

# Effect of mechanical abrasion in polar-molecular electrorheological fluids

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**Abstract.** Mechanical abrasion is a phenomenon which commonly occurs during the application of polar-molecular electrorheological (PMER) fluids. We experimentally investigate its effect by milling PMER particles for different times. We find that this effect can significantly reduce electrorheological effects of PMER fluids made of butyrolactone-modified TiO<sub>2</sub> particles. This reduction results from the reduced interaction between PMER particles due to the loss of polar molecules on the surface of TiO<sub>2</sub> particles. It is further revealed that adding proper amount of suitable polar molecules to the host fluid may compensate for the reduction of yield stress which can be about 100% at high electric fields.

**PACS.** 47.65.Gx Electrorheological fluids – 77.22.Ej Polarization and depolarization – 62.20.fg Shape-memory effect; yield stress; superelasticity

## 1 Introduction

An electrorheological (ER) fluid is a suspension containing dielectric particles in an insulating oil (host fluid). For such systems, reversible liquid-solid transitions happen in several milliseconds when an external electric field exceeds a certain critical value [1–13]. Such smart materials have potential applications in various fields [3–6]. From a theoretical point of view, the complete theory for conventional dielectric ER fluids was thoroughly reviewed in 2003 [9]. Most recently, from both experimental and theoretical perspectives, the structure and mechanism of ER fluids have been carefully reviewed [10].

Polar-molecular electrorheological (PMER) fluids belong to the family of ER fluids with dielectric particles modified with polar molecules [4,5,7]. In 2003, PMER fluids were first discovered experimentally by coating BaTiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> with NH<sub>2</sub>CONH<sub>2</sub> suspended in silicone oil [4]. In reference [5], the authors reported two kinds of PMER fluids by using TiO<sub>2</sub> nanoparticles coated with (NH<sub>2</sub>)<sub>2</sub>CO and Ca-Ti-O nanoparticles coated with C=O and O-H groups. We also experimentally obtained a different kind of PMER fluids by modifying TiO<sub>2</sub> particles with 1,4-butyrolactone molecules [7]. The yield stress of PMER fluids was reported to reach 130 kPa at electric field 5 kV/mm [4] or even more than 200 kPa at 4.5 kV/mm when the particle size was smaller [5]. So far, much theoretical analysis has been adopted to explain the giant yield

stress of PMER fluids. Generally, the interaction between induced charges and polar molecules adsorbed on particle surfaces becomes a key factor in understanding the giant PMER effect, as revealed by Lu et al. [5].

It is known that mechanical abrasion is a common phenomenon during the application of general ER fluids. This situation may become more severe for PMER fluids than dielectric ER ones because of the existence of polar molecules on particle surfaces in PMER fluids. In this study we shall experimentally investigate the effect of mechanical abrasion in PMER fluids. The abrasion effect is taken into account by milling dry PMER particles for different times because milling can lead to particle damage. As a result, ER effect is reduced accordingly due to the reduction of particle interaction caused by the loss of polar molecules on particle surfaces. To compensate for the reduction caused by mechanical abrasion, it is proposed to appropriately add an extra amount of polar molecules to the host fluid. The feasibility of the method will be shown accordingly.

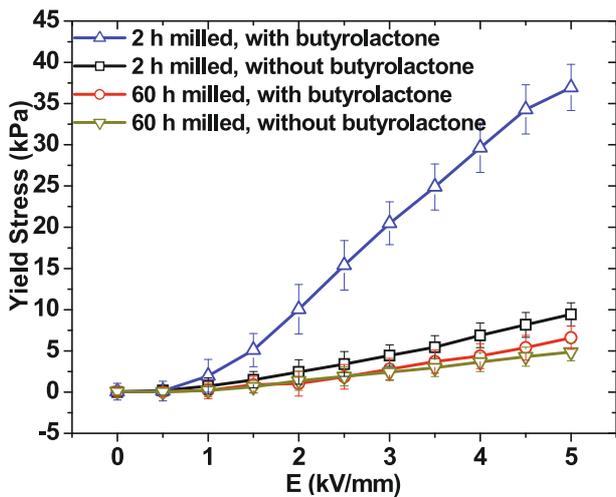
## 2 Experiments and results

### 2.1 Effect of different milling time: reduced yield stresses

Following the sol-gel method used in reference [7], we prepared butyrolactone-modified TiO<sub>2</sub> particles, and then milled the particle powder with a planet-ball mill. Several

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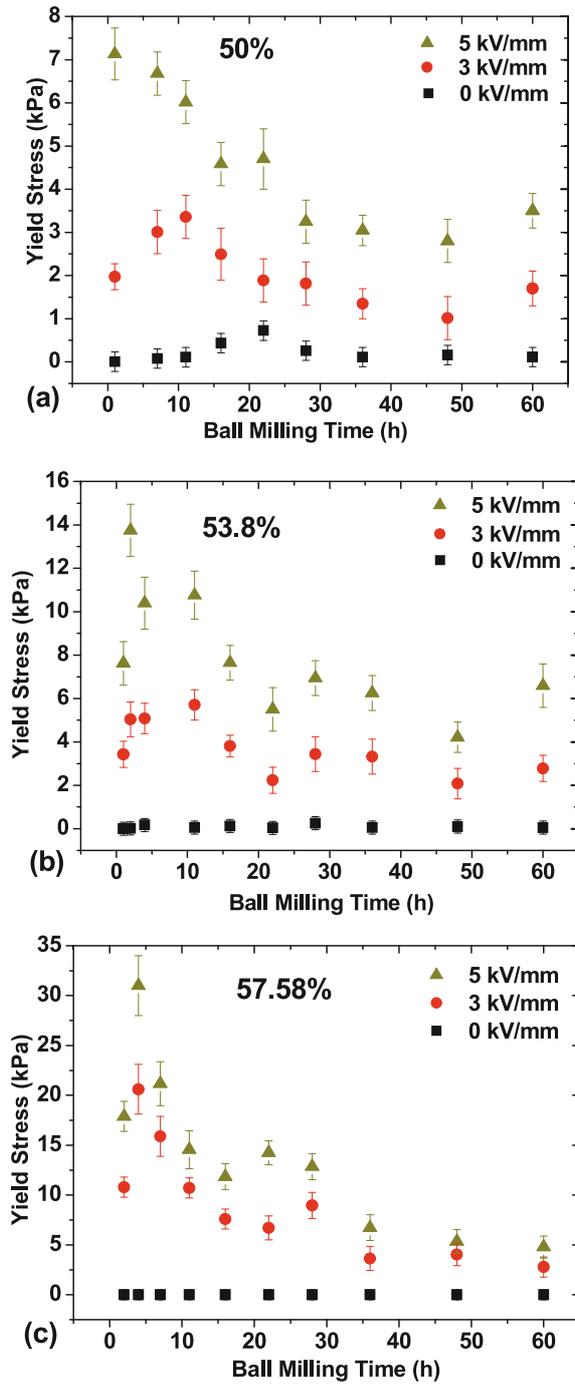
**Fig. 1.** (Color online) Yield stress of conventional ER fluids with pure  $\text{TiO}_2$  particles milled for 2 h ( $\square$ ) and 60 h ( $\nabla$ ), in comparison with that of PMER fluids with butyrolactone-modified  $\text{TiO}_2$  particles milled for 2 h ( $\Delta$ ) and 60 h ( $\circ$ ), respectively, as a function of external electric fields. The volume fraction of particles is 57.58%. The curves are drawn as a guide for the eye. Error bars are indicated in Figures 1–3.

sample powders were taken from the mill at specific time intervals ranging from 2 to 60 h, and then mixed with a host fluid (50 cSt silicone oil) so that we achieved various samples of PMER fluids. In our experiment, the diameter of particles after a short-time milling (e.g., 1–4 h) showed an evident decrease since the particle clusters were separated into fine  $\text{TiO}_2$  powders. However, the surface density of butyrolactone polar molecules was basically unchanged since the butyrolactone was homogeneously distributed in the body (not just on the surface) of the butyrolactone-modified  $\text{TiO}_2$  particles prepared with the sol-gel method. Nevertheless, longer milling time (for example from 7 to 60 h) did not cause any further change to the particle size (approximately 800–900 nm). Figure 1 shows the yield stresses of sample PMER fluids with different milling time and ingredients (volume fraction: 57.58%). The yield stress of the sample containing butyrolactone-modified and 60 h milled  $\text{TiO}_2$  particles is almost the same as that of the ER sample containing 60 h milled pure  $\text{TiO}_2$  particles, which means 60 h milling almost changed PMER particles into common dielectric ones as used in traditional ER fluids. The yield stresses of the two samples are both slightly lower than the yield stress of the sample containing 2 h milled pure  $\text{TiO}_2$  particles. The reason is that the particle size of the two former samples is about the same, but slightly smaller than that of the third sample. Since the three samples essentially belong to dielectric ER fluids, their yield stress is smaller when their particle size is smaller because of lower polarisation [9]. It is worth mentioning that in dielectric ER fluids polarisation of a particle is proportional to its volume. In contrast, the yield stress of PMER fluids can be increased when their particle size decreases [14]. This originates from the role of polar molecules.

Further, when a comparison of the two samples consisting of butyrolactone-modified  $\text{TiO}_2$  particles with different milling time of 2 h and 60 h was made, we find that a long-milling time (60 h) reduces yield stresses much more severely than a short milling time (2 h) in butyrolactone-modified particles. Owing to the role of the interaction between induced charges and polar molecules adsorbed on particle surfaces in PMER effects [5], we can safely conclude that the polar molecules (butyrolactone) on the surfaces were peeled off and volatilised during the long milling time. The results are carefully confirmed by Figure 2, which shows the yield stresses of the sample PMER fluids with different milling time and volume fractions. In general, according to Figure 2, we find that the yield stress increases with increasing electric fields and volume fractions, but decreases gradually with increasing milling time (despite some fluctuation of data). Such a decrease of yield stress can be explained as follows: when particles suffer from abrasion, both  $\text{TiO}_2$  and butyrolactone molecules are peeled off from the particle surfaces, and the butyrolactone as an organic compound will be volatilised when it is heated due to the abrasion. The  $\text{TiO}_2$  possibly remained as a sediment covering particle surfaces, which led to less polar molecules showing up on the surfaces. The loss of surface polar molecules leads to weakened interaction between particles, thus resulting in the reduction of yield stress. As mentioned above, particles were obtained by milling the dried powder prepared with the sol-gel method [7]. If the milling time is too short (for example less than 1 h), the clumps of particles are not yet separated into fine powders and the particle size can be too large to yield a high yield stress of PMER fluids [14]. On the other hand, long milling time can reduce too many polar molecules. Thus, an optimal milling time of 2–4 h for particle disagglomeration may lead to the best performance as indicated by the peaks in Figure 2.

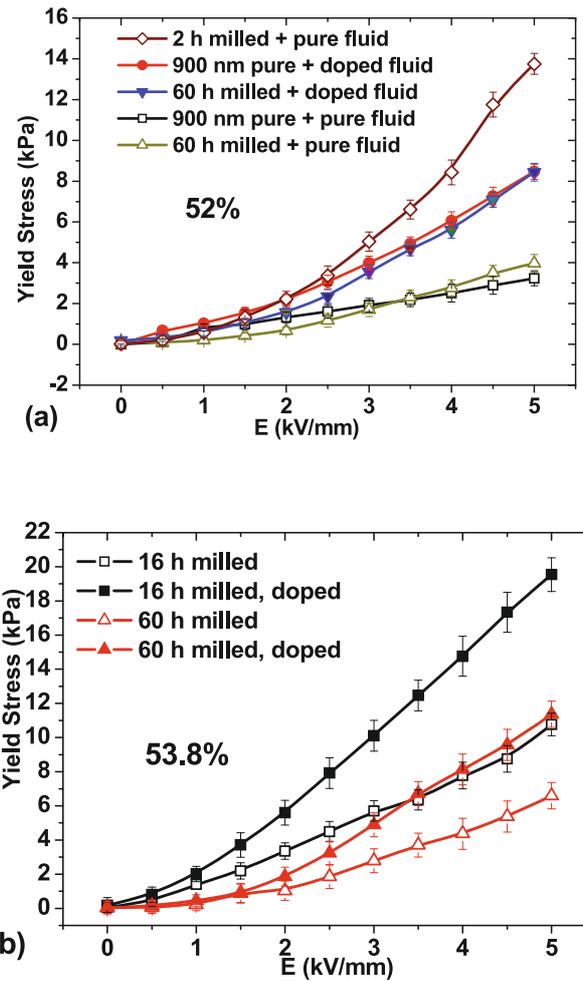
## 2.2 Effect of host fluids doped with polar molecules: enhanced yield stresses

Now we are in a position to propose a method to overcome the problem of milling-destruction by directly adding extra polar molecules into the host fluids. Using the ER fluids consisting of pure  $\text{TiO}_2$  particles with 45 nm in diameter, we have investigated the effect of adding various kinds of extra polar molecules into the systems. The tentative polar molecules were 1,4-butyrolactone [15], oleic acid, triethylamine, and isopropanolamine. The particle volume fractions in these cases are roughly 46%. As a result, adding 1,4-butyrolactone caused an electric breakdown even at low electric fields, adding oleic acid or triethylamine showed no evident enhancement in yield stresses, and only samples with added isopropanolamine had a yield-stress enhancement without electric breakdown even in a field as high as 5 kV/mm. Thus, we choose isopropanolamine as extra polar molecules in the following analysis. Incidentally the length of an isopropanolamine molecule is 0.4 nm, and its dipole moment is 2.57 Debye.



**Fig. 2.** (Color online) Yield stress of PMER samples as a function of milling time, for three external electric fields (0, 3, and 5 kV/mm) at different volume fractions of solid particles: (a) 50%, (b) 53.8%, and (c) 57.58%.

For our purpose, the suitable extra polar molecules should be those (for example isopropanolamine) with low conductivities, small sizes, and high dipole moments. Here low conductivities can be used to avoid an electric breakdown of the system in the presence of high electric fields. Owing to the requirement of minimising free energy in the whole system, polar molecules prefer to stay in a place



**Fig. 3.** (Color online) Yield stresses versus external electric fields for ER samples with volume fraction (a) 52% and (b) 53.8%. The enhancement of yield stress for each sample (except for the sample with particles milled for 2 h) is achieved by adding isopropanolamine to the host fluid with concentration of 1.1%. The symbols are explained in the text. These curves are drawn as a guide for the eye.

with a higher electric field, such as the surface between two particles. When induced charges attract added polar molecules, the molecules act as if they were absorbed on the particles with the induced charges. If polar molecules are smaller, more polar molecules can be located in the finite gap between particles. This can increase the density of local polar molecules and therefore the effective area of interaction [5] between suspended particles, thus yielding a stronger interaction between induced charges on one particle and polar molecules on the other. This can then strengthen particle interactions, resulting in an overall higher yield stress. Similarly, if the dipole moment of polar molecules is higher, each molecule can achieve stronger interactions with induced charges, and then particle interactions under electric fields can become stronger accordingly.

Figures 3a, 3b show the effect of the host fluid doped with added isopropanolamine molecules on yield stresses.

There are five PMER samples in Figure 3a: butyrolactone-modified TiO<sub>2</sub> particles milled for 2 h and mixed with un-doped host fluids ( $\diamond$ ), the same particles milled for 60 h and mixed with doped ( $\blacktriangledown$ ) and un-doped ( $\Delta$ ) host fluids, and pure TiO<sub>2</sub> particles mixed with doped ( $\bullet$ ) and un-doped ( $\square$ ) host fluids. The two samples with doped host fluids show almost the same enhanced ER behavior in the whole range of external electric fields of interest. As already shown in Figure 1, the ER fluid in which butyrolactone-modified TiO<sub>2</sub> particles were milled for 60 h has very low yield stress, which is similar to that of the ER fluid containing pure TiO<sub>2</sub> particles in pure silicone oil. This indicates that the polar molecules adsorbed on the particle surfaces were exhausted after a long milling time. Interestingly, Figures 3a, 3b convincingly demonstrates that adding proper amounts of extra polar molecules to the host fluid may indeed enhance yield stresses not only for pure TiO<sub>2</sub> particles, but also for the long-time milled samples as a compensation for the loss of polar molecules during mechanical abrasion. More relevant results are displayed in Figure 3b where the yield stresses of four samples are depicted, namely, butyrolactone-modified TiO<sub>2</sub> particles milled for 16 h and mixed with un-doped ( $\square$ ) and isopropanolamine-doped ( $\blacksquare$ ) host fluids, and the same particles milled for 60 h and mixed with undoped ( $\Delta$ ) or isopropanolamine-doped ( $\blacktriangle$ ) host fluids. The original component and structure of PMER fluids which consists of particles milled for different time are the same. Taking a sample of the PMER fluid which consists of butyrolactone-modified TiO<sub>2</sub> particles milled for 60 h in the isopropanolamine-doped host fluid, the enhancement of yield stresses will be as much as 4–5.5 kPa at 5 kV/mm, which corresponds to an enhancement ratio of 73–99% as shown in both Figures 3a and 3b. The enhancement ratio is defined as the ratio of yield stress for the ER fluid with doped silicone oil to that for the ER fluid with pure silicone oil.

It is worth mentioning that if one compares the yield stresses obtained with the 60 h milled particles in the doped silicon oil ( $\blacktriangledown$  in Fig. 3a) and the un-worn particles in the pure silicon oil (2 h-milled particles,  $\diamond$  in Fig. 3a), the yield-stress reduction induced by milling can be partially compensated upon doping the host fluid with a proper amount of extra polar molecules. In a word, we may safely conclude that, properly adding polar molecules to host fluids can enhance yield stresses of either ER fluids with pure TiO<sub>2</sub> particles or PMER fluids with different abraded particles. However, as shown by Figure 3a, the yield stress of the sample containing butyrolactone-modified particles milled for 60 h in the doped host fluid is still lower than that of the sample consisting of the same particles but only milled for 2 h. This means that the overmuch reduction can only be partially compensated. The underlying mechanism lies in polar-molecule-enhanced interactions between suspended particles, as addressed above [5].

### 3 Conclusions

We have shown that the mechanical abrasion can significantly reduce ER effects of PMER fluids made of butyrolactone-modified TiO<sub>2</sub> particles. This results from reduced interactions between PMER particles due to the loss of polar molecules on particle surfaces. To partially compensate for such reduction of yield stress, one may use a host fluid doped with proper amounts of extra polar molecules with low conductivities, small sizes, and high dipole moments. This may owe enhancing particle interactions to the extra polar molecules adsorbed on particle surfaces. The enhancement ratio can be about 100% at high electric fields.

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15. Here the “1,4-butyrolactone” means the additional one. On the other hand, the small amount of 1,4-butyrolactone molecules peeled off due to milling (except for those evaporated) can be freely suspended in the PMER system as well. However, our experiment already implies that this amount has no evident role on the enhancement of yield stress, see the experimental data represented by circles in Figure 1