FUNCTIONALIZED CARBON NANOTUBES FOR COMPOSITE MATERIALS

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Abstract

The application of carbon nanotubes as reinforcing fibers in polymeric matrices is constrained by their dispersion homogeneity within, and by the strength of their interface with, the matrix. We have investigated a number of different approaches for addressing these issues in epoxy and in polyurethane matrices. In polyurethane foam matrices, we have been able to achieve good dispersions up to approximately 4 wt.% multiwalled carbon nanotubes (MWNTs). Furthermore, we have prepared functionalized MWNTs that bear a covalently bound polyol unit derived from mannitol. Using differential scanning calorimetry, we have observed the heat of reaction between these modified nanotubes and a commercial polyurethane resin. An exotherm is observed at about 35 ˚C, and the integrated heat of this reaction scales directly with the amount of functionalized nanotube present in the mixture. We have also prepared similarly-functionalized nanotubes that bear acid chloride units, and we have investigated the reaction between this material and epoxy resins. We will present the functionalization chemistry, thermal analysis of the curing reactions, and mechanical testing results of these composite materials.

Keywords: Carbon nanotubes, chemically modified carbons, carbon composites

Introduction

Multiwalled carbon nanotubes (MWCNTs, or MWNTs) are immensely strong materials. Tensile tests of single nanotubes reveal that these structures have break stresses above 100 GPa, far surpassing that of aerospace-grade carbon fiber.(Barber *et al.*, 2005) This high strength, particularly in concert with the high thermal and electrical conductivity, make MWCNTs a very attractive reinforcing fiber for composite materials.(Qian *et al.*, 2000) However, failure analysis of nanotube-polymer composites often reveals that the nanotubes slide out from the matrix, rather than taking on the load and providing an element of reinforcement.

We are interested in chemical modification of nanotubes as a means to introduce covalent bonds between a polymer matrix and the nanotubes. Chemical treatments of nanotubes can also result in better dispersion of nanotubes into the matrix, another highly desirable characteristic for composites.

We have selected polyurethane and epoxy as 'model' polymer matrices, as these are readily available, have very different physical properties, and are used in a wide variety of applications. There is a growing body of literature describing the behavior of epoxy-carbon nanotube composites, including functionalized nanotubes in epoxy.(Gojny *et al.*, 2003; Breton *et al.*, 2002; Bai, 2003; Kim *et al.*, 2006; Zhu *et al.*, 2003; Wang *et al.*, 2006) A large number of approaches have been used to functionalize carbon nanotubes, and these have been summarized in some excellent recent reviews.(Niyogi *et al.*, 2002; Lin *et al.*, 2003; Tasis *et al.*, 2006)

We have used two different approaches that are known to produce highly functionalized nanotubes. Our first route involved the well-known oxidation of nanotubes to produce carboxylic acid terminated nanotube segments(Liu *et al.*, 1998; Chen *et al.*, 1998) followed by esterification. To further increase the number of carboxylic acid groups in the samples we mechanically processed the nanotubes to break them into shorter segments(Kónya *et al.*, 2004) and produce more 'ends' for oxidation. Mechanically-processed (shatter milled) MWNTs were treated with HNO_3, filtered and washed, then treated with H_2O_2/H_2SO_4.(Wang, 2006) This routine produces a nanotube 'ink' composed of highly functionalized nanotube segments. This material was dried and converted to the polyol polyester **2** by treatment with DCC and mannitol in DMF.

1 → Mannitol, DCC → **2**
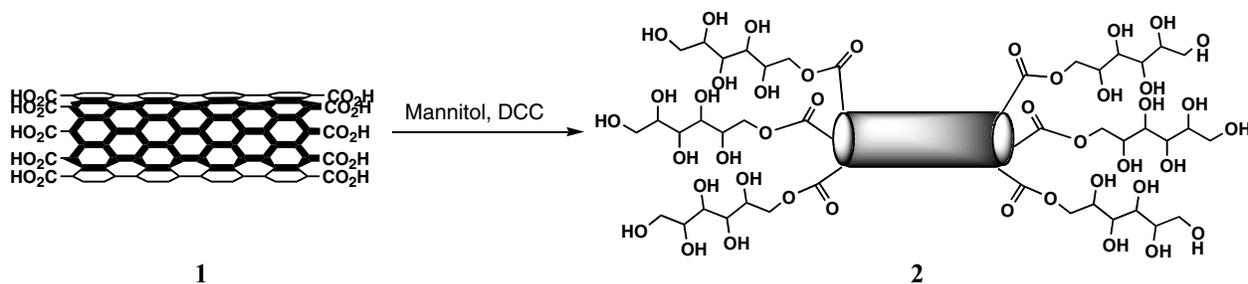
Evidence that this material reacts with the isocyanate portion of a 2-part commercial polyurethane foam kit was provided by differential scanning calorimetry (Figure 1). A mixture of isocyanate and **2** was placed in the DSC and heated (5 ˚C/min). An exotherm was observed at ~50 ˚C, a temperature that matches the exotherm produced when the polyol part of the kit is mixed with the isocyanate. No reaction was observed when unmodified MWNTs were used instead of **2**. The integrated heat flow scales with the amount of **2** present, consistent with the intended reaction between **2** and the isocyanate.
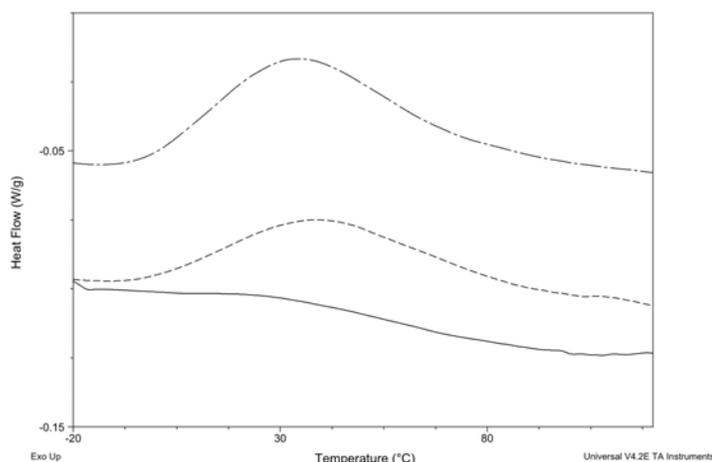

Figure 1. Differential scanning calorimetry of increasing loadings of **2** in polyurethane (isocyanate). Solid line: 1 part **2**, 20 parts polyol; Dashed line: 1 part **2**, 10 parts polyol. Dot-dashed line: 1 part **2**, 5 parts polyol.

While this reaction was encouraging and potentially useful in production of cross-linked MWNT composite materials, the difficulty in isolating **1** from the reaction mixture made it very difficult to scale up the preparation of large quantities of composites.

Dissolving metal (Birch) reduction, followed by alkylation of the resulting anions is another useful route for introducing a large number of functional groups onto nanotubes. This approach has been used for decades for alkylation of more pedestrian aromatic systems (for examples see (Hook and Mander, 1986; Rabideau and Marcinow, 1992)), and has recently been demonstrated in nanotube chemistry (for examples see(Liang *et al.*, 2004; Chattopadhyay *et al.*, 2005)). Accordingly, MWNTs were reduced with lithium metal in liquid ammonia and alkylated with ethyl bromoacetate to produce ester **3**. The esters were hydrolyzed and converted to the acid chloride by standard methods.
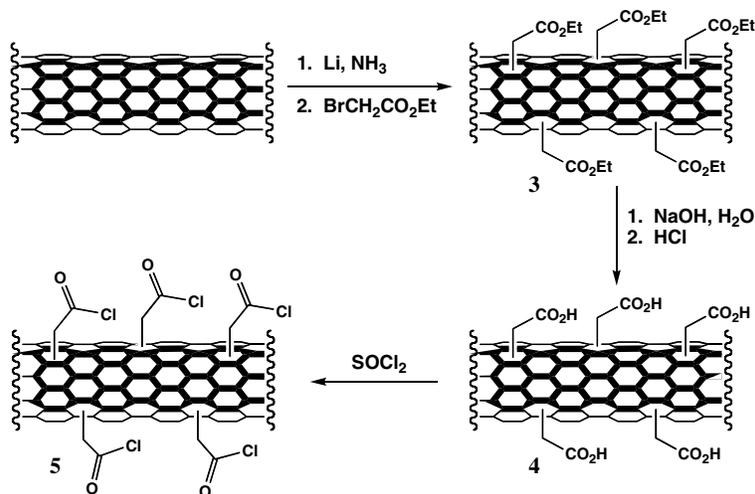
Scheme 2. Preparation of acid chloride functionalized MWNTs (**5**).

Thermal analysis provides evidence for the transformations shown in scheme 2. Thermal gravimetric analysis (in air) of a typical batch of **5** reveals the oxidative loss of ~10% of the sample mass at relatively low temperature (<400 ˚C). Oxidative loss of graphitic material (nanotubes) begins near 500 ˚C. It is safe to assume that the addition of new groups to nanotubes occurs at the ends and on the sidewall of the outermost shell. Our nanotubes are 40 shells thick on average, so significant modification of the outmost shell has been achieved.

Preparation of bulk samples for mechanical testing requires significant mixing energy. Care was taken to standardize the processing conditional for all samples in order to ensure that comparisons of mechanical properties of different samples would be valid. Accordingly, all polyurethane samples were handled in an identical manner, regardless of the MWNT loading and viscosity. Mixing of MWNTs into polyurethane resins was accomplished first by shear mixing (Silverson AV4R, 5,000 rpm, 15 minutes). Once the MWNTs were thoroughly mixed into the resins, the two parts were mixed together (Thinky planetary mixer, 25 seconds at 2000 rpm), then transferred into cardboard molds to foam and cure. After curing, 25 mm cubes were cut from the resulting foam block for test samples.

Dispersion in foams was studied by embedding small blocks in epoxy, followed by polishing and examination under an optical microscope. Dispersion in epoxy composites was studied by optical microscopy on thin disks cut from core samples taken from the cured blocks (Figure 2). Shear mixing results in dispersions that are stable (on the order of hours) and that appear homogenous to the unaided eye. Optical microscopy, however, reveals a significant number of agglomerates in samples with very high concentrations of MWNTs. The high viscosity of those mixtures precludes efficient circulation through the mixing head, and results in less than optimal dispersion. For this reason we did not exceed 2 wt% nanotubes in polyurethane.
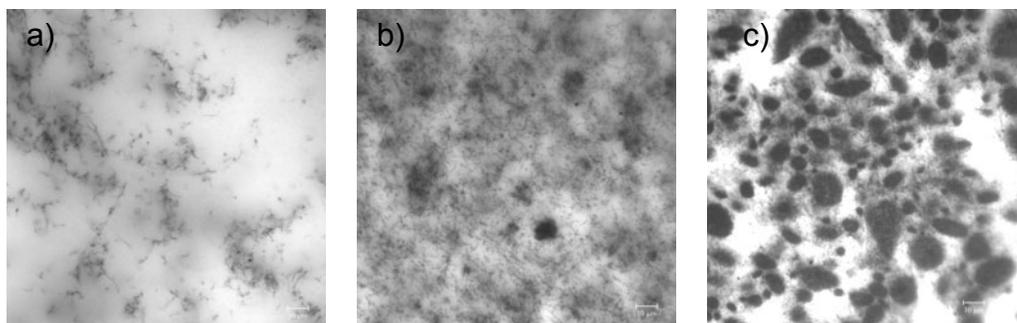

Figure 2. Examples of dispersion of MWNTs in epoxy. a) 0.1 wt% MWNTs; b) 1 wt% MWNTs; c) 5 wt% MWNTs.

Bulk samples of polyurethane composites were prepared by mixing 2 weight % nanotubes (as-produced nanotubes **1** or acid chloride nanotubes **5**) into the polyurethane components, following the mixing protocols discussed above. The foams were allowed to rise, and given several hours to cure before cutting into samples for testing. We observe a significant increase in the viscosity as nanotubes are mixed into the polyurethane components, making it very difficult to prepare mixtures with loadings higher than 2%. The chemically modified nanotubes **5** were an exception – mixtures containing **5** were much less viscous than were analogous mixtures containing as-produced MWNTs. Examination of the length distribution suggests that the nanotubes of **5** are significantly shorter than the starting as-produced MWNTs, probably as a result of unintentional shearing from magnetic stirring, filtering, and other steps.

A comparison of the compressive modulus of the different polyurethane foams with carbon nanotube loadings is given in Figure 4. Not surprisingly, we observe that higher density foams have a higher modulus. There is a general trend to lower moduli as MWNTs are mixed into the polymer. This trend is accompanied by a decrease in the density of the foam, and we suspect that the addition of MWNTs results in larger pore sizes, reducing both the density and the compressive modulus.

Quite different results were obtained from a sample prepared with functionalized MWNTs **5** blended into 16 lb/cuft foam. The density changes did not decrease in the same manner as seen in polyurethane composites made with unmodified nanotubes, nor did the compressive modulus decrease. The modulus increased to 75 MPa, which is significantly higher than the corresponding composites with as-produced nanotubes (25 MPa), and higher than the modulus of the raw polyurethane (63 MPa).
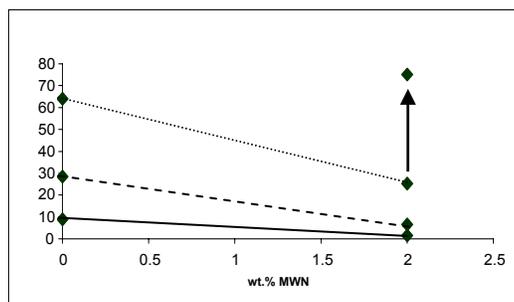

Figure 4. Compressive modulus as a function of MWNT loading in polyurethane foam. Solid line: 4 lb/cu ft foam. Dashed line: 8 lb/cu ft foam. Dotted line, 16 lb/cu ft foam. Arrow designates the increase in modulus due to crosslinking of **5** with the polyol part of the polyurethane foam.

We believe that this 300% increase in modulus is a direct result of the covalent crosslinking of nanotubes with the polymer matrix. Other non-covalent mechanisms that might be operating would be expected to be manifest with as-produced nanotubes as well as with functionalized nanotubes. The significant difference between the observed modulus most likely results from load transfer to the nanotubes. We anticipate that similar results will be obtained with crosslinked epoxy composites. Calorimetry has revealed a crosslinking reaction between a commercial epoxy resin and **5**, so we should be able to produce bulk samples of this composite as well.
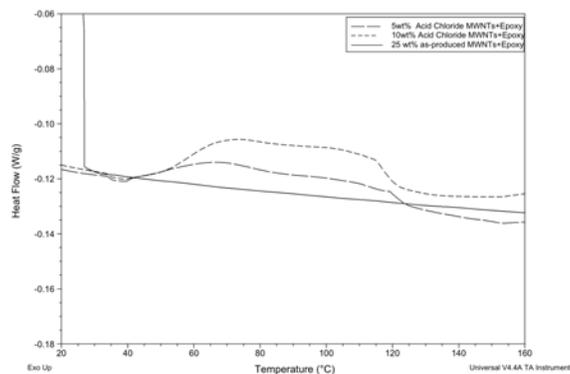
Figure 3. Differential Scanning Calorimetry of EPON 826 resin with **2** as curing agent. Solid line: control experiment: EPON826 mixed with raw, as-prepared MWNTs; b) EPON826 with 5 wt% **5** as curing agent; c) EPON826 with 10 wt% **5** as curing agent.

Conclusions

Addition of MWNT nanotubes to polyurethane foams results in a softer, lower modulus material, largely due to a decrease in the density due to an increased pore volume. Crosslinking of MWNTs to the polyurethane matrix significantly increases the compressive modulus without significantly increasing the density, supporting the notion that covalently bonded nanotubes can affect bulk material properties. This improvement occurs despite the fact that the chemical modified tubes are shorter (lower aspect ratio) than raw as-produced nanotubes. Calorimetry provides direct evidence of the heat of the crosslinking reaction, both in polyurethane and in epoxy. Mechanical analysis of epoxy composites is on-going.

Experimental

The MWNTs used in this study were prepared by a CVD method at the Center for Applied Energy Research.(Andrews *et al.*, 1999) Polyurethane foam kits (8 lb/cuft, 16 lb/cuft, 2 part) were obtained from US Composites. Epoxy resin (EPON 826) was purchased from Miller-Stephenson.

Oxidation of MWNTs. A sample of 3.11g milled nanotubes (milled for 10 minutes) was added to a mixture of 90 mL conc. H_2SO_4 and 30 mL conc. HNO_3. The mixture was stirred vigorously and heated at reflux for 25 minutes, then poured into 500 mL water. The suspension was vacuum filtered (0.2 micron nylon filter), and the filter cake was washed with water, 95% ethanol, and methanol, then dried *in vacuo* to produce 2.15 g of a fine black solid.

Esterified MWNTs (2) A sample of oxidized MWNTs was suspended in 25 mL DMF and placed in an ultrasonic bath for 5 minutes. DCC (0.20 g) was then added to the solution, and the mixture was stirred at room temperature for 30 minutes. Mannitol (0.23 g) was added and the resulting mixture was stirred overnight. The mixture was filtered (0.2 micron nylon), and washed with acetone, hot water, then acetone again before being dried *in vacuo* to produce 0.39 g of a fine black solid (**2**).

Esterified MWNTs (3) – Li Powder (6.3g, 0.9mol) was added to approximately 2500mL anhydrous ammonia and stirred for 10min; then MWNTs (10.4g, 0.85mol carbon) were added and allowed to stir for 30min. Ethyl bromoacetate (125mL, 1.12mol) was added slowly to the solution and allowed to stir and warm to RT overnight. To the resulting powder was stirred in 2000mL H_2O and sample was subsequently washed and filtered with H_2O until a neutral pH was reached. Sample was then washed with 1000mL CH_2Cl_2 and final wash with 500mL EtOH and dried under vacuum overnight.

Acidified MWNTs (4) – To a 600mL solution of 1M aqueous NaOH was added 10.5g **3** and the mixture was heated to 80 °C and stirred for 24 hr. The sample was filtered and washed with H_2O until reaching neutral pH, then washed with 500mL 10% HCl, then with 500mL EtOH, and dried under vacuum overnight.

Acid Chloride MWNTs (5) – To 500mL neat $SOCl_2$ was added 10.3g **4**, and the mixture was stirred under reflux at 80°C overnight. The excess $SOCl_2$ was then distilled off under vacuum, and the remaining solid was washed with 1000mL toluene, then with 500mL pentane and dried under vacuum overnight.

Acknowledgements

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