HYDROCARBON PROCESSING



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A compliant solution for repairing corroded acid lines with composite materials

Composite materials have been utilized for the repair of corroded or damaged piping in refineries, chemical plants and other highly aggressive operating and production plants around the world for decades. With advancements in available technologies, along with organized industry standards, this upward trend has not only continued, but has required that composite technologies push the boundaries further.

Because of the demanding conditions found in most facilities, one area of need that has been growing is for an engineered composite repair system (ECRS) that is compliant and effective with highly acidic mediums found within piping systems. Many requests for compatibility information between the pipe contents and the composite repair materials have been fielded from the industry, with sulfuric acid in high concentrations being a routine chemical in question. Due to the increasing demand for ECRSs, new formulations and fibers for composite repair systems were reviewed for feasibility and tested for material properties to determine their effectiveness and performance.

Much research and subsequent testing programs were completed to develop a specialty polymer formulation that could meet the needs of the industry, and meet qualification requirements, when used in conditions that are highly acidic in nature. This article will present the testing results, capabilities and qualifications of this advanced ECRS.

Background. As ECRSs have gained more recognition and acceptance as a reliable and beneficial repair alternative within the refining and chemical processing industry, continued advancements in materials and capabilities have also allowed for a greater range of usage—thanks in part to the development and implementation of an ASME standard (ASME PCC-2 Article 4.1) in 2006, which provides industry a great deal of guidance on material testing, qualification and design for composite repair systems. One such advancement has been in the area of chemical compatibility, specifically for the use of composites to be compatible with sulfuric acid at high concentrations. As shown in FIG. 1, there are many common uses for sulfuric acid across a variety of industries, so the demand for a repair system that can be compatible to this aggressive acid is apparent.

The wide-reaching usage of sulfuric acid and its economic impact are both major reasons why ECRSs are needed. According to Grand View Research, the global sulfuric acid market in 2016 was approximately \$10.1 B, which is forecast to increase to \$13.45 B by 2025.

With such a vast market for this raw material, it is a clear indicator that a composite repair system with compatibility would be highly beneficial. However, in many cases, the issue is not with the chemical overall, but with the concentrations at which it is utilized in facilities. Since composite repair systems are being used routinely in the oil and gas industry, it was only natural that compatibility—especially at higher concentrations—would be one of the main criteria for ECRS development. While there are some composite repair systems available that are compatible with sulfuric acid at lower concentrations, simply due to the nature of most epoxy polymers, the higher concentrations and temperatures above the standard ASTM testing conditions of 24°C (75°F) are routinely encountered in the field.

With this information, knowledge and experience in mind, a program was developed to research and test for a new composite repair system that could withstand submersion in sulfuric acid at a 98% concentration level. Industry partners have worked with the manufacturer to provide valuable insight into the specific concentrations of concern, as well as

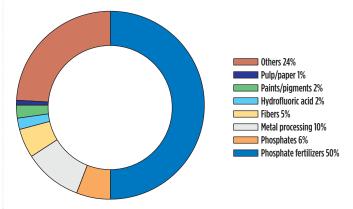


FIG. 1. Common uses of sulfuric acid. Source: The Essential Chemical Industry (online).

the overall, typical operating conditions experienced within their facilities. In addition, information was also provided for other repair alternatives, along with the reasons for developing the compatible composite repair system. These include:

- Mechanical, metallic clamp/patch/enclosure: Reasons for using a compatible composite repair system
 - · Cost—This option can be costly, depending on the full scope of repair.
 - Limitation on size—This option can have limitations based on the size of pipe requiring repair, including its overall weight.
 - · Lead times—This option can be associated with long lead times, depending on the scope of repair.
- Cut and replace: A reason for using a compatible composite repair system includes:
 - Downtime—Time spent out of operation for this option can be extremely costly to the facility due to loss of production.
- Existing composite repair systems: Reasons for using a compatible composite repair system include:
 - · Compatibility—Most existing, commercially available composite repair systems are not compatible (or not proven to be compatible) with sulfuric acid at concentrations above 40% or temperatures above 24°C (75°F).
 - Testing—Most existing, commercially available composite repair systems do not have the physical testing in place to validate claims of compatibility in operating conditions.

Development plan. Commercially available epoxy systems were reviewed for potential inclusion in the testing program; however, despite claims of compatibility, there were other

Gel time (min)
150
137.4
153
154
148.6

TABLE 2. Lap shear test results					
Sample no.	Lap shear strength (psi)				
1	1,150				
2	1,140				
3	950				
4	1,132				
5	1,023				
6	1,307				
7	1,266				
8	1,295				
Average	1,158				

hurdles that prevented them from being considered. The correct selection and combination of the epoxy resin and the hardener components determine the final characteristics and suitability of the system for a given environment, and, as such, a set of criteria was developed for review of formulations.

A newly required epoxy resin formulation was to be designed for use as both a primer and saturant on repairs, and to meet recommended operational conditions. Additionally, the chosen fibers had to be able to withstand the conditions. When a corrosive chemical comes into direct contact with a fiber, if the wrong type and grade of fiber are selected, then the chemical can degrade the fiber and destroy the resin bond, resulting in a significant reduction in structural properties. Due to known reaction levels between sulfuric acid and carbon fibers, a glass fiber was chosen for the new system reinforcement.

Among the primary goals that a development project for the repair system should include are:

- 1. Glass transition temperature of 130°C (266°F) or above
- 2. Gel time longer than 1 hr
- 3. Lap shear strength greater than 580 psi (4 MPa)
- 4. Easy to mix epoxy parts A and B
- 5. Chemical resistance to sulfuric acid up to 98% concentration.

A stringent formulation and testing process was conducted to achieve the targeted properties through various epoxy formulations. Various concentrations of base resins and advanced hardeners were mixed and tested until the desired sulfuric acid resistance, glass transition temperature (T_o), viscosity and gel times were achieved. Once the primary goal properties were obtained, it was necessary to evaluate and adjust percentages of raw materials to meet all the specific performance goals. Various fabric types, architectures and combinations were tested for sulfuric acid resistance to find the final fiber-reinforced plastic (FRP) makeup most compatible for sulfuric acid environments with concentrations up to 98%. Results of the final formulation testing, along with some developmental discoveries of the system's curing protocols, are provided in the following section. Upon completion of the initial research and evaluation of a suitable composite

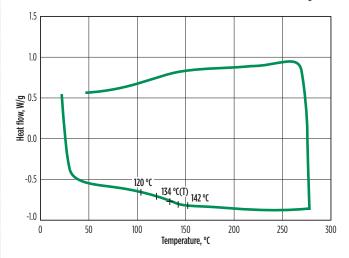


FIG. 2. T_a of epoxy, using DSC.

combination, full qualification testing to the ASME PCC-2 Article 4.1 standard (and, similarly, to the ISO 24817 standard) was completed to fully qualify and characterize the new system and its design properties and capabilities.

Material evaluation. Firstly, a thorough research was conducted to determine the appropriate epoxy formulation to be used that would theoretically perform to the primary goals and expectations for the system. Upon completing this exercise and formulating a sample batch of the determined formula, the next steps were performed to confirm that the required gel time, T_g and lap shear values were achieved with the formula.

Gel time determination. Gel time is the length of time that the two-part epoxy takes to gel after full mixing at a specified temperature. This value can be useful to determine a working time of the system so that installers know the amount of time they need to install the product correctly. The test was performed with an 80-gram mass at 24°C (75°F), using a standard laboratory gel timer for four different batches to achieve and confirm repeatability in the results. The average result for the measured gel time was 149 min, demonstrating that the goal was achieved. TABLE 1 shows the results for the gel time for the different batches.

Lap shear strength determination. Adhesion testing, using a lap shear test, is used for a specific bond strength for the epoxy system to the metallic substrate. The testing was performed according to ASTM D5868-08. Composite plates of the resin and fiber system were bonded to carbon steel plates with the epoxy of the system and, using a universal testing machine, pulled in shear until failure of the adhesion occurred. The type of failure observed was cohesive. TABLE 2 shows the results of lap shear strength for samples cured at 24°C (75°F). The average value of all eight samples tested was 1,158 psi (8 MPa), doubling the required goal.

 T_q determination. The T_g is the temperature range where a thermosetting polymer changes from a hard, rigid (or glasslike) state to a softer, more rubbery state. This is a critical value to know and understand for a composite repair system, as the system must be able to maintain its mechanical properties—consequently, upper temperature limitations should be known to ensure proper function.

The T_g of the polymer being considered was measured using differential scanning calorimetry (DSC) per ASTM E1356. FIG. 2 shows the T_g of the samples that were subjected to a heat-cool-reheat cycle from 20 °C to 260 °C, with a ramp of 10°C/min. The T_g obtained was 134°C (273°F), which demonstrated that the goal for this property was achieved [i.e., 130°C (266°F)].

In addition to these physical properties that were evaluated, the "practical" requirement for ease of use was also considered from the beginning. The requirement was for the components to be easy to mix, which meant that the viscosities should not be such that they would be too high, creating a more difficult mixture and causing difficulty in saturating the

fiber. There was not a specific target set, but an upper limit of 50,000 centipoise (cps) was the expected maximum value. Upon mixing of the epoxy, the final viscosity was measured to be approximately 25,000 cps, indicating a viscosity that could be successfully implemented within the system.

Once each of these primary goals was achieved, the next step was to test for compatibility with the 98% sulfuric acid solution.

CHEMICAL COMPATIBILITY TESTING **FOR 98% SULFURIC ACID**

Evaluating the components. Since it is paramount to the system that the polymer can resist changes in its physical properties when exposed to 98% sulfuric acid, this was the subject of the most critical testing. It is important to verify chemical compatibility of the material to ensure that the composite system can retain its mechanical and physical properties after exposure to reagents. Each component of the composite system (the epoxy and the fiber) was first tested individually, then together as the composite system. All specimens were immersed in suitable containers with a 98% sulfuric acid solution.

Different fiber types were immersed in a solution of 98% sulfuric acid at 24°C (75°F) to determine the best fit for use within the composite system. Each of the fiber samples was fully immersed in the 98% sulfuric acid. An examination of each was conducted every 24 hr while immersed. Chemical resistance of the polymer matrix system (a two-part epoxy formulation) was evaluated by measuring change in weight, appearance and Shore D hardness for pure epoxy per ASTM D543-95. After each of the individual components was thoroughly tested and deemed suitable, the full composite system was then evaluated with similar methods of physical property evaluation and by mechanical testing of the tensile properties of test coupons per ASTM D3039.

Creating the test samples. For the testing of fiber, a converted and representative "dry" fabric was tested by cutting the fabric into 6-in. × 6-in. panels. These panels were then submerged and fully immersed into the solution and monitored daily for changes. Fabrics were of various architectures based on commercial availability at the time of testing. The weave style should not influence the compatibility with the medium being tested.

For the epoxy polymer, rectangular-shaped coupons were prepared as neat epoxy bars with approximate dimensions of 76.2 mm \times 25.4 mm \times 6.4 mm (3 in. \times 1 in. \times 0.25 in.) length × width × thickness. The epoxy coupons were cured at 24°C (75°F) for 7 d before being immersed in the solution of 98% sulfuric acid for periods of 7 d and 30 d at the same temperature that was used to cure.

Finally, composite panels of 30.5 cm × 15.25 cm (12 in. × 6 in.) were also prepared with four layers (thickness) of the chosen fiber and the epoxy resin developed for this system. From these panels, tensile coupons were cut (after time spent immersed in the solution) to be tested to determine if any change in mechanical properties occurred after the chemical



FIG. 3. Epoxy before immersion (left) and after 30 d of immersion (right).

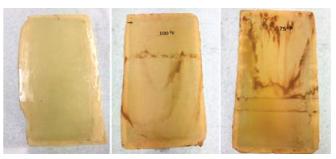


FIG. 4. Composite panel before immersion (left), after 30 d of immersion at a 38°C (100°F) cure temperature (middle) and after 30 d of immersion at a 24°C (75°F) cure temperature (right).

soak. Panels were post-cured at 38°C (100°F), immersed in the chemical, and then cut into coupon panels for tensile testing.

Results of initial testing. Results of the dry fiber testing indicated only two potential candidates to be used within the final composite system (TABLE 3). Based on these results (along with literature research, economic considerations and manufacturing capabilities), a proprietary, specialty glass fiber—which was developed for use in acidic/corrosive environments—was selected for use within the system.

The results of the neat epoxy coupon samples for this system indicated that the compatibility between the epoxy polymer and the 98% sulfuric acid was excellent (TABLE 4). This rating is from best practice standards for evaluating the resistance of plastics to chemical reagents based on protocol considered by the ASTM D543-95 standard. Resistance ratings were assigned as follows:

- 0%–15% change in properties = Excellent (E)
- 16%–30% change in properties = Good (G)
- 31%–50% change in properties = Acceptable (A)
- > 50% change in properties = Not recommended (NR).

A view of the coupon sample before immersion and after 30 d is shown in FIG. 3.

For the composite panel test, panels cured at various temperatures and at different immersion times were also evaluated. This allowed for a review of the effect of cure temperature on both short- and long-term immersion conditions. Results for the different test panels and parameters are shown in TA-

TABLE 3. Dry fiber immersion results						
Fabric weave	Appearance after immersion in 98% sulfuric acid					
0°/90°	Fibers broke down					
stitched	after 24 hr					
0°/90°	Fibers broke down					
plain weave	after 24 hr					
0°/90°	Fibers broke down					
stitched	after 5 d					
0°/90°	Fibers broke down					
plain weave	after 5 d					
0°/90° plain weave	No negative results after 7 d					
0°/90°	No negative results					
plain weave	after 12 d					
	Fabric weave 0°/90° stitched 0°/90° plain weave 0°/90° stitched 0°/90° plain weave 0°/90° plain weave 0°/90°					

TABLE 4. Neat epoxy immersion results							
Time immersed, d	Hardness change, %	Weight change, %	Surface condition	Resistance rating			
7	1.3	-2.8	No change	E			
30	1.2	-3.5	Slightly discolored	E			

BLE 5. A view of the composite panel before immersion, after 30 d of immersion at a 38°C (100°F) cure temperature and after 30 d of immersion at a 24°C (75°F) cure temperature is shown in FIG. 4. A view of the composite panels after immersion for 1,000 hr, and then cured at 38°C (100°F) for 17 hr and cured for 6 hr at 100°C (212°F), is shown in FIG. 5.

The analysis of the change in appearance, weight, hardness and tensile properties reflected "excellent" chemical resistance between 98% sulfuric acid and the composite system when allowed to cure for 7 d at both temperature levels. To obtain the best properties in the system, this cure schedule may be completed. It was noted in the 1,000-hr test that the panel cured at the lower temperature, while performing to a 'good" rating, did not perform as well as the panel cured at the higher temperature level, with regard to color retention (although mechanical properties were within the parameters of "excellent" rating), confirming that the level of cure of the epoxy polymer will still dictate the overall performance in long-term usage, and that the higher level of cure achieved, the better the system will perform. If the polymer system is fully cured, which is based on time and temperature, then it will meet the requirements, but may take longer to do so.

However, due to requirements of how the system would be used in a field environment, the recommended method would be to post-cure the system at temperatures between 38°C (100°F) and 134°C (273°F), which is the established $T_{\rm g}$ of the epoxy system to speed the full curing of the system to a more practical timeline. To characterize how this can be achieved with target temperatures and time, a study of the cure schedule at various temperatures was completed.

Determining the cure schedule options. Two methods for evaluating levels of cure were used to determine the required curing time and temperature of the composite system: Shore D hardness studies, and Fourier-transform infrared

TABLE 5. Composite panel immersion results						
Time immersed	Time at temperature curing	Hardness change, %	Weight change, %	Modulus change, %	Surface condition	Resistance rating
7 d	7 d at 38°C (100°F)	0.2	-4.9	-0.21	Slightly discolored	Е
7 d	7 d at 24°C (75°F)	0.8	-5.3	-0.8	Discolored	Е
1,000 hr	17 hr at 38°C (100°F)	-6.2	10.1	-2.7	Color changed	G
1,000 hr	6 hr at 100°C (212°F)	-0.4	1.5	-0.6	Slightly darkened	Е



FIG. 5. Composite panels after 1.000-hr of immersion and then cured at 38°C (100°F) for 17 hr (left) and cured at 100°C (212°F) for 6 hr (right).

(FTIR) spectroscopy tests to measure percent of reduction in epoxy peak. The hardness of a composite system is a direct result of the resin matrix type and how well it is cured. The more rigid the resin, the higher the level of hardness achieved—whereas, the more flexible laminate will have a lower hardness level. Although hardness increases with degree of cure, this method is not enough to fully analyze the cross-linking reaction. For example, it is possible for an epoxy to appear solid, but to have not cross-linked to a degree that it will successfully resist the harsh chemical environment. Thus, the Shore D hardness study was complemented with the FTIR test to overlay the values and find the minimum recommended cure schedule for the ECRS.

In the FTIR results, the presence of the epoxy group on the infrared (IR) spectra is proven from the presence of a strong band at 912 cm⁻¹. Once the epoxy is fully cured, this peak should disappear, eliminating the area under the curve. It was demonstrated by the previous tests that, in these conditions, the system is chemically resistant to 98% sulfuric acid (TABLE 5). To ensure a fully cross-linked system (i.e., a fully cured system), the ultimate T_o must be reached, which is achieved by curing the epoxy at the measured T_g of 134°C (273°F). Note that successful usage may not require full cross-linking, but only a specific percentage. While this study is not fully vetted in this article, it should be considered for the practical application capacity of a system. This phenomenon can be seen in FIG. 6, where each line represents the FTIR spectroscopy of a different cure temperature. The top line represents a specimen cured at 100°C (212°F) for 19 hr, where there is no epoxy peak at 912cm⁻¹ because the resin is fully cured. The

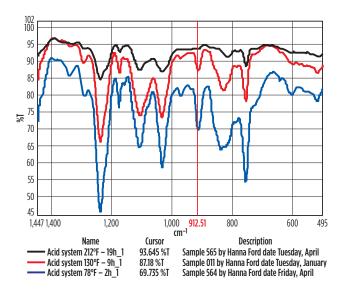


FIG. 6. FTIR spectroscopy of epoxy cured at different temperatures.

red line has a small peak at 912cm⁻¹, which corresponds to a specimen partially cured at 55°C (130°F) for 9 hr. Finally, the blue line was cured at 24°C (75°F) for only 2 hr; the depth of the epoxy peak means that there is not yet a crosslinking reaction between the epoxy and amine, indicating that the sample is not fully cured. The area under the epoxy peak curve is what is considered for calculation purposes—the smaller it is, the more cured the sample is until it disappears, indicating a fully cured resin.

If this is not possible in the field of use conditions that this ECRS will be subjected to, then a minimum cure must be known. Since it was determined that chemical compatibility was successful at the previous time and temperature values, these were used as the baseline to plot expected cure curves for the system. TABLE 6 displays the correlation of time with Shore D hardness values and percent reduction in FTIR peak values at three of the primarily reviewed temperatures. FIGS. 7 and 8 show the change in hardness and the FTIR peak, respectively, over time. As can be seen within the figures, the previous statement regarding hardness being only one piece of the puzzle for cure measurement is shown to be true. Specifically, the samples cured at 24°C (75°F) reached their full hardness in 2 d or less, while the associated FTIR peak measurements took up to 7 d to reach the minimum levels to be considered to have a resistance to the 98% sulfuric acid.

Based on this information, it can be determined that specific curing protocols should be used for this system when it is going to be used with 98% sulfuric acid to ensure adequate resistance. The graphs can provide some ideas and indica-

Cure temp = 24°C (75°F)			Cure temp = 38°C (100°F)			Cure temp = 55°C (130°F)		
Time, hr	Shore D hardness	Reduction of FTIR peak, %	Time, hr	Shore D hardness	Reduction of FTIR peak, %	Time, hr	Shore D hardness	Reduction of FTIR peak, %
1	7.4	0	1	11	0	1	13	2
3	24	-	3	29	18	3	36	22
5	39	15	4	50	21	5	69	53
7	48	-	6	62	27	6	73	55
16	55	-	8	67	36	7	75	56
24	61	22	10	67	41	8	76	62
29	65	-	12	72	45	9	82	67
30	68	30	13	76	46			
31	71	-	14	76	46			
48	80	-	15	76	47			
168	85	57	16	77	49			
			17	78	56			

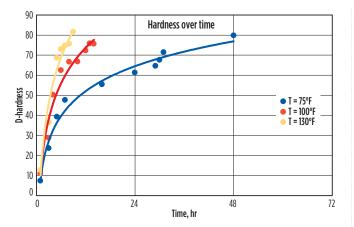


FIG. 7. Graph of hardness change over time.

tions of how to monitor and ensure that this cure level has been met when utilized in the field for repairs.

Qualifying the final ECRS. Upon completing the validation testing, and successfully characterizing the requirements and meeting the primary goals set forth, the last phase is to complete the full qualification testing to the ASME PCC-2 Article 4.1 and ISO 24817 standards for ECRSs. While this article will not go into the details of each test, the summary of all the completed qualification tests and achieved values are provided in TABLE 7.

Discussion. This article provides a detailed insight into the process and steps followed for the development of a system that is resistant to sulfuric acid in concentrations of 98% at ASTM conditions of 24°C (75°F). The main objective of this project was to create an ECRS that could be used as a valid and qualified pipe repair option for pipe systems operating with 98% sulfuric acid, which has been achieved. Numerous discoveries were made along the way—the most important of which was the effect of cure time and temperature on the resistance of the system to the chemical solution.

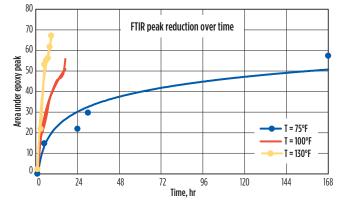


FIG. 8. Graph of FTIR peak reduction over time.

Upon full completion of the development and validation testing of the system, the full qualification testing was completed on the system. In addition, once completed with the initial validation, subsequent chemical compatibility testing programs were started to widen the scope of chemical solutions that could be used compatibly with this system—regarding both chemical compatibility and temperature ranges.

Takeaway. ECRSs are being utilized as a routine repair option for many process piping facilities, from refineries to fertilizer plants to steel mills. Because of the harsh conditions found in many of these facilities, advanced and thoroughly tested materials are required to be used successfully. Advancing technology requires commitment and persistence, as well as good cooperation between industry and the manufacturer. By fully characterizing and testing the composite materials across a spectrum of temperatures and other environmental conditions, users can be confident in the repair system's ability to successfully function as desired. The development of this new system is considered a breakthrough for its compatibility with sulfuric acid at 98% concentration, as it is the first composite repair system fully tested and proven to be resistant at such a level.

Property	Test methods	Results
Per ply thickness	Determined from the ASTM 3039 tensile tests	0.46 mm (0.018 in.)
Tensile strength (circumferential direction)	ISO 537-1, ISO 527-2 or ASTMD 3039	631.6 MPa (91.6 ksi)
Tensile modulus (circumferential direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	37.7 GPa (5.5 Msi)
Tensile strain to failure (circumferential direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	1.8%
Poisson's ratio (circumferential direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	0.11
Tensile strength (axial direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	158.6 MPa (23 ksi)
Tensile modulus (axial direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	16.1 GPa (2.3 Msi)
Tensile strain to failure (axial direction)	ISO 527-1, ISO 527-2 or ASTMD 3039	1.52%
Shear modulus of polymer	ASTM D5379	0.96 GPa (139 ksi)
Shear strength of polymer	ASTM D5379	32.9 MPa (4.77 ksi)
Shore D hardness	ISO 868, ASTM D 2583 (ASTM D2240-04)	87
T _g of saturant	ASTM D6604	138°C (280°F)
Thermal expansion coefficient (circumferential direction)	ISO 11359-2, ASTM E831	7.1 ppm/°C (3.9 ppm/°F)
Thermal expansion coefficient (axial direction)	ISO 11359-2, ASTM E832	18.9 ppm/°C (10.5 ppm/°F)
Energy release rate	ASTM D1599	543 J/m2 (3.1 in.*lb/in.2)
Impact performance	ASTM G14 Modified, ASTM D1599	Passed
Short-term spool test	ASME-PCC 2	Passed for 314 bar (4,524 psi)
Lap shear strength (lap adhesion)	EN 1465, ASTM D3165 (ASTM D5868)	Short term: 7.98 MPa (1,158 psi)
Lap shear adhesion strength (1,000 hr of immersion in water)	ASTM D5868	Long-term 90°C (194°F) water: 5.23 MPa (759 psi)
Lap shear adhesion strength (1,000 hr of immersion in air)	ASTM D5868	Long-term 100°C (212°F) air: 7.47 MPa (1,083 psi)
Compressive modulus (filler)	ASTM D695	0.24 Msi

NOTES

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MATT GREEN is the Vice President of Technical Services at CSNRI. He leads the company's global technical department for the composites business unit, which encompasses engineering, training and education. Since 2006, he has presented training and education seminars around the world on non-metallic composite repair systems and their applications on pipelines and piping networks. As a member

of the Non-Metallic Composite Repair Subcommittee for ASME PCC-2 Articles 4.1-4.3, which writes and edits the ASME standards for composite repair systems related to the repair of pipelines and pipework, Mr. Green is active in shaping the industry and its future. He has published numerous papers, and is a regular contributor of technical articles for industry-related publications. He earned a BS degree in engineering physics from Northeastern State University in Oklahoma.



RUTH RODRIGUEZ is the Research and Development Project Leader at CSNRI. She earned a Bch degree in chemical engineering and an MS degree in business administration from Keiser University, Florida. She has deep experience in product development, bringing new products to the market and developing epoxy resins for composite repair systems. During the past decade, she has been focused not only on developing

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