DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY FLAME RETARDED POLYMER COMPOSITES

SUMMARY OF PHD THESIS

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1 INTRODUCTION

The continuous increase in consumption of polymeric composites is in connection with the growing range of application fields. The prominent strength/weight ratio, corrosion resistance and low cost belong to the main driving forces of this development. About 35-40% of the annually produced fibre reinforced polymeric composites is made of thermoplastics, generally reinforced by glass, carbon or natural fibres, while the rest is made of high-tech carbon or glass fibre reinforced thermosets. These are mainly applied in the transportation and E&E industries. Besides the indisputable advantages, however, the use of such multi-component polymeric composites is accompanied with several serious environmental, sustainability and safety issues:

(1) The petrol-based polymer production contributes to the depletion of fossil fuel reserves.

(2) The use of dissimilar materials in the reinforced composites largely encumbers their reprocessing and recycling. Enormous amount of end-of-life plastic (ELP) waste is being generated, the current treatment of which, due to the low volume/weight ratio and shortage of recycling, greatly burdens the landfills.

(3) The number and danger of fire risk scenarios has been dramatically increased with the expansion of plastic usage endangering our everyday life.

To serve the realization of sustainable development, the industries will be forced by increasingly strict environmental-focused legislation to replace their conventional (e.g. glass fibre reinforced) polymer composites by more environmental-friendly alternatives; the use of recyclable or biodegradable polymeric materials is urged. Therefore, developments towards recyclable and biodegradable polymer composites with good mechanical properties and a low environmental impact are nowadays extensively examined by researchers. Nevertheless, in order to reduce the number and danger of fire risk scenarios, flame retardancy needs to be improved simultaneously with the mechanical performance of the newly developed polymer composites.

In this work, developments towards improvement in competitiveness of environmentally friendly polymer composites were addressed. Following the principles of “eco-design”, recyclable self-reinforced composites, and bio-based composites with biodegradability potential were produced. During the composite development process, besides striving for achieving competitive mechanical performance, safety, environmental and economic aspects were considered as well, with the aim to increase the chance of the studied recyclable and bio-based composites to serve as real (or better) alternatives for conventional, petrol-based counterparts.
2 LITERATURE REVIEW, AIMS

2.1 SELF-REINFORCED COMPOSITES

The concept of self-reinforced composites referred to “one polymer composite” has been introduced by Capiati and Porter in 1975 [1]. The basic concept of self-reinforcement is the creation of highly aligned molecular or supramolecular (reinforcing) structures with mechanical properties superior to those of the isotropic (matrix) polymer. In the case of semi-crystalline polymeric materials the basis of self-reinforcement is the oriented crystallization. The basic condition of oriented crystallization is a high molecular orientation [2], which can be obtained by the solid-state deformation.

One of the greatest challenges in using thermoplastic fibres to reinforce thermoplastic matrices is in their combination in to a well-consolidated composite, which, normally achieved by thermal means, is complicated by the inherent similarity between the melting temperature of the matrix and that of the reinforcing fibres [3]. It is crucial that the loss of the mechanical properties of the reinforcement is minimised during composite production in order for the performance of the final composite to be maximised. Therefore, it is imperative to widen the processing window, inside which the composite consolidation would be feasible. There are a wide range of features, including variations in molecular weight, tacticity, crystallinity, copolymerisation, polymorphism, etc., which can be exploited to ensure a suitable processing window for SRC preparation. The relevant aspects have been recently comprehensively reviewed by Karger-Kocsis et al. [4].

It was shown that self-reinforced polymer composites have various advantages over conventional composites, including high mechanical performance to weight ratio and recyclability, however, the need for unique and well-controlled processing techniques makes their production rather costly, which currently largely reduces their competitiveness. Therefore, new solutions are required in the quality assurance of SRC prefabricates and parts. For high-throughput, in-line quality inspection, only non-destructive techniques can be considered, still these have been rarely studied in the literature.

Self-reinforced polymer composites have found mainly applications in transportation and electronics fields, where fire hazard is an issue. Although the application of self-reinforced composites, made entirely of highly flammable polymeric components, is accompanied with a high fire-risk, to date no research were conducted towards their flame retardation.

2.2 NATURAL FIBRE REINFORCED BIOCOMPOSITES

The use of natural fibres as reinforcement in biopolymer matrix offers the advantage of creating fully bio-based and/or biodegradable (“green”) composites of improved mechanical properties. A large variety of such natural fibre-biopolymer combinations are being investigated in the literature as potential materials for industrial applications.

THERMOPLASTIC STARCH-BASED BIOCOMPOSITES

Starch can be processed into thermoplastic starch (TPS), a low-cost thermoplastic biopolymer, in presence of plasticizer such as glycerol, glycol, sorbitol and sugars and under action of high temperature and shear. Various natural cellulosic fibres, such as sisal, cotton, bamboo, jute, straw, kenaf, wood, etc. were used to increase the modulus and impact toughness and reduce the water uptake of TPS based composites. The improvement of the tensile properties of starch-based biocomposites varies depending on the type and nature of the fibre, its orientation (random or unidirectional), form (fibre or fabric) and volume fraction and type of blending/plasticizer used) [5].

TPS is often blended with other (bio)polymers with the aim to reduce the overall cost of the final product. Besides, TPS can act as toughening agent by reducing the rigidity of the associated polymer [6]. Furthermore, a special feature of starch was utilized by Reti et al.; i.e that starch is a suitable biobased carbon source necessitated in an intumescent flame retardant system [7].

POLYLACTIC ACID BASED BIOCOMPOSITES

Today, PLA is the most extensively researched and utilized biodegradable thermoplastic polyester. This is mainly due to its attractive mechanical properties, i.e comparable strength and stiffness with conventional synthetic polymers, excellent thermoforming capability, easy processing by conventional equipment, high industrial production capacity, UV-stability, no toxicity, low emission of greenhouse gases, low amount of energy used for production and potential biodegradability. Based on its mechanical strength and stiffness, PLA would be a promising candidate even for engineering applications (e.g. in construction or transportation fields), however, its inherent poor toughness [8] needs to be significantly improved in order to render PLA or its composites resistant to dynamic or impact stresses as well.

A range of polymers, additives and fillers have been successfully combined with PLA in order to enhance mechanical performance, reduce costs, provide unique properties and expand PLA into new applications. Natural fibre reinforcement, both in yarn and woven form, was found to improve the impact resistance of PLA. In addition, as proposed by Nodo

et al. [9], self-reinforcement seems to be a promising way to toughen PLA without the addition of modifiers or plasticizers which would affect the degradability of PLA.

2.3 **Phosphorus-based flame retardancy of biocomposites**

It is revealed that phosphorus-based additives represent an environmentally-friendly solution in the flame retardancy of biopolymers and natural fibres. Phosphorus as a flame retardant can act in the gas phase through flame inhibition, and in the condensed phase by enhancing char, by yielding intumescence, or through inorganic glass formation. In fact, for many phosphorus-based systems a significant action has been determined in both the gas and condensed phases.

Recently, the intumescent flame retardants (IFRs) have found an important place in the flame retardant market. On burning, these additives develop a foamed char on the surface of the polymeric material. The proposed mechanism assumes that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the polymer to volatile combustible products. It is revealed that a minimum of 20-22 wt% IFR is needed in order to achieve acceptable levels of flame retardancy in polyolefins. Several chemical substances, mainly heavy metal ions and silicon-containing species, have been studied as synergetic effect additives when combined with IFR systems. Thus the required amount of IFR can be somewhat, but not drastically, lowered.

*Horrocks* et al. [10] were the first to draw attention to the beneficial interaction of cellulose based and other char-forming polymer fibres and intumescent substances, while *Gallo* et al. [11] have shown recently that the char promoting behavior of kenaf fibres, combined with phosphorus-based flame retardants, can be utilized in laminated composite structure. However, the possibility for using thermoplastic fibres such as polypropylene for enhancing the flame-retardant efficiency of an intumescent system was not yet proposed.

The survey of the literature shows that up to now there are only few papers devoted to the flame retardancy of PLA, the most promising biopolymer for durable applications. The best fire retardant performance was reached by intumescent approach. Replacement of conventional petrol-based carbonizing agents with polyols originating from renewable resources proved to be a promising way towards green flame retardant systems. However, generally high loadings (20-30 wt%) were necessitated to reach the required level of flame retardancy. Therefore, exploring new approaches and mechanisms in the flame retardancy of PLA is a hot research area. It is also noteworthy, that the flame retardancy of green composites, composed of biopolymer matrix and natural fibre reinforcement, is barely studied in the literature. The researchers in this field have to face the challenges of low thermal stability and candlewick effect of natural fibres and compatibility issues as well.

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3 METHODS

3.1 EQUIPMENT USED FOR SAMPLE PREPARATION

INTERNAL MIXER
   Brabender Plasti Corder PL 2000 equipped with a 50 and a 350 cm³ mixing chamber.

TWIN SCREW EXTRUDER
   Labtech Scientific LTE 26-44 type twin-screw extruder with a screw diameter of 26 mm and a L/D ratio of 44.

FLAT FILM LINE
   Labtech Scientific LCR 300 type flat film line.

LABORATORY HOT-PRESS
   Collin P200E type laboratory hot press equipped with plane tools.

HOT-PRESS MACHINE
   Schwabenthan Polystat 300S type hot-press machine.

INJECTION MOULDING
   Arburg Allrounder Advance 370S 700-290 type injection moulding machine was used to manufacture dumbbell and plaque specimens.

3.2 CHARACTERISATION METHODS

FURIER TRANSFORM INFRARED SPECTROMETRY (FTIR)
   Bruker Tensor 37 type Fourier transform infrared (FTIR) spectrometer equipped with DTGS detector with a resolution of 4 cm⁻¹.

LASER PYROLYSIS-FTIR COUPLED GAS PHASE ANALYSIS (LP-FTIR)
   The system comprises of CO₂ pyrolyser laser (10.6 nm, SYNRAD 48-1) unit coupled with Bruker Tensor 37 type FTIR spectrometer.

REACTIR
   Mettler-Toledo ReactIR™ in situ Fourier transform infrared spectroscopic (FT-IR) apparatus equipped with a multi-reflection diamond attenuated total reflectance (ATR) insertion sensor.

RAMAN SPECTROMETRY
   Horiba Jobin-Yvon LabRAM system coupled with an external 785 nm diode laser source and an Olympus BX-40 optical microscope.

MASS SPECTROMETRY (MS)
   Perkin Elmer Sciex API 365 LC/MS/MS system.

NUCLEAR MAGNETIC RESONANCE ANALYSIS (NMR)
   Bruker AV-300 NMR spectrometer operating at 300.13 MHz, 121.50 MHz and 75.48 MHz for ¹H, ³¹P and ¹³C, respectively.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)
   Setaram DSC 92 instrument.
THERMAL GRAVIMETRY (TGA)
Setaram Labsys TG DTA/DSC instrument.

MELT FLOW RATE MEASUREMENT (MFI)
Ceast 7027.000 type computer controlled capillary viscosimeter.

LIGHT MICROSCOPY (LM)
Olympus BX51M type microscope.

SCANNING ELECTRON MICROSCOPY (SEM)
JEOL JSM-6380 LA type apparatus equipped with an energy dispersive spectrometer (EDS) unit.

DYNAMIC MECHANICAL ANALYSIS (DMA)
TA Instruments Q800 dynamic mechanical analyser.

TENSILE TEST
Zwick Z020 universal testing machine.

BENDING TEST
Zwick Z020 universal testing machine.

INTERLAMINAR (SHEAR) STRENGTH TEST
Zwick Z020 universal testing machine.

INSTRUMENTED FALLING WEIGHT IMPACT TEST (IFWI)
Ceast Fractovis 6785 type equipment.

LIMITING OXYGEN INDEX MEASUREMENTS (LOI)
Limiting oxygen index measurements were carried out according to the MSZ EN ISO 4589-1 and 4589-2 (2000) standards.

UL 94 FLAMMABILITY TEST
UL94 flammability tests were performed according to ISO 9772 and ISO 9773 standards.

MASS LOSS TYPE CONE CALORIMETRY (MLC)
MLC tests were carried out by an instrument made by Fire Testing Technology Ltd., following the procedures of ISO 13927 standard method at a constant heat flux of 50 kW/m² and using spark igniter in all cases.

COMPRESSSION TEST OF CHARRED POST-COMBUSTION RESIDUES
AR2000 Rheometer with special adjustment was used for structural and mechanical characterization of post-combustion residues.
4 RESULTS AND DISCUSSION

4.1 NON-DESTRUCTIVE CHARACTERISATION OF ALL-POLYPROPYLENE COMPOSITES USING POLARIZED RAMAN SPECTROMETRY

Our investigation aimed at elaboration of a non-destructive (structure and mechanical performance) assessment method for self-reinforced polymer composites, being especially sensitive to manufacturing and application conditions.

Polarized Raman spectrometry was found to be a suitable method for characterizing the structure of reinforcing PP fibres of all-PP composites in a fast and non-destructive way. The orientation states of the embedded iPP fibres were determined by CLS modelling with real reference spectra. The strong correlation (Figure 1), evinced between the tensile moduli of the all-PPCs and the estimated orientation degrees of the iPP fibres, served as proof for the adequacy of the elaborated method. The process control based on polarized Raman spectrometry is expected to gain application in self-reinforced composite manufacturing and quality assessment, and also in other fields where ordered structure of macromolecules is relevant.

![Figure 1 a) Relative degree of orientation obtained from the CLS model and b) strong correlation between the tensile moduli and the estimated relative degree of orientation values](image)

4.2 FLAME RETARDANCY OF RECYCLABLE ALL-POLYPROPYLENE COMPOSITES

Our work aimed at development of flame retardant SRCs and investigation of their flammability properties together with their mechanical performance. We have investigated the flame retardancy possibilities of multi-layered (film-stacked) SRCs made both of primary polypropylenes and secondary polyolefins, furthermore flame retarded injection moulded all-PPCs were studied as well. Commercially available APP based intumescent flame retardant systems were used in the matrix materials in all cases in order to diminish the flammability of the composites (made entirely of PP).
STUDY ON THE SYNERGISM BETWEEN HIGHLY ORIENTED POLYPROPYLENE TAPES AND INTUMESCENT FLAME RETARDANT SYSTEMS

Special synergistic flame retarding effect was observed as the result of physical interactions between APP based intumescent flame retardants and highly oriented PP fabrics in multilayer SRCs. Such interaction between a flammable polymer and a flame retardant, which is normally much less active than in the studied SRC systems, was not observed earlier. As low as 9 wt% additive concentration, less than half of the normally necessary amount of IFR, is enough to achieve V-0 classification of a PP SRC according to the UL-94 classification. This result is accompanied with noticeably higher LOI values and significantly lower peak of heat release rates when compared to the non-oriented PP samples with the same intumescent flame retardant contents.

Based on comprehensive analyses, performed to study the ignitability, char forming process, burning behaviour and post-combustion remains of flame retarded SRCs, important conclusions were drawn for better understanding of the phenomenon behind their outstanding flame retardancy. It was established that the significant shrinkage, exhibited by the highly-stretched PP tapes when exposed to heat, is the key factor behind the self-extinguishing behaviour of flame retarded SRCs with surprisingly low additive content (only 9 wt% IFR). As a consequence of the shrinkage, which is fairly noticeable both during horizontal and vertical ignition (Figure 2), the elongation of the molten specimens, and thus the formation of virgin polymer surfaces, is hindered. In this case the evolving compact charred surfaces can act as a barrier of increased efficiency against heat and fuel transport, resulting in immediate fire extinction. Testing SRCs with slightly relaxed PP fabrics confirmed that the degree of molecular orientation plays a key role in the char promoting effect of fibres participating in the IFR mechanism.

The prepared flame retarded SRCs, despite the presence of IFR additives, exhibit prominent tensile properties and shock resistance: a tensile strength of 90 MPa, and perforation energy of 24 J/mm, accompanied with a ductility factor of approximately 38% is achievable.
It was concluded that the embedding of additive-free, highly-stretched (oriented) fibres into the polymer matrix can basically change the burning behaviour (ignitability, char forming process, migration effects, etc.) of a flame retarded polymer system. It was proposed that the described advantageous phenomena can be utilized in other polymer types/systems, with other flame retardants, or in other self-reinforcing structures (e.g. in injection moulded all-polymer composites).

**DEVELOPMENT OF FLAME RETARDED ALL-POLYPROPYLENE COMPOSITES FROM PLASTIC WASTE**

The mechanical properties of polyolefin waste have been successfully improved by applying reinforcing polypropylene fabrics: 5 times higher tensile strength, 2 times higher flexural strength and 4 times higher perforation energy were achieved. Although the tensile and flexural strength of the recycled matrix could be more effectively increased using glass fabric reinforcement, the prepared self-reinforced composites are given preferences from environmental aspects considering that their density is much lower, and in opposition to glass fibre reinforced composites, they are easy to recycle by simple reprocessing methods at the end of their life-cycle.

Significantly reduced flammability was obtained by applying intumescent flame retardant additives and the prominent mechanical properties of the recycled multilayer composites have not been remarkably influenced by the FR content of their matrix layers. The special beneficial effect on the activity of the applied phosphorus-based intumescent flame retardant additive was evinced in the recycled self-reinforced system at 18 wt% concentration, resulting in flame-extinguishing behaviour during horizontal and vertical burning (UL-94) test, accompanied by LOI of 30 vol%, time shifted and reduced (by 75%) peak of heat release rate (pkHRR) during combustion (Figure 3).

![Figure 3](image)

**Figure 3 (a) Heat release rate and (b) mass loss (of the combustible content) measured during burning of flame retarded recycled samples**

**STUDY ON THE FLAMMABILITY PROPERTIES OF INJECTION MOULDED ALL-POLYPROPYLENE COMPOSITES**

Self-reinforced composites were manufactured by injection moulding method for the first time in flame retarded form. By this means, besides the conventional processing methods resulting in 2D all-PP sheets, the production of 3D products becomes also
realizable. Optical microscopic photographs taken from the polished cross-sections of the injection moulded all-PPCs revealed homogeneous distribution of both reinforcing fibres and flame retardant additives (Figure 4). Such products can meet the requirements of the increasingly strict safety regulations, both from mechanical and flame retardancy aspects, furthermore, such end-of-life products are easily recyclable.

![Figure 4 Optical microscopic images of the polished cross-sections (perpendicular to the flow direction) of (A) SR-PP, (B) SR-PP_FR10 and (C) SR-PP_FR15](image)

Nevertheless, in the case of the short fibre reinforced injection moulded sheets, the synergistic effect observed between longer oriented fibres and the intumescent flame retardant system proved to be rather moderate. Based on these results it was concluded that the reinforcing fibre length and alignment and the lay-up (structure) of intumescent flame retarded self-reinforced composites are of key importance regarding their fire performance.

### 4.3 Flame Retardancy of Biodegradable Composites

**Development of Flame Retarded Thermoplastic Starch Based Composites**

In this work, the flame retardancy of natural fibre 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 was evinced 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 (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>UL-94 classification*</th>
<th>LOI vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-G</td>
<td>HB</td>
<td>23</td>
</tr>
<tr>
<td>TPS-GOP</td>
<td>V-2</td>
<td>31</td>
</tr>
<tr>
<td>TPS-GOP_BFibre</td>
<td>HB</td>
<td>29</td>
</tr>
<tr>
<td>TPS-GOP_BFibre_AP</td>
<td>V-0</td>
<td>32</td>
</tr>
<tr>
<td>TPS-GOP_BFabric</td>
<td>HB</td>
<td>30</td>
</tr>
<tr>
<td>TPS-GOP_BFabric_AP</td>
<td>V-0</td>
<td>32</td>
</tr>
</tbody>
</table>
Chopped flax fibres and plain-woven linen-hemp fabrics were used as reinforcement in the obtained flame retardant TPS matrix. The TPS composites, reinforced by neat natural fibres showed increased flammability, such as UL-94 classification remained HB, and decreased LOI (Table 1), therefore before embedding into the matrix the biofibres were surface treated with ammonium phosphate (AP) 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 fibres proved to be non-flammable when exposed to 50 kW/m² heat flux under the conditions of a mass loss type cone calorimeter.

With the AP-treatment the candlewick effect of natural fibres in composites was effectively suppressed. The best V-0 classification, LOI as high as 32 vol% (Table 1), reduced heat release rates and after combustion high amount of charred residue of TPS composites were achieved, as a consequence. The AP-treated, well-dispersed, chopped flax fibres 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 of combination of flame retarding effect plasticizer and flame retardant surface treatment of natural fibres to obtain fire-safe and biodegradable thermoplastic starch composites was found to be promising, thus worth for further investigation in other polymer types, such as in polylactide as well.

FLAME RETARDANCY OF POLY(LACTIC ACID) BASED COMPOSITES WITH MULTIFUNCTIONAL ADDITIVE SYSTEM

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

The synthesized phosphorus-containing polyol, glycerol phosphate, was used as plasticizer to obtain thermoplastic starch of reduced flammability. This modified starch proved to have enhanced char promoting capability when applied in PLA, and thus provided improved flame retardancy to PLA/TPS blends. On the other hand, a newly synthesized reactive flame retardant modifier (PSil) of flax fibres allowed the phosphorus–silicon synergism to be utilized. The LOI value of both PLA/TPS and PLA/TPS–GP blends decreased when neat flax fibres were embedded. This harmful candle-wick effect of the applied fibrous substances ceased completely due to the treatment of fibres with the synthesized phosphorous-silane. Significant charring activity of biofibres was achieved (47% charred residue at 500°C in TGA) without noticeable decrease of the thermal stability of the cellulosic fibres.
When the flame retardant plasticizer was applied in combination with the PSil-treated flax fibres, 30% reduction was achieved in pkHRR compared to the phosphorus-free reference biocomposite (Figure 5). The flame retardant capability exerted by the P-content of only the plasticizer and the fibre modifier (approximately 0.65 wt%) was insufficient to provide self-extinguishing character to the biocomposites. However, the addition of as few as 10 wt% of APP proved to be sufficient to achieve V-0 rating, and a LOI value as high as 33 vol% was reached this way.

![Figure 5 Heat release rate curves of the prepared PLA/TPS based composites](image)

The phosphorus containing species, being present both on the surface of the reinforcing flax fibres and in the biodegradable matrix material resulted in adequate strength and stiffness in the case of the effectively flame retarded biocomposites. In general, the mechanical performance of the prepared flame retarded biocomposites is comparable with that of a common polypropylene, at least regarding tensile and flexural properties.

4.4 Development of recyclable and biodegradable all-polyactic acid composites in flame retarded form

The preparation of flame retarded self-reinforced PLA composites proved to be a promising way to overcome two serious drawbacks, brittleness and flammability, of PLA, simultaneously. Self-reinforced PLA composites were manufactured by film stacking of highly crystalline PLA multifilament yarns and fully amorphous PLA matrix films, also in flame retarded form. Self-reinforcement provided PLA with outstanding impact resistance without compromising its strength, stiffness, recyclability or biodegradability, while the combined application of IFR additives and MMT clays in the matrix films resulted in significantly reduced flammability compared to the readily combustible PLA.

FR loading of 16 wt% ensured self-extinguishing behaviour for the PLA-SRC both when horizontally or vertically ignited, i.e. UL-94 V-0 rating, LOI value as high as 34 vol% was
achieved, and a 50% reduction of pkHRR and a 40% of tHR were measured by cone calorimeter. The PLA fibres are the main load bearing substances, therefore the FR particles in the matrix films did not cause noticeable deterioration in the tensile and flexural strength of the PLA-SRCs, in contrast, the stiffness of the composites increased with increasing additive contents. Furthermore, enhanced consolidation quality was obtained in the case of the flame retarded PLA-SRCs as a result of the significantly increased fluidity of the matrix films in the presence of the used FRs. Consequently, the impact resistance of the PLA-SRCs further increased with the FR loading; the effectively flame retarded composite (PLA-SRC_FR16) exhibits an outstanding perforation energy of 16 J/mm (Figure 6).

![Figure 6](image)

*Figure 6 a) Typical thickness related load-time curves recorded during the IFWI tests and b) perforation energy and ductility factor of the developed PLA-SRCs*

Besides their indisputable environmental benefits such as renewable source, recyclability and probable biodegradability, the manufactured self-reinforced PLA composites prove to have competitive mechanical characteristics with conventional petrol-based polymeric composites, both in respect to static (tensile and flexural strength and stiffness) and dynamic mechanical properties (impact resistance and temperature dependent storage modulus), especially when flame retarded.
5 THESIS FINDINGS

1. The structure of all-polypropylene composites was characterized by non-destructive Raman spectrometry, which method has not been used previously to study self-reinforced composites. Strong correlation was shown between the orientation degrees estimated based on multivariate data analysis of the spectra and the Young’s moduli of the composites [XV, XXXI, XXXIV].

2. Flame retarded self-reinforced composites were prepared for the first time. It was shown that less than the half amount (9%) of additives is sufficient to achieve self-extinguishing behaviour (i.e V-0 rating) in self-reinforced polypropylene composite than in non-reinforced polypropylene, which is owing to a previously unknown flame retardant mechanism. The efficient flame retardancy is provided by the compact surface-protecting layer, which is formed as a result of the synergistic action of the heat-initiated expansion (foaming) of the intumescent flame-retarded polymer and the simultaneous heat-initiated shrinking (relaxation) of the reinforcing fibres, and the structure of which is influenced by the orientation degree of the polymer fibres [III, IV, VIII, X, XIV, XVIII, XXVI, XXVIII, XXIX].

3. Recycled composites of increased value were developed from mixed automotive polyolefin waste by self-reinforcement (five-fold tensile strength, two-fold flexural strength and four-fold falling weight impact perforation energy compared were achieved to the non-reinforced recyclate). In the case of self-reinforcement, also the synergism proposed in Thesis 2 was applicable but its efficiency, due to the impurities, was somewhat less [I, II, IV, VI, VII, XVI, XVII, XVIII, XXV].

4. Flame retarded self-reinforced injection moulded product was prepared for the first time. The prominent consolidation quality of the thus prepared composites was ascertained. With the addition of 15 wt% flame retardant the peak of heat release rate was reduced by 50%, furthermore, the limiting oxygen index was significantly increased (to 29.5 vol%). A four-fold increase was achieved in tensile strength and a six-fold increase in tensile modulus when the flame retarded self-reinforced injection mould products were compared to the matrix material [XXIX, XXXI].

5. Multifunctional – plasticizing and flame retarding – effect was shown for phosphorus-containing polyols (Exolit OP560 and glycerol-phosphate) when applied in starch. Using these additives a flame retarded material can be obtained that is processable by thermomechanical methods. With the combination of the flame retarded thermoplastic starch (containing the mixture of glycerol and OP560 in a ratio of 11 to 15) and 27 wt% ammonium-phosphate-treated flax fibres, self-extinguishing (V-0 classified) biocomposites can be obtained without using additional flame retardants [II, V, IX, XVII, XIX, XXVII].

6. It was shown that polyactic acid can be flame retarded by blending it with glycerol-phosphate-plasticized thermoplastic starch, which functions as charring agent in the
system. In the case of polylactic acid/thermoplastic starch blend of a mass ratio of 4 to 1, an increased limiting oxygen index and a 20% reduction in the peak of heat release rate were achieved. In addition, the flame retarded blend have higher tensile and flexural strength, and greater elongation at break (by 15, 30 and 30%, respectively) then their reference systems, which can be explained by the improved compatibility of the combined polymers [XI, XXXII].

7. A new phosphorus-containing silane adduct (PSil) was synthesized by the addition reaction between a phosphorous polyol (Exolit OP560) and 3-(triethoxysilyl)propyl isocyanate. The product was applied as a reactive surface-treating agent to flame-retard chopped flax fibres. It was shown by thermogravimetric analyses that the surface treatment with the newly synthesized PSil largely facilitates the charring of flax fibres without reducing their thermal stability. This phenomenon was explained by the advantageous combined action of P and Si atoms in the charring polymer phase. By incorporating the PSil-treated flax fibres into a polylactic acid/thermoplastic starch blend of 4 to 1 weight ratio, the necessary amount of flame retardant for achieving self-extinguishing biocomposites could be reduced to 10% [IV, XI, XIII, XXXII].

8. Flame retarded self-reinforced polylactic acid biocomposite was prepared for the first time. This composite reaches the self-extinguishing (V-0) category, its limiting oxygen index is significantly higher (34 vol%), furthermore, its peak of heat release rate (measured at 50 kW/m² heat flux) is around the half of the corresponding values of the additive-free polylactic acid and of the self-reinforced composites made thereof. By applying self-reinforcement and flame retardancy, the impact resistance (characterized by perforation energy) of the inherently rigid polylactic acid increased multi-fold (about thirty-fold) [IV, XII, XVIII, XX, XXX, XXXIII].
6 APPLICATION OF THE RESULTS

The recycling of polymer wastes was promoted by an EU7 framework project entitled “Magnetic sorting and ultrasound sensor technologies for production of high purity secondary polyolefins from waste” (W2PLASTICS, No. 212782), and by Recytech project (TECH_08_A4) called "Elaboration of Recycling Technologies for non-metallic automotive and electronic wastes avoiding further deposition of organic materials subsidized by the "National Technology Programme" of Hungarian National Office for Research and Technology.

Significant parts of the research work described in this PhD thesis was performed on the request of industrial partners, including the Cargo-Lakk Festékipari Kft, the Magyar Suzuki Zrt, the full biocomposite developer and manufacturer Meshlin Composites Zrt, and the aircraft manufacturer Dassault Aviation SA company, thus there is a good chance for direct utilization of the results in various segments of the industry.

7 PUBLICATIONS

7.1 Related scientific book chapters

[I] K. Bocz, H. Erdélyi, P. Anna, M Wladyka-Przybylak, K. Bujnowicz, G. Marosi Fibre reinforcement and fire retardancy in polypropylene
In Recent Advances in Flame Retardancy of Polymeric Materials, Editor: C. A. Wilkie

[II] G. Marosi, B. Szolnoki, K. Bocz, A. Toldy
Reactive and additive phosphorus-based flame retardants of reduced environmental impact

[III] K. Bocz, T. Bárány, Gy. Marosi
Development of flame retarded self-reinforced polymer composites
In Flame Retardancy and Protection of Materials: Recent Advances and Current Perspectives, Editor: S. Duquesne
Springer, France, 2014 in press

[IV] G. Marosi, B. Szolnoki, K. Bocz, A. Toldy
Fire retardant recyclable and bio-based polymer composites
In Novel fire retardant polymers and composite materials: Technological advances and commercial applications, Editor: D. Y. Wang
7.2 Related scientific articles

IN IMPACT FACTOR JOURNALS

[V] B. Bodzay, B.B. Marosfoi, T. Igricz, K. Bocz, G. Marosi
Polymer degradation studies using Laser Pyrolysis-FTIR microanalysis
IF: 2.311, I: 26 (21)

Development of flame retarded self-reinforced composite from automotive shredder plastic waste
Polymer Degradation and Stability 97 221-227 (2012)
IF: 2.770, I:11 (7)

Upgrading of recycled polypropylene by preparing flame retarded layered composite
IF: 2.294, I: 4 (2)

Self-extinguishing polypropylene with a mass fraction of 9% intumescent additive – A new physical way for enhancing the fire retardant efficiency
Polymer Degradation and Stability 98 79-86 (2013)
IF: 2.633, I:13 (7)

Flame retardancy of biocomposites based on thermoplastic starch
Polimery 58 (5) 385-394 (2013)
IF: 0.617, I: 5 (1)

[X] K. Bocz, T. Igricz, M. Domonkos, T. Bárány, G. Marosi
Self-extinguishing polypropylene with a mass fraction of 9% intumescent additive II - Influence of highly oriented fibres
Polymer Degradation and Stability 98 2445-2451 (2013)
IF: 2.633, I: 2 (0)

Flax fibre reinforced PLA/TPS biocomposites flame retarded with multifunctional additive system
Polymer Degradation and Stability 106 63-73 (2014)
IF: 3.163, I: 7 (4)

Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance
IF: 3.071 (in 2014), I: 4 (3)
Development of natural fibre reinforced flame retarded epoxy resin composites
*Polymer Degradation and Stability* 119 68-76 (2015)
IF: 3.163 (in 2014), I: 2 (0)

[XIV] K. Bocz, T. Krain, G. Marosi
Effect of particle size of additives on the flammability and mechanical properties of intumescent flame retarded polypropylene compounds
*International Journal of Polymer Science, 2015, article ID:493710, 7 pages*
IF: 1.195 (in 2014)

Non-destructive characterisation of all-polypropylene composites using polarized Raman spectrometry
*Materials Letters, under review*
IF: 2.489 (in 2014)

**FURTHER RELATED ARTICLES**

[XVI] Bocz K., Bodzay B., Toldy A., Bárány T., Marosi G.
Égésgátolt szöveterősítéses kompozitok készítése vegyes műanyag hulladékból
*Műanyag és Gumi* 48 84-87 (2011)

[XVII] Pataki H., Patyi G., Bocz K., Bodzay B., Marosi G.
Polimer-alapú gyógyszertanológiai és környezetbarát fejlesztések
*Műanyag és Gumi* 48 451-454 (2011)

[XVIII] Bocz K., László Zs., Bárány T., Víg A., Marosi G.
Égésgátolt önerősített kompozitok fejlesztése
*Műanyag és Gumi* Évkönyv 11 72-77 (2013)

Lenszál erősítésű, termoplasztikus keményítő kompozitok égégsátlási lehetőségeinek vizsgálata

[XX] Bocz K., Domonkos M., Igricz T., Kmetty Á., Bárány T., Marosi G.
Önerősített politejsav kompozit kifejlesztése és égégsátlása
*Műanyag és Gumi* 50 463-466 (2013)
7.3 Further articles

[XXI] B. Bodzay, K. Bocz, Zs. Báráki, G. Marosi
Influence of rheological additives on char formation and fire resistance of intumescent coatings
*Polymer Degradation and Stability* 96 (3) 355-362 (2011)
IF: 2.769, I: 24 (23)

In vitro dissolution-absorption evaluation of an electrospun cyclodextrin-based formulation of aripiprazole using microFlux™
IF: 3.650 (in 2014)

Comparison of spray drying, electroblowing and electrospinning for preparation of Eudragit E and Itraconazole solid dispersion
IF: 3.650 (in 2014)

Politejzav alapú habok szuperkritikus széndioxidral segített extrúziós előállítása és vizsgálata
*Polimerek* (2015) accepted

7.4 Oral presentations

[XXV] K. Bocz, A. Toldy, B. Bodzay, F. Ronkay
Multilayer flame retarded composites from recycled automotive shredder plastic waste
*14th European Conference on Composite Materials*
7-10. June 2010., Budapest, Hungary

New factor in mechanism of fire retardancy: Synergism of fibres with intumescent flame retardants
*7th International Conference on Polymer Modification, Degradation and Stabilization*
2-6. September, 2012., Prague, Czech Republic

Flame retardancy of natural fibre reinforced fully biodegradable composites
*23rd International Federation of Associations of Textile Chemists and Colourists International Congress*
8-10. May, 2012., Budapest, Hungary

[XXVIII] K. Bocz, Zs. László, T. Bárány, G. Marosi
Development of flame retarded self-reinforced polymer composites
*14th European Meeting on Fire Retardancy and Protection of Materials*
K. Bocz, G. Marosi
Development of flame retarded self-reinforced polypropylene composites
Korea-Japan Joint Workshop on Advanced Materials
16. December, 2013., Hamamatsu, Japan

K. Bocz, M. Domonkos, T. Igricz, Á. Kmetty, T. Bárány, G. Marosi
Preparation and characterisation of flame retarded self-reinforced poly(lactic acid) composites
2nd International Conference on Biobased Polymers and Composites

K. Bocz, D. Vadas, T. Á. Kmetty, T. Bárány, G. Marosi
Oriented polymer fibres for improving the flame retardant efficiency of intumescent additive systems
8th International Conference on Polymer Modification, Degradation and Stabilization
31. August- 4. September, 2014., Portorož, Slovenia

K. Bocz, D, Vadas, B. Szolnoki, G, Marosi
Synthesis and application of multifunctional flame retardant additives
FLARETEX Scientific Workshop on „Characterisation of flame retardant textile and related materials”
7. October, 2014., Dubrovnik, Croatia

K. Bocz, D. Vadas, G. Marosi
Preparation and characterisation of flame retarded self-reinforced poly(lactic acid) composites
FLARETEX Scientific Workshop on „Advances in Flame Retardancy of Polymeric Materials”
4-6. February, 2015., Madrid, Spain

7.5 Poster presentation

K. Bocz, A. Farkas, D. Vadas, T. Bárány, G. Marosi
Non-destructive characterisation of structure of reinforcing fibres of all-polypropylene composites using polarized Raman spectrometry
Augsburg-Budapest PhD Workshop