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Abstract

CHARACTERIZING THE MECHANICAL PROPERTIES OF CALLAWAYS FORGED CARBON FIBER REINFORCED SHEET MOLDING COMPOUND

Bradley Jones, Prof. Dr. London, Callaway Golf

Callaway Golf receives a proprietary blend of prepreg material from Quantum Composites. Callaway processes the prepreg in-house and supplied 254mm x 254mm x 1.3mm panels of carbon fiber sheet molding compound (CFSMC) for characterizing. Tensile strength was analyzed by conducting tensile tests per ASTM D3039. Tensile coupons were cut to 254mm long by 25.4mm wide. Tabs were constructed from 1.6mm thick GFRP printed circuit board material. A commercial grade two part epoxy was used to bond the tabs to the CFSMC. Tensile results were inconclusive due to consistent fractures occurring outside the gauge lengths of the specimens.

Flexure strength was analyzed by conducting 3-point bend tests per ASTM D790. ASTM D790 calls for a larger than normal support span-to-coupon thickness ratio of 32:1 for high strength composites. The support span was therefore set to 42.6mm. The crosshead rate was calculated to be set constant at 1 mm/minute. Six samples were calculated in order to determine the scatter and consistency of the material’s mechanical properties. The mean flexure stress at maximum flexure load was 756.42 MPa with a standard deviation of 213.34 MPa. The mean maximum flexure load was 214.61 N. The Quantum composite data sheet reads that this material exhibits flexure strengths of 792 MPa, and tensile strengths of 421 MPa.
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List of Key Words

1. Composite
2. Sheet Molding Compound
3. E-Glass
4. Carbon Fiber
5. Vinyl Ester
6. Carbon-Fiber Sheet Molding Compound
7. Compression Molding
8. Charge
9. Cure
10. Glass Transition Temperature
11. Interlaminar
12. Void
13. Resin
14. Fillers
15. Matrix
16. Polymer
17. Thermoset
18. Thermoplastic
19. Cross-linking
20. Toughness
21. Modulus
22. Van der Waal’s Bond
23. Graphitization
24. Printed Circuit Board
25. Repeatable
1.0 Introduction

Golf drivers have made considerable breakthroughs in their ability to adapt specific design characteristics to launch the ball farther down the fairway in recent history. The sport began by using wooden clubs - mostly made of hickory. These early woods did not exceed 195 cm$^3$ in volume and the biggest detriment to these clubs was weather. It was more often than not that players spent most of their time straightening their waterlogged clubs from damp and humid weather.

It was not until 1931, when steel entered the picture, did material selection demonstrate its importance to the game. The most notable change that came with the advent of steel driver’s was its manufacturability. The largest benefit added to drivers with the increased manufacturability was the ability to create hollow driver heads$^1$. In a typical club swing, when the club hits the ball, the ball will deflect in diameter much more relative to the face of the driver. The ball is therefore responsible for the greatest amount of loss energy during a swing. A critical design factor for drivers is the amount of deflection in the club face; the more deflection in the club face will yield less deflection in the ball – reducing the amount of loss energy and increasing ball velocities$^2$. For the most part, professional golfers are some of the only people who can consistently hit the ball with the center of the club face to produce maximum club-face deflection – this center is known as the “sweet spot”. Designers soon began to maximize the size of the sweet spot so amateurs could achieve more consistent shots. There are many factors that are considered when designing a driver head (which are outside the scope of this report), but the one that will make steel an obsolete material for driver heads is face size.
Driver head designers want to give the golfer the biggest opportunity for hitting the sweet spot, and the smallest chance for an off-center shot. This entails maximizing the driver face size. Since we want to maximize the face dimensions, steel is not the optimal material of choice considering its high density. In general, we want to reduce the weight of the driver. As we reduce the weight of the driver we are able to increase the swing speed of the club, creating higher ball velocities with less force. One of the most notable additions to the golf industry was the titanium driver. Titanium is about half the density of steel and allowed designers to explore many design options that were limited by the heavier steel drivers. To go even lighter, the industry is beginning to move toward “hybrid” drivers. Hybrid drivers utilize a combination of composite and titanium materials to achieve specific material properties in specific areas of the golf club. Composites will also further reduce the weight of the driver allowing for even higher club speeds.

Callaway Golf is currently developing a new driver utilizing Forged Composite™ materials in the sole and crown of the driver head (Figure 1.3). This material provides much
higher strength and modulus-to-density ratios which allow the designers to control the weight
distribution of the club head while lengthening the shaft in order to increase swing speeds\textsuperscript{4}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{callaways_forged_composite_driver.jpg}
\caption{Callaway’s Forged composite driver.}
\end{figure}

Today, the composite industry is growing quickly due to new and improved methods of
manufacturing. Most composites come in the form of laminates and are manufactured by layup
processing. Layup processing allows for several plies of pre-preg to be stacked on top of each
other which allows the fiber orientation to be rotated, giving the composite anisotropic
characteristics. Sheet molding compound (SMC), on the other hand, is an isotropic material
consisting of discontinuous fibers randomly dispersed in a matrix. Typically, SMC materials
utilize chopped E-glass fibers and are processed by compression molding.

SMC’s

SMC materials are beginning to see a wider range of applicability. One area in particular
where they are seeing more use is the automotive industry. SMC materials are used for body,
chassis, and engine components\textsuperscript{4}. They typically utilize chopped E-glass fibers that are randomly
dispersed within a polyester or vinyl ester matrix. Two reasons for using SMC’s over steel
automotive components include not only significant weight reductions, but also lower tooling costs. Compression molded SMC components will typically have 40% - 60% lower tooling costs than steel stamping\(^5\).

**Carbon Fiber-Vinyl Ester SMC**

The move from E-glass to carbon fiber SMC (CFSMC) materials has been retarded in recent years mainly due to cost. As a result, their use has been secluded to highly specialized applications utilizing processes with small volume outputs. Due to heightened research at carbon fiber developing companies and increased research funding from federal grants, CFSMC materials are experiencing more diverse applications due to an increase in production\(^6\).

The 2003 Dodge Viper (Figure 4) was an innovative application of CFSMC materials. The primary objective of using CFSMC’s was to further reduce the weight of the vehicle. The modulus of commercial-grade carbon fibers is approximately 230 GPa, which is approximately 3 times more than E-glass. This increase in modulus, and decrease in weight, will yield thinner and lighter components for the Viper\(^7\).
Compression Molding

Compression molding is a processing method used for SMC materials. Compression molding enables the production of complex composite components at fast rates. For this reason, many industries are rapidly adopting SMC materials, as described in the automotive industry, to be incorporated to their products. Compression molding begins with several rectangular plies, known as a charge, being placed onto the bottom half of a pre-heated mold cavity. The charge must cover 60%-70% of the mold surface area, which sits on the bottom fixed mold half (Figure 1.5), in order to fill the cavity during the cure process. 

Figure 1.4: Image of the 2003 Dodge Viper highlighting the use of different carbon and glass fiber SMC materials

Windshield Frame Outer and Inner Panel (Carbon-Glass Hybrid)
Sill to Fender Brackets R&L
Door Inner Panel R&L (Carbon-Glass Hybrid)
Fender Supports R&L
Headlamp Supports R&L

= Carbon Fiber Composites
= Glass Fiber Composites

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When the mold begins to close, the top half is lowered at a constant rate and presses down on the preheated mold cavity until it reaches a preset pressure. Once the mold is closed, the charge begins to cure. The charge will subsequently flow and fill the cavity of the mold. It is important to know the exact details of the charges’ cure process: For instance, when the charge begins to flow (T_g) and when it begins to harden and end the cure cycle. During compression molding, there are three areas of the charge to be aware of when considering cure behavior – surface, subsurface, and centerline layers. When heat is transferred to the SMC, it can intuitively be inferred that the heat will first be in contact with the surface. It will then travel through the subsurface, and eventually be conducted to the centerline layers. The centerline layers are located in the middle of the charge and experience different cure rates compared to the surface layers (Figure 1.6).
Optimally, all the layers of the charge would have uniform cure behaviors to avoid pressure building up from the different cure rates between the surface, subsurface, and centerline layers. In order to achieve uniform resin flow throughout the mold, fast molding speeds should be utilized to ensure uniform flow\(^\text{10}\). If the material does not attain a low viscosity before gellation (hardening of the resin), flow in mold is restricted. Premature gellation can create an incomplete part with high void contents, thereby inducing interlaminar cracking. Voids can be introduced to an SMC in the following ways: (1) in the resin paste during mechanical blending of the liquid resin and fillers, (2) at the fiber-resin interface owing to inefficient wetting, (3) in the SMC sheet during compaction between carrier films, (4) between layers of SMC sheets in the charge, and (5) in the closed mold\(^\text{11}\). Voids are a detriment to mechanical integrity for composite materials (Figure 1.7).
Matrix

A composite is typically comprised of fiber reinforcement and a resin matrix. The role of a matrix serves several purposes, namely to (1) keep the fibers in place, (2) transfer stress between the fibers, (3) provide a barrier against an adverse environment like chemicals and moisture, and (4) protect the surface of the fibers from mechanical degradation. The matrix plays an important role influencing compressive and interlaminar shear strength of a composite system\textsuperscript{12}. Matrix selection is critical when considering the interaction between with the fibers. This is because most processing defects incurred during manufacturing depend strongly on the behavior of the matrix\textsuperscript{13}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure17.png}
\caption{Effect of void volume fraction on the interlaminar shear strength of a composite laminate}
\end{figure}
Polymer Matricies

The SMC under observation for this report utilizes a vinyl ester matrix. Vinyl esters are thermoset polymers which differ from thermoplastics because of cross linking. In thermoplastics, individual molecules are held together by weak secondary bonds intermolecular forces like Van der Waals bonds. Thermosets, on the other hand, have chemically linked molecules. This phenomenon is known as cross-linking, which is formed during the cure cycle of the resin. Cross-linked molecules form rigid, three-dimensional network structures (Figure 1.8) that cannot be melted once the cure process has been initiated with the application of heat.

![Amorphous](image)

![Semi-Crystalline](image)

*Figure 1.8: Arrangement of molecules in (a) amorphous polymers and (b) semicrystalline polymers*

Generally, the mechanical properties of polymers depend strongly on both the ambient temperature and the loading rate. Changes in temperature cause the polymer to respond to stress differently, especially when the temperature of the polymer is brought close to its glass transition temperature ($T_g$). $T_g$ is the temperature at which the polymer loses its semi-crystalline molecular structure, and where amorphous structures become more predominant. Over a temperature range close to $T_g$, a polymer’s modulus will decrease by as much as five orders of
Typically, the polymer will change from having brittle properties to more soft or ductile characteristics near $T_g$. Therefore, when an external load is applied, a polymer will exhibit elastic deformation followed by a slow viscous deformation. With increasing temperature, the polymer subsequently exhibits rubber-like behaviors which are characteristic of large elastic deformations. By applying even higher temperatures, the polymer will be changed into a highly viscous liquid, however, thermosets demonstrate different behavior at this temperature range. Unlike thermoplastics, which have melting temperatures ($T_m$), thermoset polymers do not. Instead, thermosets will char and burn as they chemically degrade with increasing temperatures. The $T_g$ of thermosets, however, can be controlled by varying the amount of cross-linking between the molecules. Understanding how to manipulate $T_g$ will be critical for understanding the cure parameters and manufacturability of the composite.

**Vinyl Ester Resin**

Vinyl ester is made by reacting an unsaturated carboxylic acid with an epoxy (Figure 1.9). This SMC utilizes a proprietary vinyl ester resin composition from Quantum Composites. In vinyl esters, the carbon-carbon double bonds are known as unsaturation points, and are located at the ends of the vinyl ester molecule (Figure 1.9). This makes cross-linking less predominant compared to a polymer like polyester, and will allow a vinyl ester to be more flexible and have higher fracture toughness. The cross-links in vinyl esters are formed first by dissolving the resin in styrene monomer, thereby reducing viscosities. During polymerization (resin hardening during the cure cycle), styrene coreacts with the vinyl ester resin to form the cross-links between unsaturation points in surrounding vinyl ester molecules (Figure 1.0.1).
Vinyl esters share similar advantages of both epoxies and unsaturated polyester resins. They demonstrate properties like good chemical resistance, tensile strengths, low viscosities during curing, and fast cure rates, however they also exhibit several critical disadvantages. Some disadvantages include low adhesive strengths (compared to epoxies) which will impair the ability to form complex structures with bonded components. They also exhibit high volumetric shrinkages of around 5%-10%. Although this will allow an easier release of the part from the mold, the difference in shrinkage between the resin and the fibers results in uneven depressions on the surface.

Carbon Fibers

Carbon fiber composites usually have their fibers oriented in a continuous fashion throughout a matrix. This SMC will use discontinuous fibers that are chopped to lengths of approximately 1 inch. These fibers have several advantages such as high tensile strength-to-weight and high tensile modulus-to-weight ratios, low coefficient of linear thermal expansion, high fatigue strengths, and high thermal conductivity. Some disadvantages include low strain-
to-failure, low impact resistance, and high electrical conductivity. Carbon fibers are comprised of a blend of amorphous carbon and graphitic carbon. Their high tensile modulus is due mostly to the graphitic carbon structures. In the graphitic form, carbon atoms are in a crystallographic structure consisting of parallel planes (Figure 1.0.2). Strong carbon-carbon covalent bonds exist in-plane, however, Van der Waal’s bonds are responsible for bonding the layered planes together which are considerably weaker. The result is highly anisotropic properties in the graphite unit cell which comprises the carbon fiber.

![Figure 1.0.2: Arrangement of carbon atoms in a graphitic crystal](image)

Carbon Fibers are typically processed from either PAN or PITCH precursors. This SMC is a polyacrylonitrile (PAN) based fiber. PAN based fibers are drawn from a process known as wet spinning (Figure 1.0.3), and are subsequently stretched and heat treated. This is the first out of a 3 steps in creating PAN based carbon fibers.
The wet spinning and stretching process is followed by a heat treatment where temperatures range between 200°C - 300°C for about 2 hours. During this stage, polymer chains are aligned in the filament direction and CN groups, located at either side of the molecule, begin to combine and form the more stable ladder structure. The next stage is known as carbonization.

Carbonization begins by heating the PAN filaments at temperatures of 1000°C - 2000°C in an inert atmosphere. The fibers remain stretched in order to prevent shrinkage as well as improve the fibers’ molecular orientation. The goal of this stage is to rid the filament of impurities like nitrogen and oxygen, making the filament almost purely carbon. The carbon atoms then orient themselves in aromatic ring patterns in parallel planes (Figure 1.0.3).

*Figure 1.0.3: PAN based precursor undergoing the first out of a 3 step process in becoming a carbon fiber*

*Figure 1.0.3: Ladder structure in an oxidized PAN molecule. (a) Molecular structure of PAN and (b) rigid ladder structure*
Neighboring planes, however, are not yet ordered and the filaments have relatively low tensile moduli. The final stage is known as graphitization. Graphitization begins by heat treating the carbonized PAN filaments to temperatures over 2000°C. Their structure begins to become completely ordered and now have high tensile moduli with low tensile strengths. Higher strengths can be attained by hot stretching which aligns graphitic planes in the filament direction.

2.0 Experimental Procedure

Two mechanical properties were requested by Callaway in order to characterize the mechanical behavior of the SMC: flexure strength and tensile strength. Flexure and tensile tests were performed to measure these properties.

Bend Test Setup

The 3-point bend test was conducted per ASTM D790\(^{21}\). A 32:1 support span to thickness ratio was utilized in order to observe failure occurring in the outer surface of the SMC. This support span ensured that failure occurred solely to the bending moment developed by the crosshead (Figure 2.1). With a 1.3 mm thickness, our support span was set to 42.6 mm. The crosshead motion was set to move downward at a rate of 1.0 mm/min. Each sample was measured for thickness and width, and these dimensions were entered into the software before each test.
Flexure Specimen Preparation

Callaway provided 254 mm x 254 mm flat panels of carbon-fiber SMC material to be tested. Each sample was cut to 12.7 mm wide and 63.5 mm long. The length dimension was determined from the standard to be at least 10% longer than the support span. The width dimension was predetermined by the standard for materials with thicknesses less than 1.6 mm. The samples were cut with a composite jet saw to the aforementioned dimensions. 35 samples were prepared and tested in two separate runs. The first run tested 15 samples and the second tested 20 samples.

Tensile Test Setup & Sample Preparation

Tensile testing was conducted per ASTM D3039\textsuperscript{22}. Width, thickness, and length were entered into the software before testing each tensile coupon. Using the 25.4 cm x 25.4 cm flat panels, tensile coupons were cut with the composite jet saw to 25.4 mm wide and 254 mm in length. Tabs were used to distribute the stress induced from the tensile grips over the grip area and to avoid the development of stress concentrations during testing (Figure 2.2). Literature research
suggested using an epoxy-based glass-fiber-reinforced composite as tabbing material. 0.16 mm thick printed circuit board (PCB) material was therefore used as the tabbing material.

![Figure 2.2: Image of tabs that were placed on each tensile specimen](image)

The PCB material was 127 mm wide and was long enough for the entire grip to be placed over an appropriate amount of the tensile coupon to ensure a sufficient grip area on the tab. The as-received panels were abraded with sand paper and then cleaned with acetone. An adhesive was then applied to the surface of the panel, and subsequently the tabs were pressed down onto the adhesive. Initially a commercial-grade two part epoxy was used as the adhesive. After repeated invalid tests (due to fractures occurring outside the gauge length), a 3M structural adhesive was used for improved adhesive strengths. Weight was applied to the tabs in order to squeeze out any entrapped air between the tab and the SMC panel. The tabs were then aligned with the edges of the panel until flush. The coupons sat for 2 days in order to allow the adhesive to fully cure. They were then placed in the grips and tested until failure.

Following suggestions from ASTM D3039, we began tensile testing without tabs on our samples. It soon became apparent after several tests, that without tabs, the problem arose that either we would clamp too hard on the sample and create a stress concentration where we would consistently observe failure outside the gauge length which was indicative of an invalid test. If we did not clamp down the grips hard enough, the sample would slip from the grips; this was evident from the drop off in stress as seen in Figure 3.5.
We then began to use a commercial grade two-part epoxy in order to bond the PCB tab material to the tensile coupons. When we first began testing these tabbed coupons, it was clear there were problems with our tensile testing methodology. Almost immediately after starting the tensile test, we could hear cracking occurring from the test. Figure 3.5 demonstrates the inconsistency of data from our testing methodology and suggests that there is a problem with our samples. Our immediate speculation was that some fibers were failing, however, it soon became apparent that it was actually the epoxy failing. It clearly was not strong enough. We then moved to using a 3M structural adhesive in order to create a stronger bond between the tabs and the tensile coupons. This stronger bond was used in hopes that the material would fail before the bond, allowing us to observe the failure stress of carbon-fiber SMC.

3.0 Results

The two different flexure testing sessions produced two stress-extension graphs (Figure 3.1 & 3.2). The goal of this report is to determine the scatter of mechanical strengths between batches of material received from Callaway. Before this can be done, the scatter must first be determined within a single batch of material.
Figure 3.1: First set of flexure data. Notice the concentration of flexure strengths in the 400-500 MPa Range

Figure 3.2: Second set of flexure data. Notice this set of data follows a similar distribution of flexure strengths as seen in Figure 2.3

Tables I and II provide data correlating with Figures 2.3 and 2.4 and include standard deviation calculations.
Table I: First set of flexure data reflecting the data from Figure 2.3

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</table>

This data reflects two different test sessions in order to ensure this data was repeatable. These specimens were all gathered from the same batch of material received from Callaway.

Tensile testing was also conducted in order to analyze the scatter of tensile strengths observed within a given batch of material. The tensile methodology, however, was determined to be inconclusive once the data was observed (Figure 3.5). This methodology is incomplete, and several problems arose during testing. One problem was the choice of adhesive, therefore, two different tensile tests were conducted each using a different adhesives for the specimen tabs. These problems, as well as potential solutions, will be analyzed in the discussion. Figure 2.6 shows post-test tensile specimens. This group of specimens includes both successful and unsuccessful tests which can be determined by observing failures either inside or outside the gauge length.
Figure 3.3: Post-test tensile specimens utilizing the structural adhesive. Notice where the fracture occurs in each specimen.

Figure 3.4: Tensile test utilizing 3M structural adhesive for bonding tabs to the SMC tensile samples. Group 1 represents successful tests, Group 2 represents fractures outside the gauge length, and Group 3 represents non-linear slopes with fractures in the middle of the gauge length.
Figure 3.5: Tensile test utilizing commercial grade two-part epoxy for bonding tabs to the SMC tensile samples. Notice the linear slope in the initial stages of the test. They then slowly begin to curve as the epoxy failed.

4.0 Discussion

Flexural Strengths

The original goal of this project was to determine the scatter of mechanical properties between batches of carbon-fiber SMC; however, due to time constraints we were only able to characterize the scatter within a given batch of material. The reason for this characterization is due in part to the nature of the material at hand, and also to the way this material is processed. Quantum Composites (Bay City, MI) supplies the carbon-fiber SMC prepreg to Callaway. Quantum keeps the detailed characteristics of the prepreg proprietary, and provided Callaway with a data sheet containing the SMC’ s tensile and flexural strengths. Quantum listed the flexural and tensile strengths to be 606 MPa and 282 MPa respectively. Since 35 flexure strengths were measured, a histogram was produced to observe the distribution of flexural strengths (Figure 4.1).
From Figure 4.1 we can see that in any given batch of material, we may observe a relatively normal distribution of flexure strengths. With outliers in the 750 and 250 MPa range, it is clear that most of our samples reside between 400-600 MPa. It is clear, however, that Quantum’s data sheets may not accurately represent the flexural strength of this material. From this distribution, claiming that the strength is single valued at 606 MPa may be somewhat misleading. From the first and second run of flexure tests, Tables I and II provide us with and overall mean of 494.6 MPa which is significantly lower than the 606 MPa value listed by Quantum. It could be that a single-value of around 500 MPa would be a better indicator of the flexural strengths of this SMC.
Tensile Testing Discussion

From Figure 2.7 we can observe three trends in the data: First are the successful tests. The two successful tests are deemed successful for two reasons: 1. Failure occurred directly in the middle of the gauge length, and 2. Quantum lists their tensile strength to be 282 MPa. With these two tests failing close to 250 MPa, and considering the scatter of strengths observed in the flexure data, it is likely that the strengths observed are representative of the material. The next group of specimens in consideration is the middle group which all had fractures occurring outside the gauge length. All of these samples had similar, linear slopes with the same outcome. It is clear that further investigation as to what is causing this trend is needed to be done in order to conduct accurate tensile tests. The third group of data shows two samples that demonstrated relatively higher extensions. These two samples also have non-linear slopes; however, the peculiar characteristic of these tests is that they both fractured in the middle of the gauge length. It is also important to note that these two samples also demonstrated no slipping from the grips (which is evident on the tabs when long scratches can be seen on them); however, as observed in the epoxy tests, slipping was consistently correlated with non-linear behavior observed on the graphs (Figure 3.5). The main difference between the two is that slipping usually occurs with a gradual drop off from non-linearity as the slope begins to level off as observed in the epoxy tests, whereas the 3M adhesive experiences no linear behavior at all.

Further research has been conducted to begin answering why these trends are occurring. There is some speculation on the use of aluminum tabs; however this was not confirmed to solve the problem. Using “dog bone” geometry samples or otherwise altering sample geometries has also been speculated to solve our problem, but again this has also not been confirmed.
Future Research

As previously discussed, Callaway ultimately wanted to characterize the mechanical behavior between multiple batches of material. Callaway also showed interest in compression testing to further characterize mechanical behavior of this SMC. Due to the test parameters that influence the cure reaction in compression molding, it will also be important to understand the cure characteristics of this material. Characterizing $T_g$ was therefore an important physical property requested by Callaway also to be measured. Both of these properties, as well as finalizing the tensile method, can all be prompts for ongoing research in order to finally characterize this carbon-fiber SMC between batches.

Broader Impacts

This product will help improve the driving capabilities of players of all skill levels. The lighter driver will allow for the design of larger sweet spots which will allow more novice players to hit farther drives. This product will also allow for faster swing speeds as opposed to steel clubs; therefore, no matter your size or strength, this driver will undoubtedly suit a vast range of players seeking to improve their game.

5.0 Conclusions

1. Scatter of flexural strengths observed within a given batch of material to be over 100 MPa.
2. It may be more reasonable for Quantum Composites to list their single-value flexure strength at around 500 MPa as seen from the distribution
3. Unlike the epoxy, the structural grade adhesive was strong enough to withstand tensile testing.
4. Tensile testing methodology near completion. Further procedural variables: Try using aluminum tabs and/or different sample geometries
References


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