

Complex Properties and Composition of Electrorheological Fluids

F. E. FILISKO*

*Materials Science and Engineering, Macromolecular Science and Engineering,
The University of Michigan, Ann Arbor, MI 48109-2136*

S. HENLEY

Macromolecular Science and Engineering, The University of Michigan, Ann Arbor, MI 48109

G. QUIST

Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109

ABSTRACT: Various base ER fluid compositions are shown to have dramatically enhanced shear stresses when dispersed into poly(hexyl isocyanate)/xylene solutions as compared to being dispersed into polystyrene/xylene solutions. The concentration of the PHIC solutions was 4.5% which is well below that for liquid crystallinity. Further, the addition of small amounts (1–3%) of other particles to the suspensions show significant enhancement of the shear stresses for softer particles.

INTRODUCTION

ER fluids are most commonly described as suspensions of certain dielectric particles in a dielectric fluid which under an electric field (E) demonstrate a Bingham like behavior, i.e., solid behavior below a certain critical shear stress, T_c , 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 the observed buildup of a structure of particles between the electrodes apparently associated with the E field induced increased interactions between the particles. These induced interactions were initially associated with the ionic or dipolar polarization of the particles and related to the corresponding permittivity difference between the particles and the matrix liquid via a point dipole approach (Gast and Zukoski, 1989). This has, for the most part, been replaced by mechanisms associated with Maxwell-Wagner-Sillars interfacial polarization (Maxwell, 1892) resulting from mobile charge carriers restricted for the most part to the particles. The interactions are then related not only to the corresponding interfacial polarizations but also 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 focussed upon synthesis of particles containing mobile charge carriers. The best known of these are the polyacene quinones of Block (1988) which as intrinsic semiconductors, contain mobile electrons; the polymeric electrolytes of Bayer (Bloodworth and Wendt, 1995)

which presumably contain polyethylene oxide sequences in a copolymer which allow significant dissolution of inorganic salts, thus producing 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 are solid electrolytes and contain mobile ions as part of their chemistry (Breck, 1974); and certain (dry) polyelectrolytes where localized ion mobility has been proposed (Treasurer, Radzilowski and Filisko, 1991). Many other systems have been reported, of course, but if intrinsic they either fall broadly into one of the above categories or involve the addition of an activator such as water or a dopant. In any case, however diverse the types of particles used, the maximum strengths of the fluids remain around 3–5 kPa. Few would accept this as an insurmountable barrier but all agree that we do not understand why this limit exists. The basic science of the phenomenon is not well enough understood to allow theoreticians to make realistic predictions and experimentalists to design experiments to overcome or test them.

An alternate approach might be to explore aspects of these fluids which for the most part have been overlooked. One of these is the matrix fluid which has served 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 such as thermotropic liquid crystal fluids (Lacy et al., 1996; Inoue and Maniwa, 1995) or lyotropic liquid crystalline solutions, specifically solutions of LC polymers. Another area is that of the particles. Most types of fluids contain chemically one type of particle which are spherically symmetric and one av-

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*Author to whom correspondence should be addressed.

erage size. It is commonly observed that larger particles (100 microns) result in fluids of higher strengths than the most common ones of around 5 microns, the reasons being unknown. It was also first shown by Sillars (1937) that ellipsoidal particles produce much more intense loss peaks due to interfacial effects rather than spherical. Further, this dielectric dispersion has been related (Filisko and Schubring, 1996) to ER activity but a study for instance of ER activity vs. particle aspect ratio has not been done, one reason being the limited number of intrinsic materials which are also available in fibers of various aspect ratios. In this study we will report on some aspects of ongoing studies into exploring effects of matrix fluids and particle characteristics on properties of ER fluids.

EXPERIMENTAL

The poly(hexyl isocyanates) used were synthesized in our laboratories by procedures similar to but not identical with those reported by Shashoua et al. (1960) and Aharoni and Walsh (1979). They were, however, purified to remove low molecular material by successive solution and precipitations in toluene and methanol respectively. The xylene used was as received except it was always stored over molecular sieves. The 3A zeolites were obtained from UOP, dried at 400°C for 24 hours, quickly removed from the oven and allowed to cool in a vacuum dessicator (without dessicant) which was quickly pumped down and then isolated from the pump. When cool, the vacuum was quickly released with dry air and the liquid added immediately, taking care in mixing not to beat air into the fluid. The polystyrene used was as received from Polysciences, Inc. Concentrations of the polystyrene/xylene solutions were adjusted so that they had essentially the same zero field viscosity as the PHIC solutions. The 3A ER fluid contained 3 gms of powder to 10 ml of either PHIC/xylene solution or polystyrene/xylene solution.

The sulfonated polystyrene, poly(sodium 4-styrene sulfonate), was obtained directly from Aldrich Chemical as (approx. 14 micron) powder and dried at 120°C for 24 hours under vacuum. The material designated polyisoprene was obtained by thoroughly washing a latex surgical glove and

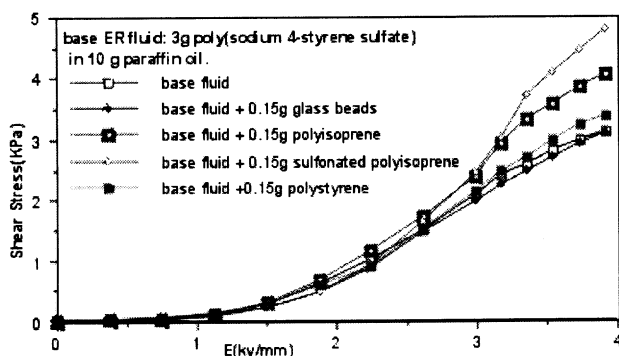


Figure 1. Effect of adding 5% of the solid content of various diverse particles to a sulfonated polystyrene ER fluid. Shear rate = 110/sec.

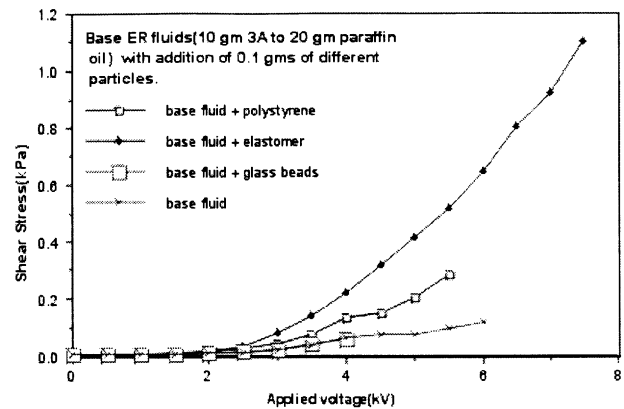


Figure 2. Effect of adding 1% of the solids content of various particles to a 3A/paraffin oil ER fluid suspension. Shear rate = 110/sec.

grinding it with a Retsch Model ZM-1 ultracentrifugal mill under liquid nitrogen to 40 micron or smaller particles. The material designated elastomer was a black test tube stopper which was ground also under liquid nitrogen in the mill. The ground samples were sieved through an 80 micron sieve although the screen used in the mill was for 40 micron powders. The powders were all subsequently dried for 24 hours at 120°C under vacuum. The sulfonated polyisoprene was obtained by exposing some of the above powder to 9M sulfuric acid at 80°C for 10 minutes followed by washing. It was then exposed to a 9M NaOH solution, washed, filtered, and dried at 120°C for 24 hours under vacuum.

Rheological measurements were made on a Weissenberg-Rheogoniometer especially modified for ER measurements, equipped with a couette cell, depth 25 mm, cup ID 27.3 mm, and 1.25 mm gap. Results illustrated in Figures 1 and 2 were obtained at angular speeds of 113 rev./min. or shear rates of 110/sec.

RESULTS

Addition of Small Amounts of Particles

Figure 1 illustrates the effect of adding small amounts (5% 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 or no effect on the properties of the base fluid. The addition of the same percentage of 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 amount of polystyrene particles due to their lower density. 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 4 kV/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 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.

Figure 2 illustrates a similar study involving addition of these particles to a different ER base fluid, i.e., 3A zeolite particles suspended into paraffin oil. The trends are similar but the relative magnitudes are much greater. The polystyrene particles result in an increase of nearly 300% in the shear stress over the base fluid, whereas the rubber particles result in an increase of nearly 600%. It should be noted that the overall strengths of the base fluids containing the sulfonated polystyrene particles are much stronger than those containing the 3A zeolites, even after the rubber particles are added.

Active Matrix Liquids

Possibilities for active matrix fluids include low MW thermotropic liquid crystalline materials as well as lyotropic polymeric solutions. Various constraints limit these to a few possibilities primarily because of the high voltages to be applied, i.e., they must be essentially non-conducting. The material we used for 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, i.e., no particles are necessary. Here we are exploring the effect of using these solutions as the matrix phase in suspensions of ER active particles, therefore not concentrating on the ER properties of the PHIC/xylene solutions which are considered elsewhere (Yang and Shine, 1992a,b). 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.

Figures 3(a) and 3(b) illustrate the shear stress vs. shear rate at 2.23 kV/mm and 3.73 kV/mm for a 4.5% PHIC/xylene solution, an ER fluid containing 3A zeolite particles dispersed into the PHIC/xylene solution, and the same concentration of 3A zeolite particles dispersed into a polystyrene/xylene solution of the same room temperature viscosity as the PHIC/xylene solution. The PHIC/xylene solution is

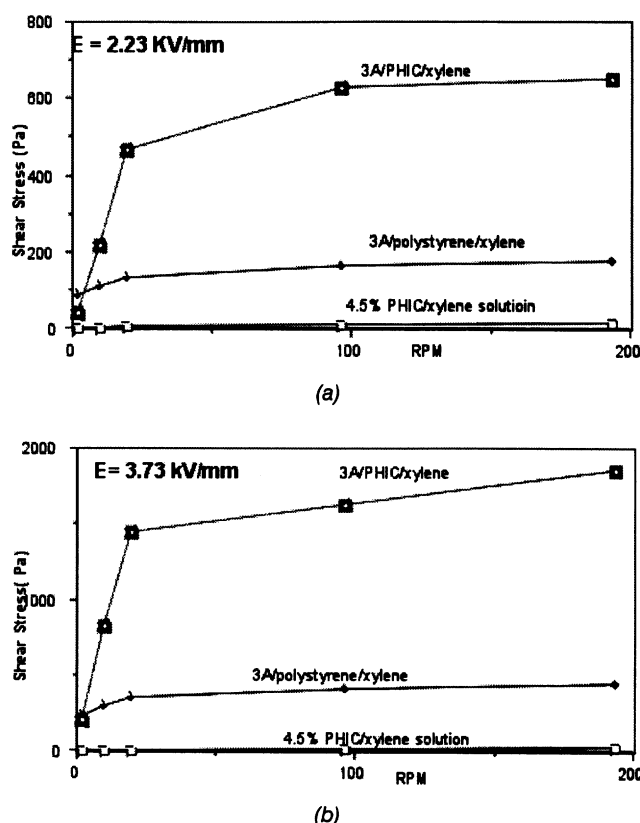


Figure 3. Shear stress vs. shear rate for a 4.5% PHIC/xylene solution and 3A zeolite based ER fluids in the PHIC/xylene solution and in a polystyrene/xylene solution at (a) 2.23 kV/mm and (b) 3.73 kV/mm.

ER active but much less so than the 3A zeolite suspension. It should be noted that the concentration of the PHIC solution (4.5%) is well below that for the onset of a mesophase which is 25–30%. This is intentional so the potential additional parameter of the presence of liquid crystalline domains may not complicate the observations or interpretations.

The PHIC/xylene solution, although ER active, is relatively weak with respect to both 3A suspensions. At 193/sec., the pure PHIC solution registers shear stresses of 15.7 and 24.5 Pa at fields of 2.23 and 3.73 kV/mm respectively, whereas the 3A/polystyrene/xylene ER fluid registers values of 178 and 449 Pa. Further the 3A/PHIC/xylene fluid registers stresses of 653 and 1859 Pa under the same conditions. If as might be expected in the simplest case, the field induced viscosity increases of the PHIC solutions simply added to the shear stress values for the 3A/PS solution ER fluids, then the net increase would be trivial, e.g., at 2.23 kV/mm from 178 to 193.7 Pa. However, the effect of the PHIC solution is much more significant, even with a low 4.5% concentration. Both figures are very similar to the behavior observed for ER fluids in other studies at shear rates above 100/sec for the 2.23 kV/mm curve and about 25/sec for the 3.73 kV/mm curve, i.e., the data are linear above these shear rates and the slopes are nearly independent of the field. These lines extrapolate to 0 shear rate to positive values of the shear stress. The major effect of the field is to shift the data up with field. At lower shear rates, the data at both fields do not continue to decrease

linearly but drop off much more rapidly, apparently approaching zero shear stress at zero shear rate. This deviation from the higher shear rate linear behavior begins at a lower shear rate (25/sec) at 3.73 kV/mm and at 100/sec for 2.23 kV/mm.

At both fields the 3A/PS/xylene ER fluids show standard behavior for ER fluids with shear rate. The slopes are very nearly the same as for the PHIC/xylene solution as expected since the PS/xylene solutions were mixed to have the same 0 field viscosity as the PHIC/xylene solutions. The stresses at 193/sec are 198 and 446 Pa at 2.23 and 3.73 kV/mm respectively, demonstrating the ER activity of these 3A/PS/xylene suspensions.

DISCUSSION

The data presented in Figures 1 and 2 are representative of a much greater number of studies beginning with the effect of adding particles of different shapes to ER fluids. The rationale for this study came from observations that ER strengths could be significantly enhanced by the addition of small amounts of larger and irregularly shaped particles. The initial study 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. In flow visualization studies it was observed 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.

At present we have no satisfactory explanation for these observations. We are exploring the possibility that selective migration of the minor particles toward the walls or internal slip planes, which develop in flow of ER fluids under field, may occur and increase the resistance to slip.

It is clear from Figures 3(a) and 3(b) 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

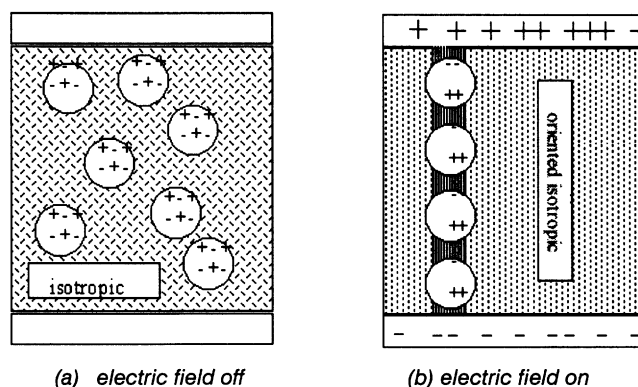


Figure 4. Illustration of a suspension of particles with mobile charge carriers dispersed into a PHIC/xylene solution (a) with 0 field applied, (b) with a field applied. Under field, the isotropic solution orients but a greatly enhanced birefringence is observed between the particles.

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. This is illustrated in Figure 4. 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 by Conrad (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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