

# Technical Paper

## MACT Compliant Acrylic Backing Resins

### Abstract

The composites industry has been under pressure for some time to reduce HAPS (Hazardous Air Pollutants) in their shops. Marine MACT (Maximum Achievable Control Technology) implementation took affect August 2004. The final Reinforced Plastics Composites Production MACT Rule defined by the US Government, for other composite applications, takes affect April 26, 2006. Fabricators must comply by that date.

Resin manufactures have been very active in their Research and Development laboratories designing and optimizing MACT Compliant replacement resin systems.

A "new generation" of acrylic backing systems has been designed that meets the criteria established by the MACT Ruling.

The modified orthophthalic polyester will be introduced and discussed in this paper. Rheology, cure progression, adhesive strength, flexural and tensile strength, percent elongation and heat distortion temperature will be compared to traditional higher styrene content acrylic backing systems. The properties of the modified orthophthalic resin system will be presented using a variety of filler types to demonstrate the robustness of the system.

Data will be presented showing that the new polyester meets the MACT requirements but does not dramatically alter the finished properties and were designed as a direct "drop in" replacement in the fabricator's shop.

### Introduction

Fabricators are looking at ways to meet the new government imposed MACT Standards, which has mandated allowable level of HAPS or Hazardous Air Pollutants. There are many methods that the composites industry can employ to meet the government regulations on styrene emissions. Many open molders are evaluating, to some degree, closed mold processes such as RTM or Infusion. For those fabricators whose desire is to retain an open mold environment, the use of non-atomized spray equipment and styrene-suppressed resin is also an option.

The Maximum HAP content for non-atomized mechanical application is 38.4%. For fabricators who use polyester or vinyl ester resins, styrene is the big concern. Historically, in laminating systems, the only HAP present is styrene.

Styrene is a reactive diluent monomer used to reduce the viscosity of the thermoset resin to achieve characteristics that allow for the resin system to be processed in a manufacturing environment.

One can replace the styrene with an alternate monomer such as vinyl toluene or paramethyl styrene, however, studies have shown that the replacement monomer is not a 1:1 exchange. In fact, the level of alternate monomer needed is much greater to achieve the same viscosity as the styrene system. Styrene replacement monomers are much more costly than styrene, thus increases the cost of the formulated product. Test results indicate that the use of alternate monomers can dramatically impact physical properties as well.

A new family of low styrene acrylic bonding resins has been developed to meet the MACT Standards. These polyesters have been carefully designed to closely match performance of higher styrene systems.

Fabricators have different application methods in backing acrylic. Some fabricators back the acrylic with a vinyl ester barrier or skin coat before applying the bulk laminate. Worth mentioning is that there are low styrene vinyl ester system available that comply with the MACT rule. Secondly, there are the fabricators that choose to use a non-filled "neat" resin system that is applied directly behind the acrylic for bulk lamination. Lastly, and more popular, are fabricators who use filler in their resin system for bulking behind the acrylic.

### Development Objectives

The following criteria were established for new product development.

- maintain the physical properties of conventional acrylic back up resin systems
- demonstrate excellent adhesion to acrylic
- have less than 38.4% HAP content
- be capable of being used as a neat system
- be capable of being filled with any type of filler
- match the cure profile of conventional acrylic back up systems

### Experiment

Simply reducing the styrene content of a conventional acrylic backing system will not work as demonstrated in table 1. The viscosity is too high to process and properly wet out the laminate.

The most logical approach for developing a low strength content formulated product that bond to acrylic is to explore alternatives using available polyester and vinyl chemistries. Current commercially available acrylic bonding resin systems were used as the controls systems throughout the development process. All liquid property testing was conducted at 25°C.

Several different chemistries of resins of resins were evaluated during the screening and development stage. The test group contained dicyclopentadienes, orthophthalic, isophthalic polyesters and vinyl esters in various levels of reactivity, molecular weight and styrene content.

Blended combinations at various ratios of the different chemistries of resins were explored. Commercially available micro additives that claim to increase adhesion were incorporated into the blended formulations. Each formulated product was initially screened for:

- liquid properties in both neat and filled applications
- adhesion to acrylic
- flatwise tensile testing

The different available polyesters or blended polyester combinations did not meet the basic criteria established to move forward with new product development and introduction. One system in the study did show promising results in that the bond strength to acrylic was acceptable, however, lacked fiber presence upon visual inspection. This system was taken to polymer synthesis for design improvements.

Targeting similar mechanical and physical properties as conventional acrylic bonding resins, a new polymer was designed for acrylic bonding applications. Several synthesis cooks were screened based on the previously mention criteria.

Reactivity and viscosity of the polymer was modified by careful selection of glycols with saturated and unsaturated diacids. The polymer molecular weight and composition were adjusted to allow for low HAP content. This adjustment enables the system to be used in neat systems or with a range of fillers. The formulation was optimized for storage stability, viscosity and gel time stabilization properties.

The new polymer was blended into a neat application, meeting the specifications of a traditional non-filled system. Adhesion properties were tested and compared to the traditional system as well. Tests results indicated good adhesion to acrylic via ASTM method C297 with 100% fiber tear. Reference Table 2.

The viscosity and thix index were measured along with the cure profile. The new polymer is a match for a typical conventional system. Reference table 3.

#### REFERENCE TABLE 4.

Then next objective was to incorporate filler to the system and compare properties to traditional filled systems.

Many fabricators employ inorganic filler with the resin. This is done for economic reasons, reduced shrinkage, which enhances dimensional stability on the finished part, reduction in VOC emissions during application and cure, opacity and flame retardancy.

The most popular types of fillers are calcium carbonate (CaCO<sub>3</sub>), calcium sulfate (CaSO<sub>4</sub>) or alumina trihydrate (ATH) or a blend of these.

There is a common misperception that inorganic fillers are interchangeable in the manufacturing process. To the contrary, filler selection (type and brand) is a critical element of product design, and is an integral part to product consistency. Alternating fillers in a resin system changes the viscosity, thix and gel time, and may impact the adhesion to acrylic.

ATH is the most popular filler used for flame and smoke reduction. CaSO<sub>4</sub> is the second most popular filler for flame and smoke reduction. ATH and CaSO<sub>4</sub> have water that is chemically bound, which makes them a choice for fabricators who need flame and smoke reduction properties. These two fillers, upon combustion, decompose and give off water to quench the flame.

CaCO<sub>3</sub> decomposes to carbon dioxide, which displaces the oxygen needed for fire, thus reduces the flame properties. ATH is the most expensive filler followed by CaSO<sub>4</sub> then CaCO<sub>3</sub>. Some fabricators choose to blend ATH with CaCO<sub>3</sub> or CaSO<sub>4</sub>.

Viscosity, thix and cure characteristics matched those of conventional acrylic bonding systems. Reference Table 5.

Physical properties were tested and compared to the control. As seen in table 6, no significant drop in physical properties occurred, and based on end use application, are acceptable.

Flatwise tensile testing via ASTM C297 was measure on the laminates prepared on vacuumed-formed acrylic. This test is critical for an acrylic backing system as it demonstrates the adhesive bond to the acrylic by the backing system. Regardless of filler type, the flatwise-tensile results indicate excellent adhesion to acrylic. Reference table 7.

These properties will give the fabricator an added advantage of being able to incorporate the new polymer into his process without costly modifications to his existing process and equipment.

## Conclusion

The ultimate test of any new resin is the performance of that resin in an actual production environment. Field trials leading to full product conversion from higher styrene systems to the new MACT Compliant system have proven the product successful as a replacement polymer. The added value in the new system is that it is designed as a direct replacement or "drop in" a fabricator's process without any modification necessary.

Best Practices are always recommended for acrylic backing applications.

**Table 1**

	Conventional System	Reduced styrene version of Conventional System
Styrene Percent	<b>45</b>	<b>38</b>
Viscosity, LV#3 @60, cps	500	1250
Thix Index, 6/60	2.5	2.5

**Table 2**

Neat Flatwise Tensile System ASTM C297	Conventional System	MACT Compliant System
psi	1400	1400

**Table 3**

Neat System	Conventional System	MACT Compliant System
Viscosity, LV#3@ 60, cps	500	500
Thix Index, 6/60	3.0	3.0
Styrene Percent	<b>45</b>	<b>38</b>
Gel time, 100g, 1.5% MEKP-9, minutes	22.0	20.0
Gel to Peak, minutes	13.0	15.0
Peak Temperature, °F	300	280

**Table 4**

Physical Properties* Neat Resin	Conventional system	MACT Compliant system
Tensile Strength, psi ASTM D638	8,900	9,200
Tensile Elongation, % ASTM D638	2.3	2.2
Flexural Strength, psi ASTM D790	15,400	18,700
Flexural Modulus, psi ASTM D790	580,000	590,000
HDT, °C	64	65

**Table 5**

	50% Sulfate	50% Carbonate	50% ATH
Viscosity, RV#3 @20, cps	1568	1600	1870
Thix Index, 2/20	2.7	3.4	3.1
Gel time, 100g, 1% M-50, minutes	16.0	18.5	15.3
Gel to Peak, minutes	18.0	17.0	16.0
Peak temperature°F	224	241	225
40g hardness at 1 hour	30 HB	40 HB	32 HB

**Table 6**

Physical Properties Filled Resin*	Sulfate System	Carbonate and ATH System
Tensile Strength, psi ASTM D638	9,800	8,600
Tensile Modulus, psi ASTM D638	560,000	550,000
Elongation, % ASTM D638	1.9	1.9
Flexural Strength, psi ASTM D790	14,300	12,700
Flexural Modulus, psi ASTM D790	550,000	560,000
HDT, °C	69	67

\*Clear Casting

**Table 7**

Filled Flatwise Tensile ASTM C297	50% Sulfate	50% Carbonate	50% ATH
psi	1500	1300	1600