Development of Innovative and Environmental Ways for Reactive Fire Retardancy of Polymer Systems Reinforced with Bio-fibres

Final report of the project

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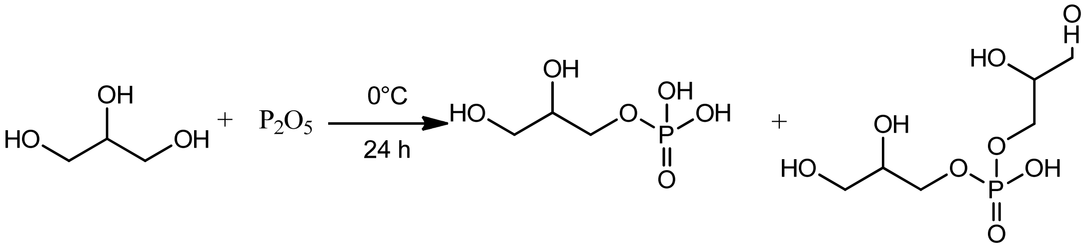
The aim of this project was to develop environmental and fire-safe alternative of the currently used flammable polymeric materials. The main approach to achieve this target included the application of new reactive fire retardancy (FR) methods for modifying novel polymer composites, development of FR-active biofibre-reinforced and FR-synergistic self-reinforced polymers. The role of modified interfaces/interphases (IP) in governing the structure-property relationship also needed to be determined.

1 Synthesis and modification of additive systems

Additives of reactive functionality and efficiency for flame retardant and interface modification were synthesized. For the up-scaling of their syntheses, computer controlled reactor, equipped with in line Raman/FTIR detection was applied.

1.1 Reaction of inorganic phosphorus compounds with organic substances

For the flame retardation of biopolymers, mainly of thermoplastic starch and PLA, P-containing FR agents were synthesized. As TPS can be easily plasticized by glycerol, the aim was to prepare glycerol phosphate (GP), which can serve both as plasticizer and flame retardant [1]. GP was synthesized through the green, addition-type reaction between glycerol and phosphorus pentoxide (see in **Scheme 1**). For neutralizing the formed acidic P-bonded hydroxyl groups, ammonia gas had been passed through the reaction mixture until the increase of the pH stopped at pH 4.5.



Scheme 1 Reaction between glycerol and phosphorus pentoxide

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

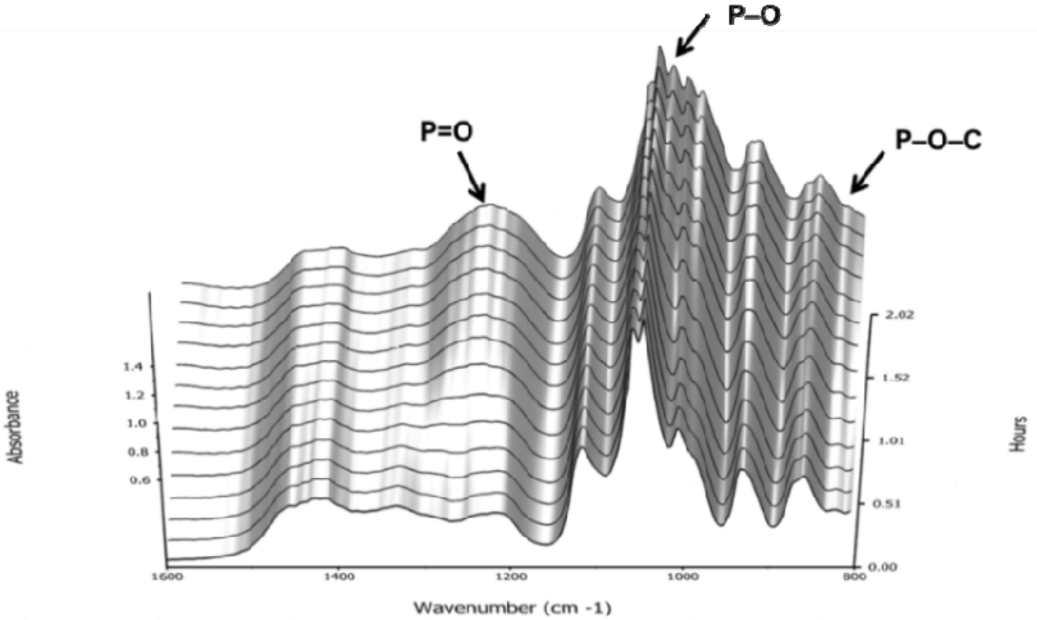


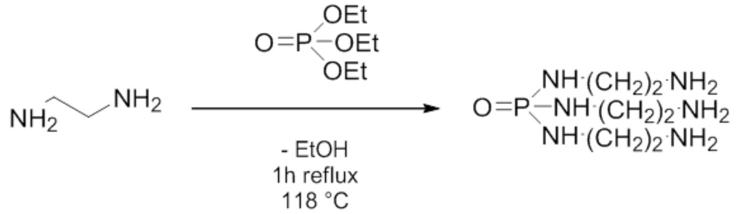
Figure 1 Joint IR spectra obtained during the reaction between glycerol and phosphorus pentoxide

Besides glycerol phosphate, several aliphatic and aromatic, mono- and bifunctional compounds were also synthesized with the reaction of the corresponding alcohols or phenols with phosphorus pentoxide, and applied as additive-type flame retardants in bio-based epoxy resins. By their application in low (up to 10 mass%) concentrations, the flame spreading rate of the reference epoxy composition could be significantly decreased.

1.2 Synthesis of organophosphorus reactive FR compounds by green synthesis methods

Phosphorus-containing aliphatic and aromatic amines were synthesized, which can act both as flame retardants and as crosslinking agents in epoxy resins. In general, these materials are prepared by the very exothermic reaction between phosphorus(oxy)chlorides and amines, producing large amount of halogenated and corrosive by-products. We aimed at finding an alternative route for synthesizing such amines, possibly suitable for industrial scale-up.

As first trial, the transamidation of triethyl phosphate (TEP) was attempted with ethylene diamine (EDA), according to the **Scheme 2**:

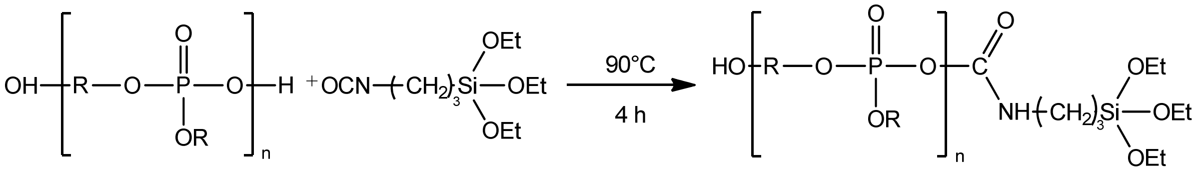


Scheme 2 Synthesis of TEDAP from $P(O)(OEt)_3$

As aromatic P-containing amines, TMPDAP and TOPDAP were synthesized, starting out from *m*-phenylene diamine and *o*-phenylene diamine, respectively, applying the same reaction method. The synthesized compounds were analysed by infrared spectrometry [2], ^{31}P-NMR and MALDI-TOF. The flame retardant efficacy of the synthesized components was investigated in a pentaerythritol-based epoxy resin system [3]. The prepared flame retardant amine proved to be more effective FR than other, commonly applied reactive (DOPO) and additive (APP) type flame retardants. In carbon fibre reinforced composites the application of TEDAP as crosslinking agent resulted in prominent FR properties, despite the fact that carbon fabric plies hinder the intumescence of the resin [4].

1.3 Reaction of siloxane compounds with cellulose/starch

Reactive modification of the reinforcing cellulose based biofibres was carried out in order to improve the adhesion between the matrix and reinforcing fibres. For a multipurpose application, a novel reactive modifying agent was synthesized by a simple addition reaction between a commercial phosphorus polyol, Exolit OP560 and 3-(triethoxysilyl)-propyl isocyanate (TESPI). The phosphorous silane adduct (PSil, **Scheme 3**) acts both as stabilizer and compatibilizer, furthermore as effective FR agent for the biofibres [1].



Scheme 3 Synthesis of the reactive phosphorous surface modifier (PSil)

It was shown that by the application of PSil for surface-treatment of natural fabrics, both the thermal stability and the charring capability of the biofibres increases significantly resulting in better processability but significantly reduced flammability compared to unmodified biofibres.

1.4 Synthesis of Diels-Alder adduct-type interfacial modifiers for nanofillers

The aim of the present task was to prepare in-situ nano-sized flame retardant (n-$Mg(OH)_2$), applicable in several thermoplastic polymers. The idea was the modification of linoleic acid with maleic anhydride through Diels-Alder cycloaddition and use as emulsifier in the synthesis of nano FR. The aim was to precipitate nano-sized $Mg(OH)_2$ from $MgCl_2$ (by slowly adding saturated NaOH solution) in the presence of the prepared Diels Alder adduct, as it can promote the emulsification of the reactants and thus the formation of FR additive of decreased particle size. Toluene was applied as precipitant of nano-$Mg(OH)_2$. Despite the insolubility of the forming NaCl by-product in toluene, due to the surfactant effect of the Diels-Alder adduct no chlorine-free nano FR could be prepared, thus the further application of the prepared compounds was discarded.

2 Preparation of environmentally friendly FR composites

Broad selection of flame retarded green composites were developed by combining components (matrix materials, reinforcing agents and flame retardants) originating from secondary or renewable resources. Recyclability and biodegradability aspects prevail in the composite design phase thus environmentally friendly final products were developed.

2.1 Composites comprising recycled matrix

With the aid of different composite manufacturing techniques such as injection moulding, two-component injection moulding, hot-compression of multi-layered structures, etc. the upgrading recycling of mixed plastic waste was successfully performed. Composites comprising of secondary raw materials (even above 80 mass%) accompanied with improved flame retardancy and mechanical performance were developed [5,6,7,8].

2.2 Composites comprising recycled FR components

Recycled polymers (such as PUR and rubber), originating from automotive shredder waste, were effectively applied as components of FR-additive systems. Despite their inherent easy flammability, both PUR and rubber show intensive charring in presence of phosphorus, as a result, the introduction of these components significantly improved the FR performance of composites made of recycled polyolefines [8,9,10,11].

2.3 Composites comprising biofibre reinforcement

Cellulose and starch can be used as inexpensive, biobased fillers in different polymer systems. Beside their filler function they can act also as reinforcement, or as charring agents in terms of flame retardancy. Cellulose was applied in a thermoplastic elastomer, in order to improve the tensile and bending properties, while maintaining the outstanding elastic properties [12]. The combination of the two kinds of materials resulted in improved strength and the results of the cyclic tests revealed that the individual deformation components changed in a direction of greater energy efficiency.

Sorbitol-based epoxy resin, originating from renewable resources, was reinforced with different natural fabrics, comprising hemp, jute and flax of different weave types [13]. Due to the natural fabric reinforcement all the examined mechanical properties increased significantly, however, the glass transition temperature of the prepared composites proved to be fairly sensitive to the water-content of the embedded biofibres.

We have shown both in thermoplastic [14,15] and thermosetting structures (**Table 1**), that natural fibres can function not only as suitable reinforcing agents but their charring ability can significantly contribute to the flame retardant efficiency of a phosphorous based additive system at the same time. Furthermore, as a new concept, the reinforcing natural fibres were successfully utilized also as physical [14] (via capillary) or reactive (when chemically bonded to the surface hydroxyl groups) carriers of flame retardant species [1].

Table 1 Cone calorimetric data of the reference and flame retarded composites

	TTI (sec)	pHRR (kW/m^2)	pHRR time (sec)	THR (MJ/m^2)	residue (%)
NHF_ref	41	1342.22	113	84.91	1.8
THF_ref	40	994.29	109	62.63	7.4
SiTHF_ref	31	1004.63	107	77.09	9.6
NHF_FR	33	777.74	107	45.89	20.1
THF_FR	30	674.48	123	45.62	20.4
SiTHF_FR	30	620.77	153	49.52	23.2

NHF: non-treated hemp fabric, THF: thermotex-treated hemp fabric, SiTHF:sol-gel and thermotex-treated hemp fabric. Ref stands for reference epoxy matrix, while FR for flame retarded epoxy matrix of the composites

2.4 Fully recyclable composites

Self-reinforced PP composites (SRCs) of prominent mechanical performance were developed in flame retarded form, which, being composed entirely from PP compounds, can be easily recycled by common thermo-mechanical methods. As low as 9 mass% additive concentration, less than half of the normally necessary amount of intumescent flame retardants in PP, proved to be enough to achieve the UL94 V-0 classification in the case of a PP SRC. This result is accompanied with noticeably higher LOI values and significantly lower heat release rates comparing to the non-reinforced PP samples with the same intumescent flame retardant content [16]. The outstanding FR efficiency was explained by the physical interactions between the expanding process caused by intumescent fire retardants and the shrinking of the highly-stretched reinforcing tapes. Polymer systems with these components, when exposed to heat, form a special, compact charred surface layer, which hinders the release of pyrolysis gases and where the flame retarding action of P- and N-containing compounds occurs at smaller volume, and thus at higher concentration, resulting in effective fire extinction [17]. The observed new synergism was investigated in further polymeric systems [18] such as in SRCs composed of secondary [7] and renewable raw materials (PLA [19]). Self-reinforcement proved to be an adequate method to overcome the inherent brittleness of PLA (especially when flame retarded) and to adjust prominent impact resistance (an impact perforation energy as high as 16 J/mm was achieved, as shown in **Figure 2**) to the biopolymer without compromising its strength, stiffness or biodegradability.

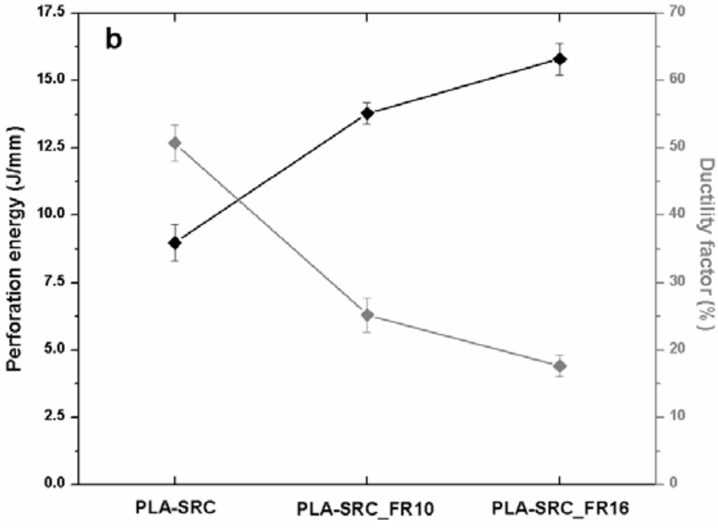


Figure 2 Perforation energy and ductility factor of flame retarded PLA-SRCs

2.5 Fully biodegradable composites

Fully biodegradable composites were manufactured on the one hand by applying the concept of self-reinforcement on the biodegradable PLA [19], and on the other hand by combining TPS and PLA (or their blend) as matrix material with reinforcing natural fibres. Novel phosphorus-containing additives were synthesized with the aim to provide flame retardancy to natural fibre reinforced biocomposites in an economical way. A phosphorus-containing polyol, glycerol phosphate (GP), was synthesized and used as plasticizer to obtain thermoplastic starch of reduced flammability [14]. This modified starch proved to have enhanced char promoting capability when applied in PLA, and thus provided improved flame retardancy to PLA/TPS blends. A newly synthesized reactive flame retardant modifier (PSil) of flax fibres (**Figure 3**) allowed the phosphorus-silicon synergism to be utilized. The harmful candle-wick effect of the cellulosic 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. Additionally, the novel phosphorus containing species, when being present both on the surface of the reinforcing flax fibres (PSil) and in the biodegradable matrix material (GP), provided adequate strength and stiffness to the effectively flame retarded biocomposites [1].

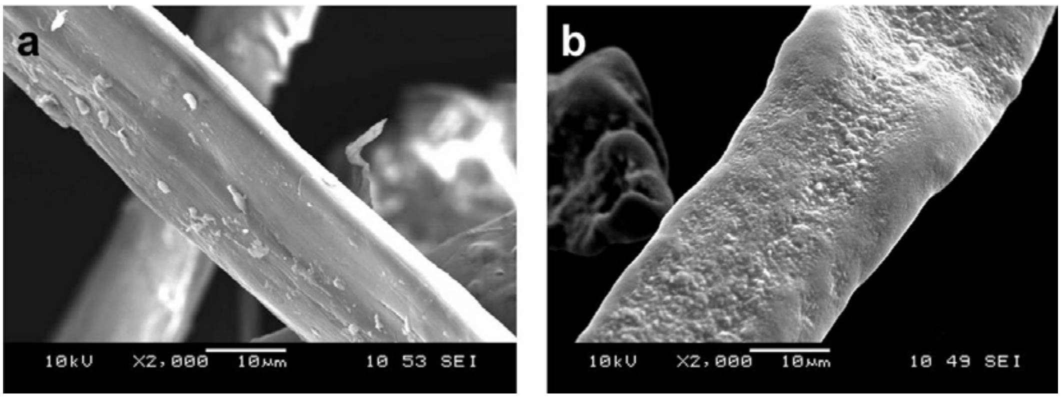


Figure 3 SEM images of the surface of (a) neat and (b) PSil-treated fibres.

3 Modification of interphases

Phosphorous flame retardants act as fillers or plasticizers in polymer matrices often accompanied with compatibility and migration issues, respectively. In this project, **modified interphases** were developed aiming at improved compatibility and avoidance of undesirable migration effects.

3.1 Nanocompatibilization

The success of the synthesized reactive FR (e.g. TEDAP) in phosphorylated epoxy resin (PEP) suggested the idea of using this polymer as FR additive in thermoplastics such as polypropylene (PP). The epoxy resin and PP are, however, seriously incompatible (see **Figure 4 a**). As a solution, organo-clays of high aspect ratio (500-1000:1) and large surface area (700-800 m^2/g) were added, aiming at nanocompatibilization. The plate-like nanofillers created sites for interaction with the polymer chains leading to the formation of a thermodynamically stable organic-inorganic multilayer interphase. Beyond the thermodynamic factors the increased viscosity and local shear forces in presence of nanofillers also contribute to the improvement of the miscibility of incompatible polymer phases [20,21]. The impressive result can be seen in **Figure 4 b**. Furthermore, the montmorillonite nanoclays, introduced to improve dispersion, proved to be advantageous also from flame retardancy aspects. Improved FR performance was achieved comparing to the reference systems, which was ascribed to homogeneous char forming action of PEP interlayer. The prospect of this nanocompatibilization concept for the fire retardancy of environmentally friendly thermoplastic polymers is discussed in two book chapters [21,22].

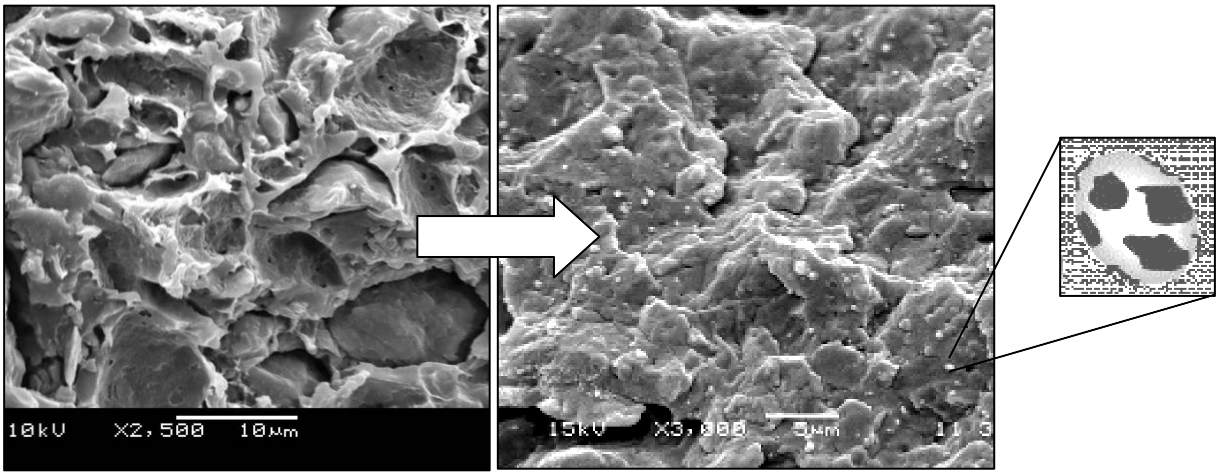


Figure 4 Compatibilization of immiscible PP and PEP polymer phases with nanoclay: a) SEM image of the blend without montmorillonite, b) SEM image of the blend with montmorillonite, c) scheme of the interfacial region with montmorillonite nanolayers

3.2 Reactive compatibilization

In order to improve the adhesion between reinforcing fibres and embedding matrices, reactive modification of the reinforcing cellulose based biofibres was carried out. Besides the application of common coupling agents such as vinyl silanes and aminosilanes, a new phosphorus containing silane (PSil) was synthesized, which, besides its compatibilizing effect, allowed the well-known P-Si synergism to be utilized and provided significantly enhanced fire performance to biocoposites comprising PSil-treated biofibres [1]. It was evinced that the simultaneous presence of P and Si in the treating agent results in well-balanced thermal behaviour of natural fibres; namely the thermal stabilizing Si effectively protects the cellulosic substrate from P induced early decomposition, thus eliminates the occurrence of thermal stability issues during processing.

3.3 Skin technology

Skin technology was investigated as a simple alternative to the responsive interlayers. Similarly to the protective coatings formed generally by laminating, co-injection moulding and co-extrusion processing methods or even by plasma treatment, the electrospinning method, was proposed for performing skin technology. Silica nanofibrous mats, prepared by sol-gel process, were deposited on the surface of PLA sheets. Because of their low thermal conductivity, electrospun nanofibre mats were found to act as a protective surface that delays ignition and distributes the intensity of heat emission in time (**Figure 5**).

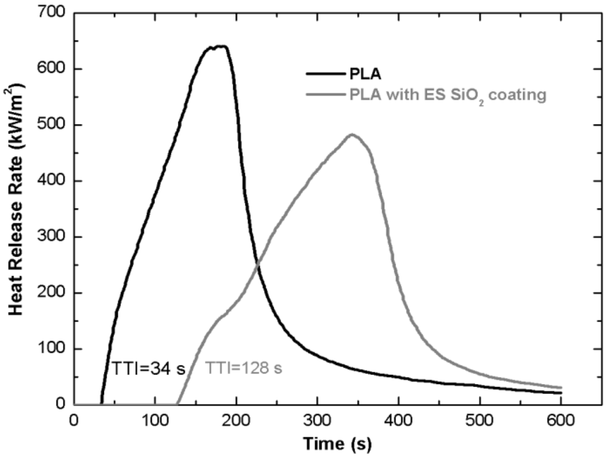


Figure 5 Heat release rate curves corresponding to PLA sheet without and with electrospun fibrous nanosilica coating

4 Development of new analytical methods

New analytical methods were developed, which, either due to their decreased time and/or sample demand or due to their increased sensitivity outperform the currently available common analytical techniques.

4.1 High speed microanalysis for identifying the degradation products in the gas phase

The lases pyrolysis(LP)-FTIR coupled method (**Figure 6**), recently developed in our research group, was successfully adapted to the flame retarded biocomposites prepared in this project to analyse the gaseous products evolved during their thermal degradation. Both the gas phase and the solid-state flame retarding action of the applied phosphorous flame retardants could be followed by LP-FTIR method. The performance of this new method was compared to the traditional techniques commonly used in the field of fire retardancy such as with cone calorimetry and also with the more relevant competitor, the TG-FTIR coupled method. On the example of TPS based samples we evinced that the obtained LP-FTIR spectra of TPS based samples fit well to the previously reported TG-FTIR features of glycerol plasticized starch, additionally, using LP-FTIR method also the vapours of glycerol could be unambiguously detected. When compared with the TG-FTIR coupled method, where the glycerol can condense between the TG and FT-IR equipments, in the case of LP-FTIR the direct connection between the pyrolysis zone and the analysing unit allows the immediate and in situ analysis of the degradation products without loss of any components. It has to be also highlighted that, in contrast to the much more time-consuming TG-FTIR method (several hours), the LP-FTIR experiments generally took only less than 1 minute per sample [14].

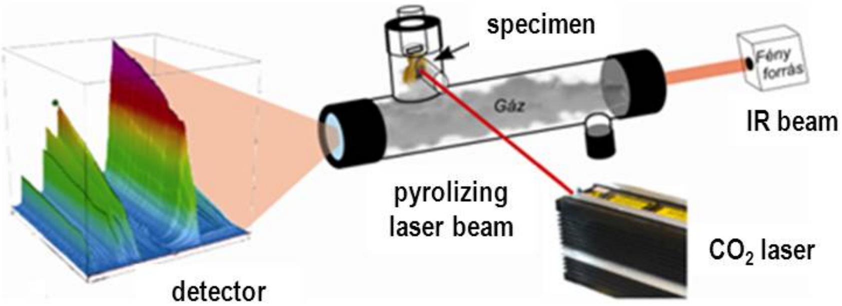


Figure 6 LP-FTIR setup

4.2 High-resolution qualitative characterisation of multicomponent polymer systems

A novel evaluation method was developed for Raman microscopic quantitative characterization of polymer systems. Heterogeneous, multicomponent systems, such as recycled plastics and biopolymers blends, were investigated by Raman mapping, which is capable of detecting the components being present even in low concentration [23,24,]. An automated method was elaborated for pixel classification, which helps to detect the different polymer phases, crystallinity, degraded areas, impurities, etc. present and enables rapid assignment of each pixel to the appropriate chemical composition. Several methods were tested to provide a basis for the pixel classification, among which multivariate curve resolution-alternating least squares (MCR-ALS) provided the best results. The MCR-ALS based pixel identification method was then used for the quantitative characterization of each component, where it was found that the automated method yields accurate results in a very short time [25].

4.3 Complex analytical protocols

Complex analytical protocols were elaborated and applied for comprehensive analyses of the prepared multicomponent systems and structural features [26,27]. (Micro-) Thermal analytical and (micro-) Raman spectrometric methods combined with chemometric evaluation supported the mechanistic understanding of the relevant flame retardant actions.

5 Relationship between the effect of additives and thermal degradation

The effect of all the FR modifications was examined on the thermal stability and decomposition pathway of the issued substrates, i.e. natural fibres and polymer matrices. The chemical changes that occur during the combustion and the degradation products were also evaluated. Based on comprehensive analytical results obtained using thermogravimetric analysis, the recently developed laser pyrolysis-FTIR coupled method, mass loss type- and conventional cone calorimetry, differential scanninc calorimetry, UL-94 and LOI measurements, significant consequences regarding FR mechanisms were drawn as well.

5.1 Comparison of the efficiency of reactive and additive type flame retardants

The effect of additive and reactive-type FRs was compared in the case of a thermoplastic and a thermosetting matrix material, and reviewed in a book chapter [22]. In thermoplastic polyurethane, the prepared multicomponent additive system proved to be more effective in terms cone calorimetric measurement (**Figure 7**), but reached the same (V0) classification as the reactive one, which provides a much more simple, and cost-effective way for the flame retardancy of TPU [28].

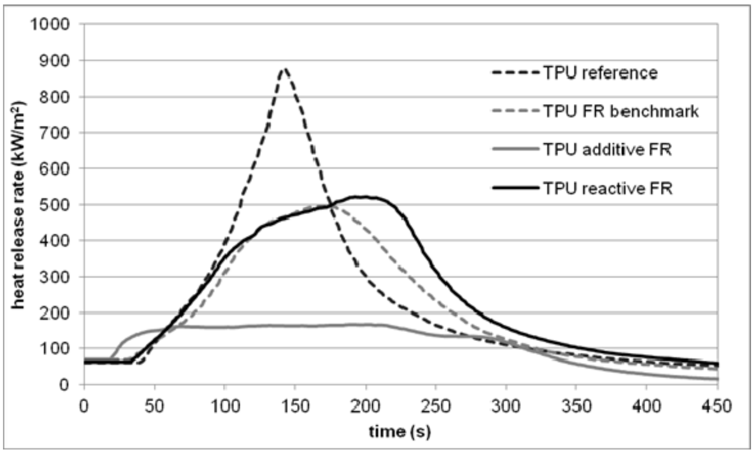


Figure 7 Heat release rate results of the chosen flame retarded systems compared to reference TPU and flame retarded benchmark TPU system

In the case of epoxy resin matrix material, the synthesized reactive amine-type flame retardant (TEDAP) proved to be much more effective than the commonly applied reactive FR (DOPO) and the additive APP (**Figure 8**) [3]. In the case of the TEDAP, V0 could be reached at even 3 mass% P-content, while for APP 5 mass% was necessary, and in the case of DOPO only HB ratings were reached.

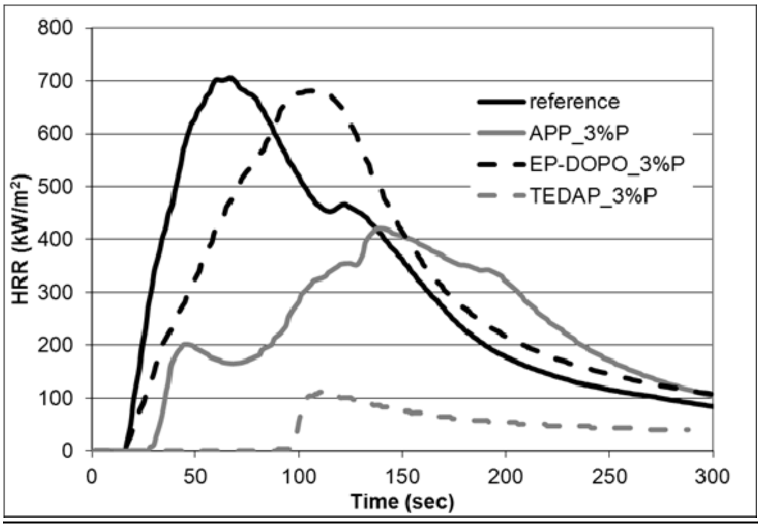


Figure 8 Comparison of the heat release curves of different flame retardants at 3 mass% P-content

5.2 *Effect of FR treatment of natural fibres*

Phosphorus compounds such as ammonium phosphates [14,15], Si-based coupling agents such as vinyl silanes and aminosilanes and their combination, a newly synthesized phosphorous silane (PSil [1]), were studied as surface treating agents for natural fibres.

The phosphorous compounds effectively initiated the charring of fibres and promoted the formation of solid residue, at the same time, significantly (even by 90°C) lowered the initial decomposition temperature and increased the weight loss rate of the fibres indicating the P induced dehydration and decomposition of cellulose. It was found that the earlier (low temperature) liberation and dissipation of flammable gases results in decreased amount of volatile combustive products, i.e. fuel supply necessary for combustion, and consequently in increased char yield. The reduced thermal stability, however, can be a serious issue, both from mechanical and aesthetic aspects, when the natural fibres are intended to be used as fillers or reinforcements in polymer composites, especially when thermoplastic matrices with processing temperatures above 160 °C (such as PP, PA, PET and also PLA) are considered.

The surface treatment with silanes resulted in increased thermal stability, as expected, however did not exhibit considerable flame retarding action. Therefore, the application of a combined treatment, by utilizing P and Si synergism, was elaborated in this project for the flame retardant modification of reinforcing natural fibres.

When the synthesized phosphorous-silane (PSil) was applied as surface treating agent, significant charring activity of biofibres was achieved (47% charred residue at 500°C in TGA, **Figure 9**) without noticeable decrease of the thermal stability of the cellulosic fibres. Furthermore, the harmful candle-wick effect of the applied fibrous substances ceased completely when PSil-treated natural fibres were embedded in polymer matrix [1].

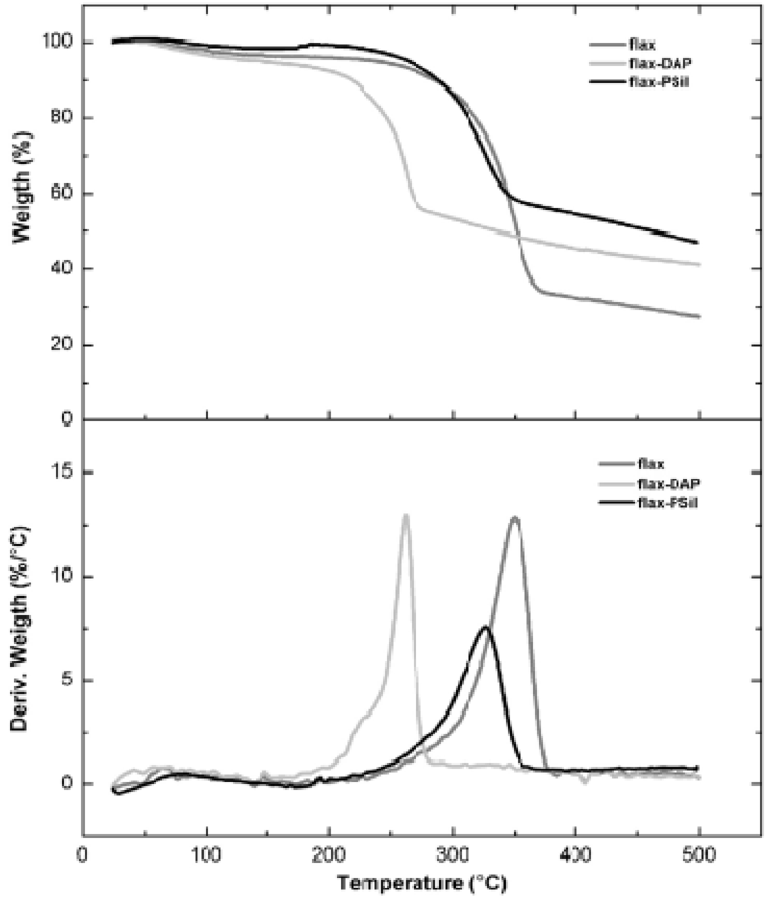


Figure 9 TG and DTG curves of neat, DAP-treated and PSil treated flax fibres

5.3 *Effect of nanoadditives*

The effect of nano-sized mineral clays of different morphology (plate-like: OMMT and fibrous: PAL, SEP) were investigated on the char formation and fire resistance of intumescent flame retarded polymer systems. It was observed that the addition of nanoparticles changes the char formation process, the height, the mass, the structure and also the fracture behaviour of the protecting shield, and therefore the fire protecting efficiency of the expanded char. In the case of palygorskite (PAL) the catalytic effect of Fe ions accelerated the thermal decomposition, therefore the fire resistance of the PAL containing system decreased. The plate-like montmorillonite reduced the extent of the intumescent char, whereas also improved the mechanical and sustained heat resistance of the fire protecting shields. The fibrous sepiolite of low Fe content assisted the development of an efficient protecting shield, which exhibited optimal cell structure, suitable thickness, and thus ensured increased heat-insulating performance [29].

The plate-like MMT proved to have prominent compatibilizing effect in PP – epoxy resin system. It was found that both thermodynamic factors and the modified rheology of the MMT containing system contribute to the improvement in the miscibility of the inherently incompatible polymer phases [21].

5.4 *Effect of FR-fibre interactions*

The FR-fibre interactions were studied in several composite structures both regarding the matrix material (epoxy, PLA, TPS, PP), reinforcing agents (carbon fabric, natural fibre and fabric, PP fabric, PLA multifilament) and FR species (reactive and additive types).

In the case of flame retarded carbon fabric reinforced epoxy composites, it was found that the rigid carbon fabrics hinder the development of a highly expanded foam structure and thus a more compact char layer is formed on the surface of the sample. As the heat insulating property of an intumescent char mainly depends on its thickness (a thicker layer gives more insulation), the formation of compact foams is associated with higher heat release rates during combustion. Still, the UL94 V-0 rating could be ensured when P-containing crosslinking agent, TEDAP, was applied [4].

Natural fibres can act not only as reinforcement, but also as charring agents in phosphorus-based flame retardants both in thermoplastic, and thermosetting matrices [14,15]. It was shown that, as a result of the reaction between the phosphorous species and the cellulosic fibrous substance, noticeably greater amount and mechanically stable fire protecting char forms, which acts as effective barrier against heat and fuel transport. It was evinced that by utilizing this beneficial interaction, smaller amount of FR additives is needed to achieve the required levels of flame retardancy in the studied polymeric systems.

Noticeably enhanced flame retardancy of multilayered self-reinforced composites, flame retarded with common ammonium polyphosphate based intumescent system, was observed by our research group [16]. The observed novel flame retardant synergism between intumescent additive system and highly oriented polymer fibres was comprehensively investigated. Based on the extensive analyses, performed to study the ignitability, char forming process, burning behaviour and postcombustion remains of flame retarded SRCs, important conclusions could be 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 mass% IFR). As a consequence of the shrinkage, which is fairly noticeable both during horizontal and vertical ignition, the elongation of the molten specimens, and thus the formation of virgin polymer surfaces, is hindered. In this case the forming compact charred surfaces can act as a barrier of increased efficiency against heat and fuel transport, resulting in immediate fire extinction. In a cone calorimeter, where the composites are exposed perpendicularly to heat flux, further effects of the embedded PP tapes could be confirmed. It was concluded that the embedded (additive-free) PP fabrics hinder the migration of flame retarding substances towards the top of the polymer bulk, resulting in somewhat higher initial rates of heat emission, but suppressed peak of heat release rates and higher amount of residual chars compared to their unreinforced counterparts of the same compositions. Also the post-combustion charred residues are of different character for flame retarded PP mixtures and SRCs. In the case of compounded flame retarded PP samples loose foam structures were observed, which was attributed to the intensive gas release and instantaneous foaming process occurring at the initial stage of burning. While in the case of multilayered SRCs the abrupt gas escape and expansion is hindered and the char formation process became prolonged in time. Mainly closed cell structure is characteristic for such char. Compression tests showed evidence for the more compact and rigid character of the charred residues obtained after combustion of the flame retarded SRCs. 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 [17].

6 Determination of the rate of biodegradation

The flame retardant modification of the polymers can alter the biodegradation process. To investigate the effect of the surface treatment of the natural fabrics and the FR modification of the polymer matrices, the biodegradability of several reference and FR composites were evaluated at the polish partner (INF), according to standard EN ISO 846:1997 Plastics – Evaluation of the action of microorganisms. The samples sent to INF covered the utmost of the investigated composites (TPS, PLA and epoxy; with reference and flame retarded matrix; with unmodified and surface-treated natural fabric reinforcement).

6.1 Resistance against the action of fungi

First, the resistance to fungi action was determined, as well as the fungistatic effect of the prepared composites. The samples of tested composites were exposed to the action of the following mould fungi mixture: *Aspergillus niger van Tieghem*, *Chaetomium globosum Kunze*, *Gliocladium virens Miller*, *Paecilomyces variotii Bainier* and *Penicillium funiculosum Thom*. Three batches were compared: a control batch, stored at ambient temperature and humidity; a non-sterile batch, which was inoculated with mould fungi suspension, then incubated; and a sterile batch, which was first treated with a bactericidal solution of water and ethanol, and non-inoculated with fungi, incubated the same way as the non-sterile batch.

Based on the visual assessment both by naked eye and microscope, by the determination of the degree of mould fungi growth and the mass change of the samples, the following conclusions could be drawn: the starch-based composites (TPSG, **Figure 10 a**) were completely decomposed, as expected. PLA, both with unmodified and surface treated natural fabric reinforcement contain nutrients for the growth of the fungi. In the case of flame retarded PP fungi growth could be seen only on the edges of the specimens, where the natural fibres were in contact with the agar medium. In the case of the epoxy resin, when neither the natural fabric, nor the matrix was flame retarded, a small degree of contamination could be observed (EP_NT_ref, **Figure 10 b**), due to the direct connection of the fibres with the agar medium. When both the matrix and the fabric were FR-modified, the sample decomposed completely, however when the natural fibres were sol-gel treated with an aminosilane-type coupling agent, no fungi growth could be observed.

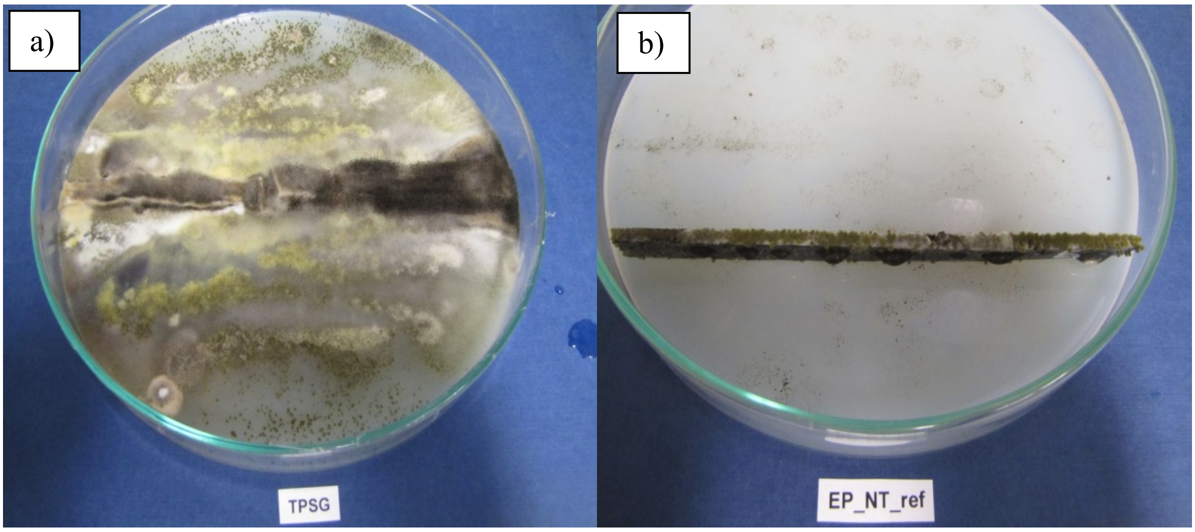


Figure 10 Samples after fungi test. a) TPSG, b) EP_NT_ref

6.2 Resistance against the action of bacteria

The determination of resistance to bacteria action was also examined, by exposing the samples to the suspension *Pseudomonas aeruginosa* strain of density 10^6jtk/ml on bouillon. Based on the results, in case of all tested composites no inhibition zone around the tested samples could be seen, and no antimicrobial activity of them was observed.

6.3 Resistance to soil microorganisms

Burial test for determination of resistance to soil microorganism was performed in the case of PLA reinforced with flame retarded (thermotex-treated) natural fabric (PLA_TT). Three batches were compared: Batch I, when non-sterile samples were buried; Batch S, when the samples were sterilized by immersion in o-phenylphenol solution and then incubated, and a Batch 0 control sample, stored at ambient temperature. The composite samples with the control strap of a reference cotton fabric were placed in jars (two samples in each jar) and covered with soil at water content of 36% at 60% water capacity of the soil. Additionally, the jars with S samples were sterilized in an autoclave at 120 °C (2 bars) for 30 min, in three consecutive days.

Figure 11 Soil test and residues

In comparison with control samples of composite (batch 0), after 6 month of soil burial test, signs of decay caused by soil micro-organisms were observed both on the surfaces of the tested samples and on their edges adjacent to the natural filler - linen-hemp fabric (batch I and S). The changes in the appearance of the tested samples were observed i.e. small cracks and discoloration on their surfaces (**Figure 11**). Soil micro-organisms caused complete decomposition and break-up of control cotton fabric in case of non-sterile samples (batch I). For comparison sterile samples of control cotton fabric did not undergo degradation. As a conclusion, the composite PLA_TT contains nutrients for the growth of soil micro-organisms - it is not resistant to fungi and bacteria present in soil. Soil micro-organisms caused the changes in the appearance of the tested composite samples and also their substantial mass change.

Based on the results of the biodegradability tests, it can be concluded that the flame retardant modification of the matrix materials do not affect the behavior of the composites in biological circumstances, however in the case of the reinforcing natural fabrics, the sol-gel-type surface modification fully inhibited the biodegradation.

7 Feasibility of application at various fields

The laboratory scale experiments and model studies allowed predicting the economical safety and environmental benefits of the new methods for different industrial segments. After collecting the special requirements of industrial companies, adjustment of the elaborated concepts and recipes were performed. For example the described advantageous reactive flame retardant+crosslinker combined phenomena initiated us to elaborate a scalable (i.e. industrializable) method for the green synthesis of such compounds [30]. The original principle of self-reinforcing+flame retardant combination is under evaluation for other polymer types/systems and other flame retardants (e.g. in injection moulded all-polymer composites). It is already proven that high amount of flame retardant additives can be spared this way and cost-effective flame retardancy of car elements can be formed. On this basis we intend to improve, as a continuation of this project, fire resistance of polymeric materials used in the construction and transportation industries.

Furthermore some of the results could be transferred even to the pharmaceutical industry. The technology and engineering of the applied biopolymer nanocomposite systems started to be adjusted to the needs of pharmaceutical formulation [31]. The continuous technologies, such as formation of bionanofibers by electrospinning, applied in the course of this project could be translated to similar pharmaceutical technologies, where such approaches are revolutionary compared to the conventional batch processes of that field [32]. The industrial implementation of the nanocomposites required concrete application-oriented model studies and evaluation of the feasibility of in-process control using the elaborated analytical methods. The control strategies developed for the synthesis of flame retardants proved to be feasible for crystallization of active substances [33]. The analytical method elaborated for determining the distribution of components in multicomponent polymer systems, based on Raman spectrometry, could be applied also for characterizing tablets produced by the pharmaceutical industry [34].

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