CHAPTER VII

STRAIN-HARDENING IN THE OSCILLATORY SHEAR DEFORMATION OF A POLYANILINE ELECTRORHEOLOGICAL FLUID

7.1 Abstract

An electrorhological (ER) fluid, consisting of polydisperse polyaniline (PANI) particles, having irregular shapes, dispersed in a silicone oil, was subjected to cyclic strain annealing treatments under an external electric field, involving application of oscillatory shear (strain γ = 1%, deformation frequency ω = 1 rad/s) for sequential time periods of increasing duration, during which the storage and loss moduli were monitored. After each annealing period, the sample was subjected to a controlled strain sweep, to determine the yield stress, and erase the ER structure. During each annealing period, the storage modulus was observed to increase, and the loss modulus to decrease, each eventually approaching an asymptotic constant value. The yield stress was also observed to increase following each annealing period. These observations seem consistent with literature reports of shear-enhanced yield stress in a model ER fluid using sequential creep-recovery cycles. After three annealing cycles, a gradual decrease in the initial storage modulus, following each prior strain sweep was observed, apparently reflecting some irreversible change in ER properties (e.g. agglomeration and sedimentation of the marginally-stable PANI particles).

KEYWORDS: Electrorheology, Creep, Conductive polymer, Polyaniline

6.2 Introduction

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 (Winslow, 1949). 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 (Bohon and Krause, 1998, Papadopoulos, 1998, Akella and Cutkosky, 1995, Choi *et al.*, 1998). 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 (Otsubo and Edamura, 1994, Choi *et al.*, 1999, Hao, 2002, Chotpattananont *et al.*, 2006). Polyaniline 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 (Gow and Zukoski, 1990). Its viscoelastic properties have been explored in terms of its yield stress (Gow and Zukoski, 1990, Gozdalik *et al.*, 2000), as well as the oscillatory shear moduli and steady shear viscosity (Jang *et al.*, 2001, Cho *et al.*, 2004, Hiamtup *et al.*, 2006). Recently, we explored the viscoelastic behavior of a PANI/silicone oil ER fluid through the liquid-solid transition driven by increase of the electric field strength (Hiamtup *et al.*, 2006). 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 (Hiamtup *et al.*, 2006), fast, fully reversible switching of the ER response is obtained.

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 (Lau *et al.*, 2003, Shi *et al.*, 2006). 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 (Lau *et al.*, 2003, Shi *et al.*, 2006). The authors infer that shear annealing 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 pre-yield region (Hiamtup *et al.*, 2007). 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.

Here, we report evidence supporting a similar shear-enhanced yield stress 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.

7.3 Experimental

7.3.1 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. 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 desiccator prior to use.

7.3.2 Polymerization Procedure

PANI was synthesized via an oxidative coupling polymerization according to the method of Cao *et al.* (1989). 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. It should be noted that after this treatment, the PANI particles have irregular shapes and exhibit a range of particles sizes with mean diameter 23.5 μm, and standard deviation 2.37 μm (Hiamtup et al., 2006).

7.3.3 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 minutes at 25 ^{o}C. The PANI suspensions were then prepared at a volume fraction of 0.05. The suspensions were stored in a dessiccator and redispersed by ultrasonification for a period of 10 minutes at 25 ^{0}C before each experiment.

7.3.4 Rheological Measurements

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).

7.4 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. Oscillatory strain (frequency ω = 1 rad/s) was increased from 0.1-1000%. Values of the storage and loss moduli, (G' and G"), and the shear stress developed were recorded and are plotted in Figure 7.1. 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 breakdown of the field-induced fibrillar structure. From the location of the inflection point in shear stress, as shown by broken lines in Fig. 7.1, we can determine the yield stress, σ_y = 20.4 Pa, and yield strain, γ_y = 6.2%. Based on this experiment, we chose to perform the shear annealing process using a fixed shear amplitude γ = 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.

Next, the electric field was turned off and the sample was subjected to steady shear at 300 s^{-1} for 90 mins in order to destroy all ER structures. Following this, in the absence of shear, the field was turned on again and maintained for 10 mins, after which the yield stress was determined by a strain sweep test (test#1, γ = 0.1-100%). Subsequently, oscillatory shear annealing cycles were performed, each of which involved application of oscillatory shear (γ = 1%, ω = 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).
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 Figure 7.2, we show the variation in G', G" and tan δ = 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. 7.2, 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. Figure 7.2 also indicates that the increase in modulus is substantially complete after 100 s

annealing and fully complete after 200 s. As further support, in Figure 7.3, 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 between the first three annealing runs. These results point to a strain-hardening effect, which is presumed analogous to the stress-enhanced enhancement of the yield stress reported by Tam and coworkers (Lau *et al.*, 2003, Shi *et al.*, 2006). A distinction is that, whereas the ER fluid studied by Tam et al. consisted of spherical 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) (Hiamtup *et al.*, 2006).

As noted by Tam et al. (Lau *et al.*, 2003, Shi *et al.*, 2006), 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 (Tao and Sun, 1991, Dassanayake *et al.*, 2000, Pan and Mckinley, 1997), 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 (Pan and Mckinley, 1997). In the case of thePANI 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, more mechanically-strong 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, but the final value of G' (and the subsequent yield stress) decrease slightly in parallel with the decrease in initial stress, as indicated in Table 7.1, where we summarize values of σ_y and γ_y, determined after all ten test runs.. 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).

7.5 Conclusions

Strain-hardening is demonstrated in a polyaniline-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 (γ_y = 6%), the storage modulus G' is observed to increase with annealing time, and tan δ to decrease, each reaching a constant value after approximately 150 sec. 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. During subsequent annealing cycles, the initial value of the storage modulus was observed to decrease, attributed to agglomeration and sedimentation of the marginally stable PANI particles.

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7.7 References

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Table 7.1 Values of σ_y and γ_y of PANI/Silicone oil suspensions, determined after all ten test runs.

Run Number	Yield strain (%)	Yield stress (Pa)
1	6.18	20.4
2	6.16	26.2
3	6.15	26.1
4	6.16	25.5
5	6.17	24.7
6	6.17	24.1
7	6.17	24.0
8	6.17	22.8
9	6.19	22.7
10	6.19	20.0

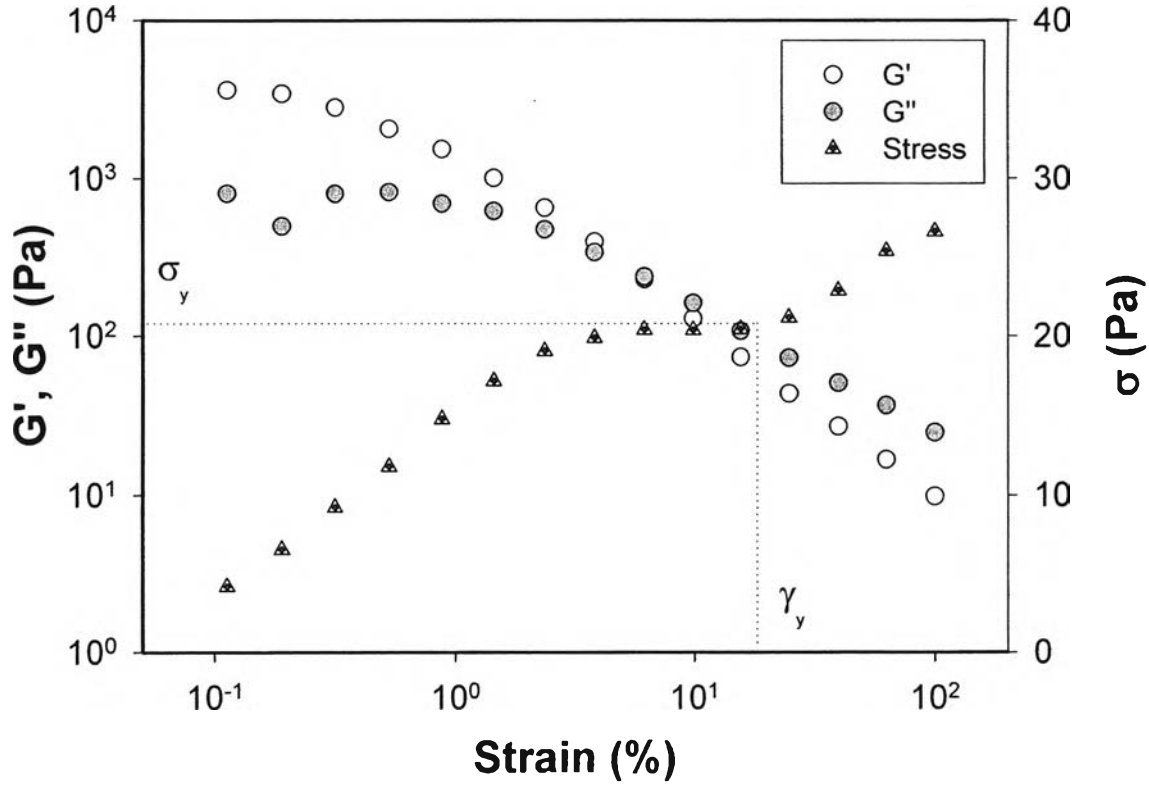

Figure 7.1 Strain dependence of G', G", and shear stress for PANI/silicone oil ER fluid (concentration = 5% vol.) at temperature of 298 K in the presence of an electric field of E = 1000 V/mm. Gap = 0.2 mm.

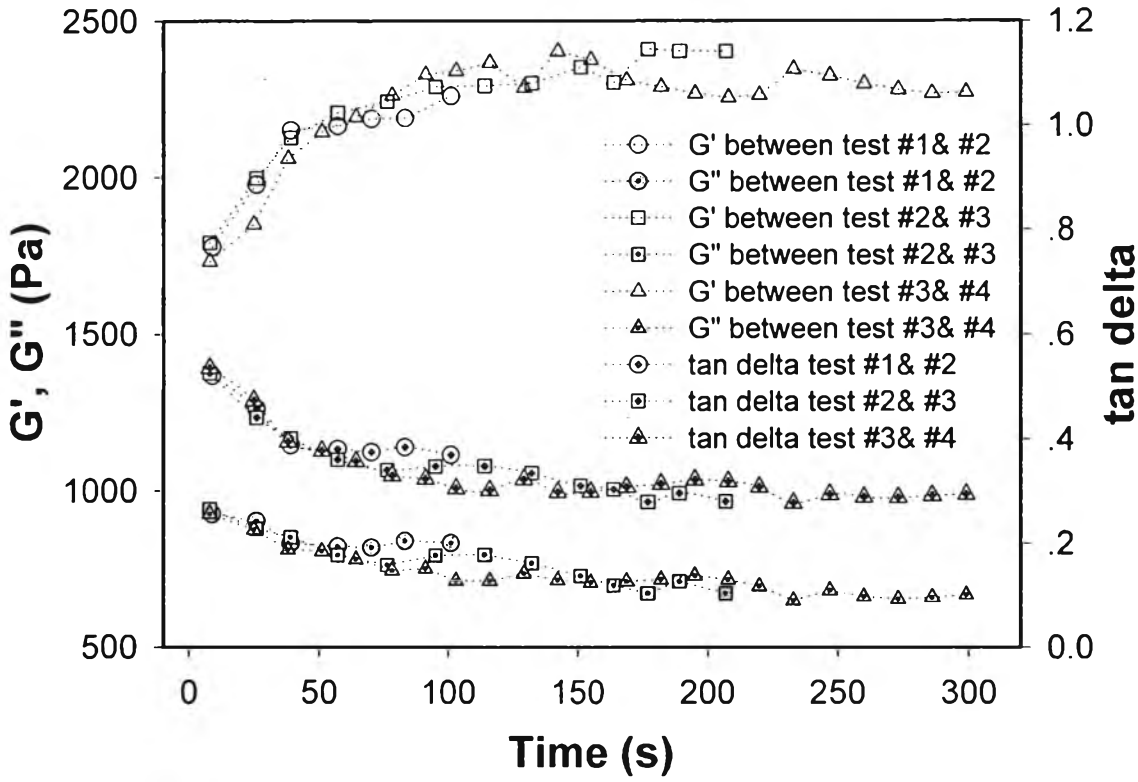

Figure 7.2 Time dependences of G', G" and tan δ for PANI/silicone oil ER fluid (concentration = 5% vol.) at temperature of 298 K in the presence of an electric field of E = 1000 V/mm. Gap = 0.2 mm.

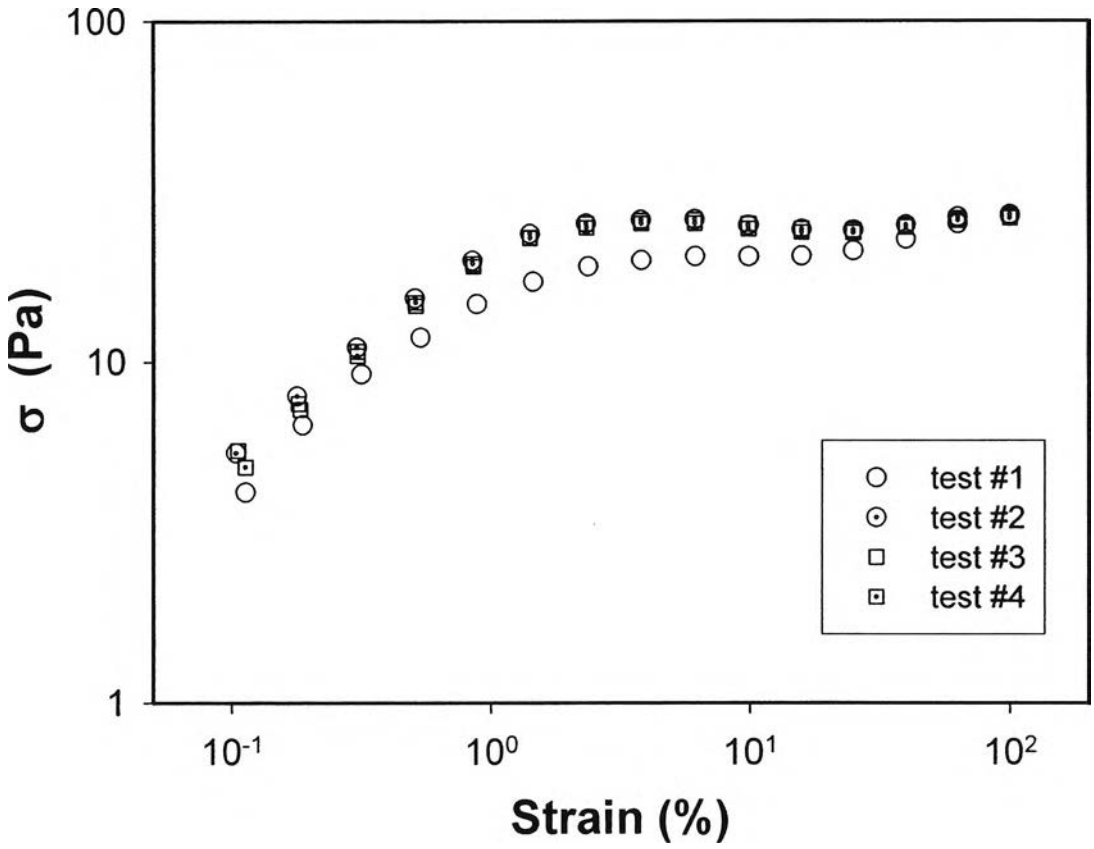

Figure 7.3 Strain dependence of shear stress for PANI/silicone oil ER fluid (concentration = 5% vol.) at temperature of 298 K in the presence of an electric field of E = 1000 V/mm. Gap = 0.2 mm.