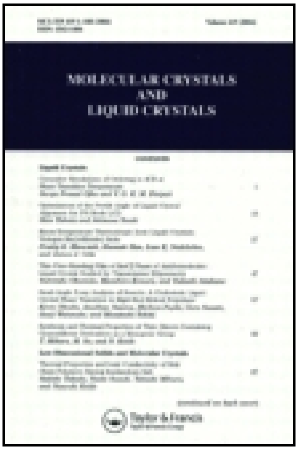

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Electrically Conducting Polymeric Microspheres Prepared by Adsorption of Multiwalled Carbon Nanotubes

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Electrically Conducting Polymeric Microspheres Prepared by Adsorption of Multiwalled Carbon Nanotubes

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Multiwalled carbon nanotubes (MWCNTs) were incorporated onto the surface of polystyrene (PS) microspheres by a simple and potentially scalable process. PS microspheres, 3.0 μm in diameter, were prepared using a dispersion polymerization method. These were adopted as the suspended particles for electrorheological (ER) fluids, in which the electrical conductivity was mainly derived from the conducting MWCNTs layers coated on the surface of the microspheres. The MWCNT/PS composite suspensions in silicone oil showed the typical characteristics of an ER fluid, forming a chain-like structure under an applied electric field (0.8 kV/mm). The MWCNTs/PS composite microspheres exhibited a conductivity of about 2.0×10^{-4} S/cm, which is in the typical range for ER fluids. This phenomenon can be explained by the interfacial polarizability of the MWCNTs adsorbed on the surface of the polymeric microspheres.

Keywords: electrical conductivity; electrorheological fluids; microspheres; multiwalled carbon nanotubes; polystyrene

INTRODUCTION

In general, electrorheological (ER) fluids are suspensions of particles with a higher dielectric constant and/or conductivity than that of the suspending medium, which is generally a fluid with a low dielectric constant and a low viscosity. They exhibit a drastic and reversible change in their rheological characteristics in response to an applied

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electric field, because the ER particles are attracted to one another and this leads to the formation of fibril structures aligned in the direction of the applied electric field [1]. A microstructural transition of the suspension from a liquid-like to solid-like state is obtained by controlling the strength of the applied electric field [2,3]. According to the polarization model, the suspended particles are polarized as a result of the dielectric mismatch between the particles and the suspending fluid under the applied electric field [4,5]. The interaction among the polarized particles causes them to align themselves in the form of strings along the electric field direction [6].

Carbon nanotubes (CNTs) have attracted a great deal of interest in engineering applications such as electronic devices, biosensors, field emission displays, hydrogen storage and composites, due to their extraordinary physical, chemical, and structural properties, such as their good electrical, mechanical and thermal characteristics [7]. Many of these outstanding properties of CNTs can best be exploited by incorporating them into some form of matrix, and the preparation of CNTs-containing composite materials is now a rapidly growing area of research [8–11]. Polymer composites reinforced with CNTs are believed to have many potential engineering uses, ranging from battery electrodes and electronic devices to applications demanding much stronger composites than those currently in use [8–13].

In this study, surface-conductive microspheres consisting of a polystyrene (PS) (3.0 μm) core and multiwalled carbon nanotube (MWCNT)-adsorbed shell were prepared using a simple process involving the blending of two colloidal solutions; an aqueous MWCNT dispersion with surfactants and an aqueous PS microsphere colloid. These microspheres were adopted as the suspended particles for ER fluids, in which the electrical conductivity is mainly derived from the conducting MWCNT layers coated on the surface of the microspheres.

EXPERIMENTAL

Materials

Styrene (Junsei Chemicals, Japan) was distilled under reduced pressure and stored in a refrigerator prior to use. Poly(*N*-vinylpyrrolidone) (PVP-40T; weight-average molecular weight = 40,000; Sigma Chemical Co.) was used as the steric stabilizer. Ethanol (Samchun Chemical Co., Korea) was used as the reaction medium. 2,2-azobisisobutyronitrile (analytical grade, AIBN; Junsei) was used as received.

Preparation of PS Microspheres

PS microspheres with a number-average diameter of 3.0 μm were synthesized using 1.0 and 1.5 wt% of AIBN using a well-established dispersion polymerization method in ethanol medium for 24 hrs at 70°C. The amount of PVP used as a steric stabilizer was fixed at 12 wt% relative to styrene. The polymerization was carried out in a 500 mL three-neck reaction vessel at a constant stirring speed of 150 rpm under a nitrogen atmosphere. After completing the polymerization, the resulting mixture was repeatedly rinsed with methanol and water, following which the fine PS microspheres were obtained by a filtration process.

Purification of MWCNTs

The MWCNTs (Iljin Nanotech Co., Korea) were synthesized by a thermal chemical vapor deposition (CVD) method. The purity of the pristine MWCNTs, as received, was 97%. In order to eliminate the impurities in the MWCNTs (such as metallic catalysts), they were treated in 3 M HNO_3 at 60°C for 12 h, followed by refluxing them in 5 M HCl at 120°C for 6 h. The purity of the acid-treated MWCNTs was measured to be 99% using thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK).

Preparation of MWCNT Dispersion

0.5 mg/mL of the pristine and functionalized MWCNTs were dispersed in water containing cetyltrimethylammonium bromide (CTAB) (0.3 wt%). Ultrasound was then applied to the MWCNT dispersion using an ultrasonic generator (Kodo technical research Co., Ltd., Japan), which has a nominal frequency of 28 kHz, with a power of 600 W for 7 h at 25°C.

Characterizations

The surface morphology and shape of the microspheres were observed using field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The FESEM images were obtained by collecting the microspheres on an aluminum SEM disk, which was then coated with platinum. The acceleration voltages and working distances for each image were 15 kV and 6 mm, respectively. The average diameter of the PS microspheres was determined by counting 100 individual particles from the electronic SEM images using Scion Image® Analyzer Software.

Electrical Conductivity of MWCNT-adsorbed Microspheres

The electrical conductivity of the pressed disk-type MWCNT-coated polymer particles was measured by a four-probe method using a picoammeter with an internal voltage source (487, Keithley, USA) and an impedance analyzer (4284A, HP, USA).

ER Characterization

The MWCNT-adsorbed PS microspheres were washed several times in pure water to extract the remaining surfactants and dried in a vacuum oven at room temperature. The ER fluids were prepared using the dried microspheres dispersed in silicone oil (10 vol%) by sonication. No stabilizers were added to the microspheres dispersion in silicone oil. A DC high voltage source was used to apply a voltage to the sample. The gap between the two parallel electrodes was fixed precisely at 370 μm. The microstructure image of the ER fluid was obtained by optical microscopy (BX51, Olympus, Japan).

RESULTS AND DISCUSSION

PS microspheres were prepared using a dispersion polymerization method, which is one of the most popular methods of producing monodispersed polymer particles (Fig. 1(a)) [14–17]. CNTs generally form stabilized bundles as a result of the van der Waals force, resulting in the formation of hollow ropes. Therefore, obtaining a good dispersion of CNTs is one of the key issues involved in using CNTs in composites [18]. In this study, surfactants were used for the purpose of dispersing the MWCNTs in water, in order to preclude the impact that chemical modification would have on the inherent properties of the

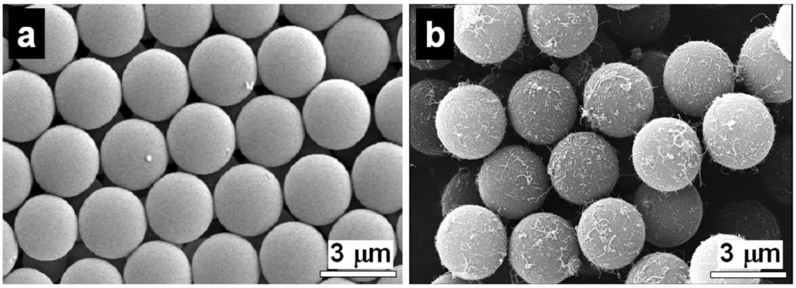

FIGURE 1 SEM images of (a) PS microspheres and (b) CNT-adsorbed PS microspheres.

individual MWCNTs. The MWCNTs were sonicated in aqueous solutions of a surfactant, such as CTAB, in order to stabilize them against thevan der Waals attractive force [19–20]. The concentration of the surfactant was approximately 0.3 weight% and the MWCNT concentration was 0.02 wt% (MWCNT powder weight per water weight), in order to form a homogeneous dispersion of the MWCNTs in an aqueous solution.

Once a homogeneous aqueous dispersion of the MWCNTs was obtained, the dispersion of the PS microspheres was blended with the MWCNT dispersion containing the surfactants. The blended dispersions were kept under ambient conditions for 48 h, during which time the MWCNT-adsorbed PS microspheres underwent slow sedimentation to the bottom of the glass containers. The MWCNTs-adsorbed PS microspheres were withdrawn, rinsed several times in deionized water to desorb the surfactants, air-dried and then vacuum-dried at room temperature overnight. The surface morphology of the microspheres was observed by FESEM, as shown in Figure 1(b). The MWCNTs were densely adsorbed on the surface of the PS microspheres (Fig. 2 (a)). Even after sonicating the MWCNT-adsorbed microspheres in deionized water, the individual MWCNTs remained strongly adhered to the PS microsphere surfaces (Fig. 2 (b)).

The electrical conductivity of these MWCNT-adsorbed microspheres was measured by a four-probe method using pressed disk-type specimens. The four-probe electrical measurements of the specimens gave a DC conductivity (σ_{DC}) of about 1.9×10^{-4} S/cm at room temperature, based on the total cross-sectional area. The actual quantity of adsorbed MWCNTs was measured using thermogravimetric analysis (TGA) at 600°C under a nitrogen atmosphere, as shown in Figure 3. Note that the PS decomposed almost entirely at this temperature.

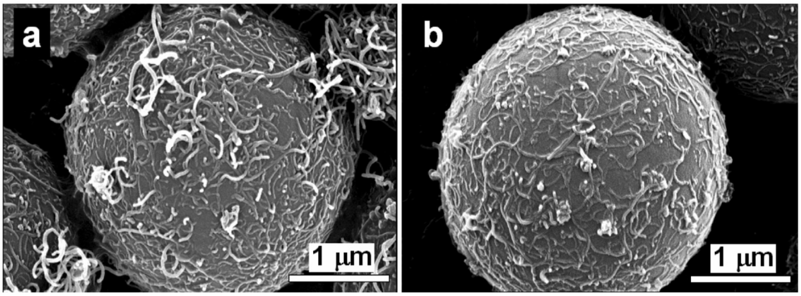

FIGURE 2 SEM images of CNT-adsorbed PS microspheres (a) before and (b) after their sonication in water.

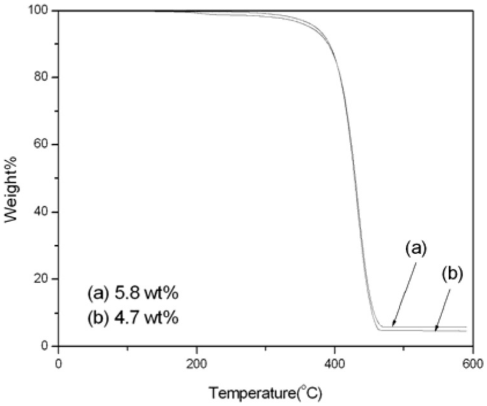

FIGURE 3 The quantity of CNTs adsorbed on the PS microspheres measured by TGA (a) before and after sonication.

The ER fluids were prepared by sonication using the dried MWCNT-adsorbed microspheres dispersed in silicone oil (10 vol%). No stabilizers were added to the MWCNTs-adsorbed microspheres dispersion in the silicone oil. A DC high voltage source was used to apply a voltage to the sample. The gap between the two parallel electrodes was fixed at 370 μm. The microstructure image of the ER fluid was obtained using an optical microscope. The behavior of the particle chain (resulting from the so-called 'fibrillation' process), based on the interfacial polarization within the MWCNT-adsorbed PS microspheres in silicone oil, was demonstrated under an electric field of 0.8 kV/mm applied for 5 s (Fig. 4). The MWCNTs-adsorbed PS microspheres

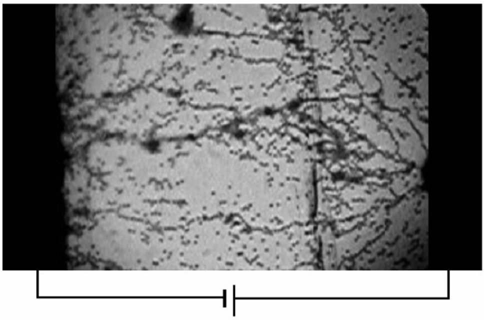

FIGURE 4 Optical microscopic images of the CNT-adsorbed PS microspheres dispersed in silicone oil 5 s after the application of an electric filed with a strength of 0.8 kV/mm. Gap distance between the two parallel electrodes; 370 μm.

formed thin and dense chains of particles under the applied electric field within one second, and the structure remained stable as long as the field was applied. The fibrillated chains were observed to span the two electrodes. It is possible that the fibrillated chain structure might provide a path for transporting the mobile carrier, and would therefore determine the conducting behavior of the ER fluid.

CONCLUSIONS

Surface-conductive microspheres consisting of a PS core (3 μm of diameter) and MWCNT-adsorbed shell were prepared using a simple process involving the blending of two colloidal solutions, viz. an aqueous MWCNT dispersion with a surfactant and an aqueous PS microsphere colloid. These microspheres were adopted as the suspended particles for ER fluids owing to the electrical conductivity of the MWCNT layers on the surface. The PS/MWCNT composite suspensions in silicone oil showed the typical characteristics of an ER fluid, forming a chain-like structure under an applied electric field (0.8 kV/mm).

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