*COMPOSITES & POLYCON 2009*
*American Composites Manufacturers Association*
*January 15-17, 2009*
*Tampa, FL USA*

# The Effects of HAP Content, Temperature, and Substrate Type on the Adhesion Qualities of Vinyl Ester Resin to Acrylic Substrates

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## Abstract

Changes to the EPA's Clean Air Act standards and the MACT regulations have shifted open molders to using lower HAP products. Shower/tub, spa, and hot tub manufacturers apply vinyl ester resins behind the acrylic substrate as a way of adhering the acrylic substrate and structural reinforced plastic composite. However, low HAP vinyl ester resins do not have the same adhesion quality to acrylic substrates that traditional, higher HAP vinyl ester resins have. The wide range of application and material temperatures found in open molding shops also plays a large role in the adhesion of resin to acrylic substrate.

This research explores the adhesion quality of vinyl ester resins with a variety of HAP contents to extruded, cell cast, and continuously cast acrylic substrates. Panels were constructed over a range of typical shop temperatures. A quantifiable method was used to test the adhesion. The results will be statistically evaluated for each of the study's variables.

## Introduction

Polymeric acrylic substrates are used for the surfaces of many reinforced plastic composites, which range from hot tubs, spas, and whirlpools to vehicle dashboards, swimming pool steps, and many more. The acrylic substrate gives the parts a decorative colored surface and provides UV and water resistance to the finished composite parts.

There are three basic manufacturing processes typically used to make the acrylic sheets which are used in these applications. These are extrusion, continuous cast, and cell cast. Each manufacturing process provides properties and cost points that make one of the corresponding materials the choice for specific end-use applications. The extruded product is lower cost and typically the lowest in molecular weight. It is used in bathtubs, shower surrounds, and swimming pool steps where the thermoforming process does not involve any deep draws, characterized as being less than 0.6 meters. These sheets provide several desired properties for the end-use applications. This version is the lowest molecular weight acrylic sheet used by this market. The continuous cast products are mainly used for parts that require very deep draws in the thermoforming process such as hot tubs and large bathtub-and-shower units. Typically, the draw ranges from 0.6 meters up to 1.2 meters, and the finished surface can be as thin as 0.5 mm. Stretching the acrylic during the thermoforming process requires a higher molecular weight acrylic to maintain a continuous film for the surface of the part. The acrylic manufacturers do sell some of these sheets to tub and shower manufacturers as well. The third type of acrylic sheet is the cell cast. It can provide the highest performance material, used in applications like ports and viewing areas of residential and commercial aquariums, impact resistant glass, aircraft windows, orthopedics, and many other applications. The highest performing cell cast acrylic is only bent in the thermoforming process and not stretched. The cell cast process can be used to make some lower molecular weight acrylic sheets for hot tubs and the other applications mentioned above.

The acrylic products discussed are all used in composites manufactured with unsaturated polyester thermoset resin and/or vinyl ester resin fiberglass reinforced laminate bonded to the acrylic. The fiberglass laminate adheres to the acrylic and provides strength and stiffness to the finished composite. Getting a suitable bond between the acrylic sheet and the laminate is critical for making a quality finished part. In many cases, especially in parts that have a deep draw and that are designed for exposure to water, a thin (1.5 mm) vinyl ester laminate is used to provide adhesion to the acrylic and because of its ability to stand up to water. (1,2) Lower cost resins such as dicyclopentadiene (DCPD) or orthophthalic unsaturated polyester are used in combination with fillers like calcium carbonate or calcium sulfate and fiberglass to provide acrylic shells with stiffness and strength and to lower the overall cost compared to composites made entirely from acrylic and vinyl ester resin.

Adhesion failures occur when the strength of the bond between the acrylic and laminate is weak, so that bond is critical to the long term performance of the finished part. These failures can occur during the manufacturing process, shipping, installation, or regular use by the consumer, and they can be caused by an impact to the acrylic surface by a heavy object or by vibrations created by tools when vent holes and drains are cut during the manufacturing process. Repairing a failure whether in the manufacturing plant or in the field and achieving a quality repair is costly and in many cases impossible, so when that bond fails on the production line, the part is scrapped.

The adhesion properties of high styrene containing (45-50%) vinyl ester resins are known to be very robust over a range of molding conditions and application methods. These vinyl ester products have historically provided the premium performance for the market and failure due to debonding was never an issue when they were used. The recent challenge for these manufacturers has been driven by the mandated reduction of HAP content for open molding thermoset resins used by this market. The Fiberglass Composites Open Molding MACT Standard has mandated the use of lower HAP (maximum of 38.4%) in "non-corrosion and/or not high strength" open molding resin when used with non-atomized spray-up equipment. The HAP limit is a maximum of 46.2% for "corrosion and/or high strength resins", among which the vinyl ester is classified, when applied as non-atomized spray, and a maximum of 40% for manual (bucket and brush) application techniques.

As the industry has been converting to vinyl ester resins with lower and lower HAP levels, bonding failures in manufacturing shops have increased. These failures have been isolated to instances where the manufacturers' shop conditions were cooler.

## Experimental

Three vinyl ester resins were used for this study. The resins have similar viscosities and thixotropic indices. Each resin was formulated for a 100-gram cup gel time of 15:00 to 20:00 minutes run at 25°C when an aliquot of 1.2 grams of methyl ethyl ketone peroxide initiator is added.

Resin A: A conventional HAP vinyl ester resin (~48% styrene)

Resin B: A low HAP vinyl ester resin (<40% styrene and VOC)

Resin C: A low HAP vinyl ester resin (<40% styrene and VOC) designed for improved adhesion to acrylic

A total of four acrylic substrates from two acrylic manufacturers were tested in this study:

Acrylic I: WRT 31, acrylic sheet manufactured by Evonik CYRO, off-white, extruded, 4.5 mm thickness

Acrylic II: WT020, acrylic sheet manufactured by Evonik CYRO, white, extruded, 4.5 mm thickness

Acrylic III: WM30, acrylic sheet manufactured by Evonik CYRO, white, cell-cast, 4.5 mm thickness

Acrylic IV: Altair I-300, acrylic sheet manufactured by Aristech, 6385 white, continuous cast, 3.175 mm thickness

The adhesion was measured with a PosiTest Adhesion Tester, described as "self-aligning tester type V" in ASTM D4541-02. See step three of the sample preparation below for more specifics on how the samples were prepared for this test.

Samples were prepared with the following method:

1. The film was removed from the acrylic sheet and the surface wiped with a clean, dry cloth. The acrylic test surface was free of contaminants before any lamination was done.

2. The laminate consisted of two plies of 460 g/m$^2$ chopped strand mat, approximately 260 x 105 mm, applied to the acrylic.

a. Ambient Temperature Tests: The acrylic sheet and resin were brought to 25°C before lamination. The resin was thoroughly mixed with the MEKP initiator and the laminate rolled out at 1 part fiberglass and 2 parts resin. The sample was allowed to cure at ambient conditions for 24-32 hours. Following the ambient cure it was post-cured for 4 hours at 49°C.

b. Low Temperature Tests (18°C): The acrylic sheet was conditioned at 18°C in an ECHOtherm chilling incubator. The resin was adjusted to 18°C before application. The acrylic sheet was removed from the incubator, the laminate was applied to the substrate, and the laminate/acrylic sheet was immediately returned to the incubator, where it was allowed to cure for 24-32 hours. Following the curing at 18°C, it was post-cured for 4 hours at 49°C.

c. Low Temperature Tests (13°C): The acrylic sheet was conditioned at 13°C in an ECHOtherm chilling incubator. The resin was adjusted to 13°C before application. The acrylic sheet was removed from the incubator, the laminate was applied to the substrate, and the laminate/acrylic sheet was immediately returned to the incubator, where it was allowed to cure for 24-32 hours. Following the curing at 13°C, it was post-cured for 4 hours at 49°C.

3. For the adhesion test a 20 mm diameter circular test area was created in the laminate by using a Lenox drill bit to form 3 mm wide circular grooves that penetrated the laminate to the acrylic sheet/laminate interface around the test area. The 20 mm circular test area conforms to the 20 mm diameter base of the dolly used for

the adhesion test. The dollies were adhered to the laminate test area with Plexus MA320 (ITW) (10:1) two-component methacrylate adhesive. The bottom surface of each dolly was abraded with 3M 60 grit aluminum oxide sandpaper before being adhered to the laminate. The adhesive was allowed to cure for a minimum of 16 hours before tests were run.

The adhesion test was run with the PosiTest Adhesion Tester in compliance with ASTM D4541-02. Four replicates were run for each resin/substrate combination. The manual pumping of the PosiTest Adhesion Tester was carried out at a rate of 0.34-1.03 MPa/second. Maximum stress was reached in less than 100 seconds. The readings were recorded immediately following each pull.

## Results and Discussion

The liquid properties of the resins are reported in Table 1. These properties are typical for products used by the industry.

The suppliers of the four acrylics gave a basic description of the molecular weight. Dynamic Mechnical Analysis (DMA) was done to determine the Tg of each material and that information is reported in Table 2. Acrylic I and Acrylic II, the extruded samples, are much lower in molecular weight than the other products. Acrylic III is cell cast, and it has the highest starting molecular weight and a Tg that is higher than I and II. The manufacturer of the continuously cast product reported that the starting molecular weight is lower than I and II and that the reaction continues in the casting process. The final molecular weight of IV is much higher than its starting point.

The PosiTest adhesion properties are reported in Table 3. PosiTest results sorted by application temperature and substrate are reported in Table 4. Analysis of all 25°C, 18°C, and 13°C readings showed averages of 5.24, 5.06, and 4.17 respectively. These results are reported in Table 5. Statistical analysis of this data showed no significant difference between the 25°C and 18°C results, but an extremely significant difference between the 25°C and 13°C results.

A comparison of the overall adhesion strengths of the three resins to the four acrylic substrates showed differences which are reported in Table 6. Comparing the average adhesion strength results for all three temperatures sorted by Acrylic I, Acrylic II, Acrylic III, and Acrylic IV, the averages are 5.34, 5.47, 4.63, and 3.85 respectively. It was noted that the two extruded acrylic substrates showed similar and the highest adhesion strength. There was a drop in the average adhesion strength of 0.7 MPa for Acrylic III compared to I, and an even larger drop of about 1.5 MPa for Acrylic IV compared to I.

A comparison of the two low HAP versions (Resins B and C) to the high HAP standard (Resin A) is shown in Table 7. A statistical analysis of the overall adhesion strength of the resins showed that Resins A and C have comparable adhesion strength, with averages of 5.04 and 4.92 MPa respectively. Resin B showed a statistically significant lower average of 4.51 MPa.

## Conclusions

One of the major conclusions is that the acrylic plays a major role in the ability of the resin to adhere to it. The adhesion results for continuous-cast and cell-cast acrylics were worse, so the selection of an extruded acrylic improves the resin's ability to adhere.

The selection of the proper resin is key to getting the proper adhesion. Zero loss of adhesion properties can be achieved when converting from a high HAP resin to a low HAP/low VOC vinyl ester resin, however, simply converting to such a product does not assure good adhesion. Based on statistical analysis, the selection of a low HAP, MACT-compliant vinyl ester product designed to have excellent adhesion to acrylic yielded comparable results to the previous industry standard high HAP product used in acrylic adhesion applications.

The three different processes used to make acrylic sheet yield products with different performance attributes. This includes the ability of resin products to adhere to the surface.

Statistical analysis showed no significant difference in the resins' ability to adhere to the acrylic substrate over an application temperature range of 25°C to 18°C, but an extremely significant difference between 25°C and 13°C.

The PosiTest Adhesion testing protocol gave reproducible results. This validated the use of this test and equipment as a tool to screen new materials, and it should also be applicable as a QC test for incoming materials.

## Acknowledgements:

Aristech Acrylics, LLC and Evonik CYRO, LLC for contributing acrylic sheet to the project.

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## Appendix 1: Tables

**Table 1: Vinyl Ester Liquid Properties**

| | **Resin A** | **Resin B** | **Resin C** |
|---|---|---|---|
| Viscosity, cp | 484 | 574 | 628 |
| Thixotropic Index | 2.45 | 2.68 | 2.52 |
| Percent HAP | 45.7 | 34.7 | 38.3 |
| Percent VOC | 45.7 | 37.7 | 38.3 |
| | | | |
| 100-gram Gel Time @25°C with 1.2 grams of MEKP initiator | | | |
| Gel Time | 17:17 | 18:13 | 17:07 |
| Gel to Peak Time | 10:08 | 9:35 | 9:37 |
| Peak Exotherm, ˚C | 179 | 181 | 179 |

**Table 2: Acrylic Sheet Characterization**

| | **Acrylic I** | **Acrylic II** | **Acrylic III** | **Acrylic IV** |
|---|---|---|---|---|
| Process | Extrusion | Extrusion | Cell Cast | Continuous Cast |
| Molecular Weight | 140,000 | 140,000 | 1,500,000 | 130,000* |
| Tg. °C | 104 | 107 | 115 | 104 |
| * The starting molecular weight is 130,000 and the polymerization reaction is continued in the mold to ultimately achieve a very high molecular weight polymer. | | | | |

**Table 3: Adhesion Results**

| Resin → | 25˚C PosiTest Adhesion Results (MPa) | | | 18˚C PosiTest Adhesion Results (MPa) | | | 13˚C PosiTest Adhesion Results (MPa) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Resin A | Resin B | Resin C | Resin A | Resin B | Resin C | Resin A | Resin B | Resin C |
| **Acrylic Sheet** | | | | | | | | | |
| **Acrylic I** | 5.12 | 6.41 | 5.77 | 6.09 | 4.57 | 5.90 | 5.33 | 4.56 | 5.28 |
| | 5.81 | 4.79 | 5.22 | 5.79 | 5.48 | 5.81 | 5.19 | 5.12 | 4.69 |
| | 5.38 | 5.41 | 4.92 | 5.95 | 5.01 | 5.55 | 5.02 | 4.24 | 4.76 |
| | 4.99 | 6.31 | 5.94 | 5.39 | 5.55 | 5.71 | 5.12 | 4.89 | 5.21 |
| Average | 5.33 | 5.73 | 5.46 | 5.80 | 5.15 | 5.74 | 5.17 | 4.70 | 4.99 |
| Std Dev | 0.36 | 0.77 | 0.47 | 0.30 | 0.46 | 0.15 | 0.13 | 0.38 | 0.30 |
| **Acrylic II** | 6.43 | 6.37 | 6.63 | 4.71 | 6.08 | 5.23 | 4.77 | 5.49 | 5.21 |
| | 5.94 | 5.43 | 5.43 | 5.77 | 4.41 | 5.72 | 4.54 | 5.14 | 4.55 |
| | 6.35 | 6.05 | 5.58 | 5.95 | 4.72 | 6.58 | 4.46 | 4.54 | 6.04 |
| | 6.64 | 6.26 | 5.32 | 5.39 | 5.03 | 4.99 | 5.61 | 5.12 | 4.59 |
| Average | 6.34 | 6.03 | 5.74 | 5.46 | 5.06 | 5.63 | 4.85 | 5.07 | 5.10 |
| Std Dev | 0.30 | 0.42 | 0.60 | 0.55 | 0.72 | 0.70 | 0.53 | 0.39 | 0.70 |
| **Acrylic III** | 6.68 | 4.91 | 5.53 | 5.46 | 3.97 | 5.46 | 4.21 | 2.96 | 4.18 |
| | 4.72 | 3.82 | 5.31 | 5.30 | 6.02 | 5.25 | 4.16 | 2.08 | 4.01 |
| | 5.35 | 4.79 | 6.03 | 4.46 | 5.14 | 5.66 | 3.89 | 1.90 | 4.31 |
| | 4.09 | 5.21 | 4.61 | 5.62 | 3.92 | 5.88 | 4.68 | 2.95 | 4.04 |
| Average | 5.21 | 4.68 | 5.37 | 5.21 | 4.76 | 5.56 | 4.24 | 2.47 | 4.14 |
| Std Dev | 1.11 | 0.60 | 0.59 | 0.52 | 1.01 | 0.27 | 0.33 | 0.56 | 0.14 |
| **Acrylic IV** | 4.97 | 3.29 | 4.46 | 4.46 | 3.74 | 4.10 | 2.86 | 3.04 | 3.32 |
| | 5.24 | 3.43 | 4.19 | 4.62 | 3.66 | 3.99 | 2.87 | 3.70 | 2.48 |
| | 5.41 | 3.74 | 4.18 | 5.23 | 3.03 | 3.70 | 3.81 | 2.45 | 2.52 |
| | 4.98 | 3.84 | 4.43 | 4.57 | 4.17 | 4.15 | 2.76 | 3.82 | 3.56 |
| Average | 5.15 | 3.57 | 4.31 | 4.72 | 3.65 | 3.99 | 3.08 | 3.25 | 2.97 |
| Std Dev | 0.22 | 0.26 | 0.15 | 0.35 | 0.47 | 0.20 | 0.49 | 0.64 | 0.55 |

**Table 4: Average Adhesion Strength**

| | 25˚C | 18˚C | 13˚C |
|---|---|---|---|
| Acrylic I | 5.51 | 5.57 | 4.95 |
| Acrylic II | 6.04 | 5.38 | 5.01 |
| Acrylic III | 5.09 | 5.18 | 3.61 |
| Acrylic IV | 4.35 | 4.12 | 3.10 |

**Table 5: Adhesion Strength, Application Temperature**

| | Average | Std. Dev. |
|---|---|---|
| 25˚C | 5.24 | 0.88 |
| 18˚C | 5.06 | 0.81 |
| 13˚C | 4.17 | 1.03 |

**Table 6: Adhesion Strength, Acrylic**

| | Average | Std. Dev. |
|---|---|---|
| Acrylic I | 5.34 | 0.51 |
| Acrylic II | 5.47 | 0.69 |
| Acrylic III | 4.63 | 1.07 |
| Acrylic IV | 3.85 | 0.80 |

**Table 7: Adhesion Strength, Resin**

| | Average | Std. Dev. |
|---|---|---|
| Resin A | 5.04 | 0.90 |
| Resin B | 4.51 | 1.15 |
| Resin C | 4.92 | 0.94 |