# Polyurethane Nanocomposites Containing NCO-Functionalized Carbon Nanotubes and NCO-Functionalized Nanoclays

**T. Nguyen, B. Pellegrin, A. Granier, and J. Chin**
**National Institute of Standards and Technology, Gaithersburg, MD, USA**
**Email: tinh.nguyen @nist.gov**

## ABSTRACT

We have developed an effective method to covalently functionalize CNTs and nanoclays that carry free isocyanate (NCO) groups, which readily form covalent bonds with polymer matrices containing hydrogen–active groups. The functionalization employs a diisocyanate molecule in which the two end NCO groups have different reactivities. By controlling the reaction conditions, the more reactive NCO groups form covalent bonds with hydrogen-active species on the nanoparticles surface, while the less reactive NCO groups are available for reacting with the polymers. Mechanical properties and photodegradation under UV radiation of an acrylic polyurethane (PU) containing NCO-functionalized (*f*) (MWCNTs and nanoclays) have been evaluated. Tensile moduli of composites containing NCO-*f* nanopartciles are much higher than those without or with unfunctionalized nanomaterials. The incorporation of functionalzed or unfunctionalized MWCNTs at 1 % mass fraction appears to stabilize the degradation of PU under UV light, but clay nanoparticles even at 5 % mass fraction have no effect on the UV resistance of this polymer. The results show that NCO-*f*(MWCNTs and nanoclays) greatly enhance the stress transfer efficiency of acrylic polyurethanes.

*Keywords*: nanocomposites, NCO, functionalization, polyurethane, nanotubes, nanoclays

## 1 INTRODUCTION

Carbon nanotubes (CNTs) and nanoclays are being studied intensively as the ultimate reinforcing materials for polymeric composites because of their exceptional mechanical properties and high aspect ratio. For this application, the nanofillers must be well dispersed in the polymer matrix and/or form strong interfacial bonds to effectively transfer load from the matrix to the nanofillers. To meet these requirements, considerable effort has been devoted to chemically functionalize these materials (1-4). We have developed a method to covalently attach an organic molecule to the MWCNTs and nanoclays surfaces that carry free isocyanate (NCO) groups. Such functionalized nanoparticles are highly desirable because NCO is very reactive towards hydrogen-active species such as OH, NH, and COOH, which are common in synthetic and natural polymers. The uniqueness of this functionalization method is the use of a diisocyanate

molecule containing two end NCO groups that have different reactivities. By controlling the reaction conditions, the more reactive NCO groups will form covalent bonds with hydrogen-active species on CNTs and nanoclays surfaces, while the less reactive NCO groups will be available for reacting with the polymer matrices of interest. Further, since the diisocyanate molecule contains a large hydrocarbon chain, this functionalization would lead to better dispersion of nanoparticles in polymers. For polyurethane (PU) nanocomposites, it is expected that the NCO-terminated nanofillers will react readily with the polyol component during curing to form covalent bonds (urethane linkages) between the matrix and the nanofillers. This should increase the load transfer efficiency of PU/CNTs and PU/nanoclays composites. This paper reports on the mechanical and photodegradation performance of an acrylic urethane containing NCO-*f*(MWCNTs and nanoclays).

## 2 EXPERIMENTAL

### 2.1 Materials

Multi-walled nanotubes (purity > 95%, diameter 10-30 nm, length 0.5-40 μm, and synthetic nanoclays (Laponite, chemical compositions in mass fraction: 66.2 % $SiO_2$, 30.2 % MgO, 2.9 % $Na_2O$, and 0.7 $Li_2O$) were obtained from commercial sources. Isophrone diisocyanate (IPDI) was used for the NCO functionalization. One particular characteristics of this diisocyanate is one NCO group is substantially more reactive than the other (5). Dibutyltin dilaurate was used as the catalyst. The polymer matrix was an acrylic polyurethane typically used in automobile coatings, consisting of an acrylic polyol and a biuret hexamethylene tri-isocyanate. After curing, this PU forms a crosslink network. Anhydrous acetone and ethylene glycol dimethyl ether (DME) were used as the solvents for the functionalization of CNTs and nanoclays, respectively. Anhydrous reagent grade acetone was used for composite processing.

### 2.2 NCO Functionalization of MWCNTs and Nanoclays

The procedure used to functionalize MWCNTs and nanoclays that carry terminal NCO groups is summarized in the schemes shown in Figs. 1a and 1b. More complete descriptions of the functionalization are given elsewhere

(6,7). Since the covalent functionalization requires that hydrogen-active species must be present in the nanoparticles, MWCNTs were first oxidized to generate COOH groups on their surface (COOH-*f*MWCNT) by sonicating and refluxing as-received MWCNTs (AR-MWCNT) in 9.5 mol/l HNO$_3$ solution for 1 h, followed by 24 h reflux with constant stirring at 125 °C. The suspended CNTs were then filtered, washed thoroughly with water and dried in vacuum. This procedure produced about 4.5 % mass fraction of COOH groups on the surface of CNTs. For nanoclays, surface SiOH species serve as the reactive sites for the functionalization. Because of its pellet structure, nanoclays were first exfoliated to increase the number of reactive sites before functionalization. This was accomplished by sonicating clay nanoparticles in DME for 30 minutes, followed by refluxing at 85 °C for 4 h under constant stirring.
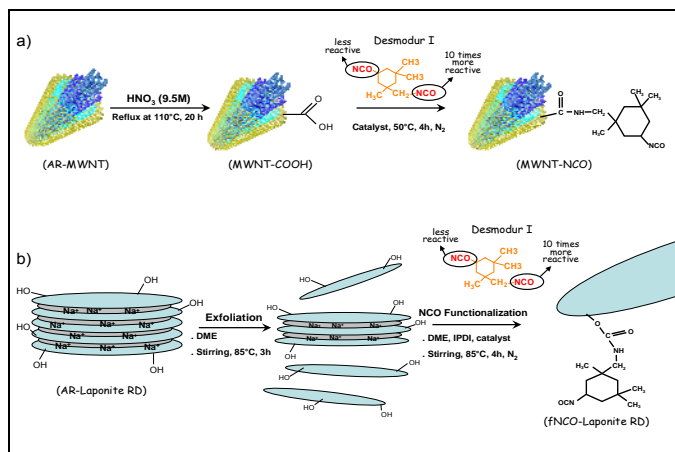


Figure 1. Steps and conditions used for NCO functionalization of MWCNTs (a) and nanoclays (b).

The NCO functionalization was carried out by placing COOH-*f* CNTs or DME-containing exfoliated nanoclays in a three-neck flask containing appropriate amounts of dibutyltin dilaurate catalyst and solvents (acetone for CNTs and DME for nanoclays). The suspension was heated for an period of time (50 °C and 7 h for CNTs and 85 °C and 4 h for nanoclays), under constant stirring and N$_2$ atmosphere. As shown in the schemes, amide linkages are generated between the diisocyanate (IPDI) molecule and the COOH-*f*CNTs, and these bonds may be formed on both the sidewalls and ends of the carbon nanofillers, because the COOH groups could be generated on both locations (8). On the other hand, urethane bonds are formed between the IPDI and clay nanoparticles. After cooling to room temperature, NCO-*f*(MWCNTs and nanoclays) were filtered, sonicated in acetone for 1h, and washed with acetone. These steps were repeated at least three times to ensure that most of the physically-sorbed and excess IPDI molecules have been removed from the functionalized

materials. After drying in a vacuum oven at 70 °C for 12 h, the functionalized materials were stored in N$_2$ at 4 °C until use.

## 2.3 Preparation of Polyurethane Nanocomposites

PU nanomposites were fabricated at 0.5, 1, and 2 % mass fraction loadings for MWCNTs and at 0.5, 1 and 5% loadings for nanoclays. The amounts of nanofillers added to the matrix were based on the effective mass of the nanoparticles, which were obtained by thermogravimetric analysis (TGA). In addition to NCO-*f*(MWCNT and nanoclays), composites containing AR (MWCNT and nanoclays) were also made for comparison. PU/MWCNT and PU/nanoclay composites were prepared using NCO:OH ratios of 1.3:1 and 1:1, respectively.

Figure 2 illustrates the steps and conditions used for preparation of PU/MWCNT and PU/nanoclay composites. Nanofillers were first sonicated in large amount of anhydrous acetone for 2 h. After adding polyol, the nanofiller suspensions were stirred and sonicated for an additional 1 h using an 80 KHz tip sonicator. The suspension was then subjected to high shear mixing at 210 rad/s (2000 rpm) for 30 min at room temperature (24 °C) to further break up nanofillers aggregations. The triisocyanate component was then added to the suspension and stirred at 315 rad/s (3000 rpm) for another hour. After degassing for 1 h at room temperature, the mixture was placed on a release paper and drawn down using an applicator. All coated films were cured at ambient conditions (24 °C and 45 % RH) for 4 days, followed by post-curing for 4 h at 130 °C in an air-circulating oven. FTIR analysis showed no further decrease of the NCO band intensity at longer curing times. All cured films had a thickness between 75 μm and 100 μm.
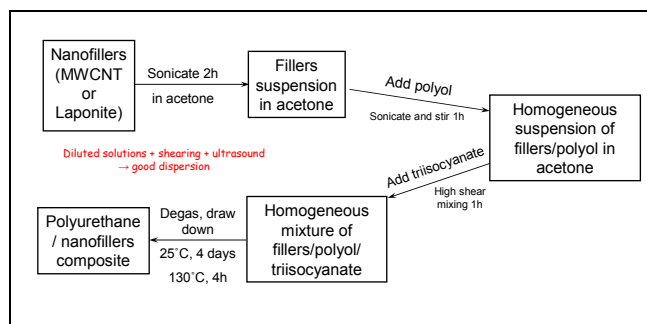


Figure 2. Steps and conditions used for preparation of PU/MWCNT (a) and PU/nanoclay (b) composites.

## 2.3 Characterization of NCO-*f*(MWCNTs and Nanoclays) and Polyurethane Nanocomposites

NCO-functionalized nanoparticles were characterized by transmission Fourier transform infrared (FTIR)

spectroscopy and TGA; the latter can provide the amounts of IPDI attached to the nanofillers. Tensile modulus, tensile strength, elongation at break, and glass transition temperature ($T_g$) of PU nanocomposites were measured by Dynamic Mechanical Thermal Analysis (DMTA). The mechanical properties were measured on 45 mm x 5 mm samples (thickness was measured for each sample) with an extension rate of 0.02 mm s$^{-1}$. $T_g$ was obtained on 30 mm x 10 mm samples at 5 Hz and 0.1 % strain, from 30 °C to 170 °C. $T_g$ was taken as the maximum of the tan δ curve. At least five samples were analyzed for each composite. The standard deviations of the mechanical properties and $T_g$ were ± 10 % and ± 1 %, respectively. The UV resistance of PU and its nanocomposites were investigated using a 2 m integrating sphere-based weathering device, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) (9). This device utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m$^2$ in the 290 nm to 450 nm range. This device can also precisely control the relative humidity and temperature. In this study, film samples of 2 cm x 2 cm μm were exposed in the SPHERE UV chamber at 50 °C and 70 % relative humidity. They were removed at specified time intervals for photodegradation measurement using FTIR in the attenuated total reflection mode (FTIR-ATR).

## 3  RESULTS AND DISCUSSION

### 3.1 Mechanical Properties of PU Composites Containing NCO-*f*(MWCNTs and Nanoclays)

FTIR and TGA results clearly showed that this approach is effective for covalently attaching IPDI monomer to the CNTs (both SWCNTs and MWCNTs) and nanoclays (6,7). We have also demonstrated that if the two or three end NCO groups in the di or triisocyanate molecules have the same reactivity such as diphenylmethane 4,4'-diisocyanate (MDI), no free NCO groups are observed (6). Therefore, such isocyanate molecules are not suitable for the NCO functionalization. NCO-f(MWCNTs and nanoclays) have been prepared, and the performance of PU composites containing these functionalized materials has been evaluated. Figures 3a and 3b show the effects of 1 % mass fraction loading of NCO-*f*(MWCNTs and nanoclays) on mechanical properties and $T_g$ of PU. Results for unfilled PU and composites containing AR(MWCNT and nanoclays) are included for comparison.

The addition 1 % mass fraction of both unfunctionalzied and functionalized (MWCNTs and nanoclays) substantially increases the modulus of PU. However, NCO-functionalized materials have a greater influence. For example, the modulus increases nearly 40 % and 65 % after incorporating 1 % NCO-*f*MWCNTs and NCO-*f*nanoclays, respectively, but only 23 % and 42 % for the corresponding unmodified nanoparticles. On the other

hand, the addition of NCO-*f*nanoparticles decreases the elongation at break of both types of nanocomposites, with NCO-*f*MWCNTs appear having a greater effect. Figure 3 shows little effect of unfunctionalized or functionalized (MWCNT or nanoclays) on $T_g$ of PU. The modulus increase with NCO-*f*(MWCNTs and nanoclays) suggests that this functionalization is effective in improving the stress transfer in these PU nanocomposites.
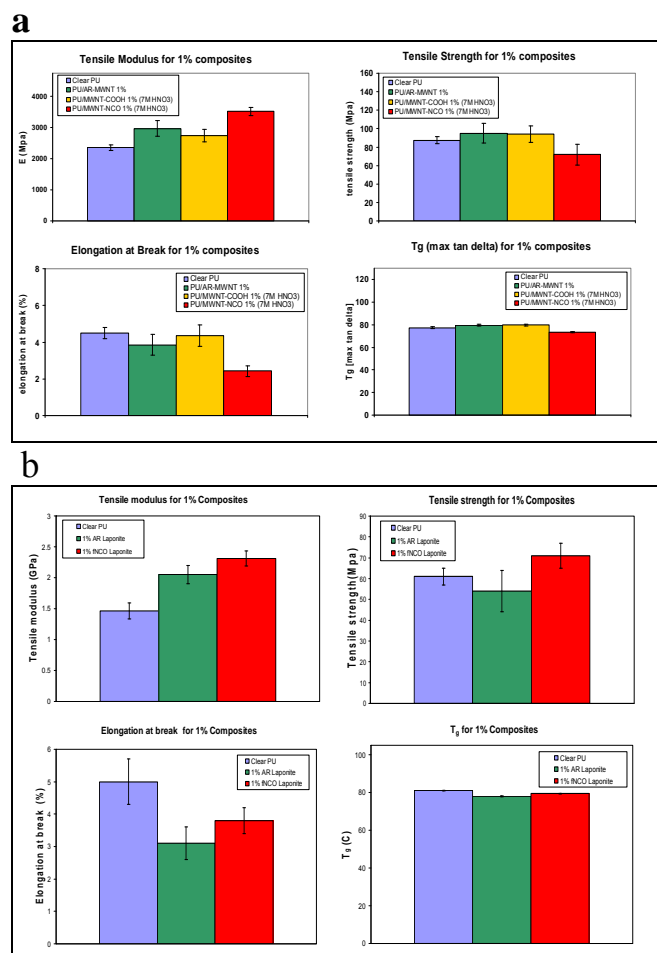
Figure 3. Tg and mechanical properties of NCO-*f*MWCNT (a) and NCO-*f*nanoclay (b) composites. Results of unfilled and PU filled with unfunctionalized nanoparticles are included for comparison.

### 3.2  Photodegradation of PU Composites Containing NCO-*f*(MWCNT and Nanoclay)

The effects of NCO-*f*(MWCNTs and nanoclays) on UV resistance of PU are displayed in Figs. 4a and 4b. This figure presents relative changes of the 1520 cm$^{-1}$ band (NH group) of the PU film with and without 1 % mass fraction of NCO-functionalized and unfunctionalized (MWCNTs and nanoclays) as a function of time exposed in the SPHERE UV chamber. A decrease of the 1520 cm$^{-1}$ band

intensity is attributed to an increase in the chain scission of the PU polymer. The intensity changes have been normalized to both the initial absorbance and that of the least-changed band (1172 cm$^{-1}$, due to C-O) to minimize the effects due to thickness differences between samples and contact variations by the ATR probe on the sample. The identification of the least-changed band was provided by a transmission FTIR analysis on a 7 μm thick film on a CaF$_2$ substrate exposed to the same UV/RH/temperature conditions. As seen in this figure, adding 1% mass fraction of unfunctionalized or NCO-*f*MWCNT in PU greatly enhances the UV resistance of this polymer. The reason for the adverse effect on photodegradation by the AR-MWCNTs at 2 % mass fraction loading is unknown and being investigated. The addition of nanoclays, functionalized or unfunctionalzied, even at 5% loading, has little effect on the UV resistance of this PU.
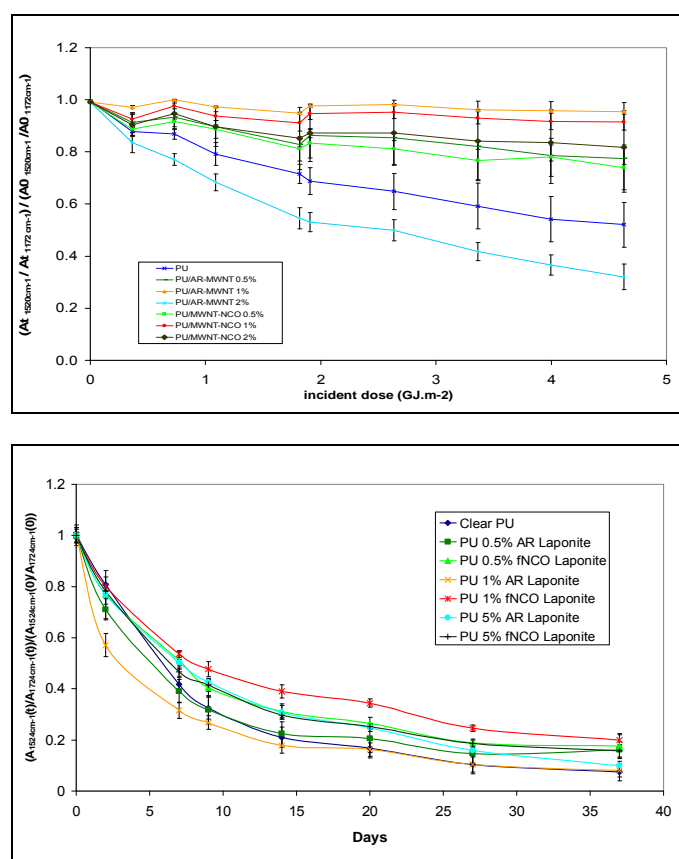


NCO groups, which can readily form covalent bonds with polymer matrices that contain hydrogen active species. Iincorporation of functionalized or unfunctionalized MWCNTs at 1 % mass fraction appears to stabilize the degradation of PU under UV light, but nanoclays even at 5 % mass fraction loading have no effect on the UV resistance of this polymer. The results show that NCO-*f*(MWCNTs and nanoclays) substantially increase the modulus and enhance the stress transfer efficiency of acrylic polyurethanes.

## 5 REFERENCES

1.  S. B. Sinnott, Chemical Functionalization of Carbon Nanotubes, *J. Nanosci. Nantech.*, 2 (2002) 113-123.
2.  K. Balasubramanian and M. Burghard, Chemically Functionalized Carbon Nanotubes, *Small,* 1 (2005) 180-192.
3.  M. Park, I.K. Shim, E.Y. Jung, J.H. Choy, Modification of external surface of Laponite by silane grafting, *J. of Phys. & Chem. Solids,* 65 (2004):499-501.
4.  N.N. Herrara, J.M. Letoffe, J.P. Reymond, E. Bourgeat-Lami, Silylation of Laponite clay particles with monofunctional and trifunctional vinyl alkoxysilanes, *J. Mater. Chem.,* ,15 (2005) 863-871.
5.  O. Lorentz, H. Decker, G. Rose, *Angew Makcromol. Chem.,* 122 (1984) 83.
6.  A. Granier, T. Nguyen, N. Eidelman, J. Martin, *Proc, Adhesion Society Meeting,* 2007, p. 346.
7.  B. Pellegrin, A. Granier, and T. Nguyen, *Proc Adhesion Society Meeting,* 2008, p.199.
8.  B. Zhao, H. Hu, E. Bekyarova, M. Itkis, S. Niyogi, R. Haddon, Carbon Nanotubes: Chemistry, *Dekker Encyclopedia of Nanoscience and Nanotechnology,* 2004, pp 493-505.
9.  J. Chin, E. Byrd, N. Embree, J. Garver, B. Dickens, T. Fin, and J. W. Martin, Accelerated UV Weathering Device Based on Integrating Sphere Technology, *Review Scientific Instruments,* 75 (2004) 4951-4959.

Figure 4. FTIR intensity changes as a function of time exposed to UV light for PU/NCO-*f*MWCNT (a) and PU/NCO-*f*nanoclay (b) composites. Results of unfilled and PU filled with unfunctionalized nanoparticles are included for comparison.

## 4 CONCLUSION

We have developed an effective method to covalently functionalize (CNTs and nanoclays) that carry terminal