Resin to Fiber Ratio - Maximizing Tensile Properties in a Water-Activated, Polyurethane/Carbon Fiber Composite Repair System

M. A. GREEN, M. U. FAROOQ AND C. J. LAZZARA

Neptune Research, Inc., 1346 S. Killian Dr., Lake Park, FL 33403, Ph: 561-683-6992 3Defence Research & Development Canada–Valcartier, Quebec City, QC, Canada

ABSTRACT

Composite repair systems are being heavily utilized for the repair of a wide variety of piping systems at high internal pressures. The strength of a composite material plays a critical role in the determination and qualification of the repair thickness for a given repair. Industry standards such as the ASME PCC-2 and the ISO/TS-24817 have been published which give some general guidelines on the usage, qualification and application process of composite materials. These standards specifically outline the required testing parameters and qualification data that must be obtained for the repair of high pressure piping systems with non-metallic composite materials.

Through intense testing based on current industry standards, as well as extensive knowledge, experience, and history with impregnating fabrics, the ideal resin to fiber ratio has been determined which will yield the maximum tensile characteristics of this water-activated polyurethane/carbon fiber composite repair system, while maintaining ease of application in real-world field applications. This allows for the design of a more conservative and cost effective repair system for the pipeline system owner/operator.

This paper discusses the mechanical testing completed on this material to achieve the optimum resin to fiber ratio with regards to strength, applicability, and performance. Included are descriptions of the performed testing and comparison of the test results from the various ratios which have been tested, as well as various sizing of the fibers for compatibility.

1. Introduction

Composite technology has gained a large amount of support and acceptance as a viable option for pipeline owners and operators to repair corrosion and mechanical damage defects in their pipeline systems. This acceptance has come to fruition as a result of several composite repair system manufacturers completing thorough testing programs to qualify and validate the composite repair systems. This was originally completed largely by the manufacturers of the systems independently as there was no governing standard specific to this type of repair system, as there was for other repair techniques such as welded sleeves or simply replacing the damaged section. This had the drawback of the manufacturers spending additional time and money performing ala carte testing as each pipeline would have different and very specific opinions or needs as to what is important regarding composite repairs. While this was effective in gaining knowledge of the individual system's characteristics, it was still lacking as a general qualification rule that all pipelines could utilize as a regulatory standard. This changed once the ASME and ISO organizations both introduced standards specifically for the qualification testing, validation, application, inspection, and certification of composites as used in the repair of high risk pipelines.

The ASME PCC-2 document, containing the article specific to composite repairs (Article 4.1 – Nonmetallic Composite Repair Systems for Piping and Pipework: High Risk Applications)[1] was originally released in 2006. It has since published a revised document in 2008, and is expected to release a new revision in

2010 or early 2011. The ISO/TS 24817 (Technical Specification for Petroleum, petrochemical and natural gas industries — Composite repairs for pipework — Qualification and design, installation, testing and inspection)[2] was also released in 2006. It has not yet released a revision, but is expected to have the first revision publish in 2010 or 2011. Each of these documents outlines all requirements for a composite system to be qualified, as well as the installation technician to be properly trained and certified, in great detail. These documents have allowed pipelines all over the world to have a set industry guideline on which to base their decisions and, in essence, judge whether a composite repair system has been properly tested and validated.

One of the most important and most frequently tested characteristics of a composite system which is to be used as a pipe repair system is the tensile properties. The tensile properties of the composite play a large role in determining the required thickness of the composite repair system. In direct relation to the tensile properties is the ratio of fiber to resin content within the composite system. Because of this, maximizing the resin to fiber ratio to gain optimum strength while maintaining practicality of a field applied, out of autoclave composite system becomes an important function in the manufacturing process.

2. Composite Systems for Pipe Repair

There are two basic types of composite repair systems for pipe in use today; "pre-cured" and "wet lay-up." A pre-cured system consists of a rigid laminate that has been cured in a coiled manner and is then adhered to the pipe using an adhesive resin. A wet lay-up composite is a system which is either pre-impregnated or is saturated on-site and then applied to the pipe to be cured in place. The pre-cured system was one of the original systems to be utilized in the pipeline industry, but trends today are tending toward the wet lay-up systems for a variety of reasons, but should be discussed in another forum. The pre-cured system obviously can place very tight controls on the resin to fiber ratio of the coiled portion of the composite, but must then be adhered with a separate resin system. The field impregnated system does not have very strict controls on resin to fiber ratios simply due to the application process. For the purpose of this paper, we will be focusing on the pre-impregnated composite system, which can place tight controls on resin to fiber ratios, while maintaining the benefits of having a wet lay-up composite system.

3. Development History

Neptune Research, Inc. (NRI) was the original developer and patent-holder on a fiberglass woven material pre-impregnated with a moisture-cured polyurethane resin. This system has been on the market for over 25 years. With recent technological developments making carbon fiber a more cost effective and accessible material, it was only a matter of time until it was adopted into the repair system as the reinforcing fiber. As a part of the testing and development of the carbon fiber system, the proper resin to fiber ratio had to be determined in order to gain the optimum strength and modulus characteristics, while still maintaining ease of application for a field technician in a practical setting.

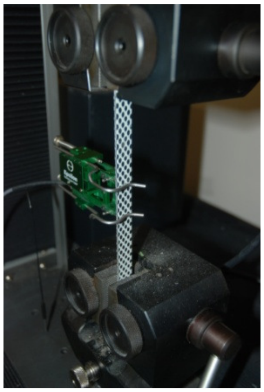
With state of the art manufacturing processes, the resin delivery can be micro-controlled and the percentage can be exacted to obtain what is desired in the composite system. Testing was completed on a variety of different resin to fiber percentages in order to determine the optimum ratio. The various percentages tested are shown in Tables 1 and 2. The percentage that yielded the best tensile properties, while maintaining ease of application in a real world environment, was eventually selected to be the ratio used in the production of the repair system. The starting percentages were determined based on previous manufacturing history using polyurethane resin and fiberglass, as well as documented testing completed for fiber volume fraction on closed mold composites [3].

Another aspect of the system which was considered in the process was the sizing used on the fibers prior to the impregnation of the polyurethane resin system. The sizing of the fibers will also play a role in determining the proper resin content, as this will directly affect the bonding capabilities of the resin to the individual fibers. Fiber manufacturers have the ability to size the fibers which are used in the composite system to suit the type of resin that is being used as the adhesive material. There were two types of sizing considered during the development process: one which is compatible with epoxy resins (GS) and the other one is compatible with polyurethane resins (GP).

4. Testing Procedures

4.1 Tensile Testing

Tensile testing for strength determination was completed using the ASTM D3039[4] standard. Tensile specimens were created by laying up a composite panel of dimensions 6×12×0.09 (in.) (4 layers of the carbon fiber/fiberglass fabric). A smaller panel of 4×9.5×0.09 (in.) was then cut from this and placed in a tabbing fixture for the application of pull tabs which insure protection from "biting" of the composite by the grips of the 10kips ADMET tensile testing machine (Fig. 1). This prevents premature failure due to the grips damaging the composite structure. The surface of the tabbing material and area of composite where the composite was to be tabbed was roughened with emery paper of fine grit and then cleaned with iso-propanol wipes. A two part epoxy adhesive was to bond tabbing material with composite and a uniform separation distance of 0.025 inch was kept using glass beads. Samples were allowed to cure for 48 hours to insure complete curing of the adhesive. Tensile specimens of 0.5 in. width were cut using a water-jet cutting machine and were insured to have straight fibers and straight cuts in the specimens. Waterjet is also the preferred way to cut the samples as it creates the minimum amount of induced stress on the specimen which could cause premature delamination during tensile testing (see Fig. 2).



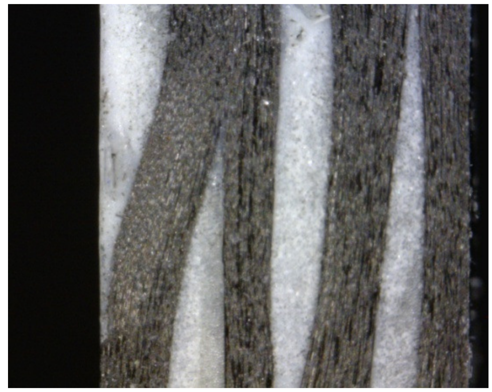
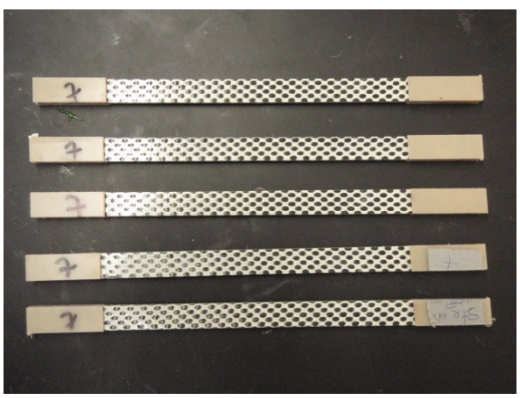


Figure 1 – Tensile Testing Fixture

Figure 2 – Edge of Sample Cut by Waterjet

Each panel yielded 3-5 acceptable coupons per test panel, which insures accurate and repeatable results (see Fig. 3, 4).



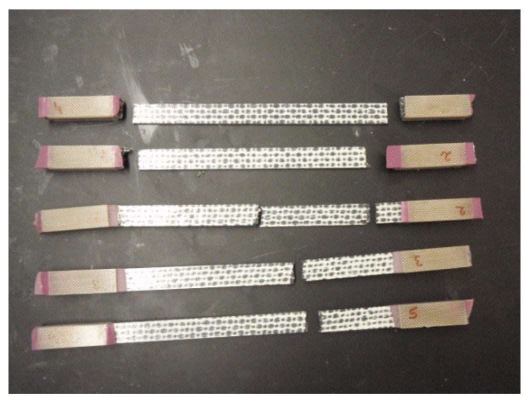


Figure 3 – Tensile Specimens (before)

Figure 4 – Tensile Specimens (after)

After each tensile specimen was pulled, the resulting tensile strength was calculated using the equation [5]:

$$\sigma = {}^{P_{max}}/_{A} \qquad \textbf{Eq. 1}$$

Where:

σ = Tensile Strengh (ksi)
P_{max} = Maximum Load Prior to Failure (lb)
A = Average Cross-sectional Area of Coupon (in^2)

4.2 Burn Testing

Resin content of the tested specimens was obtained by placing 1×1×0.09 (in.) pre-weighed samples in ceramic crucibles, ignited at 1000° F (538° C) for five minutes using a torch. Only ash and fibers remained when the burning ceased. The crucibles were then cooled to room temperature and weighed to the nearest 1.0 mg. Initial and final weights of the samples were measured on a high precision (±0.001g capacity) weight balance AE ADAM PGW 253e. The ignition loss of the specimen was calculated in weight percent as follows and the average of three specimens was taken to obtain the sample average [6].

$$Ignition\ Loss\ (Weight\ \%) = \left[\frac{W_1 - W_2}{W_1}\right] \times 100 \qquad \textbf{Eq. 2}$$

Where:
W_1 = weight of specimen in grams
W_2 = weight of residue in grams

5. Results

5.1 Testing Results

Table 1 shows some initial results of hoop and axial tensile testing with Toray Carbon fiber with GS sizing compatible with epoxy. Hoop strength is typically governed by the tensile strength of fibers, while for axial direction, the specimens fail by crack propagation through the matrix and/or fiber/matrix interface within the composite system[5]. It is observed that 38.6% is optimum resin content for maximum hoop tensile strength. The axial tensile strength in Table 1 is only approximately 6% of the hoop tensile strength.

Direction of Fibers	Tensile Strength (ksi)	Resin Content (%)	Fiber Sizing Type
Hoop (0°)	109	38.6	GS
Hoop (0°)	105	30.5	GS
Hoop (0°)	101	36.7	GS
Hoop (0°)	100	35.2	GS
Axial (90°)	6	38.6	GS
Axial (90°)	6	35.2	GS
Axial (90°)	5	36.7	GS
Axial (90°)	5	30.5	GS
Axial (90°)	4	37.6	GS

Table 1: Tensile Testing per Resin Percentage using Carbon/Glass Fiber/Polyurethane System[7]

Table 2 shows tensile properties of Carbon/glass fiber/Polyurethane system using Carbon fiber from Hexcel Fibers with GP sizing compatible with polyurethane resin. Here the resin content of 33% shows higher tensile strength as well as higher comparable modulus and strain values. The axial tensile strength is approximately 25% of the hoop tensile strength, but has been increased by 400% over the initially tested fabric shown in Table 1.

Direction of Fibers	Tensile Strength (ksi)	Resin Content (%)	Modulus (Msi)	Strain	Fiber Sizing Type
Hoop (0°)*	101.5	33	11.3	1.14	GP
Hoop (0°)	92.6	38	14.3	0.7	GP
Hoop (0°)	89.0	29	12.8	0.83	GP
Axial (90°)*	24.9	33	2.0	1.8	GP
Axial (90°)	16.8	38	1.8	1.56	GP
Axial (90°)	13.8	29	1.7	1.63	GP

** 3rd party testing, Exova OCM, CA*

Table 2: Tensile Testing per Resin Percentage using Carbon/Glass Fiber/Polyurethane system

5.3 Hands-On – "Feel" Testing

During the impregnation process, it was observed that different resin content percentages had different surface textures which gave each one a different "feel." It was noted that a resin content of 29% is too dry, which makes the field application difficult and could cause possible issues with interlaminar shear strength due to lack of resin between layers (see Fig. 5); while 38% is too slippery from the applicator's point of view and could cause possible issues with excess foaming during the curing process which would degrade the strength of the composite due to air pockets getting trapped between layers (see Fig. 6). Therefore the average of these two numbers was taken and this was the starting point at which the bulk of the testing was completed.

Figure 5 – 29%: Appears "Too Dry"

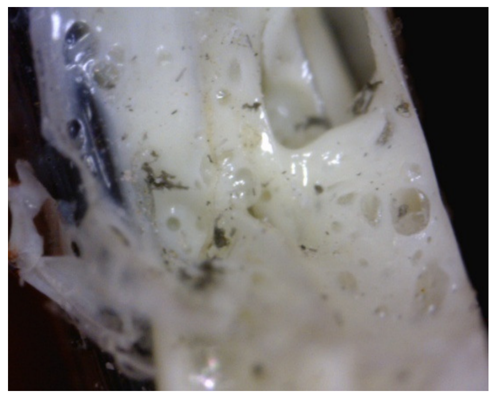


Figure 6 – 38%: Appears "Too Wet"

Figure 7 – 33%: Acceptable Appearance

Figure 8 – 33%: Closer Look

6. Discussion

The manufacturing process and ease of application, in addition to the tensile properties, all play a major role to the determination of the optimum resin content amounts for a nonmetallic, composite repair system when being used for the repair of pipes. During the initial testing phases, the manufacturing process and "feel" for the various percentages were used as a gauge to locate a high and low resin content percentage. These were determined to be at approximately 29% for the low and 38% for the high. Using these values as a beginning range, tensile testing for a variety of resin content percentages within this range was completed.

This first round of testing was completed on a fabric which had minimal fibers in the axial direction. This is the reason for the small tensile strengths reported in Table 1. However, it was decided to change to a different fabric which would give a more substantial strength in the axial direction. This was decided due to the nature of the intended use of this product (i.e., the repair of pipes) as some axial strength is a benefit in the usage of the product. By comparing the benefits of increasing the axial strengths versus the cost of losing some of the hoop strengths, it was decided that the increase of approximately 400% in axial strength was well worth the cost of only 7% loss in hoop strength. This also resulted in a change in the ideal resin content as the initial testing showed the optimum strength at a higher resin content. One would then assume that any change in a composite system, regardless of how small, should always be re-tested and re-qualified to verify validity of the composite system as a whole.

Once this change was made, the testing was completed once again using the three major resin content percentages, which are shown in the graph (Fig. 4) below. The tend of the graph appears to be parabolic in nature and can be assumed that the peak of the curve represents the optimum resin content percent, although, this particular graph lists only the three major values tested, and so may not be 100% accurate representation as to exact strengths. This is because for the purpose of this testing, the manufacturing process and usability of the end product are also considered.

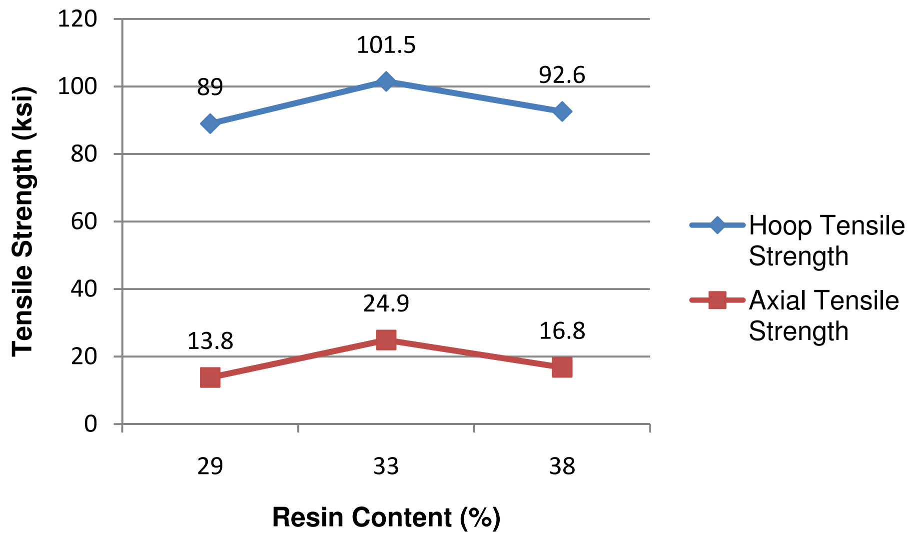


Figure 9 – Tensile Strengths vs. Resin Content

7. Conclusion

After completing the testing to determine optimum resin to fiber percentage, it was determined that the optimum resin content, which achieved the best tensile properties while maintaining ease of application, was 33%. By precisely controlling this aspect of the composite repair system during the manufacturing process, it is possible to guarantee strengths in practical, field applications that match the strengths that are achieved in the laboratory setting. This is a critical aspect for this type of composite repair system and can only be accurately done to such a degree by pre-impregnating the fabric during the manufacturing phase rather than by impregnation onsite. By manufacturing products in this way, it allows the user a great deal of confidence that the strength of each application can be controlled and guaranteed from one wrap to the next.

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