CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci

Creep and Recovery Behaviors of Polyaniline/Silicone Oil Suspension Under Electric Field

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The creep response of PANI/silicone oil suspensions is investigated. The suspensions exhibit a linear viscoelastic response only low applied stress. As the magnitude of applied stress increases, a viscous plastic behavior is rather striking. The system shows no recovery when the deformation strain exceeds 0.4-0.5. The quasi equilibrium compliance, J_e, is plotted vs. the applied stress in order to determine the effect of operating temperature. A raise in temperature is additionally observed to increase the pliability of ER structure.

1. Introduction

Electrorheological (ER) fluid consists of a suspension of dielectric particles in a liquid of low dielectric constant whose viscosity increases upon the application of electric field (Winslow, 1949). Such change is caused by the formation of an internal chain-like structure that is formed by the rearranging of dispersed particles within the fluid. Its variable flow rate or force characteristics have been utilized in many applications. It is noteworthy that in some crucial applications such as damper and controllable absorption operate under loading conditions below the yield stress or under oscillations with small amplitude and some assumptions working well for high stain system do not accurately describe these fluid behaviors (Kamath and Werely, 1997). Thus, creep experiments and behaviors are required to determine the fluid critical limit and to understand the deformation mechanisms of the solid structure (Otsubo and Edamura, 1994). Polyaniline is one of conducting polymers which has been used as the dispersed particle due to its ease of synthesis and conductivity control, good thermal, and environmental stability (Jang et al., 2001) and none of them investigated the effect of temperature on creep behavior.

In this paper, we shall report the ER behavior in creep of polyaniline/silicone oil suspensions under applied electric field. The temperature is reported and discussed.

2. Experimental

2.1 Materials

Aniline, C_6H_7N (AR grade, Merck) was vacuum-distilled and used as the monomer. Ammonium peroxydisulphate, $(NH4)_2S_2O_8$ (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 fluids, silicone oil (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosity of 100 cSt were vacuum-dried and stored in a desiccator prior to use.

2.2 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% NH4OH 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.

2.3 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 volume fractions of 0.092. The suspensions were stored in a dessiccator and redispersed by ultrasonificator for a period of 10 minutes at 25 ^{o}C before each experiment.

2.4 Yield stress and creep measurements

The creep and recovery behaviors were studied using a stress controlled rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry. The gap for the geometry used was 0.2 mm for each and DC voltage was applied during the measurements using a high power supply (Bertan Associates Inc., Model 215). For the initial conditioning, the suspensions were subjected to a steady shearing at 300 s^{-1} for 120s and then the flow was stopped before the electric field was applied for 10 minutes to obtain an equilibrium fibrillar or columnar structure before each measurement was taken. A constant stress was then instantaneously applied, maintained for 200 s, and then suddenly removed. The quasi equilibrium values of strain were measured at t = 200s as functions of temperature.

3. Results and Discussion

3.1 Creep behavior of polyaniline suspension: Effect of operating temperature

The effects of temperature on the creep and recovery PANI suspension was investigated. The suspensions were prepared at the volume fractions of 0.092 in silicone oils. The dedoped (emeraldine base form) specimen of PANI used in our work has a electrical conductivity value of 2.93 x 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 a current leakage in the system.

We define the creep compliance as;

$$\gamma(t) = J(t)\tau \qquad (1)$$

where J(t) is the creep compliance, a material parameter, and τ is the applied stress. Under a certain shear stress, higher compliance means the material deforms more easily (Yanju et al., 2001). Je is the quasi equilibrium creep compliance measured after the stress is applied beyond the duration of 200s, while Jr is the recovery compliance measured after the stress was removed at 300s.

Figure 1 shows the dependence of applied stress on Je parameter of the suspensions at various temperatures. Je curves shift to the right as temperature increases from 15-85 °C which implies that the creep resistance increases as the operating temperature increases. This improvement of material mechanical properties with increasing of temperature seems to be unusual as thermal energy is a well-known factor to enhance the Brownian motion, leading to structural instability (Parthasarathy and Klingenberg, 1996). In order to see the effect of temperature on structure deformability, natural logarithm of Je is plotted versus applied stress. Within that range of temperature, the stress dependence of Je parameter can be written as;

$$J_e = J_{e,0} e^{\frac{\alpha\sigma \cdot d^3}{k_B T}} \tag{2}$$

where $J_{e,0}$ is a hypothetical creep at $\sigma = 0$ Pa, or at absolute temperature ($T = 0$ K). The exponential argument represents the relative contribution between the electrostatic force and the thermal force. $k_B = 1.38\text{x}10^7$ $\text{PaA}^{o3}\text{K}^{-1}$ is a Boltzmann constant, T is temperature in Kelvin, and d is the particle diameter which is $23.4\text{x}10^4$ A^o. The values of α vary between $7.81\text{x}10^{-8}$ and $1.52\text{x}10^{-7}$; presumably α is expected to be constant.

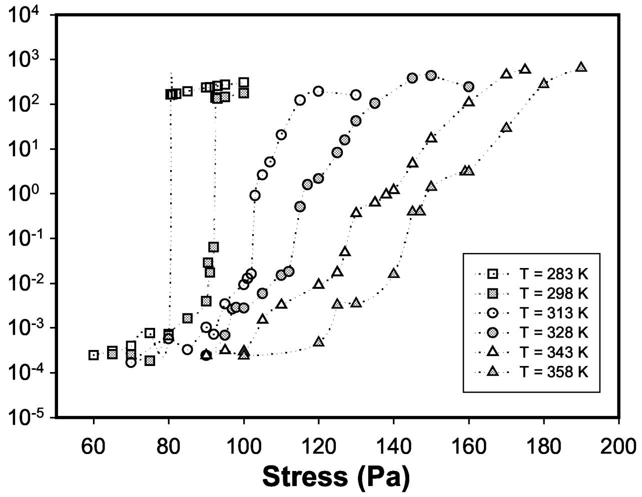

Figure1 *Stress dependence of creep compliance parameter, Je , of PANI/Silicone oil suspension, vol% = 9.2 at E = 2 kV/mm at various temperatures.*

Most of electrorheological systems having polyaniline as a polarizable particle have been reported to have an optimum operating temperature, occurring around 45-60 °C (Yanju et al., 2001; Lee et al., 1998), where the particle conductivity reaches the maximum point (Mzenda et al., 2002). Although there are some evidence about an increasing of yield stress of silicone oil base ER suspension due to the heating below

100 °C as the result of change in water content in the oil (Wu and Conrad, 1996), it is unusual that the ER efficiency of our system continue to increase after 60 °C. This phenomenon will be further investigated.

3.2 Recovery of polyaniline suspension after stress removal

According to a nonlinear viscoelastic-plastic model for ER fluids as proposed by Kamath and Wereley in 1997 (Kamath and Werely, 1997), the field responsive suspension behaves as a viscoelastic fluid in the pre-yield domain and as a viscous fluid in the post-yield domain in which the yield point are determined by the strain level. Additionally, the number of spring and dashpot in the viscoelastic model can be used to describe its behavior in the pre-yield domain which depends largely on the strain levels.

The % recovery can be determined by this following equation;

$$\%recovery = \frac{(\gamma_i - \gamma_f)}{\gamma_i} \times 100 \qquad (3)$$

where γ_i is the acquired total strain before stress removal and γ_f is the average of remaining constant strain. The dependence of % recovery on the total or equilibrium strain of the suspensions at different particle concentrations and field strengths is shown in Fig 2. The recovery decreases monotonically with increasing total strain and it reaches zero at the yield condition where there is no recovery above this point. Moreover, it is noted that the recovery after stress removals disappears when the strain is higher than the critical values ~ 0.4-0.5 which is consistent with the literature, reported by Otsubo and Edamura, 1994.

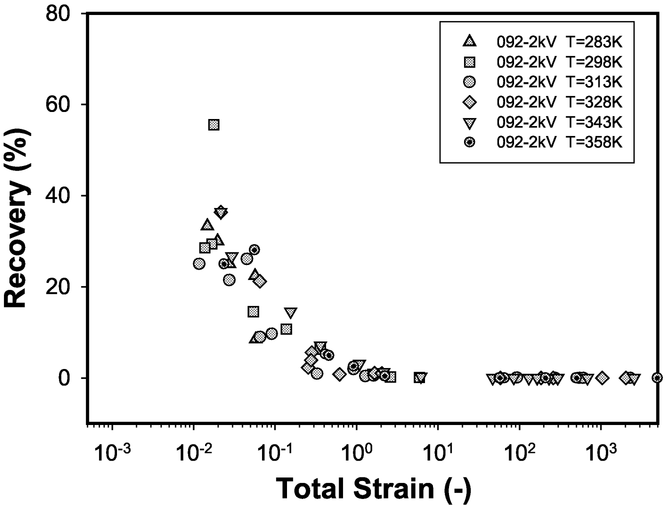

Figure 2 *Percentage of the recoverable strain to the equilibrium strain of the suspensions at various temperatures.*

4. Acknowledgement

The authors would like to acknowledge the financial support provided by The Thailand Research Fund (TRF) in the RGJ grant no. PHD/0234/2544, Conductive & Electroactive Polymers Research Unit, and the Petroleum and Petrochemical Technology Consortium.

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