PHENOLIC SMC FOR AUTOMOTIVE FIRE RESISTANCE

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Abstract

Phenolic resins that meet REACH compliance and contain lower free-formaldehyde are safer to handle, compound, and mold. These resin systems do not contain any styrene or require any fillers to achieve their rated fire resistance. A commercial phenolic sheet-molding compound (SMC) is presented that achieves a 2-minute cycle time and addresses the unique requirements in an electrified vehicle architecture. This new SMC material includes all the industrially relevant considerations including material processing, shelf life, and surface finish. Other topics such as material hybridization and comparison to incumbent materials also discussed.

The resin system uses a water-based phenolic resole which is acid-cured. This chemistry presents several unique challenges and opportunities for the industry such as managing formulation pH and appropriate methods for quality control.

A demonstrator battery cover highlights the superior fire performance, impact resistance, and light weighting that is achieved with this resin technology. The phenolic SMC formulation is compatible with already established engineering fibers and textiles resulting in low-shrink, creep-resistant composites. The mechanical performance demonstrates strength and impact energy absorption greater than cast aluminum, with over 65% property retention after fire testing. Most importantly, the material economically meets the most restrictive automotive fire performance standards.

Background

Electrified vehicle architectures are now being deployed globally with forecasts indicating a rising trend in consumer automobiles. While current fire protection standards such as the European ECE R100 and Chinese GB/T 31467.3 help define the expected minimum performance of battery encasements, even more aggressive battery run-away testing is expected to push the requirement higher. Fire resistance is no longer an optional characteristic, but a high-performance requirement.

Previous development work with phenol-formaldehyde (PF) resins resulted in a now commercial material system that can exceed all current performance requirements [1]. The resin system is a combination of four components, as shown in Figure 1, comprising a <0.1% free-formaldehyde phenolic resole, an acid-based catalyst package, a compatible internal mold release, and a color-stable black pigment.

The compounded system with glass fiber exhibits excellent mechanical properties, passes automotive fire requirements, has a shelf life of greater than two weeks, and requires no EHS labeling requirements. Additionally, a sub-2-minute cure time has been demonstrated on a large complicated geometry representative of production.

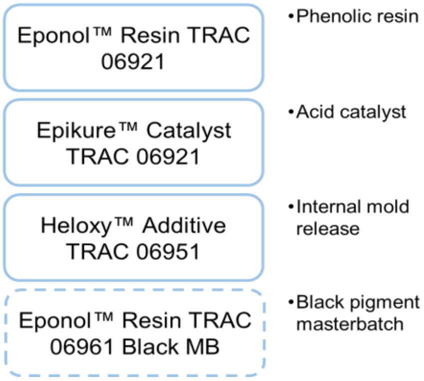

Figure 1: The components of a phenolic resin for SMC

In addition to the performance envelope for such a fire-retardant SMC, strong commercial value is necessary to gain acceptance in the automotive market. This paper goes into some of the design considerations toward minimizing the cost of a battery enclosure.

Hexion's Unique Material Value Proposition

Pigment comparison

One of the major challenges in developing a suitable resin system for automotive is to deal with some of the customer-centric requirements such as requirements for color uniformity and stability over the lifecycle of the vehicle. Almost all phenolics strongly yellow as they age, more so if they are exposed to sunlight. To this end, any colorant system such as inks or pigments must be equally color stable as well as being compatible with the resin system, which in this case also means withstanding the presence of the acid catalyst.

A series of benchtop trials were conducted to mold small coupons of the phenolic SMC system with different concentrations (0.4 up to 3.0 parts per hundred resin) of a selection of pigments thought to be suitable for this application. A viable pigment had three broad requirements: acidic so as not to inhibit the curing reaction, stable so that a strong acid would not cause the pigment to degrade or separate while the SMC is matured, and soluble in a phenolic resole so that it evenly disperses and provides uniform pigmentation.

A fabricated exemplar is shown in Figure 2; the samples were composed of the resin system hand-layed with a symmetric glass fiber plain weave stitched to a random fiber mat and subsequently hot-press molded. Once the samples were fully cured, they were left in direct sunlight for 7 days to examine the color as well as mechanically tested following the test methods below.

Figure 2: A set of color pigment concentration samples prior to being cured; each sample is 300 x 80 x 2.5 mm

Figure 3 presents three of the tested pigments in terms of the pigment concentration in the resin paste versus the resulting cured mechanical properties. While the properties are taken from partially continuous fiber laminates, the normalized results with respect to fiber volume fraction are directionally informative for discontinuous fiber composites. Here even small concentrations of piment cause a decrease in mechanical performance. Similar results were observed with varying amounts of internal mold release. The reduction in properties informs the formulation strategy: use as little pigment and internal mold release as possible to achieve the desired production requirements while maintaining the mechanical properties as much as possible.

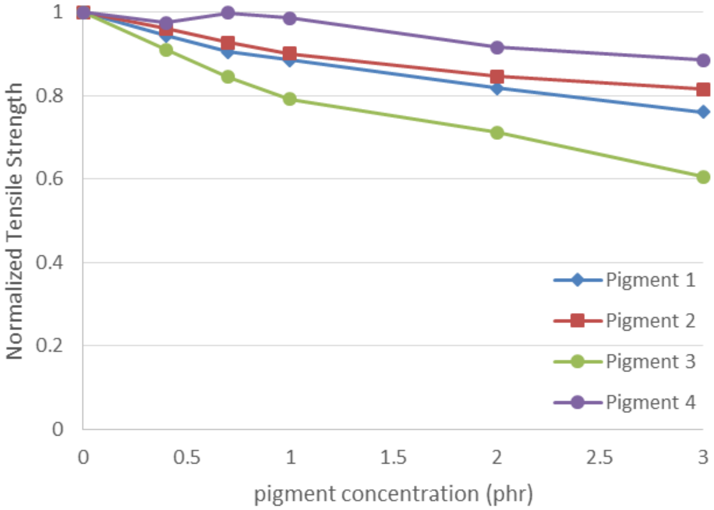

Figure 3: Pigment concentration impacts vs. normalized mechanical performance for two selected pigments

Further testing was conducted to determine the complicated interactions with the internal release candidates, suitable fillers, and catalyst package. A sensitivity analysis of all the tested components revealed a strong pH dependence overall. Whereby it is critical to keep the system pH within a narrow range to as to balance a desire for a long shelf life compound with a fast cure. The selected pigment 4 was a refined version of pigment 1 which demonstrated the best colour-fastness, did not overly interfere with the cure reaction, and was able to be adjusted to further minimize the mechanical performance impact.

Industrial scale-up

The next step toward completing the commercial formulation validation is to bring the material into service on an industrial line. Using the Dieffenbacher SMC line (Figure 4) at the Fraunhofer Project Center, a series of increasingly larger batches were compounded to first check the handle-ability of the material and second the storage and maturation robustness. Without any changes to the equipment, and without any heating or other specialized functionality, the phenolic resin was able to compound 4800 tex glass and 50k carbon fiber at relatively high basis weights of 5000 and 3000 g/m^2 respectively. In electric vehicle applications, the glass fiber is the more important design choice since it represents the lowest cost solution, though there are several niche applications for the carbon fiber variant. Unidirectional fiber variants were also run in order to understand the options of hybridized and reinforced designs. Much of the success of the compounding is due to the lack of fillers in the paste which enable the low viscosity resin to easily wet out high fiber content SMC.

Figure 4: Phenolic SMC being fabricated for scale-up testing

The compound was matured at room temperature for a period of 3-5 days until the complex viscosity of the compound reached at least 40 million centipoise via B-stage reaction. The ambient temperature during the first 12 hours after compounding is the most important to minimize the initial exotherm, and can be done by keeping the roll or festoon below 40°C.

Panels were initially molded at 135°C for 5 minutes, before brining the cure time down to 2 minutes over the course of several molded panels. Square panels (457 millimeters square, Figure 5) of a variety of thicknesses and mold coverages were produced to check the mold flow within the tool, the cure speed, the surface finish, and document various molding parameters. A complex geometry battery box was also produced for demonstration and for customer testing. Mold coverages down to 40% were obtained with tuned process conditions.

Figure 5: Sample phenolic/glass SMC plate molded at the Fraunhofer Project Center, dimensions 457x457x2.5 mm

While the phenolic resin formulation is designed to be user friendly, there are several important industrial considerations to use the material successfully:

- The SMC carrier film needs to be compatible with the resin system such that it will not disintegrate in contact with an acidic system and will release once the phenolic has properly matured.
- The mold surface needs also to be resistant to corrosion so as not to foul the tool.
- Quality control methods for the resin and compound will need to align to the unique properties of this formulated system.

Material Characterization

The molded phenolic SMC plates were fully characterized compared to current materials typically used in fire retardant applications. The tension testing follows ISO 527-4, the fiber content analysis came from ISO 7822 testing, and the impact analysis was conducted in accordance with ISO 6603-2. Panels were molded to yield planar isotropic properties. The two commercial incumbent materials also commonly seen in lower-performance battery protection applications are an ATH-filled (Aluminum TriHydrate) unsaturated polyester/vinylester resin blend and A356 cast aluminum.

Table 1: Selected material properties of phenolic/glass SMC directly against incumbent materials

Parameter	Unit	PF SMC	PF Prepreg	UPR/VER SMC w/ATH	A356 cast aluminum
Fiber Weight Fraction	%	56	60	41	N/A
Density	g/cm^3	1.78	1.85	1.8	2.7
Tensile Strength	MPa	220	630	90	240
Tensile Modulus	GPa	16	30	11	74
Impact Energy Absorption	kJ/m^2	68			45
Melting Temperature	°C	N/A	N/A	N/A	600

Case Study: OEM Battery Box concept

The previous work [1] already went into some detail regarding the superior fire performance associated with phenolic resins. Here, a business case is constructed to link the value of the material to this increased performance. All figures in the cost model are to be taken as directional and not prescriptive to give an overall picture of the expected cost/weight/performance ratios that can be obtained. The model does assume that each design is optimized for the given material and process method and uses a simple weight-cost estimate as the underlying calculation.

A large monolithic battery case is hypothesized to have average rectangular outer dimensions of 1.18 x 0.83 x 0.13 meters (length x width x depth). Such a construction will have a given wall thickness depending on he material, how it is molded, and other process, material, or engineering requirements such as minimizing deflection and side impact attenuation. Figure 6 shows a graphical depiction of the overall battery box geometry used for this analysis. Tooling costs are by simple allocation and some post-processing is included to determine an expected raw, per-part cost.

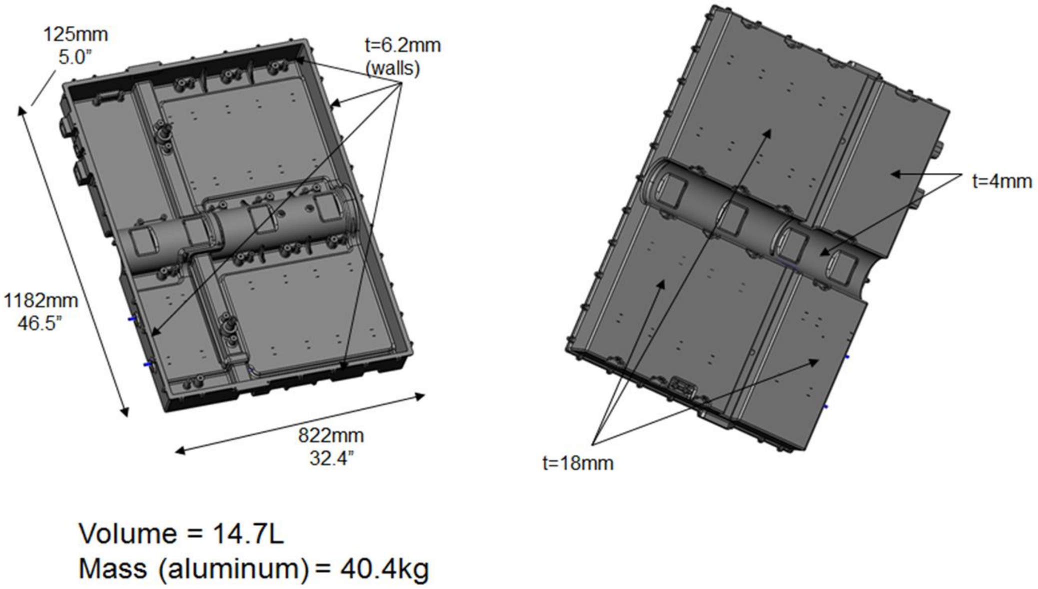

Figure 6: Hybrid vehicle battery box design for case study comparison; thickness indicated for aluminum version.

The aluminum die cast part has large wall thickness due to tooling limitations in filling the large component. All three metal designs are assumed to require an equal amount of machining. The ATH-filled unsaturated polyester and slightly increased performance unsaturated polyester/vinyl ester blend both require an intumescent coating to be able to achieve the requisite fire resistance. Insulation is not included in this model as this is not deemed to be a universal OEM requirement, though it is noted the SMC products would have an advantage here as well. While the model inputs are obfuscated, the resulting categorical costs are displayed in Figure 7, along with the calculated weight and overall part cost.

	Cast Aluminum	**GF UPR SMC w/ATH**	**GF PF SMC**	**GF PF SMC+FABRIC**
	$165.12	**$148.90**	**$91.10**	**$154.19**
Raw Material	$100.86	$70.01	$75.71	$138.81
Machining, Post Processing	$55.00	$14.59	$14.59	$14.59
Intumescent Coating, Insulation	$1.26	$63.50	$0.00	$0.00
Tooling Allocation	$8.00	$0.80	$0.80	$0.80
Part Weight (kgs.)	43.6	26.5	12.5	10.4

Figure 7: EV battery box part summarized cost model

From the constructed model, all materials are somewhat viable as their resulting costs are within the same order of magnitude. The metallic solutions are generally the cheapest raw goods per unit mass, but also have significant component weight and require secondary machining. Stamped aluminum represents the lowest piece weight and steel the lowest cost of the metal solutions. The metals are the current majority in terms of market share and are praised for their relative ease in design freedoms.

The unsaturated polyesters can be molded into highly complex, net-shape parts resulting in a low part cost. Much of the benefit is the further weight savings over a cast aluminum fabrication. If the fire performance is not a strong requirement, and an intumescent coating is not required, the current fire-retardant SMC solutions are excellent, low-cost alternatives. They can integrate multiple parts in their construction, offer multi-functionality, and can result in low-cost, low-mass components.

In a best of both worlds result, the phenolic SMC does not require filler to achieve its fire performance, and like the SMC materials, can produce the same complex, net-shape parts. With the increased performance, a smaller wall thickness is needed achieve the same overall component properties, and therefore an important cost and weight savings result. Here the component has the highest cost per unit raw material, but the lowest weight and still the lowest piece cost where fire protection is of utmost importance. A further weight savings is possible by incorporating continuous glass fiber, but this results in a cost premium for the design, though still competitive to the aluminum variant.

Another way to visualize the overall result is in Figure 8 with a stacked bar chart showing the cost buildup of the battery box structure for three different materials. Here it is easy to understand the relative impact of material, processing, and secondary assembly steps with respect to the piece price and part weight. Though many automotive OEM's are loathe to pay for weight savings, there exists a strong argument for good material selection in new EV platforms to achieve weight savings with a cost savings rather than a cost premium.

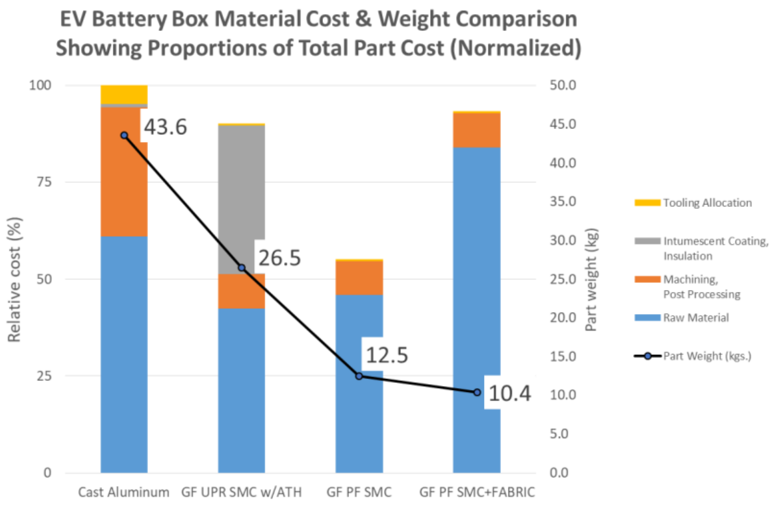

Figure 8: Down-selected cost and weight performance for the three most common battery box materials: cast aluminum, ATH-filled UPR SMC, and the phenolic SMC

The focus around SMC as a viable material format is further accentuated with the extended options toward fully structural designs by incorporating continuous fiber. The phenolic SMC is readily co-molded with the same compatible resin system in a prepreg material format to yield a substantial further increase in weight savings and even a slight cost savings over the incumbent metallic solution. This is unique to the phenolic SMC since it is formulated without filler and can easily impregnate unidirectional fiber whereas the filled UPR resins cannot.

Summary

A newly commercialized phenolic SMC resin system was demonstrated with respect to the formulating and production capabilities. Several industrially relevant concerns are highlighted in using this uncommon resin system and a path toward commercial acceptance is presented. The material performance is presented as compared to several incumbent materials. The Phenolic SMC is shown to achieve best in class fire performance without sacrificing the mechanical properties. The system is cost-competitive against both metal and incumbent SMC systems alike and offers several key benefits.

The strong mechanical performance of the phenolic is on par with the strength of cast aluminum and even exceeds the aluminum in absorbed impact energy. The phenolic SMC is a versatile tool that can be directly deployed into the current molding infrastructure and result in lightweight component design with the best-in-class fire resistance. The commercial system presented is formulated and optimized for fast cycle time molding.

Future work will focus on a complete lifecycle assessment to validate the environmental and sustainability aspects of this material system as well as provide potential solutions toward the recycling options.

References

1. Swentek I, Greydanus S, Colclough P, and Ball C, (2018) Phenolic SMC for Automotive Fire Resistance. Automotive Composites Conference and Exhibition, ACCE 18, Novi, Michigan.