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Creep and recovery behaviors of a polythiophene-based electrorheological fluid

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Abstract

We investigate the creep response of poly(3-thiopheneacetic acid) (PTAA) particles doped with perchloric acid. With increase in applied stress, these suspensions exhibit an evolution from a linear viscoelastic response, with three components of instantaneous elastic strain, retarded elastic strain and viscous strain, to a nonlinear viscoelastic response, where the retarded elastic and viscous strains monotonically decrease and a plastic contribution to the instantaneous strain grows, followed by a viscoplastic solid behavior, with fully plastic instantaneous strain, and finally a transition from plastic solid to a plastic liquid at the yield stress. With increase in electric field strength at fixed particle concentration and applied stress, the viscoplastic response diminishes, and more elastic behavior ensues. For highly doped samples, at high-electric field strengths, a fully elastic solid response is observed in the linear viscoelastic regime. The equilibrium compliance, J_C and steady state recoverable compliance J_R, were investigated as a function of electric field strength, particle concentration and particle conductivity. The results are interpreted in terms of the field-induced formation of thick fibrillar aggregates spanning the gap between the electrodes, each consisting of bundles of particle strings. Strings, which are fully connected to both electrodes generate an elastic response to the applied stress, whereas strings which are attached at only one end or are unattached generate a viscoplastic response. The net effect of an increase of the electric field strength, particle concentration, or particle conductivity is an increase in elasticity, i.e. predominantly creation of fully connected particle strings.

Keywords: Conjugated polymer; Creep; Electrorheology

1. Introduction

Electrorheological (ER) fluids composed of polarizable colloidal particles dispersed in a non-conducting fluid have attracted considerable recently [1,2] because many applications based on ER technology are possible, including the active elements of clutches, breaks, shock absorbers, engine mounts, valves, and flow pumps [3–5]. Upon the application of an electric field, chain-like or fibrillar aggregates of the suspended particles are oriented along the direction of the electric field, thereby inducing viscoelasticity and a drastic increase in viscosity [1,2]. Such ER fluids have typically used hydrated organic or inorganic particulates, in which the polarisability arises from ion motion in adsorbed water. More recently, ER fluids have been developed based on semi-conducting polymers, in which the polarisability is due to motion of electrons within the suspended particles. Examples include polyaniline (PANI) and its derivatives [6–10], polypyrrole [11,12], and poly(*p*-phenylene) [13]. Extensive studies have been carried out on the rheological properties of the ER fluids under steady shear and oscillatory shear flows [1,2,6–13], and have established that the suspensions in the presence of an electric field exhibit a yield stress, which increases with particle concentration and field strength, and above which the suspension exhibits viscous flow. In the pre-yield region, a predominantly elastic response to deformation is observed, and, at small strains, a linear viscoelastic description can be adopted. In the post yield region, plastic flow occurs.

Relatively little attention has been paid to the deformational (creep) response, which can provide insight into the mechanistic origin of the flow of ER fluids. Otsubo and Edamura [14] demonstrated that the creep behavior of an ER fluid consisting of TiO_2/polymer composite particles in silicone oil, appears to exhibit an instantaneous elastic response, followed by a retarded elastic deformation, and then viscous flow. At higher

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stress, closer to the yield point, unexpectedly, the creep shows an elastic solid response, and at still higher stress, in the yield region, the strain increases with time in a stepwise fashion, suggesting sequential rupture and restoration of the fibrillar structure was taking place. A similar behavior was observed for a magnetorheological fluid by Li et al. [15], who further clarified that the creep behavior exhibits a transition from a linear viscoelastic response at the lowest shear stresses, where the instantaneous stress is completely elastic, i.e. fully recoverable, to a nonlinear viscoelastic response at higher stress, where there is a nonrecoverable plastic contribution to the instantaneous stress, which increases in magnitude with increasing stress. At stresses just below the yield point, the material behaves as a viscoplastic solid, i.e. the instantaneous strain is dominantly plastic in nature, and rapidly approaches an equilibrium value, and there is negligible recovered strain on removal of the stress. Finally, at the yield stress, the strain increases continuously in a stepwise fashion with no detectable elastic recovery, corresponding to a transition from a viscoplastic solid to a plastic fluid. See et al. [16] have confirmed the presence of a retardation strain in an MR fluid and point out that this phenomenon is not predicted by current rheological models of field-responsive fluids. Lau et al. [17] report that the yield stress of a model ER fluid based on silica spheres in a silicon oil is enhanced when subjected to repeated cyclic creep tests in the linear viscoelastic regime.

Recently, we reported rheological studies of an ER fluid based on a new semiconducting candidate ER material, poly(3-thiophene acetic acid) (PTAA), doped with perchloric acid ($HClO_4$) [18,19]. $HClO_4$-doped PTAA/silicone oil suspensions show typical Bingham flow behavior upon application of an electric field. The static yield stress increases with electric field strength, E, and particle volume fraction, ϕ, according to the scaling law, $\tau_y \propto E^{\alpha}\phi^{\gamma}$ [19]. The scaling exponents α and γ approach the values of 2 and 1, respectively, predicted by the polarization model [20,21], at low fields, and when the particle volume fraction and the doping level decrease [19]. The frequency-dependent moduli at different electric field strengths and conductivities, when scaled according to the model of Parathasarathy and Klingenberg [22], approximately collapse into master functions of the dimensionless frequency [18]. In the present study, we investigate the creep and recovery behaviors of this ER fluid. The creep and creep recovery behaviors of $HClO_4$-doped PTAA/silicone oil suspensions are investigated as a function of applied stress level, electric field strength, $HCLO_4$ doping level, and particle concentration.

2. Materials and methods

2.1. Materials

3-Thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride, $FeCl_3$ (AR grade, Riedel-de Haen) was used as the oxidant. Chloroform, $CHCl_3$ (AR grade, Lab-Scan) and methanol, CH_3OH (AR grade, Lab-Scan) were dried over CaH_2 for 24 h under the nitrogen atmosphere and then distilled. The perchloric acid dopant, $HClO_4$ (AR grade, AnalaR) was used as received. The dispersing phase was silicone oil (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosity of 100 cSt, and was vacuum-dried and stored in a desiccator prior to use.

2.2. Preparation of ER fluid and creep measurements

Poly(3-thiopheneacetic acid), PTAA was synthesized by the oxidative-coupling polymerization according to the method of Kim et al. [23]. PTAA particles were doped with perchloric acid at various amounts to vary particle conductivity [24]. The electrorheological, ER, fluids were prepared by dispersing the $HClO_4$ doped PTAA particles in silicone oil (density 0.96 g/cm^3 and kinematic viscosity 100 cSt) with an ultrasonicator for 30 min at 25 °C.

The creep and recovery behaviors were investigated using a stress-controlled rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry at 25 ± 0.1 °C. The gap for the geometry used was 0.1 mm for each measurement. A DC voltage was applied during the measurements using a high-voltage power supply (Bertan Associates Inc., Model 215). In our sample conditioning, the suspensions were subjected to a steady state shear at 300 s^{-1}, and then electrified in a quiescent state for 5 min, to ensure the formation of equilibrium fibrillar structure before a measurement was taken. A constant stress was then instantaneously applied, maintained for 180 s, and then suddenly removed. The time dependent strain was measured at various electric field strengths. Each measurement was carried out at a temperature of 25 ± 0.1 °C and repeated at least two or three times.

3. Results and discussion

The effect of stress level, particle concentration, and particle conductivity on the creep and recovery properties of the suspensions were investigated. Particle concentrations investigated were 5, 10, and 20% by weight (corresponding to volume fractions of 0.025, 0.048, and 0.092, respectively) at a specific conductivity of 7.5×10^{-2} S/cm (HPT5, HPT10, and HPT20). To explore the influence of conductivity, the particle concentration was fixed at 20% by weight and the particle conductivity values varied from approximately zero (undoped, designated UPT20), 2.0×10^{-4} S/cm (low doping, designated LPT20), and 7.5×10^{-2} S/cm (high-doping, designated HPT20), respectively (Table 1).

First, a series of creep and recovery experiments were conducted using a sequence of step stresses. Creep is the time-dependent evolution in strain (γ) of a viscoelastic material under constant stress, σ_0, [25]. On the removal of stress, some of the time-dependent deformation may be recoverable. A creep test is, therefore, characterized by two distinct phases: the creep phase and the recovery phase. In the creep phase, a constant stress (σ_0) is applied instantaneously to the sample and maintained at that level for a fixed period. For a viscoelastic material, in general, the time dependence of the strain (γ_C) can