperature. After the iron particles settle and a cake is formed, the cake hardness is measured with a micromechanical testing instrument (DMA-7e, PerkinElmer, Waltham, MA). The test is carried out by the depression of the probe into the settled iron cakes of CMRFs with coating iron particles, CMRFs without coating iron particles, and commercially available MRFs with the force increasing at a rate of 10 mN/min, and the displacement of the probe is measured. The largest probe displacement into the settled cake indicates easily redispersibility.

RESULTS AND DISCUSSION

Compressibility

Compressibility tests were performed with an Instron 8821S hydraulic shaker to determine the bulk

TABLE II
Various Components of the CMRFs

Sample	Components	Functions	wt %	Viscosity (cP)
1	Silicone oil	Carrier fluid	20	10
	Iron particles	Magnetic particles	79.75	
	Microspheres (expanded 091 DE 80 d30)	Additive	0.25	
2	Silicone oil	Carrier fluid	20	10
	Iron particles	Magnetic particles	80	
3	Silicone oil	Carrier fluid	100	10
4	PAO	Carrier fluid	20	10
	Iron particles	Magnetic particles	79.75	
	Microspheres (expanded 091 DE 80 d30)	Additive	0.25	
5	PAO	Carrier fluid	20	10
	Iron particles	Magnetic particles	80	
6	PAO	Carrier fluid	100	10

modulus of the fluids. Six fluids were synthesized and characterized. Their compositions are given in Table II. These fluids were tested and compared to the carrier base fluid. The table shows the components of the PAO-based and silicone-oil-based CMRF samples.

In Figure 2, the compressions of various MRFs are presented as a function of the pressure inside the cylinder. The pressure inside the cylinder was calculated on the basis of the recorded force data. Silicone-oil-based and PAO-based CMRFs demonstrated the highest compressibility. For a cylinder pressure of approximately 8.3 MPa, the PAO-based CMRF had a compressibility of approximately 23.5%, whereas the silicone-based CMRF had a compressibility of 25%. These values were about 10-fold higher than those of the carrier fluids and MRFs. Therefore, the addition of microspheres significantly improved the compressibility of the MRFs. The error measurements were performed on the basis of six

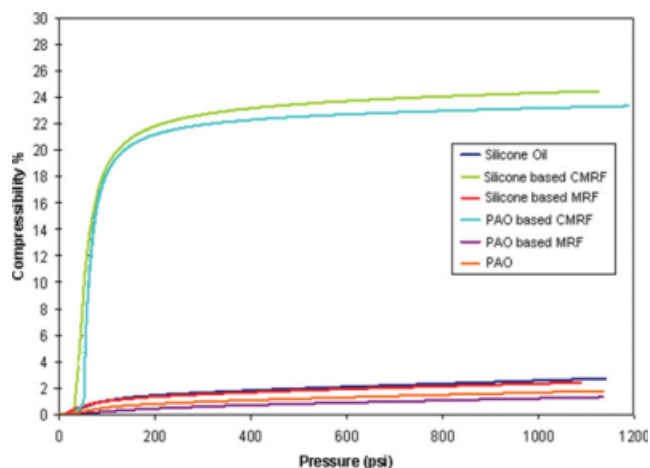


Figure 2 Compression versus the pressure for CMRFs with carrier fluids and MRFs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

experimental measurements for each datum taken with the Student *t* distribution theory. After error computation by the standard deviation function, all data fell within a 1.84% range of error.

Shear yield stress

The shear yield stress of silicone-oil-based and PAO-based CMRFs was determined with a magnetic rheometer. A magnetic rheometer is an instrument designed to carry out rheological measurements under a controlled magnetic field. Figure 3 shows the shear stress of various fluids as a function of the shear rate. The shear stress data of silicone-oil-based and PAO-based CMRFs were compared with those for commercially available MRFs at a 0.55-T magnetic field strength. The shear yield stress of the commercial MRF was 25,600 Pa, whereas the silicone-oil-based CMRF had a slightly reduced shear yield stress of 24,100 Pa. The PAO-based CMRF demonstrated the highest shear yield stress of all at 28,200 Pa.

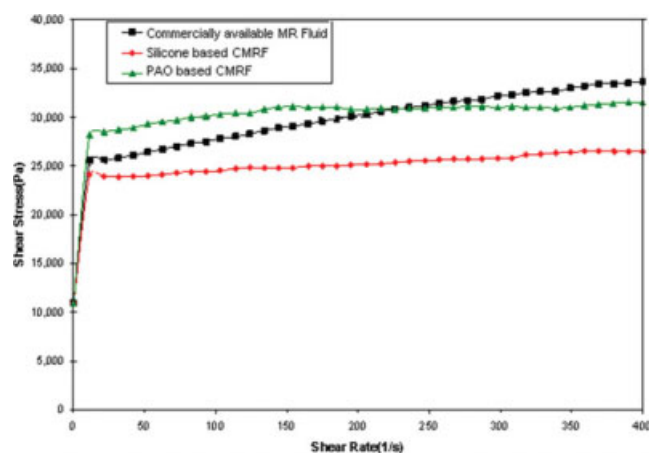


Figure 3 Shear stress versus the shear rate for CMRFs and a commercial MRF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

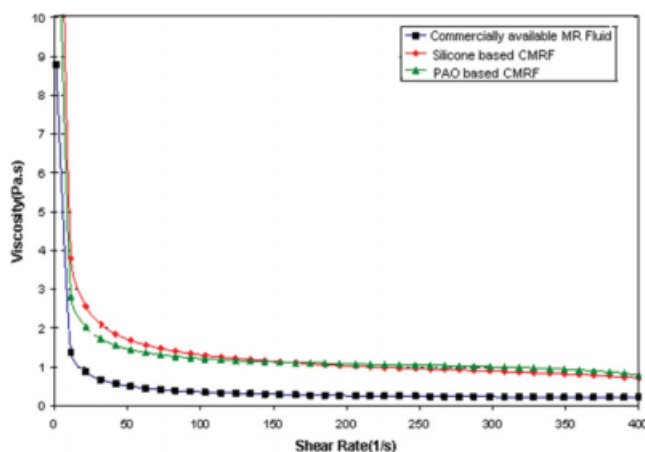


Figure 4 Viscosity versus the shear rate for CMRFs and a commercial MRF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Tangent viscosity of CMRFs

The tangent viscosity can be determined from the slope of a shear stress/shear rate curve. The viscosities of the silicone-oil-based CMRF, PAO-based CMRF, and commercially available MRF are presented in Figure 4. The commercially available MRF had a viscosity of 0.22 Pa s at a shear rate of 400 s^{-1} . The silicone-oil-based CMRF had a viscosity of 0.72 Pa s and the PAO-based CMRF had a viscosity of 0.80 Pa s under the same conditions. The higher viscosities of the CMRFs were due to the addition of microspheres. This viscosity range is reasonable for use in a shock absorber or damper.²³

Accelerated settling test (fluid durability)

The sedimentation of magnetic particles due to gravitational forces leads to a lower iron particle concentration and therefore lower permeability in the upper layer. Thus, the sedimentation velocity of the particles can be estimated via the change in the mag-

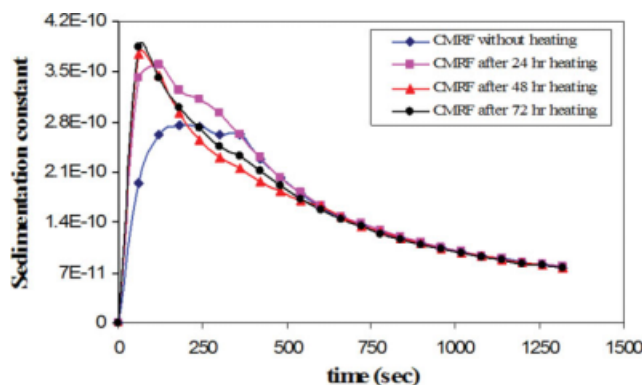


Figure 5 Plot of the sedimentation constant as a function of time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

netic permeability. With this approach, it is assumed that all the particles settle at a constant velocity. Figure 5 compares the settling rates of the magnetic particles in CMRFs by estimating the sediment constant curves after thermal cycling. These fluids were heated to 100°C for various times and then allowed to cool to room temperature for sedimentation measurements. The figure shows the sedimentation constant as a function of time. From the data, we can observe that the settling rate was lower at room temperature than at a higher temperature. At 100°C , the settling rate was almost the same after 24, 48, and 72 h of heating. This indicates that the CMRF was stable at higher temperatures even after several days of heating.

SEM image of the coated iron particles

To coat the surface of the iron particles, ATRP, a living polymerization technique, was used. As mentioned previously, this was a two-step process, with the first step requiring the immobilization of the initiator (CTCS) onto the particles, which was followed by the surface graft polymerization of 2,3,4,5,6-pentafluorostyrene onto the particles. The 2,3,4,5,6-

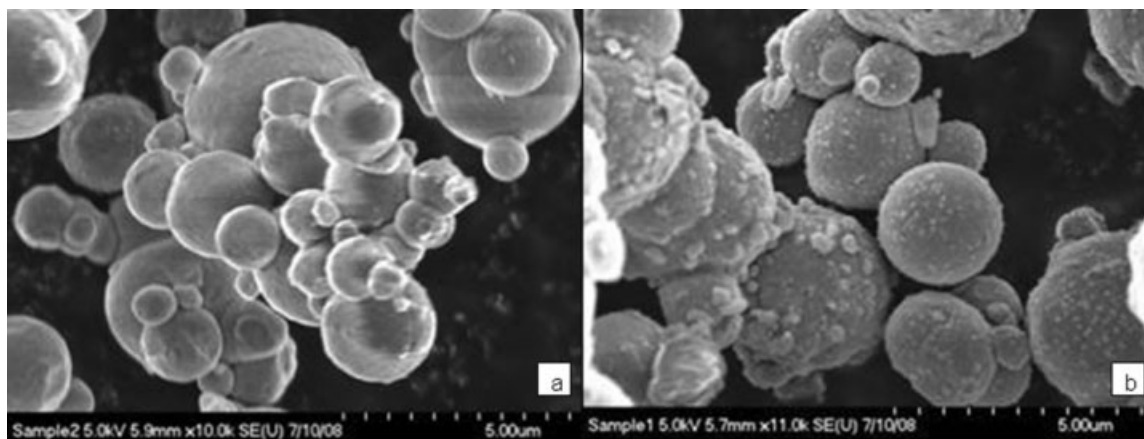


Figure 6 SEM images of (a) pure iron particles and (b) 2,3,4,5,6-pentafluorostyrene-coated iron particles.

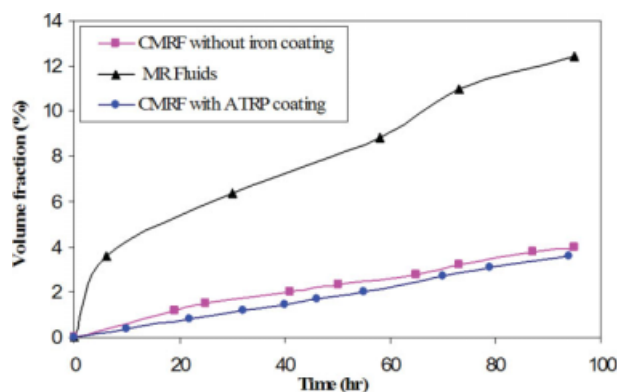


Figure 7 Clear fluid layer volume fraction as a function of the time at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pentafluorostyrene-coated iron particles were characterized with field-emission SEM to investigate their morphological properties.

Figure 6 shows the SEM images of pure iron particles and ATRP-treated iron particles. After the surface-initiated ATRP reaction, we observed that nano-size polymer particles had been grafted onto the surface of the particles rather than the core-shell structure; the polymer particles had an average size of about 200 nm. One of the causes of the particulate nature of the polymeric particles might be the hydrophilic and hydrophobic interaction between the OH group on the surface of the iron and the hydrophobic polymer.²⁴ Initially, OH groups (hydrophilic) were well dispersed on the surface of the iron particles. When the polymerization reaction occurred on the surface of the iron particles, because of the hydrophilic and hydrophobic interactions, polymer particles formed on the surface of the iron particles instead of forming a core-shell structure.

Particle settling analysis by visual observation

Sedimentation is a significant problem in the development of CMRFs. With smaller iron particles, the settling rate decreases, but at the same time, the yield stress of CMRFs also decreases. In general, the settling rate is governed by the rheological characteristics of the carrier fluids, surface properties of the iron particles, and presence of compressible additives. Also, the particle size and the volume fraction of the iron particles can affect the initial settling rate.

To prevent aggregation and reduce settling, magnetic particles are usually coated with surfactants or polymers. The stability of CMRFs depends on a balance between attractive forces, such as van der Waals and dipole-dipole interactions, and repulsive forces, such as steric and electrostatic interactions. Through the coating of the surface of iron particles

with a polymer, the steric repulsion that forms between the coated particles (which acts as a physical barrier for the particles) stabilizes the CMRFs.²⁴ In this study, 2,3,4,5,6-pentafluorostyrene-grafted magnetic particles were synthesized to provide the balance between these forces.

As mentioned previously, the settling rate is determined by the measurement of the rate of formation of a clear fluid layer free of iron particles. This is measured as a volume fraction as the iron particles settle into the carrier fluid. The rate of change in the clear fluid volume percentage is measured as a function of time. Normally, the larger the clear fluid volume fraction is, the higher the settling rate is.

Figures 7 and 8 show the settling behavior of CMRFs without the surface coating of iron particles. These CMRFs contained 2,3,4,5,6-pentafluorostyrene-coated iron particles and MRFs (without microspheres). All samples contained iron particles (79.75 wt %). These three fluids were kept in three identical cylinders and were left at room temperature for several days. The formation of the clear fluid volume was measured at different times. The same procedure was repeated when these fluids were placed into an oven at 100°C. From these graphs, we can observe that the incorporation of microspheres into typical MRFs reduces settling, but coating the surface of iron particles with a polymer reduces the settling even further. The settling behavior of CMRFs with 2,3,4,5,6-pentafluorostyrene-coated iron particles depends on the fraction of the polymer coating on the iron particles. Particle settling can be reduced by an increase in the fraction of the polymer on the surface of the iron particles. However, increasing the amount of the polymer coating on the surface of the iron particles will decrease the shear yield stress of the CMRF.¹⁸ Therefore, optimization is required between reducing the settling rate and achieving a high shear yield stress. For optimization, 1.5 wt % 2,3,4,5,6-pentafluorostyrene was used to coat the

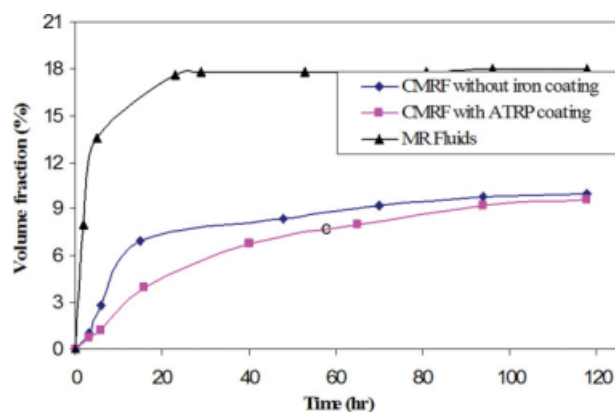


Figure 8 Clear fluid layer volume fraction as a function of the time at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface of the iron particles. From the graph, we can observe that the ATRP CMRFs showed less sedimentation than the CMRFs without a coating of iron particles. For example, the sedimentation was 3.5% at 80 h for a CMRF without a coating, whereas it was about 3% for ATRP CMRF with polymers (1.5 wt %) deposited onto the particles.

Redispersion measurement

Settling of iron particles occurs because of the large density difference between the iron particles and the carrier medium. When iron particles settle, they agglomerate, and cake formation results. Settling is not a major issue if they can be redispersed easily after settling, and the fluid can be used effectively in different devices such as dampers.

Agglomeration occurs because of attractive van der Waals force between particles closely approaching each other. To prevent agglomeration and hence stabilize the CMRF system, iron particles must be stabilized through forces of repulsion. The two known forces of repulsion are electrostatic and steric forces. Steric stabilization is achieved by polymer molecules adsorbing or attaching to the surface of magnetic particles. In a sterically stabilized system, each iron particle is coated with physically or chemically adsorbed surface layers that hinder the approach of particles to one another at distances at which van der Waals force dominate.¹⁸ The thickness of the adsorbed layer is determined by the length of the polymer chain. When two particles containing an adsorbed layer approach each other at a separation distance that is less than twice the adsorbed layer thickness, interference of the chains occurs. This interaction leads to repulsion of the particles.²⁵

It is believed that the hardness of the cake of carbonyl iron particles formed by the settling and agglomeration of iron particles is related to the ability to redisperse the particles. The harder the cake is, the more difficult it is to redisperse the compressible magnetorheological suspensions. To accelerate the settling process, a CMRF without a coating of iron particles was kept in a beaker and stored for 7 days at room temperature. To compare the redispersion of this fluid, a CMRF with a coating of iron particles and commercially available MRFs were also kept in a beaker for 7 days. The hardness after settling was measured with a micromechanical testing instrument (DMA-7e, PerkinElmer). The test was carried out by the depression of the probe into the settled iron cake with the force increasing at a rate of 10 mN/min, and the displacement of the probe was measured. Larger displacement of the probe indicated a more easily compressible magnetorheological suspension redispersion.

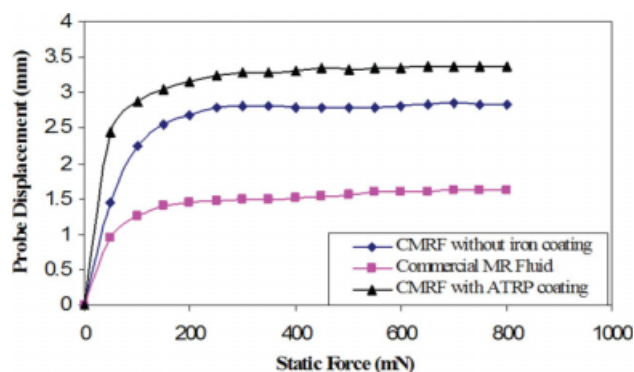


Figure 9 Redispersion curve after 7 days of settling at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9 shows the force–displacement curves of CMRFs versus commercially available MRFs. From this graph, we can observe that the probe position for the CMRFs with coated iron particles had greater displacement than the other fluids. At 800 mN of force, the probe displaced the 2,3,4,5,6-pentafluorostyrene-coated CMRFs by about 3.5 mm, the CMRFs without a coating of iron particles by about 3 mm, and the commercially available MRFs by only 1.5 mm. Thus, grafting 2,3,4,5,6-pentafluorostyrene onto iron particles significantly improved redispersibility. A possible explanation for this behavior is that the formation of the polymer layer on the surface of the iron particles acts as a stabilizing layer and sterically prevents coagulation.

CONCLUSIONS

A CMRF has been developed for use with vehicle dampers and springs. The CMRF is synthesized by the suspension of iron particles in a silicone oil or poly(α -olefin) with the inclusion of compressible microspheres to increase the compressibility. The compressibility was investigated with mechanical testing instrumentation, and 23–25% compressibility resulted at 8.3 MPa of pressure, whereas a commercial MRF was only 1–2% compressible at the same applied pressure. The shear yield stress was nearly the same as that of the commercially available MRF, but the viscosity was slightly higher because of the incorporation of microspheres. An investigation of the thermal stability was carried out at high temperatures, and the fluid was stable up to 100°C. The settling rate was investigated at both room temperature and 100°C and compared with that of a commercially available MRF. The redispersion of the CMRF was greatly improved by the incorporation of microspheres. Finally, the surface of the iron particles was coated with 2,3,4,5,6-pentafluorostyrene, a polymer that has high thermal stability. SEM imaging of the coated iron particles indicated that the polymer nanoparticles were attached to the surface of the

microparticles. These nanoparticles repulsed one another and hindered the iron particles from approaching one another. This reduced the settling of iron particles and greatly improved the redispersion of the CMRF. On the basis of compressibility and other characterization methods, this CMRF is an excellent candidate for springless dampers.

References

1. Jolly, M. R.; Bender, J. W.; Carlson, J. D. SPIE 5th Annual International Symposium on Smart Structures and Materials, San Diego, CA, March 1998.
2. Ginder, J. M. Encyclopedia of Applied Physics; Wiley: New York, 1996; Vol. 16, p 487.
3. Ginder, J. M. MRS Bull 1998, August, 26.
4. Carlson, J. D. U.S. Pat. 5,054,593 (1991).
5. Jennifer, O. Ind Phys 2004, 9(6), 14.
6. Hong, S.; Wang, G.; Hu, W.; Werely, N. J Automobile Eng 2006, 220, 1019.
7. <http://www.clearcoproducts.com/pdf/library/compressibility3.pdf>.
8. Coombs, J. D.; Edmondson, J. R. U.S. Pat. 6,988,599 (2006).
9. Itou, N.; Masukawa, T.; Ozaki, I.; Hattori, M.; Kasai, K. Colloids Surf 1999, 153, 311.
10. Macintyre, F.; Besenius, P.; Sherrington, D. C. Ind Eng Chem Res 2007, 46, 3219.
11. Schmidt, W.; Roessling, G. Chem Eng Sci 2006, 61, 4973.
12. <http://www.expancel.com/english/product/Default.htm>.
13. Masaharu, Y.; Ohata, M. Prog Org Coating 1996, 27, 277.
14. Ma, M.; Zhang, Y.; Yu, W.; Shen, H. Y.; Zhang, H. Q.; Gu, N. Colloids Surf A 2003, 212, 219.
15. Kim, N. Y.; Jeon, N. L.; Choi, I. S.; Takami, S.; Harada, Y.; Finnie, K. R.; Girolami, G. S.; Nuzzo, R. G.; Whitesides, G. M.; Laibinis, P. E. Macromolecules 2000, 33, 2793.
16. Jang, I. B.; Sung, J. H.; Choi, H. J.; Chin, I. J Mater Sci 2005, 40, 3021.
17. Fuchs, A.; Hu, B. Master's Thesis, University of Nevada Reno, 2005.
18. Hu, B.; Fuchs, A.; Huseyin, S.; Gordaninejad, F.; Evrensel, C. Polymer 2006, 47, 7653.
19. Liu, P.; Su, Z. Carbohydr Polym 2005, 62, 159.
20. Fuchs, A.; Xin, M.; Gordaninejad, F.; Wang, X. J.; Gregory, H. H.; Gecol, H. J Appl Polym Sci 2004, 92, 1176.
21. Gorodkin, S. R.; Kordonski, W. I.; Shorey, A. B.; Jacobs, S. D. Rev Sci Instrum 2000, 71, 2476.
22. Munoz, B. C.; Adams, G. W.; Ngo, V. T.; Kitchin, J. R. U.S. Pat. 6,203,717 (2001).
23. Kormann, C.; Schwab, E.; Laun, M. U.S. Pat. 5,505,880 (1996).
24. Fang, F. F.; Choi, H. J Phys Status Solidi 2007, 204, 4190.
25. Burke, N. A. D.; Stover, H. D. H.; Dawson, F. P. Chem Mater 2002, 14, 4752.