

Development of Fire-Resistant Polymer Composites for Decorative Building Materials and Comprehensive Evaluation of their Fire-Technical and Service Properties

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Abstract: This study focuses on improving the fire-technical and mechanical performance of decorative polymer composite materials based on unsaturated polyester resin. CaCO_3 , SiO_2 , marble granules, Ammophos, and, in selected formulations, $\text{Al}(\text{OH})_3$ were used as functional fillers and flame-retardant additives. Four compositions (Polyester-1 to Polyester-4) were evaluated by limiting oxygen index (LOI), UL-94 vertical burning classification, time to ignition (TTI), total heat release (THR), flexural behavior, and tensile properties. All formulations achieved UL-94 V-0. LOI increased from 27.8 to 35.4%, TTI increased from 24 to 41 s, and THR decreased from 76 to 58 MJ/m². Polyester-3 exhibited the highest flexural load capacity together with substantial deformability, whereas Polyester-4 produced the strongest fire-performance indicators. The results show that a combined mineral-phosphorus-aluminum-hydroxide system can be used to balance fire safety and service performance in decorative construction composites. The proposed formulations are promising for artificial marble, decorative slabs, interior wall panels, and related finishing elements.

Keywords: Unsaturated Polyester Resin; Polymer Composite; Decorative Material; Flame Retardancy; Ammophos; Aluminum Hydroxide; CaCO_3 ; SiO_2 ; Limiting Oxygen Index; Mechanical Strength.

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I. INTRODUCTION

Decorative materials made from polymer composites are increasingly used in construction because of their low mass, ease of shaping, corrosion resistance, broad aesthetic possibilities, and comparatively low processing temperature. Unsaturated polyester resins (UPRs) are particularly attractive matrices for panels, coatings, artificial marble, and interior finishing components because they combine practical processing behavior, adequate strength, and economic efficiency [1]-[5]. Their principal limitation is the organic nature of the matrix, which leads to high combustibility. Conventional UPR has a limiting oxygen index of approximately 19%, and in fire conditions it can contribute heat, smoke, and volatile decomposition products [6]-[14].

Halogen-free flame-retardant systems based on phosphorus- and nitrogen-containing additives, ammonium phosphates, metal hydroxides, and their synergistic combinations can delay ignition and promote the formation

of a protective carbonaceous residue. However, high additive loadings may increase viscosity, disturb curing, reduce mechanical strength, and impair surface quality. Surface modification, synergistic mineral combinations, and rational filler selection are therefore important for obtaining high flame-retardant efficiency without unacceptable losses in service properties [15]-[22]. Mineral fillers, including marble waste and silica-containing phases, can additionally improve thermal stability, stiffness, dimensional stability, and the decorative appearance of composites.

The aim of this work was to develop mineral-filled polyester composites with improved fire behavior and to evaluate fire safety together with flexural and tensile performance. The study therefore considered LOI, UL-94 classification, TTI, THR, flexural load capacity, elastic response, tensile strength, and deformation. Particular attention was given to identifying a practical balance between maximum fire resistance and preservation of mechanical functionality.

The relevance of this combined evaluation is particularly high for decorative products because these materials simultaneously perform visual, protective, and structural functions. A formulation suitable for artificial marble or an interior panel must retain dimensional stability and acceptable load-bearing capacity during handling and installation, while also limiting ignition and heat release during fire exposure. For this reason, composition-property relationships were considered more informative than a single isolated fire or mechanical parameter.

The present experimental program also reflects a practical materials-engineering constraint: the fraction and type of mineral phase affect not only combustion behavior but also resin demand, curing, interfacial bonding, porosity,

and the appearance of the finished surface. Accordingly, the compositions were evaluated as complete multicomponent systems rather than as a simple polymer matrix containing an individual flame-retardant additive.

II. MATERIALS AND METHODS

➤ Composite Formulations

Four UPR-based compositions were prepared. CaCO_3 powder, SiO_2 , and 0.5–3 mm marble granules were used as mineral phases. Ammophos (AP) was introduced at 10 wt.% as the phosphorus-containing flame retardant. Polyester-3 and Polyester-4 additionally contained 5 wt.% $\text{Al}(\text{OH})_3$. The formulations were normalized to 100 wt.% and are summarized in Table 1.

Table 1 Composition of the Polyester-Based Decorative Composites (wt.%)

Component	P-1	P-2	P-3	P-4
Polyester resin	29.31	36.84	27.68	34.79
CaCO_3 powder	54.63	-	51.60	-
SiO_2	5.86	18.87	5.54	17.82
Marble granules, 0.5–3 mm	-	34.14	-	32.25
Accelerator	0.02	0.02	0.02	0.017
Hardener	0.18	0.13	0.16	0.123
Ammophos (AP)	10.00	10.00	10.00	10.00
$\text{Al}(\text{OH})_3$	-	-	5.00	5.00
Total	100.00	100.00	100.00	100.00

The Polyester-1/Polyester-3 and Polyester-2/Polyester-4 pairs provide a useful comparison of formulations without and with $\text{Al}(\text{OH})_3$. Because the polyester and mineral fractions also change slightly between paired formulations, the observed effects should be interpreted as compositional and synergistic rather than attributed solely to $\text{Al}(\text{OH})_3$.

The matrix content varied from 27.68 to 36.84 wt.%. Polyester-1 and Polyester-3 were highly filled CaCO_3 - SiO_2 systems, whereas Polyester-2 and Polyester-4 contained marble granules together with SiO_2 . This distinction is important because fine CaCO_3 powder and coarser marble particles generate different packing structures, specific surface areas, and polymer-mineral interfaces. In highly filled UPR systems, these features can influence void formation, curing uniformity, stiffness, and fracture behavior.

The mineral fraction also contributes indirectly to fire performance by reducing the relative amount of combustible organic matrix. However, simply maximizing mineral content is not sufficient: a useful decorative composite must still wet the particles adequately, cure without excessive defects, and retain a surface quality appropriate for finishing applications. The selected formulations therefore represent different balances of matrix fraction, mineral packing, and flame-retardant chemistry.

➤ Fire and Mechanical Testing

Fire-technical properties were evaluated using the limiting oxygen index, UL-94 vertical burning behavior, TTI, and THR. The study followed the methodological approaches of ISO 4589-2:2017 for LOI and ISO 5660-1:2015 for ignition and heat-release measurements. Flexural and tensile tests were used to characterize elastic modulus, maximum load, tensile stress, elongation, and strain. The numerical results were compared across all formulations and with a reference material to establish composition-property trends.

III. INTEGRATED FIRE-SAFETY DESIGN APPROACH

The proposed safety concept reduces fire risk at the material-composition stage rather than relying only on organizational or building-level protective measures. Ammophos promotes condensed-phase charring, while $\text{Al}(\text{OH})_3$ provides an endothermic heat sink, releases bound water during decomposition, and leaves a relatively stable alumina-containing residue. In combination with the mineral fillers, these effects reduce the combustible polymer fraction, delay ignition, suppress combustion, and limit heat release. The approach integrates formulation design, fire testing, and mechanical verification in a single material-selection procedure.

This combined design is important for finishing panels and artificial-marble products because a formulation with the highest LOI is not necessarily the formulation with the best mechanical response. Therefore, the target should be application-specific optimization of fire resistance, strength, deformation capacity, surface quality, and manufacturability rather than maximization of one indicator in isolation.

From a fire-safety-management perspective, this approach shifts part of the risk-control function into the material itself. Delayed ignition provides additional time before sustained burning develops, while lower THR reduces the total thermal contribution of the material to a fire. At the

same time, V-0 classification indicates rapid self-extinguishing behavior under the UL-94 vertical test conditions. These indicators describe complementary aspects of fire performance and should therefore be interpreted together.

Mechanical verification is equally important because a fire-retardant formulation that becomes excessively brittle or loses load-bearing capacity may be unsuitable for real decorative elements. Integrating fire and mechanical measurements makes it possible to identify compositions that provide a usable safety margin during both normal service and thermal exposure.

IV. RESULTS AND DISCUSSION

➤ Fire-Technical Performance

Table 2 Fire-Technical Properties of the Developed Composites

Indicator	P-1	P-2	P-3	P-4
LOI, %	27.8	29.8	32.5	35.4
UL-94	V-0	V-0	V-0	V-0
TTI, s	24	28	37	41
THR, MJ/m ²	76	64	60	58

A clear composition-fire-performance relationship was observed (Table 2). LOI increased progressively from 27.8% for Polyester-1 to 35.4% for Polyester-4, while every formulation achieved UL-94 V-0. Compared with the reported LOI of about 19% for conventional UPR, the developed systems therefore demonstrate a substantial improvement in resistance to flaming combustion.

The effect was especially pronounced in formulations containing $\text{Al}(\text{OH})_3$. From Polyester-1 to Polyester-3, LOI

increased by 4.7 percentage points (16.9% relative), TTI increased from 24 to 37 s (54.2%), and THR decreased from 76 to 60 MJ/m² (21.1%). A similar trend was obtained for the marble-containing pair: from Polyester-2 to Polyester-4, LOI increased from 29.8 to 35.4%, TTI increased from 28 to 41 s, and THR decreased from 64 to 58 MJ/m². These changes correspond to an 18.8% relative LOI increase, a 46.4% increase in TTI, and a 9.4% decrease in THR.

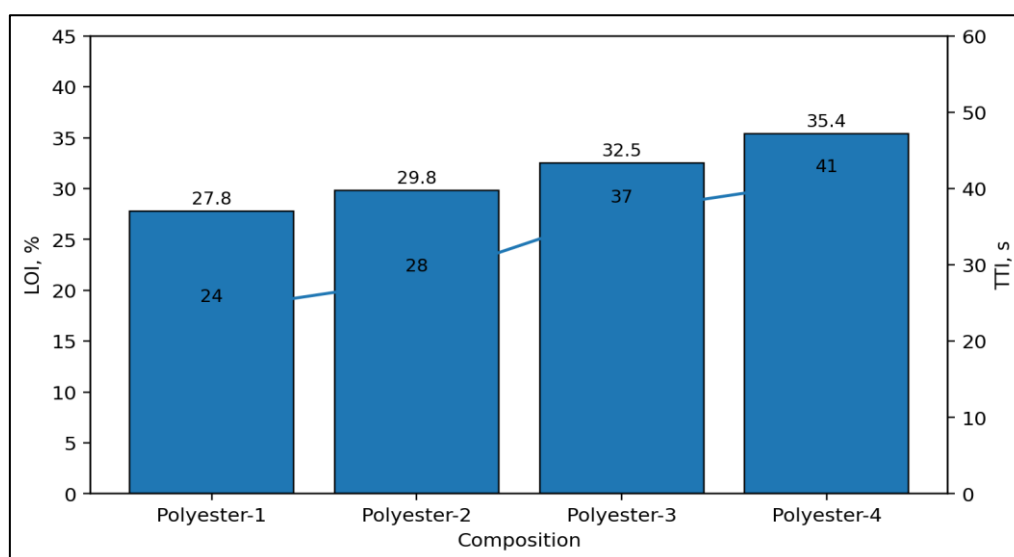


Fig 1 LOI and Time-to-Ignition Values of the Polyester Composites.

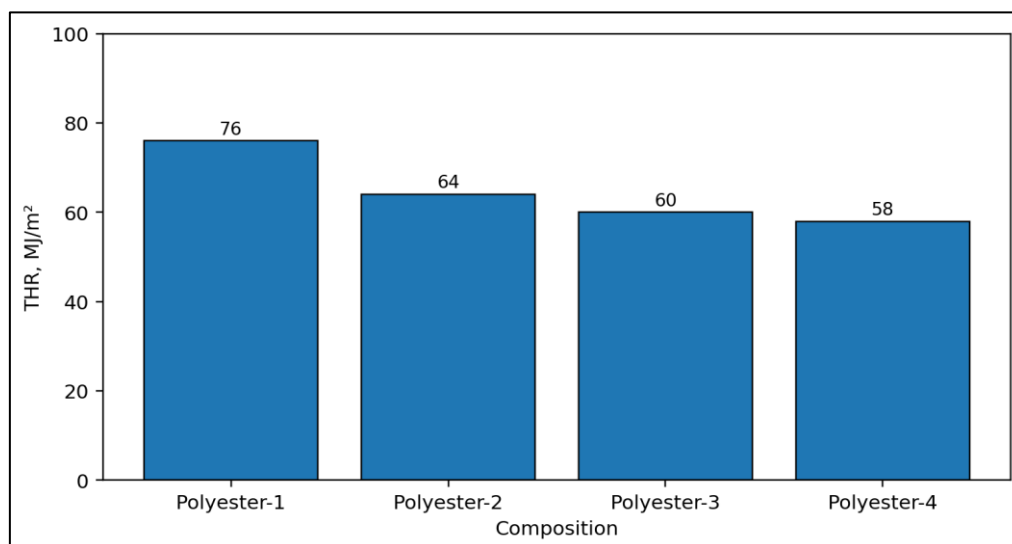


Fig 2 Total Heat Release (THR) of the Polyester Composites.

Polyester-4 had the highest LOI (35.4%), the longest TTI (41 s), and the lowest THR (58 MJ/m²). Relative to Polyester-1, its LOI was 7.6 percentage points higher, ignition time was 70.8% longer, and THR was 23.7% lower. The simultaneous improvement in all three parameters indicates both greater resistance to ignition and a reduced thermal contribution during combustion.

The stepwise increase in LOI from Polyester-1 through Polyester-4 is consistent with a progressively less flammable composite environment. At an LOI of 27.8%, Polyester-1 already requires a more oxygen-rich atmosphere for sustained burning than conventional UPR. Polyester-3 and Polyester-4 move this requirement further upward to 32.5% and 35.4%, respectively. Although LOI is not a direct simulation of a building fire, the trend provides a useful comparative measure of the effectiveness of the combined filler and flame-retardant systems.

The TTI data provide a second perspective. Extending ignition from 24 s to 37-41 s means that the $\text{Al}(\text{OH})_3$ -containing systems absorb and dissipate a larger amount of incident heat before a self-sustaining flame develops. This behavior is consistent with the endothermic decomposition of aluminum hydroxide and with the larger inert fraction of the composite. Because the formulations differ in more than one component, the improvement should be understood as the response of the overall formulation rather than as a single-additive effect.

THR decreased in the same direction as LOI and TTI improved. The drop from 76 MJ/m² for Polyester-1 to 58 MJ/m² for Polyester-4 indicates that the optimized system releases less total heat during the cone-calorimeter exposure. For interior finishing materials, this reduction is relevant because heat release is directly associated with the ability of a burning product to contribute energy to fire growth.

The fire-retardant action of $\text{Al}(\text{OH})_3$ is associated with endothermic decomposition and water release, which slows heating and dilutes combustible gaseous products, while the residual inorganic phase restricts heat and mass transfer. Phosphorus-containing flame retardants promote carbonization and formation of a protective condensed-phase layer. Literature reports for modified UPR systems similarly show that combined phosphorus/mineral or ATH-containing approaches can produce LOI values near or above 30% together with V-0 classification [8], [9], [14]-[18], supporting the mechanism inferred from the present results.

The mineral fillers may further stabilize the condensed phase by acting as a noncombustible skeleton beneath the charred surface. CaCO_3 - and silica-rich formulations reduce the proportion of volatile organic material per unit mass and may hinder heat penetration by increasing the thermal mass of the composite. Marble granules can provide a similar dilution effect while also contributing to the decorative texture required for artificial-stone products.

Comparison with earlier UPR studies is also instructive. Published phosphorus- and silicon-modified systems have reported LOI increases from about 19% to above 30% together with V-0 behavior, while combined DMMP/ATH/APP formulations have likewise reached LOI values around 30%. The present Polyester-3 and Polyester-4 results fall within or above this performance range, while retaining useful mechanical characteristics.

➤ *Flexural Properties*

Table 3 Selected Flexural Properties of the Composites

Sample	Elastic modulus, N/mm ²	Maximum force, N
Polyester-1	197675	1456.21
Polyester-2	270261	1589.05
Polyester-3	565525	1861.94
Reference	454597	1545.04
Polyester-4	213685	1295.05

The influence of the flame-retardant/mineral system on flexural response was not uniform. Polyester-3 reached the highest maximum force, 1861.94 N, exceeding the reference value of 1545.04 N by approximately 20.5%. Polyester-2 also

slightly exceeded the reference (1589.05 N, about 2.8% higher), whereas Polyester-1 and Polyester-4 were lower than the reference by approximately 5.7% and 16.2%, respectively.

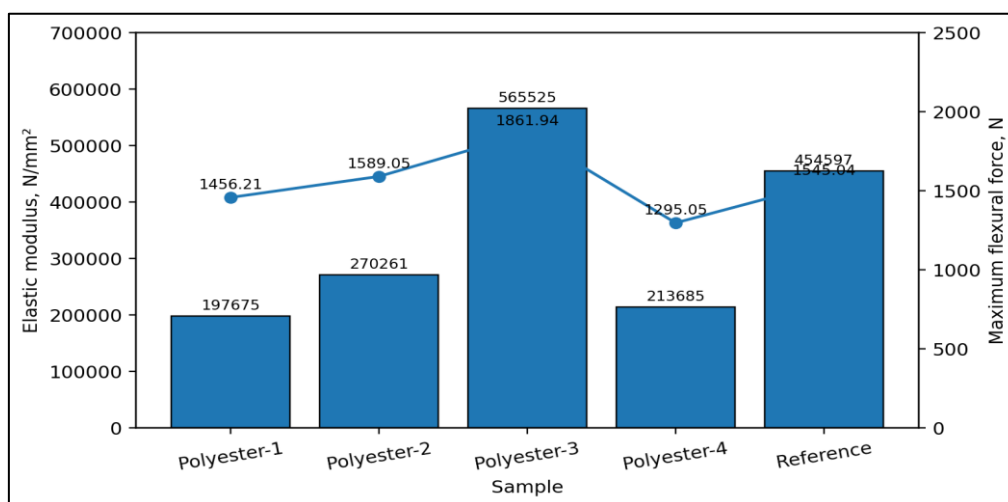


Fig 3 Elastic Modulus and Maximum Flexural Force of the Investigated Composites.

The contrasting behavior of Polyester-3 and Polyester-4 shows that introducing $\text{Al}(\text{OH})_3$ does not produce the same mechanical effect in every mineral system. The CaCO_3 - SiO_2 formulation of Polyester-3 combined improved fire resistance with increased flexural load capacity, whereas the marble- SiO_2 formulation of Polyester-4 achieved the strongest fire indicators at the cost of lower flexural load resistance. This difference is consistent with the importance of particle type, size distribution, interfacial adhesion, and microstructural defects in determining the mechanical response of highly filled UPR composites.

The elastic-modulus data reinforce the same interpretation. Polyester-3 exhibited the largest modulus value among the developed formulations, indicating a stiff load-bearing structure under flexure, while Polyester-4 showed a substantially lower value. Such differences can arise from the packing efficiency of the mineral phase, local resin-rich regions, interfacial bonding, and the presence of microvoids. In a highly filled thermoset, a small change in particle distribution can alter the stress-transfer path even when the overall additive package is similar.

Polyester-2 is also noteworthy because its maximum flexural force slightly exceeded that of the reference without containing $\text{Al}(\text{OH})_3$. This suggests that the marble- SiO_2 phase can provide useful mechanical reinforcement when the matrix-filler balance is favorable. In contrast, the lower flexural value of Polyester-4 demonstrates that the strongest fire-retardant formulation may require further optimization of particle packing or interfacial adhesion if higher structural loading is expected.

Polyester-3 is particularly notable because it combined $\text{LOI} = 32.5\%$, V-0 , $\text{TTI} = 37$ s, $\text{THR} = 60$ MJ/m², and a maximum flexural force of 1861.94 N. It therefore represents a balanced formulation for decorative elements in which fire resistance and flexural reliability are both important.

➤ *Tensile Strength and Deformation*

Table 4 Selected tensile properties of the composites

Sample	Maximum tensile stress, MPa	Strain at break, %
Polyester-1	8.050	6.364
Polyester-2	8.146	12.160
Polyester-3	4.316	14.889
Reference	6.007	5.060
Polyester-4	5.694	8.399

Tensile tests further demonstrated the trade-off between strength and deformation. Polyester-2 had the highest maximum tensile stress (8.146 MPa), followed by Polyester-1 (8.050 MPa); these values were approximately 35.6% and 34.0% higher than the reference value of 6.007 MPa.

Polyester-3 had a lower maximum tensile stress (4.316 MPa) but the greatest deformation capacity, reaching 14.889% strain at break—approximately 2.93 times the reference value of 5.060%.

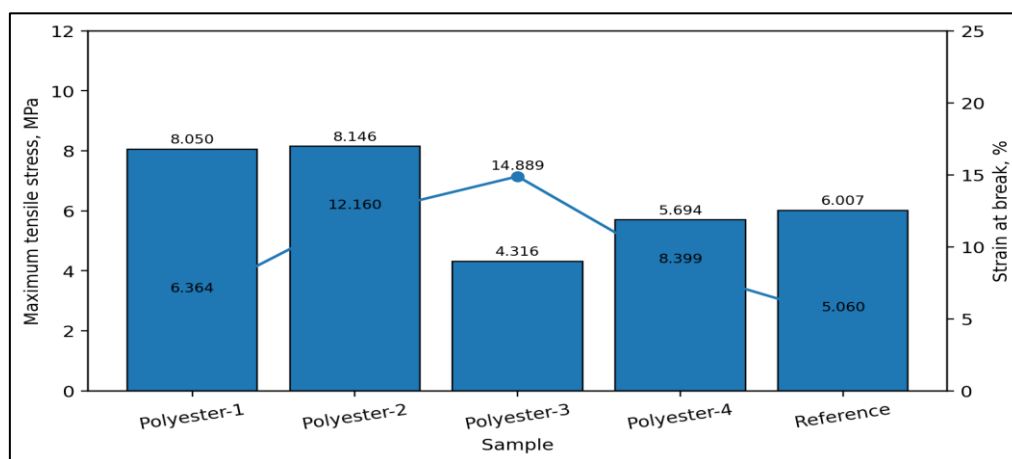


Fig 4 Maximum Tensile Stress and Strain at Break of the Investigated Composites.

Polyester-2 combined high tensile stress with 12.160% deformation, indicating simultaneous retention of strength and ductility. Polyester-4 reached 5.694 MPa and 8.399% strain at break; compared with the reference, tensile stress was about 5.2% lower while deformation capacity was about 66% higher. The increased deformability may be beneficial for decorative slabs during transport, installation, and short-term service loading because it can improve the redistribution of localized stresses.

The tensile results therefore separate the formulations into different response types. Polyester-1 is relatively strong but less deformable, Polyester-2 combines the highest tensile stress with considerable deformation, and Polyester-3 sacrifices tensile stress in exchange for markedly greater strain capacity. Polyester-4 occupies an intermediate position and still exceeds the reference in deformation. This range of responses confirms that the mineral and flame-retardant phases alter not only strength but also the way the composite accommodates strain before failure.

For brittle decorative materials, additional deformation capacity can be advantageous because local stresses arise around fasteners, edges, transport supports, and contact

points during installation. The almost threefold increase in strain at break observed for Polyester-3 relative to the reference indicates a substantially different failure response, which may help the material tolerate short-duration mechanical disturbances even though its tensile stress is lower.

➤ *Scientific Novelty and Practical Significance*

The scientific contribution of the study is the experimentally established relationship between composition and the combined fire-technical and mechanical properties of the polyester resin-mineral filler-phosphorus flame retardant-aluminum hydroxide system. Addition of $\text{Al}(\text{OH})_3$ to mineral-filled composites containing 10% Ammophos enabled LOI values of 32.5-35.4%, maintained V-0 behavior, increased TTI to 37-41 s, and reduced THR to 58-60 MJ/m². At the same time, the results demonstrate that improved flame retardancy does not necessarily require a uniform decrease in mechanical performance.

For practical selection, Polyester-4 is the formulation with the strongest measured fire-performance indicators, whereas Polyester-3 provides the most favorable balance of fire resistance, flexural load capacity, and deformation

capability. Polyester-2 is also of interest when tensile strength and deformation must be preserved together. The developed compositions are consequently relevant to artificial marble, decorative panels, interior wall elements, and furniture-related finishing components.

The results also show why formulation selection should be linked to the intended product. A wall-facing panel for which flame resistance is the dominant requirement may reasonably prioritize the Polyester-4 type of formulation. A component exposed to handling, bending, or local deformation may instead benefit from the Polyester-3 balance. Where tensile strength and deformation must be maintained simultaneously, the Polyester-2 response is attractive. This application-oriented selection strategy is more informative than declaring a single composition universally optimal.

The present results are comparative and are based on the measured formulations and test methods reported here. Further scale-up work should preserve the same integrated approach by verifying processing stability, surface quality, water resistance, thermal aging, and repeatability under production conditions. These additional service factors were identified as relevant to practical use but were not quantified in the present dataset.

➤ *Comparative Interpretation of Composition-Property Relationships*

Taken together, the four formulations demonstrate that the fire and mechanical responses are controlled by the complete composite architecture. Polyester-1, based mainly on CaCO_3 and SiO_2 with 10% Ammophos, provides the baseline for the fine-mineral system. Polyester-3 retains the same principal mineral phases but adds $\text{Al}(\text{OH})_3$ and slightly adjusts the matrix and filler fractions. The resulting increase in LOI, ignition delay, and reduction in THR occur together with a pronounced increase in flexural load capacity and deformation capability. This indicates that, in this specific CaCO_3 - SiO_2 system, the flame-retardant modification did not inherently compromise mechanical functionality.

The comparison between Polyester-2 and Polyester-4 is different. Both are based on marble granules and SiO_2 , and both contain 10% Ammophos; however, Polyester-4 also contains 5% $\text{Al}(\text{OH})_3$ and a slightly lower polymer and mineral fraction. Fire performance improves strongly, but maximum flexural force decreases. This contrast illustrates why the effects of $\text{Al}(\text{OH})_3$ cannot be generalized independently of the surrounding mineral structure. The same additive can interact differently with a fine-powder network and with a coarser marble-granule network because the interfacial area, packing density, and local resin distribution are different.

The behavior of Polyester-2 is also important in this comparison. It achieved the highest tensile stress among the investigated materials while retaining a strain level substantially above the reference. Its fire performance was lower than that of the $\text{Al}(\text{OH})_3$ -containing formulations, but LOI still reached 29.8% and the sample remained V-0. Thus,

Polyester-2 represents a composition in which mechanical strength is emphasized without losing the principal fire-retardant benefit of the phosphorus/mineral system.

Polyester-3 occupies another functional position. Its tensile stress is lower than that of Polyester-1, Polyester-2, and the reference, yet its strain at break is markedly higher, and its flexural maximum force is the highest of all samples. These apparently different trends are not contradictory because tensile and flexural tests emphasize different stress states and failure mechanisms. In a heterogeneous filled thermoset, particle packing and interfacial bonding may resist bending loads effectively while allowing greater strain accumulation under direct tension. The source data therefore support evaluating more than one mechanical indicator before selecting a formulation.

The fire indicators similarly provide complementary information. LOI describes the oxygen concentration required to sustain burning; TTI describes resistance to ignition under the specified external heat flux; THR measures the cumulative energy released during burning; and UL-94 provides a classification of vertical burning behavior. The consistent improvement of LOI, TTI, and THR toward Polyester-4, together with V-0 for all formulations, gives a stronger basis for judging fire performance than any individual indicator alone.

The combined dataset therefore establishes a practical composition-property map. Increasing fire resistance is feasible without an automatic loss of mechanical performance, but the outcome depends on filler type and the balance among matrix, mineral phase, phosphorus-containing flame retardant, and $\text{Al}(\text{OH})_3$. This finding is central to the design of decorative composites because the target property set depends on whether the product is expected mainly to resist ignition, carry bending loads, tolerate local deformation, or combine these functions.

➤ *Practical Implementation and Further Validation*

For artificial marble and decorative slab production, the mineral fillers used in this study are compatible with the visual and structural concept of highly filled polyester materials. Marble granules can generate the stone-like appearance required for decorative products, while CaCO_3 and SiO_2 contribute to packing, rigidity, and dimensional stability. The fire-retardant package can therefore be incorporated into a material architecture that already serves a decorative function rather than being treated as a separate protective coating.

The source study also emphasizes that practical selection should consider processing and service requirements in addition to laboratory fire performance. High concentrations of inorganic particles can change mixture viscosity, curing behavior, and surface finish. For industrial application, the formulation must remain sufficiently processable to achieve uniform filler distribution, adequate wetting, low porosity, and a consistent decorative surface. These factors are particularly relevant for panels and

artificial-marble products, where visible defects may be unacceptable even when fire and strength criteria are met.

Water resistance, thermal stability, and long-term service behavior are additional factors identified as important for the intended application. They were not numerically characterized in the dataset used for the present comparison and therefore should be verified before large-scale implementation. The same applies to production cost: mineral fillers can reduce resin demand, but the economic effect of specialized flame-retardant additives and additional processing steps must be assessed at manufacturing scale.

For products in which maximum fire safety is the principal design objective, the measured performance of Polyester-4 provides the strongest basis for further development because it combines the highest LOI, the longest TTI, the lowest THR, and V-0 classification. Where mechanical reliability under bending and the ability to accommodate deformation are equally important, Polyester-3 provides a more balanced measured response. The data therefore support a family of application-specific formulations rather than a single universal recipe.

Future validation should preserve the integrated testing strategy used here. Fire tests should be repeated together with flexural and tensile measurements after any change in particle size distribution, resin content, additive concentration, or production method. In this way, improvements in one performance domain can be checked immediately against possible losses in another. Such an approach is consistent with the central objective of the study: simultaneous management of fire safety and service properties through rational control of composite composition.

V. CONCLUSION

Mineral-filled unsaturated polyester composites with combined phosphorus- and aluminum-hydroxide-based fire-retardant modification showed substantial potential as decorative construction materials. CaCO_3 , SiO_2 , and marble granules reduced the fraction of combustible polymer while contributing to dimensional and mechanical performance. The Ammophos/ $\text{Al}(\text{OH})_3$ combination produced the strongest improvements in fire behavior: LOI reached 32.5-35.4%, all formulations remained at UL-94 V-0, ignition was delayed to 37-41 s in $\text{Al}(\text{OH})_3$ -containing systems, and THR decreased to 58-60 MJ/m².

Mechanical testing confirmed that the optimum formulation depends on the intended service condition. Polyester-3 combined high fire resistance with the highest flexural load capacity and the greatest tensile deformation, while Polyester-4 provided the best measured fire-technical performance. The results therefore support composition-specific optimization rather than a single universal formulation and provide a scientific basis for designing fire-safer artificial marble, decorative slabs, wall panels, and interior finishing products.

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