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Electrically Conductive Polymeric Nanocomposites Prepared in Alcohol Dispersion of Multiwalled Carbon Nanotubes

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In this study, electrically conductive microspheres were prepared by the adsorption of multiwalled carbon nanotubes (MWCNTs) on the surfaces of polymeric microspheres (polystyrene and poly(methylmethacrylate)) in MWCNT-dispersed alcohols (methanol, ethanol, and isopropanol) without surfactants. The stability of the MWCNT dispersions was measured using a recently developed multiple light scattering measurement instrument (Turbiscan). The individual MWCNTs on the surfaces of the microspheres were observed by scanning electron microscopy. The contents of MWCNTs in the composites were determined by thermogravimetric analysis and were found to range from 1.6 wt% to 4.5 wt%. The electrical conductivity and surface charge of the composite microspheres were also investigated.

1. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) and the determination of their outstanding mechanical, electrical, and thermal properties, which are particularly important in nanocomposites, they have been considered as very promising conductive fillers [1,2]. However, the advantages of CNTs have not been fully realized due to the difficulties encountered in producing nanocomposites with well-dispersed CNTs [3]. CNTs tend to form aggregates owing mainly to their extreme van der Waals force interactions and high aspect ratio. In addition, the poor dispersibility of CNTs in either aqueous or organic solvents

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has limited their practical applications. To overcome this impediment, researchers have focused on achieving the dispersion of CNTs in solvents by either the addition of surfactants or by modifying the CNT surface chemistry. However, utilizing surfactants to obtain a CNT dispersion was found to be unsuitable in many applications, because they need to be removed from the final product [4,5].

In this study, we prepared well dispersed multiwalled carbon nanotubes (MWCNTs) dispersions without a surfactant in various alcohols. Furthermore, we measured the stability of the MWCNTs in alcohol using an optical analyzer (Turbiscan), which is able to detect the destabilization of an opaque dispersion by multiple light scattering [6]. We also prepared MWCNT-adsorbed polymeric microspheres using the solutions of the MWCNTs in various alcohols. The morphological and electrical properties of the MWCNT-adsorbed microspheres were characterized by scanning electron microscopy (SEM) and a four-probe resistivity meter, respectively. The surface charge of the microspheres and MWCNT-adsorbed microspheres was also investigated.

2. EXPERIMENTAL

2.1 Materials

Styrene (Aldrich, USA) and methyl methacrylate (MMA, DC chemical co. Ltd., Korea) were used as the monomer of the dispersion polymerization. Methanol, ethanol, and isopropanol were purchased from DC chemical co., Ltd., Korea. Polyvinylpyrrolidone (PVP, M_w : 360,000 g/mol, Aldrich, USA) was used as a stabilizer without further purification. 2,2-Azobisisobutyronitrile (AIBN, Junsei, Japan) was used as an initiator and was dissolved in ethanol to remove the inhibitor, followed by precipitation at -10°C , and stored in a refrigerator before polymerization.

2.2 Preparation of Polymeric Microspheres

Polystyrene (PS) and poly(methylmethacrylate) (PMMA) microspheres were synthesized in a 250 mL three-neck round-bottom flask with mechanical stirring at 100 rpm under a nitrogen atmosphere at 70°C for 24 h and 63°C for 24 h, respectively [7–9]. A pre-weighed amount of ethanol was charged in the reactor, followed by the addition of the monomer and PVP. Then, the AIBN dissolved in ethanol was added and the polymerization was initiated. The withdrawn polymerization products were rinsed off with ethanol, centrifuged repeatedly

to remove the non-reacted materials and dried in a vacuum oven at 60°C for 2 days.

2.3 Preparation of Acid Treated MWCNTs

To eliminate any impurities within them such as metallic catalysts, the MWCNTs were treated with acid using the following typical procedure [10]. The MWCNTs were treated in an acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 60°C for 24 h. As a result of the purification process, carboxylic and hydroxyl functional groups are introduced onto the surface of the MWCNTs [11].

2.4 Adsorption of MWCNTs onto PS and PMMA Microspheres

The acid treated MWCNTs were sonicated in various alcohols (methanol, ethanol, and isopropanol) without surfactants to bring about their adsorption onto the PS and PMMA microspheres. The solution of the MWCNTs had the appearance of black color ink, indicating that the MWCNTs were well dispersed and stable in the alcohol. The maximum concentration required for forming a homogeneous dispersion of the MWCNTs in an alcohol solution was 0.02 wt% (weight of MWCNTs per weight of alcohol). Then, the dispersion of PS and PMMA microspheres was dropped into a glass bath containing the MWCNT dispersion using a syringe pump at a rate of 0.5 mL/min. During this process, the MWCNT dispersion was gently stirred. While the blended dispersions were kept at ambient conditions for 48 h, the MWCNT adsorbed PS and PMMA microspheres underwent slow sedimentation to the bottom of the glass vials. During the sedimentation of the PS and PMMA microspheres, the MWCNT dispersion also turned into a clear solution. The MWCNT adsorbed PS and PMMA microspheres were withdrawn, rinsed several times in alcohol and then air-dried and vacuum dried at room temperature overnight. The melt-compounded composite samples were also prepared for comparison with samples prepared by adsorption method. The compounding was performed with a Brabender (Plastograph[®] EC, Brabender[®], Germany) at a temperature of 170 and 250°C during 5 min and the mixer rotation rate was 300 rpm.

2.5 Characterization

The stability of the MWCNTs dispersed in alcohols was investigated using a Turbiscan (Turbiscan Lab, Formulaction, France) at 25°C for

120 h. The MWCNT dispersions were poured into a 30 ml cylindrical glass vial to an approximate height of 50 mm and then the vial was put into the Turbiscan analyzer. The stability of the MWCNT dispersions was monitored by measuring the transmittance and back scattering of a pulsed near infrared light ($\lambda = 880$ nm) from the MWCNTs dispersions. The transmittance detector was positioned at 180° to the light source and received the light passing through the dispersion, while the back scattering detector received the light scattered backwards by the dispersion at an angle of 45° . The detection head scans the entire height of the sample, acquiring transmittance and back scattering data at intervals of $40\text{ }\mu\text{m}$ [6]. Back scattering was not considered in this study, because the MWCNT dispersions had a jet-black color and absorbed almost all of the back scattered light. The morphology of the MWCNTs on the microspheres was observed using SEM (Hitachi, S-4300, Japan) after pre-coating the sample with a homogeneous Pt layer by ion sputtering (Hitachi, E-1030, Japan). Thermogravimetric analysis (TGA, TA instruments, Q50, UK) was used to measure the MWCNT contents in the MWCNT adsorbed microspheres. The measurements were performed at a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 600°C . To measure their electrical conductivity, the MWCNT adsorbed microspheres were prepared in the form of disc-type pellets with a thickness of 0.7 mm by applying a pressure of 1 ton at room temperature using a Carver laboratory press (Model #3912, Carver Inc., Wabash, IN, USA). The electrical conductivity of the microsphere nanocomposite was measured by a four-probe method with a resistivity meter (Mitsubishi chemical co., Hiresta-up MCP-HT450, Japan). The zeta potentials of PS, PMMA, PS/MWCNT and PMMA/MWCNT were measured using an electro-phoretic light scattering spectrophotometer (Otsuka electronics, Photal ELS-8000, Japan).

3. RESULTS AND DISCUSSION

The starting point for the preparation of the MWCNT adsorbed microspheres is the preparation of a stable aqueous dispersion of the MWCNTs. First, we prepared a dispersion of the MWCNTs in alcohol by acid treatment. This acid treatment facilitates the dispersion of the MWCNTs in organic solvents or aqueous media, because of their increased solubility [11–13]. The stability of the MWCNTs dispersed in alcohols was characterized by a multiple light scattering method (Turbiscan).

Figure 1 shows the transmittance profiles, plotted as the transmittance intensity vs. time, obtained from the pristine MWCNTs

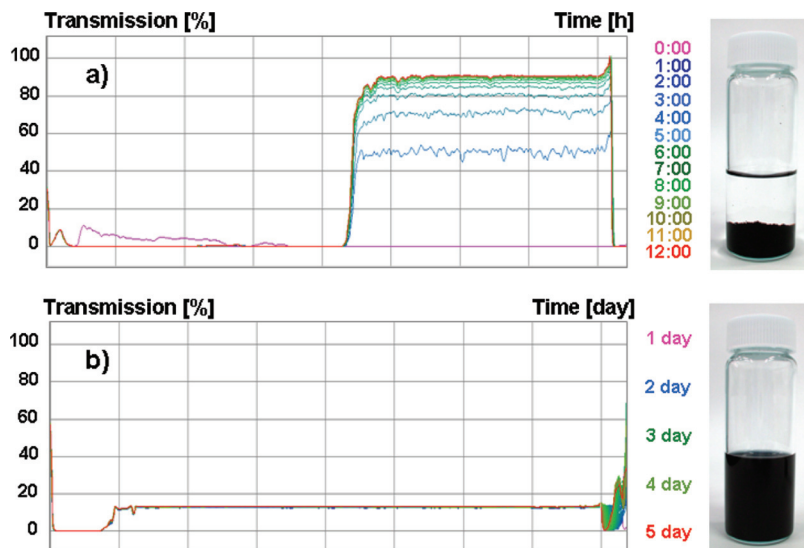


FIGURE 1 Turbiscan transmittance profiles of (a) pristine MWCNTs in methanol and (b) acid treated MWCNTs in methanol.

and acid treated MWCNTs in methanol, respectively. The pristine MWCNTs aggregated severely within an hour and the transmittance of their dispersion gradually increased up to $\sim 90\%$ with time due to sedimentation. After 12 h, the most pristine MWCNTs were completely precipitated at the bottom of the vials. However, the functionalized MWCNTs remained in a well-dispersed state in the alcohols, with the transmittance ($\sim 10\%$) remaining constant with time. As shown in the photograph, the acid treated MWCNTs were highly dispersible in methanol. These results indicate that the acid treated MWCNTs were more stable in alcohols than the pristine MWCNTs.

The morphology of the microspheres and MWCNT adsorbed microspheres is shown in Figure 2. We synthesized the polymeric microspheres by dispersion polymerization. The microspheres were successfully prepared with a spherical shape. The average sizes of the PS and PMMA microspheres were 2.8 ± 0.3 and $11.6 \pm 0.4 \mu\text{m}$ ($N = 100$), respectively. From the SEM observation (Fig. 2), the surface of as-polymerized microspheres was very clear and slick, and no impurities were observed on their surface. The MWCNT adsorbed microspheres prepared from the MWCNT dispersion in methanol, ethanol and isopropanol, respectively were also observed. The SEM images show that the MWCNTs were densely adsorbed on the surface of

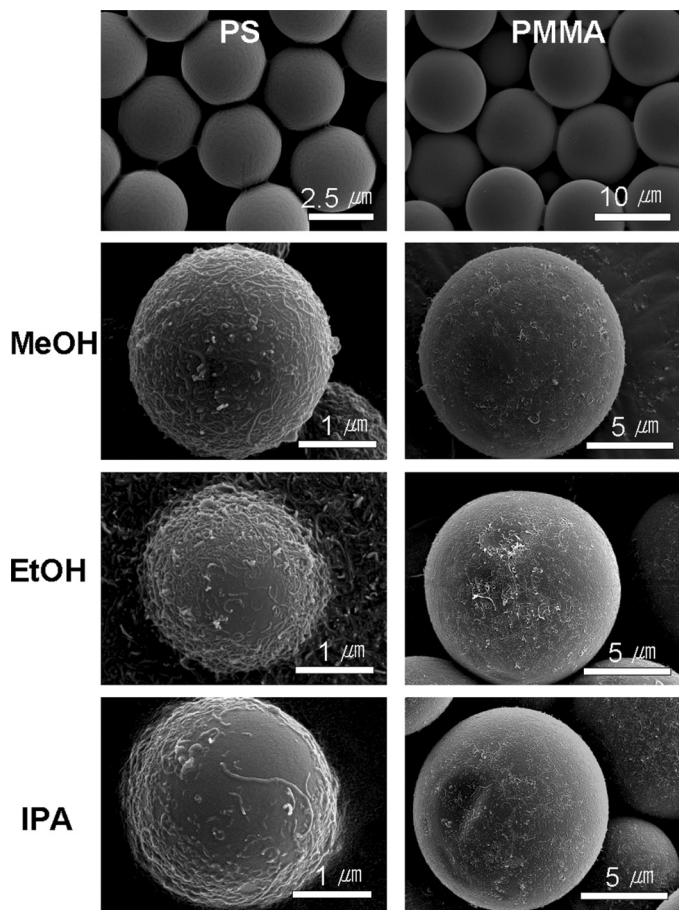


FIGURE 2 SEM images of the microspheres. PS, PMMA, and MWCNT-adsorbed PS and PMMA microspheres in various alcohols (MeOH; methanol, EtOH; ethanol, IPA; isopropanol).

the microspheres. Even after sonicating the MWCNT-adsorbed microspheres in alcohol, the individual MWCNTs remained strongly adhered to the microsphere surfaces, as shown in Figure 3. The adhesion of the MWCNTs to the PS and PMMA microsphere surfaces was believed to be related to the interfacial interaction between the microspheres and the MWCNTs, such as electrostatic and Van der Waals interactions [14].

The contents of MWCNTs on the surface of the microspheres and electrical conductivity of the MWCNT adsorbed microspheres are

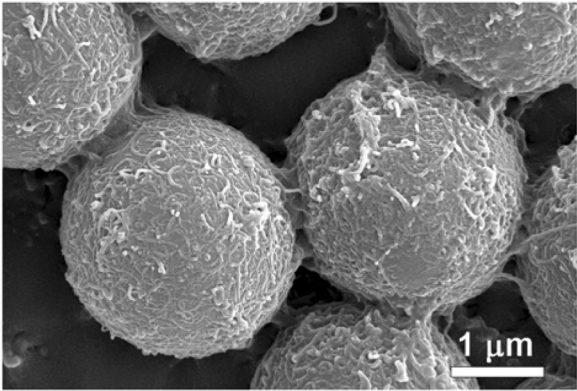


FIGURE 3 SEM image of MWCNT-adsorbed PS microspheres after sonication.

summarized in Table 1. The MWCNTs contents were calculated to be 4.2~4.5 wt% on the PS microspheres in the various alcohols. In the case of PMMA, the MWCNTs contents were calculated to be 1.6~2.3 wt%. The contents of the adsorbed MWCNTs were only slightly dependent on the various alcohols. However, the results show that the contents of MWCNTs on the surface of the PS microspheres were higher than those on the surface of the PMMA microspheres, because the average size and surface area of the PS microspheres were bigger than those of the PMMA microspheres. The electrical conductivity of the MWCNT adsorbed microspheres was measured by the four-probe method at room temperature. The pure PS and PMMA microspheres have very low electrical conductivities of the order of 10^{-17} and 10^{-15} , respectively. However, the conductivity of the PS/MWCNT composites ranged from 2.9×10^{-2} to 4.4×10^{-2} S/cm. In the case of PMMA, the conductivity of the composites was in the

TABLE 1 MWCNT Contents on the Surface of the PS and PMMA Microspheres and their Conductivity

	Contents of MWCNT (wt%)		Conductivity (S/cm)	
	PS/MWCNT	PMMA/MWCNT	PS/MWCNT	PMMA/MWCNT
Methanol	4.2	1.9	4.4×10^{-2}	6.7×10^{-6}
Ethanol	4.2	1.6	3.0×10^{-2}	2.0×10^{-7}
Isopropanol	4.5	2.3	2.9×10^{-2}	1.4×10^{-6}

TABLE 2 The Electrical Conductivity of PS/MWCNT and PMMA/MWCNT Composites Prepared by Melt Compounding

Samples	Contents of MWCNT (wt%)	Conductivity (S/cm)
PS/MWCNT	4.2	6.7×10^{-5}
PS/MWCNT	4.5	2.6×10^{-4}
PMMA/MWCNT	1.6	8.1×10^{-9}
PMMA/MWCNT	1.9	8.9×10^{-9}
PMMA/MWCNT	2.3	5.2×10^{-7}

range from 1.4×10^{-6} to 2.0×10^{-7} S/cm. The electrical conductivity was related to some extent to the content of MWCNTs adsorbed on the microspheres. The melt-compounded PS/MWCNT and PMMA/MWCNT composites were also prepared for the comparison. The electrical conductivities of the composites prepared by adsorption method were higher than the composites prepared by melt compounding in the same range of MWCNTs contents (Table 2). This result might be attributed to the poor dispersion of MWCNTs in the polymer matrix, when the composites were prepared by melt compounding. The surface charges of the microspheres and MWCNT adsorbed microspheres in methanol were determined by a zeta potential analyzer for the purpose of comparison. Table 3 shows the measured surface charges of the microspheres and those of the MWCNTs adsorbed in various alcohols. We observed that the zeta-potential of the MWCNT adsorbed microspheres was lower than that of the pure microspheres. Hence, the zeta-potential of the MWCNT adsorbed microspheres confirmed that the adsorption of the MWCNTs was properly attained.

TABLE 3 Zeta-Potential Values of Acid Treated MWCNTs, Microspheres and MWCNT Adsorbed Microspheres in Alcohol

Samples	Value of ζ -potential (mV)
Acid treated MWCNTs	-29.01
PS microspheres	-0.67
PMMA microspheres	-1.23
PS/MWCNTs prepared with methanol	-5.37
PMMA/MWCNTs prepared with methanol	-4.22
PS/MWCNTs prepared with ethanol	-5.19
PMMA/MWCNTs prepared with ethanol	-3.78
PS/MWCNTs prepared with isopropanol	-5.21
PMMA/MWCNTs prepared with isopropanol	-4.00

4. CONCLUSION

MWCNTs could be directly dispersed in various alcohols after simple acid treatment. The MWCNT-adsorbed polymeric microspheres were successfully prepared using the adsorption method, as confirmed by SEM and TGA characterization. The electrical conductivities of the PS/MWCNT and PMMA/MWCNT composites were measured to be approximately 10^{-2} and 10^{-6} S/cm, respectively. The surface charge of the microspherical composites was also enhanced by the adsorption of the MWCNTs.

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