Colloid Polym Sci (2003) 282: 198–202
DOI 10.1007/s00396-003-0998-7

SHORT COMMUNICATION

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Polyaniline microsphere encapsulated by poly(methyl methacrylate) and investigation of its electrorheological properties

Received: 17 June 2003
Accepted: 9 September 2003

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Abstract Microspheres consisting of a poly(methyl methacrylate) (PMMA) shell wrapping the conductive polyaniline (PANI) particle as a core were prepared by an insitu suspension polymerization method and then adopted as an electrorheological (ER) material. The polymerization reaction and encapsulation were confirmed by Fourier transform infrared spectrum analysis. The rod-like PANI particles were synthesized via an emulsion polymerization protocol and observed by transmission electron microscopy. In addition, a spherical shape of encapsulated PANI/PMMA (core/shell) microspheres was observed by scanning electron microscopy. The thermal stability of PANI/PMMA particles was examined by use of thermogravimetric analysis. The PANI/PMMA particle-based suspension in silicone oil exhibited typical ER behavior. The conductivity of PANI/PMMA particles was much lower than that of the rod-like PANI.

Keywords Polyaniline · Poly(methyl methacrylate) · Electrorheological fluid · Microsphere · Suspension · Encapsulation

Introduction

The choice of particle-type and suspending fluid, and the magnitude of the electric field, dramatically affect the rheological properties of electrorheological (ER) fluids. ER fluids are suspensions of dielectric (or polarizable) particles in a nonconducting liquid [1, 2, 3, 4, 5, 6], and exhibit a remarkable change in rheological properties, including a drastic increase in apparent viscosity and the formation of reversible microstructures, under an applied electric field [7, 8]. Due to their fast response time and controllable or tunable shear viscosity, ER fluids have been used as smart and intelligent materials for various engineering applications, including shock absorber, actuator, brake, and seismic controlling frame structures. Recently, various anhydrous ER fluids [9] containing semiconductive polymers such as polyaniline (PANI) [10, 11, 12] and its derivatives [13], poly(acene quinone) radicals [14], polyphenylenediamine [15], poly(*p*-phenylene) [16], polypyrrole [17], and inorganic materials [18, 19, 20] have been investigated. These ER materials possess advantages over a wide working temperature range, and reduced device abrasion operated at a relatively low current density, and have intrinsic charge carriers in either the bulk particles or their surfaces that can move locally under an applied electric field [21].

The surface modification of the dispersed particles is known to be important to the ER performance, regardless of core material [22, 23]. In reality, the electrical properties of the core have a significant effect on ER properties in suspension [24]. To improve the particle preparation method for PANI the method of microencapsulating PANI particles with melamine–formaldehyde resins has been investigated. This microencapsulation was observed to control the conductivity of the ER fluid without doping and dedoping steps, which are very time consuming, generally taking a week [25]. On the other hand, insulating core/semiconductive shell particles revealed a weaker interaction strength than seen for homogeneous semiconductive particles under an applied electric field [24]. Previously, we studied a PANI-coated PMMA (PMMA/PANI) (core/shell) based ER suspension. Among various ER fluids, PANI has advantages over others with respect to density, conductivity control, and thermal stability. In addition, PANI has been used extensively due to its inexpensiveness, ease of synthesis, and environmental stability [26, 27, 28]. To control the conductivity of PANI in a semiconductive range for ER application, the PANI particles are dedoped by reducing the pH of the aqueous medium. Additional doping and dedoping steps are required to control the conductivity of the particles for improved ER performance.

In this work, highly conductive PANI, encapsulated by the insulating PMMA, was synthesized and adopted as suspended particles (PANI/PMMA) for ER fluids. Their ER properties were examined and compared with those of PMMA/PANI- and PANI-based ER fluids.

Experimental

Emulsion polymerization of PANI in methyl methacrylate (MMA) solution

The PANI particles were synthesized following the method of Kinlen et al. [29] Initially, an emulsion solution containing aniline, MMA, acetone, and dodecylbenzene sulfonic acid in water was placed in a 1-L reactor. Polymerization of aniline was then initiated by addition of an aqueous solution of ammonium peroxysulfate (APS), $(NH_4)_2S_2O_8$, to the emulsion solution. The molar ratio of APS to aniline was fixed at 1.25. The polymerization reaction was kept at 0 °C and was continued for 5 h. As soon as the agitation stopped after the reaction, the emulsion mixture spontaneously separated into two phases. Most of the synthesized PANI particles were in the upper organic layer and the aqueous lower layer contained oxidized APS and some water-soluble components. Therefore, we can easily obtain PANI dispersion in MMA by decanting the upper organic layer.

Polymerization of MMA with PANI particles

2,2′-Azobisisobutyronitrile (AIBN), a radical initiator, was dissolved in the PANI suspension with MMA and the resulting suspension was slowly added to poly(vinyl alcohol) (PVA, molecular weight of 70,000 g mol^{-1}, degree of hydrolysis 88 mol%) solution in deionized water. The reaction system was heated to 70 °C and kept at 70 °C for 5 h, with a constant agitation speed of 300 rpm. The synthesized encapsulated polymer beads were filtered and washed three times with water and methanol. Finally, the products were dried in a vacuum oven at 25 °C.

Characterization

The success of polymerization was confirmed by a Fourier transform infrared spectrum analysis (FT-IR, Perkin Elmer System, USA) and the shapes of both PANI and PANI/PMMA particles were observed by scanning electron microscopy (SEM, S-4200, Hitachi, Japan). The thermal stability of the PANI/PMMA particles was examined by thermogravimetric analysis (TGA, Q50, TA, USA) with a heating rate of 20 ° min^{-1} from 25 °C to 905 °C. The shape of the PANI particles was also observed, by transmission electron microscopy (TEM, CM200, Philips, Netherlands). The electrical conductivity of both the PANI and PANI/PMMA particles was measured (with a pressed disk of the samples) via a two-probe method with a picoammeter having an internal voltage source (487 picoammeter, Keithley, USA). The ER fluid was prepared by dispersing the synthesized PANI/PMMA particles (10% *v*/*v*) in silicone oil having kinematic viscosity of 50 cS. The ER properties were measured by means of rotational Physica rheometers (MC 120, Paar-Physica, Germany) with concentric cylinder geometries (Z3-DIN and Z4-DIN) and equipped with a high-voltage generator (HVG 500). The flow curve (shear stress vs. shear rate) was measured in a controlled shear rate mode for the shear rate range of 0.1 to 1000 s^{-1}, with a stepwise increment (each step taking approximately 6 s).

Results and discussion

Figure 1 shows the FT-IR spectra of PANI, PMMA, and PANI/PMMA particles determined via KBr pellets. The peak at 1740 cm^{-1} originates from the carbonyl peak of PMMA and the peak at 1600 cm^{-1} is due to amine stretching of the PANI. Both carbonyl and amine peaks confirm the completeness of polymerization and encapsulation.

Figure 2 shows the TGA diagrams of PMMA, PANI, and PANI/PMMA weights as a function of temperature. The PMMA is almost decomposed at 400 °C, but most (95%) of the initial weight of PANI remains at that temperature. Therefore, we can calculate the content of PANI in the PANI/PMMA microsphere from the second plateau in the thermograms. As a result we found that approximately 10% (*w*/*w*) of the PANI is dispersed

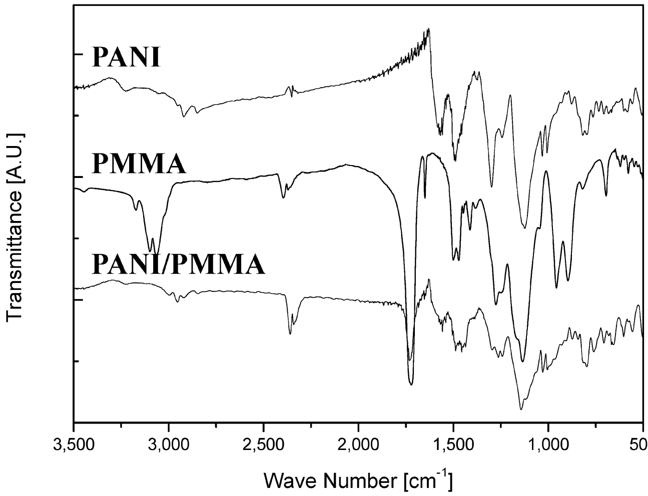

Fig. 1 FT-IR spectra of PANI, PMMA, and PANI/PMMA particles

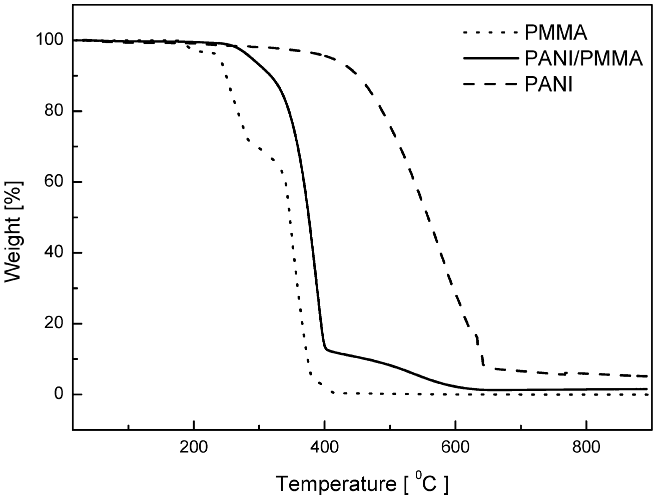

Fig. 2 TGA diagram of PANI, PMMA, and PANI/PMMA particles

in PANI/PMMA particles. Contrary to this conventional conductivity control, an encapsulation technique is adopted. Encapsulation, a well-known process by which tiny particles (or droplets) are coated [30, 31], has been successfully applied within the pharmaceutical and biomedical areas.

Figure 3 is the TEM image of the pristine PANI particles prepared via an emulsion polymerization method prior to encapsulation. The specimen for the TEM measurement was prepared by casting the PANI suspension obtained on to a copper grid coated with carbon. The observed PANI particles were appeared rod-like, with dimensions of about 100 nm thickness and 1–2 μm length.

Figure 4 is the SEM image of the encapsulated PANI/PMMA particles. The particles were spherical and of different diameters, which are characteristic of suspension polymerization, and the particle surfaces appear smooth since almost all of the PANI particles were encapsulated by the PMMA during the encapsulation process. No PANI particle without a PMMA encapsulation was found in the microscopic views, indicating that all PANI particles had been encapsulated. The PANI/PMMA particles appeared transparent with green coloring, suggesting the rod-like PANI particles were uniformly dispersed in the PMMA domains.

The dc electrical conductivity was measured as 1.8×10^{-2} S cm^{-1} via the two-probe method, using a compressed disk of the pristine PANI synthesized, while the conductivity of PANI/PMMA particles was less than 10^{-9} S cm^{-1}. This low conductivity of PANI/PMMA compared with that of PANI indicates additional evidence for the complete encapsulation of PANI particles by the PMMA. Because of the low conductivity in a semiconducting regime, the encapsulated PANI/PMMA particles were adopted directly as ER materials, without further treatment to reduce the conductivity (cf. PANI-based ER fluids).

Fig. 3 TEM image of precipitated PANI particles

Figure 5 illustrates the flow curves (shear stress vs. shear rate) for the 10% *v*/*v* PANI/PMMA particles dispersed in silicone oil under various electric field strengths. The shear stress increases with electric field strength for the entire shear rate range. In the absence of an electric field, the ER suspension behaves as a

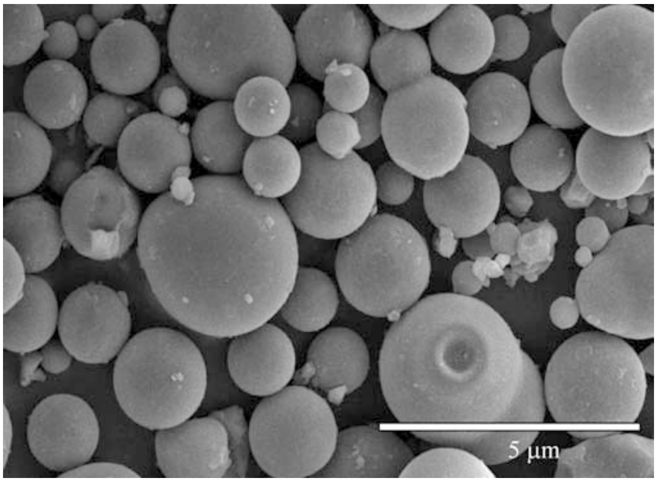

Fig. 4 SEM image of spherical PANI/PMMA particles

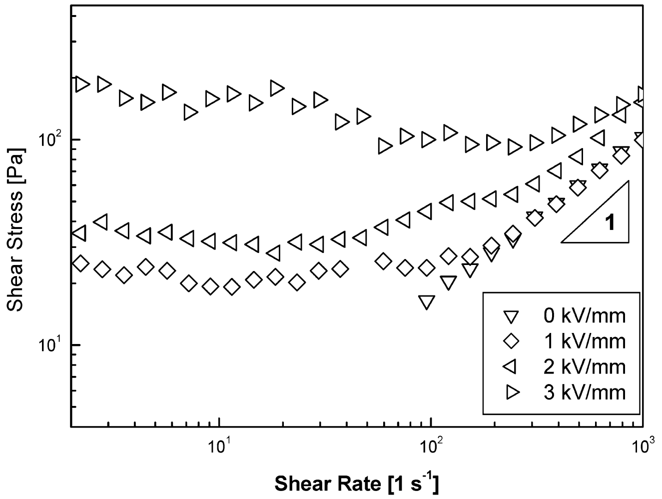

Fig. 5 Shear stress vs. shear rate for 10% *v*/*v* PANI/PMMA suspended in silicone oil at various electric field strengths

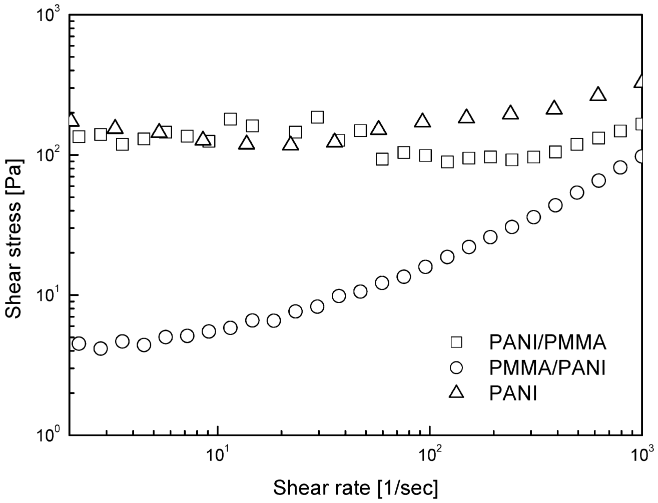

Fig. 6 Shear stress vs. shear rate for 10% *v*/*v* PANI, PMMA/PANI and PANI/PMMA in silicone oil at an applied electric field strength of 3 kV mm^{-1}

Newtonian fluid with a slope of 1.0. When electric fields were applied to the suspension, it behaved like a Bingham fluid, as given in Eq. (1):

$$\begin{aligned} \tau(\dot{\gamma}, E_0) &= \tau_0(E_0) + \eta\dot{\gamma} \quad \text{for} \quad \tau > \tau_0, \\ \dot{\gamma} &= 0 \qquad\qquad\quad\;\; \text{for} \quad \tau < \tau_0 \end{aligned} \tag{1}$$

where E_0 is the applied electric field strength, $\dot{\gamma}$ is the shear rate, $\tau(\dot{\gamma}, E_0)$ is the shear stress, $\tau_0(E_0)$ is the yield stress, and η is the shear viscosity. While shear stress at 1 kV mm^{-1} converges to the measured value without an electric field over shear rate of 100 s^{-1}, the effect of the electric field strength on shear stress still exists up to the shear rate of 1000 s^{-1} at 2 and 3 kV mm^{-1}.

Furthermore, to compare ER performance for the particles of PANI(core)/PMMA(shell) examined in this study with the data for both the particles having inverse structure PMMA(core)/PANI(shell) and the homo PANI particles, the controlled shear rate mode of rheological measurement using a rotational rheometer was applied for these three different ER suspensions. The spherical, monodisperse polymer microsphere consisting of a PMMA core and a PANI shell (PMMA/PANI) was prepared and adopted as dispersed material for ER fluid, in which electrical conductivity originated primarily from the surface-coated conducting PANI layer. Detailed explanation of the preparation method and characteristics of this PMMA/PANI can be found in our previous works [24, 32]. Figure 6 shows flow curves of the ER fluids with PANI/PMMA, PMMA/PANI and homo PANI particles dispersed in silicone oil with the same particle concentration (10% *v*/*v*) at an applied electric field strength of 3 kV mm^{-1}. Even though the PANI content in PANI/PMMA particle was about 10% *w*/*w*, the PANI/PMMA suspension in silicone oil shows ER performance quite similar to that of homo PANI suspension system. The ER properties of PANI/PMMA-based ER fluid are better than those of PMMA/PANI ER fluid. This result indicates that location of the electrically insulating PMMA and highly conductive PANI in either core/shell or shell/core system and the surface smoothness of the particles synthesized influence their ER properties. Any model to explain difference in ER properties of PANI, PANI/PMMA and PMMA/PANI suspensions remains to be tested by future experiments.

In conclusion, the PANI particles were synthesized by emulsion polymerization and PANI/PMMA (PANI encapsulated by PMMA) were prepared via suspension polymerization method using PVA as a stabilizer. The highly conductive PANI was controlled by the electrically insulating PMMA. The PANI/PMMA suspensions showed typical ER properties under an applied electric field, suggesting that the shear stress increases with the electric field strength for broad ranges of shear rate. Compared to ER properties using the homo PANI, PMMA/PANI, and PANI/PMMA particles, it could be seen that the ER effect of the PANI/PMMA is larger than that of the PMMA/PANI. The PANI/PMMA with 10% *w*/*w* PANI and homo PANI ER fluids show flow behavior similar under 3 kV mm^{-1}. The electrical properties of the core rather than the surface are found to be a more dominant factor for obtaining better ER performance. Therefore, a nonconductive surface with a conductive core is recommended not only for obtaining improved ER properties but also simplifying the method of preparation the ER materials without doping and dedoping processes.

Acknowledgement This study was supported by research grants from both the National Research Laboratory (NRL) program (2001), Korea, and the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), Korea.

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