Electrorheology and magnetorheology

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(Received March 26, 2001)

1. Introduction

Scientists and engineers are most familiar with single-crystal or polycrystialline field-responsive materials responses typically occurring while the materials remain in the solid state. These materials demonstrate dramatic changes in their rheological properties including yield stress, loss and storage moduli etc. in response to an externally applied electric or magnetic field are known as electrorheological fluid (ERF) or magnetorheological (MRF), respectively. ERF and MRF exhibit a very fast, reversible transition from a free-flowing liquid state to a solid like state. This behavior is often described as Bingham plastic characteristics having shear modulus and yield stress dependent on external field that must be overcome to initiate gross material deformation or flow.

The majority of the electrorheological fluids (ERF) are composed of solid particles suspended in nonpolar liquids. General particles used in preparing ERF are silica, titania, zeolites and the medium used in preparing ERF are silicone oil, mineral oil, cast oil. MR fluids are based on ferromagnetic or ferrimagnetic, magnetically nonlinear particles including iron, nickel, cobalt, and ceramic ferrites dispersed in organic or aqueous liquids. In electric or magnetic field, each particle acquires an induced dipole. When aligned along the field direction, the particles attract one another, whereas the particles in the plane perpendicular to the field direction repel one another. The dipole-dipole interactions cause chain structures in direction parallel to the field vector. Physical properties of ER, MR under external field are due to the formation of this chains and columns of the field responsive constituent. Mechanical energy from shocks or vibrations can be absorbed by these materials under external field. The influence of external electric or magnetic field on the deformation or flow properties of certain fluids has been a subject of scientific or practical interest for many years. The change in viscosity and other macroscopic properties has been investigated in a number of systems including molecular polar liquids

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(Andrade and Dodd, 1939; Andrade and Hart, 1954; Honda and Sasada, 1977; Hayes, 1988), magnetic dispersions or ferrofluids (Hayes, 1974; Hess et. al., 1984; Rosensweig, 1969), electrorheological fluid (Gast and Zukoski, 1989; Jordan and Shaw, 1989) and magtetorheological suspensions (Shulman et. al., 1986; Promislow and Gast, 1996). Among the class of these field-responsive fluids, special focus has been placed on the materials having the features such as rapid, reversible, and tunable transition from a liquid-like state to a solidified state upon the application of an external electric or magnetic field. These materials are known as electrorheological (ER) or magnetorheological (MR) fluids, respectively. When sufficiently strong external field is applied to these systems, they undergo remarkable changes in their rheological properties as a result of the formation of patterned structures from the random dispersion of particles. They exhibit a strong field-dependent shear modulus and a yield stress which must be exceeded in order to initiate the deformation or flow. The availability of fluids with yield stress or apparent viscosity controllable over many orders of magnitude by applied fields enables the development of many mechanical applications, such as high-speed valves, active damping system, brakes, and miniature robotic joints due to the advantage of fast response time and simplicity of devices. Unlike the ER or MR fluids, magnetic fluids (or ferrofluids) do not develop a yield stress on the application of a magnetic field since they are stable dispersion of nano-sized superparamagnetic particles governed by the influence of Brownian force. Application of ferrofluids are primarily in the area of sealing devices (Rosensweig, 1989).

While these materials are fascinating, the fundamental science of these materials the relationships between synthesis and processing and the connections between micro structural evolution and the rheological properties is very complex and is not fully understood.

2. Electrorheological fluids

Electrorheology is a phenomenon whereby a suspension of fine polarizable particles (0.1-100 μm in diameter) in a dielectric liquid undergoes orders of magnitude increase in

viscosity upon application of an electric field. This effect was first reported by Winslow in 1949 and is sometimes termed the "Winslow effect". As Winslow reported, apparent viscosities can increase by several orders of magnitude when electric fields of the order of 1 kV/mm are applied. The rheological changes are rapid and reversible and consume very low current, as has been reviewed in several recent publications (Deinega et al. 1984; Block et al. 1988, Gast et al. 1989; Jordan et al. 1989; Kreiger et al. 1992, Halsey et al. 1992; Weiss et al. 1993; Zukoski et al. 1993).

For the case of a Newtonian fluid, the steady shear viscosity is constant. Non-Newtonian fluids exhibit a shear rate dependent viscosity and may be characterized as either pseudoplastic (shear thinning) or dilatant (shear thickening). Electrorheological fluids tend to be pseudoplastic-the apparent viscosity decreases as the shear rate increases (Deinega and Vinogradov, 1984; Marshall et. al., 1989; Uejima, 1972; Klass and Martinek, 1967). At low shear rates the relationship is $\eta_a \propto 1/\dot{\gamma}$ (Marshall et al.,1989; Klass and Martinek, 1967; Shulman et. al., 1989), where η_a is apparent viscosity. This implies a constant shear stress in the region of sufficiently low shear rates and reflects the solid-like nature of the ER suspension in the presence of strong fields. Typical behavior of electrorheological fluid under the influence of external electric field is characterized as the Bingham fluid model (Klass and Martinek, 1967; Shulman et. al., 1981; Marshall et al.,1989) This means that flow is observed only after exceeding a minimum yield stress. The constitutive equation for a Bingham fluid is

$$\tau = \tau_y + \eta_p \dot{\gamma} \tag{1}$$

where τ_y is the dynamic yield stress, η_p is the plastic viscosity, and $\dot{\gamma}$ is the shear rate. Upon application of an electric field to the ER fluid, the yield stress increase dramatically while the plastic viscosity remains essentially unchanged (Marshall et al., 1989). The yield stress for a truly plastic material is often obtained by extrapolation of the flow curve (τ vs. $\dot{\gamma}$) to zero shear rate, but recent work has demonstrated that the method should be confirmed by a direct determination (Yoshimura and Prudhomme, 1988). The Bingham model suggests the solid like behavior below the yield stress and liquid like behavior at stress above yield stress. The observed dynamic yield stress represents the ER effect substantially and is scaled to the square of the electric field strength (Winslow, 1949), but other kinds of dependency are also reported (Block et. al., 1990).

However, the behavior of ER fluid below yield stress is completely overlooked in the Bingham model (Sprecher et. al. 1987). This pre-yield behavior can be effectively characterized by the modulus. More specifically, dynamic studies conducted with sufficiently small sinusoidal shear strains suggest that ER fluids deform as viscoelastic bodies

(Brook et al., 1986; Gamota and Filisko, 1991; Shulman et al., 1989; Vinogradov et al., 1986). Moreover, it is generally accepted that under a dynamic stimulus of low amplitude the structure formed in response to the electric field is virtually undisturbed. These studies have also reported that the viscoelastic parameter, i.e. storage shear modulus, loss modulus and phase angle, are functions of the field strength, ER fluid composition, strain frequency, and strain amplitude.

The stress response of electrorheological fluid subjected to a sinusoidal strain of small amplitude and an intermediate electric field shows a linear viscoelastic behavior (Gamota and Filisko, 1991). The response becomes, however, nonlinear with increasing strain amplitude due to the break of chain structure induced by the electric field. In a word, the viscoelastic parameters (G', G'') of ER suspension with electric field strongly depend upon the strain amplitude. In the case of ER fluids, the limiting strain of the linear viscoelasticity is usually 1.0%. Jordan et al. (1992) reported the dependence of G' and G'' on the strain amplitude and explained the viscoelsticity of ER fluids with a string model. Vinogradov et al. (1986) and Shulman et al. (1989) reported that both loss and storage moduli increase with electric field for a diatomite in silicone oil subjected to sinusoidal strain in the frequency range of 0.1 to 1.0 Hz. They also reported that the increase in the level of moduli depends on the particle volume fraction, strain amplitude and frequency. Such an analysis on the viscoelastic behavior needs the high resolution of measuring devices due to the relatively narrow window of the linear viscoelasticity of ER materials.

Recently, two new approaches have been tried to enhance yield stress of electro-rheological fiuid. Chin and Park introduced the effects of dispersed drop in the electrorheological (ER) behaviors of a polyaniline particle suspension (Chin et al.2000). Oil-in-oil emulsions, which have difference in the electrical conductivity and dielectric constant, were employed for the liquid bi-phase in the present study. We examined the yield stress behaviors of ER suspension under steady shear and electric field. Only when the dispersed drop with a higher conductivity formed the dispersed liquid phases in the presence of dispersed polyaniline particles, synergistic effect in the yield stress is observed, giving a better ER performance and reduced current density. This is due to the unique microstructures in a complex composed of particles and deformed emulsion drops. Not only the magnitude but also a dependence on the electric field strength of yield stresses were strongly affected by the change in relative composition of particulate and liquid drop phases. Based on the direct observation of microstructural evolution in these ER suspensions, we have explained the associated mechanism of ER response in particle-drop bi-dispersion based on the relationship between microscopic change of structures and
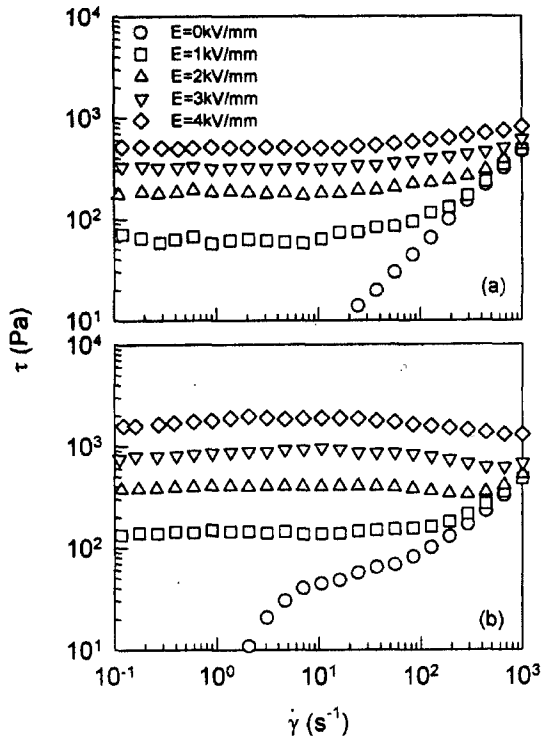
Fig. 1. Steady shear stress versus shear rate for polyanilne particle suspension under various electric field strengths. (a) 13 vol% polyaniline particle is suspended in pure silicone oil (Φ=0). (b) 13 vol% polyaniline particle and 30 vol% Celeclor s45 drop are suspended in silicone oil (Φ=0.3) ; Φ denotes the volume fraction of Celeclor s45 based on the total volume of liquid phase.

macroscopic rheological properties. Figure 1(a) illustrates the shear stress curve of polyaniline suspensions versus shear rate (0.1~1000 s^{-1}) under electric field strength of 0.0~4.0 kV/mm. For a 13 vol% of polyaniline particle dispersed in the single liquid phase (silicone oil), Bingham plastic behaviors under the steady shear flow and electric field can be clearly observed. Figure 1(b) represents the same type flow-curve for the ER fluid containing 13 vol% of polyaniline particle (ϕ_p = 0.13), 30 vol% emulsion drop of Celeclor s45, Φ = 0.3) in the silicone oil, giving a increased stress response overall the range of shear rate and electric field strength measured. The increase of shear stress was dominant in the range of low shear rate, whereas only small enhancement is observed at the high shear region in which hydrodynamic force dominates. Here the volume fraction of particle (ϕ_p), which is defined on the basis of total volume of suspension, was identical for the two cases. Another new approach is introduced by Kim et al. (1999) using Polyaniline/Clay (MMT) composites with intercalated nanostructure. But the value of yield stresses is lower than that of conventional ER system. For further improvement of ER yield stress, polyaniline coated clay

nanocomposite was synthesized as new polyaniline (hereafter PANI)/organoclay (aminosilane surface treated) nanocomposite particles and prepared electrorheological (ER) fluids by dispersing the particles in silicone oil (Park et al. 2001). Distinct enhancement in yield stress was observed due to the presence of PANI coated clay particles. The effects of delaminated clay to the ER yield stress were investigated and compared with other ER fluid systems which use PANI particles only or simply intercalated PANI/clay nanocomposite.

Gow and Zukoski (1990) studied the ER behavior of suspensions composed of polyaniline particles treated with aqueous sodium hydroxide at pH 6~9. Polyaniline suspension with optimal conductivity of particle [O(10^{-9})S/m] shows relatively high ER-yield stresses, low current density and wide working temperature range. Moreover, dispersion stability of the polyaniline suspension in oils can be improved by the use of non-ionic surfactants, which are chemically adsorbed on the surface of particles (Lee et al., 1998). Although these non-ionic surfactants can partially reduce the sedimentation and aggregation of dispersed polyaniline particles, methods of preparing stabilized polyaniline particle dispersion is still necessary for ensuring the long-term stability of ER particle suspensions.

There have been several reports on the dispersion polymerization methods for the synthesis of stable polyaniline colloids. Conventional polymeric stabilizers like poly (vinyl alcohol-co-acetate), methyl cellulose, and poly (vinyl pyrrolidone) are, however, unsuccessful since they adsorb poorly on the surface of polyaniline. To overcome such a problem, Armes et al. (1990) used tailor-made stabilizer which undergo graft copolymerization with aniline, and therefore anchored polyaniline particle dispersions of improved stability were obtained. Benerjee et al. (1995) reported the dispersion polymerization of aniline using ammonium persulfate as the oxidant and poly (vinyl methyl ether) (PVME) as the polymeric stabilizer in a aqueous and non-aqueous media, yielding stable dispersions of colloidal polyaniline particles depending on the types of solvent. PVME is an effective stabilizer which enables the re-dispersion of dried and separated polyaniline particles in both aqueous and organic media, since it is soluble in a number of organic liquids as well as water. Furthermore, PVME stabilizes the polyaniline dispersion even when used at sufficiently low concentration, suppressing the possible formation of defects in conjugated structures of particles. Benerjee et al. (1995) obtained the oblong rice-grain shape of the primary polyaniline colloids, which appear to result from the association of the precursor spherical particles. The average size of the aggregated particles was decreased with increasing the concentration of stabilizer. In their report, particle size, morphology, and the electrical conductivity of polyaniline were characterized with respect to the PVME content and the types of oxidants/continuous

media.

Recently, Chin and Park (2001) synthesized polyaniline particle suspensions stabilized by PVME in order to develop a stable electrorheological fluid. Dispersion polymerization of aniline was performed in an aqueous reaction media using ammonium persulfate oxidant and various concentrations of PVME. Particle size and its distribution as well as the morphology were investigated in order to examine the effects of PVME as a steric stabilizer during the polymerization of aniline. Then, dispersion stability of suspension was investigated by employing the sedimentation ratio test and explained in terms of the size distribution and morphology of polyaniline stabilized by PVME. The yield stresses and current density of concentrated polyaniline suspensions were characterized with a wide range in electric field strength.

3. Magnetorheological fluids

MR fluids represent an exciting family of smart materials that possess the unique ability to undergo rapid (within a few milliseconds), nearly completely reversible, and significant changes in their strength (yield stress change from ~0 to 100 kPa) upon application of an external magnetic field. MR fluids typically consist of fine (~1-10 μm) particles of a magnetically soft material (e.g., iron or ceramic ferrites) dispersed in an organic medium such as silicone oil

Magnetoheological (MR) fluids were first developed in the late 1940s (Rabinow, 1948). They have recently a revival of interest as high-shear-strength, low-voltage counterparts of electrorheological suspensions. Yield stresses of order 100 kPa, some two orders of magnitude higher than in practical ER fluids, can be obtained in MR fluids under magnetic field strength about 3 kOe, which can readily be supplied using the electro- or permanent magnets (Carlson et. al., 1993). The substantial field-induced yield stresses exhibited by the MR fluids make some applications possible, such as clutches and rotary brakes that are not practical with existing ER fluids.

Magnetorheological materials are normally comprised of magnetically soft ferromagnetic or paramagnetic particles, typically greater than 0.1 μm in diameter, dispersed in a career fluid. When the size of particles becomes smaller, the destabilizing effect of Brownian motion can become significant, leading to a decrease in the yield stress as the temperature of MR fluid increases. Particles larger than 10 μm makes it difficult to prepare MR suspension stable against the sedimentation. Typical volume fractions of dispersed phase that produce the respectable yield stresses tends to be about 0.3–0.5. In order to maximize the volume fraction of MR fluids without causing the unacceptable increase of the zero-field viscosity, selecting the particles with size distribution will be also advantageous.

The possible maximum yield stress induced by magnetorheological effect is mainly determined by the magnitude of saturation magnetization of dispersed particles. Iron and carbonyl ion has been a popular choice as dispersed phase due to the high saturation magnetization of Fe element ($\mu_0 M_s$ = 2.1 Tesla). Using Fe-Co alloys (composition of 50 wt% Fe, having the highest saturation magnetization about 2.4 Tesla), and Fe-Ni alloys can lead to MR fluids with much higher strength. As a ferrimagnetic material, such as Mn-Zn ferrite, Ni-Zn ferrite and cerramic ferrites, have relatively low saturation magnetization and therefore exhibit reduced maximum yield stress. However, these materials can be used to prepare the stable nano-MR fluids, commonly by adsorption of polyelectrolytes (Phule, 1998).

For the practical application of MR fluids, they must have the good stability and re-dispersibility. Most of the early MR fluids suffered from irreversible aggregation of the suspended particles. Therefore although the MR effect could be demonstrated practical device applications could not be developed. In the 1980s, Shulman, Kordonsky, and co-workers performed detailed research concerning physical properties and dynamics of MR fluids. In the last few years, novel MR fluid compositions of significant stability and redispersibility have been developed. Without special additives, most MR fluids based on the micron-sized particles, undergo significant problems due to the settling and formation of tightly packed sediment or a irreversible "cake". It is extremely hard to re-disperse the formed "cake", and the primary reason for this strong aggregation is the remnant magnetization of between the MR particles, which is not disappeared even without magnetic field. Additives such as polymeric surfactants and introducing a nano-structured composite with silica would be possible methods to enhance the stability of MR fluids. Pradeep Phules article summarized the salient features of the synthesis and processing of MR fluids. The use of different types of soft magnetic materials the importance of particle size, particle size distribution, shape of the magnetic particles on the properties of MR fluids is discussed. Also the choice of continuous phase and the role of nano-structured additives on the stability and redispersibility of MR fluids are discussed.

Recently, two kinds of works for improving MR stability were introduced. Rankin et al. (1999) reported the use of viscoplastic media for the preparation of stabilized MR fluids. Stability of MR fluids using viscoplastic medium against sedimentation and aggregation was satisfactory compared with that of ordinary MR fluids using Newtonian media. Small amount of nanosized ferromagnetic particles was added in an effort to enhance the dispersion stability of MR suspensions by Chin et al. (2001). Stabilizing additives composed Co-γ-Fe$_2$O$_3$ (Toda Chem.) and CrO$_2$ (Du Pont) nano-sized particles (used in the commercial ferrofluids) were employed in order to improve the

dispersion stability of concentrated MR suspension without affecting the MR efficiency, and the evaluation of the related synergistic effects were discussed. For further improvement of stability and reducing the aggregation, we introduced a new MR system (Park et al., 2001). Water in oil emulsion is adopted as a continuous phase, and magnetic particles are treated to have hydrophilicity. In terms of thermodynamics, emulsions are induced unstable systems. However, the time scale for coarsening can vary depending upon the systems. In certain cases, this time is very long. So novel MR materials based on hydrophilic treated carbonyl iron used as magnetic particles and water in oil emulsion were prepared as a continuous phase. By using the interaction between the water droplet in continuous phase and hydrophilicity of magnetic particles, the stabiliy effect is studied and the rheological behavior in steady shear flow was experimentally investigated using a parallel-plate type commercial rheometer with a magnetic induction iron yoke.

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