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Toward Advanced Biocomposites Based on Thermoplastic Biopolyester and Halogen-Free Flame-Retardant Additives for Industrial Solutions

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ABSTRACT

This work investigates halogen-free flame-retardant biocomposites based on poly(butylene succinate) (PBS) containing magnesium dihydroxide (MDH) and aluminum trihydroxide (ATH). Hybrid MDH/ATH systems (1:1, 1:2, 1:3) show synergistic flame-retardant and smoke-suppressive effects due to their different thermal activation ranges, outperforming single fillers while maintaining acceptable processability. PBS composites with ~60 wt.% metal hydroxides were prepared by melt mixing. ATH dispersed better than MDH, which showed irregular morphology and impurities. All fillers reduced peak heat release rate, improved ignition resistance, and suppressed smoke. MDH/ATH hybrids exhibited strong synergies via stable char formation, achieving significant heat reduction and near-complete smoke suppression. Despite reduced ductility at high filler loading, all composites showed shear-thinning behavior and acceptable processing performance. Overall, this study shows that MDH and ATH act as effective halogen-free flame-retardant additives, transforming highly flammable PBS into flame-retardant bio composites suitable for several industrial applications supporting the development of environmentally friendly materials.

1 | Introduction

In recent years, polymer-based materials have been extensively used in a wide range of applications such as transportation, buildings, textiles and packaging due to their excellent versatility and processability properties. Recently, to overcome the issues caused by pollution, researchers have investigated new pathways for plastics, such as the production and processing of bio-derived and bio-degradable matrices, switching the trajectory toward environmentally compliant pathways that align with the principles of sustainability [1]. Yet, plastic materials are intrinsically extremely flammable, causing serious safety concerns, especially in indoor usage of the product where flame

ignition and spread must be strictly minimized [2]. According to the state of the art, composites based on flame retardant (FRs) additives are industrially mostly mixed on polyolefins such as polyethylene (PE), Polypropylene (PP), Ethyl-vinyl-acetate (EVA), and polycarbonate (PC) at very high concentrations for coatings, for electric cables, or for sheathing applications [3]. The growing challenges associated with the disposal of petroleum-based plastic waste, together with heightened environmental concerns, have spurred significant interest in the development and utilization of biodegradable polymers [4].

Among these, poly(butylene succinate) (PBS) has emerged over the past decades as a promising candidate due to its derivation

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from renewable feedstocks, relatively low production cost, and suitability for large-scale manufacturing [5–8]. PBS exhibits favorable mechanical and thermal properties, enabling its use in packaging materials, bags, films, fibers, and biomedical devices [9]. However, like other aliphatic biopolyesters, PBS is intrinsically highly flammable, which limits its applications in sectors such as automotive, electronics, and electrical engineering. Therefore, enhancing the fire resistance of PBS is essential to broaden its applicability [10, 11].

According to Market Reports World, in 2023, the global PBS market was valued at approximately USD 1.23 billion, with projections indicating a rise to USD 2.9 billion by 2032 [12]. In agreement with the statistical data, biodegradable packaging is the largest and most mature segment of PBS, but agriculture, consumer goods, textiles, medical, and specialty applications are expanding. Although PBS is an eco-friendly material with market growth, its market penetration is challenging because of: (i) high resin cost, compared to commodity plastics like PE or PP, (ii) composting infrastructure gaps that slow end-of-life utility, (iii) feedstock volatility, considering that the costs of succinic acid or bio-based inputs can influence price competitiveness.

A typical intumescent flame-retardant system for PBS consists of an acid source (e.g., ammonium polyphosphate), a blowing agent (e.g., melamine), and/or a carbonization agent (e.g., natural fibres or pentaerythritol) [10, 13–15]. Research efforts focus on balancing fire resistance with bio-derived or bio-degradable materials characteristics, while maintaining mechanical performance and economic feasibility [14, 16–19].

Flame-retardant (FR) additives are generally classified according to their chemical composition: organic FRs, halogenated or phosphorus-based, primarily act in the gas phase by disrupting radical chain reactions and promoting char formation; whereas inorganic FRs, such as metal hydroxides, borates, and silicon-based compounds, operate mainly in the condensed phase through endothermic decomposition and residue formation [20].

It is worth noting that recently, the European Chemical Agency (ECHA) has added 1,1'-(ethane-1,2-diyl)bis[pentabromobenzene] (DBDPE) to the list of substances of very high concern (SVHC) for both human health and the environment. Furthermore, companies are responsible for managing the risks of these chemicals and giving customers and consumers information on their safe use [21].

Metal hydroxides, such as magnesium di-hydroxide (MDH, chemical formula: $\text{Mg}(\text{OH})_2$) and aluminum tri-hydroxide (ATH, chemical formula: $\text{Al}(\text{OH})_3$), have been progressively penetrating the fire-safety sector, as they represent an effective replacement for halogen-based compounds [22–25]. Therefore, both MDH and ATH exhibit excellent compatibility with many commodity thermoplastics, such as PE, PP, EVA, PVC, as well as with elastomers and thermosets used in wires, cables, sheathings and building materials [26–30]. The fire-safety properties of metal hydroxides (e.g., MDH and ATH) can be summarized by several key mechanisms. First, the MDH and ATH act as heat sinks, cooling the burning surface due to endothermic decomposition reactions and the release of water molecules. Second, the released water vapor from decomposition dilutes the combustion gases

and helps reduce the intensity of the fire. Additionally, protective layers of magnesium oxide (MgO) or aluminum oxide (Al_2O_3) can form, creating an insulating barrier between the flame and the underlying material. Furthermore, using MDH and ATH reduces smoke emissions during polymer combustion, thereby enhancing the material's overall safety [31].

According to the literature, MDH is widely used as an environmentally friendly flame retardant, offering enhanced flame resistance and smoke suppression thanks to its low cost, high thermal stability, low toxicity, and effective thermal insulation [32, 33]. Zaghoul et al. [34] examined the role of magnesium hydroxide in high-density polyethylene, showing that the addition of MDH, ranging from 5 to 50 wt.%, significantly affected the mechanical behavior of the resulting HDPE composites. Similarly, Fan Ren et al. [35] demonstrated that increasing both the MDH content and the fineness (mesh number) of the filler led to a progressive improvement in the flame-retardant performance of MDH-modified asphalt.

Interestingly, Yew et al. [36] explored the synergistic effect of an acrylic binder combined with flame-retardant additives, namely aluminum hydroxide ($\text{Al}(\text{OH})_3$) and titanium dioxide (TiO_2), in solvent-based coatings formulated for steel substrates. The study demonstrated that this combination markedly enhanced both fire protection and thermal stability, achieving a limiting oxygen index (LOI) of 34, indicative of strong flame-retardant performance.

The global aluminum hydroxide market size was estimated at USD 12,051.5 million in 2024 and is projected to reach USD 15,309.5 million by 2030, growing at a CAGR of 4.1% from 2025 to 2030. The increasing demand for products is mainly driven by their uses in pharmaceuticals, water treatment, and flame retardants [37]. Interestingly, the global magnesium hydroxide market size was estimated at USD 1,356.1 million in 2024 and is projected to reach USD 2,063.6 million by 2030, growing at a CAGR of 7.3% from 2025 to 2030. The market is driven by its applications in wastewater treatment and low-cost flame retardants [38].

A very interesting study by Chen et al., investigated the effect of different $\text{Mg}(\text{OH})_2$ particle morphologies, ranging from 500 nm to 20 μm , on the fire resistance properties of PBS-based composites, the authors demonstrated that PBS/ $\text{Mg}(\text{OH})_2$ composites filled with different $\text{Mg}(\text{OH})_2$ amounts, medium-sized, petal-like $\text{Mg}(\text{OH})_2$ ($\approx 5 \mu\text{m}$) exhibited slightly better flame retardancy compared to both larger ($\approx 20 \mu\text{m}$) and nano-sized ($\approx 500 \text{ nm}$) particles, due to the ability of the morphology to build an effective and less cracked char layer under cone calorimeter conditions. Furthermore, the authors conducted the investigation in PBS-based composites containing the filler ranging from 10 to 60 wt.% and demonstrated that the highest filler loading guarantees acceptable LOI values and V-0 (according to UL-94), regardless of the morphology of the $\text{Mg}(\text{OH})_2$ particles. The authors concluded that the highest filler loading (i.e. at 60 wt.%) ensures appropriate fire-retardant properties that the neat PBS does not possess [39].

The combination of high-cost, biodegradable yet highly flammable bioplastics with low-cost, halogen-free flame

retardants, such as metal hydroxides, may enable the development of cost-effective formulations. However, these materials must comply with several market requirements beyond just fire-resistance properties, as it has been mainly investigated in the literature so far. In this context, this study aims to thoroughly characterize the mechanical, thermal, rheological, and fire-resistance performance of natural milled magnesium di-hydroxide (MDH) and precipitated aluminum tri-hydroxide (ATH) as halogen-free flame-retardant additives (HFRs) in PBS-biocomposite formulations. MDH and ATH, either separately or in hybrid compositions, e.g., MDH/ATH at different weight ratios of 1:1, 1:2, 1:3, were introduced at high concentrations, at approximately 60 wt.%, into the bio-derived matrix, such as poly(butylene succinate) (PBS), via melt mixing. The biocomposites were then characterised in their rheological, morphological, thermal and mechanical behavior. Particular attention was given to fire resistance and photo-oxidation weathering of the PBS-based formulations containing metal hydroxides. Interestingly, good results were obtained by introducing a single MDH or ATH, and even better results were obtained using hybrid compositions of MDH/ATH; the synergistic effect of the inorganic fillers in the PBS matrix was also investigated. These resultant biocomposites exhibit superior fire-resistant characteristics and smoke suppression capabilities of pristine samples, while maintaining adequate processability and solid-state performance.

2 | Materials and Methods

2.1 | Materials

Polybutylene-succinate (PBS), BioPBS FZ91PM with a melt flow index of 5g/10min (MFR (190°C, 2.16 kg), a density of 1.26g/cm³, and a melting temperature of 115°C, was supplied by Mitsubishi Chemical Co. (Tokyo, Japan).

Magnesium Di-Hydroxide (MDH) with chemical formula: Mg(OH)₂, HYDROFY G 2.5, has been produced by milling natural mineral brucite and kindly supplied by Nuova Sima (Genga, AN, Italy). It features a specific surface area (BET) of 8.5 m²/g, a median particle size (D₅₀) of 3.5 µm, a bulk density (tamped) of 0.64 g/cm³, and a 2.36 g/cm³ specific gravity/density.

Aluminium Tri-Hydroxide (ATH) with chemical formula: Al(OH)₃, MARTINAL OL-104 LEO, is a finely precipitated aluminium hydroxide produced by Huber Corporation, Germany, sourced from high-purity alumina. It features a specific surface area (BET) of 3–5 m²/g, a median particle size (D₅₀) of 1.7–2.1 µm, purity ca. 99.4%, and a 2.4 g/cm³ specific gravity/density.

An antioxidant (AO), SABOSTAB AO 1010 produced by Sabo, was used in this research. It is a sterically hindered phenolic antioxidant, specifically pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), widely used to stabilize polymers against thermal and oxidative degradation.

Table 1 reports the main features of ATH and MDH, such as particle size, surface area, specific gravity/density, bulk density, and water content, sourced from available commercial sheets.

2.2 | Formulations of Composites

Before compounding, PBS, ATH, and MDH have been dried overnight at 75°C under vacuum to avoid hydrolysis phenomena, then, the biocomposite formulation was carried out using a batch mixer (Brabender model PLE330, Duisburg, Germany) at 135°C with a mixing speed of 50 rpm for 10 min with simultaneous addition of particles and polymer matrix previously mixed in solid phase. Sample codes with relative polymer and filler concentrations are described in Table 2. To characterize the biocomposites, pellets of all materials were dried in a vacuum oven under the same conditions as above and then compression molded using a Carver Laboratory Press (Carver, Wabash; IN; USA) at a temperature of 135°C at about 20 atm for about 3 min.

2.3 | Characterizations of Composites

2.3.1 | Rheological Analysis

Rheological tests were performed using a strain-controlled rheometer (ARES G2, TA Instruments, New Castle, DE, USA) in parallel plate geometry (plate diameter 25 mm). Frequency scans from 10⁻² to 10² rad/s were performed to measure complex viscosity (η*) and storage (G') and loss (G'') moduli at the same processing temperatures. The strain amplitude was set at 5%, which was found to be low enough to be in the linear viscoelastic regime in preliminary experiments with strain sweeps.

2.3.2 | Morphological Analysis

Particle morphology was analyzed by scanning electron microscopy (SEM) (Quanta 200 F ESEM, FEI, Hillsboro, USA). All samples were sputter-coated with a thin layer of gold to make them conductive. The crystal size distribution (CSD) was determined using ImageJ software from several SEM micrographs of the hydroxide particles, and the resulting data were processed with Origin 8.5 to obtain the particle size distribution curve.

A scanning electron microscope (SEM, Quanta 200 ESEM, FEI, Hillsboro, OR, USA) was used to examine the microstructure of the PBS-based biocomposites. Prior to the SEM analysis, the samples were fractured in liquid nitrogen. To avoid electrostatic charging under the electron beam, the fractured surface of each sample was sputtered (Scancoat Six Edwards, Crawley, UK) with a thin layer of gold for 90 s in an argon atmosphere.

2.3.3 | Differential Scanning Calorimetry

The melting enthalpies of all samples were measured by DSC using a Shimadzu (Japan) DSC-60 instrument at a heating rate of 10 °C/min from T ambient to 190°C. All samples of similar weight (~7 mg) were subjected to heating/cooling/ heating, and the thermal parameters were evaluated on the second heating scan, erasing the previous thermal history. The PBS crystallinity, χ_c, was calculated using the equation:

$$\chi_c = \frac{\Delta H_m}{\Delta H_{100} \times W_p} \times 100 \quad (1)$$

TABLE 1 | Particle size, surface area, specific density, bulk density and water content; according to [25].

	<i>Particle size</i>			<i>Surface area</i>	<i>Specific density</i>	<i>Bulk density</i>	<i>Water content</i>
	<i>Dry laser diffraction</i>						
	D₁₀ [μm]	D₅₀ [μm]	D₉₀ [μm]				
MDH	1.14	4.03	12.3	7.7	2.36	0.64	0.33
ATH	1.07	2.18	4.11	3-5	2.40	0.4-0.5	0.18

TABLE 2 | Sample code name with relative weight concentrations.

Sample code	PBS [%]	MDH [%]	ATH [%]	AO [%]
PBS	100	0	0	0
PBS MDH	39.82	60	0	0.18
PBS ATH	39.82	0	60	0.18
PBS MDH/ATH 1:1	39.82	30	30	0.18
PBS MDH/ATH 1:2	39.82	20	40	0.18
PBS MDH/ATH 1:3	39.82	15	45	0.18

where ΔH_m is the enthalpy of fusion, ΔH_{100} is the enthalpy of fusion of 100% crystalline polymer, and W_p is the weight fraction of polymer. For PBS, $\Delta H_{100} = 110.5 \text{ J gr}^{-1}$ [40].

2.3.4 | Monoaxial Tensile Test

Monoaxial tensile tests were conducted with Instron 3360 on rectangular samples (10 mm width, 0.3–0.4 mm thickness, and with a gauge length of 30 mm) produced by compression molding. The crosshead speed was 1 mm/min. Tests were performed at 23°C and 50% humidity, according to the ASTM D882 method. Ten samples were tested for each material, and the deviations were calculated on rectangular samples.

2.3.5 | Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal tests (DMTA) were carried out in tensile configuration through a dynamic mechanical analyzer model DMA + 50 (Metravib, Limonest, France). The test was performed on three specimens (10 mm × 30 mm) of each composite from room temperature to 140°C at a heating rate of 5°C/min. The frequency was set at 1 Hz, and the dynamic displacement was set at 5×10^{-5} m.

2.3.6 | Thermo-Gravimetric Analysis

Thermal Analysis was conducted in a Netzsch Jupiter F1 STA 449 (NETZSCH B.V & Co. Holding KG, Selb, Germany) in the range 25–1200°C with a heating rate of 10°C min⁻¹ by fluxing 20 mL min⁻¹ of nitrogen and 20 mL min⁻¹ of air during the analysis.

2.3.7 | Cone Calorimeter Test Setup

The cone calorimeter test was the key method used to dynamically assess the flame-retardant properties and smoke suppression capabilities of the materials by measuring the heat release rate. In this setup, the polymer was exposed to a radiant heat flux of 50 kW/m² at a distance of 25 mm from the heat source, corresponding to a surface temperature of approximately 780°C. The exposure lasted 1200 s in ambient air with a constant airflow of 24 L/min.

Each sample was prepared and mounted in the following configuration (from bottom to top): metal support – glass wool – aluminum foil – sample – metal grid – upper metal support. An electric arc was used as the ignition source.

Prior to testing, the airflow was calibrated to 24 L/min at 0 atm relative pressure (i.e., without vacuum or overpressure). The airflow was measured using a Venturi tube equipped with a diaphragm at the constriction and two pressure sensors positioned before and after the restriction. A small portion of the airflow was diverted through a capillary tube and directed to the oxygen analyzer, after passing through a paper filter and a fiberglass filter.

Before reaching the oxygen analyzer, the airflow passed through a cold trap to condense moisture, followed by a series of adsorbent filters: silica gel to capture water vapor and soda lime (a mixture of calcium hydroxide and sodium hydroxide) to remove carbon dioxide. The saturation of the adsorbent beds was monitored visually by color changes: silica gel turned from beige to green, and soda lime from white to violet. When saturation exceeded half the filter height, the materials were replaced.

A SERVOMEX paramagnetic oxygen analyzer was used. To ensure accurate analysis, the air was filtered to prevent the entry of polar compounds. The analyzer was first calibrated with clean air at a flow rate of 3.25 L/min, corresponding to an upper oxygen concentration limit of 20.95%. Then, nitrogen was introduced at the same flow rate to lower the oxygen concentration to 0%, establishing the lower calibration limit. The oxygen concentration in the extracted air was monitored over time to determine oxygen consumption, which was then converted into heat release data.

The heat flux calibration was performed using a blackbody with a reflective surface facing the cone. The distance from the cone was first precisely set to 25 mm. The temperature was then adjusted until the irradiance reached 50 kW/m². In this case, the cone temperature was set to approximately 783°C.

A methane calibration was conducted to determine the c-factor, a coefficient related to the measured heat release. A controlled methane flow was introduced horizontally under the cone and ignited using an electric arc. The ConeCal 5 software measured the c-factor, which had to fall within the range of 0.042–0.046. If values were outside this range, the exhaust hood was cleaned, and the filters were replaced.

Smoke suppression properties were evaluated using a laser-based detection system. The laser was first obscured to set the zero-transmittance baseline. A 60-s pre-test interval was recorded to establish the baseline signal. During the test, light transmittance was measured and correlated with smoke production.

2.3.8 | Photo-Oxidation Behavior

All samples were subjected to photo-oxidation again using a Q-UV/se accelerated weathering tester (Q-Labs Corp., Westlake, OH, USA) with eight UVB-313 lamps. The samples were exposed at 70°C to an irradiance of 0.89 W/m² (at a wavelength of $\lambda = 313$ nm) and monitored.

The progress of the photo-oxidation as a function of time of pure PBS and all the PBS-composites was monitored by ATR-FTIR spectroscopy analysis. Therefore, the spectroscopy analysis was carried out using ATR-FTIR equipment (Perkin-Elmer FT-IR/NIR Spectrum 400, Waltham, MA, USA), and 16 acquisitions were made for each measurement.

3 | Results and Discussion

3.1 | Processability and Morphology

Oscillatory test analyses have been carried out to investigate the processability of PBS-based biocomposites and the effect of adding magnesium dihydroxide (MDH) and aluminum trihydroxide (ATH) powders on the rheological behavior. Figure 1 shows (a–b) the complex viscosity and (c–d) the storage (G') and loss (G'') moduli of the PBS-based biocomposite containing MDH, ATH, and MDH/ATH, as a function of angular frequency, in comparison to pure PBS. As expected, the complex viscosity of pure PBS remains unchanged at low frequencies and varies slightly within the high-frequency range. In contrast, the PBS-based biocomposites demonstrate non-Newtonian behavior across the entire investigated frequency range. Among the samples, PBS MDH shows the highest viscosity, in comparison to pure PBS and PBS ATH, across the entire frequency range, indicating that the addition of MDH increases the resistance to flow, likely due to stronger filler–matrix interactions or a more interconnected microstructure. PBS ATH also exhibits higher viscosity than pure PBS, but lower than PBS MDH, indicating a less pronounced reinforcement effect of ATH, especially at high frequencies, as shown in Figure 1a. Regarding the PBS-based biocomposites containing MDH/ATH at different weight ratios of 1:1, 1:2, 1:3, see Figure 1b, all samples exhibit higher viscosity values than that of the pure PBS in the whole investigated frequency range, and however, this is more pronounced at low frequencies, confirming the structuring effect of the well-dispersed inorganic fillers and the well-pronounced interaction filler–matrix. Furthermore, all

PBS MDH/ATH systems exhibit a shear-thinning behavior, characteristic of pseudoplastic fluids due to progressive disruption and alignment of the polymer–filler network under flow. The PBS MDH/ATH at different concentrations 1:1, 1:2, 1:3 exhibit similar rheological behavior among them, suggesting that their processability is mainly governed by the presence of both MDH and ATH, and in turn, the complex viscosity trends appear comparable to the trend of PBS ATH, albeit with a less pronounced slope of shear thinning.

Therefore, the storage (G') and loss (G'') moduli trends of all the samples investigated, see Figure 1c,d, highlight some interesting results. More specifically, the PBS and PBS ATH samples exhibit liquid-like behavior across the entire investigated frequency range, i.e. there is no crossover between G' and G'' moduli, see Figure 1c. In contrast, the PBS MDH sample exhibits a crossover between G' and G'' at approximately 70 rad/s, indicating a transition to solid-like behavior, see Figure 1c. It is worth noting that all the PBS MDH ATH at different weight ratios 1:1, 1:2, 1:3, exhibit intermediate behavior among PBS MDH (solid-like) and PBS ATH (liquid-like), and G' and G'' at 100 rad/s show almost the same values, see Figure 1d. This highlights that the rheological behavior of PBS MDH/ATH samples is governed by both MDH and ATH, and their interactions with biopolymer chains.

In addition, Table 3 reports the viscosity values at $\omega = 0.1$ rad/s (low frequency) and $\omega = 100$ rad/s (high frequency) and MFI values. Although the viscosity values are higher due to the presence of metal hydroxides, this does not affect the use of these materials in melt processing, such as extrusion and/or injection moulding, highlighting the industrial feasibility of these fire-resistant PBS-based composites.

Prior to the morphology investigation of the PBS-composites, an accurate SEM analysis was performed on both MDH and ATH, and crystal size distribution (CSD) was estimated. Figure 2 reports the SEM micrographs (a,c) of the two metal hydroxides along with their corresponding crystal size distributions (b,d). The distributions were obtained by processing several SEM micrographs with ImageJ software, and the resulting data were analyzed using Origin 8.5 to generate the crystal size distribution curves. The MDH particles exhibit a rough surface and a markedly irregular morphology, consistent with their preparation by milling of a natural mineral. The milling process causes crystal fracture, leading to the formation of crystal particles with irregular size and shape distributions. This green and simple process, which does not require the use of chemicals, is responsible for the observed irregular fragmentation of the crystals and the broad size distribution. This observation is consistent with the size distribution curve shown in Figure 2b, where the most populated class falls within the 1–1.5 μm range, although pieces up to 7.5–8 μm in size are also present. In contrast, the ATH pieces display a more regular morphology, see Figure 2c. The precipitation-based synthesis process promotes the formation of crystals with controlled dimensions and uniform shapes. This observation is supported by the distribution reported in Figure 2d, which shows a significantly narrower curve compared to MDH, with the most populated class in the 0.5–1 μm range. Moreover, these findings are consistent with the BET measurements reported in the technical data sheets from manufacturers.

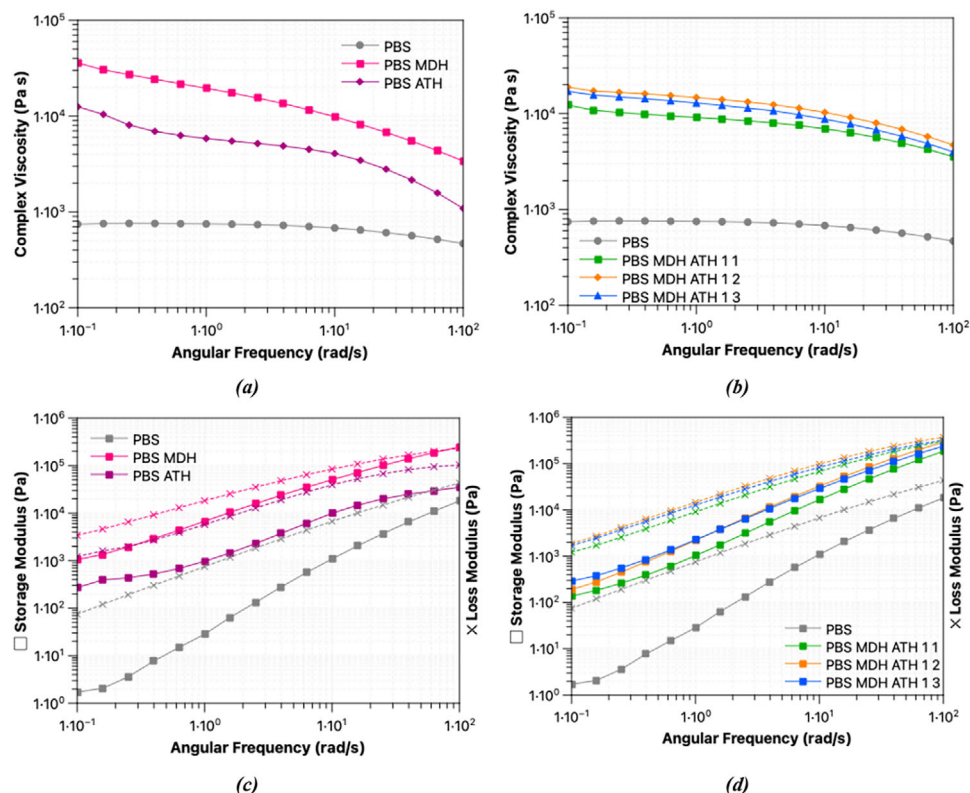


FIGURE 1 | (a,b) Complex viscosity and (c,d) G' storage ($\square$) and G'' loss ($\times$) moduli of pure PBS and PBS-based biocomposites.

TABLE 3 | Viscosity values at $\omega = 0.1$ and 100 rad/s and Melt Flow Index (MFI) of PBS and PBS-based composites.

Sample	$\eta_{\omega = 0.1 \text{ rad/s}}$ [Pa*s]	$\eta_{\omega = 100 \text{ rad/s}}$ [Pa*s]	MFI _{@190 °C, 2.16 lg} [g/10 min]
PBS	$0.7 \cdot 10^4$	$0.5 \cdot 10^3$	5.00
PBS MDH	$3.6 \cdot 10^4$	$3.4 \cdot 10^3$	1.22
PBS ATH	$1.3 \cdot 10^4$	$1.1 \cdot 10^3$	1.76
PBS MDH/ATH 1:1	$1.2 \cdot 10^4$	$3.7 \cdot 10^3$	1.54
PBS MDH/ATH 1:2	$1.9 \cdot 10^4$	$4.7 \cdot 10^3$	1.61
PBS MDH/ATH 1:3	$1.7 \cdot 10^4$	$4.0 \cdot 10^3$	1.56

In Figure 3, morphologies of PBS-based biocomposites obtained by SEM observation are shown. Pure PBS shows a homogeneous morphology characterised by smooth regions alternated with wavy structure. The morphology observed for the PBS MDH composite appears to be jagged and contains MDH grains in order of diameter that were expected from the crystal morphology, shown in Figure 2a, some of which are integrated within the matrix, while others appear to be detached. The fracture surface of the PBS ATH composite exhibits a relatively smooth morphology compared to pure PBS, with the presence of numerous small voids and cavities distributed across the surface. These voids likely correspond to detached ATH crystals or poor interfacial adhesion zones between the filler and the polymer matrix. The morphology of the polymer matrix in the hybrid composite with a higher MDH content (i.e., PBS MDH/ATH 1:1) results in a similar and consistent appearance to that of the polymer matrix in

the composite filled only with magnesium hydroxide, PBS MDH. Similarly, the PBS matrix in the PBS MDH/ATH 1:3 biocomposite, which contains a higher percentage of ATH, exhibits a comparable smooth morphology to the composite that is solely filled by ATH. In addition, with respect to SEM morphologies, the PBS MDH/ATH 1:2 displays a distinctive behavior, characterised by a jagged matrix and visible ATH particles.

However, according to rheological and morphological analyses, ATH can be easily dispersed in biopolymer and polyolefin matrices [25], and for this reason, in this work, attention has been focused on systems with increasing ATH content.

Regarding the MDH and ATH structures, our previously documented XRD analysis [25] and the literature indicate that the MDH has a brucite structure containing traces of dolomite,

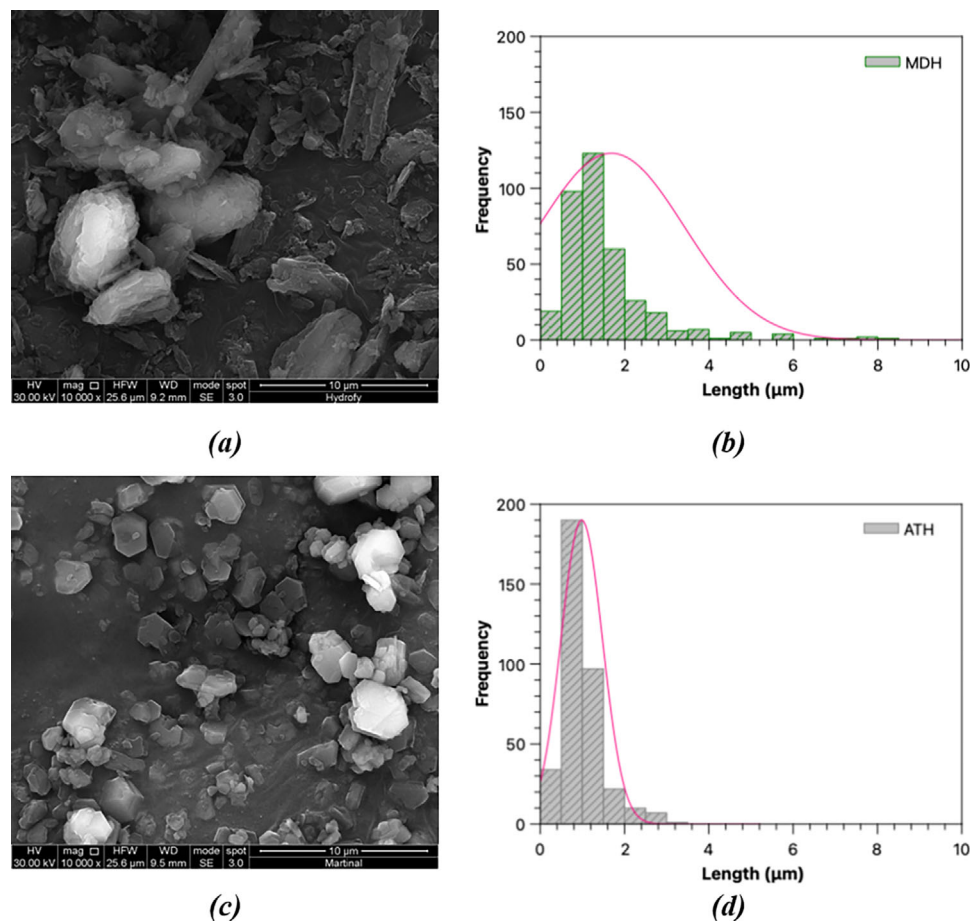


FIGURE 2 | (a,c) SEM micrographs (at 10 000× of the magnitude) and (b,d) the crystal size distribution (CSD) of MDH and ATH.

consisting essentially of magnesium and calcium carbonates. Instead, ATH emphasizes its gibbsite structure, as revealed by XRD analysis [25]. This structure–property relationship is consistent with the findings of Chen et al., who demonstrated that PBS/Mg(OH)₂ composites filled with different Mg(OH)₂ amounts, medium-sized, petal-like Mg(OH)₂ (≈5 μm), exhibited slightly better flame retardancy compared to both larger (≈20 μm) and nano-sized (≈500 nm) particles, due to the ability of the morphology to build an effective and less cracked char layer under cone calorimeter conditions [39].

3.2 | Mechanical Behavior

In Figure 4, the main mechanical properties (e.g., Young's modulus (E), tensile strength (TS), and elongation at break (EB)) of all samples investigated are shown and compared to pure PBS; on the left axis, the Young's modulus values are reported, and on the right axis, the tensile strength and elongation at break. As expected, by adding ca. 60 wt.% of metal hydroxides, the mechanical behavior is completely different, turning from a ductile behavior to a rigid one. The addition of such a high filler content results in a remarkable increase in stiffness, with the Young's modulus showing more than a three-fold rise compared to pure PBS. This highlights the reinforcing effect of the inorganic phase and the strong polymer–filler interaction. However, this enhancement comes at the expense of tensile strength and

elongation at break, which drastically decrease for all filled formulations. In particular, the elongation at break is reduced to values close to those typical of brittle materials, indicating limited chain mobility and poor polymer matrix continuity due to the high filler loading. Overall, the mechanical results underline the typical trade-off observed in highly filled biopolymer composites: increased rigidity and dimensional stability alongside a significant loss of toughness and ductility. Therefore, the increased rigidity and reduced ductility of all PBS-based biocomposites can be considered favorable for processing by compression molding to produce items that can withstand mechanical stress.

Figure 5a,b shows the storage modulus (E') curves for all the samples investigated, as determined by dynamic mechanical thermal analysis. Measurements were taken from room temperature until the materials lost their thermal stability, which occurred shortly after their melting temperature was exceeded. Over the entire temperature range, the storage modulus (E') of all biocomposites was higher than that of pure PBS. As expected, and in agreement with the rheological and mechanical data, the storage modulus at room temperature is higher for all biocomposites compared with pure PBS. Furthermore, the presence of the inorganic fillers improved the stability of the materials across the entire temperature range, shifting the onset of thermal degradation to higher temperatures. This results in an increase of approximately 15°C–20°C in the temperature at which complete

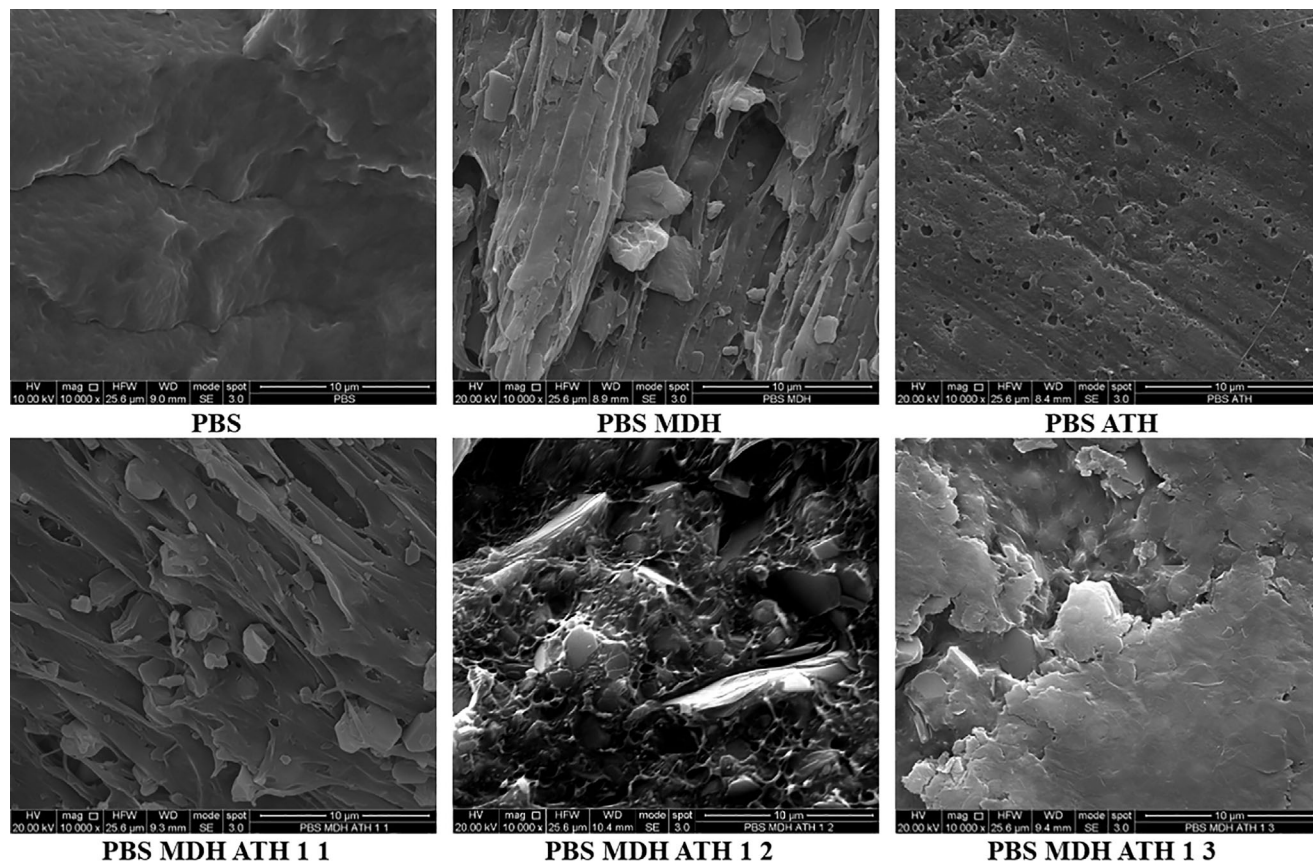


FIGURE 3 | SEM micrograph (at 10 000× of the magnitude) of pure PBS and PBS-based biocomposites.

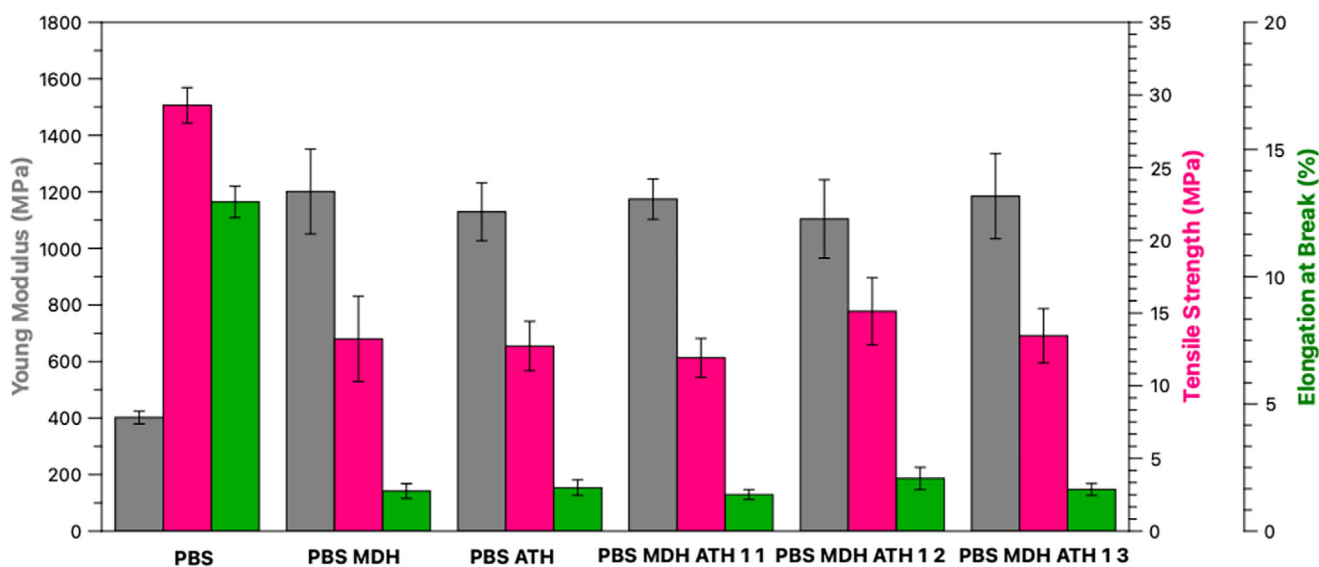


FIGURE 4 | Main mechanical properties of neat PBS and PBS-based biocomposites. Left axis: Young's Modulus (MPa). Right axis: Tensile Strength (MPa) and Elongation at Break (%).

thermal stability is lost. The reinforcing trend for the single-filler biocomposites is consistent with the rheological results; in fact, MDH particles provide the strongest reinforcing effect. For the hybrid compositions, the modulus curves are shifted to higher values compared with the composites containing only one metal hydroxide, and the differences between the three hybrid formulations appear negligible.

3.3 | Thermal Behavior and Stability

Figure 6a–d and Table 4 report the DSC curves and data of pure PBS and its biocomposites containing MDH, ATH, and MDH/ATH at different weight ratios 1:1, 1:2, 1:3, during the first heating and first cooling steps. Pure PBS shows a single melting peak at 114.6°C and a crystallisation temperature T_c of

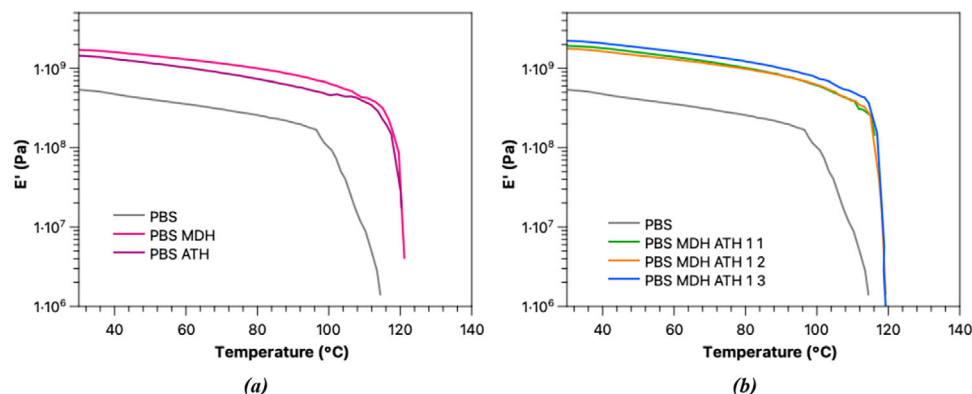


FIGURE 5 | Storage modulus (E') curves as a function of temperature: (a) pure PBS, PBS MDH and PBS ATH; (b) pure PBS and PBS MDH/ATH at different weight ratios 1:1, 1:2, 1:3.

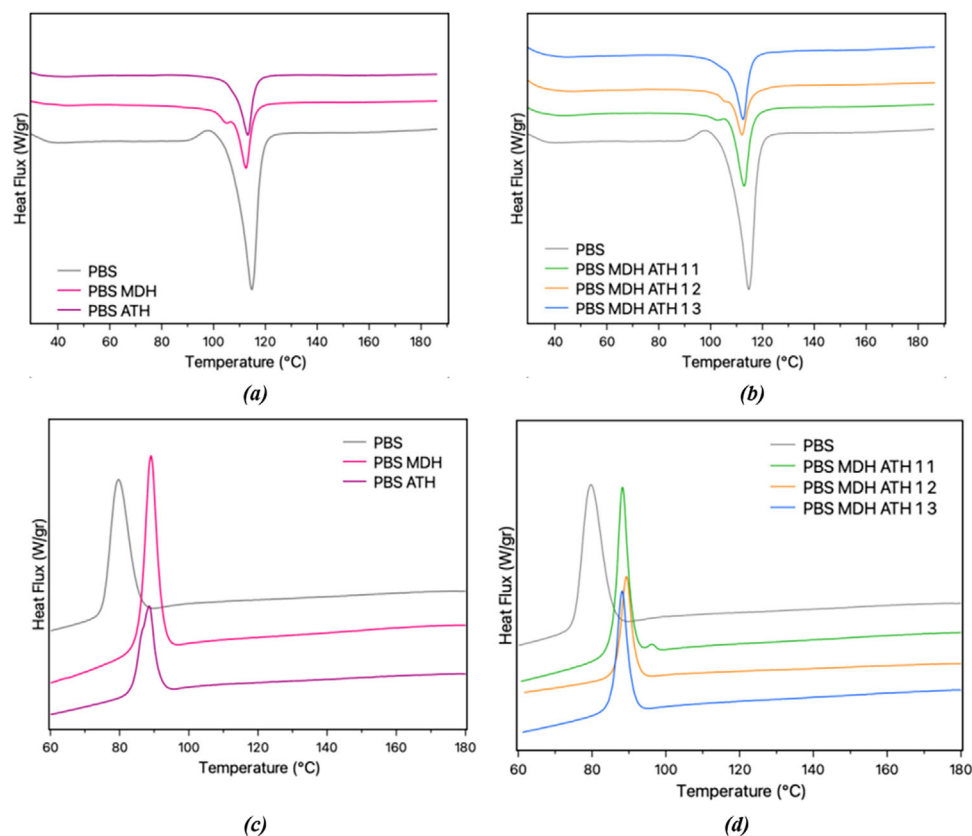


FIGURE 6 | DSC analysis of (a-b) first heating scans and (c-d) first cooling scans of pure PBS and PBS-based biocomposites.

79.9°C, with the highest enthalpy of fusion ($\Delta H_m = 84.6$ J/g) and a crystallinity χ of 74.6% (corrected for cold crystallisation). It is worth noting that PBS exhibits a small exothermic peak at approximately 97.7°C due to the occurrence of the cold crystallisation phenomenon, and this small peak is not noticeable in PBS-based biocomposites. The addition of MDH or ATH slightly decreases the melting temperature T_m , while the crystallisation temperature increases by about 10 °C. This behavior can be explained by the dual role of the filler: first, the metal hydroxide crystals act as nucleating agents, promoting an earlier onset of crystallisation phenomena, and second, they also interfere with the regular growth of the biopolymer crystals, resulting in a slight

reduction of the melting temperature. Biocomposites containing MDH, in addition to the main melting peak, display a small peak or shoulder around 105°C. This feature is observed in samples containing only MDH and MDH/ATH hybrid compositions. Table 4 also shows how it appears as a small peak (*) or shoulder $\cap$, depending on the MDH concentration in biocomposite formulations. Overall, it seems that MDH acts as a nucleating agent, increasing the crystallinity of PBS. Furthermore, an overall slight decrease in the degree of crystallinity for PBS ATH is observed, considering that ATH decreases the overall crystallinity of PBS by disrupting its crystalline structures due to its smaller crystals being able to migrate easily between the biopolymer chains.

TABLE 4 | DSC data related to the first heating scan and the first cooling scan. The crystallinity degree (χ) was calculated using Equation 1; for pure PBS was considered the cold crystallisation enthalpy ($\chi = (\Delta H_m - \Delta H_{cc}) / \Delta H_{100\%}$).

Sample	T_m [°C]	T_c [°C]	ΔH_m [J/gr]	χ [%]
PBS	114.6	79.9	84.6	74.6 [§]
PBS MDH	105.2* – 112.7	89.1	34.1	77.1
PBS ATH	113.1	88.7	29.9	67.6
PBS MDH/ATH 1:1	102.7* – 113.1	88.1	35.2	79.6
PBS MDH/ATH 1:2	106.0 [^] – 112.3	89.2	34.8	78.7
PBS MDH/ATH 1:3	105.1 [^] – 112.3	88.3	35.4	79.9

Note: (*) small peak; ([^]) shoulder; ([§]) PBS crystallinity degree was calculated by subtracting ΔH_{cc} (cold crystallisation enthalpy)

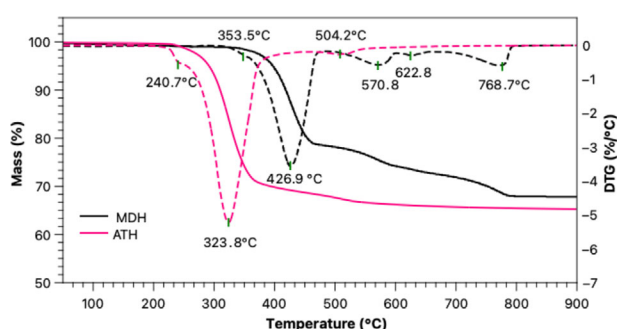


FIGURE 7 | TGA curves (left axis: weight loss) and DTG curves (right axis) of MDH and ATH.

All the PBS MDH/ATH systems exhibit slightly higher values of crystallinity in comparison to pure PBS, similar to the value of PBS MDH, indicating that the simultaneous presence of MDH and ATH promotes a more efficient reorganization of PBS crystals. The synergistic effect of MDH and ATH likely enhances nucleation density while allowing sufficient chain mobility for crystal growth, resulting in a more ordered crystalline structure.

Prior to the thermal stability of PBS-based biocomposites, the TGA/DTG analysis of the two metal hydroxides has been carried out in an inert atmosphere, and Figure 7 shows the trends. A prominent main peak in the decomposition of both aluminum and magnesium hydroxides to metal oxides and water molecules is evident, with magnesium hydroxide exhibiting significantly higher results compared to aluminum hydroxide. The main decomposition peak is located at approximately and $T_{max} = 426.8^\circ\text{C}$ for MDH and $T_{max} = 327.3^\circ\text{C}$ for ATH, corresponding to the decomposition of metal hydroxides into metal oxides, emphasising their good thermal stability.

Beyond the main peak, the MDH displays two notable peaks and one minor peak between approximately 500 and 800°C . These small peaks can be attributed to the decomposition of dolomite, a process that involves the transformation of magnesium carbonate (MgCO_3) into magnesium oxide (MgO), followed by the decomposition of calcium carbonate (CaCO_3) into calcium oxide (CaO).

In relation to ATH, a minor shoulder is observed at approximately 242.0°C , which can be ascribed to a partial dehydration of aluminum hydroxide to aluminum hydroxide oxide (also designated as aluminum oxyhydroxide), i.e., $\text{AlO}(\text{OH})$. It is evident that the degradation of aluminum hydroxide oxide $\text{AlO}(\text{OH})$ to aluminum oxide (Al_2O_3) is the underlying cause of the peak at 513.2°C .

The residual masses of the two hydroxides at 900°C are estimated at approximately 67.8% for MDH and 65.3% for ATH. The composition of these minerals is primarily metal oxides, with a loss of approximately 30%–35% attributed to the water molecules and CO_2 that were produced during the decomposition of the carbonates. The attribution of these thermal events to carbonate decomposition is consistent with the kinetic study of Smadi et al., who investigated the calcination of magnesium carbonate over a broad range of heating rates and demonstrated that MgCO_3 and CaCO_3 decarbonation proceeds through a well-defined endothermic step that forms the related oxides, MgO and CaO , and the release of CO_2 . The stoichiometric ratios between the reaction products were studied to demonstrate the mass loss in the TGA/DTG curves already discussed before [41].

The thermal stability behavior of PBS biocomposites was evaluated, and the (a-b) TGA and (c-d) DTG curves obtained under air conditions are presented in Figure 8 with the related data listed in Table 5. Pure PBS exhibits an initial decomposition temperature ($T_{5\%}$) of 351°C . The maximum rate of decomposition occurs at 406°C in a single main weight loss stage, with a small step that starts at 439°C that reduces the weight loss from 3.6% to zero, resulting in a minor shoulder in the DTG curve at 523°C . After the addition of metal hydroxides, the initial decomposition temperatures decrease, and the degradation behavior becomes more complex. The samples containing MDH or ATH show an anticipated degradation phenomenon that occurs in the range of $300 - 325^\circ\text{C}$, probably due to the occurrence of anticipated degradation phenomena of PBS in the presence of metal hydroxides, with respect to pure PBS. In accordance, the hybrid composites containing both MDH and ATH exhibit anticipated and complex degradation phenomena. This complex behavior can be attributed to the presence of the metal hydroxide crystals themselves (see Figure 7), as their thermal degradation contributes additional steps to the overall anticipated degradation process. The lower thermal stability of PBS-based biocomposites in air conditions, i.e. in the presence of oxygen, is mainly due to the premature decomposition of PBS in the presence of metal hydroxides, which can catalyze its degradation. Interestingly, the onset degradation temperature in TGA of neat PBS is said to be slightly higher than that of the PBS/MDH/ATH composite. This apparent decrease in thermal stability upon incorporation of MDH and ATH has already been reported for PBS-based systems containing Mg/Al derivatives, where the presence of metal hydroxides/oxides was shown to catalyze chain scission reactions and hydrolysis of the ester [42]. In our case, the progressive dehydroxylation of MDH and ATH during heating generates MgO and Al_2O_3 rich surfaces that provide basic sites, which can promote the thermo-oxidative degradation of PBS at the polymer–filler interface. Consequently, the composite exhibits an earlier onset of degradation in TGA compared to neat PBS, even though the overall fire performance is improved due to the endothermic decomposition of the

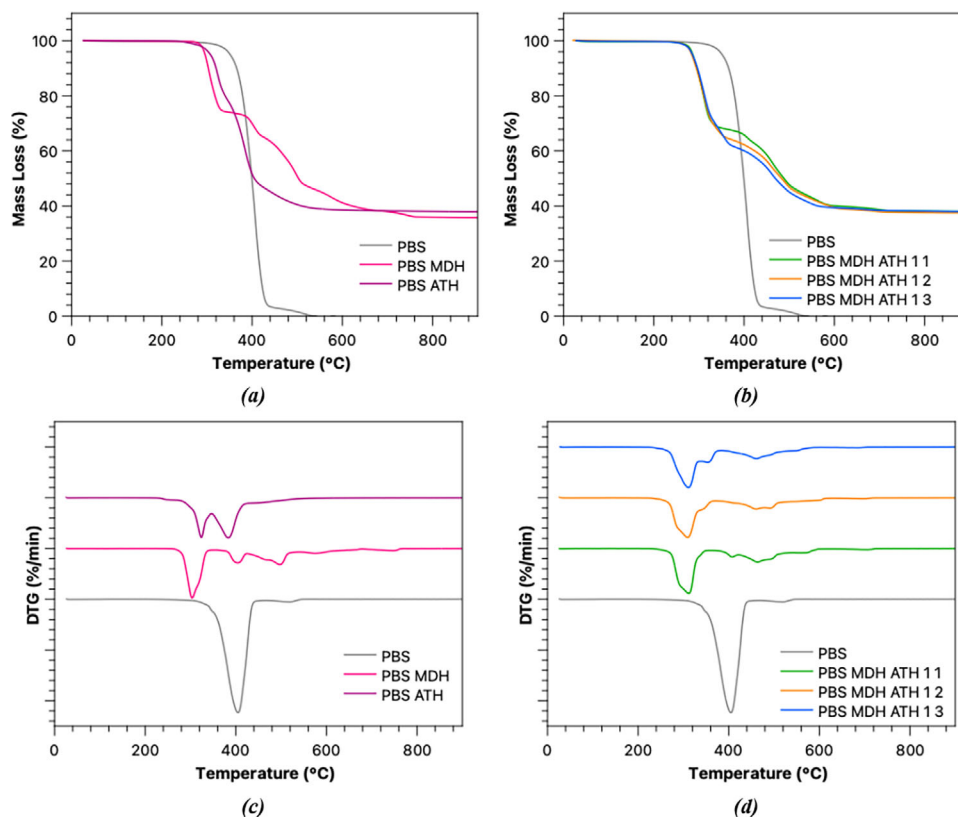


FIGURE 8 | Thermo-gravimetric analysis: (a-b) TGA and (DTG) curves of pure PBS and PBS-based biocomposites.

TABLE 5 | Data of TGA/DTA analysis, residue [%] at 900 °C and static heat resistance index (T_s).

Sample	$T_{\text{Main Peak}}$ [°C]	$T_{\text{Secondary Peak}}$ [°C]	Residue at 900			
			°C [%]	$T_{5\%}$ [°C]	$T_{30\%}$ [°C]	T_s [°C]
PBS	406	523 ^ˆ	0.1	351.2	387.1	182.6
PBS MDH	303	403–499–583 [*]	35.4	295.4	399.5	175.4
PBS ATH	324	384–457 ^ˆ	37.7	307.3	368.8	168.7
PBS MDH/ATH 1:1	309	409 [*] –469 [*] –493 ^ˆ –568 ^ˆ	37.5	286.2	330.8	153.4
PBS MDH/ATH 1:2	309	345 ^ˆ –463 [*] –493 [*] –595 ^ˆ	37.0	283.7	330.5	152.8
PBS MDH/ATH 1:3	315	357 ^ˆ –463 [*] –496 [*] –550 ^ˆ	37.5	285.4	332.1	153.6

Note: ^ˆ small shoulder; ^{*} small peak; $T_{5\%}$ and $T_{30\%}$ are the temperatures corresponding to 5% and 30% mass loss

hydroxides and the formation of a thermally stable inorganic residue.

In addition, the static heat resistance index (T_s) of PBS and PBS-based biocomposite has been calculated by using Equation 2:

$$T_s = 0.49 [T_{5\%} + 0.6 (T_{30\%} - T_{5\%})] \quad (2)$$

where $T_{5\%}$ and $T_{30\%}$ are the temperatures corresponding to 5% and 30% mass loss, all data are listed in Table 5. The T_s decreases upon the addition of both MDH and ATH, indicating a reduction in the thermal stability of the biocomposites compared to pure PBS. PBS exhibits the highest T_s (182.6°C), while the incorporation of MDH and ATH lowers T_s to 175.4°C and 168.7°C, respectively.

The hybrid composites containing both MDH and ATH show the lowest T_s values (around 153°C), reflecting the combined effect of the two additives on accelerating the initial decomposition. This decrease in static heat resistance is consistent with the premature decomposition of the metal hydroxides, forming water molecules that can catalyze the biopolymer degradation while simultaneously promoting char formation and flame-retardant action.

3.4 | Resistance to Heat and Photo-Oxidation

Figure 9 shows the (a,b) Heat Release Rate (HRR), (c,d) Smoke Production Rate (SPR), and (e,f) Total Heat Release (THR) curves

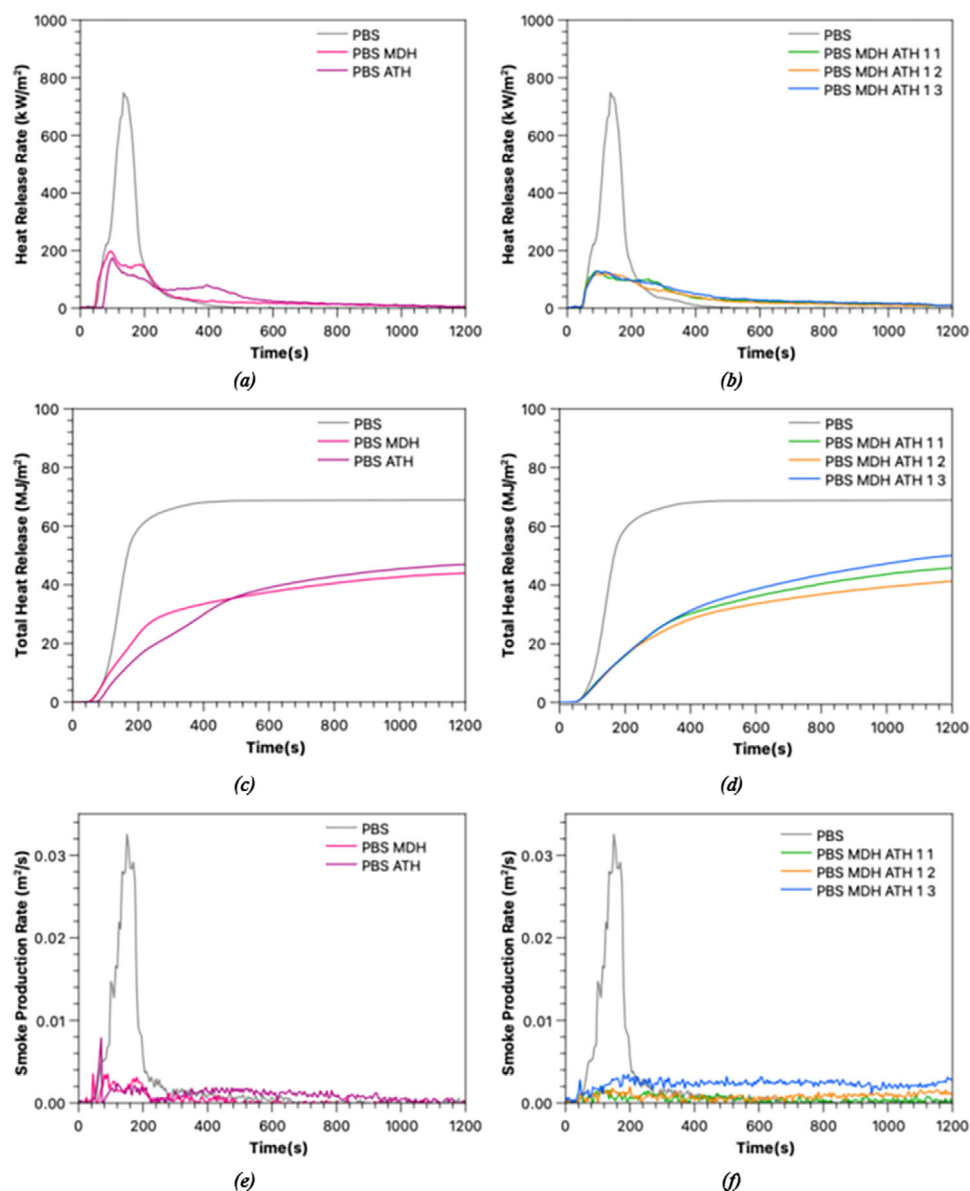


FIGURE 9 | (a,b) Heat Release Rate, (c,d) Total Heat Release and (e,f) Smoke Production Rate of pure PBS and PBS-based biocomposites at a heat flux.

of PBS and its biocomposites under cone calorimeter testing, with the corresponding data listed in Table 5. Cone calorimeter analysis allows evaluation of various parameters related to the flammability of materials. Furthermore, Figure 10 shows images of the final residue after 1200 s of combustion for all the samples investigated, while the inserts show what the samples looked like before they were burned.

As shown in Figure 9, pure PBS burns rapidly and exhibits a well-defined peak in the HRR curve, with a peak value (pHRR) of 749 kW/m², while the THR reaches a maximum of 68.84 MJ/m², similarly of what has been found by Wang et al. [14]. For the samples containing only MDH or ATH, the HRR curves display multiple peaks. For PBS MDH, the pHRR decreases to 198 kW/m², while for PBS ATH it reaches 175 kW/m². In the composites containing MDH and ATH, the first peak could be associated with the initial rearrangement of the metal hydroxide, which leads to the release of water and the formation of a protective

char layer, similar trend has been observed by PBS filled with lignin chelate composites for flame retardant applications [18]. The subsequent peaks, appearing at longer times, correspond to the partial or complete degradation of the char layer and the final combustion of the underlying polymer that had been previously shielded. The HRR curves of the hybrid composites exhibit a similar trend, characterized by a single peak attributed to the formation of an intumescent char layer. This peak gradually decreases over time, indicating the development of a more stable and efficient protective structure, also according to the literature [15]. Moreover, for the hybrid compositions, a further reduction in pHRR is observed, reaching values of 130, 121, and 130 kW/m² for PBS MDH ATH 11, 12, and 13, respectively.

Figure 9c,d shows the total heat release (THR) as a function of time for neat PBS and its composites. A clear decrease in THR is observed for the PBS-based composites compared to neat PBS. The rapid combustion of pure PBS is evident from the comparison

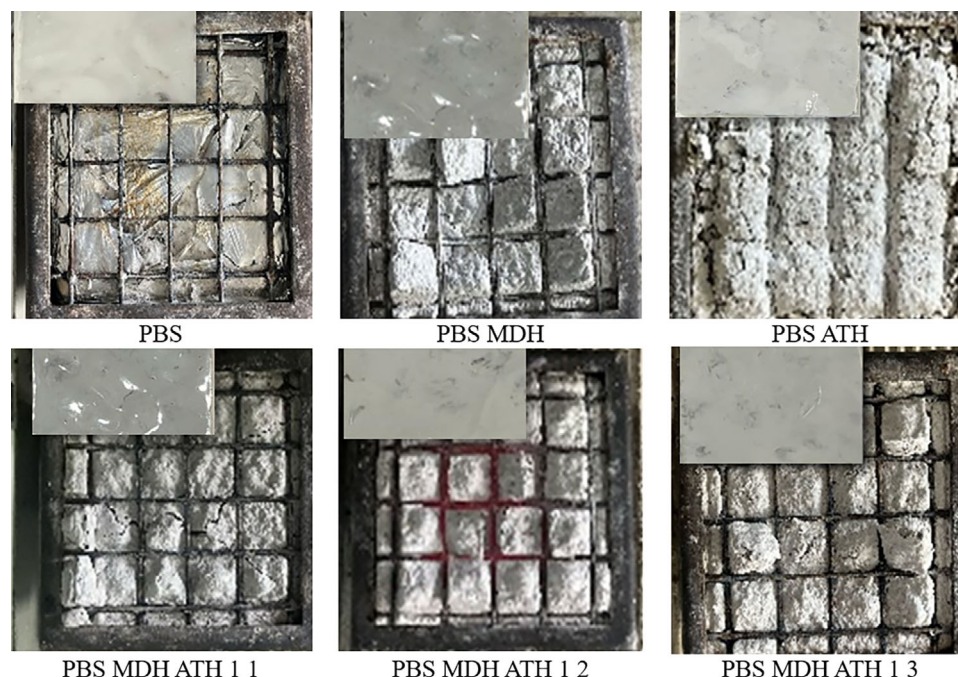


FIGURE 10 | Images of the final residue at 1200 s after combustion (inserts show the sample before combustion) of pure PBS and PBS-based biocomposites.

of the THR values at 600 and 1200 s, which appear nearly identical, indicating that the combustion is essentially completed within the first few minutes. In contrast, the composites exhibit a slower and more gradual heat release, particularly the PBS ATH sample, which shows the slowest combustion kinetics. The presence of ATH in the hybrid composites further contributes to reducing the overall burning rate of the material. A higher THR value indicates a greater amount of heat released during combustion, which increases the risk of secondary fires. The results show that the addition of hydroxides significantly reduces the THR, with the lowest value observed for PBS MDH ATH 1 2, compared to 68.84 MJ/m² for neat PBS (see Table 6 for complete data). This reduction suggests that the composites possess an enhanced ability to suppress heat release and thereby lower the potential for secondary ignition.

The smoke produced during combustion is particularly critical, as it can dramatically reduce visibility at the fire site and hinder evacuation, while the inhalation of toxic gases poses a severe health risk. Pure PBS starts to release smoke at around 54 s, shortly after ignition, which occurs at 45 s, and the smoke generation continues until approximately 285 s. Compared to pure PBS, the presence of hydroxide maintained approximately constant the starting time of releasing smoke, and the time to ignition, except for the PBS ATH sample, for which the TTI is equal to 72 s. A marked reduction, by at least one order of magnitude, in the peak of the smoke production rate (SPR) is observed for the composites compared with neat PBS. The incorporation of natural magnesium hydroxide significantly suppresses smoke generation, while ATH shows a similar but less pronounced effect, particularly in the hybrid sample PBS MDH ATH 1 3, where the total smoke production at 1200 s is comparable to that of pure PBS. Overall, compared to polyolefin-based systems (see our previous work), the use of PBS as the polymer matrix leads to an

inherent reduction of roughly one order of magnitude in the total smoke produced during combustion.

Furthermore, the flame-retardant index (FRI) of PBS-based composites has been calculated considering Equation 3 [43], as follows:

$$\text{FRI} = \frac{[\text{THR} \times \frac{\text{pHRR}}{\text{TTI}}] \text{ polymer matrix}}{[\text{THR} \times \frac{\text{pHRR}}{\text{TTI}}] \text{ composite}} \quad (3)$$

FRI was calculated for all PBS-based composites to evaluate their overall fire retardancy performance, with neat PBS serving as the reference, and all data are shown in Table 6. The FRI is a dimensionless index that allows the comparison of flame-retardant effectiveness across different systems by simultaneously considering multiple cone calorimeter parameters, including peak heat release rate (pHRR), time to ignition (TTI), and total heat release (THR). It provides a comprehensive measure of the improvement in fire resistance relative to the neat polymer. As expected, the addition of hydroxides significantly improves the fire resistance of the polymer matrix. PBS MDH exhibits a moderate improvement, with an FRI of 5.94, indicating good flame retardancy. PBS ATH shows a more pronounced effect, achieving an FRI of 10.05, which classifies it as excellent in terms of fire-retardant performance. The hybrid composites containing both MDH and ATH display FRI values ranging from 8.25 to 11.04, reflecting a combined effect of the two additives. Among these, PBS MDH ATH 1 2 reaches the highest FRI (11.04), demonstrating the most effective flame retardant behavior. The other hybrid samples, PBS MDH ATH 1 1 (FRI = 9.27) and PBS MDH ATH 1 3 (FRI = 8.25), also show substantial improvements compared to neat PBS, although slightly lower than the best-performing hybrid. These results indicate that the synergistic combination of MDH and ATH in

TABLE 6 | Data of Heat Release Rate (HRR) and Smoke Production Rate (SPR), and final weight residue at 1200 s; radiant power = 50 kW/m².

	<i>Samples</i>					
	PBS	PBS MDH	PBS ATH	PBS MDH ATH 1 1	PBS MDH ATH 1 2	PBS MDH ATH 1 3
Heat Transfer						
Height of HRR peak [kW/m ²]	749	198	175	130	121	128
time of heat release peak [s]	135	95	100	95	125	95
total heat release (THR) at 600 s [MJ/m ²]	68.70	37.44	38.50	36.06	33.53	38.50
total heat release (THR) at 1200 s [MJ/m ²]	68.84	43.91	50.02	45.80	41.30	50.02
time to ignition (TTI) [s]	49	45	72	48	48	46
Flame Retardant Index (FRI)	—	5.94	10.05	9.27	11.04	8.25
Smoke Emission						
Height of SPR peak [m ² /s]	0.033	0.004	0.008	0.002	0.002	0.004
total smoke production at 600 s [m ²]	2.85	0.47	0.77	0.39	0.43	1.33
total smoke production at 1200 s [m ²]	2.92	0.5	1.16	0.57	0.98	2.73
Final Weight Residue at 1200 s [%]	1.68	33.86	40.37	49.36	46.14	46.41

the hybrid composites can enhance the overall flame-retardant performance, balancing reductions in peak heat release rate, total heat release, and smoke production. Overall, the FRI analysis confirms that the incorporation of hydroxides, particularly in optimized hybrid formulations, significantly increases the fire safety potential of PBS-based materials. Compared with other biodegradable-matrix FR systems like PLA- and resin-based systems, the PBS/MDH/ATH biocomposites developed in this study operate through analogous halogen-free mechanisms but achieve at least comparable, and in several respects superior, performance in terms of pHRR reduction and smoke suppression at similar or slightly higher mineral loadings. In PLA, several studies using aluminum or layered double hydroxides as sole flame retardants report a substantial but moderate reduction of the peak heat release rate (pHRR) at high filler loadings accompanied by a modest increase in char formation and only limited smoke suppression. These PLA systems also show a pronounced increase in stiffness and a strong decrease in elongation at break, similar to the mechanical behavior observed in the present PBS composite [44]. In particular, the combined use of MDH and ATH promotes the formation of a more continuous, ceramic-like protective layer, which translates into a pronounced decrease in heat release and an almost complete suppression of smoke, whereas most PLA and PBAT systems filled only with single hydroxides attain smaller pHRR reductions and retain significant smoke generation under cone calorimeter conditions. This enhanced fire performance, however, comes at the cost of a high elastic modulus and very low elongation at break, so the potential application window of the present PBS composites is mainly restricted to rigid or semi-rigid components where stiffness, dimensional stability and low smoke production are prioritized over impact resistance and ductility.

Furthermore, according to Chen et al. [39], the highest filler loading (i.e., at 60 wt.%) ensures appropriate fire-retardant properties

of PBS-based composites that the neat PBS does not possess. Chen et al. [39], as discussed before, conducted an investigation into the filler range from 10 to 60 wt.% and demonstrated that the highest filler loading guarantees acceptable LOI values and V-0 (according to UL-94), regardless of the morphology of the Mg(OH)₂ particles. In our study, MDH and ATH particles with diameters ranging from 2 to 5 µm are utilized, and given that our PBS-based composites contain MDH, ATH, or MDH/ATH at 60 wt.%, it is supposed that the fire-retardant properties could be considered comparable to those reported in the literature.

A spectroscopic analysis of neat PBS, MDH, ATH, and PBS-based composites was carried out before accelerated weathering to evaluate potential chemical interactions, and the obtained spectra are shown in Figure 11.

The ATR-FTIR spectra of the ATH (gibbsite) and MDH (brucite) structures (see Figure 11a), as reported in the literature [45–47], show good purity, although the MDH spectra reveal traces of carbonate. Concerning MDH, a strong peak can be observed at 3692 cm^{−1} related to the stretching of the OH group, which is characteristic of the O–H stretching vibration of brucite (Mg(OH)₂). There is also a peak at 1444 cm^{−1} and one at 882 cm^{−1} related to the asymmetric stretching and out-of-plane bending of the CO₃^{2−} group, which is strong evidence of carbonate impurities (e.g., magnesite, dolomite, or calcite). A peak can be observed at 1077 cm^{−1} related to the stretching of the Si–O group, which may be due to silicate minerals or secondary carbonate phases, in accordance with the peak at 964 cm^{−1} related to the bending of the OH group or the stretching of the Si–O group [46, 47]. It should be noted that the presence of carbonates does not necessarily have a negative effect, particularly when considering the role of MDH as a filler for flame-retardant applications. This is due to the fact that carbonates also undergo strongly endothermic decomposition, with the resultant release of CO₂. This contributes

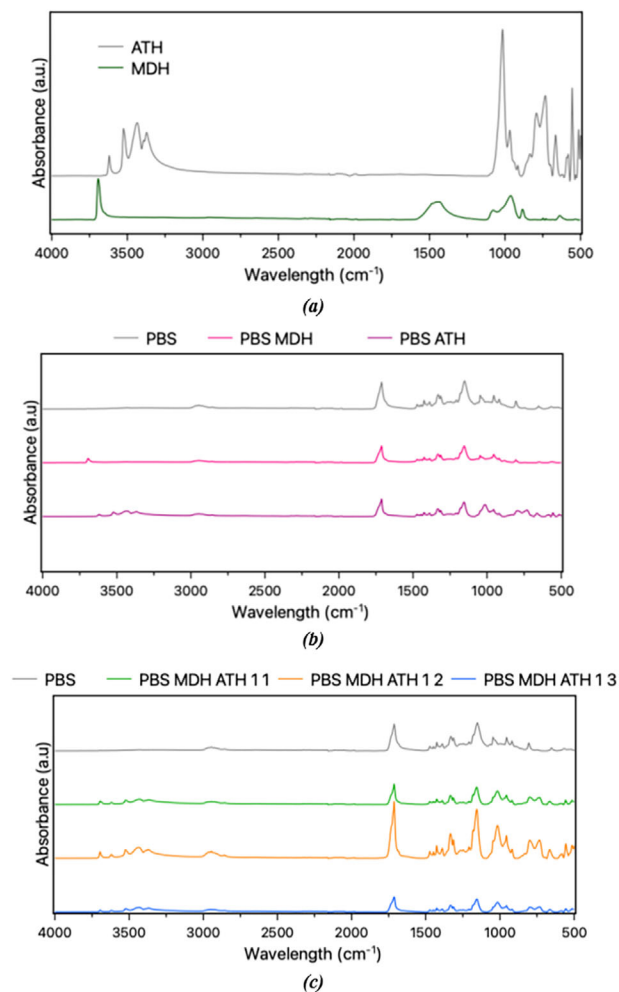


FIGURE 11 | ATR-FTIR spectra of: (a) MDH and ATH; (b) pure PBS, PBS MDH and PBS ATH; (c) pure PBS and PBS-based biocomposite with MDH/ATH hybrid compositions.

to the absorption of the heat emitted by the polymer at a different temperature with respect to MDH.

However, regarding the spectrum of ATH, the peaks at 3620 and 3524 cm^{-1} can be attributed to the $\nu(\text{OH})$ stretching of Al-OH bonds, which are typical of gibbsite. The 3435 cm^{-1} peak corresponds to the H-O-H stretching of adsorbed water, while the band at 3388 cm^{-1} is related to a broad $\nu(\text{OH})$ band due to hydrogen bonding. The 3371 cm^{-1} feature can be assigned to $\nu(\text{OH})$ stretching in an overlapping mode, still within the Al-OH or water region. Furthermore, Al-OH bending vibrations (possibly $\delta(\text{Al-OH})$) can be observed at 1016 cm^{-1} , corresponding to a characteristic in-plane OH deformation, and at 961 cm^{-1} , typically associated with $\delta(\text{Al-OH})$ bending in gibbsite. The 732 cm^{-1} band is assigned to $\delta(\text{H-O-H})$ bending of adsorbed water. Finally, Al-O bond vibrations can be detected from the peaks at 555 and 512 cm^{-1} .

As expected, all PBS-based biocomposites exhibited the typical characteristic peaks of PBS (see Figure 11b,c). The main absorption bands include the symmetric and asymmetric C-H stretching of methylene groups in the range of 2950–2850 cm^{-1} , carbonyl groups in the range 1750–1700 cm^{-1} and the vinyl group in the

range of 1000–900 cm^{-1} [48]. In particular, for samples containing MDH, a strong peak at 3692 cm^{-1} is clearly visible. For the sample containing ATH, the sequential peaks between 3620 and 3371 cm^{-1} dominate this spectral region, as they are all related to water content or to the $-\text{OH}$ functional groups of the hydroxides (see Figure 11b). Since no significant peak shifting was observed, it can be assumed that no chemical interactions occurred and that the fillers behave as inert particles within the PBS matrix.

A photo-degradation study was carried out using an accelerated weathering testing machine, exposing pure PBS and PBS-based biocomposites to UVB irradiation up to 120 h. The corresponding spectra at different exposure times are reported as supplementary files (see Figures S1–S6). Figure 12a,b shows the carbonyl accumulation (approximately 1750–1700 cm^{-1}) as a function of the photo-oxidation time for all the investigated samples.

According to the literature [49–52], depending on the environmental condition, PBS undergoes hydrolytic, oxidative, and thermal decomposition. Hydrolysis may occur through either depolymerization or random chain scission, both involving the cleavage of ester bonds along the polymer backbone upon exposure to moisture [53]. In the presence of oxygen, thermal and photo-induced degradation pathways of PBS are associated with the formation of radical species generated through hydrogen abstraction, predominantly involving hydrogen at the β -position, accompanied by cleavage of the relatively weak O-CH_2 bond. This reaction leads to the formation of succinic acid and polymer chains terminated with alkenyl segments and carboxylic acid groups [52]. Furthermore, the formation of carboxyl-containing cyclic structures has also been reported as part of the PBS degradation pathway [54]. Overall, the oxidative degradation mechanisms of PBS lead to the accumulation of large carbonyl and hydroxyl groups (e.g., formation of carboxylic acids) and alkenyl segments (e.g., vinyl saturations). Therefore, the PBS oxidative degradation could be profitably followed by monitoring the accumulation of carbonyl, hydroxyl, and vinyl groups in time, according to our previous work [53]. It is worth noting that the monitoring of the accumulation of the hydroxyl groups (approximately in the range 3600–3200 cm^{-1}) and vinyl groups (approximately in the range 1000–900 cm^{-1}) for PBS-based biocomposites is a hard matter because of the overlapping with typical peaks of MDH and ATH structures, and for this reason, the PBS photo-oxidative degradation has been monitored considering only the overall carbonyl accumulations, see Figure 12a,b. It seems that carbonyl accumulation occurs more rapidly in pure PBS than in the presence of MDH and/or ATH, which causes reduced carbonyl formation over time, even in MDH/ATH hybrid compositions. This can be explained by considering the alkaline nature of both MDH and ATH, which contrasts with the formation of succinic acid molecules.

4 | Conclusions

The production market for flame-retardant and fireproof materials is expanding rapidly, with a significant shift toward environmentally friendly compounds. In this study, PBS-MDH/ATH flame-retardant composites were studied, combining a potential bio-based, biodegradable polyester matrix with halogen-free min-

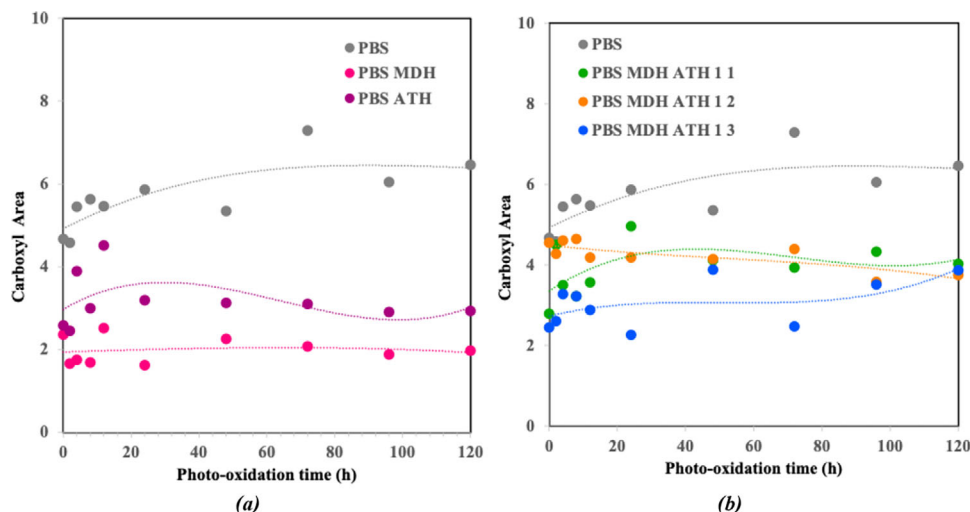


FIGURE 12 | Carbonyl area of (a) pure PBS, PBS MDH and PBS ATH, and (b) pure PBS and PBS-based biocomposite with MDH/ATH hybrid compositions.

eral flame retardants, thereby avoiding the use of halogenated additives and heavy metals.

The ATH demonstrated high purity and lamellar structures, exhibiting excellent dispersion within the PBS matrix. The MDH dispersion proved more challenging due to its rough surface. Consequently, the ATH exhibited a gibbsite structure, while MDH predominantly showed a brucite structure containing beneficial traces of dolomite (calcium and magnesium carbonates). The enhanced fire resistance of these carbonates is attributable to two principal factors. First, their high decomposition temperatures and, second, the formation of inert carbon dioxide during the process of combustion.

The investigation of all PBS-based biocomposites has demonstrated that they exhibit adequate processability and acceptable mechanical properties. Further perspectives and optimizations could rely on surface-modified hydroxides, for example $\text{Mg}(\text{OH})_2$ treated with stearic acid or stearates to improve dispersion, reduce melt viscosity, and allow lower total mineral loading while preserving flame retardancy. Stearic-acid coatings and magnesium stearate are already used at industrial scale as surface treatments and processing aids in polymer compounding, facilitating extrusion and injection molding by reducing die pressure and improving mold release, which makes these strategies directly transferable to PBS-MDH/ATH formulations. In parallel, hybrid systems combining mineral hydroxides with bio-based or phosphorus-containing flame retardants have recently shown promising fire performance in bioplastics, and could be explored to balance the inherently high modulus and very low elongation at break of the present PBS composites. Furthermore, enhanced photo-oxidative stability was observed in the presence of MDH and ATH, in comparison to the pure matrix. This phenomenon can be attributed to the contrasting alkaline properties of MDH and ATH, which are distinct from the process of succinic acid molecule formation resulting from PBS degradation. Future work should therefore include a more comprehensive durability and environmental assessment, covering not only accelerated photo-oxidative ageing but also hydrolytic degradation in fresh and salt water, as well as biodegradation tests in soil and marine

environments, in line with current standards for biodegradable plastics. Such studies will be essential to verify that the targeted fire performance can be maintained over service life and that the envisaged end-of-life scenarios are compatible with the presence of MDH and ATH, ultimately determining the feasibility of real-world applications for these flame-retardant PBS biocomposites.

It was established that both MDH and ATH were capable of reducing the peak heat release rate with effectiveness. This reduction in heat release rate resulted in enhanced ignition resistance and a significant reduction in smoke release. Furthermore, the combined MDH/ATH hybrid compositions exhibited clear synergistic effects, balancing two degradation steps to produce stable, ceramic-like char layers. This mechanism resulted in a drastic heat reduction and almost complete suppression of smoke, thereby demonstrating the high efficacy of this sustainable approach to producing flame-retardant materials. Finally, the presence of both MDH and ATH simultaneously offers the advantage of providing acceptable processability and a wide range of fire protection effects that are not offered by individual components.

Author Contributions

F.F. Formal analysis, Investigation; G.I. Conceptualization, Data curation, Formal analysis, Investigation, Validation, Writing – original draft, Writing – review & editing; G.B. Investigation, Software, Supervision, Writing – review & editing; D.T. Project administration, Resources, Supervision, Validation; L.C. Project administration, Resources, Software, Supervision, Writing – original draft; G.D.M.M. Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing; N.T.D. Conceptualization, Data curation, Investigation, Methodology, Writing – original draft; Writing –review & editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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