



Influence of compounding conditions, treatment of wood particles with fire-retardants and artificial weathering on properties of wood-polymer composites for façade applications

Arne Schirp¹ · Benjamin Schwarz^{1,2}

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Abstract

Various fire-retardants (FR) for the pre-treatment of wood flour, for example, ammonium polyphosphate and different formulations based on phosphorus- and nitrogen-compounds, as well as for application during compounding were tested for their effectiveness in injection-molded and extruded composites based on high-density polyethylene and polypropylene. Small-scale tests for flammability of polymeric materials and for determination of the limiting oxygen index were used to characterize the composite materials. Differences pertaining to the applied compounding conditions, i.e., underwater granulation versus air granulation, were determined. The amount of phosphorus leached from FR during underwater granulation was analyzed. Artificial weathering trials were performed and reaction-to-fire performance and color changes of FR-composites were evaluated. Tensile strength properties of the composites and results for cold water immersion tests are also reported. An optimized formulation based on pre-treated wood flour was developed and extruded into façade profiles for the single burning item test according to DIN EN 13823. The test showed that classification C-s3, d0 according to DIN EN 13501-1 can be achieved if pre-treated wood flour is used. The use of untreated wood flour leads to a lower classification (D-s2, d0). Fire performance of extruded façade profiles can be improved by the use of pre-treated wood flour and enables new applications in the building sector.

1 Introduction

Wood-polymer composites (WPC) are classified as normally flammable if they do not contain any fire-retardants. To improve the reaction-to-fire performance of WPC, several strategies can be used: bulk (mass) protection with fire-retardants (FR), pre-treatment of the wood particles with FR, application of a fire-retardant coating, and co-extrusion with FR only in the outer layer of the profile. The selected strategy depends on the type of polymer, amount of wood particles in the formulation and processing equipment available. A pre-treatment of the wood particles was pursued by Seefeldt and Braun (2012a, b). They impregnated unspecified wood flakes with a salt of a phosphoric acid derivative

(Disflamoll TP LXS 51064, Lanxess, Germany) and studied the interaction of the FR and a WPC material based on 40 wt% polypropylene. Cone calorimetric measurements showed that the fire behaviour of the composite material including the FR was improved compared to unprotected material. The effects of the FR were also investigated in detail by using thermogravimetry and FTIR spectroscopy.

Hämäläinen and Kärki (2014) treated spruce wood flour with two different phosphate-based FR solutions and melamine formaldehyde resin prior to combining the wood flour with polypropylene via direct extrusion. Although the fire performance was improved by wood modification, the mechanical performance of the composites deteriorated. In general, modification of wood flour for application in WPC can be accomplished, for example, by acetylation (Ibach et al. 2007), heat treatment (Ayrilmis et al. 2011), benzylation (Dominkovics et al. 2007) or treatments with silanes (Xie et al. 2013). However, these treatments were mainly focused on improving the mechanical performance, to reduce water uptake and swelling and decay resistance, while improved fire retardancy of WPC has not been sought.

✉ Arne Schirp
arne.schirp@wki.fraunhofer.de

¹ Fraunhofer-Institute for Wood Research (WKI), Bienroder Weg 54E, 38108 Braunschweig, Germany

² Present Address: GOM GmbH, Schmitzstraße 2, 38122 Braunschweig, Germany

In a recent publication by Yin et al. (2018), different routes to obtain halogen-free flame-retardant WPC based on polypropylene were investigated. All WPC with single-component flame retardants improved limiting oxygen index (LOI) values but achieved only HB classification in UL 94 tests. Fire properties and fire spread characteristics were improved by using mixtures of FR. The best overall results were obtained with mixtures based on 15 wt% expandable graphite (EG) or combinations of EG and ammonium polyphosphate (APP) at different ratios.

In another recent study, the reaction-to-fire performance of WPC made with recycled plastics was investigated using the cone calorimeter (Turku et al. 2018). Surprisingly, the composites based on recycled plastic were more thermostable than the ones based on virgin polymers. The peak heat release rate (pHRR) of the composites with recycled material was 12–25% lower which was attributed to the presence of additives in the recyclates, such as pigments and FR, as well as impurities from landfills.

Detailed information regarding the flammability of biofibres and biocomposites, strategies to achieve fire retardancy for natural-fiber reinforced composites and information regarding the mode of action of different flame retardants can be found in Kozłowski and Władysław-Przybylak (2008), Chapple and Anandjiwala (2010), Nikolaeva and Kärki (2011) and Mngomezulu et al. (2014). In general, two possible actions for a fire-retardant can be distinguished which are based on chemical or physical principles. A chemical action is targeted at interfering with free radical reactions which take place during burning (gas phase) and aim to protect internal materials from heating during char creation (solid phase). Physical actions are based on decreasing the temperature by endothermic reactions, reducing the fire distribution by fluxing oxygen with non-combustible gases. In addition, the formation of a protective surface layer is promoted.

It has been shown that the wood flour or fibre itself acts as a fire-retardant for the polymer matrix in WPC, with heat release rates decreasing as the amount of wood filler increases (Spear 2015). The heat release rate (HRR) of PP is 43 MJ kg⁻¹ whereas pine wood has HRR of 19 MJ kg⁻¹. The presence of wood also promotes the formation of a char layer on the WPC surface (Seefeldt and Braun 2012a).

In a previous research project, wood particles from fire-retardant-treated particleboard were successfully combined with thermoplastics to improve the reaction-to-fire performance of WPC (Schirp and Su 2016). Pre-treatment of thermomechanical pulp with APP was also effective to increase the fire performance of extruded profiles (Schirp and Hellmann 2019). So far, the best classification (B-s2, d0) in single-burning item (SBI) tests was achieved by using a high wood content, a pre-treatment of the wood particles with FR and by using APP as fire-retardant (Schirp and Barrio 2018). More

experimental data are required to improve our knowledge regarding the reaction-to-fire performance of WPC, especially based on large-scale tests such as the single-burning item test (SBI) according to DIN EN 13823 (2002). An important aspect which also merits further investigation is the durability of the fire-retardant treatment in WPC. It is not known yet if and to which extent fire-retardants may leach from WPC during processing and/or service life. Often, underwater granulation is used to produce granulates (pellets, compounds) for profile extrusion or injection-moulding. Potentially, FR can leach during contact with water. It was one of the objectives of this project to determine if leaching of the fire-retardant occurs when underwater granulation is used, and if this affects the reaction-to-fire performance of the materials. The underwater pelletizing system consists of a polymer diverter valve, a pelletizing unit, a water treatment and drying system and an electrical control system. The melt is flowing from the extruder to the polymer diverter valve of the underwater granulation unit and is pressed through the holes of the die plate. The strands are cut into granules directly after their exit from the die plate by rotating knives. This is occurring in the cutting chamber which is completely flooded with water. The granules are hardened due to their contact with the process water which is running over the front part of the die plate. The process water transports the granules to the centrifugal dryer where they are separated from the water and discharged. The process water is in a completely closed circulating system, hence, water loss is minimal. To analyze if leaching of the fire-retardants occurs during processing, in this project, the process water was collected during compounding and analyzed.

In summary, the objectives were to select FR for the treatment of wood particles before compounding and for the polymer matrix during compounding, to determine a potential benefit of using FR-treated wood particles, and to determine leaching of the FR during processing (compounding with underwater granulation) and during short-term weathering. The reaction-to fire performance of injection-moulded, small-scale samples as well as of large, extruded façade profiles was investigated. The selection of FR for the wood flour was done based on products available for wood particles, fibres, cellulose, paper and textiles. Preferably, the fire-retardants should be available in liquid form and halogen-free. For protection of the polymer matrix, various commercially available, halogen-free FR were sourced and tested.

2 Materials and methods

2.1 Materials

High-density polyethylene (HDPE), polypropylene (PP) and wood flour were used as main components for WPC.

Softwood flour with a main particle size between 200 and 500 μm (Arbocel C320, J. Rettenmaier & Söhne GmbH + CO, Rosenberg, Germany) was used as filler for WPC. A high-density polyethylene (HDPE) in powder form (56020S, Total Petrochemicals, Brussels, Belgium) with an average particle size of 800 μm , density of 0.952 g/cm^3 and a melt flow rate (190 °C; 21.6 kg) of 2.1 $\text{g}/10$ min was used. The PP type was PPH 9000 OG (homopolymer, off-grade type of PPH 9069, Total Petrochemicals) in pellet form with a density of 0.905 g/cm^3 and a melt flow index (230 °C; 2.16 kg) of 23.9 $\text{g}/10$ min.

The coupling agent for the HDPE-based composites was a maleic-anhydride-grafted, linear, low density polyethylene (MAPE) in powder form with MA-content of 1.5% (wt) (Scona TPPE 1102 PALL, BYK Kometra, Schkopau, Germany). For PP, a maleic-anhydride-grafted PP (MAPP) with MA-content of 1.4% (Scona TPPP 8112 FA, BYK Kometra) was used. Further additives were a blend of complex, modified fatty acid ester (TPW 113, Struktol, provided by Velox, Hamburg) used as lubricant, a UV stabilizer (Irganox B225, BASF) and a brown colour masterbatch on PE basis (74445F PE, Lifocolor GmbH, Lichtenfels).

Fire-retardants for the treatment of wood flour were ammonium polyphosphate (APP, Exolit AP 420, Clariant, Germany; phosphorus content between 12.5 and 13.5%), a nitrogen-containing salt of phosphonic acid (Aflammit MSG, Thor, Germany), zinc borate (Zinborel, Omya, Cologne, Germany), five different formulations based on P- and N-compounds (Apyrol BKW and Apyrol NCE CONC. by CHT R. Breitlich GmbH, Tübingen, Germany; VP 25623, VP 25629 and VP 25628 by IGP Ingenieurbüro Große Perdekamp, Dülmen, Germany), an organophosphorous compound (Disflamoll TP LXS 51064, Lanxess, Germany), alkali silicate (waterglass, Betol 39 T3, Wöllner, Germany), and a non-commercial by-product of the aluminum diethyl phosphinate (DEPAL) production in slurry form (Clariant, Germany). In case of the alkali silicate, this liquid was also used in combination with a catalyst (ammonium hydroxide) to accelerate the reaction with the wood flour.

The fire-retardants used for the polymer matrix were APP (Exolit AP 422, Clariant; phosphorus content 31–32%) and APP micro-encapsulated with melamine (Exolit AP 462, Clariant; phosphorus content 30.7%). In addition, the following fire-retardants were used: melamine cyanurate (Melapur MC 25, BASF, Germany); a combination of piperazine pyrophosphate, phosphoric acid and zinc oxide (AKD-STAB-FP-2200S, Adeka) which was provided as masterbatch (70% ADK-STAB-FP-2200S in a PP matrix; Mastertek GR5351, Campine, Beerse, Belgium); zinc borate (Zinborel, Omya GmbH, Cologne, Germany); magnesium hydroxide (Magnifin H5 MV; Magnifin Magnesiaprodukte, Breitenau am Hochlantsch, Austria); and a dispersion of phosphorus and nitrogen in PP (Vibatán HF 04626, W&R

Plastics). A by-product from the aluminum diethyl phosphinate (DEPAL) production (provided by Clariant) was also used as FR following drying and grinding of the slurry. Where indicated, pentaerythritol (Penta technical grade, micronized powder, Perstorp) was used as carbonific agent and melamine in powder form as blowing agent (Melafine, DSM, Geleen, Netherlands) in combination with APP.

2.2 Processing

Fire retardants (10 wt% or 20 wt%, based on solids content and dry wood flour) were added to the wood flour by using a spray nozzle attached to a plough-blade mixer. Three kg-batches with the different FR were prepared. Afterwards, batches were dried in an oven for 12 h at 30 °C. Treated wood flour was pressed into small samples (80 mm \times 10 mm \times 4 mm) using a self-made tool in a hot press. These samples were used for determination of the limiting oxygen index (LOI).

A co-rotating twin screw extruder (TSK 20, Theysohn Maschinenbau, Salzgitter, Germany) was used for compounding untreated or treated wood flour, HDPE or PP, fire-retardants and additives. Fourteen formulations (Table 1) were prepared using either underwater or air granulation (EUP-ELG 50, ECON, Weisskirchen, Austria), hence, in total, 28 formulations were processed and designated as UWG (under water granulation) or AG (air granulation). The designation was done according to the FR used for wood flour and polymer matrix, for example, AP420-AP422 means that the wood flour was treated with AP420 and the polymer matrix with AP422. The process water (eluate) during underwater granulation was collected for analysis (leaching of phosphorus).

Before injection-moulding, granulates were dried to a moisture content of approximately 1% and converted into smaller granules using a cross beater mill. A mini-injection moulding machine (HAAKE Minijet II, Thermo Fisher Scientific, Karlsruhe, Germany) equipped with a self-designed mould was used to prepare specimens of 80 mm \times 10 mm \times 4 mm for determination of LOI, UL 94-classification, artificial weathering and water uptake and swelling after 28 days of cold water immersion. Specimens of type 1A (DIN EN 527-2) with 4 mm thickness were prepared for tensile strength tests. Ten specimens were prepared for each of the tests. Processing parameters for injection-moulding are shown in Table 2. Settings were identical for most formulations, with the exception of two formulations which had to be processed with lower temperatures.

For industrial-scale extrusion trials, 180 kg of wood particles (Arbocel C320) were treated with 10% Apyrol NCE Conc. (based on solid content and wood dry weight) and dried to 5.5% moisture content by company Rettenmaier & Söhne (Rosenberg, Germany). The wood particles

Table 1 Formulations based on HDPE and PP

Designation	WF, untreated (%)	WF with exolit AP 420 (%)	WF with apyrol NCE conc (%)	HDPE (%)	PP (%)	Exolit AP 422 (%)	Exolit AP 462 (%)
Without FR	58	0	0	33	0	0	0
No FR-AP422	42	0	0	33	0	16	0
No FR-AP462	42	0	0	33	0	0	16
AP420-AP422	0	42	0	33	0	16	0
AP420-AP462	0	42	0	33	0	0	16
Apyrol-AP422	0	0	42	33	0	16	0
Apyrol-AP462	0	0	42	33	0	0	16
Without FR	58	0	0	0	33	0	0
No FR-AP422	42	0	0	0	33	16	0
No FR-AP462	42	0	0	0	33	0	16
AP420-AP422	0	42	0	0	33	16	0
AP420-AP462	0	42	0	0	33	0	16
Apyrol-AP422	0	0	42	0	33	16	0
Apyrol-AP462	0	0	42	0	33	0	16

Percentages represent wt%. Wood flour (WF) was treated with 10% of fire-retardant (FR) based on solids content and dry wood before compounding. In addition, in each formulation, 3% coupling agent (MAPE or MAPP), 3% lubricant, 2.75% colour masterbatch and 0.25% UV stabilizer were included

Table 2 Process parameters during injection moulding

Formulation	Cylinder temperature (°C)	Tool temperature (°C)	Injection pressure (bar)	Processing time (s)	Post-processing time (s)	Post pressure (bar)
PP-based: AP420-AP422; Apyrol-AP422; Apyrol-AP462	190	70	700	6	6	650
All other formulations	210	80	700	6	6	650

were compounded by company Linotech (Forst, Germany) into the HDPE-based formulation Apyrol-AP422 using a strand granulation process. The corresponding formulation without wood particle treatment but including 16% APP for the HDPE matrix was also processed. Siding (façade) profiles were extruded by company Natur-in-Form (Redwitz, Germany) using a 68 mm conical, counter-rotating extruder (Battenfeld-Cincinnati). Full siding profiles (without hollow chambers) of 18 mm thickness and a visual height of 58 mm width were extruded. Small samples (80 mm × 10 mm × 4 mm) were cut from the profiles for LOI and UL 94-tests. Extruded profiles were used for the single-burning item test.

2.3 Test methods

2.3.1 Oxygen index, UL94 tests and artificial weathering

Specimens were conditioned at 20 ± 2 °C and $65 \pm 5\%$ relative humidity for four days prior to LOI tests, UL 94 determination and mechanical tests. The oxygen index test measures the minimum concentration of oxygen in a flowing

mixture of oxygen and nitrogen that will just support flaming combustion. Determination of the LOI was done according to modified DIN EN ISO 4589-2: 2006. A small test specimen is supported vertically in an oxygen–nitrogen mixture that is flowing upward through a glass column. The upper end of the specimen is ignited, and the subsequent burning behavior of the specimen is observed. Basically, if a test specimen is hard to burn, it requires more oxygen to cause flaming combustion, and this increases its oxygen index. Horizontal and vertical UL94-tests were performed according to modified DIN EN 60695-11-10 (2014) using five conditioned test samples per formulation. The modification consisted in smaller specimen size (80 mm instead of 125 mm length) and the omission of a cotton pad under the test sample. However, development of burning droplets was carefully monitored by visual observation. LOI and UL94 tests were also performed after 300 h of artificial weathering under xenon-lamps in a Suntest XXL device (Atlas) according to DIN EN ISO 4892-2A (2009), cycle 1. After weathering, specimens were conditioned at 20 °C and 65% relative humidity for 72 h, and color measurements were taken as described in Schirp et al. (2015).

2.3.2 Tensile properties, water uptake and swelling

Tensile properties, water uptake and swelling of the test specimens after 28 days of cold water immersion were determined according to DIN EN 15534-1 (2018). Tensile strength tests were performed according to DIN EN ISO 527-2 (2012) with dog-bone shaped samples of 4 mm thickness (type 1A) using a material testing machine (BZ1-MM14740.ZW01, Zwick, Ulm, Germany) and corresponding software (TestXpert II). Rate of elongation was 1 mm min⁻¹ for the tensile modulus of elasticity and 50 mm min⁻¹ for the tensile strength. Measurement of the dimensions in thickness, width and length of the specimens (80 mm × 10 mm × 4 mm) was taken 28 days after the immersion into water at a temperature of 20 °C. Water uptake was determined by differential weighing of the test specimens.

2.3.3 Single burning item (SBI) tests

Single burning item (SBI) tests were performed according to DIN EN 13823 (2002). During SBI testing, the base layer consisted of non-flammable calcium silicate panels with 10 mm thickness. Aluminum profiles were fixed on the panels with screws, and the extruded profiles were inserted into clips which were mounted on the aluminum profiles. According to DIN EN 13823, in the longer of the two parts, there shall be a vertical and a horizontal zero-joint. Because of the presence of horizontal joints throughout the façade set-up, only a vertical joint was included.

The classification parameters of the SBI test are fire growth rate index (FIGRA), lateral flame spread (LFS), and total heat release (THR_{600s}). Additional classification parameters are defined for smoke production as smoke growth rate index (SMOGRA) and total smoke production (TSP_{600s}), and for flaming droplets and particles according to their occurrence during the first 600 s of the test. The FIGRA and SMOGRA indices were calculated as follows:

$$FIGRA = 1000 \max \left(\frac{HRR_{av}(t)}{t} \right)$$

$$SMOGRA = 1000 \max \left(\frac{SPR_{av}(t)}{t} \right)$$

where HRR_{av} is the heat release rate averaged over 30 s (in kW), SPR_{av} is the smoke production rate averaged over 60 s (in m²/s), and t is the time elapsed after the beginning of the test (in s). The units of FIGRA and SMOGRA are W/s and m²/s², respectively. Heat release-related threshold values for the FIGRA calculation were used to obtain FIGRA_{0,2 MJ} and FIGRA_{0,4 MJ} values. THR_{600s} and TSP_{600s} values were calculated over the first 600 s of the test as follows:

$$THR_{600s} = \frac{1}{1000} \sum_{0s}^{600s} HRR(t) \Delta t$$

$$TSP_{600s} = \sum_{0s}^{600s} SPR(t) \Delta t$$

where $HRR(t)$ and $SPR(t)$ are the heat release rate and smoke production rate as functions of time (in kW and m²/s, respectively), and Δt is the data acquisition interval of the measurement (in s). The units of THR_{600s} and TSP_{600s} are MJ and m², respectively. The obtained SBI results were compared with the classification criteria according to EN 13501-1 (2010).

2.3.4 Thermogravimetric analysis

Thermal stability of selected compounds was investigated by means of thermogravimetric analysis (TGA) using a TGA/DSC 1 (Mettler-Toledo AG, Schwerzenbach, Switzerland). Samples (approx. 10 mg) were weighed into a TGA crucible and subsequently placed in the TGA instrument. Samples were heated from 25 to 1000 °C at a heating rate of 10 K·min⁻¹ under a constant air flow of 50 mL·min⁻¹.

2.3.5 Leaching of phosphorous from fire-retardants during underwater granulation

The process water (eluate) collected during underwater granulation was analyzed for phosphorus content using inductively coupled plasma optical emission spectrometry (ICP-OES) according to DIN EN ISO 11885 (2009). The amount of leached phosphorous served as an indication how much of the FR was released during processing. During ICP-OES, the samples are atomized and the produced aerosol is transported into a plasma torch where the elements are excited. Using the plasma generated by inductive high frequency coupling, characteristic emission spectra are generated. The spectra are divided into lines by a grating spectrometer and analysed using a detector.

3 Results and discussion

3.1 Evaluation of fire-retardants for treatment of wood particles and polymer matrix for use in WPC

First, suitable fire-retardants were evaluated separately for the treatment of wood particles and polymer matrix. For evaluation of the wood particle treatments, the oxygen index test was chosen as method. The oxygen index is generally recognized as an indication of general flammability. Highly

flammable materials display a low oxygen index. The more oxygen required (the higher the LOI value), the more fire-resistant the material is considered to be. Since air contains 21% oxygen, polymeric materials with an LOI value lower than 21 are categorized as combustible whereas those with LOI above 21 are classified as self-extinguishing because their combustion cannot be maintained at ambient temperature without the contribution of an external energy source (Kiliaris and Pappaspyrides 2014). The oxygen index test is widely used in the plastics industry but has also been used to evaluate fire-retardant treated wood and wood products (White 1979). Results for LOI of pressed wood flour samples which were pre-treated with different FR are shown in Table 3. Overall, LOI was between 27 and 68. This is generally in the same range as results obtained by White (1979) for fire-retardant treated wood products. In Table 3, results for LOI with either 10% or 20% of FR are shown. Two concentrations of FR were tested to determine if LOI increases with higher amount of applied FR. The three FR which resulted in the highest LOI were APP (LOI: 66–67) as well as P- and N-containing compounds (LOI: 67–68). For comparison, untreated pine wood and FR-treated particleboard display an LOI of 21–22 and 68–80, respectively (Schirp and Su 2016). Phosphorus-based compounds are some of the best known fire-retardant treatments for timber and wood products. They are considered to act mainly in the condensed phase, by promoting char formation and depriving the gas phase of further volatile decomposition products (Lowden and Hull 2013).

Under the conditions of the current experiments, zinc borate, alkali silicate and DEPAL displayed the lowest values for LOI when the FR were applied to wood particles alone. Zinc borate has relatively low solubility in water and

can be easily blended with particles or strands, hence, it has often been used in the production of particleboard and OSB (Spear 2015). It has mainly been used for exterior panel products due to its low solubility. Zinc borate treatments are commonly used in the processing of WPC since they also show broad spectrum activity against wood destroying organisms and demonstrate a good environmental profile. The heat decomposition of zinc borate leads to the creation of a glassy protection layer which acts as a barrier for polymer chain oxidation (Nikolaeva and Kärki 2011). Another benefit of zinc borate is its good smoke suppressant property.

Alkali (sodium) silicate or waterglass has been used as fire-retardant coating component and as impregnation solution for wood products (Lowden and Hull 2013). The LOI of pressed wood samples with alkali silicate was slightly higher (36–37) than with zinc borate and could be further increased with ammonium hydroxide as catalyst (46–47), however, values for LOI were not as high as with some of the P- and N-containing compounds. The product used here was Betol 39 T3 (Woellner) which according to the technical data sheet is an inorganic binder based on modified sodium silicate with special additives. It is possible that higher temperature during pressing of the samples is needed to achieve a fire-retarding effect in the wood particles, or that a suitable hardener is needed. Usually, Betol 39 T3 is applied as binder for the production of insulating, fire protecting and other construction panels, and can be cured by organic or inorganic hardeners, acidic gases (e.g. CO₂) or higher temperatures.

Disflamoll TP LXS 51064 (Lanxess), a salt of a phosphoric-acid derivate, displayed intermediate values for the LOI and was close to the performance of the alkali silicate with catalyst and one of the products with P- and

Table 3 Oxygen index of pressed wood flour samples pre-treated with different FR

Type of FR	Chemical basis of FR	LOI with 10% FR	LOI with 20% FR
Exolit AP 420 (Clariant)	APP	53–54	66–67
Aflammit MSG (Thor)	Nitrogen-containing salt of phosphonic acid	42–43	59–60
Zinborel (SCL)	Zinc borate	Not tested	27–28
Apyrol BKW (CHT Bezema)	P- and N-containing compounds	37–38	40–41
Apyrol NCE conc. (CHT Bezema)	P- and N-containing compounds	38–39	67–68
VP 25623 (IGP)	P- and N-containing compounds	38–39	64–65
VP 25629 (IGP)	P- and N-containing compounds	Not tested	46–47
VP 25628 (IGP)	P- and N-containing compounds	Not tested	57–58
Disflamoll TP LXS 51064 (Lanxess)	Organophosphorous compound	Not tested	48–49
Betol 39 T3 (Wöllner)	Alkali silicate	32–33	36–37
Betol 39 T3 (Wöllner) and catalyst	Alkali silicate and ammonium hydroxide	Not tested	46–47
Slurry, non-commercial (Clariant)	Aluminum diethyl phosphinate	28–29	31–32

Either 10% or 20% of the FR was applied, based on solids content and dry wood flour. All FR were provided in liquid form, except for zinc borate, which was provided in powder form and dissolved in water. Numbers in bold represent the FR with the highest LOI, which were selected for treatment of wood flour in combination with the polymer matrix

N-containing compounds (VP 25629 from IGP). This FR was investigated in detail regarding its thermal decomposition and mode of action in WPC by Seefeldt and Braun (2012a, b). It was shown that Disflamoll TP LXS 51064 acts mainly in the condensed phase by increasing the amount of residue formed by the wood part in the WPC. Additional flame dilution is achieved by the release of water, ammonia and carbon dioxide during the decomposition of the FR. Seefeldt and Braun (2012a, b) did not determine LOI values for wood particles treated with Disflamoll TP LXS 51064.

In summary, based on the results shown in Table 3, the two FR with the highest LOI were selected for compounding trials, i.e. Exolit AP 420 and Apyrol NCE Conc.

To select FR for the protection of the polymer matrix, PP was compounded together with several types of FR. The amount of FR used was 30%, with the exception of magnesium hydroxide which was also used at 50% (wt) because it is well known that metal hydroxides need to be applied in high amounts to be effective in thermoplastics (Weil and Levchik 2016). During combustion, metal hydroxides serve to remove heat by releasing large amounts of water at the same temperature or below the temperature at which the decomposition of the polymer occurs. Thus, by absorbing heat, they slow down the polymer pyrolysis process. The generated water vapors dilute the combustible gases of polymer decomposition. Furthermore, a non-flammable layer on the surface of the material is developed which protects the substrate. Another benefit of metal hydroxides is their contribution to smoke suppression. The two most commonly used mineral flame retardants are aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH)

which was used in this project. The advantage of MDH is its higher decomposition temperature (approx. 340 °C) compared to ATH (180–200 °C). APP was used in combination with PER and melamine to obtain an intumescent system. In this case, it is recommended to use a ratio of 3:1:1 for APP:PER:melamine. Intumescent flame retardants operate in the condensed phase, interrupting the self-sustained combustion of the polymer at its earliest stage (Kiliaris and Papaspyrides 2014). Generally, intumescent systems consist of three components: (1) an acid source, e.g., ammonium polyphosphate or melamine polyphosphate, (2) a carbonization agent, e.g., pentaerythritol or starch, and (3) a blowing agent, e.g., melamine or urea. The development of a swollen char is the result of the interaction of these components. The acid source decomposes to a mineral acid that dehydrates the polyol to generate the carbon char mainly by a free radical process. The carbon char is foamed by non-flammable gases emitted during the degradation of the blowing agent.

The results for oxygen index and modified horizontal UL94-test of PP including FR are shown in Fig. 1. All formulations of this series reached classification HB according to DIN EN 60695–11–10 at a sample thickness of 4 mm. The best four formulations showed LOI values between 33 and 35, and immediate extinguishing after withdrawal of the flame. Pure PP has an oxygen index of 18 (Horacek 2012). For LOI values of approximately 25 or higher, it is not possible to determine a horizontal burning rate because above this threshold, the polymers are self-extinguishing. Figure 1 shows that there is no correlation between LOI and the horizontal burning rate if LOI is 33 or lower. The most important conclusion from Fig. 1 is that if LOI is 33 or higher, the

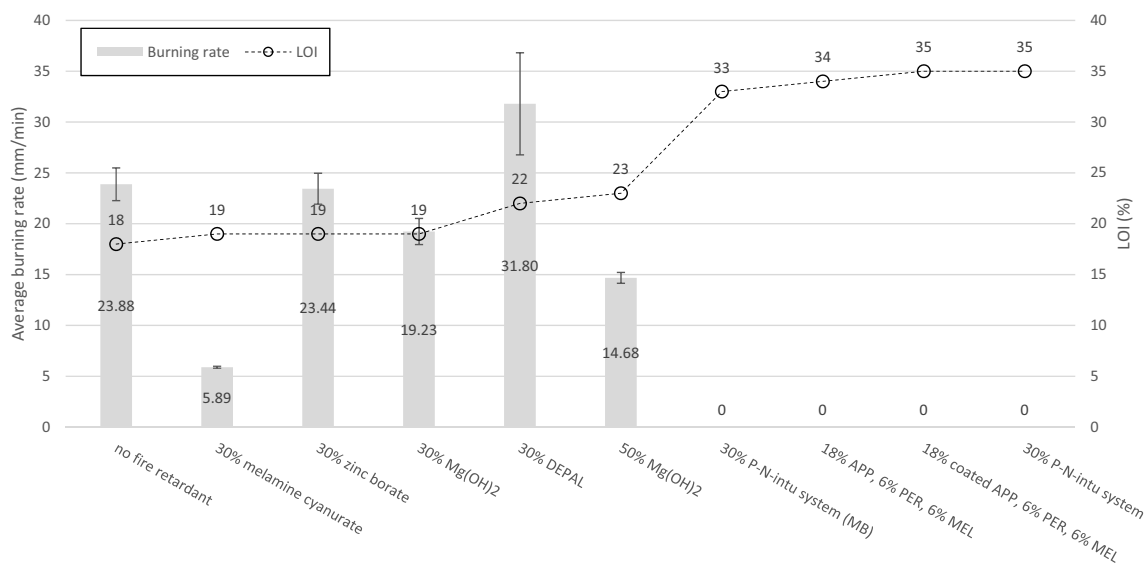


Fig. 1 Results for limiting oxygen index (LOI) and horizontal burning rate of various formulations based on polypropylene and fire-retardants (excluding wood flour). Ranking was done according to LOI

horizontal burning rate is zero and hence, it is likely that V0-classification (obtained in the vertical setup) can also be obtained. Consequently, the four best formulations were also subjected to the vertical UL94-test. The vertical test showed that V0-classification could in fact be achieved for these formulations which consisted of intumescent APP-PER-melamine and P-N-systems. Compared to these intumescent systems, other FR such as melamine cyanurate, zinc borate, magnesium hydroxide and aluminum diethyl phosphinate (DEPAL) did not perform as well in the selected PP matrix under the conditions of the present experiments. This could be due to the fact that synergists were not used. The flame retardancy of PP and other polyolefins was reviewed by Weil and Levchik (2008) and Zhang and Horrocks (2003). They conclude that in general, char-promoting additives such as PER in the presence of APP, and its combination with adjuvants, for example zinc borate or borosiloxane, may improve fire properties and flammability. This is in line with the present results which confirmed the effectiveness of the APP-PER-melamine combination for the PP used here.

PP systems based on metal hydroxide flame retardants such as aluminum trihydrate (ATH) and magnesium hydroxide have the general disadvantage that they require high FR loadings to achieve sufficient fire properties which in turn has a negative influence on mechanical properties. The required high loadings can be a problem in WPC where a high amount of filler is already present in the form of wood particles or fibres. In the present investigations, the vertical UL94 test was not performed for the formulations with magnesium hydroxide due to the relatively low oxygen index and higher horizontal burning rates compared to the APP-PER-melamine and P-N-systems.

The PP compounds with 30% zinc borate showed a relatively low LOI of 19% which was the same as for 30% magnesium hydroxide. The LOI of zinc borate could probably be increased with the addition of synergists. Zinc borate shows the best synergistic effect in combination with metal hydroxides, and good synergism has also been observed in combination with antimony trioxide (Nikolaeva and Kärki 2011). In addition to fire retardancy, borates have additional advantages such as good smoke suppression, protection against fungi and insects, and low cost.

As mentioned above, the by-product from the aluminum diethyl phosphinate (DEPAL) production was also tested in PP (without any wood particles) but did not perform as well as the intumescent systems tested and was therefore not explored further. DEPAL is often used as halogen-free FR for polyamides, polyesters and thermoset resins. If used alone, it partly vaporizes and partly decomposes to volatile diethylphosphonic acid and aluminum phosphate residue (Hörold 2014). In a fire, a predominant gas phase action was observed but the material did not reach a V0 classification. If melamine polyphosphate (MPP) is used as synergist,

V0 can be achieved because of the reaction of MPP with phosphinate.

In summary, under the conditions of these trials, intumescent FR including the two types of APP tested, performed best to protect the polymer matrix (PP). The next step was then to combine the FR which worked best for wood flour (Exolit AP 420 and Apyrol NCE Conc.) with two of the best candidates for the polymer matrix. It was decided to use Exolit AP 422 and 462 for the polymer matrix to compare the differences between these types of APP, i.e. uncoated vs. coated APP. An uncoated APP may provide the advantage of improved polar interaction with the treated wood particles.

3.2 Oxygen index (LOI) and UL 94 tests with compounds prepared using underwater or air granulation

To determine the effects of granulation (underwater versus air), the compounds based on HDPE and PP (compare list in Table 1) were investigated. The differences between underwater and air granulation could be seen clearly for the PP-based compounds by visual observation. Due to the slower cooling and heat dissipation during air granulation, the granules tended to stick together, whereas the granules from underwater granulation were separated from each other. The granules based on PP were slim, rice-grain shaped while the granules based on HDPE were in the form of platelets or flakes. In general, the colour stability of the fire-retarded formulations with PP as matrix was higher than of the formulations with HDPE which had a greyish appearance.

All formulations based on HDPE and including FR reached LOI values between 26 and 30%, indicating the self-extinguishing behaviour of the materials (Fig. 2). The reference without any FR reached a LOI value of 20–21%. In most cases, LOI values of the formulations which were processed using air-granulation were slightly higher than of the formulations which were processed with underwater granulation.

The formulations based on PP (Fig. 3) displayed a slightly lower LOI compared to HDPE which was below the threshold for self-extinguishing materials. Here, LOI for formulations processed with underwater granulation were mostly higher than for those processed with air granulation. However, the differences in LOI between air and underwater granulation were not large in general.

Three formulations based on HDPE reached V0@4 mm classification. All of these formulations contained wood flour which was treated with Apyrol. Their respective counterparts without treated wood flour did not reach V0-classification which indicates that the wood flour treatment with Apyrol increased the fire-retardancy of the composites. Apyrol is a solution based on methylphosphonic acid in combination with urea. The combination of phosphorous

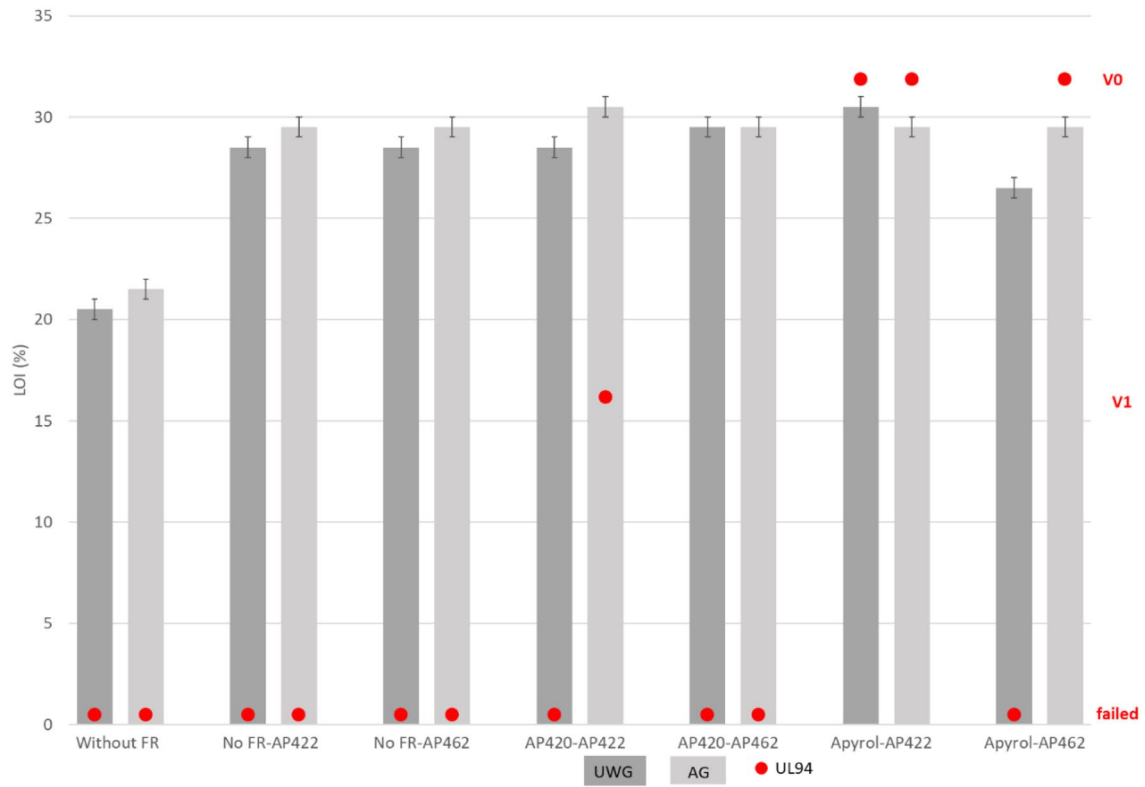


Fig. 2 Limiting oxygen index and UL94-classification of HDPE-based compounds

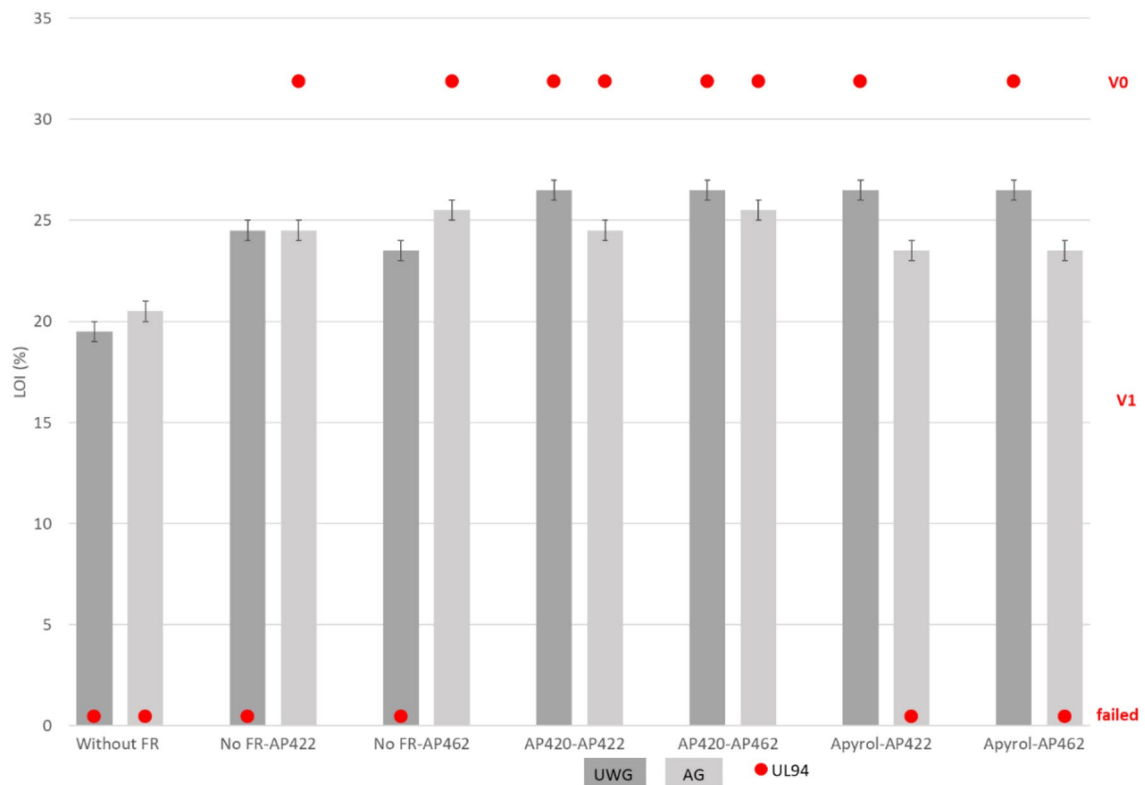


Fig. 3 Limiting oxygen index and UL94-classification of PP-based compounds

and nitrogen as used in Apyrol usually creates a synergistic effect (Stark et al. 2009). When wood is treated with this synergistic combination, the retention of phosphorous in the char is caused by cross-linking of the cellulose during the process of pyrolysis by esterification with the dehydrating agents (Nikolaeva and Kärki 2011). Furthermore, addition of nitrogen compounds to phosphorous-containing compounds may stimulate the polycondensation of phosphoric acid to polyphosphoric acid. Polyphosphoric acid in turn can act as a thermal and oxygen barrier limiting access to the material surface since it creates a viscous fluid coating (Levan 1984).

Under the conditions of this study, the pre-treatment of wood flour with APP (AP420) was not successful to confer V0-classification to the composites with HDPE. In the best case, V1 classification could be obtained (AP420-AP422; air-granulation only). Ammonium polyphosphate, the ammonium salt of polyphosphoric acid, is decomposed into polyphosphoric acid and ammonia upon heating. Hence, an intumescent protection layer is formed which prevents the oxidation of the material and improves charring. It has also been reported that APP reduces smoke production and provides resistance to flame spread (Stark et al. 2010, 2009).

In case of the PP-based formulations, a larger number of V0-classifications was obtained. Here, eight out of fourteen formulations reached V0@4 mm. Half of these eight formulations were processed with underwater granulation and half with air granulation. In contrast to the formulations based on HDPE, V0-classification could be achieved even with untreated wood flour for two formulations (no FR-AP422 and no FR-AP462; both processed by air granulation). In addition, V0-classification for the PP-based formulations was obtained with a lower LOI compared to the HDPE-based formulations. This shows that there is no correlation between the results of the LOI and UL94-test. Whereas the LOI test is used to determine the minimum concentration of oxygen, in admixture with nitrogen, that will support combustion of small vertical test specimens, in the UL94 test, the flammability rating of the material is determined. The observed differences between the UL94-results for PP- and HDPE-based WPC could be related to the melting points of the base polymers. The melting point of PP is higher than for HDPE, hence, in the case of PP, it is more energy required to heat up the same amount of polymer. In addition, differences in viscosity may play a role in flammability characteristics of the composites. Borysiak and Pauksza (2006) investigated the flammability of WPC based on PP with different MFI. Using cone calorimeter measurements, they determined that PP composites with higher MFI values have longer time to ignition, lower HRR and longer total burning time. These findings were interpreted in terms of varying degrees of wettability of wood particles by the PP matrices. One aspect that merits further investigation is why for the PP-based formulations with untreated wood flour

and with APP for the polymer matrix, only air granulation resulted in V0-classification. The corresponding formulations processed with underwater granulation did not pass the test. In the cases where the wood flour was treated with Apyrol, the opposite occurred: here, formulations processed with underwater granulation reached V0 whereas the formulations processed with air granulation failed. The reason for this is not understood yet. In the case of air granulation, leaching of the FR can be excluded. In addition, there were no differences in the moisture content of the treated wood flour since all batches were dried before compounding. Hence, it is unlikely that wood moisture was locked up in the compounds during processing which could not be removed later. In addition, compounds were dried again before injection-moulding and conditioned before LOI and UL94-tests. Further investigations using the cone calorimeter and crystallinity measurements may provide additional insight. In any case, at this stage it is an important conclusion that processing compounds with underwater and air granulation can lead to different outcomes in small-scale fire tests such as the UL94. This has important implications for the choice of processing method for fire-retarded composite materials and for formulation development of such materials in general.

3.3 Leaching of fire-retardants during processing

To determine the amount of fire-retardant which may have leached during underwater granulation, the process water was collected and analysed for phosphorus content. For treatment of the wood flour, APP (Exolit AP 420) and a formulation based on methyl phosphonic acid in combination with carbamoyl-guanidine amidino urea salt (Apyrol NCE CONC.) were used. Exolit AP 420 contains 12.5–13.5% phosphorus in a 45% solution. The phosphorus content of Apyrol NCE CONC. is not disclosed and was calculated as 8%, based on the molar mass proportion of P (16%) in the main components methyl phosphonic acid and carbamoyl-guanidine amidino urea salt (CAS 84402-58-4; $\text{CH}_5\text{O}_3\text{P}$ and $\text{C}_2\text{H}_6\text{N}_4\text{O}$) and the solids content (50%) of the solution. The amount of phosphorus in the two APP types used for protection of the thermoplastics was 32% (Exolit AP 422) and 30% (Exolit AP 462).

The maximum possible concentration of P for the formulations in the process water was determined according to the scheme shown in Table 4. The calculation is shown for the two formulations which contain the theoretically highest amount of APP, i.e., AP420–AP422. First of all, it was necessary to determine the amount of compound in contact with process water. This was done by weighing the amount of compound which was produced before the sampling process started, and subtracting this from the amount of compound after the sampling was finished. Hence, the amount

of compound in contact with process water was different for each formulation. For the two formulations shown in Table 4, the numbers were 3.77 kg and 3.59 kg, respectively. Using the calculated maximum amount of leached P and the total amount of process water, the maximum possible P concentration in the process water was calculated (1455.79 mg/l for the HDPE-based formulation and 1387.71 mg/l for the PP-based formulation). The conversion of the maximum possible concentration (mg/l) of leached P into wt.-% is shown in Table 5. The calculated amounts of leached P in the process water were 2.28 wt% for the HDPE-based formulation and 0.84 wt% for the PP-based formulation.

The results of the ICP-OES measurements show that the P concentrations of the process water (leachate) collected during underwater granulation were higher for the HDPE-based formulations compared to the PP-based formulations (Fig. 4). The highest amount of leached P (36 mg/l) was determined for formulation AP420-AP422 based on HDPE. The same formulation based on PP released only 12 mg/l phosphorus, i.e., only one third of the amount. The reference formulations without any FR were also analyzed. Here,

small amounts of P (0.34 mg/l for the HDPE-based formulation and 2.8 mg/l for the PP-based formulation; results not shown) were detected in the process water which may originate from any of the other components. These amounts were subtracted from the results for the formulations including FR when calculating the amount of P leaching in wt% (Table 5; Fig. 4). The references without any FR did not show any leaching of P and hence, are not shown in Fig. 4 because here, only the leaching of P from the FR was considered. Leaching of P was higher for the HDPE-based formulations (up to 2.5%) compared to the PP-based formulations (up to 1.7%). This could be due to the higher polarity of PP compared to HDPE which may result in stronger polar interaction of PP-based compounds with the FR compared to the HDPE-based compounds. The polar part of the surface energy is in the order of 0.3–1.3 mJ/m² for PP and in the order of 0–0.7 mJ/m² for HDPE (Anonymous 2020). If the polar part of the surface energy is higher than 1 mJ/m², a polymer is considered as polar; if it is smaller, a polymer is considered as non-polar. In most formulations with FR-treated wood flour, the amount of P leaching was higher

Table 4 Calculation of maximum possible concentration of phosphorus leached during underwater granulation for formulation AP420-AP422 with HDPE and PP matrix

Formulation	APP	Amount of P in APP (%)	Amount of APP in formulation (%)	Compound produced at start of leachate collection (kg)	Compound produced at end of leachate collection (kg)	Amount of compound in contact with process water (kg)	Calculated maximum amount of leached P (kg)	Total amount of process water (l)	Calculated max. possible P conc. in process water (mg/l)
HDPE	Added during compounding	32.0	16	1.15	4.92	3.77	*0.193	147	1312.93
	Added to wood	13.5	4.2	1.15	4.92	3.77	**0.021	147	142.86
Total									1455.79
PP	Added during compounding	32.0	16	0.89	4.48	3.59	0.183	147	1249.35
	Added to wood	13.5	4.2	0.89	4.48	3.59	0.020	147	138.36
Total									1387.71

*Calculated as: 3.77 kg multiplied by amount of APP in formulation (0.16) and amount of P in APP (0.32)

**Calculated as: 3.77 kg multiplied by amount of APP added to wood (0.042) and amount of P in APP (0.135)

Table 5 Calculation of leached amount of phosphorus during underwater granulation for formulation AP420-AP422 with HDPE and PP matrix

Formulation	Calculated max. possible P conc. in process water (mg/l)	Measured P conc. of formulation in process water (mg/l)	Measured P conc. of reference in process water (mg/l)	P conc. of formulation minus P conc. of reference (mg/l)	Calculated amount of leached P in process water (wt%)
HDPE	1455.79	36	2.80	33.20	2.28 (note: 1455.79 equals 100%)
PP	1387.71	12	0.34	11.66	0.84 (note: 1387.71 equals 100%)

Fig. 4 Amount of phosphorus (wt%) in process water from underwater granulation. For composition of formulations, see Table 1. Only leached P from the FR was considered, hence, no leaching from the two reference formulations is shown. Error bars shown represent the standard deviation of the method (1.3%)

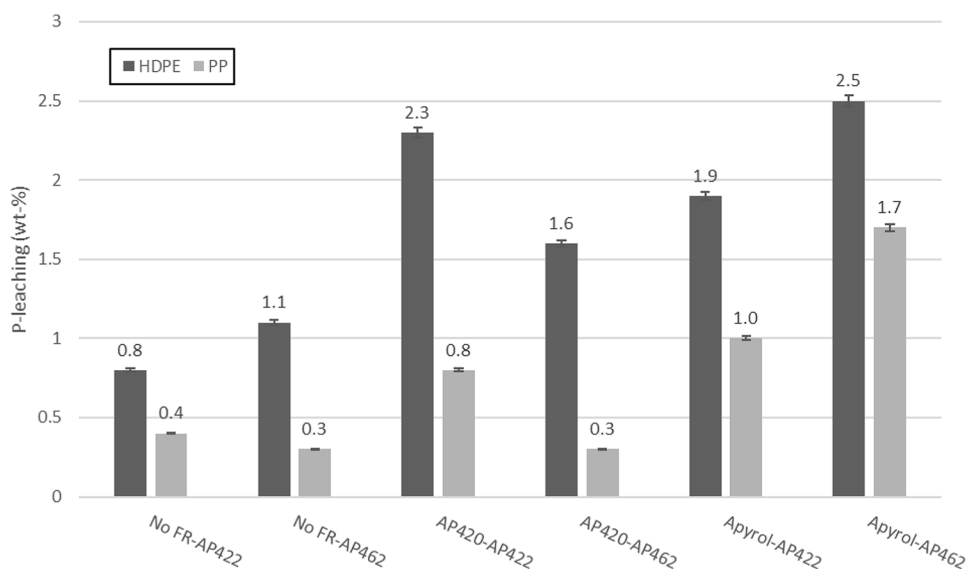


Table 6 UL94-classification, LOI and colour changes of selected formulations after 300 h xenon weathering (b.w. means before weathering, a.w. means after weathering)

Formulation	UL 94 b. w.	UL 94 a. w.	LOI b. w.	LOI a. w.	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔG
HDPE: Apyrol-AP422 (UWG)	V0	Not passed	30	24	12.4	1.0	1.0	12.5	- 5.0
HDPE: Apyrol-AP422 (AG)	V0	Not passed	29	27	14.0	1.3	0.9	14.1	- 3.3
PP: AP420-AP422 (UWG)	V0	V0	26	25	18.2	1.1	1.4	18.4	- 11.7
PP: AP420-AP422 (AG)	V0	V0	24	24	15.8	1.6	1.8	15.9	- 12.5
PP: AP420-AP462 (UWG)	V0	V0	26	26	20.9	0.5	0.7	20.9	- 12.3
PP: AP420-AP462 (AG)	V0	V0	25	25	23.2	0.8	0.8	23.2	- 11.3

For composition of formulations, see Table 1

compared to when untreated wood flour was used which can be expected. In general, leaching of P from the process water was low with values below 3 wt%. Regarding the type of APP used for the polymer matrix (uncoated AP 422 versus coated AP 462), no clear tendency could be observed for the resistance of the FR against leaching during processing. However, there may be differences during long-term exposure of the materials to water. Wang et al. (2016) investigated the differences in water solubility of a microencapsulated APP versus an uncoated APP. They determined decreased water solubility of APP after microencapsulation.

3.4 UL94, LOI and colour changes after xenon weathering

The three formulations which were processed using underwater granulation and which achieved V0-classification while displaying the lowest leaching of phosphorous were Apyrol-AP422 (HDPE), AP420-AP422 (PP) and AP420-AP462 (PP). These formulations were subjected to artificial weathering in a xenon device for 300 h and then tested again

to determine UL94-classification, LOI and colour changes. For comparison, the same formulations which had been processed using air granulation were also tested. The results are shown in Table 6. While formulation Apyrol-AP422 (HDPE) achieved V0 before weathering and failed after weathering, all formulations based on PP remained at the V0 classification after 300 h weathering. Because in the weathering test, different FR were used for the wood particles (Apyrol for the compounds with HDPE and AP420 for the compounds with PP), it is not possible to draw general conclusions. It can only be concluded that during short term weathering for 300 h in a xenon device, the compounds based on PP and with APP for the wood particles as well as for the matrix kept their UL94 classification. More long-term studies are needed to investigate the long-term durability behavior of WPC with FR. The 300 h duration is a requirement in DIN EN 15534, parts 4 and 5, if xenon weathering according to EN ISO 4892-2A is applied. In case of artificial weathering, hydrolysis of APP may occur and result in reduced fire retardancy as the formation of the intumescent network is disturbed already after exposure with an incident energy of

210 kJ cm⁻², a value which corresponds to less than 1 year of outside use in mid-Europe (Pfaendner 2014).

Colour changes (ΔE) of the tested formulations were high, with values ranging between 12.5 and 23.2. Better results in terms of colour stability and gloss (ΔG) were obtained for the HDPE-based formulation compared to the PP-based formulations. The values for oxygen index were slightly reduced for the HDPE-formulation and remained at the same level as before weathering for the PP-based formulations.

Little information is available in the scientific literature regarding the durability of FR treatments for WPC. Garcia et al. (2009) determined colour changes (ΔE) for WPC based on HDPE and with APP as FR which were in the range of 22–26 after 600 h of weathering which is much higher than the values for colour change determined here for the HDPE-based formulations. However, differences in processing, base polymer, addition and type of weathering (Garcia et al. used QUV weathering) have to be considered. The fire performance after weathering was not investigated.

Color changes after weathering of WPC based on PP and with different FR (aluminum trihydrate, zinc borate, melamine, graphite, titanium dioxide) were investigated by Turku and Kärki (2016). Duration of the weathering was 1000 h, and samples were subjected to weathering under a xenon-arc lamp source. FTIR analysis revealed that the FR did not influence the photo-oxidation mechanism of the composite. Surprisingly, it was found that FR-loaded samples showed smaller color change compared to unfilled ones.

Some recently developed flame retardants combine flame retardancy and light stabilizer functionality (Pfaendner

2014), however, the photooxidative stabilization of flame-retarded “green” composites is a complex field as the polymer, FR system, additives (processing stabilizers, antioxidants, light stabilizers, etc.) and filler have to be considered together.

3.5 Thermogravimetric analysis (TGA)

TGA was performed with compounds AP420-AP422 (HDPE and PP matrix) which had been processed using either air or underwater granulation. For comparison, the reference compound without FR was analyzed. The results are shown in Figs. 5, 6. Some differences between the compounds processed with underwater and air granulation are visible, but the differences between fire-retarded and non-fire-retarded formulations are more pronounced. Up to a temperature of approximately 200 °C, little weight loss occurred. For the compounds based on HDPE, in the temperature range between 200 and 320 °C, the fire-retarded formulation which contained wood flour pre-treated with APP plus APP for the polymer matrix showed less thermal stability than the unprotected formulation. This can be attributed to the formation of polyphosphoric acid which catalyzes the degradation of the wood flour (Abu Bakar et al. 2010). From 320 °C onwards, thermal stability of the fire-retarded formulation was higher compared to the unprotected one. Mass loss of the unprotected formulation occurred faster and resulted in lower residue (2.56% for the compound prepared using air granulation and 2.75% for the compound prepared using underwater granulation). The APP used for protection of the polymer matrix (Exolit AP 422) begins to degrade at

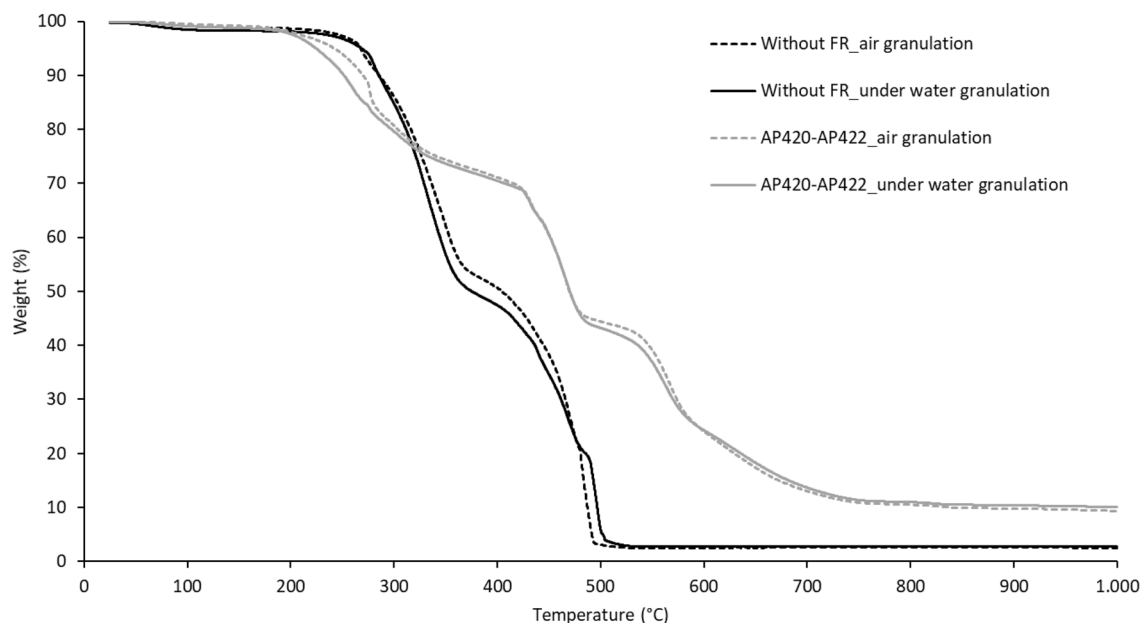


Fig. 5 TGA of HDPE-based compounds without any fire-retardant and with pre-treated wood flour plus APP

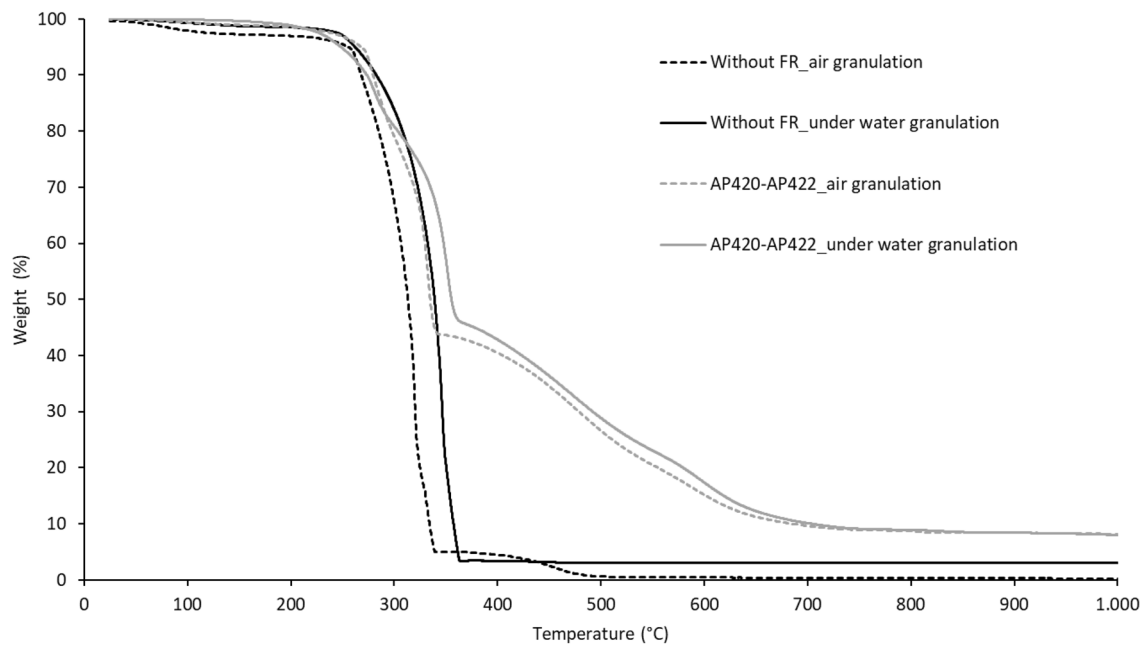


Fig. 6 TGA of PP-based compounds without any fire-retardant and with pre-treated wood flour plus APP

275 °C, according to the technical data sheet. APP begins to decompose into polyphosphoric acid and ammonia. Polyphosphoric acid acts as a char-former and a char-phosphate insulation layer is formed on the wood particle surfaces. Approximately 20% weight loss of the Exolit AP 422 is reached at 550 °C, according to the technical data sheet.

Between 400 and 600 °C, for the fire-retarded compound based on HDPE, two steps are visible in the curves, one between 462 and 471 °C, and another one between 562 and 569 °C. For the unprotected formulation, there is only one steep degradation step during this temperature range. Final residues of the fire-retarded formulation (10.68% with air granulation and 11.23% with underwater granulation) were more than three times higher than of the non-fire-retarded compounds. Mass loss of the unprotected formulation was completed at 500 °C whereas the protected formulation continued to show mass loss up to a temperature of 750 °C.

Figure 6 shows the TGA curves for the PP-based compounds. Here, higher thermal stability up to 300 °C of unprotected compounds was not visible. For the PP-based formulations, the curves show less steps compared to the HDPE-based compounds. The highest mass loss rate was obtained between 319 and 357 °C. During this temperature range, mass loss of the unprotected formulation was as high as 95–97%. In comparison, the fire-retarded formulations displayed significantly lower mass loss rate. From 350 °C onwards, stabilization of the fire-retarded formulations can be clearly seen in the curves. Final residues of the protected formulations (8.44% with under water granulation and 8.90% with air granulation) were much higher compared

to the unprotected formulations (3.41% and 0.60%). As was seen with the HDPE-based compounds, differences in thermal stability and mass loss rates were larger between unprotected and protected compounds compared to differences related to the type of granulation.

3.6 Tensile strength tests, water uptake and swelling of composites

The effects of the FR on tensile strength of the composites as well as differences between underwater and air granulation are shown in Figs. 7, 8. In general, tensile strength was not reduced due to the presence of the FR, and in some cases even increased. Only when underwater granulation was used to process HDPE-based compounds, there was a reduction in tensile strength from 35.8 N/mm² to values between 28.4 and 31.3 N/mm². This amounts to a maximum reduction of 21% in tensile strength. It has to be considered that in the reference formulations without any FR, 58% of wood particles were included whereas in the formulations which contained FR, 42% of wood particles were used. However, the total amount of filler (wood particles or combination of wood particles and FR) was identical for all formulations. It appears that the bonding between wood particles, polymer matrix and coupling agent was not affected by the presence of the FR in the formulations, with the exception of the HDPE-based compounds processed with underwater granulation. It is possible that the processing conditions affected the resulting crystallinity of the polymer matrices. Bouafif et al. (2009) showed that the addition of wood particles to

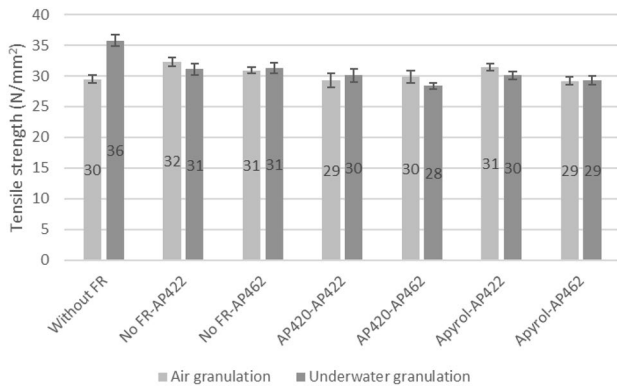


Fig. 7 Tensile strength of formulations based on HDPE (Table 1)

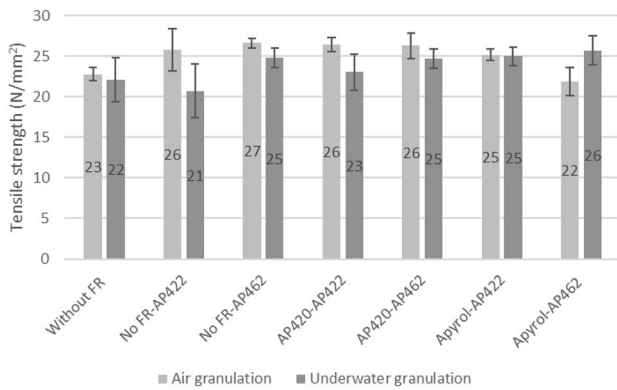


Fig. 8 Tensile strength of formulations based on PP (Table 1)

HDPE increased the crystallinity of the matrix which is due to the nucleating ability of wood particles in the crystallization of HDPE. The presence of the FR may also have an influence on the crystallinity of the HDPE. Crystallinity depends on processing parameters such as the crystallization temperature, cooling rate, nucleation density, annealing time, and fiber type (Bouafif et al. 2009). The crystallinity in semicrystalline polymers such as PE and PP is a major factor affecting their strength properties. The higher the degree of crystallization, the stronger and stiffer a moulded part may be but also the more brittle (Ehrenstein et al. 2003).

Tensile strength of the PP-based formulations was generally lower than of the HDPE-based formulations. This may partially be due to the type and shape of PP used. The HDPE was provided in powder form whereas the PP was provided in pellet form. Polymer in powder form can potentially be mixed better with wood flour, resulting in a more homogeneous distribution of the wood flour in the polymer and potentially, in higher strength. Overall, air granulation appeared to result in slightly higher tensile strength, with the exception of formulation Apyrol-AP462 (PP). The use of the FR did not result in lower tensile strength. On the contrary, in most cases, tensile strength was increased when FR was included.

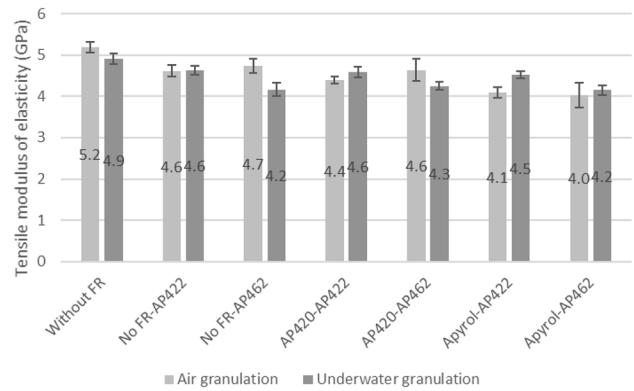


Fig. 9 Tensile modulus of elasticity of formulations based on HDPE (Table 1)

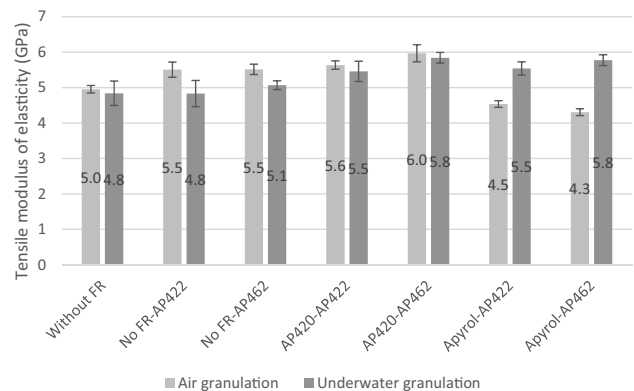


Fig. 10 Tensile modulus of elasticity of formulations based on PP (Table 1)

There was no difference in the tensile strength of PP-based formulations without FR when processed either with air or underwater granulation.

Regarding the tensile modulus of elasticity, different trends for the HDPE- and PP-based formulations were observed (Figs. 9, 10). For the HDPE-based formulations, the tensile MOE was reduced by up to 22% when a FR was included (Apyrol-AP462; air-granulation). In the formulations with FR, the FR probably interfered with the coupling agent resulting in a decrease in modulus. In addition, in the formulation without FR, a higher amount of wood flour was present which was available for bonding with the polymer via the coupling agent. In general, tensile MOE of HDPE-based formulations was between 4 and 5.2 GPa. For the PP-based formulations, except for two formulations, the tensile MOE increased with the addition of the FR.

Yin et al. (2018) determined the mechanical performance of injection-moulded, PP-based WPC samples with different FR combinations. In their formulations, either 30% wood filler (reference without FR) or 50% filler (formulations with

FR, composed of 30% wood filler plus 20% FR) were used. Hence, it is difficult to evaluate the effects of the FR. APP was used in combination with expandable graphite or red phosphorus. Under the conditions of the study by Yin et al., the combination of APP and red phosphorus retained the original flexural strength and increased flexural modulus, but Charpy impact strength was reduced significantly. In contrast, Stark et al. (2010) reported that APP had a negative effect on mechanical properties, however, in this case, polyethylene served as matrix.

Swelling and water uptake of the composites based on PP as matrix after 28 days of cold water immersion are shown in Figs. 11, 12. The reference formulation without any FR contained 58% wood particles and 33% PP (Table 1). When FR were included for the matrix, the amount of wood particles was reduced to 42%. Compared to the reference without any FR, the compounds with 16% of APP for the PP matrix and with untreated wood particles showed increased values for swelling and water uptake. For example, in the case of the compounds made with underwater granulation, water uptake of the reference was about 6%, compared to approximately 8–9% for the compounds with APP for the matrix. This increase in water uptake can be attributed to the hygroscopicity and moisture sensitivity of the APP (Wang et al. 2016). However, when the wood particles are pre-treated with FR (Exolit AP 420 or Apyrol NCE) and simultaneously, APP is added during compounding, swelling and water uptake of the composite are reduced compared to when APP is added during compounding only. In this case, it is thought that the pre-treatment of the wood particles with the FR contributes to esterification of the wood particles and consequently, the hydroxyl groups may be blocked and water uptake is reduced. Hence, the wood particle pre-treatment may have a beneficial effect regarding water uptake and swelling. The wood flour pre-treatment appears to partially counteract the negative effect of the APP addition during compounding. This was also observed for the formulations

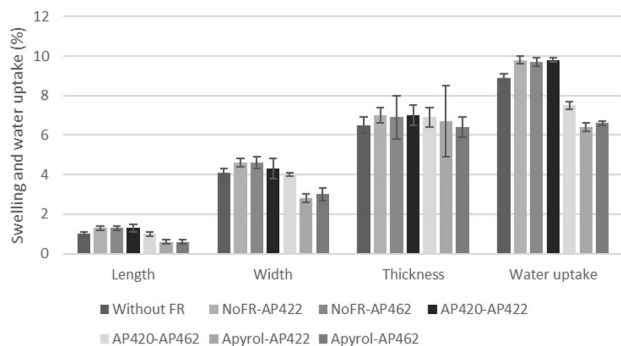


Fig. 11 Swelling and water uptake of PP-formulations (Table 1) after 28 days of cold-water immersion. Compounds were processed with air granulation

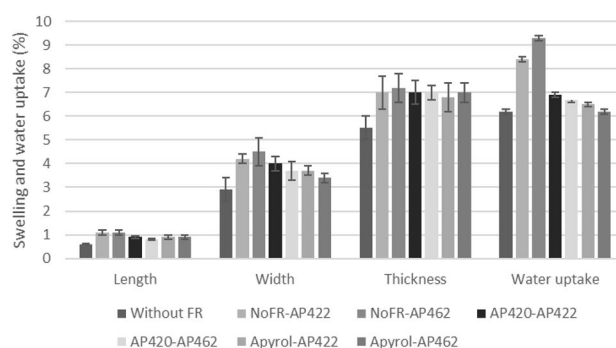


Fig. 12 Swelling and water uptake of PP-formulations (Table 1) after 28 days of cold-water immersion. Compounds were processed with underwater granulation

processed with air granulation, except for one formulation (AP420-AP422). Similar benefits for the use of modified wood flour in WPC were reported by Hämäläinen and Kärki (2014) who used phosphate-based FR solutions and a melamine formaldehyde resin for wood flour modification.

Another possible explanation for the observed reduced water uptake of compounds with pre-treated wood particles could be thermal degradation of the FR-treated wood particles. Upon heating, the APP on the wood particles can degrade into polyphosphoric acid which catalyzes the degradation of cellulose (Abu Bakar et al. 2010). The result would be particles which are less hydrophilic, similar to heat-treated wood particles. Butylina et al. (2011) have shown that WPC with heat-treated wood particles display lower water absorption compared to WPC with untreated wood.

In terms of water uptake and swelling, the most important conclusion is that it is better to use a wood particle pre-treatment plus APP for the matrix than just APP for the matrix. Since in this series, no formulation with pre-treated wood particles and without APP for the matrix was included, further experiments would be required to analyze the effects of the wood pre-treatment alone on swelling and water uptake of the composites. However, in practical terms, it does not appear to be useful to leave out the FR for the matrix if good reaction-to-fire performance of the composite is desired.

3.7 Single-burning item (SBI) tests

For the SBI test, formulation Apyrol-AP422 (HDPE-based) was chosen, based on the V0-classification (UL 94 test) achieved with air as well as underwater granulation, and due to the fact that the industrial WPC profile extrusion line used was set-up for HDPE as polymer matrix. For comparison, the corresponding formulation with untreated wood flour was chosen for the SBI test. In both formulations, APP was used to protect the polymer matrix.

Before the SBI tests were performed, small samples for oxygen index measurement and UL94-classification were taken from the profiles. Oxygen index was 32% for the profiles with pre-treated wood flour and 29% for the profiles with untreated wood flour. Samples from both formulations also achieved V0-classification in the UL94 test, hence, the results previously obtained using small injection-moulded samples were confirmed. The results for the SBI tests are shown in Table 7, and the classification criteria for SBI testing are shown in Table 8. The formulation with pre-treated wood flour reached classification C-s3, d0 according to DIN EN 13501-1 which means that the material is hardly flammable according to the German DIN 4102-1 (1998). In comparison, the formulation with untreated wood flour was classified as D-s2, d0 according to DIN EN 13501-1, i.e., the material is normally flammable according to DIN 4102-1. In both cases (untreated and pre-treated wood flour), lateral flame spread (LFS) did not reach the far edge of the long wing specimen during the first 1500 s of the test.

The formulation with 55% of wood flour listed in Table 7 was extruded in another project and differs in composition as well as in shape of the profile and processing conditions (Schirp and Barrio 2018). The profiles with 55% pre-treated wood flour achieved even better classification than the profiles with 42% pre-treated wood flour from this project and reached classification B-s2, d0. The profiles consisted of 55% pre-treated wood flour, 23% HDPE, 1% lubricant, 2% coupling agent, 19% APP (Exolit AP 422), and the shape was a hollow decking profile. In this case, the wood flour pre-treatment was done using APP (10% Exolit AP 420

based on solid content and wood dry weight). LOI of this formulation was 39–40. Despite the differences in the shape and processing of the extruded profiles, it appears that a higher wood content in WPC (55% compared to 42%) leads to better fire resistance which confirms the results by Stark et al. (2010). The wood flour or fibre itself acts as a fire retardant for the polymer matrix. As the wood filler level increases, the heat release rate decreases. In addition, the presence of wood promotes char layer formation on the profile surface (Seefeldt and Braun 2012a). Furthermore, values for the oxygen index can be used to explain why a high wood content in WPC is beneficial in terms of combustibility. The oxygen index of wood (23.9) is higher than that of pure PP (18), which indicates that a greater quantity of oxygen is required to sustain the combustion of wood. With increasing proportion of wood in WPC, the oxygen index increases, e.g., reaching 20 for 60% wood flour, indicating the presence of wood has increased the oxygen demand for combustion (Stark et al. 2010).

Seefeldt and Braun (2012a) compared hollow and solid extruded profiles regarding their reaction-to-fire performance and found that while profiles with hollow chambers reduced the fire load, they also displayed higher fire propagation. A direct comparison of hollow and solid extruded profiles based on the same composition in the SBI test would be required to clarify if there are differences in reaction-to-fire performance.

Nikolaeva and Kärki (2015) performed cone calorimetry with WPC including zinc borate, melamine and APP. Simulated FIGRA and SBI Euroclass classification results showed

Table 7 SBI results summary

Formulation	FIGRA	FIGRA	THR _{600s}	SMOGRA	TSP _{600s}	Classification		
	0.2 MJ [W/s]	0.4 MJ [W/s]	[MJ]	[m ² /s ²]	[m ²]			
HDPE: Apyrol-AP422	114.5	114.5	13.6	23.8	200.5	C	s3	d0
HDPE: no FR-AP422	165.7	165.7	16.3	17.9	168.6	D	s2	d0
HDPE*	54.6	54.6	6.4	13.7	177.3	B	s2	d0

Results are based on one test per formulation. Composition of formulations is shown in Table 1

*With 23% HDPE and 55% wood flour, which was treated with 10% AP420 (based on solids content and dry wood); in addition to differences in composition, a hollow-chamber decking profile was used (Schirp and Barrio 2018)

Table 8 Classification criteria for SBI testing

EU classification	FIGRA/THR _{600s} /LFS		SMOGRA/TSP _{600s}		Flaming droplets/particles classification
A2 and B	FIGRA ≤ 120 W/s THR _{600s} ≤ 7.5 MJ LFS < edge of specimen	S1	SMOGRA ≤ 30 m ² /s ² TSP _{600s} ≤ 50 m ²	d0	No flaming droplets
C	FIGRA ≤ 250 W/s THR _{600s} ≤ 15 MJ LFS < edge of specimen	S2	SMOGRA ≤ 180 m ² /s ² TSP _{600s} ≤ 200 m ²	d1	No flaming droplets/part. persisting > 10 s
D	FIGRA: ≤ 750 W/s	S3	–	d2	–

that the best classification achieved was class D which could be obtained by using either 30% zinc borate or 20–30% APP. The same authors also investigated the reaction-to-fire properties of coextruded WPC containing different fire retardants in the shell layer (Nikolaeva and Kärki 2016). The reference sample without fire-retardant displayed class E in the Euroclass system whereas class D was obtained when FR were included in the shell layer. The best results were obtained with APP. Hence, co-extrusion may be an efficient way to reduce costs for the FR while achieving the same Euroclass rating as with bulk protection.

4 Conclusion

Under the conditions of the present investigations, the following conclusions can be drawn:

- For PP-based WPC, it is possible to achieve V0-classification in the UL94 test at 4 mm sample thickness even without a pre-treatment of the wood flour with FR. However, to achieve the same classification for HDPE-based composites, it appears necessary to pre-treat the wood particles with organic nitrogen-phosphorus compounds.
- The values for the LOI were higher for HDPE-based composites compared to PP-based composites. For HDPE-based composites, in cases where V0-classification was obtained, LOI was 29 or higher. For the PP-based composites, a relatively low LOI of 24 leads to V0-classification@4 mm in most cases. Accordingly, there was no relationship between results obtained in LOI and UL94-tests for the wood-polymer composite formulations tested. However, this was not unexpected because the LOI test is used to determine the minimum concentration of oxygen, in admixture with nitrogen, that will support combustion of small test specimens, while in the UL94 test, the flammability rating of the material is determined.
- In general, low amounts of phosphorus leaching were observed during underwater granulation of compounds. Since exposure time of the compounds to water during underwater granulation is very short, further studies are required to investigate possible leaching of FR from the processed compounds, i.e., during service life of the products.
- After 300 h of artificial (xenon) weathering, V0-classification of fire-retarded HDPE-based composites was reduced to “not passed” whereas V0-classification of PP-based composites was maintained under the same conditions. However, color change after weathering was higher for fire-retarded PP-based than for HDPE-based composites. Color stability of fire-retarded WPC needs to be further improved.
- Single-burning item (SBI) tests showed that classification C-s3, d0 according to DIN EN 13501-1 can be achieved if pre-treated wood flour is used. The use of untreated wood flour leads to a lower classification (D-s2, d0). In the future, SBI tests with fire-retarded composites after weathering should be performed to determine the durability of the fire-retardant treatments.
- Tensile strength of fire-retarded formulations was reduced only for HDPE-based composites and when underwater granulation was used. Tensile MOE was reduced in most cases for HDPE-based composites but mostly increased for PP-based composites. These results show that it is difficult to draw general conclusions regarding the effects of FR on the mechanical performance, and that each formulation needs to be carefully evaluated, also in terms of processability.
- When wood particles are pre-treated with FR (Exolit AP 420 or Apyrol NCE) and APP is added during compounding, swelling and water uptake of the composite are reduced compared to when APP is added during the compounding step only. This may be explained with esterification of the wood particles by the FR which causes a reduction in water uptake. Hence, an important conclusion is that a combined treatment of wood and polymer provides a benefit not only in terms of fire resistance but also in terms of reduced water uptake.
- The most important conclusion is that pre-treatment of the wood particles used in extrusion (HDPE-based composites) has a positive effect on the fire performance of the composites, albeit at a higher cost. The technical benefit may outweigh the additional costs and justify the use of fire-retarded wood flour. Further research into the durability of FR-treated WPC is needed to enable the use of WPC in facades or other building products.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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