RENEWABLE RESOURCE-BASED COMPOSITES FOR THE AUTOMOTIVE INDUSTRY

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Abstract

Renewable raw materials have drawn considerable attention in the last several years for the production of bio-based composite materials. The automotive industry, in particular, has considered these materials as a viable solution to simultaneously reduce part weight, cost and reliance on foreign oil. Geopolitical instability and fluctuating costs of petroleum feedstocks further support the concept of using bio-based composites as alternatives to their petroleum-based counterparts.

This paper focuses on "green" sheet molding compound (SMC) composite materials targeted for structural and class A automotive applications. These composite materials have been prepared from renewable resource-based unsaturated polyester resins (UPR) with glass fiber reinforcements using standard SMC processing conditions. Their properties have been described and compared side-by-side with their petroleum-based counterparts. In general, results confirm that bio-based composite materials exhibit equivalent performance characteristics to their all-petroleum analogues and represent practical alternatives for existing automotive applications.

Background and Requirements

Bio-based composites have been embraced by automobile manufacturers and suppliers worldwide as a means to support their sustainability and business efforts. These efforts include vehicle weight reduction, lower fuel consumption and CO_2 emissions, cost savings and relief from foreign oil dependence. During the last several years, considerable efforts were put towards the development of thermoplastic and thermoset bio-composite materials based on natural fibers (1-3) for the production of door panels, seat backs, package trays, dashboards, headliners and various interior car parts. Although successful in some areas, natural fiber composites still cannot meet the performance requirements for exterior and structural part applications where class-A surface finish or enhanced mechanical integrity characteristics are desirable. Technical challenges such as fiber-matrix adhesion and compatibility, homogenization of fiber properties and their high moisture content still need to be properly addressed.

To address these issues, higher performing bio-based composites are needed to fill these application gaps. The concept of bio-based glass fiber reinforced composites based on UPRs derived from renewable resources (4, 5) is an alternative that has received an increasing amount of attention by those involved in the automotive manufacturing chain. Due to their sustainability efforts and corporate mandates, original equipment manufacturers (OEMs) represent a significant driver for "pull-through" development of this technology.

UPRs are an essential component in these bio-composite materials. They are styrene solutions of products of polycondensation reaction between dibasic acids or anhydrides and glycols. Until recently, starting raw materials for UPRs were exclusively petroleum based. 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. However, in recent years, rising environmental awareness and escalating petroleum prices produced a dramatic change in the way chemical and composites industries do business, and how consumers view their products (6, 7). 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.

Despite early efforts from academic researchers (8), no commercially available "green" UPRs appeared in the market until 2003. The first industrially available bio-based UPR (Envirez®[1] 1807 Resin) 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 (4, 9). Direct comparison of the resin's liquid properties (Table 1) and mechanical properties of molded SMC parts (Table 2) showed similar properties to standard petrochemical resin (SPR) counterpart, such as poly(propylene glycol maleate).

Table 1: Liquid Property Comparison between Envirez1807 Resin and Standard Petrochemical Resin (SPR)

Property	Envirez 1807	SPR
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

Table 2: Properties of Molded Standard Density Panels Prepared from Envirez1807 Resin and Standard Petrochemical Resin

Property	Envirez 1807 SMC	SPR SMC
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

[1] *Envirez® is a registered trademark of Ashland*

Since its introduction to the market, interest in “green” UPRs and composites has grown considerably and new opportunities in composites markets have opened up (9). The fact that the first “green” resin could not be formulated to meet performance requirements for all composites applications prompted Ashland to develop new generations of renewably resourced UPRs to satisfy the demand.

Diminishing petroleum reserves, crude oil price escalation, and rapid advances in white biotechnology (10) changed raw material markets to a point where renewable raw materials and bio-products can effectively compete with petrochemical analogues. 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 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

Ashland’s Composite Polymers Global Technology Group is actively working on identifying and evaluating renewable raw materials for use in UPRs and composites. We have prepared new generations of renewably resourced UPRs for evaluation. Sheet molding compound and compression molding 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 castings were removed from the mold and post-cured for 120 minutes at 150°C.

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.

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. SQ is defined by Ashland Index (AI, long term waviness parameter) and Distinctness of Image (DOI) and Orange Peel (OP) (short term waviness parameters) (11). A lower AI number coupled with a higher DOI and OP, result in better SQ.

Results and Discussion

Envirez 1807 resin and a standard 100% petroleum-based poly(propylene glycol maleate) resin (SPR) were used as bio-based and petrochemical controls, respectively, for our comparative study. These two resins were directly compared to several new renewable resourced resins, including Envirez 10418 resin and Envirez 10465 resin. Envirez 1807 resin, Envirez 10418 resin and SPR resin were comparatively studied in a structural SMC formulation. Table 3 lists comparative clear castings data for all resins, as well as surface quality (ALSA) and mechanical property data for molded SMC panels prepared from the corresponding structural SMC formulations. Results indicate that newly prepared “green” resin Envirez 10418 shows comparable heat distortion temperature (HDT) and elongation-at-break values to the petroleum-based analogue. Unlike SPR, Envirez 10418 resin has bio-content of 20% by weight on a styrene solution basis. Furthermore, its clear casting properties also show improvements in HDT and bio-content values in comparison to the bio-based control resin Envirez 1807.

Table 3: Comparative Clear Casting, Surface Quality, and Structural SMC Mechanical Properties.

	STRUCTURAL SMC		
	Green Control	**Petro-Control**	**System 1**
Resin Used	**Envirez 1807**	**SPR**	**Envirez 10418**
Clear Casting Data			
Resin HDT (°C)	134	177	175
Elongation (%)	2.10	1.25	1.40
Resin bio-content (%)	18.0	0.0	20.0
SQ Data			
AI	65-75	55-60	55-65
OP	7.7	7.7	8.2
DOI	70	85	90
SMC Mech. Prop.			
Tensile Strength (MPa)	100	95	103
Tensile Modulus (GPa)	12.2	13.6	12.0
Flex Strength (MPa)	235	260	250
Flex Modulus (GPa)	13.0	14.7	12.3
Toughness (MPa)	1.10	1.04	1.08
Elongation (%)	1.65	1.70	1.75
Glass content (%)	32.5	29.9	30.5
Shrinkage (mm/m)[2]	0.63	0.30	0.45

[2] *Positive values denote expansion*

When used in a standard density structural SMC formulation, these three resins produced molded SMC panels with comparable mechanical properties. However, due to the slightly higher glass content of the molded SMC panels of Envirez 1807 resin (32.5%), it seems that both SPR and Envirez 10418 resin SMC panels show slightly better mechanical performance. Surface characteristics of molded panels based on Envirez 10418 resin and SPR resins clearly outperform those of Envirez 1807 resin. However, while their AI values are almost the same, it is important to note that short term waviness parameters (DOI and OP) of Envirez 10418 resin SMC panels show visible improvements over SPR SMC panels.

More recently, two new “green” UPRs (A and B) were also developed and tested in Ashland’s labs for structural SMC applications. These UPRs were based on corn-derived glycols and had variable bio-content. Utilization of these resins in standard density SMC formulations showed how compositional differences affected the resins’ clear casting properties as well as mechanical properties and surface characteristics of the corresponding molded SMC panels (Table 4).

Table 4: Comparative Clear Casting, Surface Quality, and Structural SMC Mechanical Properties for newly developed “green” resins A and B.

STRUCTURAL SMC			
	Control	**System 2**	**System 3**
Resin Used	**Petro-Analogue**	**A**	**B**
Clear Casting Data			
Tensile Strength (MPa)	74	67	59
Tensile Modulus (GPa)	3.8	3.9	4.2
Flex Strength (MPa)	137	117	114
Flex Modulus (GPa)	3.9	3.9	4.3
Elongation (%)	2.27	1.90	1.55
Resin HDT (°C)	115	129	126
Resin bio-content (%)	0.0	11.0	20.0
SQ Data			
AI	101	96	89
OP	8.7	9.9	9.8
DOI	73	94	92
SMC Mech. Prop.			
Tensile Strength (MPa)	130	111	102
Tensile Modulus (GPa)	15.6	14.1	13.5
Flex Strength (MPa)	234	241	226
Flex Modulus (GPa)	14.0	14.2	14.2
Elongation (%)	1.50	1.57	1.60
Glass content (%)	28	29	30
Shrinkage (mm/m)	0.28	0.25	0.25

Clear casting results point out that increasing bio-content in resins A and B versus SPR resin improves HDTs and both tensile and flex modulus values at the expense of their corresponding strengths. Similarly, the corresponding molded SMC panels show a visible drop in tensile strength and modulus values with increasing bio-content of SMCs while flex values stayed the same. On the other hand, surface qualities of molded SMC panels showed remarkable improvement when green resins were used for their fabrication. In particular, Orange Peel (OP) and Distinctness of Image (DOI) values exhibited the greatest improvements. These examples show how complex structure-property relationships can affect performance of the final molded parts. They also illustrate how performance requirements for structural SMC applications can be met through SMC reformulation and UPR optimization.

Standard 100% petroleum-based poly(propylene glycol maleate) resin (SPR) was also used as the petrochemical control in our comparative study for the development of “green” automotive class-A SMCs. Performance of this resin was directly compared to the performance of Ashland’s class-A bio-based resin, Envirez 10465 resin in class-A SMC formulations (Table 5).

Table 5: Comparative Clear Casting, Surface Quality, and Class- A SMC Mechanical Properties for Envirez 10465 and SPR resins.

	CLASS - A SMC			
	Petro-Control	**System 4**	**System 5**	**System 6**
Resin Used	**SPR**	**Envirez 10465**	**Envirez 10465**	**Envirez 10465**
Clear Casting Data				
Resin HDT (°C)	177	193	193	193
Elongation (%)	1.25	1.16	1.16	1.16
Resin bio-content (%)	0.0	10.0	10.0	10.0
LPA bio-content (%)	0.0	0.0	0.0	14.5
SQ Data				
AI	45-50	47	40	42
OP	9.0	8.6	9.1	9.0
DOI	99	95	99	98
SMC Mech. Prop.				
Tensile Strength (MPa)	86	80	77	78
Tensile Modulus (GPa)	9.4	11.3	11.1	10.6
Flex Strength (MPa)	170	180	158	168
Flex Modulus (GPa)	10.0	11.7	10.8	11.2
Elongation (%)	1.30	1.17	1.17	1.30
Glass content (%)	29.3	29.5	28.4	28.9
Shrinkage (mm/m)	0.84	0.76	0.85	0.88

Incorporation of renewable resource components into the Envirez 10465 resin produced a 10% bio-based UPR and resulted in significant improvement in its clear casting HDT values when compared to the SPR resin. When used in class-A SMC formulations, Envirez 10465 resin gave molded panels with comparable or slightly better performance than its all-petroleum counterpart. Indeed, data show that mechanical property requirements can be achieved without sacrificing the surface quality of molded parts.

Besides good mechanical integrity, molded SMC parts intended for automotive class-A SMC applications need to provide superior surface finish. Because of that, resin performance needs to be optimized to satisfy this requirement. The base resin used in a class-A SMC formulation needs to respond properly to low profile additives (LPA) and enhancer components used for shrinkage control and provide for optimum dimensional stability of molded parts. Large shrinkage or large expansions during molding usually produce parts with poor surface quality and/or surface defects. Therefore, close to zero-shrink or small expansion is more desirable to avoid these issues. Good LPA phase-out and efficiency are important in these applications so proper choice of LPA is quite critical. Because of the multi-component nature of SMC formulations and the fact that there exist numerous interactions between all components, it is challenging to develop a bio-based SMC formulation that simultaneously meets mechanical, physical, and surface quality requirements for class-A automotive applications. Furthermore, if economic factors for making each component are thrown into the equation, the challenge becomes even greater.

During the developmental work we discovered that certain polyester LPAs made from renewable resource components, like Ashland's Envirez resins, can contribute to efficient shrink control while adding to the overall bio-content of the molded SMC parts. System 6 (Table 5), in particular, was prepared with both "green" UPR and LPA components. Performance of this class A SMC formulation proved to be equivalent to both SPR and other Envirez resin-based formulations. This example shows that sustainability of composites for automotive industry can be addressed in numerous ways. Applications can be met if the proper combination of base SMC components is in place and enough work has been done for full system optimization.

Summary

Commercially available bio-based UPRs for industrial automotive applications exist today. Corresponding structural and class-A SMC composites have been prepared and their performance compared side-by-side with all-petroleum-based counterparts. Results show that performance of these "green" composites matches or exceeds that of all-petroleum based analogues thus providing an economical and sustainable alternative to current commercial materials on the market.

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