



---

Budapest University of Technology And Economics  
Department Of Organic Chemistry and Technology  
George A. Olah Doctoral School

# Modification of Biobased Charring Agents for Flame Retardancy of Poly(Lactic Acid)

Summary of PhD thesis

Author: Kata Enikő Decsov

Supervisor: Dr Katalin Bordácsné Bocz, Research fellow

Research Group on Pharmaceutical, Environmental and Safety  
Technology  
Department of Organic Chemistry and Technology

Budapest, Hungary  
2023

# 1 Introduction

The idea of sustainability and environmental awareness increasingly permeates our everyday life. Thanks to new regulations, fewer products made from fossil materials are being used in everyday life, with a particular emphasis on single-use products. In parallel, bio-based and biodegradable raw materials are becoming increasingly popular and fashionable, from small-scale production technologies like 3D printing to the scaled-up production of durable goods.

Poly(lactic acid) (PLA) has received increasing attention among biodegradable thermoplastics because of its abundant renewable source, mechanical properties and easy processability with common processes, making PLA attractive in diverse applications as a viable alternative to petrochemical-based plastics. PLA is also applicable for producing long life-cycle devices; however, since these durable engineering products often require a remarkable flame-retardant grade, therefore developing effective flame-retardant solutions for modifying PLA is a current task to be solved.

The vision of using sustainable materials also appears in the polymer additives market. In addition to efficiency, the fact that the additives come from a renewable source is becoming increasingly important. This is especially important in the case of bio-based and biodegradable matrices, where additives can be a severe problem for compostability. For this reason, more and more research is being done on using bio-based reinforcing fillers and additives. Nevertheless, replacing traditional components such as reinforcing agents with natural-based fibres presents researchers with new challenges, such as their higher flammability. For this reason, it is essential to ensure the effective fire prevention of these composites, preferably also with biobased additives.

Intumescent flame retardants (IFRs) are considered promising halogen-free flame retardants because of their low smoke emission, toxicity, and corrosion. Bio-based excipients serving as charring agents in IFR systems are increasingly encouraged and highly preferred, especially in biopolymer composites. Substituting petrol-based charring agents with renewable char-forming materials is a prominent and viable solution to provide greener flame-retardant formulations, among others, for PLA.

## 2 Literature Review

### 2.1 Flame retardancy of polymer composites

Most polymers easily ignite when exposed to heat and burn brightly. Plastics degrade during burning; low molecular weight substances are produced from them, their viscosity decreases, and the burning is accompanied by dripping<sup>1</sup>. The dripping polymer increases the spread of the fire, and the decomposition products feed the fire, and toxic gases can be released from them<sup>2</sup>. Flame retardants interfere with combustion processes such as heat and mass transfer, polymer decomposition and chemical reactions in the condensed phase, chemical decomposition and oxidation of the pyrolysis products in the gas phase ignition or flame propagation<sup>3</sup>. The complex action mechanism inhibits several processes simultaneously to varying degrees.

#### 2.1.1 Intumescent flame-retardant additive systems

Intumescent flame retardants (IFRs) are considered promising environmentally-friendly flame-retardant systems because of their low smoke emission, toxicity, and corrosion. Intumescent flame-retardant systems generally consist of three components<sup>4</sup>:

- **Acid source** – mainly inorganic acids, or compounds that turn into acidic compounds due to heat (e.g. acids, ammonium salts, phosphates),
- **Carbonising components**, traditionally polyols such as pentaerythritol and starch, polyamides.
- **Foaming/gas-forming components**, e.g. melamine and urea.

These components work together; during heating, the acid source is converted to mineral acid, which participates in the dehydration of the carbonising compound, which forms a cellular structure as the blowing agent decomposes. Therefore, the IFR system swells when heated above its critical temperature. For this reason, these substances must start decomposing at the right temperature. This way, a carbonised layer with a foam structure is created, which forms a physical barrier and protects the underlying material from further effects of the heat flow and also acts as an obstacle in the path of oxygen and pyrolysis products<sup>5</sup>. As a result, the flame goes out since no more decomposition products are produced to feed it. Another advantage of the method is that only a limited amount of gases are formed during combustion, so the process involves the release of little smoke or toxic or possibly corrosive substances. The formed protective layer can prevent the polymer from dripping, thus preventing the further spread of the flame<sup>6</sup>.

A generally used example of an IFR system is the combination of ammonium polyphosphate (APP) and pentaerythritol (PER), where APP is both an acid source and a foaming agent, while PER is the carbonising component<sup>7</sup>. However, PER have poor compatibility with polymer matrices, and it is moisture-sensitive. Its water absorption can catalyse the hydrolytic decomposition processes of polyesters like PLA, which often results in the reduction of flame retardancy and mechanical properties of the composites. Substituting

---

<sup>1</sup> M. M. Hirschler, in *Fire retardancy of polymeric materials*, (Marcel Dekker Inc, NY, 2000), pp. 27–79.

<sup>2</sup> D. J. Irvine, J. A. McCluskey, I. M. Robinson, *Polym Degrad Stab.* **67**, 383–396 (2000).

<sup>3</sup> H. F. Mark, S. M. Atlas, S. W. Shalaby, E. M. Pearce, *Flame-Retardant Polymeric Materials*, 1–17 (1975).

<sup>4</sup> S. Bourbigot, M. Le Bras, S. Duquesne, M. Rochery, *Macromol Mater Eng.* **289**, 499–511 (2004).

<sup>5</sup> B. Schartel, *Materials.* **3**, 4710–4745 (2010).

<sup>6</sup> G. Camino, S. Lomakin, in *Fire Retardant Materials*, (Elsevier Science, 2001), pp. 318–336.

<sup>7</sup> S. Bourbigot, M. Le Bras, R. Delobel, *Carbon N Y.* **31**, 1219–1230 (1993).

PER and other petrol-based charring agents with bio-based excipients is increasingly encouraged and highly preferred to provide greener flame-retardant formulations.

However, the effectiveness and compatibility of bio-based materials with polymers are often not adequate, which is why they often need to be modified in order to create a properly effective flame-retardant system.

## 2.2 Modification of additives

### 2.2.1 Microencapsulation

The microencapsulation process is one of the most effective methods to modify the surface properties of a filler by forming an outer shell to modify the interface interaction. Also, it possibly enhances some polymer composites' flame retardancy, mechanical properties, and water resistance<sup>8</sup>.

### 2.2.2 N and P treatment

Treating the additives with nitrogen- and phosphorus-containing compounds often promotes or strengthens the flame-retardant effect, which is especially important in natural fibre-reinforced systems, where the fibres can worsen the flammability properties of the composite due to the candlewick effect.

### 2.2.3 Micronisation

It has been shown recently that the particle size of the flame-retardant additives has a significant impact on both the flammability and mechanical performance of intumescent flame-retarded polymer systems. Depending on the (relative) particle size and the dispersion of the components of an IFR system in the polymer matrix, their interaction and reaction pathways can change. Thus, carbonaceous chars of different compositions and structures can be obtained, significantly differing in flame-retarding performance<sup>9</sup>. The results of *Bocz et al.*<sup>9</sup> used grinding, and *Ribeiro et al.*<sup>10</sup> used two types of additives differing in particle size. Their results indicated 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.

### 2.2.4 Silane coupling

Silane coupling agents are generally used in natural fibre-reinforced polymer composites to promote interfacial adhesion and improve mechanical properties<sup>11</sup>. Silane treatment improved interfacial interactions, decreased moisture absorption, and improved polymeric composites' flame-retardant properties<sup>12</sup>. When combined with IFR systems, the beneficial effect of silicon-containing species relies on forming a thermally stable ceramic-like silicon-phosphate structure with an increased barrier effect and good fire performance<sup>13</sup>.

## 2.3 Biobased intumescent flame-retardant systems in PLA

### 2.3.1 Lignin and starch

*Réti et al.*<sup>14</sup> compared lignin (LIG) and starch to PER as a charring agent in PLA/APP/charring agent systems. Although PER performed the best in limiting oxygen index

---

<sup>8</sup> R.-M. Li *et al.*, *RSC Adv.* **5**, 16328–16339 (2015).

<sup>9</sup> K. Bocz, T. Krain, G. Marosi, *Int J Polym Sci.* **2015**, 1–7 (2015).

<sup>10</sup> S. P. S. Ribeiro *et al.*, *Microsc Res Tech.* **83**, 276–286 (2020).

<sup>11</sup> Y. Xie, C. A. S. Hill, Z. Xiao, H. Militz, C. Mai, *Compos Part A Appl Sci Manuf.* **41**, 806–819 (2010).

<sup>12</sup> K. Bocz *et al.*, *Polym Degrad Stab.* **106**, 63–73 (2014).

<sup>13</sup> Y. Chen, L. Li, L. Qian, *RSC Adv.* **8**, 27470–27480 (2018).

<sup>14</sup> C. Réti, M. Casetta, S. Duquesne, S. Bourbigot, R. Delobel, *Polym Adv Technol.* **19**, 628–635 (2008).

(LOI) and UL-94 flame spread tests, PLA/APP/LIG and PLA/APP/starch also showed improvement over pure PLA. They used mixture designs to optimise the intumescent formulations with only 12 wt% of APP, and high renewable content (28% starch) reached 28% in the LOI test. Costes et al.<sup>15</sup> chemically **modified lignins with phosphorus and nitrogen-containing compounds**. These modified lignins proved to be highly effective in reducing the flammability of the PLA/modified lignin composites with V-0 classification at the UL-94 test while the time to ignition (TTI) and thermal stability were maintained. Zhang et al.<sup>16</sup> synthesised **urea-modified lignin** (UM-LIG) that acts as a carbon source for an IFR system with APP. They showed that PLA/APP/UM-LIG composite could reach V-0 classification and 34.5% LOI value, and it has better flame retardancy and toughness than PLA/APP/LIG or PLA/APP systems.

Zhang et al.<sup>17</sup> also synthesised a **lignin-silica hybrid**, added it to a PLA/APP system, and optimised the ratio of the components. With the addition of lignin–silica hybrids, they reached V-0 classification and reportedly had a better char morphology with more phosphoric char. Wang et al.<sup>18</sup>, besides using starch as a charring agent, used **polyurethane microencapsulated APP** paired with a melamine resin to produce IFR-PLA biocomposites. With 30 wt% loading of this IFR system, UL-94 V-0 rating and a high LOI value of 41% were reached.

### 2.3.2 Cyclodextrins

Cyclodextrins have shown much potential as FR components in multiple polymer systems, most notably in PLA. Feng et al.<sup>19</sup> used  $\beta$ -cyclodextrin ( $\beta$ -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  $\beta$ -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. To improve the char-forming ability of  $\beta$ -CD, Zhang et al.<sup>20</sup> **modified it with phenyl phosphonic acid dichloride** through interfacial polycondensation and obtained phospholipidated  $\beta$ -CD (PCD). They found the optimum mass ratio of APP to PCD to be 5 to 1. At this ratio, with 30 wt% loading, the LOI reached 42.6% accompanied by UL-94 V-0 rating, and in mass loss cone calorimetry (MLC) test, the highest amount of char residue (71.5 wt%) was obtained besides significant reduction of peak heat release rate (pHRR) and total heat release rate (THR) values compared to the neat polymer.

### 2.3.3 Natural fibres

It is known that the so-called candlewick effect of natural fibres encumbers the flame retardancy of the biocomposites reinforced with these fibres<sup>21</sup>. Suardana et al.<sup>22</sup> fabricated **diammonium phosphate-treated** (DAP) coconut filter fibre-reinforced PLA composites. Increasing the percentage of DAP for treating the composite fibres decreased the decomposition temperature but increased the char residue. At the highest 5 w/V% DAP concentration, the lowest linear burning and weight loss rates were observed. However, the flexural and tensile strengths became lower than those of untreated fibre composites.

---

<sup>15</sup> L. Costes et al., *Eur Polym J.* **84**, 652–667 (2016).

<sup>16</sup> R. Zhang, X. Xiao, Q. Tai, H. Huang, Y. Hu, *Polym Eng Sci.* **52**, 2620–2626 (2012).

<sup>17</sup> R. Zhang et al., *High Perform Polym.* **24**, 738–746 (2012).

<sup>18</sup> X. Wang et al., *Ind Eng Chem Res.* **50**, 713–720 (2011).

<sup>19</sup> J.-X. Feng, S.-P. Su, J. Zhu, *Polym Adv Technol.* **22**, 1115–1122 (2011).

<sup>20</sup> Y. Zhang, P. Han, Z. Fang, *J Appl Polym Sci.* **135**, 46054 (2018).

<sup>21</sup> S. Li, J. Ren, H. Yuan, T. Yu, W. Yuan, *Polym Int.* **59**, 242–248 (2010).

<sup>22</sup> N. P. G. Suardana, M. S. Ku, J. K. Lim, *Mater Des.* **32**, 1990–1999 (2011).

Kaci et al.<sup>23</sup> compared neat microcrystalline cellulose (MCC) to cellulose nano-whiskers (CNW) in a PLA matrix in the presence of maleic anhydride-grafted PLA as a compatibilizer. They found that both the *aspect ratio* and the filler content affect the fire retardancy properties of PLA/cellulosic fibres. It was observed in Pyrolysis Combustion Flow Calorimeter testing that at 1wt% loading level, the CNW was more efficient in increasing the temperature of pHRR and decreasing the pHRR value. Costes et al.<sup>24</sup> investigated the effect of combining MCC or cellulose nano-fibres (CNC) with aluminium phytate in PLA, where the charring effect was enhanced in both cases. CNC's high *specific surface area* proved beneficial in promoting the formation of a better insulating charred layer.

## 2.4 Aims

The literature review showed that many researchers studied the flame-retardancy possibilities of natural fibre-reinforced PLA composites. They have analysed the effect of the surface modification of plant-based reinforcing fibres and the incorporation of additives in the polymer matrix as well. However, the optimal distribution of the flame-retardant components between the composite phases (i.e. reinforcing fibres and matrix material) has not been examined so far. Therefore, I aimed to investigate the effect of the distribution of phosphorus-containing flame retardant between the reinforcing and matrix material in detail.

Most researchers have examined the combination of cellulose fibres of a given particle size (or two different particle sizes) on the effectiveness of a flame-retardant system. So far, no comprehensive research has been done on the limitation (or potentially beneficial range) of the particle size of the biofibres, which is why I aimed to investigate this in-depth in a PLA matrix system. The effect of the cellulose fibre length on the char-forming characteristics of an IFR system was planned to be evaluated.

Due to their charring ability and thermal stability, cyclodextrins have shown effective biobased carbonising agents in multiple polymer systems, including PLA. From the literature, it is known that the particle size of a flame-retardant additive can have a significant impact on both the flammability and mechanical performance of the flame-retarded polymer system. It has been shown recently that cyclodextrins can be successfully electrospun using an aqueous high-speed technique to obtain grindable microfibers<sup>25</sup>. My hypothesis was that the high-surface area of the microfibrillar form of cyclodextrin, when used as a charring agent, could provide further benefits to the intumescent flame-retardant system. Besides, the flame-retardant surface modification of the cyclodextrin microfibers was investigated.

The literature also indicates that microencapsulation offers several advantages for formulating an additive system. For example, it can improve interfacial bonds, water resistance, and is a promising method (3 in 1) for the complex production of intumescent flame-retardant additives. In this system, the core particle is practically APP, serving as an acid source and blowing agent, while the carbonising agent forms the shell layer advantageously. I proposed for this purpose the application of a sugar-derived bioepoxy resin with good charring ability, high water resistance and good compatibility with the PLA matrix.

---

<sup>23</sup> M. Kaci, T. Aouat, E. Devaux, J.-M. Lopez-Cuesta, *AIP Conf Proc.* **2196**, 020017 (2019).

<sup>24</sup> L. Costes et al., *Eur Polym J.* **74**, 218–228 (2016).

<sup>25</sup> P. Vass et al., *J Control Release.* **298**, 120–127 (2019).

### 3 Methods

#### 3.1 Equipment used for sample preparation

Method	Equipment	Accessories/Conditions
Melt compounding	Labtech Scientific LTE 26-44 modular corotating twin-screw extruder	screw diameter of 26 mm and a length-to-diameter (L/D) ratio of 44
Film extrusion	Labtech LCR 300 laboratory flat film line	
Internal mixing chamber	Brabender Plasti-Corder Lab-Station	W50 EHT 3Z type internal mixer
	HAAKE™ Rheomix OS Lab Mixer	
Compression moulding	Teach-Line Platen Press 200E heated platen press	equipped with a square mould
	Fontjine LabEcon300 Junior heated platen press	equipped with a square mould
High-speed electrospinning (HSES)	Quick2000 Ltd. HSES	stainless steel spinneret equipped with orifices (d = 330 µm) connected to a high-speed motor
	SEP-10 S Plus syringe pump	100 ml syringe
	high-voltage power supply	45 kV
Milling	IKA MF10 hammer mill	1.0 mm sieve

#### 3.2 Characterisation methods

Measurement	Equipment	Accessories/Conditions
TGA	TA Instruments Q5000 TGA	platinum pans, nitrogen atmosphere
	TA Instruments Discovery	alumina pans, nitrogen atmosphere
DSC	Mettler Toledo 3+ type DSC	aluminium crucibles with pre-punched tops, nitrogen atmosphere
FTIR	Bruker Tensor 37	deuterated triglycine sulfate detector Specac Golden Gate ATR unit
Raman spectrometry	Horiba Jobin–Yvon LabRAM	Olympus BX-40 optical microscope, 532 nm frequency-doubled Nd:YAG laser
Mass loss type cone calorimeter	Fire Testing Technology	using the ISO 13927 standard method
Oxygen index	Fire Testing Technology	according to ISO 4589 standard
UL-94	Fire Testing Technology Fume hood	According to ISO 9772 and ISO 9773
Gel permeation chromatography	Separation Module Waters e2695	columns: Styragel HR1, HR3, HR4, WYATT Optilab® T-rEX refractive index detector
Scanning electron microscopy	SEM 6380LVa Electron microscope	Ion sputter JEOL 1200
Tensile test	Zwick Z020 universal tester	Tensile head 10 kN
Dynamic mechanical analysis	TA DMA Q800	Dual cantilever measuring clamp

## 4 Results And Discussion

### 4.1 Optimisation of the distribution of phosphorus compounds in natural fabric-reinforced biocomposites

This work investigated the flame-retardancy possibilities of multi-layered biocomposites with PLA matrix layers and plain-woven flax fabrics as reinforcement. Phosphorus-based compounds were applied both in the polymer matrix and on the surface of the reinforcing natural fibres to eliminate their candlewick effect. APP-based IFR additive was incorporated into the matrix layers, while diammonium phosphate (DAP) was combined with urea (U) to treat the natural fibres. This “DAP/U” treatment aimed to utilise the P-N synergism and compensate for the reduced heat stability of the phosphorous flame-retarded natural fibres. My measurements showed that increasing the concentration of the treating solution above 15 w/V% DAP/U is ineffective as the saturated fibre cannot absorb more FR in its internal space. To reach the optimal composition of flame-retarded biocomposites and determine the optimal distribution of P-containing compounds between the matrix and the fibrous carrier in terms of flammability and mechanical properties, various combinations of treated fabrics and intumescent PLA systems were studied by following 3<sup>2</sup> full factorial design. Several flammability features, such as limiting oxygen index (LOI), time to ignition (TTI), peak heat release (pHRR), and residual mass obtained after cone calorimeter tests revealed positive interaction between the flame-retardant-treated composite constituents, meaning that better flame-retardant performance was reached when the combined flame-retardancy approach was applied than one would expect based on the flammability features of the single constituents.

Table 1 UL-94 rating of flame-retarded biocomposites\*

<b>film fabric</b>	<b>0 wt% IFR</b>	<b>10 wt% IFR</b>	<b>20 wt% IFR</b>
<b>0 w/V% DAP/U</b>	HB (27 mm/min)	HB(-)	V-2
<b>10 w/V% DAP/U</b>	HB (17 mm/min)	V-2	V-0
<b>20 w/V% DAP/U</b>	HB (16 mm/min)	V-2	V-0

\*HB: horizontal burning, V-2: long vertical burning/flaming drips, V-0: short vertical burning, no flaming drips

Also, the V-0 rating, according to the UL-94 standard, was only achieved when both constituents (i.e. matrix and reinforcement) were flame-retardant-treated (Table 1). The reinforcing fabric can act as a char-stabilizing frame if it is charred. The volatile phosphorous compounds, originating from the matrix layers, can initiate charring of the fibres under the cone heater. Still, in the case of vertical tests, the candlewick effect can only be eliminated by the fibre treatment.

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

<sup>26</sup> K. Bocz *et al.*, *Compos Part A Appl Sci Manuf.* **70**, 27–34 (2015).

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

## 4.2 Investigation of the effect of cellulose fibre length on the efficiency of an intumescent flame-retardant system

The addition of cellulose fibres to the intumescent flame-retarded PLA composite can be a promising way to strengthen the fire-protecting carbonaceous layer. It is crucial to optimise the proportion and the size of cellulosic fibres to create an effectively flame-retarded biocomposite. Previous studies have focused on how a single or a pair of cellulose fibre sizes affect the performance of a flame-retardant system. However, the optimal range or the threshold of the fibre size has not been thoroughly investigated.

Therefore, in this study, I investigated the effects of the length of micro-sized neat and FR-treated cellulose particles in an intumescent flame-retardant system in a PLA matrix. My goal was to determine the fibre length, which enforces the candle wick effect and which fibre length can advantageously affect the barrier properties of the intumescent carbonaceous layer. While investigating the cellulose addition, besides using a constant amount (15%) of melamine polyphosphate (MPP) in the PLA matrix, the enhanced char formation of the cellulose-containing composites was revealed in thermogravimetric analysis (TGA). However, the char-promoting behaviour of cellulose fibres was only shown in the combustion characteristic of PLA composites when the fibre content was higher than 10%. At the same time, the candlewick effect of the cellulose fibres increased the flammability of the composites, which was reflected by decreased LOI values. This adverse effect was found to accelerate with increasing fibre length as a 2.0% lower LOI value was measured for the PLA composite with “C300” type 300  $\mu\text{m}$  long cellulose (25.5%) compared to that with “C8” 8  $\mu\text{m}$  long fibres (27.5%) (Table 2).

Table 2 LOI and UL-94 test results of the composite samples with differing cellulose fibre length

Sample	LOI [%]	UL-94	Sample	LOI [%]	UL-94
PLA	20.5	HB	PLA+MPP	27	V2
PLA+MPP+C8	27.5	V2	PLA+MPP+FR-C8	26.5	V2
PLA+MPP+C30	26.0	V2	PLA+MPP+FR-C30	26.5	V2
PLA+MPP+C60	26.0	V2	PLA+MPP+FR-C60	26.5	V2
PLA+MPP+C300	25.5	V2	PLA+MPP+FR-C300	25.5	V2

However, the longer fibres performed better during the mass loss calorimeter test in reducing the heat release rates of the composites. It is proposed that the higher surface area of the shorter cellulose fibres supports the chemical interactions with MPP, while for the longer fibres with higher aspect ratio, physical effects, i.e. structural reinforcement of the intumescent char, come to the fore.

The FR treatment of the cellulose fibres with P and N-containing compounds resulted in enhanced char formation and reduced flammable gas release during thermal decomposition. Yet, the FR treatment was ineffective in eliminating the candlewick effect of longer fibres (C300) and noticeably reducing the flammability of the composites. Nevertheless, the composites with FR-treated cellulose fibres had increased ignition time, shorter flaming time and significantly (by about 20%) reduced THR during combustion in the mass loss cone calorimetry. The improved barrier characteristics of the char layers are related to the effective

integration of the carbonised fibrous substances and the intumescent char, as evidenced by SEM analysis of the combustion residues.

Regarding the overall fire retardant performance of the intumescent system, the cellulose fibres with 30-60  $\mu\text{m}$  length were found to be optimal. These fibres have only a moderate candlewick effect, while during combustion, they can effectively enhance the structural integrity of the fire-protecting carbonaceous layer.

### **4.3 Application of electrospun cyclodextrin microfibre as a charring agent in intumescent flame-retarded PLA composites**

Cyclodextrins are biobased carbonising agents already used in various polymer systems, such as PLA. The literature suggests that the size of a flame-retardant additive can affect the flammability and mechanical properties of the polymer composite. Recently, it was demonstrated that cyclodextrins can be electrospun into microfibers that can be ground using a water-based high-speed method. It was assumed that due to its large surface area, the microfibrinous form of cyclodextrin when used as a charring agent, could enhance the performance of an intumescent flame-retardant system.

Therefore, in this work, microfibrinous structures were manufactured from the aqueous solution of 2-hydroxypropyl-beta-cyclodextrin (CD) by high-speed electrospinning (HSES) method and then used as a bio-based charring agent in intumescent flame-retarded PLA. The specific surface area of CD was increased nine-fold by the high throughput HSES. Furthermore, the powder and microfibrinous forms of CD were surface-treated with a phosphorous silane (PSil) with the aim of improving the thermal and structural stability of the bio-based charring agent.

The TGA results of the additives obtained this way indicated increased thermal stability of the charred residue that forms from the CD with a fibrous supramolecular structure. Furthermore, the PSil treatment was found to simultaneously accelerate the char formation and enhance the thermal stability of the char.

The neat and PSil-treated CD additives were used at 3 wt% as bio-based charring agents besides 15 wt% APP to produce flame-retarded PLA composites. SEM analyses and DMA results revealed that the high-surface-area microfibrinous CD, both in neat and surface-treated form, effectively enhances the physical interactions between the active components. Consequently, improvement in the main combustion characteristics during cone calorimeter tests (Figure 1), 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 microfibrinous 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, the TTI values decreased due to the earlier appearance of decomposition products in the gas phase initiated by the increased amount of phosphorus-containing species in the system. Moreover, the silicon-containing groups in PSil improved 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 microfibrinous CDs is assumed to contribute to the improved thermal stability of the chars.

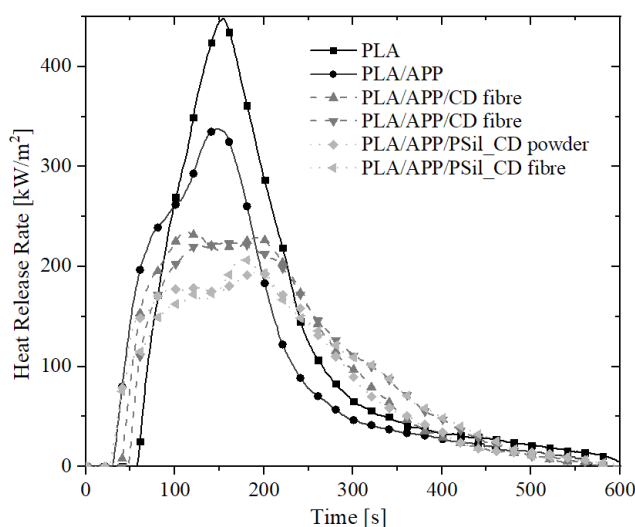


Figure 1 Heat release curves of polymer composites over time

The beneficial effects of microfibrinous structure and PSil-treatment of the used CD-type carbonising agent are most apparent when the LOI values (Table 3) 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 31.0% is reached when the CD is added in microfibrinous form. PSil-treatment of the CDs results in further enhancement; LOI values as high as 32.5% and 37.5% are achieved with 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 microfibrinous carbonising agent can be longer preserved and utilised at higher temperatures.

Table 3 The LOI values of the composite samples

Sample name	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

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.

#### 4.4 Development of bioepoxy resin microencapsulated ammonium polyphosphate for flame retardancy of poly(lactic acid)

In this work, a new type of microencapsulated APP was designed and prepared through in-situ polymerisation. Sorbitol polyglycidyl ether-based epoxy resin shell was prepared for APP not only to improve its compatibility with PLA but also as a biobased charring agent to enhance the flame-retardant efficacy of the IFR system. The effect of the thickness of the

bioresin shell of APP was investigated on the thermal properties, flame retardancy, mechanical performance, and water resistance of flame-retarded PLA composites.

The effect of the bioepoxy resin was studied in 10:1, 10:2 and 10:3 APP to resin ratios (MCAPP1, MCAPP2 and MCAPP3, respectively). The scanning electron microscopic images showed smooth, even epoxy layers on the surface of the APP (Figure 2). Nevertheless, with the increasing amount of bioresin added to the solution, the particles increasingly tended to stick together and form aggregates, which may reduce their dispersibility in the polymer matrix. The particle size analysis of the capsules also suggested that particles with thicker bioresin shell layers are prone to form aggregates since the MCAPP3 sample showed a steep increase in the particle size distribution.

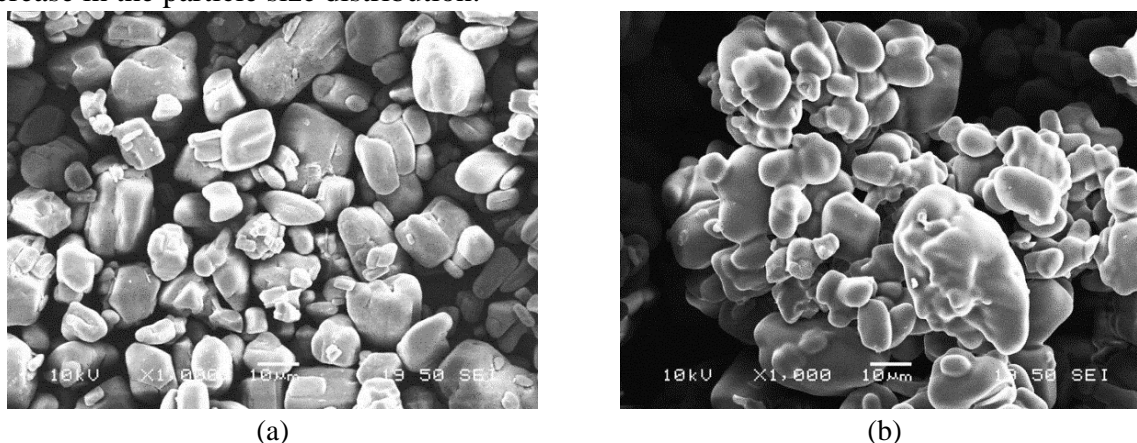


Figure 2 SEM images (a) APP; (b) MCAPP2;

The resin coating was also examined by Raman and infrared spectroscopy. Infrared spectroscopy clearly showed the difference in the thickness of the coatings, while Raman spectroscopy showed that the APP is mainly detected inside the particle, while a large amount of resin is present on the outside of it. Although the APP content was measured to be close to 90% of the calculated composition in the inner parts of the particle, the resin was detectable at every location of the surface, proving that the APP was completely covered with the resin.

The new additives were examined by thermogravimetric analysis, which showed that with increasing resin ratio, the initial decomposition temperature of the microencapsulated APP shifted to lower temperatures. This decrease in decomposition temperature showed a greater tendency than expected based on the composition of the capsules. This phenomenon can be explained by the interaction between APP and the bioepoxy resin. To further examine this phenomenon, TG-FTIR analysis was used, which showed that the decomposition of APP is facilitated by the degradation products of the bioresin.

In the PLA composites, based on the water resistance test, the microencapsulation with bioepoxy shell effectively improved the water resistance of APP and, thus, the water durability of the flame-retarded biocomposites. In the flame-retardancy test, neat APP could not reach the V-0 classification at the UL-94 test due to flaming droplets during the test, while all the microcapsule-containing composites did. The encapsulation slightly improved the LOI value, too; compared to the neat APP (28%), MCAPP2 (29%) had the best result.

In the mass loss cone calorimetric measurements (Figure 3), there was no significant difference in the TTI of either of the samples; however, a meaningful change was in the THR and the peak of pHRR values. In the case of the pHRR values, all the MCAPPs had better fire retardant efficiency than neat APP, and the MCAPP2 additive is the most effective, 19% lower than that of the untreated APP containing composite and 46% lower than that of the pure PLA.

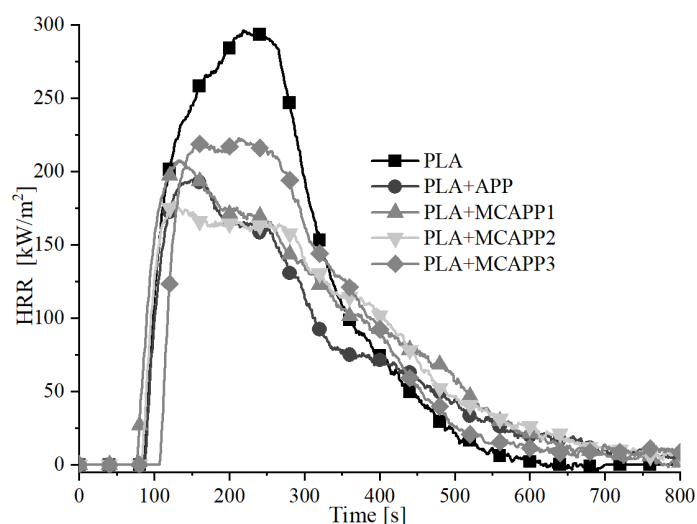


Figure 3 The heat release curves of the biocomposite samples over time under 35kW/m<sup>2</sup> heat flux

Similarly to the pHRR results, the MCAPPs successfully reduced THR too in the order of shell thickness by 32.0, 37.9 and 31.5%, respectively, compared to the neat polymer. Considering these results, the MCAPP2 additive was found to be the most effective by providing the lowest THR and 13.3% lower than the untreated APP-containing PLA sample. MCAPP2 also produced the highest amount of residue after the test. These residues were analysed using SEM. All the expanded chars showed flexible characters with mainly closed cells. The formation of such a char structure can effectively prevent heat transfer, thus protecting the underlying materials from further combustion.

Sorbitol-based epoxy resin was found to be an effective biobased charring agent and successfully applied on the surface of APP particles to create a complex (3 in 1) intumescent flame-retardant additive for PLA. Besides the noticeable improvement in the flame-retardant properties, the encapsulation of APP with bioepoxy resin provides better filler-matrix interaction, increased modulus and improved water resistance to the PLA composites.

## 5 Applicability of the results

During my thesis work, I investigated the flame-retardancy possibilities of PLA using different bio-based additives. I wanted to create effective intumescent flame-retardant systems with bio-based and/or potentially biodegradable components. I have proposed multiple synthesis routes and chemical and physical modifications of renewably sourced carbonising agents and reinforcing additives and comprehensively investigated their effects on the performance of the flame-retardant systems in PLA.

In summary, I investigated several factors influencing the flame retardancy of PLA biocomposites. My research results can help the further development of the fire prevention of biocomposites with simple methods such as the appropriate selection of the size range of the additives, the surface treatment of the additives, or the optimisation of their distribution between phases. The investigated methods can help the expansion of the use of biopolymers and the development of durable articles that require high fire resistance.

The flame-retarded flax fabric reinforced PLA composites were made and utilised within the GINOP-2.1.7-15 project in association with Meshining Engineering Kft. The aim of the project was the development of raw materials and a flame-retardant formula for PLA composites with natural fabric reinforcement. The biocomposite with an optimized composition was intended for interior design applications and to meet the requirements of the DIN 4102 and MSZ EN 13501-1 standards.

## 6 Thesis Findings

1. I found that the distribution of flame-retardant components between the composite phases (surface layer of the reinforcing fibres and polymer matrix) affects the flammability and mechanical properties of biocomposites. **I showed a beneficial interaction between flax fabrics treated with ammonium phosphate and a poly(lactic acid) matrix containing ammonium polyphosphate: the fire resistance of the biocomposites flame retarded with the combined method increases to a greater extent, and their mechanical characteristics (tensile strength and Young's modulus) improve significantly compared to systems containing flame retardant in only one phase.** [II]

2. I showed that in the case of flame-retarded poly(lactic acid) composites incorporating cellulose, in addition to the proportion of cellulose fibres, the size (characteristic length) of the fibres also significantly affects the efficiency of the intumescent flame-retardant additive system. Based on the flammability tests of poly(lactic acid) composites with 15% melamine polyphosphate and 10% cellulose of different fibre lengths, untreated or surface-treated with phosphorus- and nitrogen-containing compounds, I found that as the length of the cellulose fibres increases, the flammability of the composites significantly increases (the limiting oxygen index decreases) due to the candlewick effect. **I have shown that cellulose fibres with a length of 30-60  $\mu\text{m}$  increase the structural integrity of the charred fire-protecting layer formed under heat exposure, thereby increasing the efficiency of the intumescent flame-retardant system;** with their application, the maximum rate of heat emission is reduced by about 25% and the total amount of heat emission by about 15% compared to the flame-retarded poly(lactic acid) composite that does not contain cellulose. [VI]

3. **I was the first to point out that the surface-to-volume ratio of a carbonizing additive has a significant effect on the effectiveness of the intumescent flame-retardant system.** In poly(lactic acid) (PLA) matrix, in addition to 15% ammonium polyphosphate (APP), I compared the effects of 3% (2-hydroxypropyl)- $\beta$ -cyclodextrin (CD) type carbonizing component in the form of granular powder and micronized, ground fibre form, obtained by high-speed electrospinning, respectively. I found that compared to the effect of adding the same amount of conventional powder, the microfibrinous CD significantly increased the limiting oxygen index value of the flame-retarded PLA (from 28.0% to 31.0%) and also resulted in a larger amount of charred residue both during the thermogravimetric analysis and the cone calorimeter test. The advantage of the unique microfibrinous structure of the oligosaccharide charring agent lies in the effective interaction with APP and the formation of a carbonaceous protective layer with increased thermal and mechanical resistance. [III, V]

4. **I prepared a new CD-PSil flame-retardant additive by the reactive modification of (2-hydroxypropyl)- $\beta$ -cyclodextrin (CD) with a phosphorous silane (PSil) compound.** 3% CD-PSil used in poly(lactic acid) with 15% ammonium polyphosphate ensures the V-0 classification according to the UL-94 flammability standard and increases the limiting oxygen index from 25.0% to 32.5%. I showed that the flame-retardant effect of CD-PSil can also be enhanced by increasing the surface-to-volume ratio of the additive. The microfibrinous CD-PSil additive, produced by high-speed electrospinning of CD and subsequent reactive surface treatment with PSil, increases the limiting oxygen index of poly(lactic acid) from 25.0% to 37.5% when applied at 3% with 15% APP. [V]

5. I developed a process for the microencapsulation of ammonium polyphosphate with a sorbitol-based bioepoxy resin. The microencapsulated additive with an optimized composition forms an easy-to-use (combined) intumescent flame-retardant additive system in which the bioepoxy resin plays the role of the charring component. I proved the increased flame-retardant efficiency of the microencapsulated additive in poly(lactic acid). Additional advantages of coating the ammonium polyphosphate with bioepoxy resin are that it provides a better interfacial interaction between the poly(lactic acid) matrix and the additive, increases the tensile modulus of the composite, and also reduces the water sensitivity and leaching of the flame-retardant additive. [I, IV]

## 7 Publications

### 7.1 Related scientific articles

- I. Decsov K, Bocz K, Szolnoki B, Bourbigot S, Fontaine G, Vadas D, Marosi G (2019) Development of Bioepoxy Resin Microencapsulated Ammonium-Polyphosphate for Flame Retardancy of Polylactic Acid. *Molecules* 24:4123. <https://doi.org/10.3390/molecules24224123> . IF: 3.346; C:19, IC:15.
- II. Bocz K, Szolnoki B, Farkas A, Verret E, Vadas D, Decsov K, Marosi G (2020) Optimal distribution of phosphorus compounds in multi-layered natural fabric reinforced biocomposites. *Express Polymer Letters* 14:606–618. <https://doi.org/10.3144/expresspolymlett.2020.50>. IF: 3.531; C:9, IC:8.
- III. Decsov K, Takács V, Marosi G, Bocz K (2021) Microfibrinous cyclodextrin boosts flame retardancy of poly(lactic acid). *Polymer Degradation and Stability* 191:109655. <https://doi.org/10.1016/j.polymdegradstab.2021.109655>. IF: 4.980; C:19, IC:17.
- IV. Nguyen Thanh TT, Decsov KE, Bocz K, Marosi G, Szolnoki B (2022) Development of Intumescent Flame Retardant for Polypropylene: Bio-epoxy Resin Microencapsulated Ammonium-polyphosphate. *Periodica Polytechnica-Chemical Engineering* 66:313–324. <https://doi.org/10.3311/PPch.19468>. IF: 1.620; C:3, IC:3.
- V. Decsov KE, Ötvös B, Marosi G, Bocz K (2022) Microfibrinous cyclodextrin boosts flame retardancy of poly(lactic acid) II - phosphorous silane treatment further enhances the effectivity. *Polymer Degradation and Stability* 200:109938. <https://doi.org/10.1016/j.polymdegradstab.2022.109938>. IF: 6.137; C:5, IC:5.
- VI. Decsov KE, Ötvös B, Nguyen TTT, Bocz K (2023) The Effect of Cellulose Fibre Length on the Efficiency of an Intumescent Flame Retardant System in Poly(lactic acid). *Fire* 6:97. <https://doi.org/10.3390/fire6030097>. IF: 3.140; C:-, IC:-.

### 7.2 Further articles

- VII. Bocz K, Decsov KE, Farkas A, Vadas D, Bárány T, Wacha A, Bóta A, Marosi G (2018) Non-destructive characterisation of all-polypropylene composites using small angle X-ray scattering and polarized Raman spectroscopy. *Composites Part A-Applied Science And Manufacturing* 114: 250–257. <https://doi.org/10.1016/j.compositesa.2018.08.020>. IF:6.993; C:7, IC:5.
- VIII. Bordácsné Bocz K, Ronkay FG, Decsov KE, Molnár B, Marosi G (2021) Ütésálló poli(etilén-tereftalát) előállítására hulladék felhasználásával. *MŰANYAGIPARI SZEMLE* 2021/0 (1). pp. 1-17. ISSN 1785-7856:

- IX. Bocz K, Ronkay F, Decsov KE, Molnár B, Marosi G (2021) Application of low-grade recycle to enhance reactive toughening of poly(ethylene terephthalate). *Polymer Degradation And Stability* 185:109505.  
<https://doi.org/10.1016/j.polymdegradstab.2021.109505>. IF: 4.980; C:8, IC:5.
- X. Lukács N, Decsov KE, Molnár B, Ronkay F, Bocz KB (2023) Increased processing temperature assisted reactive toughening of poly(lactic acid). *Express Polymer Letters* 17:169–180.  
<https://doi.org/10.3144/expresspolymlett.2023.12>. IF: 3.141; C:-, IC:-.

### 7.3 Oral presentations

- XI. Decsov K, Bocz K, Marosi G; "Raman spectroscopic characterisation of self-reinforced polypropylene composites", 13th International Conference "Students for Students", 2016 Apr 13-17, Cluj-Napoca (Romania)
- XII. Decsov K, Bocz K, Baranyi B, Bourbigot S, Szolnoki B, Fontaine G, Vadas D, Marosi G; "Development of bioepoxy resin microencapsulated ammonium polyphosphate for flame retardancy of polylactic acid", International Conference on Bio-based Polymers and Composites, 2018 Sep 2-6, Balatonfüred, (Hungary)

### 7.4 Poster presentations

- XIII. Decsov K, Bocz K, Baranyi B, Bourbigot S, Szolnoki B, Fontaine G, Sarazin J, Vadas D, Marosi G; "Development of bioepoxy resin microencapsulated ammonium-polyphosphate for flame retardancy of polylactic acid", European meeting on fire retardant polymeric materials 2019 Jun 26-28, Turku (Finland)
- XIV. Decsov K, Bocz K, Baranyi B, Bourbigot S, Szolnoki B, Fontaine G, Sarazin J, Vadas D, Marosi G; "Development of bioepoxy resin microencapsulated ammonium-polyphosphate for flame retardancy of polylactic acid", 1st George Olah Conference 2019 Sep 23, Budapest (Hungary)
- XV. Decsov K, Ötvös B, Marosi G, Bocz K; "Phosphorus-treated microfibrillar cyclodextrin boosts flame retardancy of poly(lactic acid)", 2nd George Olah Conference, 2021 Sep 15, Budapest (Hungary)
- XVI. Decsov K, Ötvös B, Marosi G, Bocz K; "Phosphorus-treated microfibrillar cyclodextrin boosts flame retardancy of poly(lactic acid)", European Meeting on Fire Retardant Polymeric Materials, 2021 Aug 29, Budapest (Hungary)
- XVII. Decsov K, Ötvös B, Marosi G, Bocz K; "The effect of cellulose fibre length on the efficiency of an intumescent flame retardant system in poly(lactic acid)", 3rd international conference on eco-friendly flame retardant additives and materials, 2022 May 17-18, Alés (France)
- XVIII. Decsov K, Ötvös B, Marosi G, Bocz K; "Development of silica microfibrillar and application as flame retardant additives in poly(lactic acid)", Fire and Polymers – 2022 Jun 5-8, Napa (USA)
- XIX. Decsov K, Ötvös B, Marosi G, Bocz K; "Development of silica microfibrillar and application as flame retardant additives in poly(lactic acid)", 4th George Olah Conference, 2022 Sep 26, Budapest (Hungary)
- XX. Decsov K, Cserni V, Marosi G, Bocz K; "Development of an alginate-based additive for flame retardancy of polylactic acid", European Meeting on Fire Retardant Polymeric Materials, 2023 Jun 26-29, Zürich, Switzerland