RECENT DEVELOPMENTS IN BORON FIBER-REINFORCED COMPOSITE MATERIALS

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ABSTRACT

Boron fiber was originally developed in the 1960s as a high strength, high modulus reinforcement for composite aerospace structures. It is produced by a chemical vapor deposition process as a relatively large diameter (100-140 μm) monofilament. New enhancements to boron composite prepreg manufacturing methods have enabled compatibility with automated fiber placement machines, thus allowing increased flexibility in the tailoring of composite mechanical and thermal properties. Boron fiber remains relevant for current and new aerospace structures due primarily to its very high compressive strength relative to carbon fibers. Recent development results will be presented showing the properties of boron fiber-reinforced composites in several resin systems. Results with hybrid boron-carbon composites in particular showed an 80-170% increase in compressive strength relative to the carbon-only analog composites.

1. INTRODUCTION

1.1 Boron: the original high performance aerospace composite material

Chemically vapor deposited (CVD) boron fibers [1] have been used for over four decades as a composite reinforcement in a number of structural aerospace applications. Since their original incorporation into the horizontal stabilizers of the F-14 fighter jet in the 1970s, boron fiber reinforced epoxy resin composites can be considered the first high performance composite aerospace material. Boron fiber reinforced composites have subsequently been incorporated into many aerospace applications including the F-15, B-1, Blackhawk helicopter, and the Space Shuttle.

1.2 Compressive strength of boron fiber reinforced composites

Due to its very high strength in compression, composite reinforcement using boron fiber is particularly advantageous for structures which must withstand high compressive loading. The compressive strength of uniaxial boron composites has been difficult to measure due to difficulties in proper load introduction and buckling issues. Cross-ply stacking sequencing techniques have been necessary in order to reliably determine the uniaxial compressive strength of boron fiber composites. Depending on stacking sequence, the compressive strength of boron

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composites, normalized to a fiber volume fraction of 50 %, has a previously reported [2] range from 2.5 GPa (360 ksi) to 3.9 GPa (560 ksi). Based on this analysis, the true compressive strength of a boron/epoxy resin composite at 50 % fiber volume was reported as 3.7 GPa (530 ksi) [2].

1.3 Hybridized composite of boron and carbon fibers

Today, carbon fiber reinforced composites are more prevalent in aerospace structures than boron composites. However, the very high compressive strength of boron fiber (a factor of 2 or greater than most carbon fibers) make it advantageous to hybridize boron and carbon fiber in applications and structures requiring high compressive loading. Hybrid composites of boron and carbon fibers (trade name Hy-Bor®) are employed in certain models of the unmanned Predator aircraft. Hybridized composites of boron and carbon are also used to provide stability to space structures such as the James Webb Space Telescope and the Chandra X-ray Observatory.

2. EXPERIMENTATION

2.1 Boron fiber synthesis by chemical vapor deposition (CVD)

The boron fibers used here were synthesized using a modification of a commercial CVD process [1]. A 12µm diameter tungsten wire was drawn continuously through a 2-meter vertical glass reactor that was sealed at the top and bottom by pools of mercury (Figure 1). The mercury forms both an electrical contact and a gas seal. A mixture of boron trichloride (BCl_3) and hydrogen (H_2) was admitted through an inlet at the top and spent process gases were exhausted through an

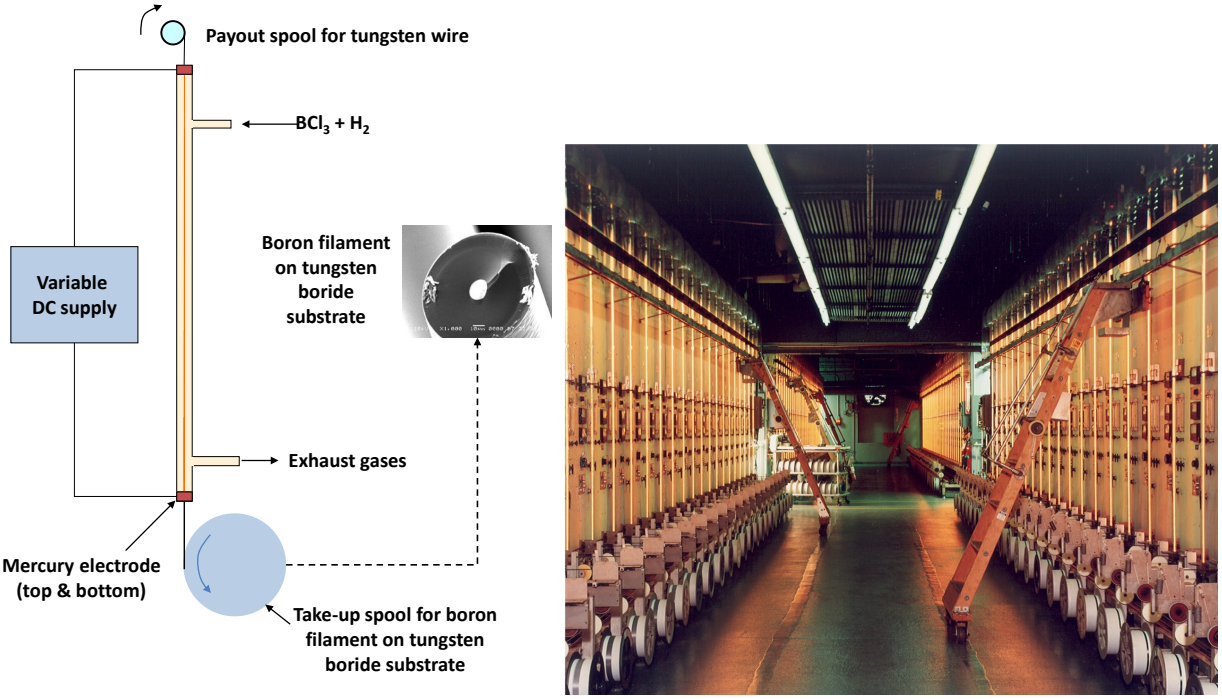


Figure 1. Process diagram showing CVD synthesis of boron fiber (left); CVD boron fiber manufacturing facility (right photo).

outlet near the bottom. The filament in the reactor was resistively heated to 1300-1400°C by application of a DC voltage (typically 2-3 kV) to the mercury seals. At this temperature, the BCl_3 was reduced by the H_2; pure, solid, amorphous elemental boron was deposited and byproduct hydrogen chloride was exhausted. The diameter of the boron produced was controlled by the draw rate of the filament through the reactor; a rate of 3-4 m min^{-1} results in a 100µm B fiber (with a reacted tungsten boride core, primarily W_2B_5) being spooled continuously at the bottom. TEM and x-ray diffraction examination [3] indicated CVD boron fibers are amorphous, exhibiting no long-range crystalline order. A scanning electron micrograph (SEM) micrograph of the boron fiber surface (Figure 2) shows fiber surface morphology. The "corn-cob" surface texture (inset to Figure 2) is indicative of macroscopic growth morphology and not the size of individual grains.

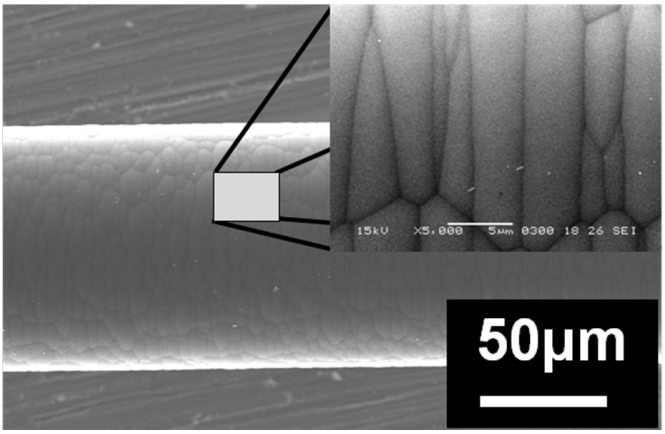


Figure 2. Surface morphology of CVD boron fiber. Inset shows a 25µm wide area of the fiber surface. The "corn-cob" texture is indicative of macroscopic growth morphology and not the size of individual grains [3].

2.2 Two-step method for boron fiber prepreg tape fabrication

Boron/resin prepreg tape is generally fabricated using two methods. The first method is called the two-step method. In the first step of this process (Figure 3), 0.64 cm (¼-inch) wide prepreg tape is fabricated by paying out individual boron filaments from a 56-position fiber creel and immersing a collimated array of boron filaments in a melt of neat resin. The collimated fibers ride over a heated coating roller that constantly rotates in a pot of melted resin. Fiber spacing is most commonly 208 filaments in^{-1} for 100 µm diameter boron fiber. Resin content can typically vary from 20 to 35 % by weight. In the second step of this process (Figure 3), two or more ¼-inch tapes are collimated and joined to make wider tapes ranging from 1.3 cm (½-inch) wide up to 15.2 cm (6 inch) wide. During the second step, backing film and/or support scrim material is applied to the tape. Traditionally, the tape fabricated in the second step of this process is in the 2 to 6-inch width range. More recently, this process has been used to fabricate narrower ½-inch wide tape that is compatible with modern automated fiber placement machines. The ½-inch boron/resin prepreg tape is typically traverse wound and collected on a 6-inch diameter take-up roll (Figure 4). For narrower tapes, the width is controlled using an in-line optical width monitor.

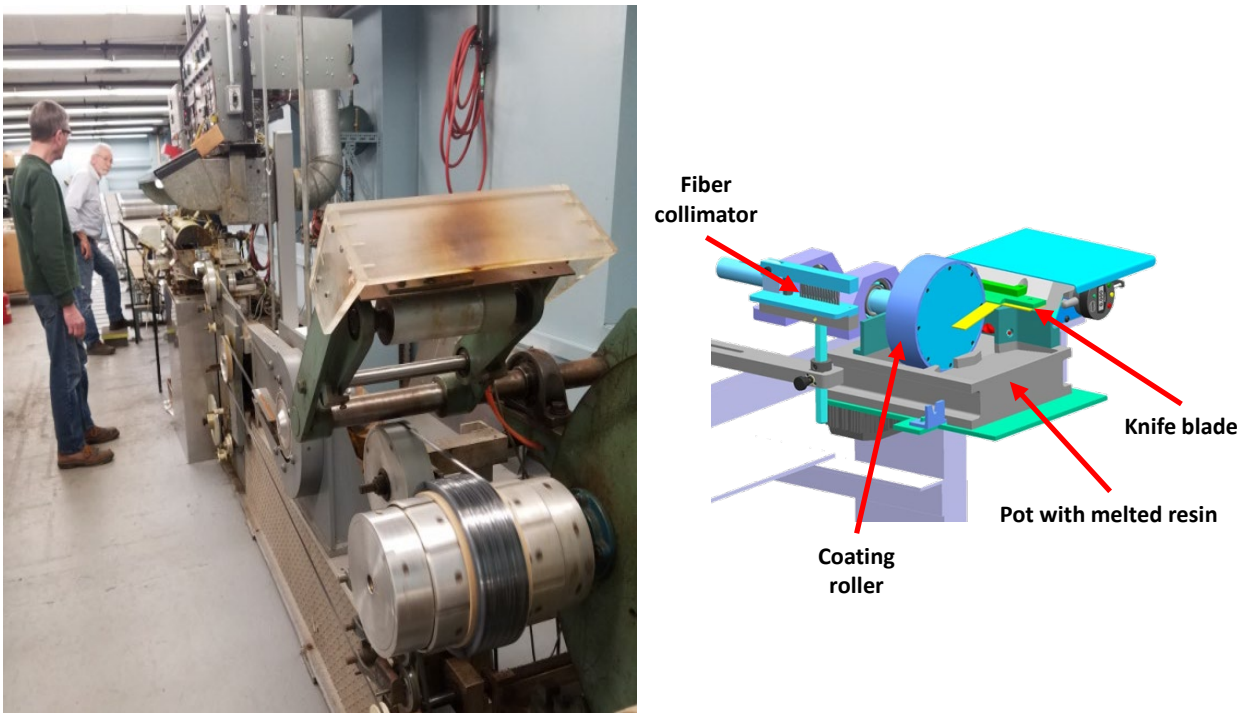


Figure 3. Quarter-inch prepreg tape fabrication (step 1 of the 2-step process) using melt dip technique (left photo); ¼-inch prepreg tape is collected on a traversed take-up roll photo bottom; the diagram shows coating roller that applies melted resin to collimated fibers that ride along the top of the roller. The knife blade adjacent to the roller controls the amount of applied resin.

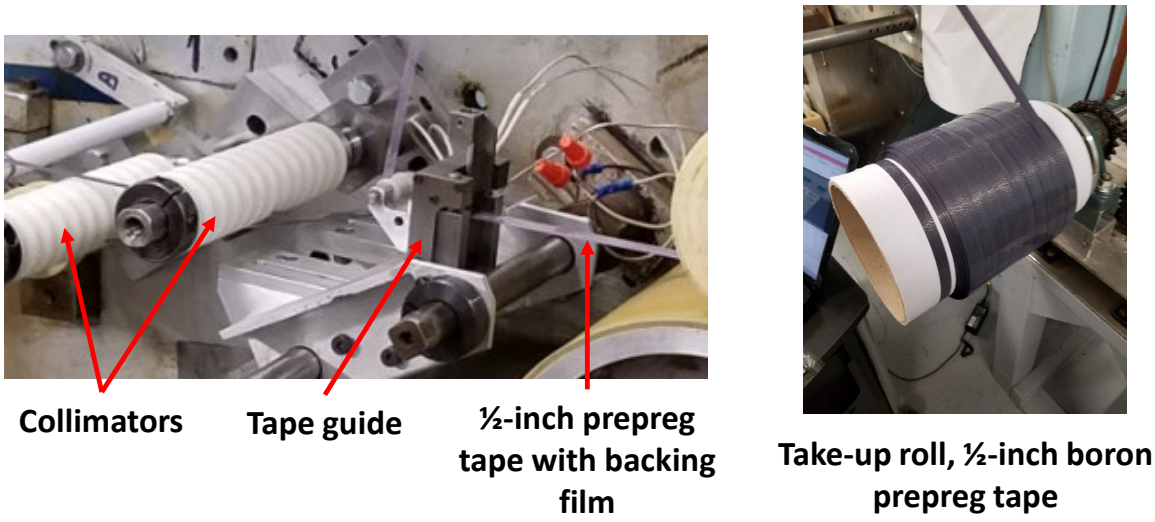


Figure 4. The second step of the two-step boron/resin prepreg tape process. Quarter-inch tapes are joined together to make wider tapes ranging from ½-inch to 6-inch wide. Above shows the fabrication of half-inch wide tape. Two ¼-inch tapes are collimated and joined together (left photo), and collected on a traversed take-up roll (right photo).

2.3 One-step method for boron and hybridized boron-carbon fiber prepreg fabrication

The more commonly used fabrication method to produce 6-inch wide boron/resin prepreg tape is called the one-step method. Hybrid boron/carbon/resin composites reported here were fabricated by this method. Individual boron filaments were paid out from a 1250 position boron fiber creel (Figure 5). The fibers were then collimated, resin was added via a resin film coated onto differential release paper; fiberglass scrim support material and backing material can be added as appropriate. In the case of boron/carbon/resin hybrid composite materials, carbon prepreg tape was added to the boron along with a topcoat of resin film and paper backing.

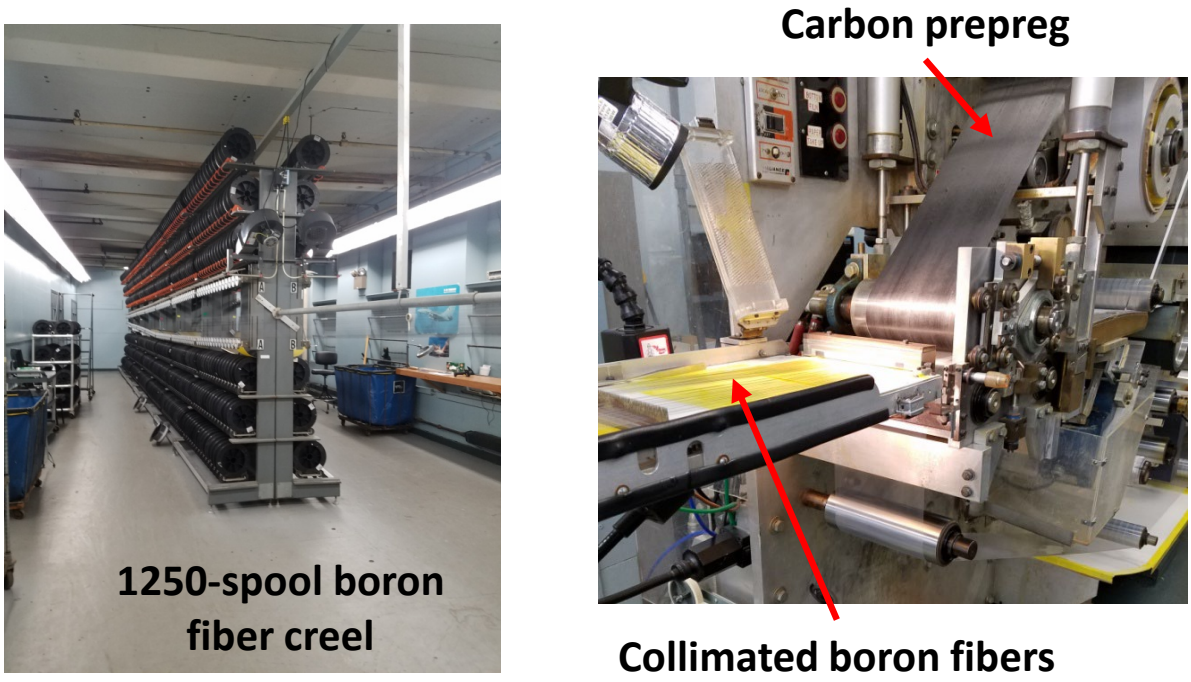


Figure 5. The one-step process to fabricate boron/resin and hybrid boron/carbon prepreg tapes. Individual 100 µm wide boron fibers from a 1250-position fiber creel are fed into a 6-inch wide collimator. Resin film, carbon prepreg tape, fiberglass scrim, and paper backing are combined as appropriate to make the final 6-inch wide boron or boron/carbon prepreg tape.

2.4 Materials used

For composite property results reported here, the boron fiber used was 100 µm (4-mil) in diameter and manufactured by the Specialty Materials CVD process. Resin systems used here included 5505 epoxy manufactured by Specialty Materials; TC350-1, a toughened epoxy resin manufactured by TenCate/Toray Advanced Composites; and TC420, a cyanate ester resin manufactured by TenCate/Toray Advanced Composites. Carbon fibers used were Toray's T1100G and Hexcel's IM7. The boron fiber spacing in all composite test pieces was 208 fibers

in^{-1} (81.9 fibers cm^{-1}) resulting in a boron fiber areal weight of 173 g m^{-2}. For all boron-carbon hybrid composites, the carbon fiber tows were spread to a carbon fiber areal weight of 65 g m^{-2}.

2.5 Test methods

For compression testing of composite panels, tests were conducted according to ASTM Standard D6641 [4] using a 21-ply panel, with layup configuration $[90/0/90]_{7,}$ and specimen dimensions of 1.27 cm (0.5 inch) x 14 cm (5.5 inch). A back-out factor was applied to obtain the values of 0° compression strength and compression modulus. Open hole compression (OHC) tests were conducted according to ASTM Standard D6484 [5] using a 24-ply panel, with layup configuration $[45/0/-45/90]_{3s}$ and specimen dimensions of 3.8 cm (1.5 inch) x 30.5 cm (12 inch) with a 0.64 cm (0. 25 inch) diameter hole centered. The fixture used for OHC testing is shown in Figure 6. Tensile and 3-point flexural testing were conducted according to ASTM Standards D3039 [6] and D790 [7], respectively. Compression testing of carbon only composites was conducted according to ASTM Standard D695 [8].



Figure 6. Open Hole Compression (OHC) test fixture

3. RESULTS AND DISCUSSION

3.1 Boron fiber strength and elastic modulus

For hybrid composite materials (Hy-Bor®) reported in section 3.3, boron fiber was used that was manufactured during 2018. Table 1 shows tensile strength and elastic modulus results of 100-µm diameter CVD boron fiber manufactured during a 10-month period in 2018.

Table 1. CVD Boron fiber mechanical properties -- 2018 data

Tensile Strength[a]		Elastic Modulus[b]	
GPa	ksi	GPa	10^6 psi
4.0	590	430	62

[a] average of 6754 fiber production runs

[b] average of 335 production runs

3.2 Hybrid boron-carbon-resin composite tensile and flexural test results

Table 2 shows tensile and flexural test results for the composites fabricated in this work. The carbon fibers investigated (T1100G and IM7) had higher tensile strengths but lower elastic moduli than that of boron fiber. The densities of the hybrid composites were generally 20 % higher than the carbon only analogs due to variations in fiber loading and/or resin content. The hybrid composites, when compared with the carbon only analogs, had lower tensile strengths, but 50 % higher values of elastic modulus. The tensile elastic modulus increase was significantly higher than the density increase, and thus can be attributed true property enhancement rather than an increase fiber loading. The limited amount of flexural test data suggests that flexural strength and modulus can be increased by the addition of boron fiber to a carbon fiber composite.

Table 2. Tensile and Flexural Properties of Hybrid Boron/Carbon Composite vs Carbon Only

		Tensile strength		Tensile modulus		Flexural strength		Flexural modulus		Composite Density (calculated)
		GPa	ksi	GPa	10^6 psi	GPa	ksi	GPa	10^6 psi	g cm^{-3}
Hy-Bor®	Boron/IM7/TC350-1	2.3	330	250	36	2.4	350	200	29	2.0
Carbon	IM7/TC350-1	2.7	390	160	23	2.3	330	120	18	1.6
Hy-Bor®	Boron/IM7/TC420	1.9	270	240	35	2.1	310	190	28	1.9
Carbon	IM7/420	2.3	340	150	21	--	--	--	--	1.6
Hy-Bor®	Boron/T1100G/TC350-1	2.3	330	240	35	2.1	310	200	29	1.9
Carbon	T1100G/TC350-1[B]	2.9	420[A]	150	22[A]	--	--	--	--	1.6

[A]Normalized to 50 % fiber volume

[B]Carbon prepreg produced at higher resin content than normal to accommodate boron addition

3.3 Hybrid boron-carbon-resin composite compression and open hole compression (OHC) test results

A scanning electron micrograph (Figure 7) of a machined section of the hybrid boron/T1100G/TC350-1 composite shows the 0° and 90° oriented plies of boron and carbon fibers. A $[90/0/90]_7$ cross-plied specimen was used for compression testing. Particularly evident in the micrograph is the large size discrepancy between the 100 μm boron fibers and the 5-10 μm carbon fibers. A compression test fracture surface (Figure 8) shows crushed boron and carbon fibers as well as fiber pullout.

Table 3 shows compression and open hole compression (OHC) test results for the composites fabricated in this work. The densities of the hybrid composites were generally 20 % higher than the carbon only analogs due to variations in fiber loading and/or resin content. The hybrid composites, when compared with the carbon only analogs, had significantly higher values of compressive strength (80-170 % higher), compressive modulus (50-80 % higher). The measured values of open hole compression strength were 100 % higher than what is typical for carbon fiber composites.

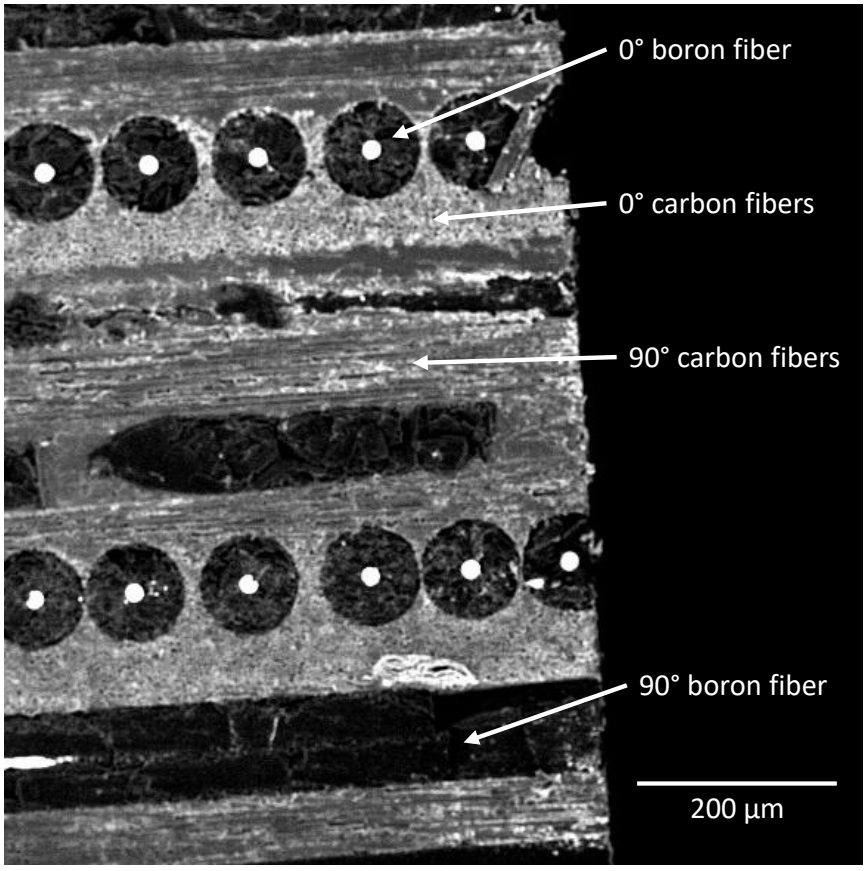


Figure 7. Machined cross section of a hybridized composite comprised of 100 μm diameter CVD boron fibers, T1100G carbon fibers, and TC350-1 toughened epoxy resin.

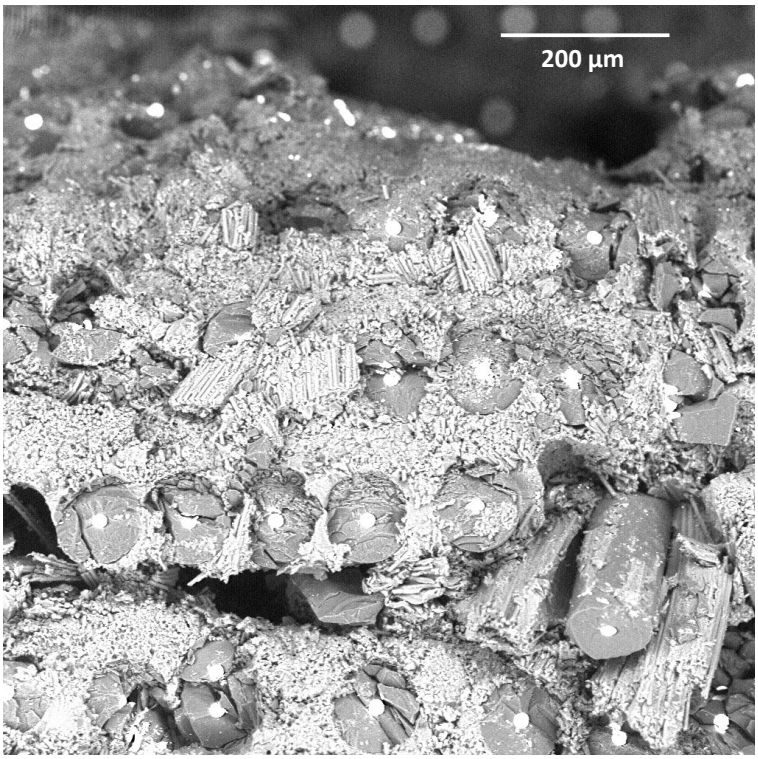


Figure 8. Boron/T1100G/T350-1 hybrid boron/carbon composite compression fracture surface showing crushed fibers and fiber pullout.

Table 3. Compression Properties of Hybrid Boron/Carbon Composite vs Carbon Only

		Compression strength[A]		Compression Modulus		Open Hole Compression (OHC)		Composite Density (calculated)
		GPa	ksi	GPa	10^6 psi	MPa	ksi	g cm^{-3}
Hy-Bor®	Boron/IM7/TC350-1	3.2	460	240	35			2.0
Carbon	IM7/TC350-1	1.7	250	150	22	310	45	1.6
Hy-Bor®	Boron/IM7/TC420	2.8	400	210	31			1.9
Carbon	IM7/420	1.1	160					1.6
Hy-Bor®	Boron/T1100G/TC350-1	2.9	420	240	35	680	98	1.9
Carbon	T1100G/TC350-1[D]	1.2	180[B,C]	130	19[B,C]			1.6
Hy-Bor®	Boron/T1100G/TC350-1, Lot 2	3.2	470	220	32	745	108	2.0
Carbon	T1100G/TC350-1, Lot 2[D]	1.2	170[B,C]	140	21[B,C]			1.5

[A]ASTM D6641 backed out

[B]Normalized to 50 % fiber volume

[C]D695 compression

[D]Carbon prepreg produced at higher resin content than normal to accommodate boron addition

4. SUMMARY AND CONCLUSIONS

A number of previously uninvestigated hybrid composites were fabricated using 100 μm diameter CVD boron fibers, T1100G carbon fibers, IM7 carbon fibers, and resin systems including TC350-1 epoxy and TC420 cyanate ester. Results reported here indicated that the hybridization of boron with carbon fibers significantly increased compressive strength and modulus as well as open hole compression (OHC) strength when compared with carbon-only reinforced composites. Uniaxial compression strengths (ASTM D6641 backed out values) of greater than 2.8 GPa (>400 ksi) and open hole compression strengths greater than 700 MPa (>100 ksi) were measured on composites fabricated in this work. The observed compressive strengths and OHC strengths are greater than twice that achievable in carbon reinforced resin composites. Work planned in the near future will investigate other newer resin systems such as the Toray/TenCate Advanced Composites TC380 toughened epoxy with enhanced hot/wet properties.

The work reported here on hybrid composites does not necessarily represent an optimized product. Parameters such as fiber loading, resin content, and ply orientation can be varied to achieve the maximum desired properties while also considering cost factors. Recent process developments have resulted in the fabrication of a narrower 1.3 cm (0.5 inch) wide boron prepreg tape that is compatible with newer, automated fiber placement machines. Boron fiber reinforced composites and boron/carbon hybrid composites, although not nearly as widely used as carbon composites in aerospace structures, remain relevant today and present opportunities to design structures that can withstand increased compressive loading and to tailor desired composite properties to match design needs.

5. REFERENCES

1. Suplinskas, Raymond J. and Marzik, James V. “Boron and Silicon Carbide Filaments.” *Handbook of Reinforcements for Plastics*, Ed. J.V. Milewski and H.S. Katz. New York: Van Nostrand Reinhold Co., 1987. pp. 340-363.
2. Ng, Yeow and Kumnick, Al. “Determination of Cross-ply Laminate Stacking Sequence for the Compression Strength Testing of a Unidirectional Boron Epoxy Material”, *Proceedings of 38th International SAMPE Technical Conference: Global Advances in Materials and Process Engineering*. Dallas, TX, November 6-9, 2006. Society for the Advancement of Material and Process Engineering. CD-ROM—6 pp.
3. Marzik, James V., Suplinskas, Raymond J., Croft, William J., MoberlyChan, Warren J., DeFouw, John D., and Dunand, David C. “The Effect of Dopant Additions on the Microstructure of Boron Fibers Before and After Reaction to MgB_2”, *Mater. Res. Soc. Symp. Proc.* Vol. 848, FF6.2.1-6, Materials Research Society, Warrendale, Pennsylvania, 2005.
4. ASTM Standard D6641 / D6641M-16e1, “Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression (CLC) Test Fixture”, ASTM International, West Conshohocken, PA, 2016, DOI: 10.1520/D6641_D6641M-16E01, www.astm.org.

5. ASTM Standard D6484 / D6484M-14, “Standard Test Method for Open-Hole Compressive Strength of Polymer Matrix Composite Laminates” ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D6484_D6484M-14, www.astm.org.
6. ASTM D3039 / D3039M-17, “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials”, ASTM International, West Conshohocken, PA, 2017, DOI: 10.1520/D3039_D3039M-17, www.astm.org.
7. ASTM D790-17, “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials”, ASTM International, West Conshohocken, PA, 2017, DOI: 10.1520/D0790-17, www.astm.org.
8. ASTM D695-15, “Standard Test Method for Compressive Properties of Rigid Plastics”, ASTM International, West Conshohocken, PA, 2015, DOI: 10.1520/D0695-15, www.astm.org.