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Novel Hybrid Organic–Inorganic Polymeric Coatings Containing Phosphonium or Acidic Groups for Improving Flame Retardancy of Wood

Vasilis Koukoumtzis ^{1,2}, Georgia C. Lainioti ^{1,2,*} , George A. Voyiatzis ²  and Joannis K. Kallitsis ^{1,2} ¹ Department of Chemistry, University of Patras, GR-26504 Patras, Greece² Foundation for Research and Technology-Hellas, Institute of Chemical Engineering Sciences (FORTH/ICE-HT), GR-26504 Rio-Patras, Greece

* Correspondence: glainioti@upatras.gr; Tel.: +30-261-099-7121

Abstract: Flame-retardant polymeric coatings with high limiting oxygen index (LOI) were prepared by combining inorganic mineral huntite (H5) and polymeric additives synthesized in the present work into a polymeric formulation. In order to improve the dispersion of the Mg- (and Ca)-based H5 particles, additives containing phosphonium and acidic groups were employed to homogenize the inorganic fillers into the polymer matrix. Specific blend combinations of the commercial matrix Ecrovin[®] LV 340 eco with huntite and the additives poly(benzyltriphenylphosphonium-co-4-styrene sulfonic acid) P(SSH-co-SSBTPB60) and poly(hexadecyltributylphosphonium-co-4-styrene sulfonic acid) P(SSH-co-SSTBHDPB80), combining acidic and phosphonium groups, led to LOI values of 34.5% and 33.5%, respectively. The novel flame-retardant polymeric coatings inhibited the combustion of the coated wood substrates, which is attributed to the combination of acidic groups that promote the dispersion of inorganic filler in the polymer matrix and phosphonium groups that support the increase in LOI values.

Keywords: phosphonium additives; acidic additives; huntite; polymer matrix; flame-retardant polymeric coatings; limited oxygen index



Citation: Koukoumtzis, V.; Lainioti, G.C.; Voyiatzis, G.A.; Kallitsis, J.K.

Novel Hybrid Organic–Inorganic Polymeric Coatings Containing Phosphonium or Acidic Groups for Improving Flame Retardancy of Wood. *Coatings* **2023**, *13*, 754. <https://doi.org/10.3390/coatings13040754>

Academic Editor: Mazeyar Parvinzadeh Gashti

Received: 21 February 2023

Revised: 29 March 2023

Accepted: 7 April 2023

Published: 9 April 2023



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1. Introduction

There is great interest in the field of polymer-based flame-retardant materials as new fire safety standards require enhanced protection in the domestic, public and industrial sectors [1]. The number of building fires and the resulting losses have increased significantly worldwide in the last decade [2–4]. The rapid spread of fires is localized in the external façade, which includes combustible ingredients that constitute potential fire hazards like wood and wood-based materials, polystyrene and polyurethane foams. In particular, the use of wood for family houses, as well as for mid- to high-rise buildings, has become very popular [5–7]. However, the high flammability of wood products has drawn scientific and industrial attention to the need to develop and use novel flame retardants for wood products [8].

There are some main ways to reduce the flammability of wood by chemical treatments: wood chemical impregnation, incorporation of the flame retardant into the glue or surface treatment with flame-retardant coatings [9–16].

In the last 40 years, the most predominant flame retardants (FRs) were halogenated flame retardants (HFRs). However, the production of carcinogens and the combustion process of those materials has led to the use of new halogen-free FRs in wood products, which are expected to be environmentally friendly and non-hazardous to human health [17–19]. These new flame-retardant additives involve phosphorus-, nitrogen-, silicone-, boron-, zinc-, iron- and aluminum-containing compounds. Phosphorus-based flame retardants are extensively used in wood products as they promote flame retardation by undergoing

dehydration and carbonization to form protective carbon layers, leading to the effective reduction of polymers' flammability [20–24]. Some of the phosphorus-based FRs that are commonly used are phosphine oxides, red phosphorus (RP), phosphines, phosphates, phosphonates, ammonium phosphate and phosphites [25–27].

In recent years, the basic understanding and development of essential knowledge have led to the combined use of phosphorus compounds with minerals, giving rise to flame-retardant coatings to be used for wood applications [28–32]. The use of flame retardants leads to the alteration of polymers' decomposition route aiming at the reduction of combustible volatiles' concentration by promoting char formation. The char may be intumescent, offering heat and fire resistance until it reaches a critical temperature above which it burns [33].

Huntite and hydromagnesite have been used as flame-retardant additives in various polymers such as polypropylene, polyethylene, ethylene propylene copolymer, ethylene vinyl acetate (EVA), vinyl ester resin and poly vinylchloride [34–36]. Huntite minerals occur naturally in economically significant reserves in a variety of environments, such as in Türkiye [37] and Greece [38]. There are many studies on the usage of huntite/hydromagnesite mineral mixtures as FR additives for various applications [39]. Their mixtures have endothermic decomposition, which is similar to the flame retardants mostly used [40]. Actually, the mixture of hydromagnesite and huntite provides a broad decomposition range from ~220 °C to ~750 °C. During these decomposition reactions, approximately more than half of the original mass of the mixture of hydromagnesite and huntite is released as carbon dioxide and water. Huntite-enriched minerals are also reported as effective smoke suppressors, and although introduced to the market in the last decades [41], they are candidates, especially in the plastic and textile industries, for the production of sustainable, bio-based and halogen-free FR products.

In the literature, huntite and hydromagnesite (HH) have been mostly used as mixtures and have been combined with some phosphorus-based FRs in order to increase the flame-retardant effect of HH with synergistic effects. Savas et al. [42] studied the effect of microcapsulated red phosphorus (mRP) on the flame-retardant properties of thermoplastic polyurethane composites containing huntite and hydromagnesite. They found that when HH and mRP are used together, a synergistic interaction was observed, with the highest LOI value (32.5%) observed at 7 wt. % mRP and 43% HH loading in the final mixture. Liodakis and Antonopoulos [43] also found that the fire retardation efficiency of diammonium phosphate seemed to have a better overall performance with the addition of huntite/hydromagnesite. The combination of phosphorus-based FRs with inorganic filler, such as huntite, may lead to flame-retardant properties with essential characteristics, such as halogen free and environmentally friendly.

In the present work, the development of new flame-retardant additives was studied, which help the better dispersion of the rich-in-huntite inorganic filler H5 (mixture of huntite, $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$, ~88 wt. % and hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, ~12 wt. %) for the preparation of flame-retardant coatings. More specifically, phosphonium and acidic groups were combined in copolymers in order to enhance the compatibility between the inorganic fillers and the polymer matrices. The polymeric additives synthesized are the functional copolymers poly(benzyltriphenylphosphonium-co-4-styrene sulfonic acid) and poly(hexadecyltributylphosphonium-co-4-styrene sulfonic acid). The polymer matrices employed in the present work were poly(methyl methacrylate) (PMMA), poly(methyl methacrylate-co-butyl acrylate) (P(MMA-co-BA)), poly(vinyl acetate) (PVAc) and the commercially available Ecrovin[®] LV 340 eco. The new coatings were mainly examined in terms of the combustibility of materials by measurements of the limiting oxygen index (LOI) of solid specimens.

It is worth noting that the combination of phosphorus compounds with acidic groups and minerals based mainly on huntite may lead to new selective additives.

Their synergistic action will contribute to the avoidance of side effects, such as water picking up the deceleration of swelling, which may lead to a decrease in the resulting

protective layer and a change in the combustion behavior towards residue-forming materials [44].

2. Materials and Methods

2.1. Materials

The reagent triphenyl phosphine and the surfactant hexadecyltributylphosphonium bromide (TBHDPB) were purchased from Merck (Merck KGaA, Darmstadt, Germany) and used as received. The reagent benzyl bromide, as well as deuterated chloroform (CDCl_3) and hydrochloric acid (HCl), the solvents ethyl acetate $\geq 99.5\%$, toluene $\geq 99.5\%$ methyl ethyl ketone (MEK) $\geq 99.0\%$, tetrahydrofuran (THF) $\geq 99.9\%$ and ethanol 95%, were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) and used as received. The polymer poly(sodium styrene sulfonate) (PSSNa) (average $M_w \sim 70,000$) was supplied by Alfa-Aesar (Thermo Fisher (Kandel) GmbH, Kandel, Germany), while poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate-co-butyl acrylate) (P(MMA-co-BA)) were supplied by BDH Chemicals Ltd. (BDH Chemicals Ltd., Poole, UK). The polymer matrix Ecrovin[®] LV 340 eco and the dispersants Polydisp A and Loraphos PA30 were kindly provided by the company Loufakis Chemicals SA (Loufakis Chemicals SA, Thessaloniki, Greece). The mineral huntite, H5, was kindly provided by the company Sibelco (Sibelco Hellas SA, Thessaloniki, Greece) and consisted of a huntite/hydromagnesite mixture, 88/12 wt./wt. %; the ratio was calculated by neglecting minor concentrations of other minerals, mostly dolomite [14,19,45]. Ultra-pure water was obtained by means of an SG apparatus water purification unit. The wood samples used for coating were birch plywood with dimensions 90 mm \times 9 mm \times 7 mm, complying with EN 13238 [46] and with minimum knots in the surface layer (since knots may influence the test results at small-scale testing). Coating was performed at 25 °C and 50% relative humidity.

2.2. Chemical Characterization

2.2.1. Nuclear Magnetic Resonance Hydrogen Spectroscopy ($^1\text{H-NMR}$)

The Bruker Avance DPX 400 spectrometer (Bruker BioSpin GmbH, Magnet Division, Karlsruhe, Germany) was used to study the materials in terms of their structure and composition. The $^1\text{H-NMR}$ spectra were obtained at 400 MHz at 300 K. Deuterated chloroform (CDCl_3) with internal tetramethylsilane (TMS) standard was used to dissolve the samples. For analysis of NMR data, the software Topspin-3.6.1 (Bruker, Karlsruhe, Germany) was used.

2.2.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out in alumina crucibles in a Lab-sysTMTG (Caluire, France) apparatus of Setaram from 25 to 800 °C and in a platinum pan in a TA Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE, USA) and heated from 25 to 800 °C under nitrogen and at a heating rate of 10 °C/min. The TGA data analysis software was Setsoft 2000 (Setaram, Caluire, France, version 2000).

2.2.3. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR spectra were obtained from Bruker Optics Alpha-P Diamond ATR Spectrometer of Bruker Optics GmbH (Ettlingen, Germany). ATR-FTIR spectroscopy was performed at room temperature in the range between 500 and 4000 cm^{-1} . The individual polymer samples were placed onto the ATR crystal and were simply pressed by using a pressure clamp. The ATR crystal was cleaned with ethanol after every measurement to prevent sample contamination. The spectra were collected as a result of 12 running scans at a resolution of 4 cm^{-1} . ATR-FTIR spectra analysis software was Opus 7.5 (Bruker, Ettlingen, Germany, version 7.5). The format of the spectra is transmission vs. wavenumber.

2.2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM, Zeiss SUPRA 35VP instrument equipped with an EDS detector, Oberkochen, Germany) was performed to investigate the cross-section morphologies of the composite membranes. The membrane samples were frozen in liquid nitrogen, broken and sputtered with gold to produce electric conductivity before SEM examination. The cross-section of the broken parts was finally examined with SEM. The magnification level was 1.00 K X and 10.00 K X.

2.3. Synthesis of Phosphonium Flame Retardants

2.3.1. Benzyltriphenylphosphonium Bromide (BTPB)

Into a 500 mL degassed round-bottom flask, toluene (300 mL), triphenyl phosphine (80 g, 0.305 mol) and benzyl bromide (33 mL, 0.277 mol) were added. After the addition of each substance, the content of the flask was degassed through argon–vacuum cycles. The system was then placed in an oil bath at 105 °C and was left under stirring for 24 h in an argon atmosphere. Then, the temperature was reduced to 50 °C, and the system was left under stirring for 5 h in an argon atmosphere to complete the precipitation of the solid that was filtered and thoroughly washed with ethyl acetate. The final material was dried at room temperature (RT) for 2 days under vacuum. The product benzyltriphenylphosphonium bromide (BTPB) was characterized through proton nuclear magnetic resonance ($^1\text{H-NMR}$) (Figure 1a), where the characteristic peaks of aromatic protons at 7.0–7.2 ppm (e–g) and 7.8 ppm (a,b) and the protons of the phosphonium methylene group at 5.1–5.2 ppm (c) confirm the successful synthesis. Moreover, BTBP was characterized using thermogravimetric analysis (TGA) showing high thermal stability up to 400 °C (Figure 1b), while the residue at 800 °C constitutes 90% of the initial weight of the sample.

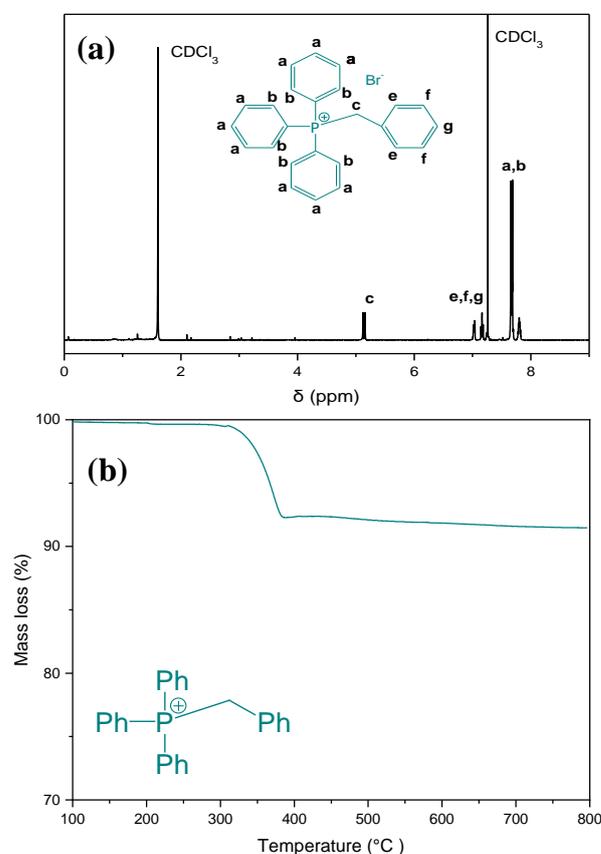


Figure 1. (a) $^1\text{H-NMR}$ spectrum and (b) TGA graph for the synthesized benzyltriphenylphosphonium bromide (BTPB).

2.3.2. Poly(benzyltriphenylphosphonium 4-Styrenesulfonate)-PSSBTPB

Into a 100 mL round-bottom flask, PSSNa (4 g, 0.0194 mol) and triple-distilled H₂O (36 mL) were added and left under stirring until the PSSNa was completely dissolved (system 1). Into a second 250 mL flask benzyltriphenylphosphonium bromide (BTPB) (9.2 g, 0.02123 mol) and ethanol 95% (72 mL) were added (system 2). After complete dissolution of BTPB, system 2 was added dropwise to System 1. After one hour, triple-distilled H₂O (300 mL) was added to the solution. The system was left under stirring for 24 h. Filtration was followed and the collected solid was dried under vacuum at 60 °C for 24 h. Characterization of the homopolymer PSSBTPB was conducted by infrared spectroscopy (ATR-FTIR) (Figure 2a) and thermogravimetric analysis (TGA) (Figure 2b).

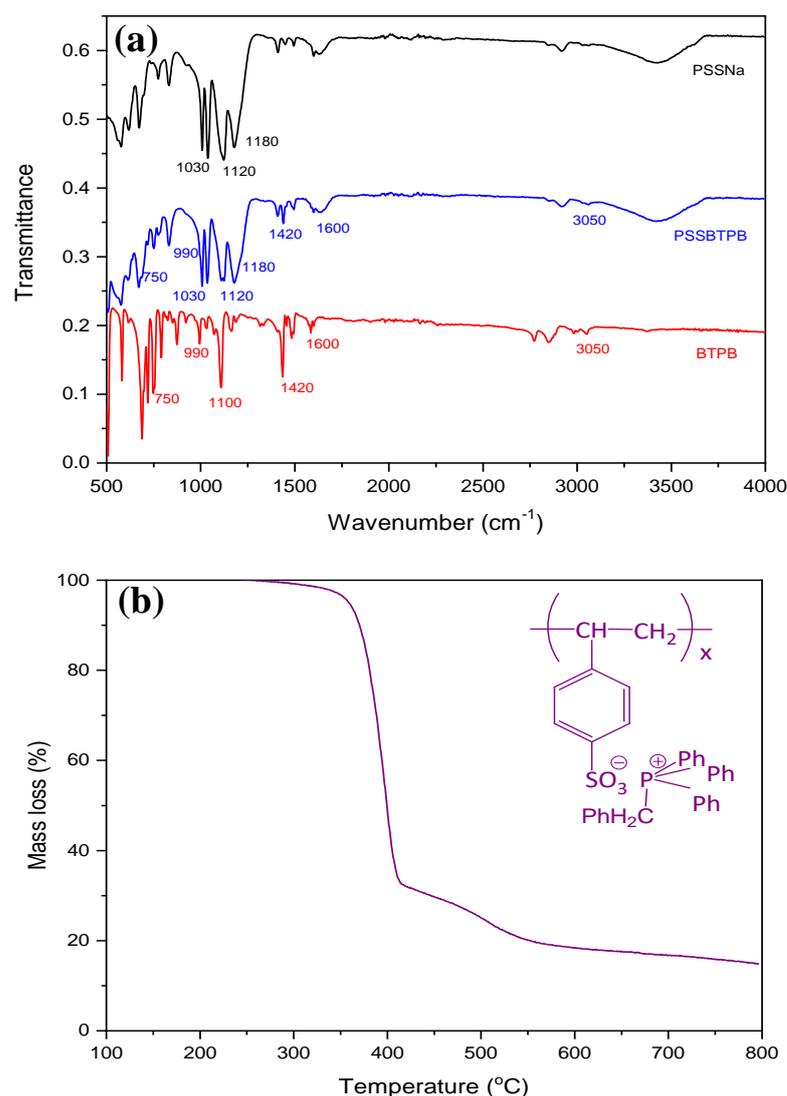
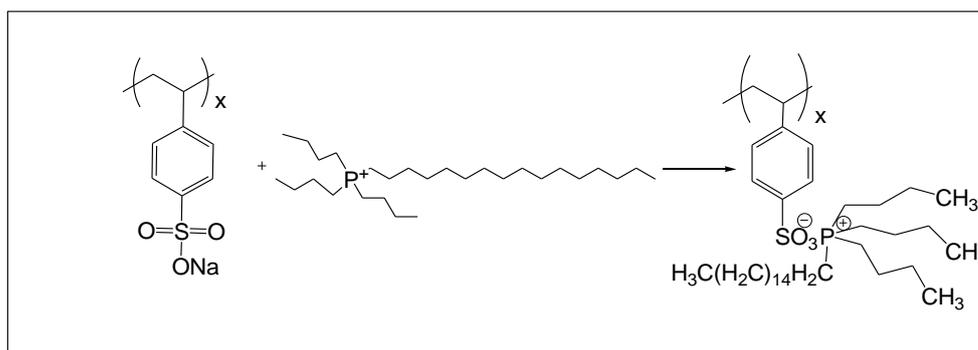


Figure 2. (a) ATR-FTIR spectra and (b) TGA graph for the synthesized benzyltriphenylphosphonium 4-styrenesulfonate homopolymer (PSSBTPB).

2.3.3. Poly(hexadecyltributylphosphonium 4-Styrene Sulfonate)-PSSTBHDPB

The homopolymer PSSTBHDPB was synthesized using PSSNa and the surfactant hexadecyltributylphosphonium bromide (TBHDPB), as reported elsewhere [47]. The synthetic procedure is shown in Scheme 1.



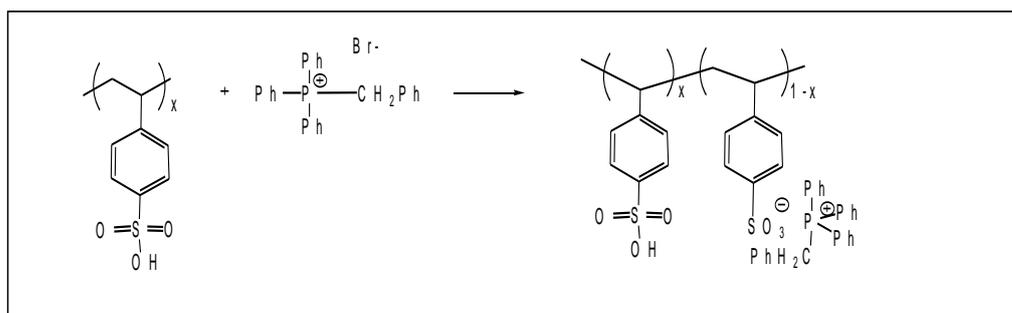
Scheme 1. Reaction between PSSNa and the surfactant TBHDPB.

2.4. Synthesis of Phosphonium-Based Oligomers

2.4.1. Poly(benzyltriphenylphosphonium-co-4-styrene Sulfonic Acid)-P(SSH-co-SSBTPB)

Into a 250 mL beaker, the homopolymer poly(sodium styrenesulfonate) PSSNa (10 g, 0.049 mol) and HCl 3 M (100 mL) were added and were left under stirring for 24 h. The solution was then transferred to a dialysis membrane and was left for 2 days. The final material was collected through a rotary evaporator and dried under vacuum at 60 °C for 24 h.

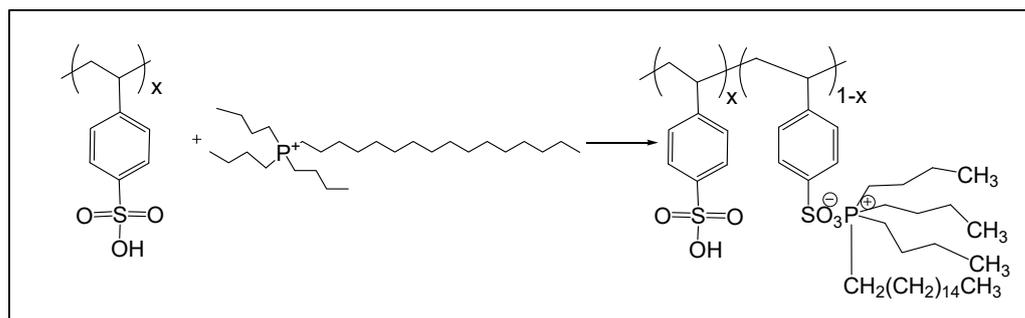
Into a 10 mL beaker, PSSH (0.1 g, 0.543 mmol) and triple distilled water (0.5 mL) were added and were left under stirring until the complete dissolution of PSSH. At the same time, into another 10 mL beaker, BTPB (0.118 g, 0.272 mmol) and ethanol 95% (2 mL) were added and the system was left under stirring until the solid was dissolved. Then, the BTPB solution was added dropwise to the PSSH solution, and the whole system was stirred for one hour. The partially modified PSSH polymer is presented in Scheme 2 and will be denoted as P(SSH-co-SSBTPB60) for simplicity, where 60 is the mol percentage of phosphonium compounds (x and $(1 - x)$ are the mol % fractions of SSH and SSBTPB units, respectively).



Scheme 2. Synthesis of the copolymer P(SSH-co-SSBTPB).

2.4.2. Poly(hexadecyltributylphosphonium-co-4-styrene Sulfonic Acid) P(SSH-co-SSTBHDPB)

Into a 10 mL beaker, PSSH (0.1 g, 0.543 mmol) and triple distilled water (0.5 mL) were added and were left under stirring until the dissolution of PSSH. At the same time, into another 10 mL beaker, the surfactant TBHDPB (0.22 g, 0.433 mmol) and ethanol 95% (2 mL) were added and the system was left under stirring. After both materials were dissolved, the TBHDPB solution was added dropwise to the PSSH solution, and the whole system was stirred for one hour. The copolymer was precipitated after the reaction completion. After rinsing thoroughly with water, the product was dried under vacuum at 60 °C. The partially modified PSSH polymer is presented in Scheme 3 and will be denoted as P(SSH-co-SSTBHDPB80), where 80 is the mol percentage of phosphonium compounds (x and $(1 - x)$ are the mol fractions of SSH and SSTBHDPB units, respectively).



Scheme 3. Synthesis of the copolymer P(SSH-co-SSTBHDPB).

2.5. Blend Preparation of Polymer Matrices and Flame Retardants

Blends of polymer matrix and phosphonium or acidic additives have been prepared. The polymer matrices that have been used were PMMA, P(MMA-co-BA), PVAc and Ecrovin[®] LV 340 eco. The phosphonium-based additives used were BTBP and PSSBTPB, whereas the acidic additives were poly(benzyltriphenylphosphonium 4-styrene sulfonic acid), P(SSH-co-SSBTPB) and poly(hexadecyltributylphosphonium 4-styrene sulfonic acid) P(SSH-co-SSTBHDPB). Precisely, the additives were dissolved in the appropriate solvent at a concentration of 10% *w/v*. After complete dissolution of the additive, the inorganic mineral H5 was added to the solution, and the system was left until complete homogenization. For selected matrices, H5 was added to the solution prior to the addition of the polymer matrix. The system was finally placed in an ultrasonic bath for 5 min in order to elaborate the dispersion of the final mixture. For PMMA blends, a solvent mixture of THF and ethanol 95% was used; for P(MMA-co-BA) and PVAc blends, the solvent was MEK; and for Ecrovin[®] LV 340, eco water was used as solvent. The total amount of the prepared polymer blends was 10 g, and the quantities of the polymer matrix, H5 and additives varied depending on the blend content (% wt.).

The final blend was poured into an aluminum or glass plate and was left at room temperature (RT) or placed in an oven at 80 °C for complete solvent evaporation. The film was removed from the plate, and visual observations in terms of its quality and integrity were made. The combustion of materials was tested through LOI measurements that were performed on plywoods of specific dimensions covered with each blend.

2.6. Application of Coatings onto Wood Substrates

After blend preparation, the plywood with dimensions 90 mm × 9 mm × 7 mm were immersed into the blend solution and were left to dry at RT for 5 min. The procedure was repeated three times until the loading of the coating was approximately 500 g m⁻². Finally, all the wood substrates were dried in an oven at 70 °C for 4 h. The coated plywood substrates are shown in Figure 3.

2.7. Limiting Oxygen Index (LOI) Tests

The standardized limiting oxygen index (LOI) test (ASTM D2863-70, standard method of test for flammability of plastics using the oxygen index method) was used to evaluate the flame-retardant properties of the coatings. The sample was placed in a vertical position, and the flame was applied to the top of the coated wood. Measurements of LOI were performed in accordance with ISO 4589.

LOI is expressed as: $LOI = 100 ([O_2] / ([O_2] + [N_2]))$.

The LOI was measured for each sample in duplicate.



Figure 3. Plywood specimens prepared for LOI measurements. Unburned specimen coated with (a) polymer matrix/H5/additive and (b) burned specimen.

3. Results

3.1. Fire Retardancy Testing of Polymer Matrices

In the first step, pure matrices were used in order to test the combustibility of materials through LOI measurements. The results are shown in Table 1.

Table 1. LOI measurements of neat matrices.

Code	Polymers	LOI (%)
I-A	PMMA	19.0 ± 0
II-A	P(MMA-co-BA)	19.0 ± 0.0
III-A	PVAc	23.0 ± 0.5
IV-A	Ecrovin [®] LV 340 eco	23.0 ± 0.0

From the results, PMMA and P(MMA-co-BA) showed LOI values of 19.0%, and the polymers PVAc and Ecrovin[®] LV 340 eco showed LOI values of 23.0%, indicating that they were easy to burn.

3.2. Characterization of Coatings with Phosphonium and Acidic Oligomers

Initially, blends of the polymer matrices with phosphonium and acidic oligomers were conducted without the addition of the inorganic mineral H5. The phosphonium-based compounds tested were BTBP, PSSBTBP, PSSTBHDPB, P(SSH-co-SSBTBP60) with 60% BTPB content and P(SSH-co-SSTBHDPB80) with 80% TBHDPB content. The phosphorus contents were calculated through the composition of the copolymers. The results are shown in Tables 2–4.

In the first step, blends of PMMA with the additives were prepared in order to test whether the additives would reduce the combustibility (LOI) of the neat polymer. Specimens with dimensions of 70 mm × 6.5 mm × 3 mm were prepared, as mentioned above. The results are presented in Table 2. As it may be seen, the addition of phosphonium or acidic additives to the polymer, in percentages 5%–10% of the total mass, corresponding to phosphorus content of 0.3%–0.6% in the mixture, seems to increase LOI by one or three percentage points. Consequently, the oligomers' addition to the PMMA matrix does not greatly alter the combustibility of the polymer since no cross-linking networks are formed between the polymer and the flame-retardant, and therefore no char is formed to protect the polymer.

Table 2. LOI measurements of PMMA blends.

Code	Polymer Matrix/Additive	Matrix Content (%)	Additive Content (%)	P Content (%)	LOI (%)
I-B	PMMA/BTPB	95	5	0.3	19.0 ± 0.3
I-C	PMMA/PSSBTPB	95	5	0.3	20.0 ± 0.3
I-D	PMMA/PSSBTPB	90	10	0.6	20.0 ± 0.2
I-E	PMMA/PSSTBHDPB	90	10	0.5	21.0 ± 0.5
I-F	PMMA/PSSH	90	10	-	20.0 ± 0.2
I-G	PMMA/P(SSH-co-SSBTPB60)	90	10	0.5	21.0 ± 0.2
I-H	PMMA/P(SSH-co-SSTBHDPB80)	90	10	0.6	22.0 ± 0.2

Table 3. LOI measurements of P(MMA-co-BA) blends.

Code	Polymer Matrix/Additive	Matrix Content (%)	Additive Content (%)	P Content (%)	LOI (%)
II-B	P(MMA-co-BA)/BTBP	95	5	0.3	19.0 ± 0.2
II-C	P(MMA-co-BA)/PSSBTPB	95	5	0.3	20.2 ± 0.1
II-D	P(MMA-co-BA)/PSSBTPB	90	10	0.6	20.4 ± 0.3
II-E	P(MMA-co-BA)/PSSTBHDPB	90	10	0.7	23.0 ± 0.4
II-F	P(MMA-co-BA)/P(SSH)	90	10	-	20.2 ± 0.3
II-G	P(MMA-co-BA)/P(SSH-co-SSBTPB60)	90	10	0.3	20.3 ± 0.5
II-H	P(MMA-co-BA)/P(SSH-co-SSTBHDPB80)	90	10	0.6	23.5 ± 0.1

Table 4. LOI measurements of PVAc blends.

Code	Polymer Matrix/Additive	Matrix Content (%)	Additive Content (%)	P Content (%)	LOI (%)
III-B	PVAc/PSSBTPB	95	5	0.3	23.0 ± 0.3
III-C	PVAc/PSSBTPB	90	10	0.6	24.0 ± 0.0
III-D	PVAc/PSSTBHDPB	90	10	0.7	24.0 ± 0.1
III-E	PVAc/P(SSH-co-SSBTPB60)	90	10	0.3	26.0 ± 0.0
III-F	PVAc/P(SSH-co-SSTBHDPB80)	90	10	0.6	26.0 ± 0.2

In a further attempt, P(MMA-co-BA) and PVAc polymer matrices were used to test LOI values for blends with phosphonium and acidic additives. As shown in Table 3, the blends with the P(MMA-co-BA) polymer matrix did not show a significant increase in LOI values in all cases.

In the case of PVAc, as shown in Table 4, the addition of PSSBTPB and PSSTBHDPB led to LOI values of 23.0%–24.0%, since the LOI of pure PVAc was 23.0%. Blends of PVAc with phosphonium and acidic additives led to higher values of LOI (26.0%). Optical observation of films indicated a good quality.

The last system studied consisted of blends with the matrix Ecrovin[®] LV 340 eco with the additives synthesized in the present work. The results are shown in Table 5.

The systems IV-B, IV-C and IV-D presented LOI values of 25.0%, whereas blends with acidic copolymers (IV-E to IV-G) led to LOI values of 26.0%–28.0%.

3.3. Addition of H5 Mineral in the Polymer Matrix/Additive Systems

In order to combine the phosphonium flame-retardant additives with polymer matrices and the inorganic filler H5, P(MMA-co-BA) and PVAc polymers were used to test the LOI values of wood coated with P(SSH-co-SSBTPB) and P(SSH-co-SSTBHDPB) additives. Both copolymers combine the action of phosphonium and acidic groups. The results are shown in Table 6.

Table 5. LOI measurements of Ecrovin[®] LV 340 eco blends.

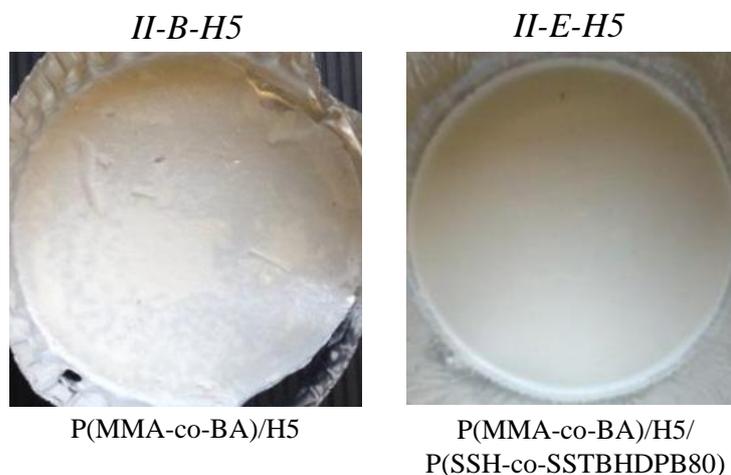
Code	Polymer Matrix/Additive	Matrix Content (%)	Additive Content (%)	P Content (%)	LOI (%)
IV-B	Ecrovin/PSSBTPB	95	5	0.3	25.0 ± 0.1
IV-C	Ecrovin/PSSBTPB	90	10	0.6	25.0 ± 0.1
IV-D	Ecrovin/PSSBHDHPB	90	10	0.7	25.0 ± 0.3
IV-E	Ecrovin/PSSH	90	10	-	26.0 ± 0.5
IV-F	Ecrovin/P(SSH-co-SSBTPB60)	90	10	0.3	28.0 ± 0.0
IV-G	Ecrovin/P(SSH-co-SSTBHDHPB80)	90	10	0.6	28.0 ± 0.1

Table 6. LOI measurements of P(MMA-co-BA) blends with H5 and additives.

Code	Polymer Matrix/Additive	Matrix Content (%)	H5 Content (%)	Additive Content (%)	P Content (%)	LOI (%)
II-A	P(MMA-co-BA)	100	-	-	0	19.0 ± 0
II-B-H5	P(MMA-co-BA)/H5	66.0	34.0	-	0	22.0 ± 0
II-C-H5	P(MMA-co-BA)/H5	50.0	50.0	-	0	23.0 ± 0.5
II-D-H5	P(MMA-co-BA)/H5/P(SSH-co-SSBTPB60)	52.6	26.4	21.0	0.8	-
II-E-H5	P(MMA-co-BA)/H5/P(SSH-co-SSTBHDHPB80)	52.6	26.4	21.0	0.9	26.0 ± 1.0

Given the fact that P(MMA-co-BA) is a polymer with very high combustibility (LOI 19%), it is important to note that the addition of H5 increased the LOI from 19% to 22%–23% compared to neat polymer. The use of P(SSH-co-SSBTPB) resulted in no film formation due to the high viscosity of the H5/additive mixture, which could not give films for further study. The addition of P(SSH-co-SSTBHDHPB) copolymer to the P(MMA-co-BA)/H5 mixtures resulted in a decrease in materials' combustibility. This was tentatively attributed both to the potential synergy between H5 and phosphorus and the better dispersion of H5 particles after modification due to specific interactions between the hydroxyl groups of the hydromagnesite portion of the mineral H5 (the inorganic filler huntite, H5, is a mixture of huntite, $Mg_3Ca(CO_3)_4$, ~88 wt. % and hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, ~12 wt. %), which is present in even a small proportion, and the acidic groups of PSSH, resulting in the formation of a more compact and cohesive char.

As shown in Figure 4, the P(SSH-co-SSTBHDHPB) copolymer also led to very good-quality films, which is already attributed to the presence of poly(styrenesulfonic acid) (PSSH) acidic groups in the solution, which can interact with the hydroxyl groups of H5, as described above. The mineral modified in this way is better dispersed in the solution, thus improving the quality of the coating.

**Figure 4.** Photographs of the films P(MMA-co-BA)/H5 and P(MMA-co-BA)/H5/P(SSH-co-SSTBHDHPB80).

In the case of PVAc blends with H5 and polymeric additives, Table 7 shows that PVAc, a polymer with LOI values of 23.0%, presented increased LOI with the addition of H5. In particular, when the polymer-to-H5 ratio was 1/1, the LOI increased up to 12 percentage points, in contrast to an increase of 7 percentage points observed at the 2/1 PVAc/H5 ratio, and the film quality remains very good. This proves the low combustibility of H5 and indicates that using it at a rate equal to or greater than that of the polymer matrix will give higher LOI values. Thus, a higher percentage of H5 is incorporated into the polymer reducing the temperature of the cracking process and releasing a higher percentage of water vapor that dilutes the combustible gases, as well as the flammable acetic acid formed during the decomposition of PVAc [48,49]. Finally, a higher percentage of char is generated through the formation of mainly MgO but also CaO, resulting from the thermal decomposition of huntite, which protects the substrate (polymeric matrix) [45].

Table 7. LOI measurements of PVAc blends with H5 and additives.

Code	Polymer Matrix/Additive	Matrix Content (%)	H5 Content (%)	Additive Content (%)	P Content (%)	LOI (%)
III-A	PVAc	100	-	-	0	23.0 ± 0.5
III-B-H5	PVAc/H5	66.0	34.0	-	0	30.0 ± 0
III-C-H5	PVAc/H5	50.0	50.0	-	0	35.0 ± 1.0
III-D-H5	PVAc/H5/P(SSH-co-SSBTPB60)	38.0	38.0	24.0	1.04	31.0 ± 0
III-E-H5	PVAc/H5/P(SSH-co-SSBTPB60)	46.9	23.4	29.7	1.29	-
III-E-H6	PVAc/H5/P(SSH-co-SSTBHDPB80)	35.7	35.7	28.6	1.2	33.5 ± 0.5

The addition of the copolymer P(SSH-co-SSBTPB60) as an additive kept the system's combustibility at low levels with an LOI value of 31%. It is worth noting that when the polymer matrix/H5 ratio was 2/1, the mixtures could not give films as a high-viscosity precipitate was formed upon the addition of PVAc, as in the case of P(MMA-co-BA) mentioned previously. On the contrary, when the polymer matrix/H5 ratio was 1/1 and the amount of mineral was higher than that of the additive in the mixture, no precipitate was formed, and the coatings were of good quality, as shown in Figure 5. The addition of P(SSH-co-SSTBHDPB) led to a further increase in LOI values but was not better than the PVAc/H5 blend.

III-E-H6



PVAc/H5/P(SSH-co-SSTBHDPB80)

Figure 5. Photographs of the film PVAc/H5/P(SSH-co-SSTBHDPB80).

Ecrovin[®] LV 340 eco polymer matrix and H5 mixtures were initially prepared in comparison to previous work [45]. Then, H5 was added to the polymer matrix at a polymer/H5 ratio of 1/1 to study the effect of the mineral on the combustibility of Ecrovin[®] LV 340 eco. The prepared mixtures are presented in Table 8.

Table 8. LOI measurements of Ecrovin[®] LV 340 eco blends with H5 and additives.

Code	Polymer Matrix/Additive	Matrix Content (%)	H5 Content (%)	Additive Content (%)	P Content (%)	LOI (%)
IV-A	Ecrovin	100	-	-	-	23.0 ± 0
IV-B-H5	Ecrovin/H5	50.0	50.0	-	-	29.5 ± 0.5
IV-C-H5	Ecrovin/H5/P(SSH-co-SSBTPB60)	38.5	38.5	23.0	0.96	34.5 ± 0.5
IV-D-H5	Ecrovin/H5/P(SSH-co-SSTBHDPB80)	38.5	38.5	23.0	1.1	33.5 ± 0.5

The addition of H5 increased the LOI up to 6.5 percentage points as hydrogen bonds are likely formed between the hydroxyl groups of H5 and the carboxyl groups of the polymer matrix, leading to better dispersion of the mineral and better integration into the polymer matrix. A reduction in materials' combustibility was also noted with the addition of oligomers to the Ecrovin[®] LV 340 eco/H5 mixture. The addition of P(SSH-co-SSBTPB60) and P(SSH-co-SSTBHDPB80) gave LOI values of 34.5% and 33.5%, respectively. As can be seen, the highest LOI values appeared in the mixture with the lower P content, the IV-C-H5 coating with 0.96% phosphorus, as it carries a larger population of acidic groups that can interact with the hydroxyls of the hydromagnesite portion of the H5 mineral. The fact that we were able to keep P content <1 wt. % is very important, since the literature reports that the extent of flame retardancy depends mainly on the phosphorus content (typically higher than 1 wt. %). Sonnier et al. [50] used phosphonium ionic liquid, which significantly reduced flammability without further addition of flame retardants due to the high amount of phosphorus (up to 3.69 wt. %).

All the films were of very good quality, and representative photographs are shown in Figure 6.

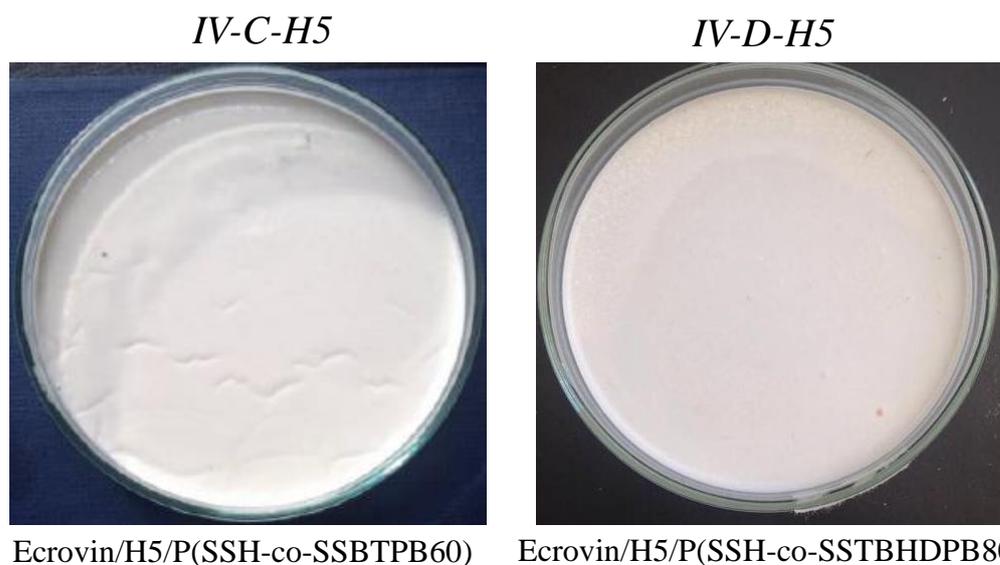


Figure 6. Photographs of the film Ecrovin/H5/P(SSH-co-SSBTPB60) and Ecrovin/H5/P(SSH-co-SSTBHDPB80).

SEM images of the Ecrovin/H5/P(SSH-co-SSBTPB60) mixture are also shown in Figure 7.

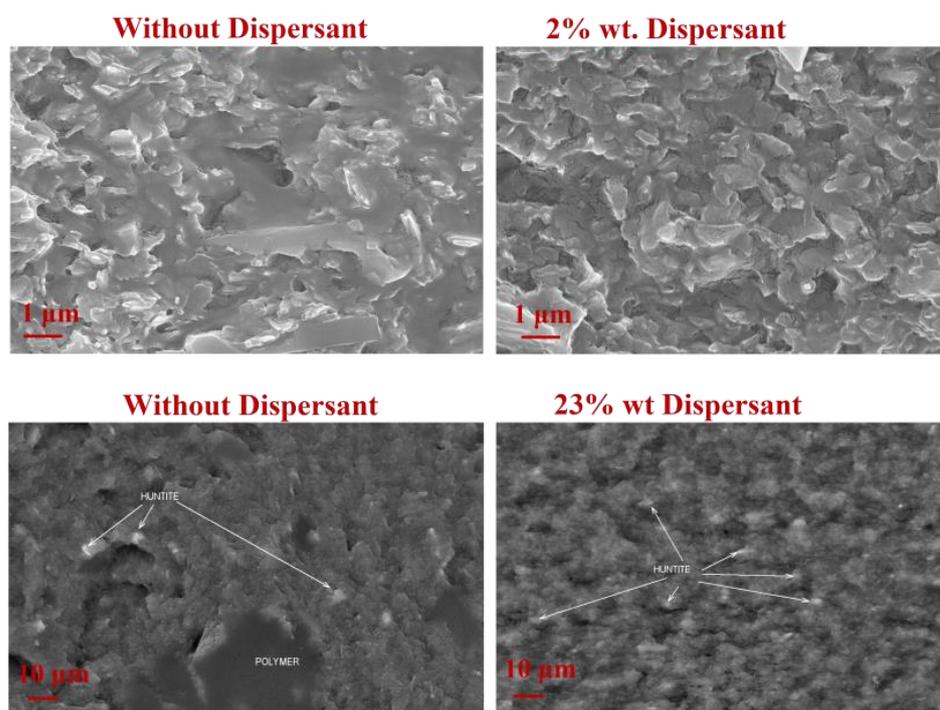


Figure 7. SEM observation of Ecrovin/H5/P(SSH-co-SSBTPB60) coating.

As shown, the good interaction between H5 and the additive led to an improved distribution of the polymer matrix as microvoids were formed. Figure 7 also revealed a high stacking density between the filler and the matrix with a short distance between the particles.

As exothermic and endothermic reactions are significant in regard to combustibility of materials, TGA analysis was performed to correlate the interactions between the polymer matrix, the huntite mineral and the additives. The most promising systems with the lowest combustibility were selected to be studied by TGA. The TGA curves are demonstrated in Figure 8. The H5 mineral consists mainly of huntite (steep loss of mass at ~ 566 °C attributed to dissociation of carbonate ions associated with Mg) with some contribution of hydromagnesite (smaller losses are observed at ~ 200 °C and 400 °C). Through thermal stabilities, it can be observed from Figure 8 that the decomposition of H5 mineral occurs at temperatures between 400 °C and 700 °C, and the polymer matrix/additive decomposes at 250–700 °C. The total residue of H5 mineral and the polymer composite sample was found to be 52 and 16–27 wt. %, respectively, due to the fact that the decomposition of H5 is lower than that of the polymer matrix/additive. Moreover, the IV-D-H5 sample, Ecrovin/H5/P(SSH-co-SSTBHDPB80), exhibits higher initial decomposition temperature and lower residue compared to the other polymer matrix/additive systems.

3.4. Use of Organic Dispersants as Additives

In order to evaluate the fire retardancy of the polymeric additives synthesized and used in the present work, the commercial additives Polydisp A and Loraphos PA 30 that are used on industrial cases were employed. In this line, coatings with Ecrovin[®] LV 340 eco and H5 were prepared, and their LOI was determined. The results are shown in Table 9. The coatings with codes IV-C-H5 and IV-D-H5 are also shown for comparison. The additives were used at contents 0.6, 2, 14 and 25 wt. %, but only the 2 wt. % content resulted in the formation of very good-quality films. Characteristic photographs of the two additives at 2 and 14 wt. % content in the blends are shown in Figure 9. The Polydisp A additive did not show higher LOI values compared to IV-C-H5 and IV-D-H5, whereas a slight increase was observed in the case of Loraphos PA30 compared to the Ecrovin[®] LV 340 eco/H5 system. This may be due to the fact that neither of these additives contains phosphorus nor interacts

with huntite to enhance the fire retardancy and simply increases the organic load of the mixture, which is easier to burn.

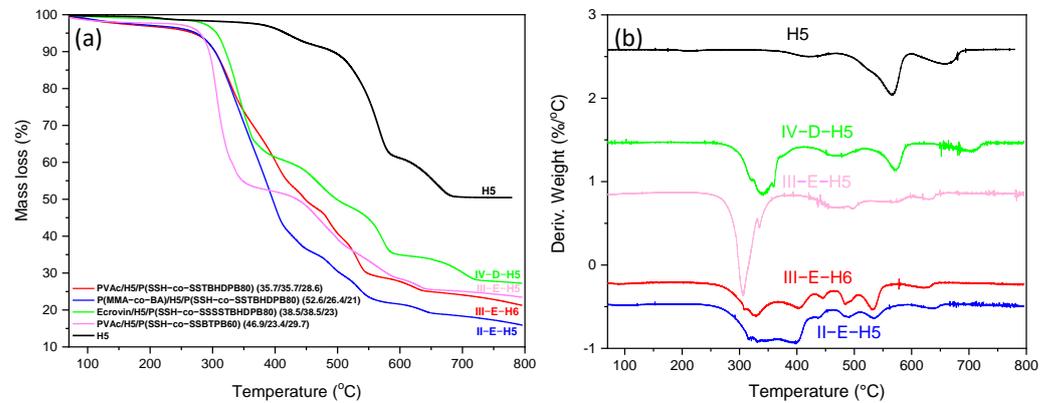


Figure 8. (a) TGA measurements and (b) the mass loss derivative as a function of temperature for neat H5 and polymer matrix/additive systems: IV-D-H5, III-E-H5, III-E-H6 and II-E-H5.

Table 9. LOI measurements of Ecrovin® LV 340 eco blends with H5 and additives.

Code	Polymer Matrix/Additive	Matrix Content (%)	H5 Content (%)	Additive Content (%)	P Content (%)	LOI (%)
V-A	Ecrovin	100	-	-	-	23.0 ± 0
V-B-H5	Ecrovin/H5	50.0	50.0	-	-	29.5 ± 0.5
V-C-H5-1	Ecrovin/H5/Polydisp A	49.7	49.7	0.6	-	-
V-C-H5-2		49.0	49.0	2.0	-	28.0 ± 0.5
V-C-H5-3		43.0	43.0	14.0	-	-
V-C-H5-4		37.5	37.5	25.0	-	-
V-D-H5-1	Ecrovin/H5/Loraphos PA30	49.7	49.7	0.6	-	-
V-D-H5-2		49.0	49.0	2.0	-	30.0 ± 0.8
V-D-H5-3		43.0	43.0	14.0	-	-
V-D-H5-4		37.5	37.5	25.0	-	-
IV-C-H5	Ecrovin/H5/P(SSH-co-SSBTPB60)	38.5	38.5	23.0	0.96	34.5 ± 0.5
IV-D-H5	Ecrovin/H5/P(SSH-co-SSBTPB60)	38.5	38.5	23.0	1.1	33.5 ± 0.5

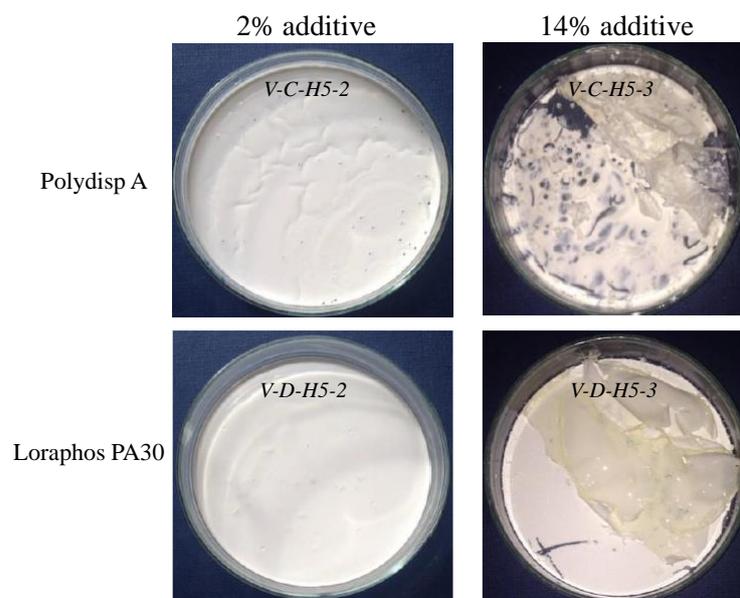


Figure 9. Photographs of the films Ecrovin/H5 with Polydisp A and Loraphos PA30 at 2% and 14% content.

4. Conclusions

In the present work, a flame retardancy test was carried out on wood coatings with phosphonium and acidic oligomers. An initial screening of polymer matrix/additive systems in terms of LOI led to the selection of systems for the addition of the inorganic mineral H5 or the commercial matrix Ecrovin[®] LV 340 eco.

The addition of hutite H5 to the P(MMA-co-BA) and PVAc polymer matrices resulted in good-quality films at polymer/H5 ratios 2/1 and 1/1. It also led to a decrease in the systems' combustibility, especially in the case of PVAc, since the LOI values increased up to 12 percentage points compared to P(MMA-co-BA), which increased the LOI values by 5 percentage points.

The addition of P(SSH-co-SSTBHDPB) to the above mixtures gave good-quality coatings in some cases and high LOI values, which may be owed to the modification between the acidic groups of PSSH and the hydroxyl groups of the mineral.

The new coatings prepared in the present work take advantage of the phosphorus flame-retardant properties and polymeric additives that have acidic groups and help the better dispersion of the inorganic filler in the polymer matrix.

Author Contributions: Conceptualization, G.A.V. and J.K.K.; methodology, V.K., G.C.L.; formal analysis, V.K., G.C.L.; investigation, all authors; data curation, V.K., G.C.L.; writing—original draft preparation, G.C.L.; writing—review and editing, G.C.L., G.A.V., J.K.K.; supervision, G.A.V. and J.K.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Commission's 7th Framework Programme under contract number FP7-SME-2012-315425. Research Funding Project: Wood FlaretCoat Flame-retardant coatings based on nano-magnesium hydroxide, huntite and hydromagnesite for wood applications.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Acknowledgments: The authors would like to thank N. Bouropoulos for the TGA analysis of the polymer matrix/additive systems.

Conflicts of Interest: The authors declare no conflict of interest.

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