

THERMOGRAVIMETRIC ANALYSIS OF SMC RESINS FOR ELECTRIC-VEHICLE BATTERY ENCLOSURE APPLICATIONS

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ABSTRACT

Sheet molding compound (SMC) composites have proven to be an excellent material choice for producing EV battery enclosure structures because of multiple benefits, such as fire retardancy (FR) properties and their ability to be molded into complex shapes. Cured SMC FR performance is typically reported as a combination of flame spread and flame extinguishing duration by some standardized flammability testing methods. However, it is challenging to assess incremental advancements in various polymer matrixes' thermal resistance with these macro-level methods. The present work investigates the fundamental thermal degradation behaviors of SMC formulations' liquid components before testing by standardized methods. Multiple combinations of the base resin and low-profile additives were cured without fiber reinforcement and measured by a thermogravimetric analysis (TGA) method. Each mixture's degradation performance was characterized by onset degradation temperatures and peak mass loss temperatures from the TGA thermographs. Comparing TGA results helps to understand each component's impact on thermal resistance properties, offering guidance in selecting optimized resin combinations and a better-defined formulating window when developing advanced FR SMC resins.

1. INTRODUCTION

Possessing a variable range of mechanical properties, density, and thermal properties, sheet molding compounding (SMC) materials are excellent material options for manufacturing automotive parts. With the electric vehicle industry boom, SMC materials attract OEMs' attention as potential materials for EV battery enclosure structures. Improving the safety and reliability of SMC materials to survive the thermal runaway conditions one of the leading R&D focuses for resin suppliers and OEMs. A previous study discussed SMC panels' response to flame testing, where the after-flame extinguishing time and after-flame spreading time were recorded as fire resistance property of the material [1]. However, the SMC matrix thermal degradation properties at elevated temperatures and impact of each component to fire retardance (FR) property is yet to be studied.

Thermal gravimetric analysis (TGA) measures a sample's mass change as a function of temperature in a controlled atmosphere. The results obtained from the measurement provide information about the thermal and oxidative stability of materials. The first important characteristic from TGA measurement is the onset weight loss temperature. Onset weight loss temperature is the transition temperature when a polymeric material decomposes, and the total weight begins to reduce. On a TGA curve, the onset weight loss temperature is defined as the temperature when the sample weight drop abruptly because of the thermal decomposition of polymeric species. A multicomponent polymeric material can display several onset weight loss temperatures because different polymers' initial degradation temperatures vary. The percent weight loss associated to each transition can be calculated from the curves for quantitative analysis. The second important characteristic of TGA analysis is the peak derivative weight loss temperature. Derivative weight loss curves are plotted to show weight loss degradation rate as a function of temperature. Peak maximums in such derivative weight loss curves show the temperatures at which the rate of degradation is the highest and is considered the peak degradation temperature. The two characteristics of TGA measurements represent the fundamental thermal degradation behavior of polymeric materials. Studying and comparing these TGA results helps researchers to understand thermal property differences between materials [2].

The TGA thermal transition properties of thermoset materials were studied for different purposes [3-5]. However, few studies investigate the correlation between thermal degradation of SMC resin and SMC FR properties. In this effort, the thermal behavior of cured liquid resin and SMC pastes of five resin systems were measured by the TGA method. The thermal properties difference was studied to evaluate each component's contribution to the overall thermal degradation resistance of SMC composites. Fire resistance properties of SMC panels made with the five SMC resin systems were tested using UL 94 5VA method [6]. Correlation between the TGA results and FR testing results are discussed and a summary of the findings are presented.

2. EXPERIMENTATION

2.1. Materials

To understand the SMC resin liquid components' impact on the thermal degradation properties, three resins were mixed with three types of low profile additives (LPAs) at a weight ratio of three to one. Table 1 lists the details of sample IDs, components and measurement of each sample. The formulations were mixed at a batch size of 100 grams, and 1.5 gram of tert-butyl peroxybenzoate (TBPB) was added as the initiator. The catalyzed resin mixtures were cured in an oven to form resin plaques. The second set of samples were made with the catalyzed resin mixture with 150 grams of Aluminium hydroxide (ATH) form SMC paste. The pastes were molded in a heated press to form paste plaques. The two sets of plaques were grounded into powders for TGA test. Corresponding SMC resins compounded with 30% glass were molded into panels with four different thicknesses of 1.6 mm, 2 mm, 2.5 mm, and 3 mm.

2.2. Dynamic thermogravimetric analysis

The thermal transition of the samples was tested on the TA instruments Discovery Thermogravimetric Analyzer. Each sample plaque was ground into fine powder, placed in a platinum pan, and mounted in the instrument for testing. The samples were heated at 10 °C/minute from 25 °C to 900 °C with either an air atmosphere purge of 25 ml/minute or a nitrogen purge of 25 ml/minute. Two replicates were measured for each sample.

1. Table 1. Materials used for the study and sample IDs.¹

Sample ID	Base Resin	LPA	Resin Plaque (TGA)	SMC paste plaque ² (TGA)	SMC panel ³ (Fire Test)
A	UPR	Poly Vinyl Acetate	X	X	X
B	VER	Poly Vinyl Acetate	X	X	X
C	Hybrid	Poly Vinyl Acetate	X	X	X
D	Hybrid	Saturated Polyester		X	X
E	Hybrid	Polystyrene		X	X

All mixtures were blended with 1.5 part of TBPB initiators and fully cured under heat.

² SMC paste plaques were made with resin/LPA mixtures and 100 parts of ATH.

³ SMC panels made were with resin/LPA mixture, 150 parts of ATH, and 30 % fiber glass.

2.3. UL 94 5VA test

SMC panels with different thicknesses were cut into bar specimens with a dimension of 125 mm by 13 mm following UL 94 specimen protocol. Samples were tested without edge smoothing. Testing was run in a non-UL certified testing lab following the UL 94 5VA testing procedures. After the fifth application of the test flame for each specimen. The after-flame and after-glow (AFAG) time were recorded. Five replicates were measured for each formulation at the specified thickness. An average after-glow and after-flame time were reported.

3.

RESULTS

This section represents the material testing results using the methods described in the previous section. The first part discusses the TGA measured thermal transitions of three cured resin plaques, listed as Sample A, B, and C in Table 1. The second part discusses the TGA results of five SMC paste plaques labeled as A, B, C, D, and E. The third section discusses the fire testing results for the five SMC formulations at different panel thicknesses. The TGA results comparison

provides information of base resin and LPA's impact on the thermal degradation behaviors of resin mixtures. The fire testing results offer a case study in the purpose of differentiating the SMC resin formulations.

3.1.TGA results of cured liquid resin

TGA for cured resin blend A, B, and C were conducted in air to identify the decomposition characteristics of the polymeric materials. The samples consist of three base resins, UPR, VER, and a hybrid resin, with the same polyvinyl acetate LPA materials. Figure 1 shows the weight losses as a function of temperature. All samples display a slight weight loss until the temperature reach 300 °C. The onset weight loss temperature of sample A and sample B are 301 °C and 311 °C. In contrast, sample C's first weight loss transition occurs at a significantly higher temperature of 363 °C. All three samples have a second weight-loss degradation reaction between 490 °C and 510 °C. Figure 2 shows the derivative weight loss curves, detailing the degradation rate of each thermal transition as a function of temperature. As one can see, two distinct degradation peak regions are identified for each sample, relevant to the two transitions in the weight loss curves described earlier. Sample A's first significant derivative weight loss occurs between 328 °C and 364 °C, with two peaks and a maximum degradation rate of 1.2 %/°C. Sample B's first derivative peak ranges from 360 °C to 394 °C, with multiple peaks. The degradation rate is about 0.6 %/°C. Sample C's first transition rate maximized at 408 °C shown as one single sharp peak on derivative TGA curve. The degradation rate at the peak temperature is 1.4 %/°C. Table 2 lists the first extrapolated onset weight loss temperature and the first peak degradation rate temperatures of liquid resin plaques. Although multiple thermal transitions are detected in the studied samples, the first weight loss reactions are the focuses of the discussion because most majority of the resin sample participate in the reaction at this stage. This first degradation transition is directly related to the overall thermal degradation behavior of the cured resin mixtures. The TGA results clearly show that the hybrid resin-based sample (Sample C) has two distinctive thermal decomposition characteristics outstanding the UPR or VER resins (Figure 2. The degradation rate of cured resin plaques. Samples A and B). Firstly, sample C has about 50 degrees higher onset weight loss temperature over Samples A and B. Secondly, once the decomposition reaction of sample C starts the reaction proceeds quickly with a high degradation rate and most of the weight loss occurs during the first thermal decomposition process.

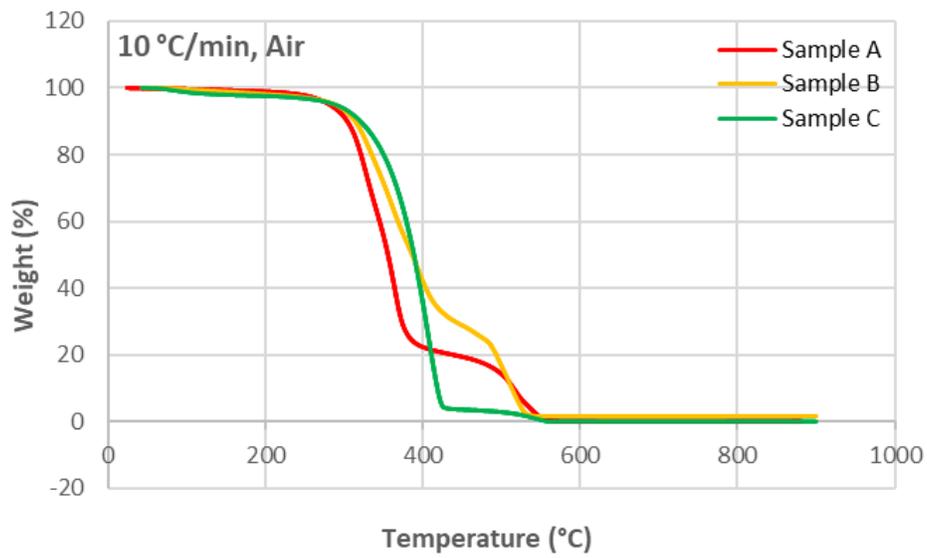


Figure 1. Weight loss of cured resin plaques.

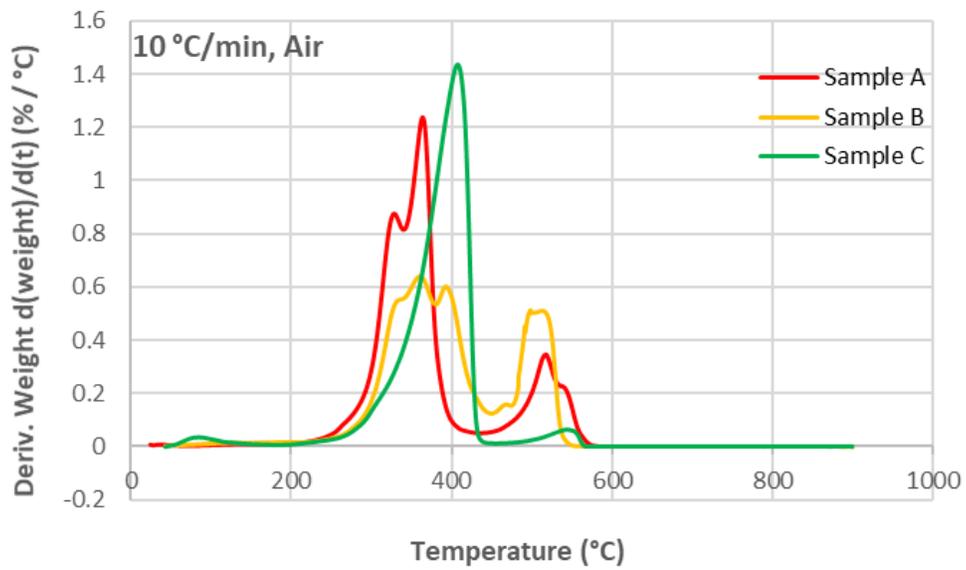


Figure 2. The degradation rate of cured resin plaques.

3.2.TGA results of cured SMC paste plaques

The SMC plaques' thermal degradation behaviors were tested twice by the TGA method, once in an air atmosphere and a second time in nitrogen. A hybrid resin mixture blended with saturated polyester LPA (sample D) or polystyrene LPA (sample E) is included. Figure 3. shows the weight loss vs. temperature profile measured in the air. The first thermal transition of all samples starts at about 250 °C, leading to approximate a 20 % weight loss. The corresponding peak degradation rate temperature is 280 °C, as shown in the derivative weight loss curve (Figure 4). This transition is related to ATH decomposition, and the weight loss is caused by the released water vapor from the representing reaction. Table 2 lists the second onset and peak temperatures measured in the paste plaques after the degradation of ATH. The second reaction step is related to the first degradation shown in the resin plaque data in section 3.1. The onset temperatures of the second curve for A and B plaques are at 330 °C, about 25 °C higher than the measured in liquid resin plaques. The onset temperatures of the second curve for A and B plaques are at 330 °C, about 25 °C higher than the measured in liquid resin plaques. The onset temperature for hybrid resin-based sample C is 343 °C, which is about 20 °C lower than that of sample C in the previous discussion. The difference between sample C, D, and E are minimal. An explanation for the degradation differences between the resin-only samples and samples with 150 PHR ATH could be two fold. Firstly, the ATH degradation curve could be masking the small beginning degradation peak shown in the resin only A and B samples, resulting in the appearance of a higher start of degradation temperature for the matrix in this data. Secondly, ATH is most likely disrupting the polymer matrix in sample C during the first degradation step, lowering the matrix beginning degradation temperature in this data compared to the resin only samples.

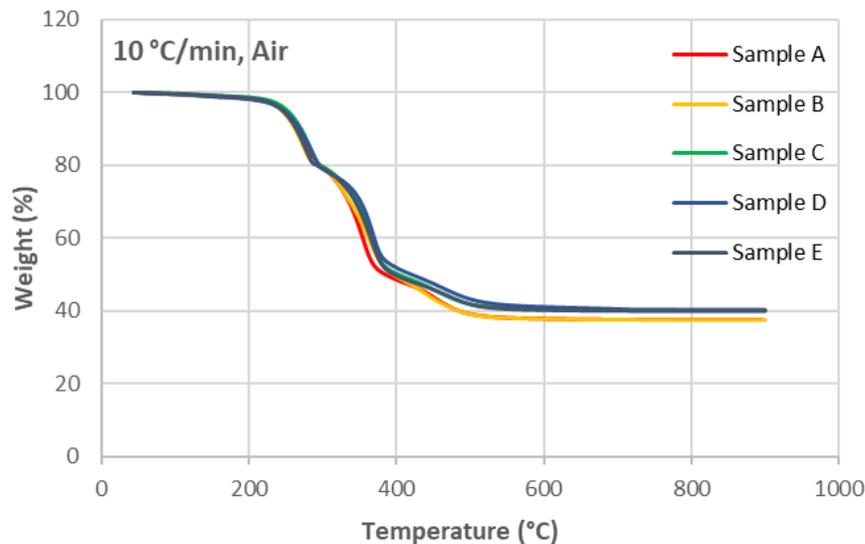


Figure 3. Weight loss of cured SMC paste plaques measured in air.

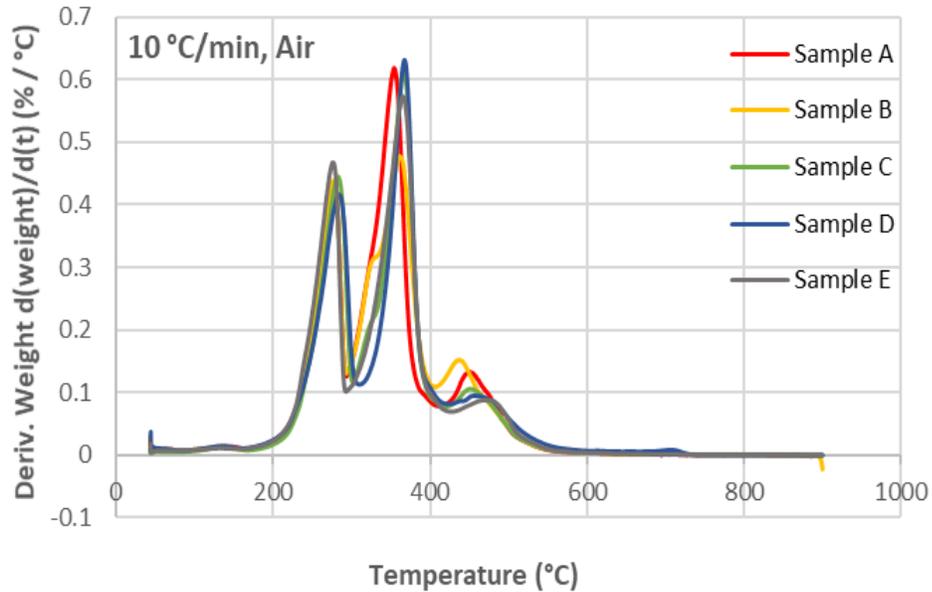


Figure 4. The degradation rate of cured SMC paste plaques measured in air.

Additionally, the char yield was found for each of the samples. The TGA profiles measured in nitrogen eliminate the oxidation process with only the pyrolysis reaction products measured, the difference between the pyrolyzed products ash yield in nitrogen is subtracted from the oxidized products ash yield in air to determine the char values. As seen in Table 3, the char yield for the samples are between 1.5 % to 2.05 %. The low char yield values indicate that the major flame retardant mechanism in the samples is from the release of water during the degradation of ATH and not from any barrier char effects.

Sample ID	The extrapolated onset of weight loss of resin plaques (°C)	Degradation rate peak temperature of resin plaque (°C)	The extrapolated onset of weight loss of paste plaques (°C)	Degradation rate peak temperature of paste plaque (°C)
A	301	328	329	356
B	311	360	329	365
C	363	408	343	367

D	-	-	348	370
E	-	-	340	368

Table 2. First onset weight loss temperature and degradation temperatures of polymeric species in resin plaques and SMC paste plaques.

Table 3. Ash values and calculated char values.

SMC Paste plaque	Ash (%) Nitrogen	Ash (%) Air	Calculated Char (%)
A	39.6	37.55	2.05
B	39.55	37.55	2
C	41.65	40.15	1.5
D	42.15	40.3	1.85
E	41.5	39.65	1.85

3.3. Fire test results for SMC panels

The discussed TGA results clearly shows thermal degradation behavior differences between the studied SMC formulations. This part of the study aims to differentiate the five SMC paste formulations by measuring the fire properties of SMC panels at different thicknesses. Table 4 lists the results of the UL 94 5VA test conducted on the panels of different thicknesses. The results include pass/fail criteria defined by the testing standard and the total AFAG time after the fifth burn. As can be seen, thick panels are more fire-resistant than thin panels. All the panels passed the UL 94 5VA test at the thicknesses of 2.5 mm and 3 mm. Formulation A and B failed the test at 2 mm thickness as both materials have a total AFAG over 60 seconds. Formulations C, D, and E passed the test with 23 seconds, 14 seconds, and 30 seconds AGAF time, respectively, at a 2 mm thickness. Comparing with the AFAG values of panels with 3 mm thickness and about 5 seconds at 2.5 mm, one can conclude that the fire extinguishing property diminishes as panels thickness is reduced. At the 1.6 mm thickness, C, D, E formulations passed the test with longer AFAG times, approaching the 60-second threshold. The results show that panels containing hybrid resin are able to pass UL94-5VA at lower thicknesses and therefore have better FR properties than the UPR or VER-based SMC formulations. Additionally, the LPA selection in the hybrid resin system did not majorly change the FR properties.

Table 4. UL 94 5VA results for sample panels with different thicknesses.

Thickness	3 mm		2.5 mm		2 mm		1.6 mm	
A	pass	3 sec.	pass	1 sec.	Fail		Fail	
B	pass	1 sec.	pass	16 sec.	Fail		Fail	
C	pass	0 sec.	pass	5 sec.	pass	23 sec.	pass	55 sec.
D	pass	0 sec.	pass	6 sec.	Pass	14 sec.	Pass	38 sec.
E	pass	0 sec.	pass	2 sec.	Pass	30 sec.	Pass	47 sec.

4. CONCLUSION

Starting at a simplistic formulation level, differences between the thermal degradative behaviour of base SMC resins was observed by TGA of resin only SMC formulations. Both the start of degradation and peak degradation temperatures were higher for the hybrid resin system than the UPR and VER resins.

After establishing a baseline for the thermal resistance of the resin systems, ATH was added as an FR additive to evaluate the resin behaviour in an FR SMC formulation. As expected, the ATH degradation curve and mechanism slightly conflated the thermal results shown in the resin only study, however the trends remained similar. The hybrid resin results still shown higher start and peak degradation temperatures compared to UPR and VER resins when formulated with ATH. The hybrid resin peak degradation temperature results were not significantly changed when formulated with different LPAs.

All formulations with ATH were analyzed under both air and nitrogen by TGA to evaluate the FR mechanism of each sample. It was found that the char yield for each formulation was 2% or less, showing that char formation is not a critical FR mechanism for any of the formulations in this study. The majority of the FR performance in these formulations is a combination of ATH loading and polymeric thermal resistance.

The results from the UL94-5VA showed that the more thermally resistant hybrid resin system outperformed both the UPR and VER resin systems. At larger thicknesses all formulations passed UL94-5VA, however the hybrid resin system was the only formulation capable of passing at 2 mm and below. Again, the FR properties of the hybrid formulations did not significantly change with the addition of different LPAs. Additional investigation, such as cone calorimetry testing, may help to explain the fire retardancy mechanism associated to the hybrid resin.

The results from the UL94-5VA tests show a correlation with the peak thermal decomposition temperature of the resins. The SMC formulations in this study were able to pass coupon level flame testing at thinner sample thicknesses as the decomposition temperature of the base resin increased. The largest difference was seen between the UPR and hybrid resin systems. More

resin systems should be analyzed by this methodology to verify the correlation between peak degradation temperature and coupon level flame testing, however this process could stream line FR resin development for future flame resistance SMC formulations. All that may be necessary in determining the optimal base resin is to evaluate the peak degradation temperature of a resin-only sample by TGA. Additionally, the LPAs used in the formulations in this study did not show to have a major impact on the peak degradation temperature or UL94-5VA results, giving design freedom to chose an LPA for a FR SMC formulation based on other non-FR property optimizations.

5. REFERENCES

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