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Relations between carbon nanotubes' length and their composites' mechanical and functional performance

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ABSTRACT

Although carbon nanotubes have been extensively studied since 1991, it is not clear the relations between the tubes' length and their composites' functional and mechanical performance. We in this study employed ball milling to reduce the length of multi-walled carbon nanotubes (MWNTs) from a few microns to hundreds of nm through milling for different time slots. The milled tubes demonstrated a 12.0% increase in surface area. When dispersed in an elastomer matrix, MWNTs showed two types of morphology: separately dispersed and clustered. The cluster size reduced with the ball-milling time. The ball milling obviously increased the composite fracture strain, while mild increase in tensile strength was observed. When MWNT/elastomer composites were compared with carbon black (CB) composites, both showed similar strength, but the former demonstrated markedly higher strength at low strain—a highly desired property for elastomers. The MWNT composites show a strong filler–filler interaction with an unobvious Payne effect. Although the ball milling slightly reduced the electrical and thermal conductivity of the MWCNT composites, they demonstrated much higher conductivity than the CB composites. The ball-milling reduced up to 18.2% of the composite internal heat rise.

1. Introduction

Graphene, a one-atom-thick, 2-dimensional, sp2–bonded carbon sheet, features prominent fracture strength (~1 TPa) [1,2], extraordinarily high in-plane electrical and thermal conductivity [3–5], and large surface area (2675 m^2/g) [6]. Although graphene has been employed to develop polymer composites [7–10], its 2-dimensional geometry is rather limited in producing entanglement. Therefore, we in this study focus on multi-walled carbon nanotubes (MWNTs) consisting of rolled graphene layers, and study their elastomer composites. Song et al. [11] investigated the effect of dispersion of MWNTs on the thermal conductivity of epoxy composites: at 1.5 wt% MWNTs, a 112% increment in thermal conductivity was observed for a composite containing well dispersed MWNTs, while only 58% increment was recorded for the poorly dispersed sample; Huang et al. [12] injected thermally conductive silicone elastomer into MWNTs arrays, resulting in a further 282% increase in the thermal conductivity at 0.4 vol%. It is noteworthy that both chemical and physical surface modifications of MWNTs promoted their dispersion in polymer matrixes, albeit a cost involved [13–15].

In spite of these extensive studies, it remains a challenge to adopt industry-compatible methods for uniformly disentangling and dispersing MWNTs in polymer matrixes. Known solutions to disentangle MWNTs include acidification, ball-milling and thermal treatment with deposited metal oxides; of these, ball-milling is the most cost-effective due to its compatibility with industrial practice. Although all these methods inevitably reduce the MWNTs' length, the tubes can be readily dispersed and even aligned in polymer matrixes and thus increase the thermal conductivity and mechanical properties of polymers. To-date, only a few studies adopted this ball-milling method for fabrication of polymer/CNT composites. Song [16] ball-milled and mixed MWNTs with thermally conductive silicone elastomer, leading to a 174% increase in thermal conductivity at 1.6 wt% MWCNTs in comparison with 104% for the unmilled composites. On the other hand, these length-reduced MWNTs increased the percolation threshold of conductivity of their composites [17,18]. However, it is not clear the effect of MWNTs' length on their composites' mechanical and functional properties.

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Table 1
Formulations of elastomer fabrication.

Materials	Content (phr)	
Elastomer	100	100
Carbon nanotubes	5, 10, 20	N/A
Carbon black	N/A	5, 10, 20
Zinc oxide	5	5
Stearic acid	2	3
Accelerant D	0.5	0.5
Accelerant DM	0.5	0.5
Accelerant TT	0.2	0.2
Antioxidant 4010NA	1	1
Sulfur	2	2

An elastomer comprises a great number of high-molecular weight macromolecules, which are highly flexible and need to be crosslinked during fabrication to acquire desired stiffness and strength. Elastomers are not only used in industries, such as tyres, conveyor belts and hoses, but for toughening brittle polymers [19,20]. Since most neat elastomers are not mechanically strong, a number of nanoadditives have been explored, including the well-known carbon black, thermal plastics [21] and the recently explored clay [22–25] and starch [26,27]. When used in dynamic loading environments, elastomers inherently produce a huge internal heat rise which causes thermal degradation of macromolecules—the major aging mechanism for elastomeric products. Thermally conductive elastomers play a key role to solve this problem. Since MWNTs are known for providing their hosting polymers with high mechanical performance and functionalities, they are chosen in this study. In comparison with thermoplastics, it is more difficult to improve the electrical and thermal conductivity of elastomers.

Hypotheses made in this study include (i) by melt compounding MWNTs with an elastomer, the resulting composites may have highly improved electrical and thermal conductivities and mechanical performance, and (ii) there might exist an appropriate tube length for ideal comprehensive properties, since highly entangled raw MWNTs cannot well disperse in matrix while a large reduction in the tube length may pose a negative effect on the functional and mechanical performance of their composites.

In this study, we will employ ball-milling to develop a number of MWNTs with tailor-made length, identify the milling effect on the tubes' length and structure, develop their elastomeric composites using an industry-compatible method, and investigate the structure–property relations of these composites.

2. Experiment

2.1. Materials

Multi-walled carbon nanotubes were supplied by Tsinghua University with purity higher than 95%; carbon black was purchased from Tianjin Dolphin Carbon Black Co. Ltd.; an elastomer styrene–butadiene rubber (SBR 1502), a type of random copolymers featuring flexible molecular chains and high molecular weight, was obtained from Jilin Petrochemical Co. of China. Other compounding ingredients include sulfur, zinc oxide (ZnO), stearic acid (SA), an accelerant D (diphenyl guanidine), an accelerant DM (2,2'-dibenzothiazoledisulfide), and an antioxidant *N*-1,3-dimethylbutyl-*N*'-phenyl-*p*-phenylenediamine (4010NA), all of which are commercial products. Table 1 shows the elastomer compounding formulations.

2.2. Fabrication of MWNTs with different length

MWNTs of desired length were produced by a ball-milling process with different milling time. In specific, MWNTs were transferred into a stainless steel (80 ml) containing several stainless balls that vibrate in a random route at 1200 cycles per min in a typical process. The milling times were chosen at 15 min, 1 h and 5 h. The facility was paused every hr in milling to release build-up heat.

2.3. Preparation of elastomeric CNT composites

Using an industry-compatible two-roll mill, MWCNs were mixed with elastomer first, followed by cooling to room temperature to reduce internal heat rise. The mixtures were then blended with additives and curing chemicals based on the recipes shown in Table 1. It was cured by compression molding at 150 °C for an optimum curing time T_{90} which was determined by a Disk Oscillating Rheometre.

2.4. Characterization

2.4.1. MWNT morphology

The morphology was observed by scanning electron microscopy (SEM, S4700 Hitachi Co., Japan) at 20 kV, transmission electron microscopy (TEM, H-800 Hitachi Co., Japan) at 200 kV and high-

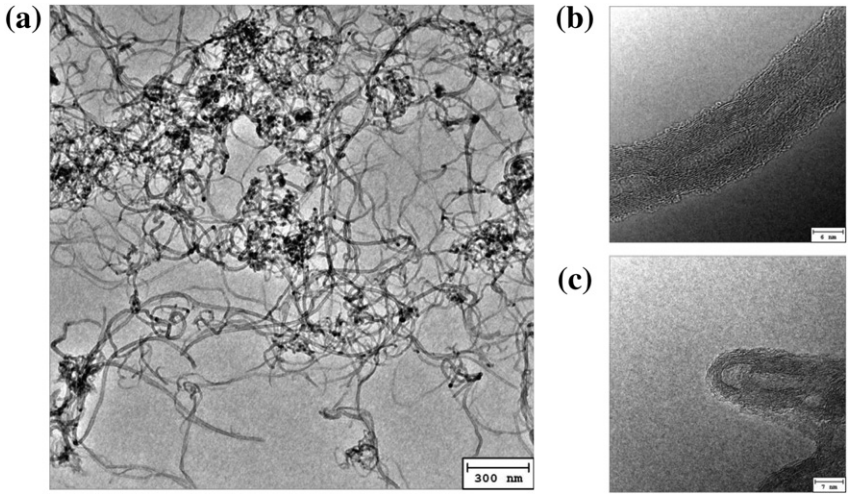

Fig. 1. TEM micrographs of pristine MWNTs: (a) an entangled state, (b) a typical wall and (c) a representative cap.