KSTLE International Journal, Vol. 8, No. 1, June 2007, pp. 7-10

Rheological Consideration of Sub-micron Sized Hollow Polyaniline Malonate Salts Suspension under the Electric Field

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Abstract: The rheological property of hollow PANI malonate suspension in silicone oil was investigated by varying the electric fields and shear rates, respectively. The hollow PANI malonate susepnsion showed a typical electrorheological (ER) response caused by the polarizability of an amide polar group and shear yield stress due to the formation of chains upon application of an electric field. The shear stress for the hollow PANI malonate suspension exhibited an electric field power of 0.90. On the basis of the experimental results, the newly synthesized hollow PANI malonate suspension was found to be an anhydrous ER fluid.

Keywords: Electrorheological fluid, hollow sphere, polyaniline malonate salt, bingham flow, amide polar group

1. Introduction

The elctrorheological (ER) fluids are such smart materials whose rheological properties (viscosity, yield stress, shear modulus, etc.) can be readily controlled using un external electric field. They can switch from a liquid-like material to a solid-like material within a millisecond with the aid of an electric field, and this phenomenon has been called the ER effect [1,2,3]. The unique feature of the ER effect is that ER fluids can reversibly and continuously change from a liquid state to a solid state[4]. ER fluids can therefore be used as electrical and mechanical interface in various industries, including torque transducer, damper, and actuator . A great deal of research interest in ER fluids and ER devices has been stimulated since the ER effect was first described by Winslow [1] in 1947.

But some of the shortcomings of these materials, such as low shear stress, poor temperature stability, easy sedimentation and high cost, have greatly restricted their industrial development. This lack severely impedes the development of new fluid formulations with improved properties. In an effort to overcome disadvantages of suspension the ER fluids, recent research interests have been mainly concentrated on anhydrous ER system providing wide operating temperature range and other advantages. Among various anhydrous ER materials, semi-conducting polymers are the leading materials exhibiting enhanced ER properties. In particular, as the conductive polymer, polyaniline (PANI) has been widely used in ER materials due to its synthetic versatility and other advantages such as a relatively low density, environmental stability, and good thermal stability [5,6]. Therefore, when it is used as the dispersed part in the ER fluid, one should expect to observe better ER performance.

In this study, we synthesized new compounds of ER material of monodisperse submicron-sized hollow PANI malonate salt form particles having low density and functional group, and prepared ER fluids by dispersing these particles into silicone oil. In the range of ER performance, the PANI malonate having functional group, amide polar group to help particle polarization is better for the ER fluids rather than PANI. In addition, it showed good thermal and electrical stability. Specifically, the ER fluid based on the modified PANI malonate as the dispersed phase showed good yield stress and electrical stability.

2. Experimental

2.1. Synthesis of hollow PANI malonate salts form

Hollow PANI malonate salts particles were prepared by synthesizing in the four step procedure. Monodispersed polystyrene (PS) spheres were synthesized by emulsion polymerization using a free radical initiator potassium persulfate (KPS, 99%, Aldrich) according to Menno *et al.* [7].

Ammonium persulfate (APS) was dissolved in the polyvinyl alcohol stabilized PS particles in a screw-cap bottle with magnetic stirring. The reaction mixture was acidified to pH 0.7 for APS, and the initial oxidant/monomer molar ratios were fixed 1.25. Aniline was added via syringe, and the polymerization was allowed to proceed for 24 h at 0°C. The pH value was maintained at 0.7 using a pH stat with 1 N HCl aqueous solution during the polymerization. And the HCl-doped PS-PANI composite particles were converted to the emerladine base form by treating it with NH_4OH aqueous solution for 12 h.

The extraction of PS particle from PS-PANI composite particle with tetrahydrofuran (THF) under stirring at room temperature for 7 days was produced.

1 M malonic acid solution was prepared for salt form. This solution and hollow PANI capsules were stirred for 5 h at room

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temperature.

The morphology and size distribution of the synthesized particles was examined by SEM and STEM.

2.2. Electrical and rheological tests

The ER fluids were prepared by dispersing the hollow PANI sphere particles into silicone oil whose viscosity was 50 cS at 25°C. The particle concentration was fixed at 10% volume fraction. The rheological properties of the suspension were investigated in a static DC field using a Physica Couette-type rheometer with a high voltage generator. The shear stress for the suspensions was measured under shear rate of 10^{-1} to 10^{3} s^{-1} and electrical fields of 0-3 kV/mm. The dc current J of PANI hollow sphere particle suspensions was determined at room temperature by measuring the current passing through the fluid upon application of the electric field E_0 and dividing the current by the area of the electrodes in contact with the fluid.

The thermal stability and degree of doping of salt in hollow PANI malonate particles was confirmed using TGA. The experimental cell was assembled by mounting two parallel copper electrodes with 1mm gap on the Teflon slide in which a drop of well mixed suspensions was dispersed and observed by a viedo camera attached to an optical microscope for ER effect.

3. Results

3.1. Chemical properties

The morphologies of the resulting sphere particles as dispersed phase synthesized in a four-step procedure are shown in Fig. 1.

Monodispersed and stable seed particles were obtained by emulsion polymerization. Fig. 1(a) and (b) shows the SEM images of PS particles with an average diameter of 100 nm and PANI-coated PS spheres with an average diameter of 200 nm. The coated spheres are as monodisperse as the PS spheres is very uniform. And the TEM image of hollow PANI spheres is shown in Fig. 1 (c). In Fig. 1 (d), the TEM image of hollow

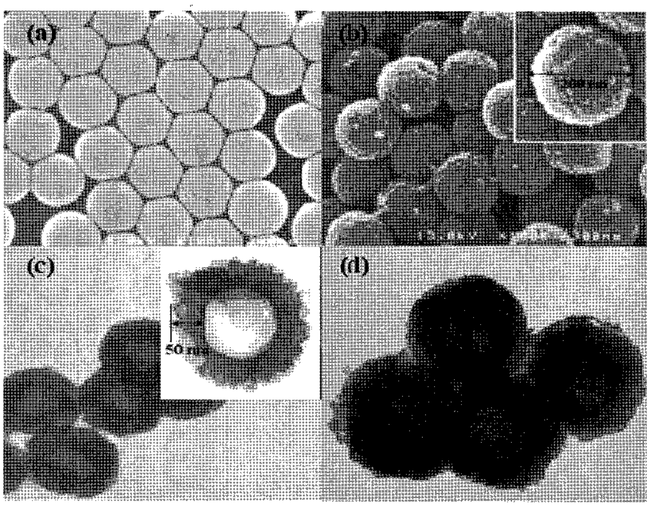

Fig. 1. Morphologies of the (A) PS, (B) PS-PANI spheres, (C) hollow PANI particles, and (d) hollow PANI malonate salts compounds.

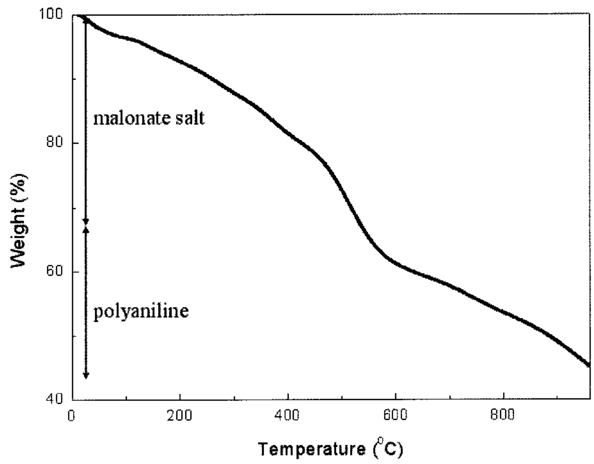

Fig. 2. TGA plots of hollow PANI malonate salts particles.

PANI malonate salt particles was observed. All the particles were very clear and highly monodisperse with a particle size distribution.

Figure 2 shows the result of TGA of the hollow PAN malonate salt particles. The weight loss processes of these samples were measured by heating them from 30 to 1000°C/ min under argon gas. The PANI has three stage weight losses in some of the samples doped with carboxylate salts. This can be explained as follows: The first weight loss of 11% observed up to 110°C is due to loss of water from the polymer. The second stage observed within the temperature 110-430°C is related to removal of dicarboxyl salt molecules from the polymer structure. The weight loss observed between 430-950°C after the removal functional group corresponded to the degradation of the PANI. The TGA clearly show PANI malonate salt particle's thermal degradation and thermal properties.

3.2. Electrical and rheological properties

The polar group of PANI particles may affect the ER behavior by playing the role of electronic donor so that the chemical structures of the organic materials become an important factor in the ER performance. The synthesized hollow PANI malonate salts suspension in this study clearly showed typical ER behavior, exhibiting Bingham fluid behavior with a yield stress under an externally applied electric field. As a representative, flow curves for 10 vol % samples ER fluid under a 0-3 kV/mm electric field at 25°C are shown in Fig. 3.

The effect of dicarboxyl salt form with respect to enhancing the yield stress is distinctively large as compared with hollow PANI suspension.

Figure 4 shows the change of current density and conductivity of the hollow PANI malonate salts nanocomposite ER fluids as a function of applied electric fields. The current density of the PANI malonate salts based ER fluids increases slightly as the electric field increases. In generally, the limitation of current density for commercial ER fluids is about 300 mA/m^2 at 6 kV/ mm. Therefore, the current density of our ER system is much less than the commercial requirement, exhibiting better electrical stability. The range of conductivity of the hollow PANI

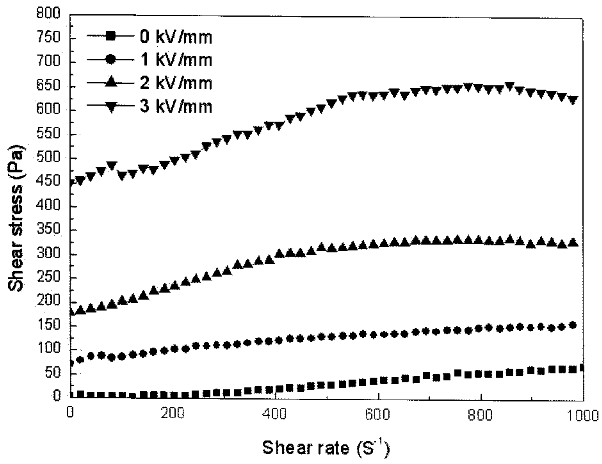

Fig. 3. Shear stress vs. shear rate on the electric fields for hollow PANI malonate salts suspension (10 vol.-%).

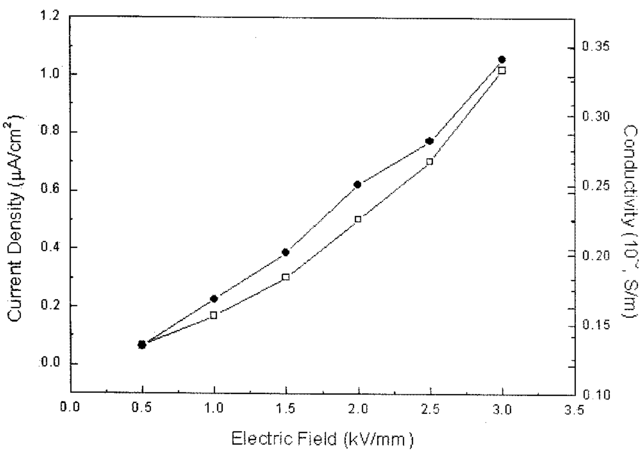

Fig. 4. Effect of the electric fields on current density and conductivity of hollow PANI malonate salt form suspension (10 vol. -%).

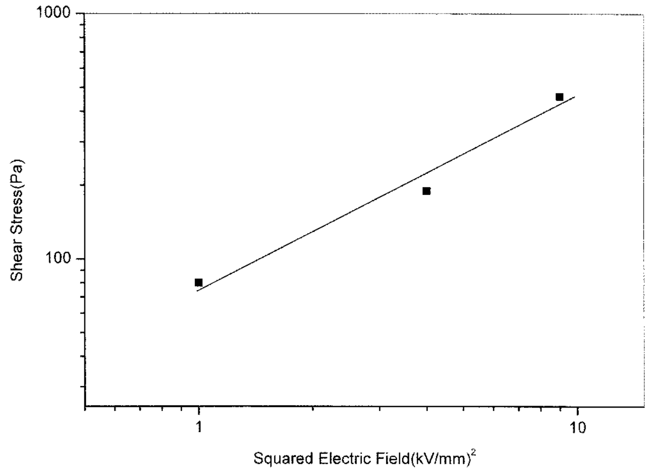

Fig. 5. Effect of squared electric field on shear stress for suspension.

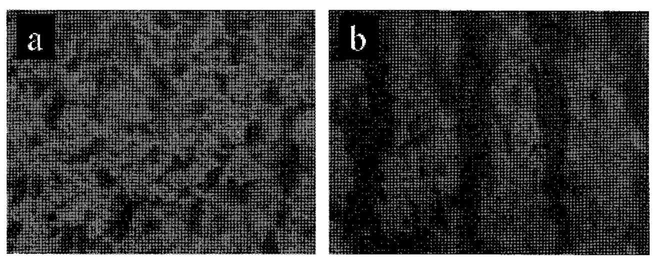

Fig. 6. The structure of particles chains without (a) and with (b) an electric field.

malonate salts suspensions are from 1.2×10^{-6} to 3.5×10^{-6} S/m under a 0-3 kV/mm electric field. Also the resulting of dielectric constant (ε) was 3.05. In contrast with the PANI malonate salts form is comparatively higher values of electrical tests due to the presence of carboxyl group.

Figure 5 shows a log-log plot of the shear stress versus the square of the electric field for hollow PANI malonate suspensions. The results in Fig. 5 indicate that the shear stress was proportional to an electric field power of 0.90 in hollow PANI malonate suspension , this is, $\tau \propto E^{0.90}$. This follows from the fact that the interaction force for the dipole in an electric field is proportional to the electric field intensity.

Figure 6 shows changes in the structure in a dilute hollow PANI malonate suspension without (Fig. 6-a) and with (Fig. 6-b) electric field and In Fig. 6-b, the chain like particle structure could be observed. These partial fibrils are thought to contribute to the viscosity increase, since an attempt to move one electride relative to the other would be hindered by the drag of the dangling fibrils. And the resulting, the suspension was acted as the ER fluid.

4. Discussion

Many researchers have investigated ER performance for ER fluids and demonstrated the polarization models based on the polarization particle chains which are formed by interactive force between the polarized particles in a dielectric fluid upon application field. The polarization model of ER fluids can be described by the equation mentioned below [2,3,5,8]

$$\tau_E \propto \phi K_f E^2 \beta^2 \quad (1)$$

where t is the shear stress, f the volume fraction of particles, K_f the dielectric permittivity of the base fluid , E the electric field and b is the relative polarization at dc or low frequency at ac fields given by [3,9]

$$\beta = (\sigma_p - \sigma_f) / (\sigma_p + \sigma_f) \quad (2)$$

where σ_p is the conductivity of particles and σ_f the conductivity of base fluid [9].

Polarization models based on a point-dipole approximation, with a focus on the mismatch between the real components of the dielectric permittivities of the particles and the based fluid, have been proposed to explain the behavior and can be described by Eq. (1).

To explain the ER mechanism of the hollow PANI malonate suspension under an electric field, the results obtained with the suspension were examined based on the assumption that the base fluid and particles behaved as ideal dielectric materials, and the particles were aligned in chains or columns between electrodes. Using these assumptions, the theological analysis of Conrad *et al.* [3] for the polarization component of the shear yield stress gives

$$\tau_E = 44.1\ A_s\ \phi\ e_o K_f\ (\beta E)^2 \Big|\ \{\exp[(14.84 - 6.165\ (R/a))b^2]\} \times 1/(R/a)^8\ (1 - 4/(R/a)^{10})^{1/2} \Big|_{max} \quad (3)$$

where A_s is taken to be the structure factor pertaining to the alignment of the particles.

This is equal to one for perfectly aligned single-row chains and can have a value of the order of ~10 for multi-chains or columns. K_f is the dielectric constant, β the relative polarizability (≅1), and R/a the ratio of the separation of the particle center to the radius (≥2.05). The structure factor, A_s is obtained from the ratio value of the measured to the calculated shear stress using Eq. (3), that is, $A_s = \tau_{meas.}/\tau_{calc.}$. $A_s = 1$ was obtained for all the test conditions at a shear stress of 10 s^{-1}, electric fields of 1 to 3 kV/mm, and a volume fraction of 0.1, which may have been due to the formation of chains aligned between the electrodes [10].

5. Conclusion

This study was conducted to infer the ER behavior of the hollow PANI malonate salts form with submicrometer-sized as the disperse phase, and to investigate the ER mechanism as an anhydrous ER fluid.

The following is a summary of the results:

(1) Hollow PANI malonate suspensions in silicone oil showed an ER response upon the application of an electric field and the suspension exhibited a Bingham flow behavior. The hollow PANI malnate suspension showed higher than hollow PANI suspension. This was considered to result from the polarizability of the branched polar amide group.

(2) The shear stress of hollow PANI malonate suspension was proportional to an electric field power of 0.90.

(3) The value of the structure factor in hollow PANI malonate suspension, A_s was 1 and this may have been due to the formation of chains aligned between the electrodes upon the application of an electric field.

(4) The hollow PANI malonate suspension showed good thermal and electrical stability.

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