

Weight Reduction and Cost Savings Using Hybrid Composites Containing High Modulus Polypropylene Fiber

by

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Abstract

Hybrid composites containing high modulus polypropylene fiber are shown to give improvements in toughness, weight, dielectric constant and ballistic resistance, depending on what other fiber type they are mixed with. In hybrid composites with carbon fiber, the composite has a great increase in toughness with a small weight penalty and a significant cost decrease. In hybrids with glass, weight is decreased and toughness increased. In hybrids with aramid fiber, the ballistic properties are maintained at a significant cost savings. Experiments detailing each of these composites, their mode of manufacture and performance are shown.

Introduction

Innegrity has developed a new class of high modulus polyolefin multifilament yarn^{1,2} which possesses an exceptional combination of high toughness and low weight. Produced at relatively high throughput from commodity polymers, the cost/performance benefits of the yarn are substantial when it is used in tough, impact resistant composites where glass, carbon and aramid fibers are traditionally used. For example, hard, thermoplastic panels containing almost 80% Innegra S (Innegrity's high modulus polypropylene (HMPP) yarn) and 20% aramid fibers display the same Level IIIA ballistic performance as panels containing 100% aramid fibers, but at about 40% of the cost.

The high-modulus/low-density properties of HMPP filaments arise from a number of unique structural and morphological characteristics imparted by the novel fiber forming process. The purpose of the present paper is to describe these characteristics in relation to composite properties and to highlight structural differences between conventional glass, carbon, or aramid panels, and those augmented with HMPP fibers.

Method

Fibers: Fibers were made according to the method described in US Patent Nos. 7,074,483, 7,445,834 and 7,445,842 (1). These fibers were then twisted and woven into fabrics as described below.

Carbon: One small 4in by 4in test panel and two large 12in by 12in test panels were constructed in epoxy resin, which had a 5 to 1 ratio of resin to catalyst, using the following fabric combinations:

- 100% plain weave carbon
- 100% plain weave carbon shell with a 50/50 plain weave carbon HMPP hybrid core
- 50/50 plain weave carbon HMPP hybrid
- 100% plain weave carbon shell with a 100% plain weave HMPP core

The test panels were laid up in a vacuum bag so that the warp of all of the fabric pieces ran along the same axis of the test panel.

Aramid: A construction of hard test panels- HMPP, using 2800 denier and 225 filaments, was twisted at approximately 1 twist/inch and woven into plain weave fabric of 15 picks per inch and approximately 12.5 ounces/square yard. Test panels were constructed by layering a polyolefin film (0.003") between layers of fabric and using the following fabric combinations:

- 100% plain weave aramid
- 25/75 plain weave aramid HMPP layered hybrid
- 50/50 plain weave aramid HMPP layered hybrid
- 25/75 plain weave aramid HMPP layered hybrid
- 100% plain weave HMPP.

The test panels were laid up and compressed at 100 psi and 140° Celsius for 30 minutes, resulting in panels with approximately 12% resin content and an areal density of 1.5 lbs/ft². The layup format consisted of 15 layers, with aramid fabric being behind the HMPP fabric in the case of hybrid test panels, and so that the warp of all of the fabric pieces ran along the same axis of the test panel.

For soft panels, HMPP of 625 denier and 50 filaments, was twisted at approximately 1 twist/inch and woven into plain weave fabric of 26 picks per inch and approximately 4.4 ounces/square yard. Test panels were constructed by layering of the fabric, edge-sewing and then sewing in an "x" pattern from corner to corner using the following fabric combinations:

- 100% plain weave aramid
- 25/75 plain weave aramid HMPP hybrid
- 50/50 plain weave aramid HMPP hybrid
- 25/75 plain weave aramid HMPP hybrid
- 100% plain weave HMPP

The layup format consisted of 15 layers, with aramid fabric being behind the HMPP fabric in the case of hybrid

test panels, and so that the warp of all of the fabric pieces ran along the same axis of the test panel.

Glass: HMPP fibers of 1600 denier and similar properties to those described above were woven into a narrow weave, 2" wide with 12 dents per inch in the warp, with a normal polypropylene fiber in the weft. The fabric was surface treated using an Enercon Plasma3 plasma system in an oxygen/helium gas at moderate power. These fabrics were cut into 8" strips, dipped into unsaturated polyester marine resin mixed with curing agent and pressed into a mold. The resulting composites had 50% +/- 5% fiber content. A series of four composites were fabricated, each panel made with eight layers of fabric, including

- a) eight layers of glass
- b) four glass and four HMPP
- c) two glass and six HMPP
- d) eight layers of HMPP

Testing: Fiber shrinkage was measured in a dynamic mechanical analyzer (DMA). Flexural testing for all samples was performed according to ASTM D790. Density was measured using the method found in ASTM D 2734 part 7.1.3. Gardner impact testing was performed according to ASTM D5420. Izod impact testing was performed according to ASTM D256. Ballistic testing was conducted according to the V₅₀ method in accordance to NIJ standard 01.01.04 using 0.44 magnum SWC projectiles for the hard test panels and full metal jacket 9mm projectiles for the soft test panels. Ballistic testing was conducted at US Testing Laboratories.

Results

Fibers: The fibers as produced are white, and, other than as described here, have the properties of their base polypropylene polymer. They are able to be twisted, woven, and otherwise post-processed in all normal textile processing techniques.

The fibers are composed of highly elongated, nanoscale fibrillar crystals. Under both small- and wide-angle x-ray scattering, the fibers exhibit both very high orientation and very high crystallinity. Despite having a high level of crystallinity and orientation, the apparent density of the HMPP fibers is about 0.67 g/cm³, which is well below the density of iPP in the amorphous state (0.85 g/cm³). The reason for the low fiber density is the presence of short, microscale cracks running parallel to the fiber axis between nanoscale crystals (Figs. 1, 2 and 3).

A water influx technique, where water under high pressure (100 psi) flows through an HPLC column containing the fibers, can be used to estimate the true density of the fiber without voids. In this technique, water fills the microcracks, and an approximate density of the polymer

is determined. By this method, the polymer density of the fiber was found to be 0.93 g/cm³ and the "microcrack density" was determined to be 0.26 g/cm³, or about 30% of the fiber volume. Moreover, by using the amorphous and crystalline densities of polypropylene (0.85 g/cm³ and 0.95 g/cm³ respectively), the volume fraction of crystalline PP was determined to be about 0.8, in good agreement with the WAXS measurement.

The high microcrack void volume results in an unusually high surface area of 1.5 m²/g when measured by BET, which is about eighteen times higher than would be expected from a void-free fiber of equal diameter and 0.93g/cm³ density. Put another way, the HMPP fibers, which have a measured mean diameter of 52 μm, have a specific surface area equivalent to fibers with a mean diameter of ~3 μm.

HMPP fibers display high dimensional stability, with negligible axial shrinkage up to 70°C, and less than 5% shrinkage at 150°C (Figure 4). Conventionally spun-drawn polypropylene fibers typically shrink by about 30% at this temperature, and literature data indicate that the shrinkage of Spectra® 900 and Spectra® 1000 polyethylene fibers at 143°C is about 23% and 9% respectively (2).

The major advantage of HMPP yarn lies in its combination of high modulus (~200g/d, ~15GPa), high tenacity (~9g/d, ~0.7GPa), high toughness (~0.7g/d, ~50MPa) and low fiber density (0.67 g/cm³). The micro-scale cracks are short, discontinuous, and parallel to the axis of the fiber. Thus, they do not have a negative impact on the tensile properties of the fibers, and appear to exert a positive effect by blunting crack propagation during fiber failure.

Carbon Composites: Hybrid panels of HMPP and carbon processed similarly to all-carbon panels. The density of panels decreased as the volume fraction of HMPP fiber increased as shown in Figure 5. Overall panel density dropped from 1.46 g/cm³ for the all-carbon composite to 1.28 g/cm³ with 25% HMPP fiber and 1.05 g/cm³ with 50% HMPP fiber. In panels of equal thickness, flexural modulus and flexural strength also dropped significantly as shown in Figure 6, but these changes are less important than the drop in density as discussed below.

Panel stiffness is proportional to the cube of its thickness (the beam effect), while the panel weight is directly proportional to the thickness. This beam effect is used to greatly increase panel stiffness with small increases in panel thickness by placing the stiffening reinforcement as far as possible from the neutral axis. If HMPP fiber is placed judiciously in carbon composite panels of equal stiffness, the associated thickness increases are mostly offset by the reduced density of the fibers. Actual weight

increases when HMPP fibers are incorporated into panels of equal stiffness (and varying thickness) are shown in Figure 7.

In carbon composites, a major advantage of HMPP fiber is lower cost, as the total fiber cost of these panels decreases strongly with increasing HMPP fiber content. This is shown in Figure 8, using representative fiber prices of \$6/lb for HMPP fiber and \$25/lb for carbon fiber.

In addition to cost savings, the hybrid panels demonstrate significant improvements in impact properties as determined by both Gardner and Izod impact tests. Room temperature impact test results are shown in Figure 9. Gardner impact energy increases 38% from 8.53 ft*lbs/in for the carbon composite (sample a) to 11.81 ft*lbs/in for the sandwich hybrid (sample d). Izod impact energy increases by 77% from 20.33 ft*lbs/in in the carbon composite (sample a) to 35.96 ft*lbs/in in sample c. The improvements in impact energy were achieved with less than 5% increase in weight and a substantial cost savings, as shown in Figures 7 and 8.

Aramid Panels: Panels were fabricated by laying-up various combinations of aramid and HMPP fabrics for testing as both hard and soft ballistic protection.

Ballistic V_{50} results (using 0.44 magnum SWC projectiles) for hard panels are shown in Table 1 and Figure 10. Panels containing 100% HMPP fabric provide 86% of the V_{50} performance of similarly constructed 100% aramid panels of equal weight. In hybrid panels, ballistic performance is statistically indistinguishable from the 100% aramid panels when up to 75% of the aramid fabric is replaced with HMPP, providing a significant cost savings. In these preliminary results, the HMPP fiber has not been optimized for fabric construction, twist level, resin content or type, or other variables. With HMPP fiber having a cost 1/4 to 1/3 that of aramid, each of the hybrid configurations shown in Table 1 would bring a significant reduction in cost.

Soft ballistic panels were constructed from aramid and HMPP fabrics and tested against a 9 mm full metal jacket round. Ballistic V_{50} results are shown in Figure 11.

The average denier, tenacity, elongation and initial modulus of the HMPP yarns before and after weaving are shown in Table 2. Comparable data is shown for aramid and ballistic nylon fabric in Table 3. The weaving and finishing process had a significant impact on the properties of aramid, losing 28% of the initial fiber tenacity in the warp and 38% in the weft. Ballistic nylon breaking strength was also reduced. In contrast, the HMPP fibers retained 100% of their initial tenacity after weaving and finishing.

HMPP fabrics provide significant ballistic protection on their own, comparing favorably to ballistic nylon. However, in hybrid panels with aramid fabrics, they provide the opportunity for significant cost savings and fabric design opportunities over panels made with 100% aramid. It is likely that this result is not limited to aramid fabrics and could be applied to hybrids containing ultra-high-molecular-weight polyethylene (UHMWPE), such as Dyneema® or Spectra®.

Glass Composites: Glass and hybrid glass/HMPP composite panels were prepared and tested for flexural strength and modulus, density, dielectric constant, and Izod impact energy.

Composite density was measured according to ASTM D792, and is shown in Figure 12. The measured panel densities follow the rule of mixtures, dropping from 1.9 g/cm³ for the full glass composite to 1.0 g/cm³ for the 100% HMPP composite. Component densities were 2.6 g/cm³ for the glass fiber, 0.67 g/cm³ for the HMPP fibers, and 1.3 g/cm³ for the resin.

The dielectric constant was measured on the same composites according to IPC TM-650. In Figure 12, Dielectric results follow the rule of mixtures for the various materials. The dielectric constant for the 100% glass composite is 4.7, and it drops to 2.7 for the 100% HMPP composite panel. The dielectric constant of the resin is 3.1.

Flexural modulus and strength were measured according to ASTM D2344 on the glass/HMPP composite panels as shown in Figure 13. Flexural modulus ranges from 16 GPa for the 100% glass composite to 5 GPa for the 100% HMPP composite. Flex strength ranges from 190 MPa to 85 MPa respectively.

The change in flex modulus with substitution level of HMPP does not follow the rule of mixtures due to the strategic placement of the low density fibers at the neutral axis of the composite panel. In this location, they function like a light weight composite core. As noted earlier, the stiffness of a panel is proportional to its thickness cubed. Thus, by using lightweight HMPP in the panel core and stiff fiberglass on the outside, panel thickness is increased slightly, panel weight is reduced, and panel stiffness is maintained. Interestingly, flex strength is also retained on panels fabricated with 50% HMPP in the core and 50% glass fiber in the outer layers.

The Izod impact energy of the composite panels was also measured according to ASTM D256-00. The 8-layer 100% fiberglass composite panel broke cleanly, absorbing 19.7 ft lb/in of energy. The 4/4 HMPP/fiberglass hybrid absorbed a similar amount of energy (20.5 ft lb/in), but the HMPP fabric in the core of the panel remained

intact after impact, while the glass fibers on the surface fractured. Test coupons after impact testing are shown in Figure 14. The photograph on the left shows a 100% glass fiber reinforced composite which has been completely severed at the notch. The photograph on the right shows the 8-layer hybrid composite, where the glass fiber has broken but the HMPP fabric remains intact.

Discussion

Benefits: HMPP fibers offer several benefits when used synergistically with other fibers in composite structures. The benefits incorporating HMPP fibers into carbon fiber/epoxy composites include:

- Lower Density: ability to reduce the density from 1.46 g/cm² to 1.05 g/cm².
- Reduced Cost: Up to 40% reduction in fiber cost compared to 100% carbon fiber while maintaining panel stiffness and weight.
- Increased Toughness: A substantial increase in toughness (38% Gardner, 77% Izod) at a reduced panel weight. At equal panel weight (compared to 100% carbon fiber), panel toughness is even higher.

In ballistic panels fabricated as an aramid/HMPP hybrid, benefits include:

- Reduced Cost: In both hard and soft panels, a dramatic cost reduction can be achieved by replacing up to 75% of the aramid fabric with HMPP fabric. This cost reduction is achieved while maintaining equivalent ballistic performance.

Finally, in hybrid composites fabricated from glass fiber and HMPP fibers, benefits include:

- Weight Reduction: Panel weight can be reduced up to 20% at equal stiffness compared to 100% glass.
- Increased Toughness: After impact, hybrid panels remain intact.

The value proposition for the HMPP fiber can be summarized nicely by comparing panels of equal stiffness made from S-glass, E-glass, carbon and aramid fibers, with hybrids made from E-glass/HMPP and carbon/HMPP. In Figure 15, the cost of the fiber component for each panel was calculated and plotted against the weight reduction achieved compared to an aluminum panel. The HMPP hybrid panels offer a weight and cost advantage that cannot be achieved by current market materials, or by combining them via rule of mixtures (black line). In addition, HMPP hybrids offer a considerable toughness increase compared to glass and carbon composites.

Note on Processability: In order to achieve the stated benefits, the HMPP fabric must be processible. We have processed the material in hybrid composites through hand lay-up, vacuum bagging, vacuum infusion, resin

transfer molding, thermoplastic compression molding, and in prepregs (250 F cure resins only).

Acknowledgments:

Several groups and individuals helped with the work that is included in this paper. Fabric was woven at Hexcel (now JPS Composite Materials), Barrday and High Tech Specialty Materials. Electrical testing on the glass composites was done at Arlon. SEM micrographs were obtained at the Clemson Materials Science Laboratory. Fiber shrinkage was measured by Innegrity Europe GmbH.

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References:

1. B. Morin, U.S. Patent No. 7,074,483, September 2007, B. Morin, US Patent Nos. 7,445,834 and 7,445,842, October 2008.
2. D.C. Prevorsek in "Handbook of Fiber Science and Technology", M. Lewin, J. Preston and L. Lewin (Eds.), Vol. 3 (1996) p. 105.

Figures:

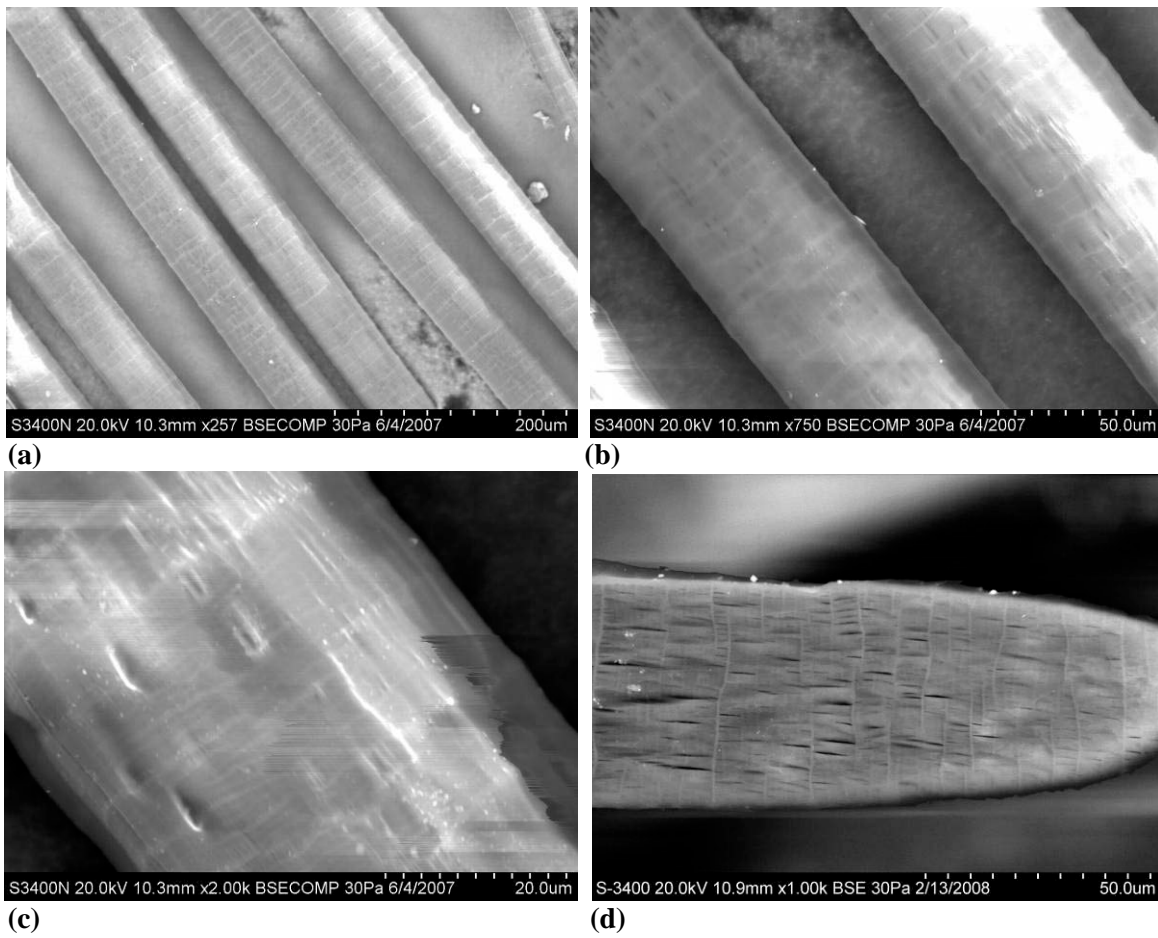


Figure 1. SEM images of HMPP fiber at (a) x257, (b) x750, (c) x2000, and (d) x1000 in quasi cross-section view.

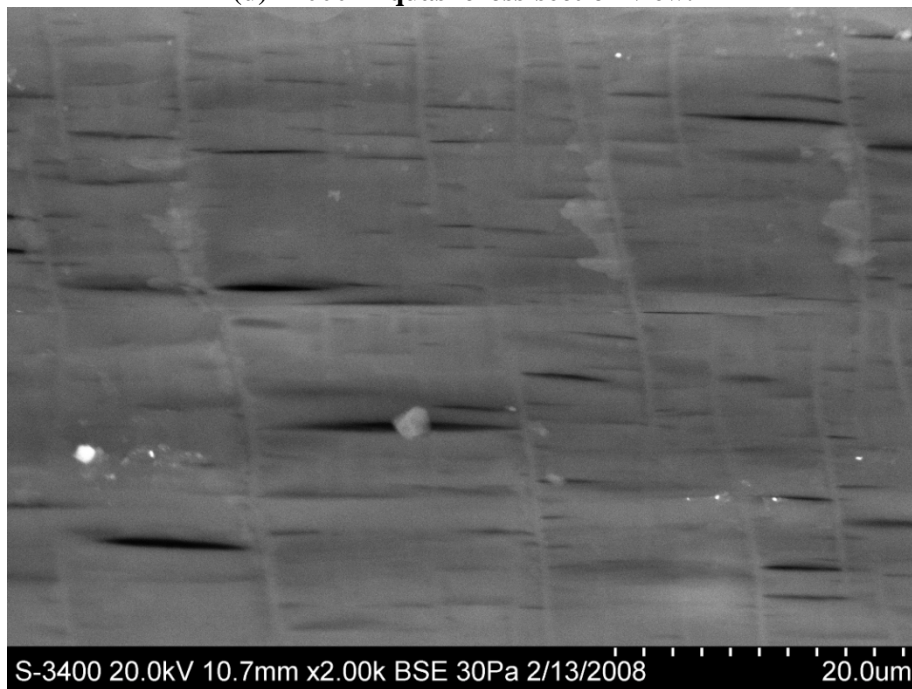


Figure 2. SEM image of HMPP fiber in quasi cross-section view.

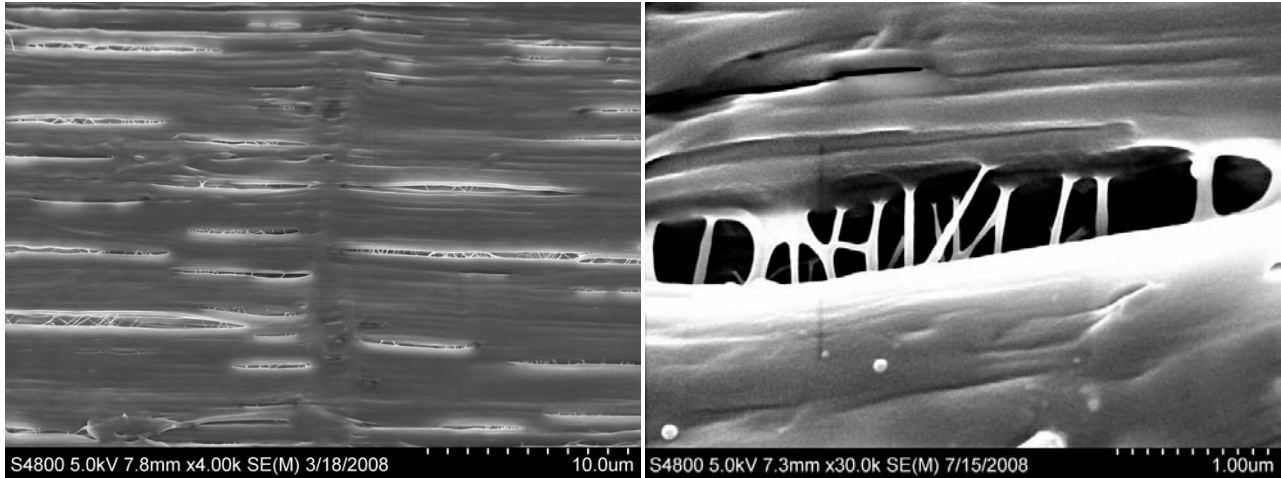


Figure 3. Cracks spanned by nanofilaments, x4000 left, x30,000 right.

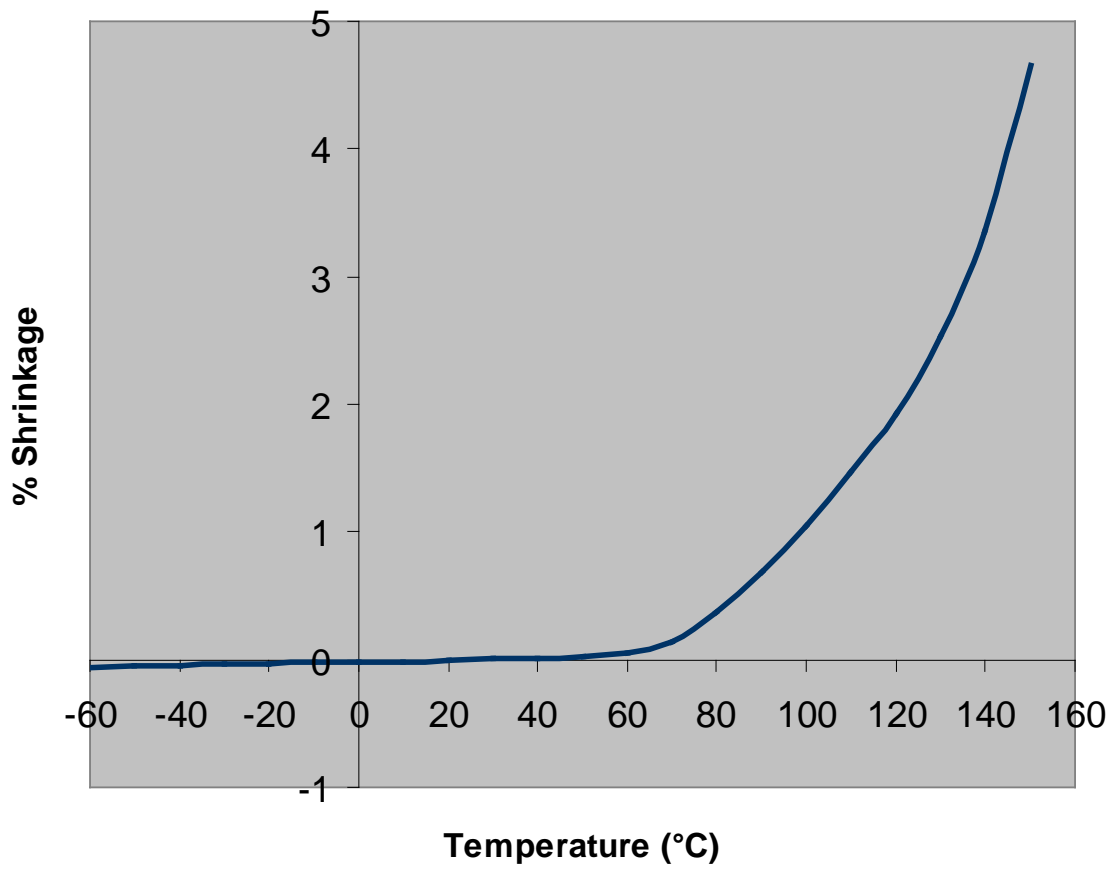


Figure 4. Thermal shrinkage of HMPP fiber. (Mean of 5 TMA measurements.)

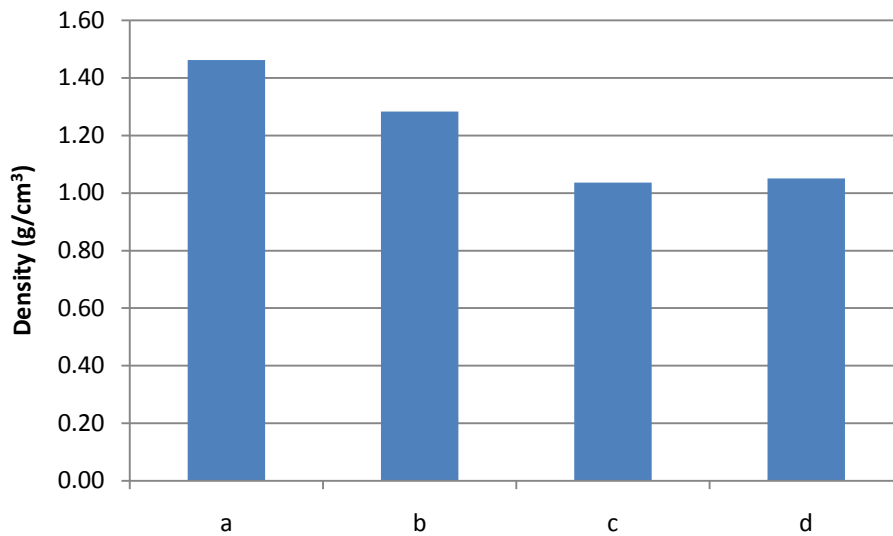


Figure 5. Density of Carbon/HMPP hybrid composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

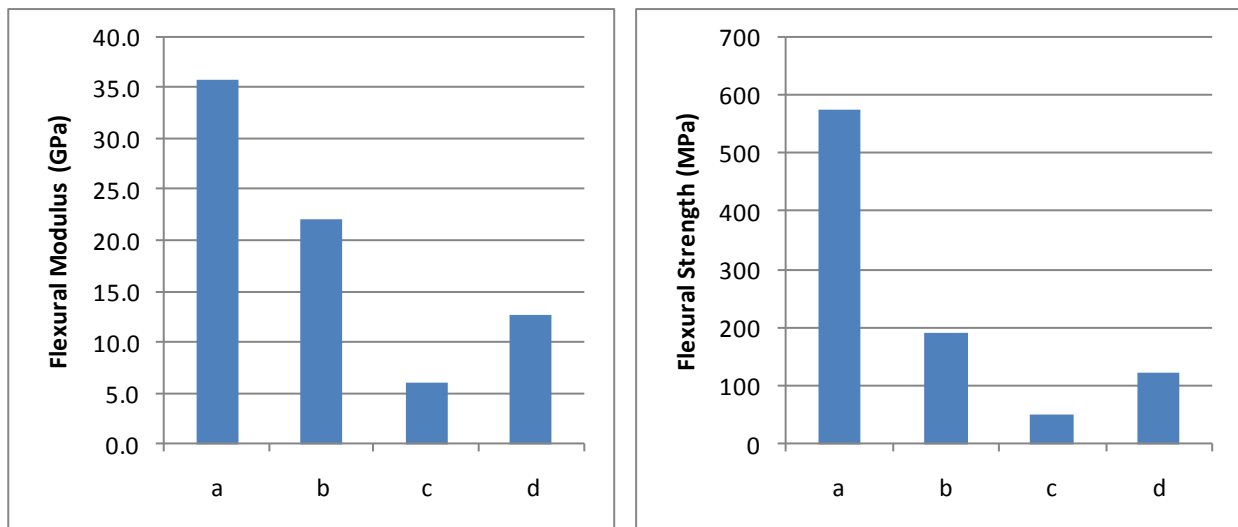


Figure 6. Flexural modulus and flexural strength of HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

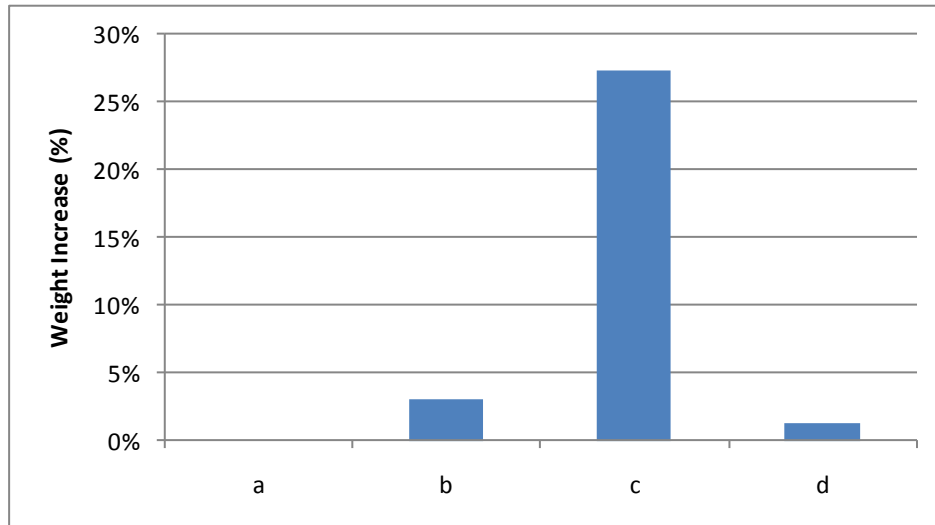


Figure 7. Weight increase at equal panel stiffness for HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

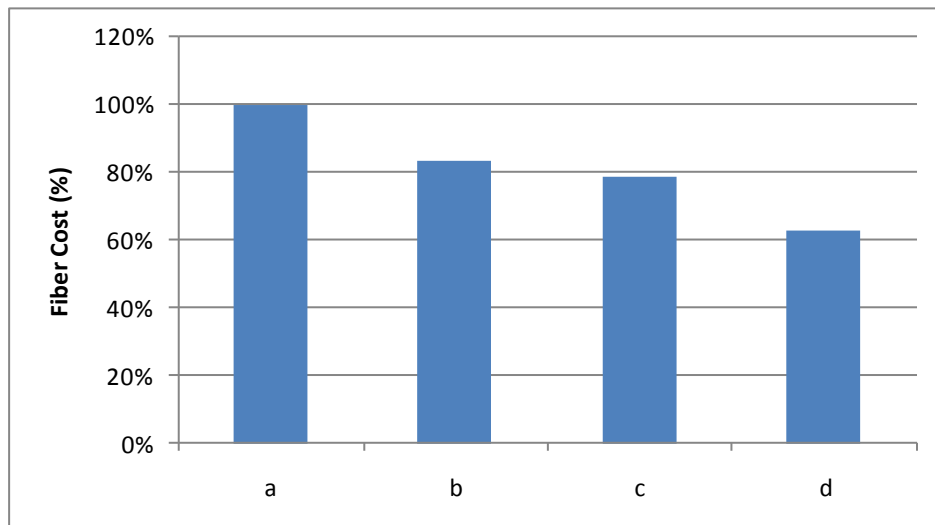


Figure 8. Fiber cost at equal panel stiffness for HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

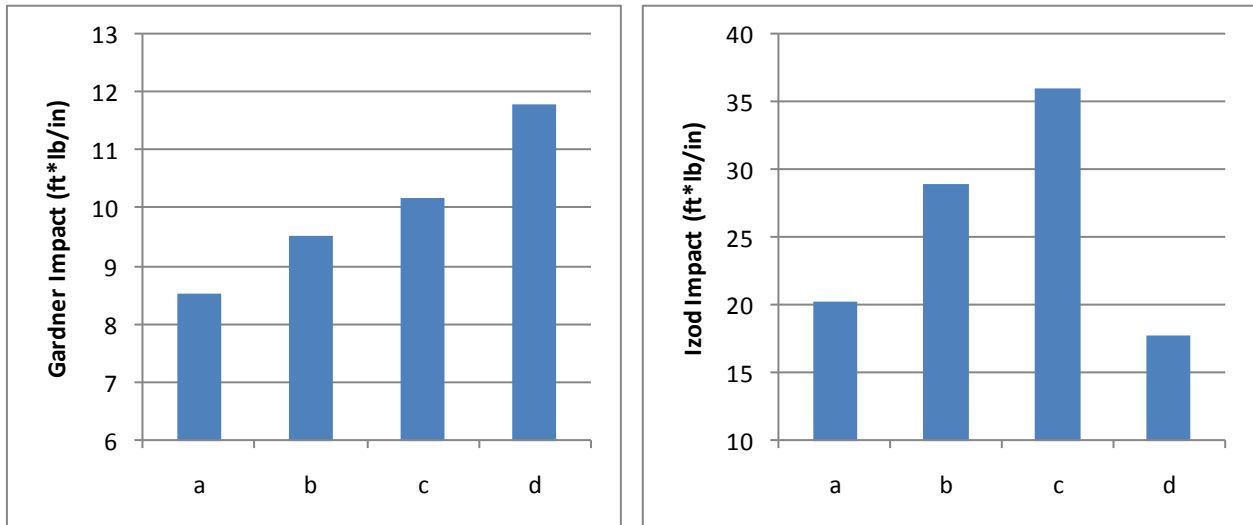


Figure 9. Gardner and Izod impact strength of HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

Material	# layers	Construction	Areal Density (lbs/sq ft)	V50 (ft/sec)
Aramid	14	Layered	1.5	1469
Aramid– HMPP hybrid-75%	11/4	Aramid behind HMPP	1.5	1477
Aramid – HMPP hybrid-50%	8/7	Aramid behind HMPP	1.5	1469
Aramid – HMPP hybrid-25%	4/11	Aramid behind HMPP	1.5	1498
HMPP	15	Layered	1.5	1258 ⁴

Table 1. V₅₀ ballistics results for a 0.44 magnum SWC projectile on aramid and HMPP hard panels.

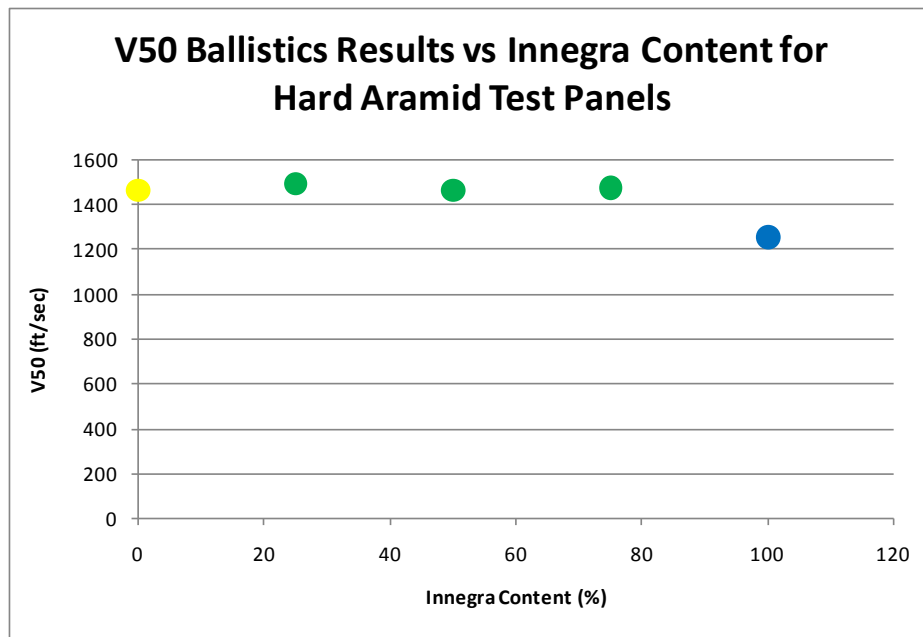


Figure 10. Aramid – HMPP ballistic performance of hard panels as a function of the % of HMPP included in the panel.

⁴ Average of two samples with V₅₀ of 1247 and 1268.

Property	Units	Fiber	Warp	Weft
Denier	denier	634		
Tenacity	grams/denier	7.44	8.02	7.70
Elongation	%	6.97	8.94	7.24
Modulus	grams/denier	151	128	149

Table 2. Properties of HMPP fiber before weaving, and after twisting and weaving.

Property	Units	Kevlar KM2 ²	Kevlar KM2 ³	Ballistic Nylon ⁵	Ballistic Nylon ⁶
Denier	denier	600	617/618		2225
Tenacity	grams/denier	26	16.2/18.8	9	7.5/8.3
Elongation	%	4	5.4/5.0	18	24/23
Modulus	grams/denier	600	608/580	60	57/65

Table 3. Properties of aramid and ballistic nylon fiber and properties of yarn removed from fabrics.

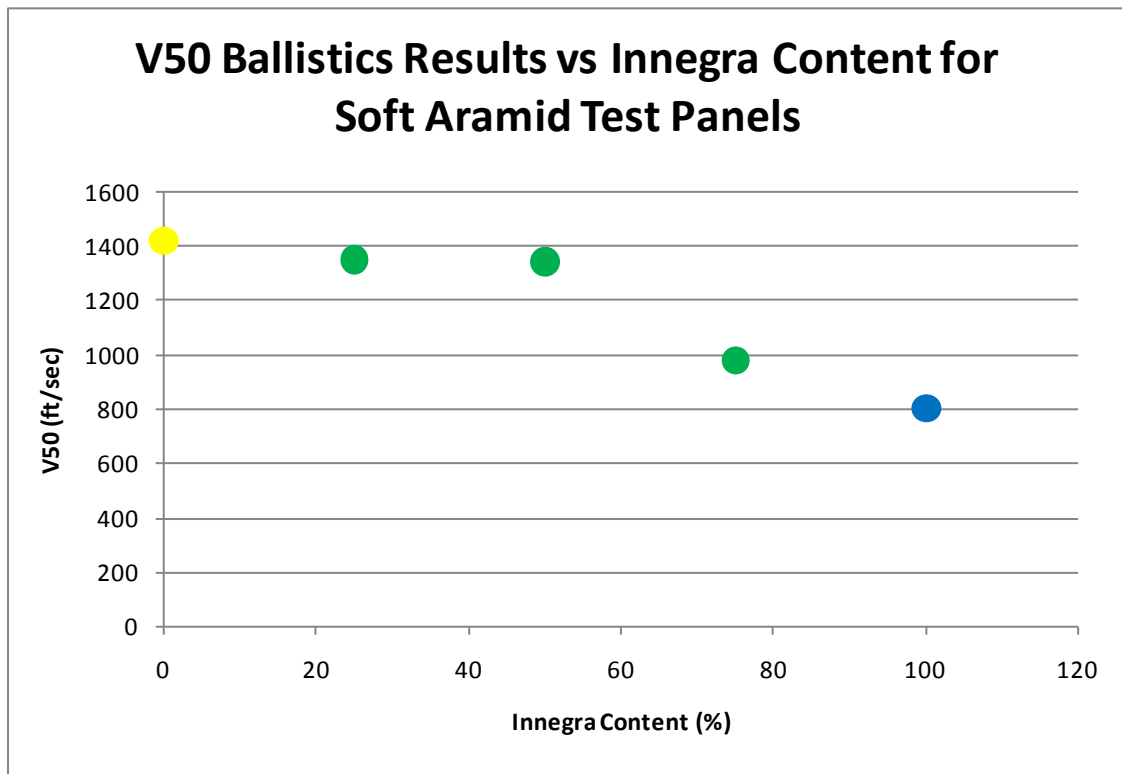


Figure 11. Aramid – HMPP ballistic performance of soft panels as a function of the % of HMPP included in the panel.

² *Lightweight Ballistic Composites: Military and Law-Enforcement Applications*, A. Bhatnagar, Woodhead Publishing Limited, Cambridge, 2006, pp 338.

³ Fibers removed from tested fabrics; results reported warp “/” weft.

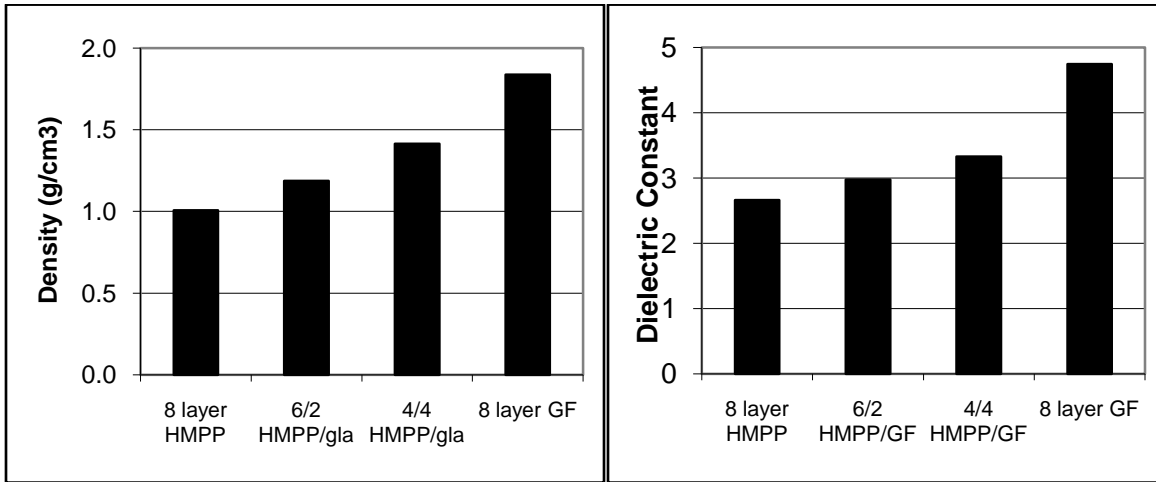


Figure 12. Comparison of density and dielectric constant for glass – HMPP hybrid composites.

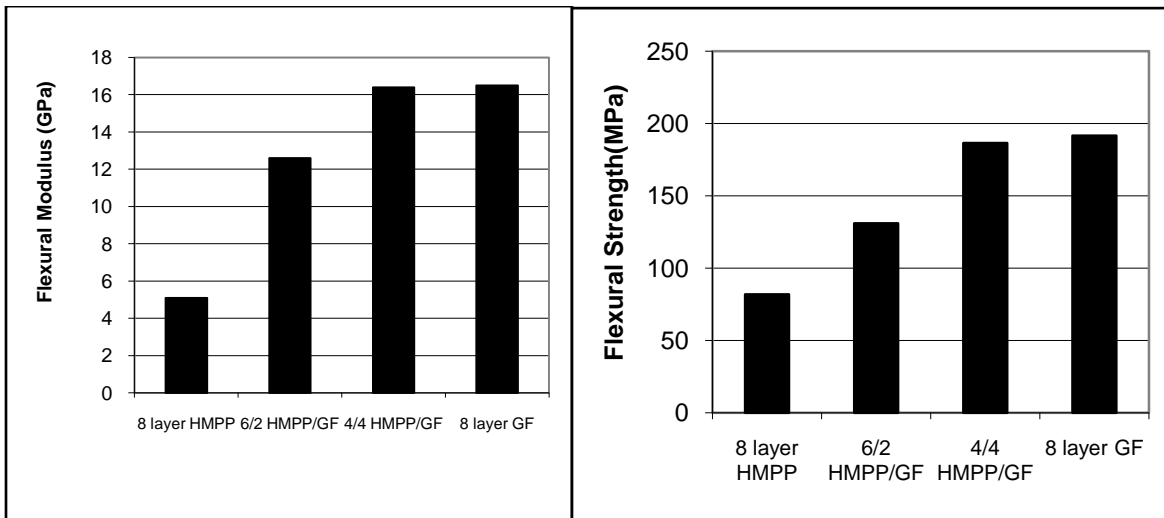


Figure 13. Comparison of Glass fabrics using flex modulus (GPa) and flex strength (MPa).

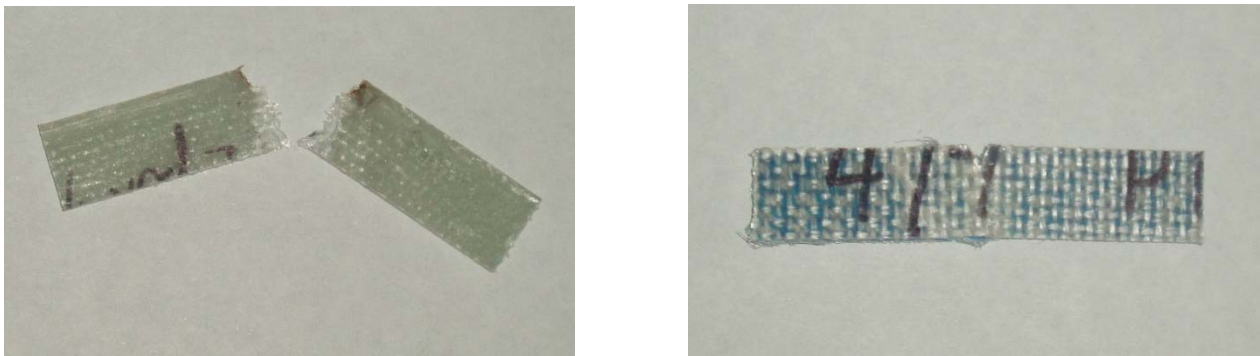


Figure 14. Broken samples from a notched Izod impact test. The left photo is of a glass fiber reinforced composite, showing a clean break with broken fibers. The right photo is of a hybrid composite using HMPP as the core fabric. In this break, the glass layers broke, but the HMPP fibers remained intact.

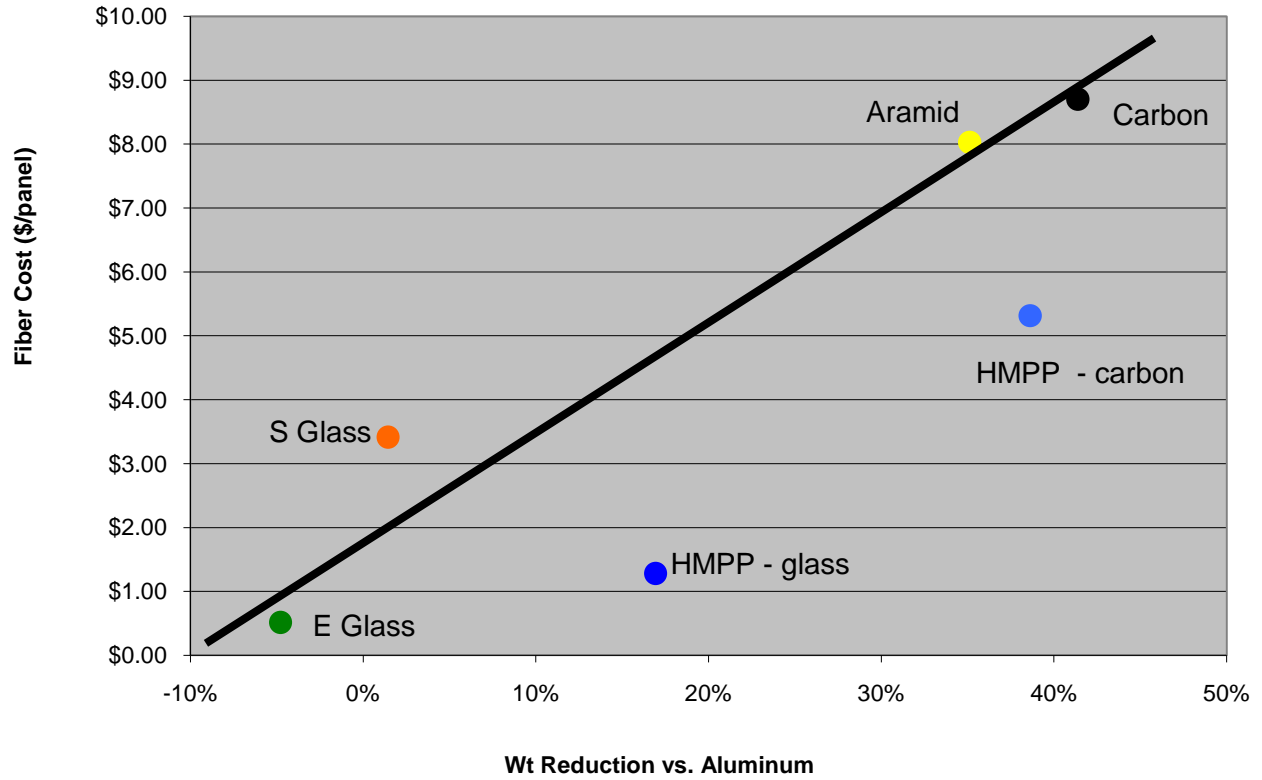


Figure 15. Comparison of fiber cost and weight reduction compared to aluminum of panels of equal stiffness. HMPP hybrid composites reduce cost and weight by comparison to current market materials.