

Secondary Bond Strength of FRP to a Variety of Substrates

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Abstract

One of the most frequent ways in which corrosion-resistant FRP equipment has been known to fail is at secondary bonding sites. The use of primer systems is one commonly accepted method of reducing the incidence of secondary bond failure. Polyisocyanate primer and an elastomer-modified vinyl ester primer with 20% elongation were found to offer improved secondary bond strength compared to laminates applied to prepared but unprimed surfaces. In addition, unprimed secondary laminates based on urethane-modified vinyl ester resin demonstrated significantly improved bond strength compared to bisphenol-epoxy vinyl ester resin laminates on PVC, CPVC and ABS substrates.

Introduction

Secondary bonding is often used in the manufacture and repair of corrosion-resistant FRP structures, and to apply a rigidizing layer of FRP to formed thermoplastics. While secondary bonding greatly expands the versatility of FRP, it has been implicated as a major source of corrosion-resistant FRP equipment failure¹, and requires that special procedures be used to ensure successful bond formation. The importance of secondary bond strength has been recognized in the industry-leading ASME RTP-1 standard for corrosion-resistant FRP equipment, which stipulates that technicians who apply secondary bonds must be tested and prequalified for performing this task, and further requires that these tests be repeated every 3 years for laminators to retain their qualification².

One technique for improving secondary bond strength that is frequently used involves application of a primer. Given that many of the corrosive media to which FRP can be exposed will permeate the laminate to some degree, it is necessary for the primer to be somewhat corrosion-resistant in addition to its primary role of improving bond strength. Two of the most popular types of primer in general use are elastomer-modified vinyl ester resins and a two-component polyisocyanate system (ATPRIME® 2). This paper presents results of a study designed to characterize the bond strength to several FRP and thermoplastic substrates formed by a two-component polyisocyanate primer and two elastomer-modified vinyl ester resin primers, one with 10% elongation (10%MVER, DION VER® 9084), and another further modified to provide 20% elongation (20%MVER, DION VER® 9085). These bond strengths are compared with those formed by laminates based on bisphenol-epoxy vinyl ester (VER, DION VER® 9100) and urethane-modified vinyl ester (UVER, ATLAC® 580-05A) without the use of primers. FRP substrates using VER, UVER and novolac vinyl ester resin (NEVER, DION VER® 9480) were evaluated. In addition, non-FRP thermoplastic substrates comprised of PVC, CPVC, and ABS were tested.

Background

Secondary bonding refers to the bond formed between a freshly applied FRP laminate and a substrate that does not have an air-inhibited surface comprised of a similar fiberglass-reinforced thermosetting resin. The substrate may be a dissimilar material such as steel, concrete or a thermoplastic, or it may be FRP that is fully cured and cannot form a primary bond with a subsequently applied laminate. The significance of air inhibition is that this process yields an FRP surface that is substantially uncured at the surface, leaving residual double bonds that can react with newly applied, catalyzed resin, thus forming a directly crosslinked, continuous material.

In the absence of available double bonds in the substrate, there are still several types of chemical interaction that can facilitate development of a secondary bond. Interactions between acidic and basic sites on the substrate surface, hydrogen bonding, interactions with surface hydration of ionic solids, bonding between π bonds and transition metals, and covalent bonding with reactive species such as hydroxyl or carboxyl groups present in the substrate are some of the chemical mechanisms that can facilitate development of a strong secondary bond³. Furthermore, if the surface to which bonding is desired is roughened, a mechanical bond can be formed as well.

Proper preparation of a surface for secondary bonding is crucial, both to maximize chemical and mechanical bonding and to eliminate factors that may inhibit bonding. Preparation typically involves grinding or machining FRP substrates down to a clean, roughened state, preferably with glass fibers exposed to further facilitate bonding, and wiping the surface with styrene monomer. Wiping with styrene is useful for removing residual dust off of the FRP, and may facilitate penetration of the surface by the resin or primer that is applied to it⁴. It is crucial to use clean styrene for this, since any contamination in the styrene will be evenly deposited over the substrate and may function as a release agent. Non-FRP substrates are also rough-

ened prior to bonding to remove surface contamination and increase the surface area in the region to which the bond will be applied. Roughening the surface improves the ability to form a mechanical bond and also increases the area over which chemical bonding can occur.

Primers function by creating a strong bond with the substrate while providing a new surface that can form a primary bond with freshly applied FRP. Elastomer-modified vinyl ester resins contain hydroxyl groups and additional carboxyl functionality (from the elastomer modification) which may participate in polar interactions with the substrate. They also provide additional toughness at the interface between substrate and laminate. This can facilitate mechanical bonding by taking up stresses formed at the interface. Given that they are applied as a thin film, elastomer-modified vinyl ester primers provide an air-inhibited surface to which a subsequent laminate can readily form a primary bond.

Two-component polyisocyanate primer uses a totally different mechanism for priming a surface. Isocyanate groups are known to react with moisture to form highly polar, chain-extended molecules. They can also react directly with hydroxyl and carboxyl groups, forming stable covalent bonds. Many substrates, including various cured resins, contain carboxyl and hydroxyl functionalities that are available for reaction. Polar groups in the chain-extended polyisocyanate can also bond with polar sites at the substrate surface. In these ways, chemical as well as mechanical bonding can occur with the substrate⁴. The polyisocyanate primer system evaluated in this study includes unsaturation that does not participate in the primer curing mechanism, and is therefore available for bonding with the subsequently applied FRP laminate.

Test Methods

Forces can act on a secondary bond both in-plane with the bond and perpendicular to the bond to produce bond failure. In-plane forces can be both tensile and compressive. Attempts were made to measure all components of secondary bond strength. In-plane strength was measured using ASTM D 3846-79 Standard Test Method for In-Plane Shear Strength of Reinforced Plastics. This method stipulates that two laminates, joined with a secondary bond, be cut into test strips and notched on either side. These notches allow a tensile or compressive force to be applied to the test strip in a manner that concentrates shear forces on the secondary bond. Failure occurs at the secondary bond when bond strength is less than the burst strength of the laminate.

Laminates used for in-plane shear testing were comprised of four plies of 1.5 oz mat and a 30% resin content for both substrate and secondary laminates. Resins were adjusted to a 20-minute gel time, and vinyl ester primers used a 10-minute gel time. Polyisocyanate primer was used according to the manufacturers instructions⁵. For testing with thermoplastic substrates, laminate thickness was increased to five plies. This was done in order to maintain similar material thickness on both sides of the secondary bond. Substrate FRP laminates were made with a non-air exposed mylar surface, post-cured at 100°C for four hours, and roughened with #300 grit sandpaper prior to secondary bonding. A 6-mil film of primer was then

drawn down onto the surface and allowed to cure for 16-24 hours. After applying the secondary laminate and allowing it to cure at room temperature, all test samples were conditioned at 40°C for 16 hours prior to testing. Secondary laminates using VER and UVER were tested without primer. Given that the primers tested all provide direct crosslinking to secondary laminates, VER resin was used on all laminates applied onto primers to facilitate comparison.

Bond strength perpendicular to the laminate was measured by drawing down a 6-mil film of primer onto a surface prepared substrate and allowing it to cure for 16 hours. At this point, a metal dolly was affixed to the primer using a two-component epoxy adhesive*. The adhesive was allowed to set for 24 hours, after which the force required to vertically lift the dolly off of the laminate was measured with an Elcometer™ adhesion tester.

*Reichhold 37-140 epoxy, 37-622 hardener

Substrate laminates used for perpendicular bond strength tests had a resin-rich surface made using one ply of C-veil. Test surfaces were prepared on Mylar™ film to create a fully-cured surface, were post-cured for four hours at 100°C prior to priming, and conditioned at 40°C for 16 hours prior to testing. Surfaces were roughened with #300 grit sandpaper prior to secondary bonding. VER, NVER and ABS substrates were tested by this method.

Observations

Results of in-plane tensile shear strength testing is listed in Table #1, while compressive strength results are listed in Table #2. Perpendicular bond strengths are shown in Table #3.

Both test methods yielded useful information, but they also have their limitations. In-plane shear strength is useful up to the point of laminate failure, at which time it simply indicates that the bond between resin and glass has failed. In tension, the test specimen has a tendency to distort, twisting the specimen and thus focusing stress on the edges of the laminate and secondary bond. In compression, much higher yield strength was observed since less distortion occurs. The distortion that does occur tends to force the laminates together, thus imposing additional stress on the substrate and secondary laminate, and biasing test results toward substrate/laminate failure. Perpendicular bond strength measurement suffers from a similar phenomena. Vertical force causes the substrate to bow upwards, again focusing stress, this time on the circumference of the adhesion tester dolly. Once a crack has been initiated, it immediately propagates, yielding a result that is difficult to quantitatively interpret.

Discussion

The mode of failure clearly must be factored into any conclusions derived from this study. Given the stress concentration effect of both test methods, and the fact that crack propagation energy is far less than that required for crack initiation, limited

quantitative and comparative conclusions can be drawn from tests ending in substrate or laminate failure. In these cases, secondary bond strength can be considered to be greater than that obtained from the test result, but cannot be assumed to be greater than the cohesive strength of the substrate or laminate. Where two or more tests end in substrate and/or laminate failure, it is not possible to derive conclusions as to the relative secondary bond strengths. Despite these limitations, useful data can be extracted from the test results, and is discussed below.

FRP Substrates

UVER provided interesting test results, both when used as a substrate and a secondary laminate. The best in-plane shear results on a UVER substrate, both in tension and compression, were obtained when 20%MVER primer was used, with laminate fracture noted in both cases. Applying a UVER secondary laminate with no primer yielded results that were equal to or better than the other primers tested. The 20%MVER significantly outperformed 10%MVER, indicating that elastomer modification improved bonding to this substrate. Where no primer was used, UVER significantly outperformed VER in tensile, though not compressive testing.

VER substrates demonstrated a different response to secondary bonding. Laminate rupture was the predominant mode of failure in in-plane shear testing, with only the two MVERs producing primer failure. While this would appear to indicate that either no primer or polyisocyanate primer would be the best approach, perpendicular bond testing showed a significant improvement in bond strength as elastomer modification was increased, and recorded a bond strength with polyisocyanate primer that was similar to 20%MVER. Both 20%MVER and polyisocyanate primer produced significantly greater bond strength than unprimed VER in perpendicular bond testing. Overall, the polyisocyanate primer appears to be the best choice for VER laminate substrates.

NVER substrates responded to secondary bond testing in a manner more similar to VER than UVER substrates. Interestingly, 10%MVER results, while nominally the lowest strength, all involved substrate/laminate failure and hence cannot be considered to be inferior to the other systems. In perpendicular bond testing a significant correlation between increasing elastomer modification and improved bond strength was noted. Perpendicular bond strength was greatest with 20%MVER and polyisocyanate primers.

Thermoplastic Substrates

In-plane shear testing was more effective when thermoplastic substrates were evaluated. All of the materials tested are considered to be difficult to create a secondary bond to, with PVC overall forming the weakest secondary bonds. When no primer was used, UVER provided roughly twice the in-plane shear strength of VER, and was the equal of all of the primed samples except the one that used 20%MVER. Elastomer modification demonstrated a significant benefit, with 10%MVER outperforming VER and 20%MVER providing the best overall bond strength.

In-plane shear testing of CPVC substrates demonstrated an even more significant difference between the two unprimed vinyl ester laminates. When VER was used, the secondary bond was not able to withstand sample preparation, and secondary bond strength was therefore below detectable limits. UVER, on the other hand, provided substantial bond strength. Inferences related to the performance of the MVER and polyisocyanate primers are more difficult to draw, given the extent of substrate failure in tensile testing and the standard deviation of the compressive test results. Nevertheless, each of the primers significantly outperformed UVER and provided a bond strength that obviously exceeds VER.

The ABS substrate continued some of the trends established with the other thermoplastics, but with notable differences. Once again, in-plane shear testing demonstrated that UVER significantly outperformed VER where no primer was used, and increased levels of elastomer modification appear to have improved the bonding characteristics of MVER resin. Polyisocyanate primer also bonds well to this substrate. While substrate failure in the polyisocyanate primed samples resulted in a low compressive shear result, perpendicular bond strength tests demonstrated impressive performance with polyisocyanate primer as well as a direct correlation between elastomer content and MVER bonding performance.

Conclusions

Evaluation of secondary bond strength remains a challenging issue, particularly for FRP substrates. The various forces applied to a secondary bond, such as thermal cycling and impact, and the tendency of stress concentrations to skew applied forces towards laminate and/or substrate failure, make it difficult if not impossible to realistically quantify bonding strength. Furthermore, exposure of FRP to aggressive chemical environments may alter secondary bonding in a way that may impact the relative utility of a primed versus unprimed bonding system. Substantial anecdotal evidence suggests that both polyisocyanate and elastomer-modified vinyl ester primers significantly improve secondary bond strength; by and large these results appear to confirm this.

Increased levels of elastomer modification did correlate with improved bond strength in vinyl ester primers. Overall the 20%MVER (DION VER[®] 9085) and polyisocyanate (ATPRIME[®] 2) primers provided the best bond strength.

The performance of UVER (ATLAC[®] 580-05A) compared to VER (DION VER[®] 9100) in thermoplastic bonding suggests that dual laminate equipment may be enhanced by use of UVER, at least insofar as unprimed CPVC, PVC and ABS substrates are concerned. Further secondary bond strength improvement can also be realized by the use of one of the primer systems considered in this study.

References

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Table #1

In-Plane Shear Tensile Test Results

Substrate	UVER Laminate			VER Laminate			10%MVER Primer			20%MVER Primer			Polyisocyanate Primer		
	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail
UVER	860	47.6	i,l	565	31.7	i	468	92.2	pr	874	53.7	l	781	27.1	pr
VER	1140	68.9	l	990	59.7	l	883	108	pr,l	937	125	pr	1036	55.6	l
NVER	891	30.5	l	928	38	l	845	117	pr,l	932	132	pr	1139	57.9	l
PVC	356	38	i	184	21	i	217	43.6	pr	422	36.4	t	317	101	pr
CPVC	601	154	i	771	31	t,pr	591	99.7	t	980	132				pr,l
ABS	246	62	i	109	9.9	i	760	59.8	l	888	15.3	l	894	22	l,t

Failure Mode

i = failure at interface

pr = primer failure

l = laminate failure

Table #2

In-Plane Shear Compressive Test Results

Substrate	UVER Laminate			VER Laminate			10%MVER Primer			20%MVER Primer			Polyisocyanate Primer		
	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail	Strength	S Dev	Fail
UVER	4870	504	i	4500	413	i	3640	1180	pr	5810	878	pr,l	5020	227	pr
VER	6580	386	l	6020	335	l	5190	671	pr	5360	1020	pr	7200	1540	l
NVER	5900	945	l	7930	1420	pr,l	5300	484	l	6100	930	pr,l	5850	323	l
PVC	2840	1023	i	1220	402	i	2560	710	pr	4310	1220	pr	2460	642	pr
CPVC	2310	230	i	0			3990	457	pr	4850	1090	pr	4100	221	pr
ABS	1700	254	i	972	248	i	3380	276	pr	3920	442	pr	2000	73.8	t

Failure Mode

i = failure at interface

pr = primer failure

l = laminate failure

Table #3

Elcometer Adhesion Test Results

Substrate	VER Strength	S. Dev.	Primer 10%MVR Strength	S. Dev.	20%MVER Strength	S. Dev.	Polyisocyanate Strength	S. Dev.
VER	220	58	300	110	350	62	370	52
NVER	160	33	210	29	280	41	310	39
ABS	120	27	170	22	420	280	820	160