



Adsorption Behavior of Carbon Nanotubes on Polystyrene Surfaces

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Polystyrene (PS) was prepared using two different polymerization methods (dispersion polymerization and seed polymerization) to investigate the steric stabilizer effect during the adsorption process of carbon nanotubes (CNTs) on the surface of PS microspheres. Experiments with different microsphere diameters and different types of CNTs were conducted to analyze the curvature effect of the spheres on the adsorption mechanism. The results showed that PS microspheres prepared through dispersion polymerization exhibited preferable adsorption behavior compared to PS spheres prepared through seed polymerization, suggesting that poly(N-vinylpyrrolidone) led to improved adsorption interactions between the CNTs and the PS microspheres in the CNTs dispersion. Additionally, the PS diameter and CNT curvature were examined with respect to the adsorption behavior between the PS microspheres and the CNTs. Multiwalled carbon nanotubes (MWCNTs) were found to be well adsorbed on the surface of PS microspheres measuring 2 μm . However, the MWCNTs were adsorbed much less on the surface of submicron-sized PS microspheres, compared with thinwalled carbon nanotubes (TWCNTs). On the other hand, TWCNTs were found to be suitable for adsorption on submicron-sized PS microspheres. These results also indicate that the curvature of the CNTs and the polymer microspheres are important to the CNT adsorption process.

Keywords: Carbon Nanotubes, Polystyrene, Microsphere, Adsorption, Curvature, Dispersion Polymerization, Seed Polymerization.

1. INTRODUCTION

Carbon nanotubes (CNTs) have been the subject of much research due to their unique electrical, thermal and mechanical properties.^{1,2} Many of these outstanding properties can be best exploited through the incorporation of the nanotubes into some form of the matrix, and the preparation of composite materials containing CNTs is now a rapidly growing research subject. A number of studies have used carbon nanotubes as fillers in the polymer matrix, and these polymer composites reinforced with carbon nanotubes are believed to have many potential uses in engineering.

Melt compounding,³ solution casting,⁴ adsorption,⁵ and *in-situ* polymerization⁶ methods have been employed to prepare polymer/CNTs composites. Compared with other methods, adsorption method can maintain morphology of pristine polymer, and incorporate CNTs in selective location.

Recently, polymer microspheres have attracted a great deal of attention as substrates to carbon nanotube (CNT)

adsorption.^{7,8} Multiwalled carbon nanotubes (MWCNTs) with polymeric spheres have shown extra functional properties, including increased mechanical properties.⁹ Jin et al. created polymer/MWCNTs microspheres that showed electrorheological properties via adsorption method.¹⁰ Jung et al. researched the location-selective incorporation of MWCNTs in polycarbonate microspheres.¹¹ These microspheres incorporated MWCNTs in selective locations so that they exhibited high electrical conducting properties at low concentration. Additionally, polymer/CNT composites have been prepared through an adsorption method using various polymer forms (fiber, film etc.). Kim et al. prepared electrically conductive polyamide-6 nanofibers that were coated with MWCNTs through electrospinning.¹² Saran et al. created an extremely simple method for obtaining thin, strongly adherent films of SWCNTs bundles on flexible, transparent plastic substrates of poly(ethylene terephthalate).¹³ Kaempgen et al. researched CNTs thin networks that were sprayed onto glass or plastic substrates in order to obtain a conductive transparent coating.¹⁴

This work demonstrates that the adsorption behavior of CNTs onto substrates is related to the properties of the

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substrate and the CNTs. Two polymerization methods were employed to form microspheres with different chemical properties to analyze the chemical effect on the adsorption property. Films and microspheres were prepared as polymeric substrates, and thinwalled carbon nanotubes (TWCNTs) were used in comparisons with MWCNTs.

2. EXPERIMENTAL DETAILS

The acid-treated CNT-dispersed aqueous solution was prepared using a previously published process.^{10,15} Carboxylic and hydroxyl functional groups were introduced on the surface of the MWCNT during the purification process.¹⁶ The polystyrene (PS) microspheres were synthesized with 2,2-azobisisobutyronitrile (Junsei, Japan) using a well-established dispersion polymerization method in an ethanol medium for 24 h at 70 °C. Poly(N-vinylpyrrolidone) (PVP-40T; Sigma Chemical Co.) was used as a steric stabilizer. The polymerization process was carried out in a 500 mL three-neck reaction vessel at a constant stirring speed of 150 rpm under a nitrogen atmosphere. After the polymerization was complete, the resulting mixture was repeatedly rinsed with methanol and distilled water and the final PS microspheres were subsequently obtained through filtration. Stabilizer-free PS microspheres were synthesized using the seed polymerization method. The polymerization procedure was conducted in a reaction flask that was mechanically stirred under a nitrogen atmosphere. Distilled water and styrene with the inhibitor removed were added to the reaction flask, and potassium persulfate (KPS, DC chemical Co., Korea) was used as an initiator. After polymerization, additional styrene and water were charged in the reactor. The polymerization process was conducted at 350 rpm and 60 °C. Upon completion of this process, the obtained PS microspheres were washed with methanol and dried under a vacuum for 24 h.¹⁷ The adsorption of CNT on the surface of microspheres was performed using described procedure in a previous work.¹⁰

The surface morphology of the microspheres was observed using field emission scanning electron microscopy (FESEM, S-4300 with EDS KEVEX, Hitachi, Japan) at an accelerating voltage of 15 kV. The chemical structures of the prepared microspheres were characterized using a Fourier transform infrared spectrometer (FT-IR, Spectrum 2000, Perkin-Elmer, USA). Elemental analysis of the microspheres was performed using EA1110 (CE instrument, Italy) at the National Center for Inter-University Research Facilities of Seoul National University, Seoul, Korea.

3. RESULTS AND DISCUSSION

Figure 1 shows the different surface morphologies of the MWCNT-adsorbed microspheres via FESEM. These

microspheres were prepared using dispersion and seed polymerization methods. Figure 1(a) shows that a large number of MWCNTs were adsorbed on the PS microsphere surface prepared using the dispersion polymerization method. On the other hand, Figure 1(b) shows that a small amount of MWCNTs were adsorbed on the PS microsphere surface prepared via the seed polymerization method. These results may be related to the differences in the chemical properties caused by the different polymerization methods.

The chemical properties of the PS microspheres were analyzed using an FT-IR spectrometer in both cases (Fig. 2). A C=O peak was observed at 1670 cm^{-1} due to the presence of PVP in the PS sphere. Therefore, the PVP was not completely washed off the prepared PS microspheres, indicating that the PVP had grafted to the PS molecules. Thus, the behavior observed in the case of the extrapolated initial intercepts may have been caused by the formation of an in-situ-grafted PVP-PS copolymer upon the initiation process during the nucleation stage.¹⁸ Additionally, Table I shows the elemental analysis results for PS microspheres formed through both dispersion and seed polymerization after seed polymerization. Therefore, PVP molecules were present in the PS microspheres prepared using the dispersion-polymerization method. These results show that CNTs were well adsorbed

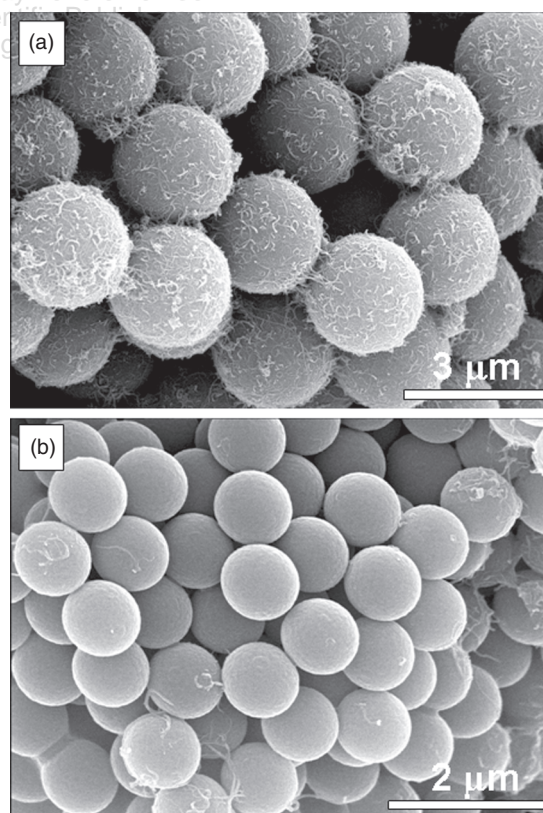


Fig. 1. FESEM images of the MWCNT-adsorbed (a) dispersion-polymerized microspheres and (b) seed-polymerized microspheres.

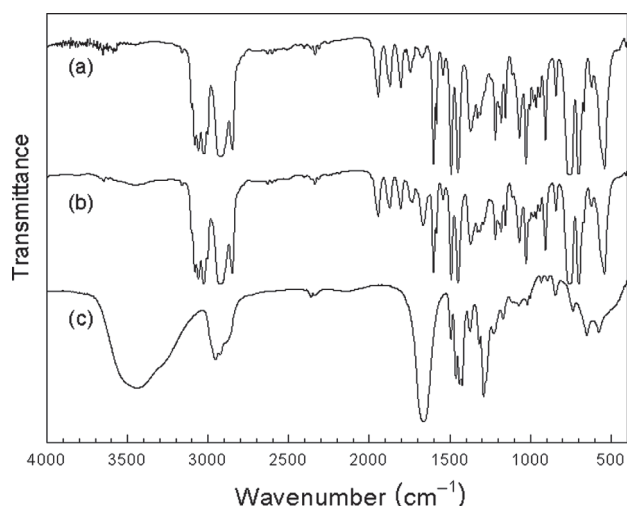


Fig. 2. FT-IR spectra of (a) seed-polymerized PS, (b) dispersion-polymerized PS and (c) PVP.

on dispersion-polymerization PS microspheres without additional processes.

In Figure 2 and Table I, the dispersion-polymerized PS spheres contained some residual PVP because the PVP reacted with the styrene monomer during dispersion polymerization.¹⁹ Therefore, the dispersion-polymerized PS microspheres showed a weak positive charge in water (Table II). On the other hand, the seed-polymerized PS spheres exhibited a strong negative charge in water. These differences in the zeta potential values were caused by the presence of PVP on the surface of PS microspheres. Therefore, the presence of the stabilizer on the surface of the microspheres was one of the critical factors that caused the dispersion-polymerized PS microspheres to exhibit less electrostatic repulsion to CNTs compared to the seed-polymerized PS microspheres. Additionally, microspheres were prepared using the seed-polymerization method to minimize the effect of the stabilizer.²⁰ The adsorption of MWCNTs onto the surface of the microspheres was related to the electrostatic interaction between the PS microspheres and the MWCNTs. Therefore, MWCNTs were not adsorbed onto the seed-polymerized PS microspheres as a consequence of electrostatic repulsion. For this reason, the zeta potential values of the MWCNTs and the PS microspheres had a considerable impact on the MWCNT adsorption characteristics.

Figure 3 shows the adsorption results of polymer matrices with different shapes. These samples were prepared using the dispersion-polymerized PS microspheres.

Table I. Elemental analysis of the PS microspheres for the different polymerization methods.

	N (%)	C (%)	H (%)
Dispersion-polymerized PS spheres	0.15	92.05	7.80
Seed-polymerized PS spheres	—	92.16	7.84

Table II. Zeta potential value of the MWCNTs and the PS microspheres.

Sample name	Zeta potential (mV)
Received MWCNTs	0.36
Acid-treated MWCNTs	-16.23
Seed-polymerized PS microspheres	-19.55
Dispersion-polymerized PS microspheres	+0.12
PVP	+1.39

In Figure 3(a), a large amount of MWCNTs was adsorbed on the surface of the PS microspheres. However, for PS film prepared by using a solvent casting method with tetrahydrofuran, the CNTs were only slightly adsorbed (Fig. 3(b)). The different adsorption behavior of the polymeric spheres and films was influenced by the shape of the polymer substrate. Generally, MWCNTs have curved structures. Therefore, MWCNTs have a larger curved surface contact area than a flat surface contact area. Therefore, the MWCNTs were more stably adsorbed onto the curved surface than they were onto the flat surface.

On the other hand, PS microspheres with different diameters were prepared to determine the relationship between the microsphere diameter and the adsorption behavior. Figure 4 shows the adsorption behavior of two kinds of CNTs which have different diameters and the PS

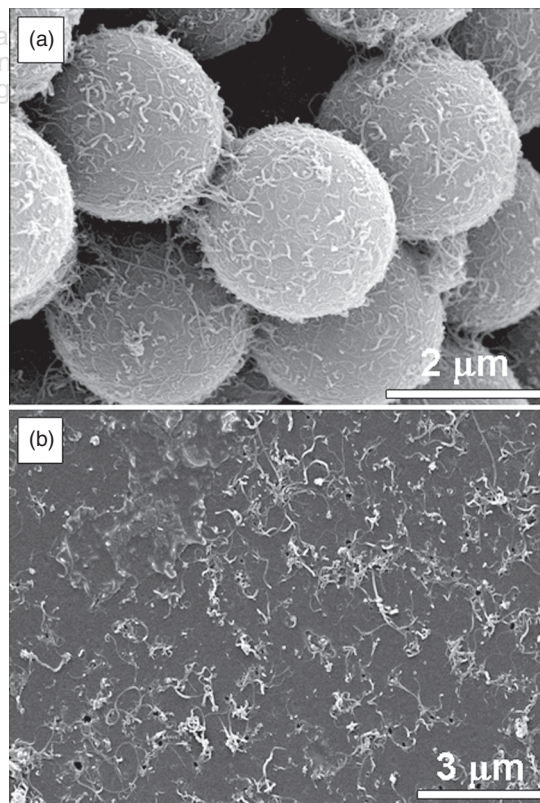


Fig. 3. FESEM images of (a) the MWCNT-adsorbed dispersion-polymerized PS microspheres and (b) the MWCNT-adsorbed film created using the solvent casting method with dispersion-polymerized PS microspheres.

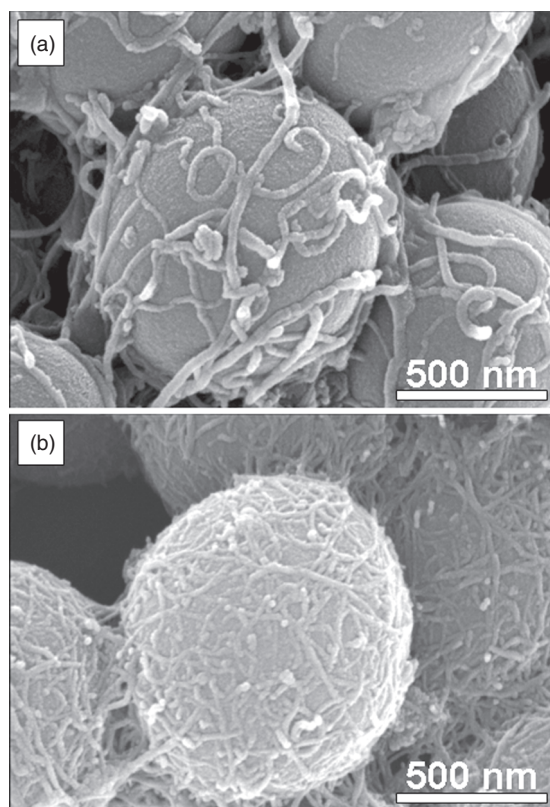


Fig. 4. FESEM images of (a) the MWCNT-adsorbed PS microspheres and (b) the TWCNT-adsorbed PS microspheres. The diameters of the PS microspheres were $0.7 \mu\text{m}$.

microspheres. In Figure 3(a), the MWCNTs were densely adsorbed onto the surface of the $\sim 2 \mu\text{m}$ PS. However, fewer MWCNTs were adsorbed onto the $\sim 700 \text{ nm}$ PS microspheres (Fig. 4(a)). Figures 3(a) and 4(a) show that the MWCNTs are more densely adsorbed on the $\sim 2 \mu\text{m}$ PS microspheres than on the submicron-sized PS microspheres. However, Figure 4(b) showed the thin-walled carbon nanotubes (TWCNTs) were feasibly adsorbed by the submicron-diameter microspheres. Thus, TWCNTs were adsorbed more densely onto the microspheres compared to the MWCNTs.²¹ The diameter of the TWCNTs ranged from 4 to 8 nm. From these results, the MWCNTs are suitable for $\sim 2 \mu\text{m}$ PS microspheres and the TWCNTs are suitable for the submicron-sized PS microspheres due to the curvature of the CNTs. The adsorption of the CNTs can be improved by selecting an adequate diameter for the CNTs. Therefore, the compatibility between the substrates and the CNTs was believed to depend on the curvature points.

4. CONCLUSION

Polymer/CNTs nanocomposites can be simply prepared in CNT dispersion using an adsorption method. Therefore, this work examined the adsorption behavior between the

polymer matrix and the CNTs in aqueous system. PS microspheres were prepared using two different polymerization methods to investigate the steric stabilizer effect during the adsorption process. The PS microspheres prepared through dispersion polymerization were preferable to the PS microspheres prepared through seed polymerization in terms of CNT adsorption on their surfaces. Additionally, the sizes of the PS microspheres and the diameters of the CNTs were also considered with respect to the adsorption behavior between the microspheres and the CNTs.

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