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HALOGEN-FREE HYBRID FLAME RETARDANCY OF MIXED PLASTIC WASTE REGRIND

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A major obstacle to the value-added recycling of mixed polyolefin regrinds recovered from post-consumer packaging waste (MOHU cap regrind) is the intrinsically high flammability of these polymers. In this study, a halogen-free intumescent flame-retardant system was investigated based on the synergistic action of ammonium polyphosphate (APP) as an acid source and melamine polyphosphate (MPP) as a blowing agent. Hybrid composites containing 5–20 wt% additives were prepared by twin-screw extrusion and injection molding, followed by comprehensive rheological, mechanical, and thermal (TGA) characterization. The results demonstrated that the hybrid formulation containing 15 wt% APP and 5 wt% MPP provided the most favorable flame-retardant performance. The horizontal flame-spread rate was reduced to nearly half that of the neat waste matrix. Thermogravimetric analyses confirmed that chemical synergy promoted the formation of a thick, thermally stable char shield that effectively suppressed the combustion process. Although additive incorporation reduced toughness through weakened phase boundaries, the increase in flexural modulus confirmed that the developed system was able to retain the original stiffness of the base matrix even at the maximum filler loading. The findings demonstrate that, by applying an optimized intumescent additive system, secondary raw materials suitable for technical applications can be produced from heterogeneous post-consumer waste streams.

Keywords: mixed plastic waste, recycling, flame retardancy, polyolefins, intumescent system

1. Introduction

Synthetic polymers are essential raw materials for modern industry, and their global production has increased exponentially in recent decades [1]. Although current research is placing increasing emphasis on the development of bio-based variants, the overwhelming majority of global production still relies on hydrocarbons derived from fossil energy carriers [2]. Owing to their low production cost, excellent processability, and broad tailorability, these macromolecules have become dominant in almost every industrial sector, particularly in packaging [3]. However, the short life cycle of packaging materials, especially single-use products, represents a major technological and environmental challenge for global waste management. Under natural conditions, synthetic polymers are practically non-biodegradable; therefore, waste released into the environment can persist for centuries. Accumulating landfill waste burdens the environment, inhibits vegetation development, and fragments released into the environment can act as physical traps for wildlife. This macroscopic damage is further aggravated by the presence of microplastics generated during physical fragmentation, which already represent a persistent and difficult-to-remediate global ecological hazard [4].

Processing mixed plastic waste originating from post-consumer selective collection faces substantial thermodynamic and technological limitations. The directives of the European Union identify waste reduction and the achievement of a circular economy as primary objectives [5]. In Hungary, since the introduction of the MOHU concession system and the DRS network, noticeably cleaner fractions and larger quantities of feedstock have been returned to the waste-management cycle [6]. Nevertheless, during the material recovery of mixed waste streams, the principal challenge is no longer simple recyclability but the extension of service life and the achievement of broader industrial applicability. The technological challenges are primarily associated with unidentified foreign plastic fractions that induce phase separation, which is further exacerbated by the thermodynamic incompatibility of the main constituents, high-density polyethylene (HDPE) and polypropylene (PP) [7]. Although both polymers belong to the polyolefin family, their different crystallization and rheological characteristics hinder homogeneous

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blending; consequently, phase separation occurs in the melt. During cooling, weak interfacial adhesion develops between the phases, which deteriorates the mechanical load-bearing capacity of the composite at the macroscopic level [8]. Compatibility problems are further aggravated by thermo-oxidative, mechanical, and hydrolytic degradation experienced during previous life cycles of the materials, leading to chain scission and a reduction in molecular weight [9]. Consequently, the properties of secondary raw materials recovered by conventional mechanical recycling are inferior to those of primary raw materials. The objective of value-added recycling is to produce engineering composites approaching the performance of virgin polymers through targeted technological interventions [10]. For higher-value technical and construction applications, however, compliance with strict industrial fire-safety requirements is indispensable [11]. Due to their chemical structure, polyolefins are highly flammable; when exposed to fire, polymer chains undergo rapid depolymerization, forming a low-viscosity melt. Until the end of the twentieth century, halogenated, particularly brominated, flame retardants were widely used. These materials exhibited excellent flame-extinguishing ability owing to their gas-phase radical-trapping mechanism [12]. During processing or in the event of fire, however, corrosive and toxic gases are released; therefore, tightening environmental regulations have made the use of halogen-free alternatives necessary [13].

From a materials-science perspective, the most effective route for flame retarding polyolefins is to promote char formation in the condensed phase [14]. Because these plastics almost completely pyrolyze into volatile gases during thermal decomposition, intumescent, i.e., heat-foaming, systems represent the most advanced technological direction among halogen-free solutions. The operation of these complex systems is based on the coordinated chemical synergy of three fundamental components: an acid source, a carbon source, and a blowing agent [15]. Upon heating, the acid source decomposes at a lower temperature and generates a strong inorganic acid within the polymer matrix, catalyzing dehydration of the carbon source. In parallel, the blowing agent reaches its decomposition temperature, and the released inert gases foam the melt. The resulting thick, cellular char shield acts as a physical barrier: it protects the underlying layers as a thermal insulator, hinders oxygen diffusion, and traps combustible pyrolysis gases [16]. In practical industrial applications, ammonium polyphosphate (APP) has proven to be one of the most reliable acid sources. Its type-II crystalline structure provides a high degree of polymerization and excellent thermal stability, preventing premature decomposition in plastic-processing equipment [17]. When used alone, the flame-retardant efficiency of APP may be limited in certain cases; to overcome this, a major current research direction is the development of hybrid systems combined with nitrogen-containing synergists [18]. For this purpose, melamine polyphosphate (MPP) is a highly suitable synergist, acting both as an additional acid source and as a primary blowing agent. Nitrogen and ammonia gases are released precisely within the temperature window in which polyphosphoric acid has already formed a viscous melt. The carefully adjusted combined application of the two additives promotes the formation of a continuous polyaromatic carbonaceous structure that provides an effective physical barrier against fire-induced thermal loading [19].

During practical implementation, the most complex challenge is the harmonization of the rheological effects of the additives [20]. The melt viscosity is critical for the proper development of the intumescent foam layer. If the melt viscosity is excessively low, the generated gases escape without foaming the carbonizing layer. Conversely, if the material is too rigid, the gas pressure cannot uniformly expand the char shield, and the gases escape through local cracks instead of forming a protective layer. In addition to improving fire-safety parameters, minimizing mechanical compromises is a fundamental engineering task [21]. The inorganic powder additives required for effective flame retardancy substantially modify the morphology of the composite. Microscopic voids form at the phase boundaries between the rigid additive particles and the nonpolar polyolefin matrix; these voids act as stress concentrators and lead to embrittlement of the composite [22]. Although the chemical operation of intumescent flame-retardant systems has already been investigated in virgin polymers, few publications are available on the flame retardancy of degraded waste streams [23].

The main objective of the present study is to develop a concept for converting mixed post-consumer plastic waste into engineering composites through the incorporation of halogen-free hybrid intumescent systems. The study provides a detailed analysis of the synergistic effect of APP and MPP additives on the melt-flow behavior, mechanical integrity, and thermogravimetric parameters of the polyolefin matrix. The strategic objectives of the circular economy require the safe and value-added reintegration of the highest possible proportion of polymer waste streams into industrial production [24]. The results of this study aim to contribute to this process by providing a scientific basis for the future practical applicability of flame-retarded mixed secondary raw materials.

2. Experimental

This section presents the experimental materials used in the study, the manufacturing steps applied for specimen preparation, and the parameters of the characterization methods. The experimental work comprised a comprehensive analysis of the morphological, rheological, mechanical, and thermal properties of composites consisting of mixed post-consumer plastic waste and a hybrid intumescent flame-retardant system.

2.1. Materials and preparation

The base matrix used in this study was an industrially sourced, mechanically pretreated mixed plastic cap

regrind supplied by Jász-Plasztik Kft. (Jászberény, Hungary). This secondary raw material had undergone density-based aqueous separation, i.e., a float-sink process, and typically consisted of 75-85 wt% high-density polyethylene (HDPE) and 15-25 wt% polypropylene (PP). Minimal amounts of polyethylene terephthalate (PET) residues originating from the neck regions of bottles were also present in the feedstock.

A hybrid intumescent system was applied for the halogen-free flame retardancy of the polymer matrix. The primary component of the system, functioning as an acid source and char-promoting catalyst, was melamine-free ammonium polyphosphate (APP), Exolit AP 422, manufactured by Clariant (Muttenz, Switzerland). This fine powder has an average particle size of 30 µm and a decomposition temperature of 290 °C; its pH is neutral, with a value of 6.0. Owing to its low water solubility (0.1 g/100 ml) and environmentally benign composition, it is particularly suitable for industrial applications where improving fire resistance while retaining mechanical properties is required. Budit 342 melamine polyphosphate (MPP), produced by Budenheim (Germany), was used as the gas-forming, foaming synergist of the hybrid system. This powder, with a particle size of 17 µm, contains approximately 30% phosphorus pentoxide and an exceptionally high nitrogen content of 43%, ensuring the release of an optimal quantity of inert gas during combustion. The additive has a decomposition temperature of 325 °C, which enables stepwise activation of foaming. This process begins after the onset of APP decomposition at 290 °C, when the melt viscosity is already suitable for forming a robust, multicellular porous char shield.

The test specimens were prepared according to the formulations detailed in *Table 1*. In addition to the neat reference sample, a series containing only MPP, a series containing only APP at 5–20 wt%, and a hybrid series were produced; in the latter, the MPP content was fixed at 5 wt% while the APP content was increased. These samples are denoted as B10, B15, and B20.

2.2. Manufacturing process

Because of the markedly different processing-temperature window, the regrind was subjected to thorough secondary sorting before physical processing to ensure complete removal of PET residues. To avoid hydrolytic degradation and porosity in the melt, the regrind was conditioned before processing in a DEGA 2500 drying silo at 80 °C for 4 h. Melt compounding of the composites was performed using a Labtech LT 20-440 twin-screw extruder. The zone temperatures were adjusted to the thermal characteristics of the heterogeneous matrix using a gradually increasing profile between 190 °C and 220 °C, with a screw speed of 35 rpm. To minimize polymer degradation, the extruded strands were cooled by air rather than in a water bath and were then pelletized using a Labtech LZ120 unit.

Standard test specimens were produced on an Arburg Allrounder 420C Golden Edition injection-molding machine, immediately preceded by a secondary drying cycle in a Faithful WGLL 125 BE chamber at 80 °C for 4 h. During injection molding, a nozzle temperature of 210 °C, a mold temperature of 40 °C, and an injection pressure of 1000 bar were applied. Tensile test specimen geometry conforming to MSZ EN ISO 527-2 was used during production; further detailed technological settings are summarized in *Table 2*.

Table 1: Composition and designation of the tested samples

Sample designation	Base matrix [wt%]	Clariant Exolit AP 422 [wt%]	Budenheim Budit 342 [wt%]
Ref	100	0	0
Ref5MPP	95	0	5
A5	95	5	0
A10	90	10	0
A15	85	15	0
A20	80	20	0
B10	90	5	5
B15	85	10	5
B20	80	15	5

2.3. Characterization methods

For materials-structure characterization of the composites, the melt flow index (MFI) was determined using a CEAST 7023 melt-flow indexer according to MSZ EN ISO 1133 at 230 °C under a 5 kg load. To ensure the reliability of the results, three parallel rheological measurements were performed for each composition.

Table 2: Injection molding parameters

Description	Unit	Value
Temperature profile (from hopper to nozzle)	°C	170 – 190 – 200 – 210
Nozzle temperature	°C	210
Mold temperature	°C	40
Injection pressure	bar	1000
Injection speed	mm/s	40
Holding pressure	bar	600
Holding pressure time	s	15
Residual cooling time	s	20
Clamping force	kN	150

The morphological structure and additive dispersion were analyzed on fracture surfaces using a Zeiss Discovery V20 stereomicroscope, revealing possible agglomerates and interphase relationships. Mechanical properties were investigated with an Instron 5582 universal testing machine. Tensile tests were performed according to MSZ EN ISO 527, and three-point flexural tests according to MSZ EN ISO 178. During the static mechanical tests, five specimens were tested for each sample type. Surface hardness was measured with a Sauter HDD 100 Shore D device in accordance with MSZ EN ISO 868; for each sample, the mean value was calculated from measurements at 10 points. Dynamic toughness, i.e., Charpy specific impact energy, was measured using a Ceast 6545 pendulum impact tester (MSZ EN ISO 179) on specimens with a 2 mm V-notch, using an impact energy of 15 J and five parallel specimens. Flame resistance was assessed by horizontal UL-94 burning tests, recording the flame-spread rate as the average of three specimens per sample. Thermo-oxidative stability and thermal decomposition processes were monitored with a Derivatograph Q-1500 D thermogravimetric (TGA) analyzer between 25 °C and 1000 °C at a heating rate of 10 °C/min in an air atmosphere, evaluating decomposition peak temperatures and residual ash content.

3. Results and discussion

This section presents and discusses in detail the results of the materials-science characterization of the developed hybrid flame-retardant systems. The analysis begins with the investigation of melt-rheological and morphological properties, followed by the evaluation of static and dynamic mechanical performance. Finally, the efficiency of hybrid synergy in the mixed polyolefin matrix is assessed based on the data from horizontal burning tests and thermogravimetric measurements.

3.1. Results of rheological and morphological investigations

Appropriate processability, governed by melt-flow behavior, is an essential prerequisite for the industrial applicability of flame-retardant additives. The dispersion of solid, non-melting particles and their interaction with the polymer matrix fundamentally influence flow characteristics. Based on the experimental results, the use of halogen-free intumescent systems clearly reduced the MFI of the melt, i.e., increased the flow resistance, for all investigated compositions, as shown in *Figure 1*. Whereas the average MFI of the neat reference matrix was 16.10 g/10 min, this value decreased to the range of 14.12-8.05 g/10 min for the modified systems. In the A series containing only ammonium polyphosphate, the MFI decreased monotonically with increasing filler content. The highest flow resistance was observed for the 20 wt% sample, with an MFI of 8.05 g/10 min. This macroscopic phenomenon confirms that the additive present as solid particles hinders the sliding of

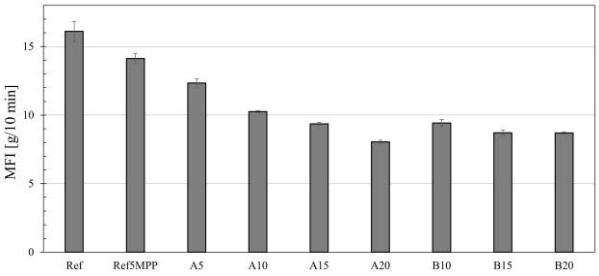


Figure 1: Melt flow index (MFI) values of the investigated samples

macromolecules past one another, thereby reducing flow tendency. The gas-forming melamine polyphosphate also exhibited a flow-inhibiting effect on its own, as confirmed by the MFI value of 14.12 g/10 min for the sample containing only 5 wt% additive.

In the B series containing hybrid systems, at the same total additive content of 10%, the hybrid formulation exhibited a lower MFI (9.42 g/10 min) than the purely APP-based sample (10.25 g/10 min). This difference can be related to the finer particle size of the additives used and to the probable tendency of the particles to agglomerate. In the 15–20% additive range, however, the decrease in MFI of the hybrid systems slowed and the values stagnated at approximately 8.7 g/10 min.

From a processing perspective, the reduced flowability necessitates optimized temperature and pressure profiles during extrusion. From the viewpoint of combustion behavior, however, the decrease in MFI is explicitly advantageous. The sudden melting and flaming dripping of polyolefins under fire exposure represent one of the main safety risks. A denser, less readily flowing melt with a lower MFI provides increased structural integrity to the matrix, delaying dripping and creating an optimal time window for the intumescent chemical reactions and for the formation of a continuous protective char layer.

Microscopic images of the fracture surfaces provide insight into the distribution of the additives and the morphology of the fracture surface (*Figure 2*). The neat reference sample is characterized by an essentially continuous matrix structure without solid inclusions. This observation directly confirms the efficiency of the secondary sorting performed prior to processing, since higher-melting PET residues would appear as solid inhomogeneities on the fracture surface. Owing to the heterogeneous polyolefin composition, particularly the thermodynamic incompatibility between polyethylene and polypropylene, only slight phase boundaries and wrinkles are visible on the surface.

The morphology of the filled samples is closely related to the particle size and surface energy of the applied flame retardants. Whereas APP with the larger average particle size (30 μm) is distributed relatively uniformly in the polymer, the finer MPP particles (17 μm) tend to agglomerate because of their larger specific surface area. The substantial polarity difference between the nonpolar polyolefin matrix and the polar

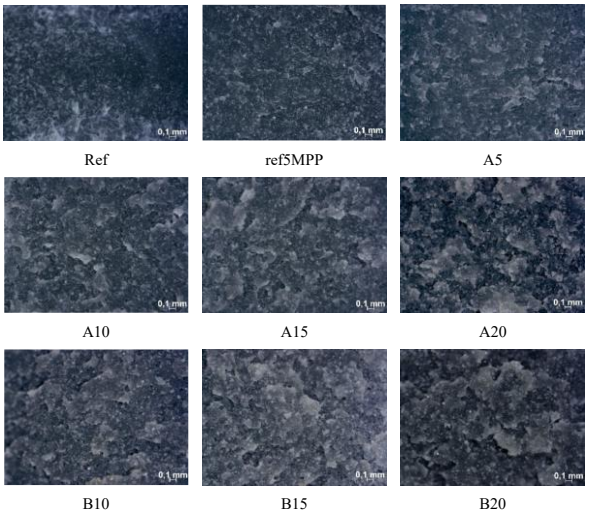


Figure 2: Microscopic images of the fracture surfaces of the composites

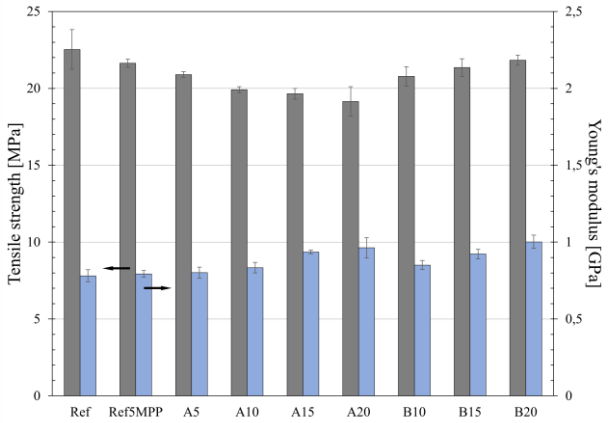


Figure 3: Results of the tensile test

inorganic additives hinders proper wetting, resulting in enhanced agglomeration and the formation of sharp phase boundaries. At the maximum filler levels of 15 and 20 wt%, these heterogeneous, irregular particle clusters occur more frequently in the matrix. Microscopic voids are also clearly visible on the fracture surfaces, indicating the traces of rigid particles pulled out of the polymer because of weak interfacial adhesion. As confirmed in the literature, a high concentration of rigid solid additives incorporated into the matrix creates stress-concentration sites that hinder polymer-chain sliding under mechanical loading, thereby leading to embrittlement of the composite and a reduction in specific impact energy [22],[25].

Morphological inhomogeneities also fundamentally influence burning behavior. Although the macroscopic viscosity described previously increases as a result of additive incorporation, at the microscopic level large agglomerates disrupt the continuity of the matrix. Under fire exposure, this structural loosening may weaken melt cohesion and thus promote hazardous dripping combustion. The efficiency of the hybrid flame-retardant system essentially depends on the success of the foaming process. This expanded layer acts as a physical bridge between the different polymer phases, effectively compensating for the structural weaknesses of the heterogeneous matrix.

3.2. Mechanical performance

Under static tensile loading, the neat reference sample exhibited an average tensile strength of 23.18 MPa. Incorporation of the additives moderately reduced this parameter. In the A series containing only ammonium polyphosphate, strength decreased monotonically with increasing filler content, falling to 19.51 MPa at the maximum additive loading of 20 wt% (*Figure 3*). The hybrid B series followed a similar trend, with a value of 19.68 MPa recorded for the B20 sample. The reduction in load-bearing capacity can be attributed to weak interfacial adhesion between the nonpolar polyolefin matrix and the polar rigid additive particles. The solid particles disrupt the continuity of the polymer matrix and act as stress-concentration sites, reducing resistance under tensile loading.

The elastic modulus, which characterizes material stiffness, did not follow a consistent trend. More relevant information on the embrittlement tendency and fracture mechanism was provided by morphological analysis of the fracture surfaces. Whereas the stiffness of the neat reference was 1.29 GPa, at lower and intermediate filler contents the modulus decreased to values between 1.09 and 1.19 GPa. This slight softening suggests that, at low concentrations, finely dispersed powders increase free volume and loosen the interactions between polymer chains. With increasing filler content, however, the volume-filling effect of the large number of solid flame-retardant particles became dominant, and the stiffness of the material began to increase again. The average modulus of the composites with the highest, 20 wt% filler content reached 1.31 GPa (A20) and 1.30 GPa (B20). Considering the scatter ranges and the substantial overlap of the error bars, these values do not differ statistically significantly from the stiffness of the initial matrix, which was 1.29 GPa. Overall, the tests confirm that the developed intumescent systems can retain the original stiffness of the matrix even at the maximum filler loading of 20 wt%, while causing only a moderate decrease in tensile strength (*Figure 3*).

The three-point flexural test results confirmed the structural changes identified during tensile testing. Because tensile, compressive, and shear stresses arise simultaneously in the specimen during bending, this method provides an appropriate approximation of the practical dimensional stability and load-bearing capacity of the composites. The measurements reveal different mechanical behavior for purely APP-based and hybrid flame-retardant systems. The flexural strength of the neat reference waste matrix averaged 22.53 MPa. In the A series, APP addition led to a gradual reduction in load-bearing capacity, decreasing to 19.15 MPa for the A20 sample with 20 wt% filler content. This decrease can be

attributed to the weak interfacial adhesion discussed in the morphological analysis, which promotes crack initiation under flexural loading. In contrast, the hybrid B series showed more favorable mechanical stability. After an initial slight decrease, flexural strength began to increase with increasing filler content, and the value of 21.83 MPa measured for B20 approached the load-bearing capacity of the starting material.

The results indicate that, by combining APP and MPP, a high flame-retardant loading of 20 wt% can be achieved in the B20 sample while retaining mechanical strength. The evolution of flexural modulus, which characterizes composite stiffness, follows classical composite theory, since incorporation of rigid additive particles increases the resistance of the system to deformation. Compared with the value of 0.78 GPa for the neat reference, an increase was observed in both series as the filler content increased (*Figure 4*). The highest stiffness values were obtained at 20 wt% concentration, where A20 reached 0.96 GPa and the hybrid B20 sample reached 1.01 GPa. Although the mean values suggest that the combined system is stiffer, the measurement error bars do not allow a clear distinction to be made between the effects of the two flame-retardant systems on flexural modulus.

As a complement to the stiffness increase observed in the tensile and flexural tests, Shore D hardness measurements were used to determine the resistance of the material to surface deformation. The results confirm that the presence of solid flame-retardant additives enhances surface hardness. The solid particles form direct mechanical obstacles and thereby increase the resistance of the polymer matrix to indenter penetration. The average hardness of the neat reference sample was 63.91 Shore D. Incorporation of flame-retardant particles increased surface resistance in parallel with increasing filler content, as shown in *Figure 5*. At low additive levels of 5–10%, the change in hardness remained moderate; however, at 20 wt% filler content, the A20 sample reached 64.92 Shore D and the hybrid B20 composite reached 65.35 Shore D. The highest average value was observed for the hybrid B15 sample, with 65.75 Shore D.

Because the measured data varied within a relatively narrow range, one-way analysis of variance and Tukey's post hoc test were applied for objective evaluation. The statistical analysis (Tukey's post hoc test) confirmed that the hardness increase of the sample containing 5% MPP only and that of the A series containing APP only did not differ significantly from the neat reference ($p > 0.05$). A significant surface-hardening effect ($p < 0.05$) relative to the control was detected only for the B series (B10, B15, B20) using the synergistic hybrid system. The hybrid B15 sample exhibited the highest mean value, which, according to Tukey's post hoc test, represents a statistically significant increase compared with the neat reference, Ref5MPP, and A5 samples. This outstanding value can presumably be explained by a more favorable spatial distribution of the two flame retardants at a total concentration of 15 wt%. The very low standard deviation observed at higher filler

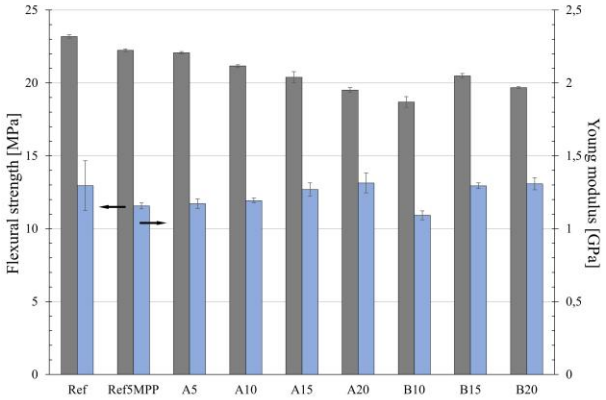


Figure 4: Results of the bending test

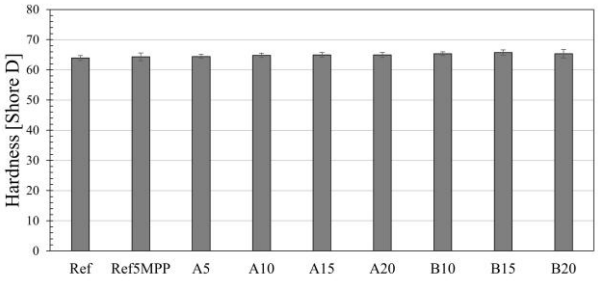


Figure 5: Results of the hardness test

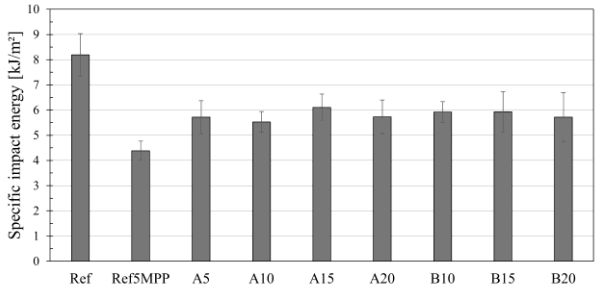


Figure 6: Specific impact energy results

levels indicates homogeneous additive distribution. This is technologically favorable because it shows that the solid flame-retardant particles were incorporated uniformly into the matrix, avoiding pronounced local inhomogeneities. Although the change is mathematically confirmed, the actual physical increase in hardness is moderate, since even the hardest sample showed only a 3% increase relative to the reference. From a practical perspective, this means that the addition of flame-retardant additives did not impair the original surface characteristics of the plastic, while the surface became more resistant to local mechanical effects such as scratching.

The Charpy specific impact energy test most clearly demonstrates the embrittling effect of powder fillers on the matrix (*Figure 6*). The results show a pronounced decrease in toughness relative to the reference; however,

further increasing the additive content did not produce a monotonic decline, and the values stagnated within the range of 5.5–6.1 kJ/m². The neat reference waste matrix exhibited relatively good toughness, with an average impact energy of 8.19 kJ/m². The addition of 5 wt% melamine polyphosphate nearly halved this value, reducing it to 4.38 kJ/m². In the A series containing ammonium polyphosphate, a decrease in toughness was observed. However, further increasing the filler content no longer caused a monotonic reduction; the values fluctuated between 5.53 and 6.10 kJ/m². At the maximum additive level of 20 wt%, a value of 5.73 kJ/m² was measured. The data for the hybrid B series show close agreement with the values of the A series at medium and high filler levels. For example, the B20 sample with a total filler content of 20 wt% yielded 5.72 kJ/m², almost identical to the 5.73 kJ/m² value of the purely APP-based A20 composite. The observed loss of toughness is attributed to solid particles embedded between the polymer chains, which act as stress concentrators and deteriorate dynamic load-bearing capacity.

Under dynamic impact, microcracks can initiate at the particle-matrix interface and propagate rapidly along agglomerates under sudden loading. This process leads to premature specimen fracture before the plastic can absorb substantial energy through macroscopic plastic deformation. The continuity of the matrix is presumably already sufficiently disrupted at relatively low powder contents, such that further increases in filler loading no longer cause additional deterioration. Statistical evaluation (Games-Howell test) revealed that even the lowest additive level of 5 wt% caused a significant decrease in specific impact energy compared with the neat reference. At the same time, within the 5–20 wt% range, toughness showed no further monotonic decline and the values stagnated between 5.5 and 6.1 kJ/m².

From a materials-science perspective, this means that after the initial loss of toughness, further increasing the filler content did not cause additional statistically verifiable embrittlement in the composite structure. The statistical analysis indicates that at the maximum filler level the total amount of solid phase determines toughness loss, whereas the precise chemical composition of the flame-retardant system no longer has a substantial influence on fracture behavior.

3.3. Flammability characteristics and results of the UL-94 test

The primary objective of the research was the halogen-free flame retardancy of heterogeneous mixed plastic waste and the elimination of the flaming dripping characteristic of polyolefins. Horizontal UL-94 flammability tests were performed to evaluate flame propagation in the composites. In this phase of the research, the main emphasis was placed on modifying the flame-spread rate, because slowing fire propagation is a key safety consideration in industrial applications. The efficiency of the applied intumescent flame-retardant system can be evaluated from the bar chart summarizing the results (*Figure 7*).

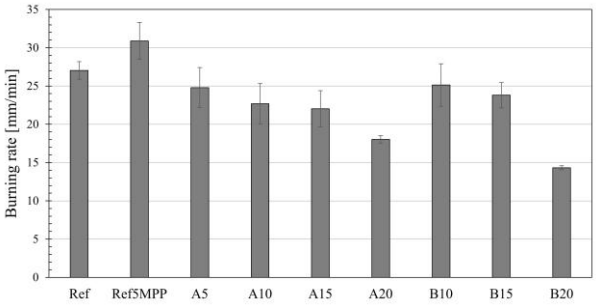


Figure 7: Results of the burning rate

The flame-spread rate of the neat mixed waste without a flame retardant averaged 27.03 mm/min. For the sample containing only 5 wt% melamine polyphosphate, this value did not decrease but instead increased to 30.88 mm/min. This accelerated combustion can be explained by the fact that, in the absence of a sufficient amount of carbon source and acid source, the gas-forming effect of melamine polyphosphate merely loosens the polymer structure at the microscopic level. As a result, the local oxygen supply to the flame may improve and heat can penetrate the material more readily, ultimately leading to faster fire propagation.

In contrast, incorporation of the complex flame-retardant systems resulted in a substantial reduction. In the A series containing only ammonium polyphosphate, the flame-spread rate gradually decreased with increasing filler content, in parallel with the decrease in MFI. Whereas the sample containing 5 wt% additive burned at a rate of 24.78 mm/min, the flame-spread rate of the A20 sample with 20 wt% concentration was reduced to 18.03 mm/min. This improvement confirms that the increasing amount of acid source is capable of forming a more stable charred layer on the burning surface.

The lowest flame-spread rate was observed at the maximum filler level of the hybrid B series. The B20 composite exhibited a flame-spread rate of only 14.32 mm/min, representing a reduction to nearly half of the value of the starting material. This substantial shift supports the synergistic intumescent mechanism described in the literature [16],[26]. The 20 wt% hybrid additive concentration provided a sufficient thermochemical basis for the system to form a more continuous and thicker charred protective layer under the influence of heat. This layer functioned as a thermal-insulation shield, isolating the melt from atmospheric oxygen and acting as a physical barrier that hindered the release of combustible decomposition gases. The reduction in flame-spread rate can be attributed not only to chemical effects but also to macroscopic physical factors. This relationship is illustrated in *Figure 8*, which plots MFI and flame-spread-rate values in a common system. A positive relationship is observed in the diagram: as the melt-flow tendency decreases, the flame-spread rate also visibly decreases.

From a thermophysical perspective, this correlation is consistent with the operating principle of intumescent

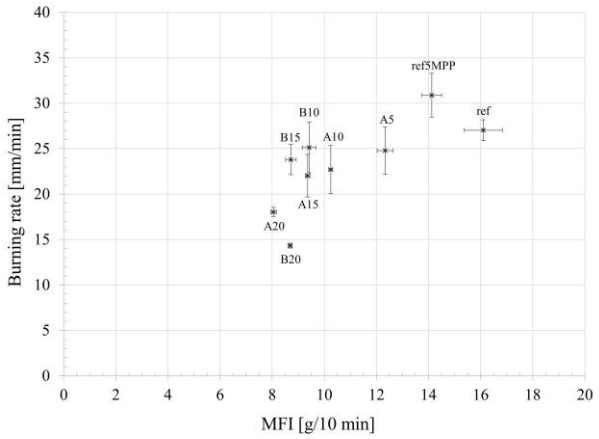


Figure 8: Burning rate as a function of the melt flow index (MFI)

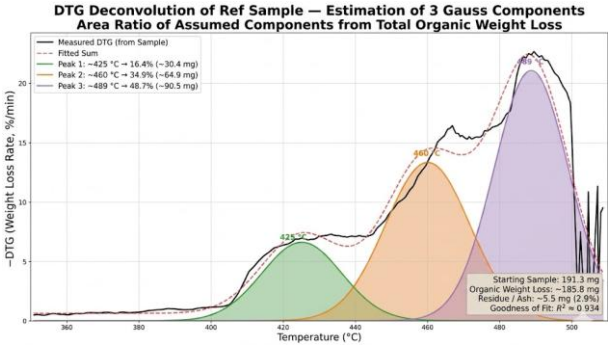


Figure 9: Deconvolution of the DTG curve for the ref sample

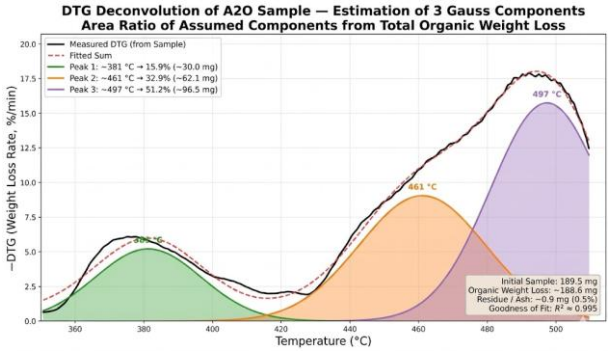


Figure 10: Deconvolution of the DTG curve for the A20 sample

systems in polyolefin matrices. Under fire exposure, plastics are inherently prone to rapid melting and flaming dripping, which exposes fresh polymer surfaces to combustion. The denser, lower-MFI melt produced by the solid flame-retardant powders, however, mechanically holds the specimen together more effectively. The less readily flowing material cannot drip as easily, which is critically important for fire protection. This reduced flow tendency creates favorable conditions for intumescent reactions to proceed. Although the resulting charred layer did not lead to complete self-extinguishing, it acted as an effective physical barrier that reduced heat and mass transport, thereby slowing the flame-spread rate. The results highlight that, for the mixed waste investigated, successful flame retardancy is based not only on chemical composition but also on targeted modification of flow characteristics.

3.4. Thermogravimetric investigations and analysis of decomposition processes

The thermal stability and thermo-oxidative decomposition mechanisms of the composites were investigated by thermogravimetric analysis. The structure of the waste-based polymer matrix used is inherently complex because it consists of a heterogeneous mixture of polyethylene and polypropylene fractions with different molecular weights and different degrees of degradation from previous life cycles. Consequently, chain scission of the macromolecules is an extended process, and several partially overlapping decomposition stages can be distinguished on the derivative thermogravimetric curves. Mathematical deconvolution was applied to approximately separate the individual processes and determine their corresponding mass-loss fractions on the DTG curves. This procedure is suitable for more precise characterization of the complex decomposition processes of heterogeneous polymer blends.

On the deconvoluted curve of the neat reference sample, decomposition of the mixed matrix can be divided into three main components, as illustrated in *Figure 9*. For the reference sample, the first peak, appearing at approximately 425 °C, can be associated with the least thermally stable fractions of the system. This stage typically represents the decomposition of shorter-chain branched polymers or chain segments that had already been oxidized and weakened during previous processing cycles. The second peak at 460 °C identifies the base components decomposing at intermediate temperature, whereas the largest peak at 489 °C indicates the presence of high-thermal-stability polyolefin fractions forming the backbone of the matrix. In the absence of a flame-retardant additive, the aliphatic hydrocarbon chains are converted almost entirely into volatile gases during thermo-oxidation; therefore, the residual mass at the end of the process is only 2.9%.

The decomposition kinetics of the A20 sample containing ammonium polyphosphate are shown in *Figure 10*. The presence of ammonium polyphosphate visibly modifies the initial stage of degradation, since the first decomposition peak shifts to a much lower temperature, 381 °C. This kinetic shift results from the characteristic thermal behavior of the additive, which decomposes between 300 and 450 °C. During this process, polyphosphoric acid is released, catalyzing early chain scission in the polyolefin chains and the formation of double bonds required for charring. At the same time, the largest peak, indicating the main decomposition process of the polymer matrix, remains in the highest

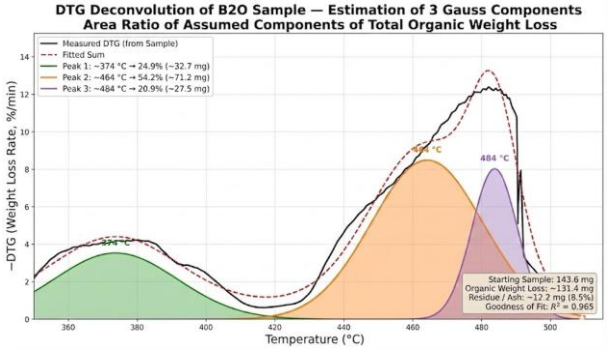


Figure 11: Deconvolution of the DTG curve for the B20 sample

temperature range. This result indicates that although APP initiates early chain scission through acidic catalysis, the main mass of the polymer matrix retains its original thermal stability and leaves as volatile decomposition products rather than forming a solid carbon skeleton. This is also supported by the extremely low solid residue of the A20 sample, only 0.5%. It can therefore be concluded that APP alone, without an appropriate gas-forming component, cannot form a continuous and stable protective layer in this mixed polyolefin blend.

The thermo-oxidative behavior of the B20 sample containing the hybrid intumescent system confirms the pronounced synergy between the two additives, as shown in *Figure 11*. Here, the onset of mass loss also falls within the lower temperature range; however, compared with the purely APP-based system, a fundamental rearrangement of the component distribution can be observed. The main decomposition stage shifted from the highest temperature region to the intermediate range at 464 °C, while the fraction of the high-temperature peak decreased substantially. This kinetic shift indicates that the use of melamine polyphosphate as a gas-forming synergist results in a more complex and more efficient decomposition mechanism. The combined action of polyphosphoric acid formed from APP and inert gases released during MPP decomposition foams the melt and initiates the formation of an intumescent char shield. Among the investigated samples, the hybrid B series produced the highest solid residue, with a value of 8.5%. This increased solid residue indicates that the APP/MPP system forms an effective charred protective layer. This layer functions as a thermal-insulating shield on the surface, isolating the polymer melt from external radiant heat and minimizing the escape of combustible volatile gases into the oxygen zone. In summary, the significant improvement in thermal stability and flame resistance is attributed to the condensed-phase protective mechanism of the hybrid intumescent system.

4. Conclusion

In this study, halogen-free flame retardancy of mixed polyolefin packaging wastes originating from post-consumer collection was successfully achieved using intumescent additive systems. The scientific results indicate that the synergistic hybrid system of ammonium polyphosphate and melamine polyphosphate can effectively address the different processing and combustion-related behavior of heterogeneous matrices. One of the main outcomes of the work is the targeted modification of the rheological properties of the polymer melt, where the increased melt viscosity resulting from the volume-filling effect of the solid additive particles provided a physical barrier against the hazardous flaming dripping characteristic of polyolefins.

Based on the thermal and combustion tests, the most outstanding performance was achieved with 20 wt% hybrid additive loading, which reduced the horizontal flame-spread rate of the reference sample to nearly half. Thermogravimetric analysis showed a solid residue of 8.5%, which is consistent with the formation of a stable protective layer on the surface of the hybrid composite. This thick charred foam layer thermally and physically isolates the flammable macromolecules from oxygen and from the radiant heat source, thereby suppressing the combustion chain reaction. In addition to optimizing fire-resistance characteristics, the tests defined the technological window within which additive-induced embrittlement does not yet endanger the mechanical stability of the material. According to the statistical evaluation, incorporation of solid additives causes a significant reduction in toughness compared with the neat reference already at a concentration of 5 wt%. At the same time, the results confirm that further increasing the filler content within the 5–20% range does not lead to any additional statistically verifiable embrittlement; thus, the dynamic resistance of the material remains stable within this broad additive window. In parallel, the elastic modulus characterizing dimensional stability increased with filler loading. Based on the results, the optimized formulation enables the production of a composite with reduced flammability from low-value mixed waste, which may be suitable for the secondary-raw-materials market as a potential engineering feedstock.

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