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Flame retardancy of biocomposites based on thermoplastic starch

Summary — The flame retardancy of fully biodegradable, natural fiber reinforced thermoplastic starch (TPS) composites was studied in this work. Thermoplastic starch of significantly reduced flammability could be prepared by using a phosphorus containing polyol for plasticizing starch. The thermal degradation of the obtained flame retarded TPS was compared to conventional glycerol-plasticized TPS using not only TGA and DSC but also LP-FTIR (Laser pyrolysis FT-IR coupled method) measurements, which allowed the identification of all the gaseous degradation products. The flame retardant TPS matrix was reinforced with chopped flax fibers and woven linen-hemp fabrics. Due to the embedding of biofibers significant increase in tensile and impact properties of TPS could be achieved, however, the flammability characteristics of the biocomposites, measured by *LOI*, UL-94 and cone calorimetric tests, become inferior to those of the unreinforced TPS matrix, thus the flame retardant treatment of the reinforcing natural fibers was indispensable. The thermal behaviour and flame retardancy of biofibers, investigated by TGA and cone calorimetry, showed substantial improvement as a consequence of their phosphorous surface treatment. The prepared fully biodegradable biocomposites, comprising of TPS matrix plasticized with P-polyol and P-treated biofibers, exhibit increased mechanical performance accompanied with excellent flame retardancy: pass V-0 rating in UL-94 test, reach *LOI* of 32 vol. %, and show with 45 % reduced pk*HRR* during combustion than the unreinforced TPS reference.

Keywords: biocomposites, thermoplastic starch, natural fiber reinforcement, flame retardancy, plasticizer, phosphorous polyol, ammonium phosphate, thermal degradation.

UNIEPALNIANIE BIOKOMPOZYTÓW NA BAZIE SKROBI TERMOPLASTYCZNEJ

Streszczenie — Przedmiotem pracy była ocena ognioodporności całkowicie biodegradowalnych kompozytów skrobi termoplastycznej wzmacnianej naturalnymi włóknami. Termoplastyczną skrobię (TPS) o ograniczonej palności otrzymywano stosując w charakterze plastyfikatora poliol zawierający fosfor. Porównano przebieg degradacji termicznej uniepalnionej TPS z degradacją termiczną skrobi uplastycznionej konwencjonalnie przy użyciu glicerolu, stosując metody TGA, DSC oraz LP-FTIR, umożliwiające identyfikację wszystkich gazowych produktów rozkładu. Uniepalnioną matrycę skrobi termoplastycznej wzmacniano ciętymi włóknami lnu lub warstwami tkaniny lniano-konopnej. Dzięki wzmocnieniu osiągnięto znaczne zwiększenie wytrzymałości na rozciąganie oraz udarności wytworzonych biokompozytów, jednak ich odporność na palenie [ocenianа na podstawie indeksu tlenowego (*LOI*), testu UL-94 oraz za pomocą kalorymetru stożkowego] uległa znacznemu pogorszeniu w stosunku do ognioodporności niewzmacnianej skrobi termoplastycznej. Badania TGA oraz metodą kalorymetru stożkowego wykazały, że udział fosforu w zastosowanym plastyfikatorze, a także we włóknach naturalnych modyfikowanych związkami fosforu użytych jako wzmocnienie, wpływa na poprawę odporności na ogień wytworzonych biokompozytów (klasa palności V-0 w teście UL-94, indeks tlenowy 32 %, maksymalna szybkość wydzielania ciepła mniejsza o 45 % niż w przypadku niewzmacnianej TPS), a jednocześnie pozwala na zachowanie ich korzystnej wytrzymałości mechanicznej.

Słowa kluczowe: biokompozyty, skrobia termoplastyczna, naturalne włókna wzmacniające, opóźniacze palenia, plastyfikator, poliol funkcjonalizowany fosforem, fosforan amonu, degradacja termiczna.

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INTRODUCTION

The enormous plastic usage worldwide is accompanied with several serious environmental and sustainability issues. Therefore, in recent years increasing attention arose to biodegradable and renewable materials. In the market many biodegradable polymers, such as polylactic acid (PLA), polycaprolactone (PCL), polyhydroxyalkanoate (PHA), *etc*., are already available; however these are generally less cost-effective than their traditional petrochemical based counterparts (PP, PE, PET, *etc*.). In this sense, starch-based thermoplastic biopolymers are promising for a wide range of application fields [1] due to their wide availability and low cost. The most commonly used plasticizers for starch are water and glycerol, but also several low molecular weight polyols (such as glycol, xylitol, mannitol, sorbitol, *etc*.) have been already employed. However, the use of polyol functionalized with heteroatom, such as P of flame retarding effect, as plasticizer seems to be a novel idea.

In order to increase the originally weak mechanical performance of the thermoplastic starch (TPS) matrix by a way that preserves the environmental friendly character of the final material the usage of natural lignocellulosic reinforcements is a logical choice [2]. The availability, renewability, low density, and price as well as satisfactory mechanical properties make the biofibers an attractive and ecological alternative to glass, carbon and other man-made fibers [3, 4]. The combination of TPS matrix with different type of natural fibers is increasingly investigated by researchers, and has been also reviewed recently by Faruk *et al*. [5].

Biocomposites, comprising of biodegradable matrix materials and reinforcing biofibers, are presumed to be increasingly used in industries (such as transportation and construction) where the development of safe and environmental friendly flame retardant composites is of great importance. Still, the flame retardancy of starch-based biopolymers was barely studied until recently, only a few papers have been published in this field [6—9]. On the other hand, according to earlier reports, reinforcing biofibers (without flame retardants in the polymer matrix) increase the heat conductivity and decrease the apparent stability of the composite, and thus ignition becomes easier [10]. Candlewick effect of natural fibers represents a big challenge for flame retardation thus its suppression is required for improving the flame retardancy of the natural fiber reinforced biocomposites [11, 12]. Phosphorous compounds [such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), monoammonium phosphate (MAP) and diammonium phosphate (DAP)] proved to be adequate to effectively flame retard cellulose based fibers [13—16].

In this work, the flame retardancy of fully biodegradable, natural fiber reinforced TPS composites of increased mechanical performance is investigated. To overcome the candlewick effect of biofibers and effectively reduce the flammability of the biocomposites phosphorus-based chemical substances were used both on the surface of the reinforcing biofibers and in the TPS matrix.

EXPERIMENTAL

Materials

Commercially available corn-starch (Natura Reformélelmiszer Kft., Hungary) of 19 % amylose content was modified. Two types of TPS matrices were prepared. One of them was plasticized with 30 wt. % glycerol (obtained from Azúr Vegyszerbolt Kft., Hungary) by itself (marked as TPS-G) that served as TPS reference; while the other (marked as TPS-GOP) was plasticized with the combination of 11 wt. % glycerol and 15 wt. % phosphorus-containing polyol (Exolit OP 560, produced by Clariant Ltd., Germany). The applied phosphorous polyol, owing to its high phosphorus content (10—13 wt. %), exhibit high flame retardant performance besides its plasticizing functionality.

As reinforcement 2—3 mm long chopped flax fibers (with diameters ranging from 20 μm to 60 μm) and linen-hemp plain woven fabrics (areal weight: 325 g/m^2), both received from the Institute of Natural Fibres and Medicinal Plants (Poznan, Poland), were used, respectively.

Fiber treatment

Flax fibers (BFibre) and linen-hemp fabrics (BFabric) were washed with water to remove dust and impurities and then dried in oven at 70 °C for 12 h. For flame retardant treatment the used fibers and fabrics were preheated at 120 °C for two hours, than immersed in cold phosphoric acid (PA) solutions with concentration of 17 % of PA for 5 minutes. The ratio of fiber to PA solution was 1 g fiber to 10 cm^3 PA solution. The fibers were then washed with 5 % ammonium hydroxide solution so that to form ammonium phosphates (AP) on the fibers (as the acid would trigger long-term degradation in cellulose fiber structure). The excess of solutions were removed by pressing the fabrics in a foulard. After treatment, the fibers and fabrics were dried in air. The amount of the absorbed phosphorus (P) was determined by the mass increase. It was set to 1.75 wt. % of P.

Sample preparation

The components of TPS matrices (TPS-G and TPS-GOP) were homogenized in a Brabender Plasti Corder PL 2000 type internal mixer at 150 °C, with a rotor speed of 60 rpm until major decrease occurred in mixing torque demand. The obtained blends were then hot pressed to form 4 mm thick reference specimens in a Collin P200E type laboratory hot press.

Two types of natural fiber reinforced TPS composites were prepared comprising of TPS-GOP matrix: short flax fiber reinforced composites (TPS-GOP_BFibre) and plain-woven linen-hemp fabric reinforced multilayer composites (TPS-GOP_BFabric). The weight fraction of both types of natural fibers in the TPS composites was fixed at 27 %. In the case of TPS-GOP_BFibre marked samples 27 wt. % of fibers were added to the plasticized starch blend and mixed for additional 3 minutes in the internal mixer. The fabric reinforced composite samples (TPS-GOP_BFabric) were prepared trough several steps. First 500 μm thick sheets were compression moulded from the TPS-GOP matrix material at 150 °C in a Schwabenthan Polystat 300 S laboratory hot press. The multilayered natural fabric reinforced composites were then manufactured by laminating 4 matrix sheets and 3 woven linen-hemp fabrics. The packages were hot-pressed to form multilayer composites (in the same hot press) at a temperature of 130 °C and a pressure of 0.25 MPa for 5 minutes.

Methods of testing

— Setaram Labsys TG DTA/DSC instrument was used for thermal characterization: differential scanning calorimetric (DSC) tests and thermogravimetric analysis (TGA). DSC and TGA measurements of plasticized starch samples were carried out in the temperature range of 25—400 °C, while TGA measurements of biofibres were carried out in the temperature range of 25—500 °C at a heating rate of 10 °C/min under nitrogen gas flow rate of 30 cm^3/min. About 15—20 mg of sample was used in each test.

— Infrared spectra (4000—400 cm^{-1}) of untreated and AP-treated biofibers were recorded using a Bruker Tensor 37 type Fourier transform infrared (FT-IR) spectrometer with resolution of 4 cm^{-1}, and equipped with DTGS detector. Before testing, the powder of fiber samples was mixed with potassium bromide (KBr) powder and cold-pressed into a suitable disk for FT-IR measurement.

— Laser pyrolysis (LP)-FT-IR [17] method was used for the investigation of the pyrolytic degradation products of TPS matrices. The system comprises CO_2 pyrolyser laser (10.6 nm, SYNRAD 48-1) unit coupled with Bruker Tensor 37 type FT-IR spectrometer.

— The samples for SEM analysis were broken at the temperature of liquid nitrogen. The fracture surfaces of the composite samples were coated with gold-palladium alloy and then examined using a JEOL JSM-5500 LV scanning electron microscope.

— Comparative static tensile tests were performed on rectangular specimens of 10 mm × 150 mm (width × length) using a Zwick Z020 universal testing machine with a crosshead speed of 2 mm/min (according to the ISO 527-4:1997 standard).

— Instrumented falling weight impact (IFWI) tests were performed using a Fractovis 6785 instrument (Ceast, Pianezza, Italy) on the following settings: maximal energy: 228.64 J, diameter of the dart: 20 mm, diameter of the support rig: 40 mm, weight of the dart: 23.62 kg and drop height: 1 m (according to the ISO 6603-2:2001 standard). Square specimens with dimensions of 70 mm × 70 mm were subjected to IFWI tests. From the IFWI tests the specific perforation energy [E_p (J/mm)] and the ductility factor [D_r (%)] were determined.

$$E_p = \frac{E_{max}}{h} \tag{1}$$

$$D_r = \frac{E_{max} - E_{F_{max}}}{E_{max}} \cdot 100 \tag{2}$$

where: E_{max} *— total energy of break [J], h — thickness of the specimen [mm],* E_{Fmax} *— energy at maximal force [J].*

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

— The flame retardant performance of the prepared TPS matrices and composites was characterized by limiting oxygen index (*LOI*) measurements according to the ASTM D 2863 standard. 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. UL-94 classification is used to determine dripping and flame spreading rates.

— Mass Loss type cone calorimeter tests were carried out by an instrument made by FTT Inc. using the ASTM E 906 standard method. Specimens (100 mm × 100 mm) were exposed to a constant heat flux of 50 kW/m^2 and ignited. Heat release values and mass reduction were continuously recorded during burning.

RESULTS AND DISCUSSION

According to the literature the inclusion of fire retardant additives into fully biodegradable polymer systems is generally accompanied with the reduction of the mechanical properties. There was a need to apply multifunctional additives being able to combine essential functions, such as plasticizing and fiber treatment, with fire retardancy.

Flame retardancy of TPS

For improving fire resistance of TPS, the substitution of generally used glycerol plasticizer by a phosphorus-containing model plasticizer (OP560 type) was studied.

The plasticizing effect of the applied chemical substances could be followed by recording the torque during mixing. It can be seen in Fig. 1 that the two types of polyols as plasticizers acted differently. In the case of glycerol, when used by itself, the torque increases continually right after starting the mixing indicating the continual decrease of hydrogen bonding between the polymer

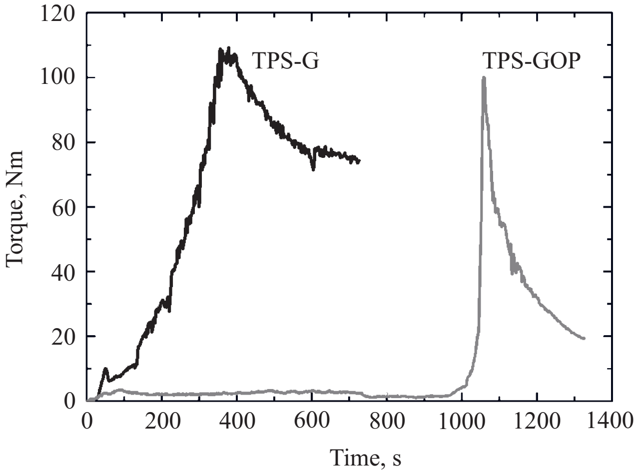

Fig. 1. Torque curves recorded during plasticizing starch with 30 % glycerol (TPS-G) and with the mixture of 11 % glycerol and 15 % OP560 (TPS-GOP)

chains and the continuous increase in molecular space. The maximum of torque demand appeared typically at 380 ± 30 s, when the gelatinization begins, *i.e.* starch molecules start getting released from the granule structure, and behave similarly to thermoplastic synthetic polymers [18]. On the contrary, the incorporation of the long-chain phosphorous polyol (OP560) between the starch chains proved to be more time-consuming. Significant increase in torque demand could not be measured until 1060 ± 60 s, when in all cases a sharp peak of torque indicated the beginning of plasticization process. The observed different plasticizing phenomenon of a short--chain and a long-chain polyol can be explained by the kinetically controlled interaction process between starch and plasticizers; the smaller molecule (in this case glycerol) penetrates the starch chains more easily [19]. It is visible that the energy necessary for plasticizing corn starch is about the same for the two types of plasticizer. However, after reaching the plateau, the equilibrium torque for P-polyol plasticized starch is considerably lower than that of the glycerol plasticized starch, which indicates that the mobility of starch chains has been increased significantly when OP560 was used as plasticizer causing remarkable change in the viscosity and resulting in somewhat sticky specimen comprising of TPS-GOP matrix.

The obtained two types of TPS blends were compared through thermal analyses. The DSC, TG and DTG curves are shown in Fig. 2. The onset temperatures of the decomposition steps of glycerol plasticized starch (TPS-G) can be seen, both in DSC and TG curves, at 155 °C and 250 °C. These correspond to the endothermic decomposition of glycerol and corn starch, respectively. It is visible that the addition of OP560 has remarkable influence on the thermal degradation of the obtained TPS. The TPS plasticized with addition of OP560 (TPS-GOP) decomposes at lower temperature than the glycerol-plasticized TPS, namely the temperatures of maximum mass loss rates for TPS-G and TPS-GOP are 314.5 °C and 264.5 °C, respectively. However, beyond the temperature of 318 °C, TPS-GOP is more stable than TPS-G, moreover, the residue left at 500 °C for TPS-GOP is 41.8 % which is much higher than that of TPS-G reference (25.4 %).

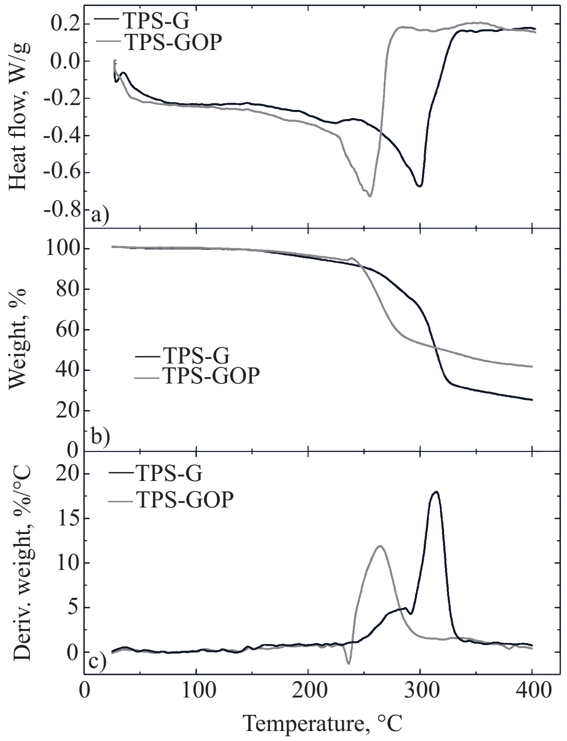

Fig. 2. a) DSC, b) TG and c) DTG curves of TPS plasticized with 30 % glycerol (TPS-G) and with the mixture of 11 % glycerol and 15 % OP560 (TPS-GOP)

LP-FTIR method was used to analyze the gaseous products during the pyrolytic degradation of TPS matrices. The FT-IR spectra of the pyrolysis products of the two types of plasticized starch are shown in Fig. 3. The LP-FTIR spectrum of TPS-G fits well to the previously reported TG-FTIR features of degradation gas products of PLA/glycerol-plasticized TPS [8]. Furthermore, besides the characteristic degradation products of starch such as

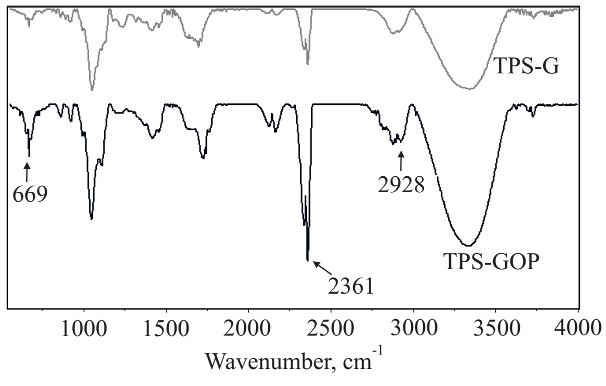

Fig. 3. FT-IR spectra of gas phase in the pyrolytic degradation of TPS matrices obtained after 45 sec laser pyrolysis with a laser power of 0.75 W for 45 s

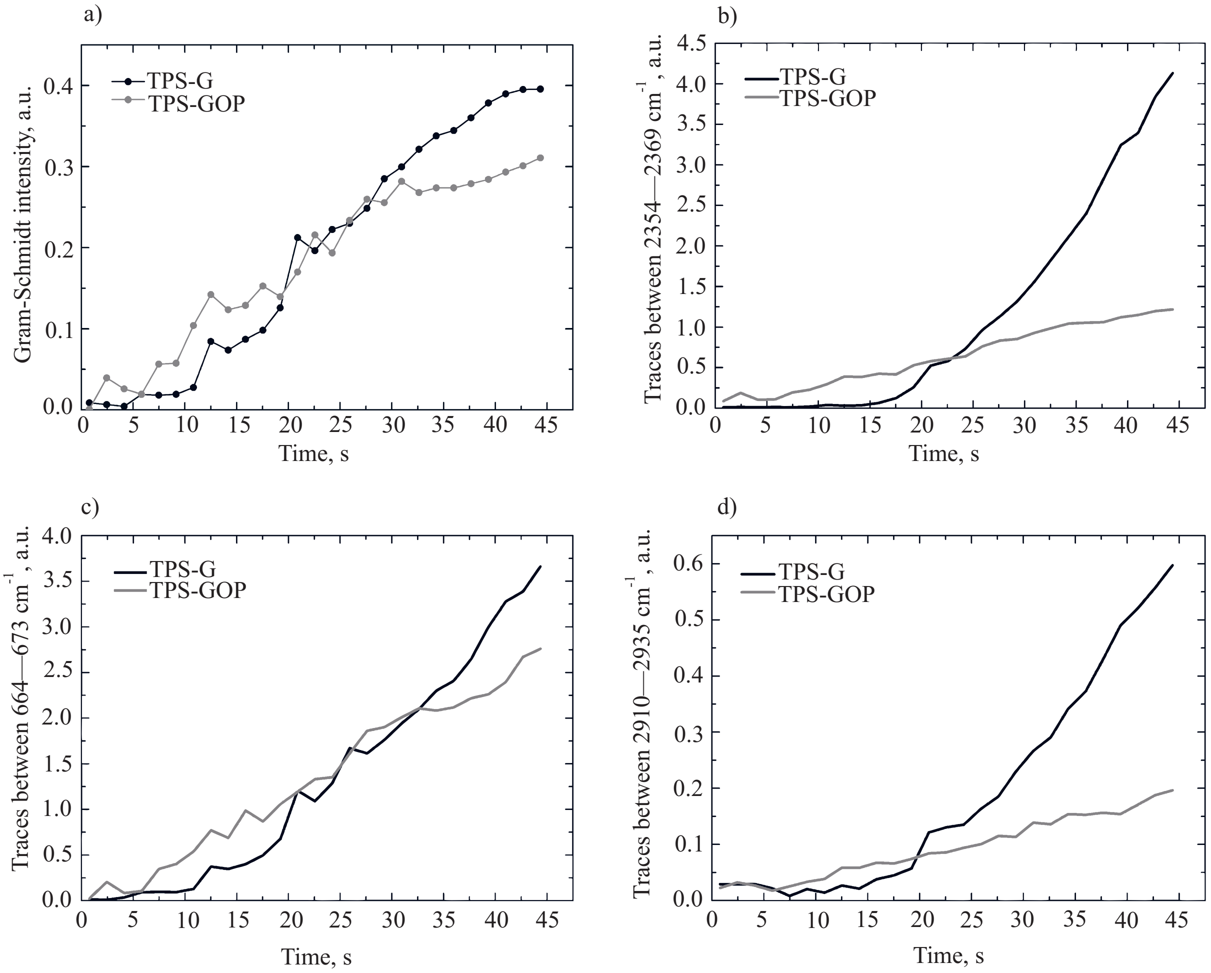

Fig. 4. Traces of pyrolytic degradation products as a function of time during laser pyrolysis with 0.75 W for 45 seconds: a) total (Gram-Schmidt Intensity), b) CO_2, c) hydrocarbons and d) CH_3OH

H_2O (3400—4000 cm^{-1} and 1200—2200 cm^{-1}), hydrocarbons (2800—3000 cm^{-1}), CH_2O (C-H stretching, 2780 cm^{-1}; C-O stretching, 1745 cm^{-1}), CO (2173 cm^{-1}), CO_2 (2280—2400 cm^{-1}), and CH_3OH (C-O stretching, 1050 cm^{-1}; O-H deformation, 669 cm^{-1}) using LP-FTIR method the vapours of glycerol (such as at 861, 923, 1111 and 1418 cm^{-1} wavenumbers) could be also unambiguously detected. When compared with the TG-FTIR coupled method, where the glycerol can condense between the TG and FT-IR equipments [8], in the case of LP-FTIR the direct connection between the pyrolysis zone and the analyzing unit allows the immediate and *in situ* analysis of the degradation products without loss of any components [17]. It has to be also highlighted that, in contrast to the much more time-consuming TG-FTIR method, the presented LP-FTIR experiments took only 45 seconds per samples.

It is well-known that dehydration and depolymerization are the two main processes associated with the thermal degradation of polysaccharides [20]. In the process of dehydration, the sample may release water, and in the process of depolymerization, the main decomposition products are CO_2, CO, CH_3OH, and hydrocarbons, *etc*. As the TG measurements reveal (Fig. 2), also the LP-FTIR analysis confirmed that the P-containing OP560 additive catalyze the thermal decomposition of TPS at the beginning. The amount of selected gas components could be compared through the integrated traces of FT-IR peaks. Comparing the quantity (Fig. 4 a) and ratio of the pyrolytic degradation products presented in Fig. 4 b, c and d, it can be established that in the first 20—25 seconds of laser pyrolysis the OP560 containing TPS release more CO_2 (2361 cm^{-1}), hydrocarbons (2928 cm^{-1}) and CH_3OH (669 cm^{-1}), *etc*. compared with the glycerol-plasticized starch (see also in Fig. 3). However, after 25 seconds of pyrolysis the char promoting effect of the P-polyol prevails and the rapid decomposition of the TPS-GOP sample ceases, meanwhile the thermal decomposition of the glycerol-plasticized starch (TPS-G) increases furthermore exponentially in time. Consequently, the solid-state flame retarding action of the P-containing plasticizer could be confirmed by the LP-FTIR method.

Flame retardancy of natural fibers

Chopped flax fibers (BFiber) and plain woven linen-hemp fabrics (BFabric) were used for reinforcing TPS. In order to reduce the flammability and diminish the candlewick effect [11, 12, 21, 22] of the fibrous substances,

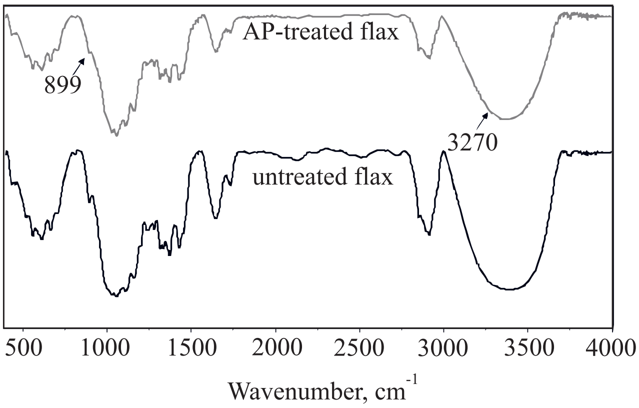

Fig. 5. FT-IR spectra of untreated and AP-treated flax fibers

the natural fibers were treated with ammonium phosphate (AP) model surface treating agent according to the above described method. It is presumed that AP is mainly physically adsorbed on the surface and in the capillaries of the biofibres, however, also chemical interaction could be confirmed by FT-IR spectroscopy between phosphoric acid and the hydroxyl groups of cellulose and lignin containing fibers. Fig. 5 shows the spectra of the untreated and AP-treated flax fibers in accordance with the results published by Suardana *et al.* [15]. The untreated fibers show sharp peaks at 2919 cm^{-1}, 1377 cm^{-1} and 895 cm^{-1} corresponding to the absorption peaks of cellulose. The peak at 3413 cm^{-1} is due to the stretching vibration of hydroxyl (O-H) group of lignin. The presence of AP on the surface of fibers resulted in decrease in transmittance. It can be noticed that the primary and secondary hydroxyl groups of cellulose and lignin in the fiber has been partially replaced by phosphate groups by phosphorylation from phosphoric acid forming phosphorus ester (899 cm^{-1}) [13]. The FT-IR spectrum of the AP-treated fiber also showed the vibration of N-H group at 3270 cm^{-1}.

The thermal degradation of the untreated and AP-treated flax fibers were analyzed by TGA measurements. The TG and DTG curves are presented in Fig. 6. As expected [23], AP significantly lowered the initial decomposition temperature of flax, and also the peak temperature of the DTG curve corresponding to the maximum weight loss rate of AP-treated biofiber, which is 262 °C (90 °C lower than that of untreated flax fibers). These shifts to lower temperatures cause an earlier liberation and dissipation of flammable gases, before their ignition temperature is reached [24]. On the other hand AP promoted the formation of solid residues and char. The char amount at 500 °C for AP-treated fibers was 41.1 %, one and a half times higher than that of untreated flax fibers. The phosphorylation reaction of AP with cellulose, which is accompanied with release of water and ammonia, can also be recognized as a shoulder peak at 235 °C in the DTG curve [25]. This phosphorylation inhibits the formation of flammable levoglucosan, and consequently reduces the fuel supply necessary for combustion [26].

The flammability of untreated and AP-treated biofibers was compared in mass loss type cone calorimeter which test models fairly well the real burning conditions. The curves of heat release rates are presented in Fig. 7. As it is visible, the AP-treatment contributed to high level of flame retardancy of natural fibers. After ignition the flame of the AP-treated flax extinguished almost immediately, thus also the sharp peak of heat release rate (pk*HRR*) of untreated biofibers could be completely diminished. After burning both type of flax fibers glowed for a long time, however, while the untreated fibers disintegrated completely and formed grey ash, the AP-treated fibers turned black, formed char and maintained their fibrous form even after combustion. The enhanced flame retardancy of AP-treated biofibers can be explained by the esterification of phosphoric acid and primary hydroxyl groups of the cellulosic fibers when exposed to heat, which promotes the char formation [13].

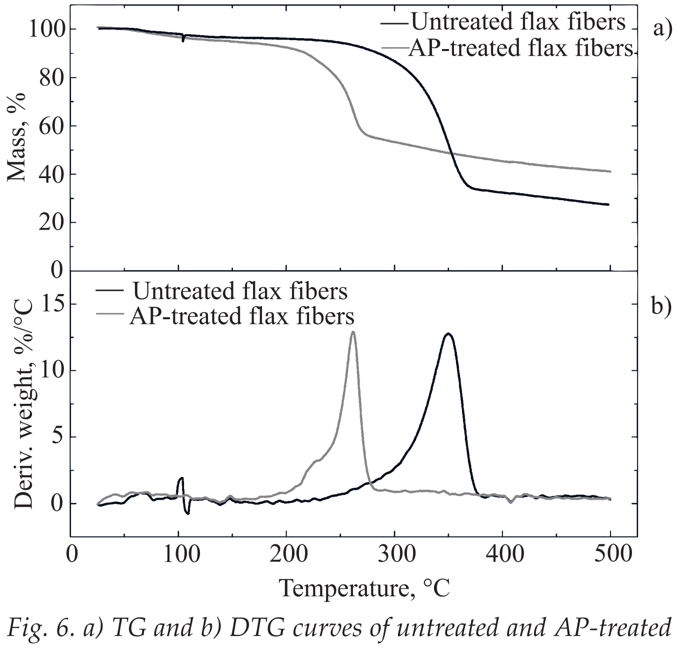

Fig. 6. a) TG and b) DTG curves of untreated and AP-treated flax fibers

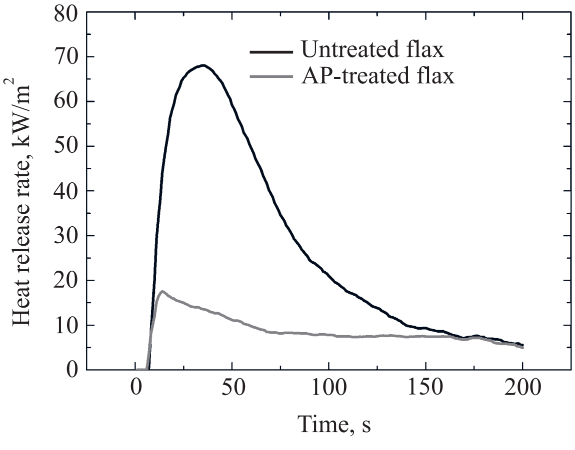

Fig. 7. Influence of AP-treatment on the heat release rate of the reinforcing biofibers

Characterization of flame retarded, natural fiber reinforced TPS composites

The fire retardancy of biofiber reinforced thermoplastic starch composites was accomplished with the combination of P-containing plasticizer and surface treatment of biofibers. The microstructure of the two forms of prepared composites can be seen in Fig. 8. The chopped fibers (Fig. 8 a) are well distributed in the TPS matrix and the adhesion between the phases is rather good. The fabric layers (Fig. 8 b) are also well embedded into the matrix but, as expected, the wetting of individual fibers cannot be achieved in this case.

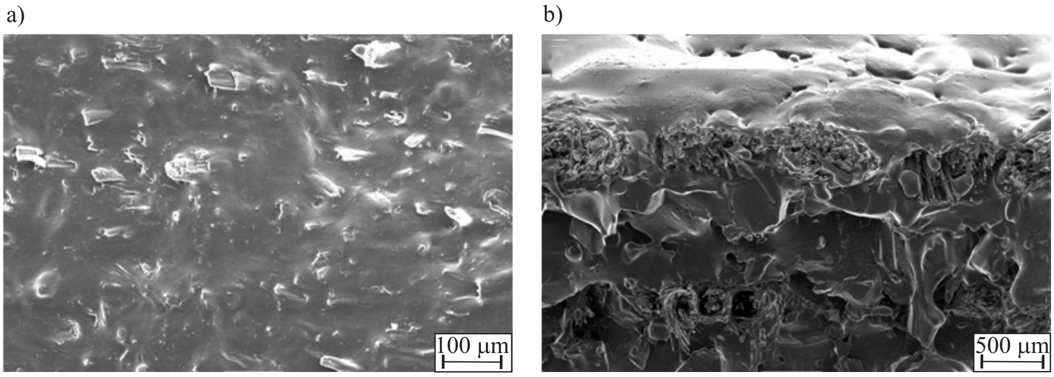

Fig. 8. SEM images of TPS composites prepared with a) chopped cellulosic fibers and b) with cellulosic fabrics

The influence of the flame retardant modifications on the mechanical properties of the biocomposites was investigated by tensile and IFWI tests (Fig. 9). It is visible, that the usage of OP560 as plasticizer reduced both the tensile strength and modulus, but increased the perforation energy of TPS matrix. It is presumed that the P-containing plasticizer improves the mobility of the polymer chains (in accordance with the lower torque shown in Fig. 1).

It can be noticed, that the same (27 %) percent of reinforcing fibers in form of woven fabrics, proved to be much more efficient in increasing the tensile strength of the TPS composites because, compared to short and randomly orientated flax fibers, the long continuous fibers aligned in the direction of loads carry and transfer these better (Fig. 9 a). As a consequence, also a 7-fold increase in perforation energy could be achieved when woven fabrics were embedded into the TPS matrix, while the chopped flax fibers had no significant effect on the impact resistance (Fig. 9 c). Nevertheless, the failure of both types of natural fiber reinforced composites can be characterized with fairly high ductility factor (Fig. 9 d), *i.e.* these natural fiber reinforced TPS composites have high ability to withstand plastic deformation, which could be very advantageous from application aspects. On the other hand, the tensile modulus values (Fig. 9 b) of the chopped fiber reinforced composites are superior to those of the fabric reinforced TPS samples. Probably the wetting and thus the immobile-interface formation is more general in the case, when the chopped fibers are thoroughly dispersed in the matrix.

Considering the tensile and IFWI test results, it can be concluded that the surface treatment of the natural fibers with AP, in contrast to the reasonable anticipation [27], slightly increased the tensile strength, the stiffness, the impact resistance (expressed in perforation energy) and the ductility of biofiber reinforced composites. It was concluded that the degradation of the cellulosic fibers at the low processing temperature is not significant, while the phosphorous compounds in both phases improve probably their interaction and mechanical cooperation. Suardana *et al.* [15] also observed that PLA composites reinforced with DAP-treated fibers show greater flexural modulus than those with untreated natural fibers and ascribed this increase in stiffness to the biofiber-DAP-PLA interaction. In our case, similar interaction can occur, which can result in good compatibility among AP-treated fibers and the embedding starch matrix.

T a b l e 1. UL-94 classification and *LOI* values of biofiber reinforced TPS composites

Sample	UL-94 classification*)	*LOI*, vol. %
TPS-G	HB (19.6)	23
TPS-GOP	V-2	31
TPS-GOP_BFiber	HB	29
TPS-GOP_BFiber_AP	V-0	32
TPS-GOP_BFabric	HB	30
TPS-GOP_BFabric_AP	V-0	32

*) In parenthesis the horizontal burning rates (mm/min), if measurable, are indicated.

The results of the UL-94 and *LOI* flammability tests are given in Table 1. It is visible that the flame retardancy of TPS-G reference could be significantly increased by the

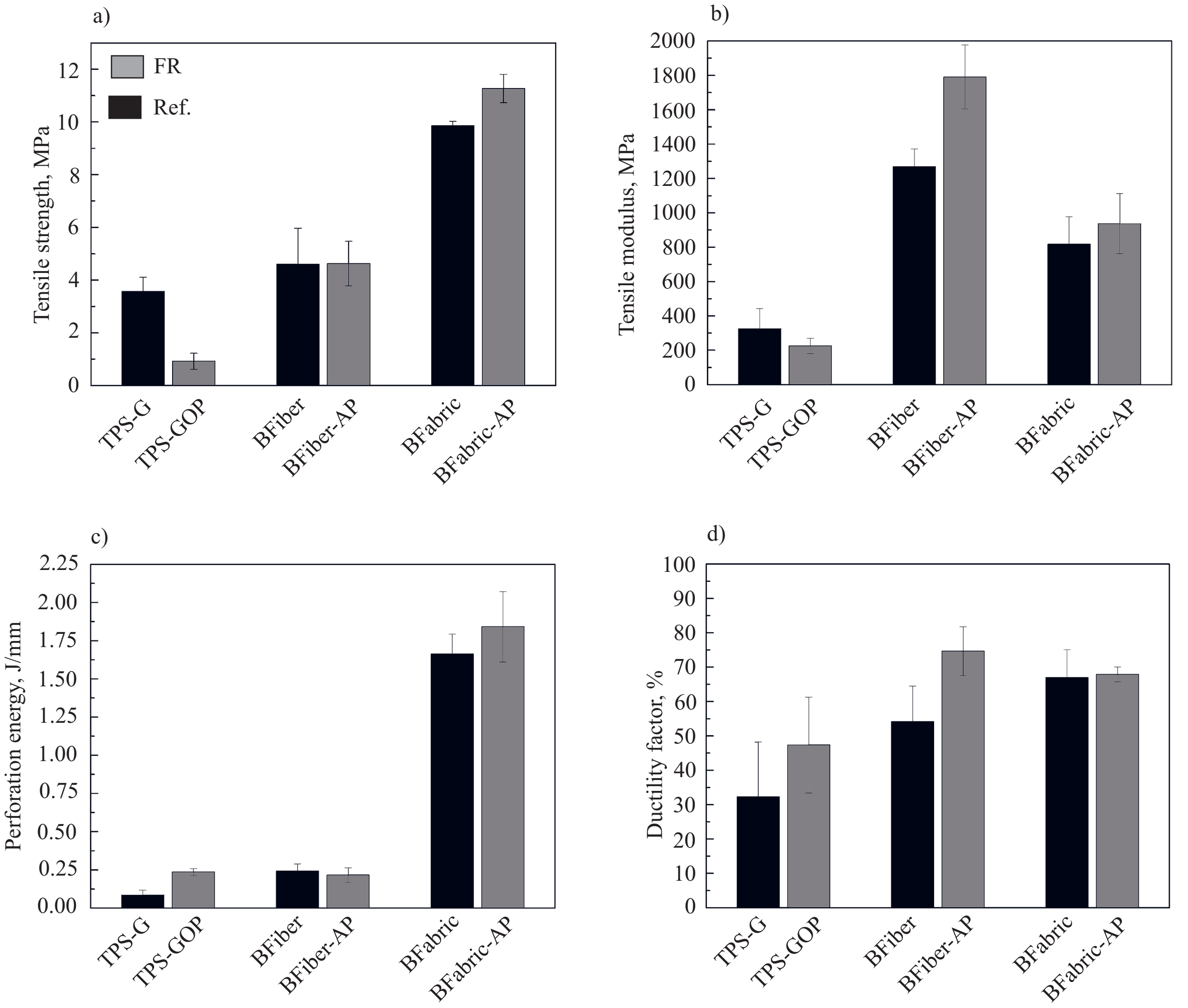

Fig. 9. a) Tensile strength, b) tensile modulus, c) perforation energy and d) ductility factor of biofiber reinforced TPS composites

partial replacement of its conventional glycerol plasticizer with a P-polyol. As a result of using OP560 as plasticizer, the horizontal burning of the highly flammable (UL-94: HB) TPS-G sample could be completely diminished, thus V-2 rating according to the UL-94 test and *LOI* as high as 31 vol. % could be achieved in the case of the TPS-GOP sample. However, when neat natural fibers or fabrics were used as reinforcement, the UL-94 classification remained still HB and also the *LOI* values decreased noticeably compared to the unreinforced TPS-GOP matrix. The moderate flammability properties of these TPS composites could be attributed to the observed long-term glow of fibers during and after burning in the specimens ascribed to the so-called „candlewick effect" [11, 12, 21, 22]. However, when additional FR active components were used on the surface of the cellulosic fibers (AP-treatment) the heat and flame propagation along the fibers could be effectively suppressed, thus the extinction of the candlewick effect was possible. As a consequence, the TPS composites reinforced with both AP-treated natural fibers and fabrics (TPS-GOP_BFiber-AP and TPS-GOP_BFabric-AP) could

Table 2. Results combustion tests executed on biofiber einforced TPS composites

Sample	*TTI*, s	pk*HRR*, kW/m^2	pkHRR_{time}, s	Residue, wt. %	t*HR*, MJ/m^2
TPS-G	36	446	161	0.8	84.1
TPS-GOP	23	402	170	3.3	76.2
TPS-GOP_BFiber	36	287	200	14.9	63.7
TPS-GOP_BFiber-AP	37	302	192	19.3	64.1
TPS-GOP_BFabric	26	314	187	7.6	68.4
TPS-GOP_BFabric-AP	22	242	174	12.1	61.4

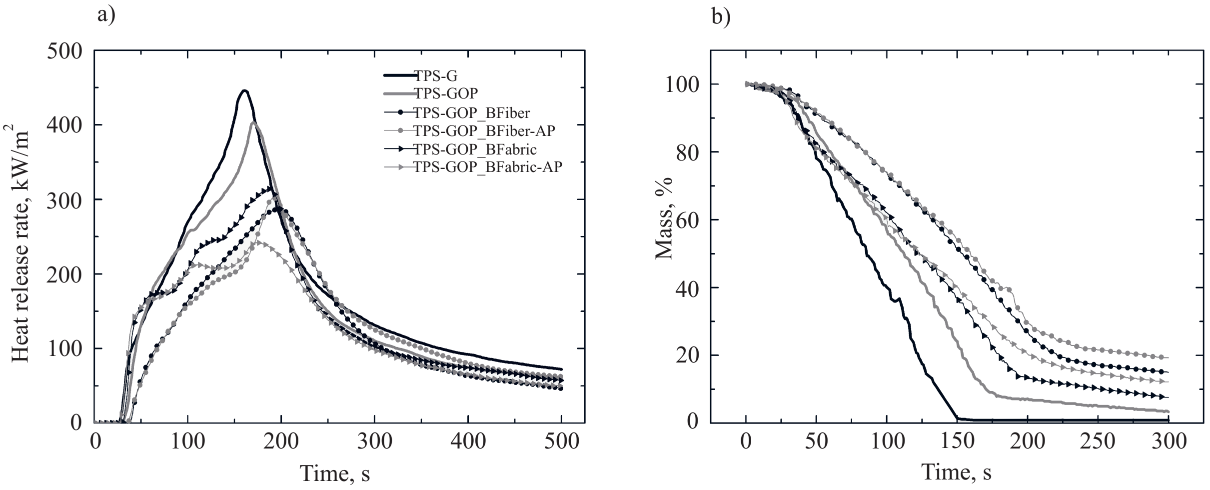

Fig. 10. a) Heat release rate curves and b) mass loss rate curves recorded during the burning of biofiber reinforced TPS composites

reach *LOI* of 32 vol. % accompanied with the best UL-94 V-0 classification. Similar flammability properties (V-0 and 33 vol. % *LOI*) of TPS composites could be achieved by Matkó *et al.* [6] with the addition of 10 % of ammonium polyphosphate, which acts, however, neither as plasticizer nor as reinforcing agent in contrast to the present formulation.

The flame retarded natural fiber reinforced composites were also characterized under the conditions of a Mass Loss type Cone Calorimeter. The recorded heat release rate (*HRR*) and mass loss rate (*MLR*) curves are shown in Fig. 10 a and b, respectively, and additional combustion characteristics are presented in Table 2. When comparing the burning behaviour of the prepared TPS matrices (TPS-G and TPS-GOP) significant difference can be observed between the time to ignition (*TTI*) values. The early inflammation in the case of the OP560 plasticized TPS can be ascribed to the initial char layer formation that is accompanied with fast volatilization of flammable substances at the initial stage of heating, as also observed when evaluating the TG curves in Fig. 2. The charring of TPS-GOP sample resulted also in higher amount of residual mass after combustion than that of the glycerol-plasticized TPS. With the partial substitution of glycerol by P-polyol for plasticizing starch 10 % reduction of both pk*HRR* and total heat release (t*HR*) could be observed.

Further considerable reduction of both the pk*HRR* and the t*HR* of TPS-GOP matix were visible when biofibers were introduced. The FR-treatment of both the biofibers and fabrics resulted in higher amount of residual mass, furthermore in the case of AP-treated fabrics additional significant reduction of pk*HRR* and t*HR* could be achieved at the same time. Considering the *TTI* values, the multilayered composites act similarly to the unreinforced matrices, while in the case of the TPS samples filled with AP-treated chopped flax fibers, the *TTI* increased significantly. Also the *HRR* and *MLR* curves of fabric reinforced samples are wavy as the single layers get into the burning zone one by one, while the homogeneously dispersed chopped fibers modify the burning behaviour, thus also the *MLR* and *TTI* values, of the entire sample. Because the well dispersed short fibers can influence the burning behaviour of the embedding TPS matrix more effectively, they can also contribute to the increase of burning residue of the flax fiber reinforced samples after combustion in higher extent.

As a consequence, with the preparation of TPS composite plasticized by OP560 and reinforced by AP-treated fibers (TPS-GOP_BFabric-AP), beside the considerable increase in mechanical properties, the best UL-94 classification accompanied with *LOI* of 32 % were achieved, furthermore pk*HRR* and t*HR* could be reduced by 45 % and 27 %, respectively, and with 11.3 % more solid residue remaining after combustion when compared to conventional glycerol plasticized TPS (TPS-G).

CONCLUSIONS

In this work, the flame retardancy of natural fiber reinforced TPS composites was investigated. Starch was plasticized with the combination of glycerol and a phosphorus-containing polyol (OP560 model compound) to obtain TPS matrix of reduced flammability. The incorporation of OP560 caused 11 min delay in the beginning of gelatinization process comparing to the effect of glycerol plasticizer. The solid state char promoting effect of OP560 could be detected by both TGA and LP-FTIR methods. Consequently flame retarding action was realized by the introduction of 15 wt. % OP560 as plasticizer achieving V-2 rating in UL-94 flammability test and 8 vol. % higher *LOI* value than that of the glycerol plasticized TPS.

Chopped flax fibers and plain-woven linen-hemp fabrics were used as reinforcement in the obtained flame retardant TPS matrix. The TPS composites, reinforced by neat natural fibers showed increased flammability, such as UL-94 classification remained HB, and decreased *LOI*, therefore before embedding into the matrix the biofibers were surface treated with ammonium phosphate model compound. The flame retardant treatment of flax resulted in lowered initial decomposition temperature, but with approx. 14 % higher amount of residual char, as measured by TGA. The AP-treated fibers proved to be non-flammable when exposed to 50 kW/m^2 heat flux under the conditions of a mass loss type cone calorimeter.

With the AP-treatment the candlewick effect of natural fibers in composites could be suppressed. The best V-0 classification, *LOI* as high as 32 vol. %, reduced heat release rates and after combustion high amount of charred residue of TPS composites could be achieved, as a consequence. The AP-treated, well-dispersed, chopped flax fibers contributed to the reduction of flammability of TPS composites even better than the AP-treated woven fabrics in layered composite structure, however, the natural fabric reinforcement proved to be more efficient in increasing the tensile strength and impact resistance of the biocomposites. The natural fabric reinforced self extinguishing TPS composites exhibit approx. 3-times higher tensile strength and modulus, and about 8-times higher perforation energy than those of the unreinforced TPS reference.

Such safe and environmentally friendly biocomposites are supposed to find increased use in engineering applications in the near future. The exemplary concept, presented in this work, of combination of flame retarding effect plasticizer and flame retardant surface treatment of natural fibers to obtain fire-safe and biodegradable thermoplastic starch composites is promising, however, in order to solve the water-sensitivity problem and improve the outward appearance of such biocomposites further intensive research towards finding adequate modifiers is needed.

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