

## Toughened Polymer Coating Technology (PCT)

by

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### Abstract

Cracks in the exterior coating occur in a relatively small fraction of gel coated FRP parts. However, when exterior coating cracks do occur they can lead to significant rework and warranty costs for the FRP parts manufacturer. Cracking in the exterior coating of FRP parts is related to movement due to stresses on the laminate. The sources and reasons for laminate stresses and movement are complex and can involve every element of a FRP parts life cycle from design, production and usage. Numerous laboratory test methods have been developed to evaluate properties of materials and FRP parts that are believed to be related to cracking.

New polymer coating and barrier technologies are designed to be more resistant to cracking when laminates are stressed and movement occurs. These new technologies have superior toughness and impact resistance in comparison to industry standard gel coats and barrier coats. These new coatings are MACT compliant for both marine market applications, as well as the stricter reinforced market applications (less than 30% HAPS). The new coating technologies will require some process modifications, but are applied similarly to conventional gel and barrier coats. In addition to crack resistance these new coating and barrier technologies offer a number of other benefits including gloss retention of the coating after weathering, water resistance, and wear resistance of the coating.

### Types and Sources of Cracking

Cracks in the exterior coating occur in a relatively small fraction of gel coated FRP parts. These surface cracks do not affect the structural integrity of the FRP

part. The exterior coating of a FRP part is a thin cosmetic shell that is not structural and is not accounted for in composites strength calculations. The exterior coating of a FRP part does add aesthetic qualities important to the consumer and also protects the underlying laminate. When cracks in the exterior surface coating do occur, they can lead to significant rework prior to sale as well as post-sale consumer dissatisfaction and warranty costs for the FRP parts manufacturer.

Exterior coating cracks are due to stress induced movement of the laminate. The types of cracking and sources of stresses that occur in FRP parts have been previously described in the literature, including references 1 to 4. A summary is provided.

One of most common types of exterior coating cracking seen in FRP parts is linear cracking. These types of cracks are generally caused by flexural stress. Linear cracks can occur during manufacture of FRP parts as well as after the parts are in service. One of the most common causes of linear cracks is over-application of gel coat. Gel coats, like all coatings, are designed to be used in a narrow thickness range. If the gel coat is applied too thin, it could cure poorly making it more susceptible to cracking. Conversely a thick un-reinforced layer at the surface of the part is more prone to cracking when stressed than a film of appropriate thickness.

Part design is also a key factor. Loading scenarios throughout the part's lifecycle must be accounted for in the design of a FRP part. For example, the process of de-molding and in-process handling of a glass fiber part (See Figure 1 and 2.) can cause different and higher stresses than will occur when the part is put into service. A glass fiber part without its structural support elements (ribs, stiffeners, etc.) is extremely fragile. Even small mishaps in handling these parts can result in enough stress to cause laminate movement and initiate cracks.

Properly designed cradling and supports are critical when transporting all types of glass fiber composite products. For example, boat hulls are designed to be supported by water on all sides not by two fork lift tongues. Storage tanks are designed to carry a static load not swing from a crane. It is relatively easy to over-stress a composite part during shipping. Designs that do not consider all of the possible stresses are likely to produce cracks.

Part complexity is another design issue that can be a source of cracking. While glass fiber fabrication does offer the versatility to combine many complicated shapes into one larger part, there are practical limits to these unitized designs. Complex part shapes are more difficult for gel coat application (deep draws are hard to gel coat with a consistent thickness), lamination and especially in de-mold.

Under-cure of properly applied coatings and resins in a glass fiber composite can lead to cracking. The mechanical strength of a glass fiber composite laminate builds with time as the thermosetting polymers in the resins, gel coats, adhesives, cores, and putties cure. If the cure is slowed by either low temperatures or incorrect catalyst levels, or if the part is de-molded too quickly, cracking can occur because the “green strength” of the part is not sufficient to prevent the part from moving during the stress of de-molding.

Glass fiber reinforcements add strength and stiffness to composite parts. Cracks can occur if the glass fiber content is too low, too high or inconsistent, or if the glass fiber reinforcements are oriented incorrectly.

Assembly of glass fiber parts can be a great source of stress on the laminate. While composite parts can be flexed for fitting and joining, this builds stress into the parts. Use of jigs while bonding structural elements such as ribs and stiffeners can deform the glass fiber parts beyond their designed limits. Cracking can occur from improperly designed jigs or from the resulting shrinkage during cure of the adhesives or putties.

Unintended usage, misuse, and abuse are often times the sources for cracking once the glass fiber part is put in service. Repeated cracking in the same area on multiple copies of a composite part might be an indication of either a laminate construction deficiency or a design flaw that is concentrating stresses in that area. Cracks in under-designed parts generally originate in the laminate, but first appear to the manufacturer or consumer as exterior coating cracks.

Radial cracks are generally associated with an impact to the coated laminate. A reverse impact or impact to the non-gel coated side of the laminate generally appears on the gel coated side of the laminate as several cracks extending from a central point. These types of cracks resemble a spider web. Impacts of the gel coated side of the laminate often create cracking in a concentric circular pattern. While radial cracks are generally caused by excessive impacts, they can occur in more routine situations if there are issues with part fabrication and design as described above.

Temperature extremes are another source of cracking for FRP parts. These thermal cracks can form in parallel or random patterns and are the result of differing thermal expansion rates of various layers of a laminate. Thermal cracking can occur when FRP parts are exposed to rapid changes in temperature, such as when FRP molds stored outside in a cold weather environment are moved into a warm shop. Another example of rapid temperature change is the use of steam to remove ice from a part stored outside in cold weather.

Stress riser cracks are cracks that extend from a cut-out or fastener location. The cut-out shape or fastener serves to concentrate strain in a localized area.

## Cracking Test Methods

Although laminate movement and stressing issues that result in exterior coating cracks are the result of design, manufacturing and field abuse issues, FRP parts fabricators and materials suppliers have worked and continue to work to make FRP parts and materials more crack resistant. Concepts for improved crack resistance are generally evaluated in a laboratory setting and numerous laboratory methods have been developed to test properties of coating and laminate matrix materials that relate to cracking. These properties include elongation, flexure and impact and more recently, thermal cycling. Descriptions of test methods and the type of cracking that they represent are discussed below.

Two common test methods for the evaluation of linear cracking are elongation and flexure to first audible crack. Elongation testing is designed to assess the flexibility of the coating film. A typical test method is described in Reference 5. Strips of coating film are formed into loops and passed through a caliper. The caliper setting through which the loops pass with and without breaking are determined. A schematic of the test is shown in Figure 3. Elongation is calculated as shown below.

$$\%Elongation = 100 \times \left[ \frac{t}{D-t} \right]$$

Where:

t = thickness of gel coat strip

D = Diameter of loop measured to the outside of the loop

Flexure to first audible crack is a modified version of ASTM D790 Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. Test sample construction depends on the test objective. For comparison of coatings a consistent laminate construction must be used for all samples. Test specimens are machined from the laminate per dimensions defined in ASTM D790. Testing is conducted per ASTM D790. The coating side of the sample is in tension. A schematic of the test is shown in Figure 4. Loading of the specimen is stopped at the first audible crack. Results are generally expressed as toughness or the ability of the material to absorb mechanical energy until fracture.

$$U_t = \int_0^{\varepsilon(\text{crack})} \sigma d\varepsilon$$

Where:

$U_t$  = Modulus of Toughness

$\sigma$  = stress

$\varepsilon$  = strain

$\varepsilon(\text{crack})$  = strain at first audible crack

Radial cracking properties of FRP components are generally evaluated by impact testing. Numerous impact test methods exist and each has its own merit. For purposes of this paper, we will focus on reverse impact testing where the impact is applied to the non-coated side of the laminate. A major marine manufacturer is using reverse impact testing to screen coatings materials. This company believes that coating performance in reverse impact test is a key parameter in reducing the level of warranty claims for cracking issues.

A reverse impact test apparatus is shown in Figure 5. Test samples are loaded into the apparatus with the coating side down. Test samples are then impacted and visually examined for cracking. Impact heights and weights are varied until passing and failing heights and weights are identified. The passing height is the maximum impact height at which no cracks occur. The failing height is the minimum impact height at which cracking begins.

Thermal cracking can be evaluated by subjecting test laminates to thermal extremes. This can be done as single exposures or test samples can be exposed to numerous thermal cycles. Single elevated temperature thermal exposures can be created by application of heat guns or heat lamps. Single cold temperature exposures can be created by use of freezers or dry ice. Thermal cycling can be accomplished by physically moving parts between hot and cold sources. However, thermal cycling is more readily done using mechanized or automated equipment.

One apparatus for evaluation of thermal cracking characteristics of composites is described in Reference 6. This device consisted of a carousel which rotated test panels between hot air guns and cold air from a heat exchanger cooled by dry ice. A picture of the apparatus is shown in Figure 6.

Frequent operation of this device has not been found to be cost effective. Constant attention is required to ensure that consistent temperatures are maintained particularly on the cold air portion of the cycle. The device even with enhancements consumes a significant amount of dry ice.

Another type of apparatus being used for evaluation of thermal cracking characteristics of composites is a thermal shock chamber like Espec Corporation's TSA-71-S-A. The TSA-71-S-A is shown in Figure 7. It is a fully programmable, single test chamber thermal shock unit. The unit has a hot air reservoir above the test chamber and a cold air reservoir below the test chamber. Doors between these reservoirs and the test chamber open and close depending on programmed cycle. Heating and cooling of the test chamber is very rapid, typically 1 to 3 minutes depending on the test temperature. Specimens are placed in baskets in the test chamber.

It is important to remember that the test methods described above are useful for materials evaluations, but their correlation to actual FRP parts performance and cracking is a matter of debate.

## Polymer Coating and Barrier Technologies

One concept for reducing cracking in FRP parts is the use of tougher coatings that are more resistant to cracking when a FRP part is bent, flexed or impacted. This is the concept behind development of a new toughened polymer coating technology (PCT) and a new polymer barrier technology (PBT). Typical liquid properties of the PCT and PBT are shown in Figure 8. Properties of a typical isophthalic gel coat and VE barrier coat as shown as a comparison. Both the PCT and PBT meet EPA NESHAP requirements for the Marine and Reinforced markets. In addition, the cure and tack-free time of the PCT and PBT are significantly shorter than other commercially available gel coat and barrier coat products. This faster tack-free time and cure has the potential to allow for more rapid part production while maintaining or improving part cosmetics and performance.

Use of the PCT and PBT requires some process modifications in comparison to conventional gel coats and barrier coats. These modifications include use of spray units specifically designed for these technologies. The actual spray application of these materials is similar to conventional gel and barrier coats. A spray application of 20 mils wet is recommended for the PCT. A spray application of 60 mils wet is recommended for the PBT.

Examples of elongation, flex to first crack, impact, and thermal shock testing on the PCT and PBT are summarized below.

Elongation properties of the PCT and PBT were evaluated. An industry standard isophthalic gel coat was included as a control for the PCT and a typical MACT compliant vinyl ester barrier coat product was included as a control for the PBT. Film strips were prepared by spraying the test coating on to a glass mold and using a

draw down bar to obtain a consistent film thickness of  $18\pm 2$  mils wet. When the lay-up time of the film was reached a razor blade was used to cut 0.25 in wide strips of film. These strips were post-cured at  $150^{\circ}\text{F}$  for 16 hours. Strips were tested as described above. Test results are shown in Figure 8. The elongation of the PCT is equivalent to the industry standard isophthalic gel coat. The elongation of the PBT is 3 times that of the vinyl ester barrier.

Flexure to first crack properties of the PCT and PBT were evaluated as described above. Several additional materials were included in the testing for reference.

- Isophthalic Gel Coat
- Isophthalic Gel Coat (2 layers)
- Isophthalic Gel Coat with VE Barrier Coat

Test samples were prepared by spraying the exterior coating onto a glass mold. The coating was drawn down to a consistent thickness of  $18\pm 2$  mils wet. For samples with barrier, the coating was backed by the barrier which was also drawn down to a consistent thickness. The coating and/or barrier were backed by a laminate consisting of 2 plies of 1.5 oz. glass mat with a general purpose dicyclopentadiene (DCPD)/ Orthophthalic laminating resin. The target glass content for the laminate was 33-35%. Samples were cured at room temperature followed by a post cure of 4 hours at  $150^{\circ}\text{F}$ . Test specimens were cut and tested per ASTM D790 with the gel coat side in tension.

In all cases the failure mode was cracking in the un-reinforced layer(s). For specimens with an exterior coating only the crack was limited to this coating and did not extend into the laminate. For specimens with both exterior coating and barrier the failure crack extended through both un-reinforced layers, but did not extend into the laminate. Toughness results are shown in Figure 9. These results show the following.

- Increasing the thickness of the gel coat decreased the toughness of the test laminate.
- Use of a VE barrier coat increased toughness of a test laminates
- A test laminate fabricated with the PCT/PBT system had nearly twice the toughness of laminates fabricated with Isophthalic Gel Coat and VE Barrier Coat

Laminates for reverse impact testing were constructed as shown in Figure 10 and as follows. As for the other tests, laminates having industry standard isophthalic gel coat and vinyl ester barrier coat were included for reference. Laminates were prepared by spraying exterior coating on to a glass mold. The coating was drawn down to a consistent film thickness of  $18\pm 2$  mils  
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wet. For samples with barrier coat the barrier was applied and drawn down behind the coating. For laminates with the skin laminate the skin was applied behind the exterior coating. The skin was allowed to cure overnight prior to bulk laminate application. The bulk laminate was applied in two steps with half the bulk thickness applied in each step. The target glass content was 33-35%. Panels were cured at room temperature for a minimum of 48 hours prior to testing. Three inch by three inch test specimens were cut from the laminates. Twenty four samples were tested for each sample construction. Samples were impacted using a 4 pound weight at varying heights.

Reverse Impact results are shown in 11. Results are shown as passing and failing impact heights. The results show incremental improvements for use of VE Barrier coat and VE-DCPD skin coats in comparison to isophthalic gel coat by itself. PCT and PBT had by far the highest pass and failure height results approximately 2.5 times those of Isophthalic gel coat and 2 times those of an Isophthalic gel coat and VE/DCPD skin laminate combination.

Laminates for thermal shock were patterned after a typical marine deck laminate. The construction was the same for all laminates with the exception of the external coating. Two laminates were fabricated using an industry standard isophthalic gel coat. Two laminates were fabricated using PCT. The external coating was spray applied to a glass mold and drawn down to a consistent film thickness of  $18\pm 2$  mils wet. A 3 ply 1.5 oz. CSM mat was applied using a DCPD-VE skin laminating resin. The target glass content for the skin was 31-35%. The skin was allowed to cure until reaching a barcol hardness of 20 minimum prior to bulk laminate application. The bulk laminate consisted of 3 layers of 1.5 oz. CSM, 1 ply of Coremat and 3 additional layers of 1.5oz. CSM. A general purpose DCDP/ortho laminating resin was used for the bulk laminate. The target glass content of the CSM mat portion of the laminate was 31-35%.

Thermal shock test panels were trimmed into 12 by 12 inch test specimens with a wet saw and beveled to a  $45^{\circ}$  angle to prevent edge cracking from affecting the testing. Screws were installed in two specimens, one isophthalic gel coat specimen and one PCT specimen, to provide a starting point for radial cracking. Stainless steel sheet metal screws, sizes #8 and #10, were used. Pilot holes were drilled for each screw as follows:

- #8 – 0.110 in.
- #10 – 0.125 in.

Four screws of each size were installed in each panel, two without countersink and two with countersink. Cracks initiated on all samples around the non-countersunk screws during screw installation. Cracking

did not occur on any sample around the non-counter sunk screws during installation.

Specimens were post-cured for 16 hours at 150°F. The specimens were placed in baskets in the test chamber and were cycled between -30°F to 160°F for 150 cycles. One cycle is 30 minutes at each temperature plus the transition time between hot and cold and vice versa.

After completion of the thermal cycling, the panels were visually examined for cracks. No cracking was found in panels without screws. For the panels with screws no cracking occurred around the counter sunk holes. The installation cracks around the non-counter sunk holes did not propagate. Evaluation of thermal shock properties of composites is continuing.

### **Additional Properties of PCT and PBT**

Weathering of PCT has been evaluated using QUV-A accelerated exposure methods. Weathering samples were prepared by spraying the coating on a glass mold. The coating was drawn to thicknesses of 18±2 mils wet and 40 mils wet. After the coating was tack free, a laminate consisting of 4 layers, 1.5 oz. CSM was applied using a standard DCPD/Orthophthalic laminating resin.

Panels were weathered per ASTM G154 Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials, cycle 1. Panels were evaluated for gloss and color prior to exposure and after every 500 hours of QUV-A exposure. Two thousand five hundred hours of QUV-A Exposure is approximately equal to 1 year in Florida.

Gloss results are shown in Figure 12. Color results are shown in Figure 13. Color is reported as  $\Delta E$ , total color change. Results for an industry standard isophthalic gel coat are also included for comparison. The PCT shows excellent gloss retention over the exposure period where as the Isophthalic gel coat shows a significant loss of gloss. The PCT shows minimal color change in comparison to the Isophthalic gel coat. The majority of the color change that did occur in the PCT occurs very early in the exposure. After this initial color change the PCT color is relatively stable. Exposure of the isophthalic gel coat was stopped after 1000 hours due to loss of gloss.

Water resistance of the PCT and PBT were evaluated per Reference 7. An industry standard isophthalic gel coat and VE barrier coat are included for comparison. Laminates for water resistance testing were prepared by spray application of the exterior coating onto a glass mold. Coatings were drawn down to provide consistent thickness. Half of each panel was drawn down to a film thickness of 18±2 mils wet. The other half of each panel was drawn down to a film thickness of approximately 40

mils wet. The coating was backed by barrier which was also drawn-down to a consistent thickness. After barrier cure, a laminate was applied consisting of chopped glass and a general purpose DCDP-Orthophthalic laminating resin.

For water resistance testing, the exterior coating of the laminate was exposed to boiling water for 100 hours. The panel was then visually evaluated for blistering, color change, print, cracking and gloss retention. Results are shown in Figure 14. Both systems tested have excellent water resistance.

Wear resistance of PCT and an industry standard isophthalic gel coat were evaluated using a Taber Industries Model 5135 Rotary Abrasor with CS-17 Calibrase Wheels, S-11 refacing discs and S-12 brush. Samples were prepared by spraying applying the exterior coatings onto glass molds. The coatings were drawn down to a consistent film thickness of 18±2 mils wet. After the coatings had reached their lay-up time, a laminate consisting of 4 plies 1.5 oz CSM was applied. A DCPD/orthophthalic laminating resin was used and the laminate glass content was 33-35%.

Wear resistance testing was conducted in accordance with ASTM D4060 for 1000 total cycles. Samples were checked for weight loss after 500 and 1000 cycles. Results are shown in Figure 15. The PCT600 showed 42% less weight loss than the Isophthalic gel coat after 500 cycles and 34% less after 1000 cycles.

### **Conclusions**

Cracking in the exterior coating of FRP parts is related to movement due to stresses on the laminate. Although cracking of the exterior coating occurs in a relatively small fraction of FRP parts this issue has a high visibility with consumers and can result in significant rework and warranty issues for FRP parts producers.

Various types of exterior coating cracks and some of the sources of laminate movement and stresses have been discussed. Laboratory test methods, used by FRP parts manufacturers and materials suppliers, to evaluate crack resistance of FRP parts and materials have been reviewed. These test methods have been used to evaluate new toughened polymer coating and barrier technologies (PCT and PBT). Test results show that the PCT and PBT have superior toughness and impact resistance in comparison to industry standard materials. The new coating and barrier technologies also have a number of other benefits including exceptional gloss retention, water resistance, and wear resistance.

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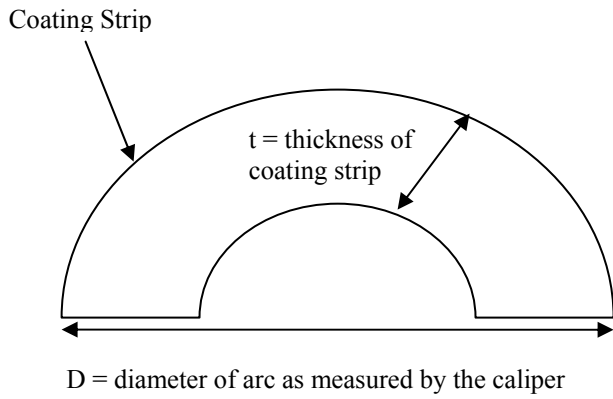
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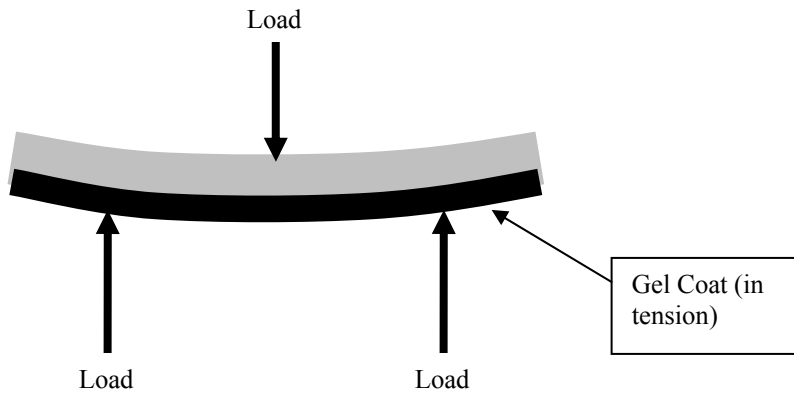
**Figure – 1. De-molding of Boat Deck.**



**Figure – 2. De-molding of Boat Deck.**



**Figure – 3. Elongation Test Schematic**



**Figure – 4. Flexure to First Crack Test Schematic**



**Figure – 5. Gardner Variable Height Impact Tester**



**Figure – 6. Carousel Thermal Shock Test Apparatus**



**Figure – 7. ESPEC Thermal Shock Chamber.**

<b>Property</b>	<b>PCT</b>	<b>Iso Gel Coat</b>	<b>PBT</b>	<b>VE Barrier</b>
100 g mass Gel Time, 77°F, minutes	8	13	1.5	10
Film Gel Time (77°F, 60 mils), minutes	20	20	3	15
Lay-up Time (77°F, 60 mils), minutes	45	50	7	45
Weight/gallon, lbs/gal.	10.8	10.8	9.9	9.6
HAP Content, %	27.9	35.7	24.1	32.3
Elongation, %	1.9	1.8	4.5	1.3

**Figure – 8. PCT and PBT Properties.**

Property	Iso Gel	Iso Gel (2 Layers)	Iso Gel / VE Barrier	PCT/PBT
Coating Thickness, mils	15-20	25-30	15-20	15
Barrier Thickness, mils	N/A	N/A	10-12	40-50
Toughness, in*lb/in <sup>3</sup>				
Average	123.3	105.1	128.1	237.9
Std. Dev.	13.1	34.4	21.6	51.1

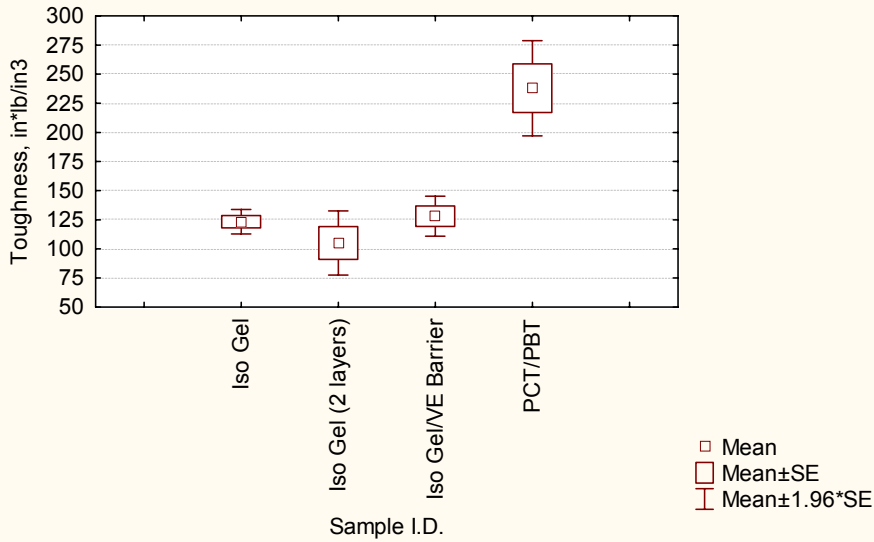


Figure 9. Flexure to First Crack Toughness Results

Coating	Barrier Coat	Skin Laminate	Bulk Laminate
Iso Gel Coat	None	None	<ul style="list-style-type: none"> <li>• DCPD/Ortho</li> <li>• 12 Plies 1.5 oz. CSM</li> <li>• 33-35% glass</li> </ul>
Iso Gel Coat	None	<ul style="list-style-type: none"> <li>• VE/DCPD</li> <li>• 2 plies, 15 oz. CSM</li> <li>• 33-35% glass content</li> </ul>	<ul style="list-style-type: none"> <li>• DCPD/Ortho</li> <li>• 10 Plies 1.5 oz. CSM</li> <li>• 33-35% glass</li> </ul>
Iso Gel Coat	VE Barrier	None	<ul style="list-style-type: none"> <li>• DCPD/Ortho</li> <li>• 12 Plies 1.5 oz. CSM</li> <li>• 33-35% glass</li> </ul>
PCT Coating	PBT Barrier	None	<ul style="list-style-type: none"> <li>• DCPD/Ortho</li> <li>• 12 Plies 1.5 oz. CSM</li> <li>• 33-35% glass</li> </ul>

Figure – 10. Reverse Impact Laminate Construction.

Property	Iso Gel	Iso Gel / VE Barrier	Iso Gel / VE-DCPD Skin	PCT/PBT
Pass Height, inches	49.6	51.2	63.8	131.3
Failure Height, inches	59.6	61.7	73.8	141.3

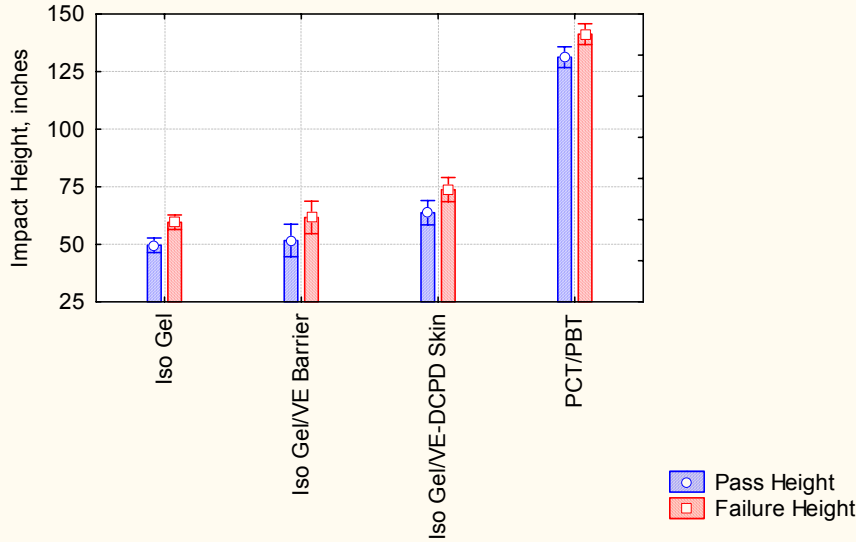


Figure – 11. Reverse Impact Test Results

Product Description	Coating Thickness	Gloss (60 Degree)					
		0	500	1000	1500	2000	2500
PCT	15 mil	90	91	91	92	89	78
PCT	30 mil	92	92	91	92	90	82
Iso Gel Coat	15 mil	98	84	48	Failed	Failed	Failed
Iso Gel Coat	30 mil	98	87	14	Failed	Failed	Failed

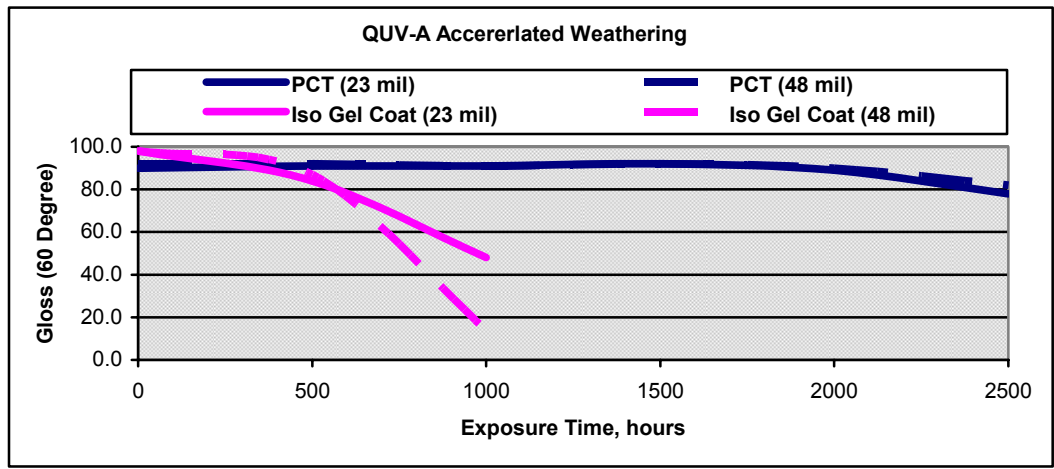


Figure – 12. Gloss Change after QUV-A Exposure.

Product Description	Coating Thickness	Total Color Change					
		0	500	1000	1500	2000	2500
PCT	15 mil	0	1.40	1.78	2.14	2.30	2.45
PCT	30 mil	0	1.24	1.85	2.22	2.78	3.40
Iso Gel Coat	15 mil	0	2.03	5.01	Failed	Failed	Failed
Iso Gel Coat	30 mil	0	2.91	6.28	Failed	Failed	Failed

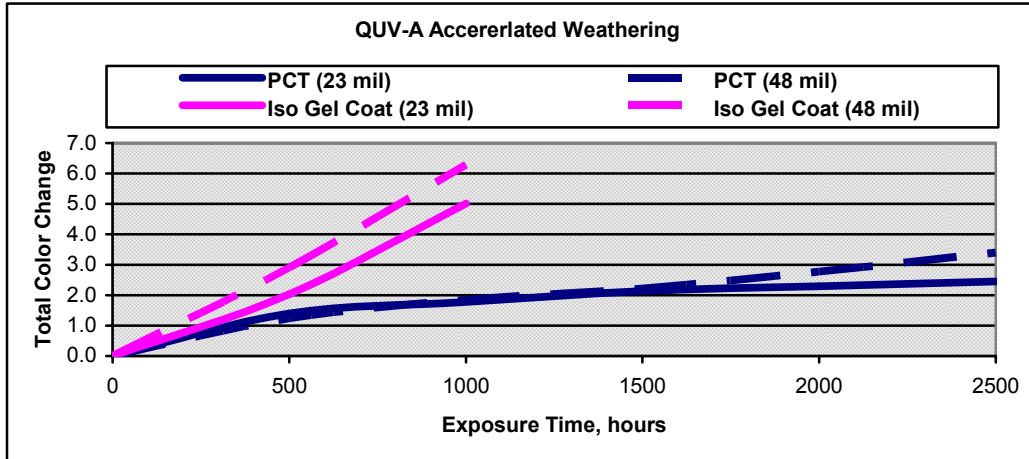


Figure – 13. Color Change after QUV-A Exposure.

	Iso Gel Coat and VE Barrier		PCT and PBT	
Exterior Coating Thickness	15 mils	30 mils	15 mils	30 mils
Barrier Coat Thickness	20 mils	20 mils	60 mils	60 mils
Blisters	0.5	0.5	0.5	0.9
Color Change	1.0	1.0	1.0	1.0
Changed of Fiber Prominence	0.5	0.5	0.2	0.2
Cracks	0	0	0	0
Loss of Visible Gloss	0.5	0.5	0.5	0.5
Total Rating	2.5	2.5	2.2	2.6

Figure – 14. Water Resistance Ratings.

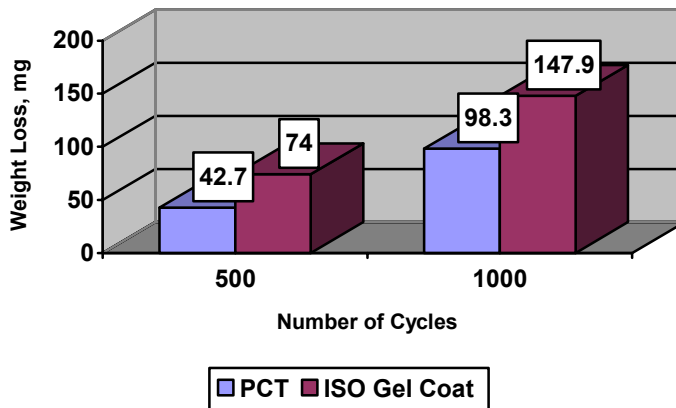


Figure – 15. Wear Resistance.

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