Poptube Technology: Enabling Next Generation Multiscale and Multifunctional Structural Composites

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ABSTRACT

This study explores a novel nanoengineering technique, Poptube technology, and to use this method to manufacture multiscale, multifunctional structure composites with superior mechanical performance and durability. The PopTube technology is a novel approach to fast grown CNTs on reinforcing fibers in large volume. In this technique, only a single chemical is used to provide both the carbon source and catalyst of CNT growth. Microwave is used to directly heat carbon fibers/fabrics to provide fast and energy-efficient heating. This technique takes only 15-30 seconds to grow CNTs under the microwave irradiation at room temperature in the air, with no need of any inert gas protection, and additional feed stock gases, typically required in chemical vapor deposition (CVD) approach. Experimental studies have revealed that the interlaminar fracture toughness of composite laminates can be significantly enhanced by this technology. Compared with existing CVD method, PopTube technology enjoys many advantages. It requires very simple equipment, can be easily scaled up for large-scale manufacture, and is highly energy-efficient and cost-effective. PopTube Technology has great potential to enable large-scale application of CNTs in nest generation multiscale, multifunctional structural composites.

CHALLENGES IN APPLICATION OF CARBON NANOTUBE IN STRUCTURAL COMPOSITES

Fiber reinforced polymers (FRPs) have been extensively implemented in the fields of aerospace, automotive, electronic, renewable energy, civil infrastructure, and sports equipment for their higher specific strength and stiffness, lighter weight, and better fatigue and corrosion resistance. A typical FRP composite consist of reinforcing microfibers/fabrics, polymer matrix, and an interphase zone developed between the fiber and matrix [1]. Although the fiber-dominated properties of FRPs (longitudinal tensile strength and elastic modulus) of a well-designed FRP are excellent, they also have some drawbacks. Since the matrix and the interphase zone

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FRPs are often poor, including the transverse tensile strength and longitudinal compressive strength, fracture toughness, the interlaminar shear strength, and the load threshold for damage initiation. These poor properties severely limit the overall performance and applications of FRPs.

With an aim to overcome the weakness of FRP composites, extensive studies have been conducted in last decade to reinforce FRPs using carbon nanotubes (CNTs) because of CNTs' extraordinary mechanical properties and excellent thermal and electrical properties. Compared with other conventional structural materials, CNTs have much higher strength (tensile strength > 100 GPa), stiffness (Young's modulus of ~ 1.5 TPa), and flexibility (20%-30% at failure) [2]. CNT reinforcements have the potential to produce much stronger and tougher materials than traditional reinforcing materials. The excellent thermal and electrical properties of CNTs can provide materials with functional advantages such as self-sensing abilities, flame retardancy, wear resistance, electrical and thermal conductivity, electromagnetic interference shielding, and improved thermal stability. When nanoscale CNTs are used alongside with microscale carbon or glass fibers as reinforcement, hierarchical multifunctional composites are formed.

In this type of composites, the microfibers are primary reinforcements and the CNTs are used to improve the mechanical performance of the matrix, to strengthen the transverse direction of the composites, to enhance the stress transfer between the primary fibers and the matrix, and to add multifunction to the composites. To reach these goals, two basic schemes have been used in the current research to incorporate the CNTs into polymer composites. As shown in Fig. 1, these two schemes are: a) CNT/Fs dispersed entirely through the matrix of the composite, and b) CNTs/Fs grown on the primary fibers.

Scheme *a* is most straight forward and adopted most widely in the literature [3-5]. By using this scheme, improved mechanical properties such as strength, elastic modulus, and fracture toughness and lower coefficient of thermal expansion of the matrix can be obtained. However, these improvements have fallen short of predicted values. One major reason responsible for the disappointing reinforcing effects of CNT/Fs has been identify by many authors as poor dispersion of high loading fractions of CNT/Fs in the matrix. Due to strong van der Waals forces between CNT/Fs, CNT/Fs are easy to conglomerate to form bundles and ropes. It has been shown that poor dispersion and rope-like entanglement of CNTs can weaken composites significantly. For this reason, results on CNT/Fs reinforcing reported are not consistent. A homogeneous dispersion of CNT/Fs into matrix is the key to reach ideal reinforcing effect.

To avoid the difficulty of dispersing CNTs as described above, the Scheme b, directly growing CNTs on fibers has been proposed recently. Thostenson and Chou [6] first successfully grew CNTs on the surface of carbon fibers using a thermal chemical vapor deposition (CVD) method. After that, a number of studies were carried out to study the detail of this technique [7]. This technique was also extended to grow CNTs on various substrates, including ceramic fibers, glass fibers, alumina fibers, and Portland cement particles. Besides fibers, CNTs were also successfully grown on the surface of fabrics.

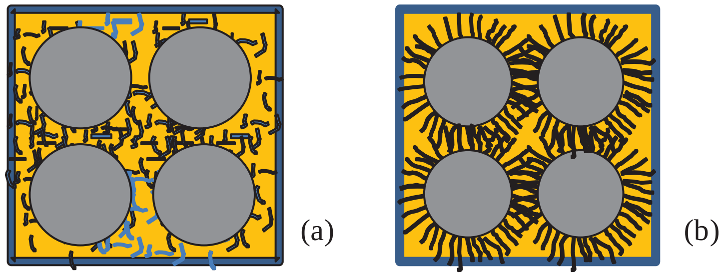

Figure1. CNT reinforcing schemes: (a) CNTs dispersed in matrix; (b) CNTs grown on fibers

Compared with dispersion of CNTs thoroughly in the matrix, growing CNTs on reinforcement fibers has many advantages. First, the extreme difficulty of dispersion of CNT/Fs is eliminated, and high loading fraction of CNT/Fs through this technique is possible. Secondly, the CNT/Fs are radically aligned around the fiber. This direction is ideal to reinforce the transverse direction of the fiber reinforced composite. This alignment can also prevent micro-buckling of the fiber, which is a critical failure mode of the fiber under compression. Thirdly, stress transfer between the fiber and the matrix is improved significantly due to the increased surface area, mechanical interlock, and local stiffening created by the CNTs on the fiber. Due to these advantages, directly growing CNTs on microfibers has become the focus of current research.

Existing research so far has focused on demonstrating the great potential of CNTs to improve the performance of FRPs at laboratory set-up. For real structural application, however, existing techniques to integrate CNTs into FRP composites must be scaled up for large-scale manufacturing/processing. CVD method and its variations are predominately used to grow CNTs on fibers [8-13]. By using this method, the catalysts are first prepared on fibers. These fibers are then put in a furnace and heated to desired reaction temperature. The carbon source is provided by a feed gas such as benzene, methane, acetylene, or carbon monoxide. When the feed gas passes through the furnace, it will be cracked and decomposed over the catalysts to form CNTs directly on the fibers. It is difficult to scale-up the laboratory set-up of CVD for large-scale processing of fibers/fabrics since the whole reaction must be finished in a closed reaction chamber, and inert gas and combustible gases are used under high-temperatures. Two recent studies explored the possibility to scale up the laboratory CVD system to grow CNTs on fibers [14-15]. Villoria et al. [14] verified that CNTs can be grown on moving substrates within a CVD chamber. However, their system cannot produce CNTs continuously. Malecki et al [15] designed an "open-ended" CVD chamber allowing for possible reel-to-reel growing CNTs on fibers. However, their system is complicated and has to use large amount of N_2 gas to ensure very low concentration of O_2 in their open-ended reaction chamber. A processing technique which meets need of large-scale manufacturing capacity is nonexistent

POPTUBE TECHNOLOGY

To address the three challenges in application of CNTs in structural composites and overcome shortcomings of existing CNT manufacture methods, an innovative method, PopTube technology [16] is exploited to grow CNTs directly on the surface of carbon fabrics in this study.

Working Principle

Aiming to integrate CNTs into cementitious materials, the authors invented a new approach to grow CNTs on substrate such as fly ash particles using microwave heating [16]. The working process of this method is illustrated by Fig. 2: i) a layer of conducting polymer is in-situ deposited on the surface of the substrate (particle/fiber); ii) the resultant particle/fiber with conducting polymer coating are then mixed well with ferrocene in solid state; and iii) upon microwave irradiation, the conducting polymer layer absorbs the microwave irradiation, and the temperature rises quickly to a level high enough to decompose ferrocene to iron and cyclopentadienyl groups. In this environment, iron nanoparticles serve as the catalyst; and the carbon atoms pyrolyzed from cyclopentadienyl ligand serve as the carbon source for CNT growth. Using this method, it takes only 15-30 seconds to grow CNTs on fly ash particles at room temperature in the air, with no need of any inert gas protection, and additional feed stock gases, typically required in CVD approach. This approach requires very simple equipment, can be easily scaled up for large-scale manufacture, and is highly energy-efficient and cost-effective.

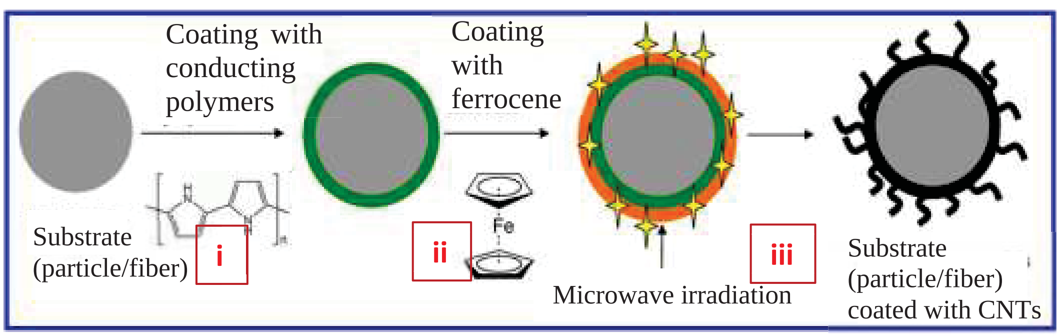

Figure 2. Growing CNTs on substrate (particle/fiber) using microwave irradiation

Using this microwave approach, CNTs has been successfully grown on fly ash particles, as shown in Fig.3. Spaghetti-like, hollow CNTs were observed with outer diameter in the range of 30-50 nm. Although some of the catalyst nanoparticles were trapped in the CNTs, more catalyst nanoparticles were capped at the tip of the tubular structures, which are the bright dots in the scanning electron microscopy (SEM) images. High resolution transmission electron microscopy (TEM) image (Fig. 4) shows that the CNT manufactured by this method is mainly multi-walled nanotubes (MWNT) in nature, with around 20 layers of coaxial carbon lattice.

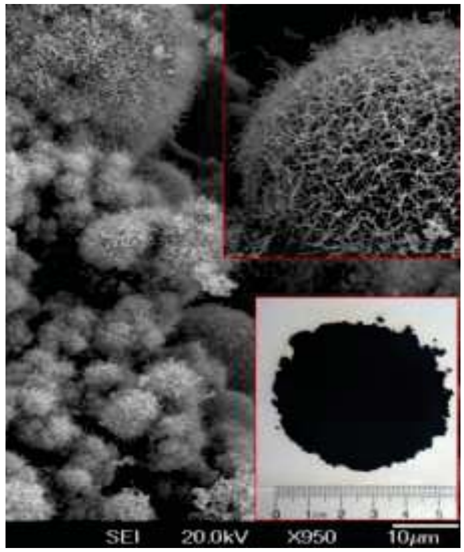

Figure 3. SEM images of as produced CNTs on fly ash, inserts: (top) zoom-in SEM image of the CNTs on fly ash; (bottom) produced 10 g fly ash grown with CNTs

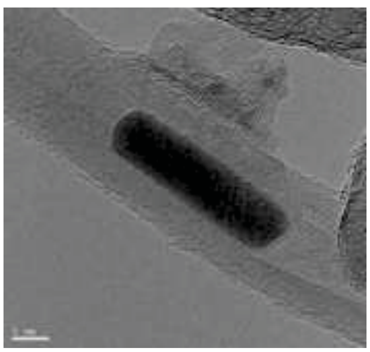

Figure 4. TEM image of as-produced CNTs

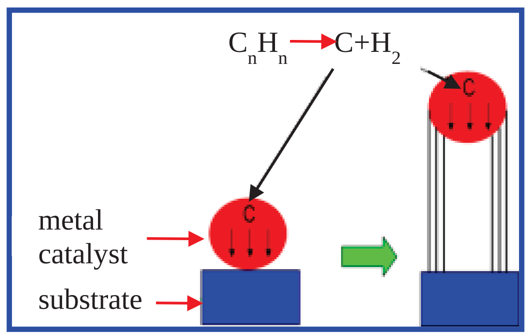

Figure 5. Tip-growth mechanism of CNT

By reviewing TEM images, we found the catalyst particles are at the tip or middle part of the CNTs, indicating that those CNTs are in the tip-growth mode (Fig 5) instead of base-growth mode [17]. The C_nH_n is actually from the decomposition of ferrocene, which generates Fe catalyst as well. The reason for a tip growth while not base-growth could be due to the weak interaction of the iron catalyst and the conducting layers, e.g., conducting polypyrrole coating.

Advantages of PopTube Technology

Compared with existing CVD based methods, PopTube Technology enjoys three distinct advantages:

1. It requires very simple equipment for large-scale and high-yield manufacture. The entire process is conducted in the ambient condition with a microwave.
2. It is highly energy-efficient. Unlike in the CVD method where most of energy is consumed in heating the furnace enclosure, the microwave energy can be selectively absorbed by carbon fabrics. In addition, the microwave has a high

efficiency of energy transfer compared to the traditional thermal heating methods.

3. It is highly cost-effective. Only one inexpensive chemical, ferrocene, is employed to serve as both the catalyst and the carbon source. The industrial level price of ferrocene is approximately $3.6/lb (see http://www.yuancailiao.net/trade/offerdetail-254191.aspx). Together with the simple equipment and high energy-efficiency, this microwave method can make CNTs at a cost significantly lower than any other existing methods. It has the potential to make it affordable to reinforce bulky structural materials using CNTs.

GROWING CNTS ON CARBON FABRICS

In this study, microwave heating approach described above is used to grow CNTs on carbon fibers/fabrics, one of most important reinforcements for FRP composites. Because carbon fibers/fabrics have moderate conductivity (10^{-2}~10^{2}Ω•m) similar to conducting polymers, they can be directly heated by microwave too. The conducting polymer coating shown in Fig. 2 is not needed in growing CNTs on carbon fibers/fabrics. Therefore, only two simple steps (ii, and iii in Fig. 2) are needed to grow CNTs on carbon fibers/fabrics using the microwave heating method.

CNTs were successfully grown CNTs on carbon fabrics using this new method, as shown in Fig. 6. Figure 6(a) shows a carbon fabric after growing CNTs using microwave heating. Figure 6(b) shows a SEM image of CNTs grown on the carbon fabric.

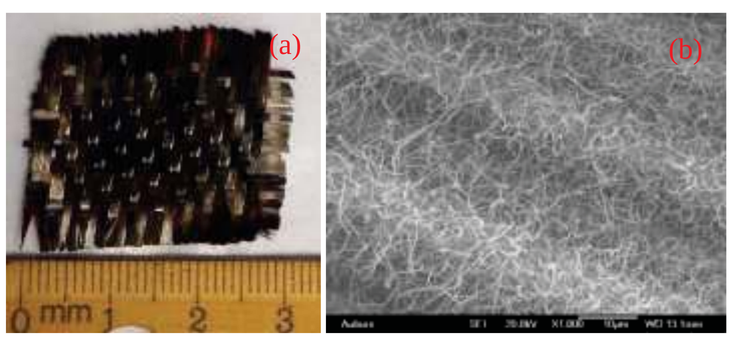

Figure 6. (a) carbon fabrics grown with CNTs using microwave; (b) SEM image of CNTs grown on carbon fabrics

Interlaminar Fracture Toughness Enhanced by PopTube Technology

A laminated composite panel was manufactured using 14 layers of 3K standard wave fabrics grown with CNTs using microwave heating method. A release film was inserted between layers 7 & 8 to create pre-crack in the panel. This panel was then cut into three double cantilever beam (DCB) specimens (Fig. 7) to measure the mode I interlaminar fracture toughness of this laminated composite according to

ASTM D5528-01. The specimen edges were painted with white brittle coating, and vertical lines were marked every *1 mm* to record the crack length with loading, as shown in Fig. 7. As control group, another three DCB specimens were laminated composite panels were manufactured with 14 layer virgin carbon fabrics. The dimensions of the specimens, testing conditions, and measured mode I fracture toughness are presented in Table 1. It can be seen that after growing CNTs on fabrics using microwave heating, the average interlaminar mode I fracture toughness has been increased by 44%.

TABLE I. MODE I INTERLAMINAR FRACTURE TOUGHNESS MEASURED FOR DCB SPECIMENS WITH AND WITHOUT CNTS

Specimen	AVG THICKNESS [in]	AVG WIDTH [in]	LENGTH [in]	TEMP/ HUMIDITY [^{o} F/ % RH]	G_{IC} [KJ/m^2]	G_{IC} AVG
Fabrics without CNTs	0.126	1.001	5.5	78 ^{o} F/55%	0.6967	
	0.133	1.002	5.5	78 ^{o} F/55%	0.6395	
	0.135	1.001	5.5	78 ^{o} F/55%	0.6882	0.6748
Fabrics with CNTs	0.113	1.001	5.5	78 ^{o} F/53%	0.9977	
	0.118	1.001	5.5	78 ^{o} F/53%	0.9550	
	0.122	1.001	5.5	78 ^{o} F/53%	0.9706	0.9744

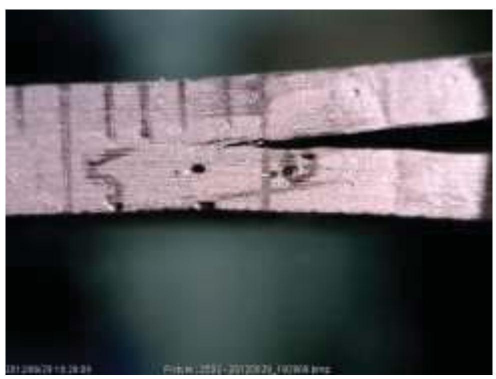

Figure7. DCB specimen used to measure model I fracture toughness

Damage on Fibers

Since carbon fibers are heated in open air in this technique, there is a concern on whether any significant damage can be induced to the carbon fibers. To evaluate the possible damage induced to the carbon fibers by microwave heating, we used SEM to check virgin fibers (Fig. 8(a)) and the ones (Fig. 8(b)) microwaved with the same duration as in growing CNTs. The virgin carbon fibers are relatively smooth with shallow groves and some manufacturing imperfection, as shown in Fig. 8(a). After microwave heating in air, the surfaces of the carbon fibers become rougher because of the oxidation of the carbon. No any pits which could affect the tensile strength of fibers can be identified from this figure, indicating that microwave heating may cause very little damage to the fibers. This is not surprising since the microwave heating to grow CNTs only lasts for less than 30 seconds. With such a short period of heating, the oxidation of the carbon surface is very limited. Interestingly, no manufacturing defect can be found on microwaved fibers, suggesting that microwave heating may improve the quality of the carbon fibers by removing weak boundary layer. Indeed, oxidation the carbon fibers has been explored as a surface processing technique to enhance the bonding between the fibers and the matrix. Oxidation and gasification of carbon fibers during the CNTs growing process should be even lower because: 1) fibers are protected by a layer of ferrocene from the open air, and ii) a large amount of heat is absorbed by the gasification of ferrocene and the growth of CNTs.

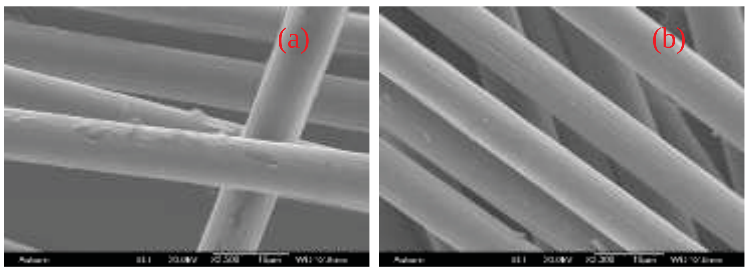

Figure 8. (a) carbon fibers before microwave irradiation; (b) carbon fibers after microwave heating

CONCLUSIONS

The PopTube technology will lead to revolutionary advances to the existing CNT manufacturing technologies and will enable surface modification of engineering materials through providing a novel, highly energy-efficient and cost effective method to grow CNTs on fibers/fabrics in large-scale. The PopTube technology can effectively overcome major challenges hampering the application of CNTs reinforcement, enabling large-scale manufacturing of the next generation CNT reinforced structural composites. These new materials will possess superior mechanical performance and many novel properties, and will immediately find their applications in many areas critically needed by our nation, such as energy, defense, and civil infrastructure systems.

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