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Date: September, 25-27, 2002

Technical Paper

Development Of A New Polyester Resin For Acrylonitrile Butadiene Styrene (ABS) Bonding Applications

Abstract

Polyester resins that bond well to vacuum formed acrylic have been present in the market place for years. The challenge is to develop an unsaturated polyester resin that bonds to vacuum formed acrylonitrile butadiene styrene, commonly known as ABS, with adhesion characteristics that are at least comparable to the current acrylic back up resin systems. In addition, an alternative test method is necessary that can be performed in the fabricator's shop that will demonstrate good adhesion to ABS sheet.

Product development and introduction as well as new methodology for demonstrating adhesion to ABS will be presented in this technical paper.

Preface

Traditionally urethane and urethane hybrids are used to back ABS systems for bathtubs, shower stalls, whirlpools, spas, hot tubs or similar end use products. For liner applications that use ABS, the vacuum formed thermoplastic sheet is either all ABS or a co-extruded or cast sheet that combines ABS with an appearance layer of acrylic that does not come in contact with the urethane back-up system. The development of an unsaturated polyester resin that will bond to ABS at strengths equal to an acrylic bonding polyester resin system would offer the composite fabricator a lower cost alternate to urethane or urethane hybrid systems.

Unsaturated polyesters offer the fabricator some advantages over urethane systems. In general, urethane systems require greater process controls from the fabricators who must precisely mix and react polyol and isocyanate raw material components. Application thickness may be difficult to control because the urethane system gel time is very rapid. In addition, high peak temperatures are achieved at exotherm, which may have a negative impact on the surface of the part. One must be aware of the heat distortion temperature of the acrylic or ABS to which the urethane is being applied. If the exotherm temperature of the urethane system exceeds that of the surface substrate, warping and shrinking can occur along with areas of delamination. Furthermore, because of the heat generated, dimensional stability of the finished part can be compromised. Handling of the urethane is also an issue and requires additional personal protective equipment due to the isocyanate component.

The development of unsaturated polyester that bonds to ABS would offer the fabricator a more cost effective alternative to urethane systems without the potential negative effects from rapid and high peak exotherm. The addition of filler to extend the resin makes the polyester even more cost effective.

Development Objectives

The following criteria were established for new product development. The new unsaturated polyester resin that bonds to ABS should:

- maintain the physical properties of conventional acrylic back up resin systems
- have less than 37% 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

An additional research objective is to develop a test method that fabricators can use to effectively demonstrate the adhesive properties of the new resin system.

Experiment

The most logical approach for developing a new

formulated product that bonds to ABS is to first explore alternatives using current polyester resin chemistries available.

ABS and acrylic have similar end use applications. Therefore, current commercially available acrylic bonding resin systems will be used as the testing controls throughout the development process.

Several different chemistries of resins were evaluated during the screening and development stage. The test group contained dicyclopentiadienes, 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 were also explored. Commercially available micro additives that claim to increase adhesion were incorporated into the blended formulations. Each formulated product was tested for:

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

The test results using different resin chemistries and blended ratios did not display a strong adhesion to ABS, however, one of the systems did have higher bond strength but lacked fiber tear at the ABS FRP interface.

Based on the aforementioned results, polymer design was returned to the synthesis laboratories to develop a new base resin. Targeting similar mechanical and physical properties as conventional acrylic bonding resins, a polymer was designed for ABS bonding applications. The reactivity and viscosity were modulated by careful selection of glycols with saturated and unsaturated diacids to enable use in neat systems or with a range of fillers. The polymer molecular weight and composition were adjusted to allow for low HAP content. The formulation was optimized for storage stability, viscosity and gel time stabilization properties.

The new polymer base resin was formulated and tested for liquid properties and adhesion to ABS. The tests results indicated good adhesion to ABS via ASTM method #C-297 with 100% fiber tear. (Actual values compared to acrylic systems are listed on table #4).

The new polymer blend was tested as a neat resin system, then filled at 40% with carbonate, sulfate and aluminum tri-hydrate. The addition of filler offers two advantages; First, the incorporation of filler extends the resin system thus reducing costs for the fabricator. Second, some types of filler offer flame-retardant properties that are necessary for certain types of manufactured products.

Viscosity, thix and cure characteristics matched those of conventional acrylic bonding systems. These properties will give the unsaturated polyester customer the added advantage of being able to incorporate the new polymer into his process without costly modifications to his existing process and equipment.

Clear castings were made and tested for physical properties. (Table 3) The flexural strength and elongation is higher than acrylic systems with slightly lower tensile and heat distortion values.

The new polymer was also tested in neat and filled application on vacuumed-formed acrylic. Those results indicated excellent adhesion to acrylic as well as ABS. As a result, manufacturers who fabricate with ABS and acrylic thermoplastic can benefit from the new polyester using one resin system for both applications. The product can also be used behind gel coat, making it even more versatile.

Test Method for Adhesion Properties

Traditionally fabricators wedge the two substrates apart by inserting a screwdriver between the layers and prying them apart to confirm adhesion. Another method consists of drilling circular sections out of the construction and prying the substrates apart with a knife. These practices have been in place for years, but may not necessarily reflect true adhesion due to the forces applied or technique.

An alternate method to check for adhesion was used in this experiment along with the traditional wedge test and the ASTM Flatwise tensile method. Specimens were cut out of a finished part after cure and placed surface side up in a 120C oven for ½ hour. The temperature of the oven is maintained above the heat distortion temperature of the acrylic or ABS thermoplastic. When the samples are placed in the elevated temperature environment, the thermoplastic exhibits its "sheet" memory and wants to shrink

back to its preformed state. The unsaturated polyester laminate is relatively stable at this temperature and will not shrink or change shapes. Under these tests conditions, the thermoplastic, if not bonded well, will shrink away and pull apart from the composite thermoset layer. A sample has been tested in this manner and is displayed in figure 2.

- Figure 1 demonstrates poor adhesion to ABS via the wedge method and the newly described method.
- Figure 2 is an example of the new method which shows good adhesion to ABS
- Figure 3 is vacuumed-formed ABS backed acrylic tub that displays the unsaturated polyester laminates adhesive properties to ABS

Conclusion

The new unsaturated polyester resin meets the development objectives and offers many added value attributes. The product has a styrene content of 35%, which is much lower than traditional acrylic back-up systems.

The new polymer is multifunctional in that, it can be used neat or filled using carbonate, sulfate or aluminum trihydrate, and will work as a gelcoat back up resin as well.

Fabricators that are using ABS and acrylic thermoplastic should consider the new polymer as a cost-effective alternative to urethane or urethane hybrid systems

Figure 1

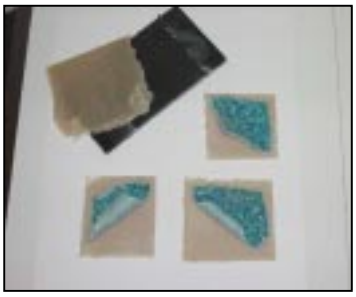

Figure 2

Figure 3

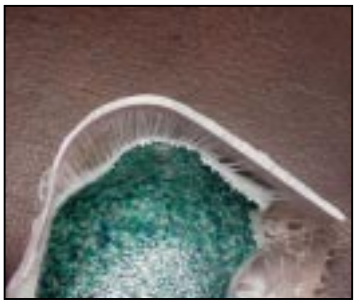

Table #1	ABS Bonding System	Conventional Acrylic Bonding	Low Styrene Acrylic Bonding	Low Styrene, High filler loading Acrylic Bonding
25C Viscosity, LV#3 @60	1200	1700	1200	900
Thix Index, 6/60	2.5	4.5	2.0	2.2
Styrene %	35%	47%	35%	45%
Filler loading	40%	50%	50%	55%

Table #2	New	Conventional Acrylic Bonding	Low Styrene Acrylic Bonding	Low Styrene, High filler loading Acrylic Bonding
25C 100g Gel time, 1% MEKP-9	15	16	12	13
Cure Interval	17	18	17	17
Peak temperature	216F	199F	210F	212F

Table #3	New	Conventional Acrylic Bonding	Low Styrene Acrylic Bonding	Low Styrene, High filler loading Acrylic Bonding
ASTM-D790 Flexural Strength Psi Mpa	 18,000 124.1	 17,000 117.2	 16,000 110.3	 15,100 104.1
Flexural Modulus Psi Gpa	510,000 3.5	620,000 4.3	500,000 3.4	490,000 3.4
ASTM D638 Tensile Strength Psi Mpa	 7,700 5.3	 10,000 69.0	 9,200 63.4	 9,300 64.1
Tensile Modulus Psi Gpa	510,000 3.5	520,000 3.6	450,000 3.10	580,000 4.0
ASTM-D638 Elongation, %	3.7	2.8	2.1	2.3
HDT °C/F	53/127	57/135	76/167	80/176

Table #4 ASTM C297	New	Conventional Acrylic Bonding	Low Styrene Acrylic Bonding	Low Styrene, High filler loading Acrylic Bonding
Flatwise Tensile Strength Psi	1300	1200	1300	1400