PHENOLIC SMC FOR AUTOMOTIVE FIRE RESISTANCE

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Abstract

Phenolic materials have long been known to achieve the best fire, smoke and toxicity performance of the available commodity polymers. However, these materials are known to have more complex process requirements, with lower mechanical properties than epoxies, risks from formaldehyde exposure, and long cure schedules. New developments in resin chemistry have resulted in exceptionally low free-formaldehyde resins (less than 0.1%) and new acid catalyst formulations to achieve safe, high volume production. With improved formulation, phenolic composites represent a new opportunity to meet the demanding automotive fire resistance specifications without compromising the composite mechanical performance. Even at full-scale, this material passes the toughest fire exposure testing where other material systems regularly fail. A new phenolic SMC is compared to other fire retardant materials at both bench-level testing and full-scale testing and an attempt is made to connect these length scales. The mechanical performance pre-exposure and post-exposure is examined to fully describe the fire retardant characteristics in relation to current material systems to validate a production-ready compound.

Background

Phenol-formaldehyde (PF) resins are thermosets that, when cured, achieve a high crosslink density. This property gives phenolics excellent thermal stability and chemical resistance, but typically at the expense of toughness and ductility. Resoles, one of the primary types of PF resins, generally contain an acid-based catalyst. As part of the condensation cure reaction, which has a moderate reaction rate, free-formaldehyde can be volatilized and form hazardous vapors [1].

To deal with these issues a new generation of phenolic resoles have been developed with extremely low, <0.1% free-formaldehyde. Additionally, with snap-cure latent acid catalysts, the resin shelf life is prolonged while reducing the in-mold cure time to a couple of minutes. Together this process yields safe, intrinsically fire resistant material that can be processed at automotive rates.

The advent of vehicular electrification has created the need for materials that meet fire, smoke and toxicity (FST) requirements typically found in aerospace or rail, but can be made into parts at much greater manufacturing rates. The European ECE R100 and Chinese GB/T 31467.3 standards specify the need for battery-powered vehicles to be able to withstand collision, fire emergencies, and allow occupants time to safely evacuate. Because of the size of the battery systems, materials that previously passed benchtop fire testing standards are no longer suitable in large-component deployment. So the development of new material formulations is required to meet these new regulations.

Experimental Procedure

Process Design of Experiments

Hexion has introduced a new class of phenolic resins suitable for a variety of manufacturing process routes including sheet molding compound and prepreg compression molding. The basic building blocks are the same and based on Hexion Cellobond™ Resin J6021X01 paired with a suitable latent acid catalyst. Fillers are not required to achieve any of the mechanical or thermal performance but can be added to improve moldability, surface finish, color, and/or other functionality as needed. For the present study, the resin was previously compounded in 20kg batches with a standard e-glass roving chopped in 25 mm lengths and provided as a ready-to-mold sheet from an industrial SMC line.

To assess this new material for the SMC process, a small design of experiments was conducted examining the temperature, pressure and mold coverage of the phenolic SMC. The molding was carried out on a chromed 457x457 mm square plaque tool with a volume of compound to yield 2 mm thick panels. The conditions for the 2^3 full-factorial experiment are summarized in Table 1. The panels were ranked on the appearance, size, and impact of observed defects. Additional panels and test articles were produced using the best molding parameters for further characterization and component testing.

Table 1 – Phenolic SMC molding trial DoE variables

Parameter	Unit	Low Condition	High Condition
Mold Temperature	°C	135	150
Mold Pressure	Bar	50	100
Mold Coverage	%	50	90

Fire Testing

Fire resistance was assessed in several ways: quick bench-level tests, moderate “scientific” tests, and full-scale article testing. Some of the bench testing was also extended to a highly filled vinyl ester SMC and a flame retardant epoxy to give context to the results. The bench tests were performed following UL 94 and FAR 25.853 to assess the horizontal and vertical burn respectively as well as heat release and smoke density. Cone calorimetry following ISO 5660 was also performed to capture the heat release rate and total heat of combustion. Finally, article-level testing following ECE R100 Section 8E and GB/T 31467.3 subsection 7.10 was performed on a portion of a molded battery box cover from a legacy production electric vehicle; the setup is shown in Figure 1. The battery box used for the full-scale fire testing was molded a 3.0 mm thickness.

Figure 1 – Fire testing setup after ECE R100 & GB/T 31467.3

In Figure 1, the battery box cover is sitting atop a 0.20 m^2 pre-heated trough filled with high-octane gasoline and is subjected to direct flame for 2.5 minutes. Panels of molded material were also exposed to fire in this way to measure mechanical properties post flame exposure. For several of the articles burned in this way, data was collected form thermocouples previously affixed to the sample. The thermocouples were placed in direct path of the fire on the underside of the battery box and also opposite that on the interior of the box. Another was placed in a small pilot hole drilled to a depth of roughly half the box thickness while the last thermocouple was placed on the interior side wall 25 centimeters further from the flame. Additionally, a FLIR imaging camera shot full 640x480 infrared video at 15 frames per second that simultaneously captured the temperature at each pixel location. This allowed for a full-field view of the temperature distribution, thermal conductivity and flame spread.

Material Characterization

Panels of consecutively molded material, native and post-burn, were sectioned into test specimens for tensile, flexure, impact, DMA and other analysis as in Figure 2. The tension testing follows ISO 527-4, the flexure testing followed ISO 14125, the fiber content analysis came from ISO 7822 testing, and the impact analysis was conducted in accordance with ISO 6603-2. Since the panels were molded without maintaining the ‘machine direction’ of the SMC (a preferential alignment of fiber along the length of the material roll), the panels can be treated as planar-isotropic, and hence the samples were machined in one direction only.

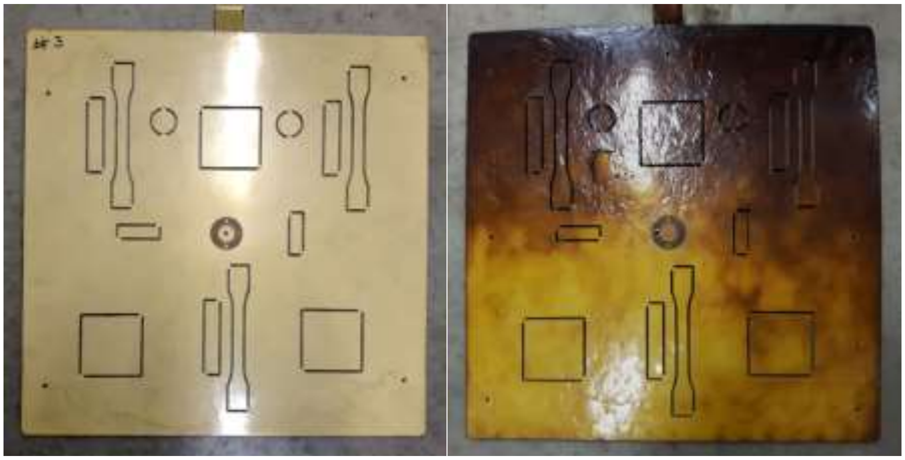

Figure 2 – Native and post-burn panels after sample pattern machining

Results and Discussion

A summary image of all the molded panels from the design of experiments is in Figure 3. The DoE analysis indicated no correlation with the molding pressure, low correlation with the cure temperature (with the lower temperature being in the direction of improvement), and high correlation with the mold coverage (with lower coverage better). The presence of the brown ring in the center of the panel is from the air poppet in the tool, which is not chromed, and causes oxidation of the resin from the tool surface. Potential oxidation or a secondary reaction of the fiber/sizing/matrix interface has led to the discoloration in the molded part present only in the higher temperature moldings (top row), and warrants further investigation.

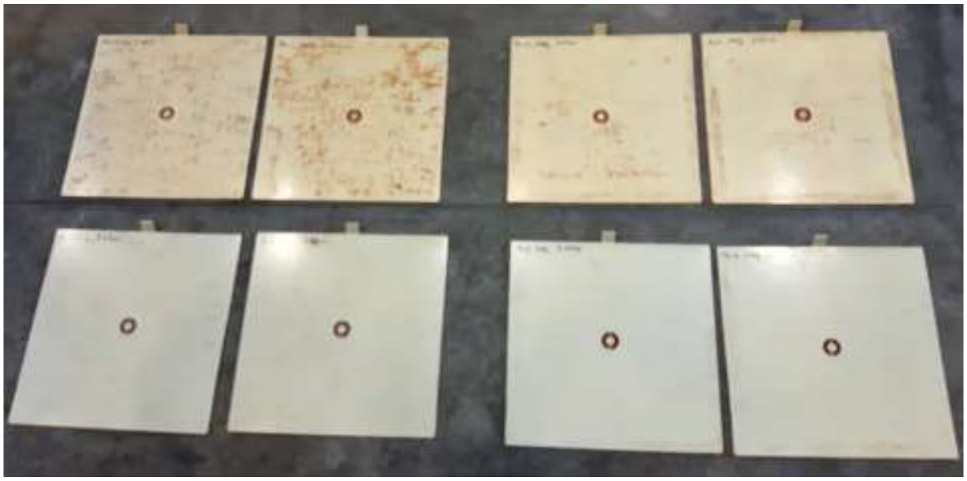

Figure 3 – Mini-DoE molded panels examining temperature, pressure and mold coverage

The measured mechanical properties in Table 2 are for both the phenolic SMC and also the same phenolic matrix paired with continuous fiber perhaps better thought of as phenolic prepreg. Though the strength and stiffness are average for a glass reinforced polyme, the fire resistance, smoke, and toxicity performance leave all other contenders well behind without a significant increase in the cost of the material.

Table 2 – Selected material properties of new phenolic composites with glass fiber reinforcement

Parameter	Unit	PF SMC	PF Prepreg
Fiber Weight Fraction	%	40	48
Density	g/cm^3	1.8	2.0
Tensile Strength	MPa	130	400
Tensile Modulus	GPa	15	30
Tensile Elongation	%	1.7	3.0
Impact Strength	kJ/m^2	53	95

The fire test results, Table 3, is where the phenolic performance really begins to shine, easily passing the most common fire testing standards by a healthy margin. The unfilled FR epoxy has a reasonably good fire resistance and is most suited to applications where mechanical performance is most important or you need a styrene-free and phenol-free solution. The filled vinylester (but this could just as easily be a filled unsaturated polyester) does not easily pass all the fire testing; however, as a commodity material is the first solution typically attempted in cost-conscious applications or where performance is not as critical.

Table 3 – Selected thermal properties of different material systems from 2mm plates

Test	Unit	PF SMC	FR Epoxy	Filled VE
Tensile Modulus	GPa	15	30	13
UL 94		Pass, V0	Pass, V0	Pass, V1
FAR 25.853		Pass	Pass	Conditional
Heat release, peak	kW/m^2	24	77	85
Heat release, 2 min. total	kW.min/m^2	2	62	81
Smoke Density		0.2	59	72
ECE R100 Annex 8E GB/T 31467.3 §7.10		Pass	TBD	Fail

In the image of the post-burned phenolic panel (Figure 2b) you can see the surface still has a luster from the reflected overhead lights – an indication that resin is still present and that the matrix has retained some performance characteristics. From the material testing results, the post-burn phenolic SMC panels maintain greater than 65% of their original tensile and impact strength.

Data from the thermocouples attached to one of the battery boxes is presented in Figure 4. Though the flame temperature increases to nearly 900°C within the 150 second test, the phenolic SMC is a good insulator and the material centerline temperature climbs just shy of 400°C. At this scale of thermal energy exposure most polymer systems would be partially or completely incinerated. Further, the phenolic SMC self-extinguished any flame in under 5 seconds following the 2.5 minute burn where all other materials failed to self-extinguish in a reasonable time and continued to smolder from the high heat. The test in which this data was generated can be seen in a short video documenting the event: https://www.youtube.com/watch?v=3eQcWGnJk_g

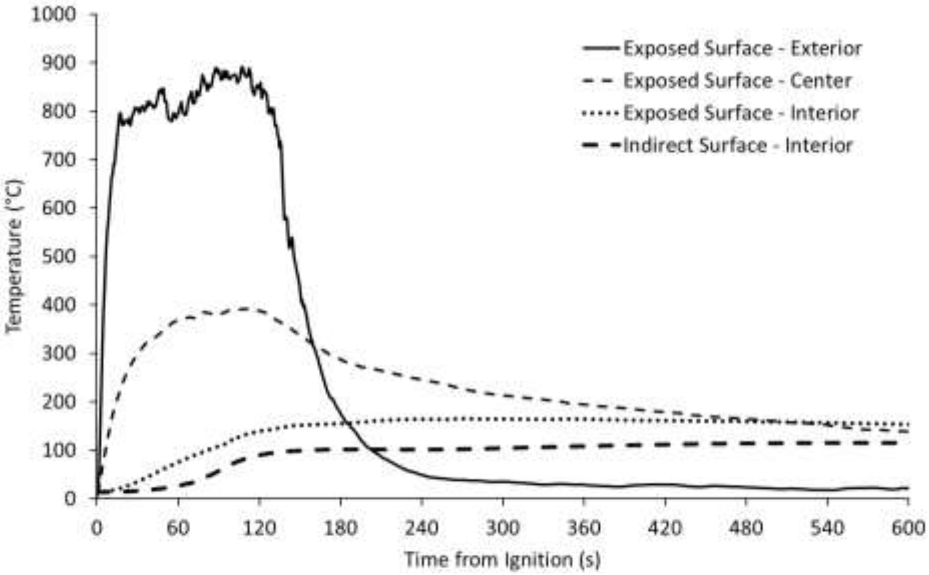

Figure 4 – Thermocouple data from battery box under 150-second direct flame exposure

Passing the full-scale fire testing is of particular note given the use of cast aluminum today in many smaller components. Most cast aluminum will melt around 560 °C and would fail if tested in this larger component format. Many materials can be made to pass this test with the use of intumescent coatings or other heat-shielding methods, but all come at additional expense and processing steps as compared to this as-molded phenolic SMC.

Summary

A new phenolic material is presented that withstands the toughest automotive fire, smoke and toxicity requirements. The phenolic SMC can be deployed on existing infrastructure as documented in the molding design of experiments and with minimal risk. This new combination of extremely low free-formaldehyde and latent acid catalyst results in a safe but suitably reactive material for current high-throughput manufacturing processes at automotive production rates.

This phenolic SMC has superior performance even in the most demanding fire resistance applications.

Acknowledgements

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References

1. Gardziella A, Pilato LA, Knop A, (2000) Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology, Springer, Berlin.