Microfibrous cyclodextrin boosts flame retardancy of poly(lactic acid) II - phosphorous silane treatment further enhances the effectivity

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A B S T R A C T

Recently, the flame retardant effectiveness of a 2-hydroxypropyl-β-cyclodextrin (CD) type bio-based carbonising agent has been evinced to noticeably increase when used in a microfibrous form, as obtained by electrospinning method. In the present research, the flame retardant performance of the electrospun CD was further enhanced by reactive surface modification with a phosphorous silane (PSil) compound. Surface-treated and untreated CD-based carbonising agents were compared, both in powder and in microfibrous form, besides ammonium polyphosphate (APP) to form an intumescent flame retardant system for poly(lactic acid) (PLA). The Limiting Oxygen Index (LOI) of the flame-retarded PLA composites increased outstandingly, from 25.0% (corresponding to the 15 wt% APP containing PLA) to as high as 37.5%, as a result of adding only 3 wt% of PSil-treated microfibrous CD to the system. Also, the main combustion characteristics improved; compared to neat PLA, about 50% reduction in the peak heat release rate (pHRR) and 25% reduction in total heat release (THR) were achieved, accompanied by an increased amount of char residue after combustion. The beneficial effect of the PSil-treated CD microfibre relies mainly on its enhanced physical and chemical interaction with APP and its increased charring ability and thermal stability, which contribute to the formation of a fire protecting char of increased structural integrity.

1. Introduction

The dynamically growing demand for biobased, compostable polymers makes poly(lactic acid) (PLA) one of the most researched polymers due to its biodegradability, excellent mechanical properties, and thermoplastic processability. Nevertheless, for durable PLA-based products [1], improved flame retardant properties are often necessitated. Therefore, more and more studies focus on developing bio-sourced flame retardant additives [2–5]. The most researched ones are the intumescent flame-retardant systems (IFRs) that form an expanded char layer on the surface of the polymer matrix, blocking the heat and gas transport [6]. In these systems, ammonium polyphosphate (APP) can act both as an acid source and a blowing agent, generally in combination with a polyalcohol type carbonisation agent. The use of char forming materials of renewable origin is a promising way to provide environmentally benign flame retardant (FR) formulations, amongst others, for PLA [7–11].

Cyclodextrins and their derivatives are widely used in many fields, such as food, pharmaceutical, and chemical industries [12]. They have also shown great potential as flame retardant components in various polymer systems [13–17], most notably in PLA [18–20]. *Feng* et al. [18] used β-cyclodextrin (CD) as a green carbon source in combination with APP and melamine (MA) at different weight ratios and showed that these compositions exhibit outstanding char-forming ability in PLA. The FR system, consisting of CD, APP, and MA at a weight ratio of 1:2:1 respectively, when used at 20 wt% loading in PLA, reached an LOI value of 34.2 and passed UL 94 V-0 rating.

Vahabi et al. [19] developed a novel organic-inorganic hybrid flame retardant system (BSDH) from the combination of β-cyclodextrin, triazine ring, and nanohydroxyapatite. When applied in PLA, 2.5 wt% BSDH besides 7.5 wt% APP was found to increase flame retardancy significantly; in cone calorimeter tests, about 50% reduction in both peak heat release rate and total heat release rate was measured compared to neat PLA. The formation of an increased amount of thermally stable residue was assumed to be

the critical parameter explaining the synergistic effect of APP and BSDH on effectively improving the flame retardant performance of PLA.

With the aim to improve the char forming ability of β-cyclodextrin, *Zhang* et al. [20] modified it with phenyl phosphonic acid dichloride and obtained phospholipidated β-cyclodextrin (PCD). APP and PCD loading of 30 wt% with an APP to PCD mass ratio of 5:1 was found to be optimal in terms of thermal and flame retardancy properties of PLA/APP/PCD blends. With this formulation, LOI value as high as 42.6% and UL-94 V-0 rating were achieved, and the total heat release of PLA was reduced by 80%. At reduced additive content of 20 wt%, UL-94 V-0 rating was still achievable. The increased charring ability and thermal stability evinced for PCD were attributed to the in situ formation of phosphoric acid during its thermal degradation. Furthermore, the efficient interaction between APP and PCD contributed to forming a more significant amount and compact intumescent char that provides increased fire protection to the matrix material.

Silane coupling agents are generally used in natural fibre reinforced polymer composites, mainly to promote interfacial adhesion and improve mechanical properties [21]. Silane treatment was found to improve the interfacial interactions, decrease moisture absorption [21], and also improve the flame retardant properties of polymeric composites [22]. When combined with IFR systems, the beneficial effect of silicon-containing species relies on the formation of a thermally stable ceramic-like silicon-phosphate structure of increased barrier effect and good fire performance [23,24].

Multiple researchers showed that the particle size of the flame retardant additives affects the flame retardant performance. For example, better flame retardancy results were achieved when finer metal hydroxide particles were used [25–27]. The results of *Bocz* [28] and *Ribeiro* [29] indicate that improved chemical interaction and, by this means, significantly improved flame retardant performance can be achieved in an IFR system if the used APP is of smaller particle size, mainly due to the increased contact area between the components.

It has been shown in our previous research paper [28] that the flame retardant efficiency of an intumescent flame retardant system can be significantly enhanced by using the polysaccharide type carbonising agent in microfibrous form, i.e., with noticeably increased specific surface area compared to the conventional powder form.

In this work, powder and microfibrous forms (manufactured by high-speed electrospinning) of 2-hydroxypropyl-beta-cyclodextrin (CD) were surface-treated with a phosphorous silane (PSil) with the aim to improve the thermal and structural stability of the biobased charring agent and then used besides APP to produce flame retarded PLA composites. Our hypothesis was that the PSil-treated microfibrous CD could form a thermally stable network of charred ceramic-like microfibers during combustion, which was expected to improve the integrity and barrier properties of the intumescent protecting layer without compromising its swelling ability. The PSil-treated CD additives and the obtained flame retarded PLA composites were comprehensively characterised with particular regard to the size effect and the role of surface treatment of the used CD type charring agent in terms of the flame retardant performance of the polymeric system.

2. Material and methods

2.1. Materials

Ingeo™ Biopolymer 4032D PLA was received from Nature-Works LLC (Minnetonka, MN, USA). Exolit® AP 422 (Clariant Plastics & Coatings GmbH (Frankfurt, Germany)) type ammonium-polyphosphate (APP) was used as a flame retardant. Kleptose®
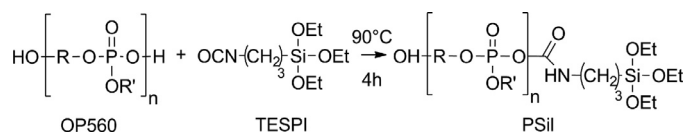

Fig. 1. Synthesis of the reactive surface modifier (PSil) [22].

HPB Roquette Pharma (Lestrem, France) type 2-hydroxypropyl-beta-cyclodextrin (CD) was used as co-additive in inherent powder form and as microfibres, produced by high-speed electrospinning (HSES) technique, respectively. For the reactive surface treatment of the two types of CD (powder and microfibre), a phosphorous silane adduct (PSil) has been synthesised from 3-(triethoxysilyl)-propyl isocyanate (TESPI) (Merck Life Science Kft, (Budapest, Hungary)) and Exolit® OP 560 phosphorous polyol, purchased from Clariant Plastics & Coatings GmbH (Frankfurt, Germany).

2.2. Preparation of CD-based additives

2.2.1. Synthesis of the phosphorus silane adduct

The reactive phosphorous silane (PSil), used for modification of CD, was synthesised by a simple addition reaction, described by Bocz et al. [22], between the Exolit OP560 phosphorous polyol and 3-(triethoxysilyl)-propyl isocyanate (TESPI). The PSil adduct was obtained by the vigorous stirring of the OP560 and TESPI (in 1:2.38 mass ratio) under anhydrous conditions at 90 °C (presented in Fig. 1). At regular intervals, samples were taken from the mixture and analysed by FTIR spectroscopy to monitor the completion of the reaction. After 4 h of stirring, the IR band corresponding to the isocyanate group of TESPI (at 2283 cm^{-1}) completely disappears from the spectrum of the adduct, and parallelly, characteristic peaks of the carbamate linkage appear with high intensity at 1534 cm^{-1} and 1721 cm^{-1}, so the reaction was considered to be completed.

2.2.2. Preparation of CD microfibres

CD microfibres were obtained according to a previously described method [30,31], namely by high-speed electrospinning from the 68 wt% aqueous solution of CD. The applied flow rate of the solution was 350 mL/h, while the rotational speed of the spinneret was 40,000 rpm. The applied voltage was 40 kV during the procedure, and a constant airflow was applied (120 m^3/h, room temperature) to transfer the fibres to the collecting cyclone. The obtained electrospun material was then ground with a hammer mill to make it suitable for blending with PLA.

2.2.3. Surface treatment of CDs

Both the powder and the microfibrous form of CD were treated with the PSil adduct by following the procedure used earlier for the reactive surface modification of flax fibres [22]. From the dried CD, 8 g was stirred in 320 ml of absolute toluene, then 16 ml of PSil was added dropwise to the suspension and stirred at 111 °C for 8 h. The solid material was filtered and washed with toluene to remove the excess PSil. The obtained materials were then heated in an oven at 130 °C for 8 h to obtain silanol moieties through the hydrolysis of the alkoxy (triethoxysilane) groups of PSil, thus enabling covalent bonding with the free hydroxyl groups of the CD structure. Fig. 2 shows the schematic representation of the preparation steps of phosphorous-silane modified CD powder and microfibres, respectively.

2.3. Preparation of flame-retarded PLA composites

2.3.1. Mixing

The flame-retarded PLA composites were prepared in 50 g batches using a Brabender Plasti-Corder Lab-Station type internal

Table 1
Formulations of the PLA composites.

Sample name	APP	CD	
		powder	fibre
PLA	–	–	–
PLA/APP	15 wt%	–	–
PLA/APP/CD powder	15 wt%	3 wt% untreated	–
PLA/APP/CD fibre	15 wt%	–	3 wt% untreated
PLAAPP/PSil_CD powder	15 wt%	3 wt% PSil-treated	–
PLA/APP/PSil_CD fibre	15 wt%	–	3 wt% PSil-treated
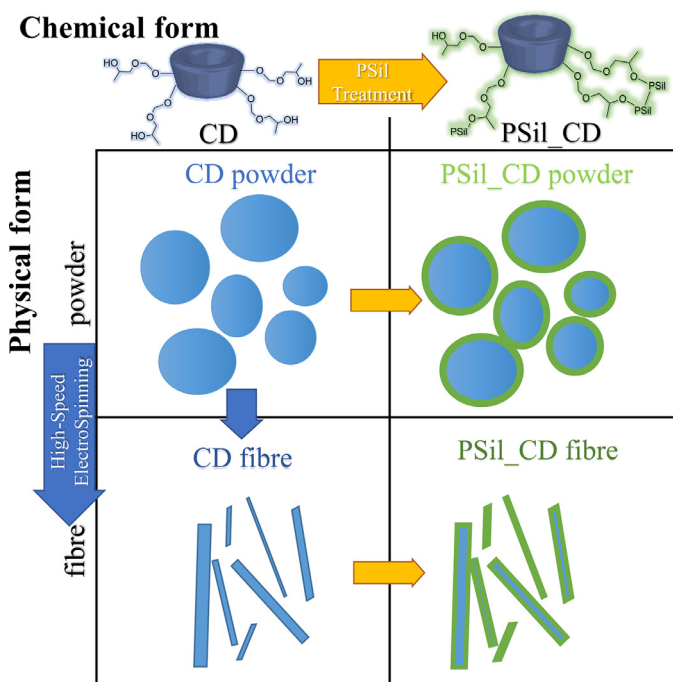
Fig. 2. Preparation of phosphorous-silane modified CD powder and microfibers.

mixer (Brabender GmbH & Co. KG, Duisburg, Germany) equipped with a W 50 EHT 3Z kneading chamber. The components were dried at 80 °C for 6 h before processing. During mixing, the operational temperature was 180 °C, and the rotor speed was 50 rpm. First, the pre-measured amount of poly(lactic acid) granules was added and kneaded until the granules fully melted, then the additives (APP and CD) were added and mixed for 10 min. The chosen ratio of APP to CD was considered based on the results of Y. Zhang et al. [20], who found the APP to PCD mass ratio of 5 to 1 to be optimal regarding the thermal and flame retardant efficiency of the system. As a reference, specimens from neat PLA and PLA containing only APP were also manufactured. Table 1 contains the composition of the manufactured PLA composites.

2.3.2. Moulding

The melt-mixed materials were dried at 70 °C, then hot-pressed using a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) heated platen press. About 40 g of each melt-mixed sample was heated to 180 °C in a mould of $100 \times 100 \times 3$ mm^3 size. The plates were compressed for 4 min with the gradual addition of pressure up to 100 bars, then cooled to 50 °C under the same pressure. The flammability and mechanical testing specimens were obtained by cutting the plates with a disk saw.

2.4. Characterisation methods

2.4.1. FTIR spectroscopy

Infrared spectra of the additives were recorded using a Tensor 37 type Fourier transform infrared (FTIR) spectrometer (Bruker Corporation, Billerica, MA, USA) with a resolution of 4 cm^{-1}. The additives were mixed with potassium bromide powder, cold-pressed into a disk, and then analysed in transmission mode in the wavenumber range of 4000–400 cm^{-1}. The liquid PSil component was analysed as a thin film layer between NaCl windows. IR spectra of the charred residues were recorded with a Specac Golden Gate ATR unit in ATR mode (4000–600 cm^{-1}). Each spectrum was an accumulation of 32 scans.

2.4.2. Scanning electron microscopy

Scanning electron microscopic (SEM) images of the powder and electrospun CD and the cryogenic fracture surface of the flame-retarded PLA composites were taken by a 6380LVa (JEOL, Tokyo, Japan) type apparatus in high vacuum at an accelerating voltage of 10–15 keV. Before examination, all the samples were fixed on the holder by conductive double-sided carbon adhesive tape and sputtered by gold with an ion sputter (JEOL 1200, JEOL, Tokyo, Japan).

2.4.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were done using a TA Instruments Q5000 apparatus (TA Instruments LLC, New Castle, NH, USA) under nitrogen gas flow rate of 25 mL/min. Samples of roughly 10 mg were placed in platinum pans. The samples were heated from 25 °C to 800 °C at a 10 °C/min rate. For thermal characterisation, two parallel measurements were carried out in all cases.

2.4.4. Tensile tests - Dynamic mechanical analysis

A Q800 dynamic mechanical analyser (DMA, TA Instruments Inc., New Castle, DE, USA) was used for dynamic mechanical analyses (DMA) of the PLA composite samples. The measurements were conducted in dual cantilever mode, and the applied span length was 35 mm. The specimens' width and length were approximately 10 mm × 60 mm. The temperature range was 25–150 °C; the heating rate was 2 °C/min while applying a deformation of 0.02% and a frequency of 1 Hz.

2.4.5. Limiting oxygen index

Limiting oxygen index (LOI) tests were performed on specimens with $100 \times 10 \times 3$ mm^3 dimensions according to the ISO 4589 standard using an apparatus made by Fire Testing Technology Ltd. (East Grinstead, UK).

2.4.6. UL-94

The UL-94 standard flammability tests were carried out according to ISO 9773. The sample dimensions were $100 \times 10 \times 3$ mm^3, and 5 samples were tested for each composition.
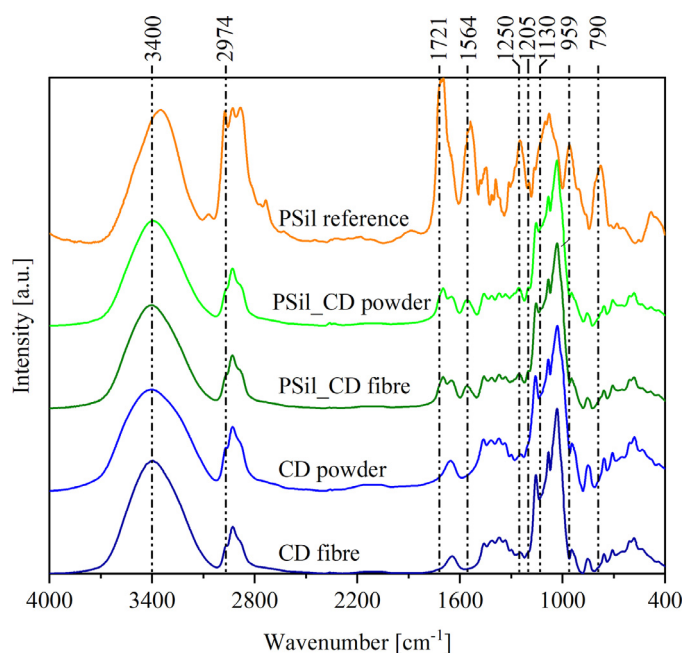
Fig. 3. FTIR spectra of the CD additives and the neat PSil adduct.

2.4.7. Mass loss calorimetry

According to the ISO 13,927 standard, Mass loss type cone calorimeter (MLC) tests were performed in a Fire Testing Technology Ltd. (East Grinstead, UK) instrument. Specimens with $100 \times 100 \times 3$ mm^3 dimensions were exposed to a constant heat flux of 35 kW/m^2. The main characteristics of fire properties, such as the heat release rate (HRR) as a function of time, the time to ignition (TTI), and the total heat release (THR), were determined. Two parallel measurements were performed, and the HRR and THR values were reproducible within $\pm$ 10%.

From the MLC data, Flame Retardancy Index (FRI) was calculated according to the following formula [32]:

$$FRI = \frac{\left[THR * \left(\frac{pHRR}{TTI} \right) \right]_{Neat\ polymer}}{\left[THR * \left(\frac{pHRR}{TTI} \right) \right]_{Composite}} \tag{1}$$

3. Results and discussion

3.1. Characterisation of the CD additives

3.1.1. FTIR spectroscopic characterisation of the CD additives

The used CD powder and fibre were characterised by FTIR spectroscopy. The spectra obtained before and after surface treatment with PSil are presented in Fig. 3. The spectra of the CDs include a broad band around 3400 cm^{-1} corresponding to the stretching vibration of OH groups. The intensity of this band decreased due to the PSil treatment in both cases. Characteristic peaks of PSil appear in the spectra of the PSil-treated CDs, such as the intensive bands at 1721 cm^{-1} (C = O stretching) and 1564 cm^{-1} (N–H bending), corresponding to the carbamate group formed from the linkage between the isocyanate (TESPI) and the phosphorous polyol (OP560). Also, the band at 790 cm^{-1} was assigned to the Si-C bond stretching vibrations, and the peak at 1250 cm^{-1} was assigned to $P = O$ bonds. The C–H stretching of the additional CH$_2$ groups at 2974 cm^{-1} confirms the presence of PSil on the surface of both types of modified CD additives. The intensive peak at 959 cm^{-1} in the
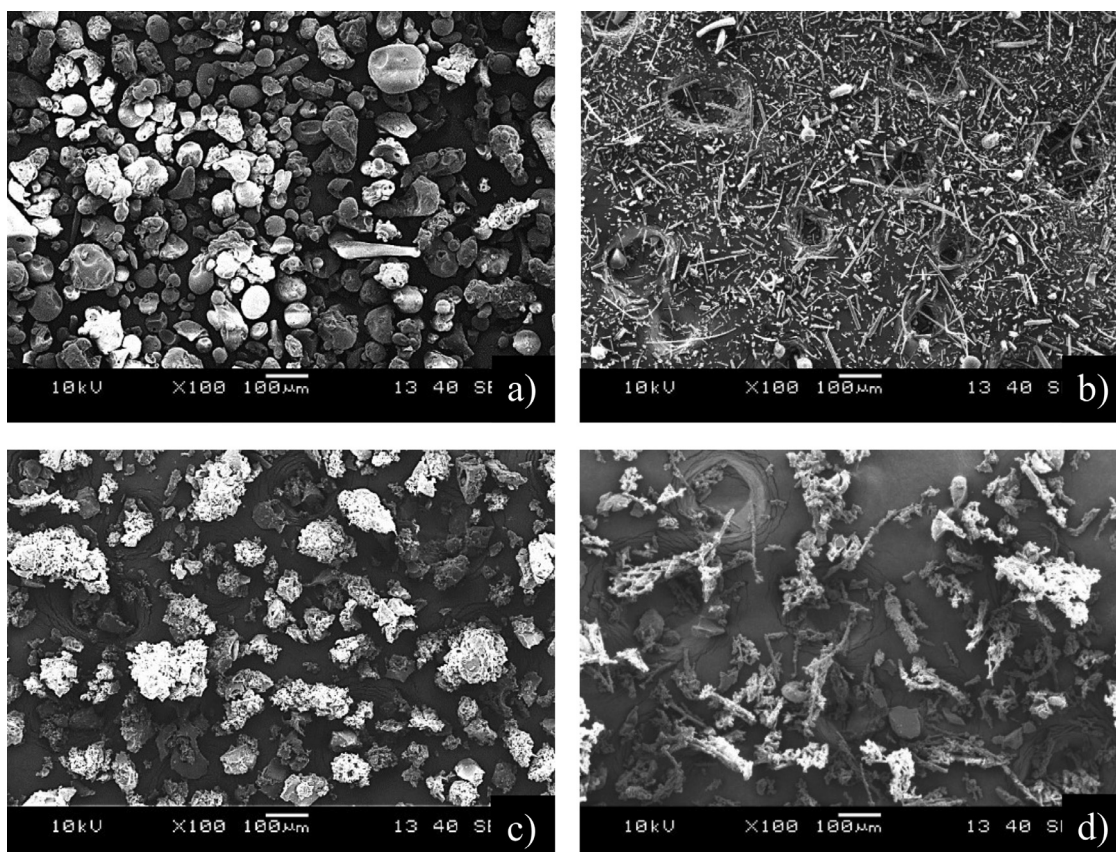

Fig. 4. Scanning electron microscopic images of the CD additives; a) untreated CD powder; b) CD fibre; c) PSil-treated CD powder; d) PSil-treated CD fibre.

Table 2
Thermogravimetric analysis results of the curves of the four types of CD additives.

Sample	Onset temperature* [°C]	Maximum degradation speed [wt%/ °C]	Temperature of maximum degradation speed [°C]	Residue at 500 °C [wt%]	Residue at 800 °C [wt%]
CD powder	320 ± 2	3.8 ± 0.2	333 ± 1	4.4 ± 0.3	1.4 ± 0.2
CD fibre	322 ± 1	3.7 ± 0.1	339 ± 0	6.3 ± 0.1	4.7 ± 0.4
PSil_CD powder	275 ± 1	1.6 ± 0.1	292 ± 1	22.6 ± 1.2	17.2 ± 1.2
PSil_CD fibre	264 ± 1	1.5 ± 0.1	284 ± 1	22.8 ± 2.1	17.8 ± 1.0

* onset temperature was determined at the point of intersection of the starting-mass baseline and the tangent to the TGA curve at the point of maximum gradient.
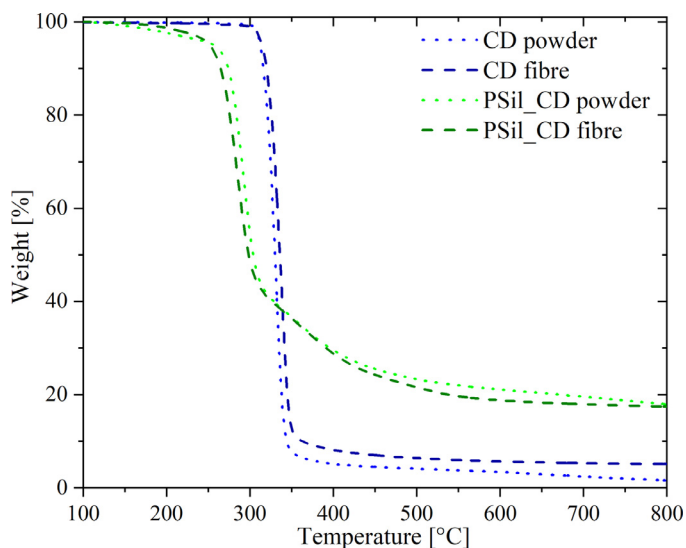

Fig. 5. Thermogravimetric analysis curves of the four types of CDs.

PSil reference spectrum is assigned to the Si-O-C_2H_5 (Si-alkoxy) vibration. The intensity of this peak significantly reduces as hydrolysis and self-condensation occur to form Si-OH. The band at 1130 cm^{-1} is assigned to the –Si-O-Si asymmetric stretching vibration and indicates that polysiloxanes were also formed on the treated CDs. The peak at 1205 cm^{-1} is assigned to the vibrations of Si-O-C and indicates the chemisorption of the modifier onto the surface of the CD particles by forming stable covalent bonds between prehydrolysed silane and the hydroxyl groups of the cyclodextrin.

3.1.2. Scanning electron microscopic analysis of the CD additives

SEM images taken from the four types of CDs, used as co-additives besides APP in PLA matrix, are presented in Fig. 4. The rougher surface is characteristic for both PSil-treated particles (powder and fibre).

Due to the relatively high CD to PSil mass ratio of 1 to 1, besides forming an even surface coating, polysiloxanes were likely formed and deposited on the treated CD particles (Fig. 4c) and d)), as also evinced by FTIR spectroscopy (see Fig. 3). The PSil-treated high-surface-area CD microfibres even tend to aggregate (Fig. 4d)). Still, there is a noticeable difference in the surface-to-volume ratio between the powder and microfibrous form of CD even after PSil treatment.

3.1.3. Thermogravimetric analysis of the CD additives

Thermogravimetric curves of the powder and microfibrous CD before and after PSil treatment are shown in Fig. 5, and corresponding data are shown in Table 2. It can be seen that PSil treatment resulted in 35–45 °C lower onset temperature of thermal degradation due to the acid-induced dehydration and decomposi-

tion of CD. Decreased amount of volatile by-products accompanies this process, and therefore, increased char yield is obtained.

Accordingly, the degradation speed of the PSil-treated CDs is significantly lower, and the charred residue at 500 °C is ∼19 wt% higher than those of the untreated powder and microfibrous CD, respectively. At 800 °C, a still noticeable amount (more than 22 wt%) of residue remains from the PSil-treated CDs, attributed to the presence of Si elements, which effectively enhance the char's thermal stability by forming ceramic-like protective structures. When the TGA results of the powder and microfibrous forms of neat and PSil-treated CD are compared, increased thermal stability can be noticed for the chars formed from the cyclodextrins with fibrous supramolecular structure.

3.2. Characterisation of the flame retarded PLA composites

3.2.1. Scanning electron microscopic analysis of the composites

Fig. 6 presents the SEM images of the cryogenic fracture surfaces of the composites. As shown in Fig. 6a), a rigid fracture is characteristic of neat PLA. In Fig. 6b), detached boundaries of APP particles indicate poor interfacial interaction with PLA. In Figs. 6c) and d), the better embedding of APP in the polymer matrix can be observed in the presence of CD particles.

It is presumed that CD particles act as interfacial adhesion agents and thus improve APP dispersion within the PLA matrix [30]. Based on the SEM images presented in Figs. 6d) and e), the APP-PLA interaction seems to be further enhanced when PSil-treated CDs are used as co-additives. During melt-processing, the CD particles are proposed to allocate around the surface of APP particles, thus enabling enhanced physical and chemical interaction between the active components, which is crucial to create an effective intumescent flame retardant system. From this respect, the high-surface-area microfibrous CD, both in neat and surface-treated form, seems to be more effective.

3.2.2. Thermogravimetric analysis of the composites

Thermogravimetric analyses were performed to characterise the thermal behaviour of the flame retarded PLA composites. The obtained TGA and DTG thermograms are presented in Figs. 7a) and b), respectively, while corresponding data are shown in Table 3.

It can be seen that the onset degradation temperature of the CD containing PLA composites decreases by about 10 °C compared to that of neat PLA or PLA/APP, which is due to the decomposition of CDs in advance. PLA shows a one-stage degradation in the range of 310–380 °C, while three degradations steps can be observed for the CD containing flame-retarded composites. The first step before 300 °C corresponds to CD decomposition. The second stage in the temperature range of 310 to 380 °C is where the decomposition of PLA and APP takes place simultaneously, while above 380 °C, the prolonged weight loss step is due to the thermal degradation of the charred residue, which forms in the presence of the flame retardants. While at 500 °C, PLA is already completely volatilised, about 10–13% char forms from the 15% APP containing composites. At the end of the heating program (at 800 °C) still, about 7–10 wt%
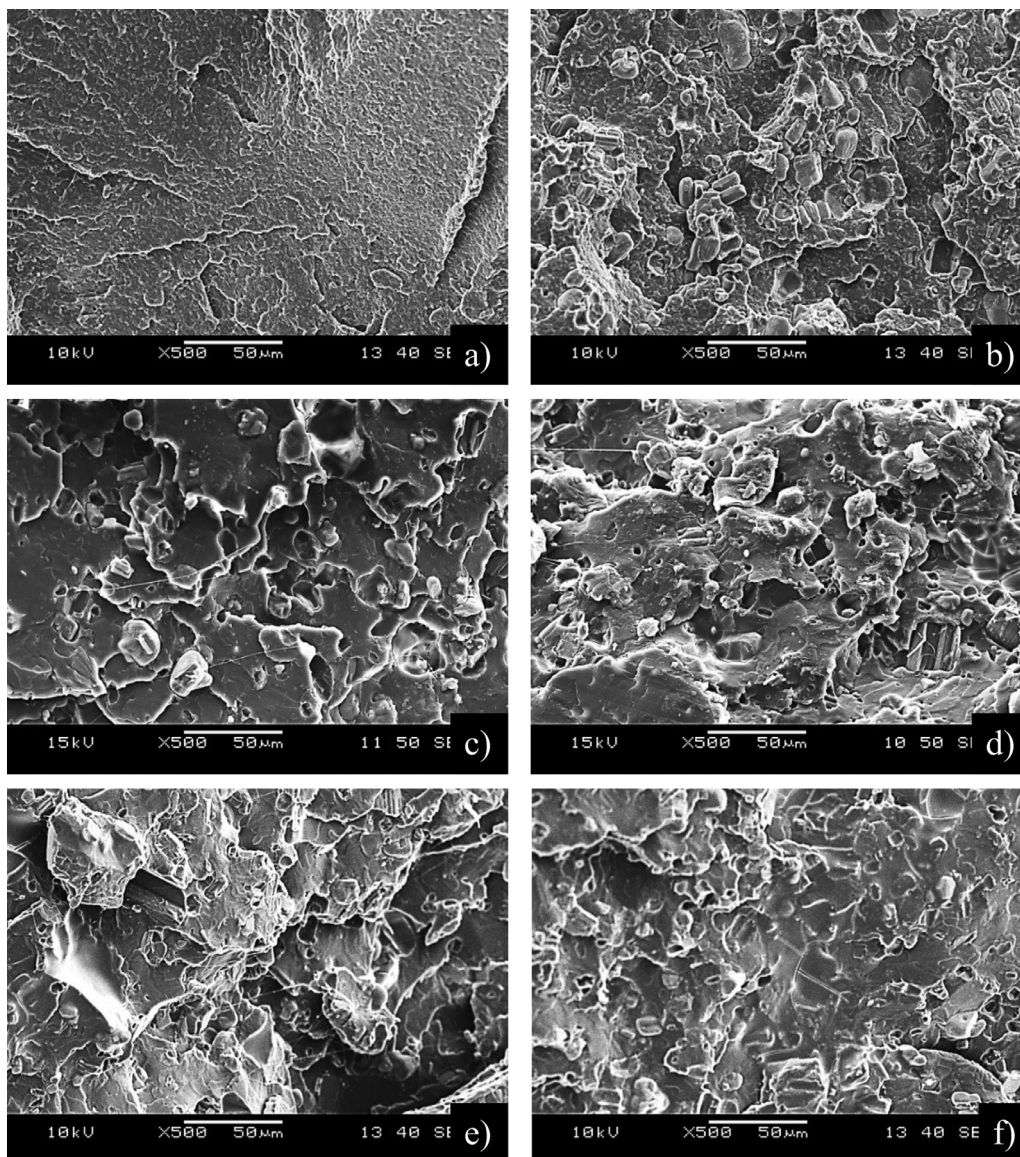
Fig. 6. Electron microscopic images of the composite samples: a) PLA; b) PLA/APP; c) PLA/APP/CD powder; d) PLA/APP/CD fibre; e) PLA/APP/PSil_CD powder; f) PLA/APP/PSil_CD fibre.
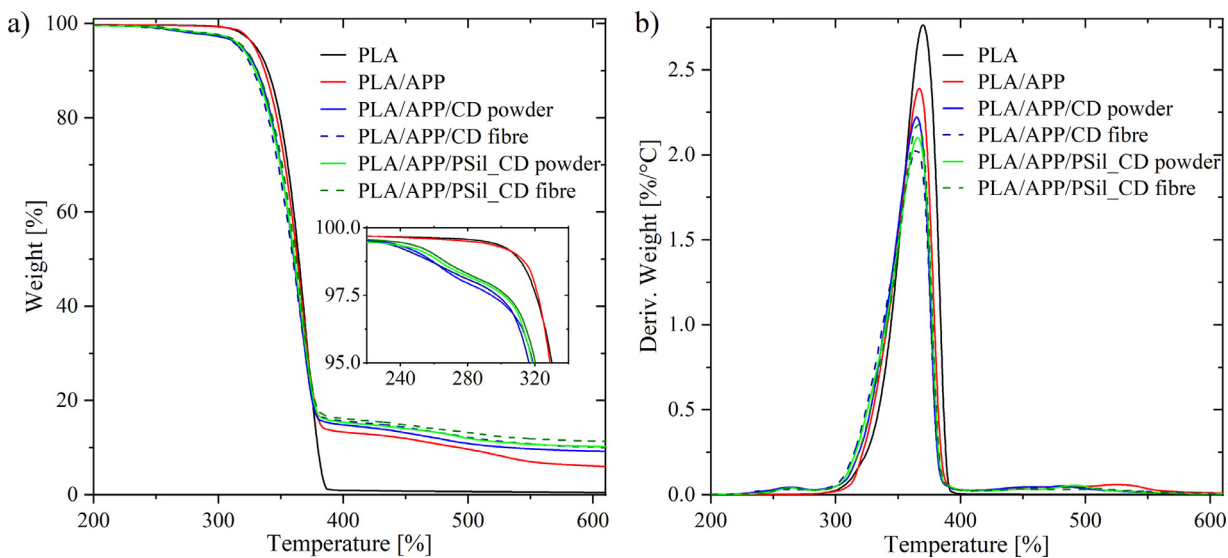

Fig. 7. a) TGA and b) DTG curves of the composite samples.

Table 3
Thermogravimetric analysis results of the composites.

Sample	Onset Temperature* [°C]	Maximum degradation speed [wt%/ °C]	Temperature of maximum degradation speed [°C]	Residue at 500 °C [wt%]	Residue at 800 °C [wt%]
PLA	346 ± 1	2.8 ± 0.0	369 ± 1	0.7 ± 0.0	0.3 ± 0.0
PLA/APP	342 ± 1	2.4 ± 0.0	375 ± 0	9.8 ± 0.1	4.1 ± 0.1
PLA/APP/CD powder	337 ± 0	2.1 ± 0.1	365 ± 0	11.2 ± 0.4	7.1 ± 0.5
PLA/APP/CD fibre	336 ± 0	2.2 ± 0.1	365 ± 0	12.1 ± 0.1	7.8 ± 0.1
PLA/APP/PSil_CD powder	337 ± 0	2.1 ± 0.0	365 ± 0	12.1 ± 0.1	8.8 ± 0.1
PLA/APP/PSil_CD fibre	338 ± 1	2.1 ± 0.1	366 ± 0	13.1 ± 0.2	9.8 ± 0.0

* onset temperature was determined at the point of intersection of the starting-mass baseline and the tangent to the TGA curve at the point of maximum gradient.
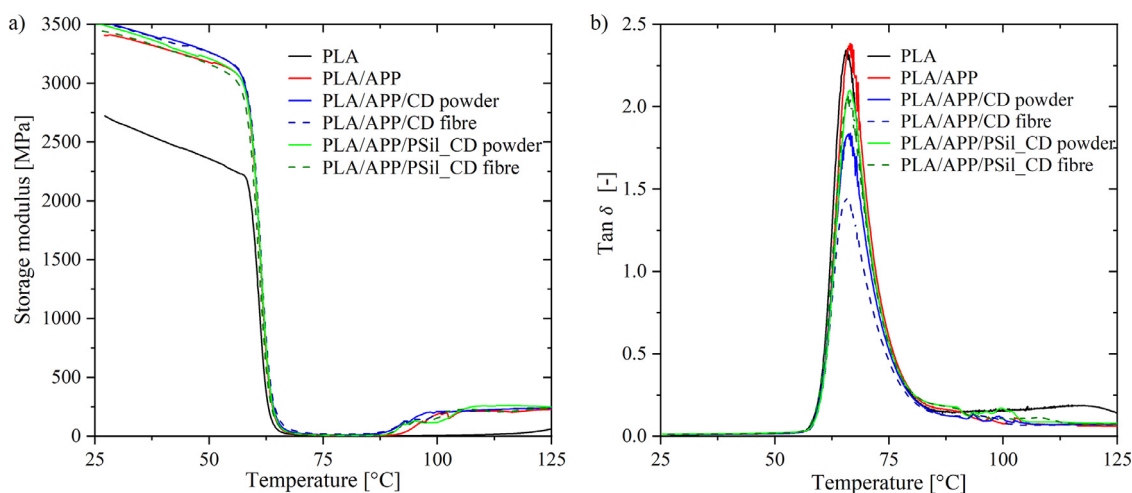

Fig. 8. a)Storage modulus and b) Tan δ results of the composite samples derived from DMA measurements.
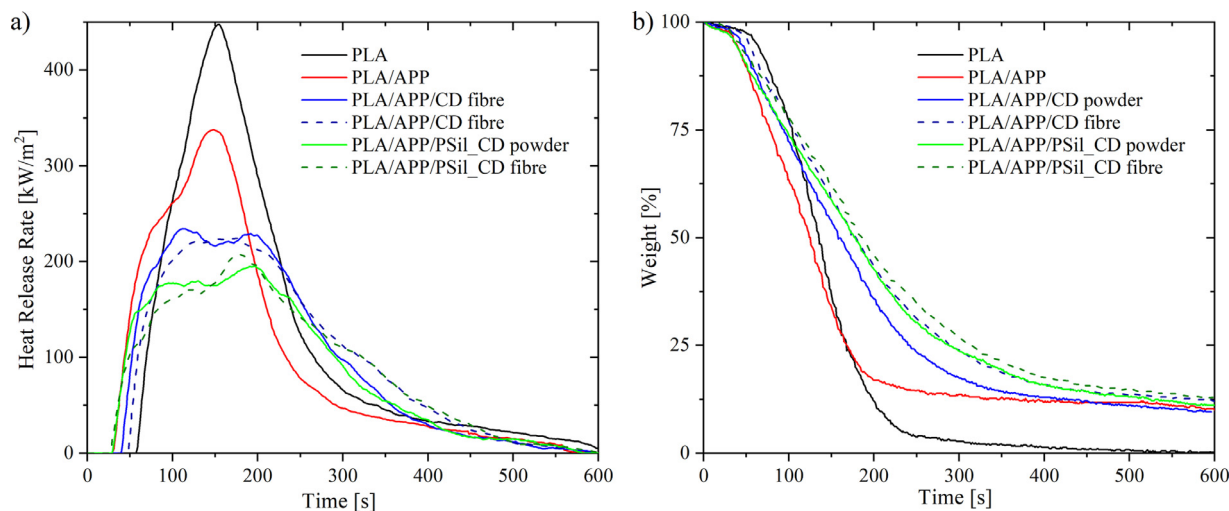

Fig. 9. a) Heat release curves of polymer composites over time; b) mass loss of polymer composites over time.

residue remains from each flame-retarded composite. The silicon-containing groups in PSil improve the residual char's stability at high temperatures, likely by forming ceramic-like structures. Also, the polymer-like supramolecular structure of the microfibrous CDs is assumed to contribute to the improved thermal stability of the residues.

3.2.3. Dynamic mechanical analysis

Dynamic mechanical analysis was performed to measure the dynamic mechanical properties and investigate interfacial interactions in the flame retarded PLA composites. As it can be seen in Fig. 8a), the flame retardant additives used at 18 wt% loading no-

ticeably increase the stiffness of PLA below the glass transition temperature of PLA; about 25% higher storage modulus is characteristic for the flame-retarded composites compared to neat PLA (Table 4).

Above 80 °C, the increment of the storage modulus values in the case of the flame retarded composites is related to the cold crystallisation transition of PLA and indicates the nucleating effect of the used additives. As shown in Fig. 8b), the damping factor (tan δ) of the composites decreases when CDs are used besides APP. This result supports our observation based on the SEM examination of the composite fracture surfaces (see Fig. 6), namely that

Table 4
Storage modulus, maximal loss modulus, and glass transition temperature values of the polymer samples.

Sample	Storage modulus at 30 °C [MPa]	Max loss modulus [MPa]	Glass transition temperature [°C]
PLA	2665	631	61.2
PLA/APP	3399	783	61.7
PLA/APP/CD powder	3487	778	61.5
PLA/APP/CD fibre	3482	754	61.5
PLA/APP/PSil_CD powder	3460	756	61.7
PLA/APP/PSil_CD fibre	3417	753	61.2

Table 5
The LOI values of the composite samples.

Sample	LOI [%]
PLA	19.5
PLA/APP	25.0
PLA/APP/CD powder	28.0
PLA/APP/CD fibre	31.0
PLA/APP/PSil_CD powder	32.5
PLA/APP/PSil_CD fibre	37.5

the presence of CD increases the interfacial interaction between the APP particles and the PLA matrix. Accordingly, the reduction of the damping factor is related to the decrease in the mobility of molecular chains at the filler-matrix interphase.

From this respect, the unmodified CDs seem more effective than the PSil-treated forms. In general, if the interfacial interactions between the matrix and the filler are strong enough, the T_g shifts towards higher temperature; however, based on the T_g values shown in Table 4, this effect cannot be clearly identified.

3.2.4. Limiting oxygen index

The LOI values of the flame retarded PLA composites are presented in Table 5. It can be seen that the LOI of PLA increases from 19.5% to 25.0% by adding 15 wt% APP. This value further increases when CD type charring agent is used, but the extent of LOI increment significantly depends on the physical form (i.e., powder or microfibre) and surface treatment of the cyclodextrin. Despite the identical CD content of 3 wt%, the LOI of the flame retarded PLA composite increases from 28.0% to 31.0% when the microfibrous CD is used instead of the inherent powder form. This "size-effect" is further enhanced when PSil-treated CDs are incorporated; the LOI increases from 32.5% (measured for PLA/APP/PSil_CD powder) to as high as 37.5% when PSil-treated microfibrous CD is used as co-additive. This value outperforms the results of Zhang et al. [20], who reported an LOI of 35.1% for the PLA composite flame retarded with 16.6 wt% APP and 3.3 wt% phospholipidated cyclodextrin (PCD). The noticeable improvement in the flammability properties, reflected by the LOI values, is ascribed, on the one hand, to the effective interaction between the well-distributed, high-surface-area microfibrous charring agent and APP, resulting in effective char formation, and on the other hand, to the improved structural and thermal stability of the phosphorous and silicon-containing char.

3.2.5. UL-94

The results of the standard UL-94 flammability tests performed on the flame retarded PLA composites are presented in Table 6. Without flame retardants, the horizontally mounted PLA specimens burn with an average flame spreading rate of 26 mm/min, and therefore neat PLA is classified as HB. When 15 wt% APP is added, the horizontally mounted specimens stop burning before reaching the second mark. In the vertical position, flaming combustion is
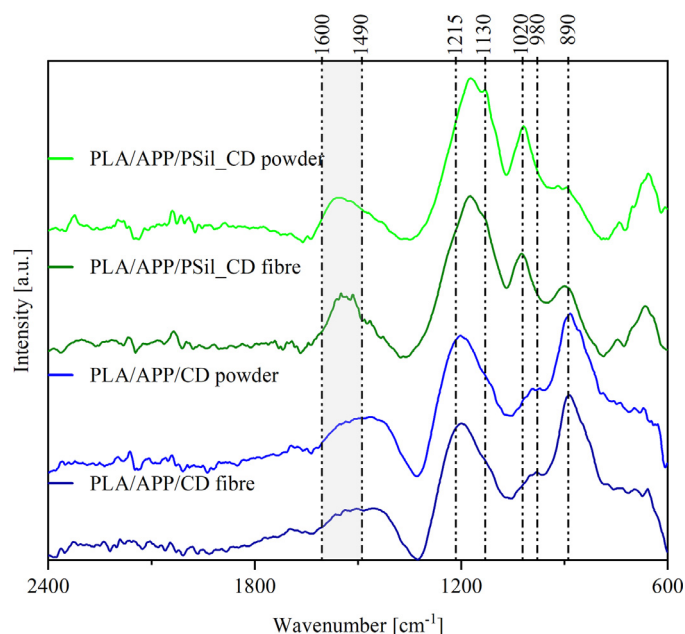

Fig. 10. FTIR-ATR spectra of the charred residues of the composite samples.

only visible for a couple of seconds; however, due to the heavy dripping of flaming particles that ignite the cotton, the 15 wt% APP containing PLA sample is V-2 rated. In the case of the CD containing samples, when APP is combined with 3 wt% untreated CD, both in powder and in microfibrous form, significant charring of the specimens occurs during testing, still, due to the flaming polymer droplets that ignite the piece of cotton wool placed underneath, V-2 rating is reached according to the UL-94 standard.

Nevertheless, PSil treatment of the CD powder reduces the flammability of the APP containing PLA composite, so the V-0 rating becomes achievable and at lower APP/CD additive content than in the literary antecedents [20]. Dripping is still characteristic for these specimens; however, immediate ceasing of flame is observable in the presence of phosphorous and silicon-containing species, and therefore flaming drips cannot occur. In contrast, when PSil-treated CD microfibres are used as co-additives, melt-dripping is more suppressed, and therefore the flame is retained longer, and as a result, flaming droplet leaves the specimens that ignite the cotton placed underneath, thus achieving a V-2 rating according to the UL-94 standard. It can be concluded that although the PSil-treated CD microfibres perform noticeably better during LOI measurement than the powder counterpart, its enhanced dripping suppressive and small flame retaining effect acts contradictory during UL-94 tests, where the specimens are ignited from the bottom.

3.2.6. Mass loss calorimetry

The heat release rate and mass loss curves gained from mass loss type cone calorimeter tests are presented in Fig. 9a) and b), respectively, while the corresponding combustion characteristics are

Table 6
Results of the UL-94 test performed on the reference and composite samples.

Sample	t_1/t_2 [s]*	Cotton ignition	Rating
PLA	-/ -	–	H.B. 26 mm/min
PLA/APP	1/2	yes	V-2
PLA/APP/CD powder	0/0	yes	V-2
PLA/APP/CD fibre	0/1	yes	V-2
PLA/APP/PSil_CD powder	0/0	no	V-0
PLA/APP/PSil_CD fibre	0/0	yes	V-2

* "-" means complete combustion for specimens.

Table 7
Combustion characteristics obtained from MLC tests and the calculated Flame Retardancy Index.

Sample name	t_{ign} [s]	pHRR [kW/m^2]	t_{pHRR} [s]	THR [MJ/m^2]	$m_{residue}$ [%]	FRI [-]	FRI classification
PLA	58 ± 5	447 ± 8	157 ± 3	67.3 ± 0.6	0.0 ± 0.0	–	–
PLA/APP	30 ± 1	337 ± 7	150 ± 5	57.0 ± 1.5	9.7 ± 0.3	0.81	*Poor*
PLA/APP/CD powder	40 ± 4	234 ± 5	117 ± 5	56.2 ± 0.4	9.6 ± 0.6	1.58	*Good*
PLA/APP/CD fibre	48 ± 5	225 ± 5	176 ± 9	56.6 ± 0.2	12.0 ± 1.2	1.96	*Good*
PLA/APP/PSil_CD powder	29 ± 4	195 ± 4	199 ± 11	50.3 ± 0.5	11.1 ± 0.6	1.53	*Good*
PLA/APP/PSil_CD fibre	26 ± 8	207 ± 18	180 ± 5	52.7 ± 1.1	12.7 ± 1.0	1.24	*Good*

summarised in Table 7. It can be concluded that a noticeable improvement in the fire retardant properties of PLA can be achieved by adding only 3 wt% CD type charring agent to the APP-based intumescent flame retardant system. About 50% reduction in the peak heat release rate (pHRR) and 25% reduction in total heat release (THR) were achieved when 15% APP was combined with 3 wt% CD. However, compared to neat PLA, the ignition time of all the phosphorus-containing composites is shorter, likely attributed to the initial char formation accompanied by fast volatilisation of flammable gases at the initial heating stage.

Compared to the CD powder additives, enhanced charring was observed for the CD fibre containing composites both in neat and PSil-treated cases. In the case of untreated microfibers, all combustion characteristics improved, while the combustion performance of the PSil treated CD fibre containing composites slightly fell below that of the corresponding powder additive (Table 7). It is assumed that the homogeneous distribution of the char forming components is crucial regarding the structure of the expanded char and its related fire retarding performance. Nevertheless, it is claimed that the differences during cone calorimeter tests are not significant, especially when considering the deviation of the duplicated test results. In summary, regarding the cone calorimeter results, the form of the used CD (powder or microfibrous) seems to be less critical.

Nevertheless, the benefits of PSil treatment of the CDs are reflected in the noticeable improvement of the main combustion characteristics, such as reduced pHRR and THR values accompanied by an increased amount of residue after combustion can be measured, except for the TTI. The decreased ignition time is due to the early appearance of decomposition products in the gas phase initiated by the increased amount of phosphorus-containing species in the system. As TTI is a significant factor in FRI calculation, the FRI values of the PLA composites with PSil-treated CD are lower than those of the neat CD-containing composites. Still, the *Poor* flame retardancy performance of the PLA/APP system increases to *Good* by the addition of 3 wt% of CD, independently of the form (powder or fibrous) or surface treatment. The noticeably reduced HRR values measured for the silane-treated carbonising agent containing PLA composites are attributed to the improved thermal and structural stability of the intumescent chars, which form as a result of effective P-Si interactions in the condensed phase.

3.2.7. FTIR analysis of the char residues

Combustion residues of the flame retarded PLA composites were analysed using ATR-FTIR method. The obtained spectra are presented in Fig. 10. Absorption bands typical for intumescent chars appear in each charred residue, such as $P = O$ (1215 cm^{-1}), P–O–P (890 cm^{-1}), P–O–C bonds (980 cm^{-1}), and IR signals related to the polyaromatic char structure in the range of 1490–1600 cm^{-1}. Meanwhile, the absorbance bands at 1020 cm^{-1} and 1130 cm^{-1} are only observable in the spectra corresponding to the decomposition product of the PSil-treated CD-containing composites. These IR bands indicate that Si-O-Si structures formed in these char layers, which are in relation to their enhanced thermal stability at high temperatures, as observed during TGA (Fig. 7) and MLC analyses (Fig. 9).

4. Conclusion

Powder and microfibrous form (manufactured by high-speed electrospinning) of CD were surface-treated with a phosphorous silane (PSil). Based on the TGA results of the additives obtained this way, the PSil treatment simultaneously accelerates the char formation and enhances the thermal stability of the char during the thermal degradation process of the cyclodextrins.

The neat and PSil-treated CD additives were then used at 3 wt% as bio-based charring agents besides 15 wt% APP to produce flame retarded PLA composites. SEM analyses and DMA results reveal that the high-surface-area microfibrous CD, both in neat and surface-treated form, effectively enhances the physical and chemical interaction between the active components. Consequently, improvement in the main combustion characteristics during cone calorimeter tests, such as reduced pHRR and THR values accompanied by increased residue after combustion, was measured for the PSil-treated CD containing PLA composites. It is proposed that the silane treatment effectively improves the structural and thermal stability of the microfibrous carbonising agent. This allows the formation of a compact intumescent char layer reinforced with a stable network of ceramic-like microfibers that provides increased fire protection. However, due to the earlier appearance of decomposition products in the gas phase initiated by the increased amount of phosphorus-containing species in the system, the TTI values decreased. Moreover, the silicon-containing groups in PSil were found

to improve the stability of the residual char formed from the PLA composites, as derived from TGA and cone calorimeter test results. FTIR analysis of the corresponding combustion residues confirmed the formation of ceramic-like structures. Also, the polymer-like supramolecular structure of the microfibrous CDs is assumed to contribute to the improved thermal stability of the chars.

The beneficial effects of microfibrous structure and PSil-treatment of the used CD type carbonising agent are most apparent when the LOI values of the PLA composites are considered. LOI of the 15% APP containing PLA increases from 25.0% to 28.0% by adding 3 wt% CD powder, but LOI of 31.0% is reached when the CD is added in microfibrous form. PSil-treatment of the CDs results in further enhancement; LOI values as high as 32.5% and 37.5% are achieved with the aid of PSil-treated CD powder and microfibre, respectively. The effective flame extinction at elevated oxygen concentrations is proposed to be related to the active phosphorus-silicon interactions in the condensed phase, which inhibit the heat and flammable gas release by forming a thermally stable graphitised char layer. Furthermore, since the silane treatment improves the thermal stability of the CD-based substance, the beneficial "size effect" of the microfibrous carbonising agent can be longer preserved and utilised at higher temperatures.

Considering all the thermal analyses and flame retardancy test results of the present study, it can be concluded that the phosphorus-silicon interactions in the condensed phase of the PSil-treated CD containing composites promote the formation of a thermally and structurally stable graphitised char layer. This layer is especially effective in small flame extinction (as indicated by the noticeably increased LOI values) but less prevalent during combustion tests, likely due to the relatively small ratio of the Si-containing excipients in the examined systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kata Enikő Decsov: Formal analysis, Investigation, Writing – original draft, Visualization, Conceptualization. **Bettina Ötvös:** Investigation, Visualization. **György Marosi:** Writing – review & editing, Supervision. **Katalin Bocz:** Writing – original draft, Supervision, Funding acquisition, Conceptualization.

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