

# Vinyl–Carbon Nanotubes for Composite Polymer Materials

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**ABSTRACT:** We report herein a simple method for attaching vinyl groups onto the sidewalls of carbon nanotubes (CNTs) and the application of vinyl–carbon nanotubes (CNT–C=C) in fabricating polymer composites. The synthesis of CNT–C=C was monitored with IR spectroscopy, Raman spectroscopy, and thermogravimetric analysis. The obtained CNT–C=C showed good compatibility with the *in situ* polymerization of poly(methyl methacrylate) (PMMA) and exhibited no tendency for phase separation in the final composite. A transmission electron

microscopy study revealed a uniform coating on the CNT–C=C tubes, indicating good grafting efficiency of PMMA. The uniform dielectric PMMA coating was responsible for the lower electrical conductivity of the CNT–C=C/PMMA composites versus that of the CNTs without vinyl modification. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1915–1920, 2008

**Key words:** modification; nanocomposites; nanotechnology; radical polymerization; reinforcement

## INTRODUCTION

Carbon nanotubes (CNTs) have attracted great attention because of their unique physical and chemical properties, such as high mechanical strength, high electrical and thermal conductivity, and high chemical stability.<sup>1–6</sup> As a result of their large aspect ratio and superior mechanical strength, CNTs have been widely considered as one of the most promising candidates as strength-enhancing fillers for novel composite materials. However, the application of CNTs has been hampered by the poor solubility of pristine CNTs in most common solvents. Meanwhile, the large surface areas of CNTs lead to large van der Waals interactions among the nanotubes, resulting in significant aggregation and phase separation in

the composite matrix. Therefore, to fabricate good CNT/polymer composites, an appropriate surface modification of CNTs is essential for achieving a homogeneous dispersion of CNTs and strong bonding between CNTs and polymer matrices. Strong bonding between CNTs and polymer matrices is a crucial task for achieving the desired mechanical, chemical, and electrical properties of the resultant composites.<sup>7</sup> It has been reported that bare nanotubes cannot produce good bonding with most polymer-based matrices, and this causes the failure of composites with respect to nanotube pullout.<sup>8</sup>

An ideal modification method is expected to give modified CNTs with high solubility and little loss of their intrinsic electrical and mechanic properties. Meanwhile, the modification will introduce an appropriate number of functional groups into the CNT side wall that will allow covalent bonding between the polymer and CNTs. In fact, because CNTs contain rich double-bond structures, they can participate in the *in situ* polymerization process in various ways. For instance, the  $\pi$ -bond of the CNT surface could be opened by free radicals that could directly initiate the polymerization process (called “grafting from”).<sup>9–11</sup> CNTs can also serve as radical absorbents to attach active oligomeric polymer chains (called “grafting to”).<sup>12,13</sup> In addition, it has also been reported that the radical of thermally decomposed benzoyl peroxide (BPO) or 2,2'-azobisobutyronitrile can be consumed by the direct formation of substituted nanotubes,<sup>12,14–19</sup> and therefore

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the number of radicals can be reduced; this results in a significant change in the gelation time.

Although modification methods have been reported, most of them either need wild reaction conditions and expensive reagents or lack control of the grafting efficiency, and this makes them less industrially practical. In this article, we report a simple and inexpensive method for preparing vinyl-group-modified CNTs (CNT-C=C). Vinyl moieties are the most important functional groups for polymer science. It is believed that good grafting efficiency and bonding can be achieved with vinyl-modified CNTs because the vinyl groups on the nanotubes should be able to take part in any alkene-involved polymer reactions. In this work, we compare CNT-C=C with other commonly available CNTs in the fabrication of CNT/poly(methyl methacrylate) (PMMA) composites via a typical free-radical vinyl polymerization process.

## EXPERIMENTAL

### Materials

Multiwalled CNTs were purchased from Shenzhen Nanotech Port, Ltd. (Shenzhen, China), and they had diameters ranging from 10 to 50 nm and lengths ranging from 1 to 2  $\mu\text{m}$ . It was estimated that these nanotubes contained approximately 15–70 graphite layers. The other reagents were all analytical-grade. Methyl methacrylate (MMA) was purchased from Tianjin Chemical Reagent Factory (Tianjin, China). MMA was washed three times with a 10% sodium hydroxide aqueous solution to remove the inhibitor reagent hydroquinone and then vacuum-distilled after the mixture was dried with anhydrous sodium sulfate overnight. Acryloyl chloride, BPO, dimethylformamide (DMF), triethylamine (TEA),  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$  were all of analytical-grade and were used as received.

### Instruments and measurements

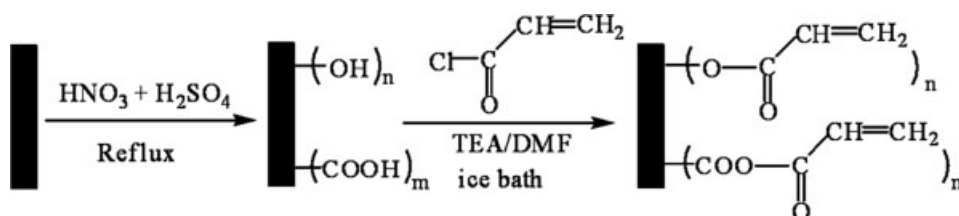
The chemical structures of the CNT samples were detected with a Fourier transform infrared (FTIR) spectrometer (Nexus 670, Thermal - Fisher, Pitts-

burgh, PA) with a KBr pellet method. Elemental analysis was carried out by Elementar Analysensystem GmbH (CHN mode, Hanau, Germany). The thermogravimetric analysis (TGA; model 1090, DuPont, Wilmington, DE) was conducted, in a nitrogen flow, from room temperature to 800°C at a heating rate of 10°C/min. The sample fracture morphology of the nanocomposites was observed via scanning electron microscopy (SEM; JSM-6380LV, JEOL, Tokyo, Japan). The effect of PMMA-grafted CNT-C=C was characterized with transmission electron microscopy (TEM; CM 200, Philips, The Netherlands). The room-temperature surface resistance of the nanocomposites films was measured with a ZC36 ultrahigh resistance meter (Shanghai, China) by the two-probe technique as described in the literature.<sup>20–22</sup>

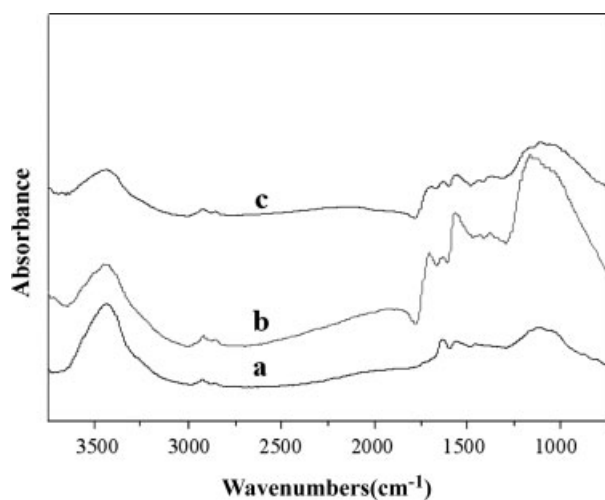
### CNT modification

Pristine CNTs (1.5 g) were added to a flask containing a 100-mL mixture of sulfuric acid and nitric acid (3 : 7 v/v). The mixture was sonicated for 3 h at the ambient temperature, and this was followed by refluxing for 12 h. The mixture was then diluted with distilled water, and this was followed by filtration through a 0.45- $\mu\text{m}$ -diameter membrane filter and washing with excess distilled water until no residual acid could be detected.

This acid treatment not only removed the impurities but also introduced some oxygen-containing functional groups into CNTs, such as hydroxyl, carboxyl, and carbonyl moieties.<sup>23–25</sup> For simplicity, the acid-treated sample is called CNT-COOH. These functional groups could further react with acryloyl chloride to provide a vinyl moiety exposed surface (Scheme 1). A 500-mL flask was charged with 100 mL of DMF, 10 mL of TEA, and 50 mg of CNT-COOH. After being ultrasonicated for 30 min, the flask was cooled to 0°C in an ice bath. A solution containing 12 mL of acryloyl chloride and 90 mL of DMF was added dropwise into the mixture in 2 h. This mixture was allowed to react at room temperature for another 24 h under magnetic stirring. The vinyl-group-modified CNTs that were produced were collected by filtration through a 0.45- $\mu\text{m}$  filter



**Scheme 1** Illustration of a possible chemical reaction producing vinyl-group-modified CNTs.



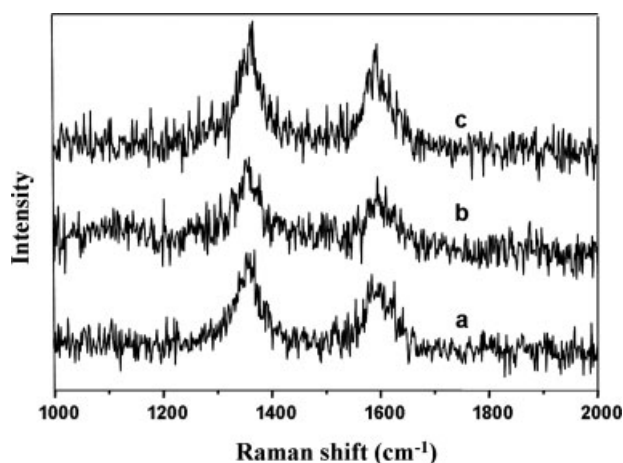
**Figure 1** FTIR spectra of (a) pristine CNT, (b) CNT-COOH, and (c) CNT-C=C.

and followed by thorough washing with distilled water and ethanol and then drying *in vacuo*.

#### Preparation of the nanocomposites

CNT/PMMA composites containing three types of CNTs (pristine CNT, CNT-COOH, and CNT-C=C) were compared. To examine the effect of the multi-walled nanotube content, we formulated CNT contents of 0.1, 0.2, 0.3, 0.5, 1.0, and 1.5 wt % with respect to the MMA content. The composites were prepared via *in situ* polymerization with BPO as an initiator. BPO was added at a concentration of about 0.11 wt % with respect to the monomer weight with CNT contents of 0.1 and 0.2 wt %, whereas the BPO amount was increased to 0.16 wt % when more CNTs were used. The CNTs were dispersed in the MMA monomer via ultrasonication for 30 min. The prepolymerization was initiated by BPO in a flask at 90°C until the viscosity was equal to that of glycerin. After prepolymerization, the mixture was sealed in a test tube and heated in a water bath at 42°C for 3 days to give the final composite.

The gelation time of prepolymerization in the PMMA/CNT nanocomposites increased with the CNT contents. Besides, it was also noticed that more BPO was needed when more CNTs were added. BPO was capable of opening the  $\pi$ -bonds of the CNTs to generate radicals on the CNT surface, which initiated the growth of PMMA chains from the CNT surface. Adding more initiator could, by itself, increase the gelation time by increasing self-termination early in the reaction when the molecular weight was still low. However, the additional consumption of BPO led to a reduction in the number of radicals during the reaction and eventually resulted in an increase in the gelation time. In addition, the increase in the gelation time may also be attributed to the fact that the pre-

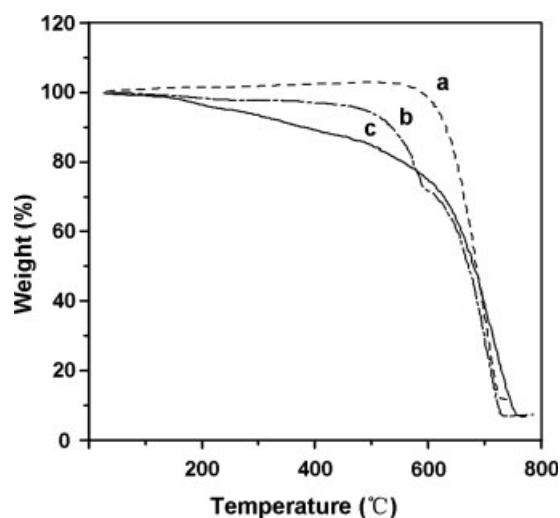


**Figure 2** Raman spectra of (a) pristine CNT, (b) CNT-COOH, and (c) CNT-C=C.

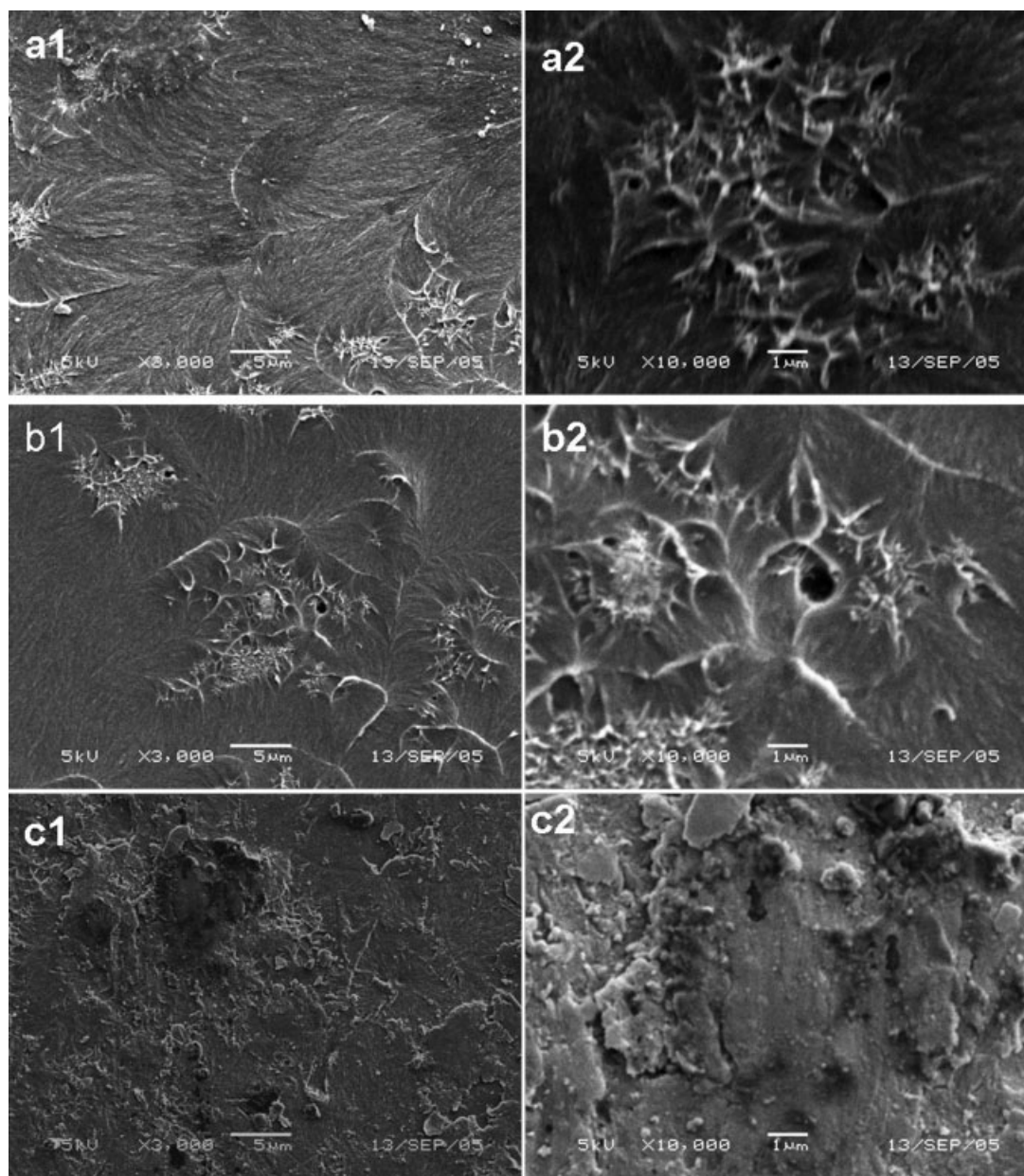
sences of more CNTs in the system could hinder the monomer diffusion to the reactive site.

#### RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of pristine CNT, CNT-COOH, and CNT-C=C. In all the spectra, the peaks around 1632  $\text{cm}^{-1}$  are assigned to the C=C-related stretching modes of the CNTs. The spectrum of CNT-COOH [Fig. 1(b)] shows a new peak at 1704  $\text{cm}^{-1}$ , which is identified as the characteristic C=O stretching from the carboxyl and carbonyl groups introduced by the acid treatment. Figure 1(c) shows that the 1704- $\text{cm}^{-1}$  peak is weaker and broader than that in Figure 1(b), suggesting that different kinds of carbonyl groups are present on the CNT surfaces after the reaction with acryloyl chloride, and this is consistent with the reaction shown in Scheme 1.



**Figure 3** TGA of (a) as-received CNT, (b) CNT-COOH, and (c) CNT-C=C. The residue weights were (a) 11.99% at 725.8°C, (b) 7.41% at 730.3°C, and (c) 8.82% at 751.7°C.

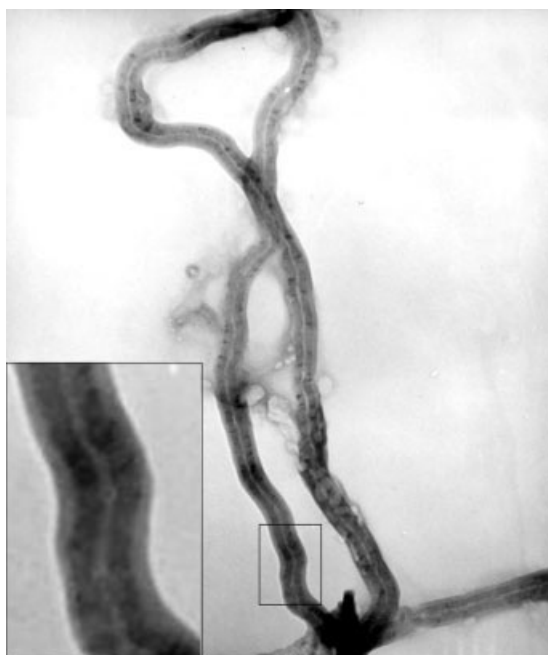


**Figure 4** SEM images of (a) pristine CNT/PMMA, (b) CNT-COOH/PMMA, and (c) CNT-C=C/PMMA nanocomposites. The CNT load was 0.5 wt % for all the samples.

The Raman spectra of the pristine and sidewall-functionalized CNTs are shown in Figure 2. The Raman spectra of CNTs possess two bands: the disorder band (D-band) around  $1350\text{ cm}^{-1}$  and the graphitic band (G-band) located around  $1580\text{ cm}^{-1}$ . Figure 2 shows that the pristine CNT, CNT-COOH, and CNT-C=C have similar band widths and peak D-band/G-band intensity ratio, and this reveals that the majority of carbon atoms in the CNTs are not affected by the chemical treatments. This effect can be understood by the fact that chemical reactions take place on only part of the outer layer, whereas most of the carbon atoms are hidden in the inner layers of the CNTs. This fact is further confirmed by

the elemental analysis. The C/O/H ratios were found to be 93.33/6.2/0.47 for CNT-COOH and 88.95/9.98/1.07 for CNT-C=C. CNT-C=C has higher oxygen and hydrogen contents than CNT-COOH, and this confirms the attachment of the acryloyl group. Meanwhile, both the Raman and elemental analyses suggest that only small amounts of the carbon atoms are affected by the modification process, and this is beneficial for retaining the intrinsic properties of the CNTs.

Additional evidence for the covalent attachment of -C=C groups to the CNTs was provided by TGA. TGA was employed to study the modifications made to the CNT samples. Because defects and attached



**Figure 5** TEM image of CNT-C=C coated with PMMA.

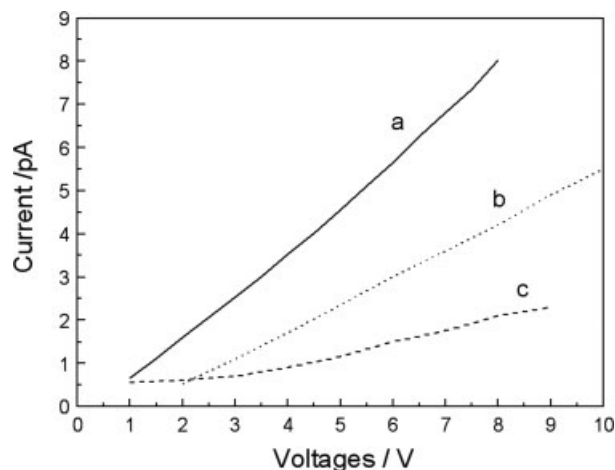
functional groups are more sensitive to oxidation than pure graphite structures on the CNTs, the shape of the TGA curves and the onset of the weight loss give good indications of the nature and quantity of the modified sites on the CNT sidewall.<sup>1</sup> In the curve of Figure 3(a), the weight remains almost constant until 550°C.<sup>26</sup> After 550°C, the weight loss is quickly accelerated because of the CNT oxidation. For CNT-COOH [Fig. 3(b)], a nearly 27% weight loss can be seen between 500 and 580°C, and it is assigned to the pyrolysis of the CNT sidewalls around the oxygen-containing functional groups. In contrast, Figure 3(c) shows a gradual weight loss starting as low as 150°C. The low decomposition temperature of the CNT-C=C sample is attributed to the relatively low bond strength of the ester linkages (Scheme 1). The TGA results prove that CNTs with different sidewall functionalizations have indeed been obtained.

To test the interaction between the CNTs and PMMA, the CNT/PMMA composites were fractured and examined with SEM. Figure 4 shows the SEM images of the cross sections of fractured PMMA composites containing 0.5 wt % CNTs. The SEM images of pristine CNT/PMMA [Fig. 4(a)] and CNT-COOH/PMMA [Fig. 4(b)] show clear evidence of phase separation. In these two samples, the CNTs aggregated into micrometer-size clusters that are clearly distinguishable from the smooth, pure PMMA regions. The texture patterns of the fractured surface reflect the interaction between the fillers and the polymer matrix. Insufficient interfacial adhesion

between the filler and matrix, corresponding to a poor dispersion of the fillers, results in a clear phase-separation-like pattern, as shown in Figure 4(a,b). In contrast, CNT-C=C/PMMA [Fig. 4(c)] shows no observable entangled clusters, and this indicates a good dispersion of the fillers. For CNT-C=C, because of the presence of the vinyl moieties, the PMMA chains can be covalently attached to the nanotube sidewalls. The PMMA chains grafted on CNT-C=C improve the compatibility between the CNTs and the PMMA matrix, allowing CNT-C=C to be uniformly embedded in the PMMA matrix. Figure 4(c) shows that CNT-C=C/PMMA gives an irregular fracture surface, indicating strong bonding between CNT-C=C and PMMA.

To examine the grafting efficiency of the polymer on the CNT surface, the CNT-C=C/PMMA composite materials were repeatedly washed with acetone to remove the unattached free polymers. Figure 5 shows a TEM image of the CNT-C=C/PMMA sample after the removal of the free polymers. The image clearly shows a uniform PMMA coating around the tube core. The diameter of the core was found to be around 30–40 nm, corresponding well to that of the pristine CNT. The polymer layer was around 10 nm with a uniform thickness, and this suggests that the reactive -C=C groups were uniformly distributed on the CNT surfaces.

Embedding CNTs in the polymer matrix is expected to improve the electrical conductivity of the composites. The surface conductance measurements of the CNT/PMMA composites show a general trend of an increase in the conductivity with an increase in the CNT load. However, different CNTs exhibit different effects on the composites' conductivity. Figure 6 shows representative current-voltage



**Figure 6** Current-voltage curves of PMMA composites with 0.5% weight fractions of (a) pristine CNT, (b) CNT-COOH, and (c) CNT-C=C as fillers.

curves of CNT/PMMA composites with a 0.5% weight fraction load of various CNTs. The pristine CNT/PMMA composite film shows the highest conductance. Under the same applied voltage, CNT-COOH/PMMA gives approximately half of the current of the pristine CNT/PMMA. In contrast, CNT-C=C/PMMA shows the lowest conductivity and also a nonlinear current-voltage curve. The different conductivities associated with different CNTs can be understood as a combination of the different nanotube dispersities in the polymer matrix and different polymer grafting efficiencies on the CNTs. As discussed previously, the pristine CNTs tend to form aggregates in the polymer matrix. Meanwhile, there is no special affinity between CNTs and PMMA; therefore, it is likely that the pristine CNTs could form a network with small gaps or even ohmic contacts between the neighboring CNTs. In contrast, because the double bonds on CNT-C=C could take part in the polymerization, the nanotubes are wrapped by a complete layer of PMMA (as shown in Fig. 5). For CNT-C=C/PMMA, electron transport is more likely to follow an electron-hopping mechanism. The relatively thick and uniform PMMA coating hampers electron hopping between the CNTs and hence results in low electrical conductivity.<sup>27</sup>

### CONCLUSIONS

The vinyl modification of CNTs using acryloyl chloride is a simple and inexpensive method that should be practical for many industrial applications. This work proves that CNT-C=C has good compatibility with the free-radical vinyl polymerization process and therefore is suitable for the fabrication of a large variety of CNT/polymer composites involving vinyl polymerization. CNT-C=C samples can be easily dispersed within the MMA monomer and form no obvious aggregates in the PMMA matrix. A TEM study has revealed a uniform coating on CNT-C=C samples, indicating good grafting efficiency of PMMA. Meanwhile, the uniformly grafted polymer layer induces a decrease in the electrical conductivity of composites. An increase in the composite conductivity may be achieved by an increase in the CNT-C=C loading or a decrease in the grafting ra-

tio. Compared with unmodified CNTs, CNT-C=C is more suitable for fabricating reinforced materials.

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