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Influence of Additives on Flame-Retardant, Thermal, and Mechanical Properties of a Sulfur–Triglyceride Polymer Composite

Perla Y. Saucedo-Oloño , Bárbara G. S. Guinati, Ashlyn D. Smith * and Rhett C. Smith *

Department of Chemistry, Clemson University, Clemson, SC 29634, USA; psauced@g.clemson.edu (P.Y.S.-O.)

* Correspondence: ashlynd@clemson.edu (A.D.S.); rhett@clemson.edu (R.C.S.)

Abstract: Plastics and composites for consumer goods often require flame retardants (FRs) to mitigate flammability risks. Finding FRs that are effective in new sustainable materials is important for bringing them to the market. This study evaluated various FRs in SunBG₉₀ (a composite made from triglycerides and sulfur)—a high sulfur-content material (HSM) promising for use in Li–S batteries, where flame resistance is critical. SunBG₉₀ was blended with FRs from several classes (inorganic, phosphorus-based, brominated, and nitrogen-containing) to assess compliance with UL94 Burning Test standards. Inorganic FRs showed poor flame retardancy and lower mechanical strength, while organic additives significantly improved fire resistance. The addition of 20 wt. % tetrabromobisphenol A enabled SunBG₉₀ to achieve the highest flame retardancy rating (94V-0), while also enhancing wear resistance (52 I_W , ASTM C1353) and bonding strength (26 psi, ASTM C482). Selected organic FRs also enhance compressive strength compared to the FR-free SunBG₉₀. This research highlights the potential of HSMs with traditional FRs to meet stringent fire safety standards while preserving or enhancing the mechanical integrity of HSM composites.

Keywords: flame retardants; sulfur utilization; composites; plant oil; animal fat; ASTM testing



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1. Introduction

Plastics and polymer composites are ubiquitous in consumer goods and construction applications. Unfortunately, many components of such structural elements are flammable, posing significant safety hazards not only to those in the immediate vicinity of a fire but also in terms of the downstream environmental damage caused by the toxic vapors produced by burning plastic and polymer composites [1,2]. These dangers can be mitigated by enhancing the material's fire safety properties via the addition of flame retardants (FRs) [3,4]. Stringent fire safety regulations often mandate the use of FRs, and meeting these regulatory standards is a legal requirement that ensures that products and materials contribute to public safety [5]. FRs inhibit the rapid spread of fire across polymer surfaces, can lower smoke production and burn time, provide valuable time for evacuation in the event of a fire, and aid firefighting efforts by containing the flames to a limited area [6–8]. The importance of FRs in polymers thus extends beyond mere fire prevention; it encompasses regulatory compliance, risk mitigation, and the enhancement of material safety and longevity across diverse industries [9].

Various industries and regions have specific fire safety standards and regulations with which materials must comply for their legal use in specific applications. The UL94 Burning Test, developed by Underwriters Laboratories (UL), is a prevalent industry standard testing protocol that evaluates how plastic materials behave when exposed to a flame ignition source while in the horizontal installation orientation (94HB) or how a vertically oriented specimen of the material reacts when exposed to a controlled flame ignition source (94V). The test evaluates the burning rate, dripping behavior, and formation of burning particles. The ratings range from V-0 (most flame-resistant) to V-2 (most flammable, but still within

set bounds), whereas materials that do not meet the criteria receive a No Rating (NR) classification. The 94HB test battery thus provides valuable information for manufacturers, regulators, and consumers about the fire safety properties of materials [10,11].

Some traditional flame-retardant additives raise environmental and health concerns [12]. Halogenated FRs, for example, may release harmful by-products during combustion, posing risks to human health and the environment [4,13,14]. There should also be a balance between performance and safety. Achieving a delicate balance between maintaining the desired performance characteristics of polymers (such as mechanical strength and flexibility) and ensuring robust fire safety is challenging [15,16]. Another challenge is that modifying a polymer to increase its flame resistance may also modify its cost and overall functionality (T_g , mechanical strength, etc.) [15,17]. While there have been significant advancements in FR technologies, there is a need for continued innovation.

The predominant categories of FRs used in commercial plastic/polymeric composite materials are halogenated organics [18,19] and phosphorus-based [16,20–24], nitrogen-based [25–29], and inorganic FRs [20,30,31]. The FR selected for a particular application is influenced by factors such as the type of polymer, its intended application, and the specific fire safety criteria being used.

Our current understanding of how traditional FRs exert their flame retardancy is based on mechanistic studies on traditional, largely hydrocarbon-based organic materials. Even though the effect of traditional FRs on sulfur–glycerol polymers has been studied, systematic research is still needed on their flame retardancy performance for high sulfur-content materials (HSMs). HSMs [32–37] have recently emerged as potential biomass [38–42] or bio-olefin-containing [43–52] replacements for plastics [53] and other structural materials, as well as in adhesives [54–56] and Li-S batteries [57–63]. Although flammability is a critical concern in many of these applications, only a few studies have evaluated the flammability of HSMs [64–67], and the influence of adding traditional FRs on the flammability and other physical properties of HSMs still needs to be explored. One of the most well-studied HSMs for structural applications is **SunBG₉₀**, a composite prepared by reacting sulfur, sunflower oil, and brown grease [68]. **SunBG₉₀** has demonstrated impressive compressive strength (35.9 MPa), low water absorption (0.83 wt. % measured according to ASTM C140), abrasion resistance (16 I_W , measured according to ASTM C1353), and thermal insulation capacity (0.126 W/m·K, measured to standard ISO 8302) [69].

In the current work, the influence of added FRs on the properties of **SunBG₉₀** were evaluated. The selected FRs (Chart 1) span the range of inorganic, phosphorus-based, brominated, and nitrogen-containing FRs. Composites of these FRs with **SunBG₉₀** were prepared and tested to the UL-94 standard. The thermal stability, thermomorphological properties, abrasion resistance, bonding, and compressive strengths of the FR-**SunBG₉₀** composites were also evaluated. This study aims to systematically evaluate the impact of different types of FRs on the flame retardancy and mechanical properties of **SunBG₉₀** composites.

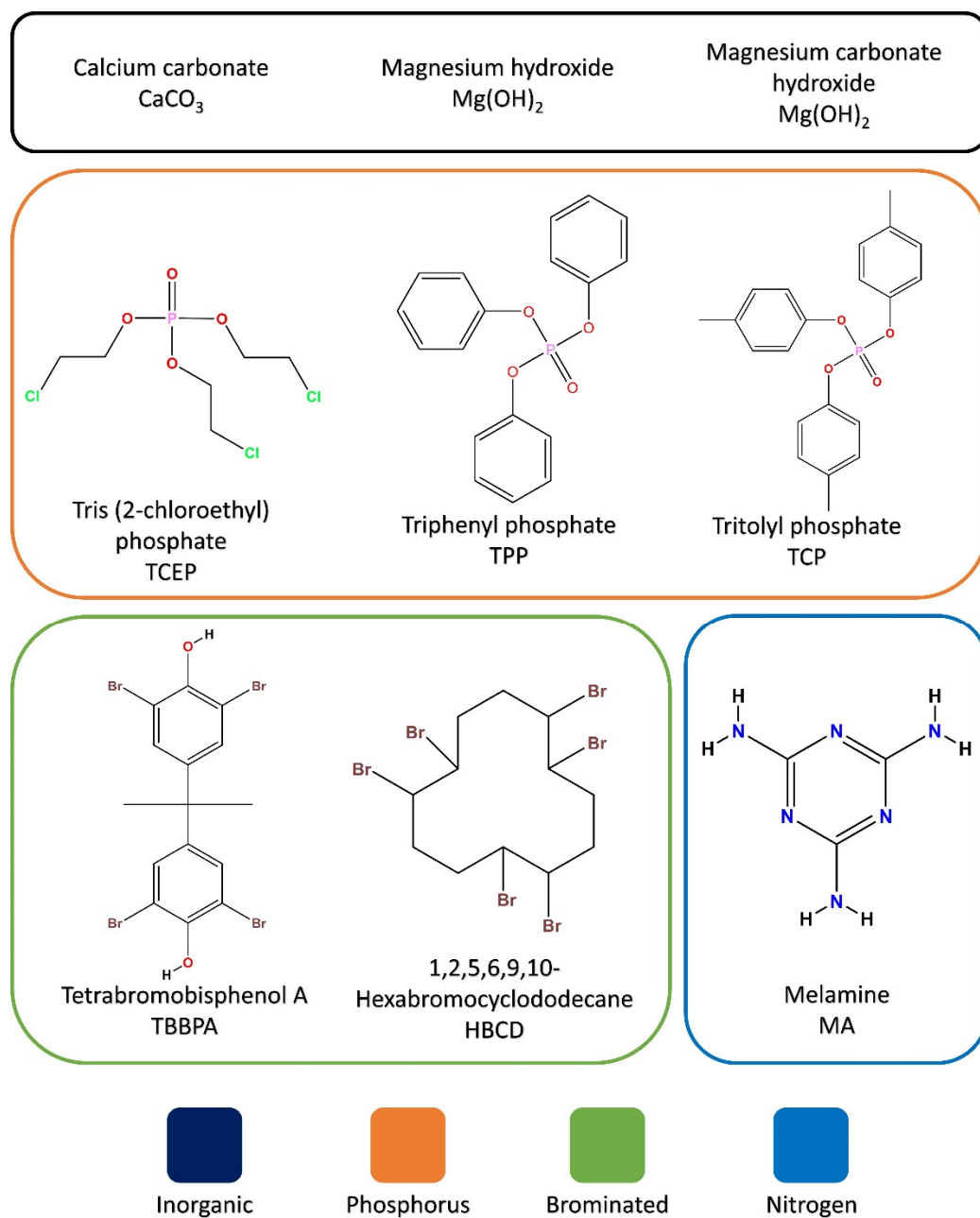


Chart 1. Flame retardants from several common categories were evaluated for use with the HSM **SunBG₉₀** in the current study.

2. Materials and Methods

2.1. Materials

Brown grease was supplied by industrial partners. All materials were used as received and without further purification. The reagents and their suppliers were: sunflower oil (Maple Holistics), sulfur (Dugas Diesel), magnesium hydroxide, *tris*-(2-chloroethyl) phosphate, triphenyl phosphate and tritolyl phosphate (Sigma Aldrich, St. Louis, MO, USA), tetrabromobisphenol A, melamine (TCI America, Montgomeryville, PA, USA), magnesium carbonate hydroxide (Thermo Scientific Chemicals, Shanghai, China), calcium carbonate and 1,2,5,6,9,10-hexabromocyclododecane (BeanTown Chemical Co., Hudson, NH, USA). **SunBG₉₀** was prepared as previously reported [68].

2.2. Design and Rationale

Among the HSMs, **SunBG₉₀** has shown promise as a structural material based on its high compressive strength, thermal insulation, and resistance to acidic degradation or water absorption [68,69]. Prior to the current study, however, the extent to which **SunBG₉₀** would comply with fire safety requirements for specified applications was largely unknown. The purpose of the current work was to assess the influence of common flame retardants (FRs) on the properties of **SunBG₉₀**. FRs were selected to represent examples from the common categories of FRs used in commercial plastic and polymer composite materials [70–72]. The phosphorus-based FRs selected were *tris*-(2-chloroethyl)phosphate (TCEP), triphenyl phosphate (TPP), and tritolyl phosphate (TCP) [73–77]. Tetrabromobisphenol A (TBBPA) and 1,2,5,6,9,10-Hexabromocyclododecane (HBCD) were selected as examples of well-known brominated FRs [78–81]. Melamine (MA), a nitrogen-based FR, aligns with the desire for FRs that offer adequate fire protection while minimizing potential health and environmental risks compared to brominated FRs [82–84]. Several common inorganic FRs—CaCO₃, Mg(OH)₂, and Mg₅(CO₃)₄(OH)₂—were also screened. The structures and abbreviations used for all FRs are provided in Chart 1.

The UL-94 test, comprising two parts—UL-94HB and UL-94V—was selected to test the **SunBG₉₀**/FR materials. The UL-94HB (horizontal burning) test is generally easier to pass than the 94V (vertical burning) test (*vide infra*); therefore, this test was employed as an initial screen method to assess the horizontal burning behavior of plastic materials. The 94HB testing employed $5 \times \frac{1}{2} \times \frac{1}{8}$ inch specimens, held at one end horizontally. A flame was applied to the free end for 30 s or until the flame front reached 1 inch. The duration of the combustion and the damaged length between 1 and 5 inches were recorded.

This test aims to replicate scenarios where a material installed as a horizontal sheet (a floor, ceiling tile, top/bottom panel of an electronic device, etc.) could encounter an ignition source. The test has metrics to help evaluate the propensity of a material to spread flames, produce flaming drips, and sustain a hot afterglow. The 94HB classification is bestowed upon materials with a thickness of less than 0.118 inches, meeting specific burning rate criteria.

The UL-94V (vertical burning) test assessed the vertical burning characteristics of materials. It employed a $5 \times \frac{1}{2} \times \frac{1}{8}$ -inches specimen, positioned vertically, and held at one end. A burner flame was administered for two 10 s intervals, with a pause for the cessation of flaming combustion after the initial application. The recorded parameters included the duration of the flaming combustion, glowing combustion, and whether flaming drips led to the ignition of cotton.

This test delivers insights into the duration of flaming combustion, the tendency for the formation of flaming drips, and the potential that a material has for igniting adjacent materials. It aids in assessing a material's performance when applied in a vertical position (as a wall panel or the sides of an electronic device) subjected to a flame. By identifying the UL-94 ratings for the **SunBG₉₀**/FR materials, this process facilitates a clear understanding for manufacturers, regulatory bodies, and consumers—enabling a straightforward comparison of flammability characteristics between different materials.

ASTM International standards (formerly known as the American Society for Testing and Materials) provide a uniform and consistent testing procedure, ensuring that tests are conducted systematically and allowing for reproducibility and comparisons across laboratories and organizations [85].

ASTM C1353 testing provides an index of abrasion resistance by determining the loss of volume from the abrasion of dimension stone. A sample undergoes abrasion through controlled rotary rubbing with regulated pressure and abrasive conditions. Evaluating abrasion resistance helps select materials that maintain their appearance and functionality in specific applications, lowering maintenance costs and assuring a more extended service life [86].

ASMT C482 testing determines the ability of a specimen to be bonded to Portland cement paste (including both face and back-mounted specimens). A flat surface sample is

prepared, and Portland cement paste is applied to create a bond assembly; then, the sample is cured and subject to increasing loads until failure occurs. Bond strength is crucial for applications where substrate adhesion must be ensured [87].

2.3. Safe Handling Warning

CAUTION: Heating elemental sulfur with organics can result in the formation of H_2S or other gases. Such gases can be toxic, foul-smelling, and corrosive. The temperature must be carefully controlled to prevent thermal spikes, contributing to the potential for H_2S or other gas evolution. Rapid stirring, shortened heating times, and the very slow addition of reagents can help avoid unforeseen temperature spikes.

2.4. Preparation of SunBG₉₀/FR Blends and Preparation of Samples for UL-94 Testing

SunBG₉₀ was prepared as previously reported [68]. Compounding of **SunBG₉₀** and FRs was accomplished by melting a sample of **SunBG₉₀** in a borosilicate glass beaker in an oil bath at 170 °C (Corning® Digital Hot Plate, Corning, NY, USA). After the **SunBG₉₀** had melted, the beaker was removed from heat and the flame-retardant additive was added. The mixture was subjected to rapid mechanical stirring (JJ-1 - Precise Strength Power Mixer, Tokyo, Japan) until a homogeneous blend was achieved, typically taking 2–5 min. Due to the nature of the instrument used for stirring, the stirring speed was not precisely controlled but maintained at a high rate to ensure thorough mixing. Specimens sized appropriately for the UL-94 tests (vide infra) were shaped by pouring the molten material into $5 \times \frac{1}{2} \times \frac{1}{8}$ -inch silicone molds and allowing the material to solidify gradually at room temperature (20 °C). The initial loading of each FR was 10 wt. %.

2.5. UL-94HB Test and UL-94V Testing Procedure

For 94HB: The test involved a $5 \times \frac{1}{2} \times \frac{1}{8}$ -inches specimen positioned horizontally. A flame was applied to the free end for 30 s or until the flame front reached 1 inch. If combustion persisted, the duration was timed at between 1 and 5 inches. If combustion stopped before 5 inches, the time and damaged length were recorded. Three specimens were tested, and a material less than 0.118 inches thick was classified as 94HB if it burned at a rate less than 3 inches per minute or stopped burning before 5 inches. If one specimen failed, a second set of three was tested, and all specimens in this set had to comply.

For 94V: This test utilized a vertical $5 \times \frac{1}{2} \times \frac{1}{8}$ -inch specimen held at one end and involved three classifications: 94V-0, 94V-1, and 94V-2. A burner flame was applied to the free end of the specimen for two 10 s intervals, with a gap equal to the time it took for flaming combustion to stop after the first application. Two sets of five specimens each were subjected to testing. The following parameters were recorded for each specimen:

1. Duration of flaming combustion after the first burner flame application.
2. Duration of flaming combustion after the second burner flame application.
3. Duration of glowing combustion after the second burner flame application.
4. Whether flaming drips ignited cotton placed below the specimen.
5. Whether the specimen burned up to the holding clamp.

The material received a rating based on its performance, ranging from V-0 to V-2, where V-0 signifies the highest flame resistance and V-2 indicates lower flame resistance. The criteria for each rating were as follows:

V-0: No flaming drips were allowed; the flame extinguished within 10 s on the specimen with cotton placed below it.

V-1: No flaming drips were allowed; the flame extinguished within 30 s on the specimen with cotton placed below it.

V-2: Drips of flaming particles were allowed; the flame extinguished within 30 s on the specimen with cotton placed below it.

2.6. Abrasion-Resistance Testing (ASTM C1353)

A specimen was secured on a rotary platform and turned on a vertical axis against the sliding rotation of abrasive wheels loaded with specific weights to simulate wear, with one abrasive wheel rubbing the specimen outward toward the periphery and the other rubbing it inward toward the center. A vacuum system was used to remove debris produced through the test. The results were reported as an abrasion index or the volume of material lost. The obtained data helps us to compare different types of stone and select the most suitable material in terms of end-use performance and specific applications where wear-resistance is critical [86].

2.7. Bond-Strength Testing (ASTM C482)

A specimen was prepared by ensuring that both the tile and cement paste were clean and contaminant-free. A layer of Portland cement paste was applied to the back of each sample and then pressed onto the substrate. Correct alignment and complete contact were visually confirmed. The bonded samples were then cured. The sample–cement paste was affixed in a testing machine capable of applying an evenly distributed and controlled load until a failure occurred, either by the specimen separating from the cement paste or the cement paste itself failing. The maximum load at which failure occurred was reported. The bond strength was calculated by dividing the maximum load by the bonded area of the sample [87].

3. Results and Discussion

3.1. UL-94 Flame Retardancy Results

Materials obtained by combining **SunBG₉₀** with inorganic FRs (CaCO_3 , $\text{Mg}(\text{OH})_2$ and $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$) resulted in poor flame retardancy and caused the **SunBG₉₀** to become soft and/or exceedingly brittle, to the extent that the test samples had to be handled with great care to avoid breakage. This observation alone precludes the practical application of these inorganics as FRs for **SunBG₉₀** in any structural context. The deleterious impact on mechanical strength in these blends was not surprising given the incompatibility between these ionic inorganic additive particles and the highly hydrophobic network comprising **SunBG₉₀**. Samples of **SunBG₉₀** to which 10 wt. % CaCO_3 , $\text{Mg}(\text{OH})_2$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$ had been added also wholly burned during UL-94 testing, so these additives proved ineffective both as flame retardants and in terms of mechanical strength retention. Only one of the organic additives, TPP, caused an obvious decrease in the physical integrity of the **SunBG₉₀**.

After observing the obvious poor performance of the initial test specimens comprising inorganic FRs, these materials were not further explored. All the other **SunBG₉₀**/FR blends were carried forward for full UL-94 testing. Table 1 summarizes the performance of all of these materials in the 94HB test, generally the easier part of the UL-94 test to pass since the flame is applied to a horizontal structure so that heat may not propagate as readily to adjacent material as in 94V. Figure S1 in the Supporting Information shows the burn length and appearance of each specimen after these tests. All the materials passed the 94HB part of the testing protocol. The 94HB classification allows for flaming drips, focusing on horizontal burning behavior. Materials can still achieve the 94HB classification even if flaming drips are observed, which might be more restrictive in other classifications like 94V. This evaluation focuses on material behavior regarding flame spread, combustion time, and the damaged length (Table 1).

Having passed the 94HB testing, samples of all blends were then tested by the 94V protocol. Table 2 summarizes these results, with the classification of each sample as 94V-0, 94V-1, or 94V-2. Figure 1 displays the materials undergoing the 94V test, demonstrating some of their behavior during the first and second ignition stages of testing. Figure S2 shows the burn length and appearance of each specimen after testing.

Table 1. Summary of UL-94HB test results for each sample.

FR Added	FR wt. %	Sample Number	Combustion Time (s) ^[a]	Damaged Length (in) ^[b]	Classification
None	0	1	3	1.125	94HB
		2	14	1	
		3	25	1	
TCEP	10	1	10	0.375	94HB
		2	20	0.437	
		3	6	0.062	
TCP	10	1	20	0.375	94HB
		2	19	0.812	
		3	16	0.125	
HBCD	10	1	8	1.500	94HB
		2	5	0.687	
		3	12	1.125	
MA	10	1	34	0.125	94HB
		2	11	0.250	
		3	9	0	
TBBPA	10	1	3	0.250	94HB
		2	11	0	
		3	12	0.500	
	15	1	4	1.375	94HB
		2	9	1.375	
		3	5	1.375	
	20	1	3	0.687	94HB
		2	2	0.875	
		3	2	1	

^[a] Combustion time excludes the 30 s in which the flame is applied to the sample. ^[b] Damaged length between the 1 and 5-inches marks.

Table 2. Summary of UL-94V test results for each sample.

FR Added	FR wt. %	Set no.	Sample No.	Flaming Combustion (s) ^[a]	Flaming Combustion (s) ^[b]	Glowing Combustion (s) ^[c]	Cotton Ignited (Y/N) ^[d]	Burned > 5-Inch Mark (Y/N) ^[e]	Classification
None	0	1	1	120	0	0	Y	Y	NR
			2	130	0	0	Y	Y	
			3	10	14	2	Y	N	
			4	150	0	0	Y	Y	
			5	38	100	0	Y	Y	
		2	1	50	64	0	Y	N	
			2	123	0	2	Y	Y	
			3	140	0	0	Y	Y	
			4	97	0	0	Y	Y	
			5	76	35	0	Y	N	
TCEP	10	1	1	15	17	3	Y	N	NR
			2	8	20	8	Y	N	94V-2
			3	52	15	2	Y	N	NR
			4	19	35	3	Y	N	NR
			5	11	45	3	Y	N	NR
		2	1	64	7	2	Y	N	NR
			2	21	8	3	N	N	94V-1
			3	20	25	3	Y	N	NR
			4	13	8	5	Y	N	94V-2
			5	15	21	2	Y	N	NR

Table 2. Cont.

FR Added	FR wt. %	Set no.	Sample No.	Flaming Combustion (s) ^[a]	Flaming Combustion (s) ^[b]	Glowing Combustion (s) ^[c]	Cotton Ignited (Y/N) ^[d]	Burned > 5-Inch Mark (Y/N) ^[e]	Classification
TCP	10	1	1	10	13	4	Y	N	94V-2
			2	17	4	2	N	N	94V-1
			3	12	27	3	Y	N	NR
			4	32	24	2	Y	N	NR
			5	16	3	2	N	N	94V-1
		2	1	38	6	4	Y	N	NR
			2	22	22	2	Y	N	NR
			3	12	8	2	N	N	94V-1
			4	23	6	3	Y	N	94V-2
			5	33	7	4	Y	N	NR
HBCD	10	1	1	6	8	2	N	N	94V-1
			2	4	3	3	Y	N	94V-2
			3	11	21	2	N	N	NR
			4	6	2	2	N	N	94V-1
			5	10	23	3	Y	N	NR
		2	1	13	8	2	Y	N	94V-2
			2	13	4	2	Y	N	94V-2
			3	6	4	2	Y	N	94V-2
			4	8	5	2	Y	N	94V-2
			5	13	6	3	Y	N	94V-2
MA	10	1	1	10	5	2	Y	N	94V-2
			2	7	8	4	N	N	94V-1
			3	5	13	3	Y	N	94V-2
			4	6	16	2	Y	N	94V-2
			5	4	37	3	N	N	NR
		2	1	11	5	2	Y	N	94V-2
			2	4	15	3	Y	N	94V-2
			3	6	14	2	Y	N	94V-2
			4	2	6	1	N	N	94V-1
			5	4	26	2	Y	N	94V-2
TBBPA	10	1	1	3	3	3	N	N	94V-1
			2	9	19	2	Y	N	94V-2
			3	7	6	4	Y	N	94V-2
			4	7	4	2	N	N	94V-1
			5	12	12	2	Y	N	94V-2
		2	1	7	6	3	Y	N	94V-2
			2	10	11	2	N	N	94V-1
			3	6	7	2	Y	N	94V-2
			4	6	17	3	Y	N	94V-2
			5	5	10	1	Y	N	94V-2
TBBPA	15	1	1	5	9	2	N	N	94V-1
			2	11	5	1	N	N	94V-1
			3	11	6	2	N	N	94V-1
			4	7	7	1	N	N	94V-1
			5	5	11	2	Y	N	94V-2
		2	1	6	6	2	N	N	94V-1
			2	5	6	2	N	N	94V-1
			3	6	6	1	N	N	94V-1
			4	7	7	1	N	N	94V-1
			5	4	5	2	N	N	94V-2
	20	1	1	3	5	0	N	N	94V-0
			2	2	3	1	N	N	94V-0
			3	1	2	0	N	N	94V-0
			4	1	2	0	N	N	94V-0
			5	2	3	0	N	N	94V-0
		2	1	4	4	1	N	N	94V-0
			2	3	4	0	N	N	94V-0
			3	3	6	1	N	N	94V-0
			4	3	3	1	N	N	94V-0
			5	1	2	0	Y	N	94V-2

^[a] Duration of flaming combustion after the first burner flame application. ^[b] Duration of flaming combustion after second burner flame application. ^[c] Duration of glowing combustion after second burner flame application. ^[d] Whether or not flaming drips ignited the cotton placed below the specimen. ^[e] Whether or not specimen burned up to holding clamp.

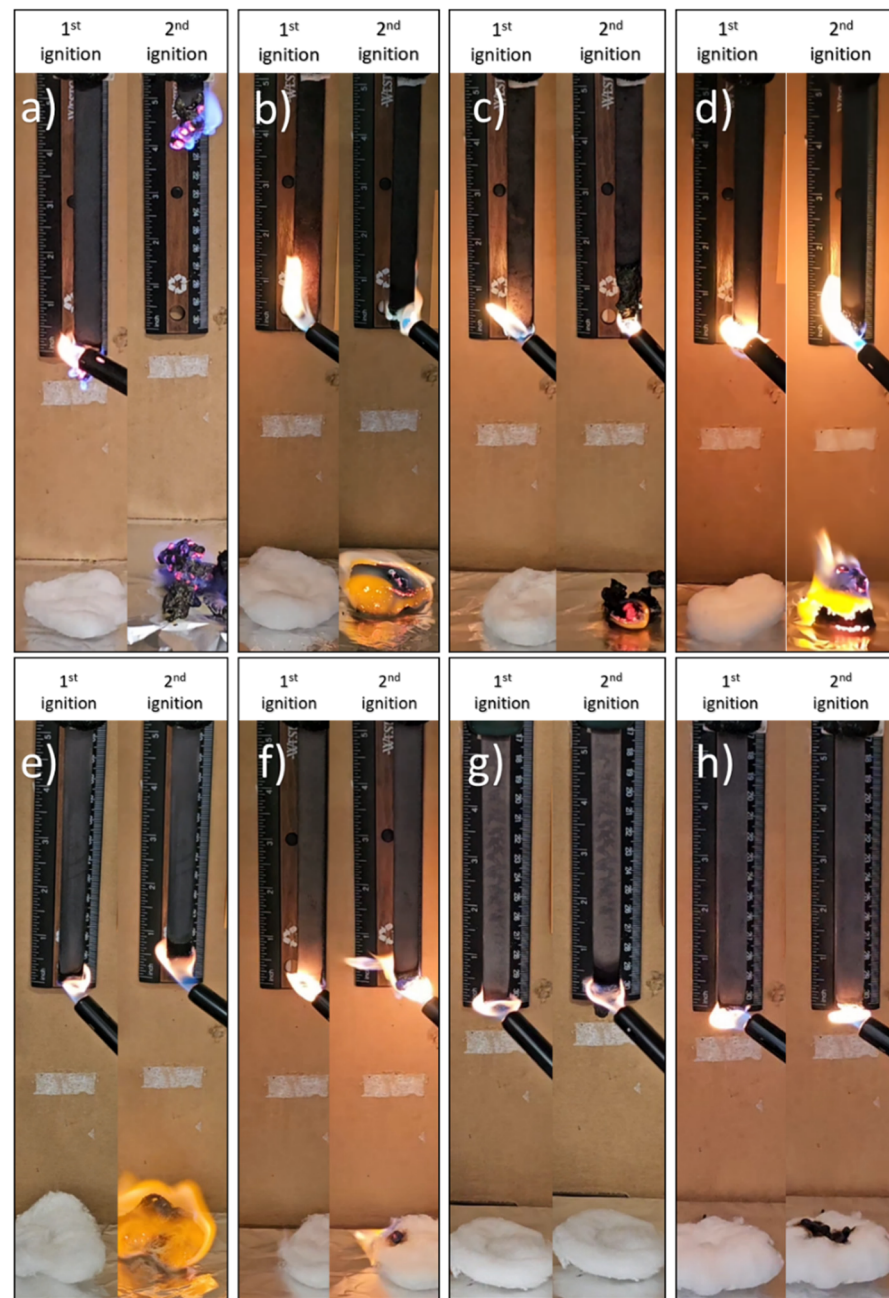


Figure 1. Materials undergoing the 94V burning test. Recorded parameters include the duration of flaming combustion, glowing combustion, and the potential ignition of cotton, providing crucial insights into the materials' response to vertically oriented flames, essential for fire safety evaluation. (a) **SunBG₉₀**, (b) **SunBG₉₀/TCEP** (10 wt. %), (c) **SunBG₉₀/TCP** (10 wt. %), (d) **SunBG₉₀/HBCD** (10 wt. %), (e) **SunBG₉₀/MA** (10 wt. %), (f) **SunBG₉₀/TBBPA** (10 wt. %), (g) **SunBG₉₀/TBBPA** (15 wt. %), and (h) **SunBG₉₀/TBBPA** (20 wt. %).

None of the specimens of FR-free **SunBG₉₀** passed the 94V test, exhibiting characteristics that allowed vertical flame propagation, suggesting a higher risk of fire spread in vertically oriented applications of **SunBG₉₀**. Flaming drips from the material were observed during the test, which may contribute to the ignition of nearby materials and increase the overall fire hazard. The flaming drips ignited the cotton placed below the specimen, further emphasizing the potential for the material to contribute to the ignition of surrounding materials. The duration of the flaming combustion exceeded the specified limits, indicating a prolonged burning behavior when exposed to a vertically oriented

flame. After the results of this test were obtained, it was decided to include flame-retardant additives in the material and test its behavior under the same conditions.

Under 94V burning test conditions, only one specimen in the first set of **SunBG₉₀/TCEP** (10 wt. %) achieved a classification (94V-2). In the second set, only two specimens achieved a classification (94V-1 and 94V-2). Almost all specimens had flaming drips after the first ignition, and the cotton placed below them was ignited. Phosphorus in TCEP can promote char formation during combustion, but the char layer may not be sufficiently stable or continuous, leading to inconsistent results.

The testing of **SunBG₉₀/TCP** (10 wt. %) revealed variability in the vertical burning behavior of the material. In the first set, only one specimen achieved the 94V-2 classification, while two specimens attained the 94V-1 classification. In the second set, two specimens received classifications of 94V-1 and 94V-2. Notably, 7 of the 10 specimens exhibited flaming drips after the first ignition, and the cotton placed below the specimens was ignited in these cases. The effectiveness of TCP may be limited by the same factors affecting TCEP, with the char layer not providing adequate protection in all cases. These findings indicate inconsistent flame resistance for this material, with potential challenges in controlling flaming drips and preventing the ignition of surrounding materials.

The **SunBG₉₀/HBCD** (10 wt. %) materials showed variable but improved performance in the vertical burning behavior of the material. In the first set, only one specimen achieved the 94V-2 classification, while two specimens attained the 94V-1 classification. However, all specimens demonstrated enhanced flame resistance in the second set, achieving the 94V-2 classification. Despite the improved classifications, 8 of the 10 specimens exhibited flaming drips after the first ignition, and the cotton placed below the specimens was ignited. HBCD's flame-retardant mechanism involves the release of bromine radicals, which can interfere with the combustion process, but the material's dripping behavior may hinder its effectiveness. These results suggest that while the material has shown progress in achieving higher flame-resistance classifications, there remains a challenge in controlling flaming drips, as with the other **SunBG₉₀/phosphorus-based FR** materials.

The analysis of **SunBG₉₀/MA** (10 wt. %) demonstrated improved vertical burning behavior over the samples that employed phosphorus-based FRs. In the first set, most specimens displayed favorable results, with one achieving the 94V-1 classification and three attaining the 94V-2 classification; only one specimen did not pass. All specimens from the second set passed to some level, with four achieving the 94V-2 classification and one receiving the 94V-1 classification. Despite the improved classifications, 9 of the 10 specimens exhibited flaming drips after the first ignition, and although seven of those nine led to the ignition of the cotton, two did not. Melamine decomposes to form nitrogen gas, diluting the flammable gases and cooling the material and improving flame resistance, and although the material showed progress over using phosphorus-based FRs in vertical flame resistance, flaming drips and the selective ignition of the cotton indicated that more improvements are needed.

The next material was **SunBG₉₀/TBBPA** (10 wt. %), which showcased consistent and positive vertical burning resistance. In the first set, all specimens passed, with three achieving the 94V-2 classification and two attaining the 94V-1 classification. The second set demonstrated a similar success rate, with all specimens passing, including four with the 94V-2 classification and one with the 94V-1 classification. Despite the overall positive results, 8 of the 10 specimens exhibited flaming drips after the second ignition, leading to the ignition of cotton in seven of those instances. While the material consistently met vertical burning standards, flaming drips and subsequent cotton ignition in some cases were still not ideal. In an effort to improve upon this result, the amount of TBBA was increased to 15 or 20 wt. %. In the evaluation of **SunBG₉₀/TBBPA** (15 wt. %), all specimens in both sets passed the 94V vertical burning test, with one obtaining the 94V-2 classification and four obtaining the 94V-1 classification for each set. Still, five of the ten specimens exhibited flaming drips after the second ignition, albeit with only two of those cases leading to the ignition of the cotton.

Examining **SunBG₉₀**/TBBPA (20 wt. %) showed that this material had even greater flame retardancy. All specimens achieved an impressive 94V-0 classification in the first set, showcasing the material's exceptional flame resistance. In the second set, while one specimen achieved the 94V-2 classification, the remaining four still exhibited a high level of flame resistance, achieving the 94V-0 classification. Despite the accomplishment of all specimens in both sets, after the second ignition, all ten specimens displayed flaming drips—in one instance leading to the ignition of the cotton.

3.2. Thermal and Mechanical Properties

Thermogravimetric analysis (TGA, details in Appendix A) and differential scanning calorimetry (DSC) were used to assess the thermal stability and thermomorphological changes of **SunBG₉₀** and its FR blends (Table 3). TGA (traces supplied in Figures S3–S8 in the SI) was employed by heating each blend from 25 to 800 °C to identify the decomposition temperature (T_d), defined as the temperature at which a 5% mass loss occurs during heating under a $N_2(g)$ atmosphere. **SunBG₉₀** displayed a decomposition temperature of 228 °C, comparable to *cyclo-S₈* (229 °C). The **SunBG₉₀**/FR materials exhibited similar T_d values of 213–217 °C, indicating the minimal influence of the FR additives on overall thermal stability, suggesting that the sulfur network dominated the initial thermal degradation.

Table 3. Thermal and morphological properties of flame-retardant added materials in comparison to **SunBG₉₀** and *cyclo-S₈*.

Material	FR wt. %	$T_d^{[a]}$ /°C	$T_m^{[b]}$ /°C	$T_g^{[c]}$ /°C
SunBG₉₀	0	228	118.5	−36.2
SunBG₉₀ /HBCD	10	213	114.1	−35.2
SunBG₉₀ /MA	10	214	118.8	NA
SunBG₉₀ /TBBPA	10	217	115.6	−36.0
SunBG₉₀ /TBBPA	15	216	114.6	−36.3
SunBG₉₀ /TBBPA	20	216	114.1	−36.7
<i>cyclo-S₈</i>	NA	229	118	NA

[a] The temperature at which 5% mass loss was observed. [b] The temperature at the peak minimum of the endothermic melting from the first heating cycle. [c] Glass transition temperature.

Thermomorphological transitions were evaluated using differential scanning calorimetry (DSC, details in Appendix A and thermograms provided in Figures S9–S20 in the SI). During the initial heating cycle, all examined samples underwent a phase transition at approximately 105 °C, indicative of an orthorhombic to monoclinic phase change for the sulfur component of the **SunBG₉₀**. A melting transition for the β -sulfur present in the **SunBG₉₀** was also observed for all samples, in a narrow range of 114–118 °C. All materials exhibited a glass transition temperature of −35 to −37 °C, unchanged from that of **SunBG₉₀** in the absence of FRs. These consistent transitions indicate that FRs do not disrupt **SunBG₉₀**'s structural properties and act mainly during combustion.

Whereas the addition of inorganic-based FRs or TPP caused significant evident deterioration of **SunBG₉₀** to the extent that the samples had to be handled gently to avoid breakage (vide supra), the **SunBG₉₀** and the other **SunBG₉₀**/FR materials could be handled as if they were cement samples without evident damage. The compressive strength for each of these samples, with more promising flame-retardant properties, was thus measured in triplicate using a mechanical test stand. The results of these trials are summarized in Figure 2 and the stress–strain curves are provided in Figures S21–S26 in the SI. Whereas a 20% decrease was observed in the compressive strength of the **SunBG₉₀**/HBCD (10 wt. %) relative to the **SunBG₉₀**, the addition of 10 wt. % MA or TBBPA to the **SunBG₉₀** actually led to compressive strength *increases* of 29% and 22%, respectively. This positive influence of FRs on the material's mechanical properties is consistent with prior studies on HSMs. A higher amorphous organic content leads to greater compressional fracture resistance due to the increased amorphous content and the better dispersion of organic FRs within

the **SunBG₉₀** matrix. The improvement in strength with the addition of FRs has its limits, however, as demonstrated by the progressive decrease in compressional strength as the amount of TBBPA was increased from 10 wt. % to 20 wt. %. Nonetheless, even at 20 wt. % of added TBBPA, the compressive strength was still equal to that of the **SunBG₉₀**.

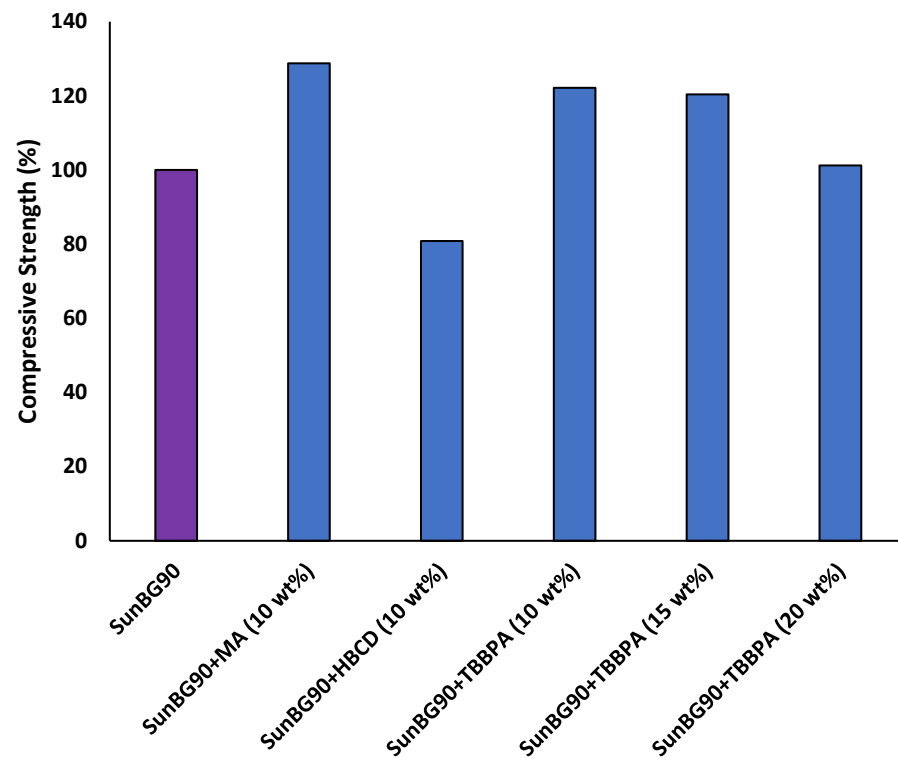


Figure 2. Impact of flame-retardant additives on the compressive strength of **SunBG₉₀**. This figure illustrates the comparative analysis of the compressive strength of **SunBG₉₀** before and after adding flame-retardant additives.

3.3. Abrasion Resistance (ASTM C1353)

Abrasion resistance is a vital characteristic determining how well a material can resist wear and tear induced by repeated contact with different materials [86]. In a previous report [69], ASTM C1353 testing was conducted on **SunBG₉₀**, yielding an abrasion resistance value of 16 (I_W , Table 4), which places it within a similar range as marble (10) and granite (25) [88–90]. The addition of 20 wt. % of TBBPA led to an increase of more than 200% relative to **SunBG₉₀**—possibly due to improved surface hardening upon curing, which can withstand abrasion better than **SunBG₉₀** alone, leading to a more robust composite and enhancing its durability in abrasive environments.

Table 4. Abrasion resistance.

Materials	Abrasion Resistance (I_W , H_A)
SunBG₉₀	16
SunBG₉₀/TBBPA (20 wt. %)	52
Limestone	10
Marble	10
Granite	25

3.4. Bond Strength (ASTM C482)

The determination of bond strength of a specimen to Portland cement paste is widely carried out, especially in applications where adhesion to cement substrate is essential [87]. Evaluating the adhesion between a sample and substrate guarantees that structures will

be long-lasting. ASTM C482 testing on **SunBG₉₀** samples revealed that bond strength significantly increased from 15 to 26 psi upon adding 20 wt. % TBBPA, showcasing a remarkable 73.3% improvement. This enhancement highlights the potential of TBBPA to influence material performance positively. While the current bond strength was below the 50 psi benchmark for mosaic and porcelain tiles (Table 5) [91,92], these promising results encourage further research and development to optimize the formulation and meet industry standards.

Table 5. Bond strength.

Materials	Bond Strength (psi)
SunBG₉₀	15
SunBG₉₀/TBBPA (20 wt. %)	26
Mosaic tile	50 or greater
Porcelain tile	50 or greater

4. Conclusions

This study systematically evaluated the flame retardancy and mechanical properties of composites formed by combining HSM **SunBG₉₀** with various FR additives. Initial results indicated poor flame retardancy and compressive strength when **SunBG₉₀** was combined with inorganic materials. All other **SunBG₉₀**/FR materials passed the UL-94HB horizontal burning test, but the more rigorous UL-94V vertical burning test revealed the susceptibility of **SunBG₉₀** to flame propagation. Subsequent experiments incorporating FRs such as TCEP, TCP, HBCD, MA, and TBBPA demonstrated varying success in improving flame resistance. While TBBPA at 20 wt. % achieved the highest 94V-0 classification, the persistent occurrence of flaming drips highlighted the need for further optimization or the development of more innovative FR systems for use with this HSM. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) provided valuable insights into the thermal stability of the composites. Mechanical testing revealed an overall improvement in compressive strength with the addition of the most protective FRs. The addition of 20 wt. % TBBPA significantly enhanced the properties of **SunBG₉₀**, increasing its abrasion resistance by over 200% and improving bond strength by 73.3%. These promising results underscore the potential for further optimization to meet industry standards.

This study also reveals several limitations: One notable limitation is the potential environmental impact of the most effective FRs, such as TBBPA and HBCD. While effective in enhancing fire resistance, these FRs are known to pose environmental concerns. Even with the best FR screened, the persistence of flaming drips underscored the need for further research on the fire safety of HSMs, which remains an underexplored aspect of this emerging class of materials. Overall, this research provides a foundation for improving fire-safety and mechanical-property balance, paving the way for future studies. Efforts to address the limitations of this study, such as exploring the effectiveness of greener FRs, are currently underway in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs8080304/s1>, Figure S1. Analysis of specimens after 94HB horizontal burning test. Each specimen provides visual insights into the effects of controlled flame exposure, with recorded data on combustion duration and damaged length.; Figure S2. Analysis of specimens after 94V vertical burning test. This image illustrates the aftermath of the 94V burning test, where two sets of five specimens underwent evaluation for vertical burning characteristics.; Figure S3. Thermogravimetric analysis (TGA) traces for **SunBG₉₀**. The inset (DTGA) shows the derivatives of the curve.; Figure S4. Thermogravimetric analysis (TGA) traces for **SunBG₉₀/HBCD (10 wt. %)**. The inset (DTGA) shows the derivatives of the curve.; Figure S5. Thermogravimetric analysis (TGA) traces for **SunBG₉₀/MA (10 wt. %)**. The inset (DTGA) shows the derivatives of the curve.; Figure S6. Thermogravimetric analysis (TGA) traces for **SunBG₉₀/TBBPA (10 wt. %)**. The inset (DTGA) shows the derivatives of the curve.; Figure S7. Thermogravimetric analysis (TGA)

traces for **SunBG₉₀**/TBBPA (15 wt. %). The inset (DTGA) shows the derivatives of the curve.; Figure S8. Thermogravimetric analysis (TGA) traces for **SunBG₉₀**/TBBPA (20 wt. %). The inset (DTGA) shows the derivatives of the curve.; Figure S9. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**. Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S10. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**. Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S11. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/HBCD (10 wt. %). Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S12. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/HBCD (10 wt. %). Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S13. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/MA (10 wt. %). Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S14. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/MA (10 wt. %). Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S15. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (10 wt. %). Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S16. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (10 wt. %). Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S17. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (15 wt. %). Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S18. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (15 wt. %). Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S19. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (20 wt. %). Three heating cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S20. Differential scanning calorimetry (DSC) traces for **SunBG₉₀**/TBBPA (20 wt. %). Three cooling cycles were collected. Endothermic transitions are downward in this thermogram.; Figure S21. Stress-strain plots for compressive strength measurements of **SunBG₉₀** after 4d at room temperature.; Figure S22. Stress-strain plots for compressive strength measurements of **SunBG₉₀**/HBCD (10 wt. %) after 4d at room temperature.; Figure S23. Stress-strain plots for compressive strength measurements of **SunBG₉₀**/MA (10 wt. %) after 4d at room temperature.; Figure S24. Stress-strain plots for compressive strength measurements of **SunBG₉₀**/TBBPA (10 wt. %) after 4d at room temperature.; Figure S25. Stress-strain plots for compressive strength measurements of **SunBG₉₀**/TBBPA (15 wt. %) after 4d at room temperature.; Figure S26. Stress-strain plots for compressive strength measurements of **SunBG₉₀**/TBBPA (20 wt. %) after 4d at room temperature.

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Abbreviations

FR	flame retardant
HSM	high sulfur-content material
SunBG₉₀	Composite made from 90 wt. % elemental sulfur, 5 wt. % sunflower oil, and 5 wt. % brown grease.

Appendix A

Instrumentation

TGA data were recorded (Mettler Toledo TGA 2 STARe System, Columbus, OH, USA) over the range 20–800 °C, with a heating rate of 10 °C·min^{−1} under a flow of N₂ (100 mL·min^{−1}). Each measurement was acquired in duplicate, and the presented results represent an average value.

DSC data were acquired (Mettler Toledo DSC 3 STARe System, Columbus, OH, USA) over the range −60 to 140 °C, with a heating rate of 10 °C·min^{−1} under a flow of N₂ (200 mL·min^{−1}). Each DSC measurement was carried out over three heat–cool cycles.

Compressional analysis was performed on a Mark-10 ES30 (Mark-10 Corporation Copiague, NY, USA) test stand equipped with a M3-200 force gauge (1 kN maximum force with ±1 N resolution), with an applied force rate of 3–4 N·s^{−1}. Compression cylinders were cast from silicone resin molds (Smooth-On Oomoo® 25 tin-cure) with diameters of approximately 6 mm and heights of approximately 10 mm. Samples were manually sanded to ensure uniform dimensions and measured with a digital caliper with ±0.01 mm resolution. Compressional analysis was performed in triplicate, and the results were averaged.

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