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Electrorheological properties of a polyaniline–montmorillonite clay nanocomposite suspension

Jun Lu[a,b] **and Xiaopeng Zhao***[a]

[a]*Institute of Electrorheological Technology, Department of Applied Physics 141#, Northwestern Polytechnical University, Xi'an 710072, P. R. China*
[b]*Department of Chemistry, Northwest University, Xi'an 710069, P. R. China.*
E-mail: lujunyue@hotmail.com

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Polyaniline–montmorillonite nanocomposite (PANI–MMT) particles were synthesized using an emulsion intercalation method and characterized by XRD and TEM spectrometry. The electrorheological properties of suspensions of PANI–MMT particles in silicone oil with a 30% weight fraction were investigated. It was found that the ER fluid displays a notable ER effect under a DC electric field.

Electrorheological (ER) fluids typically consist of electrically polarizable particles dispersing in low-dielectric oils. Application of an electric field can induce polarization of the suspended particles. As a result, a chain-like structure can be formed along the electric field direction in a very short time (a few milliseconds), and the apparent viscosity can be enhanced.[1] The increase in fluid viscosity owing to the application of the electric field is termed the electrorheological effect. Because of their controllable viscosity and short response time, ER fluids have been regarded as smart materials for active devices, whereby electrical energy can be transformed into mechanical energy. Over the past decade, ER fluids have gained much attention due to their promising potential for applications in mechanical systems such as brakes, clutches and shock absorbers.[2,3] Among various ER materials, semi-conducting polymers represent novel intrinsic ER systems since they have the advantages of reducing abrasion of the device, low cost, and relatively low current density. Recently, some semiconducting polymers have been adopted as anhydrous ER fluids.[4–9] In particular, polyaniline (PANI) has been considered as one of the most promising ER fluids. Unfortunately, available ER materials, some with relatively low shear stress and narrow operating temperature, some with poor suspension stability, are not satisfactory for engineering purposes.

In recent years, clay minerals have attracted great interest for researchers in the preparation and application of organic–inorganic microporous nanocomposites. Because of their small particle size and intercalation properties they exhibit unexpected hybrid properties, especially in the application of reinforcement materials with polymers.[10–13] The most widely used methods to prepare organic–inorganic nanocomposites are emulsion intercalative polymerization or melt intercalation of polymers into layered clays. Montmorillonite (MMT) clay, an important class of lamellar inorganic compound whose interlayer spacing can be modified by cation exchange, has been widely used for preparing organic–inorganic nanocomposites.

In this communication, from the point of the physics and chemistry design, polyaniline–montmorillonite nanocomposites were selected for further investigation. Polyaniline has better thermal stability at high temperature and more controllable conductivity. We prepared polyaniline–montmorillonite clay nanocomposite particles (PANI–MMT) with a high dielectric constant and suitable conductivity using an emulsion intercalation polymerization method.†

Fig. 1 shows the change of yield stress of PANI, MMT, a mixture of PANI + MMT and PANI–MMT ER fluids, as well as leaking current density of PANI–MMT ER fluids (30 wt% in silicone oil) with the increase of DC field at 20 °C, respectively. It can be found that the PANI–MMT ER fluid displays notable ER properties. The yield stress of PANI–MMT ER fluids is 7.19 kPa at 3 kV mm^{-1}, whereas it is 2.31 kPa for the pure PANI and 1.70 kPa for the PANI + MMT at the same electric field, respectively. This value is about 3.1 times that of PANI and 4.2 times that of PANI + MMT. In addition, the leaking current density of PANI–MMT ER fluids is less than 30 μA cm^{-2} at 3 kV mm^{-1}. Kim and co-workers[14] first reported PANI–montmorillonite composites with intercalated nanostructures. They found that the yield stress of a PANI–MMT containing 20 wt% of particles in silicone oil was less than 100 Pa at 1.2 kV mm^{-1}. This value is even lower than that of the ER system composed of pure PANI particles only.[15] We prepared the PANI–montmorillonite nanocomposite particles by emulsion intercalation as well as improved its procedures. Up to now, we have not found any other ER fluids based on PANI, which have a significantly higher yield stress value than that of the currently studied PANI–MMT suspensions.

Fig. 2 shows the variation of shear stress with the increase of shear rate of the PANI–MMT suspension under an electric field (0 ~ 3 kV mm^{-1}) at 20 °C. In the absence of an electric field, the PANI–MMT suspension is a simple suspension system, which shows Newtonian fluid behavior. When an electric field is imposed, particles in the fluid form fibrillation structures, which are oriented along the direction of the electric field. These chains are held together by interparticle forces,

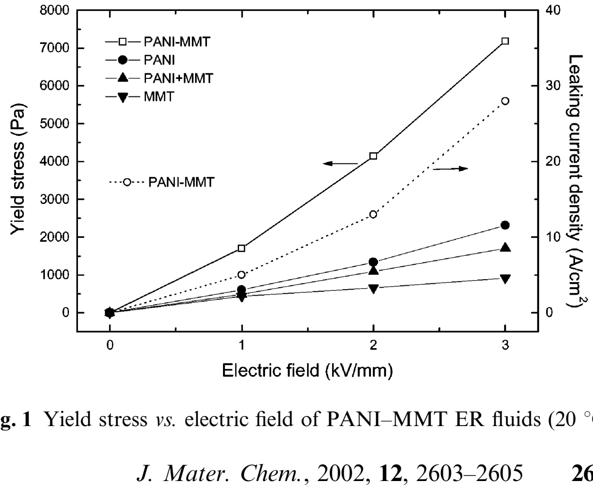

Fig. 1 Yield stress *vs.* electric field of PANI–MMT ER fluids (20 °C).

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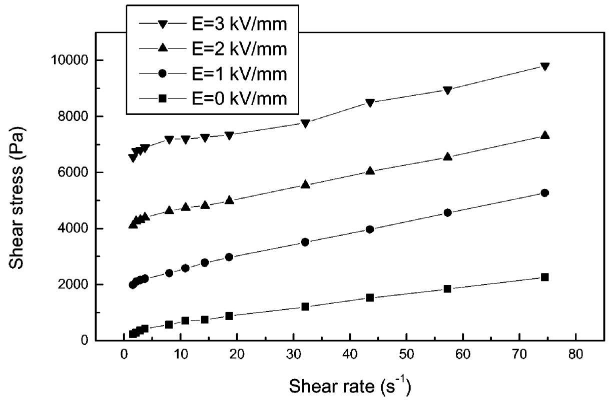

Fig. 2 Flow curves of shear stress *vs.* shear rate at different electric field strengths.

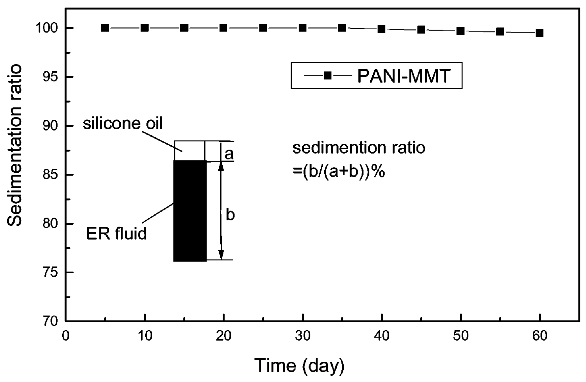

Fig. 4 The sedimentation ratio of PANI–MMT ER fluids *vs.* time.

which have sufficient strength to inhibit fluid flow, therefore, a stress is required to break the chain-like structures. This stress can be described by the Bingham plastis model, which results from the role of induced electrostatic dipoles in the bulk and surface, and is a typical rheological characteristic of ER fluids. When the shear stress strongly depends on the strength of the applied electric field, the suspension becomes a general representative of the ER property. The shear stress increases with the increasing electric field at a fixed shear rate, and it also shows an increasing stress response over the range of electric field strength, *i.e.* positive electrorheological effect.

Fig. 3 shows the variation of yield stress of PANI–MMT and MMT ER fluid with temperature under a 1.5 kV mm^{-1} (DC) field. It can be seen that the yield stress of PANI–MMT (3.1 kPa, 20 °C) increases gradually with increasing temperature, and it approach maximum (3.6 kPa) when the temperature reaches about 60 °C. After this temperature, however, the yield stress decreases gradually (2.9 kPa, 100 °C), and the leaking current density increases abruptly with temperature. In the range of 10 ~ 100 °C, the yield stress changed by 6.5% with the variation of temperature. In addition, the yield stress of MMT decreases gradually with increasing temperature.

Fig. 4 shows the sedimentation rate of the ER fluid of PANI–MMT *vs.* the static time. The PANI–MMT suspensions possess an excellent anti-sedimentation stability, and the sedimentation ratio of PANI–MMT ER fluids is about 98% over 60 days. Less than 2% oil of the total fluid volume could be observed after 60 days and longer. The sedimentation property of ER materials is one of the main criteria used to evaluate whether the materials can be commercialized.[16] Montmorillonite clay is a good suspension stabilizer due to its lamellar structure and sandwiched nanocomposite particles. The suspension ability can also be increased by the intercalation fraction of PANI. As a consequence, the PANI–MMT can be dispersed into silicone oil very well.

Fig. 5 shows the TEM spectrum of PANI–MMT. From the figure, it can be concluded that the diameter of PANI–MMT is about 100 nm. Meanwhile, from the results of X-ray diffraction and IR spectra, we found that PANI–MMT is really a nanocomposite when PANI has been inserted into the interlayer of MMT.

As we know, the higher dielectric constant (ε_p) and dielectric loss tangent (δ, >0.1 at 1 kHz) as well as suitable dielectric conductivity (σ_p, $\sim 10^{-7}$ S m^{-1}) dominate ER properties. Three basic electrical parameters (dielectric constant, conductivity and dielectric loss tangent) of the PANI–MMT nanocomposite particles were measured directly or deduced from capacitance in the range of 100 to 10^4 Hz. As shown in Table 1, the dielectric constant of the PANI–MMT nanocomposite is 75.5 and the conductivity is 38.4 $\times$ 10^{-7} S m^{-1} (f = 1000 Hz, T = 20 °C). Wheres the dielectric constant of MMT and PANI are 28.2 and 13.7, and their conductivities are 13.8 $\times$ 10^{-7} and 4.51 $\times$ 10^{-7} S m^{-1} (f = 1000 Hz, T = 20 °C), respectively. The dielectric constant of PANI–MMT is 5.5 times that of PANI and 2.7 times that of MMT; the electric conductivity of PANI–MMT is about 8.5 times that of PANI. Meanwhile, the dielectric loss of PANI–MMT and PANI particles are 0.98 and 0.59, respectively. The dielectric loss of PANI–MMT is also 1.66 times that of PANI. It is obvious that either the dielectric constant or conductivity and dielectric loss of PANI–MMT increases progressively when PANI is intercalated into the MMT interlayer.

In summary, a polyaniline–montmorillonite clay nanocomposite (PANI–MMT) with a large dielectric constant and suitable conductivity has been synthesized by emulsion polymerization and the ER properties of its silicone oil suspension have been investigated. In a 3 kV mm^{-1} field, the yield stress is

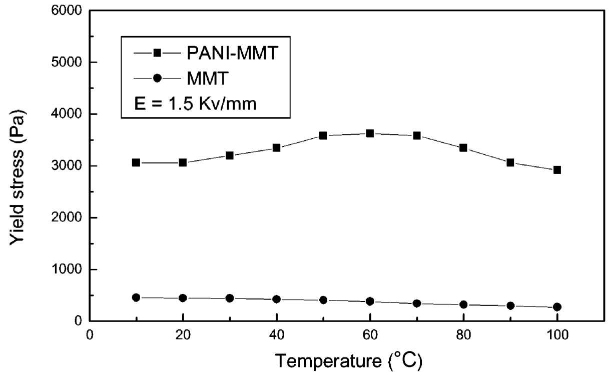

Fig. 3 Shear stress of PANI–MMT nanocomposite ER fluids *vs.* temperature.

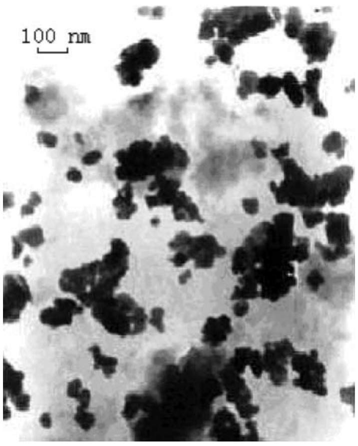

Fig. 5 TEM of PANI–MMT particles.

Table 1 Dielectric data for PANI, MMT and PANI–MMT particles (T = 20 °C)

	ε_p			σ_p ($\times 10^{-7}$)/S m^{-1}			log δ		
Sample	f = 100 Hz	1 kHz	10 kHz	f=100 Hz	1 kHz	10 kHz	f=100 Hz	1 kHz	10 kHz
PANI–MMT	146.8	75.5	45	23.2	38.4	101	3.0	0.98	0.43
PANI	21.4	13.7	9.9	2.71	4.51	12.6	2.3	0.59	0.23
MMT	61.5	28.2	16.9	7.89	13.8	39.3	2.2	0.84	0.40

7.19 kPa (20 °C), and the leaking current density is less than 30 μA cm^{-2}. Meanwhile, it was found that this anhydrous PANI–MMT ER fluid not only displays notable ER properties under DC electric field over a wide temperature range but also possess excellent anti-sedimentation stability.

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Notes and references

†Preparation of the PANI–MMT nanocomposite particles by emulsion intercalation polymerization: Firstly, 10 g Na$^+$-montmorillonite (cationic exchange capacity: CEC = 80 meq/100 g) was swelled in 500 mL deionized water and the mixture was stirred for 2 h at 80 °C. Then 2 mL aniline and 0.04 mol HCl were added, and the mixture was stirred again for 6 h at 80 °C. The resulting suspension was filtered and the collected solid was washed with deionized water until no aniline was found in aqueous solution. Secondly, the solid was dispersed into 500 mL deionized water, and the pH of the aqueous solution was adjusted to 2 using HCl solution. Then 1.6 g, 0.007 mol, $(NH_4)_2S_2O_8$ (oxidant or initiator) was added and the mixture stirred for 12 h at room temperature. The suspension was filtered, and the collected solid washed again with deionized water, EtOH, and toluene, respectively. The filter cake was immersed in aqueous NH_3 solution (pH = 10) for several hours. Finally, we obtained the PANI–MMT particles for the ER fluids by filtering, drying, and milling. ER fluids were prepared by dispersing the PANI–MMT particles in a non-conductive dielectric 30 wt% silicone oil ($\varepsilon_f = 2.60\sim2.80$, $\sigma = 10^{-12}\sim10^{-13}$ S m^{-1}, $\rho = 0.9\sim1.0$ g cm^{-3}, $\eta \approx 500$ mPa s (25 °C)), which was dried in a vacuum oven before use. The rheological properties of the ER fluids were examined *via* a system consisting of a rotary rheometer (NXS-11A, the gap between the outer cup and inner bob was 2 mm) and high-voltage DC power source (GYW-010).

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