

Recent Developments in the Properties and Composition of Electrorheological Fluids

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ABSTRACT: Recent studies suggest that an alternate if not primary way that ER fluids flow is not by chain breakage as has been assumed but by the development of slip planes parallel to the chain directions. This might help to better understand mechanisms associated with the strengths of ER fluids. This lateral slip would be essentially independent of particle interactions in the field direction. Attempts to interfere with this slip by the addition of small amounts of foreign particles have resulted in some modest but significant strength increases. An additional area of significant advancement is by making the matrix liquids ER active. Various base ER fluid compositions are shown to have dramatically enhanced shear stresses when dispersed into poly(hexyl isocyanate) solutions.

INTRODUCTION

ER fluids are most commonly described as suspensions of certain dielectric particles in a dielectric fluid which under an electric field (E) demonstrates a Bingham like behavior, i.e., solid behavior below a certain critical shear stress which is a function of the magnitude of the field. Above this shear stress the material demonstrates a liquid like behavior whose apparent viscosity is a function as well of the electric field. The solid behavior is associated with an E field induced buildup of a structure of particles between the electrodes currently associated with Maxwell-Wagner-Sillars interfacial polarization (Maxwell, 1892) involving mobile charge carriers restricted for the most part to the particles. The interactions are then related not only to the corresponding interfacial polarizations but as well to the conductivity of the particles and/or fluid and/or conductivity differences between the two (VonHippel, 1954). Effects directed upon increasing the strengths of the fluids have thus focused upon synthesis of particles containing mobile charge carriers. The best known of these are the polyacene quinones (Block and Kelly, 1988) which as intrinsic semiconductors contain mobile electrons; the polymeric electrolytes of Bayer (Bloodworth and Wendt, 1995) which contain ions as the mobile carriers; the carbonaceous fluid of Bridgestone (Ishino et al., 1995) which contain presumably pyropolymer particles and as such are semiconductors with

mobile electrons; zeolites which contain mobile ions (Breck, 1974); and certain (dry) polyelectrolytes where localized ion mobility has been proposed (Treasurer et al., 1991). Many other systems have been reported but if intrinsic they fall broadly into one of the above categories. However diverse the types of particles used, the maximum strengths of the fluids have remained around 3–5 kPa.

Recent studies in our laboratories and similar studies by Oyadiji (1996) record shear moduli of ER fluids in pre-yield in the range of 500–1000 kPa. which suggests that yielding mechanisms might be more of concern than the strength of the columns or lamellae. Current studies suggest that yielding occurs by developing slip planes either at the electrode surfaces and/or within the fluids. Thus studies are focused upon mechanisms for initiating the easy slip planes, analogous to imperfections and dislocations in crystalline ductile materials. These studies as will be demonstrated in the paper have led to the discovery of dramatically different flow profiles for ER fluids under field. Additionally attempts to exploit this new knowledge for the purpose of increasing strengths will also be presented.

A third area of new developments has been in exploring the potential of using ER active matrix liquids in the formulation of ER fluids. In common ER fluids, the matrix fluid serves primarily in a passive nature, i.e., being the liquid phase in the suspension, increasing the dielectric strength of the fluid, and supplying the low permittivity barrier between the particles. This phase could take on a more active role by itself having properties which are a function of E field. Examples being thermotropic liquid crystal fluids (Lacy et al.,

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1996; Inoue and Maniwa, 1995) or lyotropic liquid crystalline solutions, specifically solutions of LC polymers. Results obtained by compounding ER fluids using ER active liquids will be discussed as well as studies to explain the results.

EXPERIMENTAL

The flow profile photographs were obtained by using ER fluids compounded with paraffin wax as the matrix phase. These were made by adding the dried powders to molten paraffin wax at 75°C. These mixtures were then heated to a temperature of approximately 80°C and placed under a vacuum for 10 minutes to further degas the fluids. The samples were then cooled and stored in sealed containers.

The cylindrical or flat samples were prepared on a Weissenberg rheogoniometer with a couette device attached (bob = 24.77 mm dia., length = 24.13 mm, gap = 1.25 mm) but modified so high voltages could be applied over the gap. A Spellman high voltage D.C. power supply was utilized. The disc samples were prepared on a Ferranti-Shirley rheometer with parallel discs (3.0 cm diameter and 1mm gap) using a Hipotronic high voltage D.C. power supply. Samples were prepared on both instruments by melting the fluid and adding it to the device at 72°C, applying the appropriate shear and/or field for 1.5 minutes, then stopping the rotation, reducing the voltage to 500 V and allowing the sample to cool to about 49°C before it was removed. The 500 volts was maintained because the rings remained sharper. However, it was reduced to 500 V to minimize the effect of electrophoresis which will be discussed in the article. When applied, the fields were all at 2000 V/mm and both instruments were rotated only at 180 rpm which corresponds to a shear rate of 180/sec on the couette and a maximum shear rate of 280/sec between the parallel discs.

The poly(hexyl isocyanates) used were synthesized in our laboratories by procedures similar to but not identical with those reported (Shashoua et al., 1960; Aharoni and Walsh, 1979). Polystyrene/xylene concentrations were adjusted to the same zero field viscosity as the PHIC solutions. The sulfonated polystyrene, poly(sodium 4-styrene sulfonate), was from Aldrich Chemical as powder (14 micron) and dried at 120°C for 24 hours under vacuum. The polyisoprene was a latex surgical glove ground with a Retsch Model ZM-1 ultracentrifugal mill under liquid nitrogen to 40 micron or smaller particles. The powders were all subsequently dried for 24 hours at 120°C under vacuum. The sulfonated polyisoprene was obtained by exposing the powder to 9M sulfuric acid at 80°C for 10 minutes followed by washing and exposure to a 9M NaOH solution. They are then washed, filtered, and dried at 120°C for 24 hours under vacuum.

All rheological measurements were obtained on the two instruments described above.

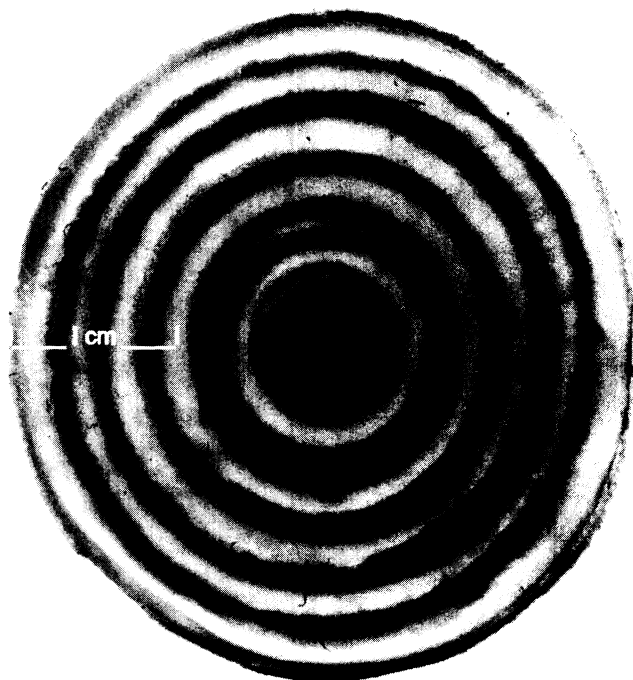


Figure 1. Flow pattern observed for an ER fluid under electric field between rotating discs at 180 rpm.

RESULTS AND DISCUSSION

Flow Profiles between Parallel Discs

Figure 1 illustrates a typical pattern assumed by the particles in an ER fluids under electric field and continuous flow. The dark rings are particles and the light regions are paraffin wax. These rings appear only under simultaneous application of shear and electric fields, i.e., they do not appear under rotation if no electric field is present nor do they appear if an electric field is present but the plates are stationary. Upon breaking these discs, it is observed that the rings extend completely through the discs in the thickness direction and are really flat cylindrical shells or washers whose axial (z direction) is the gap between the plates. The thickness of these shells and the distance between the shells are complex functions of the particle concentrations, the electric field magnitude, the shear rate, etc., and other conditions not yet resolved. Although Figure 1 shows a relatively low concentration of particles, higher concentrations as well show these distinct rings but they are much thinner with a smaller gap between them in the radial direction. It is relevant to point out that the particle chains/columns which form in the field direction are perpendicular to the plane of these discs, i.e. in the axial or thickness direction of the discs.

Figure 1 represents one example of a huge number of studies done to attempt to resolve the flow profiles in activated ER fluids and suggests an alternative if not the primary way that ER fluids flow. The common model for ER activity is that chains/columns of particles form between the

electrodes and under flow, the chains break and reform in the flow direction. An alternative to this, suggested by this research is that the chains/columns under field and flow, align themselves in tight packed geometric structures consistent with the flow field and shear dissipation occurs not by chains breaking but by these structures maintaining their integrity and shearing with respect to each other. In the case of parallel disc flow illustrated here, the many concentric cylinders of particles are randomly adhered to either the upper or lower discs of the device, thus providing the shear gradients between them. There is also a shear gradient between that surface of the cylinder which is slipping with respect to the electrode. Thus the relevant slip planes are not normal to the columns (which would occur if chains were breaking) but are parallel to the columns directions.

Addition of Small Amounts of Particles

Figure 2 illustrates the effect of adding small amounts (1 wgt % of the particles) of very hard particles (glass beads), medium hard particles (polystyrene), and soft particles (polyisoprene) to a base ER fluid containing sulfonated polystyrene suspended in a paraffin oil. The addition of the glass particles have little effect on the properties of the base fluid while polystyrene particles shows a slight increase of the shear stresses over the base fluid of about 10%. Since the amount of particles added were by weight %, this may be due to the larger volumes of polystyrene particles. Neither of these particles form ER active suspensions by themselves. The addition of an identical weight of rubbery polyisoprene however results in an increase of about 30% in the stress at 4kV/mm. As with the glass and polystyrene powders, the polyisoprene (PIP) powders by themselves do not form ER active suspensions. However, the PIP due to the presence of some unsaturations can be sulfonated to low degrees so that the particles remain elastomeric. The sodium salts of these sulfonated PIP powders do form ER active suspensions by

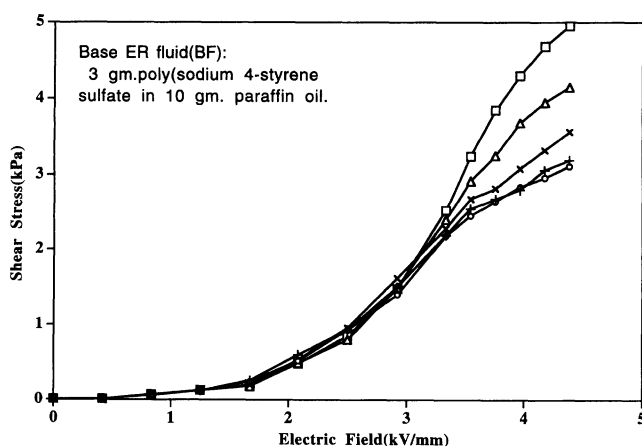


Figure 2. Effect of adding 0.15g or 1% of the solid content of various particles to an ER fluid. (○) Base fluid (BF); (+) BF and glass beads; (x) BF and polystyrene; (Δ) BF and polyisoprene; (□) BF and sulfonated PIP.

themselves and when added in small amounts to the base ER suspension used above, results in an increased shear stress at similar fields over the non-sulfonated PIP, i.e. a total increase of about 55% over the base ER fluid. Studies on the effects of concentrations of the added particles are ongoing but incomplete, however they suggest a peak in this behavior at relatively low concentrations of added (non ER active) particles, somewhere around 1% or less. Numerous other studies involved adding small amounts of fibers of various aspect ratios to ER fluids. The results of these studies are not illustrated here because they were negative, i.e. small amounts of fibers did not systematically affect the behavior of ER fluids. It was hypothesized that the fibers would orient parallel to the plates and roll or spin along their minor axes, thus not significantly disrupting the flow. Platelets of mica however did show a small but significant increase in the stresses. This could be ascribed to the platelet nature which would disrupt flow more significantly than the fibers. However the particles with the greatest effect are consistently the softer or elastomeric particles. This observation is consistent irrespective of the ER fluid composition or the type of rubber particles.

The flow profiles (as previously illustrated and discussed) obtained for the specimens containing small amounts of added particles are illustrated in Figures 3 and 4 and suggest a possible explanation for the rheological behavior. Figure 3 shows a flow profile of an ER fluid containing 1% of PIP obtained in the parallel disc rheometer and Figure 4 shows a flow profile of an ER fluid also containing 1% PIP particles obtained in the concentric cylinder rheometer. Both cases

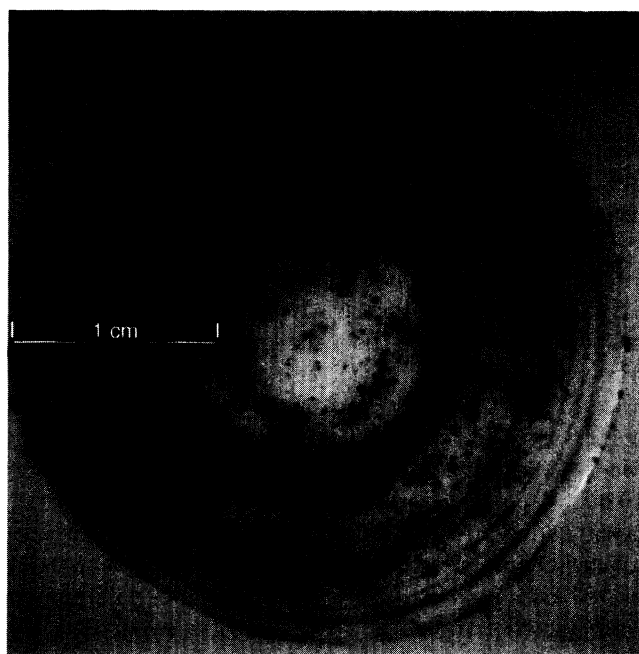


Figure 3. Flow profile observed for an ER fluid containing 1% of added polyisoprene particles between rotating discs at 180 rpm and under a field of 2kV/mm. The dark particles between the lamellae are the polyisoprene particles.

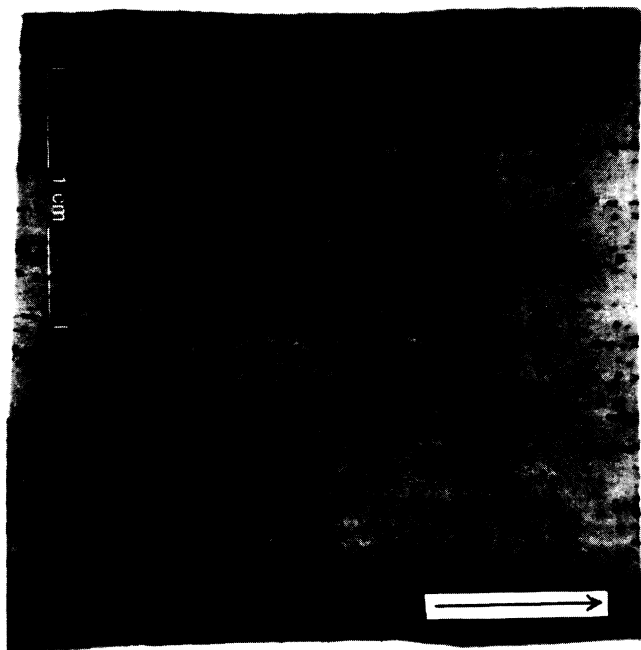


Figure 4. Flow profile observed for an ER fluid containing 1% of added polyisoprene particles between concentric cylinders at 180 rpm and under a field of 2kV/mm. The dark particles between the lamellae are the polyisoprene particles. Flow direction is from left to right as indicated by the arrow.

clearly show that the added PIP particles are all between the lamellae or rows of the primary ER particles. Apparently upon development of the lamellar flow profiles, the added particles are pushed out of or segregated from the lamellar formations and accumulate between them. If the lamellar structures were moving in phase with each other, then these particles between them would seem to make little difference in the shear stresses. However, if some of the structures were shearing with respect to each other, then the particles between them would hinder such shearing or make it more difficult. Other studies on this hypothesis are ongoing and the results seem perfectly consistent. However, what is as yet unexplained is why the elastomeric particles when present in small amounts are much more effective in increasing the shear stresses and why the rigid particles seem almost ineffective.

Active Matrix Liquids

ER active homogenous fluids include low MW thermotropic liquid crystalline materials as well as lyotropic polymeric solutions. As the matrix liquid in ER suspensions, these are limited to a few possibilities because of the high voltages to be applied, i.e., they must be essentially non-conducting. The material in these studies was poly(hexyl isocyanate) in xylene. Xylene has a very low conductivity and solutions as high as 30–35% are easily obtained which still have a relatively low viscosity, 1–5 Pa.s. at room temperature, $M_w = 74,000$. Further, this system has been shown to be ER active as a homogenous solution (Yang and

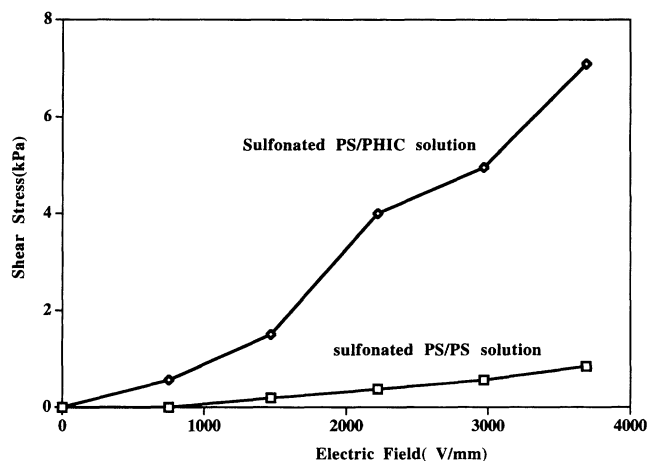


Figure 5. Shear stress vs. DC field at 1.8/sec for a sulfonated polystyrene (SPS) suspension in a PHIC/xylene solution (X), and in a polystyrene/xylene solution (O).

Shine, 1992). For purposes of ascertaining effects which may be attributable to the PHIC/xylene solution, all samples were made both in the PHIC solutions and as well in a polystyrene/xylene solution. The concentration of the polystyrene solution was adjusted so it had the same room temperature viscosity as the PHIC solution. However, the polystyrene solution was totally unaffected by the electric field and served as an inactive matrix fluid.

Figure 5 illustrates the measured shear stress at 1.8/sec for a PHIC/xylene solution, an ER fluid consisting of sulfonated polystyrene particles dispersed into the PHIC/xylene solution, and an ER fluid consisting of the sulfonated polystyrene particles dispersed into a polystyrene/xylene solution. No plot was made for the polystyrene solutions since they exhibited no ER activity as expected. Although it appears that the PHIC/xylene solution is not ER active, this is not the case but simply on this plot, the activity is very small compared to the suspensions. The apparent viscosity of the suspension of sulfonated polystyrene particles into the ER active PHIC/xylene solution is nearly 10 times greater than for the identical particles dispersed into the inert polystyrene/xylene solution. It noted that the PHIC solutions at 10% are significantly below the concentration for the spontaneous appearance of a mesophase, which is around 25–30% (Aharoni and Walsh, 1979). Data shows that the PHIC solutions are ER active at isotropic concentrations but as well are capable of inducing synergistic effects with particles in an ER fluid. It should be mentioned again that the polystyrene solutions showed neither an ER activity nor any effect on the activity of ER suspensions.

When viewed between crossed polarizers on a optical polarizing microscope as a function of electric field, the polystyrene solution showed no birefringence or orientation which of course is as expected. However, the PHIC solutions show a increasing birefringence with increasing E field up to a point where saturation or a constant birefringence is observed. Upon removing and reapplying the E field, there is

no indication that a mesophase or liquid crystalline phase is being induced and as such we describe this behavior as oriented isotropic. This is part of another ongoing study. What does seem clear however is that there is a significant ER activity associated with the E field induced orientation of the isotropic phase of the PHIC solutions as assessed by the birefringence measurements. This broadens the observations of Inoue and Maniwa (1995) which suggest that liquid crystalline domains must be present for ER activity.

Figure 5 further illustrates that the effect of the presence of the PHIC/xylene solutions as the matrix liquid in ER fluids, which are themselves ER active, are considerably greater than just the sum of the individual contributions. If simply a sum was observed, this would imply that the fluids thicken and as such would only increase the slope of the shear stress vs. shear rate data without significantly affecting the interparticulate interaction. However, the very large increases observed suggest an involvement over and above that of just acting to increase the viscosity of the matrix PHIC solutions.

Observations of the ER suspensions containing the PHIC solutions between crossed polarizers and under E fields show a greatly enhanced birefringence between the particles adjacent to points of contact. This suggests a greatly enhanced orientation of PHIC molecules in this region and probably an increased concentration as well. Such an enhanced birefringence is observed at every point of contact between the particles implying a mechanism for increasing interactions between the particles other than just in the field direction. We have observed this so far only between particles that form ER active suspensions, and never between particles that do not form ER active suspensions such as glass beads. The enhanced orientation and possibly increased concentration are a consequence of highly amplified electric fields at these points, i.e. in the first order the field strengths between successive dielectrics being inversely proportional to the permittivity, $\epsilon_1 E_1 = \epsilon_2 E_2$. This has been treated in detail (Conrad and Chen, 1995). That this occurs for metal particles is trivial but it also occurs for dielectric particles, the extent of which is proportional to the permittivity differences between the particles and the dispersing liquid. However, this effect might as well be expected to

occur for particles such as glass and polystyrene, but it does not. Thus, we expect a much greater field enhancement between the (ER active) particles due to the presence of mobile charge carriers on them, which have long been associated or suspected of being responsible for ER activity.

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