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FIRE-SAFE MATERIALS FOR ENERGY STORAGE DEVICES

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Abstract: Safety is a key parameter in various fields, especially given the rising global demand for lithium-ion batteries. The reliance on these storage systems has unfortunately brought fire accidents and the risk of thermal runaway to the forefront. This research addresses this critical need by developing novel functional coatings for battery housings, providing an essential layer of passive fire protection. The formulations utilize a polymeric matrix of pentaerythritol glycidyl ether (PGE) and Silres HP 2020, incorporating phosphorus-based flame retardants to ensure safety without using harmful halogenated compounds. Performance was rigorously evaluated through international standards, including the Cone Calorimeter Test (CCT), Limiting Oxygen Index (LOI), and UL94 flammability test. Results showed improved fire performance, specifically demonstrating an increase in protective carbonaceous residue. Crucially, the coatings exhibited excellent adhesion and successfully passed the demanding UL2596 Torch and Grit test, positioning them as strong candidates for safer energy storage device applications.

Keywords: Flame retardants, halogen free, battery safety, fire resistant, functional coatings.

1. INTRODUCTION.

The rapid expansion of electric vehicles (EVs), portable electronics, and large-scale energy storage systems (ESS) has been largely driven by advances in lithium-ion battery (LiB) technology [1]. While offering high energy density, LiBs present inherent safety challenges, primarily associated with the risk of thermal runaway [2]. This phenomenon, often triggered by internal short circuits, external impact, or overcharging, leads to a rapid, self-sustaining increase in temperature, resulting in the release of heat, toxic gases, and, ultimately, fire. The consequences of such events can be catastrophic, underscoring the urgent need for enhanced safety measures at the component level. The severity of thermal events is highly dependent on the battery's state of charge (SOC), with fully charged cells posing a maximum risk. This increasing risk has prompted regulatory bodies worldwide to introduce stricter fire resistance and toxicity standards for battery components. Therefore, the focus has shifted towards developing high-performance material solutions for battery enclosures that can withstand these extreme conditions. Furthermore, the sheer difficulty of extinguishing fires in large-scale LiB installations mandates a proactive focus on passive prevention methods to safeguard both infrastructure and personnel. The high cost of replacing damaged battery systems provides a strong economic incentive to invest in reliable external protection.

Current industry solutions often focus on active management systems. Our approach, however, focuses on passive fire protection through the application of advanced polymeric coatings directly onto the battery casing. This strategy aims to prevent or significantly delay the thermal escalation from propagating between cells or escaping the battery module.

The main objective of this research was to develop a polymeric coating (figure 1) with superior flame retardant (FR) properties specifically designed for LiB casings. A core commitment of this work was to use halogen-free additives [3], avoiding environmentally persistent organic pollutants commonly found in traditional FR systems. The final formulation integrates a synthesized or commercial phosphorus-based FR within a high-performance epoxy matrix, ensuring both fire resistance and mechanical durability suitable for industrial deployment.

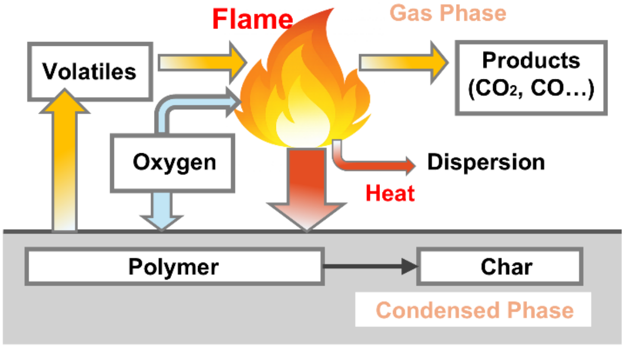

Figure 1. Combustion process.

2. METHODOLOGY.

The methodology encompassed three main stages: the synthesis of a novel FR compound, the formulation and preparation of the final coatings, and extensive characterization using thermal, chemical, and fire testing techniques. The coating system was built upon a two-component epoxy-amine system: pentaerythritol glycidyl ether (PGE) as the epoxy resin and Silres HP 2020 as the curing agent (amine). This matrix provides high mechanical strength and thermal resistance.

Beyond the experimental workflow described above, particular attention was given to ensuring the reproducibility and robustness of the coating preparation process. Each formulation was prepared under controlled mixing, viscosity, and curing conditions, allowing the identification of subtle differences in processing behavior between the synthesized and commercial flame retardants. This systematic approach also made it possible to correlate processing parameters—such as dispersion efficiency, solvent content, and cross-linking kinetics—with the final fire performance measured in subsequent tests. By integrating these considerations into the methodology, the study establishes a reliable framework for scaling the coatings toward industrial manufacturing, while also providing insight into how formulation pathways can be optimized for both performance and practical applicability.

2.1. Synthesis of Halogen-Free Flame Retardant.

A liquid, phosphorus-based flame retardant was synthesized via a chemical reaction involving phenyl dichlorophosphate, anhydrous ethylene glycol, and triethylamine [4], [5]. The synthesis process was carefully controlled to ensure a high yield of the target product, which was characterized as a clear, low-viscosity liquid. The liquid nature of the synthesized FR was crucial, as it facilitates homogeneous dispersion within the polymeric matrix and maintains the low viscosity required for the application process. This material was further purified using a rotary evaporator to remove residual solvent. and its final structure was verified using FTIR spectroscopy for quality control.

The synthesis process also revealed valuable information regarding the physicochemical behavior of the new flame retardant. As documented in the Master’s Thesis, careful control of temperature during the addition of ethylene glycol was essential to prevent premature side reactions and to ensure complete substitution of the chloride groups in the phosphorus precursor. The progressive formation of the liquid product was evidenced by the reduction in reaction mixture viscosity, while the subsequent purification step using a rotary evaporator proved crucial for removing residual solvents and unreacted amines. FTIR analysis of the final material showed the disappearance of characteristic P–Cl stretching bands and the appearance of P–O–C bonds, confirming the successful formation of the targeted phosphorus-containing structure. These observations not only validate the synthesis route but also highlight the chemical stability and compatibility of the final flame retardant with the polymeric matrices employed in the coating formulations.

2.2. Coating Preparation and Application.

Two main formulations were tested: one incorporating the synthesized FR (additives 2) and one using a benchmark commercial phosphorus-based FR (additives 1). The base formulation used a stoichiometric ratio of PGE to Silres HP 2020 calculated to achieve optimal cross-linking between the epoxy and amine functional groups (specifically, a 1:2.74 ratio of resin to curing agent). In addition to the flame retardant, inorganic solids such as Metakaolin Super and GP D255 were incorporated as synergists and fillers. These inorganic materials enhance the formation and stability of the protective char residue at elevated temperatures. The final mixture required the addition of ethyl acetate as a diluent to reduce the overall viscosity. All coatings were applied to an aluminum substrate (to mimic battery casings) using an air spray gun, necessitating a target viscosity below 200 mPa·s for industrial applicability.

2.3. Experimental Techniques.

A comprehensive suite of tests was conducted to fully characterize the coatings:

a) Viscosimetry and Curing: A rotational viscometer was used to confirm that the prepared formulations had a viscosity suitable for spraying. Differential Scanning Calorimetry (DSC) was used to monitor the curing kinetics, identifying the curing onset temperature (T_{onset}) and ensuring a complete cross-linking reaction. Fourier Transform Infrared Spectroscopy (FTIR) was used for chemical verification, confirming the structure of the synthesized FR and monitoring the disappearance of epoxy/amine functional groups after curing.

b) Thermal and Fire Performance:

- ❖ Thermogravimetric Analysis (TGA): Measures mass loss as a function of temperature. This test is vital for evaluating thermal stability and quantifying the amount of non-volatile, protective char residue formed at high temperatures.
- ❖ Limiting Oxygen Index (LOI): Determines the minimum percentage of oxygen required in the atmosphere to sustain flaming combustion.
- ❖ UL94 Vertical Burning Test: An industry-standard test that classifies a material's self-extinguishing capabilities and its propensity to produce flaming drips (figure 2).
- ❖ Cone Calorimeter Test (CCT): Provides key data such as Peak Heat Release Rate (pHRR), Time to Ignition (TTI), and Total Smoke Production (TSP).

c) Mechanical and Application Testing:

- ❖ Adhesion (ASTM D3359): Evaluates the durability of the coating on the aluminum substrate using the crosshatch method.
- ❖ UL2596 (Torch and Grit Test): A stringent test designed specifically for battery materials, combining a high-temperature torch flame with mechanical abrasion (grit). This test simulates extreme, real-world fire exposure and physical damage, and the material must maintain integrity for a defined number of cycles.

Success is confirmed by monitoring the backside temperature of the substrate, verifying the coating functions effectively as a thermal barrier against fire penetration, thus providing quantitative safety data to the battery industry

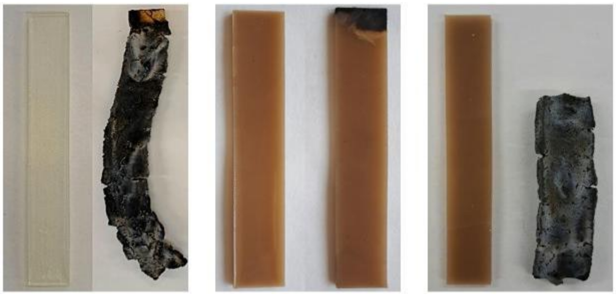

Figure 2. Reference sample for UL94 (left), sample with commercial flame retardant (center), and sample with synthesized flame retardant (right).

3. RESULTS AND DISCUSSIONS.

3.1. Physical and Thermal Characterization.

Both the commercial (additives 1) and synthesized (additives 2) formulations exhibited low final viscosities of 132 mPa·s and 122 mPa·s, respectively. These values were well within the target range, confirming their suitability for rapid, large-scale application via industrial spraying equipment. TGA analysis confirmed the effective operation of the flame retardant mechanism. The reference epoxy matrix showed a minimal residue at 700°C. In contrast, the addition of FRs and inorganic fillers significantly increased the char yield. The commercial FR formulation (additives 1) produced the highest carbonaceous residue. This char layer acts as a physical and thermal insulating barrier, slowing down the transfer of heat to the underlying substrate and preventing the release of flammable gases, thereby enhancing safety.

Furthermore, the detailed TGA assessment performed provided deeper insight into the degradation mechanisms governing each formulation. Under both air and nitrogen atmospheres, the reference epoxy showed a rapid mass loss after the onset of decomposition, leaving almost no protective residue at high temperature. In contrast, the formulations containing flame retardants and inorganic fillers exhibited a multi-stage degradation pattern, in which the early decomposition of phosphorus-containing species promoted char formation while the mineral components contributed to the structural reinforcement of the residue. Notably, the commercial FR formulation displayed the highest thermal stability in the intermediate temperature range and generated a more cohesive carbonaceous structure at 700 °C, confirming the synergy between the phosphorus chemistry and the inorganic network. These findings demonstrate that the thermal behavior of the coatings is directly linked to the composition and distribution of additives, ultimately influencing the fire performance measured in subsequent tests.

3.2. Fire Resistance Performance.

The fire tests clearly demonstrated the enhanced safety features of the functional coatings. The commercial FR formulation (additives 1) achieved the best results (table 1), with a LOI of 23.8%, a substantial increase over the reference material (20.8%). More significantly, it was the only formulation to achieve the UL94 V-1 classification, meaning the material self-extinguished relatively quickly after two separate flame applications, without the production of flaming drips.

Table 1: Results of LOI and UL94 tests.

Sample	LOI [%]	UL94
PGE (reference)	20.8	No rating
PGE + additives[1]	23.8	V-1
PGE + additives[2]	22.4	No rating

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Figure 3. Reference (left), sample with commercial retardant (center) and sample with synthesized retardant (right).

3.3. Adhesion and Extreme Fire Testing (UL2596).

The mechanical integrity of the coating is essential for long-term use. The Adhesion test (ASTM D3359 Test B) showed excellent results for both polymeric systems: a classification of 4B for additives 1 and 3B for additives 2. This performance is comparable to or better than many standard commercial paints (figure 4). The UL2596 Torch and Grit Test [6] is arguably the most relevant test for this application. It verifies that the protective layer can withstand a thermal shock while simultaneously being mechanically compromised. The performance of the developed epoxy coatings was superior to all commercial paints tested.

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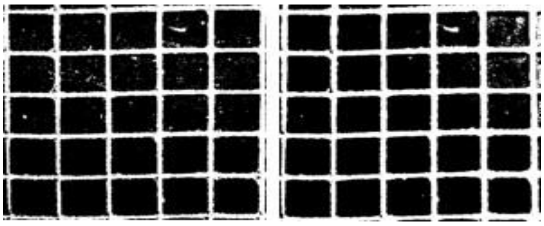

Figure 4. Image before shooting (left). Image of after using the tape (right).

These figures significantly exceed the minimum requirements of the UL2596 standard and confirm the viability of these coatings to serve as a durable, reliable fire barrier for LiB housings in extreme operating conditions (figure 5).

Figure 5. Sample before the test (left). Sample after the test on both sides (center and right).

4. CONCLUSIONS.

This research successfully synthesized a novel halogen-free flame retardant and utilized it, alongside a commercial alternative, to develop highly effective polymeric coatings for lithium-ion battery casings. Key findings confirm that the coatings provide dual protection:

1. Superior Fire Performance: The commercial FR formulation achieved a UL94 V-1 rating and significantly reduced the pHRR in CCT, demonstrating effective inhibition of combustion.
2. Robust Mechanical and Thermal Integrity: The coatings exhibited very good adhesion to the aluminium substrate and, most importantly, showed outstanding durability in the demanding UL2596 Torch and Grit Test [6], with the best formulation resisting 28 cycles.

In addition to the technical development of the flame-retardant formulations, this work offers a comprehensive understanding of how polymer inorganic hybrid systems behave under extreme thermal conditions. The experimental campaign carried out in the Master’s Thesis demonstrates that the effectiveness of a protective coating depends not only on the intrinsic chemistry of the flame retardant, but also on the combined action of synergetic fillers, curing kinetics, and the physical integrity of the coating during fire exposure. The systematic comparison between commercial materials and laboratory formulated systems highlights the importance of tailoring composition to promote char formation, delay ignition, and reduce the heat release rate, all of which are crucial parameters in preventing thermal runaway propagation in lithium-ion battery modules. This broader experimental perspective provides valuable insights for future battery safety research, reinforcing the idea that fire-safe energy storage must rely on multifunctional materials capable of delivering mechanical robustness, environmental compatibility, and reliable fire performance under realistic operating conditions.

In summary, the developed polymeric matrix coatings are solid candidates for enhancing fire safety in energy storage devices, offering a balance of high performance, environmental compliance (halogen-free) [3], and robust mechanical properties superior to existing commercial options.

5. AUTHOR CONTRIBUTIONS.

M.S.L.: Methodology, formal analysis, investigation, data curation, visualization, and writing—original draft; Y.L.: formal analysis, investigation, guidance during experimental work, visualization, and writing—review; D.W.: conceptualization, validation, supervision, and review; A.A.V.: validation, supervision and review.

6. ACKNOWLEDGMENTS.

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7. CONFLICTS OF INTEREST.

The authors declare no conflicts of interest.

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