



# The direct dispersion of granular agglomerated carbon nanotubes in bismaleimide by high pressure homogenization for the production of strong composites

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## ABSTRACT

Carbon nanotubes (CNTs) have been mass produced and widely used as fillers for advanced supercapacitor/battery electrodes and lightweight high-strength composites. Well dispersion of CNTs in the matrix is a key issue to achieve high performance composites. Developing an easy and efficient strategy to disperse CNTs in a resource-saving and environmentally benign way, especially for agglomerated CNTs, is a great challenge. Mass produced ductile and resilient multi-walled CNTs were dispersed in bismaleimide (BMI) resin by a simple high pressure homogenization process. A CNT/BMI composite with a CNT content as high as 38 wt.% was fabricated under high pressure (240 MPa) during thermal curing. The compression modulus and hardness of the composite approach to 8.5 and 0.58 GPa, corresponding to a 28.9% and 44.0% improvement compared to neat BMI resin, respectively, which reveals the feasibility of such CNTs as fillers for strong composites. This text provides a simple, efficient, and economic powder technology to directly disperse granular CNTs in matrix for advanced composites.

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## 1. Introduction

The academic research and practical engineering applications are greatly stimulated by recent successful realization of carbon nanotube (CNT) mass production and commercialization [1–3]. Among various CNT products, agglomerated multi-walled CNTs (MWCNTs), in which CNTs are entangled with each other, have been mass produced with a high yield (up to 560 tons/year) at a low cost [3]. Up to now, CNTs have been used as fillers for advanced supercapacitor/battery electrodes and lightweight high-strength composites [3]. Well dispersion of CNTs in the matrix is a key issue to achieve high performance composites. However, there are severe entanglements in the CNT agglomerates by strong van der Waals interactions. In order to break the agglomerates and realize the uniform dispersion of agglomerated CNTs, various strategies such as covalent functionalization (e.g. chemical treatments by oxidative acid) [4–6], non-covalent functionalization [7], milling [8,9], shearing [10,11] and sonication [12], have been employed to disperse CNTs. The dispersed CNTs are mixed with matrix to obtain composites. During those processes, a large amount of solvent and acid were employed [10,11]. To avoid re-agglomeration, the CNT content in the composite was always low (less than 10 wt.%), and lengths of CNTs were significantly reduced [9,11]. In some case, the graphitic CNT walls were damaged [4,5]. Those adverse treatments

hinder the availability of high-performance composites. Developing an easy and efficient strategy to disperse CNTs in a resource-saving and environmentally benign way, especially for agglomerated CNTs, is a great challenge.

Generally, high concentration well-dispersed CNTs in a matrix always bring advanced functional composites [13]. The mass produced MWCNTs are ductile and resilient, which possess good cushioning behavior [14]. If resilient CNTs are directly dispersed into a polymer matrix, the nanotubes will be surrounded with polymer chains and form a high-CNT-content composite with good mechanical performance. Based on this consideration, this research explored the idea of direct dispersing CNTs into the bismaleimide (BMI) matrix by an easy high pressure homogenization process. BMI resin is produced by a vinyl-type polymerization of a pre-polymer terminated with two maleimide groups. It was selected as composite matrix for the reason that it cures through an addition rather than a condensation reaction, thus avoiding the formation of volatiles (Fig. 1a). BMI offers high temperature performance, low cost, and maintains the epoxy-like processing, which is a promising candidate for wear-resistant and aerospace applications [15–17]. CNT/BMI composites were found to exceed the state-of-the-art unidirectional carbon-fiber-reinforced composites recently [18]. With the advantages of time-saving, easiness in continuous mode for large volumes and large scale industrial production [19], the high pressure homogenization was selected as the way to directly disperse CNTs. Thus, mass produced MWCNTs were employed as raw materials and directly dispersed homogeneously in the BMI matrix by high pressure homogenization process in this letter (Fig. 1b). After hot-pressure curing, a high performance CNT/BMI composite was fabricated.

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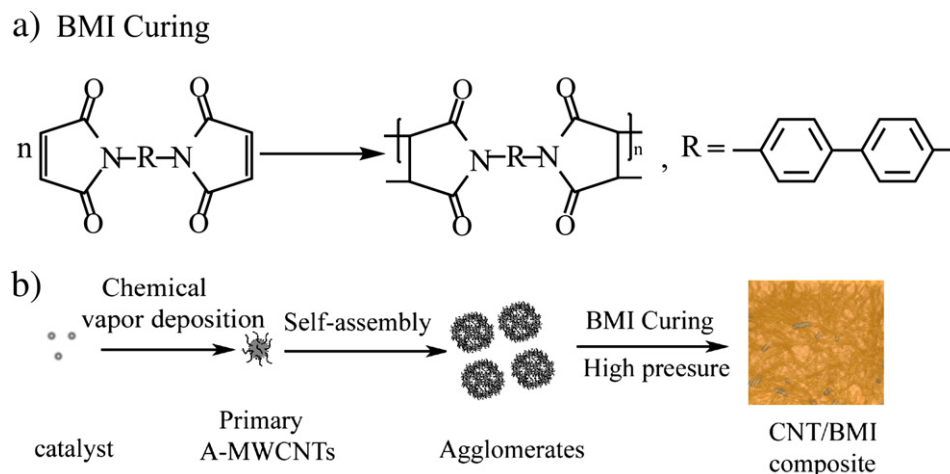


Fig. 1. Schematic illustration of (a) thermal curing of BMI resin and (b) CNT/BMI composites by the high pressure homogenization and thermal curing.

## 2. Experimental

The chemical pure, aerospace-grade BMI resin produced by Hubei Research Institute of Chemistry was used as the polymer matrix. The agglomerated multi-walled carbon nanotubes (MWCNTs) with purity of 99.5% were produced by fluidized bed and used as received for the high pressure homogenization. Firstly, to penetrate the BMI into carbon nanotube (CNTs), 4.0 g agglomerated MWCNTs were impregnated into a 500 mL BMI–acetone solution with a concentration of 1 g/L for 1.0 h. The acetone was removed under 80 °C in a vacuum oven for 4.0 h. Secondly, 5.9 g BMI powder was mixed with the BMI-modified agglomerated MWCNTs to fabricate 38 wt.% CNT/BMI composites. The as obtained powders were inserted into the cavity of a cylindrical die, and a punch was fixed at the top of the die for high pressure homogenization. Hydrostatic pressure was applied through an oil jack. To fully thermally cure the BMI, a following hot-press process with a high pressure of 240 MPa at 170 °C for 4.0 h plus 210 °C for

2.0 h was carried out. Photos of the CNT powders and blocks were taken using a Ricoh R4 video camera. The samples were characterized using a JSM 7401F scanning electron microscope (SEM) and a JEM 2010 transmission electron microscope (TEM). The nanoindentation measurements of the composite were performed on MTS Nano Indenter XP (MTS Corp., Nano Instruments Innovation Center, TN) with a continuous stiffness measurement technique. Thermo gravimetric analysis (TGA) measurement carried out on thermo gravimetric analyzer TGA 2050 instrument at a scan rate of 10 °C/min from 30 to 800 °C in air flow. Differential scanning calorimetry (DSC) measurement was performed on DSC Q2000 at 10 °C/min from 40 to 400 °C under N<sub>2</sub> atmosphere.

## 3. Results and discussion

The agglomerated MWCNTs (with a purity of 99.5%) produced by fluidized bed were received for the high pressure homogenization

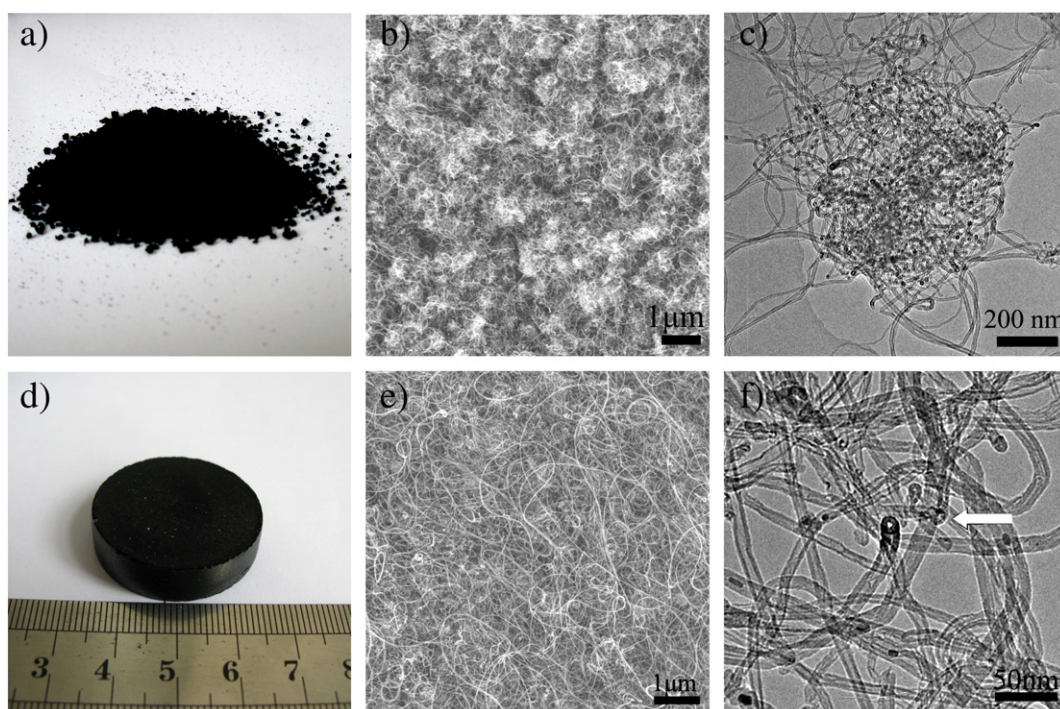


Fig. 2. (a) Photograph of the as-produced CNT powders, (b) SEM and (c) TEM images of the CNT agglomerates, (d) photograph of the CNT block after 240 MPa homogenization, (e) SEM and (f) TEM image of homogenized CNTs.

without further purification. Fig. 2a shows that the as-produced CNTs are fine powders with a size ranging from 200 to 1000  $\mu\text{m}$ . The scanning electron microscope (SEM) image (Fig. 2b) reveals that CNT powders are composed of a 3-dimensional (3D) network structure agglomerated from large amounts of CNTs. Due to the strong interaction between CNTs and catalyst supports, sub-agglomerates with sizes of ca. 1  $\mu\text{m}$  form. A further aggregation of these sub-agglomerates naturally occurs to form large CNT agglomerates due to the van der Waals forces and entanglements among CNTs [1,20]. As shown in the transmission electron microscope (TEM) image (Fig. 2c), the CNTs in the agglomerates are entangled surrounding the catalysts and form a compact core. After loading the agglomerated MWCNTs into the cavity of a cylindrical die, hydrostatic pressure was applied through an oil jack. A dense free-standing CNT pie (Fig. 2d) with a diameter of 30 mm and a thickness of 5.0 mm is fabricated under high pressure up to 240 MPa for 1.0 min in the die. The cross-section SEM image shows that CNT agglomerates collapse into a rather uniform entanglement. The original compacted cores disappear under high pressure (Fig. 2e). The fine structure of the CNT agglomerates after high pressure homogenization is shown in Fig. 2f. Clearly, the tips of nanotubes are dispersed in the agglomerates and the catalyst cores are crushed. The 3D CNT networks change into homogeneously dispersed agglomerated MWCNTs by the simple high pressure homogenization.

Fig. 3a shows that the CNTs can be well dispersed into the BMI resin matrix in a random network under 240 MPa. The weight percentage of

CNTs in the composite is ca. 38 wt.%, and CNTs with a length of less than 800 nm are exposed on the cross-section of the composite. A worm-like morphology is presented without CNTs pushed out of the matrix, indicating the well-dispersed CNTs are with good interaction with the BMI resin. In contrast, when the homogenization was conducted at 120 MPa, the cross-section of the composite shows that some CNT agglomerates glimmer on the fracture edges (Fig. 3b). Some of exposed CNTs were with a length over 5000 nm, which was attributed to the weak homogenization of agglomerated CNT hierarchical structure under 120 MPa. This indicates that high pressure homogenization at 240 MPa causes turbulent flow and cavitation of the BMI resin. This produces intense shear forces on the CNTs present in the liquid, thus breaking the CNT aggregates into dispersed units [19]; at the same time, CNT/BMI composites are in situ fabricated.

The typical applied load vs. displacement testing curves of neat BMI resin and CNT/BMI composites are presented in Fig. 4a. The

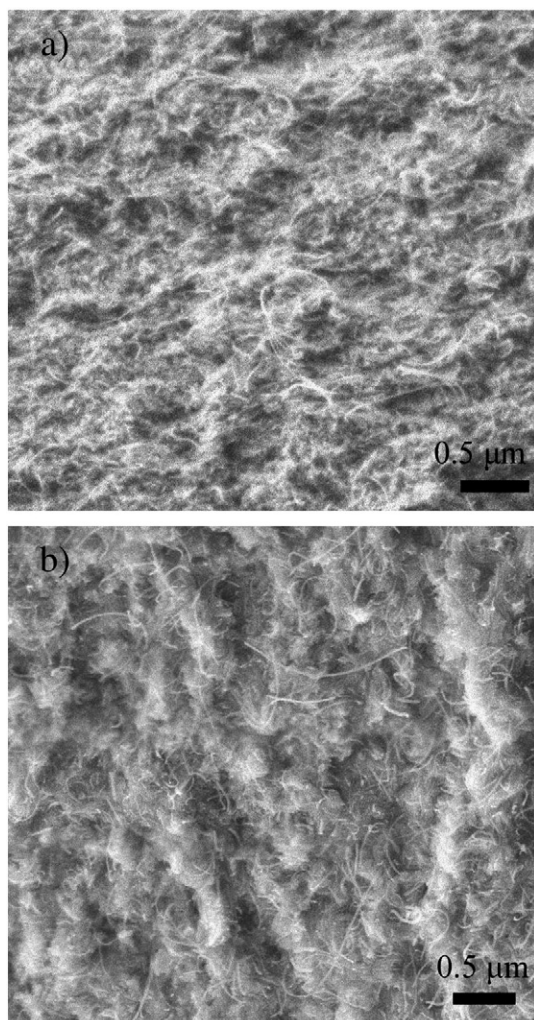


Fig. 3. SEM images CNTs in BMI matrix under (a) 240 and (b) 120 MPa.

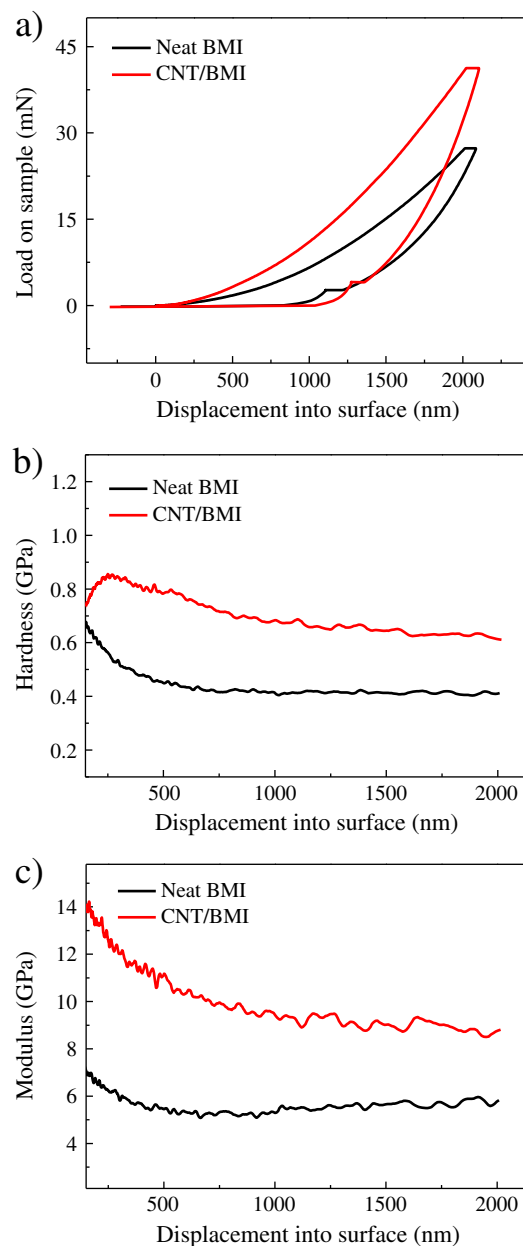


Fig. 4. (a) Typical loading–unloading curves during nanoindentation test, (b) compression hardness and (c) modulus profiles with respect to displacement into sample surface of neat BMI resin and CNT/BMI composites.

**Table 1**  
Comprehensive properties of neat BMI and long CNT/BMI composites.

Sample	CNT content	Modulus (GPa)	Hardness (GPa)	T <sub>g</sub> (°C)	2% decomposition temperature (°C)
BMI	0	5.9	0.45	305	425
CNT/BMI	38%	8.5	0.58	276	414

load on the samples increases faster when the displacement into the surface became higher. When the displacement was 2000 nm, the load was 28 and 40 mN for the BMI and CNT/BMI, respectively. The strength capacity is improved by 42% when the displacement into surface is 2000 nm. The CNT/BMI composite showed higher capacity to bear load than that of neat BMI resin. When the loading is retracted from 40 to 10 mN, the displacement decreases simultaneously. A large slope is observed for CNT/BMI resin, indicating that a resilient composite is available. Fig. 4b and c shows the compression hardness and modulus of the CNT/BMI composite. Compared to neat BMI resin, 28.9% and 44.0% improvement respectively are achieved. The homogenized CNTs in the matrix provided a uniform tough and strong network in the composites, rendering the as-obtained composites with much improvement in modulus and hardness (Table 1).

The CNT/BMI composite can bear tough high-temperature applications. Fig. 5 shows the thermal decomposition temperature (T<sub>d</sub>) of 2% weight loss at 414 °C and glass transition temperature (T<sub>g</sub>) up to

276 °C. Compared to neat BMI resin, a little decrease of T<sub>g</sub> and T<sub>d</sub> of the CNT/BMI composite derived from the high CNT loading which affected the BMI resin curing. However, the as-obtained bulk CNT/BMI still holds promising applications at high temperature.

#### 4. Conclusions

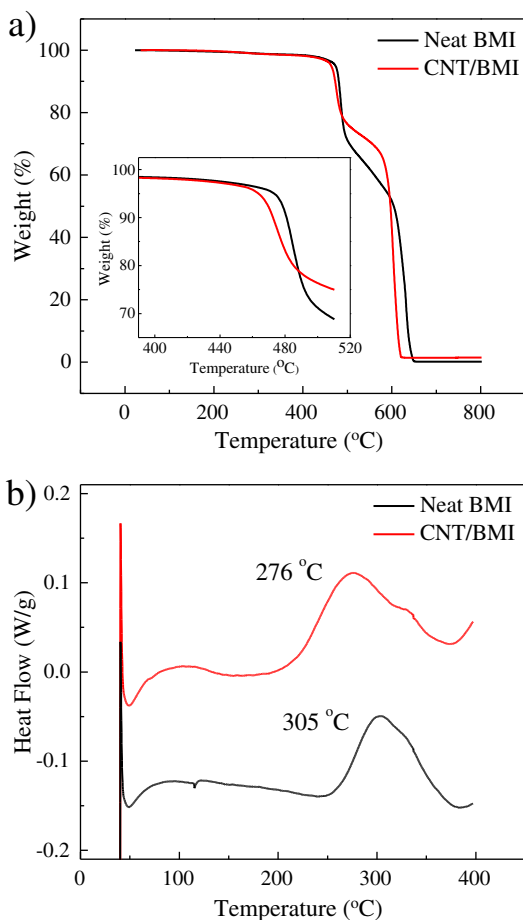
A high pressure homogenization process was adopted to disperse agglomerated MWCNTs into BMI matrix for direct fabrication of strong CNT/BMI composites. The CNTs were uniformly dispersed into the resin matrix under high pressure compression. The dense composite of ~38 wt.% MWCNT/BMI shows the compression modulus at 8.5 GPa and hardness at 0.58 GPa, corresponding to a 44% and 28.9% increase, respectively. This also provides a simple, efficient, and economic method to directly disperse CNTs in matrix for advanced composites.

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**Fig. 5.** (a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of neat BMI and CNT/BMI composites.

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