

Optimal distribution of phosphorus compounds in multi-layered natural fabric reinforced biocomposites

K. Bocz*, B. Szolnoki, A. Farkas, E. Verret, D. Vadas, K. Decsov, G. Marosi

Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

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Abstract. Flame retardancy and mechanical performance of multi-layered biocomposites, consisting of polylactic acid (PLA) matrix films and plain-woven flax fabrics as reinforcement, were investigated. Full factorial design (3^2) was applied to evaluate the effects of the distribution of P and N containing compounds between the matrix and the fibrous carrier. Composition property correlations of the composite constituents (*i.e.* flax fabrics treated in aqueous solutions of diammonium phosphate and urea with differing ratio and concentrations and matrix films with 0 to 20 wt% ammonium polyphosphate based intumescent flame retardant content) were determined by thermogravimetric analyses and open flame tests. Positive interaction between the composite constituents was revealed for green composites consisting of various combinations of treated fabrics and intumescent PLA systems. The biocomposites flame retarded with a combined approach, *i.e.* with a balanced distribution of P containing additives between the phases, were found to gain improved mechanical performance and fire retardancy. It was confirmed by tensile testing and electron microscopy as well as by UL-94, limiting oxygen index and cone calorimeter tests. As a conclusion, interpretation is given for the optimum found.

Keywords: biopolymers, biocomposites, polylactic acid, natural fibre reinforcement, flame retardancy, mechanical properties

1. Introduction

Polylactic acid (PLA) is a commercialised biopolymer, and more and more PLA products are on the market. These goods are, however, mainly related to the packaging industry even so the high strength and stiffness of PLA suggest to use it as the matrix of durable engineering composite materials. The widespread usage of PLA as high-performance composite material is restrained mainly due to its low thermo-mechanical and fire resistance, insufficient impact strength and relatively high price [1, 2]. Therefore, neat PLA is often combined with natural fibres with the aim of decreasing costs while maintaining or improving the mechanical properties [3, 4].

According to thermogravimetric analysis, PLA degrades in a single step taking place between 300 and 400 °C (the highest degradation rate is observed at

350 °C). The thermal degradation of PLA is based on a hydroxyl end-initiated ester inter-chain process and chain homolysis. In the condensed phase, the char yield is quite low (about 2 wt%) [5]. Flame retardants should, therefore, act before the degradation of PLA ($T < 300$ °C) and/or modify the degradation pathway of PLA to yield char and to avoid (or at least to decrease) the evolution of flammable products (acetaldehyde, lactide, methane etc.). For this purpose, condensed phase mechanisms of action are proposed in the literature (almost in all cases) to reduce the flammability of PLA.

Comprehensive reviews on the flame retardancy of PLA were published by Bourbigot and Fontaine in 2010 [6], by Chow *et al.* [7], and by Tawiah *et al.* [8] in 2018, respectively. Among the phosphorus-based additives, Bourbigot *et al.* [9] compared the flame

*Corresponding author, e-mail: kbocz@mail.bme.hu
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retardant effectiveness of phosphine-based flame retardants, designed for polyamides and polyesters, to ammonium polyphosphate (APP) and melamine polyphosphate (MP) in PLA matrix. The highest LOI value (34%) was measured for the 30 wt% APP containing PLA.

When bio-based fibres are used as reinforcements in polymer matrices (without flame retardants) to form biocomposites, the heat conductivity increases while the apparent stability of the polymer decreases. Thus the ignition of the composite is facilitated [10, 11]. Therefore, the understanding of the details of the flame retardant treatment of bio-fibres is essential as well. Most of the flame retardants for cellulosic fibres function via condensed phase conversion of the fibres to carbonaceous char. This reaction is considered to be acid-catalysed dehydration. Char-promoting flame retardants for cellulose typically contain phosphorus, either as acidic salts (*e.g.* ammonium phosphate derivatives) or as organophosphorus (*e.g.* phosphonium salt and phosphonate derivatives) species. On heating, they first release polyphosphoric acid which phosphorylates the C(6) hydroxyl group in the anhydroglucopyranose moiety and simultaneously act as an acidic catalyst for dehydration of these same repeat units. The first reaction prevents the formation of levoglucosan (1,6-anhydro- β -D-glucopyranose), the precursor of flammable volatiles. This ensures that the competing char-forming reaction becomes the favoured pyrolysis route [12].

A large variety of phosphorous compounds have been used to flame retard cellulose-based fibres [13–16]. Gaan and Sun [15] investigated the flame retardancy effect of six organophosphorus compounds, including Pyrovatex CP (PCP), diammonium phosphate (DAP), phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP) and triallyl phosphoric triamide (TPT) on cotton cellulose. PCP, PA and DAP were found to be more efficient in improving the limiting oxygen index (LOI) of cotton compared with the other three compounds of the same phosphorus content. Furthermore, PA, PCP, and DAP treated fabrics had a higher activation energy of decomposition, higher char content and lower heat of combustion.

The recent advances of phosphorus-based flame retardants developed for fibres and fabrics have been reviewed by Salmeia *et al.* [17]. In this survey, the newly developed additives exploiting the synergistic effect provided by the simultaneous presence of

phosphorus and nitrogen is particularly referred. Among others, urea [16, 18] has shown synergistic function with phosphorous flame retardants.

It is evident from the literature that phosphorus-containing flame retardants can efficiently initiate the charring of natural fibres, which is favourable in terms of flame retardancy. However, the application of these treatments significantly decreases the initial decomposition temperature of natural fibres [18–20]. The reduced thermal stability can be a major issue, both from a mechanical and aesthetic point of view when the natural fibres are intended to be used as fillers or reinforcements in polymer composites. Presence of water, acids and oxygen catalyses the thermal degradation of cellulose; therefore, natural fibres usually turn brown during fibre treatments. Low thermal stability is critical in case of thermoplastic matrices with processing temperatures above 140 °C, such as PP, PA, PET and also PLA.

As shown in the previous paragraphs, the flame retardancy of both PLA and natural fibres are investigated in details. Still, the flame retardancy of their green composites, consisting of PLA matrix and natural fibre reinforcement, has been barely studied in the literature yet. It is known that the so-called candlewick effect of natural fibres encumbers the flame retardancy of the biocomposites reinforced with these fibres [21, 22].

Suardana *et al.* [13] fabricated coconut filter and jute fibre reinforced PLA composites. To improve the flame retardancy of the biocomposites, the fibres were immersed in diammonium phosphate (DAP) solutions with concentrations of 1, 2.5, and 5 w/V%. Increasing the percentage of DAP for treatment of the fibres in the composites decreased the temperature required for 5% weight loss and the decomposition rate, but increased the char residue at 500 °C. The lowest linear burning rate and weight loss rate were observed for fibre treatment with 5 w/V% DAP. However, the flexural and tensile strengths became lower than those of untreated fibre composites. On the other hand, the tensile and flexural moduli of DAP-treated fibre composites increased generally.

Li *et al.* [21] compared the flammability of ramie fibre (30 wt%) reinforced PLA composites flame retarded with APP by three different processes: (1) PLA was blended with APP and combined with neat ramie fibres, (2) ramie fibres were treated with APP and then compounded with PLA and (3) both PLA and ramie fibres were flame retarded using APP

and blended together. In contrast to the identical APP loadings (10.5 wt%), significantly better flame retardancy was evinced for the composites where APP was present in both phases, which they explained by the successful elimination of the candlewick effect of the ramie fibres. The LOI of the best formulation reaches 35%, and the formulation exhibits V-0 rating.

Similar conclusions were drawn by Chen *et al.* [22], who used melamine-formaldehyde microencapsulated ammonium polyphosphate (MCAPP) to flame retard ramie fabric (30 wt%) reinforced PLA composites. Coupling agent, 3-aminopropyltriethoxysilane, was used to improve the interaction between the ramie fibre and the polymer. When MCAPP was applied both in the matrix and on the surface of the ramie fabrics, effective flame retardancy was observed. At a total MCAPP content of 10.5 wt% UL-94 V-0 rating and LOI value higher than 35% were achieved.

Based on the literature it can be concluded that achieving a good balance of the fire safety and favourable mechanical properties is a serious challenge in the case of green composites, the researchers in this field have to face the challenges of low thermal stability and candlewick effect of natural fibres and compatibility issues as well. In the present work, the flame retardancy possibilities of multi-layered biocomposites, consisting of PLA matrix layers and plain-woven flax fabrics as reinforcement, were investigated. Phosphorus-based compounds were applied both in the polymer matrix and on the surface of the reinforcing natural fibres to eliminate their candlewick effect. APP based intumescent flame retardant (IFR) additive was incorporated into the matrix layers, while in order to utilise the P-N synergism and compensate the reduced heat stability of the phosphorous flame retarded natural fibres, DAP was combined with urea (U) to treat the natural fibres. To reach the optimal composition of flame retarded green composites and determine the optimal distribution of P-containing compounds between the matrix and the fibrous carrier, in terms of flammability and mechanical properties, various combinations of treated fabrics and intumescent PLA systems were studied by following a 3^2 full factorial design.

2. Materials and methods

2.1. Materials and sample preparation

2.1.1. Preparation of flame retarded flax fabrics

Plain woven flax fabric with an areal weight of 200 g/m² was received from Meshining Engineering Kft. (Győr, Hungary). For flame retardant treatment, the flax fabrics were immersed in aqueous solutions of diammonium phosphate (DAP) and urea (U) with differing ratio and concentrations for 2 min at room temperature. The excess of the treating solutions was removed by pressing the fabrics by a foulard and then dried in an oven at 80 °C for 12 h.

2.1.2. Preparation of flame retarded PLA matrix films

Ingeo™ Biopolymer 2003D type PLA (NatureWorks, Minnetonka, MN, USA) with a specific gravity of 1.24 g/cm³ and a melt flow index (MFI) of 6 g/10 min (210 °C, 2.16 kg) was used as matrix material. The PLA resin was dried at 90 °C for 8 h prior to processing. Exolit AP462 supplied by Clariant (Muttens, Switzerland), a melamine resin micro-encapsulated ammonium polyphosphate (APP) based additive (intumescent flame retardant (IFR)) with an average particle size (D_{50}) of 20 µm was used to obtain flame retarded matrix materials.

200 µm thick PLA matrix films with increasing IFR contents (0, 5, 10, 15 and 20 wt%) were produced by melt compounding using a Labtech Scientific LTE 26-44 modular corotating twin-screw extruder (Labtech Engineering, Samutprakarn, Thailand) (temperature 170–190 °C, rotation speed 25 rpm) and subsequent film extrusion using a Labtech LCR 300 laboratory flat film line (Labtech Engineering, Samutprakarn, Thailand) with the following parameters: screw rotation speed: 22 1/min; extruder temperature profile from feed zone to die: 190, 195, 195, 200, and 200 °C, temperature of coat hanger die: 210, 205, and 210 °C; winding speed: 15 1/min.

2.1.3. Preparation of multilayered biocomposites

Multilayered flax fabric-reinforced PLA composites were manufactured by laminating 5 matrix films and 4 woven flax fabrics by alternating the warp and weft directions. The packages were hot-pressed to form 2 mm-thick multilayer composites in a Collin

P200E type laboratory hot press set to 185 °C under a pressure of 0.25 MPa for 2 minutes. An average reinforcement content of 45% was determined for the biocomposite plates by measuring the actual mass of the used fabrics and the composite mass after hot-pressing.

2.2. Characterisation methods

Thermogravimetric analysis (TGA) measurements were carried out using a TA Instruments (New Castle, NH, USA) Q5000 type instrument with a heating rate of 10 °C/min under 25 ml/min nitrogen gas flow, covering a temperature range of 25–500 °C. About 5–10 mg of sample was used in each test.

Reaction to fire of the flame retardant treated flax fabrics was evaluated based on the EN ISO 11925-2 standard. The edges of vertically mounted fabric specimens with dimensions of 90×250 mm were exposed to a 20 mm gas flame for 30 s, and the burnt length was registered (average of 4 test specimens of each type). Dripping was not characteristic for the flax fabrics.

Limiting oxygen index (LOI) measurements were performed according to the ISO 4589 standard. The LOI value expresses the lowest oxygen to nitrogen ratio, where specimen combustion is still self-supporting.

Standard UL-94 flammability tests were performed according to ISO 9772 and ISO 9773. UL-94 classification is used to determine dripping and flame spreading rates.

Mass loss type cone calorimeter tests were carried out by an instrument delivered by Fire Testing Technology Ltd., (East Grinstead, West Sussex, United Kingdom), using the ISO 13927 standard method. Specimens (100 mm×100 mm×2 mm) were exposed to a constant heat flux of 50 kW/m² and ignited. Heat release values and mass reduction were continuously recorded during burning.

Comparative static tensile tests were performed based on the ISO 527 standard on rectangular composite specimens of 15 mm×120 mm (width×length) (the gauge length was 50 mm) using a Zwick Z020 universal testing machine (Zwick GmbH & Co. KG, Germany) with a crosshead speed of 5 mm/min. Young's modulus values were determined from the stress-strain curves between the strain levels of 0.1 and 0.5%.

Scanning electron microscopic (SEM) images were taken from the cryogenic fracture surfaces of the

composites. A JEOL JSM-5500 LV type apparatus (JEOL Ltd., Akishima, Tokyo, Japan) was used for the examination with an accelerating voltage of 15 keV. All the samples were coated with gold before examination in order to prevent charge build-up on the surface.

3. Results and discussion

3.1. Characterisation of flame retardant treated flax fabrics

3.1.1. Optimisation of DAP to U ratio

As a first step, the ratio of diammonium phosphate (DAP) as char promoting flame retardant and urea (U) as a nitrogen-containing synergist in the treating solution of flax fabrics was optimised. For this purpose, the flax fabrics were immersed in aqueous solutions of constant 20 w/V% concentration but containing different ratios of DAP and U (Table 1).

The effect of the relative concentration of DAP and U on the thermal decomposition and flame retardancy of flax were examined using TGA, vertical flame tests and LOI measurements, respectively. The changes of initial degradation temperature, as measured by TGA in N₂ atmosphere, can be seen in Figure 1a as a function of increasing DAP content in the treating solution. As low as 4 w/V% DAP (and 16 w/V% U, representing 1:4 ratio) in the treating solution leads to a reduction of the initial degradation temperature of flax by 56 °C. Furthermore, even by 113 °C lower degradation temperature was measured when the solution contained 20 w/V% DAP (and no U). It has to be noted that the significantly reduced decomposition temperature of the 20 w/V% DAP treated fabric (204 °C) is too close to the composite preparation temperature (185 °C) which would unavoidably cause considerable loss of the mechanical properties. The sharply decreasing function, however,

Table 1. Composition of the 20 w/V% aqueous solutions used for fabric treatments.

Fabric treating solutions	DAP to U ratio	DAP concentration [w/V%]
1	0:1	0.0
2	1:4	4.0
3	1:3	5.0
4	1:2	6.7
5	1:1	10.0
6	2:1	13.3
7	3:1	15.0
8	4:1	16.0
9	1:0	20.0

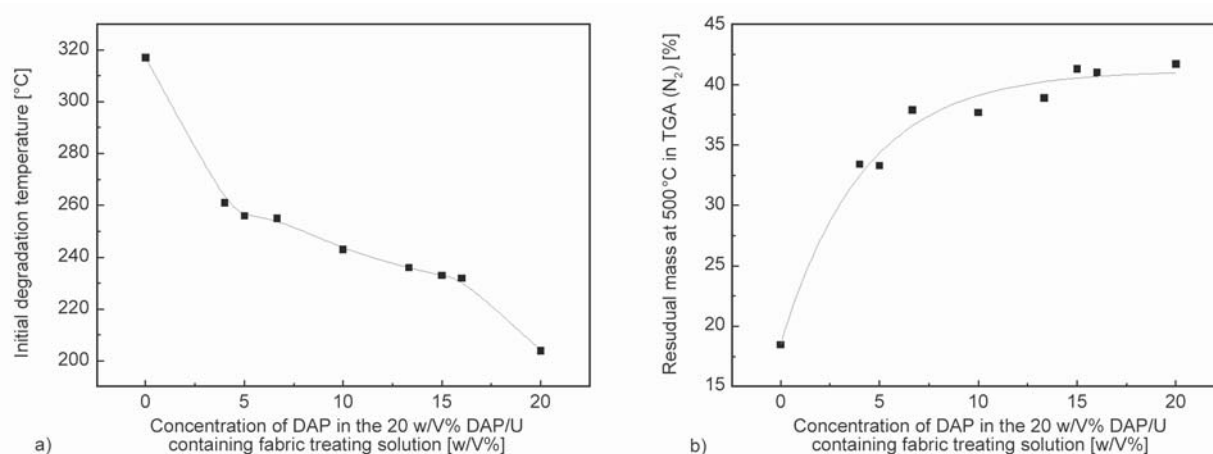


Figure 1. a) Initial degradation temperature and b) residual mass values of flax fabrics treated in 20 w/V% aqueous solutions with varying DAP and U ratio.

shows a plateau between 4 and 16 w/V% DAP concentration, where the initial degradation temperature of treated flax fabrics varies between 260 and 230 °C. In parallel, with increasing DAP ratio in the treating solution increasing amount of char formed (as shown in Figure 1b). The char promoting effect most prevails up to 6.7 w/V% DAP concentration, at which 38% charred residue was obtained, and which did not considerably increase further when the DAP to U ratio was raised above 1 to 2.

The open flame resistance of the flame-retardant-treated flax fabrics was evaluated by vertical flame tests and LOI measurements. The results of vertical flame tests are summarised in Table 2. It can be seen that the non-treated and urea-treated fabrics completely burned during testing; U alone (20 w/V%) did not provide flame retardation. In contrast, DAP alone (20 w/V%) significantly reduced the charred length without generating after-flame or after-glow.

Table 2. Vertical flame test results of flax fabrics treated in 20 w/V% aqueous solutions with varying DAP and U ratio.

DAP:U ratio in the 20 w/V% fabric treating solution	Average char length after vertical flame test (ISO 11925-2) [mm]
0:0	>150
0:1	>150
1:1	47
1:2	46
1:3	51
1:4	64
2:1	46
3:1	46
4:1	45
1:0	46

When considering the results of the DAP and U containing solutions, it can be noticed that if the DAP concentration in the solution was higher than 5% (DAP:U = 1:3), char lengths of about 46 mm were obtained, the same as by using DAP alone. Consequently, the effect of U in further reducing the char length is negligible, as also found by Nam *et al.* [16] during vertical flame testing of DAP and U treated greige cotton fabrics.

In Figure 2 the LOI values of flax fabrics are plotted as a function of the DAP concentration of the DAP and U containing 20 w/V% treating solution. The trend is just the opposite of the changes in the decomposition temperature (Figure 1a). The LOI values increase almost linearly with DAP concentration, but a local maximum can be observed at DAP to U ratio of 1 to 1, where an LOI of 38% was measured. By considering the TGA and open flame testing results, the DAP to U ratio of 1 to 1 was chosen for further optimisation of the fabric treating solution.

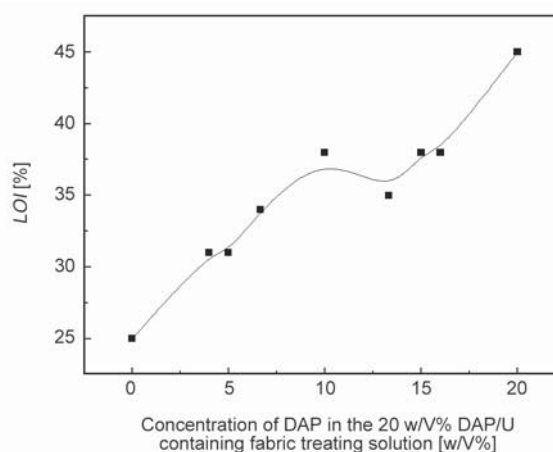


Figure 2. LOI values of flax fabrics treated in 20 w/V% aqueous solutions with varying DAP and U ratio.

Namely, at this ratio the thermal decomposition temperature of flax remained 243 °C, the achievable amount of charred residue is closely maximised (38%) and the observed local maximum of the LOI value plots can be utilised. This DAP to U ratio in the solution means a P to N atom ratio of about 1 to 3 on the surface of the fabrics, which is a well-proven P to N atom ratio for the flame retardant treatment of other cellulosic substrates such as cotton [23].

3.1.2. Optimisation of the concentration of the fabric treating solution

As a second step, the concentration of the fabric treating solution containing DAP and U with 1 to 1 ratio (marked as DAP/U hereinafter) was optimised in terms of thermal degradation and flame retardant properties of the treated flax fabrics. Figure 3 a shows the noticeable drop (about 56 °C) of the initial degradation temperature of the fabric after treatment in 5 w/V% DAP/U solution. With further increase of the solution concentration, only a slight reduction of the decomposition temperature is observable. Based on these results, it was concluded that regarding thermal stability the ratio of DAP and U has a more significant effect than the concentration of the treating solution. 5 w/V% DAP in the solution leads to about 56 °C reduction of the decomposition temperature, but at higher DAP concentrations the addition of U (by keeping the P to N atom ratio of about 1 to 3) effectively protects the fabric from further destabilisation.

The amount of charred residue obtained at 500 °C during TGA (in N₂ atmosphere) shows, however, a saturation curve as a function of increasing DAP/U solution concentration (Figure 3b). The residue of

18% remained from the non-treated flax fabric, which increased to as much as 36% when the fabric was treated in the 5 w/V% solution of DAP/U. Further noticeable increment in the amount of char, however, cannot be achieved by a further increase of the DAP/U concentration of the treating solution. Up to the examined concentration level (20 w/V% DAP/U), about 38% seems to be the maximum achievable amount of solid residue.

The charred lengths measured after vertical flame tests and the LOI values of the flax fabrics treated in solutions with increasing DAP/U concentration are shown in Table 3. Accordingly, the treating solution needs to contain at least 10 w/V% DAP/U (*i.e.* 5 w/V% DAP) to avoid complete burning. Further increase of solution concentration does not provide a noticeable improvement in the performance during the vertical flame test. In contrast, the LOI values of the flax fabrics increase linearly with the DAP/U concentration of the treating solution, at least up to the examined level of 20 w/V%. Close to 1% higher LOI value can be reached by increasing the DAP/U concentration by 1 w/V%. The increment of LOI is,

Table 3. Vertical flame test results and LOI values of flax fabrics treated in solutions with increasing concentration of DAP/U.

DAP/U concentration of the fabric treating solution [w/V%]	Average char length after vertical flame test (ISO 11925-2) [mm]	LOI [%]
0	>150	20
5	>150	25
10	49	30
15	45	34
20	47	38

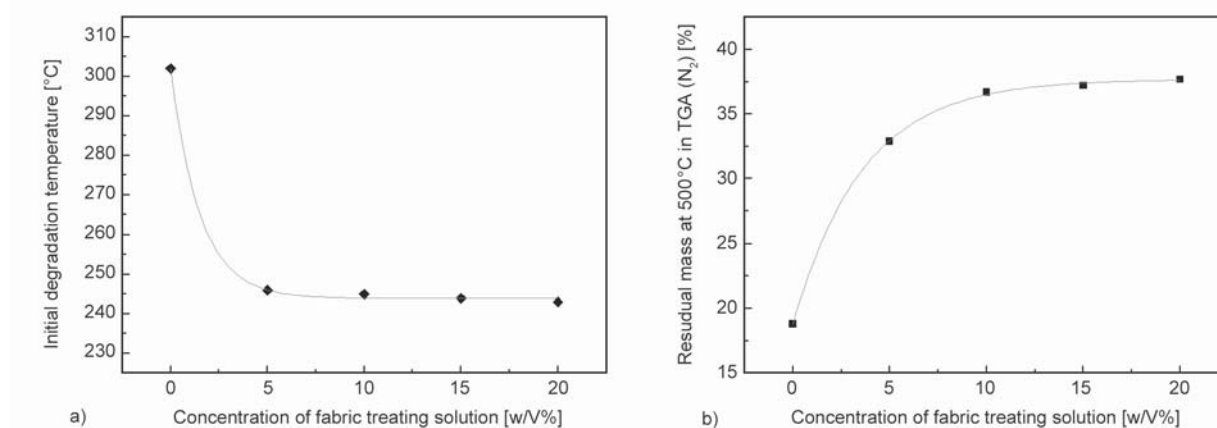


Figure 3. a) Initial degradation temperature and b) residual mass values of flax fabrics treated in solutions with increasing concentration of DAP/U.

however, accompanied by a decrease of the initial decomposition temperature, as presented (under nitrogen atmosphere) in Figure 3a. Therefore, the concentration of the treating solution needs to be optimised by finding a balance between thermal stability and flame retardancy suited for the targeted application and processing conditions.

3.2. Characterisation of flame retarded PLA matrix films

TGA curves of 200 μm thick PLA matrix films with increasing IFR contents are plotted in Figure 4. Compared to the neat PLA film, the decomposition of the IFR containing films starts at 6–10 $^{\circ}\text{C}$ lower temperature. However, this slight difference does not influence further processing or applicability of the flame retarded films. The used IFR additive effectively promoted the charring of PLA, with increasing IFR contents the amount of charred residue (obtained at 500 $^{\circ}\text{C}$ in N_2) increased proportionally, as marked in Figure 4. Also, a linear increment of LOI values of the PLA films was measured as a function of IFR content. According to the equation of the linear fit ($\text{LOI} [\%] = 0.66 \cdot \text{IFR} + 20.2$), by increasing the amount of IFR additive by 3 wt%, the LOI increases by 2%. In summary, it was concluded that in the examined range of IFR content (0–20 wt%), linear composition-property correlation of the PLA films could be expected, at least regarding the residue and flammability represented by LOI.

3.3. Optimisation of multilayered biocomposites

Before composite preparation, the effect of DAP/U treatment on the mechanical performance of the reinforcing fabrics was investigated by performing

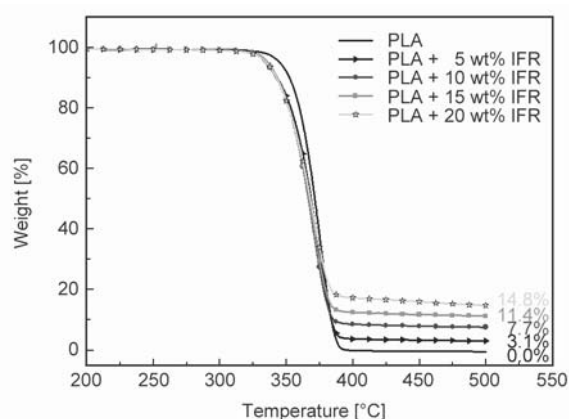


Figure 4. TGA curves of PLA films with increasing IFR content.

strip tensile tests. To simulate the effect of heat exposure during composite preparation, the strip tensile strength of fabrics after heat treatment at 185 $^{\circ}\text{C}$ for 5 min in an oven was also evaluated. It has to be noted that since these conditions do not exactly represent the actual temperature, duration and pressure of hot-pressing, the obtained results cannot be directly used to predict the mechanical performance of the fabrics used as composites reinforcements. It can be seen in Figure 5 that the flame-retardant-treatment of the fabrics caused noticeable deterioration of the mechanical performance. Reduction of 20 and 30% in the strip tensile strength was detected after immersing the flax fabrics in 10 and 20 w/V% solution of DAP/U, respectively, likely due to the acid catalysed degradation of structural cellulose. This property loss was accelerated at elevated temperature: after heat treatment, 12% lower strip tensile strength was measured for the flame-retardant-treated fabrics at both examined DAP/U concentration. While heat treatment at 185 $^{\circ}\text{C}$ did not influence the mechanical performance of the non-treated fabric, the strength of the 20 w/V% DAP/U solution treated fabric after heat processing reduced to approximately half of that of the neat fabric. Based on these results, noticeably reduced reinforcing efficiency can be expected when flame-retardant-treated fabrics are used as composite constituents.

In order to optimise the flame retardant distribution between the fibrous carrier and the polymer matrix, multi-layered composites consisting of flax fabrics and PLA films were produced by varying the amount of the phosphorus-based flame retardants between the two phases based on a 3^2 factorial design (Figure 6). In the design space, the reinforcing flax fabrics were either neat or treated in 10 or 20 w/V% solution of

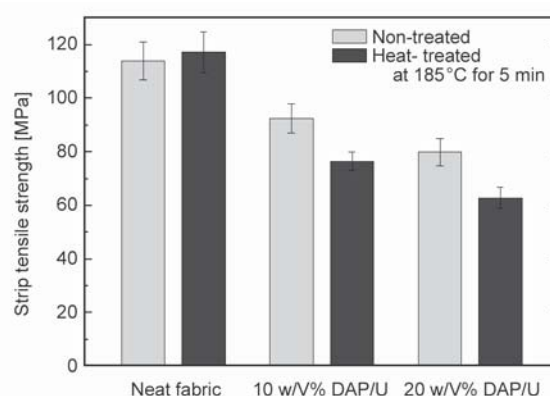


Figure 5. Strip tensile strength of neat and flame-retardant-treated fabrics before and after heat treatment.

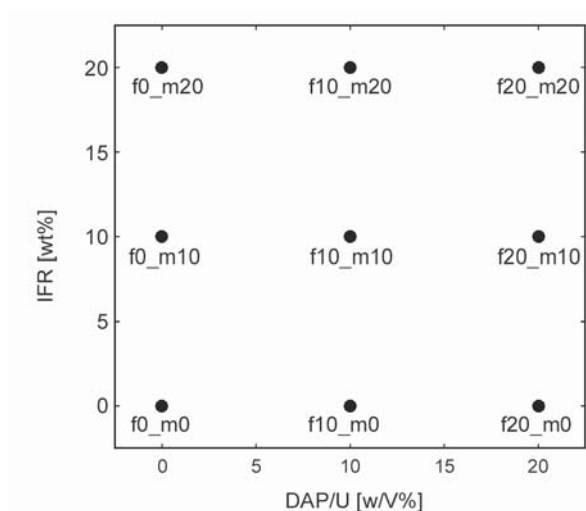


Figure 6. The three-level design with 2 factors for the sample preparation.

DAP/U (DAP to U mass ratio was kept constant at 1 to 1) while the IFR content of the PLA matrix was 0, 10 and 20 wt%, respectively. Hereinafter, fX marks the DAP/U concentration of the flax fabric treating solution and mX marks the IFR content of the matrix films.

The UL-94 ratings of the flame retarded biocomposites are shown in Table 4. It can be seen that the FR content introduced through fabric treatment is not sufficient to achieve better UL-94 rating than HB, the additive-free PLA layers burn out with noticeable flame and intensive dripping independently of the FR content of the flax fabrics. On the other hand, a V-2 rating was reached when non-treated fabrics were combined with 20 wt% IFR containing PLA films. Without fibre reinforcement, about 20 wt% IFR would be sufficient to reach V-0 rating [24], however, in these multi-layered composites, the harmful candlewick effect of natural fabrics prevail and thus the UL-94 rating of the biocomposite composed of non-treated fabrics and PLA films with 20 wt% IFR content remains V-2. In contrast, when the flax fabrics were treated in 10 w/V% DAP/U solution, the UL-94 classification increased from HB to V-2 and from V-2 to V-0 when combined with 10 wt% IFR and 20 wt% IFR containing films, respectively. This means that immersion in 10 w/V% DAP/U solution effectively eliminates the candlewick effect of flax fabrics used as reinforcements in PLA based biocomposites. Nevertheless, V-0 rating was only achieved when 20 wt% IFR was used in the PLA matrix layers.

LOI values of the biocomposites are summarised in Table 5. An LOI of 22% was measured for the

Table 4. UL-94 rating of flame retarded biocomposites.

Fabric \ Film	0 wt% IFR	10 wt% IFR	20 wt% IFR
0 w/V% DAP/U	HB (27 mm/min)	HB (–)	V-2
10 w/V% DAP/U	HB (17 mm/min)	V-2	V-0
20 w/V% DAP/U	HB (16 mm/min)	V-2	V-0

Table 5. LOI values of flame retarded biocomposites.

Fabric \ Film	0 wt% IFR	10 wt% IFR	20 wt% IFR
0 w/V% DAP/U	22	28	37
10 w/V% DAP/U	24	32*	39
20 w/V% DAP/U	27	32	45*

non-treated biocomposite, which increased by 5% when only the reinforcing fabrics were flame-retardant-treated in 20 w/V% DAP/U solution. A much greater increase of the LOI value of 15% was reached when the matrix films were loaded with 20 wt% IFR (by introducing a higher amount of P in this case), and the flax fabrics were used as received. When considering the LOI values of the biocomposites containing P compounds in both phases, it can be found that the measured LOI values are in some cases (marked with symbols) higher than expected based on the sum of the LOI increments reached by modifying only one constituent. This observation suggests positive interaction between the two flame-retardant-treated composite constituents. It is proposed that the charred fabric layers act as char stabilizing frames and enhance the structural integrity of the protecting carbonaceous foam.

Cone calorimeter tests were performed to analyse the combustion behaviour of the flame retarded biocomposites. The effects of the executed flame retardant modifications on the heat release rate curves of the composites can be seen in Figure 7.

For a better visibility, only the corner points and the centre point of the design are plotted. It can be seen that the shortest time to ignition value (19 s) corresponds to the additive-free biocomposite ($f0_m0$) and both the addition of IFR to the matrix layers and the treatment of fabrics in DAP/U solution result in a shift of ignition time. The ignition time of the biocomposite with high flame retardant content in both phases ($f20_m20$) shifted to even 99 s. It can also be observed that both the DAP/U treatment of the reinforcing fabrics and the incorporation of IFR additive

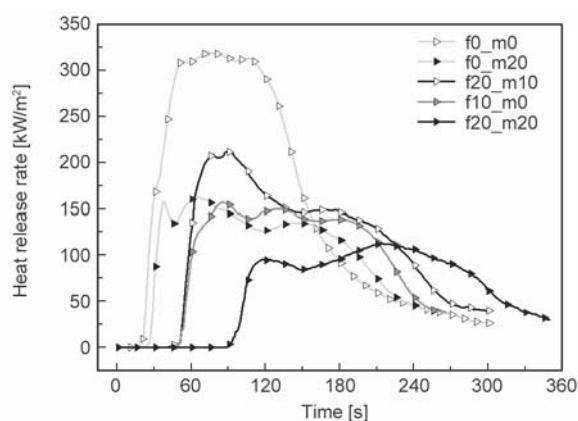


Figure 7. Heat release rate curves of the flame retarded biocomposites (*fX* marks the DAP/U concentration of the flax fabric treating solution and *mX* marks the IFR content of the matrix films).

in the PLA matrix films effectively reduced the peak of heat released rate and prolonged the combustion time of the biocomposite. The best flame retardant performance was achieved when the combined flame retardancy approach was implemented, *i.e.* in case of *f10_m10* and *f20_m20* samples. The charred residues obtained after the cone calorimeter tests are shown in Figure 8, the measured residual mass values are also indicated. It can be seen that without modification the biocomposite burned almost completely, only some grey ashes of the flax fabrics remained in the sample holder. When only the fabrics were flame-retardant-treated (*f20_m0*), the matrix films burnt out completely and only the shrunk, charred fabric layers remained indicating that the flame-retardant-treated fabrics do not affect the combustion of the adjacent PLA films.

In contrast, when IFR containing PLA films were layered with neat flax fabrics (*f0_m20*), the charring of the cellulosic fabrics is also evident together with the charred residue remaining from the flame retarded matrix layers. Based on this observation, interaction between the layers was assumed, namely the degradation products of the IFR embedded in the

matrix actively promoted the charring of the flax fabrics as well. A noticeable amount of compact charred residues were obtained when both constituents were flame-retardant-treated (*f10_m10* and *f20_m20*). It is also notable that 23.0 wt% residue remained from the *f20_m20* sample, that is more than the sum (18.3 wt%) of the residual masses obtained from the *f20_m0* and *f0_m20* samples, which also indicates positive interaction between the flame-retardant-treated components.

In order to investigate the suspected interaction and to better analyse the contribution of the flame retardant treatment of the constituents to the complex flame retardant performance of the composites, the evolution of the peak of heat release rate (pkHRR) and the total heat release (THR) values were plotted with the fitted response surface (Figure 9a and 9b). The IFR addition to the matrix layers reduces the pkHRR and THR values more effectively than the DAP/U treatment of the flax fabrics. This is not surprising as noticeably higher amount of FR active components, such as P atoms, can be introduced by incorporating into the matrix than by fixing on the surface of the reinforcement. Nevertheless, curvature of the pkHRR response surface (Figure 9a) can be seen when both constituents are flame-retardant-treated, indicating a positive correlation between the two factors. This means that lower pkHRR values are achievable when the combined flame retardancy approach is applied than the sum of the pkHRR reducing effect of the flame retardant treatment of the single constituents. Based on Figure 9a, the pkHRR of the biocomposites gradually reduces with the IFR content of the matrix films, however, to achieve best performance the concentration of the fabric treating DAP/U solution does not need to be increased above 15 w/V% (*i.e.* 7.5 w/V% DAP) as the saturated fibre cannot absorb more FR in its internal space. The charred flax fabric layers are proposed to enhance the thermal and mechanical stability of

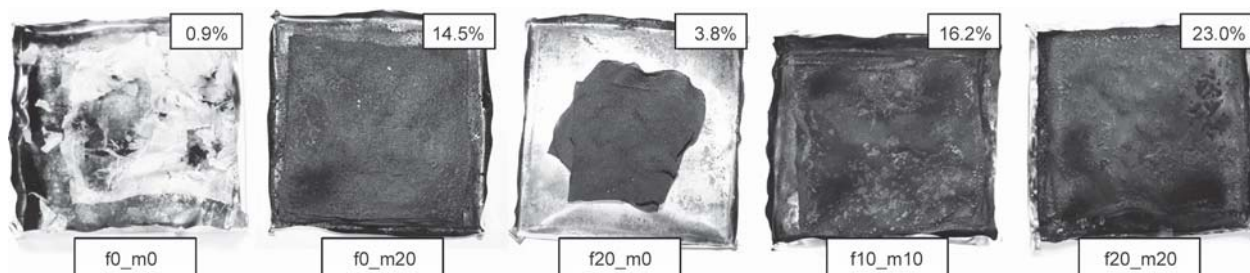


Figure 8. Charred residues obtained after cone calorimeter tests (*fX* marks the DAP/U concentration of the flax fabric treating solution and *mX* marks the IFR content of the matrix films).

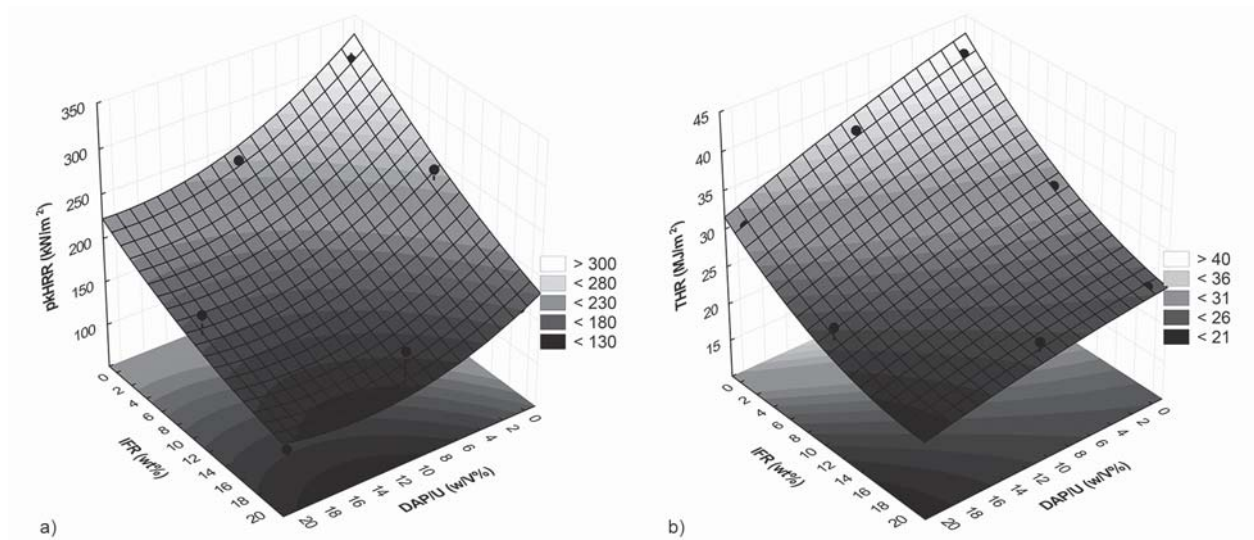


Figure 9. Quadratic model response surface for a) pkHRR and b) THR.

the carbonaceous foam structure which can thus preserve its barrier function for a longer time. According to Figure 9b, however, no relationship between the flame retardant treatments of the two phases appears in THR values. Consequently, the distribution of the FR additives influences only the ignitability and the dynamics of the burning, but these differences are compensated by the end of combustion. Figure 10a depicts the tensile strength of the flame retarded biocomposites. Beyond the expected slight decreasing effect of IFR and quadratic effect of the flame retardant treating solution of the flax fabrics on the tensile strength of the biocomposites (in accordance with the strip tensile test results of the DAP/U-treated fabrics shown in Figure 5), significant curvature of the response surface fitted on the tensile strength data can be observed. The data were statistically tested, and

there is sufficient evidence to conclude that a considerable relationship exists between IFR content and DAP/U concentration because the interaction effect was close to significant ($p=0.198$).

This newly described relationship means that better mechanical performance can be achieved when the DAP/U treated fabrics are combined with IFR loaded matrix films instead of neat PLA layers, even though the FR treatment of fabrics and the IFR loading of matrix layers alone reduce the strength of the reinforcements and composites, respectively. Similarly improved mechanical performance was observed earlier when phosphorous-silane (PSi)-treated chopped flax fibres were embedded into PLA/glycerol-phosphate modified thermoplastic starch (PLA/GP-TPS) blends [20] and also when phosphorus-treated flax fibres were combined with phosphorus-containing

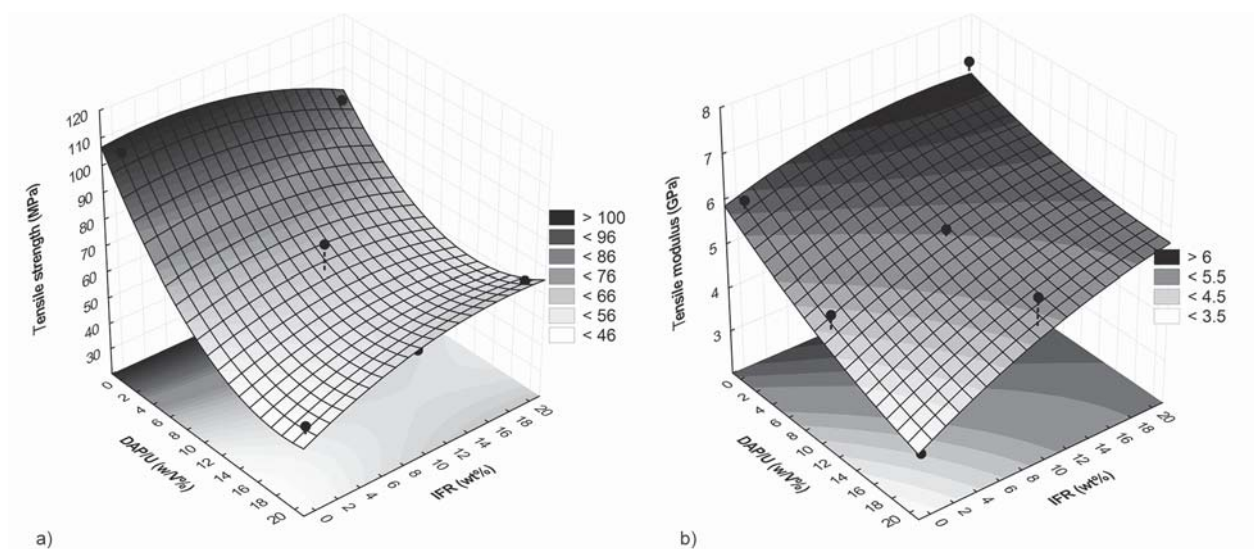


Figure 10. Quadratic model response surface for a) tensile strength and b) tensile modulus.

epoxy resin [25]. This is always a fortunate hit since the flame retardant properties also improve when the amount of additives is increased, and the combined flame retardancy approach is applied. The positive interaction between the flame-retardant-treated constituents is explained by the better compatibility between the two phosphate-treated phases providing better load transfer to the fibres.

Even though the tensile modulus is less sensitive to the fibre-matrix interactions, a similar effect can be found when considering the modulus data presented in Figure 10b. It can be seen that 20 wt% IFR content of the matrix films increases the modulus of the biocomposites by 20% when combined with non-treated fabrics, but the increment compared to the composite with 20 w/V% DAP/U treated fabrics reaches even 70%, when 20 wt% IFR is added to that one. As a result, the modulus of the biocomposite with the highest flame-retardant loading ($E_{f20_m20} = 5.48 \pm 0.22$ GPa) is only barely lower than that of the neat biocomposite ($E_{f0_m0} = 6.0 \pm 0.31$ GPa). According to these observations, it was concluded that from a mechanical point of view, the combined flame retardancy approach is beneficial.

To investigate the fibre-matrix adhesion in the composites with various flame retardant compositions, SEM micrographs were taken from the cryogenic fracture surfaces. In Figure 11, the proper embedding of the non-treated flax yarns can be seen by the additive-free ($f0_m0$) and by IFR loaded PLA matrix ($f0_m20$) alike. However, when DAP/U treated flax

fabrics were combined with additive-free PLA layers, noticeable fibre-matrix debonding can be observed ($f20_m0$). The poor fibre-matrix adhesion can be responsible for the noticeable deterioration of the mechanical properties of this composite. Nevertheless, when DAP/U treated fabrics were layered with IFR containing PLA films ($f10_m10$ and $f20_m20$), better interfacial interaction was revealed during SEM imaging. This observation confirms the conclusions drawn based on the static tensile test results, namely that the better interfacial interaction plays a key role behind the improved mechanical performance achieved in the case of the biocomposites in which phosphates are present both in fibre and matrix phase.

4. Conclusions

Composition-property correlations were analysed in flax fabric-reinforced PLA composites flame retarded with phosphorus-containing compounds by systematically varying their distribution between the phases using experimental design. Several flammability features, such as LOI, TTI, pkHRR and residual mass obtained after cone calorimeter tests revealed positive interaction between the flame-retardant-treated composite constituents, meaning that better flame retardant performance was reached when the combined flame-retardancy approach was applied than one would expect based on the flammability features of the single constituents. Also, V-0 rating, according to the UL-94 standard, was only achieved when both constituents (*i.e.* matrix and reinforcement) were

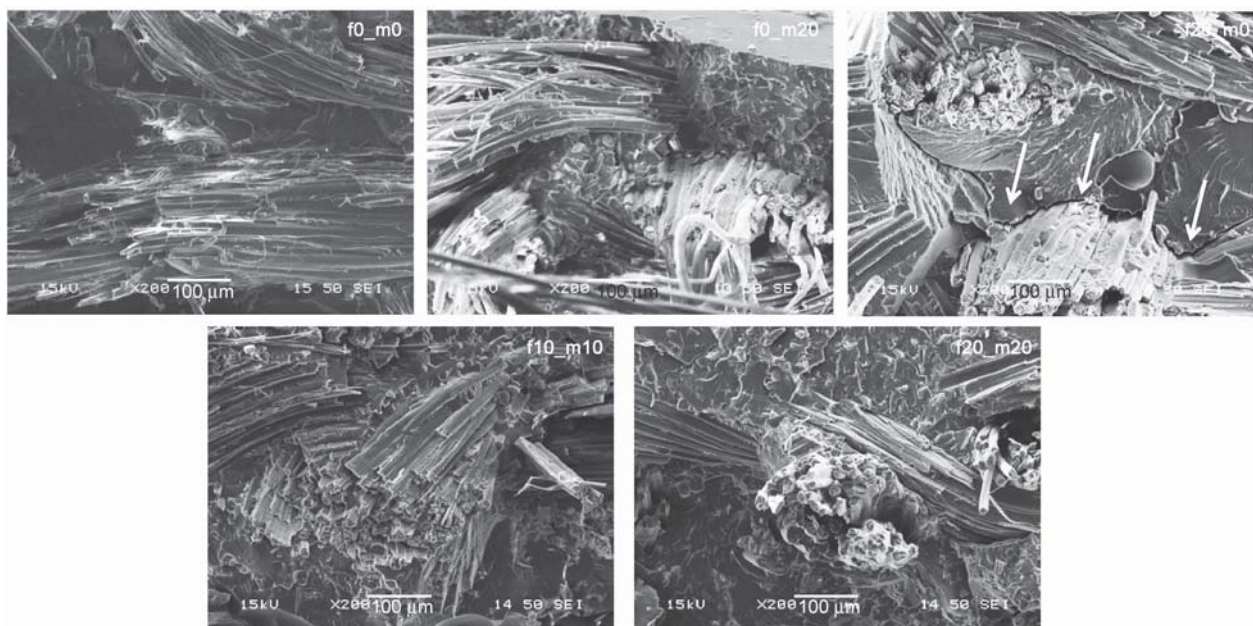


Figure 11. SEM micrographs taken from the fracture surface of the flame retarded biocomposites (fX marks the IFR content of the matrix films and mX marks the DAP/U concentration of the flax fabric treating solution).

flame-retardant-treated. The reinforcing fabric can act as a char stabilizing frame if it is charred. The volatile phosphorous compounds, originating from the matrix layers, are able to initiate charring of fibres under the cone heater but in case of vertical tests, the candlewick effect can only be eliminated by preliminary treatment. Increase of the concentration of treating solution above 15 w/V% DAP/U (7.5 w/V% DAP) is not effective as the saturated fibre cannot absorb more FR in its internal space.

Furthermore, the positive relationship between the flame-retardant-treated constituents was evinced by analysis of variance (ANOVA) of the tensile strength data of the flame retarded biocomposites with varying compositions as well. The improved mechanical performance of the biocomposites flame retarded with a combined approach is explained by the better interfacial interaction provided by the phosphates being present both in fibre and matrix phase. This interaction, which needs further investigation, can probably be attributed to the fact that the increased surface roughness of the fibres after acidic treatment with DAP (*i.e.* phosphoric acid generated from the thermal decomposition of DAP) can result in an anchoring effect only if the viscosity of PLA is decreased due to the presence of APP (as reported by the authors recently [26]).

As a conclusion, a combined approach is recommended for flame retardancy of biocomposites, since phosphorus-containing species being present both on the surface of the reinforcing flax fabrics and in the biodegradable matrix material in a well-balanced distribution result in effectively flame retarded biocomposites accompanied with improved mechanical properties.

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References

- [1] Tábi T., Tamás P., Kovács J. G.: Chopped basalt fibres: A new perspective in reinforcing poly(lactic acid) to produce injection moulded engineering composites from renewable and natural resources. *Express Polymer Letters*, **7**, 107–119 (2013).
<https://doi.org/10.3144/expresspolymlett.2013.11>
- [2] Tawiah B., Yu B., Ullah S., Wei R., Yuen R. K. K., Xin J. H., Fei B.: Flame retardant poly(lactic acid) biocomposites reinforced by recycled wool fibers – Thermal and mechanical properties. *Express Polymer Letters*, **13**, 697–712 (2019).
<https://doi.org/10.3144/expresspolymlett.2019.59>
- [3] Park J-W., Lee T-H., Back J-H., Jang S-W., Kim H-J., Skrifvars M.: Phenyl silane treatment and carding process to improve the mechanical, thermal, and water-absorption properties of regenerated cellulose lyocell/poly(lactic acid) bio-composites. *Composites Part B: Engineering*, **167**, 387–395 (2019).
<https://doi.org/10.1016/j.compositesb.2019.02.064>
- [4] Siengchin S.: Potential use of ‘green’ composites in automotive applications. *Express Polymer Letters*, **11**, 600 (2017).
<https://doi.org/10.3144/expresspolymlett.2017.57>
- [5] Zou H., Yi C., Wang L., Liu H., Xu W.: Thermal degradation of poly(lactic acid) measured by thermogravimetry coupled to Fourier transform infrared spectroscopy. *Journal of Thermal Analysis and Calorimetry*, **97**, 929–935 (2009).
<https://doi.org/10.1007/s10973-009-0121-5>
- [6] Bourbigot S., Fontaine G.: Flame retardancy of polylactide: An overview. *Polymer Chemistry*, **1**, 1413–1422 (2010).
<https://doi.org/10.1039/c0py00106f>
- [7] Chow W. S., Teoh E. L., Karger-Kocsis J.: Flame retarded poly(lactic acid): A review. *Express Polymer Letters*, **12**, 396–417 (2018).
<https://doi.org/10.3144/expresspolymlett.2018.34>
- [8] Tawiah B., Yu B., Fei B.: Advances in flame retardant poly(lactic acid). *Polymers*, **10**, 876/1–876/22 (2018).
<https://doi.org/10.3390/polym10080876>
- [9] Bourbigot S., Duquesne S., Fontaine G., Bellayer S., Turf T., Samyn F.: Characterization and reaction to fire of polymer nanocomposites with and without conventional flame retardants. *Molecular Crystals and Liquid Crystals*, **486**, 325–339 (2008).
<https://doi.org/10.1080/15421400801921983>
- [10] Le Bras M., Duquesne S., Fois M., Grisel M., Poutch F.: Intumescent polypropylene/flax blends: A preliminary study. *Polymer Degradation and Stability*, **88**, 80–84 (2005).
<https://doi.org/10.1016/j.polymdegradstab.2004.04.028>
- [11] Mochane M. J., Mokheba T. C., Mokhothu T. H., Mtibe A., Sadiku E. R., Ray S. S., Ibrahim I. D., Daramola O. O.: Recent progress on natural fiber hybrid composites for advanced applications: A review. *Express Polymer Letters*, **13**, 159–198 (2019).
<https://doi.org/10.3144/expresspolymlett.2019.15>

- [12] Horrocks A. R.: Developments in flame retardants for heat and fire resistant textiles – The role of char formation and intumescence. *Polymer Degradation and Stability*, **54**, 143–154 (1996).
[https://doi.org/10.1016/s0141-3910\(96\)00038-9](https://doi.org/10.1016/s0141-3910(96)00038-9)
- [13] Suardana N. P. G., Ku M. S., Lim J. K.: Effects of diammonium phosphate on the flammability and mechanical properties of bio-composites. *Materials and Design*, **32**, 1990–1999 (2011).
<https://doi.org/10.1016/j.matdes.2010.11.069>
- [14] Liodakis S., Fetsis I. K., Agiovlasis I. P.: The fire-retarding effect of inorganic phosphorus compounds on the combustion of cellulosic materials. *Journal of Thermal Analysis and Calorimetry*, **98**, 285–291 (2009).
<https://doi.org/10.1007/s10973-009-0307-x>
- [15] Gaan S., Sun G.: Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton. *Polymer Degradation and Stability*, **97**, 968–974 (2007).
<https://doi.org/10.1016/j.polymdegradstab.2007.03.009>
- [16] Nam S., Condon B. D., Parikh D. V., Zhao Q., Cintrón M. S., Madison C.: Effect of urea additive on the thermal decomposition of greige cotton nonwoven fabric treated with diammonium phosphate. *Polymer Degradation and Stability*, **96**, 2010–2018 (2011).
<https://doi.org/10.1016/j.polymdegradstab.2011.08.014>
- [17] Salmeia K. A., Gaan S., Malucelli G.: Recent advances for flame retardancy of textiles based on phosphorus chemistry. *Polymers*, **8**, 319/1–319/36 (2016).
<https://doi.org/10.3390/polym8090319>
- [18] Nam S., Condon B. D., White R. H., Zhao Q., Yao F., Cintrón M. S.: Effect of urea additive on the thermal decomposition kinetics of flame retardant greige cotton nonwoven fabric. *Polymer Degradation and Stability*, **97**, 738–746 (2012).
<https://doi.org/10.1016/j.polymdegradstab.2012.02.008>
- [19] Bocz K., Szolnoki B., Władyka-Przybylak M., Bujnowicz K., Harakály G., Bodzay B., Zimonyi E., Toldy A., Marosi G.: Flame retardancy of biocomposites based on thermoplastic starch. *Polimery*, **58**, 385–394 (2013).
<https://doi.org/10.14314/polimery.2013.385>
- [20] Bocz K., Szolnoki B., Marosi A., Tábi T., Władyka-Przybylak M., Marosi G.: Flax fibre reinforced PLA/TPS biocomposites flame retarded with multifunctional additive system. *Polymer Degradation and Stability*, **106**, 63–73 (2014).
<https://doi.org/10.1016/j.polymdegradstab.2013.10.025>
- [21] Li S., Ren J., Yuan H., Yu T., Yuan W.: Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber-reinforced poly(lactic acid) biocomposites. *Polymer International*, **59**, 242–248 (2010).
<https://doi.org/10.1002/pi.2715>
- [22] Chen D., Li J., Ren J.: Combustion properties and transference behavior of ultrafine microencapsulated ammonium polyphosphate in ramie fabric-reinforced poly(L-lactic acid) biocomposites. *Polymer International*, **60**, 599–606 (2011).
<https://doi.org/10.1002/pi.2986>
- [23] Willard J. J., Wondra R. E.: Quantitative evaluation of flame-retardant cotton finishes by the limiting-oxygen index (LOI) technique. *Textile Research Journal*, **40**, 203–210 (1970).
<https://doi.org/10.1177/004051757004000301>
- [24] Vadas D., Igricz T., Sarazin J., Bourbigot S., Marosi G., Bocz K.: Flame retardancy of microcellular poly(lactic acid) foams prepared by supercritical CO₂-assisted extrusion. *Polymer Degradation and Stability*, **153**, 100–108 (2018).
<https://doi.org/10.1016/j.polymdegradstab.2018.04.021>
- [25] Szolnoki B., Bocz K., Solti P. L., Bodzay B., Zimonyi E., Toldy A., Morlin B., Bujnowicz K., Władyka-Przybylak M., Marosi G.: Development of natural fibre reinforced flame retarded epoxy resin composites. *Polymer Degradation and Stability*, **119**, 68–76 (2015).
<https://doi.org/10.1016/j.polymdegradstab.2015.04.028>
- [26] Bocz K., Domonkos M., Igricz T., Kmetty Á., Bárány T., Marosi G.: Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance. *Composites Part A: Applied Science and Manufacturing*, **70**, 27–34 (2015).
<https://doi.org/10.1016/j.compositesa.2014.12.005>