Surface Modification of Carbon Nanotube by Poly(ethylene glycol) for the Preparation of Poly(vinyl alcohol) Nanocomposite

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Herein, PEGylated multi-walled carbon nanotube (MWNT) was prepared for the successive fabrication of poly(vinyl alcohol) PVA/MWNT nanocomposite film by solution casting. The surface modified MWNT showed a good colloidal stability in a polar solvent, i.e., water. Also, the PEGylated MWNT had an improved dispersion stability in aqueous PVA solution. The mixture of PEGylated MWNT and PVA dissolved in water was film casted and the dispersion uniformity and corresponding improvement of electrical conductivity were investigated. The electrical conductivity of PVA/modified MWNT composite film was three-fold higher than that of PVA/pristine MWNT composite film due to the much improved distribution uniformity of modified MWNT in PVA matrix.

Keywords: Multi-walled carbon nanotube, poly(ethylene glycol), composite, dispersion uniformity, electrical conductivity

1 Introduction

Currently, carbon nanotube composites have attracted much attention because the multi-walled carbon nanotube (MWNT) has a unique structure and remarkable mechanical (1), electrical (2), and optical properties (3). Owing to its great possibilities, MWNT is expected to substitute a variety of classical materials in the near future. To achieve full reinforcing potential of MWNT, it should be well dispersed in a matrix and possess good interfacial affinity with a matrix (4). However, MWNT with high van der Waals force, surface area, and high aspect ratio inevitably cause the self-aggregation. Moreover, it is insoluble in any organic solvents due to the pure carbon element and its stable structure (5). In order to overcome these problems, the chemical modification of the MWNT's surface or utilization of surfactants is regarded as an effective way to improve its dispersion uniformity (6,7). The chemical modification methods using covalent bonds involve the introduction of various chemical moieties on MWNT's surface to improve its solubility in solvents. Whereas the physical treatments utilize the adsorption of various chemical agents on MWNT's surface either via hydrophobic/hydrophilic interaction or coulomb attraction (8). When surfactants are employed in MWNT dispersions, surfactant molecules work by adsorption at the interface and self-accumulation into supramolecular structures, which help the MWNT dispersion retain a stable colloidal state. The MWNT uniformly dispersed in solvents can be utilized in direct conductive coating, further sol-sol process, and nanocomposite manufacturing.

It is well-known that pristine MWNT surface can be simply carboxylated by treatment with strong acids such as nitric acid (HNO_3) and sulfuric acid (H_2SO_4). This chemical oxidation can significantly increase the dispersion stability of the suspensions (9). In our previous study, we have found that the MWNT with carboxylate (COOH) was very well dispersed in polar media including water and alcohols due to the combination of polar-polar affinity and electrostatic repulsion. Recently, several studies have focused on PVA/carbon nanotube composites because a water soluble polymer, PVA, has gained much importance for environmental reasons (10).

Therefore, in this work, we introduced a hydrophilic polymer, poly(ethylene glycol) (PEG) on the surface of carboxylated MWNT via esterification reaction to improve dispersion stability of MWNT in PVA aqueous solution. Pristine and PEGylated MWNTs were dispersed in polar and

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nonpolar solvents and the change of dispersion stability was measured by employing a multiple light scattering technique. The dispersion stability of PEGylated MWNT in PVA aqueous solution was improved due to the polar-polar affinity between the surface of PEGylated MWNT and aqueous solution. And the PVA solution with MWNT was dried to prepare PVA/MWNT composite films. Since the dispersibility of PEGylated MWNT was considerably improved, the electrical conductivity of the PVA/PEGylated MWNT composite film was three-fold higher than that of the PVA/pristine MWNT composite film.

2 Experimental

2.1 Materials

Multi-walled carbon nanotube (MWNT, 95% pure by thermogravimetric analysis (TGA)) synthesized by a thermal chemical vapor deposition (CVD) was received from Hanhwa Nanotech, Korea. It has a mean diameter of 10–20 nm and length of 10–50 μm. 63% nitric acid (HNO$_3$) and 98% sulfuric acid (H$_2$SO$_4$) from Duksan Pure Chemical, Korea were used as received. Poly(ethylene glycol) (PEG) with a molar mass of 2000 g/mol was purchased from Yakuri Pure Chemicals Co., Japan and dried under vacuum before use. Poly(vinyl alcohol) (PVA) supplied by Sigma Aldrich, USA was 99+ % hydrolyzed with an average molecular weight 89,000-98,000 g/mol.

2.2 Chemical Oxidation of MWNT

MWNT (2 g), sulfuric acid (8 mL), and nitric acid (22 mL) were charged in a 250 mL one-neck round bottom flask equipped with a condenser and a magnetic stirring bar (50 mm). The flask was sonicated for 10 min with a horn-type ultrasonic apparatus. The chemical oxidation reaction was carried out at 110°C for 24 h. After acid treatment, the MWNT was functionalized with the carboxylic acid groups (COOH) on the surface. After cooling down to room temperature, the mixture was diluted with 1000 mL of deionized water, then vacuum filtered through a 0.2 μm polytetrafluoroethylene (PTFE) filter (membrane filter, Adventec®). Filtering, washing with deionized water and redispersion were repeated at least 10 times until the pH of the filtrate reached near 7. After vacuum drying the filtrate, 1.93 g carboxylated MWNT (MWNT-COOH) was achieved.

2.3 Preparation of Pegylated MWNT

For the introduction of PEG groups (HO(CH$_2$CH$_2$O)H) on the carboxylated MWNT's surface, the as-prepared 0.02 g carboxylated MWNT, 2 g PEG, 20 g ethanol as a medium, and 0.02 g HCl as a catalyst were charged into a 250 mL flask. The mixture was heated at 70°C for 3 h. The reaction

occurred via esterification between the carboxylic acid of modified MWNT and alcohol group of PEG. After cooling to room temperature, the mixture was diluted with ethanol and then vacuum filterated through the PTFE filter. Filtering, washing with ethanol, and redispersion were repeated at least three cycles until unreacted PEG was removed. After vacuum drying the filtrate, PEGylated MWNT was achieved.

2.4 Preparation of Composite Films

Free-standing PVA composite films with different MWNTs were fabricated by solution casting. First, % PVA aqueous solution was prepared by mixing PVA and deionized water at 70°C for more than 5 h. Two different MWNTs (pristine and PEGylated MWNT) solutions were prepared by adding 0.1 wt% MWNT to the deionized water. The two solutions were sonicated for 5 min using high-power ultrasonicator (750 W). And then PVA aqueous solution and MWNT solutions were mixed. After mixing, PVA/MWNT aqueous solutions were poured into PTFE dishes and dried in an oven at 30°C for 7 days. The composite films were obtained by peeling off from PTFE dishes and kept in a vacuum desiccator before measurement.

2.5 Characterization

To confirm the structure of the pristine, modified, and functionalized MWNT, a Fourier transform infrared spectroscopy (FT-IR, VERTEX 80V, Bruker) was employed. An X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermofisier) with a Mg Kα X-ray source (1253.6 eV) was used to investigate the surface chemical state of pristine, modified, and functionalized MWNT. A thermogravimetry analysis was performed on TGA Q50 (TA Instrument) at a heating rate of 20°C/min under nitrogen atmosphere. A Hitachi scanning electron microscopy (SEM, S-4300) and a videoscope (VM, EGVM-35B, EG Tech) were used to observe the morphology change of MWNT in PVA composite films. The dispersion stabilities of pristine, modified and functionalized MWNTs in the solvents were analyzed using a multiple light scattering method (Turbiscan®, Formulaction, France). Turbiscan using monochromatic near infrared of 880 nm detects the transmission and backscattering light of the samples. Turbiscan measurement was performed every 1 h for 24 h. The results are presented as the change in the transmittance of light vs. time. The electrical conductivity of the composite films was determined by a resistivity meter (Laresta-GP, Misubishi Chemical Co.).

3 Results and Discussion

The entire procedure from the chemical oxidation of pristine MWNT to the preparation of PEGylated MWNT is illustrated in Scheme 1. The chemical oxidation was
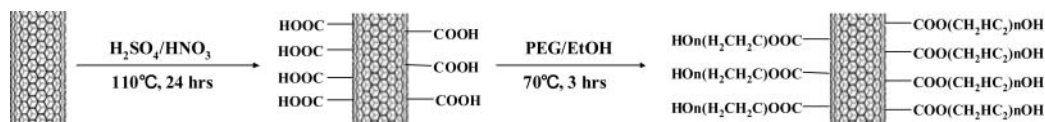
Sch. 1. The procedure for the preparation of the PEGylated MWNT through oxidation and esterification reactions.

performed using strong acids consisting of H_2SO_4 and HNO_3. After the oxidation process, structural defects occur at the MWNT's ends, and occasionally on the sidewalls ([],11). However, these defects are usually the prime sites for functionalization (12). The PEGylated MWNT was prepared by esterification between the carboxylic acid on MWNT's surface and terminal alcohol group of PEG.

To confirm the modification of MWNT, the chemical compositions of three different MWNTs' surfaces were characterized by FT-IR. Figure 1 shows the FT-IR spectra of pristine, carboxylated, and PEGylated MWNTs. The spectrum of the pristine MWNT (Fig. 1(a)) shows a broad C–H alkyl stretching peak at 2,850-3,000 cm^{-1}. After acid treatment, the spectrum of the carboxylated MWNT shows a sharp C=O stretching peak from the COOH groups at 1700 cm^{-1} and a broad O-H stretching peak between 3400 and 3600 cm^{-1}(Fig. 1(b)). In the case of the PEGylated MWNT, a C-O-C stretching peak from PEG groups appears at 1100 cm^{-1}(Fig. 1(c)). These FT-IR spectra indicate that the PEG chains were chemically attached to the carboxylated MWNT (13).

XPS spectra also provide useful information on the chemical bonding on the surface of solid. XPS analysis was performed on the carboxylated and PEGylated MWNT to obtain the information on carboxylic acid groups (–COOH) and PEG on the MWNT. The main peak (about 284.5 eV) is attributed to the C1s, and the other peaks are

attributed to –C-OH (about 285.7 eV), –C=O (about 286.5 eV), and –COOH (about 288.5 eV), respectively ([]). The XPS spectra shown in Figure 2 indicates that the functional groups of MWNT's surface were changed after the acid treatment and esterification. The XPS analysis gives the accurate atomic concentration of functionalized carbon atoms. On the pristine MWNT's surface, 14.64% of carbon atoms are bonded with an –OH group, 6.45% with a = O group, and 9.33% with a –COOH group. In comparison with pristine MWNT, the carboxylated MWNT has 10.21% of carbon atoms bonded with an –OH, 5.85% with a =O group, and 11.54% with a –COOH group. In the case of the PEGylated MWNT, 17.11% of carbon atoms are bonded with an –OH group, 6.93% with a =O group, and 5.01% with a –COOH group. The XPS result suggests that the MWNT was majorly modified with the carboxylic acid groups (–COOH) on the surface by the acid treatment, and successively functionalized with PEG on the surface by the esterification. Through these qualitative results, XPS spectra indicate that MWNT was successfully surface-modified to bear functional groups.

The SEM microphotographs (Fig. 3) compare the morphology of the pristine (Fig. 3(a)) and PEGylated MWNT (Fig. 3(b)). The evidence of the surface modification by PEG can be clearly witnessed at the high magnification on the micrograph. The diameters of pristine and PEGylated MWNT are 40.07 and 60.01 nm, respectively. The diameter of PEGylated MWNT is about three times greater than that of pristine MWNT. It indicates that PEG was well attached to the surface of MWNT.

To examine the amount of PEG bonded on MWNT, thermogravemetry analysis was performed. The weight loss curves of pure PEG, pristine, carboxylated and PEGylated MWNT are presented in Figure 4. For pristine MWNT (Fig. 4(a)), a constant weight is maintained up to 800°C under nitrogen atmosphere. After treatment with H_2SO_4 and HNO_3, the weight loss increases to about 13% at 800°C, and a continuous weight loss is observed due to the defects which resulted from reaction with strong acids. In contrast, for pure PEG, about 97% weight loss occurred between 220-420°C resulting from the thermal decomposition of PEG molecules. For the PEGylated MWNT, the transition region around 220-420°C is attributed to the structural degradation of PEG molecules, however, the weight loss before 220°C originates because of the defects resulted from reaction with strong acids as one can confirm in Figure 4(b) (carboxylated MWNT). The weight loss of PEGylated MWNT indicates that the amount of PEG bound to MWNT is about 47.3 wt%. The amount of grafted unit on
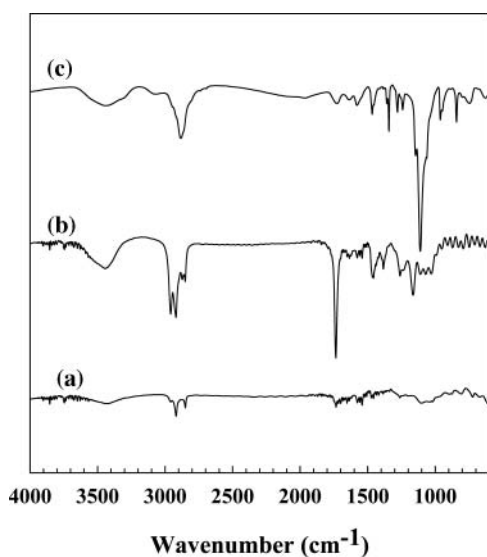

Fig. 1. FT-IR spectra of (a) pristine, (b) carboxylated, and (c) PEGylated MWNTs.

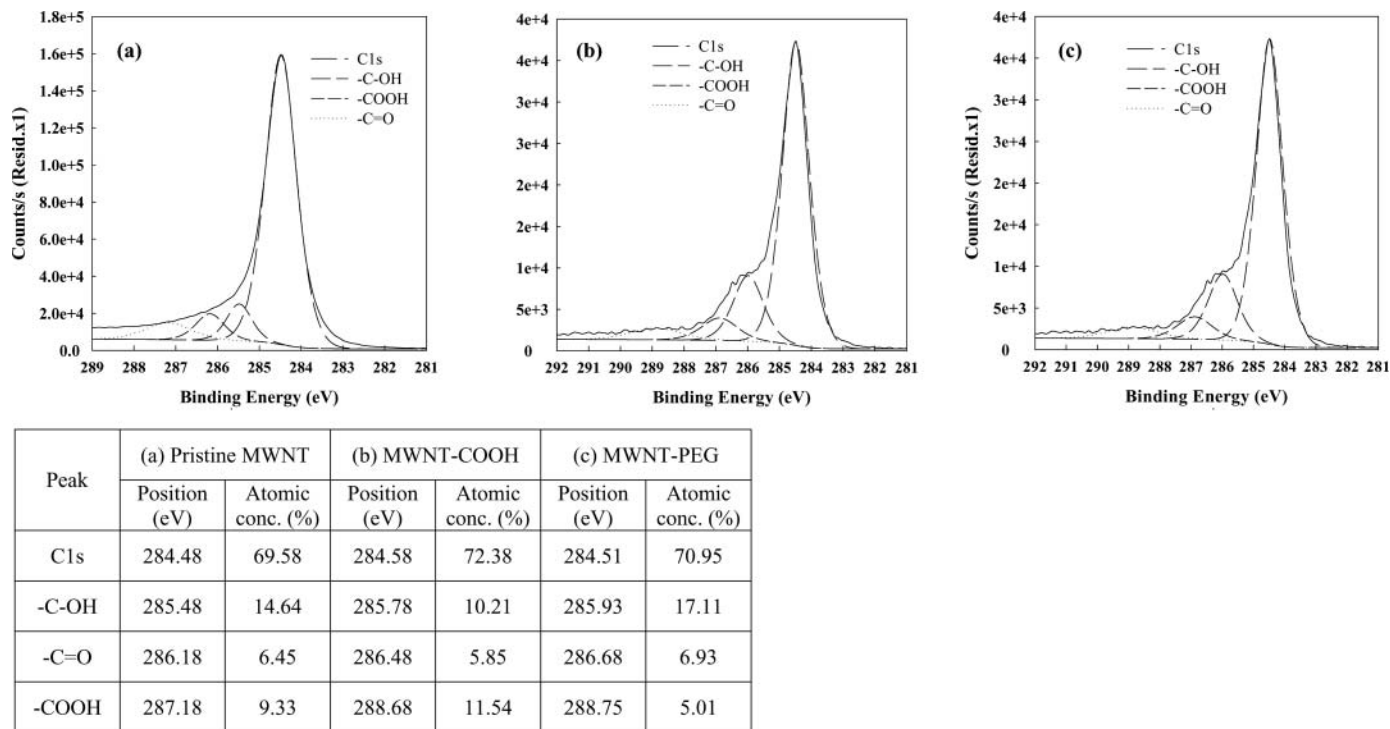| Peak	(a) Pristine MWNT		(b) MWNT-COOH		(c) MWNT-PEG	
	Position (eV)	Atomic conc. (%)	Position (eV)	Atomic conc. (%)	Position (eV)	Atomic conc. (%)
C1s	284.48	69.58	284.58	72.38	284.51	70.95
-C-OH	285.48	14.64	285.78	10.21	285.93	17.11
-C=O	286.18	6.45	286.48	5.85	286.68	6.93
-COOH	287.18	9.33	288.68	11.54	288.75	5.01

Fig. 2. XPS spectra of (a) pristine, (b) carboxylated, and (c) PEGylated MWNTs.

the MWNT's surface was calculated according to following equation:

$$[grafted\,unit]_{CNT} = \left[\frac{\frac{wt\%\ of\ grafted\ unit\ from\ TGA}{molecular\ wt.\ of\ grafted\ unit}}{\frac{100}{molecular\ wt.\ of\ carbon}} \right] \times 100$$

where $[grafted\,unit]_{CNT}$ denotes mol% of the grafted unit on the surface of CNT. From the TGA curve of PEGylated MWNT in Figure 4, the content of grafted units on MWNT is found to be 0.2838 mol% (14,15).

The dispersion stability of pristine and functionalized MWNT in polar (deionized water) and nonpolar (toluene) solvents was tested by Turbiscan.® A recently developed

optical analyzer, Turbiscan,® was successfully employed to investigate the dispersion stability of the pristine and PEGylated MWNT in deionized water and toluene. Based on the multiple light scattering principle, the dispersion state can be readily visualized even in opaque dispersions. Inside a cell, the backscattering (BS) and transmittance (T) of incident light are measured by calculating transport mean free path of photons (l^*) throughout the medium. Based on Mie theory, the BS and T can be obtained for a concentrated suspension as follows (16):

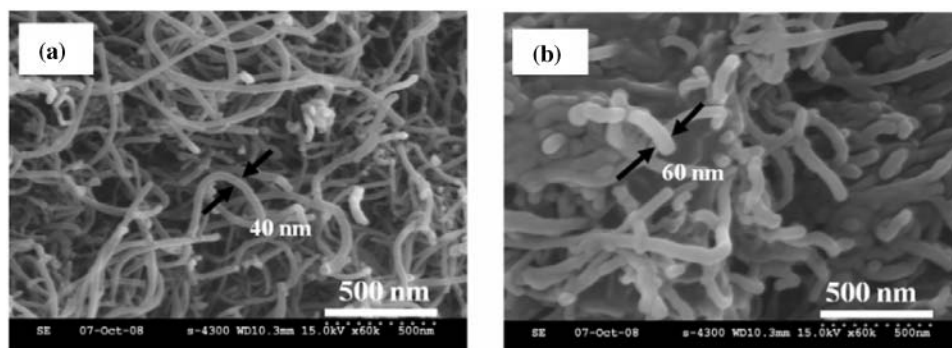$$BS \approx (1/l^*)^{1/2} \qquad (1)$$

$$T \approx \exp(-r/l) \qquad (2)$$

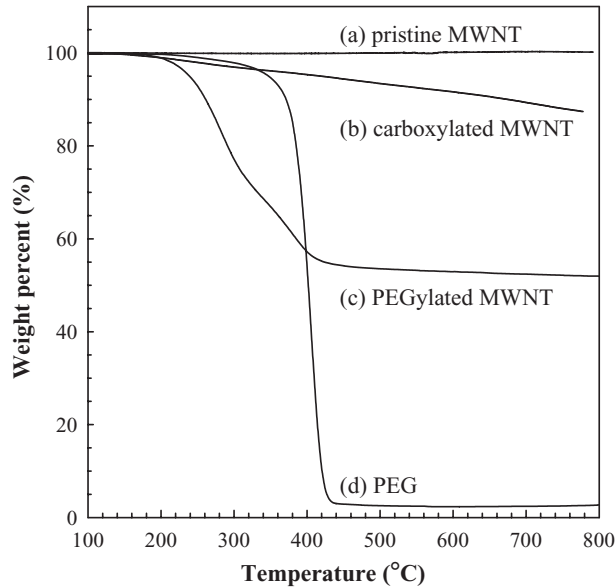**Fig. 3.** SEM microphotographs of (a) pristine and (b) PEGylated MWNTs.

Fig. 4. TGA thermograms of (a) pristine, (b) carboxylated, (c) PEGylated MWNT, and (d) pure PEG.

Fig. 6. Aggregation behavior of 0.01 wt% (a) pristine (b) carboxylated and (c) PEGylated MWNT in 5 wt% PVA aqueous solution.

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;

$$l^* = \frac{2d}{3\Phi(1-g)Q_S} \quad (3)$$
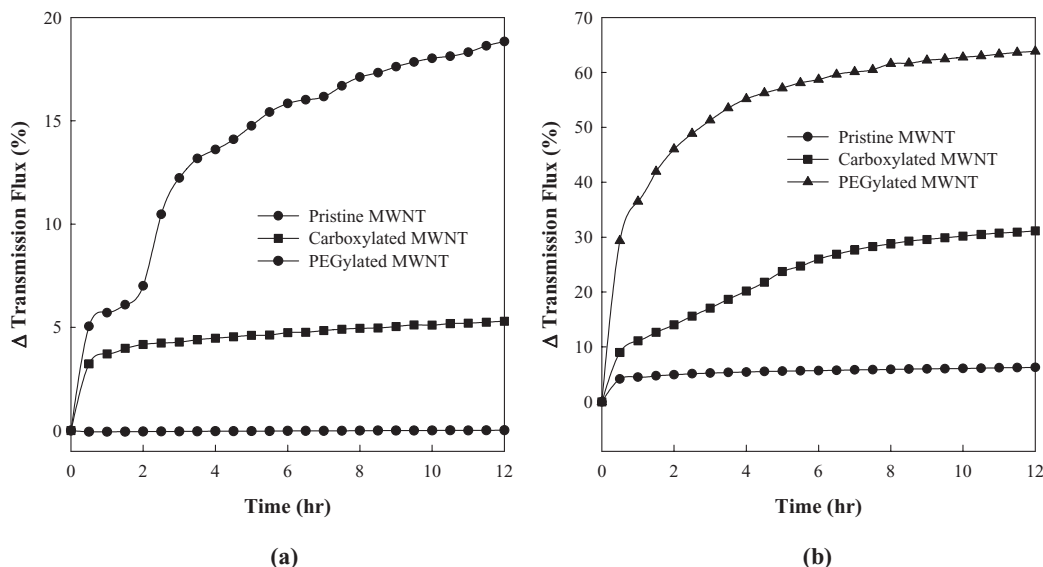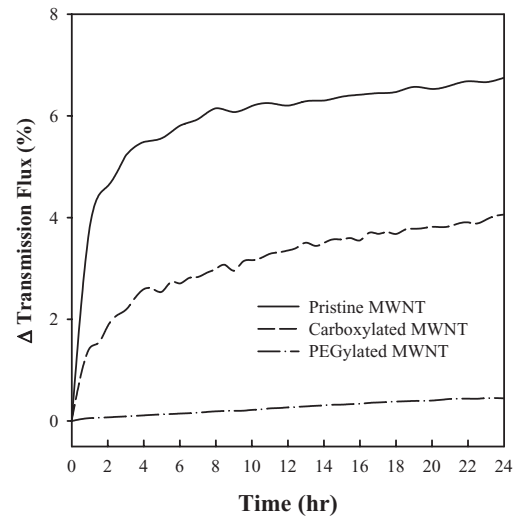
$$l = \frac{2d}{3\Phi Q_S} \quad (4)$$

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 obtained results are presented as the sedimentation profile *i.e.*, transmission flux vs. time as seen in Figure 5.

In deionized water, the transmission flux of pristine and carboxylated MWNT dramatically increases within 2 h and steadily increases with time, and no discernable change in the transmission flux with time is observed for the PE-Gylated MWNT. In contrast to the behavior in deionized water, in toluene, the transmission flux of PEGylated
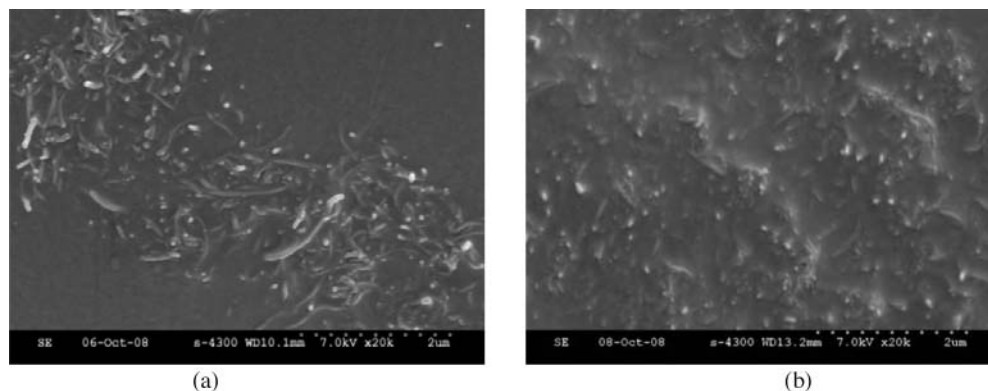

(a)

(b)

Fig. 5. Aggregation behavior of 0.01 wt% pristine, carboxylated, and PEGylated MWNT in (a) deionized water and (b) toluene.

Fig. 7. SEM microphotographs of PVA composite films with 1 wt% different MWNTs: (a) pristine and (b) PEGylated MWNT.

MWNT dramatically increases within 2 h and steadily increases with time, and the transmission flux of carboxylated MWNT increases steadily with time, whereas no discernable change in the transmission flux with time is observed for the pristine MWNT for 12 h. These results inform that the PEGylated MWNT has much improved dispersion stability in deionized water due to chemical affinity to water, and the pristine MWNT is well dispersed in a nonpolar solvent such as toluene because of their hydrophobic property. According to these Turbiscan results, we can confirm that the chemical nature of pristine and PEGylated MWNT's surface have a great effect on the dispersibility in deionized water and toluene. Therefore, the PEGylated MWNT was also well dispersed in PVA aqueous solution than the pristine and caroxylated MWNT due to a chemical affinity to water as shown in Figure 6.

Figure 7 shows the SEM microphotographs of cryogenically fractured surfaces of PVA/MWNT composite films where 1.0 wt% of pristine and PEGylated MWNT were incorporated. For the PVA composite film containing the pristine MWNT, aggregated masses of MWNT were frequently observed as seen in Fig. 7(a), whereas the

PEGylated MWNT was spatially well dispersed in the composite film as shown in Fig. 7(b). It indicates that the PEGylated MWNT maintained the initial dispersed state in PVA aqueous solution during a solution casting because of a chemical affinity between hydrophilic PEG and PVA. Figure 8 shows VM images of surfaces of PVA/MWNT composite films in a macroscale. The pristine MWNT was significantly agglomerated as shown Fig. 8(a), whereas the PEGylated MWNT was well dispersed in PVA composite film (Fig. 8(b)). It indicates that a chemical affinity between PEGylated MWNTs and PVA aqueous solution was superior.

The possibility of the PEGylated MWNT as a conducting filler in polymer composite has been successfully realized. Figure 9 shows the behavior of the electrical conductivity of three composite films with increasing MWNT loading. The electrical conductivity shows an exponential rise as MWNT was loaded into the composites. When the composite films were loaded with 1 wt% pristine, carboxylated and PEGylated MWNT, their electrical conductivities were 1.38×10^{-10}, 2.91×10^{-10} and 3.64×10^{-10} S/cm, respectively. Therefore, we confirmed
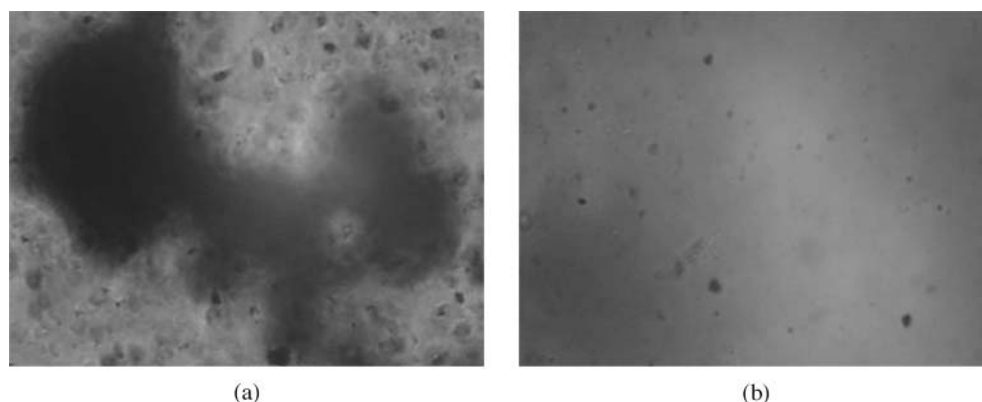

Fig. 8. Video microscope images of PVA composite films with 1 wt% different MWNTs: (a) pristine and (b) PEGylated MWNT.
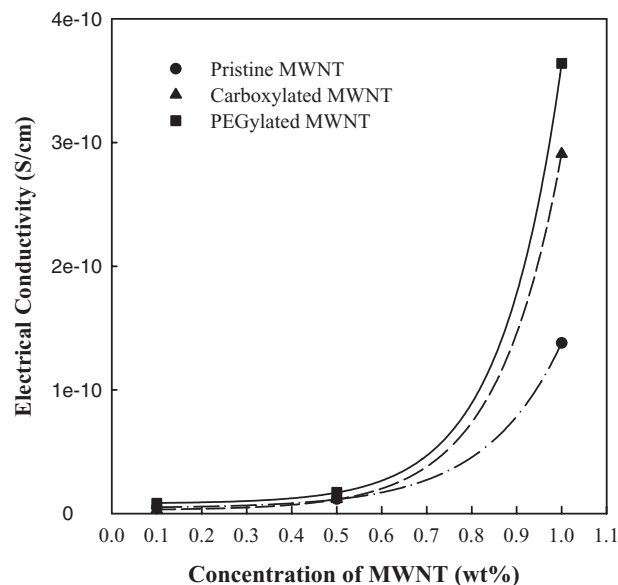
Fig. 9. Electrical conductivity of PVA composite films with 1 wt% different MWNTs: pristine, carboxylated, and PEGylated MWN.

that the electrical conductivity of PVA/MWMT composite was significantly affected by the dispersibility of MWNT.

4 Conclusions

In this study, MWNT was covalently functionalized by a hydrophilic polymer, PEG through oxidation and esterification reaction to achieve good dispersion stability of MWNT in a hydrophilic polymer matrix, PVA. The degree of surface modification of MWNT by PEG was thoroughly investigated by FT-IR, XPS, TGA, and SEM. By means of simple solution casting, PVA/PEGylated MWNT composite film was prepared. Throughout the composite film, we could confirm that the PEGylated MWNT maintained the initial well-dispersed state in PVA matrix due to a hydrophilic affinity between PEG and PVA. As the dispersibility of PEGylated MWNT in the composite film was enhanced, the electrical conductivity of PVA/PEGylated MWNT composite film was three-fold greater than that of PVA/pristine MWNT composite film.

Acknowledgments

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