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**Flax fibre reinforced PLA/TPS biocomposites flame retarded with
multifunctional additive system**

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ABSTRACT

Fully biodegradable composites were developed, possessing prominent mechanical performance and reduced flammability at the same time. The manufactured composites consisted of PLA/TPS biopolymer

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matrices reinforced with chopped flax fibres. The flammability of the prepared biocomposites was reduced by a newly synthesized multifunctional additive system. Glycerol phosphate (GP), a plasticizer of starch with flame retardant potential, and a novel phosphorous-silane (PSil), applied as a surface treating agent of the reinforcing biofibres, were successfully combined in order to reduce the flammability of the prepared biocomposites. Owing to the beneficial effect of the applied multifunctional additive system, a loading of as low as 10 wt% of ammonium polyphosphate (APP) proved to be sufficient to provide prominent levels of flame retardancy to the composites, i.e. V-0 rating according to UL94, 33 vol% LOI and a 40% reduction of heat emission were achieved. Furthermore, the combined application of the surface treated reinforcing flax fibres and plasticizer in the biodegradable, flame retarded biocomposites resulted in well-balanced strength and stiffness.

Keywords: flame retardancy, biocomposite, polylactic acid, thermoplastic starch, plasticizer, natural fibre, fibre treatment

1 Introduction

In the recent decades, the need for application of environmentally favourable biodegradable polymers, especially when originating from renewable resources, is increasingly coming to the forefront. However, even until recently, these are widely used only in the packaging industry and in the medical field. Extension of biopolymers to engineering applications would serve the realization of sustainable development; however, these new types of polymers require various modifications, including reinforcement and flame retardancy, in order to offer a reasonable green alternative the conventional petroleum-based plastics in all aspects.

Among biopolymers, polylactic acid (PLA) is one of the most promising candidates for wide-range future applications due to its multiple benefits, such as biodegradability, high degree of transparency, prominent mechanical performance and comparable processing properties to commonly used thermoplastics [1]. However, the most severe limitation of the replacement of

common polymers by PLA in greater amounts is its noticeably higher cost. For this reason PLA is often blended with cheaper biopolymers or biofillers. According to the paper published by *Huneault and Li*, blending of PLA with thermoplastic starch (TPS) not only reduces the overall cost of the final product, but it also results in decrease of the inherent brittleness and rigidity of PLA as well as in improvement of the material ductility [2]. Furthermore, as revealed by *Reti et al.*, starch can effectively contribute to the flame retardant action of an intumescent additive system acting as a biobased charring agent [3]. Several lignocellulosic fibres (jute, flax, sisal etc.) are also used in PLA to ensure better properties, such as enhanced biodegradability, lower density, higher strength and modulus, at lower cost and without compromising biodegradability [4,5].

The flame retardancy of biopolymers is of great importance when applications in electronics, construction and transportation are considered. To achieve the desired levels of flame retardancy is, however, quite challenging in the case of the most promising raw material, PLA, due to its easy flammability and intensive dripping during burning [6,7,8]. Although a few options were already proposed to form flame retarded PLA [3,9,10], these methods, applying mostly a high load of expensive flame retardants in the expensive matrix, may not be implementable for industrial use. Consequently, the need for the elaboration of new cost-effective approaches for flame retardancy of biopolymers is very urgent.

In this work, our hypothesis was that the flammability of PLA can be cost-effectively reduced by applying multifunctional active ingredients, which, besides their essential functions (such as reinforcement, filler, plasticizer, compatibilizer, stabilizer, pigment, coating, etc.), display also flame retardant activity.

Hence, in this paper two innovative approaches were studied aiming at the production of a PLA-based biocomposite of reduced flammability and adequate mechanical performance in an economical way:

- 1) replacement of glycerol, the most commonly used plasticizer of starch, by glycerol phosphate (GP) possessing flame retardant effect, and
- 2) elaboration of a novel one-step reactive flame-retardant treatment for natural fibres, which can provide considerable flame retardant activity to the cheap cellulosic reinforcements used in PLA/TPS biopolymer blends.

Our strategy relating to the use of a P-containing plasticizer in TPS relies on the recently reported study on a commercial P-containing polyol (OP560) applied successfully in TPS both as plasticizer and as flame retardant agent [11].

It is quite common to render cellulosic fibres or fabrics flame retardant by using P-containing compounds, such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), monoammonium phosphate (MAP) and diammonium phosphate (DAP) [12,13,14,15]. The non-toxic phosphorus-based compounds can effectively initiate the charring of fibres [11,12], however, due to the application of these treatments the initial decomposition temperature of natural fibres significantly decreases (even by 90 °C) [11,16]. The reduced thermal stability can be a serious issue, both from mechanical and aesthetic aspects, when the natural fibres are intended to be used as fillers or reinforcements in polymer composites, especially when thermoplastic matrices with processing temperatures above 140 C (such as PP, PA, PET and also PLA) are considered. It is well known from the literature that the surface treatment with different silanes can result in increased thermal stability of cellulosic fibres [17,18].

Therefore, the application of a combined treatment, by utilizing P and Si synergism, was selected in this work for the flame retardant modification of reinforcing natural fibres. Then, the effects of the flame retardant plasticizer and the flame-retardant-treated flax fibres on the thermal, flammability and mechanical properties of the obtained biocomposites were investigated.

2 Materials and methods

2.1 Materials and sample preparation

2.1.1 Preparation of glycerol-phosphate-plasticized starch

Anhydrous glycerol (M: 92.1 g/mol, ρ : 1.26 g/cm³) supplied by Merck (Merck KGaA, Darmstadt, Germany) and phosphorus-pentoxide (P₂O₅, M: 141.9 g/mol, ρ : 2.30 g/cm³) purchased from Sigma Aldrich (St. Louis, MO, USA) were used as received for the synthesis of the flame retardant plasticizer. NH₃ gas was received from Linde Gáz Magyarország Zrt. Budapest, Hungary, and was let through a CaCl₂-filled tube before use, in order to eliminate humidity.

Corn starch (produced by Dénes-Natura Kft, Pécs, Hungary) of 19% amylose content was plasticized in the one case with commercial glycerol (obtained from Azúr Vegyszerbolt Kft., Budapest, Hungary) and in the other case using the newly synthesized glycerol-phosphate-based plasticizer (GP) to obtain a reference common thermoplastic starch (TPS) and a flame retardant thermoplastic starch (TPS-GP) batch, respectively. In both cases, the starch and the plasticizer were mixed together in a mortar at least one day before processing. The two types of thermoplastic starch batches have been processed in a Brabender Plasti Corder PL 2000 type internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany) at 135 C with addition of 0.6 wt% stearic acid and with a rotor speed of 60 rpm, until a decreased, close-to-constant torque demand was measured during mixing.

2.1.2 Preparation of flax fibre reinforced PLA/TPS blends

PLA/TPS biopolymer blends were prepared with 80% PLA and 20% TPS contents. The used Ingeo™ Biopolymer 3052D type PLA was supplied by NatureWorks LLC., Minnetonka, MN, USA. The biopolymer blends were prepared in the same internal mixer as the plasticized starch, heated to 160 C. TPS was added once PLA was molten. After 5 minutes of

homogenization at a rate of 50 rpm, 25 wt% chopped flax fibres were added to the blends. The fibres (2–3 mm long with diameters ranging from 20 µm to 60 µm) were received from the Institute of Natural Fibres and Medicinal Plants (Poznan, Poland). In the case of the samples marked as “flax_PSil”, the flax fibres were flame retardant-treated with a newly synthesized phosphorous-silane (PSil), prior to their addition to the blend. The phosphorus polyol, Exolit OP560, and 3-(triethoxysilyl)-propyl isocyanate (TESPI), applied for the synthesis of PSil, were received from Clariant GmbH (Frankfurt am Main, Germany) and purchased from Sigma Aldrich (St. Louis, MO, USA), respectively. The obtained compositions of the prepared biocomposites are summarized in Table 1. In the case of one sample (PLA/TPS-GP/flax-PSil+APP), 10 wt% ammonium polyphosphate (APP, Exolit AP 422, Clariant GmbH, Germany) was also introduced into the biocomposite as additional flame retardant agent.

The specimens for mechanical and flammability tests were manufactured from 4-mm-thick plates prepared by hot pressing of the blends in a Collin P200E type laboratory hot press (Dr. Collin GmbH, Ebersberg, Germany) set to 160 C.

Table 1 Compositions of the prepared biocomposites

Table 1 Compositions of the prepared biocomposites

	PLA (wt%)	Starch (wt%)	Glycerol (wt%)	Glycerol phosphate* (wt%)	Stearic acid (wt%)	flax fibre (wt%)	PSil- treated flax fibre (wt%)	APP (wt%)
TPS	-	74.4	25.0	-	0.6	-	-	-
TPS-GP	-	74.4	12.5	12.5	0.6	-	-	-
PLA/TPS	80.0	14.9	5.0	-	0.1	-	-	-
PLA/TPS-GP	80.0	14.9	2.5	2.5	0.1	-	-	-
PLA/TPS/flax	60.0	11.1	3.8	-	0.1	25.0	-	-
PLA/TPS-GP/flax	60.0	11.1	1.9	1.9	0.1	-	25.0	-
PLA/TPS/flax-PSil	60.0	11.1	3.8	-	0.1	25.0	-	-
PLA/TPS-GP/flax-PSil	60.0	11.1	1.9	1.9	0.1	-	25.0	-
PLA/TPS-GP/flax-PSil+APP	52.0	9.6	1.65	1.65	0.1	-	25.0	10.0

*GP consists of 40 wt% glycerol, and has an overall P-content of 8.24 wt% and N-content of 6.0 wt%.

2.2 Methods

2.2.1 ReactIR

The ReactIR™ *in situ* Fourier transform infrared spectroscopic (FT-IR) apparatus (Mettler-Toledo, Columbus, OH, USA) allows for *in situ* real-time FTIR analysis of a reaction mixture in the mid-IR region using a multi-reflection diamond attenuated total reflectance (ATR) insertion sensor. The sensor can withstand reaction conditions over a wide temperature range (−80 to 250 C) and under pressures up to 100 bar. The spectral range for this instrument is 450 cm^{−1} to 4800 cm^{−1}. The technology is well-suited to perform kinetics experiments as data collection is very fast (resulting in accurate determination of reaction rates). The diamond sensor is compatible with several chemical environments, and *in situ* characterization of components allows detection of unstable species (those may not be measurable by chromatographic or other off-line techniques).

2.2.2 Mass spectrometry (MS)

Mass spectrometric analysis was performed on a Perkin Elmer Sciex API 365 LC/MS/MS system (Perkin Elmer, Waltham, MA, USA). The sample was introduced into the mass spectrometer with a flow rate of 10 μL/min. The instrument was operated in ESI mode with positive ionization. Mass spectra were recorded in Q1 scanning mode between *m/z* ratios of 50–500 with the following settings (voltage values with signs corresponding to the given ionization mode): declustering potential: 30 V, focusing potential: 145 V, entrance potential: 10 V, ionspray voltage: 4500 V, ion source temperature: not heated. The flow rates of the N₂ nebulizing gas, N₂ curtain gas were 8 units and 8 units, respectively. When product ion spectra acquisition was performed: CAD (collisionally activated dissociation) gas: 2 units, collision energy: 30 V.

2.2.3 Nuclear magnetic resonance (NMR) analysis

NMR spectra of the synthesized products, the flame-retardant-effect plasticizer (glycerol-phosphate) and the fibre treating agent (PSil), were recorded with a Bruker AV-300 NMR spectrometer (Bruker Corporation, Billerica, MA, USA) operating at 300.13 MHz, 121.50 MHz and 75.48 MHz for ^1H , ^{31}P and ^{13}C , respectively, and equipped with a 5 mm Z-gradient QNP (quattro nucleus probe, for $^1\text{H}/^{13}\text{C}/^{31}\text{P}/^{19}\text{F}$) probehead. For analysis, about 40 mg of sample was dissolved in 600 μL of D_2O and CDCl_3 for glycerol phosphate and PSil, respectively. All experiments were carried out at 26°C in 5-mm tubes using standard pulse sequences. Spectra were referenced relative to TMS (tetramethylsilane, 0.00 ppm) for ^1H and to the CDCl_3 solvent signal for ^{13}C (77.0 ppm). ^{31}P NMR spectra were indirectly referenced to 85 vol% H_3PO_4 , using the absolute frequency of the ^1H signal of TMS and the corresponding Ξ value, according to the IUPAC convention. A detailed description of ^{31}P referencing as well as the acquisition parameters of the 1D ^1H , ^{13}C and ^{31}P spectra are provided as supplementary information.

2.2.4 Infrared analysis (FTIR)

Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) of treating agents and biofibres were recorded using a Bruker Tensor 37 type Fourier transform infrared (FTIR) spectrometer (Bruker Corporation, Billerica, MA, USA) equipped with DTGS (deuterated triglycine sulfate) detector with resolution of 4 cm^{-1} . Before testing, the powder of fibre samples was mixed with potassium bromide (KBr) powder and cold-pressed into a suitable disk for FTIR measurement.

2.2.5 Thermal analysis (TGA)

A Setaram Labsys TG DTA/DSC instrument (Setaram Instrumentation, Caluire, France) was applied for thermogravimetric analyses (TGA). TGA measurements were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under 30 ml/min nitrogen gas flow, covering a temperature range of

25–400°C and 25–500°C in the case of the TPS batches and the natural fibres, respectively. About 15–20 mg of sample was used in each test.

2.2.6 Scanning electron microscopy (SEM)

Scanning electron microscopic (SEM) images were taken using a JEOL JSM-5500 LV type apparatus (JEOL Ltd., Akishima, Tokyo, Japan). The samples were coated with gold–palladium alloy before examination to prevent charge build-up on the surface.

2.2.7 Flammability tests

The flame retardant performance of the prepared samples was characterized by limiting oxygen index (LOI) measurements according to the ASTM D 2863 standard on 4-mm-thick test specimens. The LOI value expresses the lowest oxygen to nitrogen ratio where specimen combustion is still self-supporting.

Standard UL-94 flammability tests (ASTM 1356-90 and ANSI/ASTM D-635/77) were also performed on 4-mm-thick specimens. 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 ASTM E 906 standard method. Specimens (100 mm × 100 mm × 4 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.

2.2.8 Mechanical testing of composites

Comparative static tensile tests were performed on rectangular specimens of 10 mm × 150 mm (width × length) using a Zwick Z020 universal testing machine (Zwick GmbH & Co.

KG, Ulm, Germany) with a crosshead speed of 5 mm/min (according to the ISO 527-4:1997 standard).

Static three-point bending tests were performed on rectangular specimens of 80 mm × 20 mm using the same Zwick Z020 universal testing machine. The crosshead speed was 5 mm/min and the span length was 64 mm.

All the mechanical tests were performed at room temperature and at least five specimens were tested in all cases.

3 Results and discussion

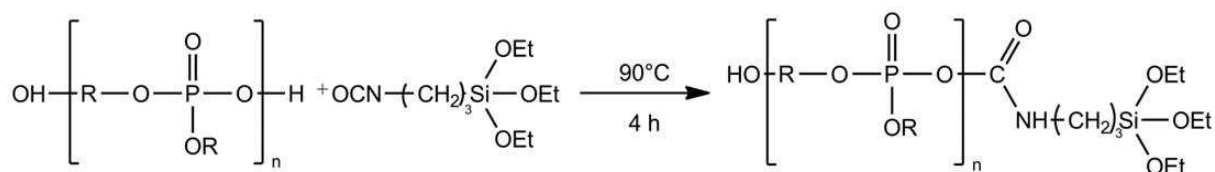
3.1 Preparation and characterization of the phosphorus containing plasticizer

3.1.1 Synthesis and structure elucidation of glycerol phosphate

As atomic efficiency (AE) is one of the most important criteria of green chemistry [19], glycerol phosphate was synthesized through the green, addition-type reaction between glycerol and phosphorus pentoxide (see in Scheme 1).

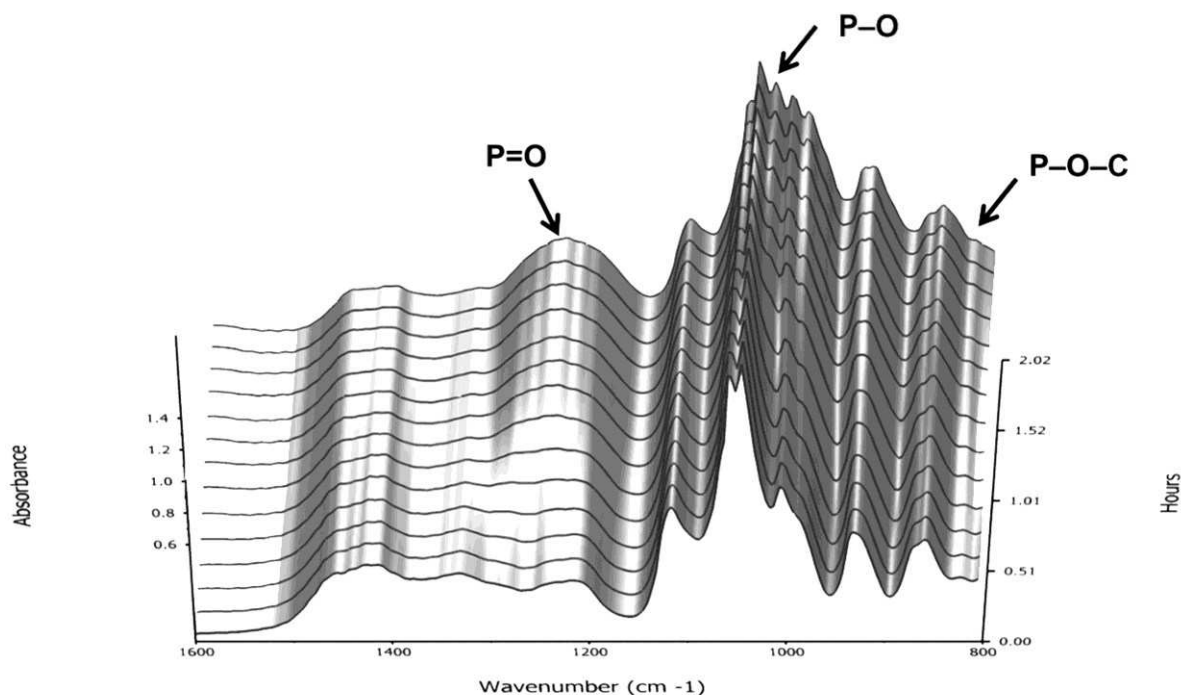
The anhydrous glycerol (92.1 g, 1 mol) was cooled to 0°C in an ice bath under continuous mechanical stirring at 200 rpm. Phosphorus pentoxide (23.66 g, 0.166 mol, glycerol to P-atom ratio: 3:1) was added in 2-g fractions to the cold glycerol under more intense stirring (500 rpm). After each feeding step, temperature of the reaction mixture increased to 10–15 °C, therefore it had to be cooled back to 0°C before the next step. After the addition of the last portion of P₂O₅, the reaction mixture was allowed to warm up to room temperature and then the mixture was stirred for 24 h to ensure complete conversion. For neutralizing the formed acidic P-bonded hydroxyl groups, ammonia gas have been passed through the reaction mixture until the increase of the pH stopped at pH 4.5.

Scheme 1 Reaction between glycerol and phosphorus pentoxide



The up-scaling of the reaction for the preparation of GP was performed in ReactIR™ in-line FT-IR apparatus. The changes in the IR spectrum during the reaction are shown in Figure 1. The formation of glycerol phosphate is easily traceable with its characteristic peaks, such as P=O (around 1220 cm⁻¹), P-O (1030 cm⁻¹) and P-O-C (810 cm⁻¹). The products can be identified after as few as 2 h of reaction; however, overnight intense stirring was necessary to ensure complete conversion.

Figure 1 Joint IR spectra obtained during the reaction between glycerol and phosphorus pentoxide



The synthesized glycerol phosphate structures were identified by ³¹P NMR and MS measurements. According to the MS and NMR results, mainly diglycerol phosphate was

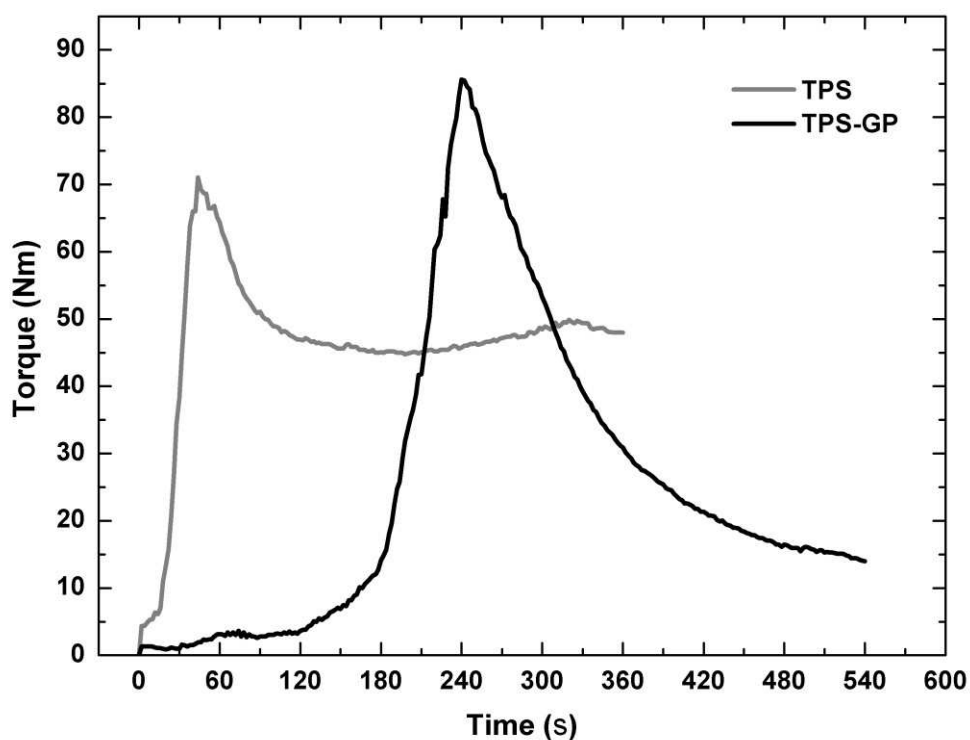
formed during the reaction (MS positive ionization: 247 m/z ; δ : -0.09 ppm, molar ratio reference: 1). Monoglycerol phosphate (MS positive ionization: 173 m/z ; δ : 0.19 ppm) and phosphoric acid (MS positive ionization: 99 m/z ; δ : 0.14 ppm) were formed in quasi-equal amounts, with molar ratios (relative to diglycerol phosphate) of 0.5. Triglycerol phosphate (MS positive ionization: 321 m/z ; δ : -0.54 ppm) was also present in the product, with a relative molar ratio of 0.2. Some other minor by-products, with an overall relative molar ratio of 0.3, were also identified using the MS spectra, i.e. a product formed by the condensation of mono- and diglycerol phosphate (MS: 401 m/z) as well as pyrophosphoric acid (MS: 179 m/z).

3.1.2 Plasticizing effect of GP

Glycerol phosphate was synthesized with an aim to study a multifunctional model plasticizer that can also display flame retardant activity in the polymer matrix. At first, the plasticizing effect exerted by the prepared glycerol phosphate on starch was investigated by continuous recording of the torque during mixing. The torque curves recorded for plasticization of starch with glycerol-phosphate (TPS-GP) and with pure glycerol (TPS) as a reference are compared in Figure 2. The sharp peak of torque demand indicates the stage when starch molecules start getting released from their granule structure followed by gelation [20]. As expected, the smaller molecule (glycerol) could penetrate the starch chains more easily [21] consequently the gelation began already after 60 ± 15 s of mixing. In the case of the glycerol phosphate both phenomena were shifted in time, appearing only after 220 ± 20 s of processing. Typically 15% greater torque was needed for glycerol phosphate to decrease the number of hydrogen bonds between the polymer chains; however, the equilibrium torque for processing the TPS-GP batch was found to be about half of that measured for the conventional glycerol plasticized TPS. This decrease in viscosity can be explained by the increased molecular space and mobility of starch chains when glycerol-phosphate is incorporated. Similar plasticizing

behaviour was observed previously, when a longer-chain phosphorus-containing polyol (Exolit OP560) was studied as a flame retardant plasticizer in starch [11].

Figure 2 Torque curves recorded during plasticizing starch with 25% glycerol (TPS) and with the synthesized glycerol phosphate (TPS-GP)

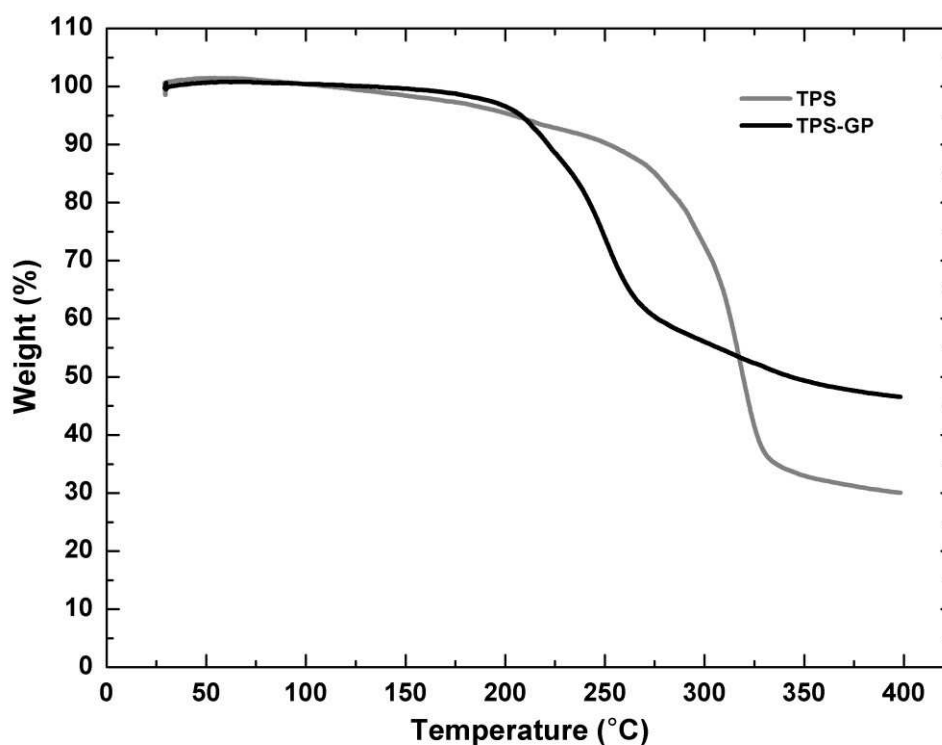


3.1.3 Thermogravimetric analysis of glycerol phosphate plasticized starch

The two types of plasticized starch blends (TPS and TPS-GP) were compared by TGA measurement. The analysis provided evidence for the significant char-promoting effect of the synthesized glycerol-phosphate-based plasticizer. It is shown in Figure 3 that the onset temperature of starch decomposition was shifted from 253 C (TPS reference) to 200 C in the case of the TPS-GP indicating the acid (of GP origin) induced dehydration and decomposition of starch. This is accompanied by a decreased amount of volatile combustible products and

consequently increased char yield. The charred residue at 400 C was 16.5% higher when TPS-GP sample was measured than in the case of the TPS reference.

Figure 3 TG curves of TPS and TPS-GP



3.1.4 Flammability characteristics of plasticized starch

The flammability characteristics of the prepared thermoplastic starch blends were studied by UL94, LOI and mass loss calorimetric methods. The UL94 ratings, the LOI values and the total heat released (tHR) data for the two types of TPS are compared in Table 2. The use of glycerol phosphate plasticizer resulted in significant improvement of flame retardancy. The approximately 1 wt% of P introduced through the plasticizer into the TPS-GP resulted in V-1 rating, high LOI value and 44% reduction of the tHR.

Table 2 Comparison of the flammability characteristics of TPS and TPS-GP

Table 2 Comparison of the flammability characteristics of TPS and TPS-GP

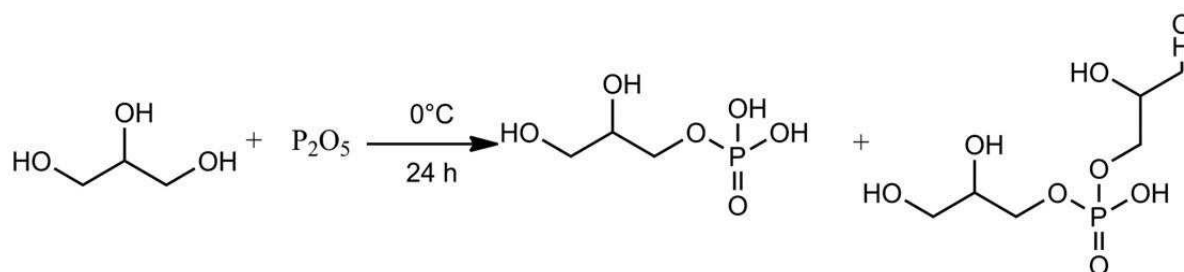
	UL-94 classification	LOI (vol%)	tHR (MJ/m ²)
TPS	HB	22	119
TPS-GP	V-1	34	67

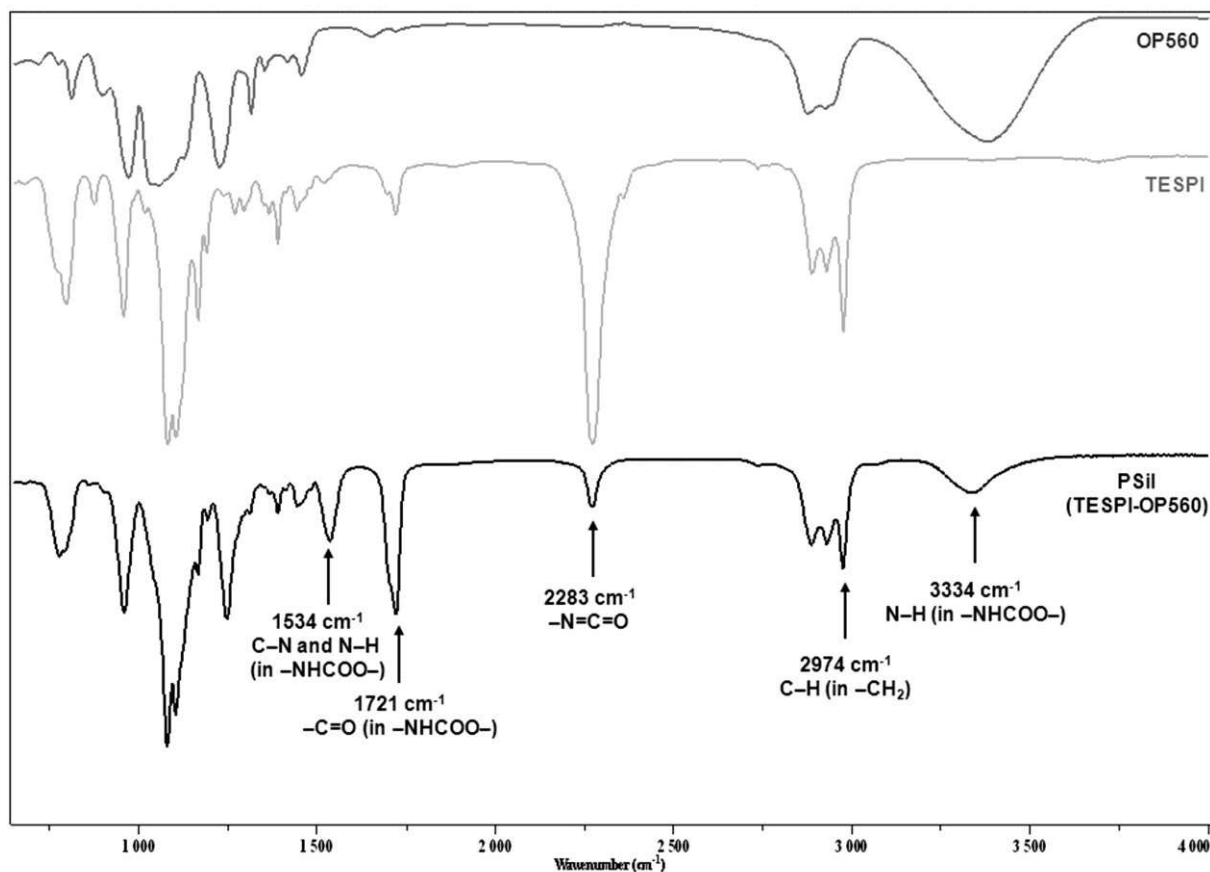
3.2 Preparation and characterization of flame retardant treated flax fibres

3.2.1 Synthesis and corresponding analyses of PSil

A novel reactive modifying agent for cellulose-based biofibres was synthesized by a simple addition reaction between a commercial phosphorus polyol, Exolit OP560 and 3-(triethoxysilyl)-propyl isocyanate (TESPI). The phosphorous silane adduct (PSil, Scheme 2) was obtained after stirring of 5 ml of OP560 with 11.9 ml of TESPI vigorously at 90°C for 4 h under anhydrous conditions. The completion of the reaction was confirmed by FTIR spectroscopy. As shown in Figure 4, the significant reduction of the intensities of both the OH groups of OP560 (at 3380 cm⁻¹) and the NCO groups of TESPI (at 2283 cm⁻¹) revealed that the reaction between the two components had taken place. Accordingly, signals indicating the formation of the PSil adduct appeared at 3334 cm⁻¹ (stretching vibration of the N-H bond), at 1534 cm⁻¹ (assigned to the C–N stretching and N–H bending vibrations), and also at 1721 cm⁻¹ (the characteristic peak for C=O stretching of carbamate linkage).

Scheme 2 Synthesis of the reactive phosphorous surface modifier (PSil)

**Figure 4 FTIR spectra of OP560, TESPI, and their adduct marked as PSil**



The successful linkage, associated with the cessation of the isocyanate group and creation of a linker carbamate group (see reaction in Scheme 2), was also confirmed by NMR spectroscopy. Appearance of a signal at 156.6 ppm was observed in the ¹³C NMR spectrum of the product (see supplementary Figure S1). This chemical shift is close to the typical values of carbamates [22] (literature examples, chemical shifts of individual carbamates, are given as supplementary information). On the other hand, no signal was detected in the ¹³C NMR spectrum of the product between 120 and 135 ppm, the typical spectral region of isocyanate signals [23] (literature examples, chemical shifts of individual isocyanates, are given as supplementary information) suggesting that no residual isocyanate remained in the product up to the detection limit of the ¹³C NMR method. (Presence of some residual, unreacted isocyanate is, however, suggested by detection of an isocyanate band in the product by FTIR. Nevertheless this can obviously be attributed to the higher sensitivity of the IR method compared to ¹³C NMR, especially in the case of such an intensive vibration band. However,

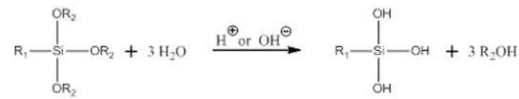
the ^{13}C NMR spectrum at least confirms that the majority of the product contained PSil and the remaining isocyanate, suggested by the FTIR spectrum, is only a minor residue, not detectable in NMR.)

3.2.2 Treatment of flax fibres with PSil

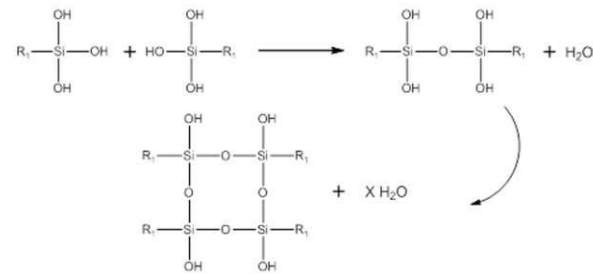
Flax fibres were treated with the new flame retardant according to the following procedure: at first, 8 g of dried fibres was stirred in 320 ml of absolute toluene for 20 minutes, and then 16 ml of PSil was added dropwise to the suspension. This toluenic mixture was refluxed at 111 C for 8 h. The flax fibres were then filtered and washed with pure toluene in order to remove PSil excess. The obtained fibres were heated in an oven at 130 C for 8 h in order to promote the hydrolysis of the alkoxy (triethoxysilane) groups of PSil to silanol moieties. The latter then would subsequently form new covalent bonds with the hydroxyl groups of the cellulosic fibres (Scheme 3) [17].

Scheme 3 Interaction of PSil with flax fibres through hydrolytic process

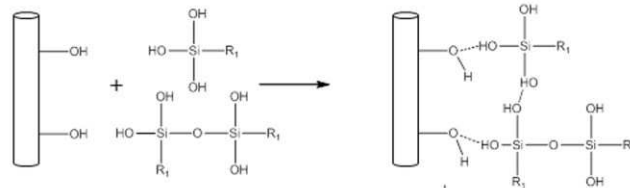
Hydrolysis:



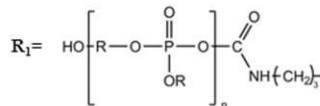
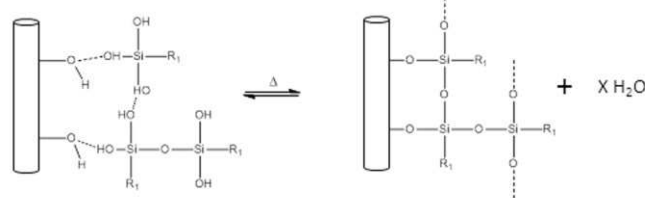
Self-condensation:



Adsorption:

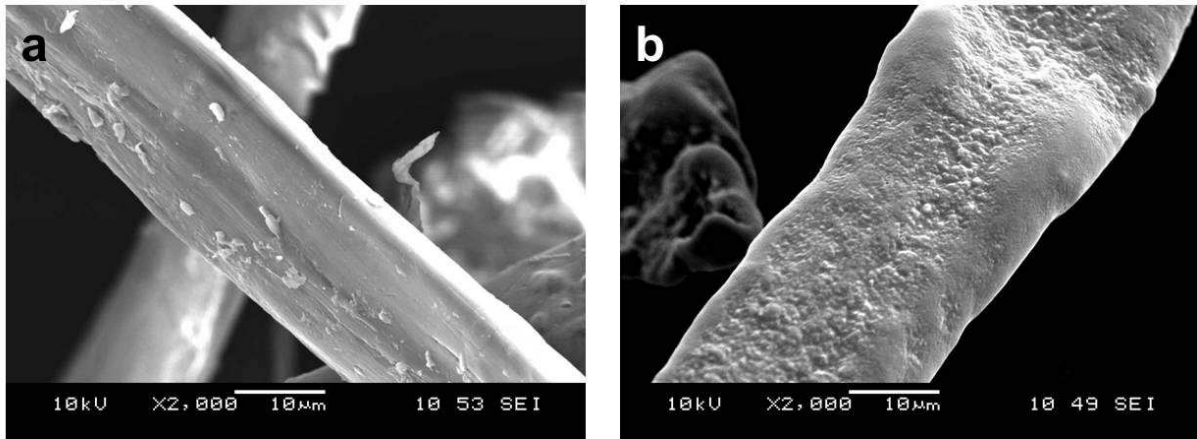


Chemically grafting:



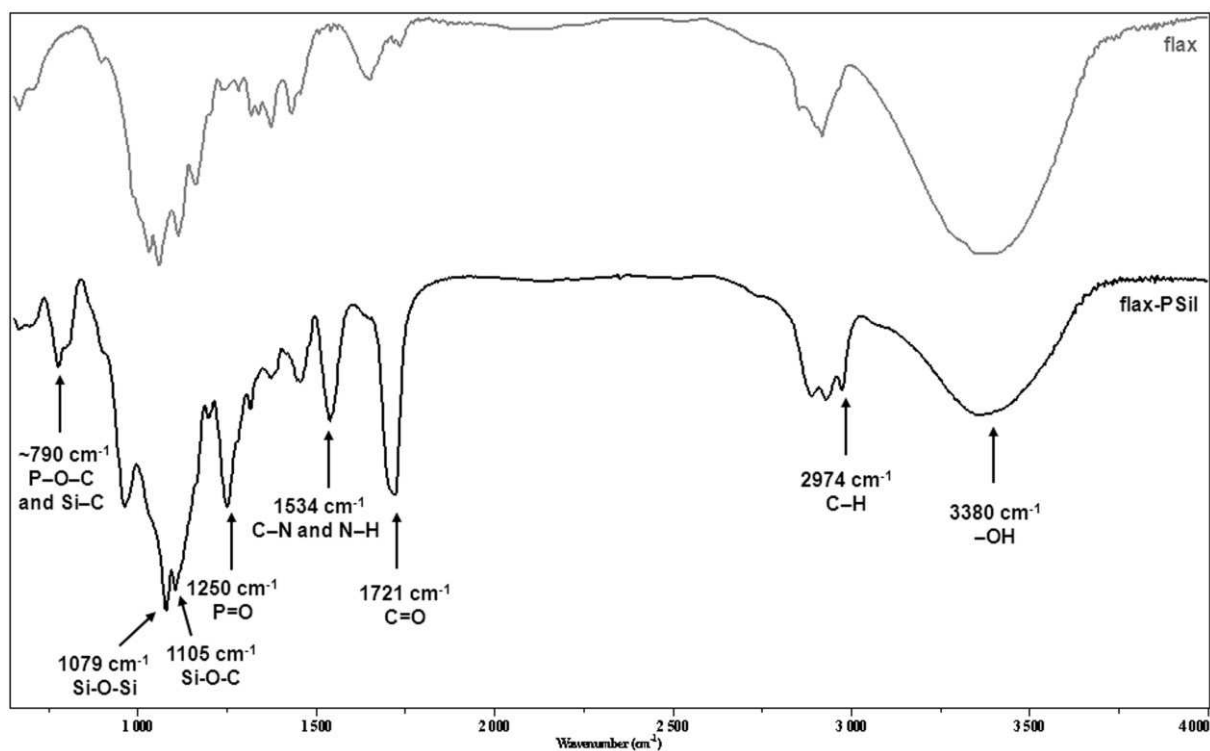
After the described procedure, an average 35% weight increase of the flax fibre indicated the immobilization of a noticeable amount of the modifier on the surface of the biofibres. Thus, approximately 2 wt% P content was introduced to the flax fibres through the PSil-treatment (a higher concentration would have caused adherence of fibres to each other and limited their dispersability). The presence of PSil on the surface of flax fibres was also confirmed by SEM (Figure 5). It was observed that the modifier covered the surface of the fibres in a relatively thick but smooth layer.

Figure 5 SEM images of the surface of (a) neat and (b) PSil-treated fibres



The chemical reaction between PSil and flax was also confirmed by comparing the FTIR spectra of the neat and PSil-treated flax fibres, as presented in Figure 6. The characteristic peaks of PSil are easily observable in the spectrum of the PSil-treated flax fibres, such as the intensive bands at 1721 cm^{-1} and 1534 cm^{-1} corresponding to the carbamate linkage between the two starting components (TESPI and P-polyol) and the presence of other characteristic peaks assigned to P=O bonds (at 1250 cm^{-1}), and to C–H stretching of the additional CH_2 groups (at 2974 cm^{-1}). The band around 790 cm^{-1} can be assigned to the overlap of P–O–C and Si–C stretching vibrations. It can be seen in the spectra that the intensity of the broad peak around 3380 cm^{-1} , corresponding to the free OH groups of cellulose, has decreased as the result of the treatment. In the case of the spectrum of PSil-treated flax fibres, the sharp peaks between 1000 and 1200 cm^{-1} are assigned to the Si–O–C and –Si–O–Si– bonds. The Si–O–C band confirm the chemical linkage between the hydrolysed silane and the hydroxyl groups of cellulose [24,25], and the chemisorption of the modifier onto the fibre surface by stable covalent bonds. The band at 708 cm^{-1} is also assigned to the –Si–O–Si– symmetric stretching vibrations and indicates that polysiloxanes were formed and deposited on the treated fibres, which explains the measured considerable weight increase as well as the SEM observations.

Figure 6 FTIR spectra of neat and PSil treated flax fibres



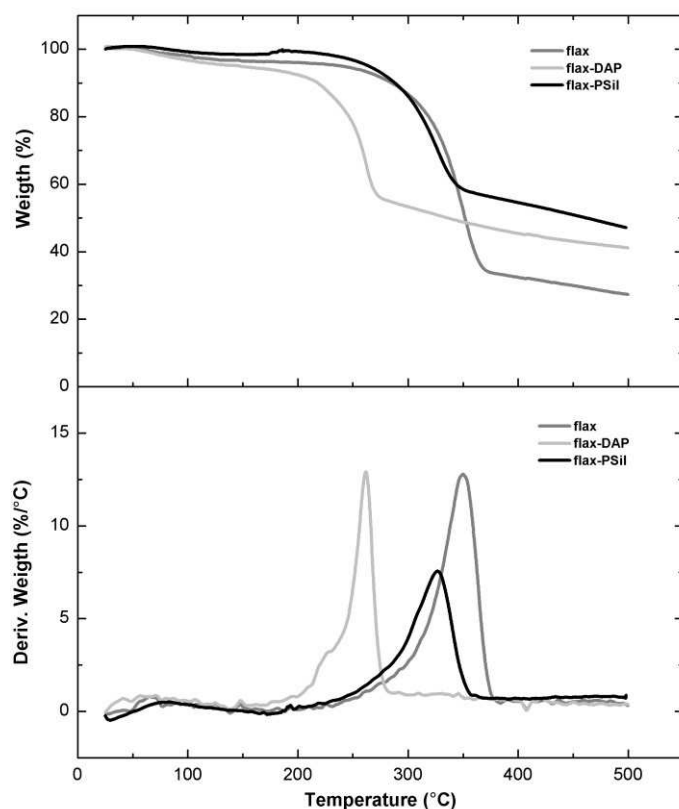
3.2.3 Thermogravimetric analysis (TGA) of PSil treated flax fibres

In Figure 7, the TG and DTG curves of neat flax fibres are compared with those of conventional diammonium phosphate (DAP)-treated and the PSil-treated fibres prepared in the present work. For comparison, the DAP-treatment of flax fibres was carried out according to the termotex procedure [26]. At first, the flax fibres were heated to 120 C which temperature was maintained for 2 h, followed by a 5-minutes-immersion into a cold 5-wt% DAP solution. The ratio of fibre to solution was 1 g/10 ml. The fibres were then separated by centrifuging and dried at 80 C for 4 h. The amount of the absorbed phosphorus (P) was determined as 1.75 wt% of P, calculated from the mass increase.

As expected, the thermal decomposition began at a significantly lower temperature in the case of the DAP-treated fibres and accordingly, the peak temperature of the corresponding DTG curve, indicating the maximum weight loss rate, was 89 C lower than that of the untreated flax fibres. On the contrary, PSil, synthesized by coupling a P-polyol with a silane, did not degrade earlier than the cellulosic substrate; the initial temperature of thermal degradation of

neat and PSil-treated fibres was about the same. The maximal rate of degradation of PSil-treated fibres occurred at a slightly (~ 23 C) lower temperature; however, its rate ($7.6\%/C$) decreased notably compared to the case of untreated flax fibres ($12.8\%/C$). Considering the residual masses obtained after heating the flax fibres up to 500 C, it can be noticed that the highest amount (47%) of residual char belonged to the PSil-treated fibres. These observations can be attributed to the well-known synergistic effect of P and Si atoms [27,28]. Based on the observed significant char promoting effect of PSil, advantageous influence was expected on the flame retardant properties of PSil-treated fibres and their composites as well.

Figure 7 TG and DTG curves of neat, DAP-treated and PSil treated flax fibres



3.3 *Characterization of flax fibre reinforced PLA/TPS biocomposites*

Several advantages of blending of PLA with TPS have already been described, such as reduced cost, decreased rigidity and brittleness, as well as improved ductility [2], moreover TPS can serve as an effective charring agent during combustion [3]. In this work, seven types of PLA/TPS biocomposites were prepared, for all the samples the PLA to TPS ratio was kept constant at 4 to 1. PLA/TPS blends were prepared either with or without flame retarded plasticizer (glycerol phosphate, GP). The obtained two types of PLA/TPS blends were reinforced either with untreated or with treated flax fibres (see Table 1). Thus, one of the obtained biocomposites even contained flame retardant agents both in the matrix material (in the form of GP based plasticizer) and on the surface of the reinforcing biofibres (i.e. the newly synthesized phosphorous-silane, PSil). Additional 10 wt% APP was introduced in the case of the sample marked with the code PLA/TPS-GP/flax-PSil+APP. The manufactured flame retarded biocomposites were then evaluated in terms of their flammability and mechanical properties.

3.3.1 Flammability

The UL94 classifications and the LOI values measured for the manufactured biocomposites, flame retarded through different ways, are summarized in Table 3. It can be seen that the best (V-0) rating according to the UL94 standard was achieved only when additional APP was applied. This is not surprising considering that the P content introduced through the GP plasticizer adds up only to approximately 0.15 wt%, while that through the PSil treatment of the flax fibres only to about 0.5 wt% of P in respect of the total mass of the composite, which is certainly not sufficient to achieve higher levels of flame retardancy. However, when the LOI values of the biocomposites are compared, the effect of each approach of flame retardancy (FR plasticizer, FR fibre treatment and FR additive) can be evaluated one by one. The blending of PLA with glycerol phosphate plasticized starch (TPS-GP) resulted by itself in

a 2 vol% higher LOI (23 vol%) than that measured for the conventional PLA/TPS blend (LOI = 21 vol%). Due to the embedding of neat flax fibres in the biopolymer blends, even when a P-containing plasticizer was applied, the flammability of the obtained composites increased noticeably, and thus the measured LOI values decreased to 20 and 21 vol%, respectively. The observed candle-wick effect [29,30,31] of flax fibres was effectively counterbalanced by their flame retardant treatment with PSil prior to embedding, thus the corresponding LOI values increased by 3 vol% both in the presence or without FR plasticizer. The addition of only 10 wt% of APP to the thus obtained biocomposites resulted in a notable increase in LOI, and ensured self-extinguishing behaviour at ambient conditions (UL94 test), which demonstrate the prominent charring capability of both starch and cellulosic fibres. In the presence of sufficient P atoms, biomaterials, which are rich in hydroxyl groups, can serve as adequate charring agents [3] in intumescent flame retardant systems. Moreover, their application is environmentally preferable, especially when flame retardancy of biopolymers is targeted.

Table 3 UL94 classifications and LOI values measured for PLA/TPS based composites

Table 3 UL94 classification and LOI values measured for PLA/TPS based composites

	UL-94 classification	LOI (vol%)
PLA/TPS	HB	21
PLA/TPS-GP	HB	23
PLA/TPS/flax	HB	20
PLA/TPS-GP/flax	HB	21
PLA/TPS/flax-PSil	HB	23
PLA/TPS-GP/flax-PSil	HB	24
PLA/TPS-GP/flax-PSil+APP	V-0	33

The flame retardant properties of the manufactured biocomposites were also characterized and compared under a cone heater applying 50 kW/m² heat flux. The *obtained heat release rate* (HRR) curves are presented in Figure 8. Additional experimental results are shown in Table 4. It can be seen that the application of GP as plasticizer of PLA/TPS blend by itself moderates the peak of heat release rate (pkHRR) by 20%. The embedding of flax fibres resulted in the

change of shape of the HRR curves (plain running and prolonged HRR data were recorded compared to the sharp pkHRR characteristic for the unreinforced matrix materials). Both the use of GP plasticizer and the flame retardant treatment of the flax fibres slightly shortened the times to ignition (TTI) of the biocomposites, but resulted in a noticeable decrease in the measured HRR and tHR values. Indeed, in the case of their combination (PLA/TPS-GP/flax-PSil), pkHRR decreased by 30% and tHR by 17% compared to the FR-free composite, which is referred to as PLA/TPS/flax. The TPS content of the biopolymer blend certainly contributed to the charring capability of the manufactured composites. When further reduction of flammability is required, the addition of 10 wt% APP to the system (PLA/TPS-GP/flax-PSil+APP) provides prominent fire retardancy to the composite. HRRs lower than 150 kW/m², by 40% reduced tHR (compared to PLA/TPS/flax) and charred residue as much as 24% were obtained in this case (Table 4). It should be noted that owing to the presence of the beneficial multifunctional agents (plasticizer, surface treating agent) applied, the total amount of FR additives needed in this case (10 wt% APP) is significantly lower than applied commonly in similar PLA based systems [9,10,32,33].

Figure 8 Heat release rate curves of the prepared PLA/TPS based composites

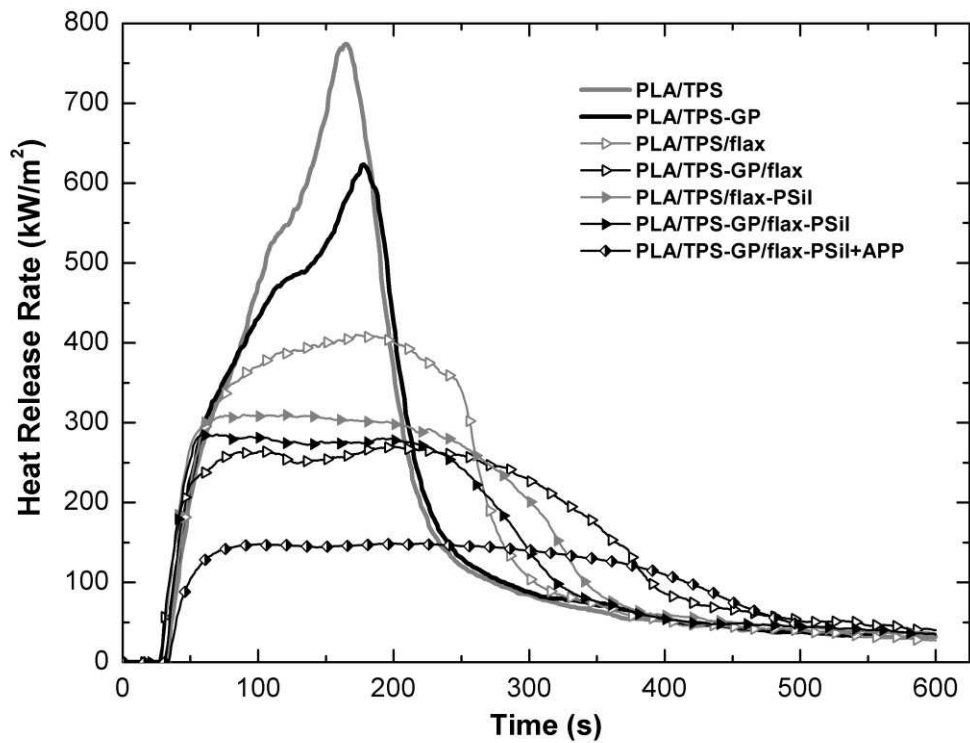


Table 4 Experimental results of the mass loss calorimetric tests

Table 4 Experimental results of the mass loss calorimetric tests

	TTI (s)	pkHRR (kW/m ²)	tHR (MJ/m ²)	residual mass (%)
PLA/TPS	33	774	105.4	0
PLA/TPS-GP	29	623	100.0	4
PLA/TPS/flax	34	410	98.1	5
PLA/TPS-GP/flax	28	270	90.3	6
PLA/TPS/flax-PSil	29	310	91.0	9
PLA/TPS-GP/flax-PSil	29	285	81.0	10
PLA/TPS-GP/flax-PSil+APP	34	149	57.5	24

3.3.2 Mechanical characteristics

The mechanical performance of the manufactured flame retardant biocomposites was characterized by static tensile- and bending tests. The measured strength and modulus values are compared in Figure 9, while the elongations measured at break during tensile tests are presented in Table 5. The blending of PLA with GP-plasticized starch (PLA/TPS-GP) resulted in noticeably better tensile and flexural properties than those of the reference

PLA/TPS blend. The strain to failure of 2.63% measured for the GP-containing blend was also noticeably greater than the elongation measured for the reference blend (Table 5). These results can be (at least partially) attributed to the decreased viscosity of TPS-GP, which improved the dispersion between the two, originally immiscible biopolymers as shown in the SEM images of Figure 10. As a consequence, the mechanical performance of the obtained flame retarded blend (PLA/TPS-GP) mostly surpasses those of the PLA/TPS blends of similar compositions reported in the literature [34,35,36].

The addition of 25 wt% neat flax fibres increased the flexural strength (shown in Figure 9 b) and stiffness (see in Figure 9 c and d) of the biopolymer blends, however it caused significant (30%) reduction of the tensile strength and a considerable decrease in the elongation at break (Table 5) of the PLA/TPS-GP blend, indicating that the presence of GP had reduced the compatibility between the cellulosic fibres and the embedding biopolymer matrix. Similar conclusions were drawn when P-containing species were used on the surface of the flax fibres embedded into the reference PLA/TPS matrix (without GP). All the studied mechanical characteristics of the latter prepared composite (PLA/TPS/flax_PSil) deteriorated due to the PSil treatment of flax fibres, compared to the composite reinforced with untreated flax fibres (PLA/TPS/flax). However, when P-containing species were applied in both phases, i.e. both in the matrix and on the surface of reinforcing fibres (PLA/TPS_GP/flax_PSil), increase of both the tensile- and flexural strength was observed (see Figure 9 a and b), as well as increased elongation at break (Table 5). Aiming at even better flame retardant properties, APP was added to the system, which, as expected, decreased the tensile strength, but increased the stiffness. The mechanical performance of this effectively flame retarded composite can still outperform their current counterparts [37].

Figure 9 (a) Tensile strength, (b) flexural strength, (c) tensile modulus and (d) flexural modulus of the flax fibre reinforced PLA/TPS biocomposites

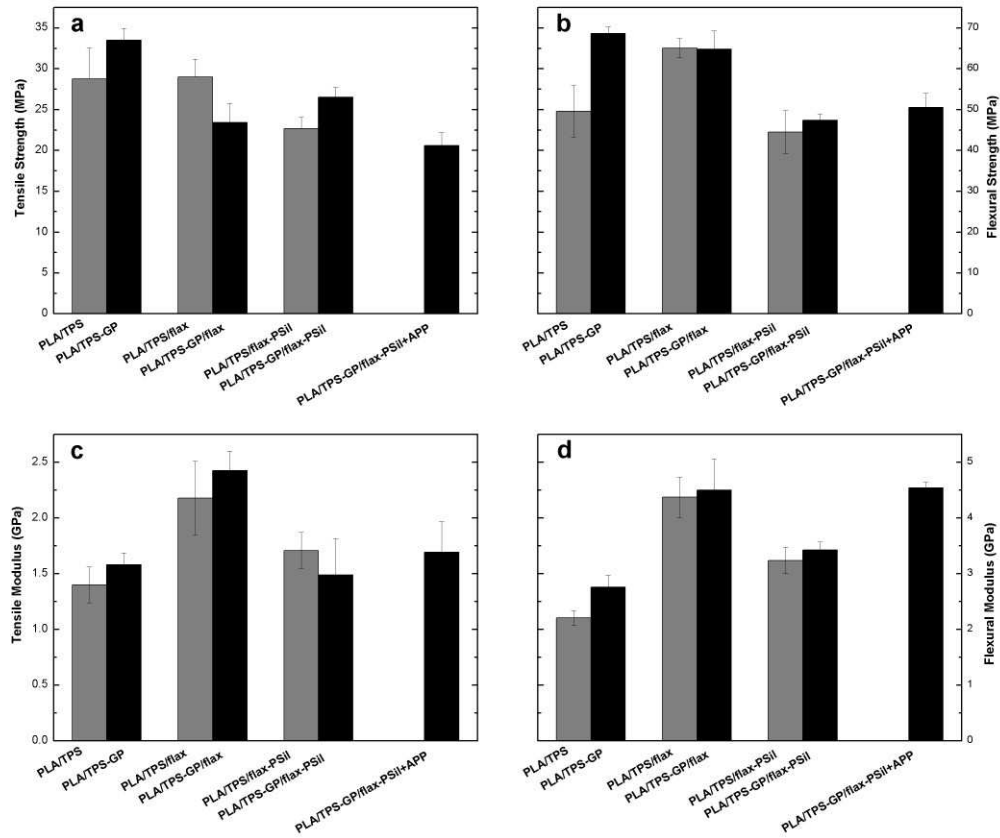
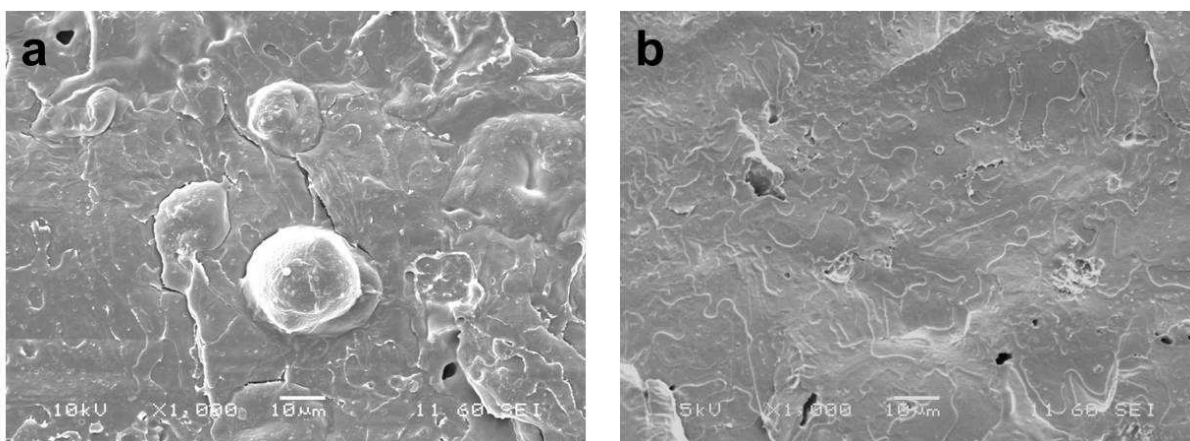


Table 5 Elongation at break measured for the flax fibre reinforced PLA/TPS biocomposites

Table 5 Elongation at break measured for the flax fibre reinforced PLA/TPS biocomposites

	Elongation at break (%)
PLA/TPS	2.05 ± 0.14
PLA/TPS-GP	2.63 ± 0.08
PLA/TPS/flax	1.25 ± 0.06
PLA/TPS-GP/flax	1.10 ± 0.10
PLA/TPS/flax-PSil	1.44 ± 0.04
PLA/TPS-GP/flax-PSil	1.89 ± 0.08
PLA/TPS-GP/flax-PSil+APP	1.32 ± 0.08

Figure 10 SEM images of (a) PLA/TPS and (b) PLA/TPS-GP blends



4 Conclusions

Novel phosphorus-containing multifunctional additives were synthesized with the aim to provide flame retardancy to natural fibre reinforced PLA/TPS biocomposites in an economical way.

The synthesized phosphorus-containing polyol, glycerol phosphate, was used as plasticizer to obtain thermoplastic starch of reduced flammability. This modified starch proved to have enhanced char promoting capability when applied in PLA, and thus provided improved flame retardancy to PLA/TPS blends. On the other hand, a newly synthesized reactive flame retardant modifier (PSil) of flax fibres allowed the phosphorus–silicon synergism to be utilized. The LOI value of both PLA/TPS and PLA/TPS–GP blends decreased when neat flax fibres were embedded. This harmful candle-wick effect of the applied fibrous substances ceased completely due to the treatment of fibres with the synthesized phosphorous-silane. Significant charring activity of biofibres was achieved (47% charred residue at 500 C in TGA) without noticeable decrease of the thermal stability of the cellulosic fibres.

When the flame retardant plasticizer was applied in combination with the PSil-treated flax fibres, 30% reduction was achieved in pkHRR compared to the phosphorus-free reference biocomposite. The flame retardant ability exerted by the P-content of only the plasticizer and the fibre modifier (approximately 0.65 wt%) was insufficient to provide self-extinguishing

character to the biocomposites. However, the addition of as few as 10 wt% of APP proved to be sufficient to achieve V-0 rating, and a LOI value as high as 33 vol% was reached this way. The phosphorus containing species, being present both on the surface of the reinforcing flax fibres and in the biodegradable matrix material resulted in adequate strength and stiffness in the case of the effectively flame retarded biocomposites. In general, the mechanical performance of the prepared flame retarded biocomposites is comparable with that of a common polypropylene, at least regarding tensile and flexural properties.

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