

## Carbon Nanotube-Adsorbed Polystyrene and Poly(methyl methacrylate) Microspheres

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Carbon nanotubes have been among the most exciting new materials since their discovery in 1991.<sup>1</sup> Their remarkable properties have attracted considerable interest from the scientific community and from industry. There is now abundant experimental evidence of the outstanding properties of carbon nanotubes such as the mechanical, electrical, and thermal properties.<sup>2</sup> Many of these outstanding properties can be best exploited by incorporating nanotubes into some form of matrix, and the preparation of nanotube-containing composite materials is now a rapidly growing research area.<sup>3–6</sup> In many cases, these composites use not only the polymer matrixes but also other matrix materials, such as ceramics and metals.<sup>3</sup> A number of studies have used carbon nanotubes as fillers in polymer sheets and fibers.<sup>3</sup> Polymer composites reinforced with carbon nanotubes are believed to have many potential engineering uses, ranging from battery electrodes and electronic devices to much stronger composites.<sup>3–7</sup> Furthermore, its electrorheological (ER) characteristics have recently been reported, in which in situ polymerized particles of carbon nanotube nanocomposite with either poly(methyl methacrylate) (PMMA) or polyaniline (PANI) were dispersed in silicone oil.<sup>8</sup>

ER fluids are mainly suspensions of particles with a higher dielectric constant and/or conductivity than that of the

suspending medium fluids with a low dielectric constant and a low viscosity. They exhibit a drastic and reversible change in their rheological characteristics as a result of an applied electric field, because the ER particles are attracted to one another to form fibril structures aligned in the direction of the applied electric field.<sup>9</sup> A suspension microstructural transition from liquidlike to solidlike is obtained by controlling the imposed electric field strength.<sup>10</sup> According to the polarization model, the suspending particles are polarized as a result of the dielectric mismatch between the particles and the suspending fluid under an applied electric field.<sup>11</sup> The interaction among the polarized particles causes them to align themselves in the form of strings along the electric field direction.<sup>12</sup>

In this study, nanotubes were incorporated onto the surface of polystyrene (PS) and PMMA microspheres by a surprisingly simple, potentially scalable process. PS and PMMA microspheres, 3.0 and 6.5  $\mu\text{m}$  in size, respectively, were prepared using a dispersion polymerization method, which is one of the most popular methods for producing monodispersed polymer particles.<sup>13,14</sup> Note that a dispersion polymerization method adopted in this study is well-known for producing monodisperse polymeric particles, as reported by Shen et al.<sup>13</sup> The nanotubes used were multiwalled carbon nanotubes (approximately 97% pure, Iijin Nanotech, Korea), which were synthesized using a thermal chemical vapor deposition method. To remove the metallic catalyst residues in the nanotubes prior to their use, the nanotubes were treated in 3 M  $\text{HNO}_3$  at 60  $^\circ\text{C}$  for 12 h, which was followed by refluxing in 5 M  $\text{HCl}$  at 120  $^\circ\text{C}$  for 6 h.<sup>15,16</sup> Although single-walled carbon nanotubes have many applications in industry, they have not been fully commercialized owing to their expense. However, multiwalled carbon nanotubes are now more than 500 times cheaper than single-walled nanotubes at a similar purity (>95%).<sup>6</sup> The electronic properties of perfect multiwalled carbon nanotubes are known to be similar

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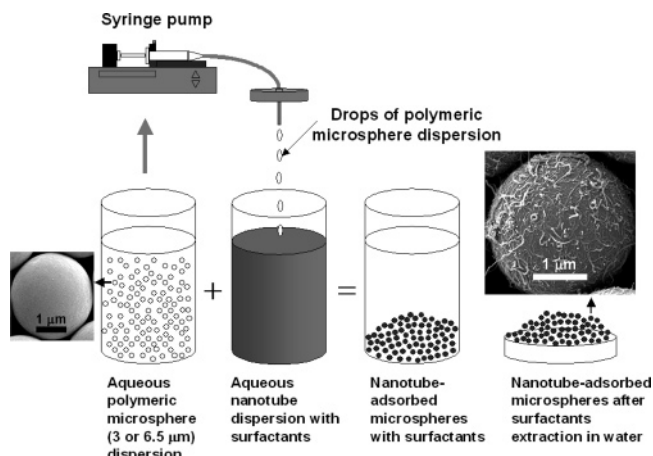
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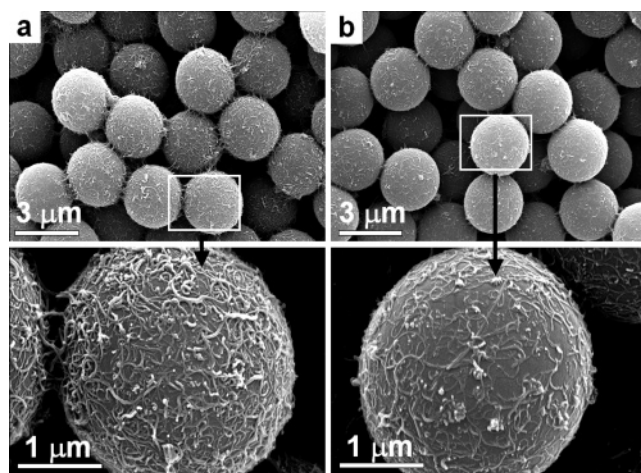
to those of single-walled nanotubes owing to the one-dimensional electronic structure and the electronic transport characteristics.<sup>4</sup>

Nanotubes 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 nanotubes is one of the key issues in using nanotubes in composites.<sup>17</sup> By introducing small amounts of nanotubes in the form of small bundles or individual tubes, the mechanical strength, electrical conductivity, and thermal conductivity of a polymer composite can be improved tremendously compared with those of the pristine polymer.<sup>18</sup> The dispersion of nanotubes in the polymer matrix has been examined from different points of view using noncovalent functionalization and by covalent functionalization as well.<sup>19</sup> On the other hand, the poor dispersibility of nanotubes in either water or organic solvents has limited their practical applications.<sup>15,16,20–22</sup> To overcome this impediment, research has been focused on the dispersion of nanotubes in solvents by either modifying the nanotube surface chemistry or by the addition of surfactants.<sup>15,16,20–23</sup> In this study, surfactants were selected for the process of dispersing nanotubes in water to minimize the impact of chemical modification on the inherent properties of the individual nanotubes and to avoid the soluble problem of PS or PMMA microspheres in organic solvents, for example, chloroform, dimethylformamide, and so forth. The nanotubes were sonicated in aqueous solutions of the surfactants such as anionic sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS), cationic cetyl trimethylammonium bromide (CTAB), and nonionic Triton X-100 to stabilize the nanotubes against the van der Waals attractive force.<sup>16,20–23</sup> The concentration of each surfactant was approximately 0.3 wt%, and the nanotube concentration was 0.02 wt% (nanotube powder weight per water weight) for forming a homogeneous dispersion of nanotubes in an aqueous solution.

Once a homogeneous aqueous dispersion of nanotubes was obtained, each dispersion of PS and PMMA microspheres was dropped into a glass bath containing the nanotube dispersion with various surfactants using a syringe pump at a rate of 0.5 mL/min (Figure 1). During this process, the



**Figure 1.** Scheme of the simple processing technique for producing the carbon nanotubes-adsorbed polymeric microspheres.



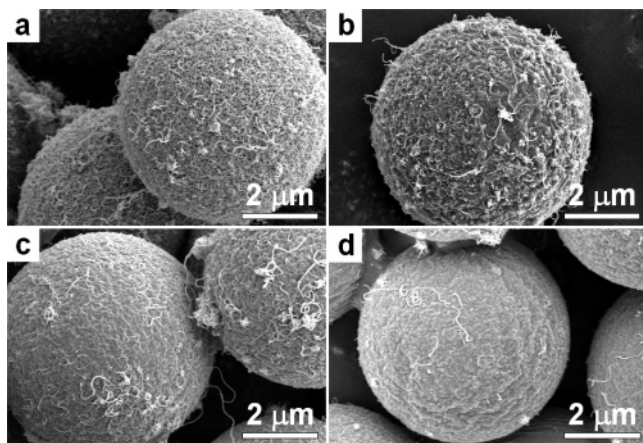
**Figure 2.** FESEM images of the carbon nanotube-adsorbed PS microspheres using the surfactants: (a) CTAB and (b) NaDDBS.

nanotube dispersion was gently stirred. After the dropping of the dispersion of polymeric microspheres was completed, the blended dispersions were kept at ambient conditions for 48 h without stirring. During this time, the nanotubes-adsorbed PS microspheres underwent slow sedimentation to the bottom of glass vials. At the same time of the sedimentation of the PS microspheres, the supernatant of the nanotube dispersion turned into a clear solution. The nanotubes-adsorbed PS microspheres were withdrawn, rinsed several times in deionized water to desorb the surfactants, and then air-dried and vacuum-dried at room temperature overnight. The surface morphology of the microspheres was observed by field emission scanning electron microscopy (FESEM). The nanotubes were densely adsorbed on the surface of the PS microspheres. The best result was obtained when the nanotubes were dispersed in an aqueous solution of either CTAB or NaDDBS (Figure 2). Aqueous dispersions of nanotubes formed with either SDS or Triton X-100 did not generate PS microspheres with strongly adsorbed nanotubes.

Even after sonicating the carbon nanotube-adsorbed microspheres in deionized water, the individual nanotubes remained strongly adhered to the PS microsphere surfaces. The adhesion of the nanotubes to the PS microsphere surfaces was believed to be related to the hydrophobic interaction between PS and the nanotubes.<sup>21</sup> Therefore, the same process

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**Figure 3.** FESEM images of the carbon nanotube-adsorbed PMMA microspheres using the surfactants: (a) CTAB, (b) NaDDBS, (c) SDS, and (d) Triton X-100.

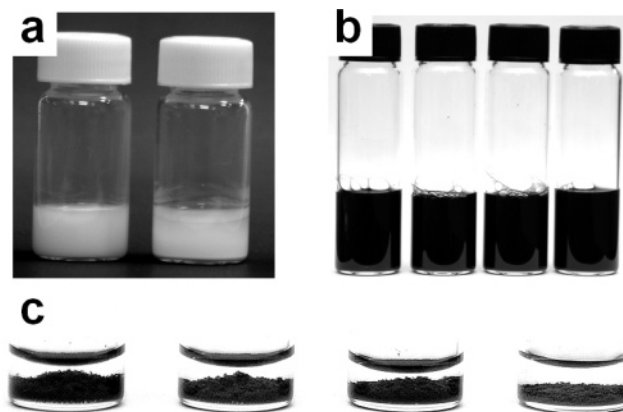
**Table 1. Quantity of Carbon Nanotubes Adsorbed on Microspheres with Various Surfactants and Their Conductivities**

	amount (wt %) of carbon nanotubes coated on microspheres		conductivities (S/cm)	
	PS	PMMA	PS	PMMA
CTAB	5.9	3.9	$1.9 \times 10^{-4}$	$6.3 \times 10^{-5}$
NaDDBS	4.7	3.6	$2.9 \times 10^{-5}$	$5.2 \times 10^{-5}$
SDS	1.8	2.1		
Triton X-100	2.3	1.6		

was applied to the PMMA microspheres prepared. Figure 3 shows SEM images of the PMMA microspheres after a treatment with a similar aqueous nanotube dispersion.

The electrical conductivity of these nanotubes-adsorbed microspheres was measured by a four-probe method using pressed disc-type specimens. The four-probe electrical measurements of the specimens gave a DC conductivity ( $\sigma_{DC}$ ) of  $1.9 \times 10^{-4}$  to  $6.3 \times 10^{-5}$  S/cm at room temperature, based on the total cross-sectional area (Table 1). When only the external shell of the nanotubes is considered, the conductivity will be much greater than those values because the electrical conductivity of the pure multiwalled carbon nanotubes is about  $2.3 \times 10^4$  S/cm.<sup>24</sup> However, the external shell thickness of nanotubes could not be calculated in this study because of the irregular feature of the nanotubes adsorbed on the surface of the microspheres. The actual quantity of adsorbed nanotubes was measured using thermogravimetric analysis at 600 °C under a nitrogen atmosphere, as shown in Table 1. Note that the PS and PMMA decomposed almost entirely at this temperature.

Although the efficiency of the four surfactants on adsorbing nanotubes on the PS or PMMA microspheres differed significantly, the precise mechanism by which the microspheres and the different surfactants interact is uncertain. It was recently reported that the interactions between the surfactant molecules and the nanotube surface were mainly hydrophobic in nature.<sup>21</sup> When the PS or PMMA microspheres were added to the nanotube dispersion, the surfactant molecules could serve as a link between the nanotubes and the microspheres, providing hydrophobic interactions that can enhance the contact at the interface. It was reported that



**Figure 4.** Images of (a) PS (2.7 wt%, left) and PMMA (2.4 wt%, right) microsphere dispersions; (b) nanotube (0.02 wt%) dispersions with the surfactants (0.3 wt%) CTAB, NaDDBS, SDS, and Triton X-100 (from left to right); and (c) blended dispersions of a polymeric microsphere and nanotube: PS/nanotubes with CTAB, NaDDBS, SDS, and Triton X-100 (from left to right).

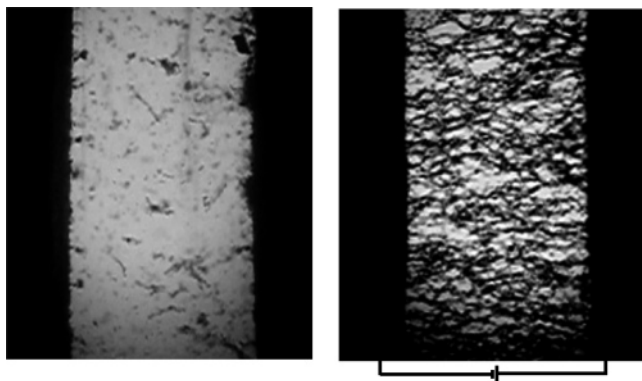
NaDDBS consisting of a benzene ring moiety or CTAB provided better stability of the nanotubes in water by an order of 10–100 compared with that of the other commonly employed surfactants.<sup>20,25</sup> Therefore, the stability of the individual nanotubes with the surfactants in water may be responsible for the fraction of adsorbed nanotubes on the polymeric microspheres. Furthermore, the nanotubes with a relatively smaller diameter (<20 nm) adsorbed more on the surface of the PS and PMMA than those with a larger diameter. The diameter of the multiwalled nanotubes used in this study ranged from about 8 to 40 nm.

The sedimentation times of the nanotubes were examined (Figure 4) at room temperature, when the PS microsphere colloid was added to the nanotube dispersion containing the four different surfactants. Unlike the long sedimentation time (>2 days) of the nanotubes with SDS or Triton X-100, the sedimentation time of the nanotubes with CTAB or NaDDBS was <1 h, when the PS microsphere colloids were added. The faster sedimentation time indicates a stronger interfacial interaction between the PS microspheres and the surfactants with the nanotubes. When the PS microsphere dispersion was added to the nanotube dispersion with the surfactants, adsorption of the nanotubes with the surfactants occurs rapidly on the surface of the PS microspheres, thereby inducing the sedimentation of the nanotubes with the surfactants.

The nanotubes-adsorbed PMMA microspheres prepared using the CTAB surfactant were washed in pure water several times to extract the remaining surfactants and dried in a vacuum oven at room temperature. The ER fluids were prepared by sonication using the dried nanotubes-adsorbed microspheres dispersed in silicone oil (10 vol%). No stabilizers were added to the nanotubes-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 350 μm. The microstructure image of the ER fluid was obtained using an optical microscope. The behavior of the particle chain (so-called

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**Figure 5.** Optical microscopic images of the nanotubes-adsorbed PMMA microsphere dispersed in silicone oil before (left) and after the application of an electric field strength of 1.4 kV/mm (right). Both sides of the horizontal black stripes represent the electrodes. The gap distance between the two parallel electrodes was 350  $\mu\text{m}$ .

“fibrillation”), based on interfacial polarization within nanotubes-adsorbed PMMA microspheres in silicone oil, was demonstrated under an applied electric field of 1.4 kV/mm for 5 s (Figure 5). The nanotubes-adsorbed PMMA microspheres form thin and dense chains of particles under the applied electric field within 1 s, and the structure remained stable as long as the field was applied. The fibrillated chains were observed and spanned two electrodes. It is possible that the fibrillated chains structure might provide a path for the mobile carrier transporting and would determine the conducting behavior of ER fluids.

Theoretically, suspended ER particles are normally assumed to be monodisperse and spherical. However, the particles used experimentally in ER fluids are often polydisperse and irregular.<sup>26</sup> These morphological factors of the dispersed phase are one of the most critical issues. Some efforts have been reported, including PANI-coated silica<sup>27</sup> and PMMA with a double-layered shell.<sup>28</sup> Spherical monodisperse polymer microspheres consisting a PMMA core and

a PANI shell were prepared from either simple chemical oxidation<sup>29</sup> or in situ graft polymerization of aniline onto a PMMA core to improve the adhesion between the shell and core.<sup>30</sup> Monodisperse and spherical PS or PMMA particles, which are only conducting on the surface, were used as the dispersed phase of the ER fluids in this study. Compared with the previously reported spherical and monodisperse ER particles with PMMA,<sup>29</sup> the carbon nanotube-coated PMMA ER particles are believed to be rather simple to prepare, and their surface conductivity is easy to control. The ER properties using a rotational rheometer under an applied electric field are currently under investigation, and the details will be reported elsewhere. It should also be noted that owing to ER fluids’ many desirable characteristics, such as a short response time, low power consumption, smoothness of operation, and simple mechanics, ER fluids have been used in many fields using electromechanical devices, including engine mounts, shock absorbers, clutches, ER valves, and robotic arms, as well as other control systems.<sup>31</sup> Despite the extensive research and development efforts, these ER devices are still in the very early stages of commercialization because of several unsolved problems, such as the colloidal instability and the inadequate yield stress. Furthermore, the process conducted under mild conditions (aqueous, room temperature, and nontoxic) does not harm the inherent properties of the polymeric microspheres and could be scaled up for high-volume production.

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**Supporting Information Available:** Detailed synthesis methods of polymeric microspheres and characterization given (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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