

# Controlled Functionalization of Multiwalled Carbon Nanotubes with Various Molecular-Weight Poly(L-lactic acid)

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Multiwalled carbon nanotubes (MWNT) were functionalized with poly(L-lactic acid) (PLLA) with different molecular weights using a “grafting to” technique. The oxidized MWNT (MWNT-COOH) were converted to the acyl-chloride-functionalized MWNT (MWNT-COCl) by treating them with thionyl chloride (SOCl<sub>2</sub>) and reacting them with PLLA to prepare the MWNT-g-PLLA. FTIR and Raman spectroscopy revealed that the PLLA was covalently attached to the MWNT, and the weight gain due to the functionalization was determined by thermogravimetric analyses (TGA). The Raman signals of the MWNT were greatly weakened as a result of the PLLA grafting. The morphology of the grafted PLLA was examined by using SEM and TEM. The amount of grafted PLLA depended on the molecular weight of the PLLA. The PLLA coated on the MWNT became thicker and more uniform with increasing PLLA molecular weight from 1000 to 3000. However, the amount of grafted PLLA became lower when the molecular weight of PLLA was further increased to 11 000 and 15 000, and the PLLA attached to the MWNT showed a squid leglike morphology forming blobs and leaving much of the MWNT surface bare.

## Introduction

Carbon nanotubes (CNT) are one of the most promising candidates for the design of novel ultrahigh strength polymer composites.<sup>1–3</sup> It is believed that the high aspect ratio, mechanical strength, and high electrical and thermal conductivity of CNT will enhance the overall performance of many polymer-CNT composites and open up new applications.<sup>4</sup> Polymer-CNT composites are easily molded, and the resulting shaped plastic articles have a perfect surface appearance compared with the polymer composites using conventional carbon or glass fibers. Good interfacial adhesion between the CNT and the polymer matrix is essential for efficient load transfer in the composite. The novel ultrahigh strength polymer composites demand uniform dispersion of the CNT in the polymer matrix without aggregation and thereby a strong CNT/polymer matrix interaction is needed. The advantages of CNT have not been fully realized due to difficulties in producing CNT/polymer composites with well-dispersed CNT.<sup>5</sup>

Both noncovalent and covalent modifications of the CNT surface have been used to improve the wetting and solubility of CNT. The noncovalent approach includes surfactant modification,<sup>6–8</sup> polymer wrapping,<sup>9–11</sup> and polymer absorption<sup>12,13</sup> where the polymers are produced by in-situ ring-opening metathesis polymerization or emulsion polymerization. The advantage of noncovalent attachment is that the perfect structure of the CNT is not damaged and their mechanical properties remain intact. The main disadvantage of noncovalent attachment is that the forces between the wrapping molecules and the CNT are very weak, which means that the load may not be transferred efficiently from the polymer matrix to the CNT filler.

The covalent functionalization of CNT is most frequently initiated by introducing carboxylic acid groups using a nitric acid oxidation method.<sup>14–18</sup> Thereafter, long alkyl chains,

polymers, and sugars can be chemically attached to the CNT by esterification and amidation reactions via the carboxylic acid moieties.<sup>19–27</sup> Tour et al. prepared polystyrene composites with functionalized CNT through the in-situ generation of diazonium compounds.<sup>19</sup> Sun et al. functionalized the CNT with poly(vinyl alcohol) and made the functionalized CNT soluble in highly polar solvents.<sup>20</sup> Haddon et al. used carboxylic acid groups to introduce long alkyl chains to CNT via amide linkages or carboxylate–ammonium salt ionic interactions.<sup>14</sup> Sun et al. successfully anchored poly(styrene-*co-p*-(4-(4'-vinylphenyl)-3-oxabutanol)) to the CNT via ester linkages.<sup>21</sup>

The functional groups attached to the CNT reported so far include fluorine,<sup>28</sup> aryl radicals,<sup>29</sup> aryl cations,<sup>30</sup> hydrogen,<sup>31</sup> nitrenes,<sup>32</sup> carbenes,<sup>33</sup> radicals,<sup>34</sup> and 1,3-dipoles.<sup>35</sup>

In a previous study,<sup>36</sup> the covalent attachment of PLLA chains to the CNT surface were accomplished by a “grafting from” technique, where a CNT-g-PLLA hybrid was synthesized using the surface-initiated ring-opening polymerization of L-lactide.

In this study, PLLAs with various molecular weights were synthesized and reacted with –COCl groups, which had previously been introduced to CNT using the “grafting to” technique. The morphology and grafting mechanisms of the resulting MWNT-g-PLLA composites were examined.

## 2. Experimental Section

**2.1. Materials.** The multiwalled carbon nanotubes (MWNTs) were provided by Iljin Nanotech Co. (Korea). The MWNTs were obtained using the chemical vapor deposition method, and the purity was >95%. L-Lactic acid (LA, TEDIA, Fairfield, OH) was used as received. Titanium(IV) butoxide (Aldrich) was used as received to catalyze the polymerization reactions. Methanol, chloroform, and *N,N'*-dimethylformamide (DMF) were obtained from Aldrich and used as received.

**2.2. Purification of MWNT.** The purity of the as-purchased MWNT was 97% according to the manufacturer. To remove

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the impurities, such as metallic catalysts in the MWNT, the MWNTs were treated with 3 M HNO<sub>3</sub> and 1 M H<sub>2</sub>SO<sub>4</sub> at 60 °C for 12 h, which was followed by a reflux process in 5 M HCl at 120 °C for 6 h. The purity of the acid-treated MWNT was determined by thermogravimetric analysis (TGA, TA Instruments, Q50) to be 99%. These acid treatments may shorten the length of the MWNT and introduce carboxylic and hydroxyl groups.

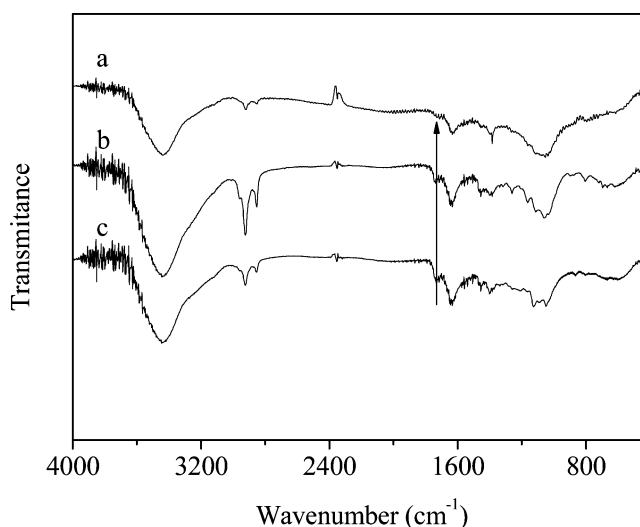
**2.3. Acid Treatment of MWNT.** A 500 mL flask charged with 2.5 g of the crude MWNT and 200 mL of a 60% HNO<sub>3</sub> aqueous solution was sonicated in a bath (28 kHz) for 30 min. The mixture was then stirred for 12 h under reflux. After the solution was cooled to room temperature, it was diluted with 400 mL of deionized water and vacuum filtered through a 0.22  $\mu$ m polycarbonate membrane. The solid was washed with deionized water until the pH of the filtrate reached approximately 7. The solid was then dried under vacuum for 12 h at 60 °C to yield 1.5 g (~60%) of the carboxylic-acid-functionalized MWNT (MWNT-COOH).

**2.4. Synthesis of Poly(L-lactic Acid).**<sup>37</sup> L-Lactic acid (LA) was added to a three-neck reactor (500 mL), which was connected to a vacuum system via a liquid nitrogen trap. The reactor was immersed in an oil bath at 100 °C under nitrogen atmosphere for 1 h in order to remove the water. The flask reactor was heated in an oil bath to 180 °C with mechanical stirring (300 rpm), and titanium(IV) butoxide (TNBT, 0.08 mL) was added to the reactor under nitrogen. The esterification reaction was carried out for a certain duration, and the reactor pressure was then gradually reduced to 500 Torr over a 4 h period. The reaction was continued at 1 Torr and 180 °C for different times in order to control the molecular weight. The resulting polymer was dissolved in chloroform and microfiltered through a 0.45  $\mu$ m pore membrane filter. The polymer was precipitated by pouring the filtrate into an excess of methanol, filtering, and drying in a vacuum oven at 60 °C to a constant weight.

**2.5. Functionalization of MWNT with PLLA.** The acid-treated MWNT (MWNT-COOH) was reacted with excess SOCl<sub>2</sub> for 24 h under reflux, and then the residual SOCl<sub>2</sub> was removed by reduced pressure distillation to yield the acyl-chloride-functionalized MWNT (MWNT-COCl). The MWNT-COCl was added to chloroform, and the mixture was sonicated for 20 min to create a homogeneous dispersion. PLLA under nitrogen was then added to the mixture, and the reactor was then immersed in an oil bath at 70 °C with mechanical stirring for 1 h to remove the solvent. The reaction was allowed to proceed for 24 h at 180 °C and 1 atm. The resulting reaction medium was dissolved in excess chloroform and vacuum filtered three times through a 0.22 polycarbonate membrane to yield the MWNT-g-PLLA hybrid by filtering the chloroform soluble substances such as the unbound PLLA. The MWNT-g-PLLA hybrids were prepared using the PLLAs with molecular weights of 1000, 3000, 11 000, and 15 000, which are represented as MWNT-g-PLLA1, MWNT-g-PLLA2, MWNT-g-PLLA3, and MWNT-g-PLLA4, respectively.

**2.6. Measurements.** Transmission electron microscopy (TEM) images were obtained using a TEM 2000 EX-II microscope (JEOL, Tokyo, Japan) operated at a 100 kV accelerating voltage to observe the nanoscale structures of the various MWNT-g-PLLA hybrids. The specimen for the TEM observations was prepared by placing one drop of the sample on a copper grid coated with carbon.

The morphology of the MWNT-g-PLLA hybrid was observed using scanning electron microscopy (SEM, Hitachi S-4300) at



**Figure 1.** FTIR spectra of (a) MWNT-COOH, (b) MWNT-g-PLLA2, and (c) MWNT-g-PLLA4.

an accelerating voltage of 15 kV after precoating the sample with a homogeneous Pt layer by ion sputtering (Hitachi, E-1030).

The grafting behavior of the PLLA onto the MWNT was monitored by Bio-rad Fourier transformed infrared spectrophotometry (FTIR, Perkin-Elmer, Spectrum 2000, USA).

Raman spectra were obtained by Neodym (Nd) laser excitation at 1064 nm (BRUKER RFS 100/S) using an InGaAs detector.

The molecular weights were measured by gel permeation chromatography (GPC, Waters 410) using polystyrene as the standard and THF as the eluent.

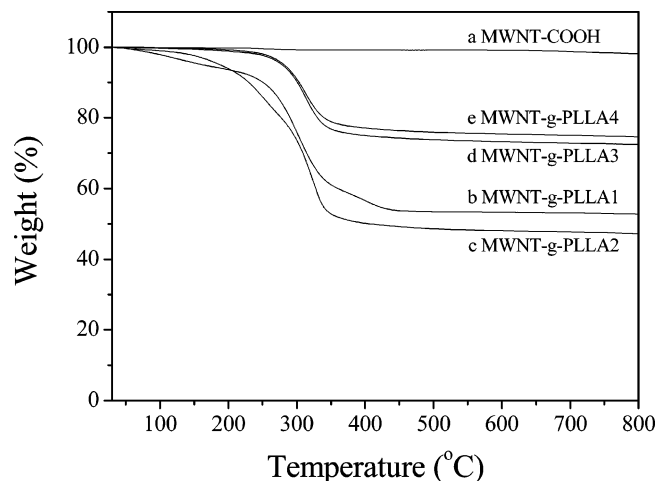
Thermogravimetric analysis (TGA) was performed using PL-TGA (Polymer Laboratories, Q50, U.K.) by scanning from 30 to 900 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

### 3. Results and Discussion

Previous studies have succeeded in grafting polymer chains such as polystyrene and poly(sodium 4-styrenesulfonate) to the surface of CNTs.<sup>38–39</sup>

This study attempted to graft PLLA chains to MWNT in a controlled manner. After the grafting reaction, the product was washed thoroughly with chloroform and filtered to remove any chloroform-soluble substances such as the PLLA unbound to the MWNT. Washing was continued until no polymer could be detected in the filtrate. The PLLA-functionalized MWNT (MWNT-g-PLLA) collected had a black color. Considerable weight gain was observed after the grafting reaction, which confirmed that a substantial amount of PLLA had been grafted to the MWNT.

The composition of the resulting MWNT-g-PLLA hybrids was confirmed by FTIR. Figure 1 shows the FTIR spectra of the MWNT as well as the MWNT functionalized with PLLA. The FTIR spectrum of the acid-treated MWNT (Figure 1a) showed the expected C=O stretching at 1736 cm<sup>-1</sup> corresponding to the carboxylic acid groups incorporated as a result of the acid treatment process. The large FTIR band observed at 3441 cm<sup>-1</sup> and the weak one at 1638 cm<sup>-1</sup> were attributed, respectively, to the asymmetric bending and scissoring vibrations as a result of trace amounts of water.<sup>40</sup> In Figure 1b, the strong carbonyl stretching band at 1737 cm<sup>-1</sup> clearly indicates that the PLLA molecules were covalently bound to the MWNT. In



**Figure 2.** TGA traces of MWNT-COOH and MWNT-g-PLLAs.

addition, the intensity of the C–H stretching frequencies at 2853 and 2925  $\text{cm}^{-1}$  corresponding to the alkyl groups was more intense in the MWNT-g-PLLA2 than in the uncoated MWNT-COOH. However, when the molecular weight of the PLLA was increased to 15 000 g/mol, the peak for the alkyl groups in the MWNT-g-PLLA4 was less intense than that in the MWNT-g-PLLA2. When the molecular weight of the PLLA was lower, the larger number of hydroxyl groups increased the reaction rate between the MWNT and the PLLA. However, the number of the alkyl groups per mole of the PLLA was smaller. Therefore, the amount of alkyl groups, that is, the amount of grafted PLLA, will increase to a maximum and then decrease with the increasing molecular weight of the PLLA, which is in line with the present observations.

It is possible that the PLLA unbound to the MWNT was almost completely removed from the product by the filtration and washing, as mentioned in the Experimental Section, because the FTIR peaks for the PLLA were not detected after the filtrating and washing in a parallel experiment where MWNT-COOH was simply mixed with a commercially produced PLLA (MW, 240 000 g/mol).

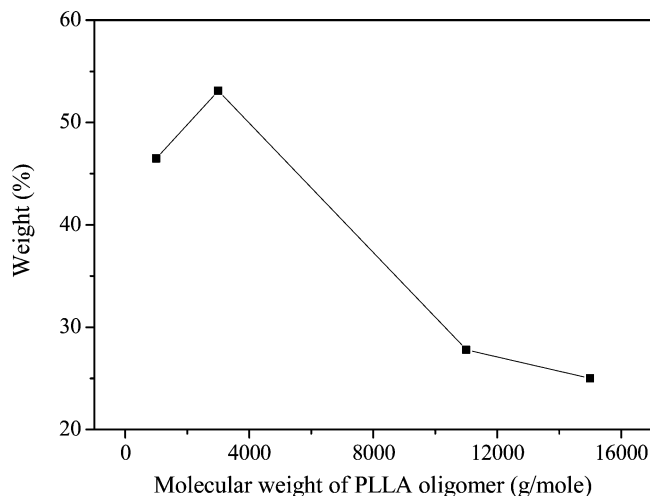
Although CNT composites with other polymers have also been investigated using a “grafting to” technique with end group functionalized polymers,<sup>41,42</sup> there are few reports detailing the effect of the molecular weight on the grafting.

The amount of PLLA grafted to the MWNT was determined through the TGA analysis. The MWNT-g-PLLA exhibited major weight loss in the temperature range of 200–350 °C due to the degradation of the PLLA grafted to the MWNT, as shown in Figure 2. The amount of the PLLA bound to the MWNT ranged from 25 and 53.1 wt % when the molecular weight of the PLLA was varied from 15 000 and 3 000 g/mol, respectively.

It is generally accepted that the molecular weight of the polymers produced from condensation polymerization depends on the reactor pressure that evacuates the condensed substances. Hence, these experiments were engineered to control the molecular weight of the grafted PLLA by keeping the reactor pressure constant at a predetermined value and by choosing the PLLA with an appropriate molecular weight.

The TGA results shown in Figure 2 indicate that the weight loss of the MWNT-g-PLLA took place rapidly near 300 °C as a result of the decomposition of the grafted PLLA. The residual fraction at temperatures above 800 °C corresponds mainly to the MWNT.

Figure 3 shows the effect of the molecular weight on the grafted amount of the PLLA determined from TGA analysis. It



**Figure 3.** Relationships between the molecular weight and the amount of PLLA grafted to the MWNT.

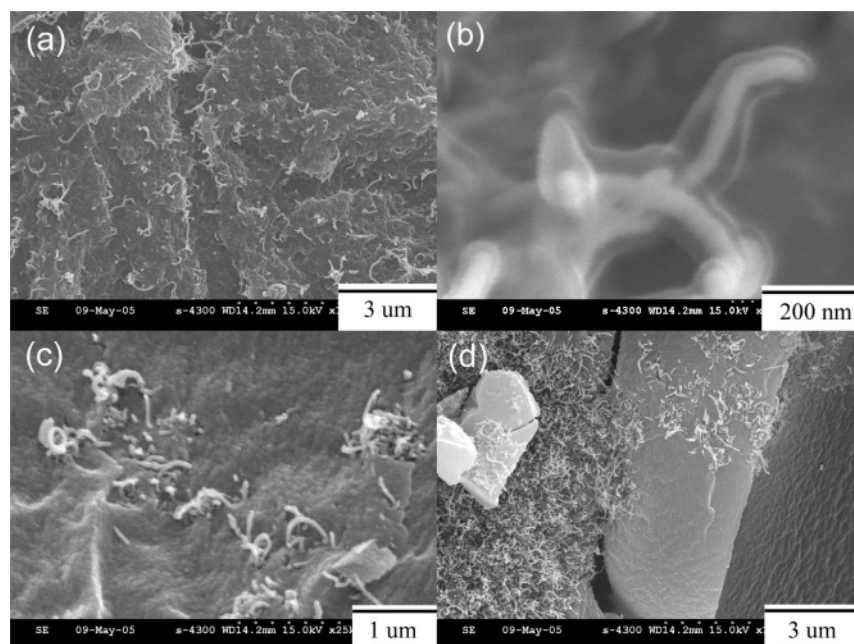
demonstrates that the amount of grafted PLLA increased from 46.5 to 53.1 wt % with increasing PLLA molecular weight from 1 000 to 3 000. However, the amount of grafted PLLA decreased when the molecular weight of the PLLA was further increased to 15 000. This suggests that there is an optimal molecular weight for the functionalization of the MWNT with PLLA. In contrast, the weight of the polystyrene bound to CNT increased linearly with increasing molecular weight in the case of the CNT surface-induced polymerization using the “grafting from” technique.<sup>38</sup>

Figure 4 compares SEM images of the MWNT-g-PLLA/PLLA composites with those of the solution-blended MWNT-COOH/PLLA composite. The MWNT-g-PLLA/PLLA composites differ from the solution-blended composite significantly revealing the higher degree of dispersion of the MWNT in the former composites. Figure 4a shows that, in the case of the MWNT-g-PLLA2/PLLA composite, a substantial amount of the MWNT was well dispersed in the PLLA matrix. The MWNT appears embedded in the PLLA matrix. A higher magnification (Figure 4b) demonstrated that the MWNT was completely coated by PLLA and that the diameter of the coated MWNT (80 nm) was much larger than that of the neat MWNT-COOH (30 nm). This suggests a strong interaction between the MWNT-g-PLLA and the PLLA matrix. Figure 4d shows SEM images of the solution-blended MWNT-COOH/PLLA composite containing 1 wt % of MWNT-COOH. Much of the MWNT-COOH appears to be completely aggregated. This is in sharp contrast to the SEM images of the MWNT-g-PLLA2/PLLA composite, where the MWNT were immobilized in the PLLA matrix and were well dispersed without any aggregation.

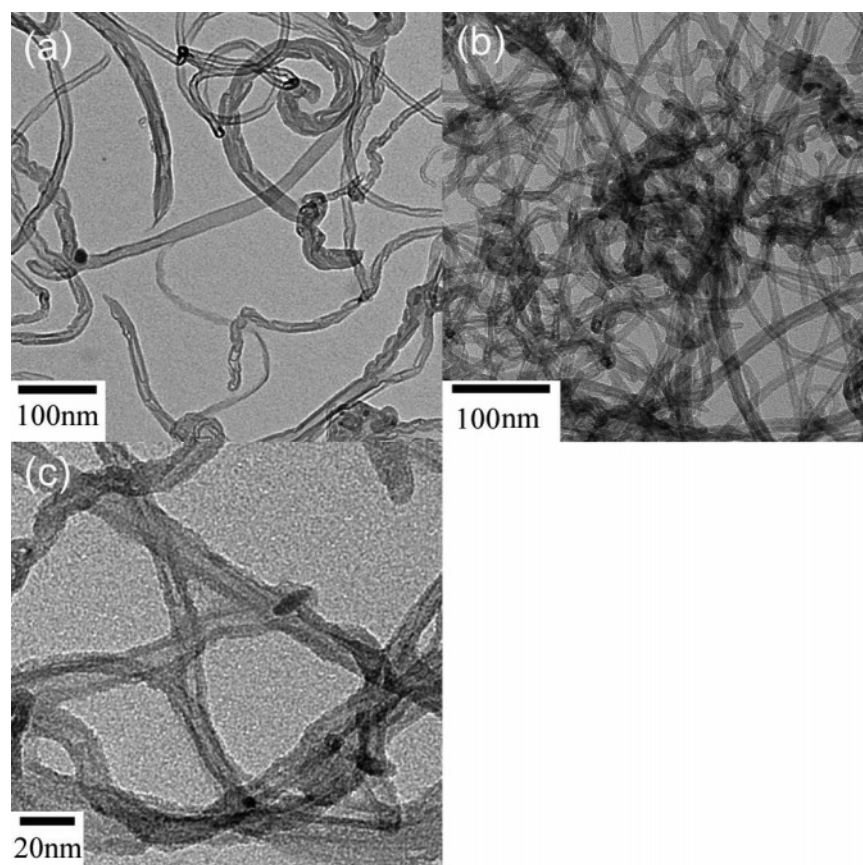
More evidence for the MWNT-g-PLLA was obtained by TEM. Figure 5 shows the TEM images of the MWNT-g-PLLA hybrids after many washings with chloroform under sonication to remove the unbound PLLA completely from the MWNT-g-PLLA/PLLA composite. In the TEM images of the neat MWNT-COOH (Figure 5a), the individual tubes were obviously separated from each other. The MWNT wall is relatively smooth and clean and does not appear covered with any extra phase. In contrast, the MWNT-g-PLLA2, shown in parts b and c of Figure 5, appears stained with PLLA and they are glued together at the intersection points. This indicates that the grafting reaction takes place not only at the tips but also on the whole MWNT surfaces.

The fine nanostructures of the MWNT-g-PLLA hybrid were further investigated at high magnification (Figure 6). The





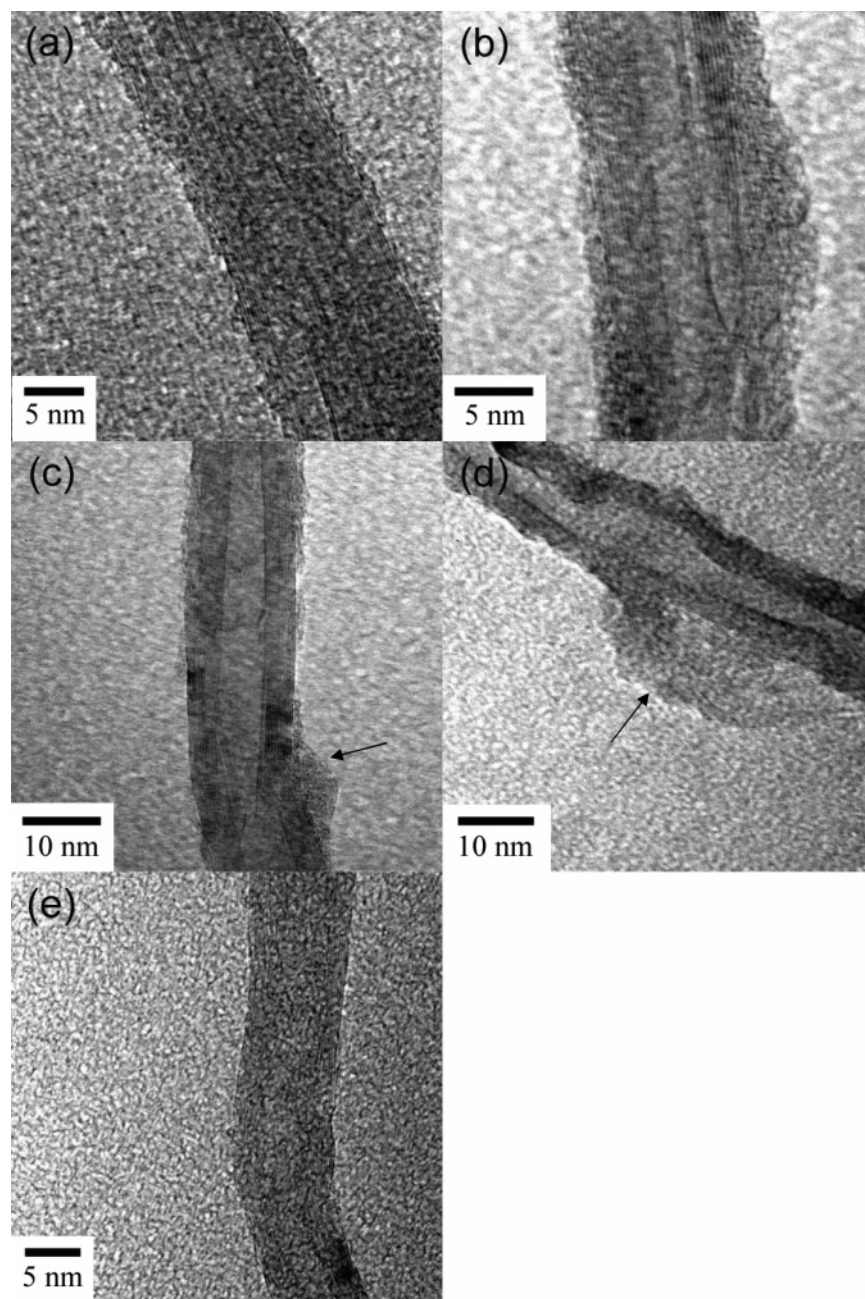
**Figure 4.** SEM images of the MWNT-g-PLLA2/PLLA composite at (a) lower and (b) higher magnifications, (c) MWNT-g-PLLA4/PLLA composite, and (d) the solution-blended MWNT-COOH/PLLA composite.



**Figure 5.** TEM images of (a) MWNT-COOH and MWNT-g-PLLA2 at (b) lower and (c) higher magnifications.

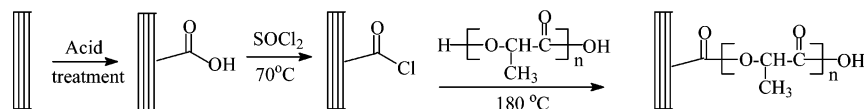
morphology of the PLLA bound to the MWNT surface appears different from each other depending on the molecular weight of the PLLA. The MWNT-g-PLLA was not uniformly covered with PLLA. In the case of the MWNT-g-PLLA1 and MWNT-g-PLLA2, the PLLA coated on MWNT was relatively uniform. As the molecular weight of the PLLA was increased from 1000 to 3000, the thickness of the PLLA coating on the MWNT increased from about 1 to 3 nm. When the molecular weight of

the PLLA was further increased, the PLLA stained only some parts of the MWNT surface with a squid leglike morphology, as shown in parts c and d of Figure 6. In contrast, the TEM image of the solution-blended MWNT-COOH/PLLA composite after washing with chloroform in the same manner as for the MWNT-g-PLLA reveals that the surface of MWNT-COOH was very clean and was not contaminated at all by any extra phase, as shown in Figure 6e.



**Figure 6.** TEM images of (a) MWNT-g-PLLA1, (b) MWNT-g-PLLA2, (c) MWNT-g-PLLA3, (d) MWNT-g-PLLA4, and (e) the solution-blended MWNT-COOH/PLLA composite after thorough washing with chloroform.

**SCHEME 1: Illustration for the Functionalization of the MWNT with PLLA**



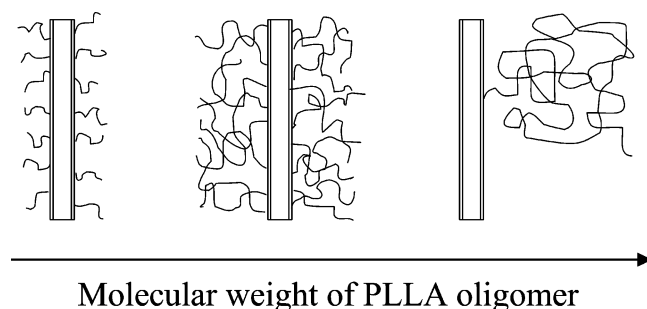
Polymer-functionalized CNTs usually show a much higher solubility or better dispersion in solvents. In the case of the MWNT-g-PLLA hybrids, the solubility in solvents appears dependent on the molecular weight of the PLLA and therefore on the grafted structure on the MWNT surface. The MWNT-g-PLLA2, which was coated thickly with the PLLA, was readily dispersed in organic solvents such as *N,N*-dimethylformamide (DMF) and chloroform. However, the MWNT-g-PLLA4 was less uniformly dispersed than the MWNT-g-PLLA2 (data not shown) in the same solvents. This was attributed to the higher PLLA content in the latter hybrid than that in the former. The squid leglike morphology of the former hybrid, as shown in

Figure 6d, may be another reason for the poorer dispersion in the solvents, which is due to the larger surface area of bare MWNT. The grafted structure of the PLLA is shown schematically in Scheme 2.

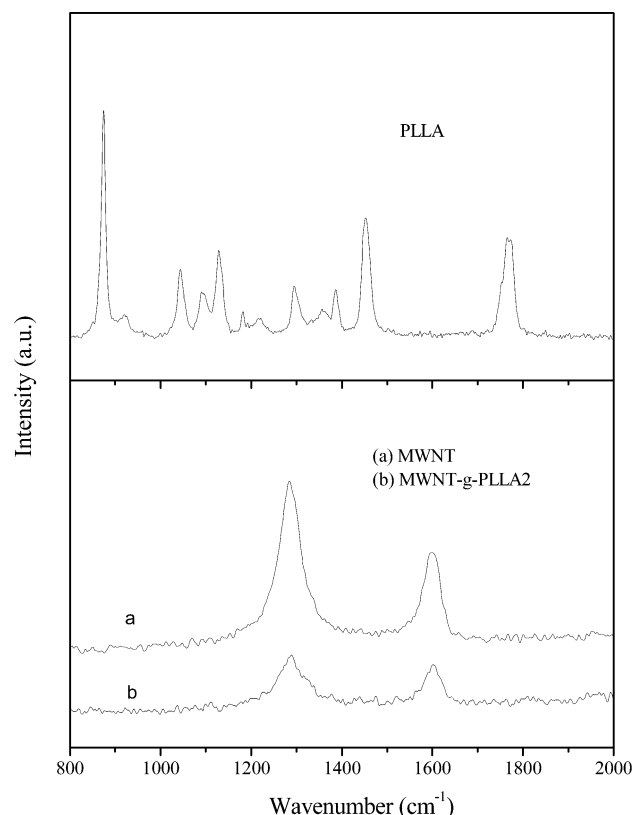
The Raman spectra shown in Figure 7 reveal the D- and G-bands of the MWNT at 1287 and 1598  $\text{cm}^{-1}$  for both MWNT-COOH and MWNT-g-PLLA2,<sup>43</sup> which were attributed to the defects and disorder-induced peaks and tangential-mode peaks.<sup>44</sup> The peak intensity of the MWNT-g-PLLA2 was much weaker than that of the MWNT-COOH, which means that the characteristic absorption peaks were strongly attenuated due to the grafted PLLA. Furthermore, Raman signals assigned to the



## SCHEME 2: Illustration of the Structure of the PLLA Grafted to the MWNT



neat PLLA were not observed in the spectrum of the MWNT-g-PLLA2. Because the Raman signals for PLLA were detected in the solution-blended MWNT-COOH/PLLA composite, it is possible that the PLLA grafted to the MWNT-COOH was completely different from the neat PLLA in terms of the Raman characteristics.



**Figure 7.** Raman spectra of the PLLA, MWNT-COOH, and MWNT-g-PLLA2.

The decrease in the Raman signals of the MWNT-g-PLLA originate neither from the low MWNT content nor from the translucence of the PLLA layer.<sup>45</sup> It might be due to energy transfer between the MWNT and the PLLA layer or to the influence of the grafted PLLA on the electronic properties of the MWNT. Further studies will be needed to fully understand the effect of polymer grafting to MWNT on the intensity of the Raman signals and the possible energy transfer mechanism.

## 4. Conclusions

MWNT were coated with PLLA at various molecular weights by reacting the PLLA with the MWNT functionalized with  $\text{-COCl}$  groups, which was prepared by treating the purified

MWNT with  $\text{HNO}_3$  followed by  $\text{SOCl}_2$ . The retention of polymer even after extensive washing with a good solvent for the polymer was evidenced by FTIR spectroscopy. The TGA and TEM observations indicated that the amount of grafted PLLA and its morphology depended strongly on the molecular weight of the PLLA. As the molecular weight of the PLLA was increased from 1000 to 3000, the PLLA coating on the MWNT became thicker and more uniform. When the molecular weight of the PLLA was increased further to 11 000 and 15 000, the surface of the MWNT was not covered wholly but was sparsely stained with the PLLA. The grafted PLLA formed blobs exhibiting a squid leglike morphology. The MWNT-g-PLLA prepared using PLLA with a molecular weight of 3000 was more readily dispersed in organic solvents such as chloroform and *N,N*-dimethylformamide (DMF) than that obtained using other PLLAs. This was attributed to the higher PLLA content and the smaller area of the bare MWNT surface.

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