

Incorporation of Multiwalled Carbon Nanotubes on the Surface of Polystyrene Microspheres via *In Situ* Suspension Polymerization

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Abstract: Polystyrene (PS) microspheres selectively coated with multiwalled carbon nanotubes (MWCNTs) were prepared by *in situ* suspension polymerization. The styrene monomer was polymerized in an aqueous matrix with poly(vinyl pyrrolidone) (PVP), MWCNTs and 2,2-azobisisobutyronitrile. PVP was used as both as an agent for dispersing the MWCNTs using a wrapping strategy in an aqueous system and as a steric stabilizer for styrene droplets. Therefore, MWCNTs wrapped with PVP were dispersed on the surface of PS microspheres. Scanning and transmission electron microscopy confirmed that the MWCNTs were located only on the surface of the S-PS/MWCNT microspheres. The electrical conductivity of the MWCNT-network on the surface of the PS microspheres was analyzed by electrical resistance measurements. Overall, PS/MWCNT microspheres can be used to produce highly concentrated MWCNT-dispersed PS films by hot compression.

Keywords: multiwalled carbon nanotubes, polystyrene, microspheres, suspension polymerization, selective incorporation.

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention owing their outstanding mechanical, thermal, and electrical properties.¹⁻⁴ Recently, substantial effort has been directed towards using CNTs as reinforcing fillers because of their attractive properties. Only a small amount of CNTs are needed to affect the polymer properties because of their low mass density and high aspect ratio.⁵ However, two important problems must be considered when producing high performance polymer/CNT nanocomposites. CNTs are poorly dispersed in a polymer matrix because of Van der Waals forces and there is the poor interfacial adhesion with the polymer. Good interfacial adhesion is essential for good load transfer.⁶ A range of mechanical and chemical methods can be used to overcome these problems. In these mechanical methods, other supporting materials, such as surfactants and polymers, can stabilize the CNTs by wrapping them.^{7,8} Chemical methods include CNT surface modifications using acid treatments and proper reactions.⁹⁻¹¹

Polymeric microspheres covered with CNT, which are one kind of polymer/CNT nanocomposite, have many useful applications, such as electrically conducting particles for electrorheological (ER) fluid¹² and precursors for CNT hollow spheres¹³ that are fabricated by the removal of polymer particles from the CNT/polymer microsphere. Additionally, ordered microspheres can be used as templates to control

CNT-networking.¹⁴ Transparent conducting films¹⁵ for electrical devices and scaffolds¹⁶ can be fabricated for tissue engineering by removing the polymer from the CNT-networked microsphere. In addition, highly concentrated CNT dispersed composite films¹⁷ can be made by melting the polymer in the CNT-networked microspheres.

Oil-in-water (O/W) emulsions,¹⁸ adsorption^{12,19} and *in situ* polymerization^{20,21} methods can be used to fabricate polymer/CNT microspheres. Unlike *in situ* polymerization methods, O/W emulsion and adsorption methods are two-step processes that consist of both polymerization and composite formation steps. In the most recent research issue, CNT-coated PS microspheres were prepared from PS nanospheres with carboxyl acid groups on the surface and the CNTs, which were grafted with poly(vinyl pyrrolidone).¹⁹ In a previous study, poly(methyl methacrylate) (PMMA)/CNT microspheres were fabricated by *in-situ* dispersion polymerization. However, the CNTs were located on both the surface and inside of the PMMA microspheres^{20,21} because the dispersion polymerization process is a one-phase system. The suspension polymerization system has a matrix and monomer phase, and polymerization occurs at the monomer droplet. Therefore, polymeric microspheres that are covered with CNTs can be fabricated if the CNTs are dispersed in a matrix. On the other hand, polymeric microspheres with CNTs inside of them can be fabricated when the CNTs are dispersed in the monomer phase.

In this study, an *in situ* suspension polymerization method was used to incorporate multiwalled carbon nanotubes

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(MWCNTs) only on the surface of the polystyrene (PS) microspheres. For this suspension polymerization, a solution consisting of two immiscible liquids, water containing the MWCNTs and the styrene monomer, was used. The two phases were stabilized using a steric stabilizer to create a uniform emulsion, whilst retaining the uniformly sized microspheres. During polymerization, the PS microspheres were produced and covered with the MWCNTs. A conducting MWCNT network formed in the PS microspheres, which increased dramatically the volume conductivity from 7.69×10^{-16} S/cm for the neat PS microspheres to 5.33×10^{-5} S/cm for the conducting composites. Highly concentrated CNT-dispersed PS films were obtained by hot compression. At a concentration of 0.85 wt% MWCNTs, orderly dispersed MWCNTs improved the electrical percolation threshold of the composite film.

Experimental

The MWCNTs (purity > 95%, Hanhwa Nanotech Co., Korea) used in this study were synthesized by thermal chemical vapor deposition (CVD). The styrene (Samchun Chemical, Korea) monomer was used to fabricate the PS microspheres. Poly(vinyl pyrrolidone) (PVP, Mw: 360,000 g/mol, Aldrich) was used as a steric stabilizer for the O/W emulsion system, and 2,2-azobisisobutyronitrile (AIBN, Junsei, Japan) was used as the initiator. Polymerization was carried out in distilled water (di-water).

Purification of MWCNTs. The MWCNTs were treated with acid using the following typical procedure to eliminate impurities in the MWCNTs, such as metallic catalysts and amorphous carbon. First, the MWCNTs were treated with a concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3/1 v/v, 95% and 60%, respectively) solution at 60 °C for 6 h. Carboxylic and hydroxyl functional groups were introduced to the surface of the MWCNTs during the purification process.²² The acid functionalized MWCNTs were washed with di-water several times using a nylon membrane filter (0.45 μm) and dried in a vacuum oven overnight at 80 °C.

Preparation of PS Microspheres via Suspension Polymerization. Suspension polymerization was carried out in a 250 mL round bottom flask at 75 °C for 6 h. PVP (1 wt%) was dissolved in di-water solution (150 mL) and loaded into the reactor. Styrene (14 g) and AIBN (0.12 g) were added, and the mixture solution was homogenized at 1,200 rpm using an Ultra-Turrax T25 (Ika Labortechnik, Staufen, Germany) to form the stable microspheres. The polymerization products were rinsed with ethanol and centrifuged repeatedly to remove any non-reacted styrene and PVP. The PS microspheres were then dried in a vacuum oven at room temperature for 48 h.

Preparation of PS Microspheres that were Covered with MWCNTs (S-PS/MWCNT Microsphere). The PS microspheres with the MWCNTs on their surface (S-PS/MWCNT

microspheres) were prepared using the following method. The process was fundamentally the same as previously mentioned for polymerizing the PS microspheres. The acid-treated MWCNTs (0.05 wt%) and PVP (1 wt%) were added separately to di-water (150 mL). The aqueous MWCNTs dispersion was ultrasonicated for 20 min at 25 °C using an ultrasonic generator (Kodo Technical Research Co., Korea) with a nominal frequency and power of 28 kHz and 600 W, respectively. As described previously, the S-PS/MWCNT microspheres were then fabricated by heating and stirring the mixture solution containing styrene and AIBN. The S-PS/MWCNT microspheres were processed in accordance with the procedures described above, including the washing and drying steps.

Preparation of MWCNT/PS Composite Film. The MWCNT/PS composite film was fabricated using the S-PS/MWCNT microspheres. The S-PS/MWCNT microsphere powders were placed between the metal plates. The plates were pressed together with an applied pressing force of 1 ton for 5 min at 250 °C using a Carver laboratory press. After hot compression, the plates were cooled to room temperature, creating a MWCNT/PS composite film between the plates.

Characterization. After pre-coating the sample with a homogeneous Pt layer by ion sputtering (E-1030, Hitachi, Japan), the morphology of the microspheres was observed using field emission scanning electron microscopy (FESEM, S-4200, Hitachi, Japan) at an accelerating voltage of 15 kV. The location of the MWCNTs incorporated in the PS microspheres was observed using transmission electron microscopy (TEM, CM200, Philips, USA) at an accelerating voltage of 100 kV. The microspheres were placed in an epoxy resin (Embed-812, Electron Microscopy Sciences, USA) and hardeners (DDSA, NMA, Electron Microscopy Sciences, USA) in an oven at 60 °C for 2 days. A microtomed slice of the microspheres embedded in the epoxy resin was placed on a copper grid and observed by TEM. The quantity of MWCNTs in the S-PS/MWCNT microspheres was analyzed by thermogravimetric analysis (TGA, Q50, TA instruments, UK), from 20 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The electrical conductivity of the S-PS/MWCNT microspheres was measured using a ring-probe method with an electrical conductivity meter (Hiresta-UP MCP-T450, Mitsubishi Chemical, Japan). The S-PS/MWCNT microsphere samples were prepared in the form of disc-type pellets with a thickness of 0.8 mm using a Carver laboratory press at room temperature and an applied pressing force of 1 ton.

Results and Discussion

Figure 1(a) and (b) show FESEM images of the PS microspheres produced by suspension polymerization. PVP was dissolved in water as a steric stabilizer for the oil-in-water

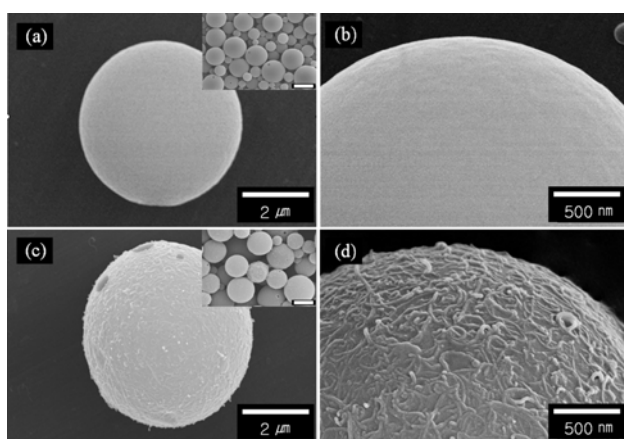


Figure 1. FESEM images of the PS microspheres and S-PS/MWCNT microspheres produced by *in situ* suspension polymerization at two different magnifications: (a), (b) PS microspheres and (c), (d) S-PS/MWCNT microspheres. The scale bars for the insets of (a), (c) are 5 μm .

system. The styrene monomer formed microspheres due to mechanical stirring and the presence of the steric stabilizer. The main-chains of the PVP molecules surrounded the styrene droplets and the side chains (pyrrolidone components) of the PVP molecules, which had a positive charge in water, headed for an aqueous phase. Therefore, the styrene droplets repelled each other and did not attach. As the temperature increased, AIBN dissolved in the styrene droplets produced radicals. Polymerization then occurred in the styrene droplets. The stirring speed determined the size of the microspheres that had formed during polymerization. The mean size of the microspheres decreased with increasing speed. The average diameter of the PS microspheres was $3.5 \pm 2.2 \mu\text{m}$ when the solution was homogenized at 1,200 rpm, as determined by measuring 100 individual microspheres from the FESEM images using image analyzer software.

Figure 1(c) and (d) show FESEM images of the S-PS/MWCNT microspheres. The S-PS/MWCNT microspheres were fabricated when the MWCNTs were dispersed in the aqueous phase. In this case, PVP functioned as both a dispersant for the MWCNTs dispersion by wrapping around the MWCNTs in the aqueous system and a steric stabilizer of suspension polymerization.^{23,24} The PVP molecules were present on the surface of the PS microspheres. Therefore, the MWCNTs were also located on the surfaces of the S-PS/MWCNT microspheres. The MWCNTs sustained their adsorption to the microspheres, even after 10 min of ultrasonication, because of the strong interaction between the PVP molecules on the surface of the PS microspheres and the MWCNTs. In Figure 1(d), the MWCNTs were well incorporated on the surface of the S-PS/MWCNT microspheres. The MWCNTs were interconnected on the surface of the PS microspheres. The mean diameter of the S-PS/

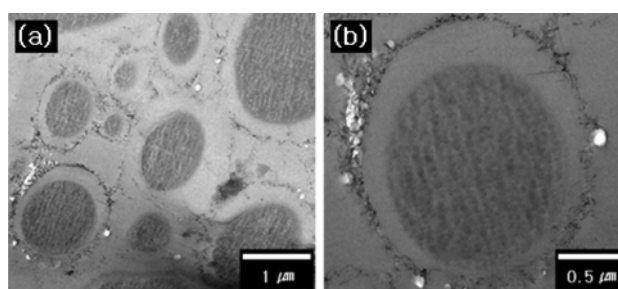


Figure 2. TEM images of the S-PS/MWCNT microspheres (a) at lower magnification and (b) at higher magnification.

MWCNT microspheres was $3.8 \pm 2.6 \mu\text{m}$, as measured using the previous method. The presence of MWCNTs increased the diameter of the microspheres.

The locations of the MWCNTs incorporated into the PS microspheres were verified by TEM. As expected, the MWCNTs were only located on the surface of the PS microspheres (Figure 2(a)). As mentioned above, the diameter of the S-PS/MWCNT microspheres increased by approximately 0.3 μm due to the addition of the MWCNTs layer. Figure 2(b) shows that the MWCNTs were interconnected, leading to the formation of a MWCNTs network. Unlike the SEM images, TEM revealed some gaps with low contrast between the outer MWCNTs layer and inner PS microspheres. The epoxy layer formed inside the MWCNTs layer because PS was dissolved in the epoxy resin that had been used to prepare the TEM samples, as mentioned in the experimental section. In addition, TEM showed that the interaction with the MWCNTs was strong enough to maintain their ordered structure when PS was dissolved. The electrical conductivity of the PS microspheres and S-PS/MWCNT microspheres was measured using the ring-probe method at room temperature. The electrical conductivity of the PS and S-PS/MWCNT microspheres was $7.69 \times 10^{-16} \text{ S/cm}$ and $5.33 \times 10^{-5} \text{ S/cm}$, respectively. In Figures 1 and 2, the MWCNTs incorporated onto the S-PS/MWCNT microspheres were interconnected, leading to the formation of MWCNTs layers, and the MWCNTs network formed electrical pathways.²⁵

As mentioned previously, suspension polymerization could control the location of the MWCNTs incorporated into the microsphere because suspension polymerization consists of two phases at the first stage of polymerization and is initiated in the monomer droplet. If the MWCNTs were dispersed in the styrene monomer, the dispersed MWCNTs were well compounded with PS during polymerization, so that they could be located inside the microspheres (I-PS/MWCNT microspheres). The MWCNTs prepared by functionalizing the surface of the MWCNTs with dodecane²⁶ were dispersed in the styrene monomer. Figure 3 shows a different dispersion of the purified MWCNTs and functionalized MWCNTs in styrene and di-water. After mixing the styrene

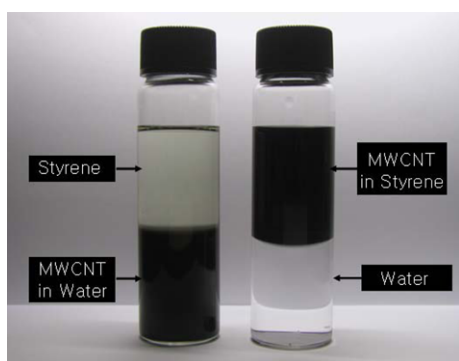


Figure 3. Optical images of the dispersion of the purified MWCNTs and functionalized MWCNTs in styrene and di-water solutions.

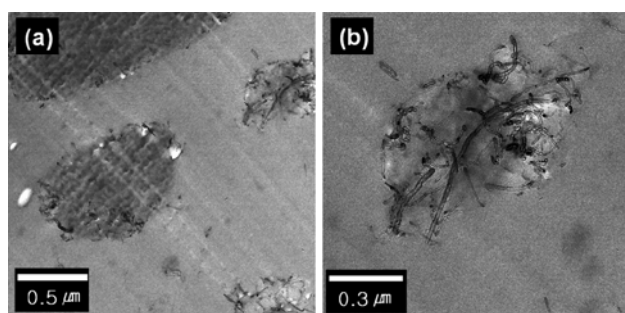


Figure 4. TEM images of the I-PS/MWCNT microspheres (a) at lower magnification and (b) at higher magnification.

monomer with di-water, the styrene monomer existed in the upper layer of the solution owing to its incompatibility and density. When the purified MWCNTs were added to the solution, the MWCNTs were dispersed in the water phase (left image). However, the MWCNTs functionalized with dodecane were well dispersed in the styrene monomer (right image). Figure 4 presents a TEM image of the I-PS/MWCNT microsphere cross-section. In contrast to Figure 2, most of the incorporated MWCNTs were inside the PS microspheres and the interface between PS microspheres and epoxy was unclear due to the similar contrast to PS and epoxy resin used for the TEM observations. Therefore, suspension polymerization controlled the location of the MWCNTs that had been incorporated in the polymeric microspheres.

TGA was performed in a nitrogen atmosphere to analyze the quantity of MWCNTs incorporated into the PS microspheres. In Figure 5, the PS microspheres began to decompose at $\sim 350^\circ\text{C}$, and had decomposed completely at $\sim 470^\circ\text{C}$.²⁷ After decomposition, the amount of ash was approximately 0.27 wt% at 500°C . At the same temperature, the amount of ash was approximately 86.82 and 1.01 wt% for the purified MWCNTs and S-PS/MWCNT microspheres, respectively, because the MWCNTs were thermally stable materials that remained even above 500°C . The amount of ash, which was used to determine the content of MWCNTs incorporated in the S-PS/MWCNT microspheres, was approximately 0.85

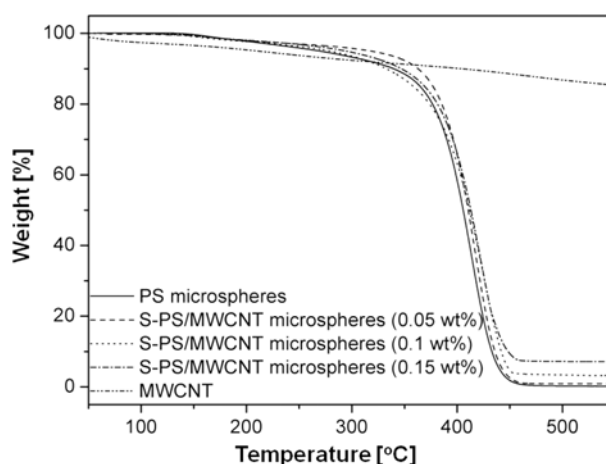


Figure 5. TGA curves of the PS microspheres, purified MWCNTs, and S-PS/MWCNT microspheres fabricated using the MWCNTs dispersion at various concentrations (0.05, 0.1, and 0.15 wt%).

wt%. In addition, the quantity of MWCNTs could be controlled using different concentrations of the MWCNTs solutions during S-PS/MWCNT microsphere preparation. The number of the MWCNTs attached to the PS microspheres was controlled by the concentration of the MWCNTs solutions. The concentration of the MWCNTs in the microspheres fabricated using the 0.1 and 0.15 wt% MWCNTs solutions was 3.59 and 7.99 wt%, respectively.

As mentioned previously, the highly concentrated CNT dispersed PS films were formed using the S-PS/MWCNT microspheres. The PS microspheres functioned as a template for maintaining the CNT-dispersion,^{16,17} as shown in Figure 6. The MWCNT/PS composite film was fabricated after the S-PS/MWCNT microspheres compression powders had melted using an applied pressing force of 1 ton at 250°C . During melting, most of the CNTs that had deposited onto the surface of the PS particles formed a conducting

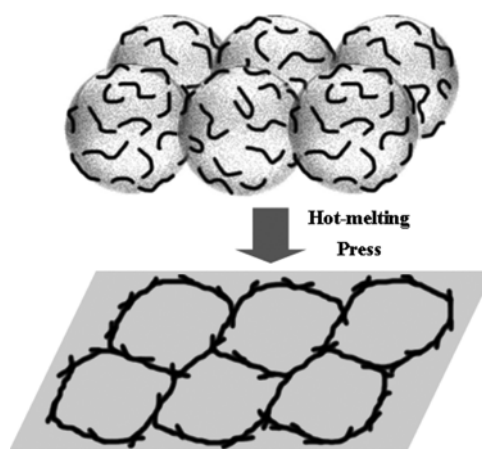


Figure 6. Schematic diagram of the MWCNT/PS composite film preparation using the S-PS/MWCNT microspheres.

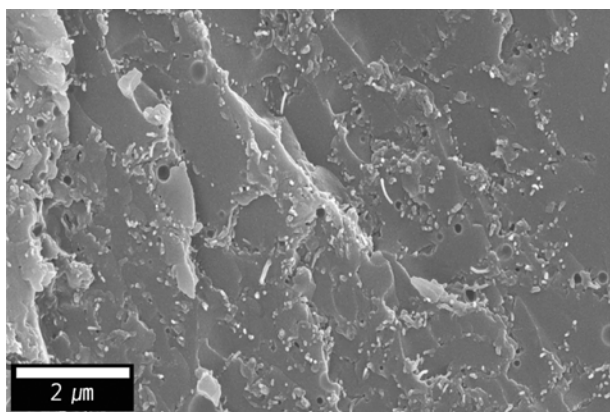


Figure 7. FESEM image of a fracture in the MWCNT/PS composite film. The MWCNTs are represented by the bright lines.

network like circles in the polymer matrix due to capillary action and the high flexibility of the CNTs. Figure 7 shows a SEM image of a fracture in the MWCNT/PS composite film. The MWCNTs are represented by the bright lines in the SEM image because of the different charging abilities for the transport of conducting MWCNTs and the insulating PS matrix. The MWCNTs were distributed homogeneously in the polymer matrix without aggregation in Figure 7. As the PS microspheres melted, the MWCNTs that were adsorbed on the surface had spread to the PS film in a spherical arrangement because the PS microspheres acted as a template for the MWCNT arrangement. The mean electrical conductivity of the MWCNT/PS composite film was 7.52×10^{-6} S/cm, which was lower than the conductivity of the S-PS/MWCNT microspheres (5.33×10^{-5} S/cm) because MWCNTs networking was rearranged as the PS microspheres melted. The MWCNT/PS composite film, which was fabricated through compression of the S-PS/MWCNT microspheres, exhibited a low electrical percolation conductivity at a concentration < 0.85 wt% MWCNTs. The concentration of MWCNTs was lower using the percolation method than with melt mixing (0.99 wt%)²⁸ and solvent casting (3.1 wt%)²⁹ methods.

Conclusions

An efficient process was developed to produce S-PS/MWCNT microspheres by *in situ* suspension polymerization in an aqueous system. The MWCNTs were well adsorbed onto the PS microspheres due to the presence of PVP wrapped around the MWCNTs. This method was advantageous because the microspheres were easily fabricated. SEM and TEM confirmed that the MWCNTs were present only on the surface of the microspheres. The electrical conductivity of the S-PS/MWCNT microspheres was remarkably high (5.33×10^{-5} S/cm) because of their structural characteristics. In addition, low electrical-percolation-thresh-

old MWCNT/PS films were fabricated using the S-PS/MWCNT microspheres. This simple method for producing S-PS/MWCNT microspheres can be extended to MWCNTs in mechanical material or electronic device applications.

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