# Chemical Modification of Single-Walled Carbon Nanotubes for the Reinforcement of Precursor-Derived Ceramics

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Single-walled carbon nanotubes (SWNTs) were incorporated into precursor-derived ceramics made from a polysilazane. To improve the dispersion of the nanotubes in the liquid precursor and finally in the ceramic matrix, the SWNTs were chemically modified by (iodomethyl)trimethylsilane via a radical reaction. The functionalization degree of the modified SWNTs was determined to be 3 atom %. Microscopic investigation combined with viscosity measurements and thixotropy tests demonstrated that the functionalized SWNTs are more homogeneously dispersed in the liquid SWNT/polymer mixtures and the solid cross-linked precursor, as compared to pristine nanotubes. SWNT/Si-C-N ceramics with nanotube contents of up to 1 wt % were obtained through pyrolysis of cross-linked SWNT/polymer composites at 1000 °C. The presence of intact nanotubes in these composites could be verified by scanning transmission electron microscopy. The high viscosity of the SWNT/polysilazane mixtures was identified as an important prerequisite for attaining good nanotube dispersion in the Si-C-N matrix.

#### Introduction

Carbon nanotubes have attracted strong attention since their discovery<sup>1</sup> owing to their excellent mechanical, electrical, and thermal properties. Incorporation of carbon nanotubes into polymeric,<sup>2–4</sup> metallic,<sup>5,6</sup> or ceramic<sup>7,8</sup> matrices has enabled to improve substantially their mechanical performance and implement useful thermal, electrical, or optical properties. In particular, mechanical studies of multiwalled carbon nanotubes (MWNTs)/Si–C–N composites reveal a remarkable increase in the fracture toughness of the ceramics.<sup>9</sup> Several studies on polymer matrix composites have shown that the reinforcement by SWNTs is often superior to that achievable with MWNTs.<sup>2</sup> This difference is mainly due to the substantially higher surface area per unit mass of the SWNTs, which allows them a greater interaction with composite matrices. Toward the production of

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composites with a ceramic matrix, conventional powder-based ceramic processing techniques might disrupt the integrity of the nanotubes besides the difficulty in achieving a homogeneous dispersion of the nanotubes throughout the matrix. Such dispersion is particularly difficult to achieve for SWNTs as a consequence of a strong cohesive force between individual tubes that leads to formation of bundles and agglomerates. Accordingly, full exploitation of the benefit of SWNTs for reinforcement requires their chemical modification in order to facilitate separation of bundles into individual nanotubes. At the same time, the attached functional groups can provide a suitable interfacial bonding to ensure efficient load transfer between the matrix and the nanotubes. Chemical modification schemes<sup>10</sup> that have been successfully used for unbundling the nanotubes and tuning their interaction with the matrix<sup>2,11</sup> comprise the covalent attachment of alkyl<sup>12–14</sup> or aryl groups,<sup>15,16</sup> amines,<sup>17,18</sup> amino acids and biomolecules,<sup>19,20</sup> as well as polymers<sup>21</sup> like polystyrene,<sup>22</sup> poly(methyl methacrylate),<sup>23</sup> and polyimide.<sup>24</sup> Moreover, siloxane modification has been achieved via reaction of chlorosilanes with oxidized MWNTs,<sup>25,26</sup> and aminosilanes have been covalently linked to fluorinated SWNTs.27

An alternative approach to ceramics, which offers various advantages over powder processing for the task of producing

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nanotube-reinforced composites, involves polymer precursorbased routes. First, the inherent relatively low process temperature<sup>28</sup> could minimize or even avoid damage of the nanotubes. Second, nanotubes are easier to be dispersed by polymer processing methods than by powder-based ones. Moreover, the polymer processing combined with the nanometer size of SWNTs enables production of complex forms in small scales like in microelectromechanical devices.<sup>29</sup> However, the pronounced tendency of SWNT agglomeration within precursor-derived Si-C-N ceramics<sup>30</sup> necessitates further improvements with respect to tailoring the nanotube/nanotube as well as nanotube/matrix interactions. In this work, we develop a chemical modification method for SWNTs wherein the organosilicon compound (iodomethyl)trimethylsilane is linked via a free radical reaction 31-33 to the nanotube sidewall. Our strategy aims at exploiting the chemical similarity between the appended moieties and the polysilazane precursor for Si-C-N ceramics to facilitate tube dispersion and processing of the nanotube/precursor polymer mixture. As a further advantage, the attached Me<sub>3</sub>Si-CH<sub>2</sub> moieties do not introduce oxygen to the Si-C-N ceramic, in contrast to nanotubes bearing, for example, Si-O groups.<sup>31</sup>

### **Experimental Section**

**Chemicals and Materials.** Purified-grade HiPco SWNTs were purchased from Carbon Nanotechnologies, Inc. with sizes ranging from about 0.8 to 1.2 nm in diameter and 0.1 to 1  $\mu$ m in length. (Iodomethyl)trimethylsilane, benzoyl peroxide (BPO), anhydrous benzene, and ethanol were purchased from Aldrich. The liquid polyureasilazane (Ceraset) was obtained from KION (USA). THF and toluene were distilled from potassium before use.

**Purification of As-Received SWNTs.** According to the product sheet, the as-received nanotubes (1) contain up to 15 wt % of iron

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Figure 1. UV-vis-NIR spectra of the pristine (1) and chemically modified SWNTs (2) dispersed in THF.

catalyst and up to 5 wt % of organic impurities. A simple acid treatment and filtration procedure<sup>34</sup> was employed for their purification. To this end, a suspension of 700 mg of the as-received SWNTs in 70 mL of HCl (6 M) and 7 mL of ethanol was placed in a 100 mL glass bottle, bath sonicated for 15 min, followed by magnetic stirring for 2 h. The resultant mixture was centrifuged, and the yellow supernatant was decanted. This procedure was repeated until the centrifuged supernatant did not show any color. The mixture was then washed with distilled water until neutral condition was observed. Finally, the residue was filtered through a 0.2  $\mu$ m PTFE membrane, washed with ethanol, THF, and toluene, and dried in vacuum at 120 °C overnight.

**Functionalization of SWNTs with (Iodomethyl)trimethylsilane.** A 36 mg amount of pristine nanotubes (1) was suspended in 45 mL of dry benzene in a 100 mL three-necked round flask under argon atmosphere with the aid of bath sonication for 30 min. (Iodomethyl)trimethylsilane (9 mmol) and BPO (3 mmol) were added, and the mixture was magnetically stirred at 78 °C for 30 h. After cooling to room temperature, the suspension was filtered through a  $0.2 \,\mu$ m PTFE membrane, washed with ethanol and THF several times, and then dried in vacuum overnight at 80 °C. The functionalization degree (atomic ratio Si/C) of the modified SWNTs (**2**) was determined by EELS to be 3%.

**Preparation of Cross-Linked SWNT/Polysilazane Solid Composites.** The suspension of 2.5 g of Ceraset with 0.75 wt % of SWNTs (i.e., 18.8 mg of 1 and 23.5 mg of 2, where in the latter case the mass increase due to chemical modification is taken into account) in 40 mL of THF was sonicated for 1 h under argon atmosphere using a tip sonicator (SONOPLUS HD2200) with a cycle of 40% and an amplitude of 4. Removal of the THF by evaporation afforded a viscous SWNT/polysilazane mixture which was transferred into Teflon molds (18 mm in diameter and 1 mm in depth). After degassing in vacuum, the molds were tightly sealed by a set of metal dies and placed in a glass vessel under argon atmosphere. The cross-linking was performed by heating the mixture to 360 °C within 20 min and subsequent annealing at this temperature for 6 h, which yielded solid SWNT/polysilazane composite discs with diameters of ~18 mm.

**Preparation of SWNT/Si-C-N Ceramic Composites.** The cross-linked SWNT/polysilazane discs were ground with SiC sand paper of 1200 grit to the thickness of 0.57–0.63 mm and then pyrolyzed at 1000 °C for 1 h under argon atmosphere (heating rate of 10 °C/h). On the basis of the weight loss of the SWNT-free polysilazane during cross-linking and pyrolysis, the SWNT content

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Figure 2. Raman spectra of the pristine (1) and chemically modified SWNTs (2).



Figure 3. Mid-IR spectra of the pristine (1) and chemically modified SWNTs (2).

in the ceramic composites is estimated to be  $\sim 1.0$  wt %. Upon pyrolysis, the discs linearly contract by about 22.0% in thickness and 25.0% in diameter, resulting in a density of around 2.20 g/cm<sup>3</sup>. According to XRD analysis, the obtained samples are amorphous.

Characterization. Fourier transform infrared (FTIR) spectra were recorded from KBr pellets using a Nicolet spectrometer. The ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were acquired with a Varian Cary 50 spectrophotometer with samples being prepared by tip sonication of the SWNTs for 2-3 min in THF. Raman spectra were obtained with a laser Raman spectrometer (DILOR labram 010 microscope) equipped with a HeNe laser ( $\lambda_{exc}$ = 632.8 nm) and an air-cooled charge-coupled device (CCD) detector. Thermal gravimetric analysis with mass spectroscopic detection (TGA-MS) was carried out with a Netzsch STA 449C instrument. For this purpose, the samples were heated in argon atmosphere from 25 to 1000 °C at a heating rate of 10 °C/min. Viscosity and thixotropy measurements were performed close to room temperature (24 °C) with a Haake Stress 1 instrument using a cone/plate sensor system (C20/1° Ti). Controlled rate (CR) modes were applied to determine the steady viscosity. The rotational rate was increased stepwise with the samples being held at each rate for 60-300 s to ensure that an equilibrium stress had been reached. Thixotropy tests were performed in the CR mode with the rotational rate being linearly increased from 0 to 36 000 rpm within 120 s followed by a linear decrease to zero within 120 s. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6300F system. For analytical electron microscopy, a VG HB501UX scanning transmission electronic microscope (STEM) operated at 100 keV was used. This microscope was equipped with an electron energy-loss spectrometer (Gatan UHV Enfina) and an energydispersive X-ray (EDX) system (Thermo Fischer Scientific, Noran SIX).



**Figure 4.** TG-DTG curves of the pristine (1) and chemically modified SWNTs (2) recorded under argon with a heating rate of 10 °C/min.



Figure 5. Ion current vs temperature measured in the course of TGA-MS analysis of the pristine (1) and chemically modified SWNTs (2) under argon using a heating rate of 10  $^{\circ}$ C/min.

## **Results and Discussion**

1. Chemical Modification of SWNTs. UV-Vis-NIRSpectroscopy. In Figure 1, UV-vis-NIR absorption spectra of 1 and 2 suspended in THF are displayed. The pristine nanotubes (1) exhibit distinguished absorption features<sup>35</sup> typical of HiPco nanotubes obtained by the catalytic decomposition of carbon monooxide.<sup>36</sup> While the bands in the range of 440-645 nm correspond to the v1  $\rightarrow$  c1 transition of the metallic nanotubes, the bands in the ranges from 600 to 800 nm and 830 to 1600 nm, respectively, belong to the v2  $\rightarrow$ c2 and v1  $\rightarrow$  c1 transitions of the semiconducting nanotubes.

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**Figure 6.** (a) Bright-field and (b) high-angle annular dark-field (HAADF) STEM images of the modified nanotubes (2). (c) Dark-field and (d) HAADF-STEM images of a corresponding bundle. EELS spectra of a typical area  $(20 \times 24 \text{ mm}^2 \text{ size})$  recorded in the energy range of the Si-L<sub>2,3</sub>, C-K edges (e) and the O-K edge (f). Note that the intensity scale for f is reduced by a factor of 10 compared to e.

The disappearance of these absorption features after chemical modification (2) testifies the successful attachment of Me<sub>3</sub>Si-CH<sub>2</sub> groups which disrupt the  $\pi$  conjugation of the nanotubes.<sup>31</sup>

*Raman Spectroscopy.* The Raman spectra of 1 and 2, depicted in Figure 2, comprise four relevant features:<sup>37</sup> (a) the radial breathing modes (RBMs) between 150 and 300 cm<sup>-1</sup>, (b) the tangential stretch G band below 1600 cm<sup>-1</sup>, (c) the disorder-induced D band at 1310 cm<sup>-1</sup>, and (d) the G' band near 2600 cm<sup>-1</sup> (overtone of the D band). The Raman spectrum of the starting material (1) with a D band of very low intensity is characteristic of nanotubes containing a low density of defects. The reaction of the nanotubes with (iodomethyl)trimethylsilane leads to a substantial increase in the D/G band intensity ratio (from 0.08 to 0.50), indicative of covalent side-wall modification.<sup>38</sup> At the same time, observation of well-defined RBM peaks after modification proves that the basic tube structure remains largely intact.

*FTIR Spectroscopy.* The mid-IR spectrum (Figure 3) of the modified tubes (2) confirms the presence of organic silane groups. In contrast to the essentially featureless FTIR spectrum of the pristine nanotubes (1), the modified SWNTs (2) exhibits two absorptions at 1260 and 801 cm<sup>-1</sup>, which can be attributed to the presence of Si-CH<sub>3</sub> motives.<sup>31</sup> Moreover, broad band in the range of 1000-1200 cm<sup>-1</sup> may arise from the bending and rocking modes of the methyl groups or Si-C bond.

TGA-MS Analysis. Further evidence for the covalent functionalization of SWNTs was gained from TGA coupled with online monitoring of the volatile products by mass spectroscopy (MS). As apparent from the TG–DTG curves in Figure 4, the pristine nanotubes (1) exhibit a noticeable weight loss of 10% upon heating to 1000 °C, which most likely originates from noncovalently bonded adsorbates. In comparison, the modified tubes (2) show a significantly larger weight loss of 30% in the same temperature range. It is thus concluded that the covalently appended groups in 2 are responsible for a weight loss of 20%, from which a functionalization degree of  $\sim$ 3% is calculated. Mass spec-

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Figure 7. Shear viscosity of pure polysilazane, 1/polysilazane, and 2/polysilazane.



Figure 8. Thixotropy test curves of pure polysilazane, 1/polysilazane, and 2/polysilazane.

troscopy revealed the evolution of  $H_2^+$  (*m*/*e* 2),  $CH_3^+$  (*m*/*e* 15),  $CH_4^+$  (*m*/*e* 16, not shown here; same position and shape as *m*/*e* 15), and  $C_2H_6^+$  (*m*/*e* 30) from the modified tubes (2), as can be discerned from Figure 5.

In order to determine the extent to which the radical initiator BPO itself leads to covalent modification of the nanotubes, pristine SWNTs were subjected to the same reaction conditions, however, without addition of (iodomethyl)trimethylsilane. The sample obtained in this manner exhibited a major weight loss at 435 °C associated with evolution of benzene and carbon monoxide and a second strong and sharp weight loss at 895 °C with concomitant evolution of carbon monoxide (data not shown). The total weight loss amounted to 30%, indicating a similar extent of reaction between the nanotubes and radicals formed from the BPO as for the reaction between the nanotubes and (iodomethyl)trimethylsilane in the presence of BPO. While addition of organic peroxide-derived radicals to SWCNTs has been reported previously,<sup>39</sup> it is an interesting observation that the two reactions do not occur simultaneously. Obviously, the radicals generated from BPO react faster with (iodomethyl)trimethylsilane than with the nanotube sidewall.

STEM-EELS Analysis. The chemical functionalization extent of the SWNTs was also determined by EELS



**Figure 9.** Optical micrographs of cross-linked discs of **1**/polysilazane and **2**/polysilazane with an approximate diameter of 18 mm.

investigation. In Figure 6, the typical morphology of the modified nanotubes **2** (Figure 6a and 6b) is shown. The Si- $L_{2,3}$ , C-K, and O-K edge spectra collected from the bundle in Figure 6c and 6d are presented in Figure 6e and 6f. From these follows a Si/C atomic ratio between 0.02 and 0.04, in good agreement with the 3 atom % functionalization degree derived by TGA analysis. For the O/C atomic ratio, a value below 2 atom % has been determined, which is evidence of a small reaction extent between the nanotubes and benzoylperoxo radicals formed from BPO.

2. Viscosity and Thixotropy of SWNT/Polysilazane Mixtures. The rheological properties of filled polymer systems are influenced by particle-matrix and particle-particle interactions, by the dispersion state of particles, as well as by the shape and orientation of dispersed particles.40,41 Therefore, rheology is a powerful technique for studying the dispersion of fillers in liquid or melt matrix. It has been reported that a better dispersion of nanotubes in polymers results in higher shear viscosities of the corresponding nanocomposites.<sup>42,43</sup> The results of the shear viscosity and thixotropy measurements on the 1/polysilazane and 2/polysilazane mixtures are shown in Figure 7 and 8, respectively. The pure polysilazane behaves like a typical Newton fluid within a wide shear rate range without noticeable thixotropy and shear thinning. Upon incorporation of the pristine or modified SWNTs, the viscosity is seen to increase especially at low shear rates and a shear-thinning behavior emerges, in analogy to observations made on liquid or melt polymer/ SWNTs composites.<sup>40,43</sup> Both samples containing nanotubes exhibit hysteresis, which is more pronounced in the case of 2/polysilazane. The thixotropy values obtained for pure polysilazane, 1/polysilazane, and 2/polysilazane are 470, 3970, and 12100 Pa/s, respectively.

Owing to their high aspect ratio and the strong tube-tube interaction, dispersed SWNTs are able to form a network superstructure,<sup>40,44</sup> which imparts some solid-like behavior, in particular at low shear rates or low oscillation frequencies. It is furthermore apparent that the covalent modification of

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Figure 10. SEM images of the fracture surface of cross-linked samples comprising (a) pure polysilazane, (b) 1/polysilazane, and (c) 2/polysilazane. In panel b, the ellipse marks a nanotube agglomerate, which is shown in b' at higher magnification.

the nanotubes increases both the shear viscosity and the shear stress of the mixtures, which can be attributed to a better dispersion, the presence of smaller bundles, and a stronger interaction of the functionalized tubes with the matrix.

3. Cross-Linked SWNT/Ceraset Composites. *Macroscopic Observations*. Although sonication treatment of the SWNTs in THF helps to some extent to disperse the SWNTs in the matrix, a number of transparent pinholes can be discerned in the cross-linked SWNT(1)/polysilazane composites (Figure 9). Obviously the tubes that have been dispersed at the beginning of the synthesis reagglomerate in the cross-linking step, during which the temperature reaches  $360 \,^{\circ}$ C and therefore the viscosity of the mixture decreases substantially. By contrast, the cross-linked composites containing 2 rarely exhibit such pinholes. This difference can be reasonably explained by the considerably higher viscosity of the 2/polysilazane mixtures, which effectively reduces the reagglomeration rate of nanotubes in the cross-linking step.

*Microscopic Distribution of the SWNTs*. In order to study the microscopic distribution of the SWNTs in the matrix, the fracture surface of the cross-linked composites was investigated by SEM (Figure 10). It can be seen that while the fracture surface of cross-linked pure polysilazane is typically smooth (Figure 10a), addition of SWNTs leads to a significant increase in surface roughness. In particular, the fracture surface of **2**/polysilazane becomes quite rough due to the bridging, pull-out, and breaking of nanotubes. For fiber-reinforced polymer or ceramic matrix composites, a rough surface in general indicates enhanced toughness, while a smooth surface is typically encountered in materials displaying brittle fraction behavior.<sup>45,46</sup>



Temperature (<sup>0</sup>C)

**Figure 11.** TG–DTG–MS traces of cross-linked SWNT/polysilazane composites (in argon, 10 °C/min): (a) TG–DTG curves of pure polysilazane and **2**/polysilazane and (b) mass ion current curves of the SWNT/ polysilazane composites.

As exemplified by Figure 10b, the fracture surface of the 1/polysilazane composite exhibits nanotube agglomerates with sizes on the order of several micrometers, which are

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Figure 12. (a) STEM image of SWNT bundles within a 2/Si-C-N composite and corresponding EELS spectra (b-d) of the ceramic matrix and the modified nanotubes.

not observed in the 2/polysilazane case (Figure 10c). This finding is in accordance with the above-described stronger aggregation tendency of the unmodified tubes during the cross-linking step.

Taken together, the above macroscopic and microscopic observations as well as the rheological data clearly demonstrate that the modified SWNTs (2) are easier to disperse into the preceramic polymer matrix, thus enabling access to more homogeneous composites.

4. Pyrolysis of Cross-Linked SWNT/Ceraset Composites. Pyrolysis of the cross-linked SWNT/polysilazane composites was monitored by TGA-MS analysis. The DTG curve of pure Ceraset (Figure 11a) exhibits two prominent weight loss stages with maxima at ~430 and ~600 °C. Polysilazane containing 1 shows also two weight loss stages at similar temperatures (data not shown), whereas in the case of 2/polysilazane, only the second stage at 600 °C is observed. The first stage is best ascribed to volatilization of low molecular weight silazane oligomers, while from the MS data (Figure 11b) hydrogen and methane have been identified as the major evolved species within the second stage, in close agreement with other reports.<sup>28,47</sup> Accordingly, the absence of the first stage in the 2/Si-C-N composite testifies a higher degree of cross-linking, which in turn leads to a higher ceramic yield of 80.5%, as compared to yields of 76.4% and 75% for the pure polysilazane and 1/polysilazane, respectively, for pyrolysis at 1000 °C under argon.

The persistence of nanotubes in the pyrolized 2/Si-C-N composites could be proven by STEM-EELS analysis. The STEM image of such a sample, shown in Figure 12a, reveals SWNT bundles with a length of up to 300 nm. In Figure 12b-d, EELS spectra recorded in the energy range of the Si-L<sub>2,3</sub>, C-K, and N-K edges from the Si-C-N matrix

and the SWNT bundles are depicted. It is noteworthy that the C–K edge spectrum<sup>43</sup> of the Si–C–N matrix displays the typical shape of amorphous carbon, while the shape of the C–K edge spectrum of the nanotube bundles is similar to that of graphite (Figure 12b).

## Conclusions

In summary, a novel chemical modification method has been developed that involves the radical addition of an organosilicon compound to the sidewall of SWNTs, which enables production of SWNT/Si-C-N composites containing homogeneously distributed nanotube bundles. It has been demonstrated that the reduced agglomeration tendency of the covalently modified nanotubes leads to an enhanced viscosity of the nanotube/polysilazane mixtures, which significantly facilitates further processing, in particular by largely preventing the reagglomeration of the tubes during the cross-linking step as well as to some extent during the subsequent pyrolysis. Despite their sizable functionalization degree of 3%, the modified nanotubes were found to resist the high pyrolysis temperature of 1000 °C. Further work aiming at optimization of the functionalization extent and processing of the SWNT/polysilazane mixtures and composites as well as determining the mechanical properties of the SWNTreinforced Ceraset-derived Si-C-N ceramic composites is in progress.

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