A Generic Organometallic Approach toward Ultra-Strong Carbon Nanotube Polymer Composites

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While carbon nanotubes (CNTs) are fascinating new materials, chemical modification is often necessary to take full advantage of their unique properties.[1] For example, it may be beneficial to covalently attach nanotubes to surfaces or molecules or to functionalize nanotubes with units such as polymers. Wrapping nanotubes by different polymers has been reported by several groups.[2] Probably the most accessible area for viable CNT applications is plastics reinforcement.[3] While CNTs are 5 times less dense than steel and approximately 30 times stronger, attempts at polymer reinforcement have been hampered by the fact that few polymers form strong interfaces with nanotubes. In this communication, we present a generic route to polymer reinforcement via the preparation of polymer-functionalized nanotubes using an organometallic approach.

It has been reported that C_{60} can react with lithium alkyl and Grignard reagents, giving alkylated metal fullerides such as $RC_{60}^- Li^+$.[4] However, while many aspects of organometallic chemistry of fullerenes have been explored, the corresponding research on nanotubes has not been developed. It is well-known that nanotubes can contain many deviations from pure hexagonal structure, which are potentially reactive and can be attacked by nucleophiles such as lithium alkyls. One early study described the interaction of fluorinated single-walled carbon nanotubes with lithium alkyls.[5] An interesting approach on usage of *sec*-butyllithium-treated single-wall carbon nanotubes as initiators of anionic polymerization for in situ preparation of polystyrene-grafted nanotubes was also recently reported by P. M. Ajayan et al.[6] Here we report use of *n*-butyllithium-functionalized multiwalled carbon nanotubes (MWNTs) for the preparation of new polymeric composite materials by a simple coupling reaction with halogenated polymers.

The MWNTs were synthesized by decomposition of ethylene at 700 °C on Co/Al_2O_3 and purified by refluxing in 40% NaOH for 24 h and concentrated HCl for 15 h, followed by annealing under vacuum at 500 °C for 5 h to remove the carboxylic groups. The purified annealed MWNTs were reacted with an excess of *n*-butyllithium in dry tetrahydrofuran (THF) under argon at −10 °C to give green solutions. The process involves binding butyl groups to the MWNT surface with the formation of very air- and moisture-sensitive adducts ($MWNT^{n-})Li^+_n$ (Scheme 1). After the treatment, the dispersability of the nanotubes in THF increases significantly because of the presence of butyl groups attached to the nanotubes. We believe that butyllithium preferentially attacks the more reactive sidewall defects, tips, and other nonhexagonal regions.

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Scheme 1. Schematic Presentation for Functinalization of MWNTs with Chlorinated Polypropylene (CPP)[a]
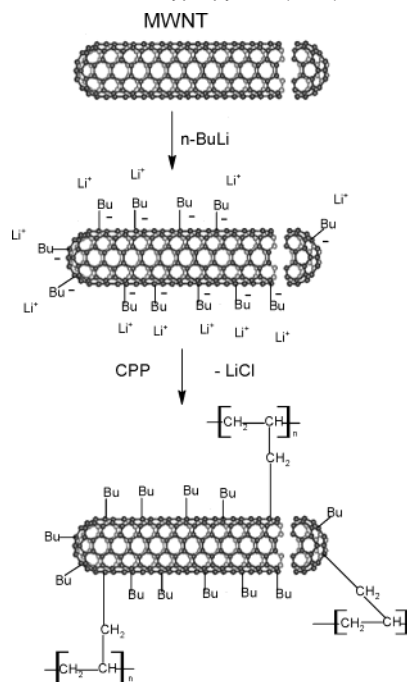
[a] BuLi is *n*-butyllithium.

The hydrolyzed lithiated MWNT samples have been studied by FTIR spectroscopy. The IR spectrum of the sample contained characteristic alkyl (CH) bands at 2970, 1480, and 1370 cm^{-1}. The butyllithium-functionalized nanotubes are susceptible to metathetic exchange reactions with halogenated species via elimination of lithium halides. Our preliminary studies of lithiated carbon nanotubes in reactions with $SnCl_4$ and $SiCl_4$ resulted in the formation of species containing Sn−C and Si−C bonds, respectively, as observed by FTIR spectroscopy, at 285 [ν(Sn−C)] and 802 cm^{-1} [ν(Si−C)] (see Supporting Information).

The butyllithium-functionalized MWNT (Scheme 1) has been further reacted with chlorinated polypropylene (CPP) to give nanotubes covalently bonded to chlorinated polypropylene (CPP−MWNT). The TGA-estimated CPP content in the grafted MWNTs was 31%. TEM images of the CPP−MWNT composite (Figure 1) have shown polymer-coated carbon nanotubes forming bundles. These materials are expected to interact strongly with a polypropylene matrix in composite systems. The covalent attachment of polymer molecules to nanotubes should facilitate processing and solve the problem of interfacial stress transfer, which is a huge bottleneck.[7] To demonstrate this, composite solutions were made by adding CPP−MWNT composite to chlorinated polypropylene
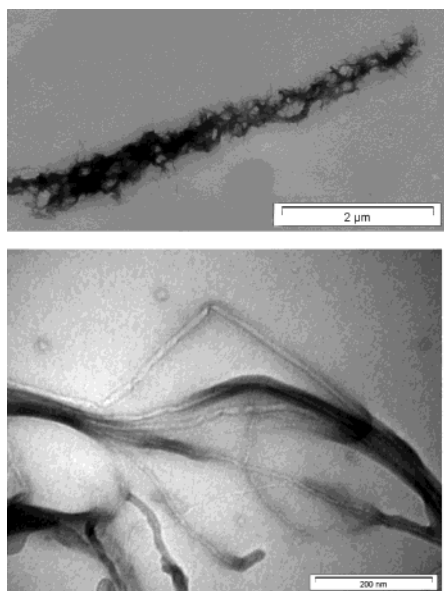
Figure 1. TEM images of MWNTs coated with the chlorinated polypropylene.
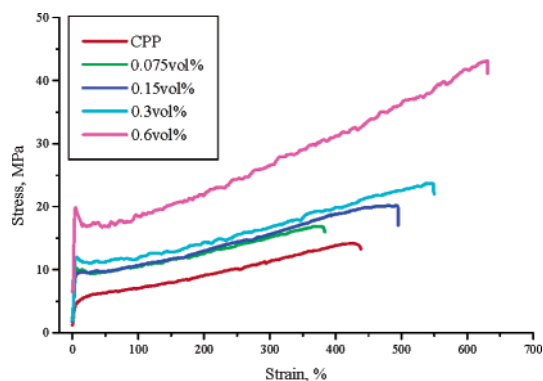

Figure 2. Stress−strain curves for the CPP−MWNT composites studied.

in THF. While untreated MWNTs were insoluble in the THF solution and rapidly sedimented out, the CPP−MWNTs could easily be dispersed in THF to give a homogeneous mixture. This solution was then blended with a polymer solution to produce blends of 0.125, 0.25, 0.5, and 1 wt % (0.6 vol %) nanotube/polymer mass ratios. They were then cast onto Teflon-coated disks to form 300 μm thick films. Tensile testing was carried out with representative stress−strain curves shown in Figure 2. Substantial increases in mechanical properties are observed as the nanotube concentration is increased. On average, as the nanotube content is increased to 0.6 vol %, the Young's Modulus increases by a factor of 3 compared to the pure polymer from 0.22 to 0.68 GPa. This is significant compared with previous results.[7] Moreover, both the tensile strength

and the toughness (energy required to break) also increase by factors of 3.8 (from 13 to 49 MPa) and 4 (from 27 J/g to 108 J/g), respectively. These results show that the covalent functionalization of carbon nanotubes enables both efficient dispersion and excellent interfacial stress transfer.

Thus, our studies have clearly demonstrated that MWNTs can be effectively functionalized using *n*-butyllithium and then chemically bonded to halogenated species. In principle, the organometallic approach is feasible for a wide range of functionalities, allowing the reinforcement of many different plastics. We anticipate the development of novel unprecedented, ultra-strong, ultra-light polymer materials using this technique. Further research on investigation of electric and mechanical properties of new materials is currently in progress.

Supporting Information Available: Some experimental details, IR spectra, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0474805