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Optimized Resins and Sizings for Vinyl Ester/Carbon Fiber Composites

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FINAL TECHNICAL REPORT

Optimized Resins and Sizings for Vinyl Ester/ Carbon Fiber Composites

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- Michelman, Inc.
- Michigan State University
- University of Dayton Research Institute
- Zoltek Corporation

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List of Acronyms

BPA	Bis-phenol A
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
FRPC	Fiber-Reinforced Polymer Composite
GPa	Giga pascals
GSM	Grams per Square Meter
IACMI	Institute for Advanced Composites Manufacturing Innovation
ILSS	Interlaminar Shear Strength
mPDA	Meta Phenylene Diamine
MPa	Mega pascals
MSU	Michigan State University
PX35	Panex 35 fibers from Zoltek
SBS	Short Beam Shear
SMC	Sheet Molding Compound
Tg	Glass Transition Temperature
UDRI	University of Dayton Research Institute
VER	Vinyl ester resin

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Executive Summary:

This report will summarize the results of a Technical Collaboration project to develop technology suitable for the fabrication of styrene-free vinyl ester / carbon fiber prepregs. Numerous combinations of resins from Ashland, sizings from Michelman, and fibers from Zoltek have been investigated at Michigan State and at UDRI, and the processing and properties of the best-performing systems are described.

The project team demonstrated an optimized vinyl ester / carbon fiber prepreg system with the following attributes/benefits:

- no styrene. The vinyl ester resins that can be used to make prepregs are hot melt resins that do not contain a reactive diluent. They are not intentionally diluted in styrene.
- long shelf life (> 23 months). The films used to make prepreg surrogates during the course of this project have been shown to be stable for at least 9 months at room temperature. The surrogates themselves have been shown to be stable for at least 7 months at room temperature. In related work outside the scope of this project, prepregs made with the same vinyl ester resins have been stable at room temperature for 23 months.
- no need for refrigeration. Unlike most epoxy prepregs, which need to be stored in a freezer, vinyl ester prepregs can be stored at room temperature.
- fast cure (≤ 3 minutes). The prepreg surrogates made in this project were compression-molded at 325-350°F and 100 psi pressure and a molding time of 3 minutes. In comparison, the molding time is 10 minutes for the epoxy/carbon system that IACMI has used as benchmark for compression-molded prepregs.
- improved resin-fiber interface. The Interlaminar Shear Strength (ILSS) values measured at Michigan State for the best-performing resin/sizing/fiber systems were near or slightly above 100 MPa. This is indicative of a strong resin-fiber interface. These values were significantly higher than an epoxy/carbon control run at MSU and higher than any values of ILSS found in the literature for vinyl ester/carbon systems. Micrographs of the fracture surfaces showed good contact between the resin and the fiber, providing further evidence of a strong resin-fiber interface.
- reduction in the amount of process scrap that needs to go to a landfill. Vinyl esters offer significant advantages relative to epoxy resins with respect to recycling and re-use. Work with Vartega has shown that their extraction process can readily remove the resin from scrap vinyl ester prepreg, enabling facile recovery of the carbon fibers. On the re-use front, it has been shown that scrap prepreg can readily be molded after an extended

period of time. It has also been shown that virgin or scrap prepreg can be co-molded with Sheet Molding Compound (SMC).

- reduction in embodied energy. The FRPC calculator developed by IACMI has been used to show that vinyl ester prepregs offer the potential for significant reductions in embodied energy relative to epoxy-based systems. Reductions as high as 33% have been calculated. This is a significant fraction of IACMI's target of a 50% reduction in embodied energy by 2020.
- cost-effectiveness. The use of industrial grade carbon fibers, the improvement in shelf life stability of the prepreg at room temperature, the lack of a need of refrigeration, the short molding time, and the ability to extract value from prepreg scrap all add up to a cost-effective alternative to epoxy/carbon prepreg systems. IACMI has calculated a 22% reduction in the cost to produce a compression-molded hood inner, and the reduction could be even higher if the recycling/re-use options for prepreg scrap are taken into consideration.

The key benefits demonstrated for the optimized resin/sizing/fiber system include long shelf life at room temperature, short compression molding times, and recycling and re-use opportunities for prepreg scrap.

The work performed in this project moved the Technology Readiness Level (TRL) for vinyl ester/carbon fiber composites from 3 to 4. A Stage 2 IACMI project should be initiated to scale-up the optimized resin/sizing/fiber system identified in the Stage 1 work described in this report. The project team should be expanded to include a prepregger who could make actual prepregs instead of prepreg surrogates and an automotive OEM or Tier 1 supplier with a specific part in mind to fabricate with the optimized system.

The Stage 2 project should also include a recycling/re-use component that would demonstrate the advantages of vinyl ester prepregs on a larger scale. This effort should include work to optimize the recovery of carbon fibers (and potentially the resin as well) from prepreg scrap and further work on the molding and co-molding of prepreg scrap.

This project is a very good illustration of how IACMI is an effective mechanism for technology development. It fosters collaboration between industry, academia and the federal labs on industrially-relevant problems.

1.1 Introduction: This project was a Technical Collaboration that began in February 2017 and ended in January 2018. The project team consisted of three industrial partners (Ashland, Michelman and Zoltek) and two IACMI centers (Michigan State and the University of Dayton Research Institute, *aka* UDRI).

The objectives of the project are listed below:

- design resins & sizings for vinyl ester / C fiber composites
- develop technology suitable for high speed production of automotive parts via prepregging
- demonstrate advantages relative to epoxy / carbon

To develop an optimized resin/sizing/fiber system, the project team brought together a resin supplier (Ashland), a sizing supplier (Michelman), and a carbon fiber supplier (Zoltek). Although there are many composite fabrication processes, the team focused exclusively on developing technology suitable for the production of prepregs which could be compression molded to produce a fabricated composite part. This technology was targeted at the automotive industry, where short cycle times are needed to produce vehicle volumes in excess of 100,000 parts per year.

The incumbent technology for many prepreg applications is epoxy/carbon fiber. This is especially true in aerospace applications, with Boeing's 787 Dreamliner being a recent, high profile example. However, going into the project, it was felt that vinyl ester resins (VERs) offered potential processing and cost advantages relative to epoxies and other prepreg systems, particularly with respect to improvements in cure speed and elimination of the need to refrigerate prepregs prior to use. Based on the literature and previous experience, it was recognized that improvements in the resin-fiber interface would be needed with a vinyl ester/carbon system.

From an energy perspective, this project fit very well with IACMI's stated goal of reducing the embodied energy of composite parts by 50% by 2020. This fit encompassed both material aspects and processing aspects. From a materials perspective, one of the shortcomings of epoxy/carbon prepreg is the high amount of prepreg scrap, which often ends up in a landfill. With carbon fiber as the reinforcement, this scrap contains a considerable amount of embodied energy that is wasted. This report will show that with vinyl esters, recycling and re-use of prepreg scrap is much more facile than with epoxies, making significant reductions in embodied energy possible.

There are also energy advantages to vinyl esters from a processing standpoint. The drive to shorter cycle times that is important to the automotive industry from a parts per year standpoint also has energy implications. It will be shown in this report that significantly shorter molding times are possible with vinyl esters relative to epoxies. Since compression molding is an energy-intensive process, shorter molding times also lead to energy savings.

1.2 Background:

The automotive industry has a long history of using compression-molded SMC (Sheet Molding Compound) to fabricate parts. Much of this work has been done using chopped glass fibers as the reinforcement and an unsaturated polyester or vinyl ester resin as the matrix.

In recent years, the automotive industry has begun to utilize compression molding of prepreg to fabricate parts such as hoods. Much of the prepreg technology that has been adopted in the automotive industry has its roots in the aerospace industry, where epoxy/carbon is the system of choice. Prepregs are typically made by either the hot-melt route or the solution route.[1]

The following paragraphs provide some background on the five partners involved in this project. They are intended to describe the "starting point" for this project and the fit for each of the partners.

Prior to the start of this project, Ashland had developed some vinyl ester resin (VER) technology targeted toward the production of prepreg via the hot melt route. Unlike most of the vinyl ester resins that are used throughout the composites industry in a wide variety of fabrication processes, the VERs employed in this project did not contain styrene as a reactive diluent. Prior to the start of this project, Ashland tested one of these VERs at Renegade Materials in Miamisburg OH, who showed that the resin processed well on their hot-melt equipment with carbon fiber unitapes, carbon fabrics and glass fabrics. This work focused on processability and did not attempt to optimize the resin-fiber interface or the mechanical properties of composite parts fabricated using the prepreg.

Zoltek is a subsidiary of Toray, whose high performance carbon fibers are used throughout the aerospace industry. Zoltek produces industrial grade carbon fibers, which are lower in performance than their aerospace counterparts but also considerably lower in cost and thus more attractive for high volume automotive applications. Zoltek does have an internal sizing development group, and prior to the start of this project, they had developed sizings that are compatible with different resin systems, including epoxies and vinyl esters. They also have a pilot line for applying sizings to carbon fiber at their plant in St. Peter's, MO.

Michelman supplies sizings to a variety of industries, including composites. They have considerable expertise in the formulation of aqueous sizings for a variety of resin systems, including thermosets and thermoplastics. Prior to the start of this project, Michelman had not developed or commercialized any sizings specifically intended for use with vinyl esters.

Michigan State has considerable expertise in the area of sizing development and characterization of the resin-fiber interface. They have done previous work with sizings intended for use with vinyl ester resins.[2-4] However, this previous work has been done with vinyl ester resins that contained significant amounts of styrene. As noted above, the VERs from Ashland employed in this project did not contain any styrene. Similarly, Adherent Technologies in Albuquerque NM has developed sizings for styrenated vinyl ester resin systems. [5]

The University of Dayton Research Institute (UDRI) is well-equipped for the fabrication of composites by a variety of methods. UDRI does not have a hot-melt prepregging unit, but they have expertise in the fabrication, molding and testing of "prepreg surrogates," which will be described later in this report.

All this experience and expertise was combined in this project to develop an optimized resin/sizing/fiber system targeted for use in vinyl ester/carbon fiber prepregs. Taking into consideration the expertise of all the partners, the Technology Readiness Level (TRL) going into this project was estimated to be 3-4.

1.2.1 Materials Employed:

Resins: Two monomer-free, styrene-free vinyl ester resins (VERs) from Ashland were used as the resin matrix. Arotran 901 was based on bis-phenol A (BPA) and had a glass transition temperature (T_g) = 147^{o}C as measured by the peak of the tan δ curve. Arotran 902 was also based on BPA, but it also contained some novolac character and had a higher T_g = 188^{o}C. Both resins were designed for prepreg fabrication via the hot-melt route. Additional information about these resins is available from Ashland.

Sizings: Thirteen different sizings were evaluated. They were aqueous dispersions based on multiple chemistries, and they were designed for enhanced adhesion/interactions with vinyl ester resins. Three of the sizings were commercially-available, fully-formulated sizings from Zoltek. The other ten sizings came from Michelman; two were commercially-available, fully-formulated sizings, and eight were developmental sizings. For nomenclature purposes, the thirteen sizings were labeled A to M. Additional information about these resins is available from Zoltek and Michelman.

Fibers: The fibers were industrial grade PX35 carbon fibers from Zoltek. These fibers are PAN-based, intermediate modulus fibers with the following mechanical properties.

- Modulus: E = 242 GPa (35Msi)
- Strength: σ = 4.14 GPa (600 ksi)

The PX35 fibers came in a 50k tow. The sizings were applied to the fibers on Zoltek’s pilot line in St. Peter’s, MO. Two different winding configurations were studied -- T grade (“ropes”) and W grade (“ribbons”). Additional information about the PX35 fibers is available from Zoltek.

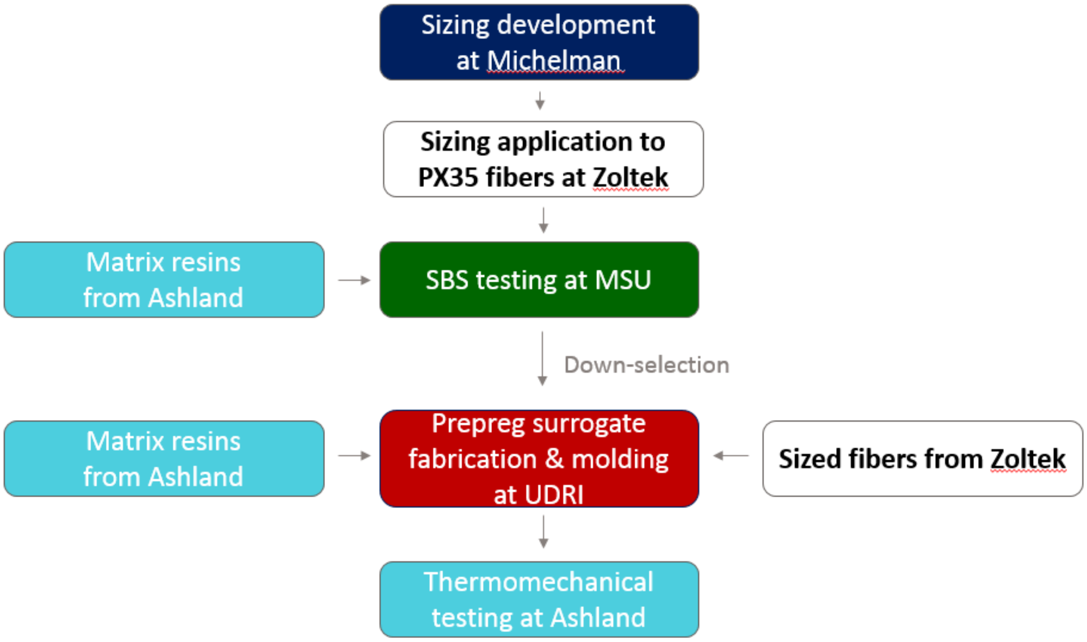
1.2.2 Process Flow: Figure 1 summarizes the responsibilities of the various partners.

Figure 1. Project team responsibilities

Partner	Responsibilities
Ashland always solving	Resin Development, Mechanical & Thermal Analysis Testing
MICHELMAN	Sizing Development
ZOLTEK Toray Group	Sizing Application to PX35 Fiber
MICHIGAN STATE UNIVERSITY	Characterization of Resin-Fiber Interface
UDRI UNIVERSITY of DAYTON RESEARCH INSTITUTE	Fabrication & Molding of Prepreg Surrogates, Project Management

Figure 2 shows the process flow during the project. Most of the sizing development work was performed at Michelman's laboratories in Cincinnati. Sizings from Michelman and from Zoltek were applied on Zoltek's pilot line in St. Peter's, MO. Spools of the sized fibers were sent first to Michigan State where they were combined with the matrix resins from Ashland to produce Short Beam Shear (SBS) specimens. The SBS samples were used to measure the Interlaminar Shear Strength (ILSS), which is a good indicator of the strength of the resin-fiber interface.

Figure 2. Process flow



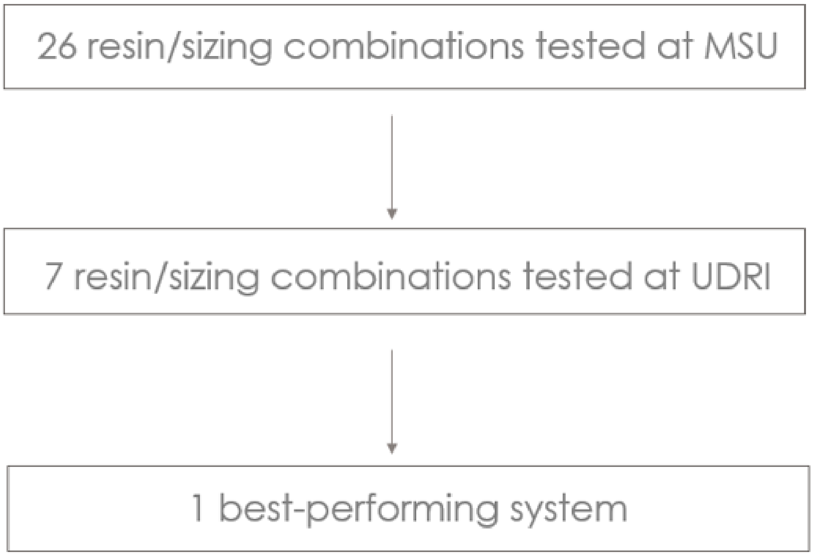
The ILSS results at MSU were used to down-select systems for further testing at UDRI, which was responsible for the fabrication and molding of prepreg surrogates. The term “prepreg surrogate” will be defined later in the experimental section for UDRI.

Compression-molded samples were sent to Ashland’s labs in Dublin, OH where the vast majority of the thermomechanical testing was performed.

In all, 26 combinations of resins and sizings were tested – 2 resins x 13 sizings. The nomenclature system used to distinguish the systems was Resin #/ Sizing letter – eg, 901/A or 902/M.

Figure 3 summarizes the down-selection process. Of the 26 systems tested at MSU, 7 were down-selected for further work at UDRI. Of these 7 systems, one system was selected as the best-performing system based on the mechanical property results and processing considerations.

Figure 3. The down-selection process



1.3 Results & Discussion

1.3.1 Sizing Development & Application

13 different sizings were tested. They were labeled A to M and are described briefly below:

A,B	Commercial, fully-formulated sizings from Michelman
C-J	Developmental sizings from Michelman spanning these chemistries – phenoxy, vinyl ester and urethane, not fully-formulated
K-M	Commercial, fully-formulated sizings from Zoltek

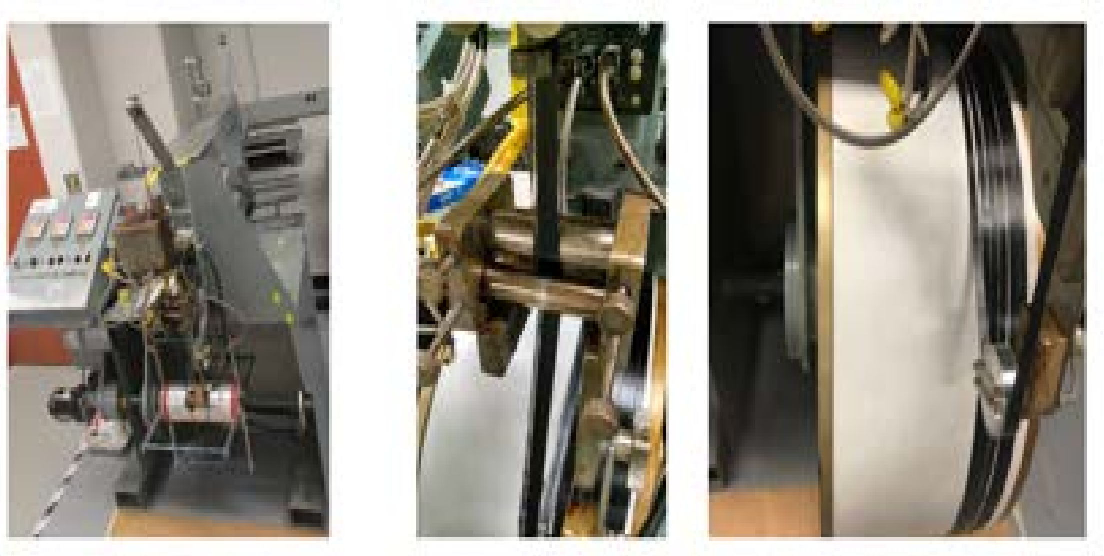
Sizings were applied on Zoltek's pilot line in St. Peter's MO. The target sizing weight was 1.0-1.5 wt% based on fiber.

1.3.2 Preparation, Characterization and Testing of Prepreg and Short Beam Shear Samples

1.3.2.1 Experimental: The following process was used at Michigan State to produce unidirectional, well-consolidated composites using an out-of-autoclave, compression molding process with PX35 fibers sized on Zoltek's pilot line in St. Peter's, MO and vinyl ester resins (Arotran 901 and Arotran 902) provided by Ashland.

1.3.2.1.1 Preparation of Prepreg: Unidirectional prepreg tape was made via a wet-winding process using the slit-die hot-melt prepregger (Research Tool, Ovid, MI) shown in Figure 4. A spool of fibers from Zoltek was mounted on a tension controlled axle that fed the tow to a heated resin pot containing a series of pins that aided in impregnation. The tow exited the pot through a slit die 0.70” wide whose thickness was adjustable via shims to accommodate various tow cross-sectional areas. After exiting the slit-die, the tow passed over two flattening pins and a guide roller before being taken up on a rotating drum covered with release paper (Loparex, Cary, NC). The resin pot, slit-die, flattening pins, and guide roller were all temperature-controlled. The prepregger drum rotation and axial displacement was controlled so that the impregnated tow was carefully placed adjacent to tow placed on the drum from the previous rotation. The process was run continuously until a desired width of adjacent tows was assembled resulting in the prepreg tape. Once the desired width was reached, the prepreg operation was stopped and a second layer of release paper covered the prepreg tape on the drum. After removal from the drum, a prepreg 74” long and with the prescribed width was produced.

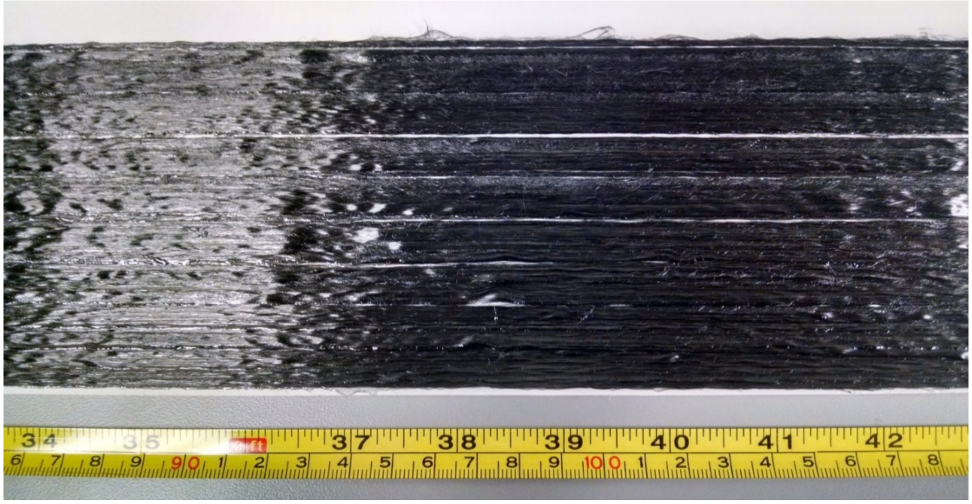
Figure 4. Equipment used to prepare Short Beam Shear (SBS) samples at MSU



Luperox P from Sigma Aldrich was used as the initiator at 1.5 wt% based on resin. The processing temperatures used for prepregging with the Arotran 901 and 902 resins were 100°C and 80°C, respectively. This included the preheating of the resins prior to adding the initiator, the temperature of the oven holding the resin prior to processing, and the settings of the prepregger’s resin pot, flattening pins and roller guide.
Rheological studies verified that the VER systems maintained a long pot life during these prepregging operations.

A section of uncured prepreg was trimmed to a 3” width and cut into 6.5” long segments; an example of uncut prepreg is shown in Figure 5. After cutting, the 74” prepreg yielded 11 plies for layup to produce a unidirectional composite.

Figure 5. An uncured prepreg made with the 901/K system



The mold used was a two-piece plug mold 3” x 6.5” in area with a 0.5” deep cavity. It was designed with a “slip-fit” between the plug and cavity which allowed excess resin to bleed-out during processing, yielding a high fiber volume fraction composite. A dry film PTFE release agent was applied to all surfaces of the mold. The mold containing the layup was placed into a preheated Carver press (100°C for the 901 resin, 80°C for the 902 resin) with the temperature monitored with a thermocouple embedded in the side of the mold. The mold was placed under compression with a contact load only. The load was maintained throughout the process cycle as the plies consolidated, and excess resin was allowed to bleed out. Once the mold reached the desired preheat temperature, it was held there for 5 minutes followed by a ramp to 160°C at 10°F per minute. After a 1-hour soak at 160^{o}C, the mold was cooled under contact load to room temperature.

1.3.2.1.2 Preparation & Characterization of Short Beam Shear (SBS) Samples: After molding, the composite panels were cut into standard ASTM test coupon dimensions using a water-cooled diamond saw. The first cuts trimmed 0.5” from the edges to remove any potentially non-uniform material. Two strips 0.5” wide were collected in the °0 direction and cut into specimens for examination via optical microscopy and for Short Beam Shear testing.

Short Beam Shear testing was performed in general compliance to ASTM Standard D2344. Ten specimens were tested for each composite.

Fiber volume fractions and the presence and quantity of voids were determined by collected cross-sectional micrographs of the composite coupons. Three specimens from each panel were embedded in metallographic mounting media and polished. A series of photomicrographs were taken of each specimen and optically stitched together to produce a single image through the thickness of the composite. The width of view of the individual photomicrographs was 1.6 mm, and they were not cropped during stitching.

The cross section of a sample obtained with Arotran 901 as the matrix resin is shown in Figure 6. The slightly darker regions located roughly perpendicular to the thickness direction are areas where the fiber concertation is slightly lower than the surrounding area and coincide with the region where adjacent plies came together under the compression consolidation step in the mold. If the plies did not deform during the compression molding step, a series of darker regions parallel to each other would have been produced.

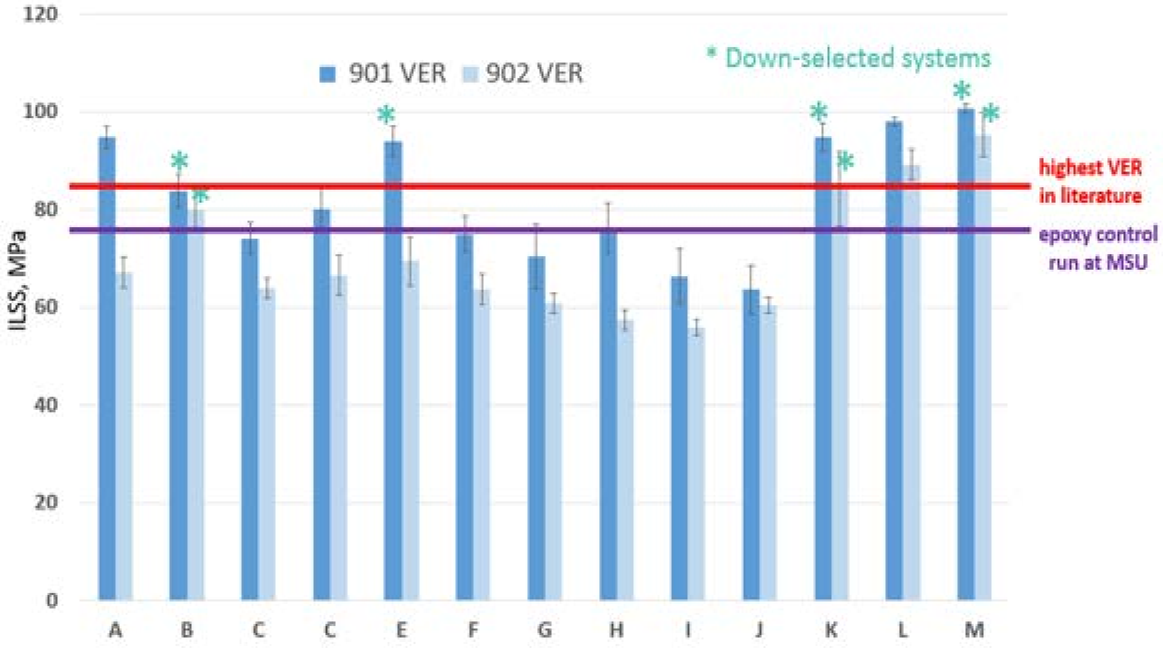
Figure 6. Cross Sections of 901/PX35 ribbon at 3 Locations (Width of View = 1.6 mm)

Location : 2 Location : 7 Location : 16

1.3.2.2 Results of Short Beam Shear (SBS) Testing: Figure 7 shows the Interlaminar Shear Strength (ILSS) results for the 26 systems tested at MSU. The values ranged from about 60MPa to slightly above 100MPa. The values near 100MPa are indicative of a strong resin interface. The red line in Figure 7 indicates the highest value for a vinyl ester/carbon fiber system found in the literature.[5]

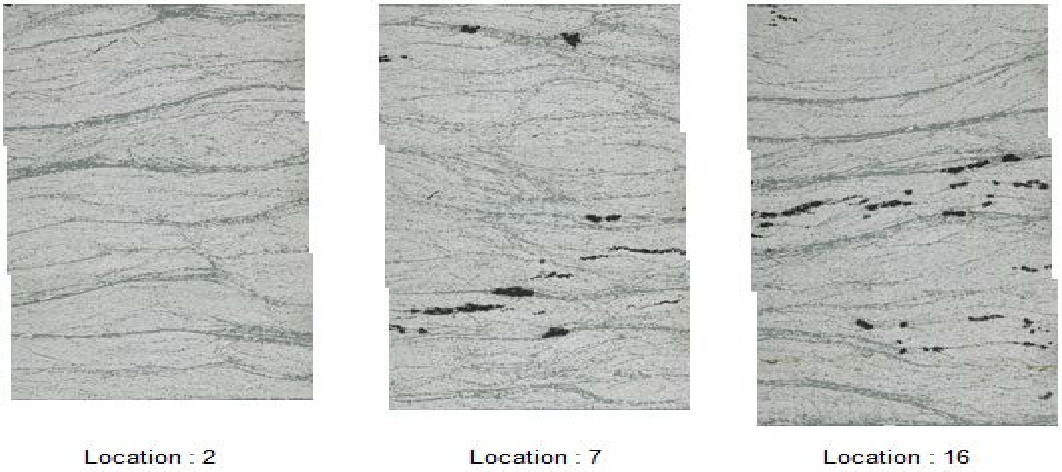
Figure 7 also includes data for an epoxy control run at MSU using the same Zoltek fibers and the same equipment used to process the vinyl ester samples. The epoxy system was based on the diglycidyl ether of bis-phenol A and meta-phenylene diamine, mPDA; it was a system that MSU had worked with in the past. The data for this system is shown as the purple line in the figure, and many of the experimental VER/C systems gave ILSS values that exceeded this value. This was taken as further evidence that a strong resin-fiber interface had been formed in some of the experimental VER/C systems.

Figure 7. ILSS results from Short Beam Shear (SBS) testing at MSU



Note that for a given sizing, the ILSS value was always higher with the 901 resin than with the 902 resin. The best explanation for this somewhat unexpected result comes from a comparison of the micrographs of molded samples prepared with 901 and 902. The micrograph of a 901-containing sample has been shown in Figure 6. Note that microstructure appears fairly uniform throughout the sample. Contrast that to the microstructure for a 902-containing sample shown in Figure 8. The dark spots in Figure 8 are voids that appear to have concentrated along the interlaminar regions. Although the overall void content is still low (<2 volume %), this concentration at the interlaminar interface could be responsible for the lower ILSS values consistently seen with the 902 resin.

Figure 8. Cross Sections of 902 / PX35 ribbon at 3 Locations (Width of View = 1.6 mm)



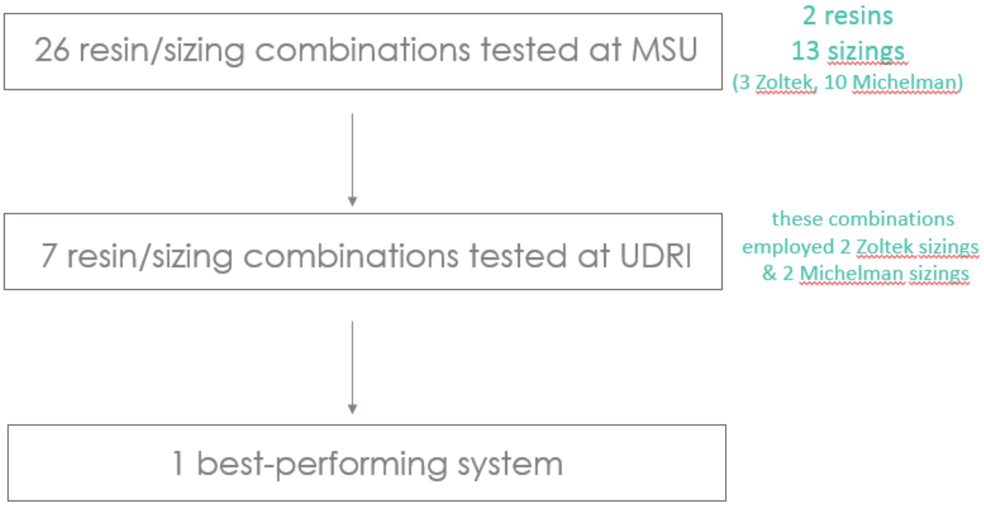
Location : 2

Location : 7

Location : 16

1.3.2.3 The Down-selection Process: Of the 26 systems tested in Figure 7, the seven systems marked with an asterisk were selected for further testing at UDRI. The seven systems were: 901/B, 902/B, 901/E, 901/K, 902/K, 901/M and 902/M. The selection of these systems enabled 1) further work with some of the systems with the highest ILSS values, 2) comparison of the same sizing with both resin systems and 3) a range of ILSS values that could be compared to resin-dominated properties measured at UDRI to see how well the data at the two sites correlated. The results of the first step of the down-selection process are summarized in Figure 9.

Figure 9. Down-selected systems from MSU

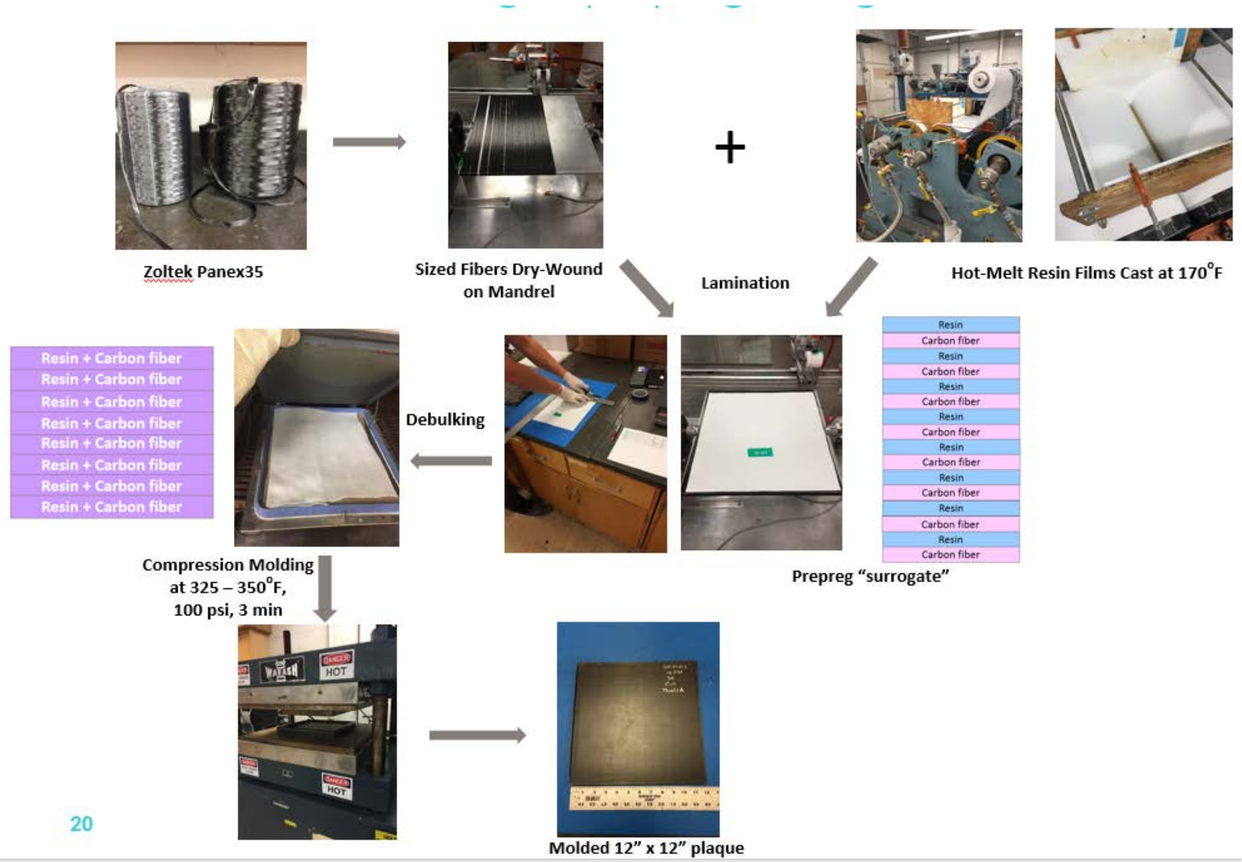


1.3.3 Fabrication & Molding of Prepreg Surrogates: UDRI was responsible for the fabrication and molding of “prepreg surrogates” with the seven down-selected systems from Michigan State.

The need to evaluate a multitude of sizing/resin combinations and the form of the fiber (bobbins) necessitated the need to prepare prepreg “surrogates”. The surrogates were intended to simulate actual prepregs during the compression molding step. In a hot-melt prepregging process, fiber or fabric is impregnated with resin to give a single layer that contains both resin and fiber. A prepreg surrogate consists of stacked, alternating layers of fiber and resin. All the ingredients of a prepreg are present, but they are not both present in the same layer. The Experimental section will describe how prepreg surrogates were produced and processed at UDRI.

1.3.3.1 Experimental: Figure 10 summarizes the preparation and molding of prepreg surrogates at UDRI.

Figure 10. Preparation & molding of prepreg surrogates at UDRI



UDRI performed fiber tow spreading and winding onto a dry tool, much like a filament winding operation. Air knives and several, non-stick roller/spreaders were implemented in order to accurately wind each ply to a fiber areal weight of 200 g/m2. Concurrently, resin films were cast on a heated, 3-roll film line (Killion KXH12-20) and then stored at room temperature ambient conditions until they were needed for panel consolidation. Both the Arotran 901 and Arotran 902 were filmed so that the prepreg surrogates would be a net resin system with a fiber weight % of 60%. Single plies of resin were then draped onto single plies of spread tow carbon fiber and cut off the mandrel. The tack from the resin was high enough to keep the fibers aligned, so no attempt at working the resin into the fibers was initially performed.

Due to the snap cure qualities of the VER systems, the prepreg surrogates did not allow for resin flow and good consolidation. After failed attempts to consolidate the panels and get good resin flow, it was decided to perform a debulking step at 170^{O}F under vacuum. This process would simulate the hot melt procedure performed at a commercial prepregger. This was performed in a Zip-Vac unit inside a Blue M (WC-9980F) oven. After winding, each ply was vacuum debulked individually at 170°F for 20 minutes. This was done in batches of 8 plies separated by Teflon coated fiberglass. Plies were stacked and debulked at 170°F for 5 minutes every 4 plies. This means that 5-minute debulks occurred at plies 4, 8, and 12. Lastly, the total panel stack was debulked at 170°F for 20 minutes before processing.

The surrogates were then loaded into a 75-ton Wabash press with digital controls and recording capabilities. A flat plate tool, 12” x 12”, was modified and bolted to the press so that the surrogates could be loaded into the heated press at 350°F and simulate a hot stamping press in a rapid manufacturing process. Figure 11 shows the processing conditions for a typical $[0/90]_{4s}$ panel fabricated in this project. A few panels were constructed with all unidirectional plies, $[0°]_8$, and those were processed at much slower conditions in order to avoid warping of the panel; the heating schedule for these panels is shown in Figure 12.

Figure 11. Cure schedule for $[0/90]_{4s}$ prepreg surrogates molded at UDRI

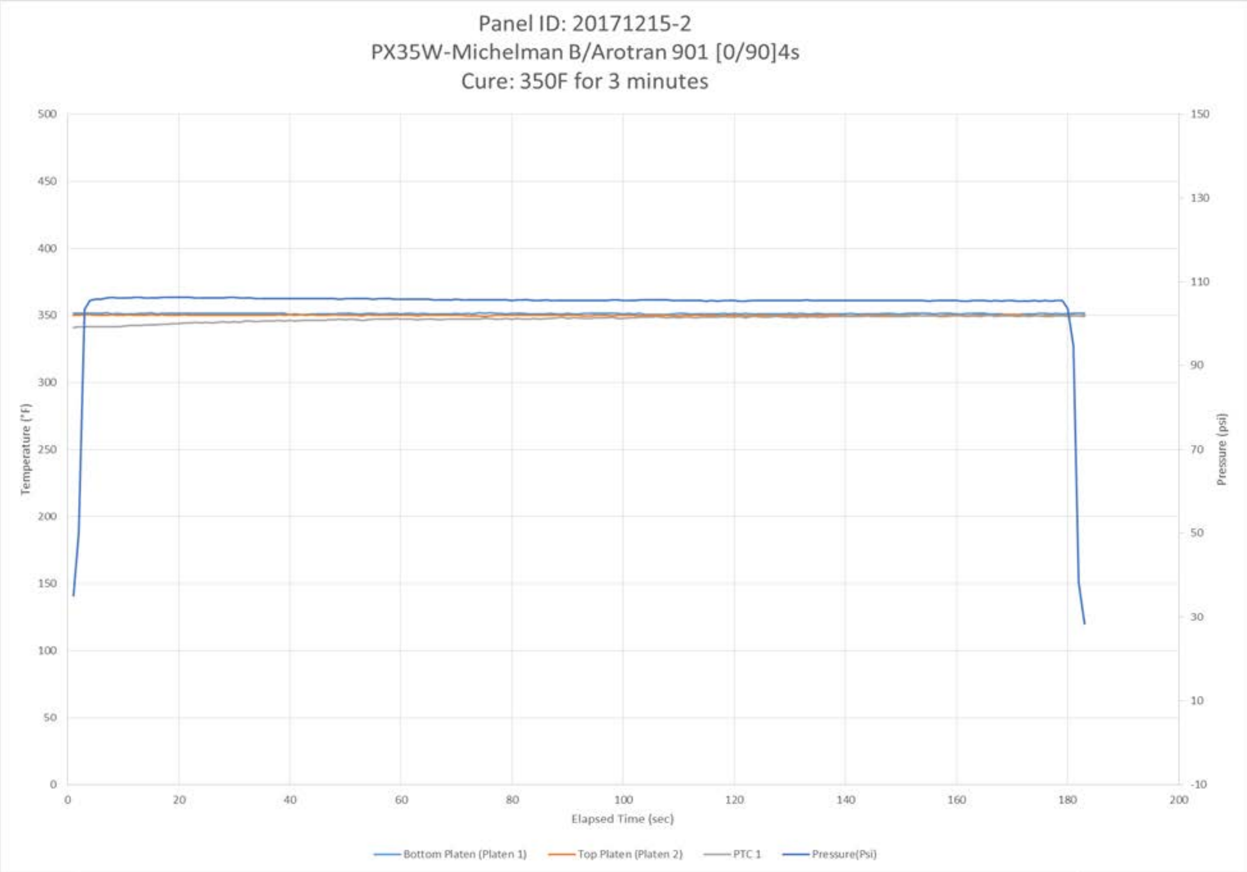
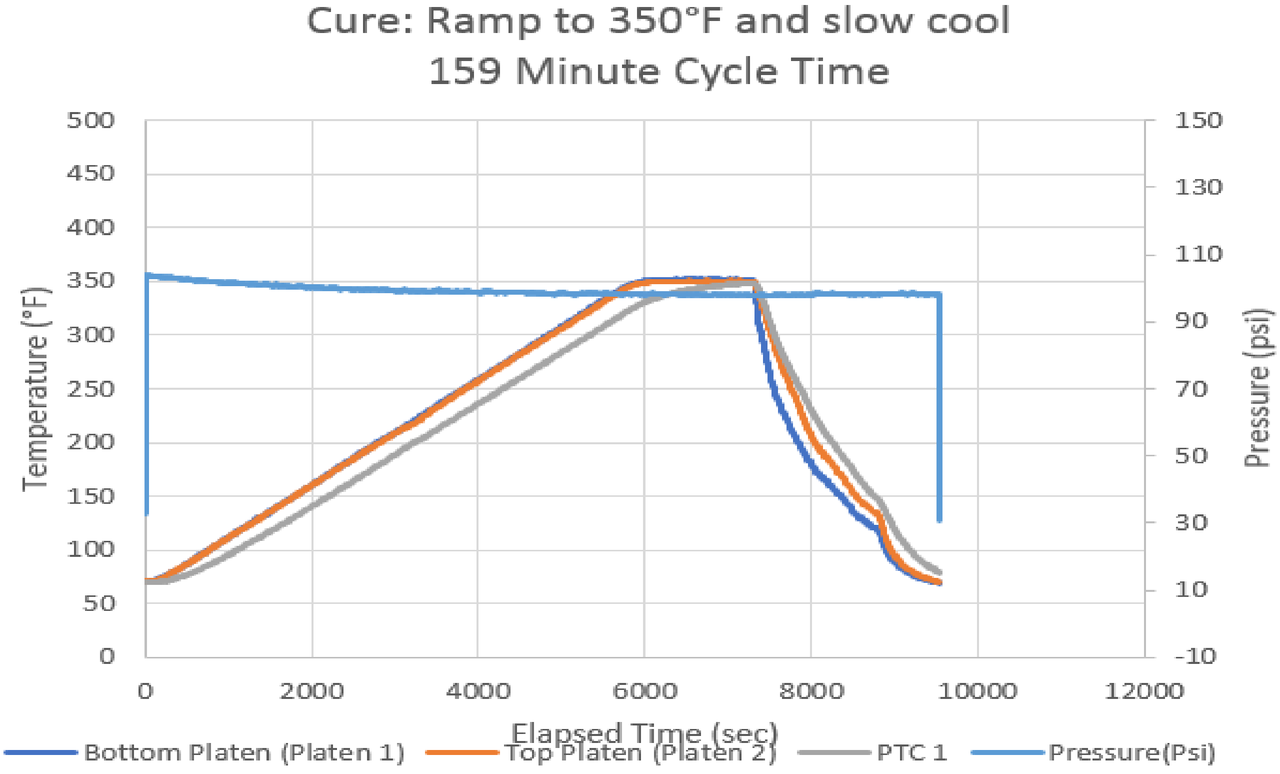


Figure 12. Cure schedule for [0]$_8$ prepreg surrogates molded at UDRI.



Once consolidated at 3 minutes with 100 psi of pressure, the panels were machined with a Dyna-Cut diamond wet saw into specimens to check for fiber volume, void content, resin content, microscopy, glass transition temperature, and a battery of mechanical testing coupons.

Unlike Michigan State, which used a wet winding process to prepare their Short Beam Shear samples, UDRI used a dry-winding process. The spools of sized fiber from Zoltek were dry wound on a spinning plate. In parallel, films of Arotran 901 and Arotran 902 were cast at 170F on a hot melt caster. Samples of these films were sent to Ashland's labs in Dublin for characterization by Differential Scanning Calorimetry (DSC).

Pieces of spun fiber were then cut and stacked with films of matrix resin to produce the surrogate structure shown in the cartoon with the alternating red and blue layers shown on the right-hand side of Figure 10.

To get from the surrogate structure to a structure more similar to an actual prepreg with a fully wet-out preform, the surrogate went through a de-bulking step. This treatment occurred under vacuum at intermediate temperatures (170°F), enabling resin to flow into the fiber layers and produce a structure more similar to the cartoon shown on the left-hand side of Figure 10.

The vast majority of the surrogates made at UDRI consisted of 16 layers with a [0/90]$_{4s}$ architecture. Unidirectional samples were produced with a [0]$_8$ architecture.

Compression molding was conducted in a Wabash press modified to enable rapid heat-up. The typical molding conditions for the [0/90]4s surrogates were 3 minutes at 350F for samples made with Arotran 901 and 3 minutes at 325F for samples made with Arotran 902, all with a uniform pressure of 100 psi. The unidirectional $[0]_8$ surrogates required a longer curing cycle to obtain flat samples. They were cured with a slow ramp (3°F/min) to 350^{0}F, a 30-minute hold, and then a slow cool (6°F/min) to reduce thermal residual stresses. Total cycle time was 2.6 hours.

1.3.3.2 Results & Discussion:

1.3.3.2.1 Production of Resin Films and Prepreg Surrogates: Films of Arotran 901 and Arotran 902 were produced at 170F. They were stored at room temperature until it was time to produce prepreg surrogates. The thickness of the films was calculated and controlled to enable the production of prepreg surrogates with 60 weight % fiber and 40 weight % resin.

Generally, it was found that the Arotran 901 resin processed easier than Arotran 902. 901 was easier to film and less prone to premature gelation.

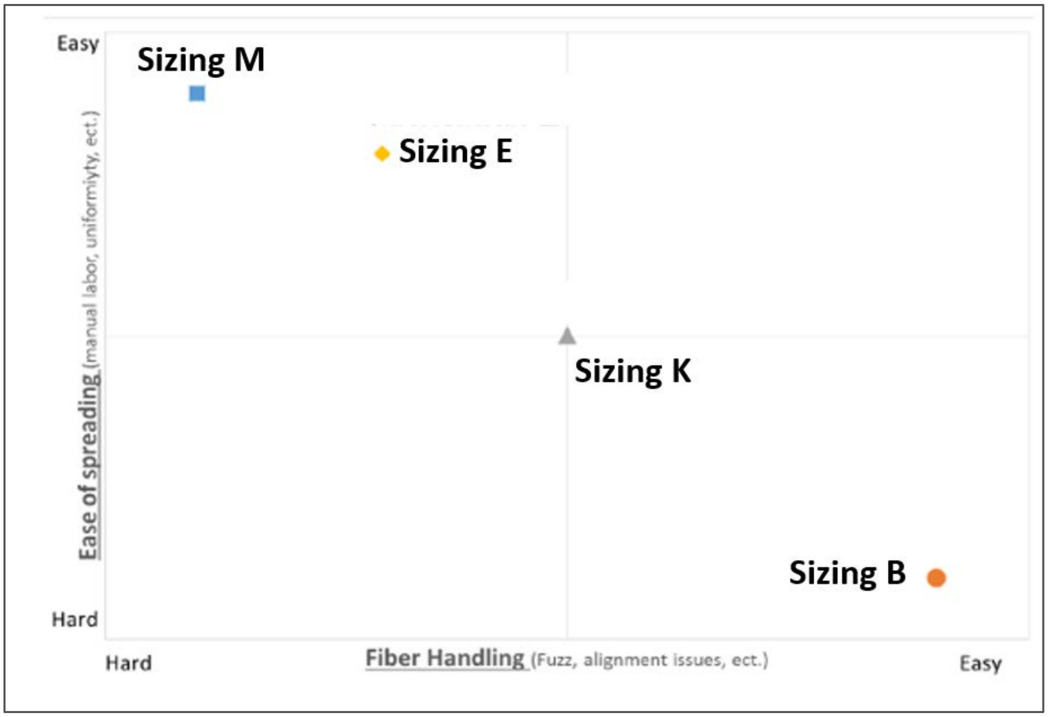
For the dry-wound fibers, UDRI targeted 190-210 gsm. UDRI (and Michigan State) both reported that the W grade fibers from Zoltek were much easier to work with than the T grade fibers. The W grade fibers have a ribbon-like structure, making them much easier to spread than the T grade “ropes.”

Surrogates were made at UDRI with four different sizings – B, E, K and M. The sizing had a very noticeable effect on the handleability and processability of the fibers during the dry-winding step. Some fibers were easier to spread, some had more fuzz, and some were more rigid or “boardier” than others. These observations, which were very important but also somewhat subjective, are captured in Figure 13 and are summarized here in easiest-to-handle to most-difficult-to-handle order.

o handleability of sized fibers: K > E > M > B

Sizing K, from Zoltek, provided the best combination of handleability and processability. It was followed by sizing E, from Michelman. UDRI reported that sizings B and M were considerably more challenging to work with. Sizing B produced fibers that were very rigid, and sizing M was very difficult to spread. The difficulties encountered with sizing M clearly manifested themselves in the mechanical properties of the molded surrogates, as will be discussed later in section 1.3.4.2.2.

Figure 13. Ranking fiber sizings based on processability and handling

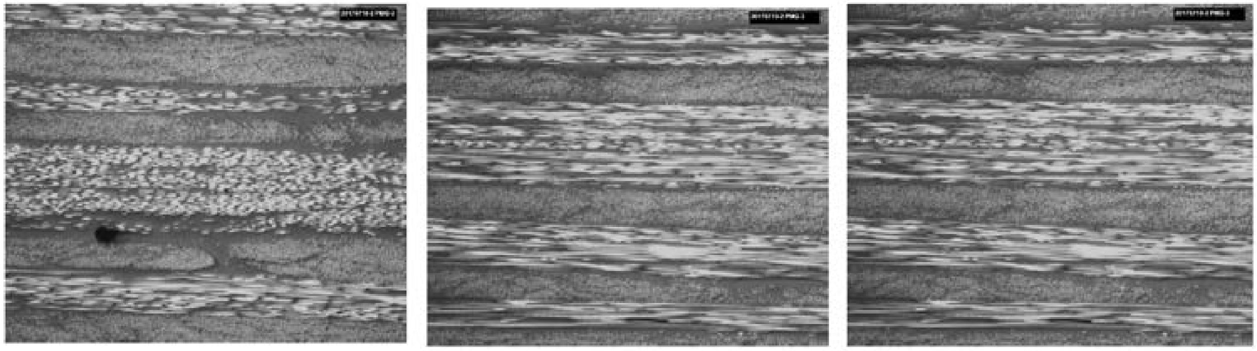


1.3.3.2.2 Compression Molding: The surrogates were molded at UDRI into 12” x 12” laminate panels. Molded samples with two different architectures were produced -- $[0/90]_{4s}$ and unidirectional.

The [0/90] laminates were cured with a 3-minute hold at 350^o for Arotran 901 and 325^o for Arotran 902. These conditions produced fully-dense laminates with low void content. A typical cross-sectional microstructure of a molded surrogate is shown in Figure 14.

In IACMI’s cost modeling of compression-molded prepreg parts (to be discussed in more detail in section 1.4., the default calculation uses a molding time of <u>10 minutes</u> for epoxy resins. The use of vinyl ester resins with a cure time of 3-minutes would enable a 7-minute (70%) reduction in molding time.

Figure 14. Cross-section of a prepreg surrogate molded at UDRI



It should be noted that longer cycle times were required to produce molded, unidirectional samples that were flat enough for mechanical testing. Further work with actual prepregs and different architectures would be part of a Stage 2 project.

1.3.4 Thermal & Mechanical Analysis: The vast majority of the thermal and mechanical analysis was performed in Ashland's labs in Dublin, OH. The SBS testing at MSU has already been described, and some additional mechanical testing was also performed at UDRI and at an external laboratory (Westmoreland in Youngstown, OH).

1.3.4.1 Characterization of Resin Films and Prepreg Surrogates: As has been previously described in Figure 10, films of Arotran 901 and 902 were cast at UDRI and used to make prepreg surrogates. The stability of the films and the surrogates (prior to compression molding) were examined as a function of time using Differential Scanning Calorimetry (DSC).

Figure 15 shows the DSC results for films of Arotran 901 and 902 stored at room temperature. The results show that the % uncured material in the films stayed essentially at 100% over a 9-month period. This is evidence that these resins are not undergoing crosslinking during storage at room temperature. This is in sharp contrast to epoxy resins, many of which need to be stored in a freezer prior to use.

Figure 15. Room temperature stability of neat resin films made with Arotran 901 and 902 at UDRI

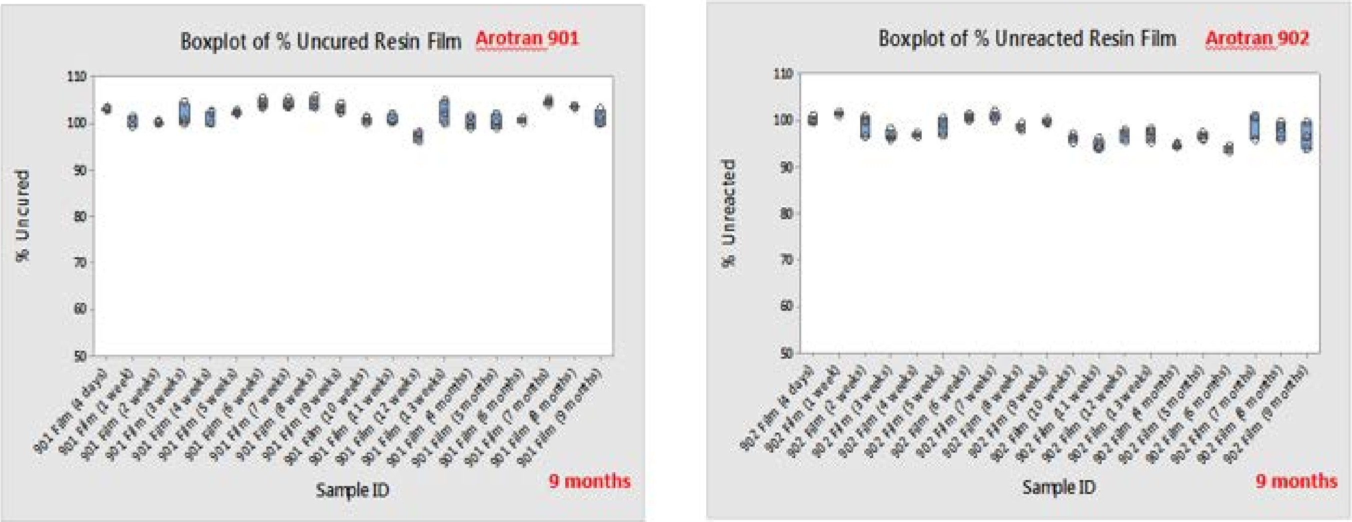
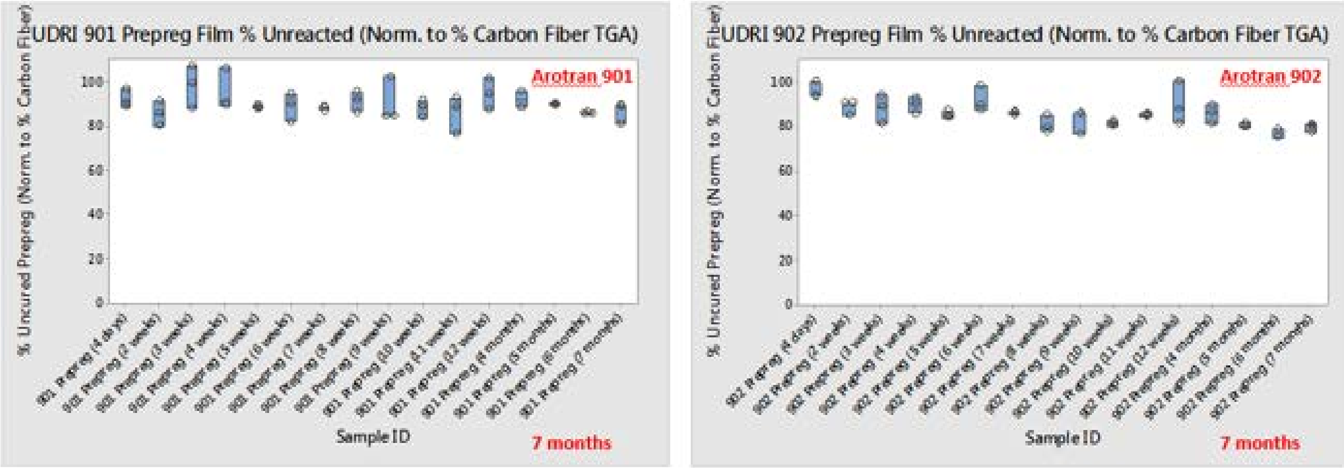


Figure 16 shows the DSC results for prepreg surrogates made with Arotran 901 and 902 at UDRI as a function of time. These surrogates were stored at room temperature and were not used in molding experiments. Again, the results show that the % uncured material in the films stayed essentially at 100% over a 9-month period. This is evidence that the resins in the laminated surrogates are not undergoing crosslinking during storage at room temperature. Again, this is in sharp contrast to epoxy resins, many of which need to be stored in a freezer prior to use.

Figure 16. Room temperature stability of prepreg surrogates made with Arotran 901 and 902 at UDRI

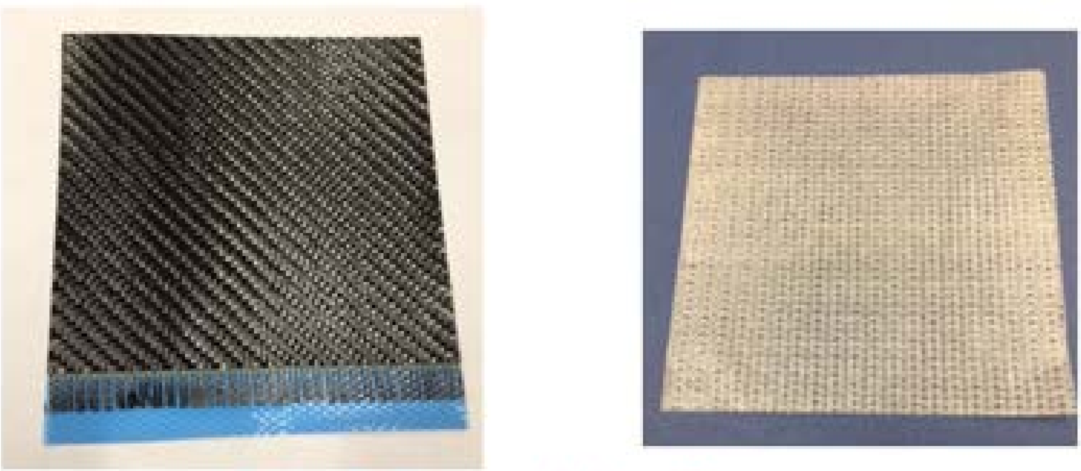


These DSC results show that Arotran 901 and 902 have exceptional stability at room temperature. This is distinctly different from most epoxy prepreg resins. For example, the area in Boeing's Dreamliner 787 production facility where epoxy prepregs are stored and then used to fabricate the aft fuselage has the tag line "From Freezer to Flight." The vinyl ester resins used in this project do not need to be refrigerated.

The DSC results described above are further supported by evidence from the field. In February 2016, Arotran 901 was used to produce prepregs at Renegade Materials in Miamisburg, OH. The prepregs were produced via the hot melt route with two different carbon fibers and with a glass fiber. No attempt was made in this work to optimize the sizing on the fibers. The purpose of the work was to demonstrate that Arotran had the processability necessary for prepreg production.

The production of prepregs at Renegade with Arotran 901 went very smoothly with all three fibers/fabrics. Pictures of a carbon fiber and a glass fiber prepreg they produced are shown in Figure 17. Renegade reported that the resin processed well and produced prepregs with acceptable tack. At the end of this IACMI project, the prepregs made at Renegade were 23 months old. After nearly two years of storage at room temperature, the prepregs were still very flexible and could be compression-molded at 350^{o}F.

Figure 17. Prepregs made with Arotran 901 at Renegade Materials in February 2016



Carbon fiber and glass fiber prepregs
prepared at Renegade Materials in Feb ‘16

Collectively, the results at Renegade and the DSC results for the resin films and prepreg surrogates made at UDRI illustrate the exceptional stability that is possible with these vinyl ester resins. This behavior is a key differentiator for vinyl esters compared to epoxy prepreg resins.

1.3.4.2 Characterization of Molded Prepreg Surrogates:

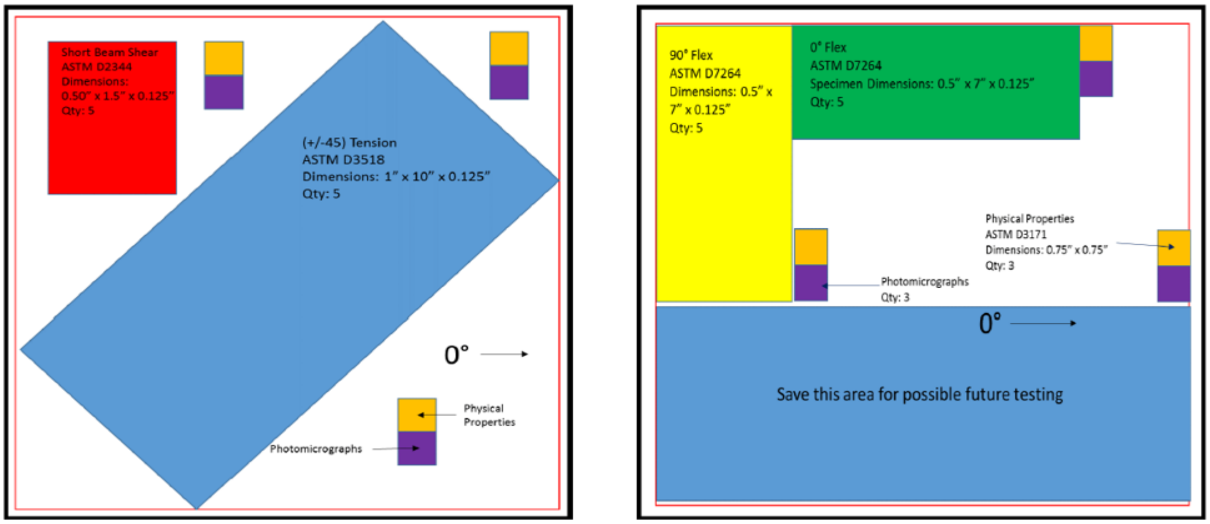
1.3.4.2.1 Mechanical Testing Protocol: Table 1 summarizes the all the thermomechanical testing that was conducted on molded samples. As seen in the table, most of this testing was conducted at Ashland.

Table 1. Summary of mechanical testing

Site	Scope	Tests	ASTM #	Architecture
MSU	Interlaminar Shear Strength (ILSS)	Short Beam Shear	D2344	$[0^{o}]_{11}$
UDRI	"QC" of Molded Prepreg Surrogates	Resin, Void & Fiber Content	D3171	$[0/90]_{4s}$, $[0^{o}]_{8}$, $[0^{o}]_{24}$
		Photomicrographs		
Ashland	In-plane Shear Strength	+/-45 Tension	D3518	$[0/90]_{4s}$
	Interlaminar Shear Strength (ILSS)	Short Beam Shear	D2344	$[0/90]_{4s}$
	Longitudinal (0^{o}) & Transverse (90^{o}) Flexural Strength & Modulus	3-Point Flex	D7264	$[0/90]_{4s}$
	Longitudinal (0^{o}) & Transverse (90^{o}) Tensile Strength & Modulus	0 and 90 Tension	D3039	$[0^{o}]_{8}$
	Fracture toughness	Mode I	D5528	$[0^{o}]_{24}$
		Mode II	D7905	$[0^{o}]_{24}$
	Glass Transition Temperature	DMA, tan δ	D4065	$[0/90]_{4s}$

Figure 18 shows how the 12" plaques molded at UDRI were carved up to provide samples for thermomechanical testing. In general, 5 replicates were conducted for each test.

Figure 18. Samples for thermomechanical testing of molded prepreg surrogates



Both resin-dominated and fiber-dominated properties were measured. The resin-dominated properties are more indicative of the quality and strength of the resin-fiber interface and will be discussed first.

1.3.4.2.2 Resin-dominated Properties: The ILSS results for the unidirectional, wet-wound, Short Beam Shear samples prepared at Michigan State have already been discussed. Short Beam Shear testing (ASTM D2344) was also conducted on the 0/90 laminates molded at UDRI. The results are summarized in Figure 19.

Figure 19. Interlaminar Shear Strength (ILSS) of [0/90] prepreg surrogates molded at UDRI

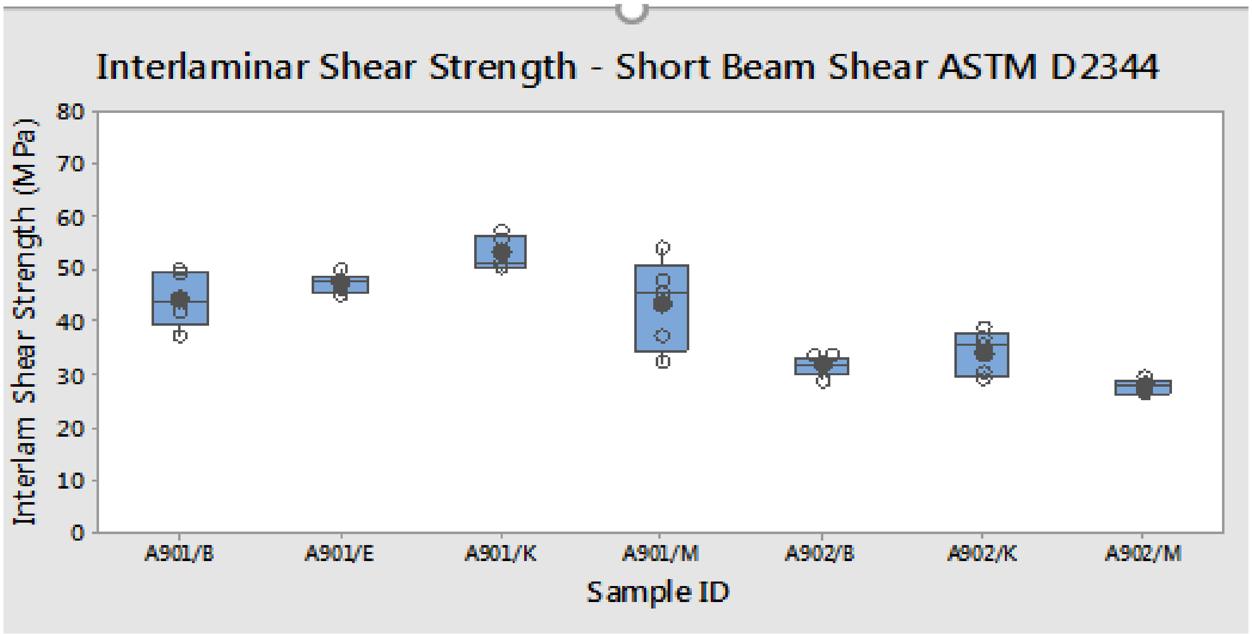


Figure 20 shows that as a group, the samples prepared with Arotran 901 had a higher ILSS than samples made with Arotran 902. This is consistent with the results from MSU. The highest ILSS measured for a prepreg surrogate molded at UDRI was 53 MPa obtained with the 901/K system.

Another resin-dominated property that is a good indicator of the strength and quality of the resin-fiber interface is +/-45 in-plane shear tension testing. Those results are shown in Figure 20. Again, the 901/K system gave the highest result, and as a group, the values for 901-containing systems were higher than for 902.

Figure 20. +/- 45 tensile stress of [0/90] prepreg surrogates molded at UDRI

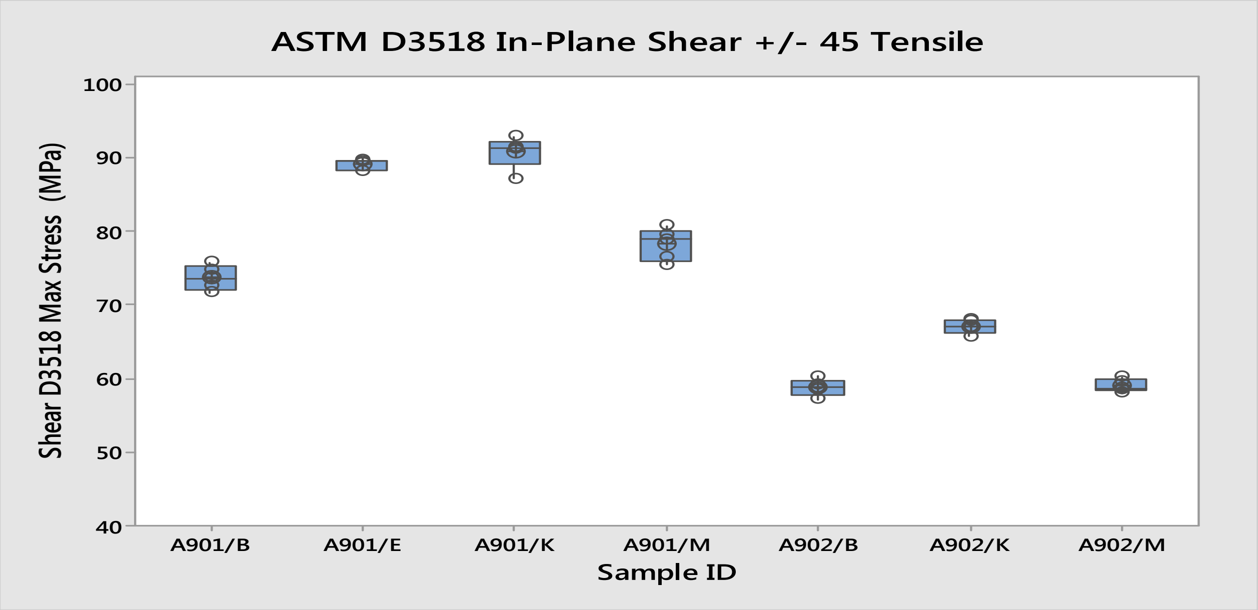
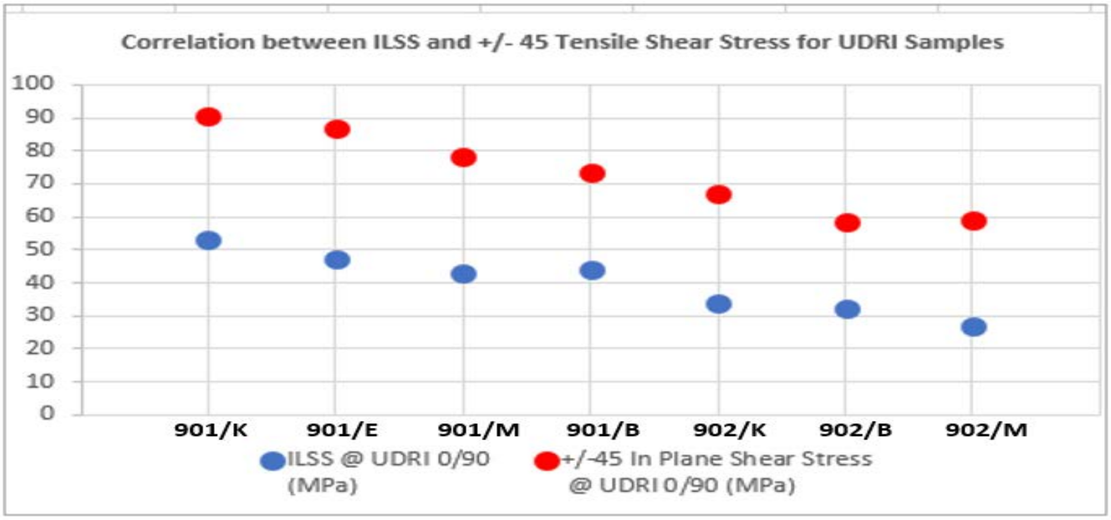


Figure 21 shows that there was very good correlation between the ILSS results and the -/-45 tensliles measured for the prepreg surrogates molded at UDRI.

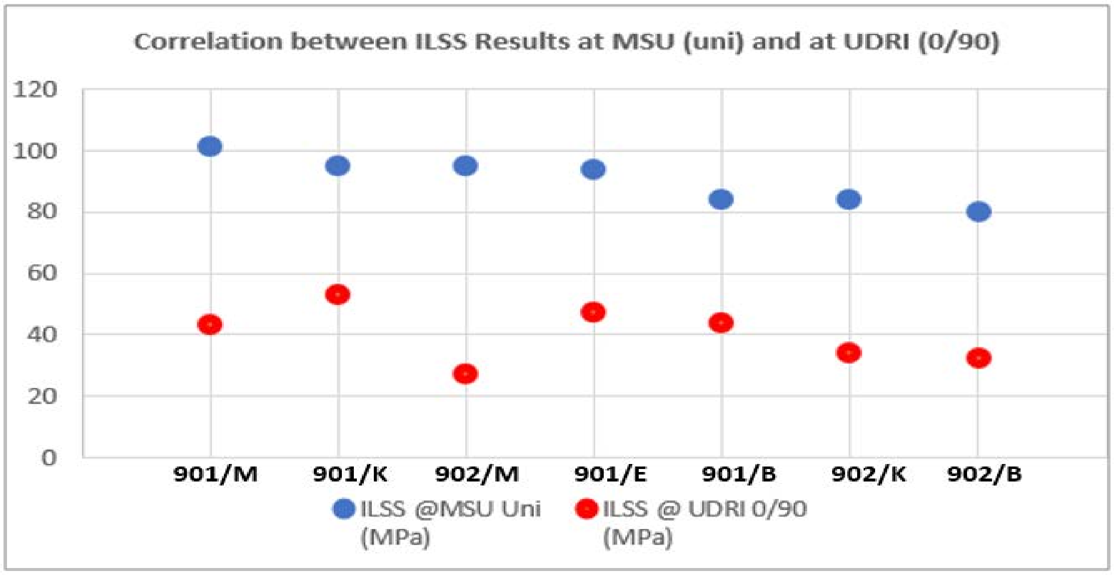
Figure 21. Correlation of ILSS and +/- 45 tensile stress of [0/90] prepreg surrogates molded at UDRI



The ILSS values measured for the UDRI samples were about half of those measured at MSU. This result is consistent with the fact that the MSU samples had a unidirectional architecture and the UDRI samples had a 0/90 architecture.

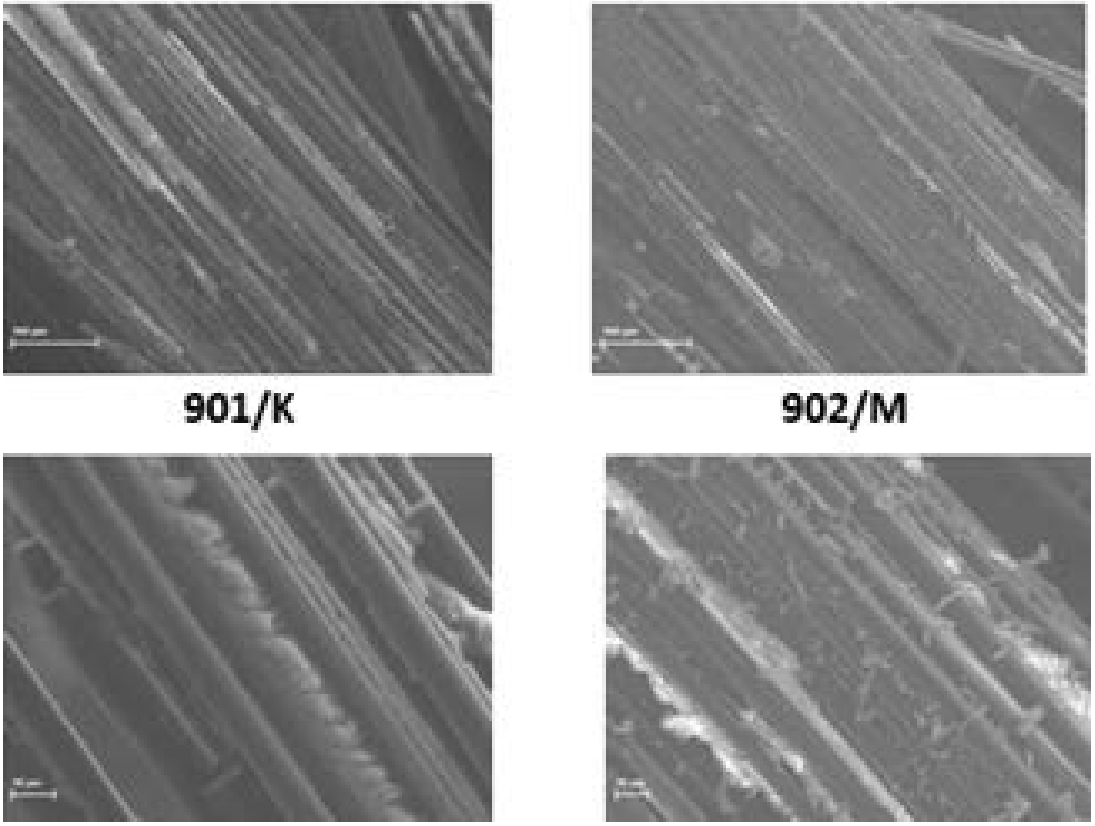
Figure 22 shows the correlation between the ILSS results obtained for samples molded at MSU and at UDRI. The correlation is quite good with two notable exceptions – the 901/M and 902/M systems. It is believed that the previously-discussed challenges associated with processability and handling experienced at UDRI with the M sizing were the reason behind this discrepancy. In comparing the results from MSU and UDRI, it became clear that resin-dominated properties were not only a function of the resin and the sizing but also a function of processing.

Figure 22. Correlation between ILSS results obtained with molded, unidirectional laminates at MSU and [0/90] molded prepreg surrogates at UDRI



Another good indication that a good resin-fiber interface had been achieved came from micrographs of the fracture surfaces of the molded samples. An example is shown for the 901/K system in Figure 23, where it is clear that there was very good contact between the matrix resin and the fiber in the region where the sample fractured.

Figure 23. Micrographs of fracture surfaces of molded prepreg surrogates



901/K

902/M

1.3.4.2.3 Fiber-dominated Properties: Figures 24 to 26 summarize the fiber-dominated flexural properties obtained with the seven down-selected systems. All of these results were obtained with the $[0/90]_{4s}$ architecture employed with the prepreg surrogates molded at UDRI.

Two general observations can be made: 1) these properties did not vary much as the resin and sizing were changed. This would be consistent with the fiber-dominated nature of these properties and 2) bigger differences were observed between the 0^o and 90^o measurements for the same resin/sizing system. The reason for the latter observation is the asymmetry in the arrangement of the plies in the surrogates. The outer ply being in the 0 or 90 degree direction to the loading nose in flex could account for some of the variability in the modulus between the 0° and 90° flex samples on a $[0/90]_{4s}$ stack-up.

Figure 24. 0^0 and 90^o flexural strength of prepreg surrogates molded at UDRI

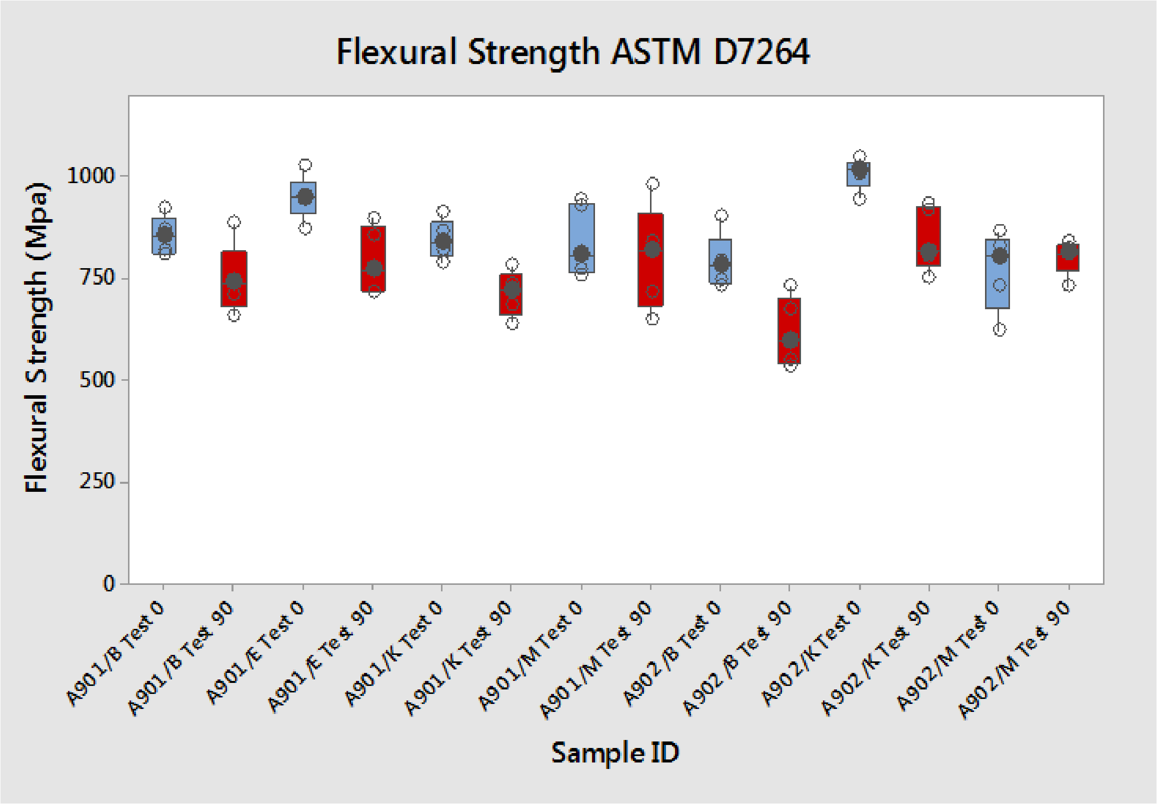


Figure 25. 0^0 and 90^o flexural modulus of prepreg surrogates molded at UDRI

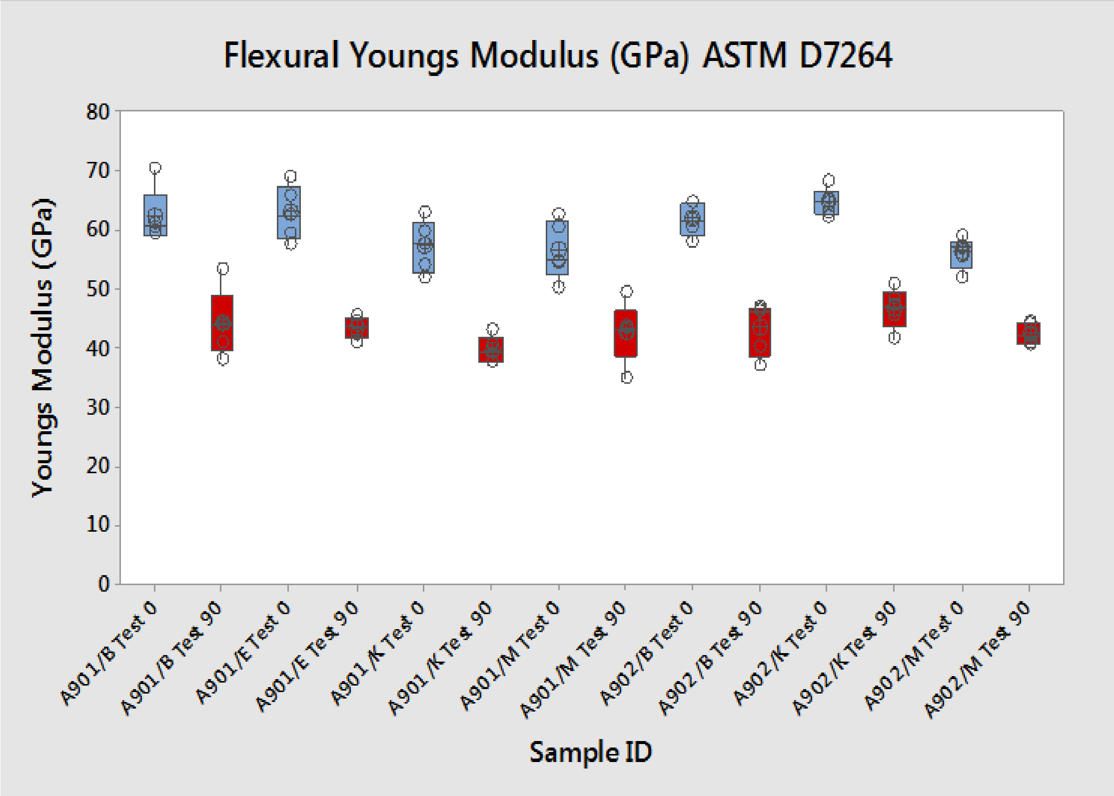
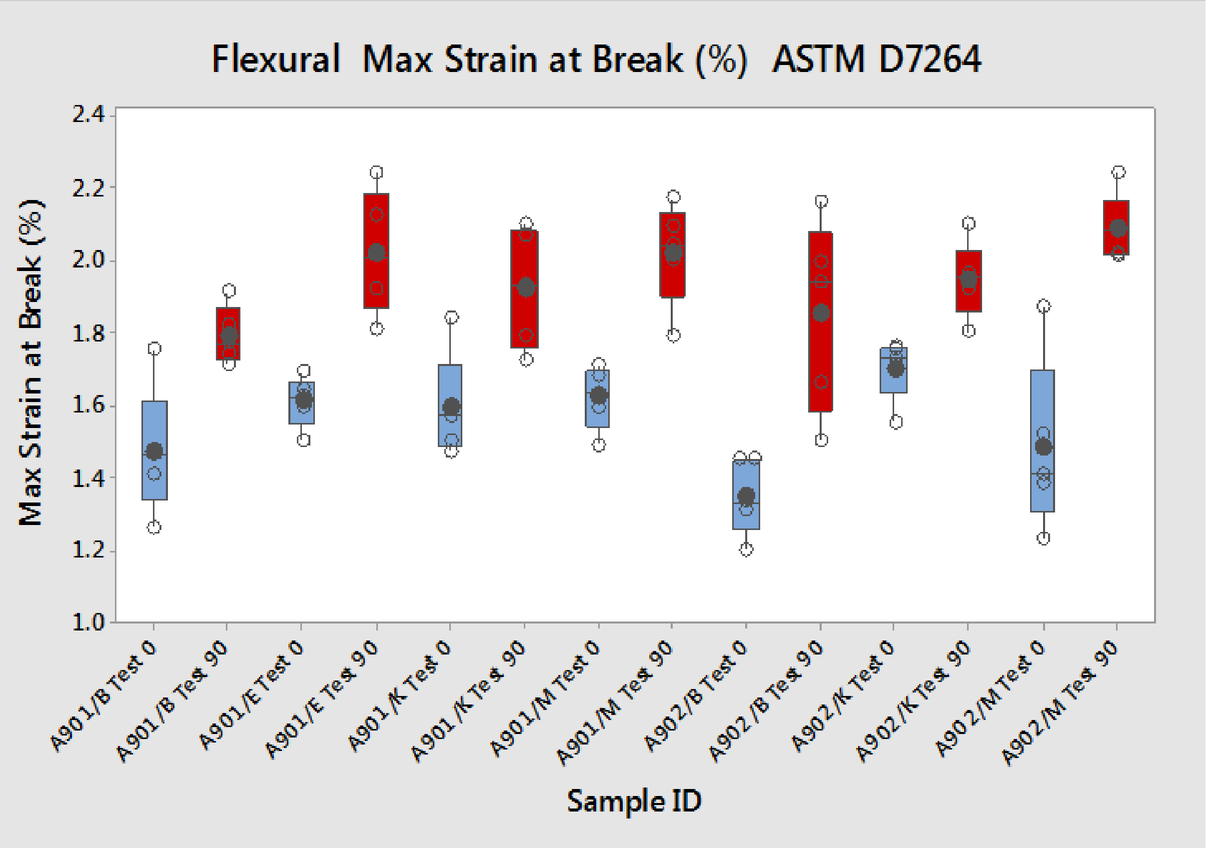


Figure 26. 0^0 and 90^o flexural maximum strain at break of prepreg surrogates molded at UDRI



1.3.4.2.4 Glass Transition Temperature Results: It was noted in the Section 1.2.1 that Arotran 902 is a higher Tg resin because of its novolac character. This was confirmed by Dynamic Mechanical Analysis (DMA) results that had been obtained by Ashland before the project began. Those results are shown in Figure 27a and Figure 28a, where the peak of the tan δ curve for 901 occurs at 147°C and at 189°C for 902, respectively.

However, when prepreg surrogates were molded at UDRI, the observed Tg values were considerably lower than expected. Figure 27b and Figure 28b show the DMA traces for 901/K and 902/M. The peak of the tan δ curve was only 119°C for 901/K and 182°C for 902/M, respectively.

Figure 27. DMA of a) neat 901 resin and b) 901/J prepreg surrogate molded at UDRI

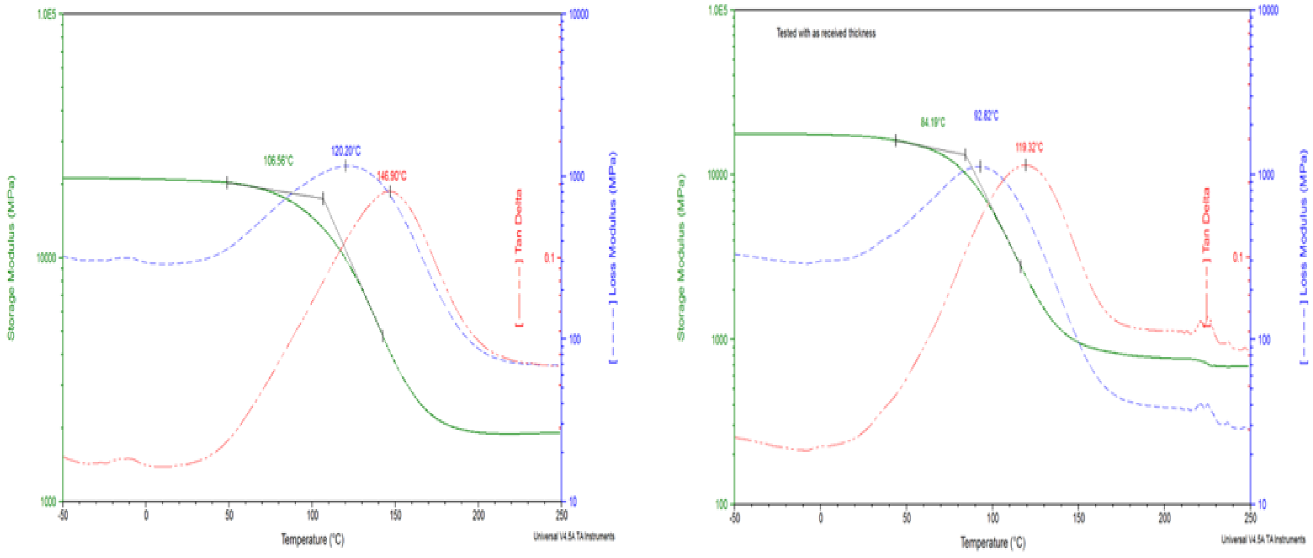
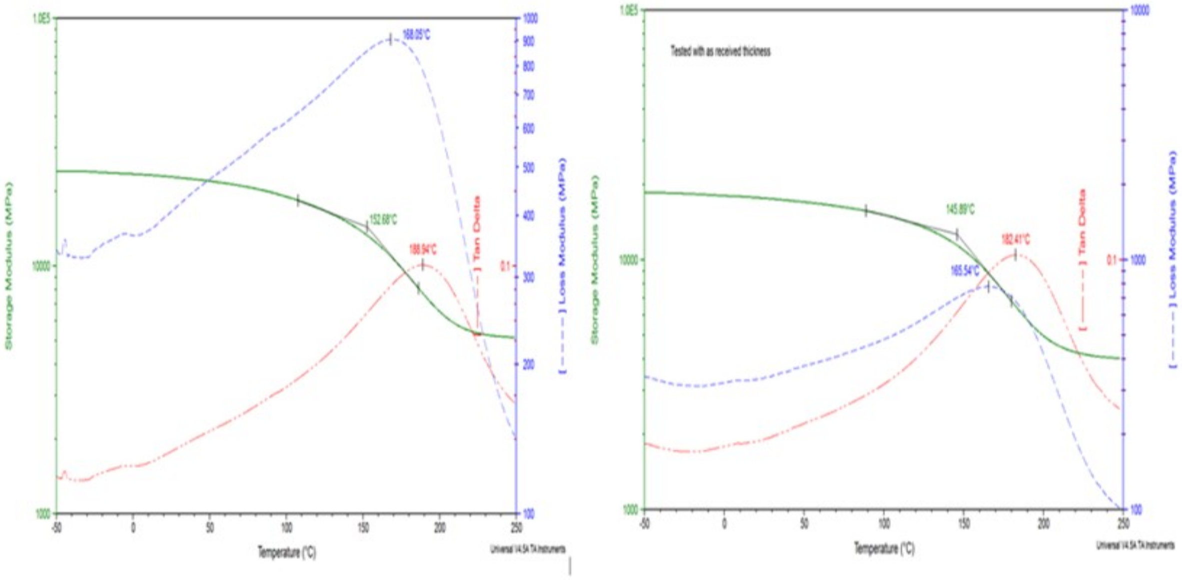

a. b.

Figure 28. DMA of a) neat 902 resin and b) 902/J prepreg surrogate molded at UDRI


a. b.

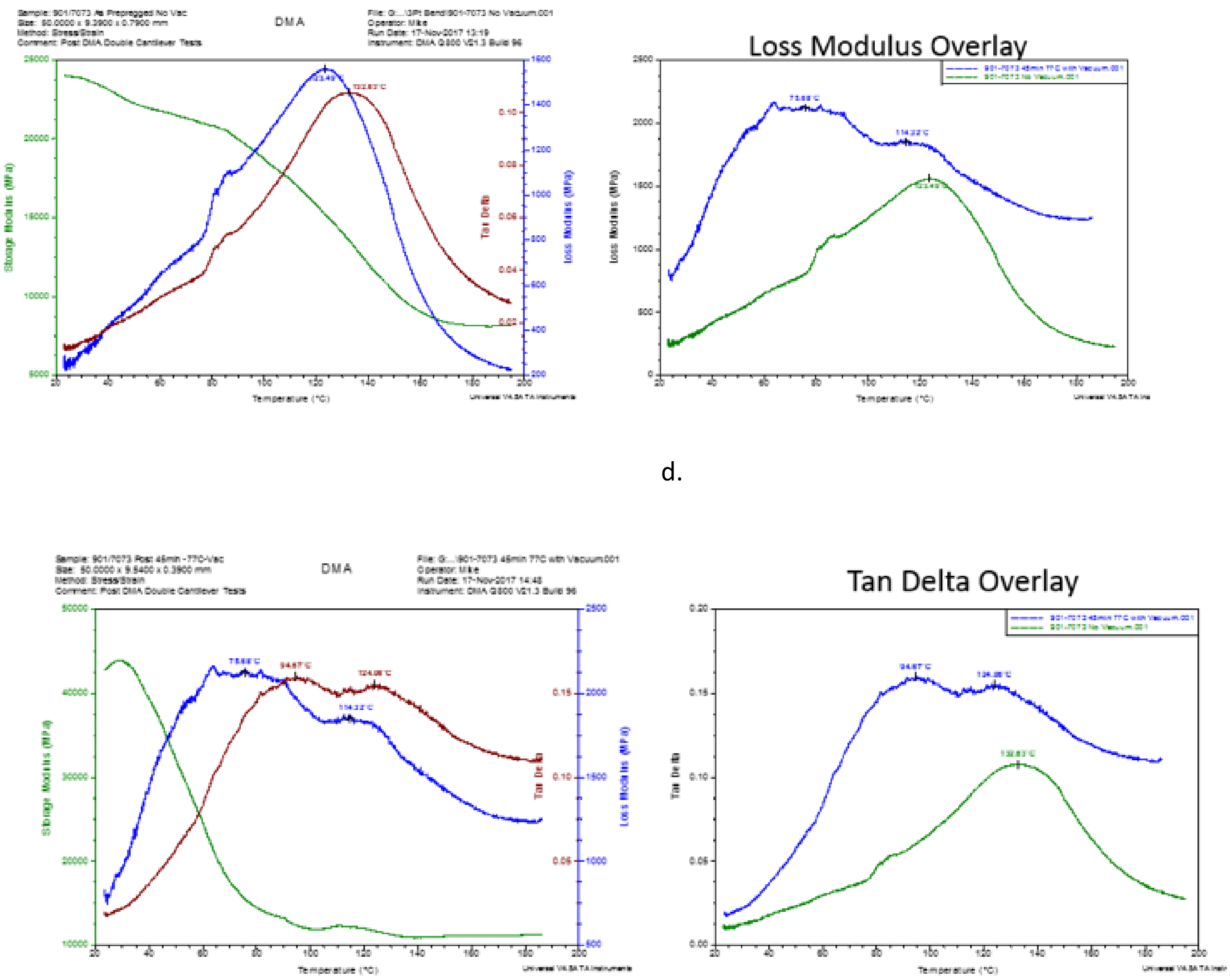
Follow-up experiments conducted at Michigan State shed light on why this might be occuring. Those experiments looked at the effect of the de-bulking step on Tg. Figure 29a and 29c compares the DMA traces of 901/J samples that were compression-molded with and without an intermediate heat/vacuum treatment step that simulated the debulking step at UDRI. These results, and especially the overlay traces shown in Figures 29b and 29d show that the inclusion of the debulking step resulted in a downward shift of the tan δ peak and the appearance of a new peak at lower temperature with the 901 resin. A similar, but smaller, depression was also observed with the 902 resin.

With prepreg surrogates, a de-bulking step was necessary to ensure good contact between the laminate layers. It is hypothesized that the extended time at elevated temperatures did cause some advancement/crosslinking of the resin before the molding step. This manifested itelf in a different degree of crosslinking in the final molded part; this phenomenon was reflected in the changes in the DMA traces.

Figure 29. DMA traces for laminates molded at MSU with and without a debulking step

a. b.

c. d.



It is expected that a similar phenomenon would not occur, or would occur to a much lesser extent, with actual prepregs rather than prepreg surrogates. This could be investigated in a Stage 2 project with actual prepregs, where the effect could be studied in greater detail and minimized to such an extent that T_gs near the values obtained at Ashland and at MSU could be realized.

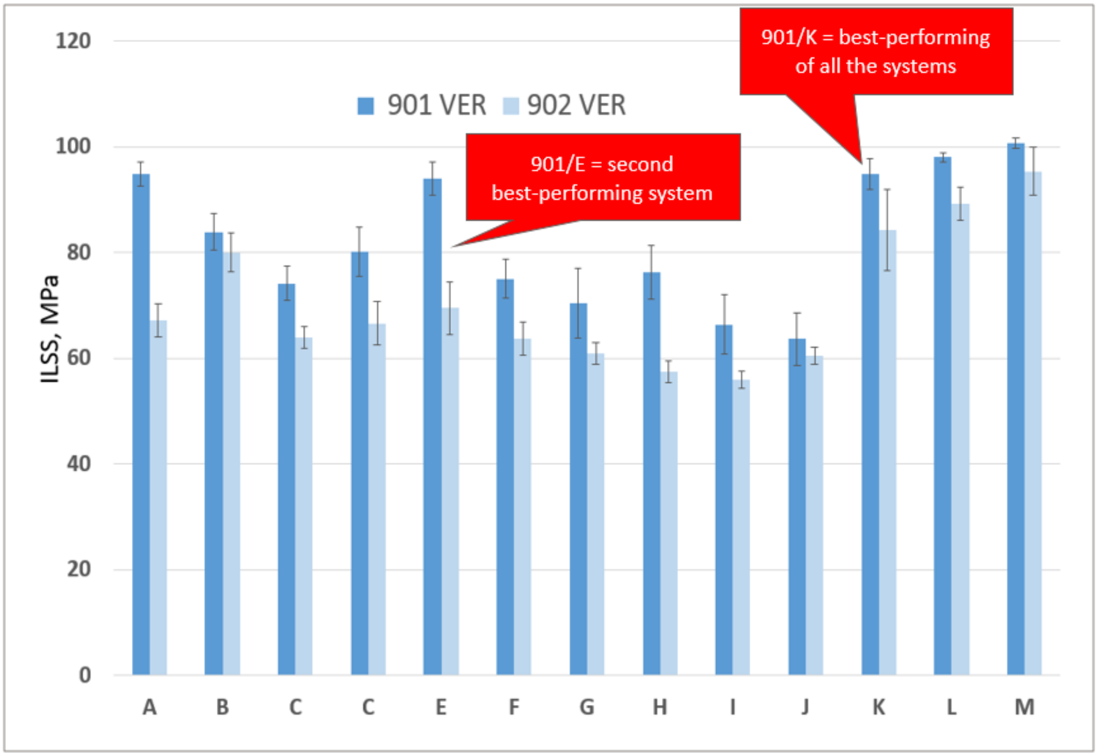
1.35 Identification of the Best-performing Resin/Sizing/Fiber System: Table 2 summarizes the mechanical property results for the seven down-selected systems tested at UDRI.

Table 2. Mechanical properties for the seven down-selected systems from MSU

Property	Architecture	901/B	901/E	901/K	901/M	902/B	902/K	902/M
ILSS (MPa), MSU	$[0]_{11}$	84	94	95	101	80	84	95
ILSS (MPa), UDRI	$[0/90]_{4s}$	44	47	53	43	32	34	27
0^{o} Flex Strength (MPa)	$[0/90]_{4s}$	853	946	843	840	788	1005	768
0^{o} Flex Modulus (GPa)	$[0/90]_{4s}$	62	63	57	57	62	65	56
90^{o} Flex Strength (MPa)	$[0/90]_{4s}$	745	790	711	798	616	843	802
90^{o} Flex Modulus (GPa)	$[0/90]_{4s}$	44	43	40	43	43	47	42
In-Plane Shear Stress (MPa)	$[0/90]_{4s}$	74	89	90	78	59	67	59
0^{o} Tensile Strength (MPa)	$[0]_{8}$			1501				
0^{o} Tensile Modulus (MPa)	$[0]_{8}$			122				
G_{1c} (N-m/m^{2})	$[0]_{24}$			455				
G_{2c} (N-m/m^{2})	$[0]_{24}$			567				

Taking these data and the observations about handleability/processability discussed in Section 1.3.3.2 into consideration, the best-performing of all 26 resin-sizing-fiber combinations was Arotran 901 with PX35 W grade fibers sized with sizing K, *aka* 901/K. The second best-performing system was Arotran 901 with PX35 W grade fibers sized with sizing E, *aka* 901/E. These systems are highlighted in Figure 30.

Figure 30. ILSS results highlighting the 901/K and 901/E systems



Sizing K was a fully-formulated, commercially-available sizing from Zoltek. Sizing E was a developmental sizing from Michelman. Additional information about these sizings is available from Zoltek and Michelman, respectively.

1.3.5.1 Properties of the Best-performing System: Table 3 summarizes the resin-dominated and fiber-dominated properties for 901/K, the best-performing of all 26 systems. The table incudes the data for the $[0/90]_{4s}$ laminates. All the fiber-dominated properties have been normalized to a fiber volume of 60%, $V_f = 60$. To gather more information about the mechanical properties of this best-performing system, additional testing was also performed with unidirectional samples. $[0]_8$ unidirectional laminates were used to obtain the tensile strength and modulus, and $[0]_{24}$ unidirectional laminates were used to obtain the fracture toughness values.

Table 3. Resin-dominated and fiber-dominated mechanical properties of the 901/K system

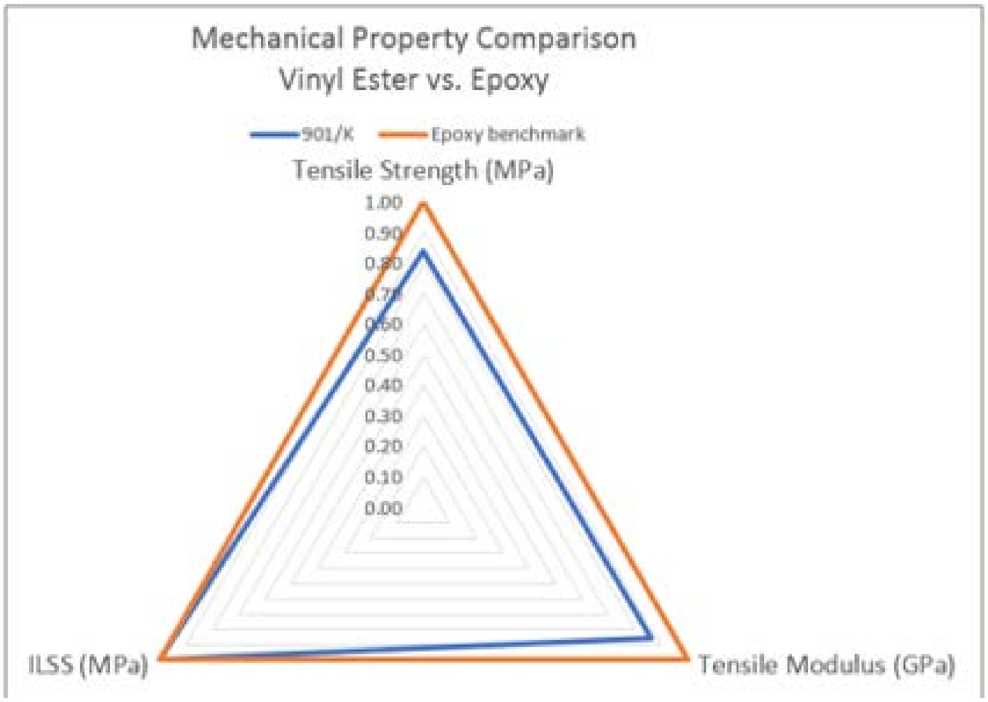
	Property	901/K	Architecture
Resin-dominated	ILSS (MPa)	95	$[0]_{11}$
	ILSS (MPa)	53	$[0/90]_{4S}$
	In-Plane Shear Strength (MPa)	90	$[0/90]_{4S}$
	Fracture toughness G_{Ic} (N-m/m^2)	455	$[0]_{24}$
	Fracture toughness G_{IIc} (N-m/m^2)	567	$[0]_{24}$
Fiber-dominated	Flexural strength (MPa)	1032	$[0/90]_{4S}$
	Flexural modulus (GPa)	70	$[0/90]_{4S}$
	Tensile strength (MPa)	1501	$[0]_{16}$
	Tensile modulus (GPa)	122	$[0]_{16}$

1.3.5.2 Comparison to Epoxy Benchmarks: In Section 1.3.2.2, it was noted that Michigan State performed SBS testing with an epoxy benchmark using the same fibers, the same unidirectional architecture unidirectional and the same process employed with the vinyl ester matrix resins. The ILSS value measured for the epoxy benchmark was 76 MPa, compared to 95 MPa for 901/K.

Other comparisons to epoxy benchmarks were made using literature values. In these cases, care was taken to compare systems prepared with the same carbon fibers (PX35) and the same architecture. In cases where the fiber volume was different, the mechanical properties were normalized to $V_f = 60$, thus enabling "apples-to-apples" comparisons with the same fiber, the same architecture, and the same fiber volume.

Barrday has used PX35 fibers with their EPH302 epoxy resin system and reported unidirectional tensile strength and tensile modulus values at $V_f = 60$ of 1778 MPa and 142 GPa, respectively. They also report an ILSS of 95MPa for this system. The spider diagram in Figure 31 compares the properties of the 901/K system with the values reported by Barrday.

Figure 31. Comparison of the ILSS, tensile strength and tensile modulus of 901/K with an epoxy benchmark from Barrday

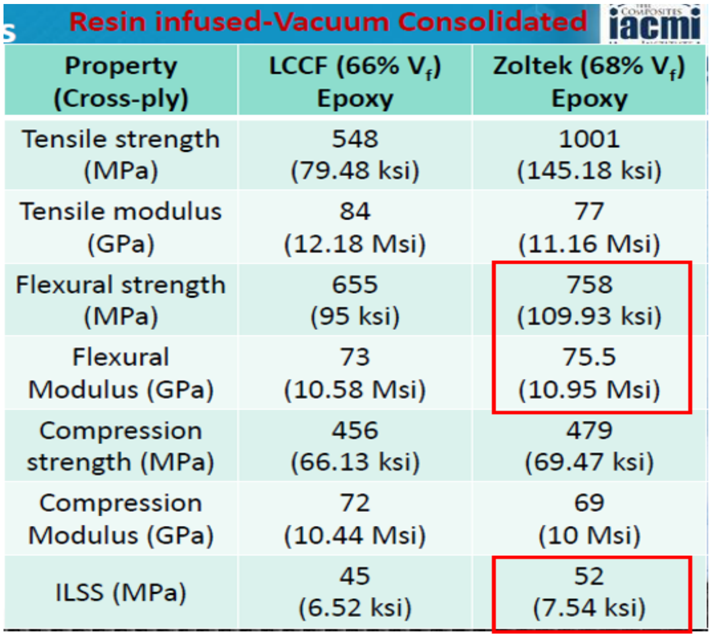


On a percentage basis, the ILSS value for 901/K was 100% of Barrday's epoxy value. The tensile strength and tensile modulus values for 901/K were both about 85% of the Barrday values. Taken as a whole, the mechanical properties in Figure 31 for the 901/K system were about 90% of the values for the epoxy benchmark that employed the same fibers, the same architecture, and the same fiber volume fraction.

It should be noted that the values for the 901/K system were obtained with prepreg surrogates, not actual prepregs. It is fully expected that the mechanical properties of the 901/K system would improve with actual prepregs, bringing the optimized resin/sizing/fiber combination identified in this work even closer to the epoxy benchmark. Nevertheless, for the purpose of the embodied energy calculations discussed in Section 1.4.1 and the cost estimates discussed in Section 1.4.2., it has been assumed that the mechanical properties of the 901/K system are 10% lower than for a comparable epoxy system, meaning that parts made with 901/K might have to be 10% thicker (and 10% heavier) than an epoxy part. This is a conservative assumption.

IACMI has also reported mechanical property values for an epoxy system reinforced with PX35 fibers from Zoltek. The data presented by U Vaidya at the 2017 semi-annual review meeting in Dayton is summarized in Table 4.

Table 4. Mechanical properties reported by IACMI for an epoxy benchmark made with PX35 fibers



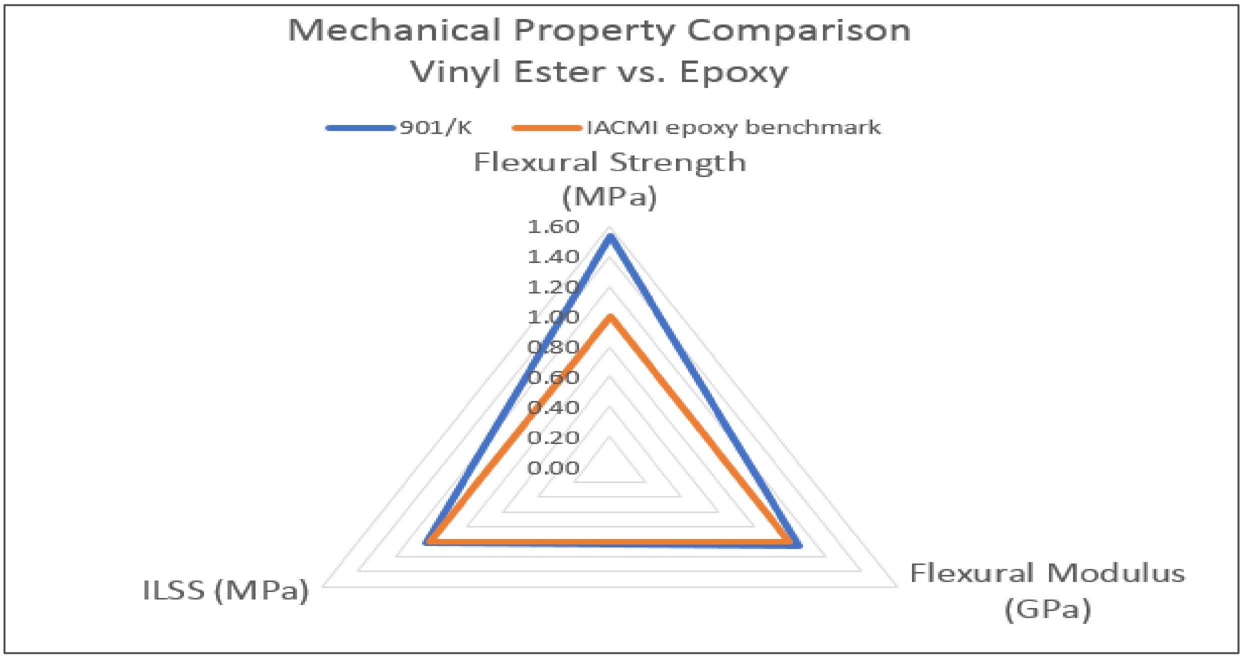
Resin infused-Vacuum Consolidated

Property (Cross-ply)	LCCF (66% V_f) Epoxy	Zoltek (68% V_f) Epoxy
Tensile strength (MPa)	548 (79.48 ksi)	1001 (145.18 ksi)
Tensile modulus (GPa)	84 (12.18 Msi)	77 (11.16 Msi)
Flexural strength (MPa)	655 (95 ksi)	758 (109.93 ksi)
Flexural Modulus (GPa)	73 (10.58 Msi)	75.5 (10.95 Msi)
Compression strength (MPa)	456 (66.13 ksi)	479 (69.47 ksi)
Compression Modulus (GPa)	72 (10.44 Msi)	69 (10 Msi)
ILSS (MPa)	45 (6.52 ksi)	52 (7.54 ksi)

The IACMI values for flexural strength, flexural modulus, and ILSS highlighted in the table were obtained with vacuum-infused samples with a cross-ply architecture. This architecture is similar to, but not identical to the [0/90] laminates prepared at UDRI with 901/K. The IACMI samples with the Zoltek fibers had V_f = 68.

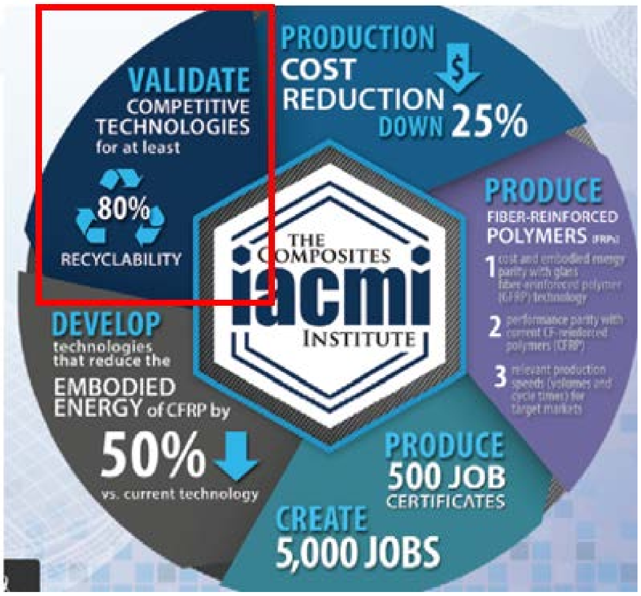
Figure 32 is a spider diagram that compares the flexural and ILSS properties for 901/K [0/90] laminates with the cross-ply data reported by IACMI. In this comparison, the values for 901/K are as good or slightly better (from an ILSS and flexural modulus perspective) and significantly (54%) better (from a flexural strength standpoint).

Figure 32. Comparison of the ILSS, flexural strength and flexural modulus of 901/K with an epoxy benchmark from IACMI



1.3.6 Recycling and Re-use Considerations: One of IACMI's stated goals is to increase the recyclability of composites into useful products by 80% by 2020. This goal is highlighted in Figure 33.

Figure 33. IACMI's recyclability goal



This is a very ambitious goal. However, it has been discovered in this project that the use of vinyl ester prepregs can help in a big way toward meeting this goal.

Vinyl ester prepregs are amenable to both recycling and re-use. The basic reason for this is that during production of the prepreg, no crosslinking occurs. This is in sharp contrast to epoxy prepregs, where crosslinking begins as soon as the epoxy resin and the curing agent (either amine or anhydride) are mixed, and crosslinking continues as the prepreg ages. This is the reason that many epoxy prepregs need to be stored in a freezer; the cold temperatures slow down the crosslinking, but they do not stop it.

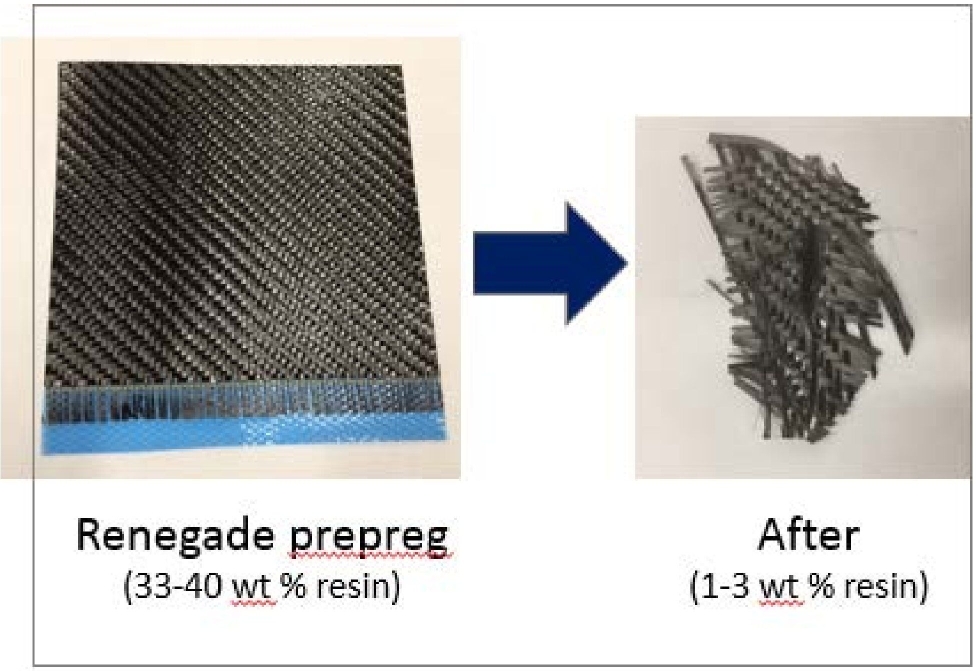
In contrast, the vinyl ester resins employed in this study are hot-melt resins that can be cast at 170^{o}F but do not undergo crosslinking reactions until the molding temperatures (325-350^{o}F) are reached. The large temperature window between casting and molding (curing) and the even bigger window between ambient temperature and molding temperature is the reason that the vinyl ester prepregs are so stable.

This absence of crosslinking, and the resultant stability, of vinyl ester prepregs has important ramifications with respect to recycling and re-use.

1.3.6.1 Recycling of Carbon Fibers: Vartega is an IACMI member focused on the recovery of carbon fiber from scrap prepreg. The scrap prepreg could be in the form of expired rolls that have gone past their recommended shelf life. It could also be out-of-spec prepreg or the unused portions of prepreg (offal) that are left over after the cutting operations. In many cases, this scrap is unusable and ends up in a landfill.

Vartega has developed a multi-step extraction process to recover the carbon fiber from scrap prepreg. Because vinyl ester prepregs are not crosslinked, they are very amenable to Vartega’s process. Figure 34 illustrates the facile recovery of carbon fiber from vinyl ester prepreg. Although the process conditions were not optimized, Vartega showed that they could readily reduce the resin content from about 30 weight % down to about 1%.

Figure 34. Recovery of carbon fiber from vinyl ester prepreg using Vartega's extraction technology



With the right choice of solvent, it may be possible to not only recover the carbon fibers but the resin in a usable form as well. This possibility needs further exploration, possibly as part of a Stage 2 project that would move the proof-or-principle recycling technology demonstrated during Stage 1 to an even higher TRL.

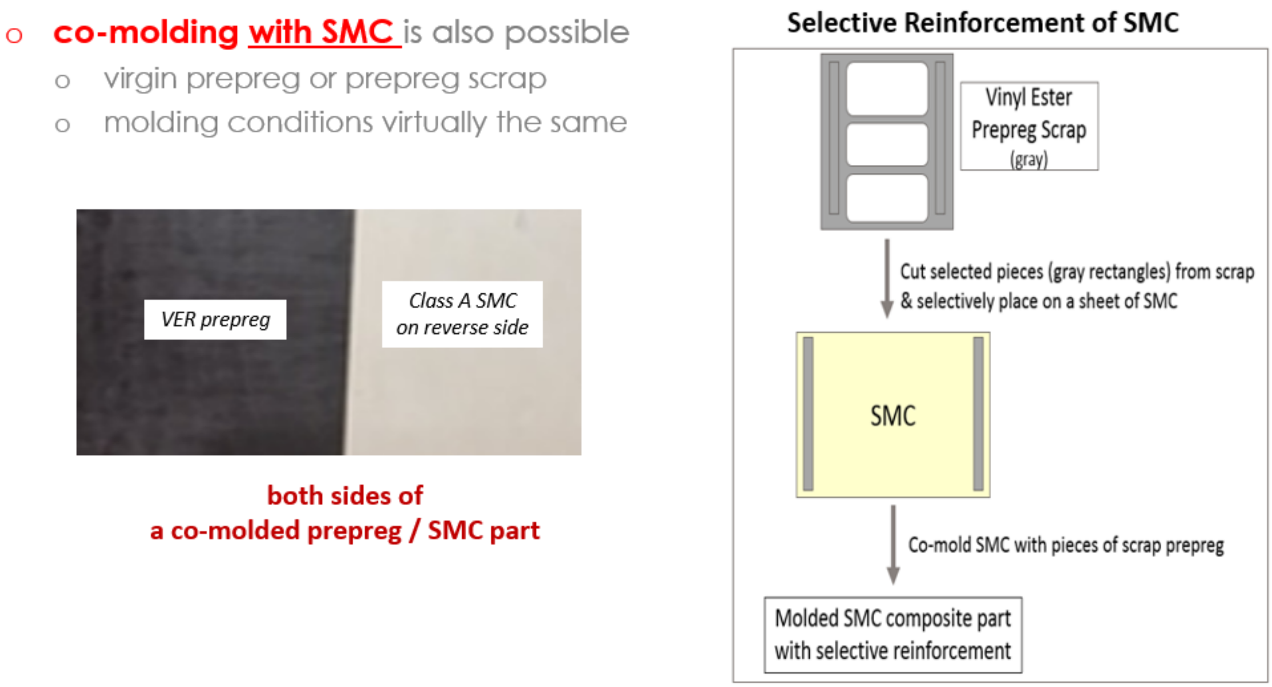
1.3.6.2 Re-use of Prepreg Scrap: It has also been shown that pieces of vinyl ester prepreg scrap (*aka*, offal) can be re-used in several different ways.

Perhaps most interestingly, it has been shown that vinyl ester prepregs can be co-molded with Sheet Molding Compound (SMC). This opens up the opportunity of selectively reinforcing SMC, which contains short, chopped fibers, with pieces of prepreg that contain continuous fibers. This process is illustrated in the diagram in Figure 35.

The process shown in Figure 35 has been demonstrated with virgin vinyl ester prepreg. The part shown in Figure 35 is a co-molded plaque with SMC on one side and vinyl ester prepreg on the other. Since virgin VER prepreg does not crosslink, it should also be possible to take pieces of scrap and co-mold them with SMC. This would be another recycling/re-use element of a Stage 2 project.

Pieces of prepreg scrap prepared with a vinyl ester resin are particularly well-suited to the process described in Figure 35. The reason is that most SMC is prepared with either an unsaturated polyester resin or a vinyl ester resin that cures with the same type of catalyst (peroxides) and by the same mechanism (free radical curing). Thus, the co-molding could occur under typical molding conditions for SMC.

Figure 35. Co-molding of vinyl ester prepreg with SMC

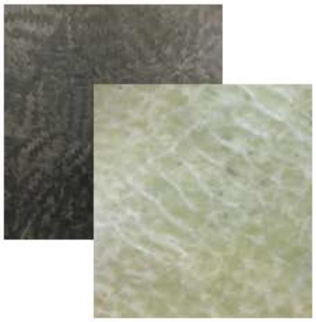


- co-molding with SMC is also possible
  - virgin prepreg or prepreg scrap
  - molding conditions virtually the same

It has also been shown that pieces of vinyl ester prepreg scrap can be molded by themselves to produce a molded part. This is shown in Figure 36 and has been demonstrated with pieces of vinyl ester prepreg made at Renegade that are 23 months old.

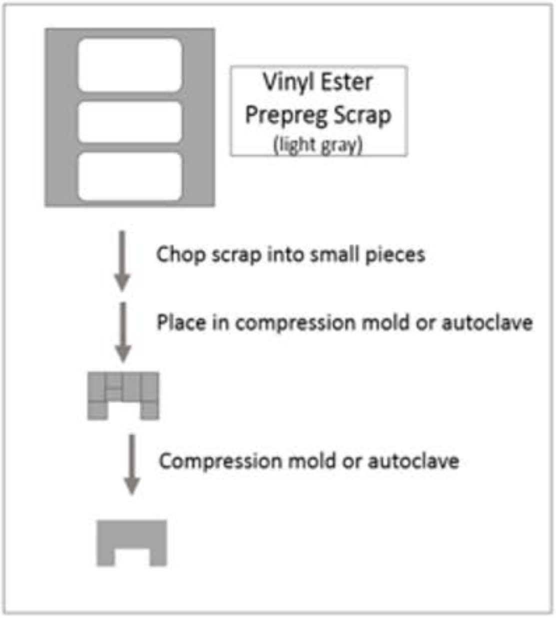
Figure 36. Molding of prepreg scrap from Renegade prepregs after 23 months

- re-use of prepreg scrap is possible
  - compression molding of scrap
  - possible due to the absence of crosslinking



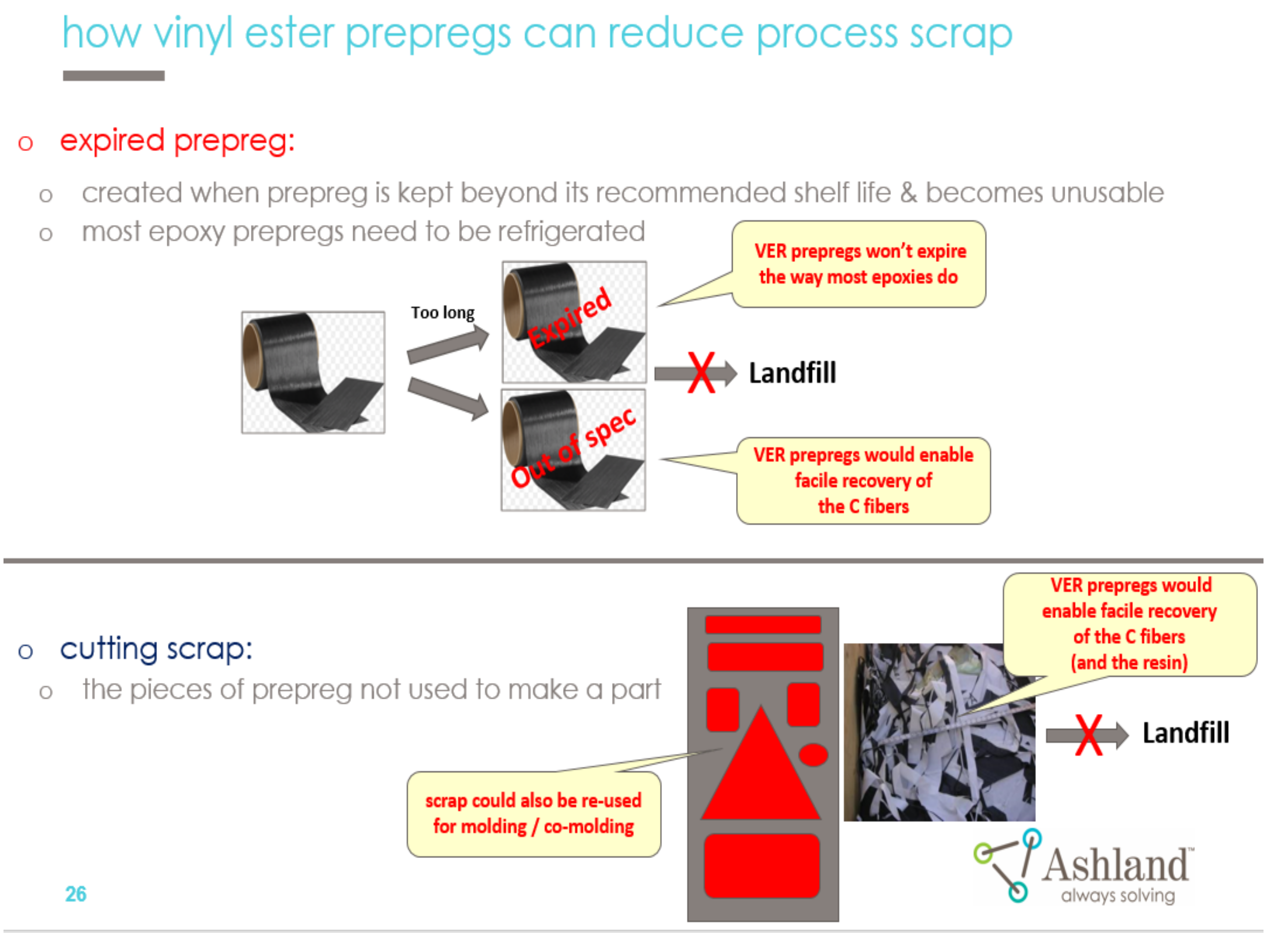
chopped pieces of Renegade prepregs molded after 23 months

Compression molding of prepreg scrap



The recycling and re-use advantages of vinyl ester prepregs are summarized in Figure 37.

Figure 37. Recycling and re-use advantages of vinyl ester prepregs



how vinyl ester prepregs can reduce process scrap

- expired prepreg:
  - created when prepreg is kept beyond its recommended shelf life & becomes unusable
  - most epoxy prepregs need to be refrigerated

VER prepregs won't expire the way most epoxies do

VER prepregs would enable facile recovery of the C fibers

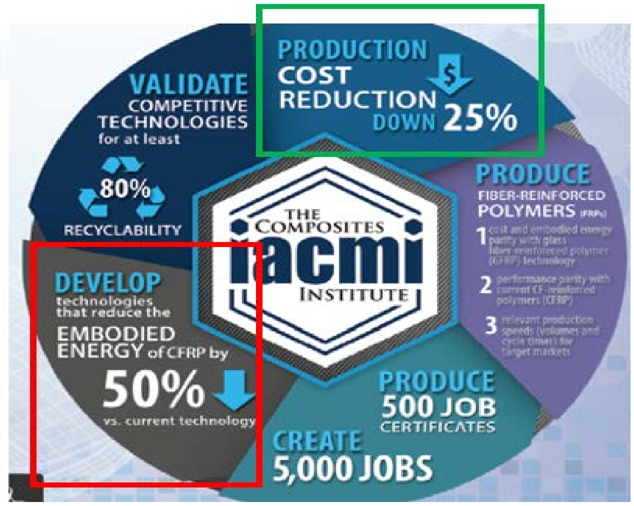
- cutting scrap:
  - the pieces of prepreg not used to make a part

VER prepregs would enable facile recovery of the C fibers (and the resin)

scrap could also be re-used for molding / co-molding

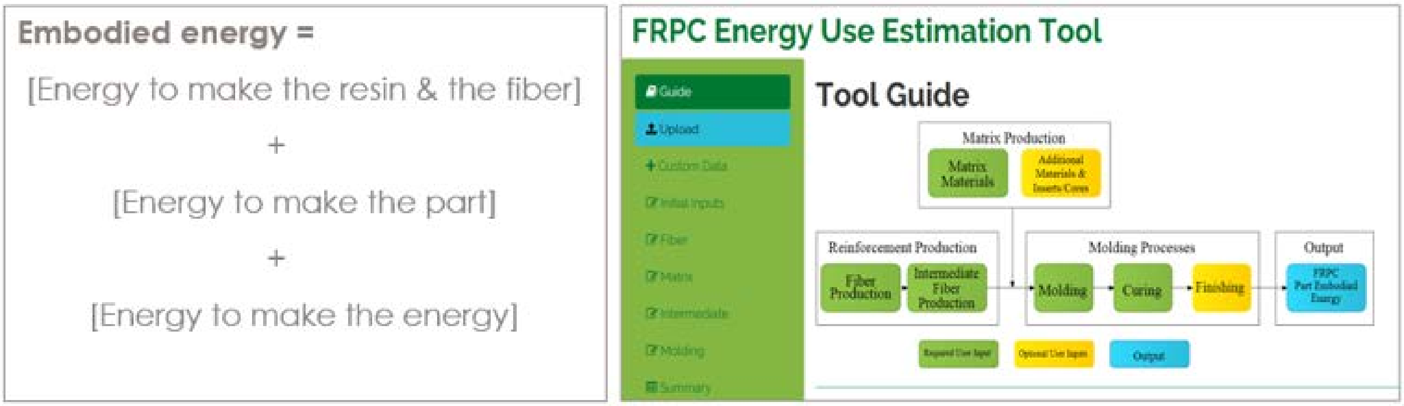
1.4 Benefits Assessment: Two of IACMI's stated goals are related to embodied energy and cost, respectively. These goals are highlighted in Figure 38.

Figure 38. IACMI's goals related to cost reduction and embodied energy



1.4.1 Embodied Energy: IACMI has developed an on-line tool that can be used to calculate the embodied energy associated with the production of composite parts made by a variety of different fabrication processes and made using a variety of different materials. The tool is known as the FRPC Energy Use Estimation tool and has been developed by Sujit Das and Kristina Armstrong at ORNL. It can be accessed at http://www.energytoolestimator.com/. Figure 39 provides a brief summary of the tool.

Figure 39. FRPC tool for calculating embodied energy


Embodied energy =

[Energy to make the resin & the fiber]

+

[Energy to make the part]

+

[Energy to make the energy]

This tool has been used to compare the embodied energy associated with the fabrication of a part by compression molding of a prepreg made with epoxy/carbon and vinyl ester/carbon systems. For these calculations, the default values in the tool have been used for the epoxy/carbon system. For the vinyl ester system, customized values have been entered. A sample calculation is shown in Appendix 1.

The assumptions made for these calculations include:

- the calculations are based on the "average primary energy" in the United States

- the vinyl ester parts are 10% heavier than epoxy parts due to the slightly lower mechanical properties
- the energy required for recycling is not included in the analysis, but it should be low for an extraction process.

The calculations have been performed with 30% process scrap, which is a commonly-used number quoted for prepreg scrap, and with 40% process scrap, which is the default value for “Manual Prepregs” in the FRPC tool. In the second and third columns of Table 5, it has been assumed that the amount of reclaimed scrap is higher with vinyl esters than with epoxies because of the recycling and re-use considerations described in Sections 1.3.6.1 and 1.3.6.2. The last column in Table 5 shows that reductions in embodied energy up to 33% should be possible by using vinyl esters. This is true even with the conservative assumption that the vinyl ester parts are 10% heavier, which may not be necessary in all applications depending on part design and performance specifications. Thus, a significant fraction of IACMI’s target of 50% reduction may be possible by using vinyl ester prepregs.

Additional calculations have shown the values in the last column in Table 5 increase by an additional 8-10% if the part weight of the vinyl ester part is assumed to be the same as that of an epoxy part. The values increase by another 1% if elimination of the energy needed to refrigerate the prepregs during storage is taken into consideration. Appendix 1 contains several spreadsheets showing these calculations.

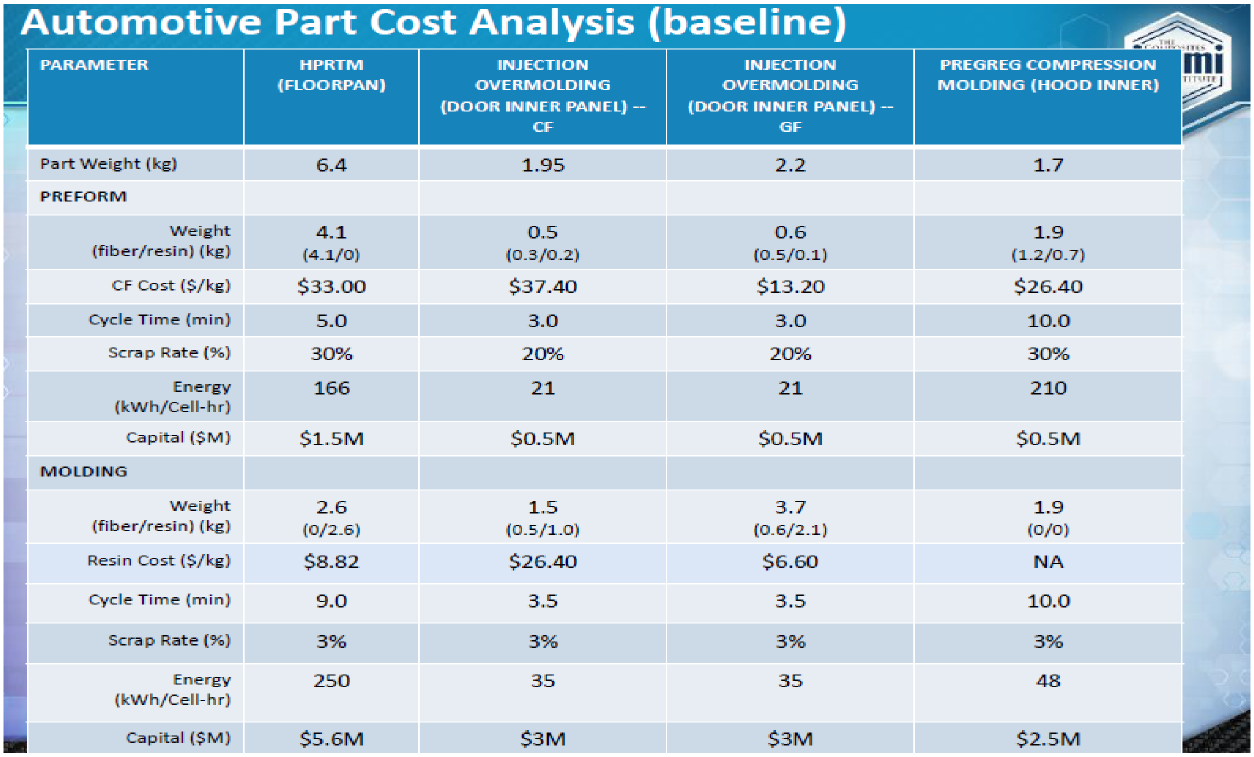
Table 5. Estimated % reduction in embodied energy with vinyl ester prepregs using the FRPC tool

% Process Scrap	% Reclaim VER	% Reclaim Epoxy	% Reduction in Embodied Energy
30	50	0	9
	100	50	6
	100	25	14
	100	0	22**
40	50	0	17
	100	50	11
	100	25	22
	100	0	33

** The output of the FRPC tool for this calculation is shown in detail in the first section of Appendix 1

1.4.2 Cost considerations: IACMI has developed a cost model for the fabrication of composite parts. (reference Brosisus). Example of these calculations are shown in Table 6. The calculation most relevant to this project is the data for a compression-molded hood made with epoxy prepreg in the far-right column.

Table 6. Automotive part cost analysis by IACMI



Automotive Part Cost Analysis (baseline)

PARAMETER	HPRTM (FLOORPAN)	INJECTION OVERMOLDING (DOOR INNER PANEL) -- CF	INJECTION OVERMOLDING (DOOR INNER PANEL) -- GF	PREGREG COMPRESSION MOLDING (HOOD INNER)
Part Weight (kg)	6.4	1.95	2.2	1.7
PREFORM				
Weight (fiber/resin) (kg)	4.1 (4.1/0)	0.5 (0.3/0.2)	0.6 (0.5/0.1)	1.9 (1.2/0.7)
CF Cost ($/kg)	$33.00	$37.40	$13.20	$26.40
Cycle Time (min)	5.0	3.0	3.0	10.0
Scrap Rate (%)	30%	20%	20%	30%
Energy (kWh/Cell-hr)	166	21	21	210
Capital ($M)	$1.5M	$0.5M	$0.5M	$0.5M
MOLDING				
Weight (fiber/resin) (kg)	2.6 (0/2.6)	1.5 (0.5/1.0)	3.7 (0.6/2.1)	1.9 (0/0)
Resin Cost ($/kg)	$8.82	$26.40	$6.60	NA
Cycle Time (min)	9.0	3.5	3.5	10.0
Scrap Rate (%)	3%	3%	3%	3%
Energy (kWh/Cell-hr)	250	35	35	48
Capital ($M)	$5.6M	$3M	$3M	$2.5M

Unlike the FRPC model for embodied energy discussed earlier, IACMI's cost model is not available on-line. However, Dale Brosius of IACMI used data from this project to calculate the estimated reduction in part cost for a compression-molded hood made with vinyl ester prepreg. Table 7 provides a summary of these calculations. A detailed summary of his calculations is included as Appendix 2.

Note: the resin and fiber costs in Table 7 are estimates based on automotive volumes of at least 100,000 vehicles per year.

Table 7. Estimated part costs for hood inner prepared with compression-molded prepregs

	901/K	Epoxy benchmark
Resin cost ($/lb)	3.00	4.00
Fiber cost ($/lb)	7.70	10.00
Molding time (min)	3	10
Part weight	1.1	1.0
$ per part	111.64	142.71

These calculations indicate that the estimated cost per part would be 21.8% lower with vinyl ester compared to the epoxy benchmark. 4.2% of this reduction comes from the fact that the raw material costs for both the resin and the fiber are lower than for the epoxy control. This is true even though the same conservative assumption has been made here as in the case of embodied energy – that the vinyl ester part is 10% heavier because the mechanical properties are not quite as good as for epoxies. The other 17.6% of the reduction comes from the reduction in cycle time.

It should be noted that these calculations do not take into account any savings associated with recycling and/or re-use of prepreg scrap and avoidance of landfill costs for disposal of scrap. If the scrap can be recycled and/or re-used with vinyl esters more easily than with epoxies, additional savings should also be possible.

1.5 Commercialization

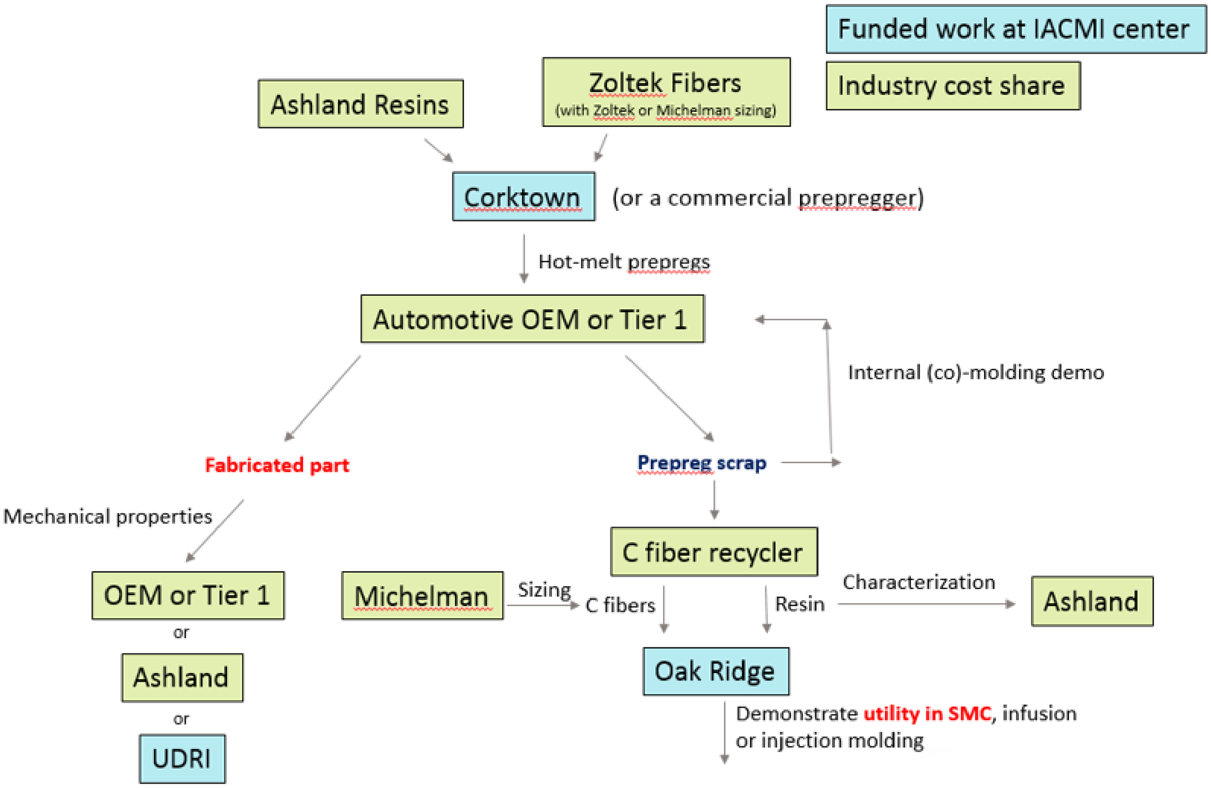
At the initiation of this project, the Technology Readiness Level (TRL) was estimated to be 3. At the conclusion of this project, an optimized resin/sizing/fiber combination had been identified and the TRL was estimated to be 4.

To move this technology further towards commercialization, a Stage 2 project has been proposed. The motivation for a Stage 2 project is the following:

- vinyl ester prepregs have an attractive value proposition from a processing, molding, recycling & re-use, and overall cost perspective
- all the Stage 1 work described herein has been done with prepreg surrogates, not prepregs
- a Stage 2 project would demonstrate utility in an actual part, not 12” square plaques
- a Stage 2 project would enable the recycling and re-use advantages of vinyl esters to be examined in greater depth

The project proposed for Stage 2 is summarized in Figure 40.

Figure 40. Flow chart for a potential Stage 2 project for vinyl ester/carbon fiber prepregs



It would involve many, if not all, of the project team members in Stage 2. It would also include new team members, specifically:

- a prepregger
- an automotive OEM or Tier 1 supplier with a specific part in mind
- a recycling partner

1.6 Accomplishments

The project team demonstrated a vinyl ester / carbon fiber prepreg system with the following attributes/benefits:

- no styrene. The vinyl ester resins that can be used to make prepregs are hot melt resins that do not contain a reactive diluent. They are not intentionally diluted in styrene. This feature adds an additional environmental benefit in that handling of styrene and control of styrene emissions is not required.

- long shelf life (> 23 months). The films used to make prepreg surrogates during the course of this project have been shown to be stable for at least 9 months at room temperature. The surrogates themselves have been shown to be stable for at least 7 months at room temperature. In related work outside the scope of this project, prepregs made with the same vinyl ester resins have been stable at room temperature for 23 months.
- no need for refrigeration. Unlike most epoxy prepregs, which need to be stored in a freezer, vinyl ester prepregs can be stored at room temperature.
- fast cure ($\leq$ 3 minutes). The prepreg surrogates made in this project were compression-molded at 325-350°F and 100 psi pressure and a molding time of 3 minutes. In comparison, the molding time is 10 minutes for the epoxy/carbon system that IACMI began using in 2015 as a benchmark for compression-molded prepregs.
- improved resin-fiber interface. The Interlaminar Shear Strength (ILSS) values measured at Michigan State for the best-performing resin/sizing/fiber systems were near or slightly above 100 MPa. This is indicative of a strong resin-fiber interface. These values were significantly higher than an epoxy/carbon control run at MSU and higher than any values of ILSS found in the literature for vinyl ester/carbon systems. Micrographs of the fracture surfaces showed good contact between the resin and the fiber, providing further evidence of a strong resin-fiber interface.
- reduction in the amount of process scrap that needs to go to a landfill. Vinyl esters offer significant advantages relative to epoxy resins with respect to recycling and re-use. Work with Vartega has shown that their extraction process can readily remove the resin from scrap vinyl ester prepreg, enabling facile recovery of the carbon fibers. On the re-use front, it has been shown that scrap prepreg can readily be molded after an extended period of time. It has also been shown that virgin or scrap prepreg can be co-molded with Sheet Molding Compound (SMC).
- reduction in embodied energy. The FRPC calculator developed by IACMI has been used to show that vinyl ester prepregs offer the potential for significant reductions in embodied energy relative to epoxy-based systems. Reductions as high as 33% have been calculated. This is a significant fraction of IACMI's target of a 50% reduction in embodied energy by 2020.
- cost-effectiveness. The use of industrial grade carbon fibers, the improvement in shelf life stability of the prepreg at room temperature, the lack of a need of refrigeration, the short molding time, and the ability to extract value from prepreg scrap all add up to a cost-effective alternative to epoxy/carbon prepreg systems. IACMI has calculated a 22% reduction in the cost to produce a compression-molded hood inner, and the reduction could be even higher if the recycling/re-use options for prepreg scrap are taken into consideration.

1.7 Conclusions

- The best-performing resin/sizing/fiber system identified in this work consisted of Arotran 901 resin from Ashland, sizing K from Zoltek, and W grade PX35 fibers from Zoltek. Selection of this system, referred to as 901/K, took into account mechanical properties and handleability/processing considerations.
- The second best-performing system consisted of Arotran 901, sizing E from Michelman, and W grade PX35 fiber. This system, referred to as 901/E, gave good mechanical properties, but fibers sized with E were not as easy to handle as those sized with K.
- The composition of the sizing had a significant effect on the resin-dominated mechanical properties of compression-molded laminates. The processability of the sized fibers played a big role in obtaining good parts/properties.
- W grade PX35 fibers (ribbons) from Zoltek were easier to process than T grade (ropes).
- Arotran 901 always outperformed Arotran 902 in resin-dominated mechanical tests. These included ILSS and in-plane shear strength measurements at UDRI and ILSS measurements at MSU. On a more subjective note, both MSU and UDRI also reported that 901 was easier to handle and process than 902.
- The hot-melt vinyl ester resins employed in this project do not crosslink during prepreg fabrication. This behavior, which is distinctly different from epoxy prepregs, manifests itself in the long shelf life observed at room temperature and the recycling and re-use advantages of vinyl ester prepreg scrap relative to epoxies.
- The debulking step, where prepreg surrogates were heated under vacuum prior to compression molding, appeared to cause a reduction in glass transition temperature of the molded parts.
- In the closest “apple-to-apples” comparison to an epoxy prepreg system, the mechanical properties of the 901/K system were about 10% lower. The mechanical properties of the 901/K system would be expected to improve if prepreg surrogates were replaced by actual prepregs.
- The TRL for vinyl ester/carbon fiber composites increased from 3 to 4 as a result of this work. This project is a very good illustration of how IACMI is an effective mechanism for technology development. It fosters collaboration between industry, academia and the federal labs on industrially-relevant problems.

1.8 Recommendations

- A Stage 2 IACMI project should be initiated to scale-up the optimized resin/sizing/fiber system identified in the Stage 1 work described in this report. The project team should be expanded to include a prepregger who could make actual prepregs instead of prepreg surrogates and an automotive OEM or Tier 1 supplier with a specific part in mind to fabricate with the optimized system.
- The Stage 2 project should also include a recycling/re-use component that would demonstrate the advantages of vinyl ester prepregs on a larger scale. This effort should include work to optimize the recovery of carbon fibers (and potentially the resin as well) from prepreg scrap and further work on the molding & co-molding of prepreg scrap.
- Other elements of future work should include:
    - additional work on optimizing the amount of the sizing in the best-performing systems
    - additional work on mechanical property measurements of unidirectional samples. This should include compressive strength measurements and measurement of the transverse tensile and flexural properties of unidirectional samples that have been fast-cured
    - work to understand and minimize the effect of the debulking step on glass transition temperature
- A similar, structured approach to identifying the optimized resin/sizing/fiber combination in a styrenated vinyl ester resin system should be undertaken.

Acknowledgements

We would like to acknowledge all the team members from the various partners for their collaborative spirit, hard work, and dedication to this project. They are listed below.

Ashland: Jon McKay, Jim Emrick, Allison Michaels, Tom Grentzer, Laura Littlejohn, Stephanie Fulmer, and Nicole Clark

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Zoltek: Phil Schell and David Corbin

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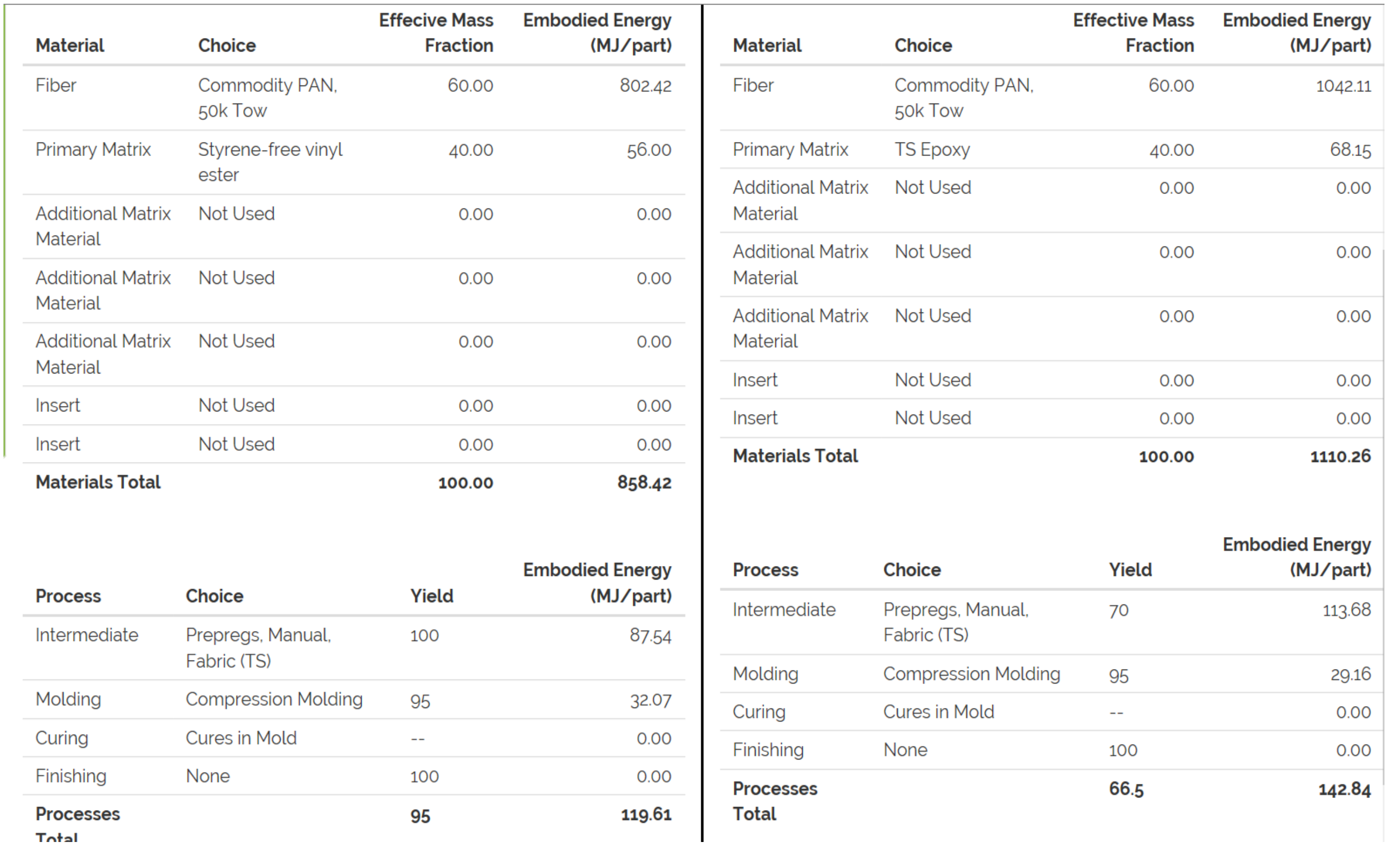
8. From presentation by Dale Brosius entitled “IACMI Baseline Cost and Energy Metrics.” IACMI semi-annual meeting, Denver, February 2017. Slide 14.

Appendix 1 FRPC Calculations

The output from the FRPC for the fourth entry in Table 5 is shown below.

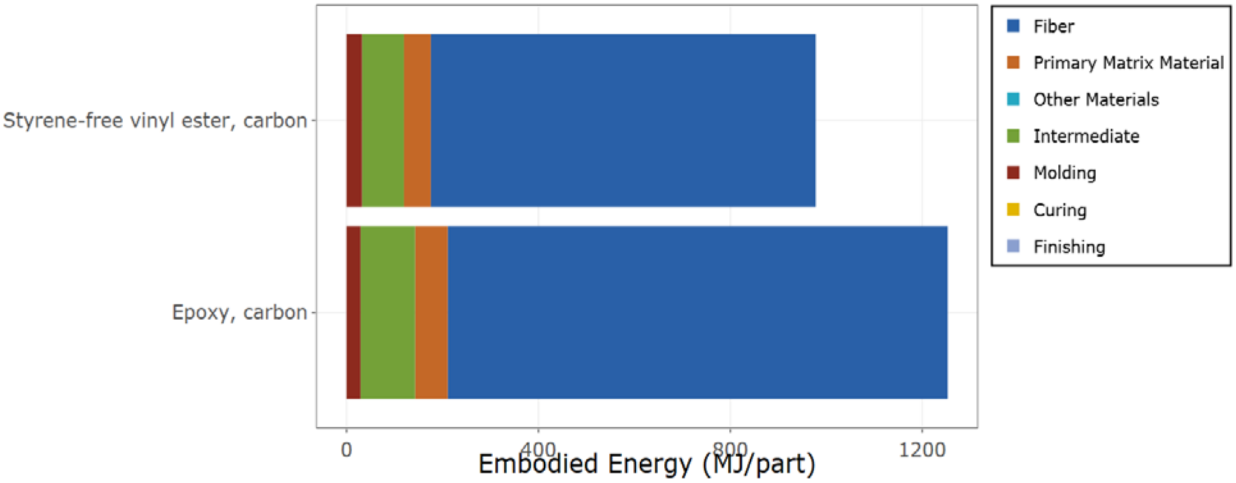


Material	Choice	Effective Mass Fraction	Embodied Energy (MJ/part)
Fiber	Commodity PAN, 50k Tow	60.00	802.42
Primary Matrix	Styrene-free vinyl ester	40.00	56.00
Additional Matrix Material	Not Used	0.00	0.00
Additional Matrix Material	Not Used	0.00	0.00
Additional Matrix Material	Not Used	0.00	0.00
Insert	Not Used	0.00	0.00
Insert	Not Used	0.00	0.00
Materials Total		**100.00**	**858.42**

Process	Choice	Yield	Embodied Energy (MJ/part)
Intermediate	Prepregs, Manual, Fabric (TS)	100	87.54
Molding	Compression Molding	95	32.07
Curing	Cures in Mold	--	0.00
Finishing	None	100	0.00
Processes Total		**95**	**119.61**

Material	Choice	Effective Mass Fraction	Embodied Energy (MJ/part)
Fiber	Commodity PAN, 50k Tow	60.00	1042.11
Primary Matrix	TS Epoxy	40.00	68.15
Additional Matrix Material	Not Used	0.00	0.00
Additional Matrix Material	Not Used	0.00	0.00
Additional Matrix Material	Not Used	0.00	0.00
Insert	Not Used	0.00	0.00
Insert	Not Used	0.00	0.00
Materials Total		**100.00**	**1110.26**

Process	Choice	Yield	Embodied Energy (MJ/part)
Intermediate	Prepregs, Manual, Fabric (TS)	70	113.68
Molding	Compression Molding	95	29.16
Curing	Cures in Mold	--	0.00
Finishing	None	100	0.00
Processes Total		**66.5**	**142.84**



				Vinyl Ester Prepreg				Epoxy Prepreg			
Case	Scrap %	% Reclaimed VER	% Reclaimed Epoxy	Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)		Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)	% Reduction with VER
1	30	50	0	1009.9	135.06	1144.96		1110.26	142.84	1253.1	9%
2		100	50	858.42	119.61	978.03		914.33	122.78	1037.11	6%
3		100	25	858.42	119.61	978.03		1002.81	131.84	1134.65	14%
4		100	0	858.42	119.61	978.03		1110.26	142.84	1253.1	22%
5	40	50	0	1073.02	141.49	1214.51		1295.3	161.79	1457.09	17%
6		100	50	858.42	119.61	978.03		971.47	128.63	1100.1	11%
7		100	25	858.42	119.61	978.03		1110.26	142.84	1253.1	22%
8		100	0	858.42	119.61	978.03		1295.3	161.79	1457.09	33%

assumptions: 10% thicker part with VER. There are no energy savings associated with elimination of refrigeration. Styrene-free VER = 120.9

These are the values shown in Table 5

				Vinyl Ester Prepreg				Epoxy Prepreg			
Case	Scrap %	% Reclaimed VER	% Reclaimed Epoxy	Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)		Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)	% Reduction with VER
9	30	50	0	1009.9	117.89	1127.79		1110.26	142.84	1253.1	10%
10		100	50	858.42	105.02	963.44		914.33	122.78	1037.11	7%
11		100	25	858.42	105.02	963.44		1002.81	131.84	1134.65	15%
12		100	0	858.42	105.02	963.44		1110.26	142.84	1253.1	23%
13	40	50	0	1073.02	123.26	1196.28		1295.3	161.79	1457.09	18%
14		100	50	858.42	105.02	963.44		971.47	128.63	1100.1	12%
15		100	25	858.42	105.02	963.44		1110.26	142.84	1253.1	23%
16		100	0	858.42	105.02	963.44		1295.3	161.79	1457.09	34%

assumptions: 10% thicker part with VER. **There are energy savings associated with elimination of refrigeration.** Styrene-free VER = 120.9. Intermediate ee = 105.

The elimination of refrigeration buys you another 1% reduction.

				Vinyl Ester Prepreg				Epoxy Prepreg			
Case	Scrap %	% Reclaimed VER	% Reclaimed Epoxy	Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)		Materials Embodied Energy (MJ/kg)	Process Embodied Energy (MJ/kg)	Total Embodied Energy (MJ/kg)	% Reduction with VER
17	30	50	0	918.09	107.18	1025.27		1110.26	142.84	1253.1	18%
18		100	50	780.38	95.47	875.85		914.33	122.78	1037.11	16%
19		100	25	780.38	95.47	875.85		1002.81	131.84	1134.65	23%
20		100	0	780.38	95.47	875.85		1110.26	142.84	1253.1	30%
21	40	50	0	975.47	112.05	1087.53		1295.3	161.79	1457.09	25%
22		100	50	780.38	95.47	875.85		971.47	128.63	1100.1	20%
23		100	25	780.38	95.47	875.85		1110.26	142.84	1253.1	30%
24		100	0	780.38	95.47	875.85		1295.3	161.79	1457.09	40%

assumptions: **Equal part thickness and there are energy savings associated with elimination of refrigeration.** Styrene-free VER = 120.9. Intermediate ee = 105.

Equal part thickness results in signicantly greater reductions in the totla emboded energy.

Appendix 2. Cost Calculations by IACMI

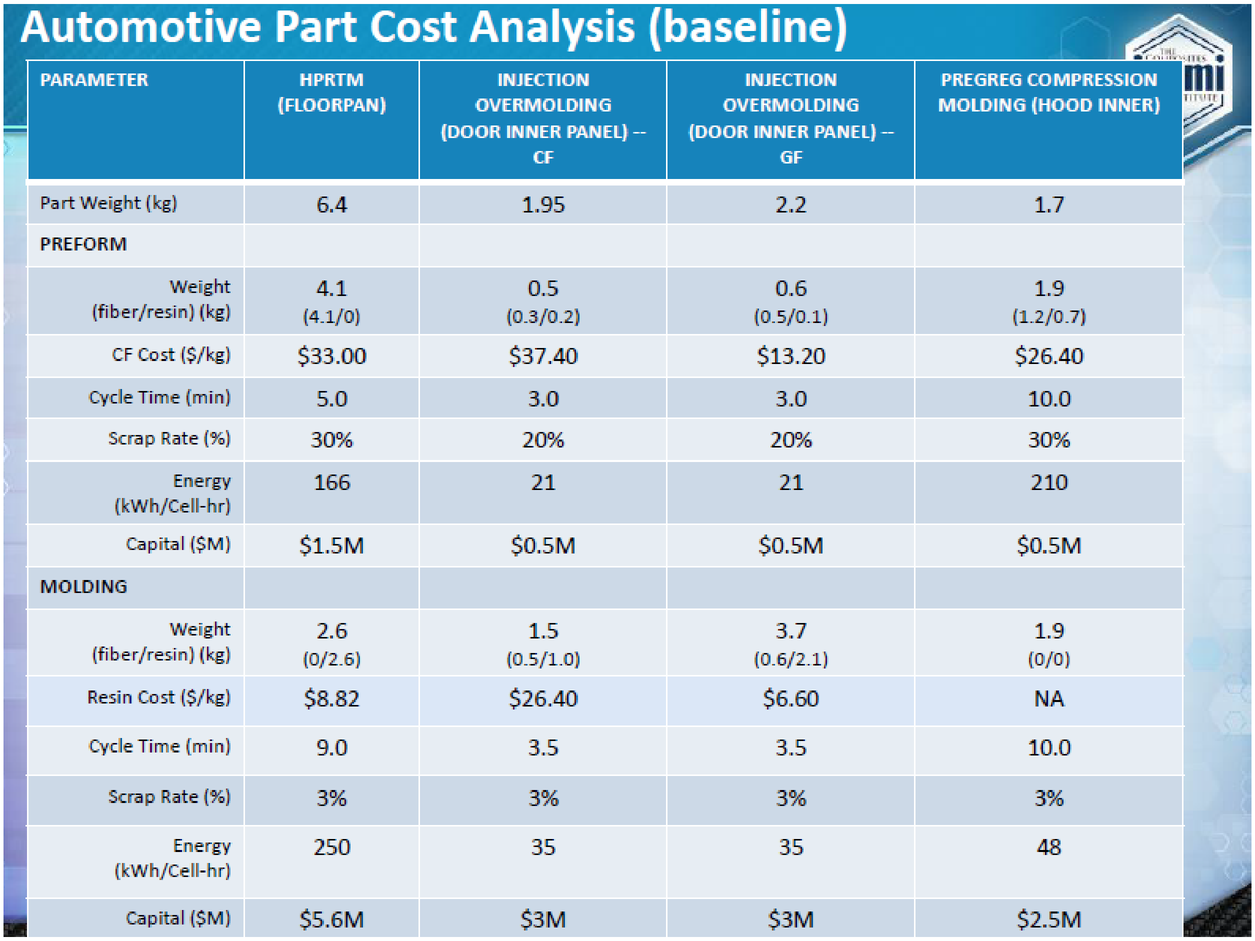
January 30, 2018

To: Joe Fox, Ashland

From: Dale Brosius, IACMI

SUBJECT: Cost Reduction Estimate for VE/CF prepreg compression molding

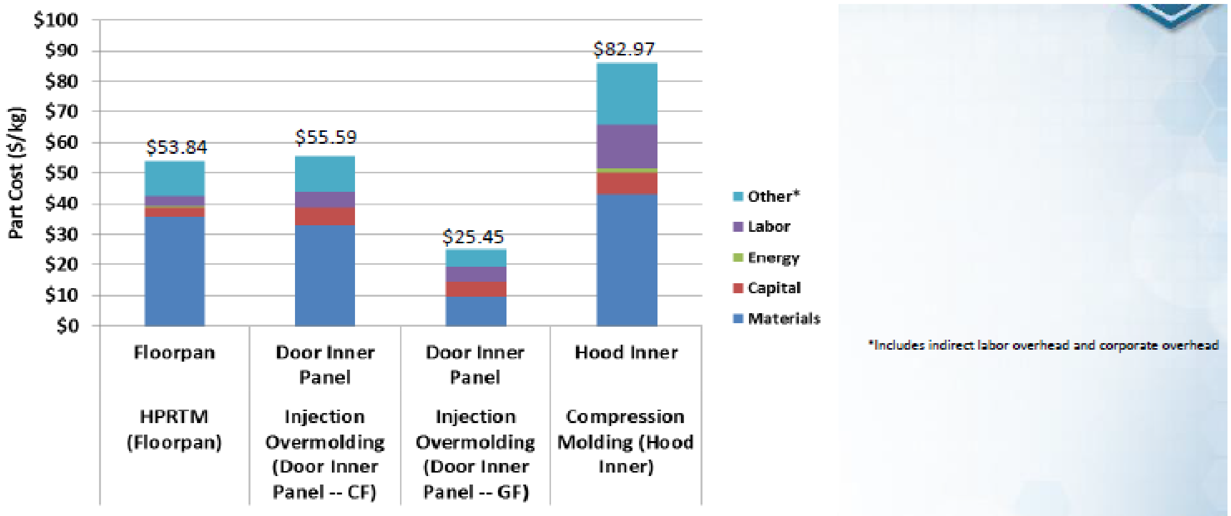
The charts in the baseline metric document can be used to estimate the effects of improvements on cost of various molding processes. For the purposes of estimating the impact of the change in material cost and molding cycle time for the baseline hood inner, we need only three charts:



Automotive Part Cost Analysis (baseline)

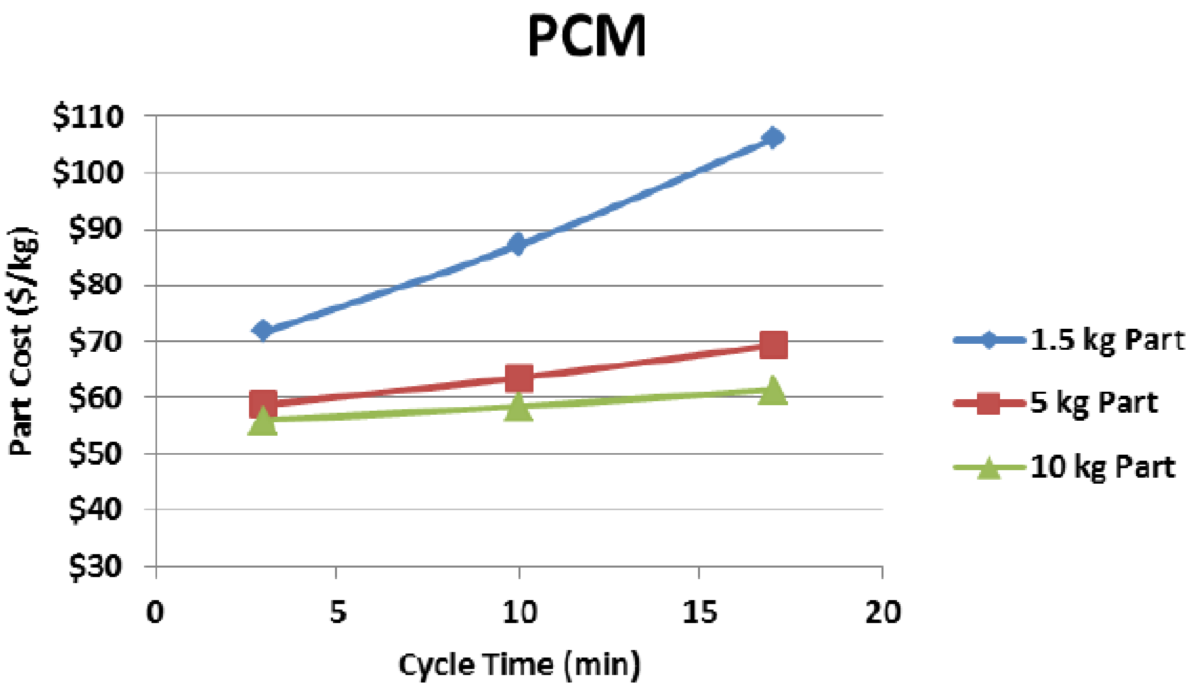
PARAMETER	HPRTM (FLOORPAN)	INJECTION OVERMOLDING (DOOR INNER PANEL) -- CF	INJECTION OVERMOLDING (DOOR INNER PANEL) -- GF	PREGREG COMPRESSION MOLDING (HOOD INNER)
Part Weight (kg)	6.4	1.95	2.2	1.7
PREFORM				
Weight (fiber/resin) (kg)	4.1 (4.1/0)	0.5 (0.3/0.2)	0.6 (0.5/0.1)	1.9 (1.2/0.7)
CF Cost ($/kg)	$33.00	$37.40	$13.20	$26.40
Cycle Time (min)	5.0	3.0	3.0	10.0
Scrap Rate (%)	30%	20%	20%	30%
Energy (kWh/Cell-hr)	166	21	21	210
Capital ($M)	$1.5M	$0.5M	$0.5M	$0.5M
MOLDING				
Weight (fiber/resin) (kg)	2.6 (0/2.6)	1.5 (0.5/1.0)	3.7 (0.6/2.1)	1.9 (0/0)
Resin Cost ($/kg)	$8.82	$26.40	$6.60	NA
Cycle Time (min)	9.0	3.5	3.5	10.0
Scrap Rate (%)	3%	3%	3%	3%
Energy (kWh/Cell-hr)	250	35	35	48
Capital ($M)	$5.6M	$3M	$3M	$2.5M

This one gives us the baseline values we need for the epoxy/CF hood inner.



*Includes indirect labor overhead and corporate overhead

This one tells us the baseline inner costs $82.97 per kg for a 1.7kg (net) inner panel



This chart says that for a 1.5 kg part using the same materials and assumptions as the hood inner, the cost for a 10 minute cycle is roughly $88/kg and for a 3 minute cycle is roughly $71, or a difference of $17/kg. Since our finished part weight of 1.7 kg is fairly close to 1.5 kg, this serves as a reasonable proxy for estimating the cycle time impact.

The impact of material costs can be directly calculated based on the information provided. The one tricky part is estimating the prepreg cost. For our baseline carbon/epoxy prepreg, we used a price of $12.00/lb, for a 60-62% by weight carbon fiber prepreg. This included a fiber cost of $10/lb and a resin cost of about $4.00/lb as formulated. The cost of the resin and fiber in this prepreg are $4.00 x 0.4 + $10.00 x 0.6 = $1.60 + $6.00 = $7.60. To reach $12, an add-on of $4.40/lb gives us $12.00.

If we use $3.00 for VE resin and $7.70 for fiber, we get a material cost of $5.82. With a similar add-on, we have $10.22, so, for estimating purposes, we can use $10.00/lb for the VE carbon UD tape.

To be fair, we could use $7.70 for the fiber in the epoxy prepreg, and this would give us a prepreg cost closer to $10.50/lb, but the goal of this exercise is to compare against the baseline values from 2015.

If we assume the VE part has to be 10% heavier, as you suggest, then our 1.72kg part becomes 1.89kg.

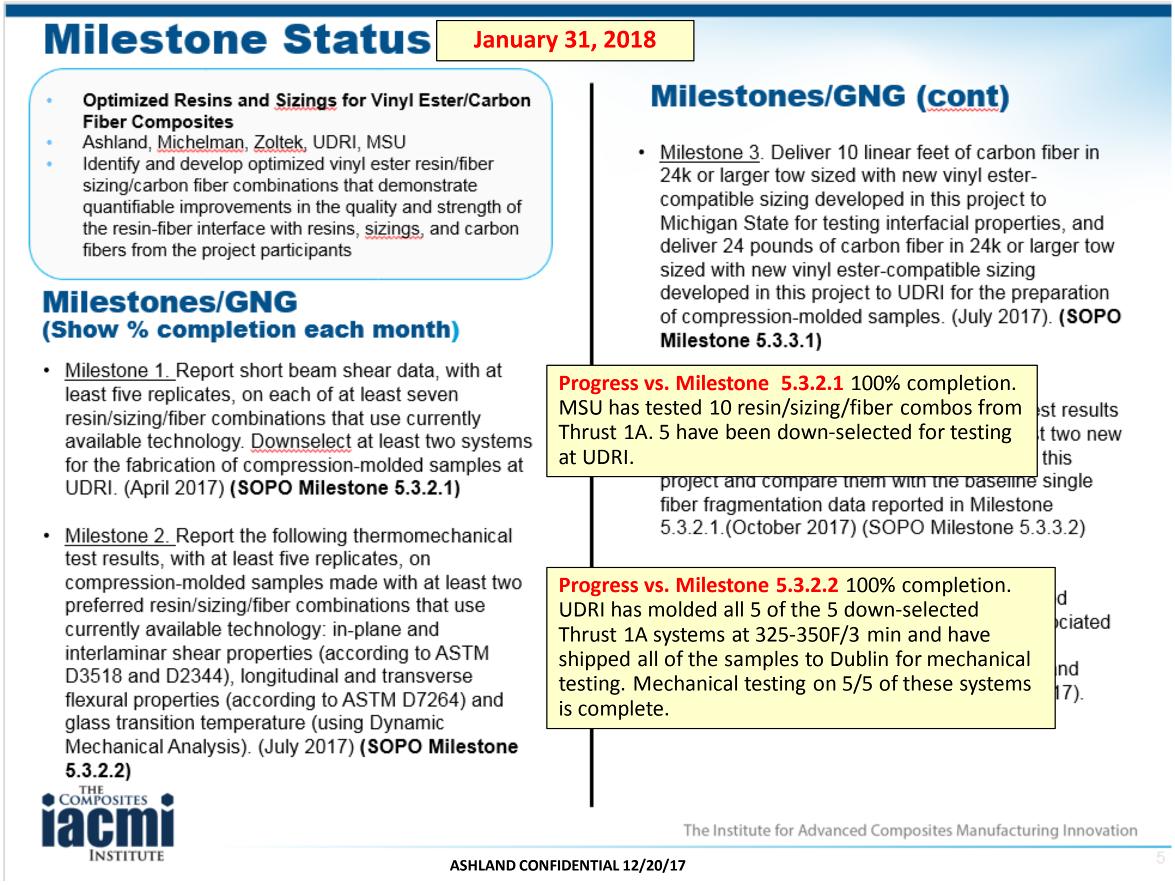
Now, we can run the following comparative calculations:

	Baseline Epoxy/CF	VE/CF
Net part weight	1.72kg	1.89kg
Preform weight (before final trim)	1.9kg	2.09kg
Scrap (pattern cutting/offal)	30%	30%
Material required	2.71 kg	2.99 kg
Material price	$26.40/kg ($12.00/lb)	$22.00/kg ($10.00/lb)
Total material cost per part	$71.66	$65.69
Material cost per kg (net part)	$41.66/kg	$34.76/kg
Molded part cost (10 min cycle)	$82.97/kg (baseline)	
Molding cost (part less material)	$41.31/kg	
Reduction for 3 minute cycle	($17.00)	
Molding cost for 3 minute cycle	$24.31/kg	
Estimated cost for VE/CF part (material plus molding cost)		$59.07/kg
Overall part cost (cost/kg x wt)	$142.71 (baseline)	$111.64
Savings		$31.07 (21.8%)
Savings from material cost		$5.97 (4.2%)
Savings from cycle time reduction		$25.10 (17.6%)

Note that switching to VE/CF is 29% lower on a cost/kg basis ($59.07/$82.97 =0.71), but this is offset due to the higher part weight, so the net <u>per part</u> savings is about $22%.

What is not taken into account here is what happens to the 30% scrap of the vinyl ester prepreg, which represents 0.9 kg per part, or $19.70. If 75% of this material can be recovered and remolded into a useful part, this could result in an additional $19.70 x 0.75 = $14.78/part savings, less any costs of collecting, sorting and reprocessing of the waste prepreg. Ideally, this could result in an additional savings of 10% of the original part cost.

Appendix 3   Progress vs. Milestones



Milestone Status

January 31, 2018

- **Optimized Resins and Sizings for Vinyl Ester/Carbon Fiber Composites**
- Ashland, Michelman, Zoltek, UDRI, MSU
- Identify and develop optimized vinyl ester resin/fiber sizing/carbon fiber combinations that demonstrate quantifiable improvements in the quality and strength of the resin-fiber interface with resins, sizings, and carbon fibers from the project participants

Milestones/GNG
(Show % completion each month)

- Milestone 1. Report short beam shear data, with at least five replicates, on each of at least seven resin/sizing/fiber combinations that use currently available technology. Downselect at least two systems for the fabrication of compression-molded samples at UDRI. (April 2017) **(SOPO Milestone 5.3.2.1)**
- Milestone 2. Report the following thermomechanical test results, with at least five replicates, on compression-molded samples made with at least two preferred resin/sizing/fiber combinations that use currently available technology: in-plane and interlaminar shear properties (according to ASTM D3518 and D2344), longitudinal and transverse flexural properties (according to ASTM D7264) and glass transition temperature (using Dynamic Mechanical Analysis). (July 2017) **(SOPO Milestone 5.3.2.2)**

Milestones/GNG (cont)

- Milestone 3. Deliver 10 linear feet of carbon fiber in 24k or larger tow sized with new vinyl ester-compatible sizing developed in this project to Michigan State for testing interfacial properties, and deliver 24 pounds of carbon fiber in 24k or larger tow sized with new vinyl ester-compatible sizing developed in this project to UDRI for the preparation of compression-molded samples. (July 2017). **(SOPO Milestone 5.3.3.1)**

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project and compare them with the baseline single fiber fragmentation data reported in Milestone 5.3.2.1.(October 2017) (SOPO Milestone 5.3.3.2)

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17).

Progress vs. Milestone 5.3.2.1 100% completion. MSU has tested 10 resin/sizing/fiber combos from Thrust 1A. 5 have been down-selected for testing at UDRI.

Progress vs. Milestone 5.3.2.2 100% completion. UDRI has molded all 5 of the 5 down-selected Thrust 1A systems at 325-350F/3 min and have shipped all of the samples to Dublin for mechanical testing. Mechanical testing on 5/5 of these systems is complete.

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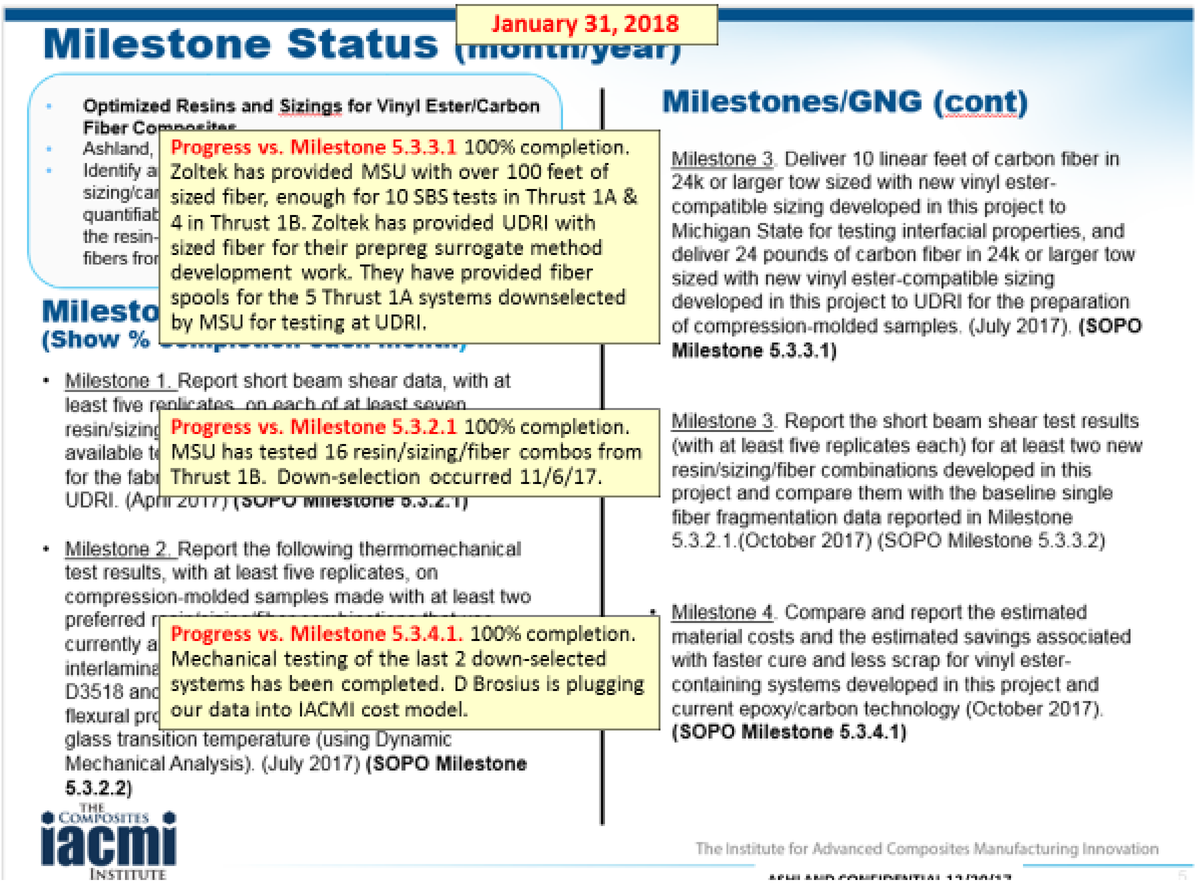

Milestone Status (month/year)

January 31, 2018

- **Optimized Resins and Sizings for Vinyl Ester/Carbon Fiber Co**
- Ashland,
- Identify a sizing/car quantifiab the resin- fibers fro

Progress vs. Milestone 5.3.3.1 100% completion. Zoltek has provided MSU with over 100 feet of sized fiber, enough for 10 SBS tests in Thrust 1A & 4 in Thrust 1B. Zoltek has provided UDRI with sized fiber for their prepreg surrogate method development work. They have provided fiber spools for the 5 Thrust 1A systems downselected by MSU for testing at UDRI.

Milesto (Show %

- Milestone 1. Report short beam shear data, with at least five r resin/sizing available t for the fab UDRI. (Apr

Progress vs. Milestone 5.3.2.1 100% completion. MSU has tested 16 resin/sizing/fiber combos from Thrust 1B. Down-selection occurred 11/6/17.

- Milestone 2. Report the following thermomechanical test results, with at least five replicates, on compression-molded samples made with at least two preferred r currently a interlamina D3518 and flexural pr glass transition temperature (using Dynamic Mechanical Analysis). (July 2017) **(SOPO Milestone 5.3.2.2)**

Progress vs. Milestone 5.3.4.1. 100% completion. Mechanical testing of the last 2 down-selected systems has been completed. D Brosius is plugging our data into IACMI cost model.

Milestones/GNG (cont)

Milestone 3. Deliver 10 linear feet of carbon fiber in 24k or larger tow sized with new vinyl ester-compatible sizing developed in this project to Michigan State for testing interfacial properties, and deliver 24 pounds of carbon fiber in 24k or larger tow sized with new vinyl ester-compatible sizing developed in this project to UDRI for the preparation of compression-molded samples. (July 2017). **(SOPO Milestone 5.3.3.1)**

Milestone 3. Report the short beam shear test results (with at least five replicates each) for at least two new resin/sizing/fiber combinations developed in this project and compare them with the baseline single fiber fragmentation data reported in Milestone 5.3.2.1.(October 2017) (SOPO Milestone 5.3.3.2)

- Milestone 4. Compare and report the estimated material costs and the estimated savings associated with faster cure and less scrap for vinyl ester-containing systems developed in this project and current epoxy/carbon technology (October 2017). **(SOPO Milestone 5.3.4.1)**

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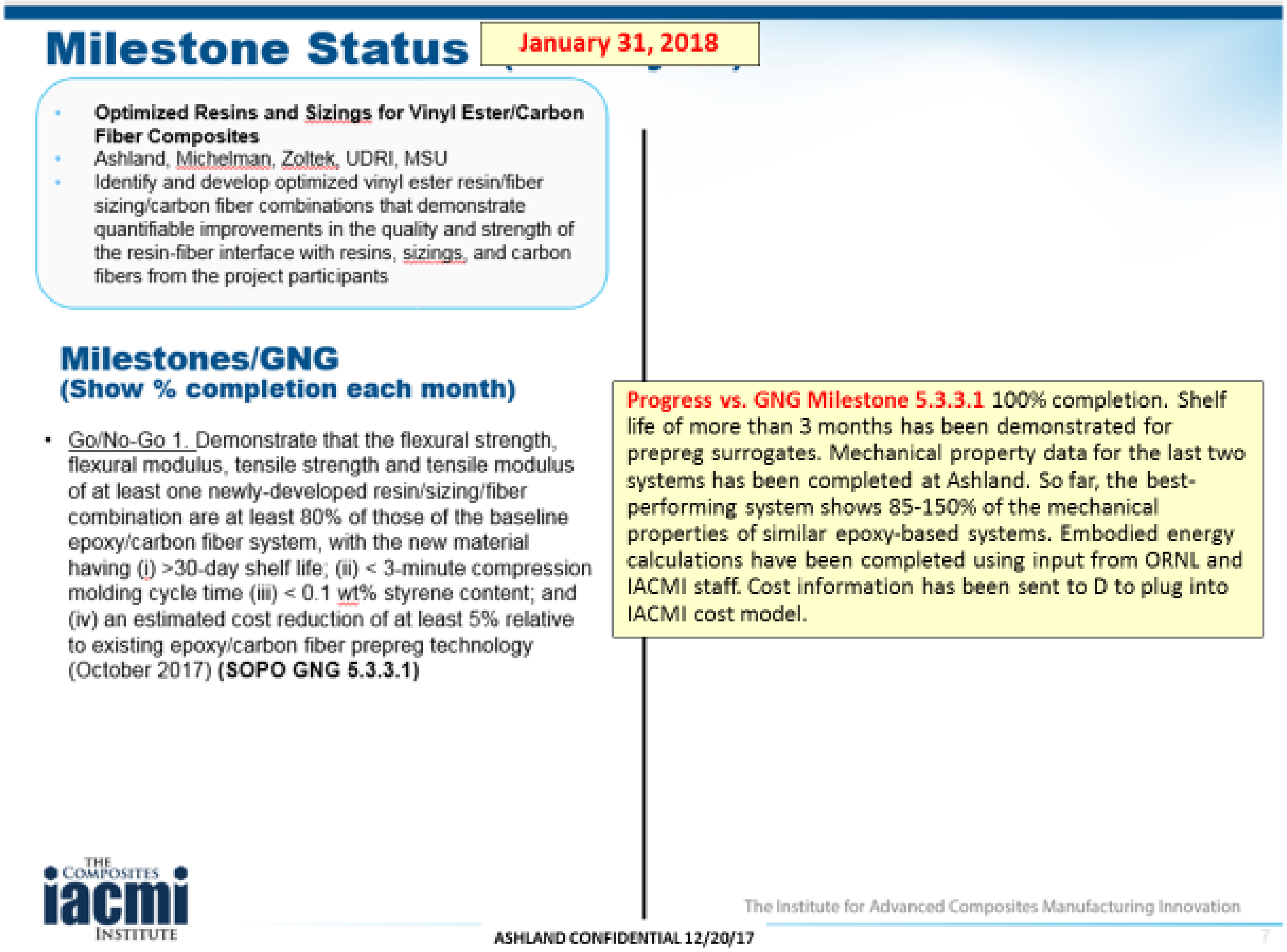

Milestone Status

January 31, 2018

- **Optimized Resins and Sizings for Vinyl Ester/Carbon Fiber Composites**
- Ashland, Michelman, Zoltek, UDRI, MSU
- Identify and develop optimized vinyl ester resin/fiber sizing/carbon fiber combinations that demonstrate quantifiable improvements in the quality and strength of the resin-fiber interface with resins, sizings, and carbon fibers from the project participants

Milestones/GNG

(Show % completion each month)

- Go/No-Go 1. Demonstrate that the flexural strength, flexural modulus, tensile strength and tensile modulus of at least one newly-developed resin/sizing/fiber combination are at least 80% of those of the baseline epoxy/carbon fiber system, with the new material having (i) >30-day shelf life; (ii) < 3-minute compression molding cycle time (iii) < 0.1 wt% styrene content; and (iv) an estimated cost reduction of at least 5% relative to existing epoxy/carbon fiber prepreg technology (October 2017) **(SOPO GNG 5.3.3.1)**

Progress vs. GNG Milestone 5.3.3.1 100% completion. Shelf life of more than 3 months has been demonstrated for prepreg surrogates. Mechanical property data for the last two systems has been completed at Ashland. So far, the best-performing system shows 85-150% of the mechanical properties of similar epoxy-based systems. Embodied energy calculations have been completed using input from ORNL and IACMI staff. Cost information has been sent to D to plug into IACMI cost model.

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