EVALUATING PHENOLIC COMPOSITE IN BENCHTOP THERMAL RUNAWAY TESTING

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Abstract

To enable future mobility, electric vehicles continue to increase their driving range using more energy-dense battery packs with greater quantities of individual cells. These batteries pose a potential safety risk in the unlikely scenario where they experience an electrical short that leads to a thermal runaway condition. The newest automotive design standards are now detailing the required performance of an electric vehicle battery enclosure regarding the minimum thermo-mechanical safety constraints. The design of the battery enclosure thus becomes critical in preventing and safeguarding against a thermal runaway.

A phenolic sheet molding compound is compared against traditional enclosure materials to evaluate their high temperature resistance up to 1600 °C. Two different protocols are adopted that mimic real-world lithium-ion batteries undergoing a thermal runaway but are safe to perform and repeatable within the lab. Commercially available materials were selected from an aluminum battery enclosure, a fire-retardant sheet molding compound using a hybrid unsaturated polyester / vinyl ester blend, and a phenolic sheet molding compound. Direct thermocouple measurements and indirect thermal imaging were used on a range of thicknesses for each material to evaluate their overall thermal resistance. Mechanical testing was also conducted to compare the material performance metrics.

The phenolic composite is shown to be the best-in-class high temperature, fire-resistant material for electric vehicle battery module structures. It is the only material capable of delivering the required thermal performance without secondary countermeasures.

Background

Fire protection standards for electric vehicles (EVs) continue to mature while new safety requirements are imposed on the market. The thermal runaway standard in China, GB 38031, represents the newest, and most restrictive standard that requires a battery enclosure to withstand at least 5 minutes of battery thermal runaway without any external fire spread or smoke intrusion into the passenger compartment. This standard was released in 2020 but not enforced until January 2021 to give automakers a chance to adapt their material selection and designs to meet these more stringent requirements.

There already exist several materials on the market that are being used in battery enclosures including steel, aluminum, and glass-reinforced thermoset composites with fire retardant additives. Steel is a natural first choice as it is low cost, readily available, and has a very high melting temperature. However, steel is susceptible to corrosion and it is dense resulting in a high-weight component. Aluminum overcomes some of steel's deficiencies being much less susceptible to corrosion and having a lower density. Both metals suffer from a lack of thermal insulation, require extra energy, and have more manufacturing steps to weld and machine the components to final shape. Aluminum also suffers from a low melting temperature that poses a high risk for use in battery thermal runaway protection. Hybrid polyester / vinyl ester sheet molding compound (SMC) would typically be quite flammable, but manufacturers have learned that if they can add sufficient quantity of aluminum trihydrate (ATH), they can instill a measure of fire resistance upon the material. This ATH-filled SMC then becomes a lower-density alternative to aluminum and can achieve more complex compression molded geometry; the main drawback is the greatly reduced mechanical performance from adding the ATH, followed closely by severe molding limitations. Phenolic SMC aims to have increased performance over the ATH-filled SMC without any of the drawbacks. Cured phenolic resin is intrinsically fire retardant and the lack of filler results in a composite with retained high mechanical performance. Additionally, the SMC can be net-shape molded and is thermally insulative thus eliminating multiple processing and assembly steps associated with metallic designs.

Previous development work with phenol-formaldehyde (PF) resins resulted in a now commercial material system that can exceed all current performance requirements. Eponol™ Resin TRAC 06921 is the only phenolic-based SMC resin system on the market that is specifically designed to support high volume EV battery enclosure applications. Among other features, the patented system has exceptional FST (fire, smoke, toxicity) performance, is lighter and less dense versus aluminum, offers greater design flexibility, and has a lower total cost than solutions requiring secondary thermal protection countermeasures.

The key requirement necessitating the use of a phenolic resin is the strict and exceptional high temperature resistance. Advanced battery technologies such as lithium-ion cells are susceptible to a rapid and uncontrollable exothermic reaction if they are under-charged, over-charged, short-circuit, or exceed their operational temperature. Additionally, a short circuit may have several potential ignition sources including puncture and moisture. When one such battery experiences a thermal runaway reaction, the instantaneous temperature can peak above 2000 °C, and first-minute average temperatures in the range of 1200-1400 °C. These cells are self-oxygenating and cannot be extinguished by common means. Finally, most automotive battery module designs require many multiple cells arranged in close proximity; a single cell experiencing a thermal runaway can easily lead to a catastrophic cascade failure across the entire battery module. There is a strong need for materials with high thermal resistance for vehicular occupant safety and for battery cell isolation.

Thermal Runaway Testing

Protocol Development

Testing very high temperature, uncontrollable reactions is inherently dangerous. With lithium ion batteries there is an added risk of toxic vapors and the spontaneous and variable nature of a rupturing cell distributing molten lithium ion salts in every direction. Therefore, a protocol needed to be developed to simulate the expected thermal exposure in a controlled, repeatable, and operator-safe manner. Proprietary customer data and multiple vendor approaches were combined to yield the following two protocols. These protocols can be conducted safely, rapidly, and allow for a simplified method to screen and objectively compare material performance. The tests do provide strong evidence and confidence in expected high temperature behavior and conform to the Chinese thermal runaway testing requirements. From a conformance perspective, the approach is to apply a test condition slightly more stringent than the actual standard to ensure a result is directly applicable toward a fully scaled automotive solution.

The developed protocols, listed in Table 1 below, are designed to test the two main concerns observed in real-world testing, the high temperature performance and how the resistance to additional mechanical load in the form of a distributed pressure or ablative element while at temperature. Protocol A is a straight, elevated temperature burn, while Protocol B adopts a heat cycle with intermittent sandblasting to simulate a pressure and ablative load acting on the material as might be expected from an exploding lithium battery. Protocol B also attempts to mimic the progressive and cascade failure of a battery pack by simulating sequential cell runaway events in succession.

Table 1: Thermal runaway testing protocols

	Protocol A	Protocol B
Method	1. Set torch to 1400°C 2. Burn until hole observed in panel or > 5 minutes reached 3. Repeat with different panel thickness 4. [optional] repeat with different temperature	1. Set torch to 1600°C for 12s 2. Withdraw torch; apply sandblast 8s at same point as directed flame 3. Set torch to 800°C for 40s 4. Repeat until hole observed or > 5 cycles reached 5. Repeat different panel thickness
Reported outcome	• Rear temperature over time at a given thickness • Average burn through rate per unit thickness	• Number of cycles until failure per unit thickness

This test is candidly not a ground truth of what might occur in the field, but it does provide a systematic approach to comparing material performance and creates a framework from which other standardized tests might build their more precise approaches.

Test Apparatus

The thermal runaway test apparatus was developed in-house. An oxy-acetylene torch was mounted horizontally to a linear rail as in Figure 1. The heat and safety shroud are composed of stainless steel, while a Lexan particle shield (not visible) further protects the operator from any debris. Mild steel comprises the bulk of the frame and test stand. The apparatus accepts a 23 cm^2 sample of variable thickness up to 12 mm with toggle clamps mounted on the rear to keep the front of the sample in a consistent plane with respect to the directed heat source.

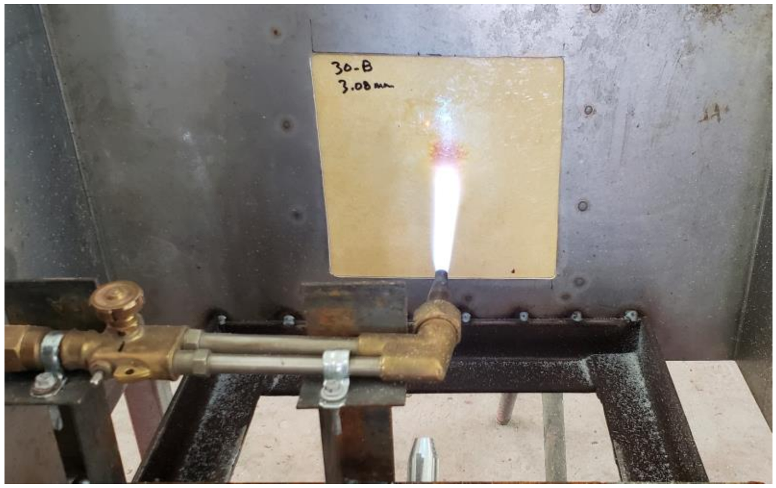


Figure 1: Thermal runaway test apparatus containing a phenolic test plate. An oxy-acetylene torch is mounted to a guided rail and the sandblast nozzle is visible in the lower center of the image.

A sandblast nozzle is mounted at an upward angle of 30 degrees and positioned such that its focus point is coincident with the mounted torch flame. Both the sandblast nozzle and the torch nozzle are set for standard operation at a distance of 25 cm from the sample.

The whole apparatus is mounted to a mobile trolley with locking castors to be both mobile and elevated off the ground. A 2 m radius was kept clear around the test apparatus and the tests were always conducted with appropriate ventilation.

Calibration

The first step to calibrating the test is to calibrate the parameters for the oxy-acetylene torch to enable a consistent flame dimension, temperature and pressure. A fresh cylinder of oxygen regulated to 350 kPa and a fresh cylinder of acetylene regulated to 40kPa provided a repeatable and stable flame cone. A fiducial template was used to ensure the produced flame cone was always 20 cm long and with a 5mm bright inner flame. The positions on the gas flow nozzles was marked and a stop block installed such that a consistent flame could always be produced so long as enough gas was in the cylinders.

To calibrate the testing temperature, a high temperature K-type thermocouple from Omega was selected; model number TJ36-CAXL-18E-12-SB-SMPW-M. This thermocouple has a maximum rated temperature of 1250 °C, but can allow for short excursions up to 1400 °C. Thus, calibrating beyond 1400 °C was the result of an extrapolation from a power law fit of the positional offset data seen in Figure 2. The temperatures were independently verified by an FTIR thermal imaging camera acting on a piece of blackened steel.

To generate the calibration curve, 10 positions of the linear rail (from the sample plane) were marked and with a fixed flame, the steady-state temperatures were recorded. This was repeated several times to generate the position dependent temperature curve. Temperatures from 600-1600 °C in 200 °C increments were converted to their respective positions along the linear rail and marked accordingly. Stop blocks were were installed along the linear rail and a program was developed to ensure moving from one position to a second position was uniform and repeatable.

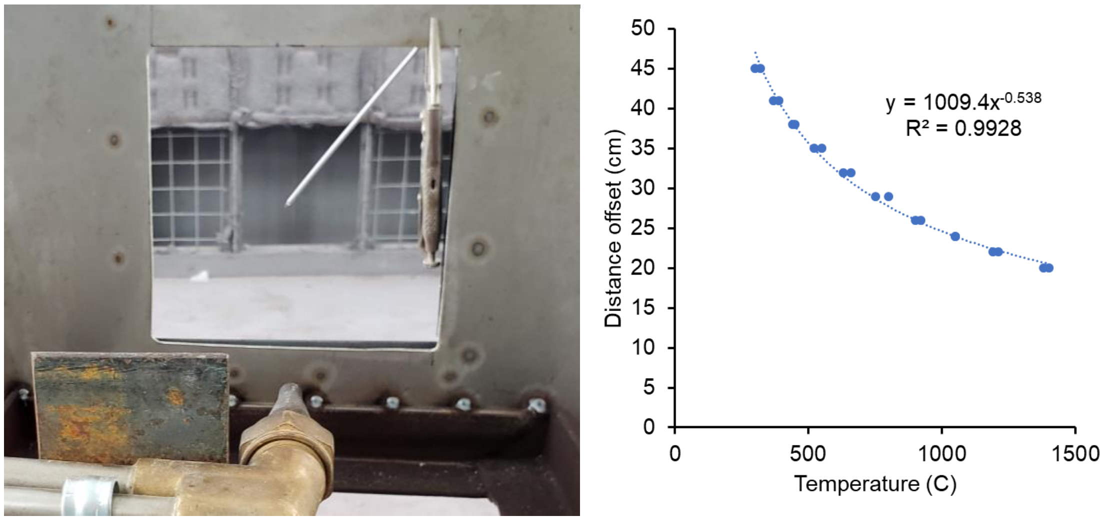


Figure 2: a) Mounted thermocouple for temperature calibration b) resultant calibration curve

The final calibration is in respect to the sandblast configuration. The setpoints for this portion of the test are as follows:

- 5 mm ceramic nozzle diameter
- Large grit screened sand, average particle size µ = 0.25 mm
- Air pressure regulated to 0.4 MPa

One final note is that the test is governed by a thin wall assumption and no attempt is made to correct advancing damage. The torch applied temperature positional setpoint and the position of any applied sandblasting were effectively static for the duration of a given test. The implication is that an infinitely thick material would never fail this test and materials beyond 5 mm thick experience a diverging focal target between the torch and sandblast. As a test progresses and a material degrades, the temperature experienced by the material decreases because the exposed surface of the material recedes away from the heat source.

Measurement

For a given thermal runaway test, a fresh sample was positioned and locked within the test fixture. Video capture for every test was used to both record the test and mark the time of data capture. Thermal imaging data of the whole of the rear sample was also recorded. One challenge in FTIR data capture is in relation to calibrating the material emissivity. For example, a white reflective ATH-filled sample would turn black and burn through the course of the thermal runaway test. Measuring emissivity is very challenging, but we could infer the emissivity value by independent temperature measurement of the material surface. This was accomplished by using the previously mentioned contact thermocouple positioned on the rear of the sample to record the temperature of the center of the sample.

All the materials were subjected to near identical mechanical testing (appropriate to the material and test standard). All the samples were machined (as opposed to waterjet cutting which can impart delamination in composite materials). For the SMC materials, tension testing was conducted in accordance with ASTM D3039, the flexure testing followed from ASTM D790, the fiber content analysis came from ASTM D2584 testing, and the impact analysis was conducted in accordance with ASTM D6110. The cast aluminum followed parallel standards for tension, flexure, density, and impact, but using the metal-specific equivalent. All the testing was conducted on the same respective load frames by the same operator to minimize any bias. At least 3 samples were taken for each measurement and the average is reported.

Materials

The two SMC materials were directly molded into 457 mm square plaques and sectioned for either the thermal runaway testing or the mechanical properties testing. The AA365 cast aluminum was sourced from a commercial battery enclosure and sectioned into pieces of roughly flat topologies. Uniform thin sections (~3.4 mm) were used for the mechanical testing since we did not want to machine any of the surfaces and so damage the surface grain structure. Sections with minor ribbing or embossments was selected for the thermal runaway testing.

Results and Discussion

Mechanical Testing

The collected material properties are shown below in Table 2. The density of the cast aluminum is highest at 2.71 g/cm^3 while both SMC products are below 2.0 g/cm^3. This would falsely imply that SMC could yield components of a much lighter weight than their metal counterpart. A more nuanced statement would stem from the material specific strengths: Cast Aluminum 68 [kN·m/kg], ATH-filled SMC 28 [kN·m/kg], and phenolic SMC 147 [kN·m/kg]. Now it is clear that the ATH-filled SMC, though low in density is also low in strength and has the lowest light-weighting potential. The cast aluminum falls in the middle, while the phenolic SMC has a very high specific strength. For reference, modern steels regularly achieve specific strengths around 120 [kN·m/kg].

Table 2: Comparison of material properties between cast aluminum, 60% ATH-filled SMC and phenolic SMC

Parameter	Unit	AA365 cast aluminum	60% ATH-filled SMC	Phenolic SMC
Fiber Weight Fraction	%	-	20	60
Density	g/cm^3	2.71	1.95	1.78
Tensile Strength	MPa	185	55	262
Tensile Modulus	GPa	75	7	17
Flexure Strength	MPa	359	129	459
Flexure Modulus	GPa	50	9	21
Notched Charpy Impact Strength	kJ/m^2	142	101	154

Another false assumption would be that phenolic SMC can automatically produce the lightest, strongest battery enclosure. These materials are subject to both the optimized component design and a fully-tuned manufacturing process to yield the best overall use of each material. For example, the cast aluminum has several fundamental limits on the achievable wall thickness in casting before this material needs to be machined. Similarly, the fiber-reinforced composite materials can be molded with continuous fiber to stabilize a major load path. These process-property relationships and geometric design limitations are outside the scope of the present analysis, but the fundamental material properties can be used to understand which material has the best potential in design and how to use the combination of material properties and high temperature resistance to achieve a specific design intent.

Generally, thermoset polymers are more brittle than metals. However, the Phenolic SMC is observed to have similar impact energy absorption compared to cast aluminum. In fact, phenolic composites retain up to 65% of its impact resistance after a full fire event [1]. Much of this improvement is attributed to the increased fiber reinforcement in the composite, which in turn is made possible by not requiring any fillers or additives to enable the resin fire resistance.

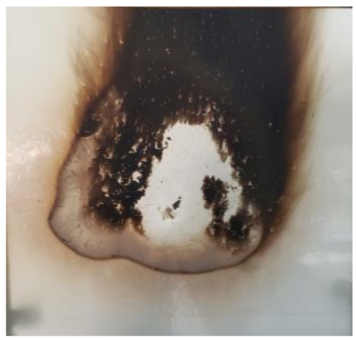
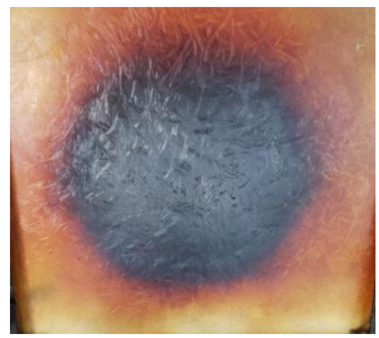
Thermal Exposure

Similar thickness panels thickness were selected for direct comparison in their high-temperature resistance. The cast aluminum section had a thickness of 3.40 mm (ignored rear ribs), the ATH-filled SMC had a thickness of 3.24 mm, and the phenolic SMC had a thickness of 3.20 mm. The results of the protocol A testing at 1400 °C are presented pictorially in Table 3, below. Here the aluminum, with its rear rib structure and moderate melting temperature failed a little after two minutes into the test with a hot slug of molten aluminum dripping away from the target and leaving a large hole. The ATH-filled SMC did resist the heat fairly well, but mid-way through the test the rear side burst into flames and a hole finally appeared around three and a half minutes into the test. The phenolic SMC appeared to reach a steady state in regards to both colour change and apparent damage progression. Though the test was left on the test stand for twice its intended length of time, there was still no identifiable failure after ten minutes of exposure. After the panel cooled, there still appeared to be a neat resin surface on the rear of the phenolic SMC panel, while the ATH-filled panel partially disintegrated upon removal from the test fixture.

Ninety seconds into the test, the rear-side temperature of each panel was: aluminum 565 °C, ATH-filled SMC, 420 °C, and phenolic SMC 200 °C. For a lithium-ion cell, the typical onset of thermal runaway from high-temperature exposure is around 350 °C. To prevent a cascade failure of a neighboring battery cell array, the barrier material must successfully insulate a thermal runaway event. Only the phenolic SMC is observed to be capable of this property.

In the protocol B testing, the aluminum survived for a little over 1 cycle, the ATH-filled SMC survived for 2 cycles, and the phenolic SMC survived for 7 complete cycles. Both the protocol A and protocol B testing is best seen in the compiled video showcases available by contacting the author.

Table 3: Post-burn images of the front (torch-facing) side and the rear with their recorded burn-through time following protocol A testing.

	Cast Aluminum	ATH-filled SMC	Phenolic SMC
Front			
Rear			
Failure Time (s)	122	193	> 600 (no failure)

Summary

A newly commercialized phenolic SMC resin system was demonstrated with respect to its high temperature resistance. Two thermal runaway test protocols were developed and presented that allow for a safe, industry-relevant test capable of being performed in the lab. This testing approach was utilized on three current battery enclosure materials to compare their performance. Each material's mechanical performance is also presented to best understand the strengths and deficiencies of each product. 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 commercial resin system presented is formulated and optimized for fast cycle time molding targeting high volume automotive production. Phenolic SMC is a versatile tool that can be directly implemented into the current molding infrastructure and results in lightweight component design with the best-in-class fire resistance. This material is found to be the only material capable of delivering the require thermal performance to successfully mitigate a thermal runaway exposure.

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., Ball, C., Greydanus, S., and Nara, K., "Phenolic SMC for Fire Resistant Electric Vehicle Battery Box Applications," SAE Technical Paper 2020-01-0771, 2020, https://doi.org/10.4271/2020-01-0771.