Poptube Technology, enabling multifunctional hybrid composites for next generation aircrafts

NASA Award Number: NNX13AB80A; 11/15/2012-06/30/2014

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Purpose

The purpose of this study is to use a novel nanoengineering technique, Poptube technology, to manufacture multiscale, multifunctional structure composites with superior mechanical performance and durability. The PopTube technology is a scalable, highly energy-efficient and cost effective approach to fast grow 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 grown 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.

Background

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. Since the matrix and the interphase zone are much weaker than the fibers, the matrix and interphase-dominated properties of 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. 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. 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. A processing technique which meets need of large-scale manufacturing capacity is nonexistent.

To meet the need of real, large-scale applications of CNTs in FRP composites, this study proposes a simple, highly energy-efficient, and highly cost-effective nanoengineering technique to grow CNTs on fibers/fabrics. This research will lead to a new paradigm of integration of CNTs with conventional micro-size fiber reinforcements to form high-performance, highly durable, multifunctional, hierarchical hybrid structural composites. The novel PopTube technique provides a much-needed solution for real application of CNTs reinforcement in large-scale structural composites for next generation aircrafts.

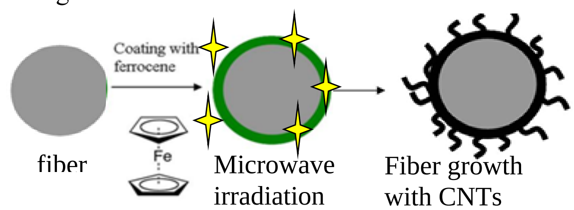


Figure 1 Grow CNTs on carbon fiber using PopTube technology

Approach

PopTube method is a novel approach to grow CNTs using microwave irradiation. The approach to grow CNTs on carbon fibers/fabrics can be described in Figure 1: i) mixing carbon fibers/fabrics well with ferrocene in solid state; and ii) microwaving the resulted fibers/fabrics with ferrocene. Upon microwave irradiation, the carbon fibers/fabrics will absorb the microwave irradiation, and the temperature will rise very quickly to a level high enough to decompose ferrocene to iron and cyclopentadienyl groups. In this environment, iron nanoparticles will stick on the surface of the heating layer, serving as the catalyst; and the carbon atoms pyrolyzed from cyclopentadienyl ligand will serve as the carbon source. This novel technique for manufacturing CNTs is very similar to make popcorn in your kitchen. For this reason, we refer this technique as Poptube technology.

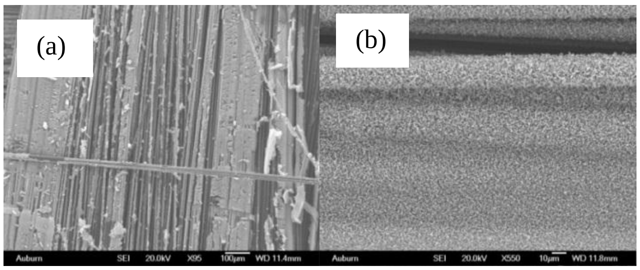
Accomplishments

We have accomplished all proposed studies in Phase I and reached two milestones: 1) successful growing CNTs on carbon fabrics using Poptube Technology; and 2) evaluating mechanical behaviors of hybrid composites made from carbon fibers grown with CNTs using Poptube Technology. Two accomplishments exceed our Phase I goals: 1) Poptube Technology is significantly simplified for carbon fabrics; and 2) "fuzzy tubes" are also be produced by Poptube Technology.

1) PopTube technology has been simplified to grow CNTs on carbon fibers/fabrics

Poptube Technology has been simplified for growing CNTs on carbon fabrics. The conducting polymer layer used in original Poptube technology is eliminated since carbon fibers can absorb microwave directly (Fig. 1). Figure 2(a) shows that CNTs have been successfully grown on as-received carbon fabrics using the simplified Poptube Technology. Optimal growing conditions of CNTs have also been determined. Study also shows that we can control the coverage and morphology of CNTs grown by Poptube Technology through pretreating the carbon fabrics with acetone and adding extra carbon source such as hexane, as shown in Fib. 2(b).

Fig.2 CNTs grown on carbon fabrics using simplified Poptube Technology: (a) CNTs grown on as-received carbon fabrics; (b) CNTs grown on acetone treated carbon fabrics with addition of hexane



2) Metallocene with transition metal other than iron can be used to replace ferrocene to grown CNTs.

Bis(cyclopentadienyl) cobalt has been used to replace ferrocene to successfully grow CNTs, as shown in Fig. 3. Since cobalt doesn't react with carbon, using cobalt based metallocene to replace ferrocene to grow CNT to reduce damage to fibers.

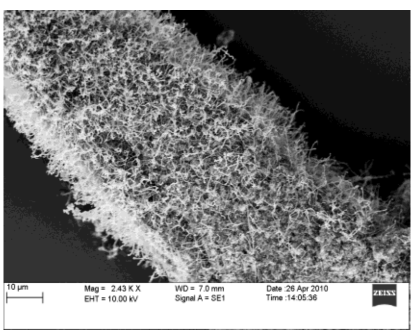


Fig. 3 CNTs grown on carbon fiber using Bis(cyclopentadienyl) cobalt

3) ***Hybrid composites manufactured from carbon fabrics grown with CNTs by Poptube Technology have better resistant to Mode I delamination***.

A laminated composite panel was manufactured using 14 layers of 3K standard wave fabrics grown with CNTs using Poptube method with a pre-crack between layers 7 & 8. This panel was then cut into three double cantilever beam (DCB) specimens to measure the mode I interlaminar fracture toughness of this laminated composite according to ASTM D5528-01. As control group, another three DCB specimens were laminated composite panels were manufactured with 14 layer virgin carbon fabrics. As shown in Table 1, the average interlaminar mode I fracture toughness of the laminated has been increased by 44% due to the treatment of using Poptube technology. More significant improvement can be achieved if optimal growing conditions are used.

End Notched Flexural (ENF) specimens have been used to measure the mode II interlaminar fracture toughness and results are provided in Table 2. It can be seen that there is no essential difference in initial mode II fracture toughness between the specimens treated by Poptube technology and the virgin one with growing CNTs. Tensile strength of the hybrid composite and the composite using virgin fabrics were measured and shown in Table 3. The tensile strength of the hybrid composite is about 20% lower than that of the virgin composite.

The reduction in Mode II fracture toughness and tensile strength in hybrid composite could be induced by two possible reasons. Firstly, the poor CNTs coverage on carbon fabrics can reduce, if not improve the Mode II fracture toughness and stress transfer between carbon fibers and the matrix. SEM analysis shows CNTS coverage on the fabrics is not uniform and in some area, no CNTs were formed on the treated carbon fabrics. Secondly, CNTs grown on the fabrics can reduce the wettability of the fabrics. Because hand layup was used to manufacture the hybrid composite, much higher porosity can be observed in the interphase zone between the carbon fiber and the matrix. These two reasons may actually weaken the interface rather than strengthen the interface.

Table 1. Comparison of Mode I interlaminar fracture toughnesses of hybrid composites and controlled group

Speci-men	AVG THK. [in]	AVG WID. [in]	LEN. [in]	G_{IC} [KJ/m^2]	G_{IC} Ave.
Fabrics without CNTs	0.126	1.001	5.5	0.697	
	0.133	1.002	5.5	0.640	
	0.135	1.001	5.5	0.688	0.675
Fabrics with CNTs	0.113	1.001	5.5	0.998	
	0.118	1.001	5.5	0.955	
	0.122	1.001	5.5	0.971	0.974

Table 2 Comparison of Mode II interlaminar fracture toughnesses of hybrid composites and controlled group

Specimen	G_{IIC} (KJ/m^2) Initial	G_{IIC} (KJ/m^2) propagation
Virgin	1.17	0.97
Treated	1.07	0.70

Table 3 Comparison of tensile strength of hybrid composites and controlled group

specimen	Tensile strength (MPa)	Failure strain	Modulus of Elasticity (GPa)
Virgin	676	0.0024	281
Treated	536	0.0020	270

To overcome these two problems, our current research in Phase II are focusing on using industrial microwave to grow CNTs, which will produce much better quality control on the CNTs growth because of its capacity to produce uniform microwave energy field. Advanced manufacturing technology will be used to manufacture the hybrid composite, in which pressure will be applied to ensure fully wet of the fabrics after grown with CNTs.

4) ***Poptube Technology introduces only minor damage to carbon fibers.***

Single fiber tensile tests were conducted to quantify any damage induced to the fibers by the microwave irradiation. Single fiber tensile testing results are summarized in Fig. 4. Microwave heating on three different fibers are compared in these figures: 1) fiber as received without any treatment to simulate the microwave heating on virgin fibers; 2) fibers after soaking in acetone to remove sizing to simulate microwave heating on fibers without sizing; and 3) fibers soaked in acetone and then coated with ferrocene to simulate the CNTs growth using PopTube Technology. Three microwave heating duration are used in these testing: 15s, 30s, and 45s, corresponding to the minimum, optimal, and maximum time needed in the PopTube Technology, respectively. All data shown in Figure 4 are average of five duplicate specimens.

Figure 4 shows that microwave heating can cause some damage on carbon fibers. To grow CNTs on carbon fabrics using the proposed technology, 15s can reduce the tensile strength of the carbon fiber to 92%, and an extended microwave heating of 45s can reduce the tensile strength further to 86%. The damage on the carbon fiber induced by the PopTube technology is much lighter in comparison with the commonly used CVD method, which has been reported to reduce the strength of the carbon fibers over 50%. This may be because of the short heating period used in the proposed method. It is also interesting to pointed out that after soaking the carbon fibers in Acetone, 15s microwave heating can even enhance the strength of the carbon fiber. This may be caused by the healing effect of Acetone on the fiber and annealing effect of the microwave heating.

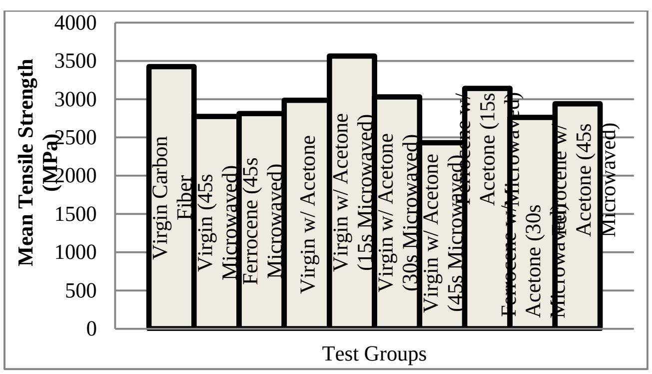


Figure 4 effect of microwave heating on the tensile strength of carbon fibers

5) ***Invention: Three-dimensional nano-carbon "fuzzy tubes" have been produced by the Poptube Technology.***

A new type of nano-carbon reinforced material, "fuzzy tubes" was invented in this Phase I study. We successfully demonstrated that Poptube Technology can produce not only "fuzzy fibers", but also "fuzzy tubes". Figure 5 shows these "fuzzy tubes" produced in our Phase I study, in which secondary CNTs are grown on the primary CNTs. "Fuzzy tubes" extends the concept of "fuzzy fibers" from the micrometer scale to the nanometer scale. The advantages of "fuzzy tubes" over regular CNTs are similar to those of "fuzzy fibers" over regular fibers. For example, stress transfer from the matrix to the CNTs can be significantly improved if "fuzzy tubes" are used. This can effectively overcome another barrier preventing practical application of CNTs in composites: low bond strength between CNTs and matrix. "Fuzzy tubes", as three-dimensional nano-materials, have great potential to be developed into a next-generation nano-reinforcement to replace currently used one-dimensional CNTs. To the knowledge of the PIs', there is no other existing method that can produce "fuzzy tubes" at similar cost and quantity as Poptube Technology.

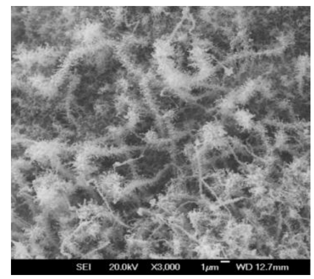


Fig. 5 "Fuzzy tubes" produced by the Poptube Approach in which secondary CNTs are grown on primary CNTs

Current TRL: 3

Applicable Programs/Projects

A number of NASA research programs/projects might benefit from this research:
Aviation Safety Program: Vehicle Systems Safety Technologies Project
Fundamental Aeronautics (FA) Program: The fixed wing project
NASA Glenn Research Center at Lewis field: Advanced Composite Mechanics, Environmental Durability of Advanced Materials, Polymers and Polymer Matrix Composites, Structural Integrity.

Publications and Patent Applications

1. Jialai Wang, Xinyu Zhang, 2013. Enable carbon nanotube reinforcement in infrastructure material using Poptube Approach. Presented at Engineering Mechanics Institute Conference, ASCE, August 4-7, 2013.
2. Jialai Wang, Xinyu Zhang, 2013. Poptube Technology: Enabling Next Generation Multiscale and Multifunctional Structural Composites. ASC 28th annual technical conference, Sept 9th – 11th, 2013, State College, PA, CD-ROM proceeding (9 pages).

Awards & Honors related to LEARN Research

Graduate student Will Guin who worked on this project won the first place of three-minute dissertation competition of The University of Alabama and "People's Choice" of the same competition of the Southeastern Region.