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Strain-hardening in the oscillatory shear deformation of a dedoped polyaniline electrorheological fluid

Piyanoot Hiamtup · Anuvat Sirivat · Alexander M. Jamieson

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Abstract An electrorheological (ER) fluid, consisting of polydisperse dedoped polyaniline (PANI) particles, having irregular shapes, dispersed in silicone oil, was subjected to cyclic strain annealing treatments using oscillatory shear, under an external electric field. After each annealing period, the sample was subjected to a controlled-strain sweep, to determine the yield stress, and to erase the ER structure. During each annealing cycle, the storage modulus and the yield stress were observed to increase, and the loss modulus to decrease, each eventually approaching an asymptotic constant value. These observations in oscillatory shear complement our previous observations of a strain-hardening effect in a PANI/silicone oil ER fluid subjected to unidirectional creep tests.

Introduction

Electrorheological (ER) fluids typically consist of dielectric particles dispersed in an insulating fluid. Application of an electric field polarizes the particles, driving them to aggregate into fibrillar structures, spanning the distance between the electrodes [1]. This typically results in a transformation from a Newtonian liquid into a Bingham plastic solid. The resulting change in viscoelastic properties has been utilized in applications such as shock absorbers, clutches, brakes, actuators, artificial joints, and robotic controls [2–5]. In such applications, key factors are, first, that the strength of the ER structures be sufficiently high and, second, that the formation and dissipation of the ER structures be fully reversible. Viscoelastic measurements are fundamentally useful in exploring the relationship between ER properties and the ER structures [6–9]. Polyaniline (PANI) is a conducting polymer which has been used to form the dispersed particles in an ER fluid, due to its ease of synthesis and conductivity control, good thermal and environmental stability [10]. Its viscoelastic properties have been explored in terms of its yield stress [10, 11], as well as the oscillatory shear moduli and steady shear viscosity [12–14]. Recently, we investigated the viscoelastic behavior of a PANI/silicone oil ER fluid through the liquid–solid transition driven by increase of the electric field strength [14]. The transition was observed to occur at a critical electric field strength, in the range $E_c =$ 50–200 V/mm, whose value depends on particle concentration and host fluid viscosity. When the field was switched off we found that a residual structure remained, with a yield stress smaller than that in the presence of the field, but which increased with the strength of the applied field and particle concentration. When the applied stress exceeds the yield stress of the residual structure [14], fast, fully reversible switching of the ER response is obtained. In addition, in controlled-strain, oscillatory shear, the relationship between the G'–G'' crossover frequency, ω_c, and the electric field strength was investigated as a function of matrix viscosity and shear strain [15]. We found that ω_c increased with increasing field strength, and decreased with increase of matrix viscosity and strain amplitude. These observations reflect the dynamic character of the particles within the field-generated fibrillar aggregates, and are in qualitative agreement with a theoretical model [16, 17],

P. Hiamtup · A. Sirivat (✉)
The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
e-mail: anuvat.s@chula.ac.th

A. M. Jamieson
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

which relates the relaxation mechanism to the competition between hydrodynamic and electrostatic forces between PANI particles within the fibrillar structures.

This note is prompted by recent reports that the strength of ER structures in a model ER fluid, consisting of 2.5 μm silica spheres dispersed in silicon oil, can be enhanced by a shear-annealing method [18, 19]. These studies observed that the yield stress of the ER fluid could be increased by application of sequential creep recovery cycles under the external electric field. For a specified number of cycles, the magnitude of the enhancement increased with increase in applied stress level up to the yield point of the unstressed fluid; for a specified applied stress level, the magnitude of the enhancement increased up to a maximum enhancement [18, 19]. The authors infer that shear-annealing process enables the particles in the ER fluid to form better aligned and denser columns, leading to the increased yield stress. Recently, we carried out creep experiments on a PANI/silicone oil ER fluid, in which an apparent discrete increase in the equilibrium compliance was observed at a critical applied stress, σ_c, in the preyield region [20]. Measurements of the yield stress after the sample was annealed at stresses levels above σ_c support the interpretation that this effect is due to a strain-hardening effect.

The above experiments were performed under controlled-stress conditions, and it is of interest to establish that a similar strain-hardening phenomenon is present in controlled-strain oscillatory shear. Here, we report evidence indicating that a shear-enhanced yield stress indeed occurs in the PANI/silicone oil ER fluid, following cyclic oscillatory shear-annealing treatment, each cycle involving, first, the application of oscillatory strain in the presence of an electric field for a specified annealing time, and, subsequently, destruction of the ER structure by a strain sweep experiment from which the yield strain was measured.

Materials and methods

Materials

Aniline, C_6H_7N (AR grade, Merck) was vacuum-distilled and used as the monomer. Ammonium peroxydisulphate, $(NH_4)_2S_2O_8$ (AR grade, Merck) was used as the oxidant and 38% Hydrochloric acid, HCl (AR grade, Labscan); 25% solution of ammonia, NH_4OH (Ar grade, Merck), and methanol, CH_3OH (AR grade, Labscan) were used as received. The base fluid, a silicone oil (AR grade, Dow Corning) with density 0.96 g/cm^3 and kinematic viscosity of 100 cSt was vacuum-dried and stored in a desiccators prior to use.

Polymerization procedure

PANI was synthesized via an oxidative coupling polymerization according to the method of Cao et al. [21]. After the course of polymerization, the precipitate was then dedoped by immersion in 3% NH_4OH in order to adjust its conductivity, before being vacuum-dried and passed through a 38-μm sieve shaker to control the particle size and its distribution. Extensive characterization of PANI specimens subjected to this dedoping treatment has been reported in prior publications [14, 15, 20]. The resulting PANI particles have irregular shapes and exhibit a range of particles sizes with mean diameter 23.5 μm, and standard deviation 2.37 μm [14]. The electrical conductivity was determined to be 2.93×10^{-9} S/cm. PANI of low conductivity was chosen in order to be able to investigate ER behavior at high-electric field strength without current leakage in the system.

Preparation of ER fluids

Prior to mixing in silicone oil, PANI powder was dried for 2 days at room temperature to remove moisture in a vacuum oven at room temperature. The particles were then dispersed in the silicone oil with an ultrasonicator for 30 min at 25 °C. The PANI suspensions were then prepared at a volume fraction of 0.05. The suspensions were stored in a desiccator and redispersed by ultrasonification for a period of 10 min at 25 °C before each experiment.

Rheological measurements

As in our previous studies of PANI fluids [14, 15, 20], the viscoelastic properties of the blends were investigated using a modified melt rheometer (ARES, Rheometric Scientific Inc.) with parallel plates (diameter of 25 mm) attached via insulating spacers to the transducer and motor. A DC electric field was applied across the gap between the plates by a function generator (GFG-8216A, Instek) and a high-voltage amplifier (Model 609E-6, Trek). The system parameters (volume fraction, field strength, and conductivity level) were selected so that we could monitor the crossover from linear to nonlinear viscoelastic behavior, and ensure that the yield strain occurred in the experimentally accessible range.

Results and discussion

Initially, a strain sweep experiment was performed on the PANI/silicone oil ER fluid (concentration = 5 vol%), at 298 K in the presence of an electric field of $E = 1000$ V/mm to assess the yield stress of the as-formed ER structure.

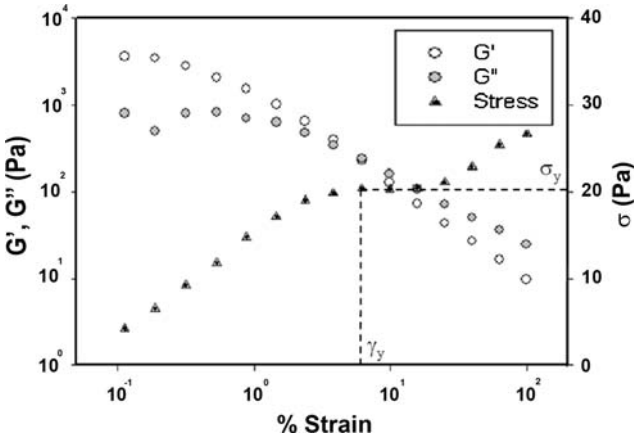

Fig. 1 Strain dependence of G', G'', and shear stress for PANI/silicone oil ER fluid (concentration = 5 vol%) at temperature of 298 K in the presence of an electric field of $E = 1000$ V/mm. Gap = 0.2 mm

Oscillatory strain (frequency $\omega = 1$ rad/s) was increased from 0.1 to 1000%. Values of the storage and loss moduli, (G' and G''), and the shear stress developed were recorded and are plotted in Fig. 1. Evidently, the shear stress increases uniformly with increasing strain, and shows an inflection between strain values of 6–15%, after which it continues to increase. The inflection encompasses the strain where the G'–G'' crossover occurs, indicating a transition from predominantly elastic to predominantly viscous behavior. We may define the onset of the inflection point in shear stress, as shown by broken lines in Fig. 1, as the yield point, and hence determine the yield stress, $\sigma_y = 20.4$ Pa, and yield strain, $\gamma_y = 6.2\%$.

It is of interest to compare our results with prior experimental and theoretical large-amplitude oscillatory shear (LAOS) results in the literature. Ahn and coworkers [22, 23] have investigated the LAOS response of diverse polymeric fluids and distinguish four types of behavior at the crossover from linear to nonlinear viscoelasticity: type I, strain thinning (G', G'' decreasing); type II, strain-hardening (G', G'' increasing); type III, weak strain overshoot (G' decreasing, G'' increasing followed by decreasing); type IV, strong strain overshoot (G', G'' increasing followed by decreasing). As noted by Ahn and coworkers [22, 23], previous ER experiments by Parthasarathy and Klingenberg [24] on a suspension of acid alumina particles in poly(dimethylsiloxane) exhibit type III behavior at low values of the scaled oscillation frequency $\tilde{\omega} = \omega/E^2$, evolving toward type I behavior at higher values of $\tilde{\omega}$. Our ER results, shown in Fig. 1, indicate type I behavior. We note that several features of our results are quite consistent with both the experimental data of Parthasarathy and Klingenberg, as well as their accompanying particle dynamic simulations of the LAOS ER experiments [24]. Specifically, the onset of nonlinear viscoelasticity occurs at a very small critical strain $\gamma_1^{\text{crit}} \sim 10^{-3}$; second, the G'–G'' crossover corresponds to a transition from nonlinear viscoelasticity to viscoplastic deformation, and occurs at a second critical strain, γ_2^{crit} when $G'(\gamma_2^{\text{crit}}, \omega)/G'(\gamma \to 0, \omega) = 0.1$; third, in the viscoplastic regime, power-law strain dependence of G' and G'' is observed, with exponents of the order -1.0 for G' and -0.8 for G'' at small $\tilde{\omega}$. Ahn and coworkers [22, 23] do not discuss the strain dependence of the stress in LAOS experiments. Typically, in type I systems, the stress will increase strongly in the linear viscoelastic regime ($\sigma \sim \gamma$, up to the onset of nonlinearity, and then increase more slowly thereafter; in type II, systems, the stress will increase linearly and then more strongly in the nonlinear regime; in type III, the stress response typically shows an increase with strain up to the point where strong shear thinning ensues and then the stress exhibits a maximum and subsequently decreases. In type IV, the variation in stress with strain should be similar to that in type III, except that a broader maximum may be observed. Parthasarathy and Klingenberg also [24] do not discuss the evolution of stress with strain in their paper, but an approximate estimation of the total stress, σ, from their published $G'(\omega)$ and $G''(\omega)$ data, using the equation $\sigma = \gamma(G' \sin \omega t + G'' \cos \omega t)$, indicates the stress exhibits typical type I behavior, i.e., it increases linearly up to the onset of nonlinearity and then increases more slowly thereafter. Thus, the presence of a distinct inflection in the strain dependence of σ in an ostensibly type I fluid (Fig. 1) appears to be novel, but not unexpected in view of the above discussion, i.e., it is a behavior intermediate between that of Types 1 and III.

Based on results of the strain-sweep experiment, we chose to perform oscillatory shear annealing using a fixed strain amplitude $\gamma = 1\%$, substantially below the yield strain, and to limit the shear sweep experiments to the range 0.1–100% strain, sufficient to determine the yield strain and ensure the destruction of the ER structure between each run. First, the electric field was turned off and the sample was subjected to steady shear at 300 s^{-1} for 90 min in order to destroy all ER structures. Following this, in the absence of shear, the electric field was turned on again and maintained for 10 min, after which the yield stress was determined by a strain sweep test (test #1, $\gamma = 0.1$–100%). Subsequently, oscillatory shear-annealing cycles were performed, each of which involved application of oscillatory shear ($\gamma = 1\%$, $\omega = 1$ rad/s) for a specified time period, followed by a strain sweep to determine the yield stress of the annealed sample. For the first three cycles, the following protocol was utilized:

1. Oscillatory shear for 100 s, followed by a strain sweep test (test #2).
2. Oscillatory shear for 200 s, followed by a strain sweep test (test #3).

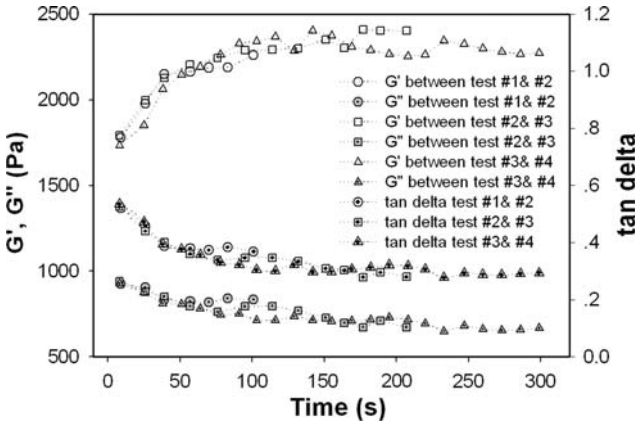

Fig. 2 Time dependences of G', G'', and tan δ for PANI/silicone oil ER fluid (concentration = 5 vol%) at temperature of 298 K in the presence of an electric field of $E = 1000$ V/mm. Gap = 0.2 mm

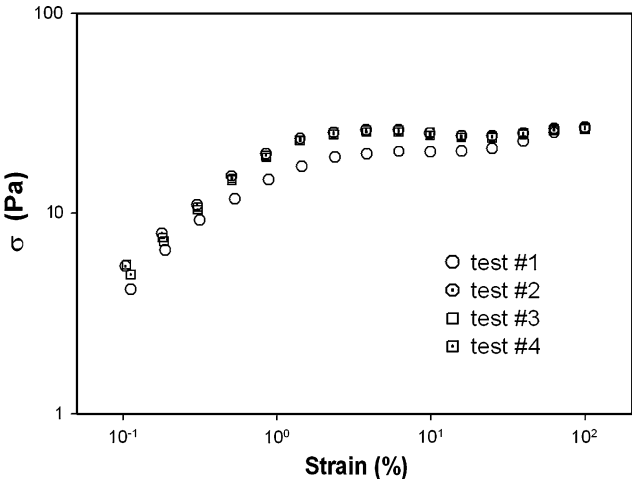

Fig. 3 Strain dependence of shear stress for PANI/silicone oil ER fluid (concentration = 5 vol%) at temperature of 298 K in the presence of an electric field of $E = 1000$ V/mm. Gap = 0.2 mm

3. Oscillatory shear for 300 s, followed by a strain sweep test (test #4).

All subsequent cycles involved shear annealing for 300 s followed by strain sweep tests (tests #5–10).

In Fig. 2, we show the variation in G', G'', and tan $\delta = G''/G'$ during the first three annealing periods. First, we note that the initial G' and G'' values, prior to annealing, are the same within experimental error, for all three runs, indicating that the shear-induced ER structure is completely erased during the prior strain sweep test. Second, we see that the value of G' increases, and that of G'' decreases, to an asymptotic value during the annealing period. It follows, as also shown in Fig. 2, that tan δ decreases from an initial value of ~ 0.5 to a value ~ 0.3. This is clear indication that oscillatory shear results in strain-hardening of the ER structure. Inspection of Fig. 2 further indicates that the increase in modulus is substantially complete after 100 s annealing and fully complete after 200 s. As additional support, in Fig. 3, we compare the results of strain sweep tests performed on the unannealed ER fluid (test #1) versus those performed after the first three annealing treatments (tests #2, #3, and #4). Clearly the yield stress, measured as the low-frequency maximum value in the shear stress, increases substantially in the annealed samples. It is also evident that there is no substantive difference in the magnitude of σ_y and γ_y among the first three annealing runs. These results point to a strain-hardening effect, which is presumed analogous to the stress-enhanced increase of the yield stress reported in a silica ER fluid by Tam and coworkers [18, 19] and in the PANI fluid by Hiamtup et al. [20]. It is noted that, whereas the ER fluid studied by Tam and coworkers consisted of spherical silica particles, relatively uniform in size (mean diameter = 2.5 ± 0.1 μm), the present PANI suspension has highly irregular particles with a relatively broad distribution in size (mean diameter = 23.5 ± 2.37 μm) [14].

As pointed out by Tam and coworkers [18, 19], on application of the electric field, the columnar structures formed may be viewed as metastable structures, with many defects. The application of shear strain may remove such defects via slippage and restructuring, leading to mechanically stronger columns. In addition, analysis of the crystalline organization of the columnar structures induced by the electric field [21, 25–27], suggests that deformation may transform the crystal structure from some lower energy structure to a different stronger one; e.g., face-centered or body-centered tetragonal may transform to a hexagonal close-packed lattice. Finally, it has been suggested that, after deformation, the ER structure may consist not only chains of particle columns spanning the electrode gap along the field direction (primary chains), but may also have secondary structures, short tilted chains which interconnect the primary chains, and which strengthen the ER structure [28]. In the case of the PANI ER fluid, the irregular, highly polydisperse nature of the PANI particles appears to preclude the formation of an ordered lattice-like structure. However, clearly strain-hardening can still take place, presumably via rearrangement of the PANI particles within the fibrils, to form a denser, mechanically stronger organization.

After the first three annealing cycles, we observed that the initial stress value after the prior stress sweep systematically decreases slightly in each subsequent test run. One still observes an increase in storage modulus during the oscillatory strain annealing steps, i.e., strain-hardening still takes place in each test run, but the final value of G' (and the subsequent yield stress) decreases slightly, in parallel with the decrease in initial stress. Table 1, summarizes the

Table 1 Yield strains and yield stresses after annealing cycles

Run number	Yield strain (%)	Yield stress (Pa)	$\frac{\text{Yield stress}}{\text{Initial stress}}$
1	6.18	20.4	7.1
2	6.16	26.2	7.6
3	6.15	26.1	8.1
4	6.16	25.5	8.2
5	6.17	24.7	6.5
6	6.17	24.1	7.1
7	6.17	24.0	7.0
8	6.17	22.8	7.2
9	6.19	22.7	7.2
10	6.19	20.0	11.2

values of σ_y and γ_y, determined after all ten test runs, and also lists the ratio of the yield stress to the initial stress. The latter ratio illustrates that strain-hardening in the form of an increased yield stress occurs in each run. Evidently some irreversible change in ER properties has developed (mechanical fatigue, or agglomeration and sedimentation of the PANI particles, which form only a marginally stable dispersion in silicone oil) [14].

Conclusion

Strain-hardening is demonstrated in a PANI-based ER fluid using a shear-annealing cycles under oscillatory strain. Thus, during application of oscillatory strain at a frequency of 1 rad/s and strain amplitude 1%, substantially smaller than the yield strain ($\gamma_y = 6.2\%$), the storage modulus G' is observed to increase with annealing time, and tan δ to decrease, each reaching a constant value after approximately 150 s. Likewise, the yield stress σ_y, measured via strain sweep tests after each of the first three annealing cycles, increases substantially over the unannealed specimen. Strain-hardening was also manifested in the strain sweep tests as an increase in stress beyond the yield point. During subsequent annealing cycles, strain-hardening continues to be observed, but the initial value of the storage modulus and the resulting yield stress are each observed to decrease slightly, attributed to agglomeration and sedimentation of the marginally stable PANI particles.

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