

초음파를 이용한 PVA에 의한 다중벽 탄소나노튜브의 수상 그래프팅

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Sonochemical Grafting of Poly(vinyl alcohol) onto Multiwall Carbon Nanotubes in Water

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초록: 초음파를 이용한 수중 반응을 통하여 친수성 고분자인 poly(vinyl alcohol) (PVA)를 다중벽 탄소나노튜브 표면에 개질하였다. 초음파 인가 시 PVA는 라디칼을 지닌 상태로 절단되며 탄소나노튜브는 일반적으로 라디칼 스캐빈저 역할을 하므로 생성된 PVA 라디칼과 반응하여 PVA 사슬이 탄소나노튜브 표면에 그래프트 된다. PVA의 그래프트 반응을 조절하기 위하여 초음파 인가 조건을 300과 500 W로 선택하였으며, 인가 시간은 최대 50분으로 하였다. 탄소나노튜브 표면에 그래프트된 PVA는 FTIR, TGA, SEM, 및 TEM을 통하여 분석하였다. 또한 PVA로 개질된 탄소나노튜브의 분산안정성을 분석하였다. 그래프트된 PVA의 양은 초음파의 인가 출력과 인가 시간에 비례하여 증가하였으며, PVA로 개질된 탄소나노튜브는 물 속에서 매우 안정적인 분산성을 보였다. 이는 복잡한 화학반응 과정 없이 초음파를 이용하면 탄소나노튜브를 고분자로 간단히 개질할 수 있음을 보여준다.

Abstract: Multiwall carbon nanotubes (MWCNTs) were modified with a water soluble polymer, poly(vinyl alcohol), PVA, using a simple ultrasonic wave in water. Under the irradiation of ultrasound, PVA chains were severed as macroradicals and instantly grafted onto the surface of MWCNTs due to the radical scavenging effect of MWCNTs. To control the grafting PVA onto MWCNTs, the ultrasonication power and irradiation time were changed from 300 to 500 W and from 10 to 50 min, respectively. The grafted PVA onto MWCNTs was confirmed by FTIR, TGA, SEM, and TEM. Dispersion stability of the modified MWCNTs was monitored by Turbiscan. The amount of grafted PVA on MWCNTs increased with the increase in the sonication power and irradiation time. The grafted PVA on MWCNTs induced the improved dispersion stability of the modified MWCNTs in water. These findings exhibit that ultrasound can be readily used for the grafting polymer chains on MWCNTs.

Keywords: multiwall carbon nanotubes, poly(vinyl alcohol), surface modification, ultrasound, dispersion stability.

Introduction

Carbon nanotubes (CNTs) have attained great interest to material industry and academic society in the last few decades since their discovery in 1991.¹ CNTs have high elastic modulus about 1 TPa comparable to that of diamond (1.2 TPa) and strength of 100 times that of steel.¹⁻³ And they have relatively high electrical conductivity (10^5 - 10^7 S/m).⁴ These superior properties of the CNTs in combination with their nanoscale structures, low mass density, and high aspect ratio (typically

>1000), make them excellent candidates for a number of applications such as electromagnetic shielding devices, field emission display, gas sensors, hydrogen storage, and polymer composites.⁵⁻⁷ Especially, the CNTs have been used to reinforce mechanical and electric properties of polymer composites or solution since they can modulate weak and insulating polymers into strong and conducting polymer composites at even low loading.^{8,9} For the improvement in properties of polymer composites, the CNTs have to be well-dispersed in polymer matrices or organic solution with a good affinity.¹⁰ However, the CNTs are usually poorly dispersed in these surroundings. First of all, the CNTs have weak interfacial bonding with them. And the strong van der Waals force and

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the high aspect ratio of the CNTs easily cause the self-aggregation.^{11,12}

The modification of the surface of CNTs is considered as an effective method aiming to solve these critical problems. The modification of CNTs with polymers is divided into “non-covalent” and “covalent” modification. The non-covalent modification is the physical adsorption or wrapping the CNTs using surfactants or polymer chains. This method does not destroy genuine structures of the CNTs. However, the interactions achieved by physical treatment are weak and not permanent. In a different way, the covalent modification induces a strong chemical bonding between the CNTs and polymers. Most covalent modification methods of the CNTs use toxic chemicals such as strong acids. Consequently, this chemical process is environmentally harmful and causes the serious deterioration of the structure and properties of the CNTs.

Ultrasonic degradation of polymer chains in solution has a long standing history since 1939.¹³ The effects of ultrasound on chemical transformations are not the result of any direct coupling of the sound field with the chemical species involved on a molecular level. The ultrasound is able to cause chemical effects through cavitation phenomenon.¹⁴ When microbubbles created by the cavitation collapse, tremendous energy is gushed out and various chemical and mechanical effects arise.¹⁵⁻¹⁷ For last 3 decades, many researchers have paid attention to the reduction of molecular weight of polymer in solutions under ultrasound, called ultrasonic degradation. For example, Smith *et al.* reported the reduction of the molecular weight of polystyrene in various solvents under ultrasound irradiation.¹⁸ Gronroos *et al.*, reported ultrasonic depolymerization of poly(vinyl alcohol) (PVA) as a functions of frequency, and sonication power.¹⁹ Lately, Gogate *et al.*, investigated the reduction of intrinsic viscosity of carboxymethyl cellulose and PVA solutions.²⁰ The ultrasonic degradation of the polymer is often expressed as the reduction in the molecular weight of polymers under ultrasound. An interesting fact is that the polymer chains are severed statistically around the middle of them, leaving polymeric radicals at the ends.²¹

It has been known that CNTs have a radical scavenging capacity. Maztinez *et al.*, unveiled the free radical scavenging activity of singlewall CNTs (SWCNTs) with different structures through electron transfer reactions.²² And Fenoglio *et al.* discovered that multiwall CNTs (MWCNTs) are very effective scavengers.²³ This suggests that CNTs can react with the polymeric radicals severed by ultrasound, to generate polymer-grafted CNTs. In this work, aqueous solution of PVA con-

taining MWCNTs was exposed to ultrasound to graft PVA onto MWCNTs. Grafting of PVA onto MWCNTs were experimentally verified and the dispersion stability of modified MWCNTs in water was significantly improved. This result suggests that a simple “grafting onto” modification of CNTs is possible using ultrasound in water.

Experimental

Materials. The MWCNTs synthesized by a thermal chemical vapor deposition method was used (95% pure; Hanwha Nanotech, S. Korea). The MWCNTs have a diameter of 10-20 nm and a length of 10 to 50 μm . PVA (Mw: 89000-98000 g/mol, Aldrich, USA) was used to modify the MWCNTs. Double distilled deionized water was used.

Modification of MWCNTs Using PVA in Water. 5 g of PVA and 94.75 g of water were charged into a 100 mL glass reactor. In order to make a homogeneous PVA aqueous solution, the mixture was stirred vigorously with a magnetic stirrer at 70 °C for 15 min. After cooling down to room temperature, 0.25 g of MWCNTs were added into the mixture. The mixtures were dispersed and sonicated with a horn-type probe (VC 750 ultrasonic processor, Youngjin, S. Korea). In order to induce the ultrasonic degradation of PVA and chemical grafting of PVA chains on MWCNTs, the ultrasound powered at 300 W (intensity: 105.8 W/cm²) and 500 W (intensity: 176.3 W/cm²) was irradiated for 50 min. After sonochemical reaction, modified MWCNTs were completely suspended in the water without sedimentation. Unreacted PVA molecules were separated by Soxhlet extraction using DDI water for 3 days. Finally, pure PVA modified MWCNTs were obtained and dried *in vacuo* 80 °C for 1 day.

Characterization. To confirm the functional groups of the PVA modified MWCNTs, Fourier transform infrared spectra were recorded on a FTIR Vacuum Spectrometer (VERTEX 80V, Bruker, Germany). Scanning electron microscopy (SEM) (S-4300, Hitachi, Japan) and transmission electron microscope (TEM) (CM200, Philips, The Netherlands) were used for the observation of the morphology change of MWCNTs. Thermogravimetric analysis (TGA) was performed with a heating rate of 20 °C/min under nitrogen atmosphere on a TGA Q50 (TA instruments, USA). Quantitative analysis of dispersion stability of MWCNTs was measured by Turbiscan LAB[®] (Formulation, France). 0.01 wt% of raw and modified MWCNTs were dispersed in the DDI water and the migration behavior of the MWCNTs in water was monitored by measuring the trans-

mittance and backscattering of monochromatic light ($\lambda=880$ nm) from the suspension. Suspensions in flat-bottomed cylindrical glass tubes were placed in the instrument and the transmission and backscattering of light from suspensions was periodically measured along height at room temperature every 1 h until 24 h. Inside a glass cell tube, the backscattering (BS) and transmittance (T) of incident light are measured by calculating transport mean free path of photons (l^*) throughout the medium. Base on Mie theory, the BS and T can be obtained for a concentrated suspension as follows:²⁴

$$BS \approx \left(\frac{l}{l^*}\right)^{1/2} \quad (1)$$

$$T \approx \exp\left(\frac{-r}{l}\right) \quad (2)$$

where r is an internal radius of a measurement cell. The photon transport mean free path (l^*) and photon mean free path (l) are defined:

$$l^* \approx \frac{2d}{3\Phi(1-g)Q_s} \quad (3)$$

$$l \approx \frac{2d}{3\Phi Q_s} \quad (4)$$

where d , Φ , g , and Q_s denote a particle mean diameter, the volume fraction of a dispersed phase, asymmetry factor, and scattering efficiency factor, respectively. The results were presented as the sedimentation profile *i.e.*, Δ transmission flux *versus* time.

Molecular weight of PVA from ultrasonic degradation is calculated using the Mark-Houwink equation (eq. 5) and these viscosity data were obtained from viscometer (Dial reading viscometer, Brookfield, U.S.A).

$$[\eta] = kM_V^a \quad (5)$$

$[\eta]$ is the intrinsic viscosity of polymer and ' k ' is constant which depend on the type of polymer, solvent and the temperature of viscosity determinations. To investigate defects of MWCNTs (3.2) from ultrasound, the Raman spectra were recorded with Bruker RPS 100/S FT Raman instrument. The excitation wavelength was 1064 nm from a Nd/YAG laser power of 20 mW. In order to analyze ultrasonic degradation of MWCNTs, a particle size analyzer (PSA) (ELS-Z particle size analyzer, Otsuka Electronics, Japan).

Results and Discussion

Ultrasonic Degradation of PVA Chains. Under ultrasound irradiation, polymer chains in the polymeric solutions are severed preferentially near the middle of the chains, resulting in polymeric radicals at the ends.²⁵ Sonication power, irradiation time, and frequency mainly determine the degradation of polymers, the change of molecular weight, and their limiting molecular weight.^{20,26-28} Figure 1 explains the reduction of molecular weight of PVA during ultrasonication under 300 and 500 W at different irradiation time due to ultrasonic degradation. It is noted that frequency of applied ultrasound was 20 kHz. Intrinsic viscosity and resulting molecular weight are also listed in Table 1. The degradation of the PVA chains was outstanding in stronger ultrasonication power and longer irradiation time. The increase in the degradation of the PVA chains means more active cleavage of PVA chain and more affluent generation of macroradicals from PVA.

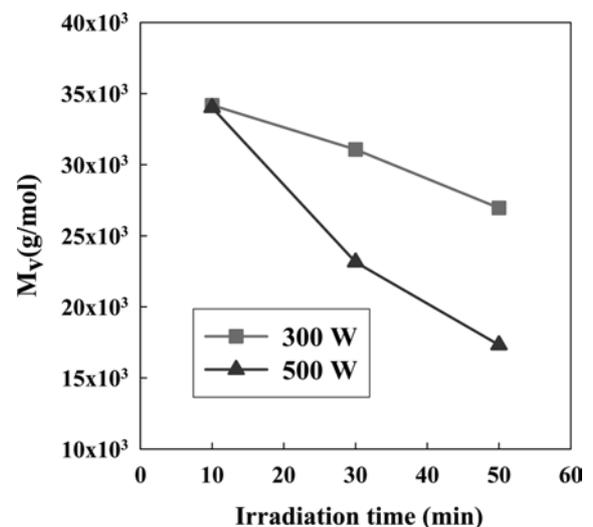


Figure 1. Change of molecular weight of PVA in water by applying ultrasound.

Table 1. Reductions in M_w of PVA Polymeric Solution by Effect of Sonication Power and Irradiation Time

Conditions	Intrinsic viscosity (dm ³ /g)	Molecular weight (g/mol)
300 W - 10 min	0.0558	34173
300 W - 30 min	0.0519	31066
300 W - 50 min	0.0466	26960
500 W - 10 min	0.0556	34012
500 W - 30 min	0.0415	23147
500 W - 50 min	0.0333	17326

Defects of MWCNTs from Ultrasound. It has been known that the great intensity of energy released by cavitation process from high power ultrasound causes a serious deformation and damage to CNTs. Strong ultrasound may strip of the outer graphitic layer and even turn CNTs to amorphous carbon.²⁹ Therefore, the structural damage of MWCNTs was investigated using FT-Raman spectroscopy as shown in Figure 2. The convenient confirmation of functionalized CNTs is to use the Raman spectroscopy.³⁰ The Raman spectra are observed at around 1300 and 1600 cm^{-1} which correspond to defective carbon band from the disordered sp^3 -hybridized carbons in the nanotube walls (D-band) and graphite carbon band from the sp^2 -hybridized (G-band) of MWCNTs, respectively.^{31,32} Peak intensity ratio (I_D/I_G) of D-band to G-band of MWCNTs is a direct indicative of the degree of structural defect of MWCNTs. In Figure 2, the intensity ratio (I_D/I_G) steadily rises in stronger irradiation power and longer irradiation time. But a range of this variation was not large. This fact suggests that the ultrasonic wave has marginal effect on the generation of defects of the MWCNTs since ultrasound power was controlled to be low in order to minimize the destruction of MWCNTs. However, the applied ultrasound was found to cut off the long MWCNTs in water in the presence of PVA. Ultrasonicated MWCNTs aqueous solution was filtered using a cellulose thimble. Since the average pore size of the filter is 8 μm and its structure is double walled thimble shape with about 2 mm of thickness, long raw MWCNTs with 10 to 50 μm length cannot pass through the filter. Figure 3 shows the opti-

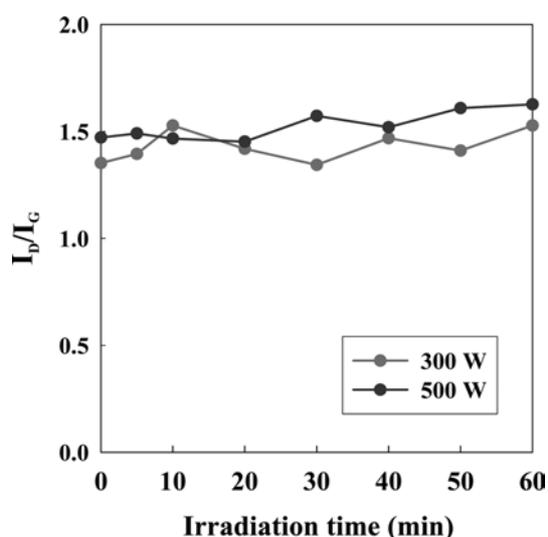


Figure 2. Degree of structural defect of sonicated MWCNTs with ultrasound irradiation time.

cal images of filtered aqueous suspensions of MWCNTs. For a weak ultrasonic condition of 300 W for 10 min, the MWCNTs suspension is almost transparent, indicating that MWCNTs were hardly shortened. However, the suspensions became darker when ultrasonic conditions were harsh. The darkness of the suspension is caused by the shortened MWCNTs due to strong ultrasonication.

Figure 4 shows the change of the size of MWCNTs in water measured using a particle size analyzer (PSA). Usually, PSA is used for estimate the size of particle-like spheres. Although the structure of MWCNTs having high aspect ratio is different with spheres, there is much room to use for MWCNTs having curvature structure. It is noted that the average size of raw MWCNTs was obtained as 25500 nm from the PSA. Con-

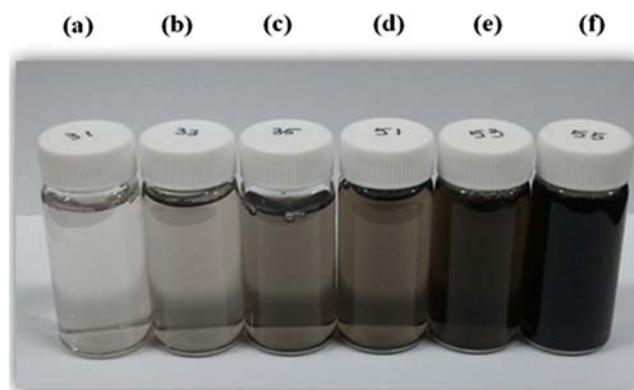


Figure 3. Optical image of the suspension of the cutted pieces of MWCNTs: (a) 300 W-10 min; (b) 300 W-30 min, (c) 300 W-50 min; (d) 500 W-10 min; (e) 500 W-30 min; (f) 500 W-50 min.

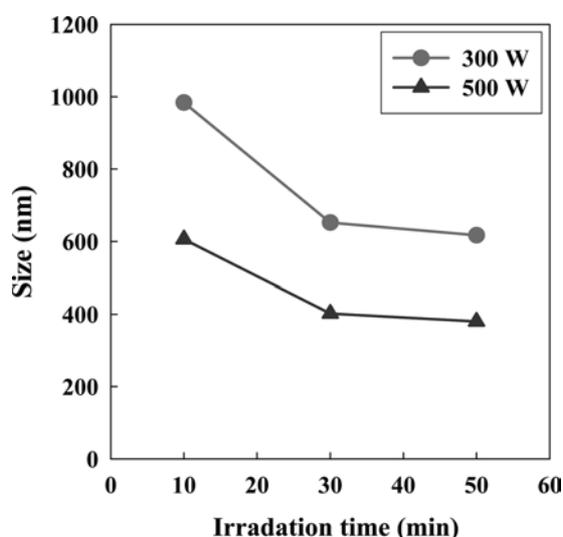


Figure 4. Average size of the cutted pieces of MWCNTs by applying ultrasound.

sidering the length of 10-50 μm for raw MWCNTs, the measured result is close to this value. The size of severed MWCNTs in the suspension decreases by sonication, which is more prominent for stronger applied power and longer irradiation time. From the information above, it can be deduced that ultrasonication conditions used in this work cause mainly size reduction rather than structural defect on the basal plane of MWCNTs.

Sonochemical Grafting of PVA. To verify the sonochemical grafting of PVA onto MWCNTs, their characteristic vibra-

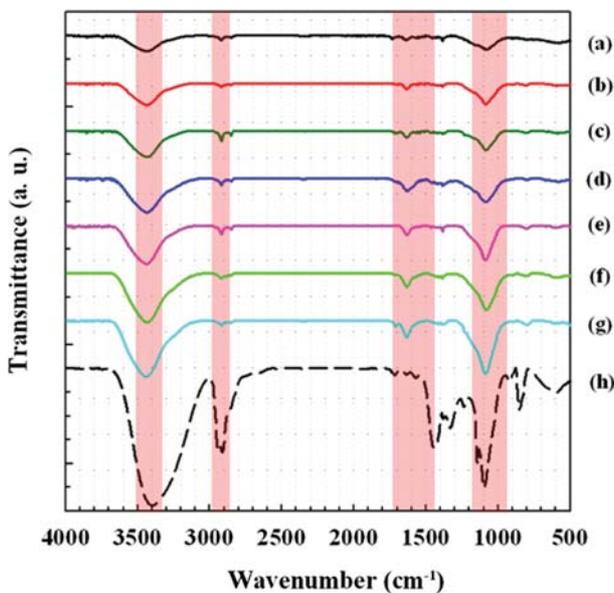


Figure 5. FTIR spectra of (a) raw MWCNTs and PVA modified MWCNTs: (b) 300 W-10 min; (c) 300 W-30 min; (d) 300 W-50 min; (e) 500 W-10 min; (f) 500 W-30 min; (g) 500 W-50 min; (h) raw PVA.

tion bands were investigated employing FTIR as shown in Figure 5. The FTIR spectrum of the MWCNTs (curve a) shows peaks of absorption bands at 3440 and 1635 cm^{-1} . The broad peak at 3440 cm^{-1} is O-H for amorphous carbon and the peak at 1635 cm^{-1} is C=C for the internal defects of MWCNTs. Raw PVA (curve h) shows absorption bands at 3400, 2940, 2912, 1733, 1626, 1570, 1445, 1377, 1330, 1236, and 1095 cm^{-1} , which are due to the O-H, C-H, C-O and C-C bonding. The PVA modified MWCNTs (curve b, c, d, e, f and g) show peaks of absorption band at 3437, 2920, 2850, 1712, 1634, 1384, and 1087 cm^{-1} . Among them, broad O-H peak at 3437 cm^{-1} and C-O peak at 1087 cm^{-1} confirms that PVA was grafted onto MWCNTs. O-H peak of modified MWCNTs at 3437 cm^{-1} is shifted from 3440 cm^{-1} for raw MWCNTs and 3400 cm^{-1} for raw PVA. C-O peak is also shifted to 1087 from 1080 cm^{-1} . Consequently, PVA chains were covalently bonded to the surface of MWCNTs.

TGA was used for a quantitative analysis of the amount of grafted PVA on MWCNTs. The weight loss curves of raw MWCNTs, raw PVA and PVA modified MWCNTs are shown in Figure 6(a). A weight of the raw MWCNTs was maintained up to 750 $^{\circ}\text{C}$. For raw PVA, a weight loss about 96% was observed for the thermal decomposition in 250 to 450 $^{\circ}\text{C}$ and the residue of PVA was about 4%. For PVA modified MWCNTs, thermograms show that the main thermal decomposition of grafted PVA occurs in 170 to 450 $^{\circ}\text{C}$ and the amount of the grafted PVA was about 30 wt%. For modified MWCNTs, the decomposition starts earlier since powerful sonication caused structural defects and size reduction. Figure 6(b) represents the effect of ultrasonication irradiation time on the sonochemical grafting of PVA on MWCNTs. The amounts

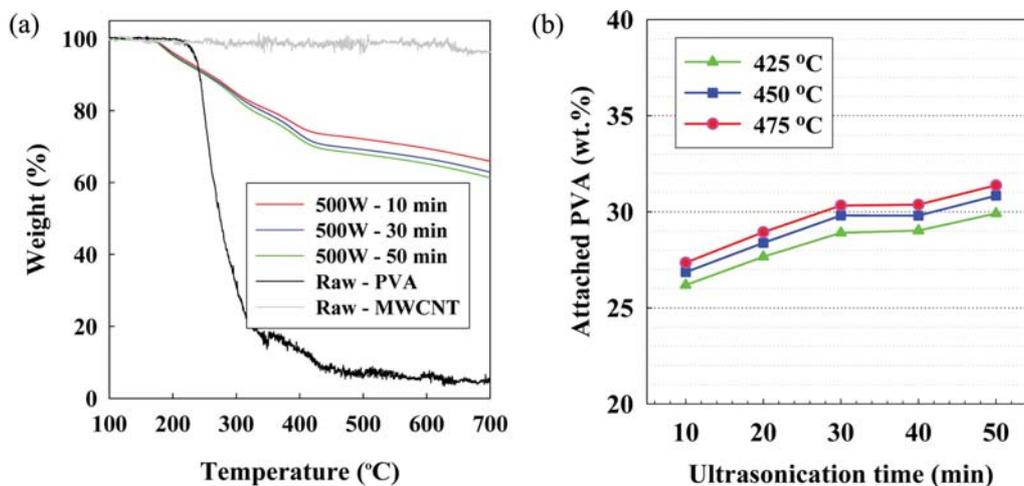


Figure 6. (a) TGA thermograms of raw PVA, raw MWCNTs, and PVA modified MWCNTs; (b) amounts of grafted PVA on MWCNTs.

of covalently grafted PVA were 26.8, 30, and 30.9 wt% for 500 W-10 min, 500 W-30 min, and 500 W-50 min, respectively. Generally, the amount of grafted PVA is linearly increased with sonication time up to 50 min however it is levelled off after 30 min. Therefore, the optimum time seems to be 30 min to induce sonochemical grafting PVA on MWCNTs.

Also, the PVA grafting was visualized in Figure 7 where the morphological change was analyzed using TEM. Figure 7(a) shows clear surface without any impurity or polymer layer for raw MWCNTs. On the other hand, Figure 7(b) evidently

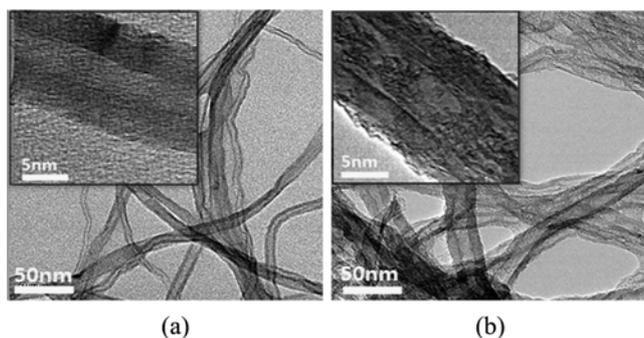


Figure 7. TEM microphotographs of (a) raw MWCNTs; (b) PVA modified MWCNTs (500 W-30 min).

shows that the PVA layer on the surface of the modified MWCNTs is roughly formed. And thickness of the PVA layer is maximum 3.5 nm and about 1.5 nm on average. SEM microphotographs of the PVA modified MWCNTs in Figure 8(a)-(c) display that the thickness of PVA layer is slightly increases compared to raw MWCNTs in Figure 8(a). Especially, it is possible to confirm that the amounts and thickness of grafted PVA on the MWCNTs were increased by greater sonication power and longer irradiation time. Figure 8(d) shows a detailed difference in morphology of the surface of layer of grafted PVA. At the relatively weak sonication power and short irradiation time, the chains of PVA are uniformly and thinly grafted on the surface of MWCNTs. However, at the relatively strong sonication power and long irradiation time, the uniform layer of PVA is already formed and then the others of the PVA chains grafted superabundantly and take the rough morphology. The reason is that possible grafting sites on MWCNTs are remarkably decreased once PVA chains are fully grafted on the most surface of MWCNTs. In the concrete, the PVA chains having radicals are more quickly grafted to the surface of MWCNTs acted as radical scavenger than the surface of the PVA layer on the MWCNTs. The PVA chains hav-

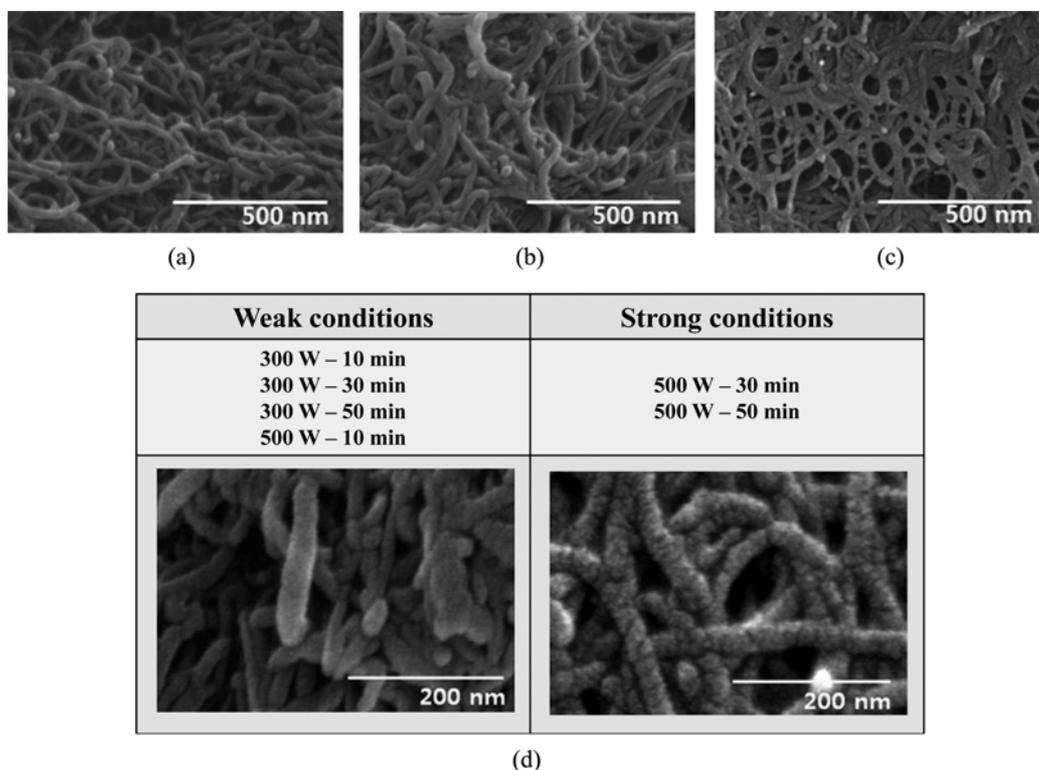


Figure 8. SEM microphotographs of (a) raw and PVA modified MWCNTs: (b) 500 W-30 min; (c) 500 W-50 min; (d) surface morphology of the PVA modified MWCNTs.

ing radicals is slowly attached to the surface of the PVA layer after the surface of the MWCNTs is fully coated. These morphology results have close relation to the TGA data in which the grafting rate of PVA was decreased with prolonged ultrasound irradiation time.

Dispersion Stability of Modified MWCNTs. Figure 9 displays optical images taken after 2 months for the dispersion stability of raw MWCNTs and PVA modified MWCNTs in water. The raw MWCNTs dispersed in water aggregated within an hour and sedimentation occurred in a day because of their high surface energy and poor affinity with water. However, the PVA modified MWCNTs showed distinctively improved dispersion stability in water due to the good chemical affinity between hydroxyl group of grafted PVA and the water. For a quantitative optical analysis, the dispersion stability of 0.01 wt% of raw MWCNTs and PVA modified MWCNTs in water monitored by Turbiscan for 24 h is

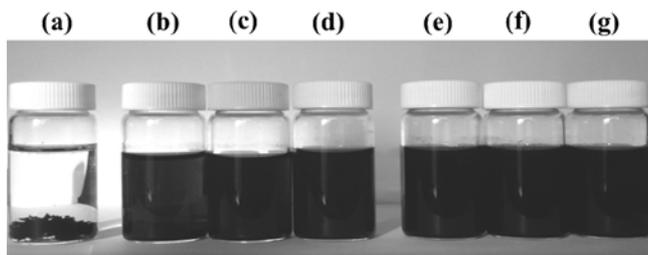


Figure 9. Optical image of dispersion stability of 0.01 wt% of (a) raw and PVA modified MWCNTs in water (two months after dispersion); (b) 300 W-10 min; (c) 300 W-30 min; (d) 300 W-50 min; (e) 500 W-10 min; (f) 500 W-30 min; (g) 500 W-50 min.

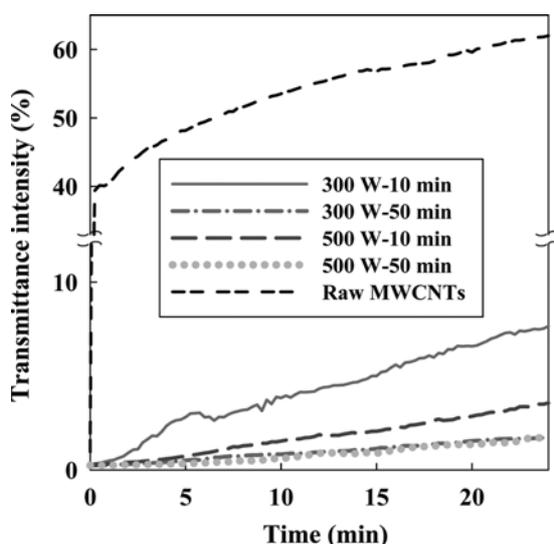


Figure 10. Dispersion stability of raw MWCNTs and PVA modified MWCNTs in water.

depicted in Figure 10. Higher transmittance implies that suspensions become transparent due to aggregation and sedimentation of MWCNTs in water and lower transmittance suggests the suspension is stable. Because raw MWCNTs severely formed the aggregated structure and occurred sedimentation, the transmittance of incident light sharply increased within an hour. On the other hand, the transmittance of suspensions containing PVA grafted MWCNTs steadily increased with time, however, the transmittance is much lower compared to raw MWCNTs. In particular, lower transmittance was achieved for higher applied ultrasound power and longer irradiation time. The much improved dispersion stability originates from the grafted PVA chains are hydrophilic and serve as steric stabilizer preventing from the aggregation of MWCNTs. Therefore, the dispersion stability of modified MWCNTs improves as the amount of grafted PVA increases.

Finally, it was found that ultrasonic degradation of polymer chains in liquids can be used to simply graft the polymers on the surface of MWCNTs which act as radical scavenger. Herein, a water soluble polymer, PVA, was grafted on MWCNTs in water and the degree of modification was investigated. The modified MWCNTs show much enhanced dispersion stability in water. The experimental findings suggest that irradiation of controlled ultrasound provides a new methodology to modify CNTs via an eco-friendly and simple process without involving sophisticated and time-consuming chemical reactions.

Conclusions

In this work, a water-soluble polymer, PVA, was grafted on the surface of MWCNTs using a simple ultrasonication process. It was found that the applied ultrasound causes slight structural defects and significant size reduction of MWCNTs. Since PVA chains are severed and generate macroradicals, MWCNTs as radical scavenger can instantly react with the polymeric macroradicals, resulting in the grafting of the polymer chains. The amounts of the grafted PVA on MWCNTs are strongly depended on the sonochemical reaction conditions such as sonication power and irradiation time. The grafted PVA was confirmed by FTIR, SEM, TEM, and TGA. The degree of grafted PVA was proportionally increased with ultrasound power and irradiation time. The amount of the grafted PVA was about 30 wt% and the thickness of PVA layer on MWCNTs was about 1.5 nm on average. The as-prepared PVA-modified MWCNTs possess much improved dispersion

stability in water since the grafted PVA chains are hydrophilic and serve as steric stabilizer preventing from the aggregation of MWCNTs. Finally, this simple method would provide the facile route to fabricate modified MWCNTs using various polymers in order to improve the dispersion stability in solvents or uniform dispersion of MWCNTs in polymeric matrices.

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