

Covalent Functionalization of Carbon Nanotubes with Diisocyanate for Polyurethane Nanocomposites

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Introduction

Carbon nanotubes (CNTs) have a wide range of potential applications due to their unique mechanical properties, high aspect ratios, and electronic structures (1). Many of these applications require good dispersion and chemical reactivity of CNT in the polymer matrices. For effective stress transfer in nanocomposites, chemical functionalization so that covalent bonds are formed between the CNT and the polymer matrix is desired (2). This paper describes a novel method to covalently functionalize CNTs that bear terminated isocyanate (NCO) group. NCO-functionalized CNT (NCO-*f*CNT) is highly desirable, because NCO is very reactive towards hydrogen-active groups, such as OH, NH, which are common species in polymer matrices. The functionalization is based on COOH-NCO chemistry, using a diisocyanate molecule in which one NCO has a higher reactivity than the other. By controlling the reaction parameters such as catalyst, temperature, etc., the higher reactive NCO group is allowed to react with COOH groups on CNTs, while the less reactive NCO group is not consumed and available for further reactions. Both NCO-functionalized single-wall CNT (NCO-*f*SWCNT) and multi-wall CNT (NCO-*f*MWCNTs) have been prepared. Fourier transform infrared (FTIR) spectroscopy and thermogravimetric (TGA) results showed that the functionalized CNTs bear a substantial amount of organic molecules and free NCO groups.

Materials and Experimental Procedures

Materials: SWCNTs and MWCNTs were from commercial sources. The diisocyanate used for functionalization was isophorone diisocyanate (IPDI), whose chemical structure is included in Figure 1. One important characteristics of this aliphatic diisocyanate is the reactivity of one NCO group (attached to the primary carbon) is 5 to 10 times more reactive than the other (attached to the secondary carbon) (3). 4,4 diphenylmethane diisocyanate (MDI) in which the two

NCO groups have similar reactivity was also used for comparison. Dibutyl amine and a polyether polyol were selected for studying the reactivity of NCO-*f*CNTs. Reagent grade acetone and dibutyltin laurate were used as the solvent and catalyst, respectively. Anhydrous, spectroscopic-grade KBr powder was used to prepare pellets for FTIR measurement. All chemicals were from commercial sources.

NCO Functionalization: the steps and conditions used to prepare NCO-*f*CNTs is illustrated in Figure 1. The first step was the preparation of COOH-*f*CNTs. This was accomplished by sonicating (at 55 kHz) CNTs in HNO₃ solutions (9.5 mol/l and 2.6 mol/l for MWCNT and SWCNT, respectively) for 1 h, followed by 24 h reflux with constant stirring at 125 °C. The suspended CNTs were then filtered, washed thoroughly with distilled water until the filtrate had a pH 5, and finally dried in vacuum at 70 °C for 24 h. This oxidation method can generate COOH groups on both side walls and ends of the CNTs (2).

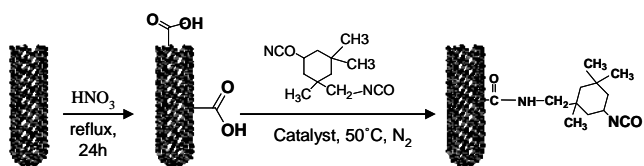


Figure 1. Steps and conditions used for preparation of NCO-*f*CNTs.

The NCO functionalization was carried out by placing appropriate amount of COOH-*f*CNTs in a three-neck flask containing catalyst and acetone. After sonicating for 20 min, IPDI was added to the flask, followed by refluxing for 7 h at 50 °C under N₂ atmosphere. After cooling down 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 two times to ascertain that most of the physically-sorbed and excess IPDI molecules have been removed from the functionalized materials.

Characterization of NCO-fCNTs: Functionalized CNTs were characterized by transmission FTIR (T-FTIR) and TGA techniques. The latter provides quantitative information about amount of IPDI molecules attached to CNTs. For T-FTIR measurement, KBr pellets containing 0.075% CNTs and having a thickness of 1 mm were prepared in vacuum. All pellets were carefully made using the same protocol. TGA measurements were conducted in nitrogen from 25 °C to 800 °C at a heating rate of 10 °C/min. The measurement uncertainties were $\pm 2 \text{ cm}^{-1}$ wavenumber and $\pm 1 \%$ absorbance for the T-FTIR and $\pm 1 \text{ °C}$ and $\pm 2 \%$ mass change for the TGA.

Results and Discussion

The NCO-functionalization method described here is based on the availability of COOH groups on the CNT surface. Therefore, the efficacy of oxidation by HNO_3 treatment is crucial. Figure 2 shows T-FTIR spectra of SWCNT and MWCNT before and after oxidation under HNO_3 . The spectrum of a CNT-free KBr pellet is also included for aid in the interpretation. KBr shows two bands near 1625 cm^{-1} and 3400 cm^{-1} , due to OH bending and OH stretching, respectively, of the adsorbed water on KBr. As-received SWCNTs or MWCNTs show a characteristic IR band near 1582 cm^{-1} , assigned to -C=C- groups (4), and a very broad, unassigned band extending from 950 cm^{-1} to 1300 cm^{-1} . After HNO_3 treatment, a prominent, broad band appears near 1723 cm^{-1} , which is due to carboxyl C=O , and the intensity of the band near 1245 cm^{-1} , assigned to C-O , increases markedly. These results suggest that a substantial amount of COOH has been formed on the CNT surfaces.

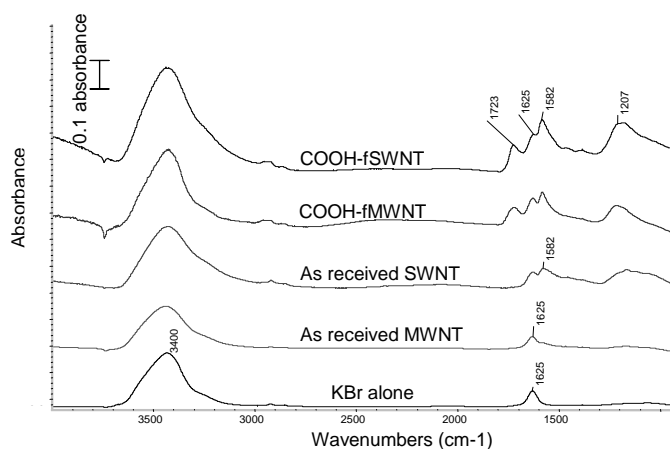


Figure 2. T-FTIR spectra of SWCNT and MWCNT before and after HNO_3 treatment; T-FTIR spectrum of KBr material is also given.

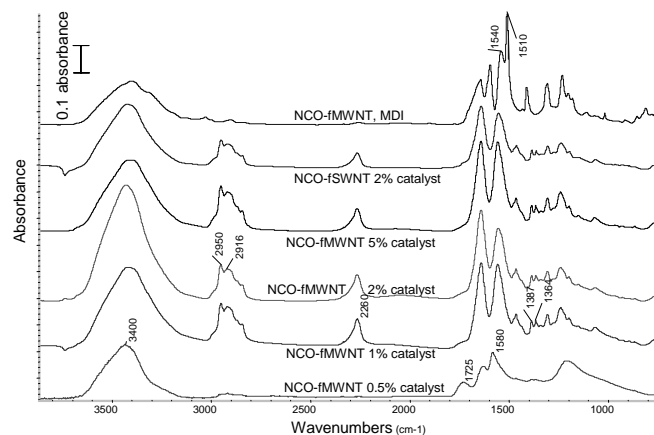


Figure 3. FTIR spectra of NCO-fMWCNT prepared using IPDI at different catalyst levels, NCO-fSWCNT at 2 % catalyst, and NCO-fMWCNT using MDI.

Figure 3 shows T-FTIR spectra of NCO-fMWCNT prepared with IPDI at different catalyst levels, NCO-fMWCNT prepared with MDI monomer, and NCO-fSWCNT functionalized with IPDI at 2 % catalyst. The incorporation of IPDI materials in the CNTs can be clearly seen by the bands at 2260 cm^{-1} , due to NCO, at 1387 cm^{-1} and 1364 cm^{-1} , due to gem-dimethyl groups, and in the CH stretching region between 2800 cm^{-1} and 3000 cm^{-1} . However, the formation of covalent bonds between the COOH-fCNTs and the diisocyanate molecules may only be ascertained by the intensity decrease of the carboxyl C=O band at 1723 cm^{-1} . The intensity decrease is due to the loss of the COOH through the reaction: $\text{R-NCO} + \text{R}'\text{COOH} \rightarrow \text{RNHCOR}' + \text{CO}_2$ with the formation of a secondary amide. The absence of the NCO and CH bands of functionalized CNTs prepared at 0.5 % catalyst observed in Figure 3, or without catalyst (not shown), indicates that little amount of IPDI was attached to CNTs at the low level or absence of catalyst. This assertion is strongly supported by the TGA data shown later.

Had the two NCO groups in the diisocyanate monomer have similar reactivity and been free of steric hindrance, both should react equally with COOH groups on CNTs, and there are no free NCO groups in the functionalized materials. This is clearly seen in the spectrum of NCO-fMWCNT using the MDI monomer (Figure 3, top spectrum). This spectrum shows little evidence of the NCO band at 2260 cm^{-1} but high intensities of the benzene ring at 1510 cm^{-1} and CH_2 at 1460 cm^{-1} . This FTIR result, together with TGA data which revealed a 60 % mass loss (not shown), indicates that the MDI monomer has been attached to the CNTs. Figure 3 results confirm the strategy used in this study; that is, in order to effectively functionalize CNTs that bear terminated

NCO groups, the two NCO groups in the diisocyanate monomer should have different reactivity.

The amount of IPDI loading on the CNTs can be estimated by TGA method, as illustrated in Figure 4, which shows results for SWCNTs and MWCNTs before and after NCO functionalization. A TGA curve of the COOH-fMWCNT is also included for comparison. In general, as-processed CNTs do not lose any significant amount of mass below 600 °C. However, COOH-fMWCNTs and NCO-fMWCNTs start to lose mass at relatively low temperatures. For example, COOH-fCNTs have a 5 % mass loss (due to CO₂ decomposition) at 300 °C. For NCO-fMWCNTs or NCO-fSWCNTs prepared with 2 % catalyst, the loss initiates at approximately 220 °C with a maximum mass loss of nearly 70 % at 320 °C. This loss is due to the amount of IPDI attached to the CNTs.

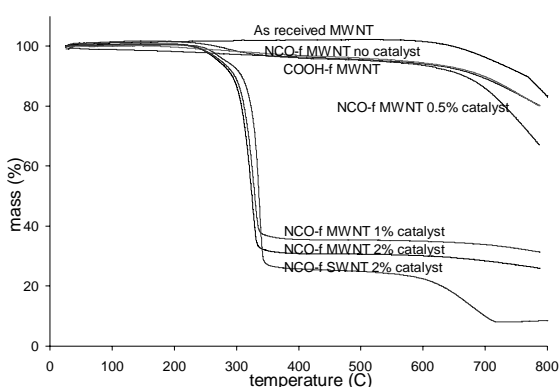


Figure 4: TGA curves of unfunctionalized and functionalized CNTs.

Assuming that only the primary NCO groups were reacted with COOH to form an amide linkage between the CNTs and IPDI, a 70 % mass gained in NCO-fCNT translates to a 13.8 % free NCO in the CNTs (for comparison, IPDI has an NCO content of 37.5 %).

Comparing TGA results of COOH-fCNTs and NCO-fCNTs made in the absence or with 0.5 % catalyst with NCO-fCNTs prepared at 1 % or 2% catalyst (Figure 4) clearly indicates that most of the mass loss is due to IPDI material covalently bonded to the CNTs. If IPDI molecules were attached to the CNTs solely by physical adsorption or trap in the bundles, they would be readily removed by washing, as can be observed in the 0.5 % and without catalyst samples.

The results presented above clearly show that this functionalization method is effective for preparing CNTs that form covalent bonds with the diisocyanate molecule and providing CNTs with terminated NCO groups. One question that needs to be addressed is the reactivity of the terminated secondary NCO group.

Examples of the reactions between the NCO-fMWCNTs with two hydrogen-active compounds are illustrated in the FTIR spectra given in Figure 5. The reaction is best observed by the intensity decrease of the NCO band at 2260 cm⁻¹. It shows a complete loss of this band in dibutyl amine and a small residual peak under polyether polyol after 4 h reaction. These results suggest that the reaction was quite fast with amine at room temperature, but slow for polyether polyol even in the presence of catalyst and at elevated temperature.

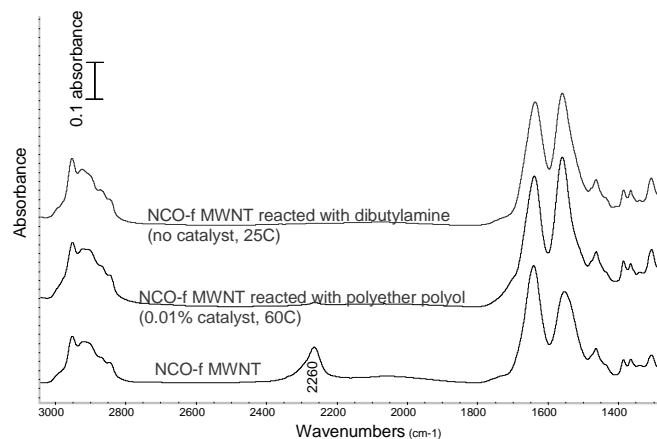


Figure 5. T-FTIR spectra of NCO-fMWCNTs after reacting with a polyether polyol and dibutyl amine (reaction time was 4 h for both compounds).

Conclusions

FTIR and TGA results have clearly shown that an effective method for covalently functionalizing CNTs bearing terminated NCO groups has been developed. The functionalization is based on the use of a diisocyanate molecule in which one NCO group is more reactive than the other. Since NCO is very reactive towards a variety of molecules, the addition of NCO-fCNTs in polymer matrices would potentially increase the CNT-polymer interfacial bonds and improve the stress transfer in polymer/CNT composites.

References

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