

# A Novel Method to Covalently Functionalize Carbon Nanotubes with Isocyanates

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## Abstract

*We have developed a novel method to covalently functionalize carbon nanotubes (CNTs) that carry free isocyanate ( $N=C=O$ ) groups. NCO-functionalized CNTs (NCO-fCNTs) are very desirable, because the NCO group is highly reactive with hydrogen-active groups, such as OH, COOH, and NH, which are commonly present in synthetic and natural polymers. The functionalization utilizes a di-isocyanate compound in which one NCO group has a higher reactivity than the other. By controlling the reaction parameters, the higher reactive NCO is allowed react with hydrogen-active CNTs, while the less reactive NCO groups remain free. Both NCO-fSWCNTs and NCO-fMWCNTs have been successfully prepared using hydrogen-active carboxylic-terminated CNTs. Spectroscopic and thermal analysis results clearly showed that the functionalized CNTs bear a substantial amount of organic molecules and free NCO groups, and that the functionalization effectiveness is strongly dependent on catalyst concentration. The NCO-fCNTs have been shown to react readily with amines and polyols. Since the NCO group is highly reactive with a variety of natural and synthetic polymers, NCO functionalization potentially opens up many new applications of CNTs.*

## INTRODUCTION

Carbon nanotubes (CNTs) have exceptional mechanical, electrical, and thermal properties.<sup>1-3</sup> These attributes together with their fiber-like structure, large aspect ratios, and low density have made CNTs particularly appealing for enhancing multifunctional performance of polymer composites.<sup>4-6</sup> For this application, the nanofillers must form a strong interfacial bond with, and disperse well in, the polymer matrices. However, unmodified CNTs, with their conjugated carbon structure, have low reactivity with most polymers and poor solubility in organic or aqueous solvents.<sup>2,3</sup> Therefore, a great deal of research has been devoted to the attachment of non-reactive and reactive functional groups and molecules on the surface of CNTs (i.e., functionalization) to improve their processability, interactions, and performances as well documented in many extensive reviews.<sup>3,7-11</sup> Two main methods are generally employed to functionalize CNTs: non-covalent functionalization (i.e., physical adsorption) and covalent functionalization. Different applications require different functionalization strategies. However, in order to increase stress transfer efficiency and retain the enhanced performance under mechanical and environmental stresses in polymer/CNT composites, chemical modifications must be performed in such a way that, not only covalent bonds are formed between the CNTs and the molecules that carry the functional groups but also between the functional groups and the polymer matrix.

Covalent functionalization can be achieved through both the sidewalls and ends of the CNTs. For polymer composite applications, chemical modification at the tube ends is preferred because such process has little effect on the mechanical and electronic properties of the CNTs.<sup>3,8</sup> Many reactive groups have been functionalized on the surface of CNTs that are capable of forming covalent bonds with the polymer matrices, such as COOH and NH<sub>2</sub>.<sup>7-11,12,13</sup> However, despite its very high reactivity and enormous commercial importance, the isocyanate (N=C=O) group, which is the main functionality of the urethane chemistry, has received little attention with respect to its use to chemically modify CNTs and nanoparticles. To the best of our knowledge, there has been only one report on functionalization of CNTs with an NCO group, but this study employed tolylene 2,4 diisocyanate (TDI), a small, aromatic molecule.<sup>14</sup> The success of this particular compound was explained as due to the steric hindrance of the two NCO groups located on the same benzene ring: the *p*-NCO is more accessible than the *o*-NCO. It was speculated that because of this steric hindrance reason, a substantial amount of the *o*-NCO

remained unreacted. We believe that the reason for the presence of unreacted NCO in this case is not due to steric hindrance but due to a decrease of the activating effect after one of the two NCO groups has already reacted, as demonstrated clearly for many diisocyanates where two NCO groups are located in the same aromatic ring.<sup>15</sup> This is because NCO is a strong activating group. Therefore, as soon as one of the two NCOs has been reacted, the reactivity of the other NCO group is significantly reduced. Therefore, no free NCO can be attached to the CNTs if the two NCO are in different rings or far apart. Regardless of the reason, TDI is not a desirable monomer for polymer nanocomposite processing and applications because its high vapor pressure and aromatic nature make it a serious health safety concern. In addition, TDI has dark color and is an ultraviolet (UV)-absorbing chromophore, which will limit its use and also lead to poor UV resistance of the nanocomposites, respectively.

This paper describes a novel method to covalently functionalize CNTs to carry free NCO groups (designated as NCO-*f*CNTs) using an aliphatic diisocyanate molecule, which is commonly used in polyurethane coatings and plastics for exterior applications. The presence of free NCO group on the CNTs is highly desirable because it is very reactive toward hydrogen-active species such as, COOH, OH and NH, which are commonly present in many synthetic and natural polymers. Such NCO-*f*CNTs will form strong interfacial bonds with the matrices containing these species. In addition, because the NCO-functionalized materials carry a substantial amount of hydrocarbon chains, this functionalization is expected to improve the dispersion of CNTs in polymers. The combined effects of strong interfacial strength by covalent formation and a large increase in the interfacial area (resulting from good dispersion) created by the NCO functionalization would enhance the load transfer efficiency and mechanical properties of polymer nanocomposites.

The NCO functionalization described here requires three essential conditions: 1) the functionalization molecule must contain two or more NCO groups that have different reactivities, 2) CNTs must carry hydrogen-active species, such as COOH-terminated CNTs (COOH-*f*CNTs), and 3) a suitable catalyst to control the reactivity of different NCO groups. The novelty and success of this approach lies in the reactivity difference of various NCO groups on the functionalization molecule, as schematically illustrated in Figure 1 for a diisocyanate. In order to form covalent bonds with the COOH-*f*CNTs and at the same time carry free NCO groups in the functionalized products, the reactivity of one NCO in the functionalization

molecule must be substantially greater than that of the other NCOs (e.g., reactivity of NCO # 1 is >> reactivity of NCO # 2 in Figure 1). By controlling the reaction parameters such as catalyst and time, the more reactive NCO groups will react with COOH on CNTs while a substantial amount of the less reactive NCO groups remain unreacted and available for forming covalent bonds with polymer matrices or other molecules of interests. Since carboxylic acids are generally less reactive towards NCO than alcohol or amine,<sup>15</sup> the degree and rates of reaction can be effectively controlled by the catalyst or reaction time or both. As clearly demonstrated later, if the two NCO groups in the diisocyanate molecule have the same reactivity, essentially no or little free NCO is observed in the functionalized product, even though a substantial amount of the isocyanate molecule has been covalently attached to the CNTs.

Spectroscopic and thermogravimetric analysis results have clearly demonstrated this functionalization method is effective to covalently and substantially attach free NCO groups to the CNTs and these free NCO groups readily react with hydrogen-active containing compounds, typically used in polyurethane manufacturing. In addition, results on mechanical properties and interfacial characteristics of polyurethane (PU) nanocomposites have also shown that the NCO- $\mu$ MWCNTs form stronger interface with the PU polymer than the unmodified MWCNTs and increases substantially the modulus of PU polymer.<sup>16</sup>

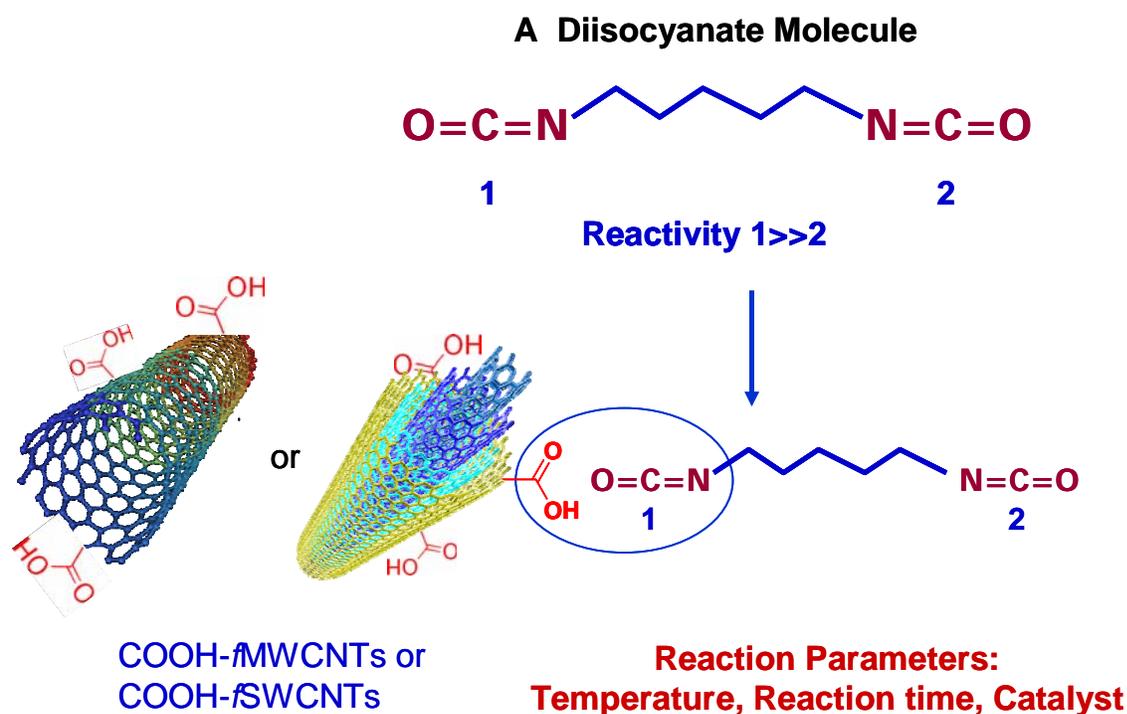


Figure 1. Strategy to covalently functionalize CNTs that carry terminal NCO groups.

## EXPERIMENTAL PROCEDURES\*\*

### Materials

Commercially-available single-walled CNTs (SWCNTs) (Aldrich) and multi-walled CNTs (MWCNTs) (Helix) were used. The average diameter of SWCNTs ranged from 0.6 nm to 1.4 nm (as measured by AFM), and that of MWCNTs was between 11 nm and 20 nm (by TEM). The amounts of residual metal catalyst in SWCNTs and MWCNTs were  $12.3 \pm 2\%$  and  $4.6 \pm 1.4\%$  (by mass), respectively, as measured by thermogravimetric analysis (TGA). The NCO-functionalization molecule was 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, a cycloaliphatic diisocyanate generally known as isophorone diisocyanate and commonly abbreviated as IPDI (Desmondur I, Bayer MaterialScience LLC, USA). The chemical structure of this molecule is included in Figure 2. One significant feature of this diisocyanate is one NCO group, which is attached to the primary carbon, is 5 to 10 times more reactive than the other NCO group attached to the secondary carbon.<sup>17</sup> The reactivity of NCO-fCNTs was studied using

dibutyl amine (Aldrich) and a polyether polyol (Multranol 4012, Bayer MaterialScience LLC, USA). Dibutyl tin laurate (Aldrich) was used as the catalyst for both functionalization and reaction with polyols. To prove the novelty of this method, functionalization was also performed using 4,4 diphenylmethane diisocyanate (MDI) (Aldrich) in which the two end NCO groups are known to have similar reactivity.<sup>15</sup> Anhydrous, spectroscopic-grade KBr powder was employed to prepare pellets for transmission FTIR spectroscopy (T-FTIR) measurement.

### **NCO Functionalization**

NCO-*f*CNTs were prepared using the process schematically illustrated in Figure 2 for MWCNTs, as an example. The first step of the functionalization was to oxidize as-received material (AR-CNTs) to produce hydrogen-active COOH-*f*CNTs using a refluxing, liquid-phase nitric acid procedure that has been suggested for both MWCNTs<sup>18</sup> and SWCNTs.<sup>19,20</sup> The nitric acid treatment first opens the end caps of the CNTs,<sup>18</sup> followed by oxidation to introduce mostly carboxylic acid (COOH) groups at the tube ends and defect sites on the side walls.<sup>21-23</sup> This treatment reportedly does not disturb the tubular structure of the CNTs,<sup>18,19</sup> which is important for polymer composite applications because treated CNTs still retain their exceptional mechanical properties and unique electronic structures. In this study, COOH-*f*MWCNTs were prepared by sonicating (at 55 kHz) as-received material in 9.5 mol/l HNO<sub>3</sub> solution for 1 h at 24 °C, followed by 24 h reflux with constant stirring at 110 °C. The same procedure was used for preparing COOH-*f*SWCNTs, except that a 3 mol/l HNO<sub>3</sub> concentration and a reflux time of 10 h were used. The suspended CNTs were filtered using a 1.2 μm tetrafluoroethylene membrane, washed thoroughly with distilled water until the CNT suspension in water had a pH = 5, and finally dried in vacuum at 70 °C for 24 h.

The NCO functionalization (Figure 2, Step 2) was carried out by placing an appropriate amount of COOH-*f*CNTs in a three-neck flask containing a known amount of catalyst and acetone (amounts of catalyst are expressed in percent mass fraction of the IPDI molecule). It should be noted that the amounts of catalyst used here were not selected based on typical COOH-NCO chemical reaction but rather based on trial and error, because the exact concentration of COOH in the reaction was not known. After sonicating for 20 minutes, the isocyanate functionalization molecule (i.e., IPDI) was added to the flask, followed by heating for 7 h at 50 °C under N<sub>2</sub> atmosphere. After cooling to room temperature, NCO-*f*CNTs were filtered,

sonicated in acetone for 1 h, and washed with acetone. The last three steps were repeated at least twice to ensure that most of the physically-sorbed and excess IPDI molecules have been removed from the functionalized products.

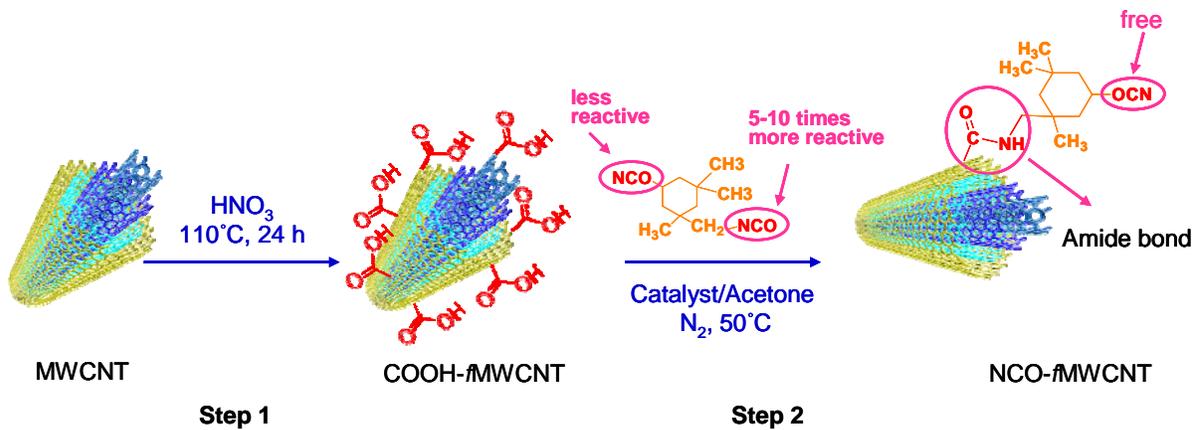


Figure 2. Steps and conditions used for covalent NCO functionalization of CNTs.

### Characterization of NCO-functionalized CNTs

NCO-functionalized CNTs were characterized by transmission FTIR spectroscopy (T-FTIR), thermogravimetric analysis (TGA), and X-ray Photoelectron Spectroscopy (XPS). T-FTIR was also used to follow the formation of COOH on CNTs by  $\text{HNO}_3$  treatment, the reactions between COOH-fCNTs and diisocyanate, and between NCO-fCNTs and model compounds containing hydrogen-active groups (i.e.,  $\text{NH}_2$  and OH). TGA provided quantitative information on the amounts of COOH and isocyanate functionalization molecule attached to the CNTs, while XPS gave quantitative data on both elemental and complex chemical species on both the unfunctionalized and functionalized CNT surface. For T-FTIR measurement, KBr pellets containing a mass fraction of 0.075 % CNTs and having a thickness of 1 mm were prepared. A vacuum was used during pressing to minimize the reaction between NCO group and water from the ambient air and the adsorption of moisture on KBr. All pellets were carefully made using the same protocol. T-FTIR spectra were the average of 128 scans, which were recorded on a Nexus 670 spectrometer (Thermo Nicolet) at a resolution of  $4\text{ cm}^{-1}$  using a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector, and dry air purge. The peak height method was employed to represent IR intensity, which is expressed in absorbance, A. The uncertainties for this measurement were  $\pm 1\text{ cm}^{-1}$  wavenumber and  $\pm 1\%$  absorbance. TGA measurements were conducted in nitrogen from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$

using a TGA 2950 analyzer (TA Instruments); the uncertainties were  $\pm 1$  °C and  $\pm 1$  % mass change.

XPS measurements of the MWCNT samples were made on a Kratos Axis-Ultra DLD spectrometer with a monochromated Al-K $\alpha$  source at a 0° angle between the sample surface normal and the analyzer lens. Samples were mounted on carbon tape. In addition, to verify that no signal from the carbon tape was contaminating the CNT signal, samples were also mounted on indium foil.<sup>24</sup> Multiple positions and duplicate spectra were obtained for each sample. At each position, a survey spectrum was taken with pass energy 160 eV, using the hybrid lens and the ‘slot’ aperture ( $\sim 300$   $\mu\text{m} \times 700$   $\mu\text{m}$ ). High resolution spectra were taken with pass energy 20 eV, using the hybrid lens and either the slot or the 110  $\mu\text{m}$  aperture. Spectra were analyzed using Kratos Vision Processing software. Data was fit with 70 % Gaussian/30 % Lorentzian peaks. For the NCO-containing samples only, charge neutralization was used, necessitating calibration of the lowest C 1s peak binding energy to 284.6 eV.

## RESULTS AND DISCUSSION

### Characterization of NCO-Functionalized CNTs

#### *T-FTIR Analysis*

The NCO-functionalization strategy described in this paper is based on the availability of COOH groups on the surface of CNTs. Therefore, the oxidation efficacy by HNO<sub>3</sub> treatment is crucial for the success of this method. T-FTIR spectra of SWCNTs and MWCNTs before (as-received) and after oxidation by HNO<sub>3</sub> are displayed in Figure 3. The spectrum of a CNT-free KBr pellet having the same mass and thickness is also included for aid in the interpretation. KBr material exhibited two bands near 1625 cm<sup>-1</sup> and 3440 cm<sup>-1</sup>, due to OH bending and OH stretching, respectively, of adsorbed water on KBr. As-received SWCNTs displayed a characteristic IR band near 1582 cm<sup>-1</sup>, assigned to -C=C- bonds of the CNTs,<sup>25</sup> and a very broad, unassigned band extending from 950 cm<sup>-1</sup> to 1300 cm<sup>-1</sup>. At the concentration of CNT in KBr used in this study, MWCNTs showed a much lower absorption in these two regions. After HNO<sub>3</sub> treatment, a prominent, broad band appears near 1723 cm<sup>-1</sup>, assigned to non-hydrogen bonded C=O of carboxylic acid,<sup>23,26</sup> and the intensity of the band near 1245 cm<sup>-1</sup>, assigned to C-O, increased markedly. In Figure 3, it is also seen that the intensity of the -C=C- band at 1582 cm<sup>-1</sup>

for both SWCNTs and MWCNTs increased noticeably after the HNO<sub>3</sub> treatment, suggesting that a modification of the tubes' chemical structure has taken place allowing the aromatic C=C bonds to absorb the infrared radiation more strongly as compared to the untreated CNTs. Based on a shift of this band, a previous study also suggested that HNO<sub>3</sub> treatment causes a change in the structure of SWCNTs.<sup>23</sup> The results of Figure 3 indicated that a substantial amount of COOH has been formed on the surface of CNTs after the HNO<sub>3</sub> treatment, consistent with TGA results to be given later.

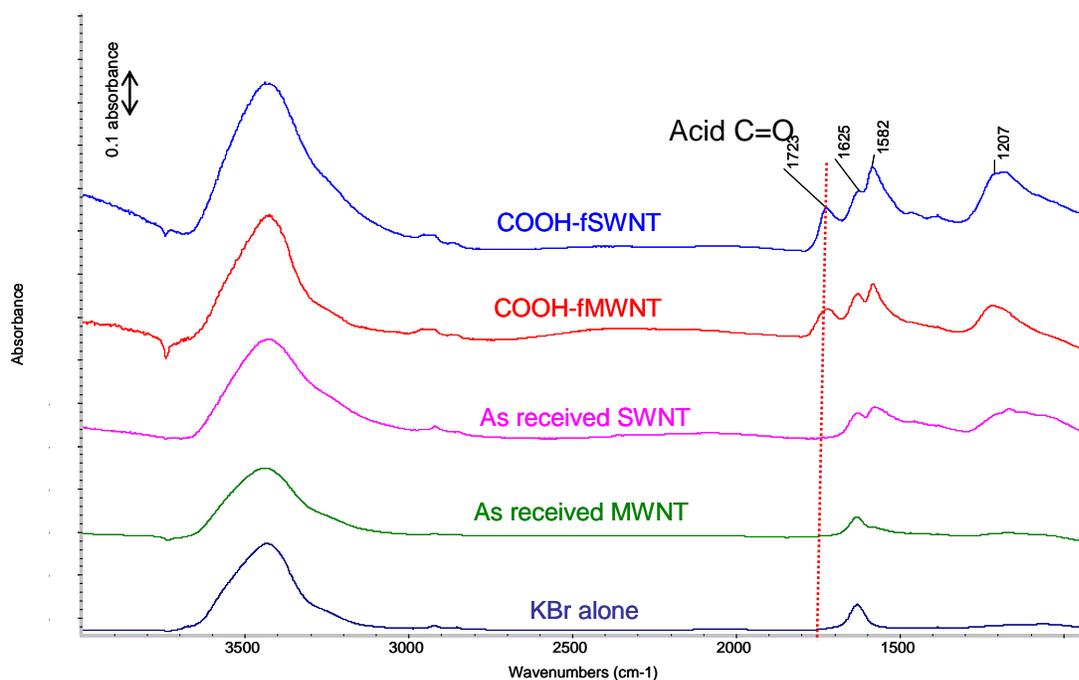


Figure 3. T-FTIR spectra of as-received and HNO<sub>3</sub>-treated SWCNTs and MWCNTs (denoted as COOH-fSWNT and COOH-fMWNT); an T-FTIR spectrum of the KBr material is also provided for comparison.

Figure 4 presents T-FTIR spectra of NCO-fMWCNTs prepared with IPDI at different levels of catalyst and NCO-fSWCNT using IPDI at 2 % catalyst. The presence of free NCO groups in the functionalized CNTs is clearly demonstrated by the strong absorption band at 2260 cm<sup>-1</sup>, due to the out-of-phase stretching of the N=C=O bonds. The attachment of IPDI hydrocarbon chain onto the CNTs can be seen by the bands at 1387 cm<sup>-1</sup> and 1364 cm<sup>-1</sup>, due to CH<sub>3</sub> deformation (gem-dimethyl), and in the CH stretching region between 2800 cm<sup>-1</sup> and 3000

cm<sup>-1</sup>. Formation of the covalent amide bonds (-CONH) between the COOH-fCNTs and the diisocyanate molecule can be ascertained by several changes in the FTIR spectra. One evidence was a substantial decrease in intensity of the carboxyl C=O band near 1723 cm<sup>-1</sup>. For the aliphatic diisocyanate used here, this intensity decrease is probably due to the following reaction:<sup>15</sup>

$R-NCO + R'COOH \rightarrow RNHCOR' + CO_2$ , in which COOH is consumed to form substituted amides. This reaction goes through mixed anhydride intermediate products, which decompose to amides.<sup>15</sup> Another evidence was the appearance of the strong absorption bands at 1640 cm<sup>-1</sup> (due to C=O stretching), 1540 cm<sup>-1</sup> (due to NH bending), and 1225 cm<sup>-1</sup> (due to mostly C-N stretching), indicating the formation of -CONH linkages, consistent with the reaction above. Similar observations have been reported for the COOH disappearance and CONH formation for NCO<sup>14</sup> and amine<sup>12</sup> functionalizations of CNTs.

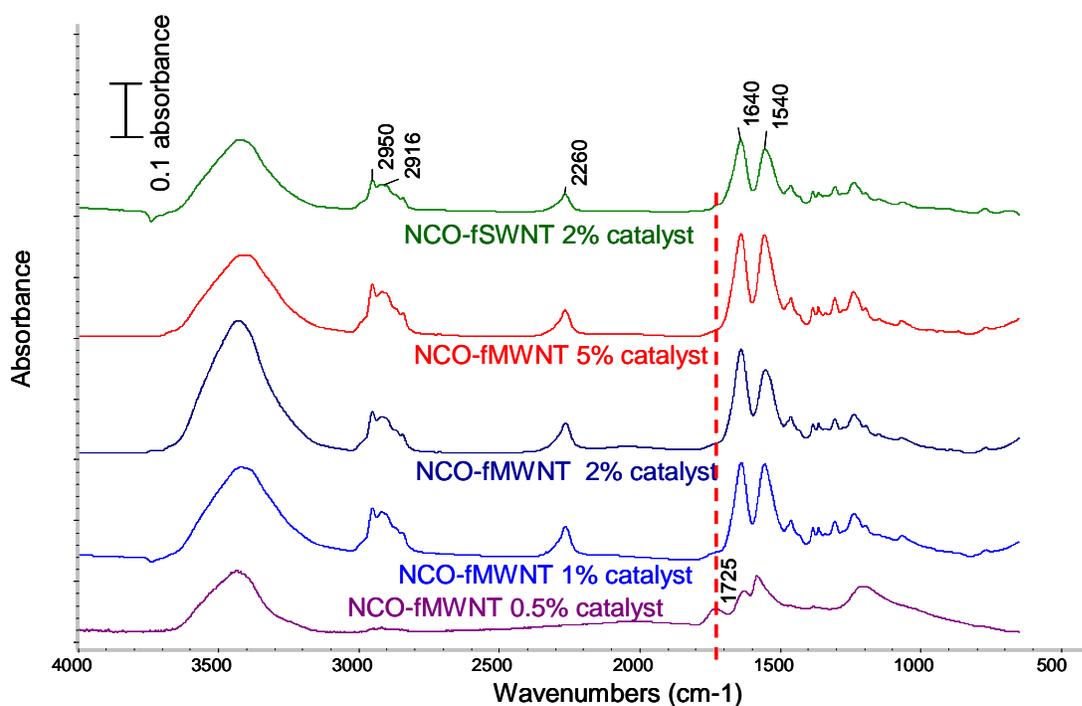


Figure 4. T-FTIR spectra of NCO-fMWCNT prepared using IPDI at different catalyst levels, and NCO-fSWCNT at 2 % catalyst.

To verify the NH assignment, an NCO-*f*MWCNT sample was exposed to D<sub>2</sub>O vapor for 8 h at 80 °C. In the presence of D<sub>2</sub>O, the NH in a CONH group or in an amine-containing compound is converted to COND or ND, respectively, and FTIR intensity of the NH is reduced, but that of the C=O band remains essentially unaffected. The spectra of the D<sub>2</sub>O-exposed sample (not shown) exhibited greatly reduced intensity of the NH band at 1540 cm<sup>-1</sup> but little change on intensity of the C=O band at 1640 cm<sup>-1</sup>, thus confirming the proper assignment of the NH band at 1540 cm<sup>-1</sup>.

In addition, to ascertain that the CONH and CH bands were due to IPDI covalently-attached to the CNTs and not from insoluble self-polymerized products of the diisocyanate material, a reaction containing 2 % catalyst but without COOH-*f*CNTs was carried out using the same reaction conditions. The solution of this reaction was clear, with no evidence (with the naked eye) of any suspended particle or precipitation at the bottom of the flask. Further, the attenuated total reflection FTIR (ATR-FTIR) spectrum of this solution was similar to that of the IPDI, with no evidence of the NH and C=O bands. These results indicated that the products observed were from the reactions between the diisocyanates and the hydrogen-active CNTs and not from the reactions among the diisocyanates themselves

One important observation in Figure 4 is the spectra of NCO-*f*MWCNTs samples prepared at 0.5 % catalyst (and without catalyst, not shown) did not show the presence of NCO, CH, or C=O bands. These results clearly indicated that little IPDI was attached to CNTs when no or low concentration of catalyst was used in the reaction. The results, which are consistent with TGA data below, strongly suggested that the washing procedure was effective for removing completely the unreacted isocyanate functionalization molecules.

### ***Thermogravimetric Analysis***

The amount of the diisocyanate functionalization molecule (i.e., IPDI) attached to the CNTs was estimated by TGA method, as illustrated in Figure 5. This figure displays mass loss as a function of temperature for 1) MWCNTs before and after NCO functionalization at different catalyst levels, 2) COOH-*f*MWCNTs, and 3) NCO-*f*SWCNT prepared at 2 % catalyst. As-received CNTs did not lose any significant mass below 600 °C. However, COOH-*f*MWCNTs and NCO-*f*MWCNTs started to lose mass at relatively low temperatures. For example, COOH-*f*CNTs had a 4.5 % mass loss, due to COOH decomposition to generate CO<sub>2</sub>, at 300 °C.

This amount of COOH attached to the MWCNTs is in line with reported values ranging from 4.0 % to 6.8 % obtained by titration for SWCNTs treated with different concentrations of  $\text{HNO}_3$ .<sup>27</sup>

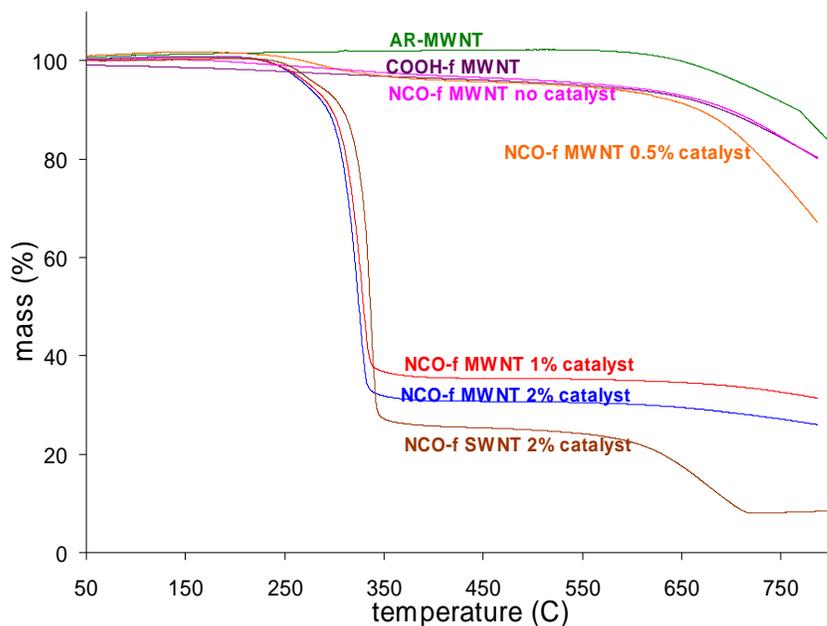


Figure 5. TGA curves of as-received and NCO-functionalized MWCNTs (denoted as NCO-fMWNT) at different catalyst concentrations. TGA curves of NCO-fSWCNTs (denoted as NCO-fSWNT) and COOH-fMWCNT (denoted as COOH-fMWNT) are also given.

For NCO-fMWCNTs or NCO-fSWCNTs prepared with 2 % catalyst, the mass loss initiated at approximately 220 °C, progressed rapidly and reached a maximum loss of nearly 70 % at 320 °C. This mass loss was due the organic IPDI molecules attached to the CNTs. Using solution phase FTIR, a previous study has reported a 55 %  $\pm$  10 % mass fraction loading of octadecylamino (ODA) was covalently attached (through amide linkage) to the COOH-fSWCNTs treated in 2.6 M  $\text{HNO}_3$  for 45 h.<sup>21</sup> The high loading was attributed to the reactions with COOH groups located at both the ends and side walls of the SWCNTs. The mass fraction of COOH with respect to CNTs of that study was only between 1 % and 2 %, <sup>22</sup> which is substantially lower than the 4.5 % observed here for MWCNTs.

A comparison of TGA results between NCO-fCNTs prepared without or with 0.5 % catalyst and those prepared using 1 % or 2 % catalyst (Figure 5) indicated that the majority of

mass loss was due to the decomposition of the IPDI material that was covalently bonded to the CNTs. If IPDI molecules were attached to the CNTs solely by physical adsorption or were simply trapped between the bundles, they would be readily removed by solvent washing, as observed in the 0.5 % catalyst and catalyst-free samples.

### X-ray Photoelectron Spectroscopy Analysis

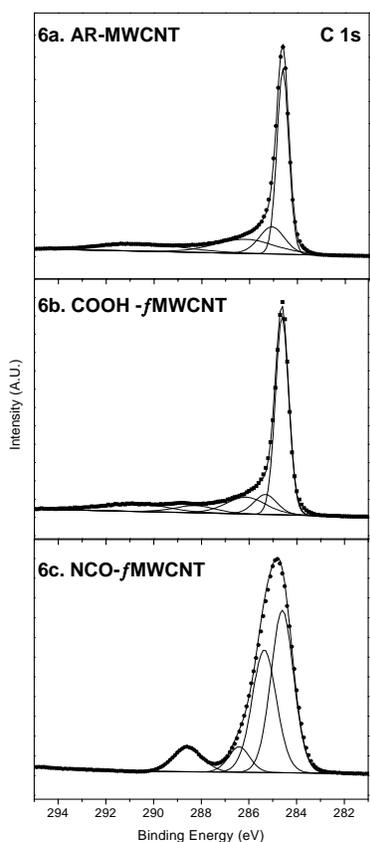


Figure 6. XPS spectra of the C 1s region of MWCNTs: (a) as-received, (b) functionalized with COOH, and (c) functionalized with –NCO group.

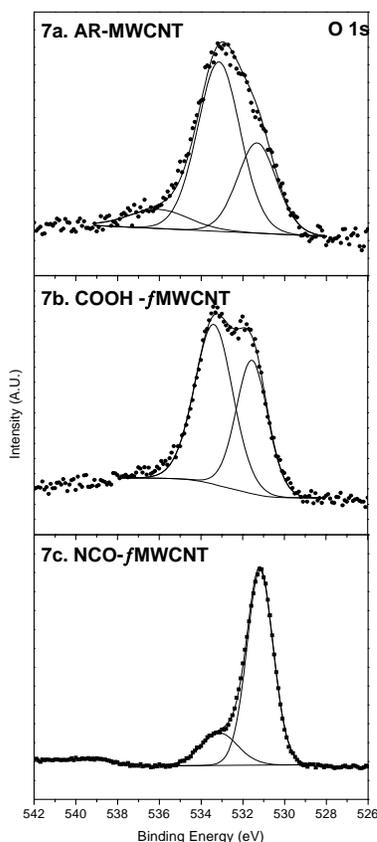


Figure 7. XPS spectra of the O 1s region of MWCNTs (a) as-received, (b) functionalized with COOH, and (c) functionalized with –NCO group.

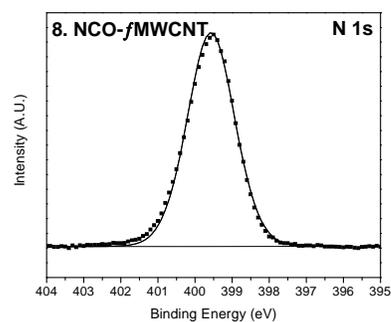


Figure 8. XPS spectrum of the N 1s region of MWCNTs functionalized with –NCO group. For all figures: lines represent fits for individual components and total fit. Circles represent the data.

Figures 6 and 7 show XPS spectra of the C 1s and O 1s region, respectively, for as-received, COOH-*f*MWCNTs and NCO-*f*MWCNTs. For the as-received and the COOH-functionalized samples, the C 1s spectra (Figures 6a and 6b) are similar to each other and to previously-published results.<sup>10, 28-30</sup> Both show peaks around 284.6 eV, 285.3 eV, 286.2 eV, and 290-291 eV which correspond to sp<sup>2</sup> C, sp<sup>3</sup> C, C singly-bonded to O, and an sp<sup>2</sup> C shake-up peak, respectively. In addition, in Figure 6b, a peak is present at 288.4 eV, corresponding to the C in the COOH group. The O 1s spectra in Figs. 7a and 7b show multiple peaks, which arise from C-O, C=O or -OH.<sup>29</sup> Figures 6c, 7c and 8 display the C 1s, O 1s, and N 1s spectra for the NCO-*f*MWCNTs. The C 1s spectrum is composed of a main peak, which includes both the sp<sup>2</sup> and sp<sup>3</sup>-hybridized C peaks at 284.6 eV and 285.3 eV, respectively. In addition, smaller components are found at 288.6 eV due to N=C=O and N-C=O groups and at 286.3 eV corresponding to C-O. Two peaks are observed in the O 1s spectrum in Figure 7c, due to C=O, and also probably some residual COOH or C-O groups. The N 1s spectrum (Figure 8) shows a peak at 399.6 eV, similar to previous result of MWCNTs containing isocyanate groups.<sup>12</sup>

Atomic percentages for C, O, and N were calculated and are listed in Table 1. Spectra taken with different spot size or mounting technique were highly reproducible and were included in the analysis. Each value represents the average of values obtained for between 6 and 9 spectra. The as-received MWCNTs were primarily (98.8 %) carbon with some residual oxygen, perhaps COOH and C-O groups, present. The COOH-*f*MWCNTs had a higher percentage of O (4.5 %), as expected. The NCO-*f*MWCNT was composed of C (81.7%), O (5.9 %), and N (12.4 %). These data are qualitatively in good agreement with T-FTIR and TGA results, and again confirmed that this functionalization approach is effective for attaching a substantial amount of NCO material on the CNT surface.

Table 1. Average atomic percentages for C, O, and N, obtained by XPS, including standard deviation of multiple measurements

| Sample       | C 1s        | O 1s       | N 1s         |
|--------------|-------------|------------|--------------|
| AR-MWCNT     | 98.82 ± .17 | 1.18 ± .17 | -            |
| COOH-f/MWCNT | 95.50 ± .46 | 4.50 ± .46 | -            |
| NCO-f/MWCNT  | 81.7 ± .38  | 5.90 ± .28 | 12.40 ± 0.17 |

### Reactions Involved in the NCO Functionalization

Based on FTIR, TGA, and XPS evidence, a plausible scheme on the reactions involved in the NCO functionalization is presented in Figure 7. The first step was the reaction between COOH and NCO to yield substituted amides (-CONH-), as indicated earlier. If amides were the primary reaction products, the mass ratio of O and N atoms should be 1. However, XPS data (Table 1) shows a ratio of N and O close to 2, suggesting that other possible reactions have taken place during the NCO functionalization, as illustrated in Steps 2, 3, and 4 in Figure 7. Step 2 involved the reaction between the substituted amide NH and excess NCO in the reaction mixture to form amidine compounds (-N=CNH-).<sup>15</sup> The IR band of the amidine C=N is very weak and located near 1650 cm<sup>-1</sup>,<sup>31</sup> which is in the same range with the high absorptivity C=O of the amides and thus could not be used to substantiate the amidine formation. Because the basic NH group is very reactive toward NCO, these groups in the amidine structure likely reacted further with NCO to form substituted urea (R-NHC=ONHR)<sup>15</sup> (Step 3), which underwent further reaction to yield more amidine compounds (Step 4). If there was enough NCO in the reaction solution, a further step similar to that of Step 3 involving with the amidine NHs likely occurred; this can account for the N/O slightly greater than 2 shown in Table 1. In addition, although the primary NCO groups likely participated in the majority of the reactions, particularly with the less reactive -COOH and CONH groups, it is reasonable to assume that some fraction of the less reactive 2<sup>nd</sup> NCO groups of the IPDI material may also have involved in some reactions, particular with the more reactive NH groups. Therefore, the NCO-functionalized CNTs likely contain a complex, highly branching chemical structure, as shown in Figure 7. This reaction

scheme is consistent with the XPS data, adequately accounts for the free NCO groups and the formation of a substantial amount of C=O and NH groups, and provides a reasonable explanation for the high loading of IPDI molecule on the CNTs.

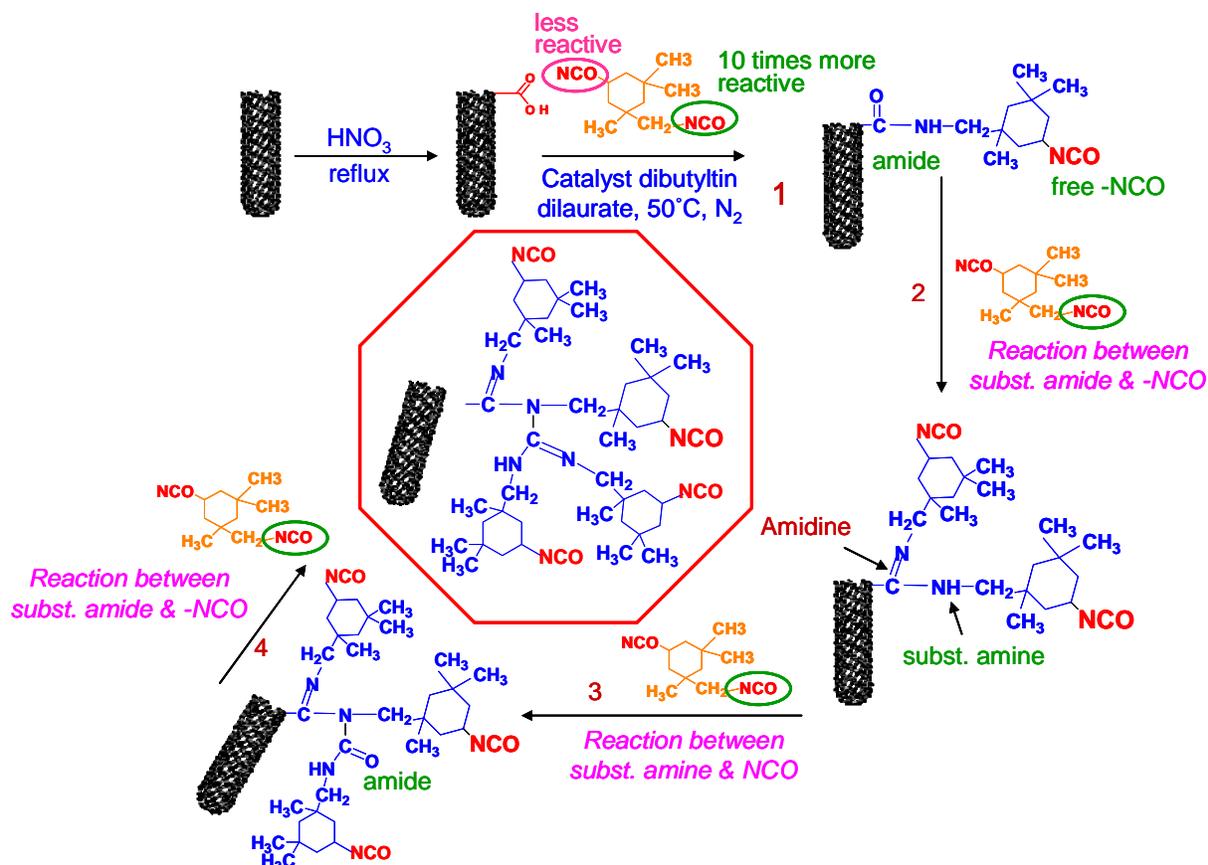


Figure 9. Plausible reactions involved in the NCO functionalization of CNTs.

### Validation of the Functionalization Strategy

Our premise is that to covalently functionalize CNTs that bear terminal isocyanate groups, the two NCO groups in the diisocyanate monomer must have different reactivities. That is, if the two NCO groups in the functionalized molecule had similar reactivities and were free of steric hindrance, both would react equally with COOH groups on CNTs and there would be no free NCO groups present in the functionalized products. This is clearly seen in the T-FTIR spectrum of NCO-*f*MWCNT functionalized using 4,4-diphenylmethane diisocyanate (MDI) (Figure 10a). T-FTIR spectra of the COOH-MWCNT and NCO-*f*MWCNT functionalized with IPDI are also included in the figure for comparison. As indicated in the experimental section, MDI monomer has two NCO groups that are far apart in the chemical structure and have similar

reactivity. The spectrum of the MWCNTs functionalized with MDI shows little absorption at  $2260\text{ cm}^{-1}$  of the free NCO group but strong absorption bands of the benzene ring at  $1510\text{ cm}^{-1}$  and the  $\text{CH}_2$  at  $1460\text{ cm}^{-1}$  from the MDI molecule. These T-FTIR results, together with TGA data (Figure 10b), which reveals a 60 % mass loss, indicated that the MDI monomer has covalently attached to the MWCNTs. However, because both the NCO groups on the MDI monomer have mostly reacted with the COOH-*f*CNTs, only a small residual IR band of the NCO group is observed in the spectrum. The results for MDI has validated our proposed functionalization strategy.

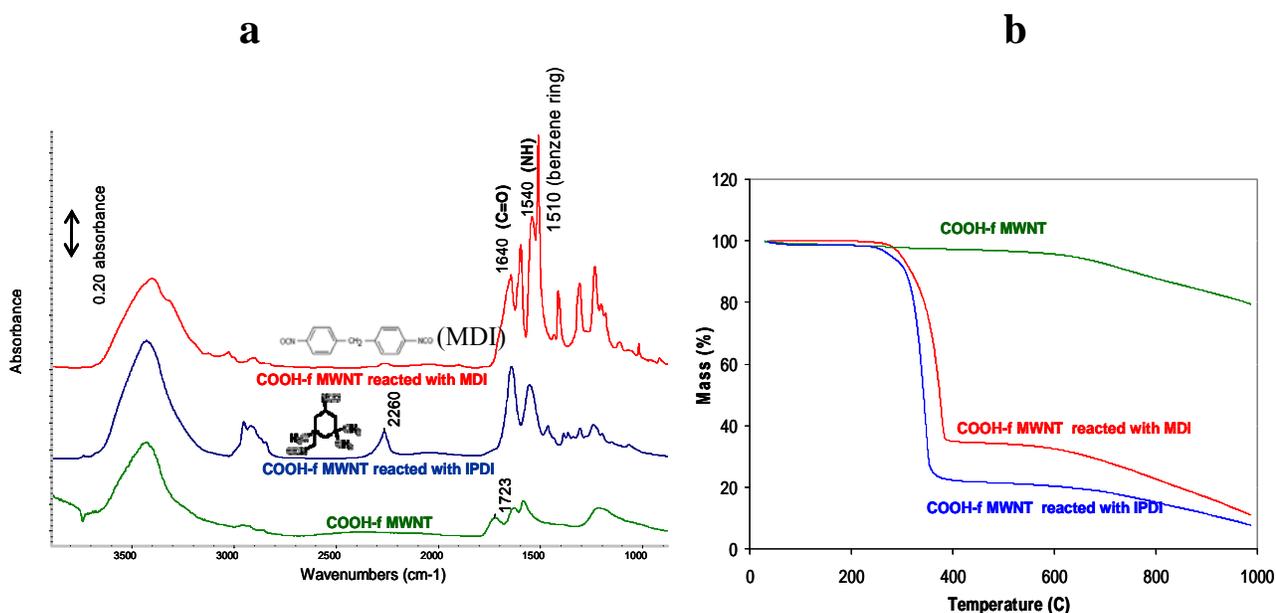


Figure 10. T-FTIR (a) and TGA (b) results for MWCNT functionalized with 4,4-diphenylmethane diisocyanate (MDI). The results for COOH-*f*MWCNTs and IPDI-*f*MWCNTs are also included for comparison.

### Reactivity of NCO-Functionalized CNTs

Spectroscopic and thermogravimetric results presented above have clearly demonstrated that this functionalization method is effective in forming covalent bonds between a CNT and the diisocyanate and in providing CNTs with terminated secondary NCO groups. One question that needs to be addressed is the reactivity of these free NCO groups. That is, are they capable of forming covalent bonds with the hydrogen-active compounds and polyurethane resins?

Examples of the reactions between the NCO-*f*MWCNTs with two hydrogen-active molecules are illustrated in the FTIR spectra given in Figure 11. The reaction is best observed by the intensity decrease of the NCO band at 2260 cm<sup>-1</sup>. Figure 11 showed a complete loss of this band in dibutyl amine and a small residual peak in polyether polyol after 4 h at 60 °C. For amine, no catalyst and room temperature (25 °C) were used for the reaction. For polyether polyol, a mass fraction of 0.01 % dibutyltin laurate catalyst (based on the mass of polyol) and 60 °C were employed. The results indicated the reaction was fast with amine even at room temperature, but quite slow for polyether polyol even in the presence of catalyst and at elevated temperature.

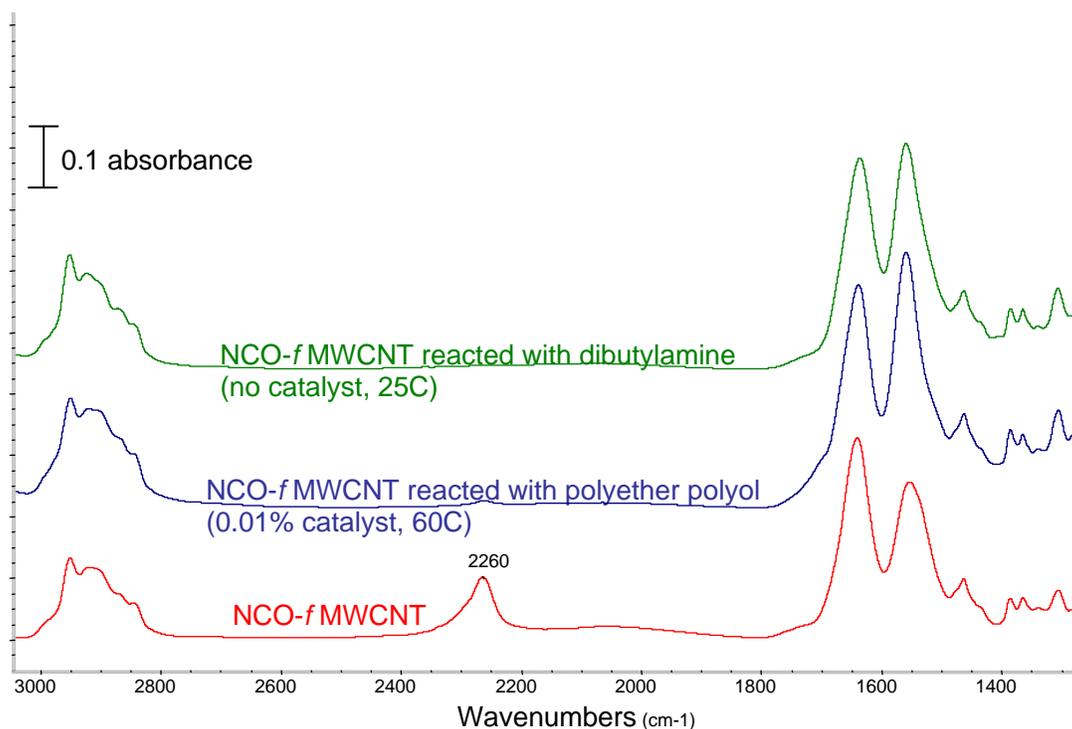


Figure 11. T-FTIR spectra of NCO-*f*MWCNTs after reacting with a polyether polyol and dibutyl amine (reaction time was 4 h for both compounds).

The storage stability of the NCO-*f*CNTs was also investigated by monitoring the NCO band at 2260 cm<sup>-1</sup> of the functionalized materials that were exposed to ambient condition (24 °C, 45 % relative humidity) and in N<sub>2</sub> at 0 °C. No change in band intensity was observed for NCO-*f*MWCNTs exposed for 18 days in the latter condition, but approximately 80 % of the intensity was lost after the same duration in ambient conditions. This was attributed to the reaction of NCO with water in the environmental air.

## CONCLUSIONS

We have developed an effective method to covalently functionalize CNTs that bear terminal NCO groups. The functionalization was based on isocyanate - carboxylic acid chemistry and the use of a di-isocyanate molecule in which one NCO group is more reactive than the other. The functionalization consisted of oxidization of CNTs to produce COOH groups on their surface, followed by reacting COOH-*f*CNTs with a diisocyanate molecule in the presence of a catalyst. Spectroscopic and thermal analysis results clearly showed that, under suitable conditions of catalyst and reaction time, covalent bonds are formed between the COOH-*f*CNTs and the diisocyanate molecule and that NCO-*f*CNTs contained a substantial amount of free NCO groups and organic chains. NCO-*f*CNTs have been shown to react readily with hydrogen-active groups OH and NH<sub>2</sub>. Since the NCO group readily forms covalent bonds with natural and synthetic polymers containing active-hydrogen species, NCO-*f*CNTs potentially open up a variety of new applications. They can be used to greatly increase the stress transfer in polymer/CNT composites and covalently attached to biological systems to increase their stability and selectivity. Our results showed that polyurethane composites containing NCO-*f*MWCNTs have a better dispersion, stronger interface, and greater modulus than the same polymer containing non-functionalized MWCNTs.

*\*\*\*\*Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.*

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