COMPOSITES & POLYCON 2009
American Composites Manufacturers Association
January 15-17, 2009
Tampa, FL USA

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 throughputs 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:

a) 100% plain weave carbon
b) 100% plain weave carbon shell with a 50/50 plain weave carbon HMPP hybrid core
c) 50/50 plain weave carbon HMPP hybrid
d) 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 the 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/ft^2. 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 an 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 made, each 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 hrinkage was measured in a dynamic mechanical analyzer (DMA). Flexural testing for all 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 V_{50} 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. 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 highly elongated and under both small- and wide-angle x-ray scattering show very high elongation and very high crystallinity. Despite having a high level of crystallinity and orientation, the density of the HMPP fibers is about 0.67 g/cm^3, which is well below the density of iPP in the amorphous state (0.85 g/cm^3). The reason for the low fiber density is the presence of extensive crack formation (Figs. 1, 2 and 3) which results in a large void volume.

A water influx technique, in which water under high pressure flows through an HPLC column containing the fibers, permits the density of the fiber to be estimated based on a fiber volume that does not include the voids. That is, it assumes all the voids are filled with water at the (~100 psi) pressure applied and provides an approximate density of the polymer alone. By this method, the polymer density of the fiber was found to be 0.93 g/cm^3, giving a "void density" of 0.26 g/cm^3, or about 30% of the fiber volume. Moreover, with the amorphous and crystalline densities of polypropylene being 0.85 g/cm^3 and 0.95 g/cm^3 respectively, the volume fraction crystallinity computed by this method is about 0.8, in good agreement with the WAXS measurement.

The high void volume results in an unusually high surface area of 1.5 m^2/g, measured by BET, which is about eighteen times higher than would be expected from a void-free fiber of equal diameter and 0.93g/cm^3 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^{o}C, and less than 5% shrinkage at 150^{o}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^{o}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/cm^3).

Carbon Composites: Hybrid panels of HMPP and carbon processed similarly to all-carbon panels. The density was lowered as more HMPP fiber was included, and is shown below in Figure 5, with overall density dropping from 1.46 g/cm^3 for the all-carbon composite, to 1.28 g/cm^3 with 25% HMPP fiber and 1.05 g/cm^3 with 50% HMPP fiber. While the flexural modulus and flexural strength dropped significantly as shown in Figure 6, this is overshadowed by the drop in density, as discussed below.

The panel stiffness is proportional to the thickness of the panel cubed, while the weight is only proportional to the thickness of the panel with no exponent. This gives rise to the possibility to make panels slightly thicker, with greatly increased panel stiffness, but only somewhat increased thickness. If, at the same time, the density of the material comes down, then the weight of the panel could change only slightly, as it does in the hybrid composites represented in samples b) and d). The weight increase of an equal stiffness panel is shown in Figure 7.

Additionally, because HMPP fiber is lower cost, the total fiber cost of these panels comes down dramatically. This is shown in Figure 8, using \$6/lb for HMPP fiber and \$25/lb for carbon fiber, as representative fiber prices.

In addition to cost savings, the hybrid panels also show significant increase in impact properties as tested in both Gardner and Izod impact tests. These results are shown in Figure 9. The Garner impact increases from 8.53 ft*lbs/in in the carbon composite (sample a) to 11.81 ft*lbs/in in the sandwich hybrid (sample d), a 38% increase. The Izod impact increases from 20.33 ft*lbs/in in the carbon composite (sample a) to 35.96 ft*lbs/in in sample c, a 77% increase. Both of these increases came at less than 5% weight increase and a cost savings, as is shown in Figures 7 and 8.

Aramid Panels: Panels were made from aramid fabrics layered with HMPP fabrics for testing in both hard and soft ballistic protection.

The results from testing (using 0.44 magnum SWC projectiles) of hard panels are shown in Table 1 and Figure 10. HMPP fabrics, alone, provide 86% of the V_{50} performance of similarly constructed aramid fabrics. In hybrid panels, the performance is statistically indistinguishable from the 100% aramid panels with up to 75% HMPP in the panels, providing a significant cost savings. Again, these initial results have not been optimized for fabric construction, twist level, resin content or type, or other variables. With HMPP costing between 1/4 and 1/3 of the cost of aramid fibers, all of these configurations represent significant cost savings.

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

The average denier, tenacity, elongation and initial modulus of the yarns, before and after weaving, are shown in Table 2, compared to similar aramid and ballistic nylon fabric. Especially in the case of aramid fabrics, the fiber tenacity diminished significantly through the weaving and finishing process, having lost 28% of the initial fiber tenacity in the warp and 38% in the weft. Ballistic nylon breaking strength was also reduced.

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 also possible that this result is not limited to aramid fabrics, but could be repeated with ultra-high-molecular-weight polyethylene (UHMWPE), such as Dyneema® or Spectra®.

Glass Composites: Glass and hybrid glass – HMPP panels were tested for flexural strength and modulus, density, dielectric constant and Izod impact testing. The composites thus prepared were measured for physical and dielectric properties.

Composite density was measured according to ASTM D792, and is shown in Figure 12. The density follows the density predicted according to the ratios of the three materials included in the composite, lowering from 1.9 g/cm^3 for the full glass composite to 1.0 g/cm^3 for the homogenous HMPP composite. These follow very closely the prediction of a rule of mixtures using densities of 2.6 for the glass fiber, 0.67 for the HMPP fibers, and 1.3 for the resin.

The dielectric constant measured on the same composites according to IPC TM-650, also shown in Figure 12, and follows the rule of mixtures for the various mateirals. The dielectric constant of the resin is 3.1. The dielectric constant for the full glass composite is 4.7, and is reduced to 2.7 for the homogenous HMPP composite.

Flexural modulus and strength was measured according to ASTM D2344 on the same composite materials, and is shown in Figure 13. Flexural modulus ranges from 16 GPa for the full glass composite, to 5 GPa for the homogenous HMPP composite, while flex strength ranges from 190 MPa to 85 MPa for the same set of materials.

In this case, the variation does not follow a simple algebraic combination of material properties, and this is due to the strategic placement of the low density HMPP fibers in the center of the composite, where they act similarly to a light weight composite core. For homogenous materials, beam stiffness is proportional to the thickness of the beam cubed. Thus, by using a lightweight material in the core of a composite, the thickness is increased without increase in weight, and the composite stiffness is maintained.

The izod impact resistance of the composites was also measured, according to ASTM D256-00. For the 8 layer glass fiber material, the composite broke cleanly, absorbing 19.7 ft lb/in of energy, while for the 4/4 HMPP/glass fiber material, the energy absorption was very similar (20.5 ft lb/in), but the HMPP fabric remained intact at the center of the composite while the glass fibers had all broken. Shown in Figure 14 are broken pieces from the Izod impact test. On the left is a broken glass fiber reinforced composite, which has been completely severed at the notch. On the right is an eight layer hybrid composite, with four glass layers (two on each skin) and four HMPP layers. The glass fiber has broken, but the HMPP fabric remains intact.

Discussion

Benefits: It is clear that HMPP fibers offer several benefits when used in the appropriate form. Benefits in hybrid composites with carbon fiber and epoxy include:

- Density: ability to reduce the density from 1.46 to 1.05.

- Cost: Up to a 40% reduction in fiber cost while retaining panel stiffness and weight.
- Toughness: A dramatic increase in toughness (38% Gardner, 77% Izod), in these cases at lower panel weight. If panel weight was increased (to be equal with 100% carbon panel), toughness would be further increased.

In ballistic panels made with hybrid of aramid and HMPP, benefits include:

- Cost reduction: 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

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

- Weight reduction: With equal panel stiffness, the panel weight can be reduced up to 20%.
- Toughness: Again at equal panel stiffness, the panel impact resistance can be improved, with the resultant impacted parts remaining intact.

To compare just the cost and weight aspects, a compareson was made of panels of equal stiffness made from S-glass, E-glass, carbon and aramid fibers, and also hybrids made from E-glass/HMPP and carbon/HMPP. The cost of the fiber included in each panel was calculated, as well as the weight reduction achieved compared to an aluminum panel. These are shown in Figure 15. As can be seen, the HMPP hybrid panels offer a weight and cost savings that cannot be achieved by current market materials, or by combining them by a rule of mixtures (which would fall on the black line). Additionally, HMPP offers a considerable toughness increase over glass and carbon materials.

Processability: In order to achieve these benefits, one must be able to process the material. 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. SEMs were tested at the Clemson Materials Science Laboratory. The 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:

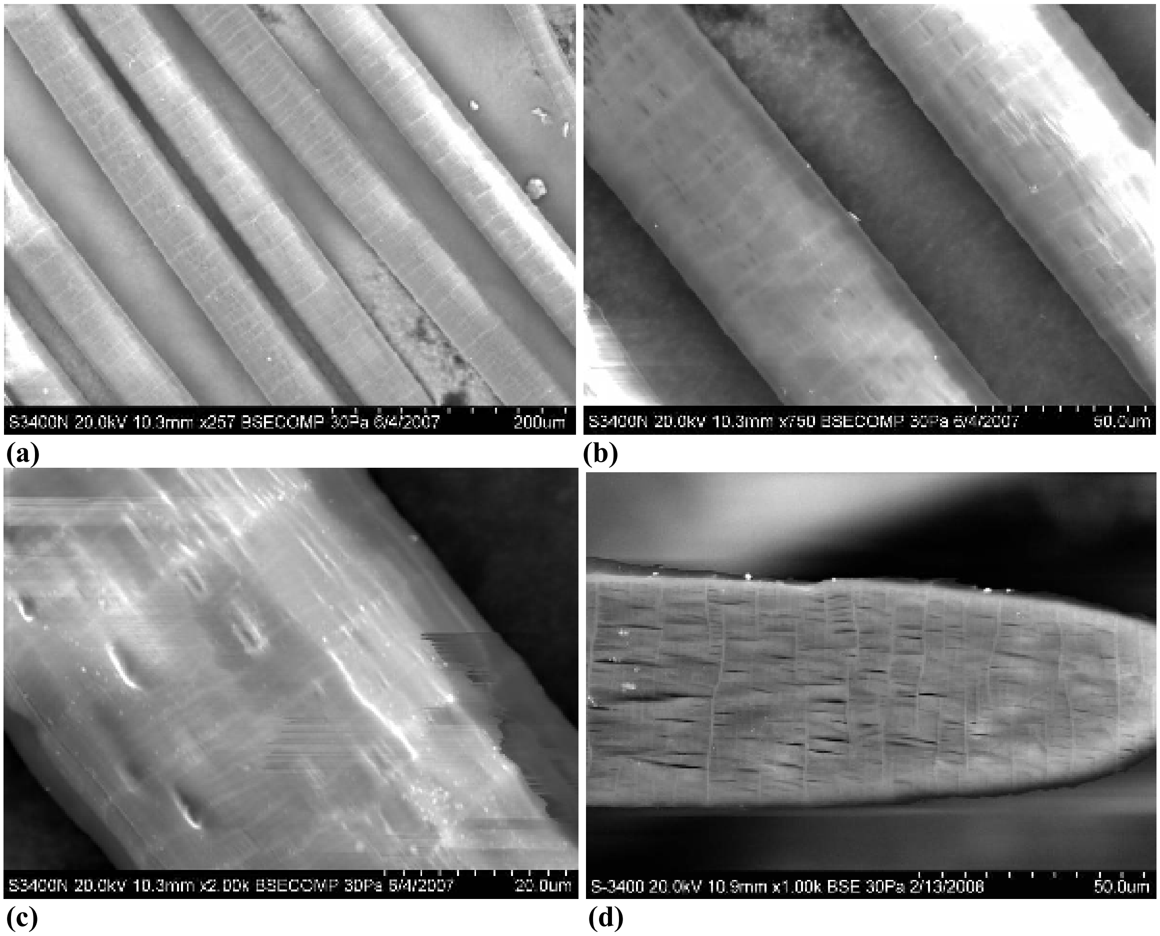

Figure 1. SEM images of HMPP fiber at (a) x257, (b) x750, (c) x2000, and (d) x1000 in quasi cross-section view.

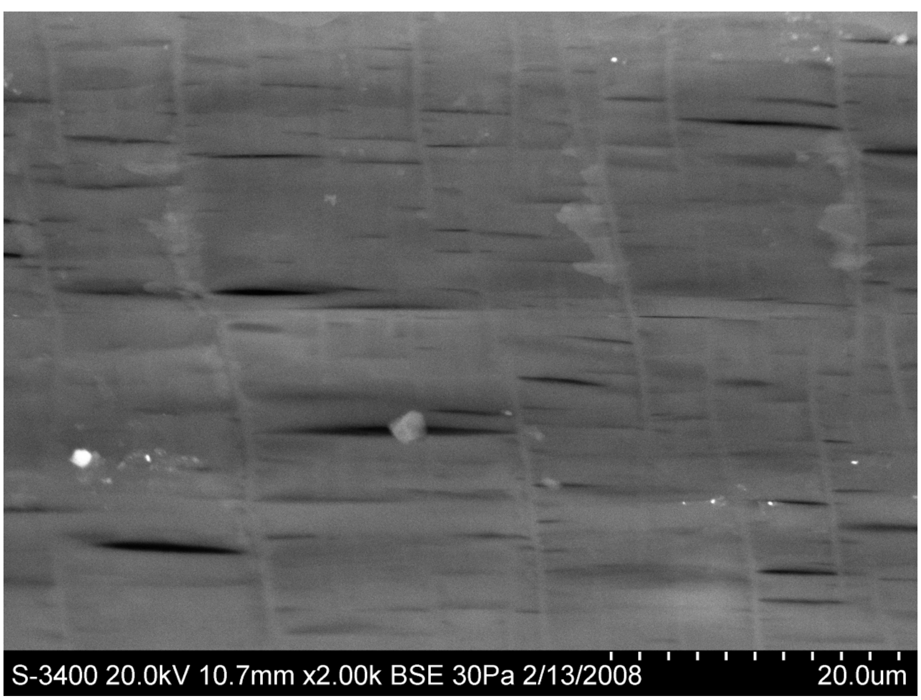

Figure 2. SEM image of HMPP fiber in quasi cross-section view.

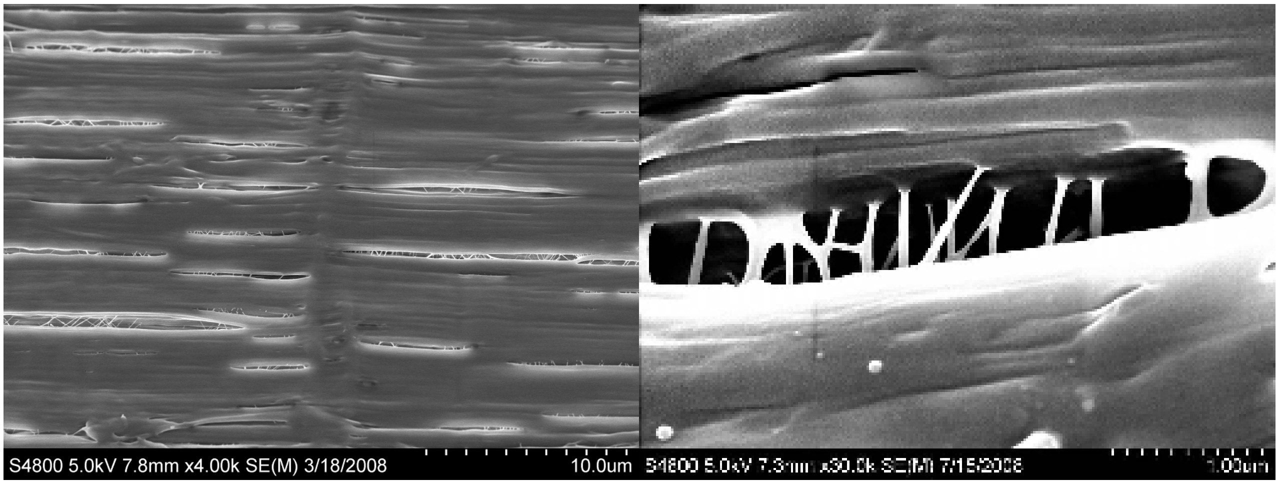

Figure 3. Cracks spanned by nanofilaments, x4000 left, x30,000 right.

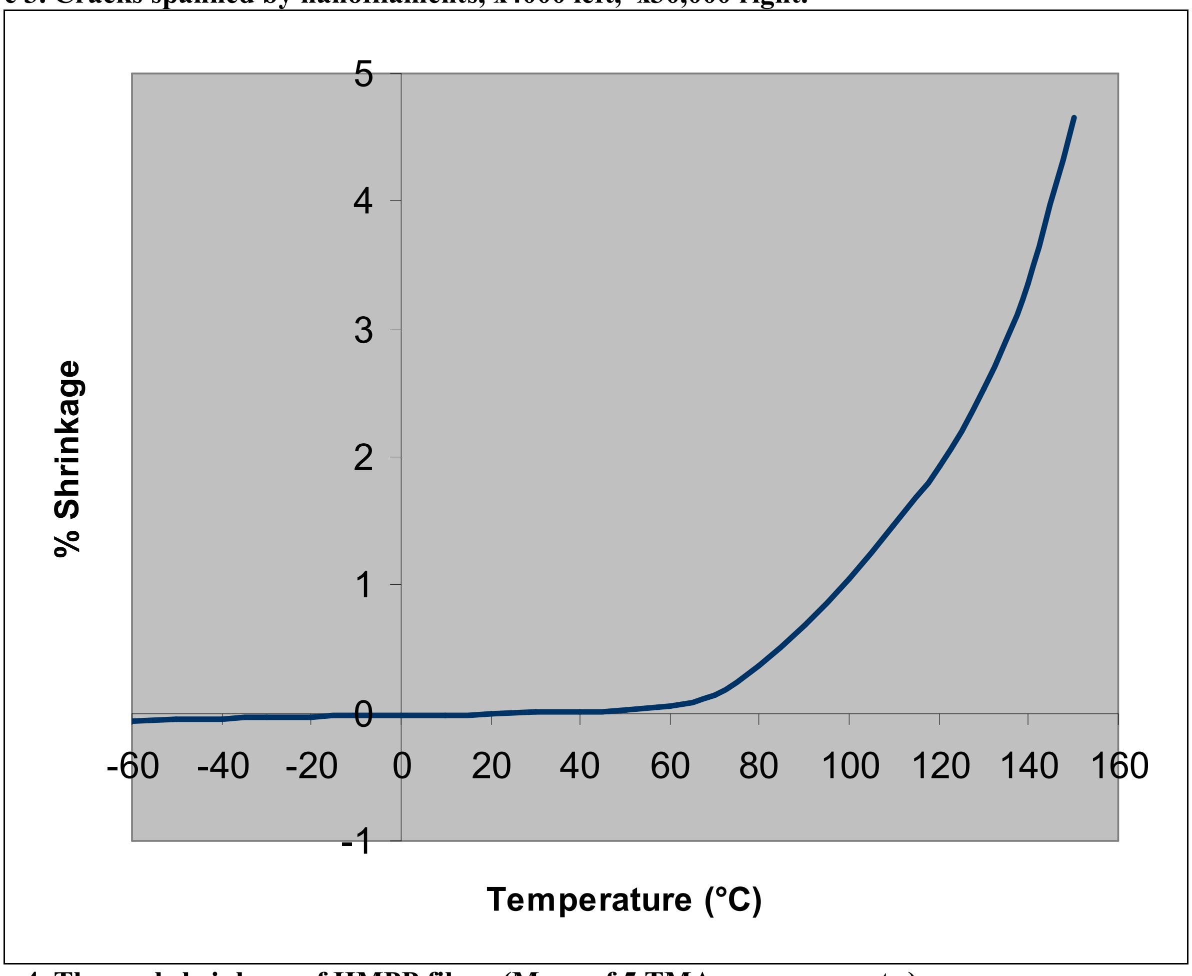

Figure 4. Thermal shrinkage of HMPP fiber. (Mean of 5 TMA measurements.)

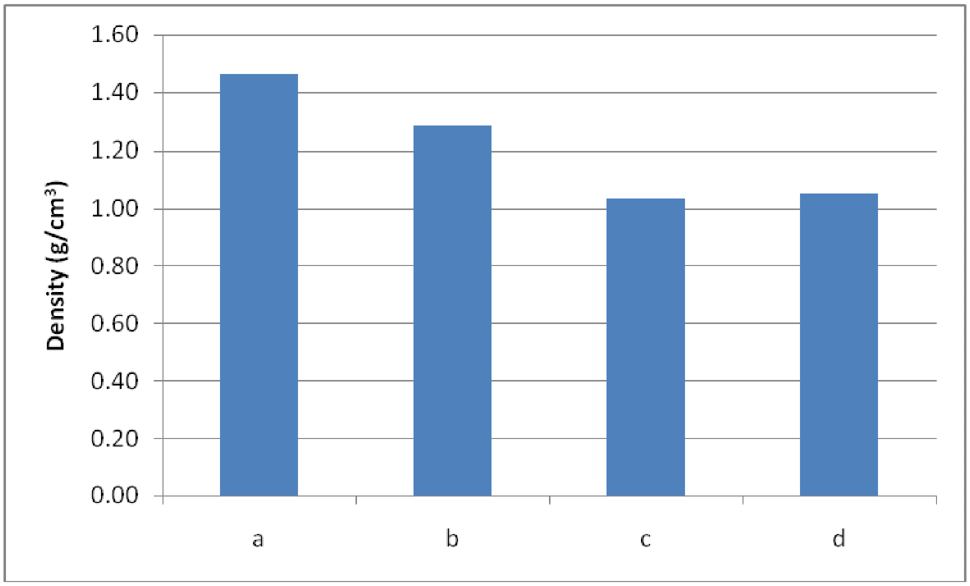

Figure 5. Density of Carbon/HMPP hybrid composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

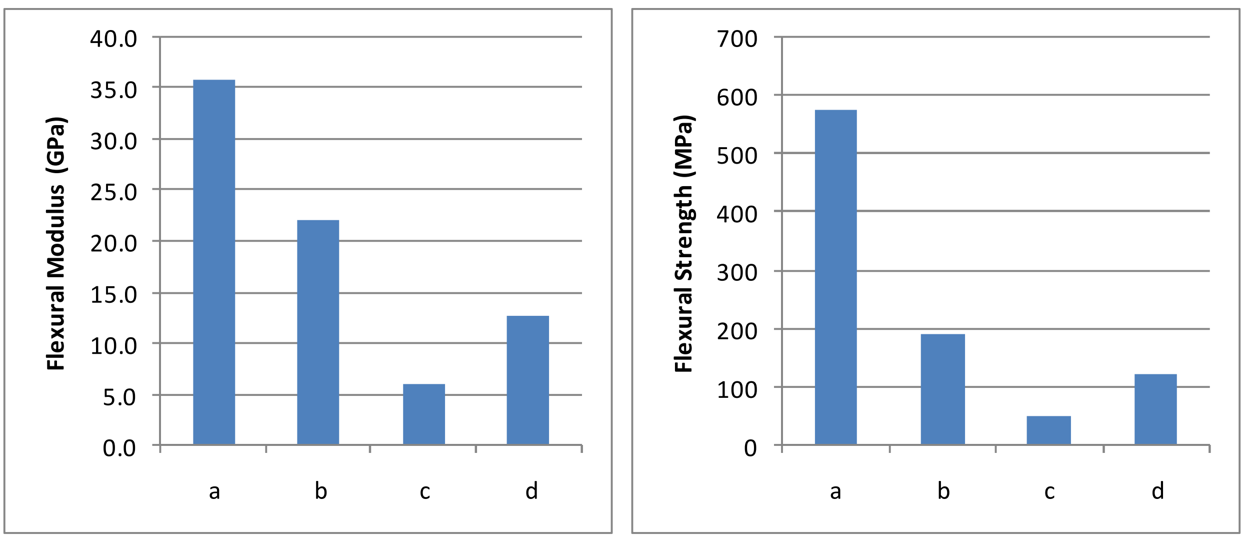

Figure 6. Flexural modulus and flexural strength of HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

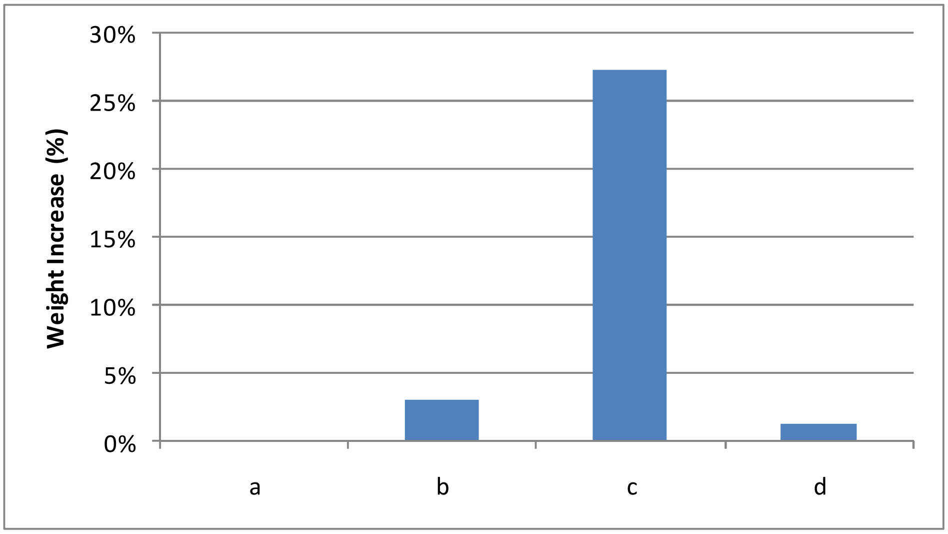

Figure 7. Weight increase at equal panel stiffness for HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

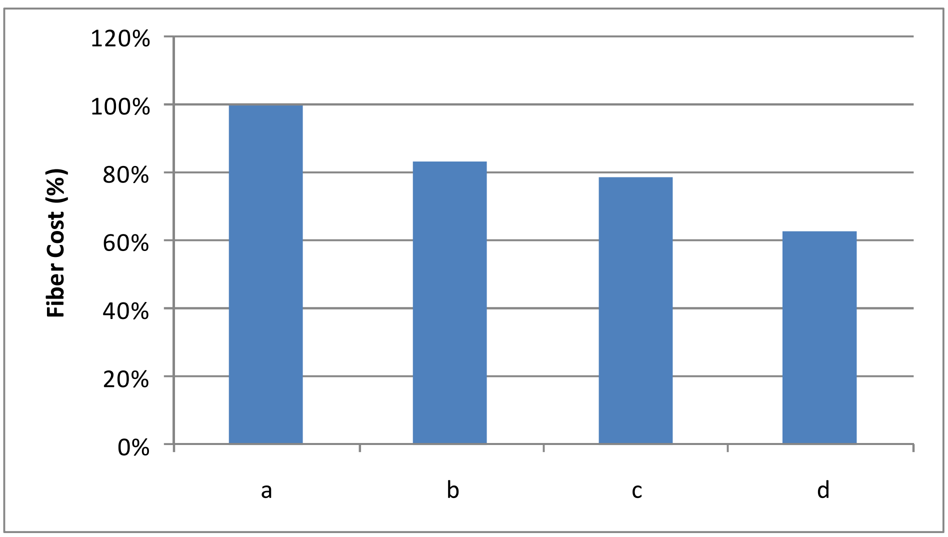

Figure 8. Fiber cost at equal panel stiffness for HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

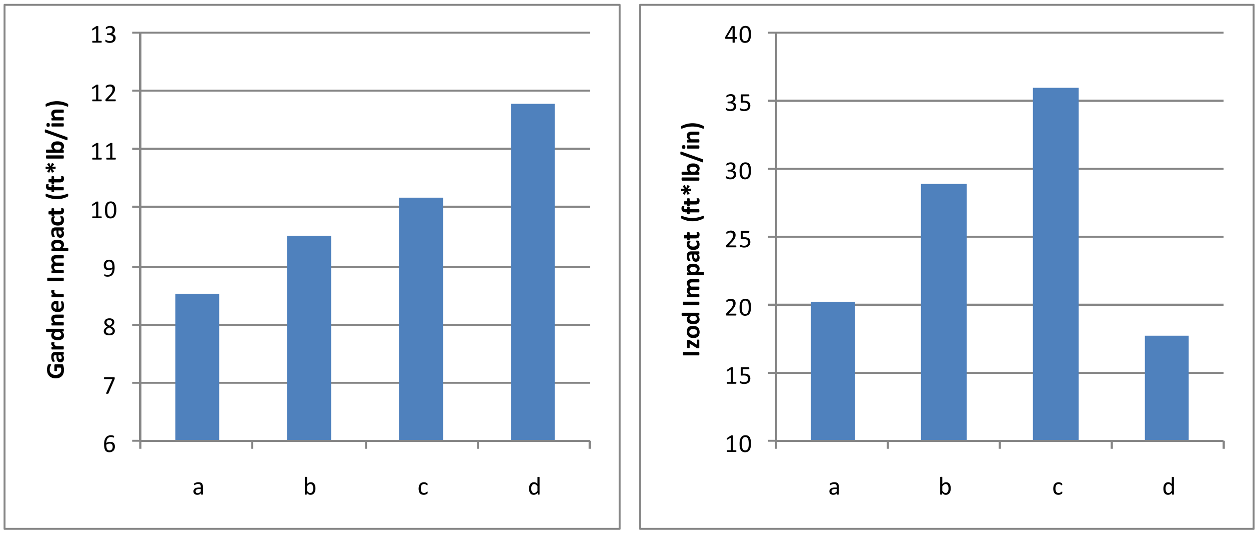

Figure 9. Gardner and Izod impact strength of HMPP/carbon composites. a) 100% carbon, b) 100% carbon shell with 50/50 carbon HMPP hybrid core, c) 50/50 carbon HMPP hybrid, d) 100% carbon shell with 100% HMPP core.

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[1]

Table 1. V_{50} ballistics results for a 0.44 magnum SWC projectile on aramid and HMPP hard panels.

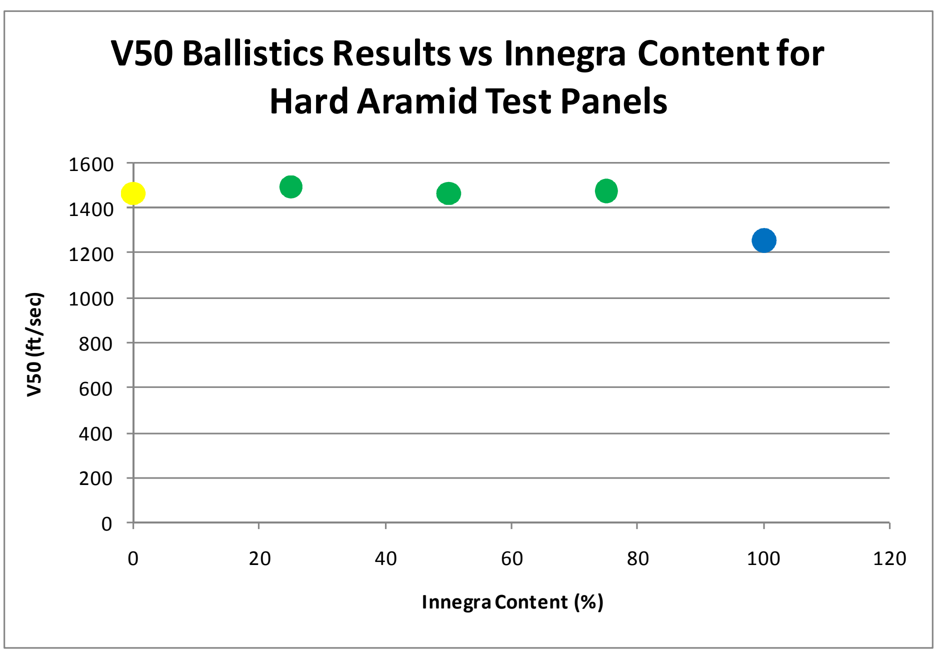

Figure 10. Aramid – HMPP ballistic performance of hard panels as a function of the % of HMPP included in the panel.

[4] Average of two samples with V_{50} 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.

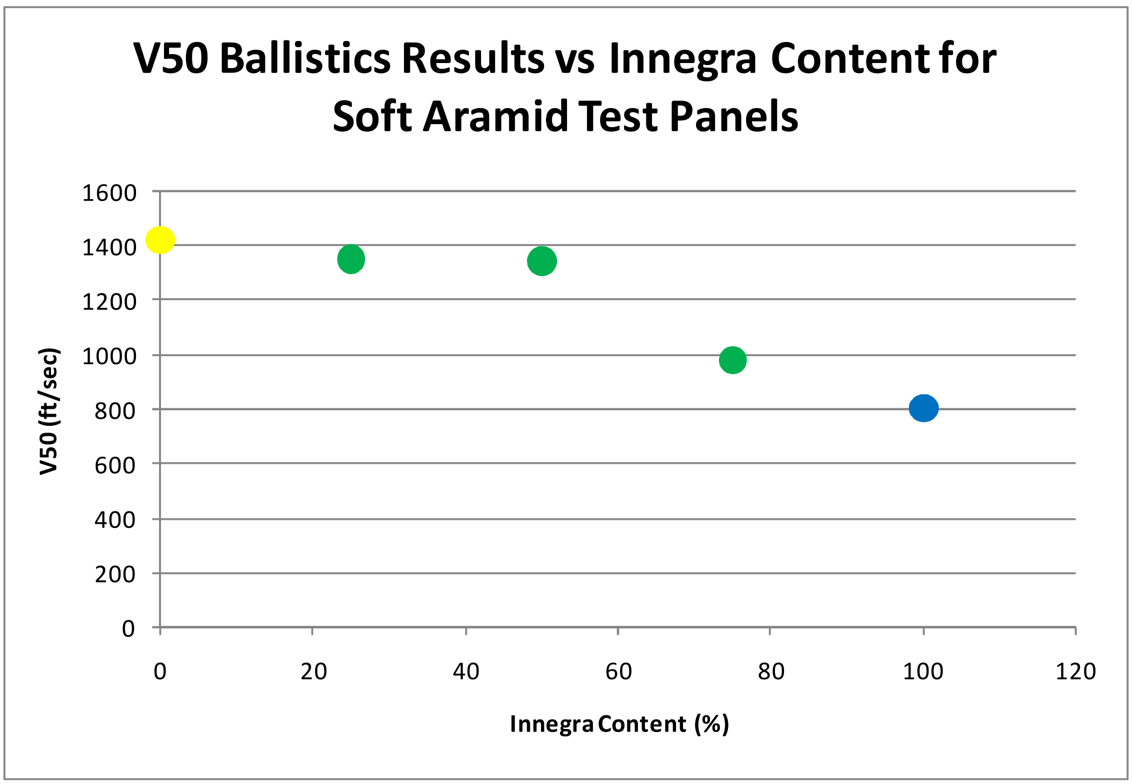

Figure 11. Aramid – HMPP ballistic performance of soft panels as a function of the % of HMPP included in the panel.

[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.

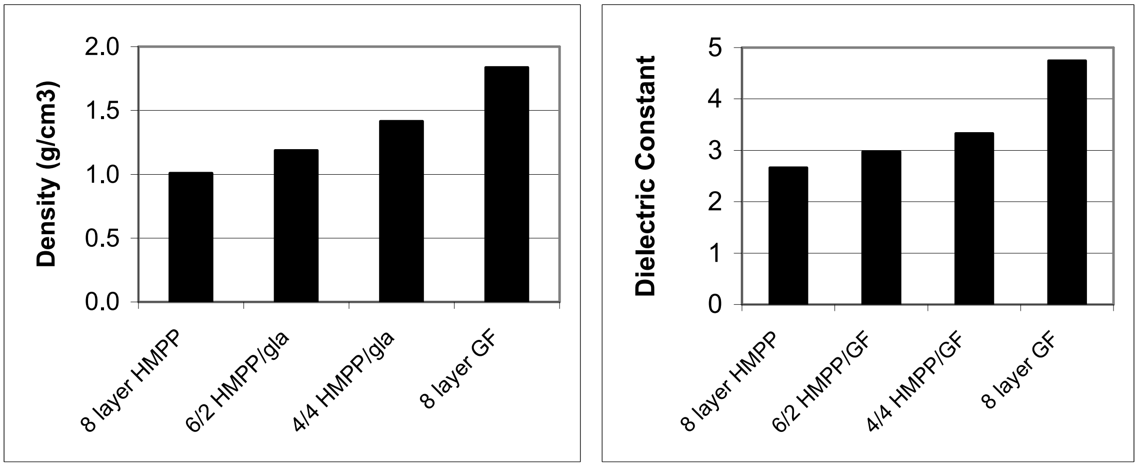

Figure 12. Comparison of density and dielectric constant for glass – HMPP hybrid composites.

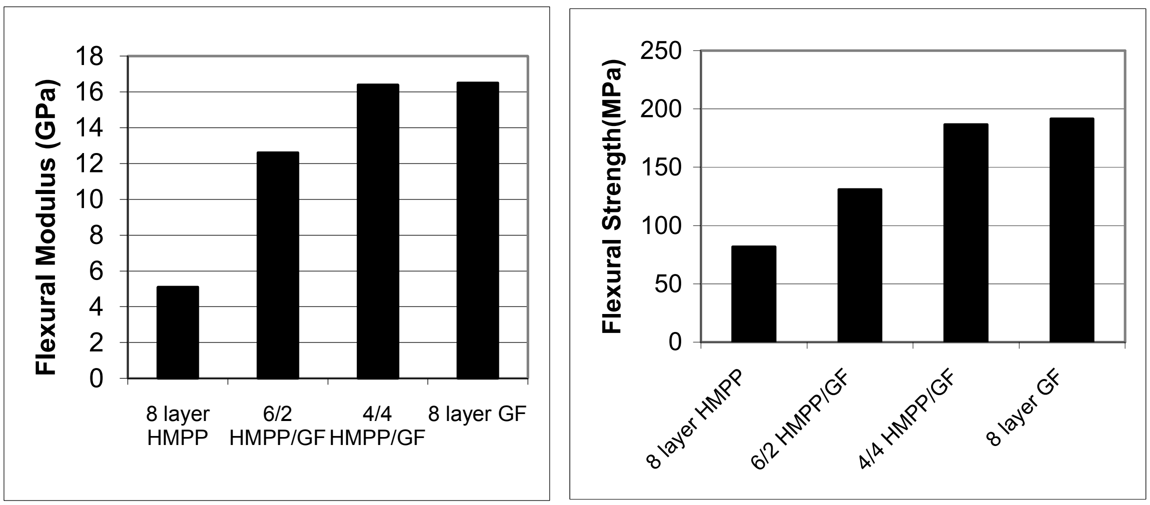

Figure 13. Comparison of Glass fabrics using flex modulus (GPa) and flex strength (MPa).

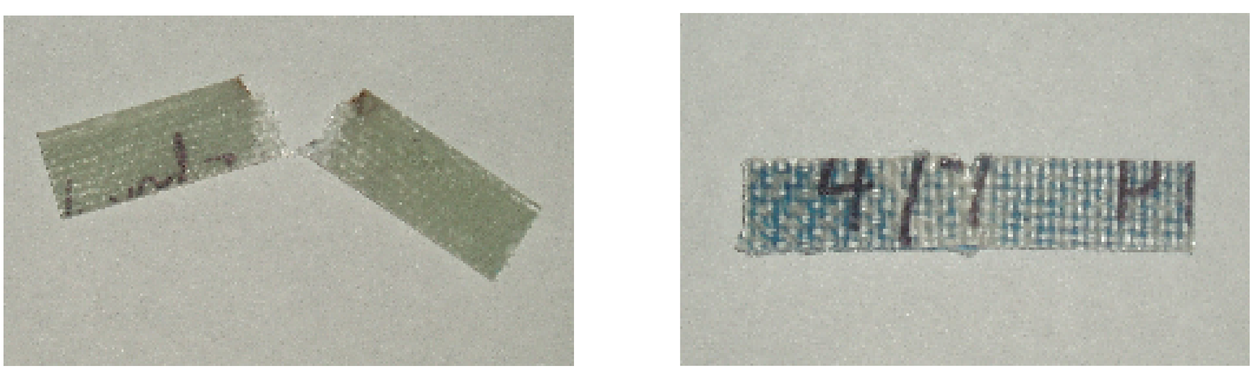

Figure 14. Broken samples from a notched Izod impact test. The left photo is of a glass fiber reinforced composite, showing a clean break with broken fibers. The right photo is of a hybrid composite using HMPP as the core fabric. In this break, the glass layers broke, but the HMPP fibers remained intact.

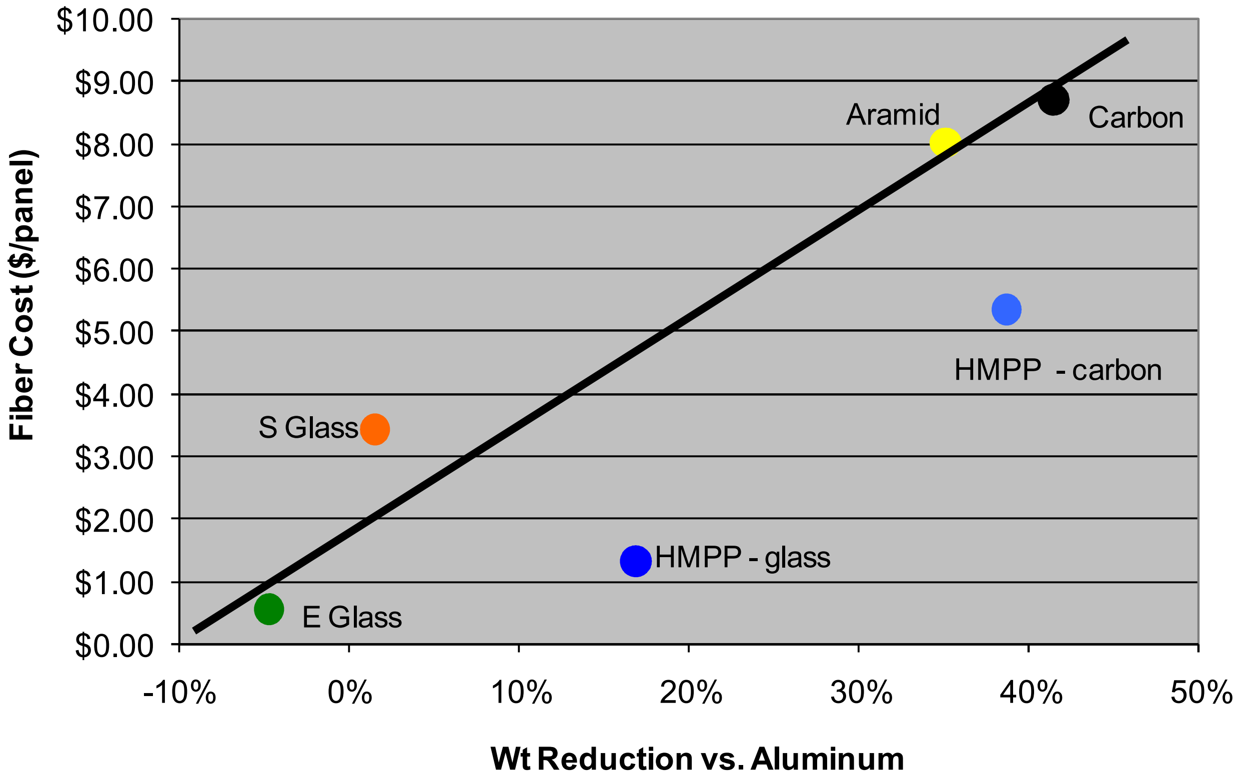

Figure 15. Comparison of fiber cost and weight reduction compared to aluminum of panels of equal stiffness. HMPP hybrid composites reduce cost and weight by comparison to current market materials.