

Unsaturated Polyester Resins Derived from Renewable Resources

by

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Abstract

The incorporation of renewable resources in composite materials is a viable means to reduce environmental impact and support sustainability efforts in the composites industry. Rising costs and dwindling petrochemical feedstocks also make renewable resource-based materials attractive alternatives to their petroleum-based counterparts. This paper focuses on unsaturated polyester resins prepared from renewable resources and their use in composite materials. Applications of these resins in the automotive and marine industries are described, including a comparison of properties and performance versus typical petroleum-based resins. Results indicate that biobased UPRs and composites generally show comparable performance characteristics to their all petroleum-based analogues. Therefore, they represent practical alternatives to 100% petroleum-based UPRs and composites.

Introduction

Unsaturated polyester resins (UPRs) are one of the most important thermoset materials used in composites industry for the preparation of molding compounds, laminates, coatings, and adhesives. Since their inception some 75 years ago (1, 2), UPRs have made significant structural and performance advances (3, 4), which resulted in their broader application in automotive, building, construction, and marine industries. One of the key advantages of UPRs is the ease of fabrication, which results in low production costs. This is mainly attributed to easily controllable and fast cure processes, which proceed via free radical polymerization mechanism.

UPRs are usually styrene solutions of unsaturated polyesters synthesized by way of polycondensation reaction between dibasic acids or anhydrides and glycols. Until recently, starting raw materials for UPRs were exclusively petroleum-based (5). This was justified by the ready availability and low cost of petroleum, as well as

processes for its conversion into useful raw materials. Low-cost petrochemical products saturated chemical and composites industries and little was done toward sustainable development and "green" alternatives. Shining examples, such as Henry Ford's all-plastic car body (6), prepared from cellulose fibers and soy-modified phenolic resin, and that of his close friend, George Washington Carver, on paints, adhesives, synthetic rubber, and plastics from renewable resources (7), were soon forgotten and the world was set on the course of complete petroleum dependence.

However, in recent years, rising environmental awareness and escalating petroleum prices caused a drastic change in the way chemical and composites industries do their business and how consumers view their products (8, 9). Utilization of renewable raw materials in UPRs and composites is becoming a feasible approach to reducing environmental impact and supporting sustainability efforts, while simultaneously creating value and building competitive advantage.

Background

Chemical tools for conversion of renewable resources into polyester resins have existed for several decades. For example, the alkyd resin industry utilizes those tools to effectively incorporate fatty acids, vegetable oils, rosin, and glycerol into their resins (10-12). Fatty acids, like tall oil fatty acids, and drying oils, such as tung oil and linseed oil, have been used frequently as renewable resource components of alkyd based paints and coatings. Unlike UPRs, alkyd resins have lower reactivity and cannot be used in traditional composites applications. However, similar chemistry tools can be used to incorporate renewable raw materials into UPRs and composites.

Fatty acids, vegetable oils, and their derivatives, which historically represented key components that distinguished alkyds from other polyester resins, have been used with UPRs in the composites industry merely as additives, such as mold release agents (13, 14), and surface profile enhancers (15) in sheet molding compounds (SMC). Only recently have these renewable components found their use for the synthesis of UPRs. Initially, academic researchers utilized synthetic pathways to convert inexpensive and readily available vegetable oils into an array of useful intermediates for UPR synthesis (16-22). These conversions were accomplished through transesterification, epoxidation, ozonolysis, hydroxymethylation, maleinization and cycloaddition reactions of plant oil triglycerides and their derivatives. However, despite the availability of chemical tools, no commercially available "green" UPRs appeared in the market until 2003. The first industrially available biobased UPR contained approximately 18% total bio-content derived from the combination of soybean oil and corn derived ethanol. This UPR was designed primarily for compression molding applications, in particular for the preparation of SMC

molded parts for agricultural equipment, such as combines and tractors (23). Direct comparison of the resin's liquid properties (Figure 1) and mechanical properties of molded SMC parts (Figure 2) showed similar properties to 100% petroleum-based resin counterpart (Resin B).

Since its introduction to the market, interest in "green" UPRs and composites has grown considerably and new opportunities in composites markets opened up (24). Because the first "green" resin could not be formulated to meet performance requirements for all composites applications, new generations of renewably resourced UPRs were needed to satisfy the demand.

Diminishing petroleum reserves, crude oil price escalation, and rapid advances in white biotechnology (25) changed raw material markets to a point where renewable raw materials and bioproducts can effectively compete with petrochemical analogues. For example, recently DuPont Tate & Lyle BioProducts announced the availability of Susterra™ propanediol (26). Susterra™ propanediol is a 100% renewably sourced glycol made from corn sugar. Utilization of this glycol in UPRs allows for improvement of "green" content. However, it is important to note that while bio-content is desirable, it is hardly the most important parameter. Mechanical, physical, and liquid properties of new resins must meet all requirements set by customers before they can even be considered for any application. Simply stated, renewably resourced UPRs must offer similar or better performance and quality than petroleum-based counterparts at similar price.

Experimental

Our group is actively working on identification and evaluation of renewable raw materials for use in UPRs and composites. New generations of renewably resourced UPRs were prepared. Sheet molding compound, compression molding, and vacuum infusion processes were used for compounding and composite preparation. Resin clear-castings were also prepared and their mechanical and physical properties determined. Mechanical and surface quality properties of "green" composite materials were directly compared to 100% petroleum-based analogues in order to assess their performance.

Clear castings of standard UPR resins were prepared in the following manner. The resin formulations were initiated with 1% benzoyl peroxide and 0.5% t-butyl peroxybenzoate. The mixture was then poured into a glass mold and cured for 30 minutes at 54°C, 60 minutes at 71°C, and 60 minutes at 82°C. The cured clear casting was removed from the mold and post-cured for 120 minutes at 150°C.

Clear castings of the low profile additive (LPA)-containing infusion resins were prepared using the following procedure. The glass mold surface was treated with mold release agent prior to resin cure. The infusion resin was initiated with 1.5% DDM-9 and poured into a glass mold. Two hours later, the clear casting was re-

moved from the mold and post-cured at 43°C for 24 hours between the two glass plates.

SMC was compounded on a 24 inch SMC machine using standard compounding protocols. Compression molding was conducted on a 100 ton hydraulic press using a 12 x 12 inch matched flat metal mold. Flat panels were molded at a thickness of approximately 0.01 inch.

Gelcoated laminate panels were prepared using a closed molding vacuum infusion process (Figure 3). The glass plate surface was coated with mold release agent before gelcoat application and cure. Gelcoat resin was initiated with 2% DDM-9 and applied onto the glass surface at about 30 mils thickness wet. Glass fiber reinforcement was laid on top of the cured gelcoat and covered with vacuum bag. The whole system was evacuated for several hours before the resin was infused. After the resin infusion, the laminate was allowed to cure for 2 hours before demolding. The gelcoated side of the laminate was used for surface quality analysis. The gelcoat was peeled off of the laminate prior to mechanical analysis.

Standard ASTM and/or ISO methods were used to determine mechanical and physical properties. Surface quality (SQ) analysis was performed using Advanced Laser Surface Analyzer (ALSA). SMC panels were analyzed at room temperature 24 hours after the molding. A minimum of five SMC panels were analyzed for each formulation and their data averaged. Gelcoated infused laminates were analyzed after the postcure treatment of seven days at room temperature and three days at 43°C. SQ is defined by Ashland Index (AI, long term waviness parameter) and Distinctness of Image (DOI) and Orange Peel (OP) (short term waviness parameters) (27). The lower the AI and the higher the DOI and OP are, the better the SQ.

Results and Discussion

The first commercial renewably resourced UPR mentioned earlier (Figure 1, A), and standard 100% petroleum-based poly(propyleneglycol maleate) resin (C) were used as biobased- and petrochemical-controls for our comparative study. These two resins were directly compared to two new renewable resourced resins (D and E). Resins A, C, and D were comparatively studied in a structural SMC formulation, while resins C and E were studied in an automotive class-A SMC formulation (Figure 4).

Figure 5 lists comparative clear castings data for all resins, as well as surface quality (ALSA) and mechanical property data for molded panels prepared from the corresponding structural and class-A SMC formulations. Results indicate that newly prepared "green" resin D shows comparable heat distortion temperature (HDT) and elongation-at-break values to the petroleum-based analogue. Unlike resin C, resin D has bio-content of 20% by weight on a styrene solution basis. Furthermore, clear casting properties of resin D also show improvements in

HDT and bio-content values in comparison to the bio-based-control resin A.

When used in a standard density structural SMC formulation, these three resins (A, C, and D) produce molded SMC panels with comparable mechanical properties. However, due to the slightly higher glass content of the molded SMC panels of resin A (32.5%), it seems that both resin C and resin D SMC panels show slightly better mechanical performance. Surface characteristics of molded panels based on resin D and resin C clearly outperform those of resin A. However, while their AI values are almost the same, it is important to note that short term waviness parameters (DOI and OP) of resin D SMC panels show visible improvements over resin C SMC panels.

Resin E, intended for automotive class-A SMC applications, shows drastic improvement in clear casting HDT value over its petroleum-based counterpart, resin C (Figure 5). This newly developed “green” resin has 10% bio-content by weight on the styrene solution basis. When used in an automotive class-A SMC formulation, resins E and C give molded SMC panels with similar surface quality and comparable mechanical properties. While both resins have similar tensile and flexural strengths, tensile and flexural modulus values of resin E SMC panels are noticeably higher than those of their 100% petroleum-based counterpart, resin C.

Resins A and C were also compared in LPA-containing infusion formulations (Figure 6). These infusion resins are typically used for above-the-water-line applications in the marine industry, such as the preparation of small boat parts, like cooler lids, hatches, and consoles. Infusion resin formulations used in this study were initiated with 1.5% DDM-9 prior to infusion. The bio-containing infusion formulation is based on resin A and has about 8% bio-content on a styrene solution basis. Economy and premium infusion formulations are standard 100% petroleum resin systems based on resin C. These two resins cover a broad spectrum of infusion resins in terms of their performance and cost, with the economy formulation being lower performing and more affordable and the premium infusion formulation being top-performing and higher priced.

Figure 6 lists liquid, clear casting, laminate and surface quality properties for all three LPA-containing infusion resin products used in this study. All three infusion resins have similar liquid properties and exhibit good laminar flow and glass wetting during infusion. In terms of clear casting mechanical and physical properties, the biobased infusion resin shows much better performance than the economy resin, but performance was still not as good as the premium resin. Interestingly, the biobased resin clear casting shows simultaneously the highest HDT and tensile elongation values compared to its petroleum-based counterparts. Additionally, typical biobased resin laminate properties show similar or better performance than both petroleum-based resins.

Surface quality of the gelcoated laminate surfaces is one of the most important performance characteristics of infusion resin systems. Visual appeal and retention of the laminate surface quality with time is highly regarded in the boatbuilding industry. Because of that, resin performance needs to be optimized to satisfy this requirement. Therefore, it is challenging to develop a biobased infusion system that simultaneously meets liquid, mechanical, physical, and surface quality requirements.

The gelcoated laminate made with a newly developed biobased infusion resin shows surface characteristics that fall between those of economy and premium infusion resins (Figure 6). SQ results show significant performance improvement over the economy class resin, with AI, DOI, and OP values in the automotive class-A range (Figure 7). However, further advances are needed to develop “green” alternatives to premium infusion systems.

Conclusions:

Commercially available renewable resource materials have been successfully incorporated into unsaturated polyester structures to yield several UPRs for automotive and marine applications. Initial raw material and manufacturing cost analyses show that “green” UPRs can be produced commercially at competitive price to their petroleum-based analogues. Comparative experiments have been conducted to show side-by-side performance of these resins and their petroleum counterparts in several automotive and marine applications. Results indicate that biobased UPRs and composites generally show comparable or better performance characteristics to their all petroleum-based analogues. As such, they represent viable alternatives to 100% petroleum-based UPRs and composites and offer means to reduce environmental impact and support sustainability efforts in the composites industry.

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Dr. Roman Loza heads up the R&D Resins group in the Composite Polymers-Global Technology Organization of Ashland Performance Materials, a Division of Ashland, Inc. Roman received his Ph.D. from the State University of New York at Buffalo in organic chemistry in 1980. After a postdoctoral appointment at the University of Chicago, he joined the R&D Department of The Standard Oil Company (now BP). There he worked in a variety of areas including enhanced oil recovery, polymer synthesis, nitrile process chemistry and epoxy and phenolic resins for aerospace applications. Roman has been with Ashland, Inc. since 1995. His work experience includes management of Ph.D. scientists and technicians; extensive experience in the development and scale-up of products (unsaturated polyesters and vinyl esters) from bench scale to pilot scale to full production. Roman has extensive experience in the use of statistical methods for process and quality control. He developed a novel process for preparing low-VOC unsaturated polyester resins using alcohol end-capping and was instrumental in the development of Ashland's ENVIREZ® UPRs. Roman holds 17 US Patents.

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Property	A	B
Viscosity @ RT (cP)	850-1050	800-1000
Non-volatiles (%)	69.0-72.0	64.0-66.0
180°F Gel Test Data		
Gel Time (min)	5.5-8.0	8.0-12.0
PET (min)	7.0-11.0	10.0-13.0
PE (°C)	196-213	216-238

Figure 1: Liquid Property Comparison between Bio-Based Resin (A) and Standard Petrochemical Resin (B).

Property	SMC-A	SMC-B
Tensile Strength (MPa)	102	81
Tensile Modulus (GPa)	10.8	13.0
Flexural Strength (MPa)	194	208
Flexural Modulus (GPa)	9.8	11.1
Impact, Notched (J/m)	940	1070
Impact, Unnotched (J/m)	1260	1270
Glass Content (%)	29	29
Shrinkage (mm/mm)	-0.0005	-0.0006
Water Absorption (%)	0.480	0.490

Figure 2: Properties of Molded Standard Density SMC Panels Prepared from Bio-Based Resin (A) and Standard Petrochemical Resin (B).

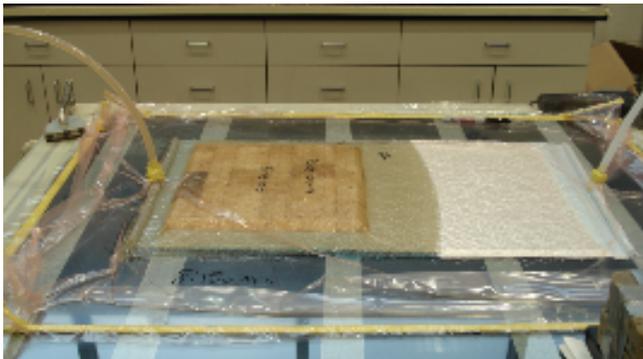


Figure 3: An Example of a Closed Molding Vacuum Infusion Setup.

	Parts by weight	Parts by weight
UPR Components	65.1	66.4
LPA Components	38.8	37.9
Inhibitor	0.02	0.6
Initiator	1.5	2.0
Mold Release	4.5	4.5
Filler	180	200
MgO dispersion	1.31	3.4
1" Chopped Fiberglass Roving (%)	30	30

Figure 4: Standard Density Structural and Class-A SMC Formulations.

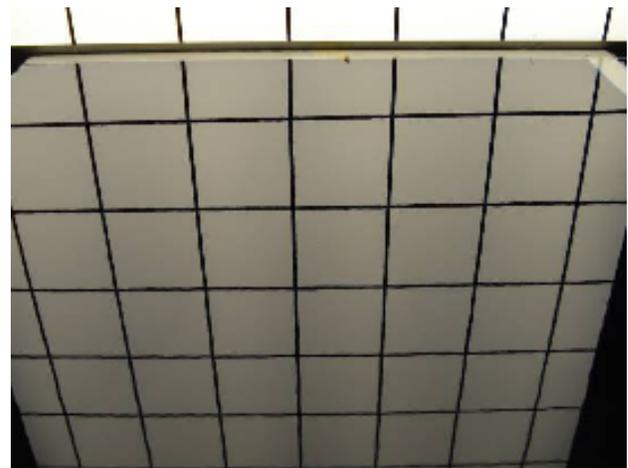


Figure 7: Distinct Image of the Light Grid in a Gelcoated Laminate Prepared with Green Infusion resin.

SMC Formulation	Structural	Class-A
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	STRUCTURAL SMC			CLASS A SMC	
	Green Control	Petro-Control	System 1	Petro-Control	System 2
Resin Used	A	C	D	C	E
Clear Casting Data					
Resin HDT (°C)	134	177	175	177	200
Elongation (%)	2.1	1.25	1.4	1.25	1.0
Resin bio-content (%)	18.0	0.0	20.0	0.0	10.0
SQ Data					
AI	65-75	55-60	55-65	45-50	45-55
OP	7.7	7.7	8.2	9.0	8.5
DOI	70	85	90	99	95

SMC Mech. Prop.					
Tensile Strength (MPa)	100	95	103	86	80
Tensile Modulus (GPa)	12.2	13.6	12	9.4	11.3
Flex Strength (MPa)	235	260	250	170	180
Flex Modulus (GPa)	13	14.7	12.3	10.0	11.7
Toughness (MPa)	1.103	1.041	1.076	0.621	0.552
Elongation (%)	1.65	1.70	1.75	1.30	1.20
Glass content (%)	32.5	29.9	30.5	29.3	29.5
Shrinkage (mm/m)*	0.63	0.30	0.45	0.84	0.76
* Expansion					

Figure 5: Comparative Clear Casting, Surface Quality, and SMC Mechanical Properties.

	Economy	Green	Premium
Resin Used	C	A	C
Liquid Properties			
LVT Visc. (cP)	165	150	145
Solids (%)	48	50	48
Resin bio-content (%)	0.0	8.0	0.0
Clear Casting Data			
Resin HDT (°C) (ISO 75)	70	78	76
Tensile Strength (MPa) (ISO 527)	17.0	32.0	40.0
Tensile Modulus (GPa) (ISO 527)	1.22	1.78	2.28
Tensile Elongation (%) (ISO 527)	2.8	3.2	3.0
Flex Strength (MPa) (ISO 178)	27.5	41.6	56.0
Flex Modulus (GPa) (ISO 178)	1.37	1.44	1.88
Laminate Properties			
Tensile Strength (MPa) (ASTM-D-638)	147	147	125
Tensile Modulus (GPa) (ASTM-D-638)	9.9	10.8	8.9
Tensile Elongation (%) (ASTM-D-638)	2.1	2.3	2.2
Flex Strength (MPa) (ASTM D-790)	154	172	199
Flex Modulus (GPa) (ASTM D-790)	9.9	9.2	7.5
SQ Data			
AI	90	60	40
OP	7.0	8.2	9.9
DOI	70	83	100

Figure 6: Comparative Liquid, Clear Casting, Laminate and Surface Quality Properties for LPA-Containing Infusion Resins.