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Rheological Properties and Stability of Magnetorheological Fluids using Viscoelastic Medium and Nanoadditives

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Abstract−In order to improve the stability of magnetorheological (MR) fluids, viscoelastic medium having 2.2 Pa yield stress has been used as a continuous phase and nanosized CrO_2 particles are added too. The rheological properties as well as the dispersion stability of MR fluids have been studied by using a stress-controlled rheometer and sedimentation test. The steady-shear MR response was independent of the continuous and nano additives and the field-induced yield stress increased subquadratically with the flux density. Since the constant stress is generated within the limit of zero shear rate, the plateau in the flow curve corresponds to the Bingham yield stress. Under an external field, the yield stress varied as $B^{3/2}$. The yield stress has an approximately linear relation with the particle volume fraction.

Key words: Magnetorheology, Yield Stress, Dispersion Stability, Carbonyl Iron, Viscoelastic Medium

INTRODUCTION

Magnetorheological fluids, consisting of magnetizable particles dispersed in the carrier medium, show unique abilities to undergo rapid, nearly completely reversible, and significant changes in their strength upon application of an external magnetic field. Typically, this change is manifested by the development of a yield stress that monotonically increases with the applied field. It has long been recognized that these MR fluids have the potential capability to radically change the way in which electromechanical devices are designed and operated. The potential applicability of MR fluids has stimulated considerable research activities in developing controllable shock absorbers, clutches, and engine mount, alternators, power steering pumps, control valves, and artificial joints [Phule and Ginder, 1999].

The MR effect is attributed to the field-induced magnetization of the disperse phase relative to the continuous phase [Ginder, 1996; Ginder et al., 1996]. Particle magnetization in an applied magnetic field can be described to leading order as a magnetic dipole. The dipolar particles align head to tail in the direction of the magnetic field, resulting in the experimentally observable fibrous structure. The fibrous structure can be broken with the external flow and the yield stress is related to the force required to break these columns.

Various materials of MR fluid systems have been described in the literature:suspensions of polymer-coated nanosize (diameter ~30 nm) ferrite particles [Kormann et al., 1996], iron-cobalt alloy particles [Margida et al., 1996], and meso-scale carbonyl iron and nickel-zinc ferrites [Phule and Ginder, 1996], carbonyl iron and nano scale magnetic particle additives (Co-γ-Fe_2O_3, CrO_2) [Chin et al., 2000].

MR fluids composed of thr above materials have high yield stress of 10-100 kpa at a strong magnetic field of 10T. However, sedimentation is a significant problem in the development of suitable MR fluids, since the particles are too dense compared to the carrier fluid. When particles settle, the field-induced particle chains form incompletely at best, severely degrading the MR response. In fact, application of conventional stabilization methods for concentrated suspension is not satisfactory. Phule and Ginder reported the effectiveness in stabilization of nanoscale additives such as silica, fibrous carbon, and other polymers, via forming a coating layer on the MR particles or making a thixotropic network [Phule and Ginder, 1996; Phule, 1998]. The use of conventional additives to produce stable dispersion is, however, not successful since the added additives may deteriorate the columnar structures of MR particles under the magnetic field.

The ability of a viscoelastic medium to suspend isolated particles has been characterized by the gravity yield parameter [Chhabra, 1993; Rankin et al., 1999].

$$Y_G=\tau_O^G/[gR(\rho_P-\rho)] \qquad (1)$$

Where τ_O^G is the yield stress of the viscoelastic medium, g is the acceleration of gravity, R is the particle radius, ρ_P is the particle density, and ρ is the density of the viscoelastic medium. Larger values of Y_G indicate better ability of the viscoelastic medium to suspend the particles. If Y_G is greater than Y_G^{crit} the medium will prevent a particle from settling. But the medium having larger values of Y_G has very high viscosity so the volume fraction of magnetic particles can be dispersed in medium and MR fluid applications are limited.

In this study, we used a viscoelastic medium that has low yield stress (2.2 Pa) as a continuous phase and carbonyl iron as magnetic particles and nano-size ferromagnetic CrO_2 particles as stabilizing modifier. The synergistic stability effect using nano-sized particles in the viscoelastic medium was studied and the rheological behav-

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ior in steady shear flow was experimentally investigated by using a parallel-plate type commercial rheometer with a magnetic induction iron yoke.

EXPERIMENTAL

1. Preparation of MR Fluids

Viscoelastic medium was prepared by mixing vacuum grease (Dow corning) and silicone oil (Shin Etsu Chemical 100cs). The medium yield stress was controlled by grease/silicone oil weight ratio. The grease was diluted with silicone oil to 10%, 25%, 40% to obtain media with dynamic yield stress of 1-13 Pa (Fig. 1). To increase miscibility of grease and silicone oil Span 80 was used as a surfactant.

Magnetorheological materials are normally composed of magnetically soft ferromagnetic or ferrimagnetic particles, typically greater than 0.1 μm in diameter, dispersed in a carrier fluid. In this system, carbonyl iron [$Fe(CO)_5$, from Sigma] with density of 4.4 g/cm^3 and diameter in the range of 4.5-5.2 μm was used. These particles were directly dispersed with specified weight fraction [which in turn converted to the volume fraction (ϕ)] in a medium.

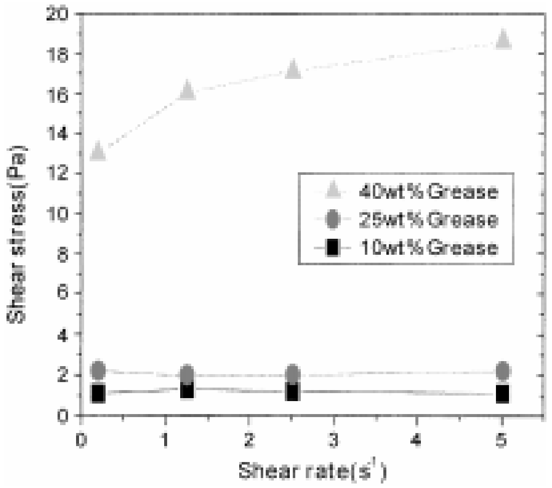

Fig. 1. Shear stress as a function of shear rate for grease was diluted with silicone oil (100cs) to 10, 25, 40 w%, with the dynamic yield stresses ranging from 1.5 to 13.

To make stabilized MR fluids using viscoelastic medium having relatively low yield stress (2.2 Pa), CrO_2 (Du Pont) particles were also used as stabilizing additives. CrO_2 particles were treated by polydimethylsiloxane bis(3-aminopropyl) terminated (Aldrich Chemical) as a surfactant and dispersed in viscoelastic medium as a 5 w%, 10 w%. These ferrofluid suspensions were agitated during 24 hr with mechanical stirrer at 1,000 rpm; the mixing bottle was filled with zirconia beads (500 g) of 2 mm diameter. The carbonyl iron suspension of ϕ=0.1-0.3 with various concentrations of CrO_2 particles were prepared and then the rheological properties and the behavior of stability were investigated.

2. Microstructure Investigation of Particles

The carbonyl iron and CrO_2 particles employed in this study were characterized by using scanning electron microscope (SEM). Fig. 2(a) and (b) shows the morphology of carbonyl iron and CrO_2 particles, respectively. The shape of the carbonyl iron is spherical but that of CrO_2 is needle like.

3. Magnetic Properties

A custom-built vibration sample magnetometer (VSM) was used to determine the quasistatic magnetic properties of MR fluids. An electric field was generated by a electromagnet driven by a switching power supply (AML) and a Hall-effect gaussmeter (Walker Scientific) was used. The sample was contained in a cylindrical volume of the glass tube between the coil bobbins. When mechanical vibration is applied to magnetic materials in a constant magnetic field, the induced voltage is generated in the pick-up coils; such voltage is proportional to the magnetic moment of materials.

4. Measurement of the Rheological Properties

Magnetic fields were generated with an electromagnet (Fig. 3), which was constructed from low coercivity iron. A thousand turns of insulated wire were wrapped around the yoke. An electric field was generated by a switching power supply. Magnetic flux was measured with a Lakeshore gaussmeter (model 450). The magnetic probe was placed between a rheometer plate and the electromagnet, with the probe tip less than 0.1 mm from the shaft. The magnetic flux was controlled by the coil current control. The relation between magnetic field and coil current is shown in Fig. 4.

The magnetorheological properties of MR suspensions were measured with a commercial parallel-plate rheometer (ARES, Rheomet-

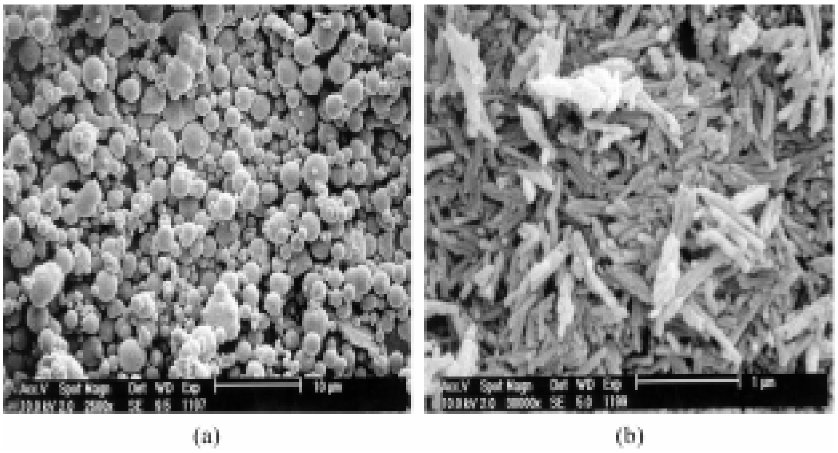

Fig. 2. Scanning electron microscope of the carbonyl iron (a) and CrO_2 (b).

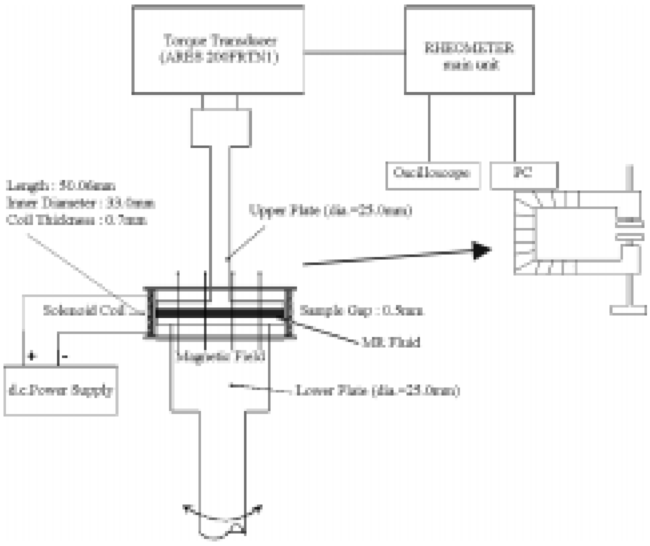

Fig. 3. Schematic diagram of the apparatus for the rheological measurement in the magnetic field along the direction of velocity gradient.

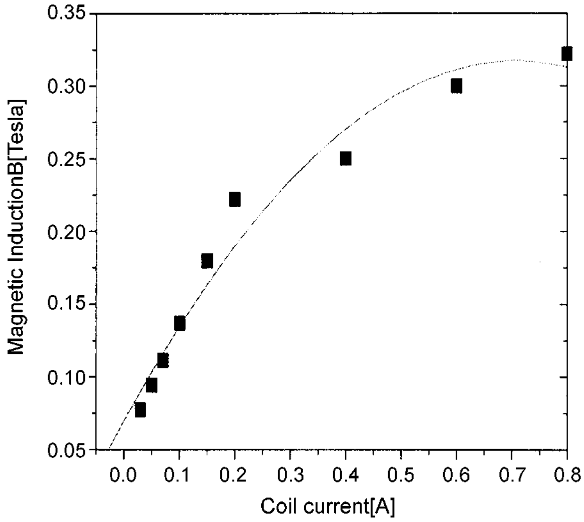

Fig. 4. Magnetic field generation as a function of coil current.

ric Scientific Co.) attached with an electromagnetic iron. Stainless steel parallel-plate fixtures were used and the gap was set to 0.5 mm. The magnetic flux perpendicular to the shear flow was generated by the electromagnetic iron. Although gravitation settling of the MR fluid samples was not observed during the tests, all samples were mixed well before the rheological measurements and changed with new ones at each measurement.

RESULTS AND DISCUSSION

1. Effect of Stabilizing Viscoelastic Medium and Ferromagnetic Particles

The gravity yield parameter Y_G [Eq. (1)] characterizes a viscoelastic fluid's ability to prevent a particle from settling. A higher value of Y_G means higher τ_G^O and higher viscosity of medium. That might limit the application of MR fluids and also the MR fluids cannot contain high volume fraction of magnetic particle because of the viscosity enhancement problem. So we used a viscoelastic medium having relatively lower yield stress and lower viscosity than that of viscoelastic medium demonstrated by Rankin et al., 1999. Instead of using a viscoelastic medium having high yield stress, we used a viscoelastic medium having 2.2 Pa yield stress and then added a ferromagnetic nano additive (CrO_2) mixture. MR fluids with CrO_2 nanoadditive for stability against gravity have been introduced by Chin et al., 2000. But the time scale of stability ranged only up to 50 hr. By using ferromagnetic nanoadditive, the synergistic effect against sedimentation of the viscoelastic medium was investigated.

Fig. 5(a) shows the effect of viscoelasticity on the dispersed stability of MR suspension. Each suspension contains carbonyl iron particles with ϕ=0.1 and no nanoadditive particles. Three kinds of medium (yield stress: 1.5, 2.2, 13 Pa) were tried as shown in Fig. 1. Fig. 5(b) shows the effect of nanoadditives for stability using viscoelastic medium having 2.2 Pa yield stress. In the present method, settling of the macroscopic phase boundary between the concentration suspension and the "supernatant" liquid was observed, since it can be simply applied without the limitation to the properties of particles/medium or the concentration. The ratio of sedimentation in

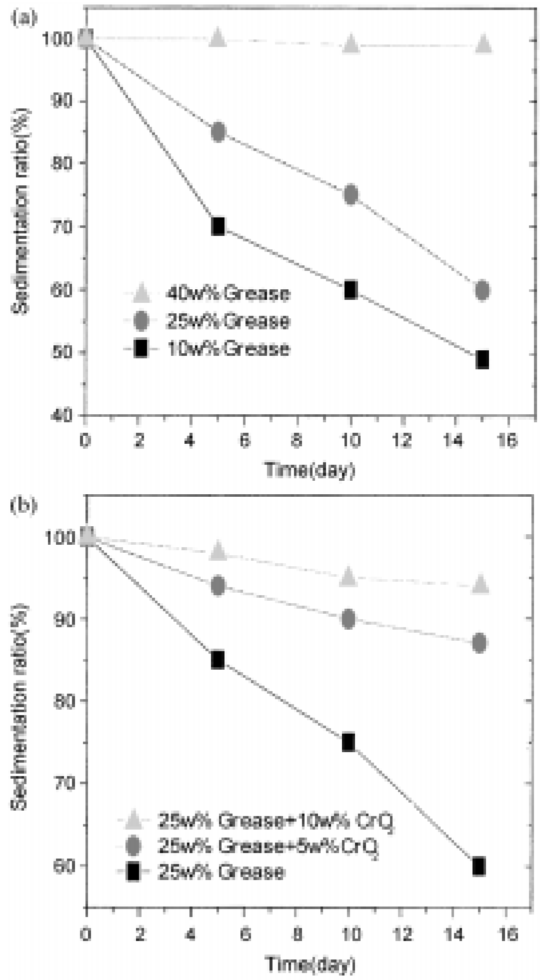

Fig. 5. Sedimentation ratio versus time for carbonyl iron suspensions (ϕ=0.2) using various viscoelastic medium and containing various percent of the CrO_2 particles.

Fig. 5(a), (b) is defined as:

$$\text{Ratio of sedimentation} = \frac{\text{volume of the supernatant liquid}}{\text{volume of the entire suspension}} \times 100 \quad (2)$$

Therefore, the sedimentation ratio test reflects the role of stabilizing additives on the bulk carbonyl iron particles and does not account for the stability of highly stabilized tiny colloidal particles [Lee et al., 1998]. The long-term stability of the MR fluids was fairly enhanced with increasing grease contents in medium as shown in Fig. 5(a). When the 2.2 Pa yield stress medium was used MR suspension showed relatively high stability. But sedimentation behavior was observed as time passed. In other words, the value of Y_G was less than the critical value (Y_G^{crit}). For further increasing stability CrO_2 particles were used as stabilizing additives in order to prevent particle aggregation, structure barriers between carbonyl iron particles. The retardation of sedimentation was observed so that it can be said that the re-dispersibility was improved greatly. Fig. 5(b) represents the effect of ferromagnetic additive materials (CrO_2). The time scale of stability is around 15 days. That means the nanoadditives effect is more powerful than that case of using newtonian medium [Chin et al., 2001].

2. Magnetic Properties of MR Suspension

Fig. 6 shows the normalized magnetic field-dependent magnetization (M-H curve) for the carbonyl iron suspension, measured at room temperature. The magnetization increases very rapidly, increasing the applied magnetic field, and at above 8 kOe, saturates to M_s. The MR effect increases with increasing external magnetic field.

3. Steady Shear and Yield Stress

Rheological behaviors of MR fluids that have stability against gravity were investigated under steady shear flow and static magnetic field. Dynamic yield stress measurements were made using the following step. The suspension was sheared ($\dot{\gamma}>10\ s^{-1}$) at zero field for 60seconds to distribute the particles uniformly. Fig. 7 shows the variation of shear stress versus shear rate as a function of magnetic field for carbonyl iron suspension $\phi=0.2$ dispersed in viscoelastic medium (grease 25 w%, CrO_2 10 w%). Without a magnetic field, the dynamic yield stress of MR fluids shows about 3-4 Pa. But with increasing magnetic field the MR fluid shows Bingham plastic behavior with yield stress 1-6 kPa, representing the stable chain structures of magnetized particles. The yield stress of the medium is negligible compared with that of the case under a magnetic field, but viscoelastic properties of the medium showed good enhancement of stability as shown in Fig. 5(a, b). Magnetic fields were generated with an electromagnet (Fig. 4), which was constructed from low coercivity iron. From the shear stress-shear rate curves, dynamic yield stress can be easily obtained by the extrapolation to zero shear rate (practically, at the plateau stress in the range of low shear rate, $\dot{\gamma}=0.1\ s^{-1}$) [Chin et al., 2000]. In Fig. 8, dynamic yield stresses of three MR fluids are shown as a function of applied magnetic field B. The yield stresses of 20 v% ($\phi=0.2$) are observed to increase with $B^{3/2}$ dependence. That value deviated a little with numerical and analytical models developed by Ginder et al., 1996. This subquadratic dependence of flux density is a consequence of the local saturation of the magnetization in the polar or contact zones of each particle. But when the magnetic field exceeds 0.25T the

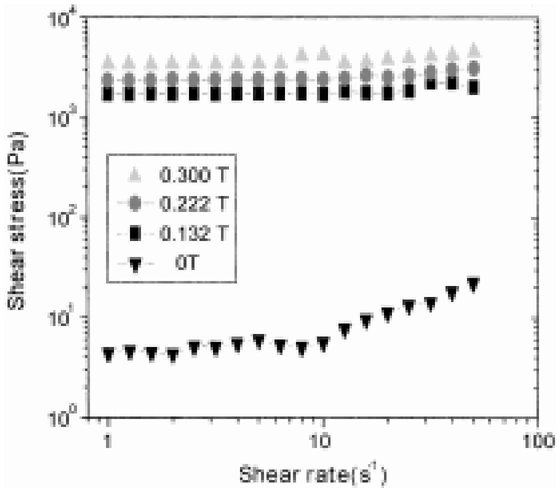

Fig. 7. Steady shear stress versus shear rate for carbonyl iron dispersed in viscoelastic medium (grease 25 w%, CrO_2 10 w%).

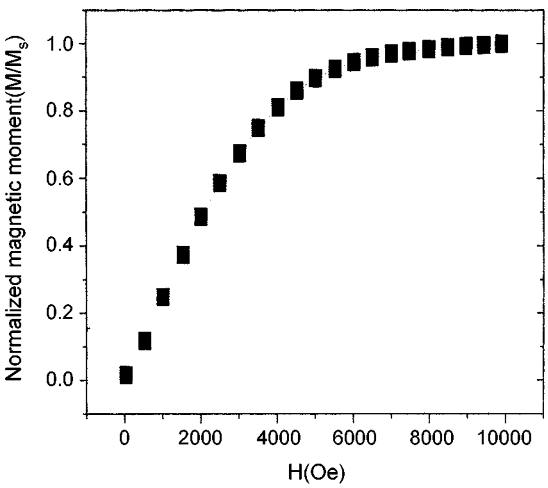

Fig. 6. Normalized magnetic moment as a function of induced magntic field (H_O) for the carbonyl iron suspension.

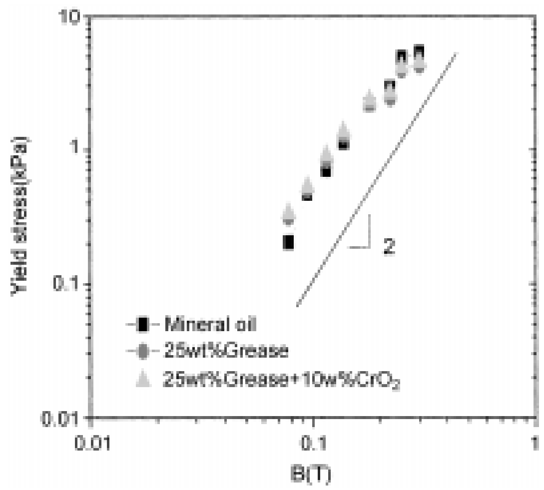

Fig. 8. Dynamic yield stress as a function of magnetic field.

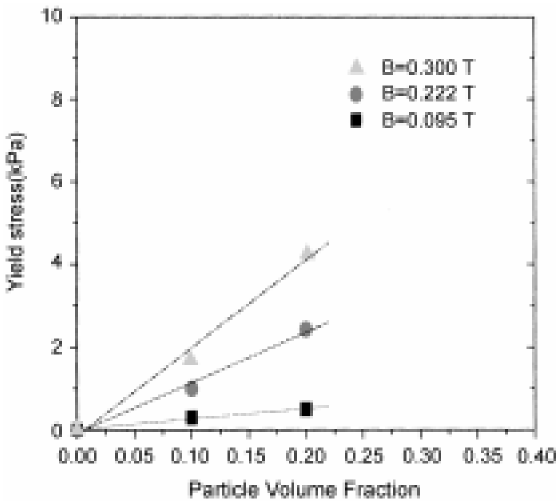

Fig. 9. Dynamic yield stress as a function of particle volume fraction using viscoelastic medium (25 w% grease, 10 w% CrO_2) at various magnetic field.

yield stress shows saturation. The yield stress of different kinds of MR fluids showed similar values. This phenomenon shows continuous phase and magnetic nano-additive particles did not affect yield stress of MR fluids. Chin et al. have shown that magnetic nanoparticles affect MR yield stress at low magnetic field. But nanoadditives could not give any synergistic effect against yield stress because of low magnetic field in Chins system [Chin and Park, 2001].

The effect of carbonyl iron volume fraction on the dynamic yield stresses for applied magnetic flux densities of 0.095, 0.222, 0.300T is plotted in Fig. 9. A medium containing 25 w% grease and 10 w% CrO_2 was used. The dynamic yield stress has an approximately linear relation with the volume fraction at this moderate flux density.

4. Viscoelastic Properties in a Small Strain

While the MR fluids exhibit Bingham plastic behaviors with an apparent yield stress, they often were described as viscoelastic materials in the range of a small strain of oscillatory flow. The response of stress in ER fluid subjected to a sinusoidal strain of small amplitude shear flow shows a linear viscoelastic behavior, where the amplitude and phase angle of the stress are dependent upon the applied electric field strength [Jordan et al., 1992; Kim and Klingenbery, 1997]. The response becomes, however, nonlinear and deviation from the viscoelasticity occurs with increasing strain amplitude, due to the break of chain [Chin and Park, 2001]. In the case of MR suspensions, Nakano et al. investigated the dynamic viscoelasticity in pressure-driven oscillatory slit flow, which is important in the design of dampers using MR valves [Nakano et al., 1998].

For two kinds of MR fluids, carbonyl iron (ϕ=0.1) dispersed in viscoelastic medium (grease 25 w%), carbonyl iron (ϕ=0.1) dispersed in mineral oil, Fig. 10(a) shows the dependence of G' and G'' on the strain amplitude (γ) for oscillatory shear flow. Small strains were employed to ensure that the suspension structure was not significantly altered by the deformation. The region of linear viscoelasticity, where G' and G'' are not dependent on the amplitude of strain, is restricted to very small strain, as shown in Fig. 10(a). G' and G'' rapidly decrease with increasing amplitude of strain, causing the non-linearity. At very small strain range (γ<0.3%), G' behavior of both MR fluids was similar. MR fluid using mineral oil as medium

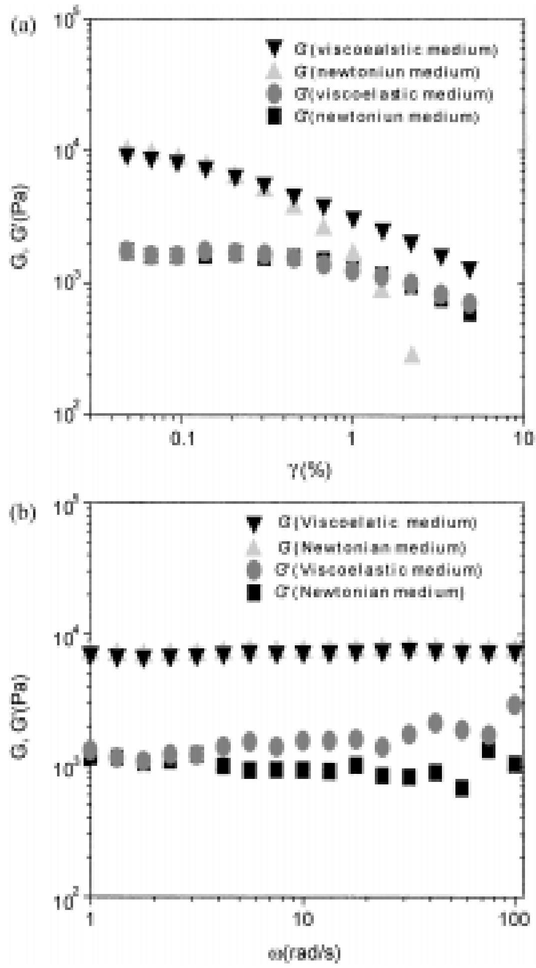

Fig. 10. (a) Storage shear and loss modulus as a function of strain amplitude for the carbonyl iron (ϕ=0.1) in viscoelastic medium (grease 25 w%) and Newtonian medium (silicone oil) under 0.078T. (b) Storage shear and loss modulus as a function of strain frequency for the carbonyl iron (ϕ=0.1) in visoelastic medium (grease 25 w%) and newtonian medium (silicone oil) under 0.078T

shows a very rapid decrease with increasing amplitude of strain. But MR fluid using viscoelastic medium shows that the decreasing of storage modulus was retarded. In other words, chain deformation of MR fluid is retarded by viscoelastic medium and so the break point of the chain cluster shifts to higher strain amplitude than that of a newtonian medium. In the linear viscoelastic region under very small strain (γ=0.1%), Fig. 10(b) shows the G' and G'' as a function of strain frequency for two kinds of MR fluids. The storage shear modulus (G') of MR fluid shows constant over wide range of driving frequencies. This behavior of G' and G'' is similar to the result of frequency-plateau of G' and G'' in typical ER (electrorheological) fluids.

CONCLUSIONS

Magnetorheological fluids that show very good enhancement of stability against gravity have been successfully prepared by using viscoelastic medium and magnetic nanoadditives (CrO_2). The rodlike, small particle seems to play a role of steric repulsion between the carbonyl iron particles so that the stability against sedimentation has been improved greatly. The stable suspension remains for very long time. Effect of the nanosized particles as a good stabilizer is much more evident in viscoelastic medium compared with the case of newtonian medium. The synergistic effect of nanoadditives in viscoelastic medium has been observed obviously without any reduction of the dynamic yield stress of MR fluids. This means that the small particles using stabilizer do not affect the chain structure at all under a magnetic field.

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