ORNL Manufacturing Demonstration Facility
Technical Collaboration **Final Report**

Solution for Carbon fiber Wet-Out Issue for Low Cost Sheet Molding Carbon Fiber Composite Production[1]

Continental Structural Plastics

Project ID:	MDF-TC-2013-022
Start Date:	8/14/2013
Completion Date:	8/31/2014
Company Size:	Large business, 2,700 employees

Summary

Poor wetting leads to underperforming composite properties and has been a major obstacle in implementing low cost carbon fibers in SMC parts. The objective of this project is to solve the technical challenge of poor carbon fiber wet-through during Sheet Molding Composite (SMC) process. Continental Structural Plastics (CSP) partnered with ORNL to develop a new sizing technique called Point Sizing (PS) that achieved an increase of a) ~25% of the short beam shear strength with Hydrosize epoxy sizing (Fig 3.), and b) 10-20% of the short beam shear strength with vinyl ester resin (Fig 4.). CSP sought an understanding for the *soundness of this technique, if scalable, and if results produced an increase in the shear strength of the composite.*

Background

Continental Structural Plastics (CSP) is a large compounder and molder of composites, mainly for the automotive industry. Carbon fibers are typically sold in the condition of being fully sized along the fiber length. Carbon fiber sizing is a highly proprietary coating and is applied at 0.5 to 5 percent of the weight of the carbon fiber-- sizing protects the carbon fiber during handling and processing (e.g., weaving) into intermediate forms, such as dry fabric and prepreg. Sizing also holds filaments together in individual tows to reduce fuzz, improves processability and increases interfacial shear strength between the fiber and matrix resin. In spite of the beneficial effect of sizing in regards to handleability and interface issues, sizing can impede the interfilamentary penetration of the resin matrix during the final stage of composite manufacturing (retards wettability, which leads to low shear strength).

The high surface energy of non-sized carbon fibers promotes wetting of the carbon fiber bundle by the matrix polymer. Highly energetic surfaces can be achieved using a gas

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phase surface treatment technique developed by ORNL to create polar groups that produce a hydrophilic surface, However, non-sized fibers typically produce fuzz and generate blockages and/or breakages in the SMC process. The approach taken in this feasibility project is the Point Sizing (coating) of carbon fiber filaments and subsequent surface treatment. The resulting filament is depicted in Fig 1.

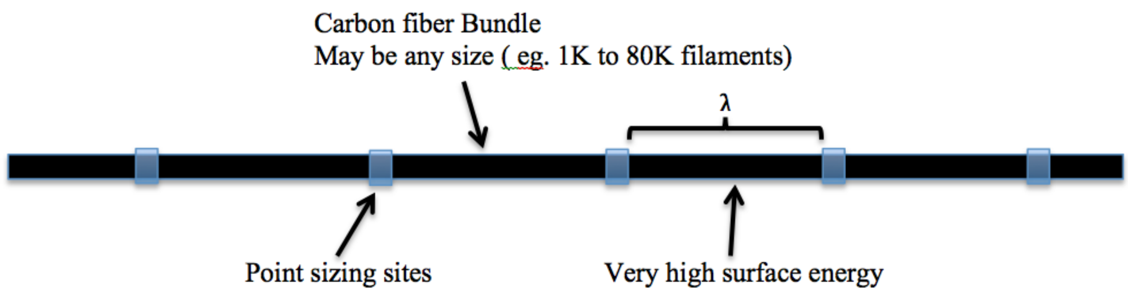

Figure 1: Point sizing of carbon fiber provides fiber bundle integrity. Subsequent surface treatment highly activates the bare carbon fiber surface between point sizing sites for wetting.

Technical Results
A carbon fiber surface modification and coating technique was investigated that resulted in improved mechanical properties of the final part. The overall objective of this project was to develop high-performance, cost-effective, carbon fiber SMC materials and associated processing techniques for high-volume automotive components with CSP.

From the two possibilities indicated in the project proposal (spraying vs. uniquely shaped rollers), the project team utilized the spraying methodology. The next step, shown in Fig 2., was the development and optimization of the point-sizing technique. In this approach, the sizing material is sprayed in spots in predefined intervals. Proper selection of materials and equipment was necessary at the initial stage of the project.

Figure 2: Carbon fibers are sized in spots using spraying technique. The intervals between the points are carbon fiber without sizing. After surface treatment, these intervals will have high surface energy ready to interact with the resin matrix in composite manufacturing.

Before experimentation could begin, preliminary work was performed, as outlined below.

1) Selection of two resin chemistry types (one Hydrosize-based epoxy, one vinyl ester resin)
2) Selection and acquisition of carbon fiber material with different characteristics (with and without sizing and surface treatment)
3) Selection of spraying equipment manufacturer and interaction to match materials to equipment (compatible chemistry, viscosity, quantity sprayed, etc.)
4) Dry run of equipment for performance verification

After this initial setup stage, a parametric evaluation was performed in order to:

5) Determine the effective point sizing intervals
6) Determine the sizing concentration
7) Optimize the sizing drying temperature
8) Optimize the surface treatment conditions for effective wet-through
9) Evaluation of the Interfacial Strength via short beam test

Coupon test specimens were fabricated for mechanically testing the effectiveness of the various surface treatment parameters. The effectiveness of surface treatment in enhancing the interfacial strength was characterized by performing interfacial shear strength (IFSS) testing using ASTM 2344.

During the parametric evaluation and test coupon analysis, a significant amount of time was required to determine the optimal set of test conditions. The required combination of sprayed sizing and novel gas phase surface treatment led to an extensive examination of a wide variety of chemistries, spray patterns and spray settings, surface treatment conditions, and coupon fabrication techniques. For example, too high a processing temperature caused over-crosslinking of the sizing chemistry applied during point sizing and excessive sprayed material covered too much of the tow length, reducing the effective of the surface treatment.

The composite making process comprises an intricate combination of thermal, chemical, and mechanical processes. Figure 3 represents data from the experiment in which a hydrosized epoxy was first sprayed on the carbon fiber tow in four inch intervals. Next, a preliminary dryer was set to a temperature of 75°C, in which the tow had a residence time of approximately 1min. At that point, the tow was surface treated using the gas phase thermochemical technique at 80°C, and collected on a spool under inert atmosphere to prevent interaction with humidity. Composites were made using a thickened vinyl ester resin labeled; Derakane 782 with a viscosity greater than 1300cP. Figure 3 summarizes the improvement in short-beam-shear-strength of composites with carbon fibers treated with ORNL point-sizing technique as compared to control carbon fibers (controlled fibers are surface treated by carbon fiber manufacturer).

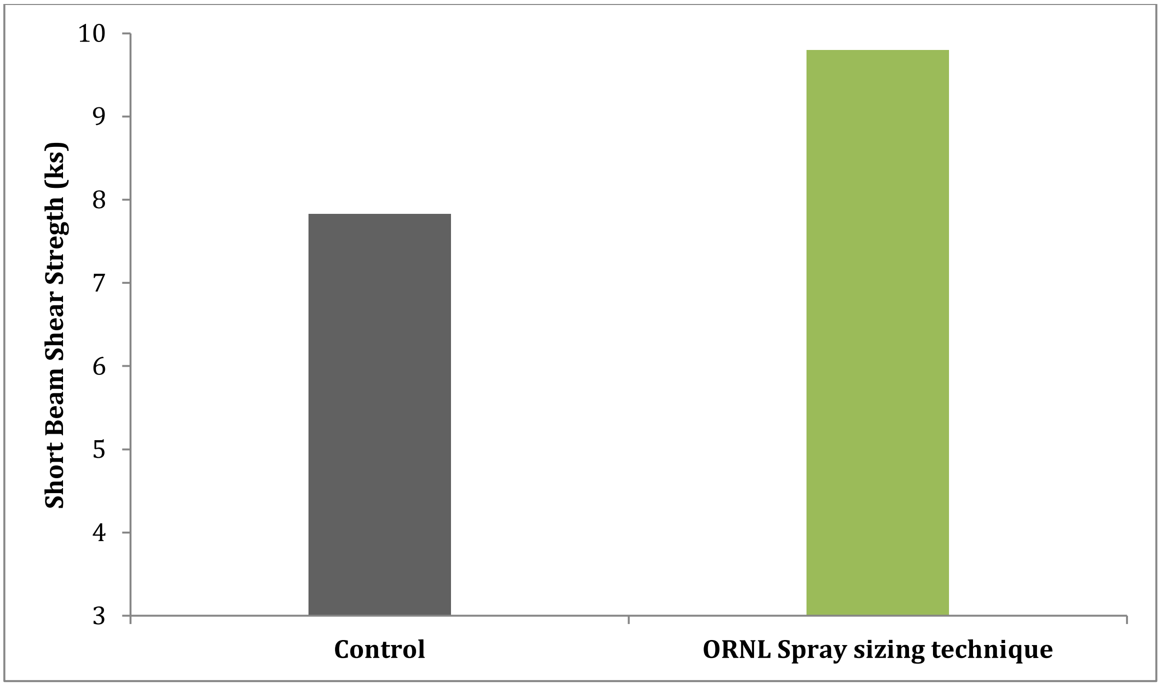

Figure 3:" Controlled" is as received carbon fiber from manufacturer. ORNL spray sizing technique: Hydrosized epoxy resin was sprayed on the carbon fiber tow, in 4 inch intervals. The dryer was set to a temperature of 75°C, collected under N2 environment to protect against humidity, and Vinyl Ester Resin Derekane 782, with a viscosity >1300cP was used to create the composites.

A second experiment (Figure 4) resulted in higher short beam shear strengths. The vinyl ester resin used to create the composites, and used for the spray sizing in the second experiment was Derakane 782; however, the viscosity of this resin was equal to 1300cP and not greater. Thus, when creating the composite, the lower viscosity helped to impregnate the fibers during the process, leading to better saturation and a better composite. The increase in strength may also be due to the increase in the processing temperature. The preliminary dryer and the surface treatment could be carried out at a higher temperature benefiting the treatment used for the addition of surface roughness on the carbon fiber tow. This seems to be promising data, but due to the intricacies of processing carbon fiber, more experimentation needs to be done in order to exhaust the full strength potential of the thermo-chemical treatment.

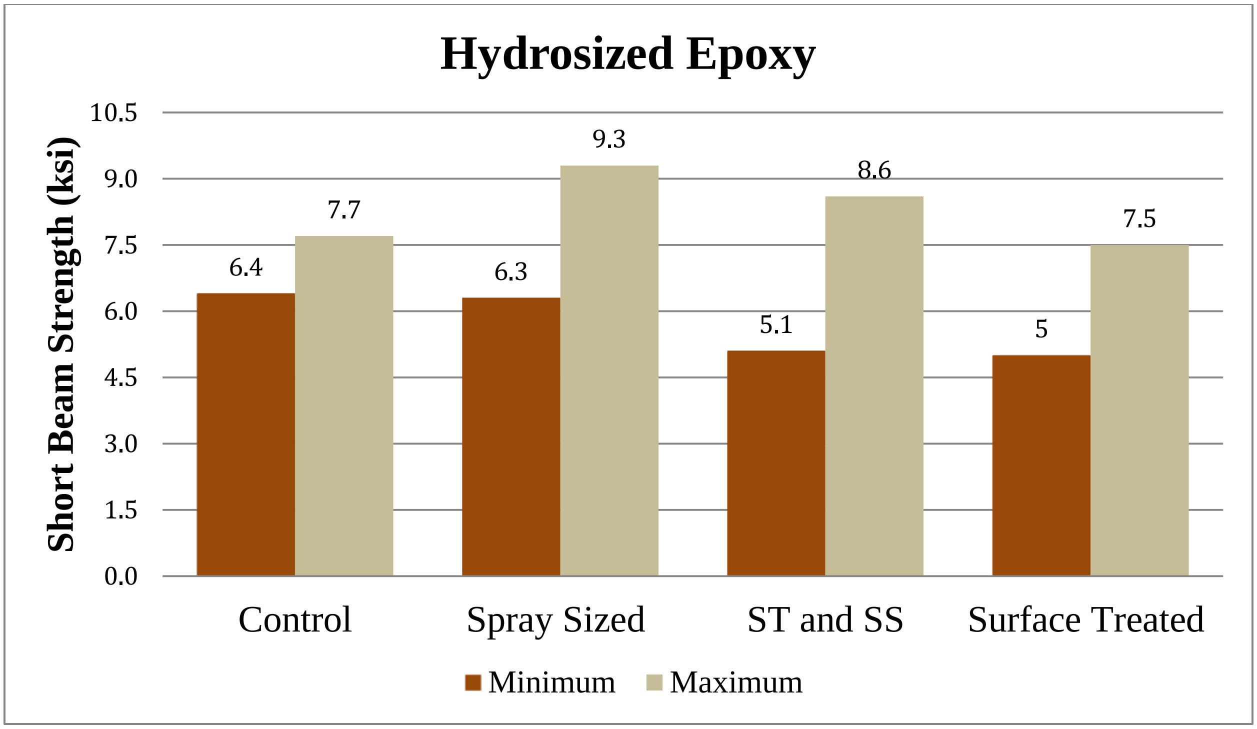

Figure 4: Vinyl Ester Resin Derakane 782 possessing a viscosity of 1300cP was sprayed at 4 inch intervals. No initiator compound was added during the spraying processes. Dryer temperature set to 90°C, ozone surface treatment at 95°C, collected under N_2 environment to protect against humidity, and Vinyl Ester Resin Derakane 782 with a viscosity of 1300cP was used to produce composites.

Subsequent work will involve actual SMC processing of this fiber. During this process, fiber chopping should be synchronized to the point sizing pattern on the fiber. The spraying interval can be selected by design. A useful adjunct to the point sizing technique would be a mechanism to spread out the fiber ends sufficiently to establish the necessary bonding with the resin matrix. ORNL has demonstrated in batch processing the successful application of electrostatic spreading of these fibers, and this will facilitate the penetration of the resin matrix and the wet-out of the carbon fiber filaments. In SMC production, where chopping and immersion must occur on a continuous basis, this technique would further improve overall part strength. This approach should be validated in subsequent work. Samples are shown in Figure 5.

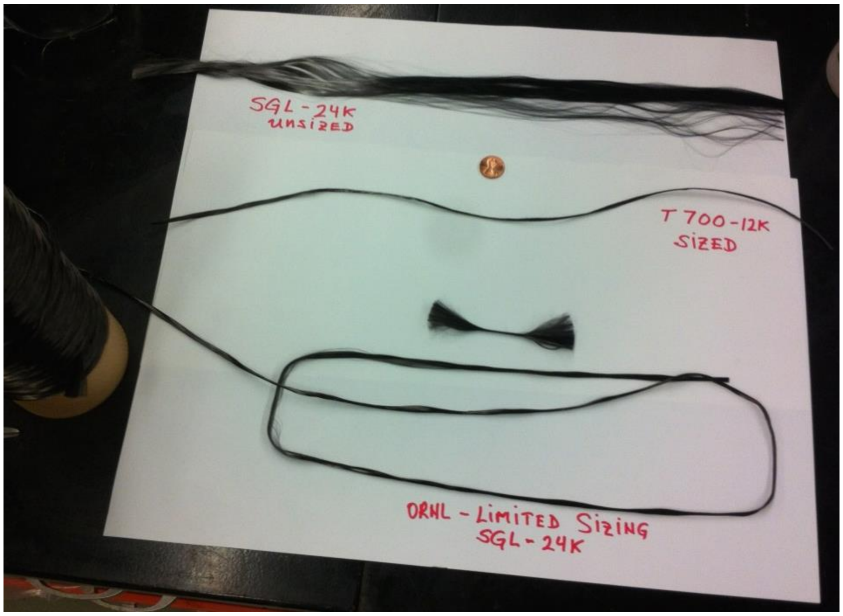

Figure 5: Fiber samples. The circled sample demonstrates the electrostatic spreading of fiber filaments

Impacts

This project directly targets the manufacturing problem of carbon fiber composites via Sheet Molding Compounding. SMC is by its nature high volume, quick cycle process as compared to any other aerospace type processes. Although widely utilized with glass fibers, SMC processes are not typically practiced with carbon fiber due to the lack of wetting of the carbon fiber which causes poor processability resulting in poor mechanical properties. Production implementation of the results of this project will contribute to making mechanically sound light-weight composite automotive parts.

Conclusions

This technology proved, when the right window of processability was identified, to be valuable for part techniques, such as SMC or continuous fiber part techniques. Feasibility of point sizing application, electrostatic fiber spreading and composite part shear strength improvement was also demonstrated. Further optimization and refinement will improve the properties significantly and is required for the implementation of this technology in the production scale.

Refinement, optimization, and scale-up of this technology towards different manufacturing processes such as SMC and other part fabrication techniques is required for commercial deployment.

The development team believes this technology has the potential to be commercially implemented in not only SMC, but many other composite part fabrication processes. Once optimized, this technology will have a signification impact in the way that some carbon fiber composites are made today by both reducing costs and increasing shear strength.

About the Company

Continental Structural Plastics is a leading manufacturer and molder of composite materials. CSP is the largest compounder and molder of SMC (Sheet Molding Composite) and LFT-D (Direct Long Fiber Thermoplastic) in North America with the primary focus being on the automotive/transportation and industrial segments. The main product lines are Class A exterior body panels, molded structural components (thermoset and thermoplastic), and pick-up boxes. Annual sales are currently in excess of $400 million. Continental Structural Plastics separate headquarters and R&D facilities are both located in Troy, MI. CSP currently operates seven plants in North America. Ship-to locations include the US, Mexico, Canada, Europe, and Japan.

ORNL and CSP were joined by SGL Group which provided carbon fiber, Michelman: which provided various sizing for spraying and RMX Technologies which provided fiber processing support and facilities.

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