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The Dispersion Stability of Multi-Walled Carbon Nanotubes in the Presence of Poly(styrene/α-methyl styrene/acrylic acid) Random Terpolymer

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Abstract: Aqueous dispersions of pristine and functionalized (COOH- and NH_2-) multi-walled, carbon nanotubes (MWNTs) were prepared by using three types of surfactants: sodium dodecyl sulfate (SDS, anionic), PEO-PPO-PEO (Pluronic P84, non-ionic), and poly(styrene/α-methyl styrene/acrylic acid) random terpolymer, i.e., alkali-soluble resin (ASR). The aggregate size, ζ-potential, and storage stability of the MWNT aqueous dispersions were investigated by using dynamic light scattering and the turbidity method at room temperature. The exfoliation of the MWNT aggregates was determined by a UV-visible spectrophotometer and the morphology of the surfactant-coated MWNTs was observed by transmission electron microscopy (TEM). In all cases, ASR showed better dispersion stability with the smallest aggregate size, compared with the other surfactants, because of its unique molecular structure, i.e., randomly incorporated carboxylic acid groups and planar phenyl groups that can be irreversibly and effectively adsorbed on the MWNT surface. A predominantly-exfoliated morphology of MWNTs was observed in the presence of ASR from the strong intensity of the UV-vis spectrum at 263 nm.

Keywords: multi-walled carbon nanotubes, alkali-soluble resin, dispersion stability, terpolymer, ultrasonication.

Introduction

Carbon nanotubes (CNTs) have attracted a great deal of attention due to their unique and versatile properties, since multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) were discovered by Iijima in 1991 and 1993, respectively.[1,2] Both MWNTs and SWNTs are, however, severely entangled and possess extremely low solubility in any solvent.[3] For practical applications, it is considered to be a significant barrier in both academic research and industrial applications. Due to the strong π-π interactions among the CNTs, it is not easy to obtain a fine and stable dispersion of CNTs.[4] Until now, many research papers have been published regarding the chemical modification and dispersion of CNTs.[3-18] Chemical modification of CNTs can impart various functional groups, such as hydroxyl, carboxyl, carbonyl, amine, and vinyl group to the CNTs; however, it often leads to significant defects on the CNT molecular structure or cutting.[11,14,19-26] On the other hand, dispersion of pristine CNTs can be prepared by simply using various anionic, cationic, and nonionic surfactants, which are adsorbed on the surface of CNTs and can effectively minimize the strong attraction among CNTs by electrostatic repulsion or steric hindrance.[27-31] Use of short-chain surfactants, however, might not be favorable due to surfactant migration during the film formation of the matrix polymer, which deteriorates the final properties of the CNTs/polymer composites. Polymer-assisted dispersions of CNTs have been previously reported in many literatures; however, most research was related to non-aqueous medium (i.e., organic solvents or polymeric media).[6,18,20,32]

In this study, fine and well-dispersible MWNT dispersions were prepared using an alkali-soluble random terpolymer [ASR, poly(styrene/α-methyl styrene/acrylic acid)]. ASR is a sort of polymeric type surfactants with having a molecular weight ranging from 10^3~10^4 $gmol^{-1}$, in which ionic moieties are randomly incorporated. They can be dissolved in water under basic conditions and they form aggregates like micelles.[33-37] Thus, ASR can play the role of both emulsifier in solvents and counter-part polymer in CNT/polymer composites (it can also be grafted with a matrix polymer via a hydrogen abstraction mechanism in free-radical polymerizations[38-40]). In the current work, aggregate morphology and the dispersion stability of MWNTs were compared with those

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prepared by using sodium dodecyl sulfate (SDS, anionic) and a PEO-PPO-PEO triblock copolymer (Pluronic P84, non-ionic). The aggregate size and the dispersion stability of the MWNTs, in an aqueous phase, were measured using dynamic light scattering, ζ-potential, and turbidity methods. The exfoliation of the MWNT aggregates was determined by a UV-visible spectrophotometer and the surfactant-coated individual MWNTs were observed by a TEM.

Experimental

Materials. Pristine MWNTs were obtained from the Il-Jin Nanotech (Diameter=10~30 nm, length=10~50 μm 95 vol% of purity). Sodium dodecyl sulfate (SDS, 90%) was purchased from Sigma-Aldrich. Pluronic P84 ($\overline{M_n}$=4,200 gmol^{-1}, HLB=14) was purchased from BASF. ASR (ESI-REZ 50, $\overline{M_n}$=9,500 gmol^{-1}, PDI=2.6, Acid number=200 mg KOH/g resin, T_g=80 °C, Cook Composites & Polymers) was donated by Gentrol Co. NaOH, HNO_3, H_2SO_4, acetone, and tetrahydrofuran (THF) were all of analytical-grade. Thionyl chloride ($SOCl_2$), triethylamine (TEA), *N*-methyl-2-pyrrolidone (NMP), and ethylene diamine ($C_2H_8N_2$, 99%) were used after dehydration with 4 Å-molecular sieves for 12 hrs. Phosphotungstic acid ($H_2PO_4 \cdot 12WO_3 \cdot H_2O$) and ruthenium (IV) oxide hydrate were used to enhance the contrast of the TEM images. Double-distilled and deionized (DDI) water was used throughout the experiments.

Preparation of Pristine, COOH-, and NH_2-Functionalized MWNTs. Pristine MWNTs were purified by using a 3 N HNO_3 aqueous solution. The MWNT solution was stirred for 6 hrs and was followed by vacuum filtering (PTFE filter, a 10 μm pore size), and washed with excess DDI water to neutral pH. The purified MWNTs were functionalized by refluxing with a mixture of H_2SO_4/HNO_3 (3:1 by volume) in a bath-type sonicator for 8 hrs at room temperature. Then, the MWNT solution was washed and filtered with the previously-mentioned method. The NH_2-functionalized MWNTs were prepared by the acylation (i.e., formation of COCl-MWNTs) of carboxylic acid group with $SOCl_2$ at 65 °C for 24 hrs. This was followed by the reaction with EDA.[22] The COCl-MWNTs dispersed in NMP were injected with a microsyringe pump at a rate of 2.5 mL hr^{-1} into the EDA, in the presence of a trace of TEA at 60 °C for 48 hrs. After COOH- and NH_2-functionalization, the MWNTs were washed several times with THF, filtered, and then dried in a vacuum oven for 24 hrs. The pristine and functionalized MWNTs were then characterized by FTIR and Raman spectroscopy analyses. A schematic of the chemical modification of the pristine MWNTs is illustrated in Scheme I.

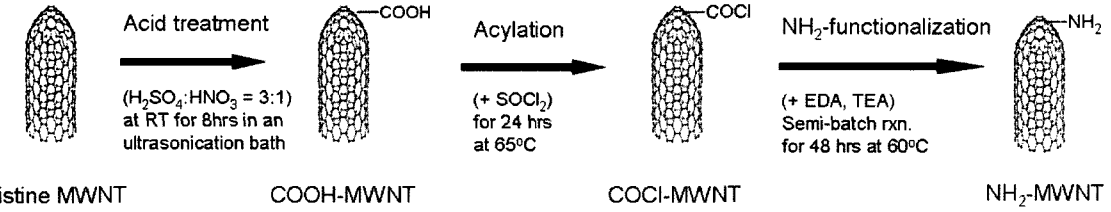
Preparation of MWNT Aqueous Dispersions. Several MWNT aqueous dispersions were prepared with three types of MWNTs and three kinds of surfactants. For each experiment, 5 g of the surfactant (each SDS, Pluronic P84, and ESI-REZ 50), 0.001 g of MWNT (each pristine, COOH-, and NH_2-MWNTs), 95 g of DDI water, and a calculated amount (for 100% neutralization) of NaOH were used. The resulting mixture was ultrasonicated by using a horn-type ultrasonicator (Sonic Vibracell, VCX 750). The frequency and power were 20 kHz ± 50 Hz and 40 W, respectively.

Characterization. FTIR spectrophotometer (Mattson Instr. Galaxy 7020A) was used to confirm the functional groups which formed after chemical modification. Raman spectrophotometer (Spex Ramanlog 9L) was used to characterize the functionalized MWNTs. The aggregate size and the ζ-potential of MWNT aqueous dispersions were measured by using a dynamic light scattering method (ELS-8000, Otsuka) at 20 °C. A UV-vis spectrophotometer (Beckman DU7500) was used to obtain qualitative results for the water dispersibility and the degree of exfoliation of the MWNTs. The degree of exfoliation can be measured by monitoring UV intensity, since individual MWNTs show greater UV absorption intensity at 263 nm than the aggregation or bundles of MWNTs. The storage stability of the MWNT dispersions was observed by a turbidity method (Turbiscan Classic, Formulations) for a 24 hrs period at room temperature. From the on-line measurements of the transmission and backscattering intensity values, the transmission flux of the MWNTs was obtained. A transmission electron microscope (H-7600, 120 kV, Hitachi) was used to observe the morphology of the MWNT dispersions which were prepared with various surfactants.

Results and Discussion

Chemical Modification of Multi-Walled Carbon Nanotubes.

FTIR Spectroscopy: Figure 1 shows the FTIR spectra of pristine and functionalized MWNTs. The spectrum of the pristine MWNTs shows a C=C stretching peak at 1663 cm^{-1}. It, however, shows no discernable peaks, indicating the for-



Scheme I. A schematic of the chemical modifications for MWNTs.

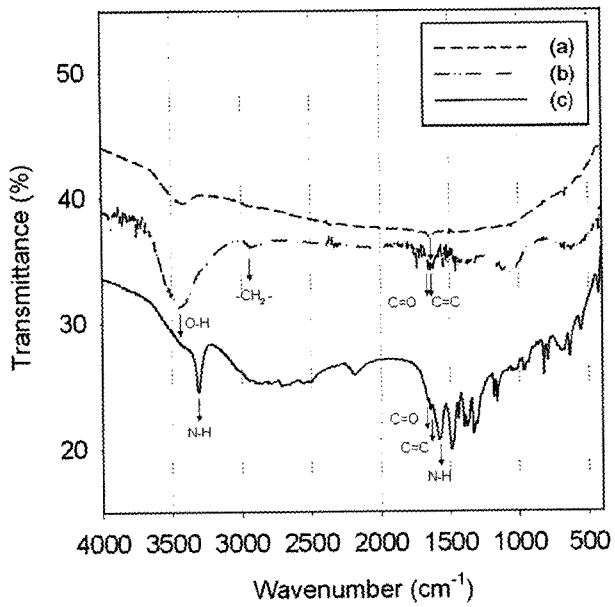


Figure 1. FTIR spectra of pristine and functionalized MWNTs: (a) pristine, (b) COOH-functionalized, and (c) NH_2-functionalized MWNTs.

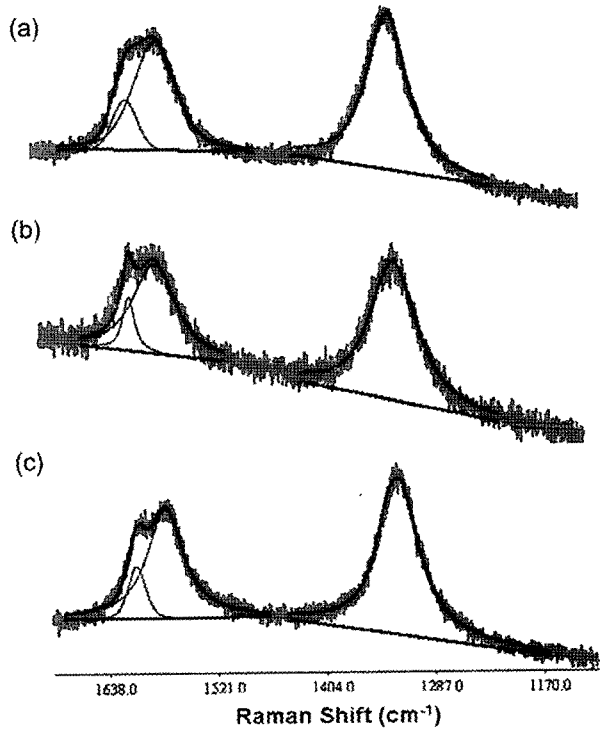


Figure 2. Raman spectra of pristine and functionalized MWNTs: (a) pristine, (b) COOH-functionalized, and (c) NH_2-functionalized MWNTs.

mation of carboxylic acids or defects after purification. The C=C stretching peaks, which indicate graphite structure of CNT, are observed in the COOH- and NH_2-functionalized MWNTs as well. After acid treatment, the COOH-MWNTs show a C=O stretching peak from the COOH group at 1710 cm^{-1} and a very broad O-H stretching peak between 3400 and 3600 cm^{-1}. The NH_2-MWNTs show a N-H stretching peak from the amide group which appeared between 3400 and 3200 cm^{-1}, a N-H bending peak from the amide group at 1590 cm^{-1}, and a C=O stretching peak at 1710 cm^{-1}.

Raman Spectroscopy: High resolution Raman spectra were recorded using an Ar^+ ion laser a wavelength of 514.5 nm. After spectrum normalization, the D (disordered, 1350 cm^{-1}) and G (ordered, 1580 cm^{-1}) peaks were fitted to a Lorentzian-Gaussian line-shape and the area ratio of the G- and D-bands (A_G/A_D) was used to quantify each chemical modification process. Figure 2 shows the first-order Raman spectra of the cleaned pristine and functionalized MWNTs. As shown in Figure 2, the D- and G-bands of the MWNTs were observed at ca. 1325 and 1573 cm^{-1}, respectively. In addition, the D'-band at 1617 cm^{-1}, which is known to be directly affected by the disorder in carbon nanotubes, also is exhibited and increased as the reaction step proceeds.[41] The ratio of A_G/A_D decreases from 0.64 to 0.61 as the chemical modification step progresses, which reveals that both the acid-treatment and sonication process increase the D-band intensity.

Aqueous Dispersions of MWNTs.

Dispersion Stability: Figure 3 shows photographic images of various MWNT dispersions after 7 days and 6 months.

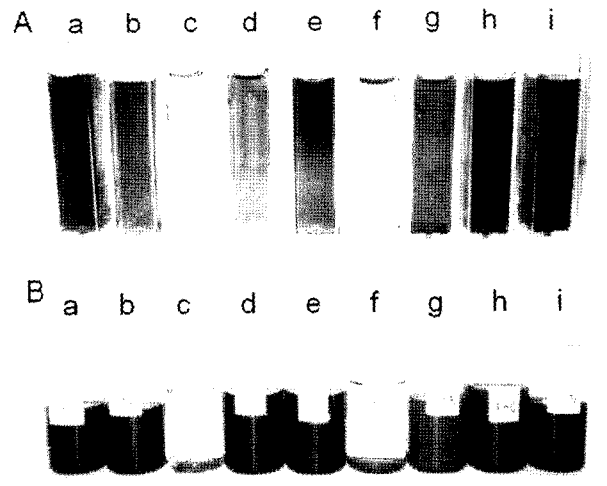


Figure 3. Photographic images of the various MWNT dispersions after 7 days (A) and 6 months (B): (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

The concentration of MWNTs in the water was 0.01 mg/mL. The dispersion state of all samples, after preparation, was

the same (which was not shown in the paper). As shown in Figure 3(A), most dispersions show good storage stability at room temperature except NH_2-MWNT (refer c and f in Figure 3(A)). Due to the charge attraction (or neutralization) between the NH_2-MWNTs and SDS, SDS shows poor storage stability, as compared with ASR (refer c and i in Figure 3(A)). Even though ASR has the same ionic moieties, it shows good storage stability regardless of the MWNTs (refer g, h, and i in Figure 3(A)). These results can be explained by the molecular structure (i.e., π-π attractive interaction between the MWNT surface and phenyl groups of styrene or α-methyl styrene units[42]) and the typical properties of polymeric surfactants (e.g., high molecular weight and high internal viscosity[35]) of the ASR. It was found that the NH_2-MWNT dispersed with Pluronic P84 shows poor stability, which might be due to attractive interaction between amine group and MWNT or poor dispersion stability of Pluronic P84. From the results, it can be concluded that the dispersion state of the functionalized MWNTs is not affected by HLB values, but by the molecular structure of the surfactants[43] even though various surfactants were not screened in this work. As shown in Figure 3(B), there's no difference in the colloidal stability of MWNTs after 6 months.

Size of Aggregates and ζ-Potential Analyses: Figure 4 shows the aggregate sizes of the MWNT dispersions measured by the dynamic light scattering (DLS) method. One can compare the relative aggregate sizes of the various dispersions form the DLS data. As shown in Figure 4, the MWNT dispersions, which were prepared using Pluronic P84 and SDS, show larger aggregates as compared with those by ASR; however, ASR shows the smallest aggregates. In the case of SDS, COOH-MWNT shows smaller aggregate size compared to pristine and NH_2-MWNTs. This result is originated from the good dispersibility of COOH-functionalized MWNT, since carboxylic acid groups support additional stability, i.e., an ionic stabilization effect of the COOH-MWNTs. The aggregate size of the NH_2-MWNTs is bigger than that of the COOH-MWNTs, which is due to charge neutralization effect between amine and carboxyl groups. Regarding Pluronic P84, functionalized MWNTs showed slightly smaller aggregate sizes compared with the pristine MWNTs. No charge effect, which was shown in the case of SDS, was observed in Pluronic P84. From the DLS data, it can be concluded that ASR can effectively stabilize all types of MWNTs. This can be proven by the effective electrostatic and steric stabilization mechanisms, which originate from a typical molecular structure of ASR as mentioned previously.[37,42]

Figure 5 shows the ζ-potential values of the MWNT dispersions measured at 20 °C. In the case of SDS, the ζ-potential values of the pristine, COOH-, and NH_2-MWNTs are -50.7, -58.3, and -38.0 mV, respectively, which is due to the nature of the ionic groups on the surface of the MWNTs. As shown in Figure 5, the MWNT dispersions prepared with SDS showed higher ζ-potential values compared with the dispersions prepared with Pluronic P84 or ASR. In the case of Pluronic P84, the ζ-potential values are -10.6, -7.7, and

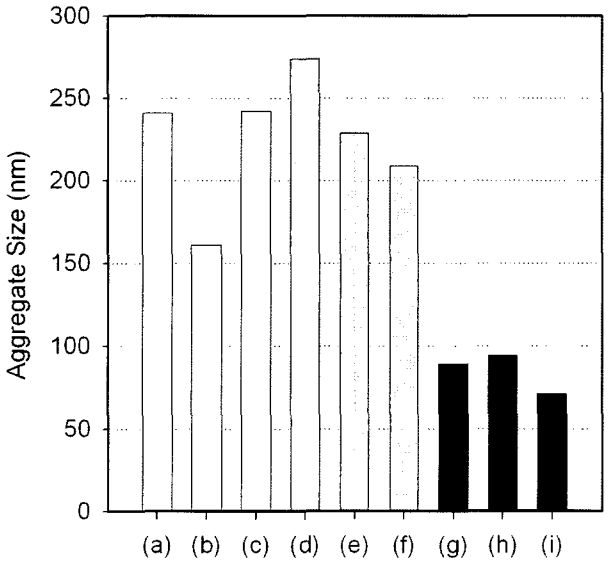


Figure 4. Aggregate sizes of various MWNT dispersions, which were measured by a dynamic light scattering method: (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

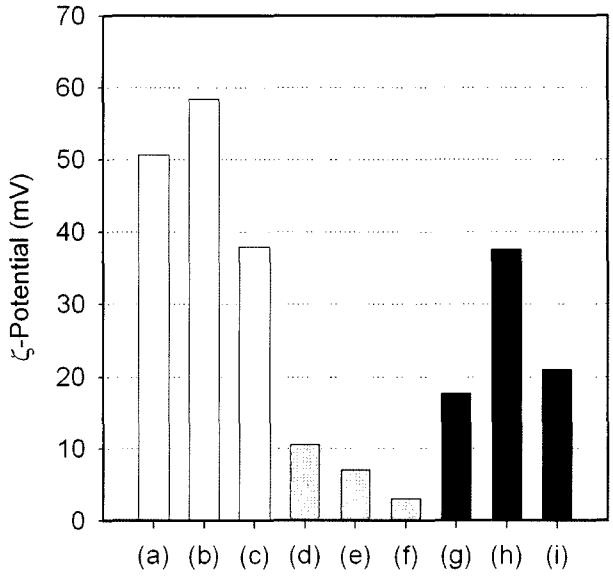


Figure 5. ζ-potential values of the various MWNT dispersions: (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

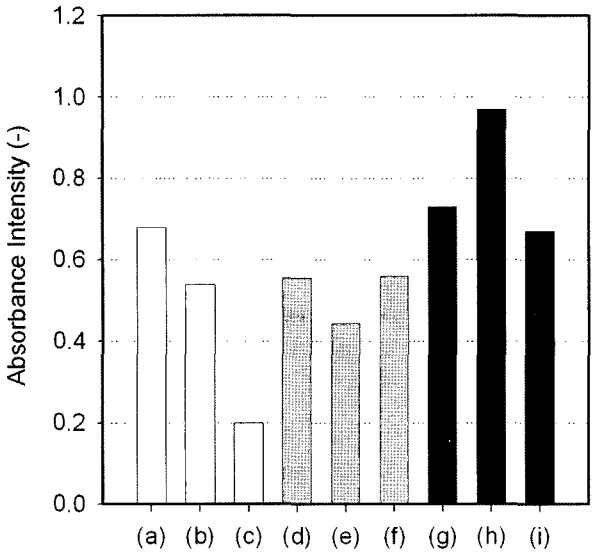


Figure 6. UV-vis absorbance intensity values of the various MWNT dispersions: (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

-3.2 mV, respectively. These results imply poor dispersion stability which corroborates the results shown in Figures 3 and 4.

Exfoliation of MWNTs: In order to investigate an effect of the type of surfactants on the exfoliation of MWNTs in aqueous surfactant solution, UV-vis spectroscopy was used to monitor the intensity variation at 263 nm. Polymer wrapping of MWNTs has received attention as a means of preventing the CNTs from aggregating into bundles, thereby improving their dispersion into a composite matrix.[44] Polymer wrapping of CNTs may also be a promising way for the manipulation and organization of CNTs into ordered structures, even of their non-covalent functionalization.[32] In Figure 6, the UV-vis absorbance intensity levels of various MWNT dispersions are shown at a concentration of 0.01 mg/mL. As shown in Figure 6, the exfoliation of pristine and COOH-MWNTs seemed to be easier than that of the NH_2-MWNTs. From an increase in the UV-absorbance intensity of the NH_2-MWNTs (c → f → i), it can be concluded that the exfoliation ability (i.e., enveloping or wrapping of the MWNT surface by surfactants) of the surfactants increases in the following order: ASR > Pluronic P84 > SDS, since ASR has many molecules that contain a planar phenyl group which can irreversibly adsorb to the surface of MWNTs.[45] Thereby, ASR showed smaller aggregate sizes and better storage stability of MWNTs in spite of the relative low ζ-potential values, as shown in Figure 5.

On-Line Turbidity Analysis. The on-line turbidity method was applied in order to get the evolution of the transmission

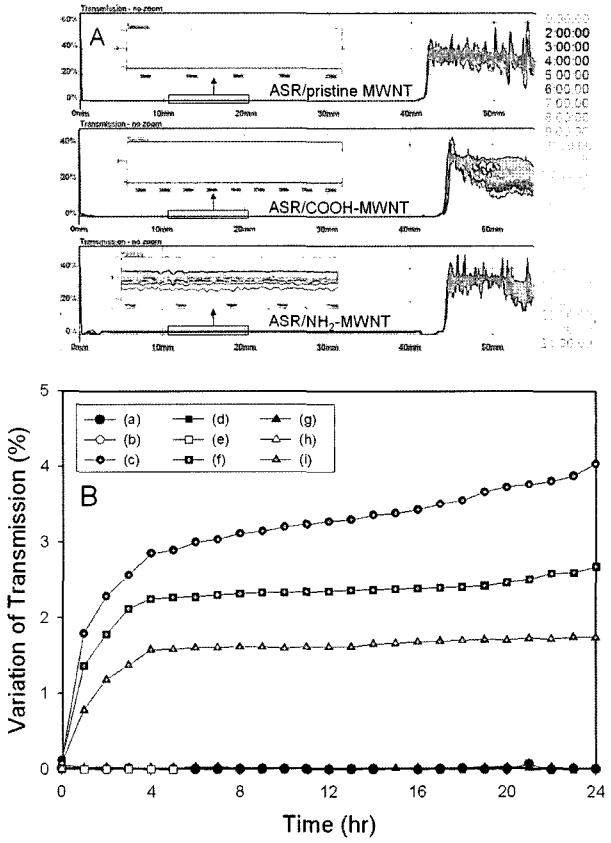


Figure 7. (A) Representative Turbiscan raw data of (a) pristine, (b) COOH-, and (c) NH_2-functionalized MWNT dispersions prepared with ASR; (B) Time-evolution transmission data of the various MWNT dispersions over a 24 hrs period: (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

of MWNT aqueous dispersions at room temperature. Representative transmission profiles of the three types of MWNT dispersions, which were prepared with ASR, are shown in Figure 7(A). The x- and y- coordinate in Figure 7(A) indicates the height (mm) of the sample bottle and the transmission intensity (0-100%), respectively. In the case of pristine and COOH-MWNTs, no substantial variations in the transmission were observed until 24 hrs had passed. In the case of NH_2-MWNTs, however, the variation was uniform throughout the whole sample bottle. This implies that MWNT aggregates initially started to flocculate in the water phase without sedimentation. Sedimentation is believed to occur when the aggregates become too large to be dispersed, even though their sizes at the beginning of sedimentation were not measured. The time-evolution of the transmission intensity levels of the MWNT dispersions was shown in Figure 7(B). From the results, both pristine and COOH-MWNTs were found to be stable regardless of the surfactant type

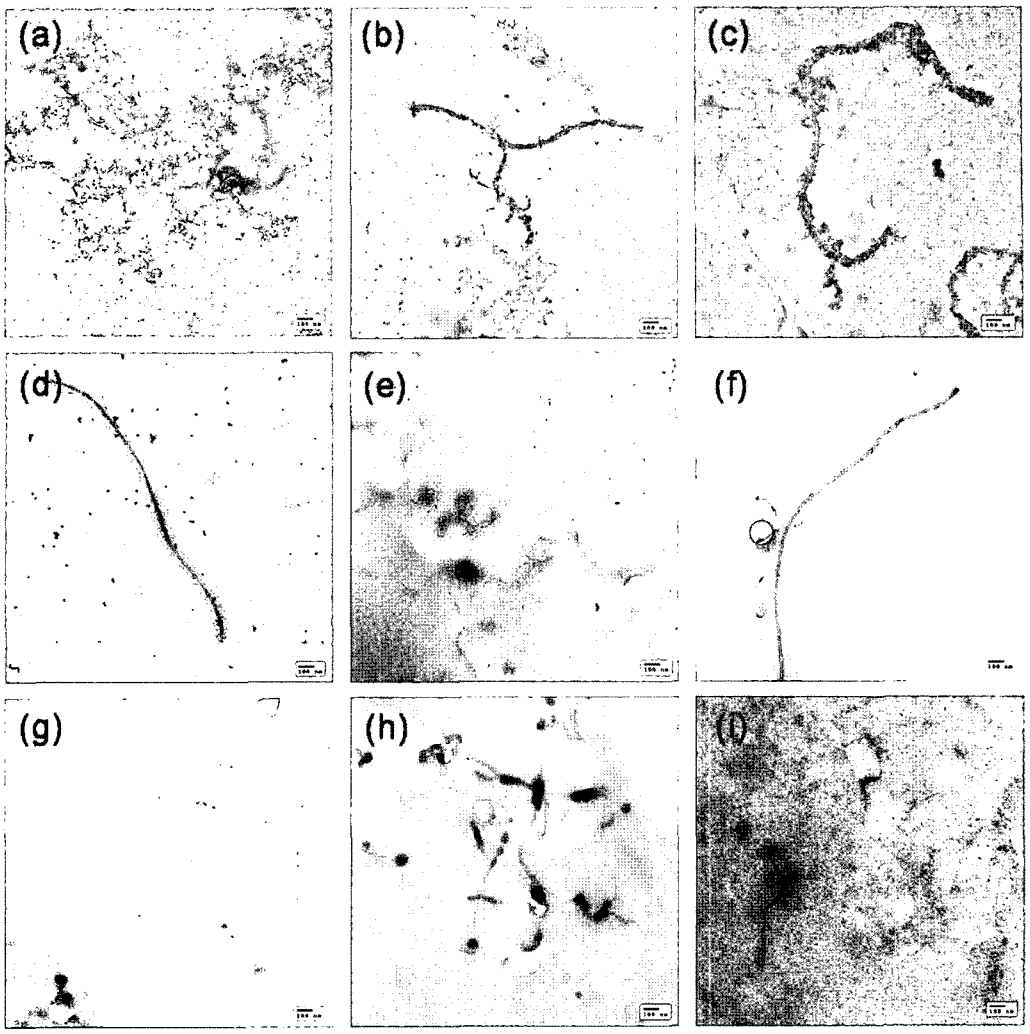


Figure 8. TEM micrographs of the individual MWNTs (scale bar = 100 nm): (a) SDS/pristine MWNTs, (b) SDS/COOH-MWNTs, (c) SDS/NH_2-MWNTs, (d) Pluronic P84/pristine MWNTs, (e) Pluronic P84/COOH-MWNTs, (f) Pluronic P84/NH_2-MWNTs, (g) ASR/pristine MWNTs, (h) ASR/COOH-MWNTs, and (i) ASR/NH_2-MWNTs.

until 24 hrs had passed. In the case of NH_2-MWNT dispersions, however, the transmission intensity levels abruptly increased at ca. 1 hr and their slopes gradually decreased. The NH_2-MWNT dispersion, prepared with ASR, showed the smallest variations in the time-evolution of the transmission intensity.

Morphology of MWNTs. Figure 8 shows the TEM images of pristine, COOH- and NH_2-functionalized MWNTs dispersions, which were prepared with various surfactant solutions. In all samples, no large bundles of MWNTs were observed in the TEM analysis, since the concentration of the MWNT was low (ca. 0.01 mg/mL) and the samples were diluted more than 20 times for analysis. As shown in Figure 8(a, b, and c), SDS surfactant molecules form large aggregates, which evenly adhere to the surface of MWNTs in a dry state. In the case of Pluronic P84 (d, e, and f), however, the surface morphology of the individual MWNTs is clearly shown without any aggregates of Pluronic P84 molecules. An individual MWNT is coated by a layer of Pluronic P84 and no substantial differences were observed between the three types of MWNTs. Considering the dispersion status of the NH_2-MWNT in Figure 3, it can be concluded that the morphology of surfactant covered individual MWNT does not reflect the colloidal stability of the MWNT aggregate. In the case of ASR, it was not easy to discern the MWNTs from the ASR matrix (because ASR forms thick film on the surface of TEM grid) due to the use of RuO_4 and phosphotungstic acid (i.e., staining materials). This is because ASR can easily be stained with RuO_4. It, however, was found that individual MWNTs are partially enveloped in thick and dense (or dark) domains, as shown in Figure 8(g, h, and i). These results are also in good agreement with the exfoliation of MWNTs by ASR, as shown in Figure 6.

Conclusions

The dispersion stability of the various MWNT aqueous dispersions and their wet properties were investigated with three different surfactants. In the case of SDS and Pluronic P84, it was found that the type of MWNTs clearly affected the dispersion stability, aggregate size, and exfoliation behavior of the MWNTs. In particular, the NH_2-functionalized MWNTs showed poorer dispersion stability. The dispersion stability of the MWNTs is clearly increased by using a polymeric type surfactant, i.e., ASR, which has many phenyl groups and carboxylic acid groups. Due to the typical molecular structure of ASR, it showed the smallest aggregate sizes and better storage stability regardless of the type of MWNTs.

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