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Green Composites Through the Use of Styrene-Free Resins and Unsaturated Polyesters Derived from Renewable and Recycled Raw Materials

by

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Abstract

Unsaturated polyester and vinyl ester resins traditionally have been wholly derived from petrochemicals and contain high concentrations of styrene, a hazardous air pollutant. Until recently, resins prepared from green feedstocks such as renewable or recycled materials, and resins employing alternate non-HAP monomers have failed to meet performance requirements. Resins presented herein are partially derived from biologically renewable resources and recycled materials, without sacrificing performance. In addition, presented here are new resin systems that have been developed to offer styrene-free and ultra-low VOC resins to produce more ecologically friendly composites. Applications of these resin systems include cured-in-place-pipe, marine, fire retardant, solid surface and general purpose laminating.

Introduction

Developments in resin chemistry have evolved to enable production of composite parts that are stronger, produced more quickly, lighter weight, more consistent with fewer defects and with lower overall unit costs. More recently, propelled by the general public’s increased interest in environmental issues, desire for green products, and in some cases by government regulations, composite fabricators have added another target to the wish list: green technologies. In addition, availability and volatile crude oil and natural gas prices have accelerated the move toward more sustainable chemistry as the backbone of composites. Green technologies presented herein represent resins that are based on one or more of the following characteristics:

- Resins derived from biologically renewable materials
- Resins derived from recycled materials
- Resins that are styrene-free

The objectives for these green resin technologies were to offer a seamless transition for the composite fabricators. Properties such as viscosity, gel time, peak exotherm temperature, catalyzed stability, and wet-out were targeted to be compatible with existing composite fabrication processes, and in many cases, identical to conventional petrochemical-derived resins. Similarly, equal physical properties compared to conventional petrochemical-derived resins were targeted such as mechanical properties and chemical resistance. Finally, multiple sources of the biologically renewable materials and recycled materials were required to ensure a security of supply.

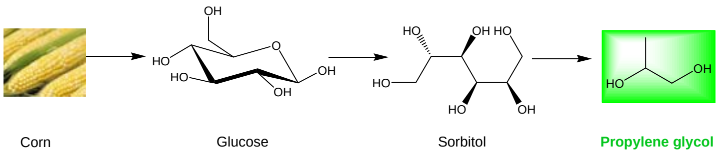
Discussion

For many years, it has been well known that soybean oil can be utilized to prepare unsaturated polyester resins. More recently, with the next step in the evolution of the chemical industry, there has been a boon in biobased chemicals, making a variety of building blocks commercially available. Some of these hydroxy, carboxylic acid, and anhydride functional materials have become available in large scale production, and have been utilized to prepare unsaturated polyester resins.

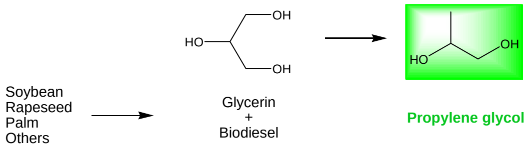
Using a variety of these biologically-derived building blocks such as soybean oil, glycerin, 1,3-propanediol, and other ingredients, unsaturated polyester resins were prepared. Liquid properties were acceptable, however mechanical properties, specifically modulus and heat distortion temperature, were inferior to some of the higher performance, conventional isophthalic acid - propylene glycol resins. In addition, corrosion resistance was expected to be inferior.

Recent developments in renewable chemistry have made propylene glycol (PG) derived from corn and plant oils commercially available. PG is a high performance building block for unsaturated polyester resins often resulting in products with premium corrosion resistance and high mechanical properties. Reacted with isophthalic acid (ISO) and maleic anhydride, PG-based unsaturated polyester resins (Figure 1) have long served as the industry benchmarks for cured in place pipe and corrosion resistant applications. Production of biobased PG is achieved by two commercial processes. Glucose from corn starch hydrogenated to sorbitol and then converted to PG is one commercial route (Equation 1).

A second pathway involves the conversion of triglycerides from soybeans and other plant oils to manufacture biodiesel. Glycerin is the byproduct that is then converted to PG through a catalytic dehydration reaction (Equation 2).



Equation 1.



Equation 2.

Consistent with commercial trends toward sustainability, post industrial recycled PG has also been brought to the market. These sources of PG derived from corn, plant oils, and post industrial recycled PG were studied extensively by a variety of analytical chemistry methods and shown to be equivalent. An example of one of these techniques, infrared analysis (Figure 2) showed greater than a 99.5% match among the PG sources.

Polyethylene Terephthalate (PET), another available recycled feedstock serves as a building block in the synthesis of these green alternatives. When used to prepared unsaturated polyester resins, PET offers the combination of good elongation with high strength and heat resistance. The resins may also be engineered to be suitable for mild corrosion resistant applications.

PG derived from these renewable sources and recycled PG were used to prepare conventional ISO-PG resins used in cured in place pipe applications. The ISO-PG resin products derived from biologically renewable PG, and recycled PG were found to be identical in every aspect compared to the wholly petrochemical-derived resin. Infrared analysis of bio-derived ISO-PG unsaturated polyester resins and petrochemical-derived ISO-PG unsaturated polyester resin confirms that the resins are a match (Figure 3).

Renewable/Recycled Cured-In-Place-Pipe

Cured in Place Pipe (CIPP) applications require resins with excellent physical properties and corrosion resistance. Most gravity cured in place liners are designed to a minimum liner thickness that is controlled by the flexural properties of the composite. CIPP liners are typically designed for a minimum of a fifty year design life so long term properties are critical for these applications. Unsaturated polyester resins made with isophthalic acid and PG have excellent long term mechanical properties making them ideally suited for CIPP applications.

Mechanical properties of 6 mm PET felt laminates made with petroleum-derived and bio-derived CIPP resins are shown in Table 1. Reactivity, stability, viscosities, density, peak temperature and all other properties of the bio-derived ISO-PG resin matched the same specifications of the petrochemical based products.
The renewable or recycled content of resins designed for CIPP ranged from 16 to 22 percent, depending on final resin formulation. The renewable or recycled content for these resins is calculated by the weight fraction of PG used to produce the unsaturated polyester polymer multiplied by the weight percentage of the unsaturated polyester polymer concentration in the total resin formulation (Equation 3).

$$\begin{array}{c}\text{Percent}\\ \text{Renewable}\\ \text{and/ or}\\ \text{Recycled}\\ \text{Content}\end{array} = \left(\begin{array}{c}\text{Weight fraction of}\\ \text{PG used to}\\ \text{produce the}\\ \text{unsaturated}\\ \text{polyester polymer}\end{array}\right) \mathbf{X} \left(\begin{array}{c}\text{Weight percentage of}\\ \text{unsaturated polyester}\\ \text{polymer in the total resin}\\ \text{formulation (monomer,}\\ \text{filler, polymer, additives)}\end{array}\right)$$

Equation 3.

Mechanical properties of the clear cast CIPP resins are shown in Table 2. Neat resins and filled resins are represented. A filled styrene free isophthalic–propylene glycol resin is also shown.

Resins produced using PG from bio-derived and recycled sources are identical to resins produced using the traditional petroleum based PG. Because the resins are the same there is no requirement to reproduce the long term corrosion and flexural creep testing found in many CIPP specifications.

Styrene-Free Cured-In-Place-Pipe

CIPP manufacturers have utilized new styrene-free resin technologies for a variety of reasons including to reduce emissions, odor, and regional requirements. Such systems are being investigated for use in potable water applications. With processing characteristics compatible with current equipment and catalyst systems, styrene-free and ultra low (< 2 %) HAP (hazardous air pollutant) resins have been developed. Table 3 summarizes the cast mechanical properties of these resins, which compare favorably to existing technologies. Liquid properties of these styrene-free systems such as viscosity, gel time, cure profile, wet-out, and initiated stability meet requirements suitable for a range of CIPP applications. Additionally, mechanical properties and corrosion resistance were found to be acceptable.

The options for replacing styrene in polyester and vinyl ester resin systems are limited to alternative reactive monomers, and the choice made impacts the processing characteristics and mechanical properties of the final product. For CIPP applications there are monomers that are similar to styrene that can be substituted directly with little change to mechanical properties, cure performance or processing. These styrene derivatives, though non-HAP, are still somewhat volatile and are not VOC-exempt. Other lower volatility monomers that may be considered ultra low HAP or VOC can be used but they often require changes due to the differences in mechanical properties or resin processing. The mechanical properties that result from using some of these alternative monomers can result in lower elongation that could potentially be a problem in CIPP applications. Using vinyl ester resins with careful monomer selection can increase the elongation of the resin to acceptable levels (table 3).

Renewable/Recycled Casting Resins

Casting resins for solid surface applications have traditionally been derived from isophthalic acid and neopentyl glycol (ISO-NPG), and are the industry standard for attributes including physical properties and stain resistance. A new resin system derived from renewable raw materials has been developed and successfully used to prepare solid surface products. The new resin, derived from 20% renewable content compared favorably to the ISO-NPG industry benchmark. The mechanical property comparison is shown in table 4. The resins exhibit similar strengths while the ISO-NPG standard has higher elongation and the renewable-derived resin has a higher HDT. All physical properties of the renewable resin are within acceptable ranges for most solid surface and engineered stone applications. Beige solid surface casts were identically prepared using the ISO-NPG standard and the renewable-derived resin. Stain resistance tests were performed according to ANSI/ICPA SS-1-2001 on each cast. Figure 4 shows the results of each test, demonstrating the renewable-derived resin performing equal to, or better than the ISO-NPG benchmark. The ISO-NPG control was graded as a 65 on the stain test, and the renewable resin was graded as 63, both passing the stain tests.

Acrylic Bonding Renewable/Recycled Resin

A new resin system derived from renewable and recycled materials is presented for use in acrylic bonding applications. This green alternative is a promoted, thixotropic polyester designed to be used with filler as a back-up laminate for acrylic sheets, typically for use in bathware applications. The resin is derived from a total of 39% renewable and recycled content. The liquid properties and mechanical properties are a close match to the conventional petrochemical-derived phthalic anhydride based-resin (Table 5). The adhesion of the unsaturated polyester resin laminate to the acrylic substrate was measured according to ASTM C 297 and the renewable-recycled product compared favorably with a relatively strong bond of 1400 psi compared to 1200 psi using the conventional resin.

Fire Retardant Renewable/Recycled Resin

A new resin system derived from renewable and recycled material is presented and designed to be blended with alumina trihydrate (ATH) to provide fire retardant properties for mass transit applications. The halogen-free resin resin is derived from renewable and recycled materials at 24% by weight. Laminates of the resin combined with ATH (1:1 by weight) were tested according to ASTM E84, test method for surface burning characterisitcs of building materials, and obtained Class 2 rating for flame spread (48) and smoke development (338). ATH-filled laminates were also tested according Underwriters Laboratory UL 94 standard for safety of flammability of plastic materials and passed a V-0 rating. The flame retardant and smoke development data of the ATH filled laminates are presented in table 6. The low viscosity (130 cP) is engineered to be compatible with high ATH loading while retaining acceptable rheological characteristics. The neat resin exhibits high heat resistance (HDT = 128 °C) and modulus. Mechanical and liquid properties are summarized in table 7.

Styrene-Free Laminating Resins

Styrene-derivatives such as vinyl toluene, tertiary butyl styrene, and paramethyl styrene have long been used as alternative non-HAP diluents for general purpose laminating resin applications. The resulting properties are similar to styrene-based composites, and the resins are typically functionally equivalent and often drop-in replacements compared to their styrene-based analog resins. The driving force for fabricators to change to these higher cost systems is decreased emissions and environmental permit limitations.

Less volatile monomers such as high boiling (meth)acrylates have also been used in combination with unsaturated polyesters to achieve ultra-low emissions with near zero volatile organic compound detection during cure. However, the properties of these cured resins usually exhibit low tensile and flexural strength and considerably lower heat distortion temperature compared to styrene-based resins used in the same applications. These inferior properties are a result of poor copolymerization between the maleate or fumarate segments in the polymer backbone with the (meth)acrylate reactive diluents.

Presented herein is a styrene-free, general purpose laminating resin, also suitable for marine applications, containing reactive diluents with low volatility. A novel polymer system was developed to be copolymerizable with the reactive diluents, resulting in a thermoset network with a crosslink density comparable to conventional resins. The mechanical properties of the styrene-free resin compare favorably to the DCPD-derived, general purpose marine laminating resins (Table 8). The higher elongation results in composite parts that are tougher, and less prone to cracking. The slightly lower heat distortion temperature is still well within the range of acceptable limits for general purpose open mold applications. Liquid properties of the styrene-free resin (table 9) are suitable for a range of open mold processes, and gel time and viscosity are easily modulated with varying concentrations of promoters and reactive diluent, respectively, similar to conventional resins. Volatile organic compound concentration was measured according to EPA Method 24 and resulted in less than 1% emission by weight. As a result of the low volatility of the components, the resin system has a flash point of > 200 °F, and has an NFPA and HMIS rating of 1 for flammability, making this a non-red label product. Thus far, the resin has been used successfully in manufacture of composites for marine and tub/shower applications. The finished products showed good dimensional stability and excellent blister resistance in 24h water boil tests.

Conclusion

There is an increasing need for green alternatives to petrochemical based products in the composites industry. Fabricators and end-users have the expectation that these alternatives will not sacrifice product performance. Previously, in many cases, the use of renewable or recycled green feedstocks in the production of unsaturated polyester and vinyl ester resins have resulted in products that failed to meet all of the necessary performance characteristics. Resins have recently been developed that use biologically derived renewable or recycled resources to produce products that are identical in structure and performance to the petroleum based counterparts. The evolution of the chemical industry with increasing production of biobased chemicals has now penetrated the composites industry, to include biobased PG unsaturated polyesters. Propylene glycol has a long history of success in the composites industry as a high performance building block for unsaturated polyesters. Recycled glycols and PET also serve as green materials for the production of polyester resins. Applications utilizing these technologies presented here such as CIPP, cast polymer, acrylic bonding and flame retardant composites have been produced with equivalent performance versus conventional petrochemical derived resins.

New styrene-free technology presented here utilizing novel polymers designed to copolymerize with alternate low volatile monomers has successfully been used in marine, CIPP and open mold laminating applications. The styrene-free resins are shown to be drop-in replacements in these applications without compromise in performance. The styrene-free and ultra low HAP resins allow CIPP contractors to meet the requirements of reduced emissions, odors, and discharge limits. The non-styrene, ultra low HAP resins may potentially allow CIPP contractors to achieve NSF 61 approval for use in potable water applications. Benefits for open molding applications in emission permitting and OSHA requirements may also be realized.

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Author

Dr. John McAlvin is an R&D manager for AOC, LLC. He has been with AOC since 2000 and has focused on development of corrosion resistant, casting, laminating, and gel coat, vinyl ester and unsaturated polyester resins for open mold composite markets.

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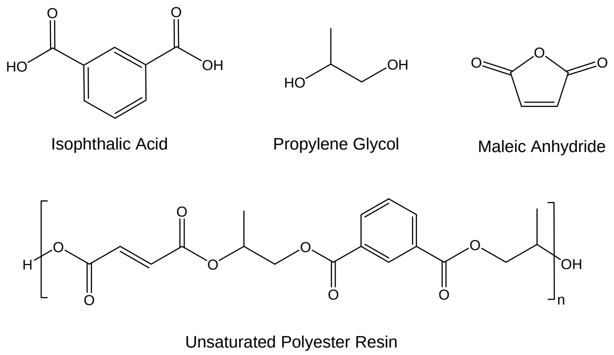

Figure 1. Raw materials and unsaturated polyester resins derived from isophthalic acid, propylene glycol and maleic anhydride

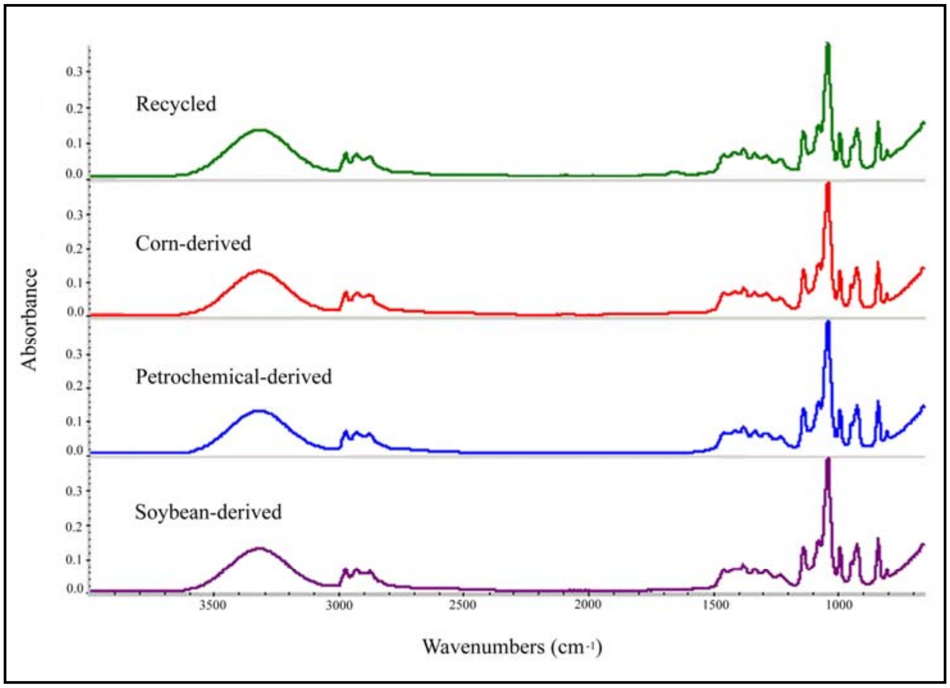

Figure 2. Comparison of infrared analysis of propylene glycol derived from various sources: recycled, corn, petrochemical and soybean.

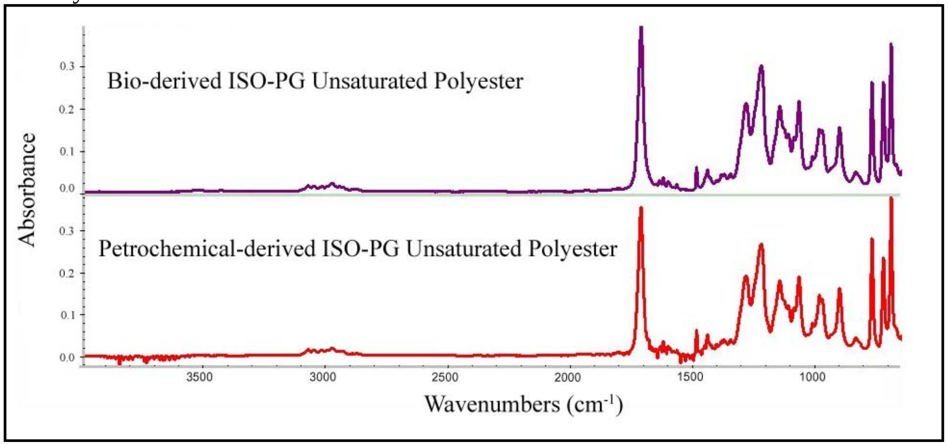

Figure 3. Comparison of infrared analysis of bio-derived ISO-PG unsaturated polyester and petrochemical-derived ISO-PG unsaturated polyester.

Property	Method	Units	6 mm PET Felt Laminate petroleum-derived ISO-PG resin	6 mm PET Felt Laminate bio-derived ISO-PG resin
Flexural Strength	ASTM D790	psi	7,800	7,900
Flexural Modulus	ASTM D790	psi	500,000	530,000
Tensile Strength	ASTM D 638	psi	4,100	4,200
Tensile Modulus	ASTM D 638	psi	560,000	630,000
Tensile Elongation	ASTM D 638	%	0.9	0.9

Table 1. PET felt laminate mechanical properties of petroleum-derived and bio-derived isophthalic propylene glycol CIPP resins.

Property	Test Method	Units	Filled Styrene-Free ISO	Filled ISO	High MW Rigid ISO
Tensile Strength	ASTM D 638	psi	8,700	8,000	13,500
Tensile Modulus	ASTM D 638	psi	670,000	730,000	600,000
Tensile Elongation	ASTM D 638	%	1.7	2.0	3.0
Flexural Strength	ASTM D 790	psi	10,800	12,000	23,300
Flexural Modulus	ASTM D 790	psi	660,000	750,000	630,000
Heat Distortion Temperature	ASTM D 648	°C	113	97	100
Renewable/Recycled Content	By weight	%	16	16	22

Table 2. Cast mechanical properties of renewable and recycled CIPP resins.

Property	Test Method	Units	Filled Styrene-Free ISO	Filled Styrene-Free VE	UV Curable Styrene-Free VE
Tensile Strength	ASTM D 638	psi	8,700	8,000	8,800
Tensile Modulus	ASTM D 638	psi	670,000	730,000	470,000
Tensile Elongation	ASTM D 638	%	1.7	1.9	2.5
Flexural Strength	ASTM D 790	psi	10,800	12,600	15,300
Flexural Modulus	ASTM D 790	psi	660,000	710,000	510,000
Heat Distortion Temperature	ASTM D 648	°C	113	117	105
Renewable/Recycled Content	By weight	%	16	0	0

Table 3. Cast mechanical properties of styrene-free CIPP resins.

Property	Test Method	Units	ISO-NPG	Renewable
Tensile Strength	ASTM D 638	psi	12,500	11,300
Tensile Modulus	ASTM D 638	psi	560,000	580,000
Tensile Elongation	ASTM D 638	%	3.7	2.4
Flexural Strength	ASTM D 790	psi	20,000	20,800
Flexural Modulus	ASTM D 790	psi	590,000	630,000
Heat Distortion Temperature	ASTM D 648	°C	78	85

Table 4. Physical property (1/8" clear cast) comparison of renewable material-derived solid surface unsaturated polyester resin and the industry standard ISO-NPG unsaturated polyester resin.

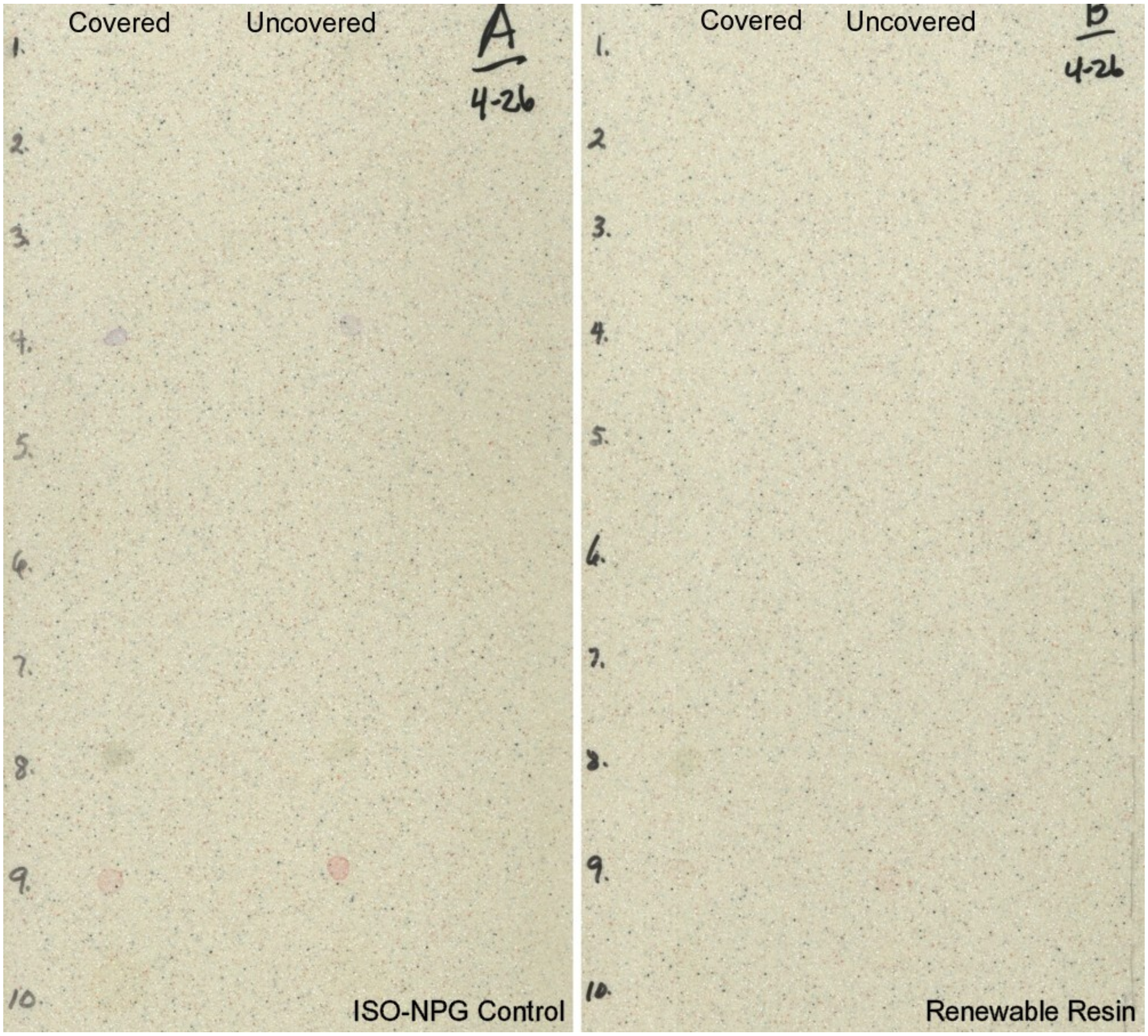

Figure 4: ANSI/ICPA SS-1-2001 Stain resistance test specimen comparison of the renewable-derived solid surface resin (right) and the industry standard ISO-NPG resin (left). Stain tests as follows: (1) black crayon; (2) black liquid shoe polish; (3) blue washable ink; (4) gentian violet solution; (5) beet juice; (6) grape juice; (7) lipstick; (8) black hair dye; (9) mercurochrome solution, 2%; (10) wet tea bag.

Property	Test Method or description	Units	Conventional Petrochemical-derived Acrylic Bonding UPR	Renewable/ Recycled-derived Acrylic Bonding UPR
Tensile Strength[†]	ASTM D 638	psi	8,800	8,800
Tensile Modulus[†]	ASTM D 638	psi	480,000	480,000
Tensile Elongation[†]	ASTM D 638	%	2.7	2.4
Flexural Strength[†]	ASTM D 790	psi	13,300	13,300
Flexural Modulus[†]	ASTM D 790	psi	510,000	490,000
Heat Distortion Temperature[†]	ASTM D 648	°C	50	54
Tensile Strength of Acrylic-UPR Sandwich Construction in Flatwise Plane[‡]	ASTM C 297	psi	1,200	1,400
Brookfield Viscosity, neat	25 °C, LV#3 @ 60 rpm	cP	510	590
Thix Index	As above, @ 6/60 rpm	-	2.8	2.5
Percent Styrene	By weight	%	38	38
Gel Time	25 °C, 100g, 1.25% DDM-9	min	24	19
Gel to Peak Time	As above	min	18	15
Peak Exotherm	As above	°C	121	129
Total Renewable/Recycled Content	By weight	%	0	39

Table 5: Property comparison of petrochemical-derived and renewable/recycled content-derived acrylic bonding resins. [†]Mechanical properties of the unreinforced (1/8" clear cast) of a conventional petrochemical-derived unsaturated polyester resin and the renewable/recycled content-derived unsaturated polyester resin. [‡]Tensile Strength specimens of the acrylic-UPR laminate sandwich constructions were each prepared and tested identically as 3 ply of 1.5 oz chopped strand mat at 35% glass behind vacuum formed acrylic sheets.

<table>
<tr><th colspan="9">Flame Retardant and Smoke Development Data</th></tr>
<tr><th colspan="3">NFPA 258 Smoke Development (ASTM E 662 NBC Smoke Density Chamber)</th><th>Flame Spread Rating ASTM E 162</th><th colspan="3">UL 94</th><th colspan="2">ASTM E 84 Test</th></tr>
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<tr><td>D_s 1.5</td><td>57</td><td>1</td></tr>
<tr><td>D_s 4.0</td><td>194</td><td>35</td></tr>
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Table 6: Flame Retardant and Smoke Development Data for laminates made from the ATH filled renewable and recycled content-derived unsaturated polyester resin. The laminates were prepared with 2 ply of 1.5 oz chopped strand mat (450g per square meter) and the ratio of ATH to the unsaturated polyester resin was 1:1 by weight.

Property	**Test Method or description**	**Units**	**Value**
Tensile Strength†	ASTM D 638	psi	9,000
Tensile Modulus†	ASTM D 638	psi	540,000
Tensile Elongation†	ASTM D 638	%	2.1
Flexural Strength†	ASTM D 790	psi	14,000
Flexural Modulus†	ASTM D 790	psi	590,000
Heat Distortion Temperature†	ASTM D 648	°C	128
Brookfield Viscosity, neat	25 °C, LV#3 @ 60 rpm	cP	130
Percent Styrene	By weight	%	37
Gel Time	25 °C, 100g, 1.0% MEKP-9	min	40
Gel to Peak Time	As above	min	5
Peak Exotherm	As above	°C	216
Total Renewable/Recycled Content	By weight	%	24

Table 7: Mechanical and liquid properties of the renewable and recycled-derived neat unsaturated polyester resin intended for ATH-filled fire retardant applications. †Mechanical properties are of an unreinforced 1/8” clear cast.

Physical Property	**Test Method**	**Units**	**Conventional Styrene-based UPR**	**Styrene-Free GP Laminating Resin**
Tensile Strength	ASTM D 638	psi	9,000	11,000
Tensile Modulus	ASTM D 638	psi	570,000	490,000
Tensile Elongation	ASTM D 638	%	2.0	3.5
Flexural Strength	ASTM D 790	psi	14,000	16,300
Flexural Modulus	ASTM D 790	psi	590,000	500,000
Heat Distortion Temperature	ASTM D 648	°C	95	87

Table 8: Mechanical properties (1/8” clear cast) of a conventional DCPD-derived styrene-based unsaturated polyester resin and the styrene-free general purpose marine laminating resin.

Property	**Test Description**	**Units**	**Nominal Value**
Brookfield Viscosity	25 °C, LV#3 @ 60 rpm	cP	650
Thix Index	6/60 rpm	-	> 2.0
Styrene Content	By weight	%	0
Gel Time	100g, 1.5% MEKP-9H	min	40
Gel to Peak Time	As above	min	7
Peak Exotherm	As above	°C	160

Table 9: Liquid properties styrene-free general purpose marine laminating resin