Katalin Bordácsné Bocz
PhD thesis

Development of Environmentally Friendly Flame Retarded Polymer Composites
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PhD Thesis

Development of Environmentally Friendly Flame Retarded Polymer Composites

Supervisor
Dr. György Marosi

Co-supervisor
Dr. András Víg

George Olah Doctoral School
Department of Organic Chemistry and Technology
Faculty of Chemical Technology and Biotechnology
Budapest University of Technology and Economics

Budapest, Hungary
2015
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ACKNOWLEDGEMENT

First of all, I would like to express my sincere gratitude to my supervisor, Prof. György Marosi for acquainting me with material science in particular with flame retardancy of polymers, and for helping my scientific work with uncountable discussions and advice, and for the encouragement in every aspect of the research.

I would like to express my appreciation to Tamás Igricz for his essential assistance and cooperative efforts during the course of this research.

I am thankful to all my colleagues in the Safety, Environmental and Pharmaceutical Technologies Research Group for their help and valuable suggestions. Also, I wish to thank the students for their enthusiastic work and contribution.

I would also like to acknowledge with much appreciation the staff of the Department of Polymer Engineering, who gave the permission to use all required equipment and the necessary materials to complete my tasks.

Last but not least I am very grateful to my family and friends, who supported me during the Ph.D. work, and my special thanks goes to my husband for his inspiration and encouragement.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A_0$</td>
<td>original cross sectional area</td>
</tr>
<tr>
<td>AE</td>
<td>atomic efficiency</td>
</tr>
<tr>
<td>AP</td>
<td>ammonium phosphate</td>
</tr>
<tr>
<td>aPMMA</td>
<td>atactic polymethyl methacrylate</td>
</tr>
<tr>
<td>APP</td>
<td>ammonium polyphosphate</td>
</tr>
<tr>
<td>aPP</td>
<td>atactic polypropylene</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>b</td>
<td>width of the specimen</td>
</tr>
<tr>
<td>CAD</td>
<td>collisionally activated dissociation</td>
</tr>
<tr>
<td>CD</td>
<td>cyclodextrin</td>
</tr>
<tr>
<td>CLS</td>
<td>classical least squares</td>
</tr>
<tr>
<td>CP</td>
<td>cross-ply</td>
</tr>
<tr>
<td>DAB</td>
<td>3,3′-diaminobenzidine</td>
</tr>
<tr>
<td>DAP</td>
<td>diammonium phosphate</td>
</tr>
<tr>
<td>DCP</td>
<td>dicumyl peroxide</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
</tr>
<tr>
<td>DOPO</td>
<td>9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide</td>
</tr>
<tr>
<td>DPER</td>
<td>dipentaerythritol</td>
</tr>
<tr>
<td>Dr</td>
<td>ductility factor</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>derivative thermogram</td>
</tr>
<tr>
<td>DTGS</td>
<td>deuterated triglycine sulfate</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$E_b$</td>
<td>flexural modulus</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive spectrometer</td>
</tr>
<tr>
<td>$E_{F_{\text{max}}}$</td>
<td>energy at maximal force</td>
</tr>
<tr>
<td>$E_{\text{tot}}$</td>
<td>total impact energy at break</td>
</tr>
<tr>
<td>EOL</td>
<td>end-of-life</td>
</tr>
<tr>
<td>$E_t$</td>
<td>perforation energy</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>F</td>
<td>tensile/axial load</td>
</tr>
<tr>
<td>$F_{\text{max}}$</td>
<td>maximal tensile load</td>
</tr>
<tr>
<td>FR</td>
<td>flame retardant</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectrometry</td>
</tr>
<tr>
<td>$F_y$</td>
<td>load at yield</td>
</tr>
<tr>
<td>GF</td>
<td>glad fabric</td>
</tr>
<tr>
<td>GP</td>
<td>glycerol-phosphate</td>
</tr>
<tr>
<td>h</td>
<td>thickness of the specimen</td>
</tr>
<tr>
<td>HDT</td>
<td>heat deflection temperature</td>
</tr>
<tr>
<td>IFR</td>
<td>intumescent flame retardant</td>
</tr>
<tr>
<td>IFWI</td>
<td>instrumented falling weight impact test</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>iPMMA</td>
<td>isotactic polymethyl methacrylate</td>
</tr>
<tr>
<td>iPP</td>
<td>isotactic polypropylene</td>
</tr>
<tr>
<td>iPVC</td>
<td>isotactic polyvinyl chloride</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>L</td>
<td>length of the support span</td>
</tr>
<tr>
<td>L₀</td>
<td>original length of the specimen</td>
</tr>
<tr>
<td>l₀</td>
<td>undrawn length</td>
</tr>
<tr>
<td>l₁</td>
<td>drawn length</td>
</tr>
<tr>
<td>LC</td>
<td>liquid chromatography</td>
</tr>
<tr>
<td>LGFPP</td>
<td>long glass fibre reinforced polypropylene</td>
</tr>
<tr>
<td>LM</td>
<td>light microscopy</td>
</tr>
<tr>
<td>LOI</td>
<td>limiting oxygen index</td>
</tr>
<tr>
<td>LP</td>
<td>laser-pyrolysis</td>
</tr>
<tr>
<td>MA</td>
<td>melamine</td>
</tr>
<tr>
<td>MAP</td>
<td>monoammonium phosphate</td>
</tr>
<tr>
<td>MCAPP</td>
<td>microencapsulated ammonium polyphosphate</td>
</tr>
<tr>
<td>MEL</td>
<td>melamine</td>
</tr>
<tr>
<td>MFI</td>
<td>melt flow index</td>
</tr>
<tr>
<td>MLC</td>
<td>mass loss calorimeter</td>
</tr>
<tr>
<td>ML</td>
<td>mass loss</td>
</tr>
<tr>
<td>MMT</td>
<td>montmorillonite</td>
</tr>
<tr>
<td>MOI</td>
<td>methacryloyloxyethyl isocyanate</td>
</tr>
<tr>
<td>MP</td>
<td>melamine phosphate</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multiwall carbon nanotube</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance analysis</td>
</tr>
<tr>
<td>o-MMT</td>
<td>organomodified montmorillonite</td>
</tr>
<tr>
<td>PA</td>
<td>phosphoric acid</td>
</tr>
<tr>
<td>PA</td>
<td>polyamide</td>
</tr>
<tr>
<td>PA6</td>
<td>polycaprolactam</td>
</tr>
<tr>
<td>PAL</td>
<td>poly(aspartic acid-co-lactide)</td>
</tr>
<tr>
<td>PBAT</td>
<td>poly(butylene adipate-co-terephthalate)</td>
</tr>
<tr>
<td>PBS</td>
<td>polybutylene succinate</td>
</tr>
<tr>
<td>PCL</td>
<td>polycaprolactone</td>
</tr>
<tr>
<td>PCP</td>
<td>Pyrovatex CP</td>
</tr>
<tr>
<td>PDLA</td>
<td>poly-D-lactic acid</td>
</tr>
<tr>
<td>PDLLA</td>
<td>poly-D,L-lactic acid</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEPBP</td>
<td>1,2-dicarboxyl ethylene spirocyclic pentaerythritol bisphosphonate</td>
</tr>
<tr>
<td>PER</td>
<td>pentaerythritol</td>
</tr>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>PHA</td>
<td>polyhydroxyalkanoate</td>
</tr>
<tr>
<td>PHB</td>
<td>polyhydroxybutyrate</td>
</tr>
</tbody>
</table>
PHBV  poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
pkHRR  peak of heat release rate
pkHRRtime time to peak of heat release rate
PLA  polylactic acid
PLLA  poly-L-lactic acid
PP  polypropylene
PPC  polypropylene composite
PPLA  phosphorus containing polylactic acid
PSil  phosphorus-silane
PVA  polyvinyl alcohol
REC  recycled polyolefin mixture
rPP  ethylene-propylene random copolymer
SEM  scanning electron microscope
SPDPC  spirocyclic pentaerythritol bisphosphate disphosphoryl chloride
SPDPM  spirocyclic pentaerythritol bisphosphate disphosphoryl melamine
sPP  syndiotactic polypropylene
sPVC  syndiotactic polyvinyl chloride
SRC  self-reinforced composite
SRP  self-reinforced plastic
TAP  triallyl phosphosphate
TBP  tributyl phosphate
TESPI  3-(triethoxysilyl)-propyl isocyanate
Tg  glass transition temperature
TGA  thermogravimetric analysis
tHR  total heat release
Tm  Melting temperature
TMS  tetramethylsilane
TPER  tripentaerythritol
TPS  thermoplastic starch
TPT  triallyl phosphoric triamide
TTI  time to ignition
UD  unidirectional
UHMWPE ultra-high-molecular-weight polyethylene
WAXD  wide angle X-ray scattering
αPP  monoclinic polypropylene
βPP  hexagonal polypropylene
γPA6  triclinic polycaprolactam
ΔLf  the amount by which the length of the object changed until failure
εf  strain at break
λ  draw ratio
σb  flexural strength
σu  ultimate tensile strength
σy  yield strength

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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 polylactic 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].
ÚJ TUDOMÁNYOS EREDMÉNYEK

1. Önerősített kompozitok vizsgálatára korábban még nem alkalmazott roncsolásmentes Raman spektrometriai módszerrel jellemeztem polipropilén szálakkal erősített kompozitok szerkezetét. Erős korrelációit mutattam ki a spektrumok többváltozós adatelemzése alapján becsült orientációfok értéke és a kompozitok Young modulusai között [XV, XXXI, XXXIV].

2. Elsőként állítottam előként önkioltó, önerősített kompozitokat. Kimutattam, hogy önerősített formában kevesebb, mint fele mennyiségű (9%) égésgátló adalékkal állítható előként önkioltó (V-0 fokozatú) polipropilén kompozit, mint erősítés nélkül, amit egy korábban nem ismert égésgátlási mechanizmussal magyaráztam. A hatékony égésgátlást a hő hatására táguló (felhabosodó) égésgátlott polimer és a hő hatására zsgorodó (relaxálódó) erősítő szálak szenzorgetikus együttes hatásának eredményeként létrejövő kompakt felületi védőréteg biztosítja, amelynek szerkezetét az erősítő polimer szálak orientációs foka befolyásolja [III, IV, VIII, X, XIV, XVIII, XXVI, XXVIII, XXIX].

3. Megnövelt műszaki értékű újrahasznosított kompozitokat fejlesztettem ki autóipari vegyes poliolefin hulladékból önerősítéssel (ötszörös szakítószilárdság, kétszeres hajlítószilárdság, négyszeres ejtősúlyos energiaélnyelő-képesség az erősítetlen reciklátumhoz képest). Önerősítés mellett érvényesült a II. tézisben említett szinerzigmus is, hatékonysága azonban kissé csökkent mértékű, amit a szennyezések jelenlétére vezettem vissza [I, II, IV, VI, VII, XVI, XVII, XVIII, XXV].

4. Elsőként állítottam előként önkioltó és égésgátló fröccstermék. Igazoltam az így előállított kompozit kiváló konszolidáltságát. A kompozit hőkibocsátási maximum értéke 15% öngégédel alkalmazásával közel 50%-kal csökkent, továbbá jelentősen megnőtt az égéshez szükséges oxigénigénye (29,5 vol%). Az égésgáltolt önkioltott fröccstermékekkel a matricanyaghoz képest mintegy négyszeres szakítószilárdság és hatszoros rugalmassági modulus növekedést ért el [XXIX, XXX].


7. Új foszfortartalmú szilán (PSil) aduktot állítottam elő foszfortartalmú poliol (Exolit OP560) és 3-(trietoxiszilil)-propil-izocianát addíciós reakciójával, amelyet reaktív felületkezelőként alkalmazt vágott lenszálok égéstőltésére. Termogravimetriás vizsgálatokkal kimutattam, hogy az új PSil-nal történő kezelés nagymértékben elősegíti a lenszálok szenesedését anélkül, hogy csökkenténé azok termikus stabilitását. Ezt a jelenséget a P és Si atomoknak a szenesedő polimer fázisra gyakorolt kedvező együttes hatásával magyaráztam. A PSil-nal kezelt lenszálat poliejsav/termoplaztikus keményítő 4: 1 arányú keverékébe ágyazva az önkijelölt biokompozitok előállításához szükséges égéstőltő adalékmennyiség 10%-ra csökken [IV, XI, XIII, XXXII].

8. Elsőként állítottam elő égéstőltőt, önerősített poliejsav biokompozitot. Ez a kompozit eléri az önkijelölt (V-0) kategóriát, az égéshely szükséges oxigénigénye (oxigénidex): lényegesen magasabb (34 v/v%), az 50 kW/m²-es hőfluxus hatására mért hőkibocsátási maximum értéke pedig közel fele, mint az adalékmentes erősítetlen és önerősített poliejsav referencia minták megfelelő értékei. Önerősítés és égéstőltés együttes alkalmazásával a rideg poliejsav (perforációs energiával jellemzett) ütésállósága többszöröseire (mintegy 30-szorosára) nőtt [IV, XII, XVII, XX, XXX, XXXIII].
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 electronic 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 toward 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.

The most efficient way to minimize the negative (or maximize the positive) sustainability impacts of polymer composites is the integration of environmental considerations in the product design and development, which concept is often referred as “eco-design”. One of the important rules in “designing for recycling” is based on selecting the smallest possible number of different constituents in a material system. In this sense, the preparation of well-designed self-reinforced composites (SRCs), in which the reinforcing fibres are made from the same substance as the matrix polymer, is one possible way to improve the mechanical properties of polymers without any limitation regarding recycling. On the other hand, new polymer composites within the perspective of eco-design or sustainable development can be developed by using renewable resource-based and/or compostable components, such as biobased and/or biodegradable polymers and natural fibres.
The literature review of this PhD thesis gives an overview on the strategy, production and application of recyclable self-reinforced polymer composites and the classification and characteristics of natural fibre reinforced biocomposites with special attention to thermoplastic starch-based and polylactic acid-based systems. Then, the flame retardancy possibilities of thermoplastic polymers are introduced. In the case of biopolymer-based thermoplastics and their composites, the application of phosphorus-based flame retardants are discussed in details, because these are environmentally favoured owing to their lower environmental impact during their entire life-cycle (including production, use and disposal) when compared to other conventional flame retardants.

In the experimental part, the development results of new, environmentally sound and fire-safe polymer composites are presented. Recyclable self-reinforced composites and thermoplastic biocomposites were developed in flame retarded form. During the present research period the application of exclusively phosphorus-based flame retardants were investigated. Green solutions utilizing synergistic effects, multifunctionality and integrated approaches are proposed to obtain sustainable flame retarded polymer systems. Furthermore, new methods to characterize the flame retardant recyclable and biocomposites and understand their thermal degradation and flame retardant mechanisms are presented.
2 LITERATURE REVIEW

2.1 SELF-REINFORCED POLYMER COMPOSITES

The most widely produced thermoplastic (isotropic) polymers, such as polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET), are unsuitable for load-bearing applications due to their inherent low modulus and insufficient strength. In order to improve their stiffness and strength, two main routes can be considered. First is by introduction of fillers/reinforcements, such as talc or glass fibres, to create polymer composite materials. However, polymer composites with varied components suffer from reduced recyclability due to the hardly feasible separation of fillers and matrices. The second route is the exploitation of the inherent molecular strength by uncoiling the molecules and orienting them in the direction of loading, so that the loading is transferred by the stiff main chain (“carbon backbone”) rather than by weak intermolecular bonds. When both fibre and matrix of composites are composed of similar or identical polymers, recycling is simplified to thermomechanical reprocessing [1].

The concept of self-reinforced composites referred to “one polymer composite” has been introduced by Capiati and Porter in 1975 [2]. Various publications describing different technologies to achieve this concept often use similar terms, such as “self-reinforced polymer composites”, “all-polymer composites”, “single polymer composites” and “one polymer composites”, which vary by research group. In this work, the use of the terms “self-reinforced composites” (SRCs) and “all-polymer composites” are preferred.

2.1.1 STRATEGY, PRODUCTION AND APPLICATION OF SELF-REINFORCED POLYMER COMPOSITES

Self-reinforced composites (SRCs) are a relatively new family of composite materials in which the polymer matrix is reinforced with highly oriented polymer fibres or tapes, both derived from the same polymer type [3]. 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, and the basic condition of oriented crystallization is a high molecular orientation [4].

2.1.1.1 POLYMER REINFORCEMENT

The structure of semi-crystalline polymers can be approximated as consisting of a crystalline phase constituted of crystal lamellae connected with tie molecules, which are embedded in the disordered amorphous phase. In the case of semi-crystalline polymeric materials with flexible chain molecules, such as PP, the reinforcement phase is created by rapid extension of melts or flow-induced crystallisation, whereby highly oriented crystalline structures, such as the so-called shish-kebab structures (Figure 2.1), extended chain fibrils and oriented folded chain lamellae are induced. The polymer molecules have high strength (high bonding energy) covalent bonds along their longitudinal axis and lower strength intermolecular...
bonds (mainly Van der Waals bonds) in the perpendicular direction, therefore increased mechanical properties (strength and modulus) can be achieved by increasing the number of oriented chain molecules and assuring their orientation in the loading direction [4].

There are multiple routes to the orientation of semi-crystalline polymers, such as gel (solution) spinning, melt drawing and solid state deformation techniques, resulting in fibrous or tape-like reinforcing structures. The simplest commercial route for the production of high tenacity polymer fibres or tapes is the solid-state deformation below the melting temperature \(T_m\), but above the glass transition temperature \(T_g\) of the polymer by drawing an extruded fibre through a hot oven. Tensile deformation is achieved by pulling a fibre through an oven with a greater speed than the fibre enters the oven. Generally, increasing mechanical properties can be achieved by increasing the draw ratio \(\lambda\), which is defined as the ratio of the drawn length \(l_1\) and the original (undrawn) length \(l_0\) (Equation 1). The obtained average orientation can be measured using techniques, such as birefringence, X-ray scattering, IR dichroic ratios, and polarized Raman spectrometry.

\[
\lambda = \frac{l_1}{l_0}
\]

Equation 1 Calculation of draw ratio

Based on drawability, the semi-crystalline polymers can be divided into two categories - the drawable apolar polymers, and the less drawable polar polymers. The interchain interactions in apolar polymers are relatively weak and therefore a high degree of drawability can be obtained. Polar polymers, on the other hand, have relatively strong interchain interactions and are therefore less drawable [5]. In both cases, the maximum drawability achieved by solid state drawing of semi-crystalline polymers drawn between \(T_g\) and \(T_m\) is limited by the presence of molecular entanglements.

To create an ideal oriented polymer, it is essential to have highly extended chain structure without any defects. As the chain ends are known to behave as defects, it is expected that higher molecular weight materials will have lower extent of defects resulting from chain ends. Thus, the molecular weight should be maximised to provide greatest molecular continuity in the loading direction. However, in practice, above a critical limit of molecular weight, for the formation of entanglements, the number of molecular entanglements rapidly increases with molecular weight. Therefore, as molecular weight becomes very large, large
numbers of entanglements limit the drawability of the polymer. In order to increase drawability and further align semi-crystalline polymer molecules, it is necessary to reduce the number of molecular entanglements by reducing the molecular weight, which results in lower mechanical properties due to lower molecular continuity in the direction of loading. Thus, the molecular weight needs to be optimized in order to achieve an optimum level of entanglement density, required for obtaining high drawability of polymer network [1]. The maximum attainable draw ratio for PP is $\lambda \sim 25$ [6]. In the case of the more polar polyethylene terephthalate (PET) and polycaprolactam (PA6), draw ratios of only about 4-7 are attainable [5].

As a result of molecular orientation during spinning and drawing, high performance polymer fibres can be achieved serving as suitable reinforcements in the structurally similar polymer matrix. In Table 2.1, the mechanical properties of polymer fibres are compared with carbon and glass fibres. It can be seen that the mechanical performance of the polymer fibres (especially of UHMWPE and aramid fibres) are comparable with those of the widely used glass and carbon fibres, however, the density of the polymer fibres is noticeably less, which is a major advantage in applications where high strength to weight ratio is required. Polymer fibres provide some other specific features, such as ease of production, low cost, recyclability and good interfacial bonding without any surface treatment. Similarly to traditional composites the stress transfer from the “weaker” matrix to the “stronger” reinforcement occurs via an interface/interphase in SRCs. In traditional composites weak van der Waals forces act across the interfacial region, which do not ensure acceptable bonding and thus the reinforcement is generally surface treated (sizing, coating) and/or the matrix is modified (coupling agent). In contrast, molecular entanglements, favourable amorphous/crystalline superstructures and even H-bonding may serve for improved adhesion and thus for stress transfer between the matrix and reinforcement via the interphase of SRCs [3].

Table 2.1 Comparison of the density and mechanical properties of polymer reinforcing fibres with glass and carbon reinforcing fibres

<table>
<thead>
<tr>
<th>Fibres</th>
<th>Density [g/cm³]</th>
<th>Tensile strength [MPa]</th>
<th>Tensile modulus [GPa]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE*</td>
<td>0.96</td>
<td>2800-3300</td>
<td>150-175</td>
<td>4</td>
</tr>
<tr>
<td>PE</td>
<td>0.96</td>
<td>1000-1500</td>
<td>40-100</td>
<td>4-18</td>
</tr>
<tr>
<td>PP</td>
<td>0.9</td>
<td>500-650</td>
<td>5-20</td>
<td>15-25</td>
</tr>
<tr>
<td>Aramid (Kevlar 49)</td>
<td>1.44</td>
<td>3300-3800</td>
<td>75-130</td>
<td>4</td>
</tr>
<tr>
<td>Glass (E type)</td>
<td>2.54</td>
<td>2500-3000</td>
<td>70-75</td>
<td>2-5</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.8</td>
<td>3400-3600</td>
<td>240-250</td>
<td>1.4-1.5</td>
</tr>
</tbody>
</table>

### 2.1.1.2 Possibilities to widen the processing window

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 [7]. The main task is to achieve
good reinforcement in the final structure while retaining the orientation in the reinforcing phase. Deterioration of stiffness and strength occurs via thermally induced shrinkage and partial melting which are accompanied with substantial changes in the morphology, and especially in that of the interphase. Moreover, the processing parameters (heating/cooling rates, pressure regime applied) are all time dependent which also strongly influence the degree of the property deterioration of the reinforcement and thus the performance of the consolidated SRC [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. The width of the process window is mainly governed by the choice of polymer systems used as well as the choice of self-reinforcement technology applied. Thus, widening of the process window may occur by exploiting some intrinsic features of the corresponding polymers and by choosing proper processing methods and conditions.

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. [3].

**Physical state**

The temperature range between the matrix and the reinforcement can be widen by applying a matrix polymer with decreased softening (when the matrix is amorphous) or melting (when the matrix is semi-crystalline) temperature compared to the reinforcement. The slow crystallization character of thermoplastic polyesters can be exploited by fast cooling operation producing fully amorphous matrix layers, the softening of which is starting above $T_g$. Two-constituent SRCs can be produced by layering crystalline reinforcements (fibres, tapes, fabrics) with amorphous films followed by hot pressing at a temperature selected between the $T_g$ of the matrix and $T_m$ of the reinforcing polymer. This concept has been demonstrated on examples of PET [8] and PLA [9].

**Tacticity**

A straightforward approach is to exploit the differences in crystallinity and melting temperature of the stereoisomers of a polymer. In PP, based on the configuration of polymer chains three distinct structures can be distinguished. The pendent methyl groups are present on the same side of the backbone in isotactic polypropylene (iPP), they are alternating in syndiotactic polypropylene (sPP), and random in atactic polypropylene (aPP). The stereoirregular aPP is amorphous, while iPP and sPP are prone to crystallize due to their highly regular chain conformations; their melting temperature is, however, different due to their differing helical conformations in their elementary cells. The melting temperature of iPP is about 165°C, while that of sPP is about 135°C. Among SRCs, several
matrix/reinforcement combinations exist exploiting the tacticity-related phenomena, such as aPP/iPP, aPMMA/iPMMA, aPVC/iPVC [3].

Polymorphism

Polymorphism is a widespread phenomenon in polymers, which may arise from the packing of chains with different conformations or different packing modes of molecular chains with identical conformation in the unit cell [10]. Four different crystalline modifications, monoclinic (α), hexagonal (β), triclinic (γ) and trigonal (δ), have been identified for iPP differing with respect to mutual chain orientation in the unit cell. These crystalline modifications possess various melting temperatures, which can be also exploited to widen the processing window of SRC preparation. The feasibility of this concept has been proven by a patent filed by Karger-Kocsis [11], who combined β-PP matrix with α-PP reinforcement to obtain PP SRC, and also by Bhattacharyya et al. [12] who applied α-PA6 multifilament yarn as reinforcement in γ-PA6 matrix to obtain PA6 single polymer composites.

Copolymers

The regularity of the macromolecular chains can be reduced by copolymerisation, resulting in lower crystallinity and less perfect and smaller crystals with lower melting temperature compared to the corresponding homopolymer. Therefore, the copolymers (such as ethylene-propylene copolymers) are suitable matrix materials in SRCs.

Besides exploiting some features of the corresponding polymers, the processing window necessary for SRC preparation can be ensured by choosing adequate processing methods and conditions.

2.1.1.3 Fabrication Methods for Self-reinforced Polymer Composites

Kmetty et al. [13] recently reviewed the self-reinforced polymeric materials and classified them according to their constituents (single- or multicomponent), their production (one-step or in multi-step procedures) and the spatial alignment of the reinforcing phase in the matrix (in one, two or three dimensions). In this work, the focus is mainly put on the industrially most relevant technologies, which mostly use different preforms (fibrous, tape-like, knitted or woven fabrics) as reinforcements with suitable thermoplastic matrices to create self-reinforced composites. In all cases the consolidation of the related assemblies occurs by hot pressing, but it has to be noted, that by using a double belt press, continuous composite manufacturing is also feasible.

Film-stacking

In the film-stacking method, the reinforcement structure is layered ("sandwiched") with thermoplastic films and consolidated under heat and pressure to fully impregnate the fibres. As it is demonstrated in Figure 2.2, using this method many layers can be stacked with a suitable number of film plies. When exposed to heat and pressure, the polymer films soften and flow between the fibres and upon cooling these films become the matrix phase, while the fibres withstand processing without significant loss in their mechanical properties and
thus remain the reinforcement phase of the composite. To guarantee the necessary
temperature window, the films are formed mostly from copolymers. Bárány et al. [14]
exploited the 15°C wide temperature window offered by the combination of α and β
polymorphs of iPP to create PP SRCs. In the film-stacking method, planar arranged
(unidirectional or cross-ply) fibres as well as random fibre mats or knitted or woven fabrics
of highly oriented and crystalline homopolymers can be applied as reinforcement [7]. The
fibre volume fraction can be well-controlled in a fairly wide range; the tensile modulus of the
obtained composites is in good agreement with the rule of mixtures theory, commonly
applied for many composite materials. The main advantage of the film-stacking method is
the large variety of applicable material combinations, and the achievable wide processing
window. This method has been successfully applied to create all-PP [15], all-PE [16], all-PA
[12], all-PET [17,18] and even all-PLA [9] composites.

Figure 2.2 Consolidation of a self-reinforced polymer composite from a stacked arrangement of
fibres and polymer films [7]

**Impregnation (melt, powder, solution)**

A commonly used technique for preparation of conventional i.e. glass or carbon fibre
reinforced polymer composites is resin infusion, mostly using an uncured thermoset matrix
as impregnating medium. This process is also feasible for thermoplastic matrices so that the
melt of the matrix polymer is forced to flow around the fibres [7]. However, the high melting
temperature and the high viscosity of the melts makes the manufacturing of thermoplastic
composites by melt impregnation process rather slow and costly. In addition, when SRCs are
targeted to be manufactured, fibre relaxation and mechanical property loss may occur due
to partial melting during melt impregnation. As a solution, large temperature window should
be guaranteed and/or low-molecular-weight polymer grades can be used [19]. The process is
shown schematically in Figure 2.3. The technique is equally applicable with any planar
arrangement of fibres such as woven fabrics and random fibre mats. The method was used
for the development of all-PE and all-PP composites [20]. It has to be noted, that besides
melt, powder [21] or solution [22] of the matrix can also be used for impregnation. The
latter one, for example, has been successfully applied to create all-cellulose composites [23].
Figure 2.3 Consolidation of a self-reinforced polymer composite from a combination of arranged fibres and a polymer melt [7]

Hot compaction

Hot compaction is a one-constituent method, during which different assemblies of fibres or tapes are compacted under pressure and upon careful heating to a temperature within the melting range, more exactly in the vicinity of the melting onset of the fibres. During processing, the exterior of the fibres melts while the core of the fibre remains intact. The molten proportion of the fibre volume flows to fill the interfibrillar space and voids, and upon cooling forms the matrix phase of the composite. This technique is advantageous due to the use of only one polymer type, however, the small processing window, typically about 5°C or below, between the feasible processing temperature and the melting temperature of the fibre means a real challenge. Excessive heating results in relaxation and hence a loss of molecular orientation, whereas insufficient heating leads to a poor interfacial bonding between the fibres/tapes. This small temperature processing window reduces the versatility of this processing route [19]. Still, hot compaction is a commonly used method, Hine and his co-workers applied it to prepare SRCs consisting of various polymers, such as PP, PE and nylon 6,6 [24,25].

Figure 2.4 Consolidation of a self-reinforced polymer composite from homogenous fibres by a hot compaction type technology [7]

Coextrusion

During this technique, bicomponent tapes with skin/core/skin cross section, fabricated by coextrusion, are consolidated by hot-pressing to create SRCs. The skin layer of the coextruded tapes is composed of a copolymer with lower $T_m$ than the homopolymer core material. During hot pressing the copolymer skin overtakes the role of the matrix, whereas the remaining core acts as reinforcement. The main advantage of this production method is the achievable very high reinforcement content (>80%), i.e. core layer, which is well
preserved during processing. Further advantages are the excellent bonding between the tapes and the enlarged processing temperature window (about 20-40°C) [19]. Disadvantage is, however, that the SRCs are manufactured in a multistep procedure (coextrusion and hot pressing) which makes the process more costly compared to the other techniques. The primary tapes can be assembled in different ways (ply-by-ply structures with different tape orientations, such as UD (unidirectional) and CP (cross-ply)), or integrated in various textile structures such as woven fabrics. Mainly all-PP composites consisting of highly oriented PP tapes have been prepared by this method [26].

Figure 2.5 Consolidation of a self-reinforced polymer composite from coextruded tapes [7]

**Microfibrillar reinforced composites (MFCs)**

MFCs are polymer-polymer composites containing constituents that are incompatible with each other and possess different melting temperatures [13]. Microfibrillar reinforced composites can be obtained from incompatible polymer blends by extrusion and orientation (the fibrillization step) followed by thermal treatment at a temperature between the melting points of the two components at constant strain (isotropization step), as shown schematically in Figure 2.6. The block copolymers formed during the isotropization (in the case of condensation polymers) play the role of a compatibilizer. Prolonged annealing transforms the matrix into a block and thereafter into a random copolymer [27]. MFCs are usually made of condensation polymers (PET, PA-6.6) working as reinforcements and polyolefins (PP, PE) acting as matrices [13]. MFCs exhibit significantly improved mechanical properties compared to those of the respective isotropic matrix; it is revealed that the mechanical properties of MFC are similar to those of short glass fiber-reinforced composites containing the same matrix [28].

Figure 2.6 Steps for the formation of microfibrillar reinforced composites [29]
2.1.1.4 Quality Assessment of Self-Reinforced Polymer Composites

During production of self-reinforced composites, there are various parameters influencing the properties of the finally formed composite. Besides the ratio and characteristics of the constituents (matrix polymer and reinforcement), the most crucial parameter is the achieved consolidation quality. Full compaction means the least void content and the theoretical maximum density is achieved. The most relevant parameters affecting the consolidation quality are the type and MFI (melt flow index) of the matrix, the type and structure (fibrous, knitted, woven, etc.) of the reinforcement, the volume fraction of the reinforcement, the temperature, pressure and holding-time applied during hot-pressing and the cooling speed. It has to be noted, that in contrast to conventional glass or carbon fibre reinforced thermoplastic composites, where improved consolidation quality can be ensured by decreasing the viscosity of the matrix by increasing the processing temperature, in the case of SRCs the melting temperature of the reinforcing polymer fibre or tape determines the upper limit of the applicable temperature. Also, the increased processing temperature will lead to molecular relaxation of fibres and consequently to loss in reinforcing efficiency. It was found by Izer et al. [30] that as a function of increasing processing temperature the consolidation quality of all-PP composites improves (as revealed by peel-strength and density measurements), and parallel the tensile and flexural strength and modulus values are also increasing (and then pass through a maximum), however the energy absorption capability (perforation energy) decreases with increasing consolidation temperature. Therefore, it is essential to find the optimal processing conditions, where the SRCs are well-consolidated and accompanied with excellent interlaminar strength in a presence of transcry stalline layer, and have prominent mechanical performance with good energy absorption at the same time. Among the above listed parameters, the volume fraction and structure of the reinforcement phase and the consolidation temperature are the most important parameters regarding the consolidation quality and mechanical performance of the achievable SRCs. With careful adjustment, the self-reinforced composites could become suitable counterparts of the corresponding glass-fibre reinforced composites, even with 30% weight reduction.

The quality assurance of SRC prefabricates and parts is a crucial issue. Quality of the products was assessed by various destructive methods (different kind of mechanical loading) coupled with further in situ (such as acoustic emission) [31] or post mortem (light and scanning electron microscopy) failure inspections so far. Non-destructive techniques were rarely used for quality management, though ultrasonic testing [32] and X-ray micro-computed tomography [33] as pioneer investigations can be found in the literature. This is still an open issue, especially if in-line quality inspection is the target [3].

2.1.1.5 Advantages and Disadvantages of Self-Reinforced Polymer Composites

Self-reinforced polymer composites have various advantages and disadvantages over conventional composites. Due to the thermoplastic nature of the reinforcement phase they
will always be much more sensitive to exposure to elevated temperatures than glass or carbon fibre-reinforced composites, however, the maximum service temperatures of the self-reinforced polymer composites can be increased by using higher melting temperature polymers, such as PA. The need for unique and well-controlled composite processing routes means that self-reinforced polymer composites are more expensive to manufacture and more sensitive to manufacturing parameters than conventional composites [7].

In contrast, the absence of “foreign” reinforcements in SRCs has several advantages over other conventional composites. The exclusive use of polymers means that the density of self-reinforced polymer composites is low, and their high performance to weight ratio can be more attractive compared to many other materials. Additionally, at the end of the product life the use of only one polymer type enables the material recycling by simple thermomechanical methods without the need for separation of fibre and matrix [7]. Bárány et al. [34] demonstrated that the reprocessing of self-reinforced PP composites is not accompanied with any property deterioration related to the properties of the matrix materials, thereby it is an excellent candidate for upcycling.

2.1.1.6 APPLICATIONS OF SELF-REINFORCED POLYMER COMPOSITES

SRCs may compete with traditional composites in various application fields based on their favoured recycling and beneficial performance/cost balance. This is the main reason for the increasing industrial and commercial interests behind the SRCs’ development.

A commercial break-through with SRPCs occurred recently. Self-reinforced PP composites are now available on the market under the trade names Curv®, Pure® and Armordon®. According to Peijs’ survey [26], the current market for these all-PP composites can be segmented into four sectors: transport (45%), electrical (35%), consumer and domestic appliances (10%), and industrial applications (10%). To date, the most commercially applied technology is based on hot compaction and marketed as Curv®, with examples of loud speaker cones, protective sports equipment, automotive panels and a major commercial range of luggage. Additionally, the use of PP coextrusion-based self-reinforced polymer composites based on the Pure® product technology, has been prototyped in applications such an automotive undertray panel and is reported to have been commercially applied to kayaks and other recreational equipment as well as in motorsports applications [7].

Also PET (polyethylene terephthalate) SRCs have been developed to give some alternative properties to PP SRCs, primarily better impact performance and higher in-service temperatures. All-PET composites are currently used to manufacture luggage, anti-ballistic and blast panels, sports goods (body protection pads) and automotive body panels. As part of the FP7 ESPRIT project [35], the injection-mouldable version has also been developed, which opens up many more possibilities for the manufacture of complex shapes with improved impact resistance for no weight penalty over standard, unreinforced PET.
2.1.2 Preparation and Characteristics of All-Polypropylene Composites

PP is a common material for thermoplastic matrix composites due to the combination of good thermal properties, high toughness, low cost and established history of use in a wide variety of applications. Accordingly, the PP-based self-reinforced composites (PP-SRCs) have generated the greatest commercial interest so far. In the scientific literature, PP-SRCs have been prepared by a large variety of processing techniques, including film-stacking method, melt-impregnation, hot-compaction, and consolidation of coextruded tapes, as also presented in Section 2.1.1. To date, there is a large selection of commercial PP fibres, yarn and tapes available in the market, and various technologies have now been commercialised to create these PP SRCs on an industrial scale.

Although the main purpose of creation self-reinforced polymer composites is to obtain improved mechanical properties compared to unreinforced polymers, in order to be commercially competitive with composites reinforced by conventional reinforcements such as glass fibres, self-reinforced polymer composites should possess similar mechanical properties. While the stiffness of highly oriented PP fibres is typically much less than that of the stiffness of glass fibres, unique fabrication methods have been developed to create self-reinforced polymer composites with fibre volume fractions of ~90%, compared to ~35% for commercial continuous glass fibre-reinforced PP composites [26]. Since the stiffness of a fibre-reinforced composite material is approximately proportional to the stiffness of the reinforcing fibres and its fibre volume fraction, the lower stiffness of the precursor PP fibres may be compensated by the very high fibre volume fraction achievable in self-reinforced polymer composites [7]. The highest mechanical properties have been reported using the coextruded tape technology, Alcock et al. [36] reported a longitudinal tensile modulus of ~13 GPa and a longitudinal tensile strength of ~385 MPa for coextruded PP tapes based (volume fraction ~ 90%) unidirectional composites. The same group reported the highest mechanical properties for bidirectionally (woven-fibre) reinforced all-PP composites; a tensile stiffness of 7.4 GPa and a tensile strength of ~230 MPa were achieved at a fibre volume fraction of ~90% [37]. These composites exhibit excellent resistance to falling weight penetration, and their specific mechanical properties were found to be comparable to those reported for commercial unidirectional glass fibre-reinforced PP composites.

From technical aspects, the main advantage of all-PP composites may be their outstanding impact resistance, which is mainly attributed to the interfacial failure between the polymer tapes/fibres; during failure, high amount of energy is absorbed by tape facture, delamination and debonding. It is shown in Figure 2.7 that the impact resistance of self-reinforced PP composites significantly outperform that of common plastics and glass fabric reinforced counterparts, both at room temperature and at -40°C.
As it is demonstrated by Figure 2.8, SR-PP composites offer a range of advantages over non-reinforced PP and traditional fibre reinforced composites such as glass fibre reinforced composites. Although SRP composites have many significant advantages, include greatly improved recyclability, low density and prominent impact performance, they are not without their disadvantages. The main disadvantage is their temperature sensitivity, which can be an issue both during processing and application.

Figure 2.7 Impact resistance of self-reinforced PP composites in comparison with other plastics [38]

Figure 2.8 Comparison of the properties of self-reinforced PP composites with (a) non-reinforced PP and (B) glass fibre reinforced composites [38]
2.1.3 Preparation and Characteristics of All-Polylactide Composites

The concept of self-reinforcement has also been applied to polylactic acid (PLA) with the aim to create fully biodegradable composites from renewable resources. As PLA is a slowly crystallizing polymer, it can easily be processed into two distinct physical forms: amorphous PLA and highly crystalline PLA. This phenomenon has been exploited by Li and Yao [9] and Jia et al. [39]; highly oriented crystalline PLA fibres and amorphous PLA films were combined to widen the processing window for all-PLA composite preparation, which was greater than 30°C in these cases. Tsuji et al. [40] proposed that a PLA stereocomplex could also be used to enlarge the processing temperature window; compared to the melting temperature of the pure polylactides (poly-L-lactide (PLLA) and poly-D-lactide (PLDA)) of 178°C, the melting temperature of the electrospun stereocomplex was found to be 220°C. Yu et al. [41,42] evaluated various physical treatments, such as cool drawing, annealing, CO₂ treatment and nucleation, and their effects on increasing the difference in melting temperature between the PLA matrix and PLA fibres in PLA-based SRCs. A thermal processing window of approximately 7-9°C was achieved after cool drawing and annealing the PLA fibres. However, these features have not been widely utilized for all-PLA composite preparation, yet.

In the literature, various methods have been proposed to create self-reinforced PLA composites, including hot-compaction [43] and textile insert moulding technique, whereby PLA fabrics are attached to the surface of PLA resin by injection-compression moulding [44], among which the film-stacking of amorphous matrix films and highly crystalline PLA fibres has been mostly applied to create all-PLA composites [9,39]. Compared to the non-reinforced PLA sheet, a noticeable improvement in tensile strength to 58.6 MPa and a Young’s modulus of 3.7 GPa was achieved in film-stacked PLA yarn (25 wt%) reinforced all-PLA composites. However, when PLA fabric (50 wt%) was used as reinforcement, although the tearing strength was significantly improved, the tensile strength of the fabric-reinforced SRCs remained almost unchanged, at about 45 MPa both before and after reinforcement, as reported by Li and Yao [9]. Similar results were obtained by Jia et al [39], their bi-directionally reinforced PLA-SRCs did not show any higher tensile properties (especially, tensile strength and strain at break) than the non-reinforced PLA, which they explained by the low fibre area density in the loading direction and by the weak points (stress concentration) caused by the yarn cross-over points. Nodo et al. reported a 400 % improvement in impact resistance for double PLA textile insert mouldings compared to neat PLA resin [44]. Despite the promising expectations and this encouraging result, surprisingly, the impact resistance of all-PLA composites is barely studied in the literature [45].

To date, PLA SRCs found applications mainly in the medical field; rods, screws and plates made of self-reinforced PLA are widely available for the fixation of cancellous bone fractures and osteotomies.
2.2 NATURAL FIBRE REINFORCED THERMOPLASTIC BIOCOMPOSITES

The development of recyclable self-reinforced polymeric composites, shown in the previous chapter, represents a significant progress in the direction of using environmentally sound polymer composites, however, the environmentally-friendly character of the obtained composite is also largely influenced by the used raw materials and the end of life options have to be considered as well. Therefore, the use of bio-based and/or biodegradable constituents in polymer composites increasingly come to the forefront.

Bio-based polymers have been defined as man-made or man-processed macromolecules derived from biological resources for plastic or fibre applications. In 2013, the bio-based polymer production of 3.5 million tons per year was reported to share about 1.5% of the total polymer production, which is expected to increase to 3%, reaching nearly 12 million tons by 2020 [46]. The most significant drivers to move from fossil based polymers to bio-based polymers are the limited fossil fuel resources that are increasingly expensive, the sustainable development and concerns about climate change and the important breakthroughs in biotechnology. The bio-route may become also economically advantageous with respect to the fossil-route if oil prices continue rising above 50 $/barrel. The cost/performance of many of the bio-based polymers is quite competitive already, furthermore it is suggested that bio-based polymers have the potential not only to replace existing polymers in a number of applications, but also to provide new combinations of properties for new applications [47].

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.

2.2.1 CLASSIFICATION AND APPLICATION OF THERMOPLASTIC BIOCOMPOSITES

Definitions (terminology)

Biocomposites can be interpreted as either biomass-based (bio-based) or biomedical materials. The most accepted definition for the former meaning originates from Mohanty et al. [48], stating that biocomposites are composite materials in which at least one of the constituents is derived from natural resources. Such biomass-based composites are available for various industrial purposes. On the other hand, biomedical composites are not necessarily biomass-based or biodegradable, but should be biocompatible and their application is limited merely to biomedical use [49]. Although according to Mohanty’s definition [48] the presence of either bio-based matrix or reinforcement allows polymer composites to be considered as biocomposites, in this work by biocomposites we mean only when both main constituents are biobased, i.e. biopolymers are reinforced with natural fibres. These materials are also commonly referred as “green composites”. More specifically, this work will only look at the subset of green composites that are commonly considered as
being biodegradable. In this context, it also has to be clarified, that the term biopolymer (or bioplastic) is defined as polymer produced from biological products issued from biomass, while the term biodegradable refers to a material that can be degraded relatively rapidly by microbes in a bio-active environment under suitable conditions.

Counter-intuitively, bio-based polymer composites are not necessarily environmentally friendly, nor biodegradable as defined by the appropriate standards (EN 13432 [50], EN 14995 [51]). Thus the assignment of the environmentally friendly label can be done only on the base of a life cycle assessment (considering also the chemicals used during processing), and not just on the base of origin. Similarly, the ability of being degraded by biological activity depends not on the origin, but rather on the chemical structure. Actually, all (bio- and petroleum-based) plastics are theoretically biodegradable; however, most materials degrade at such slow rates that they are considered non-biodegradable or durable [52].

Classification

There is a wide range of biopolymers deriving from a variety of renewable resources, including both thermosets and thermoplastics, which are promising candidates for application in a green composite, either being biodegradable or non-biodegradable. Biodegradable polymers can be classified on the basis of their properties, origin, or synthesis methodology. Depending on their origin, biodegradable polymers can be classified into agro-polymers (e.g. polysaccharides, proteins), microbial derived (e.g. PHA), chemically synthesized from agro-based monomers (e.g. PLA) and chemically synthesized from synthetic monomers (e.g. PCL). Most of the thermosets are formed by copolymerisation with synthetic monomers, and therefore they cannot be considered as 100% green materials [53].

In the case of biocomposites, the use of natural reinforcement is an obvious solution. Natural fibres are generally classified, based on their origin, into vegetable, animal and mineral fibres. Vegetable fibres are principally composed of cellulose, whilst animal fibres are composed of proteins. Some of the minerals based fibres (e.g. asbestos) are scarcely used due to their negative effects on health. Vegetable fibres are the most commonly used in composite applications and, as such, are the primary focus of this review, and are mostly referred as biofibres. Vegetable fibres can themselves be classified as either wood or non-wood. Non-wood fibres may be further subdivided into bast, leaf or seedhair fibres, depending on their origin in the plant, while wood fibre can be subdivided into softwood and hardwood fibre [54].

Properties

In Table 2.2, the properties of the most commonly used biopolymers are compared with polypropylene. It can be seen that PLA and PHB can be melt-processed in the same temperature range (and with the same equipment) as PP. It is also visible that PP outperforms TPS but it falls behind PLA and PHB in stiffness. So from mechanical aspects the bio-based PLA and PHB are real counterparts of the synthetic PP, however, their
considerably higher price makes them uneconomical for large scale applications. Also, their biodegradable nature can be problematic in long-life applications.

Table 2.2 Properties of thermoplastic biopolymers and polypropylene

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density [g/cm³]</th>
<th>Melting point [°C]</th>
<th>Tensile strength [MPa]</th>
<th>Young’s modulus [GPa]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS</td>
<td>1.1-1.4</td>
<td>110-115</td>
<td>5-6</td>
<td>0.12-0.85</td>
<td>30-45</td>
</tr>
<tr>
<td>PLA</td>
<td>1.24</td>
<td>150-165</td>
<td>25-60</td>
<td>0.5-3.5</td>
<td>2.5-6</td>
</tr>
<tr>
<td>PHB</td>
<td>1.20</td>
<td>165-185</td>
<td>25-40</td>
<td>3.5-4</td>
<td>5-8</td>
</tr>
<tr>
<td>PP</td>
<td>0.92</td>
<td>160-170</td>
<td>30-40</td>
<td>1.1-1.6</td>
<td>20-400</td>
</tr>
</tbody>
</table>

Generally, biofibres consist of cellulose, lignin, hemicellulose, pectin and wax. The main criteria for the choice of suitable fibres are the mechanical characteristics (such as stiffness, tensile strength and elongation at failure), thermal stability, adhesion of fibre and matrix, dynamic and long-term behaviour, price and processing costs. Table 2.3 gives a view of the mechanical properties of different natural fibres, also in comparison with glass fibres. The low density and particular microstructure of natural fibres are responsible for the relatively good specific mechanical properties. When considering the potential of natural fibres for composites and comparing the tensile strength, elasticity and elongation at failure with synthetic fibres, it becomes clear that hemp and flax fibres can potentially compete with glass fibres, which are commonly used in conventional polymer composites [54].

Table 2.3 Mechanical properties of natural fibres and glass fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density [g/cm³]</th>
<th>Tensile strength [MPa]</th>
<th>Young’s modulus [GPa]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>350-1500</td>
<td>25-100</td>
<td>2.7-3.2</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.47</td>
<td>550-900</td>
<td>40-70</td>
<td>1.5-4.0</td>
</tr>
<tr>
<td>Jute</td>
<td>1.3-1.5</td>
<td>400-800</td>
<td>15-25</td>
<td>1.1-1.5</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.45</td>
<td>450-700</td>
<td>10-20</td>
<td>3-7</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.54</td>
<td>2500-3000</td>
<td>70-75</td>
<td>2-5</td>
</tr>
</tbody>
</table>

Biofibres offer numerous advantages such as energy efficiency, low cost, low density, high toughness, appreciable specific strength and biodegradability. However, a major drawback is that biofibres cannot provide a consistent pattern of physical properties year by year; their properties vary from every harvesting season and region. Besides, they are hydrophilic in nature and have poor fire resistance, which disadvantages often limit their application in outdoor panels (i.e. construction) and in areas that pose fire hazard to humans (i.e. transportation) [55].

Natural fibre reinforced thermoplastics can be processed by conventional manufacturing methods such as compression moulding, extrusion and injection moulding [56]. Natural fibres can be used in the form of particulate or filler, short fibres, long fibres, continuous roving, woven fabric and non-woven fabric. The properties of a biocomposite are basically determined by the intrinsic properties of the matrix and the fibre, their volume fraction, the reinforcement architecture (fibre geometry, fibre orientation), and the fibre-matrix interface [54]. Good bonding is essential for the effective stress transfer to the reinforcement. On the other hand, the interfacial adhesion also strongly influences the toughness, i.e. the ability to
resist the propagation of cracks, of the obtained composite material. Natural fibres are, however, generally incompatible with most matrix polymers due to their hydrophilic nature. Therefore, chemical and/or physical modifications are generally introduced to promote the fibre-matrix adhesion; either the reinforcing fibres are surface-treated (such as acetylated or silylated) before composite manufacturing or compatibilising agents are used during processing.

As far as green composites have comparable mechanical performance with the synthetic ones, green composites seem to serve as real environmentally-friendly alternatives for their petrol-based counterparts. Conversely, as one would expect from biodegradable materials, green composites have limited durability. Exposure to environmental conditions can lead to a rapid degradation of the material. Accurately predicting the lifetime of green composites is a major challenge to their widespread implementation [57]. Kumar et al. [58] used amphiphilic additives such as mandelic acid and dicumyl peroxide to accelerate or delay biodegradation of flax fabric reinforced composites. They propose that suitable amphiphilic additives can be added as triggers for inducing controlled biodegradation.

Applications

Many types of bio-based thermosetting and thermoplastic polymers are nowadays already commercially available. Among the thermoplastics mainly polyesters and polysaccharide derivatives can be found; the order in terms of the production volume is as follows: bio-PET, PLA, bio-PE, starch blends, PHA and PA. To date, the packaging industry is the most important user of thermoplastic bioplastics, followed by the automotive and electronic sectors.

In parallel with the intense research of green composites at the academic level their large-scale commercialization has also begun. The first green composites appeared in the automotive sector in the early 2000’s, and the automotive applications represent the largest market for natural fibre reinforced bio-plastics ever since. Thermoplastic green composites increasingly find applications in a range of widely different fields such as in structural parts in buildings, furniture, cases for electronic devices, etc., however, their poor fire resistance often represents a critical limitation for their widespread use in structural engineering applications.

2.2.2 CHARACTERISTICS OF THERMOPLASTIC STARCH AND ITS BIOCOMPOSITES

Starch

Starch is a renewable and readily biodegradable carbohydrate, one of the most abundant polymers produced by nature. It can be found in a variety of plants like wheat, maize, potato and rice. Due to its wide availability and low cost starch is an attractive raw material for the production of biodegradable plastics, including biocomposites.

Native starch has a granular structure, which is built by two types of α-D-glucose monomeric units based polysaccharide polymers: the linear (1-4 linked) amylose and the highly
branched (with 1-6 linkage) amylopectin (Figure 2.9). Typically amylose is the minor component (about 10-20%) and amylopectin is present with a larger degree of polymerization. The short branched amylopectin chains are able to form helical structures which crystallize. Depending on the crystalline amylopectin content, which varies with the botanical origin, the crystallinity of starch granules is in the range of 15-45% [59].

![Chemical structure of amylose and amylopectin](image)

**Figure 2.9 Chemical structure of amylose and amylopectin**

Native starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding formed by the hydroxyl groups on the granule surface. They swell when they absorb water through hydrogen bonding with their free hydroxyl groups, but they still retain their order and crystallinity. However, when these swollen starch granules are heated, hydrogen bonding between adjacent glucose units is disrupted. The crystallinity is progressively destroyed. This process is called gelatinization [60]. During gelatinization, starch molecules are released from the granule structure. Plasticizers, like water and glycerol can form hydrogen bonds with the starch and thus the original hydrogen bonds between hydroxyl groups of starch molecules are destroyed. As the plasticizer penetrates into the starch granules, it disrupts the initial crystallographic structure and renders the semi-crystalline starch completely amorphous. Once the starch is gelatinized and properly plasticized, the obtained thermoplastic starch can flow just as any synthetic thermoplastic polymer and is therefore suited for conventional moulding and extrusion technologies [61].

**Thermoplastic starch**

Starch can be processed into thermoplastic starch (TPS) in presence of plasticizer and under action of high temperature and shear. Besides water, various polyols such as glycerol, glycol, sorbitol and sugars were applied as plasticizer in starch to obtain TPS. Addition of glycerol affects the onset of gelatinization and results in an increase in the activation energy for the melting of the starch crystallites, and results in higher glass transition temperatures and higher interactions forces between glycerol and starch polymers. Depending on the amount of glycerol in TPS the product may be in its glassy or rubbery state at ambient temperature. In the presence of sufficient water or glycerol under gelatinization conditions native starch becomes gel-like in appearance or properties but during the thermoplastic processing behaves like a polymer melt [62].
TPS is a low-cost biopolymer, however, it has some drawbacks while using it as a material for biodegradable products. One drawback is the so-called retrogradation and aging after being stored for a period of time. Starch retrogradation is re-crystallization of its molecules, which makes TPS fragile [63]. To prevent retrogradation of TPS, some plasticizers containing amide groups, such as formamide, acetamide and urea were successfully used [64]. The hydrophilic character of starch also retards its widespread industrial applications; once a starch product gets in contact with water, it swells and then even dissolves. The water resistance of TPS may be improved by mixing it with biodegradable polymers or inorganic materials (such as fly ash [64]). Another major disadvantage is that TPS has inherently poor mechanical properties (see in Table 2.2). It is possible to improve the mechanical properties by the addition of fillers, such as mineral clays, as demonstrated by Cyras et al. [65]. These composites could be use in packaging where good barrier and thermal properties are required. Another option is the use of natural fibres as reinforcement, which due to their similar chemical structure provide good compatibility and adhesion to the TPS matrix.

**Thermoplastic starch based biocomposites**

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. Such composites are completely biodegradable and composable and therefore considered “environmentally friendly” since, at the end of their useful life, they can be discarded without causing any damage to the environment. 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), content and form (fibre or fabric) and type of blending/plasticizer used) [66].

TPS is often blended with other (bio)polymers with the aim to reducing the overall cost of the final product. Besides, TPS can act as toughening agent by reducing the rigidity of the associated polymer [61]. 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 [67].

A number of TPS-based blends and composites have already been commercialised. Applications have tended to focus on markets for which renewability and biodegradation are value-added properties. Cost reduction resulting from starch incorporation may also be a benefit. Examples of applications where biodegradation is important include: food packaging (containers, wraps); disposable eating utensils; loose fill, antistatic, and formed protective packaging; and compostable films and bags for trash, retail, and agriculture.
2.2.3 CHARACTERISTICS OF POLYLACTIDE AND ITS BIOCOMPOSITES

Lactic acid

Lactic acid (2-hydroxypropionic acid) is a simple chiral molecule that exists as two enantiomers, L- and D-lactic acid (Figure 2.10), which differ in their effect on polarized light. Lactic acid can be produced by fermentative or chemical syntheses. The chemical synthesis is mainly based on the hydrolysis of lactonitrile by a strong acid, where a racemic mixture of the two forms (D(−) and L(+)) lactic acid is produced. The biotechnological production of lactic acid has received significant interest, since it is an attractive process in terms of its environmental impact and its combination of low production cost from sugarcane fermentation, decreased fossil-based feedstock dependency, reduced CO₂ emission, biocatalyst use, and high product specificity and, additionally, production of optically pure L- or D-lactic acid, depending on the strain selected. Approximately 90% of the total lactic acid produced worldwide is made by bacterial homo- and heterofermentation, and the remaining portion is produced synthetically by the hydrolysis of lactonitrile. The carbon source for microbial production of lactic acid can be either sugar in pure form such as glucose, sucrose, lactose or sugar containing materials such as molasses, whey, sugarcane bagasse, cassava bagasse, and starchy materials from potato, tapioca, wheat and barley. Lactic acid production has a great worldwide demand due to its versatile applications in food, pharmaceutical, textile, leather, and chemical industries and as monomer in the production of biodegradable polymers, such as polylactic acid (PLA) [68].

![L-lactic acid and D-lactic acid](image)

**Figure 2.10** L- and D-lactic acid

Polylactic acid

There are three possible ways for the polymerization of lactic acid: direct condensation polymerization, direct polycondensation in an azeotropic solution and polymerization through lactide formation [69]. The latter route is being industrially accomplished for production of high molecular weight PLA.

PLA is a linear polyester having stereocenter in its repeating unit. Due to the chiral character of lactic acid, the term “polylactic acid” refers to a family of polymers: pure poly-L-lactic acid (PLLA), pure poly-D-lactic acid (PDLA), and poly-D,L-lactic acid (PDLLA). As the biological metabolite is the L-isomer, L-lactic acid constitutes the main fraction of PLA derived from renewable sources. The stereochemistry and thermal history have direct influence on the crystallinity of PLA. PLA with PLLA content higher than 90% tends to be crystalline, while the less optically pure is amorphous. Depending on the composition of the optically active L- and
D-enantiomers, PLA can crystallize in three forms (α, β, and γ). [70]. The melting temperature ($T_m$), and the glass transition temperature ($T_g$) of PLA decrease with decreasing amounts of PLLA.

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 (see in Table 2.2), transparency, excellent thermoforming capability, easy processing by conventional equipment (which is of a commercial importance), high industrial production capacity, UV-stability, no toxicity, low emission of greenhouse gases, low amount of energy used for production, potential biodegradability. According to a life cycle assessment carried out by Vink et al. [71], PLA results in 15% to 60% lower carbon emissions and 25% to 55% lower energy consumption than petroleum-based polymers.

PLA degrades primarily by hydrolysis, after several months of exposure to moisture. Polylactide degradation occurs in two stages. First, random non-enzymatic chain scission of the ester groups leads to a reduction in molecular weight. In the second stage, the molecular weight is reduced until the lactic acid and low molecular weight oligomers are naturally metabolized by microorganisms to yield carbon dioxide and water. It is important to note, that any factor which affects the reactivity and the accessibility (such as particle size and shape, temperature, moisture, crystallinity, isomer ratio, residual lactic acid concentration, molecular weight, water diffusion and metal impurities from the catalyst) will affect the polymer degradation rate [68]. Controlling the hydrolytic degradability of PLAs is of great importance, and numerous studies have been undertaken to elucidate the effects of various components in the systems. Shinoda et al. [72] applied poly(aspartic-co-lactide) (PAL) to accelerate the degradation rate of PLA. Enhanced degradation rate was observed both in water, solid and composites with the addition of a small amount of PAL.

PLA based products are mainly produced by melt processing. Some of the examples of melt processed PLA are injection molded disposable cutlery, thermoformed containers and cups, injection stretch blown bottles, extruded cast and oriented films, and meltspun fibres for nonwovens, textiles and carpets. PLA also finds uses in other less conventional applications, such as for the housing for laptop computers electronics [70].

Although PLA is commercialised and more and more PLA products are on the market, these products are still mainly related to packaging industry, even so the high strength and stiffness of PLA suggest it to be used as the matrix of a durable engineering composite material, however, its low heat deflection temperature (HDT) and low impact strength still retards its usage as a high performance composite [73].

**Polylactic acid based composites**

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.
Ikada et al. [74] prepared various PLA blends to improve thermal resistance; the stereocomplexed PLLA/PDLA blend was found to have ca. 50°C higher melting temperature than those of pure PLLA and PLDA. Other researchers demonstrated that the thermal resistance of PLA can be increased with incorporation of fibrous substances. Iwatake and co-workers [75] demonstrated that 10% microfibrillated cellulose containing PLA composites, prepared by film-casting method, have constant storage modulus above glass transition temperature ($T_g$) (between 70 and 120°C), and suggested that the cellulose fibre network interconnected by hydrogen bonds resists the applied stress independently of the softening of PLA during dynamic mechanical analysis (DMA). Accordingly, in order to prevent the significant loss in stiffness of amorphous PLA products above $T_g$ and thus achieve increased HDT, strong fibre-matrix connection is crucial. By utilizing this approach, Tábi et al. achieved highly increased dimensional stability and storage modulus with silane-treated basalt fibre reinforced PLA composites [73].

In order to overcome the inherent rigidity and brittleness of PLA, several investigations have been conducted by researchers. PLA have been chemically modified with 2-methacryloyloxyethyl isocyanate (MOI) to prepare ductile PLA [76]. PLA have been melt-blended with plasticizers, such as adipates [77] and with tougher resins, such as a biodegradable poly(ether)urethane elastomer [78], polycaproactone, and also TPS. Blending of PLA with TPS results in improvement of the material ductility by preserving (or improving) the biodegradability and reducing the overall cost of the final product [61]. However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible, leading to poor adhesion between the two components, and thus poor and irreproducible performance. Hence, several strategies have been used to improve the compatibility of PLA and TPS such as by blending [79], using compatibilizers [80], amphiphilic molecules [81] or coupling agents [82]. Although these materials may improve the compatibility of PLA/TPS, they may not improve the mechanical properties of PLA blends enough to justify the additional cost of the material [83]. There is little information available on the use of fibre reinforced PLA/TPS blends. Teixeira et al. [83] blended PLA with increasing amount (0, 5, 10, 15 and 20 wt%) of cassava bagasse fibre reinforced TPS by extrusion and evaluated their morphological, mechanical, spectral, and thermal properties. As expected, the blending of TPS with PLA reduced the tensile strength (55.4 MPa) and modulus (2.4 GPa) of neat PLA. At 20 wt% cassava bagasse fibre reinforced TPS content the maximum strength (19.9 MPa) and tensile modulus (1.7 GPa) were reduced about 64% and 32%, respectively, compared to the PLA matrix.

Neat PLA has also been blended with natural fibres with the aim of decreasing costs while maintaining or improving the mechanical properties. Chopped natural fibres, non-woven webs as well as woven fabrics were used as reinforcements in PLA matrix.

Natural fibre/polylactic acid (PLA) composites were prepared with ramie and jute short fibre as reinforcement by Yu et al. [84]. The effect of natural fibre content was investigated on the mechanical properties of PLA composites. The best mechanical performance, such as tensile...
and flexural strength and modulus and impact strength, was found at a fibre weight fraction of 30%. At fibre content higher than 30% the tensile strength decreased even to lower value than that of neat PLA, which was explained by the poor dispersibility of high amount of fibre in the PLA matrix.

Flax fibre reinforced PLA composites with flax fibre contents of 30 and 40 wt% were manufactured with twin-screw extrusion and subsequent compression moulding by Oksman et al. [85]. The addition of flax fibres did not improve the tensile strength of PLA, which indicated poor adhesion between the flax fibres and the matrix, so that the stress is not transferred from the matrix to the stronger fibres. However, the flax fibres increased the stiffness of PLA, the tensile modulus increased from 3.4 to 8.4 GPa at 30% flax fibre content.

Bax and Müssig [86] used Cordenka rayon fibres and flax fibres to reinforce PLA. Their composites were prepared by injection moulding. The highest Charpy unnotched impact strength (72 kJ/m²) and tensile strength (58 MPa) were found for Cordenka reinforced PLA at a fibre content of 30 wt%. The highest Young’s modulus (6.31 GPa) was found for the composite made of PLA and flax. However, also poor fibre-matrix adhesion was observed for both composites using SEM.

As it can be seen, several papers reported the preparation of natural fibre reinforced PLA composites and claimed that the low compatibility of hydrophobic PLA with hydrophilic natural fibres leads to composites with poor mechanical properties. On the other hand, Faludi et al. conducted essential research in understanding the structure-property correlations in lignocellulosic fibre reinforced PLA composites [87]. They estimated the interfacial adhesion by quantitative estimation of the adhesion strength, by acoustic emission measurements and by SEM studies, and contrary to most claims published in the literature, found that interfacial adhesion between PLA and natural fibres is rather strong [88].

Generally, to improve the interfacial adhesion between natural fibres and the matrix, chemical modifications, such as silanization of natural fibres have been studied and found to improve the mechanical properties of the composites. Kumar et al. [89] investigated the effect of fibre treatment with amphiphilic additives, such as mandelic acid, benzilic acid, dicumyl peroxide (DCP) and zein, and the addition of montmorillonite (MMT) clay on the interfacial adhesion and mechanical properties of woven flax fabric (30 wt%) reinforced PLA composites. Among the tested additives, DCP was found to be the most effective in maintaining high values of tensile strength and modulus both in presence and absence of MMT.

To improve the interfacial adhesion in PLA/wood composites Faludi et al. proposed the use of two reactive coupling agents, N,N-(1,3-phenylene dimaleimide) and 1,1-(methylene-4,1-phenylene)bismaleimide and a resol type phenolic resin. All three compounds improved the properties of the composites. Stiffness, strength and deformability increased simultaneously supplying sufficient proof for coupling [90,91].
Baghaei et al. [92] prepared unidirectional hemp/PLA yarn (30 wt%) reinforced PLA composites using compression moulding and investigated the influence of fibre orientation and alkali treatment on the mechanical properties of the PLA/hemp composites. The best overall properties were achieved with 0° axial oriented, aligned alkali treated hemp/PLA yarn leading to a tensile strength of 77.1 MPa, Young’s modulus of 10.3 GPa, flexural strength of 100.9 MPa, flexural modulus of 7.1 GPa, and impact strength of 18.8 kJ/m². The results showed that the mechanical properties of the composites were highly affected by the fibre direction.

Porras and Maranon [93] produced bamboo woven fabric reinforced PLA composites using the film-stacking method. Compared to neat PLA a 30% increase in tensile strength and a 57% increase in impact resistance were measured for the PLA/bamboo fabric laminates with 51 vol% fabric content.

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. [44], 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.

Gaupner and co-workers [94] prepared PLA composites using various natural fibres such as cotton, hemp, kenaf and man-made cellulose fibres (Lyocell) and their mixtures at 40% weight proportion by compression moulding. The mechanical characteristics of the obtained composites varied markedly depending on the characteristics of the used raw fibres. While kenaf and hemp/PLA composites showed very high tensile strength and Young’s modulus values, cotton/PLA showed good impact characteristics. Lyocell/PLA composites combined both, high tensile strength and Young’s modulus with high impact strength. It was revealed that composites of fibre mixtures can combine the positive properties of different fibres, thus playing with the different fibre characteristics the design of composite properties is possible. Learning from nature what the function of a fibre in a plant is, the composite properties can be designed by adding seed fibres with high elongations for improved impact resistance or stem fibres for improved stiffness.
2.3 Flame Retardancy of Polymers

Extensive statistical researches show [95,96] that with the expansion of plastic usage the number and danger of fire risk scenarios have been dramatically increased endangering our everyday life. The time available for building evacuation was around 17 minutes in the seventies, while it is around 3 minutes nowadays. It is revealed that plastic objects are responsible for 25% of fire-caused injuries and for 40% of deaths. The fire hazard associated with the use of plastics is of particular concern among government regulatory bodies, consumers and manufacturers as well. Therefore, the use of flame retardants to reduce combustibility, smoke or toxic fume production of the polymers has become a pivotal part of the development and application of new materials, especially in the electrical/electronic, building/construction and transportation application fields [97].

The combustion of polymers is a complex physico-chemical process involving chemical reactions of polymer degradation in the condensed phase, chemical decomposition and oxidation of gaseous (pyrolysis) products and heat- and mass-transfer processes. There exist two approaches to achieve flame retardancy in polymers, i.e. to prevent combustion and to delay the spread of fire after ignition, generally known as the “additive” type and the “reactive” type. Additive type flame retardants (FRs) are generally incorporated into the polymeric matrix by physical means. This obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers. Nevertheless, a variety of problems, such as poor compatibility, leaching, and a reduction in mechanical properties, weaken their attraction. The application of reactive flame retardants involves either the design of new, intrinsically flame retarding polymers or modification of existing polymers through copolymerisation with a flame retarding unit either in the chain or as a pendant group. However, new polymer design lacks sufficient versatility in manufacturing and processing and is uneconomical mainly due to the expense associated with qualifying a new material for use. In the case of the modification approach the flame-retarding unit is covalently incorporated in the polymer backbone and the original physical and mechanical properties can be maintained [98]. The reactive type flame retardants do not migrate to the matrix surface either during high temperature processing or application and generally less FR, compared to the additive approach, is needed to achieve same level of flame retardancy, which in turn leads to reduction of toxic gas emission.

All flame retardants act either in the vapour phase or the condensed phase through a chemical and/or physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition or flame spread. Figure 2.11 demonstrates the condensed phase and gas phase actions of the mostly used flame retardants. For example, the flame retarding action of hydrated fillers is mainly based on their endotherm decomposition which cools the pyrolysis zone and the release of non-flammable gases which dilute the concentration of decomposition gases. Halogen, phosphorus and antimony act in the vapour phase by a radical mechanism to interrupt the exothermic processes and to suppress combustion. Phosphorus can also act in the condensed phase promoting char formation on the surface,
which acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air. Another major category of flame retarding mechanism is known as “intumescent”, according to which materials swell when exposed to fire or heat to form a porous foamed mass, usually carbonaceous, which in turn acts as a barrier to heat, air and pyrolysis products [97].

**Figure 2.11 Condensed phase and gas phase actions of flame retardants**

The application of halogenated components is one of the most effective methods for the preparation of flame retarded polymeric systems. However, the increasing focus on health and environmental compatibility of flame retardants has resulted in a steady decline in the acceptance of these products. According to the directives of the European Parliament from July 2006 the most used halogenated flame retardants are banned from the market [99]. The sustainable development concept applied to this field implies that fire retardants should involve a low impact on health and environment during the entire life cycle including recycling and disposal. At the same time, the rising cost pressure in industry requires cost-effective solutions. Substantial amount of research and development has been focused on the replacement of the halogen-containing flame retardants by economical halogen-free products. The water releasing inorganic additives, such as metal hydroxides, meet the health, environmental and cost requirements but the very high concentration, needed for appropriate flame retardant effect, restricts their widespread use. Today, the most intensive research is focused on the development of phosphorus-containing flame retardants of reduced ecological impact. Different kinds of additive and reactive approaches to compounds containing phosphorus are finding success, so that they are increasingly proposed as halogen-free flame retardants for various polymeric materials and applications.

### 2.3.1 MECHANISM AND APPLICATION OF PHOSPHORUS BASED FLAME RETARDANTS

The range of phosphorus containing flame retardants is extremely wide, since the element exists in several oxidation states. Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphates are all used as flame retardants.
As mentioned above, phosphorus 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 the former case hydrogen and hydroxy radicals are replaced by less reactive radicals or are rendered harmless by radical recombination in the gas phase. As a result, chain reactions of the oxidation of hydrocarbons in the gas phase are slowed down or interrupted, and thus the heat production is reduced. The PO-radical is believed to play the major role during the gas-phase action [97]. The solid-phase action of phosphorus-containing flame retardant is mainly connected to the formation of polyphosphoric acid upon heating. This acid initiates the formation of a char layer, which shields the material from oxygen, in that way preventing the formation of flammable gases [100]. However, if a char-former is present, then an additional chemical effect of char promotion exists. This is particularly the case in more complex phosphorus-containing systems, where a polyol is present to enhance the char-forming tendency. This kind of phosphorus-containing flame retardant is usually formulated as the combined acid and carbon source in intumescent systems. An intumescent char-forming system usually acts by combined chemical and physical reaction to form a rigid voluminous foamed residue or char, which offers protection to the underlying substrate from further decomposition [101]. Intumescence in polymeric materials can be used to reduce the heat release rate by slowing down the pyrolysis front velocity, or even to achieve extinction before the pyrolysis front passes through the whole specimen. In the latter case the insulation of the char decreases the temperature in the underlying material to keep it from reaching the decomposition temperature of the polymer [97].

In fact, for many phosphorus-based systems a significant action has been determined in both the gas and condensed phases. The occurrence and the efficiency seems to depend not only on the chemical structure of the phosphorous flame retardant compound itself, but also on the interaction during pyrolysis with its chemical environment, including the polymeric material and other additives. Indeed, as reported by Schartel [97], the mechanism and efficiency of phosphorous flame retardants are influenced and can be optimized by modifying the flame retardant using synergists and adjuvants and by changing the polymeric material.

2.3.2 INTUMESCENT FLAME RETARDANT SYSTEMS AND THEIR SYNERGISTS

Recently, the intumescent flame retardants (IFRs) have found an important place in the flame retardant market as safe and environmentally friendly additives providing flame retardancy to polymers. 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 (Figure 2.12). The flame then extinguishes because it is not adequately fed. The intumescence occurs with limited evolution of volatile products, thus low amount of smoke and toxic or corrosive gases are produced, and also the undesired secondary effects are minimised in the case of this condensed-phase mechanism of fire.
retardance. Furthermore, the intumescent char adhering to the molten section of the burning polymer prevents it from dripping, thus eliminating a possible source of propagation of fire [102].

![Figure 2.12 Intumescent flame retardant mechanism](image)

An IFR system is commonly composed of three components: an acid source (eg. acids, ammonium salts, phosphates), a carbonisation or char forming agent (polyols such as pentaerythritol and starch, polyamides), and a blowing agent which produces gases on heating (eg. melamine, urea). On heating, the acid source transforms to mineral acid that takes part in the dehydration of the carbonising compound that forms a cellular structure when the blowing agent decomposes. A typical IFR system is ammonium polyphosphate/pentaerythritol/melamine (APP/PER/MEL) mixture [103]. As APP acts both as the acid source and blowing agent during combustion, MEL is not necessarily used. The optimal weight ratio of APP/PER was investigated by several researchers, the best flame retardant performance was observed when the APP to PER ratio was 2:1 in the system [104].

Bourbigot and co-workers [105] investigated the carbonization mechanisms leading to intumescent phenomena of an APP/PER system in polypropylene and proposed a multi-step carbonization process. In the first stage (190°C<T<280°C) the reaction of the acidic species with the carbonisation agent takes place with formation of ester mixtures. In the second step, occurring between 280 and 350°C, the foaming agent decomposes to yield gaseous products which cause the char to swell. Then between 350°C and 430°C, decomposition of this intumescent layer occurs. At higher temperatures, there are structural changes leading to the formation of a new carbonaceous and polyaromatic species (established at the temperature about 430°C), whose carbon organisation in stacks is characteristic of a pre-graphitisation stage.

There are some problems associated with the IFR systems, such as their moisture resistance and poor compatibility with the polymer matrix. The blending of the hydrophilic PER and APP with PP leads to considerable decrease in mechanical properties as a consequence. Further drawbacks are the low thermal stability and poor flame retardant efficiency at low
IFR concentrations. In order to overcome these drawbacks and enhance the flame retardancy, new IFR systems have been developed and synergistic agents have been used in IFR systems.

Instead of the highly hydrophilic PER, Lv et al. [106] used its two derivatives, dipentaerythritol (DPER) and tripentaerythritol (TPER) of less water solubility in their IFR system. Demir et al. [107] found that surface modification of APP with 3-(trimethoxysilyl)-1-propanethiol coupling agent can improve its water resistance and the compatibility.

Synergistic effect was revealed for a large variety of chemical compounds and fillers, such as organoboron siloxane [108], polysilsesquioxane [109], iron powder [110], transitional metal oxides and other metal compounds [111], zinc borate [112], expandable graphite [113], silica [114], zeolites [115], sepiolite [116], montmorillonite [117], etc. Many researches have shown that synergistic agents can effectively increase the strength and stability of char layer by Si-O-P-C and Al-O-P-C bonds, and promote in catalyzing the reactions among IFR components in PP/IFR systems [115, 118]. It was also shown by Bertelli et al. [119] that above a given loading of fillers (hydrated silica and alumina in the studied case) there is a general tendency to a decrease in swelling and loss of the foamed structure of the char, while thermal insulation deteriorates and fire retardant characteristics worsen. On forced burning, the fillers decrease the rate of combustion. The results are tentatively interpreted on the basis of heat and mass transfer through the char as physical parameters which control the fire retardant effectiveness of the intumescent system.

2.3.2.1 INTERACTION OF FIBRES AND INTUMESCENT SUBSTANCES

Intumescence is of general application in polymers, in particularly in polyolefins, and more recently in their fibre reinforced composites as well. It was proposed by researchers that fibres, depending on their type and chemical structure, may interact with intumescent flame retardant systems. Accordingly, fibres can be classified into three groups, inert or inorganic fibres, organic char forming fibres and non-char forming fibres. Inorganic fibres, such as glass, silica or alumina, are very good protective barriers for flame and heat, they can withstand temperatures up to 1100°C for a considerable time. In contrast, conventional organic fibres or textiles are highly flammable due to their high specific surface area, which significantly enhance the rates at which pyrolytic formation of volatile fuels and subsequent combustion occurs. Char-forming organic fibres are either natural, such as cellulose and wool, or synthetic thermoplastics with aromatic structure such as some polyesters and polyamides. Other organic thermoplastic fibres, such as polyolefins, on the other hand, have poor or zero char-forming capability.

When incorporated in a polymer matrix, glass fibres cause a so called “candlewick effect”, which generally means a big challenge for the flame retardation of the thermoplastic composites [120]. Due to the candlewick effect, glass fibres are able to transfer and feed the fuel from the pyrolysis zone of the polymer matrices to the flame by capillary action, speed the heat flowing back to polymers and thus make the polymers decompose and burn faster.
Thus, to achieve UL-94 V-0 rating, the glass fibre reinforced thermoplastics need higher amount of flame retardants than neat polymers do [121]. Liu et al. [122] observed during cone calorimeter tests that long glass fibres destroy the foaming capability of the intumescent flame retardants and the continuity of the residue char, which decrease the flame retardancy of IFR in IFR-LGFPP samples.

Natural fibres, such as ramie and flax, were found to cause candle-wick effect as well [123]. The cellulosic fibres speed the transfer of the flammable mass to the burning area and make the natural fibre reinforced composites more flammable. However, it has been demonstrated by Horrocks [124], that if an intumescent is interspersed within a flame retardant fibrous assembly and both components char, then a so-called “char-bonded structure” may arise. This integrated fibrous-intumescent char structure has a physical integrity superior to those of charred fabric or intumescent alone and because of reduced oxygen accessibility, demonstrates an unusually high resistance to oxidation when exposed to temperatures above 500°C. Furthermore, these composite structures show significantly reduced rates of heat release when subjected to heat fluxes of 35 kW/m² thus demonstrating additional significant fire barrier characteristics. Le Bras et al. [125] also showed that association of charring of cellulosic material (flax fibre) and of intumescent system allows to obtain an optimised FR formulation. The effectiveness of the char-bonded structure as a flame and heat barrier is considered to be dependent on the efficiency of the interaction of fibre and intumescent char-forming substances. Similar interactions are not seen with glass fibres and non-char-forming thermoplastic fibres [126].

It is stated by Horrocks [124], that thermoplastic fibres, such as polypropylene and some polyesters, even when flame retarded using either comonomeric modifications or additives introduced during polymerisation and/or fibre extrusion stages, melt drip and/or form holes when exposed to flame. They cannot, therefore, be used in applications, such as protective clothing and barrier textiles, where sustained thermal protection via char formation is an essential requirement.
2.4 Flame Retardancy of Biopolymer-Based Thermoplastic Composites

The main deficiency of the biopolymer-based composites, similarly to mineral oil-based ones, is their flammability during their use. In order to meet the strict safety requirements of more demanding sectors as automotive and aircraft industries, their flame retardant (FR) properties have to be improved by maintaining other important characteristics as mechanical and thermal properties, and also considering environmental issues as risks for human life and environment, waste treatment and recycling.

Limited number of papers have been published until now on flame retardancy of biocomposites. Most of them are dedicated to materials using PLA as matrix [127], but the flame retardant possibilities of PBS [128] and TPS [129] based green composites have also been investigated. Flame retardants have been either incorporated into the biopolymer matrix or used on the surface of the reinforcing natural fibres by means of impregnation or grafting, but the best results were obtained when both strategies were combined. The most commonly used flame retardants in green composites are the environmentally favoured phosphorus-based compounds [130,131,132], because they are safe during their production and use, furthermore, not harmful at the end of their life. A review on inorganic polyphosphates by Kulakovskaya et al. [133] claims that APP, the most commonly used component of intumescent flame retardant systems, is a nontoxic and biodegradable compound; its degradation by hydrolysis leads to ammonium phosphates which are common plant nutrients. Therefore, it is an obvious choice to use APP-based flame retardant systems in biodegradable polymer matrices without hindering their biodegradation.

The known flame-retardant synergism between phosphorus-based additives and metal oxides, used earlier for petroleum-based plastics, has been extended recently to bio-based materials (PHBV/PBAT blends) by Gallo et al. [134]. Nevertheless, the researchers strive generally for non-toxic and green (bio-based) solutions to flame retard biopolymers in order to keep the environmentally friendly character of the final product. As for an example, lignin, chemically modified with phosphorus compounds, was found to be an effective bio-based flame retardant when applied in polybutylene succinate (PBS) [135].

2.4.1 Phosphorus-Based Flame Retardancy of Natural Fibres

Natural fibres represent an obvious choice as reinforcement for bio-based polymer matrix materials, as with their combination all-bio composites can be prepared. Lower density, renewability and biodegradability, as well as lower price and composite processing costs make them promising alternatives to the commonly applied synthetic carbon, glass or aramid fibres [136]. Kenaf, hemp, flax, jute, and sisal have attained commercial success in designing biocomposites. Among their disadvantages, such as fluctuating fibre quality, high moisture uptake, limited processing temperature range, low impact strength and durability, their flammability represents a major drawback, especially in more demanding sectors as automotive, aircraft and electronic industries.
The flammability of bio-based fibres depends mainly on their chemical composition (determining their thermal degradation), but also on their structure, degree of polymerization and fibrillar orientation. The thermal degradation of the natural fibres is a well-described phenomenon [137,138,139]. It involves several processes as desorption of absorbed water, depolymerisation of cellulose leading to dehydrocellulose and water, decomposition of the formed dehydrocellulose to char and volatiles, formation of levoglucosan and its decomposition to flammable and non-flammable volatiles and gases, tar and char. The main characteristics of the thermal degradation behaviour of the major natural fibre components and their effect on flammability are summarized in Table 2.4.

<table>
<thead>
<tr>
<th>main component</th>
<th>temperature range of thermal degradation</th>
<th>major decomposition products</th>
<th>effect on flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose</td>
<td>260-350°C</td>
<td>flammable volatiles, gases</td>
<td>increased flammability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>incombustible gases, tars, less char</td>
<td></td>
</tr>
<tr>
<td>hemicellulose</td>
<td>200-260°C</td>
<td>incombustible gases, less tar</td>
<td>decreased flammability</td>
</tr>
<tr>
<td>lignin</td>
<td>160-400°C</td>
<td>aromatic char</td>
<td>higher decomposition temperature, lower resistance to oxidation</td>
</tr>
</tbody>
</table>

As for the chemical composition of fibres, lower cellulose content and higher lignin content reduce their flammability. Concerning the fine structure of fibres, the high crystallinity of cellulose leads to formation of high amount of levoglucosan during pyrolysis and consequently to increased flammability, so from this point of view lower cellulose content is preferred. On the other hand, as more activation energy is required to decompose the crystalline structure of the cellulose, it results in higher ignition temperature. As for the degree of polymerization and orientation of the fibrillar structure higher molecular weight and orientation (resulting in lower oxygen permeability) is favourable.

As mentioned in Section 2.3.2.1, when bio-based fibres are used as reinforcements in polymer matrices (without adding flame retardants to the polymer matrix) to form biocomposites, the heat conductivity increases while the apparent stability of the polymer decreases, therefore the ignition of the composite is facilitated [125]. This is ascribed to the candlewick effect of natural fibres, which encumbers the flame retardancy of the biocomposites reinforced with these fibres [123,131]. Thus the flame retardant treatment of biofibres was found to be essential from this respect as well.

The flammability of natural fibres and composites made thereof can be decreased with flame-retardant fibre treatments. Most of the flame retardants for cellulosic fibres function via condensed phase conversion of the fibres to carbonaceous char. This reaction is considered to be an acid-catalyzed dehydration. Char-promoting flame retardants for cellulose typically contain phosphorus, either as acidic salts (e.g. ammonium phosphate derivatives) or as organophosphorus (e.g. phosphonium salt and phosphonate derivatives) species. On heating they first release polyphosphoric acid which phosphorylates the C(6) hydroxyl group in the anhydroglucopyranose moiety and simultaneously act as an acidic
catalyst for dehydration of these same repeat units. The first reaction prevents formation of laevogluscosan, the precursor of flammable volatile formation, and this ensures that the competing char-forming reaction becomes the favoured pyrolysis route [124].

A large variety of phosphorous compounds have been used to flame retard cellulose based fibres [130,140,141,142]. Gaan and Sun [141] investigated the flame retardancy effect of six organophosphorus compounds, including Pyrovatex CP (PCP), diammonium phosphate (DAP), phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP) and triallyl phosphoric triamide (TPT) on cotton cellulose. PCP, PA and DAP were found to be more efficient in improving the limiting oxygen index (LOI) of cotton compared with the other three compounds of the same phosphorus content, furthermore, PA, PCP, and DAP treated fabrics had a higher activation energy of decomposition, higher char content and lower heat of combustion.

Nitrogen-containing additives, including cyanamide [143], guanidine carbonate, melamine – formaldehyde [144] and urea [145], have shown synergistic function with phosphorous compounds. Recently also the bio-based chitosan was demonstrated to have synergism with DAP [146]. Many researchers have tried to explain how and why N additives enhance the efficiency of P-FRs, and their theories have been outlined by Gaan et al. as follows [141]:

1. N additives facilitate the phosphorylation reaction of P-FRs.
2. N additives and P-FRs interact to form P-N bonds, which have better thermal stability than P-O bonds and thus increase the retention of P and N in char. The intermediate products containing P=N or P-NH₂, which are formed during pyrolysis, efficiently phosphorylate cellulose and catalyze a dehydration reaction.

There is also a particular interest for reactive flame retardant finishes, however, the currently commercialized major durable finishes (e.g. Proban® (Rhodia) and Pyrovatex® (Huntsman)) involve the use of formaldehyde during manufacture or application with associated health risks during processing, and end-use. The recently introduced Firestop product Noflan® is formaldehyde-free alkyl-phoshoramidate stabilized as a salt adduct with ammonium chloride. It may react with cellulosic substrates via the phosphoramidate-NH₂ group, which is, however, not very reactive. For making it effective in cellulosic-based textiles, it is applied either in a resin binder or cross-linked using a methylolated resin [147]. Recently, Liu et al. [148] synthesized a novel formaldehyde-free flame retardant, poly (1,2-dicarboxyl ethylene spirocyclic pentaerythritol bisphosphonate) (PEPBP), and successfully used as reactive flame-retardant finishing agent for cotton fabrics.

It is evident from literature, that phosphorus-containing flame retardants can efficiently initiate the charring of natural fibres, which is favourable in terms of flame retardancy, however, the application of these treatments decreases the initial decomposition temperature of natural fibres significantly [145]. The reduced thermal stability can be a
major issue, both from mechanical and aesthetic point of view, when the natural fibres are intended to be used as fillers or reinforcements in polymer composites. Presence of water, acids and oxygen catalyses the thermal degradation of cellulose, therefore natural fibres usually turn brown during fibre treatments. Low thermal stability is critical in case of thermoplastic matrices with processing temperatures above 140°C (such as PP, PA, PET and also PLA). Surface treatment with silane compounds is a possible solution to increase the thermal stability of cellulosic fibres [149,150]. In the presence of moisture, the hydrolysable alkoxy groups of silanes lead to the formation of silanols, which then react with the hydroxyl groups of the cellulosic fibre, and form stable covalent bonds to the cell wall that are chemisorbed onto the fibre surface. Recently, the layer by layer assembly came to the forefront for rendering textiles flame retardant without compromising, or even increasing thermal stability [151,152].

2.4.2 PHOSPHORUS-BASED FLAME RETARDANCY OF THERMOPLASTIC STARCH AND ITS COMPOSITES

Only a few examples exist for flame retardancy of thermoplastic starch or its composites. The pioneering work has been published by our research group (Matkó et al. [129]), where the use of ammonium polyphosphate (APP) was reported to effectively flame retard glycerol plasticized TPS. Compared to the low LOI (23 vol%) of neat TPS, a LOI value as high as 33 vol% and UL94 V-0 were achieved by incorporating only 10 wt% APP. By further increasing the APP concentration to 30 wt%, a flame retardant TPS with LOI of 60 vol% was obtained.

Wu et al. [153] proposed that in PVA/glycerol-plasticized thermoplastic starch (TPS) blend and its intumescent flame retardant composites, microencapsulated form of ammonium polyphosphate is necessary in order to restrain the reaction between APP and starch during processing. These composites with only 2 wt% APP can pass V-0 in UL-94 test and their LOI value is 31 vol%.

Most of the starch-based thermoplastic polymer blends are, however, mechanically not acceptable, especially when sufficient amounts of flame retardants are introduced. Melt-blending of starch with other biodegradable polymers is rather difficult since very few polymers are compatible with starches. Fibre reinforcement is, therefore, a better way to achieve improved mechanical properties. Still, until now, in the literature only one paper by Wittek and Tanimoto [154] has been published results regarding the flame retardancy of fibre reinforced TPS based composites. They used a resin emulsion based on thermoplastic starch and polycaprolactone (PCL) as biodegradable matrix material in combination with basalt fabrics as reinforcement to obtain biocomposites. In order to enhance the fire retardancy of the biocomposites, a red phosphorus based additive and magnesium-hydroxide were applied to the bioresin. Although the 4.5 wt% flame retardant loading of both types of additives proved to be sufficient to cease the horizontal flaming of the samples, since vertically the composites burnt completely, their UL-94 rating remained HB. It can be concluded that in this field there is a particular need for further investigations.
2.4.3 Phosphorus-based Flame Retardancy of Polylactide and Its Composites

As PLA has already found applications not only in packaging but some examples appeared even in engineering fields (such as in construction, electronics and automotive industry), where the fire hazard is an issue, thus the possibilities of its flame retardancy have been extensively investigated recently.

According to thermogravimetric analysis, PLA degrades in a main apparent step taking place between 300 and 400°C (highest degradation rate is observed at 350°C). The thermal degradation of PLA is based on a hydroxyl end-initiated ester interchain process and chain homolysis. In the condensed phase, the char yield is quite low (about 2 wt%) [155]. Flame retardants should therefore act before the degradation of PLA (T < 300°C) and/or modify the degradation pathway of PLA to yield char and to avoid (or at least to decrease) the evolution of flammable products (acetaldehyde, lactide, methane etc.). For this purpose condensed phase mechanisms of action are proposed in the literature (almost in all cases) to flame retard PLA.

In 2010, a comprehensive review on the flame retardancy of PLA was published by Bourbigot and Fontaine [156]. Among the phosphorus-based additives, Bourbigot et al. compared the flame retardant effectiveness of phosphine-based flame retardants, designed for polyamides and polyesters, to ammonium polyphosphate (APP) and melamine polyphosphate (MP) in PLA [157]. The LOI of the flame retarded PLA samples increased with the additive content, the highest LOI value (34 vol%) was measured for the 30 wt% APP containing PLA. UL-94 V-0 rating was reached only at 20 wt% loading of MP and at 25 wt% loading of the combined (Al-phosphinate and MP containing) additive. The UL-94 rating of the other flame retardant compositions remained V-2 due to flammable dripping. At 30% additive content, a 33% reduction of peak of heat release rate (pkHRR) was measured for the MP containing PLA sample, while for the other flame retardants the reduction was poor. The slight reduction of pkHRR was assigned to the low viscosity of the FR PLA upon heating. It was proposed, that the charred material formed by the reaction between the additives and the polymer is not viscous enough to be expanded by the fuel consisting of the degradation gases and then to make a protective coating. These results clearly show that the flame retardancy of PLA is rather challenging.

The concept of intumescence was applied for flame retarding PLA by several researchers. A new intumescent flame retardant (SPDPM) was synthesized from spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride (SPDPC) and melamine by Zhan et al. [158]. At 25 wt% loading of SPDPM UL94 V-0 rating, LOI as high as 38 vol% and by 33% reduced pkHRR (measured by microscale combustion calorimetry) were achieved. It was reported that the flame retardant mechanism of SPDPM in PLA was not only due to the intumescent protective charred layer but also for the change of the degradation process of PLA.

In order to maximize the quantity of bioresources in a conventional, i.e. APP and PER based, intumescent flame retardant system in PLA, Reti et al. [67] investigated the substitution of
the petrol-based PER by biobased carbonization agents, lignin and starch. Surprisingly, UL-94 V0 ratings were reached only for the lignin and starch containing IFR systems, however lower LOI values and somewhat inferior flame retardant performance during cone calorimeter test were obtained for the “green” compositions compared to those of the PER containing sample. The composition of the “green” intumescent systems was optimized by an experimental design. As a result, besides maintaining the V-0 classification, a 32 vol% LOI value was obtained for the composite containing 60% PLA, 12% APP, and 28% starch.

In the green intumescent composition of Wang et al [159], microencapsulated ammonium polyphosphate (MCAPP) is used as the acid source, melamine (MA) acts as the blowing agent, while also starch functions as the carbonization agent of renewable source. In their system, APP is microencapsulated by polyurethane with the aim to improve its compatibility with PLA and also to retard the reaction between acid and carbonization agent during processing. The PLA composites containing 20 wt% IFR (composed of MCAPP and MA in a weight ratio of 2 to 1) and 10% starch reached UL94 V-0 rating accompanied with a high LOI value of 42 vol%.

β-cyclodextrin (CD), another alternative green carbon source, was used by Feng [160] in an intumescent system. The TGA results indicated that CD, as a “green” charring agent, demonstrates outstanding char formation ability in PLA when used in combination with APP and melamine. When the complex contained CD/APP/MA at weight ratio of 1/2/1 and the total amount of complex in PLA was 20 wt%, the PLA composites showed LOI values of 34.2 vol% and passed UL-94 V-0.

Polymer nanocomposites exhibit low heat release rate in cone calorimeter but they often fail at other tests, in particular at those investigating samples in vertical position (e.g. LOI, UL-94). The mechanism of protection involves the formation of char layer covering the entire sample surface acting as insulative barrier and reducing volatiles escaping to the flame. The formation of such a layer which does not form cracks when burning is critical to obtain low heat release rate from nanocomposites. It is the reason why nanoparticles have been combined with conventional flame retardants, such as intumescent systems, in order to create a synergistic effect [156].

Fontaine and Bourbigot [161] combined organomodified montmorillonite (o-MMT) and multiwall carbon nanotubes (MWCNTs) with intumescent flame retardant system composed of APP and melamine (in a ratio of 5 to 1). Significant synergistic effect was evinced when o-MMT was used, whereas antagonistic effect was observed when MWCNTs were used. At a total loading of 10 wt% UL-94 V-0 rating and LOI of 35 vol% were reached for the formulation with o-MMT. The unfavourable results with MWCNT were assigned to the imperfect dispersion of MWCNTs in the matrix, resulting in accumulation of MWCNT in the intumescent char leading to the percolation threshold. As a consequence, the apparent heat conductivity increases significantly and does not permit the intumescent coating to play its role of heat barrier.
The effects of o-MMT incorporation into an intumescent flame retardant (IFR) system on the flame retardancy and melt stability of PLA were also investigated Li et al. [162]. At a total additive loading of 20 wt% UL94 V-0 rating was achieved and LOI value increased from 20.1 for pristine PLA to 27.5 for the flame-retarded PLA. According to thermogravimetric analyses (TGA), MMT provided increased thermal stability to the PLA composites, furthermore MFI and rheological measurements indicated that o-MMT significantly enhances the melt stability of PLA, which is of key importance to suppress melt dripping. The improvement of the melt stability and restraint of the mobility of the polymer chains by adding o-MMT contributed to the formation of a continuous, dense and integrated closed honeycomb pore structure, which results in improved flame retardancy of the composites.

Besides incorporating conventional flame retardants and fillers, several possible solutions for inherent flame retardation of PLA have been also described. The copolymerization of D,L-lactic acid (LA) with 3,3’-diaminobenzidine (DAB) via melt polycondensation resulted in a copolymer with improved thermal stability [163]. By chain extension with P-containing moieties, the flame retardant can inherently be incorporated into the polymer backbone. Wang et al. developed different chain extended structures from dihydroxyl-terminated pre-PLA, either by the application of ethyl phosphorodichloridate [164], or by using hydroquinone-modified 9,10-dihydro-9-oxy-10- phosphophenanthrene-10-oxide (DOPO) and 1,6-hexamethylene diisocyanate [165]. In the first case, the synthesized P-containing PLA (PPLA) showed significantly lower peak of heat release in microscale combustion calorimeter than the neat PLA, and the peak appeared at 60°C higher temperature. The PPLA has also been used as additive flame retardant in PLA. At 10% PPLA loading, a LOI value of 34 vol% and UL-94 V-0 rating was reached [164]. The DOPO-modified PLA itself reached UL-94 V-0 rating and high, around 30 vol% LOI values, independently of the applied diol-diisocyanate ratio [165].

Achieving a good balance of the fire safety and mechanical properties is a challenge in the case of biocomposites as well. Therefore, the flame retardancy possibilities of natural fibre reinforced green composites of PLA have been also investigated. Suardana et al. [130] fabricated coconut filter and jute fibre reinforced PLA composites. To improve the flame retardancy of the bio-composites, the fibres were treated with diamonium phosphate (DAP). Increasing the percentage of DAP for treatment of the fibres in the composites decreased the temperature required for 5% weight loss and the decomposition rate, but increased the char residual at 500°C. The lowest linear burning rate and weight loss rate were observed for fibre treatment with 5% DAP. However, the flexural and tensile strength became lower than those of untreated fibre composites. On the other hand, the tensile and flexural moduli of DAP-treated fibre composites are generally higher than those of untreated fibre composites, which were attributed to the interaction between natural fibre, DAP and PLA, which indicates a good compatibility among them. The natural fibre reinforced PLA composites were found to have good flame retardant and mechanical properties but lack of wear resistance.
Li et al [123] compared the flammability properties of ramie fibre (30 wt%) reinforced PLA composites flame retarded with APP by three different processes: (1) PLA was blended with APP and combined with neat ramie fibres, (2) ramie fibres were treated with APP and then compounded with PLA and (3) both PLA and ramie fibres were flame retarded using APP and blended together. In contrast to the identical APP loadings (10.5 wt%), significantly better flame retardancy was evinced for the composites where APP was present in both phases, which they explained by the successful elimination of the candlewick effect of the ramie fibres. The LOI of the best formulation reaches 35 vol% and the formulation exhibits V-0 rating.

Similar conclusions were drawn by Chen et al. [131], who used melamine-formaldehyde microencapsulated ammonium polyphosphate (MCAPP) to flame retard ramie fabric (30 wt%) reinforced PLA composites. To improve the interaction between the ramie fibre and the polymer 3-aminopropyltrietoxysilane was used as coupling agent. When MCAPP was applied both in the matrix and on the surface of the ramie fabrics, effective flame retardancy was observed. At a total MCAPP content of 10.5 wt% UL-94 V-0 rating and LOI value higher than 35 vol% were achieved.

Because of the growing market of PLA for durable applications where flame retardancy is required, increasing number of publications are expected in this field.
2.5 SUMMARY OF THE LITERATURE REVIEW

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.

Natural fibre reinforcement is likely used to improve the mechanical properties of biopolymers. While fibre reinforcement provides improved strength and stiffness to TPS, flame retarded TPS composites have not been developed yet. In the case of natural fibre reinforced PLA composites the poor impact resistance is a serious issue. Surprisingly, the approach of self-reinforcement, which is also an environmentally sound reinforcing technique, has not been investigated to improve the impact resistance of the inherently rigid PLA.

It is revealed that phosphorus-based additives represent an environmentally-friendly solution in the flame retardancy of biopolymers and natural fibres. 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, composted 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.
3 MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 MATRIX MATERIALS

Table 3.1 Summary of the applied polymers

<table>
<thead>
<tr>
<th>Material (abbreviation)</th>
<th>Brand/marketing name</th>
<th>Producer/supplier</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>polypropylene (PP)</td>
<td>Tipplen R 959 A</td>
<td>TVK Nyrt (Hungary)</td>
<td>random copolymer, MFI = 45 g/10 min (230°C, 2.16 kg)</td>
</tr>
<tr>
<td>Ethylene-propylene copolymer (rPP)</td>
<td>Versify 4200</td>
<td>Dow Chemical Company (USA)</td>
<td>propylene-ethylene copolymer based thermoplastic elastomer with a broad crystalline melting temperature range between 55 and 100°C (peak temperature: 78°C).</td>
</tr>
<tr>
<td>recycled polyolefin mixture (REC)</td>
<td>Alcufer Kft. (Hungary)</td>
<td></td>
<td>density-separated polyolefin fraction (ρ&lt;0.92 g/cm³) of automotive shredder waste with approx. 78% PP content</td>
</tr>
<tr>
<td>starch</td>
<td>étkezési keményítő</td>
<td>Natura Reformélélmiszer Kft. (Hungary)</td>
<td>amylose content: 19%</td>
</tr>
<tr>
<td>polylactic acid (PLA)</td>
<td>Ingeo™ Biopolymer 3052D</td>
<td>NatureWorks LLC. (USA)</td>
<td>MFI = 12 g/10 min (210°C, 2.16 kg), semicrystalline</td>
</tr>
<tr>
<td>polylactic acid (PLA)</td>
<td>Ingeo™ Biopolymer 6302D</td>
<td>NatureWorks LLC. (USA)</td>
<td>MFI = 15-20 g/10 min (210°C, 2.16 kg), highly amorphous</td>
</tr>
</tbody>
</table>

3.1.2 REINFORCEMENTS

Table 3.2 Summary of the applied reinforcing materials

<table>
<thead>
<tr>
<th>Material (abbreviation)</th>
<th>Brand/marketing name</th>
<th>Producer/supplier</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>polypropylene fabric (PP fabric)</td>
<td>id. code: T-PPT-181</td>
<td>Stradom S.A., (Poland)</td>
<td>plain-woven (composed of highly stretched, split iPP tapes), $T_m = 172.4°C$, tape tensile strength: 128.8 ± 3.0 MPa (measured on a 50 mm wide strip), areal weight: 171.5 g/m²</td>
</tr>
<tr>
<td>polypropylene multifilament (iPP multifilament)</td>
<td>Stradom S.A., (Poland)</td>
<td></td>
<td>highly oriented iPP homopolymer multifilament. $T_m = 173.0°C$, single fibre diameter of 40.1 ± 1.8 μm, tensile strength of 581 ± 30 MPa and tensile modulus of 6432 ± 490 MPa (measured in single fibre tensile tests).</td>
</tr>
<tr>
<td>glass fabric (GF)</td>
<td>id. code: HexForce 01717 1050 26224</td>
<td>Hexcel Co. (USA)</td>
<td>plain woven, type of yarns: EC9 68, strip tensile strength: 142.6 ± 6 MPa, areal weight: 160 g/m²</td>
</tr>
<tr>
<td>chopped flax fibre</td>
<td>Institute of Natural Fibres and Medicinal Plants, Poznan (Poland)</td>
<td></td>
<td>length: 2-3 mm, diameter: 20-60 μm</td>
</tr>
<tr>
<td>linen-hemp fabric</td>
<td>Institute of Natural Fibres and Medicinal Plants, Poznan (Poland)</td>
<td></td>
<td>plain woven, areal weight: 325 g/m²</td>
</tr>
</tbody>
</table>
3.1.3 Chemicals and Additives

Table 3.3 Summary of the applied chemicals and additives

<table>
<thead>
<tr>
<th>Material (abbreviation)</th>
<th>Brand/marketing name</th>
<th>Producer/supplier</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonium polyphosphate (APP)</td>
<td>Exolit AP 422</td>
<td>Clariant Ltd. (Germany)</td>
<td>n &gt; 1000, P content: 31.0-32.0%, N content: 14.0-15.0%</td>
</tr>
<tr>
<td>ammonium polyphosphate (APP)</td>
<td>Exolit AP 766</td>
<td>Clariant Ltd. (Germany)</td>
<td>Combined, APP based and charring agent containing IFR additive, P-content: 23-25%, N content: 14.4-16.4%</td>
</tr>
<tr>
<td>ammonium polyphosphate (APP)</td>
<td>Exolit AP 462</td>
<td>Clariant Ltd. (Germany)</td>
<td>Melamine resin micro-encapsulated ammonium polyphosphate (APP) based additive</td>
</tr>
<tr>
<td>glycerol (G)</td>
<td>glycerol</td>
<td>Merck KGaA (Germany)</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>phosphorus-polyol</td>
<td>Exolit OP 560</td>
<td>Clariant Ltd. (Germany)</td>
<td>P-content: 10-13 wt%, hydroxyl number: 400-500 mg KOH/g</td>
</tr>
<tr>
<td>phosphorus-pentoxide</td>
<td>phosphorus-pentoxide</td>
<td>Sigma Aldrich</td>
<td></td>
</tr>
<tr>
<td>3-(triethoxysilyl)-propyl isocyanate (TESPI)</td>
<td>3-(triethoxysilyl)-propyl isocyanate</td>
<td>Sigma Aldrich</td>
<td></td>
</tr>
<tr>
<td>montmorillonite clay (MMT)</td>
<td>Nanofil® 116</td>
<td>Rockwood Clay Additives GmbH (Germany)</td>
<td>Unmodified, cationic exchange capacity (CEC): 116 mEq/100 g</td>
</tr>
</tbody>
</table>

Each yarn consists of 144 continuous filaments with a filament diameter of 20.5 ± 0.8 μm, with a crystalline melting temperature of 174°C and with a tensile yield stress of 102.4 ± 5.8 MPa, an ultimate tensile strength of 258.3 ± 16.6 and a strain at break of 44.6 ± 4.1%.
3.2 EQUIPMENT USED FOR SAMPLE PREPARATION

3.2.1 MELT COMPOUNDING

**Internal mixer**

Brabender Plasti Corder PL 2000 type internal mixer (Brabender GmbH & Co. KG, Germany) was used to prepare homogeneous compounds. The apparatus is equipped with a 50 and a 350 cm³ mixing chamber and a unit for continuous recording of temperature, time, speed and torque data during homogenization.

**Twin screw extruder**

Labtech Scientific LTE 26-44 type twin-screw extruder (Labtech Engineering Co., Ltd., Thailand) with a screw diameter of 26 mm and a L/D ratio of 44 was used to compound flame retardant containing polymer mixtures.

3.2.2 FILM EXTRUSION

**Flat film line**

Labtech Scientific LCR 300 type flat film line (Labtech Engineering Co., Ltd., Thailand) was used to obtain 50-100 μm thick films to be applied as matrix layers in composites.

3.2.3 COMPRESSION MOULDING

**Laboratory hot-press**

Collin P200E type laboratory hot press (Dr. Collin GmbH, Germany) equipped with a 100 × 100 mm or a 160 × 160 mm plane tool was used to prepare smaller composite sheets.

**Hot-press machine**

Schwabenthan Polystat 300S type hot-press machine (Maschinenfabrik Fr. Schwabenthan & Co. KG, Germany) was used to prepare multilayered composite plates of 300 x 300 mm dimension.

3.2.4 INJECTION MOULDING

**Injection moulding machine**

Arburg Allrounder Advance 370S 700-290 type injection moulding machine (Arburg GmbH., Germany) was used to manufacture ISO standard dumbbell specimens with a cross-section of 4 × 10 mm and plaque measuring 80 × 80 × 2 mm in dimension, respectively.
3.3 METHODS

3.3.1 SPECTROSCOPIC ANALYSES

**Fourier transform infrared spectrometry (FTIR)**

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

**Laser pyrolysis-FTIR coupled gas phase analysis (LP-FTIR)**

Laser pyrolysis (LP)-FTIR [166] method was used for investigation of the pyrolytic degradation products of TPS matrices. The system comprises of CO\(_2\) pyrolyser laser (10.6 nm, SYNRAD 48-1) unit coupled with Bruker Tensor 37 type FTIR spectrometer (Figure 3.1).

![Figure 3.1 LP-FTIR coupled gas phase analysis](image)

**ReactIR**

The ReactIR™ in situ Fourier transform infrared spectroscopic (FT-IR) apparatus (Mettler-Toledo, USA) allows for in situ real-time FTIR analysis of a reaction mixture in the mid-IR region using a multi-reflection diamond attenuated total reflectance (ATR) insertion sensor.

**Raman spectrometry**

Raman mapping spectra were collected using a Horiba Jobin-Yvon LabRAM system coupled with an external 785 nm diode laser source and an Olympus BX-40 optical microscope.

**Mass spectrometry (MS)**

Mass spectrometric analysis was performed on a Perkin Elmer Sciex API 365 LC/MS/MS system (Perkin Elmer, USA). The instrument was operated in ESI mode with positive ionization. Mass spectra were recorded in Q1 scanning mode between m/z ratios of 50–500.

**Nuclear magnetic resonance analysis (NMR)**

NMR spectra were recorded with a Bruker AV-300 NMR spectrometer (Bruker Corporation, USA) operating at 300.13 MHz, 121.50 MHz and 75.48 MHz for \(^1\)H, \(^{31}\)P and \(^{13}\)C, respectively, and equipped with a 5 mm Z-gradient QNP (quattro nucleus probe, for \(^1\)H/\(^{13}\)C/\(^{31}\)P/\(^{19}\)F) probehead.
3.3.2 THERMAL ANALYTICAL METHODS

Differential scanning calorimetry (DSC)
Setaram DSC 92 instrument was used for differential scanning calorimetric (DSC) test. All DSC experiments were performed under nitrogen gas flow rate of 30 cm$^3$/min with a heating rate of 10 °C/min covering the suitable temperature range. About 15-20 mg of sample was used in each test.

Thermal gravimetry (TGA)
Setaram Labsys TG DTA/DSC instrument was used for thermogravimetric analysis (TGA). All TGA experiments were performed with a heating rate of 10 °C/min in suitable temperature ranges under nitrogen gas flow rate of 30 cm$^3$/min. About 15-20 mg of sample was used in each test.

Melt flow rate measurement (MFI)
Melt flow rate measurements were performed using a Ceast 7027.000 type computer controlled capillary viscosimeter (Instron Ltd., United Kingdom) at different test temperatures but with a 2.16 kg load in all cases.

3.3.3 MORPHOLOGICAL ANALYSES

Light microscopy (LM)
Light microscopic pictures were taken using an Olympus BX51M type microscope.

Scanning electron microscopy (SEM)
SEM pictures were taken using a JEOL JSM-6380 LA type apparatus (JEOL Ltd., Japan). Before examination, the samples were coated with a thin gold-palladium alloy layer to prevent charge build-up on the surface. The used SEM apparatus is equipped with an energy dispersive spectrometer (EDS) unit capable of performing elemental analysis of the obtained residues.

3.3.4 MECHANICAL TESTS

Dynamic mechanical analysis (DMA)
Dynamic mechanical analyses were performed using a Q800 dynamic mechanical analyser (DMA, TA Instruments Inc., USA). Dual cantilever mode was applied with a span length of 35 mm. The width and length of the specimens were approximately 10 mm × 55 mm (cut by water jet), respectively. The scanning range of temperature was 20°C-160°C a heating rate of 1°C/min and a frequency of 1 Hz with a 0.02% deformation were selected.

Tensile test
Static tensile tests were performed using a Zwick Z020 universal testing machine (Zwick GmbH., Germany) with a crosshead speed of 5 mm/min in all cases.
From the stress–strain curves typically the yield strength ($\sigma_Y [\text{MPa}]$, according to Equation 2, where $F_Y [\text{N}]$ is the load at yield and $A_0 [\text{mm}^2]$ is the original cross sectional area of the specimen), the ultimate tensile strength ($\sigma_U [\text{MPa}]$, according to Equation 3, where $F_{\text{max}} [\text{N}]$ is the maximal tensile load), the Young’s modulus ($E [\text{GPa}]$, calculated by dividing the tensile stress by the extensional strain in the elastic (initial, linear) portion of the stress–strain curve, where $F [\text{N}]$ is the tensile load, $A_0 [\text{mm}^2]$ is the original cross-sectional area, $\Delta L [\text{mm}]$ is the amount by which the length of the object changes, $L_0 [\text{mm}]$ is the original length of the object (Equation 4)), and the strain at break ($\varepsilon_f [%]$, according to Equation 5, where $\Delta L_f [\text{mm}]$ is the amount by which the length of the object changed until failure) were determined.

$$\sigma_Y = \frac{F_Y}{A_0} \ [\text{MPa}]$$

Equation 2 Calculation of yield strength

$$\sigma_U = \frac{F_{\text{max}}}{A_0} \ [\text{MPa}]$$

Equation 3 Calculation of ultimate tensile strength

$$E = \frac{\sigma}{\varepsilon} = \frac{F/A_0}{\Delta L/L_0} \ [\text{GPa}]$$

Equation 4 Calculation of Young’s modulus

$$\varepsilon_f = \frac{\Delta L_f}{L_0} \ [%]$$

Equation 5 Calculation of strain at break

**Bending test**

Static 3 point bending tests were performed on rectangular specimens of 80 mm length using a Zwick Z020 universal testing machine. The crosshead speed was 5 mm/min and the span length was 64 mm in each tests.

From the stress–strain curves the flexural strength ($\sigma_b [\text{MPa}]$) was calculated according to Equation 6, where $F [\text{N}]$ is the axial load (force) at the fracture point, and $b [\text{mm}]$ is the width and $h [\text{mm}]$ is the thickness of the specimen and $L [\text{mm}]$ is the length of the support span.

The flexural modulus ($E_b [\text{MPa}]$) was calculated according to Equation 7, where $b [\text{mm}]$ and $h [\text{mm}]$ are the width and thickness of the specimen, respectively, $L [\text{mm}]$ is the distance between the two outer supports and $\Delta f [\text{mm}]$ is the deflection due to the $\Delta F [\text{N}]$ load applied at the middle of the specimen.

$$\sigma_b = \frac{3 \cdot F \cdot L}{2 \cdot b \cdot h^2} \ [\text{MPa}]$$

Equation 6 Calculation of flexural strength

$$E_b = \frac{1}{4} \cdot \frac{L^3}{b \cdot h^3} \cdot \frac{\Delta F}{\Delta f} \ [\text{MPa}]$$

Equation 7 Calculation of flexural modulus
Interlaminar (shear) strength test

Interlaminar shear strength was determined on rectangular specimens of 25 mm × 160 mm using a Zwick Z020 universal testing machine according to the ASTM D 3167-97 standard with a crosshead speed of 5 mm/min.

Instrumented falling weight impact test (IFWI)

IFWI tests were performed on Fractovis 6785 type equipment (Ceast SpA (Instron), Italy) using the following settings: maximal energy: 228.64 J; diameter of the dart: 20 mm; diameter of the support rig: 40 mm; weight of the dart: 23.62 kg and drop height: 1 m. 70 mm × 70 mm square specimens were subjected to IFWI tests. From the IFWI tests the specific perforation energy ($E_p$ [J/mm]) and the ductility factor ($D_r$ [%]) were determined according to Equation 8 and Equation 9, respectively, where $E_{tot}$ [J] represents the total energy of break, $h$ [mm] is the thickness of the specimen and $E_{F_{max}}$ [J] is the energy at maximal force.

The ductility factor was calculated as the ratio of the total impact energy ($E_{tot}$) to the energy absorbed until the maximum load ($E_{F_{max}}$). $E_{F_{max}}$ represents mainly the energy required to initiate fracture in the specimen and corresponds to the deformation at yield, while $E_{tot}$ indicates the total energy absorbed until ultimate deformation.

$$E_p = \frac{E_{tot}}{h} \left[ \frac{J}{mm} \right]$$

Equation 8 Calculation of Perforation energy

$$D_r = \frac{E_{tot} - E_{F_{max}}}{E_{tot}} \left[ \% \right]$$

Equation 9 Calculation of ductility factor

3.3.5 FLAMMABILITY TESTS

Limiting oxygen index measurements (LOI)

Limiting oxygen index measurements were carried out according to the MSZ EN ISO 4589-1 and 4589-2 (2000) standard. $LOI$ [vol%] is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer. The higher the $LOI$ the better the flame retardant property.

UL 94 flammability test

Flammability tests according to ISO 9772 and ISO 9773 standards were performed to determine the horizontal and vertical burning characteristics of plastic specimens subjected to a small flame. The UL 94 ratings group materials into categories based on their flammability characteristics such as ignitability, dripping and flame spreading rates:

- **HB**: slow burning on a horizontal specimen; burning rate < 76 mm/min for thickness < 3 mm and burning stops before 100 mm.
- **V-2**: burning stops within 30 seconds on a vertical specimen; drips of flaming particles are allowed.
- **V-1**: burning stops within 30 seconds on a vertical specimen; drips of particles allowed as long as they are not inflamed.
- **V-0**: burning stops within 10 seconds on a vertical specimen; drips of particles allowed as long as they are not inflamed.

**Mass loss type cone calorimetry (MLC)**

MLC tests were carried out by an instrument made by Fire Testing Technology ltd. (UK) (see schematic picture in Figure 3.2), following the procedures of ISO 13927 standard method. Specimens with dimensions of 100 × 100 × 4 mm were exposed to a constant heat flux of 50 kW/m² and ignited with a spark igniter placed above the sample. Heat release values and mass reduction were continuously recorded during their burning. In all cases 3 samples of identical compositions were tested, the results reported in tables or figures correspond to the mean values obtained from these parallel measurements. The error range of the calculated experimental results was in the case of peak heat release rates ($pkHRR$ [kW/m²]) and time to peak heat release rates ($pkHRR_{time}$ [s]) lower than 15%, in the case of time to ignition ($TTI$ [s]) and residual mass values lower than 10%, and in the case of total heat released ($tHR$ [MJ]) lower than 5% in all cases.

![Figure 3.2 Schematic picture of mass loss type cone calorimeter](image)
3.3.6 OTHER TEST METHODS

Compression test of charred post-combustion residues

AR2000 Rheometer (TA Instruments, USA) with special adjustment was used for structural and mechanical characterization of chars obtained from disk-shaped specimen (diameter = 30 mm) burned at 500°C under cone heater. Compression tests were carried out with a constant squeeze rate of 30 μm/s while the changes in the normal force were recorded (Figure 3.3). The diameter of the squeezing upper plate was 25 mm and the initial gap was 20 mm in all cases. As the heights of the examined chars were different, the registered normal force values were plotted against the percentage of deformation of the corresponding chars.

Figure 3.3 Compression test used for mechanical characterization of chars
4 RESULTS AND DISCUSSION

Introduction

Taking into account the shortages, challenges and potentials found in the literature survey, the following objectives were formulated, and experiments were planned accordingly.

- Investigation of the feasibility of Raman spectrometry for the non-destructive characterisation of all-polypropylene composites;
- Development of flame retarded self-reinforced polypropylene composites;
- Investigation of the interaction between polypropylene fibres and intumescent flame retardant system in self-reinforced polypropylene composites;
- Upgrading recycling of plastic waste by preparing self-reinforced composites;
- Development of self-reinforced polylactic acid composites and their flame retardation with phosphorus-based compounds; characterisation of the impact resistance;
- Experiments towards the production of flame-retarded self-reinforced composites by the more versatile injection moulding method;
- Developments towards the elimination of the candlewick effect of natural fibres in biopolymer matrices;
- Application of complex strategy, i.e. use of flame retardants both in the matrix material and on surface of natural fibres, to flame retard thermoplastic starch and PLA-based green composites;
- Synthesis and application of potentially multifunctional flame retardants in biopolymers and biocomposites;
- Use of carbonizing agents of renewable origin in intumescent flame retardant systems.

New types of recyclable and biobased composites were planned to be developed. In all cases the mechanical and flame retardancy properties were simultaneously investigated. The proposed workplan required parallel synthetic, technological, analytical and methodological developments.
4.1 Non-destructive characterisation of all-polypropylene composites using polarized Raman spectrometry

Rationale and aims

In self-reinforced plastics (SRPs), a polymer matrix is reinforced with high-tenacity fibres or tapes of the same polymer family, creating a material with enhanced strength, stiffness and impact resistance compared to the unreinforced polymer. The intensive stretching of extruded tapes or fibres results in high degree of molecular orientation in the polymer chains (both in crystalline and amorphous phase) and by this means polymer fibres of high strength and modulus can be manufactured serving as suitable reinforcing substances in SRPs. The basis of all SRPs techniques is to set a suitable processing window which exploits the difference between the melting temperatures ($T_m$) of the reinforcement and the matrix. The processing conditions (such as consolidation temperature, pressure and time) have a significant influence on the macromolecular orientation of the reinforcing polymer fibres and the consolidation quality of the composite, thus basically determine the mechanical properties of the SRPs; their optimization and monitoring are crucial in respect to the SRPs’ quality. In the industry, a significantly time and material consuming, iterative procedure (including destructive material tests) is followed to optimize the processing parameters of a SRP product. Moreover, for the quality assessment of SRPs during service only destructive or semi-destructive tests are currently available.

The following investigation aimed at elaboration of a non-destructive (structure and mechanical performance) assessment method for SRPs. The feasibility of using polarized Raman spectrometry to examine the structure of all-polypropylene composites (all-PPCs), prepared at different consolidation temperatures was studied. In our investigation, all-PPCs of highly stretched isotactic polypropylene (iPP) multifilament fibres and propylene-ethylene random copolymer (rPP) matrix were examined. The tensile modulus of reinforcing iPP fibres basically depends on the fraction of chain segments that are oriented (basically crystalline orientation) and the degree of orientation along the stress direction. Polarized Raman spectrometry has been effectively used to study regularity and structure of iPP fibres [167,168]. In the former studies, the ratio of Raman bands at 841 and 808 cm$^{-1}$ was generally used to estimate molecular orientation [168,169]. However, the structure of reinforcing iPP fibres embedded in a structurally similar polymer (rPP) matrix has not been investigated yet. For this purpose, the entire frequency range of Raman spectra collected from all-PPCs was evaluated by a multivariate evaluation method, namely the classical least squares (CLS) model, for determining the orientation state of the reinforcing fibres and thus estimating the mechanical performance at the same time.
Composite preparation

50 ± 5 μm thick films were manufactured from the rPP granules by film extrusion technique using a Labtech LCR 300 laboratory flat film line. The temperature profile from feed zone to die of the extruder was 210, 215, 215, 215 and 220°C. All-PPC sheets were prepared by filament winding followed by compression moulding process. 5 plies of matrix films and 4 iPP multifilament layers were laminated pretensioned onto a 6 mm thick aluminium core (300 × 300 mm) in a filament winding process to obtain unidirectionally (UD) aligned fibres. The all-PPCs with a thickness of 1.7 mm and a nominal reinforcing multifilament content of 65 wt% were produced by compression moulding. The filament-wound laminates were consolidated at different temperatures; at 130, 140, 150, 160, 170 and 180°C, respectively, serving as series regarding molecular orientation of fibres and mechanical performance. The film-stacked packages were inserted in between the preheated moulds and held for 300 s without pressure, then compressed for 420 s under a pressure of 1 MPa and finally cooled to 45°C (under pressure).

Spectrum collection and data analysis

Reference Raman spectra were collected from the matrix film (rPP) and from the reinforcing iPP fibre in its original, highly oriented form (iPPo-100%), and in its completely heat relaxed form (iPPo-0%) obtained after heat treating the iPP fibre at 180°C for 20 minutes. The Raman spectra of the references were collected with a 100× objective using an acquisition time of 90 s, and accumulating and averaging 3 measured spectra at each measured point.

Raman mapping was performed on the surface of the UD composites. The schematic representation of the experimental setup for Raman imaging and scattering geometry is shown in Figure 4.1. The incident laser radiation propagates in the negative Z direction with polarization in Y direction. The UD composite samples were mounted horizontally with reinforcing fibres oriented in the Y direction. The backscattered radiation, also polarized in the Y direction, travels in positive Z direction. The analysing polarizer is oriented to select only light polarized in the Y direction (identical to the incident light polarization). The spectrograph was set to provide a spectral range of 200–1400 cm⁻¹ with a 2 cm⁻¹ resolution. The maps were collected with 10× objective (laser spot size: ~3.8 μm) and 6 μm and 12 μm step size in the X (perpendicular to the fibre orientation) and in the Y direction (parallel to the fibre orientation), respectively. In each experiment the acquisition time of a single spectrum was 40 s and 3 such spectra were averaged at each pixel. The analysed area was 36 × 12 pixels, ie. 210 × 132 μm² in each case.
Before chemometric evaluation, all spectra were baseline corrected and normalized in order to eliminate the intensity deviation between the measured points. The average relative orientation degree of the reinforcing iPP fibres of the all-PPCs was determined by CLS modelling with real reference spectra collected from iPPo-100%, iPPo-0% and rPP.

Results and discussion

The reference polarized Raman spectra collected from the highly oriented iPP fibre (iPPo-100%), from the fully relaxed iPP fibre (iPPo-0%) and from the matrix polymer (rPP) are shown in Figure 4.2. The spectra collected from iPP fibre both in oriented and relaxed form match the typical Raman shifts of a semi-crystalline iPP, the vibrational assignments are given in Table 4.1 [170]. The noticeable differences in the peak intensities and ratios of the highly oriented (iPPo-100%) and relaxed iPP fibres (iPPo-0%) provide a good basis for estimating the structure formation of the reinforcing fibres during composite processing including heat and compression exposure. In contrast, the rPP matrix shows great similarity to the spectrum of the heat relaxed iPP fibre (iPPo-0%), which makes the modelling and estimation fairly difficult. As for a solution, instead of evaluating only the Raman peak intensity ratios at 808 cm\(^{-1}\) and 841 cm\(^{-1}\), as suggested by Paradkar et al. [169], CLS method was applied to the entire frequency range (200-1400 cm\(^{-1}\)), providing superior estimation for the orientation state of the iPP fibres embedded in rPP matrix. Each Raman spectrum obtained from an all-PP composite is assumed as a linear combination of the three reference spectra, and when subtracting the contribution of the matrix component, the orientation state of the iPP fibre can be estimated. It is defined regarding its relation to the reference spectra of iPPo-100%, being considered as 100% relative orientation state, and to iPPo-0% as 0% relative orientation state.
Table 4.1 Vibrational assignments for Raman bands of iPP [170]

<table>
<thead>
<tr>
<th>( \omega [\text{cm}^{-1}] )</th>
<th>vibrational assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>808</td>
<td>( r(\text{CH}_2), \nu(\text{C-C}) )</td>
</tr>
<tr>
<td>841</td>
<td>( r(\text{CH}_2) )</td>
</tr>
<tr>
<td>972</td>
<td>( r(\text{CH}_3), \nu(\text{C-C}) )</td>
</tr>
<tr>
<td>998</td>
<td>( r(\text{CH}_3) )</td>
</tr>
<tr>
<td>1151</td>
<td>( \delta(\text{C-C}), \delta(\text{CH}) )</td>
</tr>
<tr>
<td>1168</td>
<td>( \nu(\text{C-C}), r(\text{CH}_3), w(\text{C-C}) )</td>
</tr>
<tr>
<td>1220</td>
<td>( t(\text{CH}_2), w(\text{CH}), \nu(\text{C-C}) )</td>
</tr>
</tbody>
</table>

\( \delta \) = bending, \( r \) = rocking, \( \nu \) = stretching, \( t \) = twisting, \( w \) = wagging

Raman maps were collected of 0.02772 mm\(^2\) area of each all-PPCs prepared at consolidation temperatures between 130°C and 180°C and analysed using CLS method. Two typical maps of iPP\(_{100\%}\) contribution calculated for the all-PPCs consolidated at 160°C and at 180°C are shown in Figure 4.3. The dark domains of the non-oriented matrix and the light areas corresponding to the highly oriented structures are clearly visible. Based on the uneven interfaces and smaller characteristic orientation degrees estimated for the fibres embedded in the all-PPC prepared at 180°C, considerable molecular relaxation and infusion of fibre/matrix interfaces were supposed.
The average relative degrees of orientation obtained from CLS modelling the Raman maps of each examined all-PPC are shown in Figure 4.4 a. As expected, the average relative degrees of orientation estimated for the reinforcing iPP fibres of the all-PPCs showed a decreasing tendency as a function of increasing composite consolidation temperature. Below the starting temperature of the crystalline melt (158.5°C) only slight relaxation occur during heat treatment, while above 160°C the increasing mobility of the polymer chains, trying to return to the thermodynamically stable coil state, results in noticeably decreased orientation degrees. As it can be seen, the same tendency was observed when the tensile moduli of the all-PPCs as a function of composite consolidation temperatures were evaluated. Fairly strong correlation ($R^2=0.934$) was evinced between the tensile moduli and the orientation degrees (estimated based on the polarized Raman maps of the all-PPCs), as presented in Figure 4.4 b.

Consequently, it is proposed that the developed method enables to evaluate or monitor the structure of reinforcing fibres of all-polymer composites in a non-destructive way, in contrast to WAXD or birefringence methods, which are used off-line slowing down the quality control and thus the whole technology. It is presumed that Raman spectrometry can serve as core unit of an on-line controlling loop aiming at the precise control of the manufacturing process.
of self-reinforced composites, being especially sensitive to the preparation parameters (such as compaction temperature, time, pressure, etc.).

**Conclusions**

Polarized Raman spectrometry proved to be a suitable method for characterizing the structure of reinforcing PP fibres of all-PP composites, being especially sensitive to manufacturing and application conditions, 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, 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.

**RELATED PUBLICATIONS:** [XV, XXXI, XXXIV]
4.2 Flame Retardancy of Recyclable All-Polypropylene Composites

The application of reinforced polymeric composites in construction and transportation industry is continually increasing. These industries will be, however, forced to replace their conventional (e.g. glass fibre reinforced) polymer composites by more environmentally-friendly alternatives, due to the more and more strict environmental-focused legislation, thus the use of recyclable or biodegradable polymeric materials is urged. Such environmentally favourable examples are the easily recyclable self-reinforced composites (SRCs) [13,37]. It is claimed that 20-30% reduction in weight can be achieved by using SRC parts (from PE, PP, PET, PA, etc.) instead of conventional glass fibre reinforced parts of comparable mechanical properties [171]. At the same time, the importance of flame retardancy of polymeric composites, especially in technical application fields, is indisputable. However, the flame retardation of these recently developed polymer composites is not examined or solved yet.

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. As the PP fibres have proved difficult to flame retard effectively [124], flame retardant additives were used in the matrix materials in order to diminish the flammability of the composites (made entirely of PP). Commercially available APP based intumescent flame retardant systems were applied in all cases.

4.2.1 Study on the Synergism between Highly Oriented Polypropylene Tapes and Intumescent Flame Retardant Systems

Rationale and aims

When compared to conventional halogenated flame retardants, phosphorus-based flame retardants are environmentally favoured owing to their lower environmental impact during their entire life-cycle. Wide range of phosphorus-based flame retardant (FR) compounds is available for polypropylene (PP), among which the use of ammonium polyphosphate (APP) based intumescent flame retardant (IFR) system is fairly common [172]. The mechanism of such intumescent additive system (consisting of acid source, carbon source and blowing agent) has been already studied and reviewed comprehensively [101,173]. These reviews state that a minimum of 20-22 wt% IFR is needed in order to achieve acceptable levels of flame retardancy in polyolefins. However, as much as 25-35 wt% of IFR is also generally used in literature [107,174,175,176]. Several chemical substances, mainly heavy metal ions and silicon-containing species, have been studied as synergetic effect additives when combined with IFR systems [101,177,178,179,180,181]. Thus the required amount of IFR can be somewhat, but not drastically, lowered.
Horrocks et al. [124,126] 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. [182] 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.

In this section, a synergistic effect, observed between highly oriented polymer fibres and IFR systems, is described. This advantageous interaction was utilized in multilayer PP SRCs. Comprehensive analysis has been performed using several testing methods in order to contribute to deeper understanding of the found novel phenomenon and by this means to raise the possibility of the production of new, cost-effective and recyclable flame retardant composites in the future.

Composite preparation

To compare the flammability properties of simple PP mixtures and multilayer SRCs accurately, concentration series with identical compositions were prepared for both materials, with IFR contents of 0, 9, 13, 17 and 21 wt%, respectively.

The simple flame retarded mixtures were prepared by simple mixing of the required amount of IFR additive (Exolit AP 766) with PP (Tipplen R959 A) in a Brabender Plasti Corder PL 2000 type internal mixer at 190°C, with a rotor speed of 30 rpm, for 10 minutes. The blends were then hot pressed to form 4 mm thick specimens in a Collin P200E type laboratory hot press.

The SRCs were prepared through the following steps: The first step was the compression moulding of 180 μm thick matrix layers with IFR content of 16.3, 23.6, 30.9 and 38.2 wt% at 190°C in a Schwabenthan Polystat 300 S laboratory hot press. The multilayered SRCs were then manufactured by laminating 11 flame retarded matrix foils and 10 woven PP fabrics (T-PPT-181) by film stacking method. The film-stacked packages were hot-pressed to form composites (in the same hot press) at a temperature of 162°C and a pressure of 6 MPa for 2 minutes. The manufactured SRCs had a total nominal reinforcement content of 45 ± 1.5 wt%. Thus each SRC (considering the total mass of the SRCs) had the same flame retardant content as the equivalent simple PP mixtures. (For example in the case of the SRC with an IFR content of 9 wt%, 55% of the mass of the SRC was flame retarded film containing 16.3 wt% IFR, giving an overall IFR content of 0.55 × 16.3 wt% ~ 9 wt%.) The mean thickness of the prepared SRCs was 3.78 mm.

To evaluate the role of molecular orientation of reinforcing fibres in the flame retardant effectiveness of IFR systems, the PP fabrics used for reinforcement could be characterized with different degree of orientation. In the case of the SRCs marked RLX (i.e. relaxed) the commercially available highly stretched fabrics were heat-treated at 164°C with a pressure of 0.4 MPa for 10 minutes before integration into the SRC_RLX composites, while SRCs without markings used the fabrics as received. Due to the heat-treatment the tensile strength of the relaxed fabric strip was reduced from the original value of 128.8 ± 3.0 MPa.
(tensile strength of the non-treated fabric) to 76.1 ± 2.2 MPa (avoiding the fusion of the PP fibres) suggesting significantly lowered degree of molecular orientation.

Results and discussion

4.2.1.1 COMPARISON OF THE FLAMMABILITY PROPERTIES OF POLYPROPYLENE MIXTURES AND SELF-REINFORCED COMPOSITES

Concentration series with increasing IFR contents were prepared to compare the flammability characteristics of simple PP mixtures and multilayered SRCs. Significantly reduced flammability was exhibited by the SRCs compared to the simple PP mixtures of the same composition when examined with several flammability tests. As shown in Table 4.2, the results for simple PP mixtures agreed with those in literature [101]; at least 21 wt% IFR was needed in simple PP mixtures to reach V-0 classification from standard UL-94 testing. On the contrary, in the case of SRCs IFR content as low as 9 wt% proved to be sufficient for self-extinguishing behaviour (V-0 rating). Furthermore, as it can be seen in Figure 4.5, PP SRCs consistently reached higher LOI values than simple PP mixtures despite the fact that the two compounds had the same IFR concentration. It can be also noticed from Figure 4.5 that the difference between the measured LOI values increases with the additive content of the samples; while the LOI of PP-IFR9 was only a few per cent lower than that of PP-SRC-IFR9, the LOI value of PP-SRC-IFR21 was up to 7 vol% higher than the value measured for the PP-IFR21 sample.

Table 4.2 UL-94 classification of IFR containing PP mixtures and multilayer SRCs

<table>
<thead>
<tr>
<th>FR content [wt%]</th>
<th>0</th>
<th>9</th>
<th>13</th>
<th>17</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP mixtures</td>
<td>HB</td>
<td>HB</td>
<td>HB</td>
<td>V-2</td>
<td>V-0</td>
</tr>
<tr>
<td>PP-SRC</td>
<td>HB</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
</tr>
</tbody>
</table>

Figure 4.5 Comparison of LOI values of PP mixtures and SRCs as a function of their IFR contents

For demonstrating the burning behaviour of the two types of flame retarded PP samples photographs, taken during horizontal and vertical burning of samples containing 13 wt% IFR additives, are presented in Figure 4.6 and Figure 4.7, respectively. It can be seen that, despite the same FR content, the behaviour of the two types of flame retarded samples,
exposed to flame, is completely different. During horizontal test (Figure 4.6), the PP-IFR13 specimen proved to be easily ignitable, and already after 15 s of ignition noticeable flame arouse. At this initial stage of burning the formation of a charred (but fairly loose foam) structure, is also visible, which, by virtue of its weight, gets to the bottom of the specimen and in time even falls down. As the foamed char continually loses contact with the specimen, over and over virgin, molten polymer gets to the pyrolysis zone and feeds the flame. In contrast, a weak, almost colourless flame can be observed during the ignition of the flame retarded SRC system. As the Bunsen burner is taken, the PP-SRC-IFR13 specimen extinguishes immediately. The appearance of the remaining burnt surface differs a lot from that of the non-reinforced sample. Survey of the shrunk structure of the charred residue helped the mechanism behind the observed flame-extinguishing behaviour to be understood. It is proposed that the shrinkage of the heated highly-stretched PP tapes embedded in the matrix contributes to the formation of a compact surface which hinders the availability of fuel for flame.

![Figure 4.6 Horizontal burning test of PP mixture (PP-IFR13) and SRC (PP-SRC-IFR13) with 13 wt% IFR content](image)

When the specimens are vertically ignited (Figure 4.7), the shrinking operating against the force of gravity becomes more crucial for achieving prominent flame retardation. In the case of the compounded samples considerable elongation, accompanied with increasing area of easily inflammable surfaces, is characteristic for the burning specimen. Whilst, in the case of the layered composites, ignited parallel to the direction of orientation, significant vertical shrinkage is observable which hinders the elongation and the formation of virgin surfaces. In this case, the charring and the flame retarding act of the applied IFR additive, concentrates to a smaller volume resulting in immediate fire extinguishing even at low additive level.
Clear evidence for significantly better flame retardant efficiency of IFR additive in multilayer SRCs comparing to bulk compounds was provided by UL94 flammability tests and LOI measurements. Although the local concentration of IFR outside the fibres is higher (almost two-fold) compared to the homogeneous mixture, it cannot explain the observed outstanding fire performance by itself, because, for example in the case of the PP-SRC-IFR9 sample, the IFR concentration in the matrix layer (16.3 wt%) is still significantly less than needed (at least 21 wt% IFR [101]) for reaching V-0 classification when preparing simple mixtures). On the other hand, Hornsby et al. [183] studied the fire behaviour of multilayered composites consisting of fire retardant skin and unfilled core layers and did not find any noticeable enhancement in fire retardant behaviour for the benefit of the multilayered structure. Therefore, we concluded that in the case of the flame retarded self-reinforced composites another phenomenon (high degree of molecular orientation of fibres) must play the key role behind the observed significant enhancement in flame retardant behaviour.

The burning behaviour of the two types of flame retarded samples shows also noticeable differences when examined under the conditions of a cone heater. The experimental results of the cone calorimetric combustion tests are presented in Table 4.3. It is noticeable that, despite the identical IFR content of the corresponding samples, the SRCs consistently achieved lower values of peak heat release rate ($pkHRR$) than simple PP mixtures, usually by 30-45%. In the case of simple PP compounds, it was found that the time taken to reach the $pkHRR$ ($pkHRR_{time}$) increased significantly with FR content while for the SRCs this increase was moderate.
On average, time to ignition (TTI) for SRCs was 8 s less than that for compounded PP mixtures. It is known that the ignitibility of a composite at a given heat flux does not depend exclusively on the chemical stability of the matrix polymer and the type of the fibre. In order to understand the ignitibility results their thermal conductivity, the thickness of the layers and their interactions need to be considered as well [138]. In the case of the SRCs, there are two main factors that can explain the shorter TTI. The most crucial factor is the thickness of layers; the volatilization of the thin upper layers of SRCs occurs much faster than in the case of the thick bulk of simple PP mixtures. Furthermore, the IFR additive content of the upper (matrix) layers is higher. According to Li et al. [180], the formation of a char layer, initiated by the IFR, at the initial stage of heating results in quick temperature rise and fast decomposition of PP on the surface of the samples.

The amount of charred residues obtained from combustion increased with the FR content in the case of both simple PP mixtures and SRCs. The increase is greater in the case of SRCs. Although Figure 4.8 suggests larger extent of charred residue after burning of the PP mixture containing 17 wt% IFR, in fact the mass of the char corresponding to the multilayer composite (SRC-FR17) was (owing to its more dense character) considerably (by 24%) bigger. At FR content of 21 wt% the difference between the obtained residual masses of the two types of samples exceeded 38%. Table 4.3 also presents that the total heat release (tHR) was typically also by 25% lower for SRCs.

<table>
<thead>
<tr>
<th>FR content [%]</th>
<th>Sample type</th>
<th>TTI [s]</th>
<th>pkHRR [kW/m²]</th>
<th>pkHRRtime [s]</th>
<th>Residue [%]</th>
<th>tHR [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>mixture</td>
<td>38</td>
<td>880</td>
<td>171</td>
<td>0.5</td>
<td>128.0</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>30</td>
<td>751</td>
<td>180</td>
<td>0.6</td>
<td>120.7</td>
</tr>
<tr>
<td>9</td>
<td>mixture</td>
<td>34</td>
<td>587</td>
<td>416</td>
<td>2.6</td>
<td>126.1</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>24</td>
<td>413</td>
<td>351</td>
<td>3.6</td>
<td>102.7</td>
</tr>
<tr>
<td>13</td>
<td>mixture</td>
<td>33</td>
<td>514</td>
<td>513</td>
<td>2.9</td>
<td>117.3</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>22</td>
<td>295</td>
<td>464</td>
<td>4.3</td>
<td>89.7</td>
</tr>
<tr>
<td>17</td>
<td>mixture</td>
<td>30</td>
<td>340</td>
<td>750</td>
<td>5.4</td>
<td>103.4</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>23</td>
<td>227</td>
<td>468</td>
<td>7.1</td>
<td>80.2</td>
</tr>
<tr>
<td>21</td>
<td>mixture</td>
<td>28</td>
<td>222</td>
<td>843</td>
<td>8.0</td>
<td>91.5</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>22</td>
<td>160</td>
<td>509</td>
<td>12.9</td>
<td>66.7</td>
</tr>
</tbody>
</table>

Figure 4.8 Charred residues of 17 wt% IFR containing samples obtained after cone calorimetric tests.
The heat release rate and mass loss curves of the samples containing 9 and 13 wt% IFR are presented in Figure 4.9 a and b, respectively. Considering Figure 4.9 a, it can be seen that in the beginning the combustion of the compounded samples is accompanied with considerably lower heat release rates than that of the multilayered composites. However, after a while noticeable peak of heat release rate appears in all cases, which are by 30-40% lower in the case of the flame retarded SRCs. This can be explained by the different foaming processes and char structures. Highly expanded, but loose char forms from the compounds containing IFR additive, which acts, due to its porous, multicellular structure, as efficient heat insulator at the initial stage of burning. It protects the underlying molten PP from combustion. However, as this weak foam structure degrades, significant amount of PP gets into the burning zone abruptly, resulting in sharp peak of heat release rate. In contrast, similarly to the effect of inorganic fabrics [122,184], the intensive expansion is hindered by the additive-free woven PP fabrics in the case of SRC composites. When the multilayer composite is exposed to heat the shrinkage of the highly stretched tapes occurs simultaneously with the swelling of the flame retarded matrix layers. As a consequence, much denser, compact charred layer will be formed. As the heat insulation depends particularly on the thickness of the char (a thicker layer gives more insulation), the formation of compact foams in the case of SRCs is associated with higher initial heat release rates.

For further investigation of the different foam forming processes of the compounded and multilayer samples, the charred layers, formed at the early stage of burning, were examined (Figure 4.9 a). In the case of the flame retarded compound (PP-IFR13) large amount of molten PP was present (as expected) under the thick, swollen, charred layer after 180 s of combustion. In the case of the multilayer SRC (PP-SRC-IFR13), however, a completely charred full mass was obtained in the same period (only thin virgin polymer spots could be observed on certain areas of the char bottom). These observations are in accordance with the recorded heat release curves. The larger amount of pure polymer remains under the protecting layer, the larger heat releases abruptly (the higher the peak of heat release rate) after degradation of the protecting layer.
It was assumed that the migration of the flame retardant components [185] plays crucial role in the char formation process and is greatly responsible for the observed differences in combustion behaviours. In order to establish this assumption the phosphorus (P) content in the representative parts of the samples was determined using EDS. As it is presented in Figure 4.10 a, 1.35 at% P was detected on the surface of the compounded PP sample with 13 wt% IFR content. After 180 s combustion (in Cone Calorimeter at 50 kW/m²) significant amount of molten polymer remained under the formed thick charred foam. The distribution of P atoms on the upper and lower surface of this (solidified) PP layer is presented in Figure 4.10 b and c, respectively. It can be noticed that on the upper surface of melted PP (just below the char), which is directly connected to the charred foam, no P could be detected at all and on the bottom surface, being contiguous with the Al sample holder, only 0.6 at% P was measured. Considering these results, it was concluded that the applied heat flux initiated migration of the FR additives towards the surface. By the enrichment of the active species an effective heat protecting char layer can develop on the top of the compounded sample, in contrast, the flame retardant content of the underlying polymer becomes poor (insufficient). As a consequence, when the protecting shield gets damaged, the remaining molten polymer will get burnt abruptly, accompanied with the appearance of a sharp peak of heat release rate. Considering the mass loss curves, recorded during the cone calorimetric tests (Figure 4.9 b), it can be established that about 60-70% (indicated by the increased rate of mass reduction) of the original mass of the compounded samples is referred to be combusted during this accelerated burning period.
In the case of the SRCs no considerable amount of molten polymer was observed in the beginning period of burning (and during char formation) suggesting homogeneous P distribution in the cross section of the developed char. Therefore it was concluded that the migration of the IFR additives throughout the entire bulk of the multilayered sample is hindered by the embedded additive-free PP fabrics. As a consequence, the whole mass of the sample participates simultaneously in the charring and foam-forming process resulting in somewhat higher initial rates of heat emission but suppressed peak of heat release rates. In the case of the SRCs there is no polymer layer with insufficient additive content, and consequently, as it is presented in Table 4.3, the total heat emission is reduced and higher amount of residual char remains after combustion when compared to the compounded samples (in which the migration is unobstructed) of identical FR contents.

![Figure 4.10](image)

**Figure 4.10** EDS imaging of the P content of a) the prepared PP-IFR13 compounded sample, b) upper layer of the molten PP and c) lower layer of the molten PP (obtained after 180 s combustion in cone calorimeter)

The charred residues obtained after combustion were noticeably of different character. The foams corresponding to the flame retarded compounds seem to be soft and weak, while those of the SRCs were more compact and rather rigid. The structure of the two types of flame retarded samples was examined by SEM. At lower magnification it is visible that the char corresponding to the PP-IFR13 sample (Figure 4.11 a) consists of funnel-like formations and holes formed probably during the release of the gaseous degradation products. In contrast, the char of the PP-SRC-IFR13 sample (Figure 4.11 c) consists of hollow spherical formations. When applying greater magnification it can be seen that the walls of both the funnels (Figure 4.11 b) and spheres (Figure 4.11 d) are built up from spherical cells, however, while these constitute a tough, multicellular honeycomb structure in the case of the SRC (Figure 4.11 d), they are limp and apparently lack of toughness in the case of the compound (Figure 4.11 b). The observed loose foam structure, formed during the intensive gas release and instantaneous foaming process of the compounded samples, is probably in correspondence with the abrupt change of the corresponding heat release rates at 40 s in Figure 4.9 a. On the other hand, the additive-free reinforcement layers in the case of the
SRCs can hinder the abrupt gas escape and expansion, resulting in foam of mainly closed cell structure. Considering the corresponding heat release rate curves in Figure 4.9 a, it can be observed that the char formation process is prolonged compared to that of the compounded samples.

![Figure 4.11 SEM images of the charred residues obtained after the cone calorimeter tests of PP-IFR13 (a and b), and SRC-IFR13 samples (c and d)](image)

The mechanical performance of the charred residues obtained after combustion of disk-shaped specimen (with a diameter of 30 mm) in the cone calorimeter (set to 50 kW/m² heat flux) was examined through compression tests. The tests were carried out in a rheometer with a plate-plate geometry on the basis of the method used earlier for characterization of charred foams formed from intumescent coatings by our group [186]. In Figure 4.12, the recorded normal force values were plotted against the deformation percentages of each charred residues. It can be seen that the main trends of the obtained curves are similar: initial increase in normal force, corresponding to the first cracking of the foam structure; then slightly growing average normal force is needed for deformation; and finally the compaction stage. However, definite differences can be established between the compression behaviour of the chars of the two types of flame retarded samples. It can be noticed that in the case of the SRCs the step of the initial increase in normal force is much higher, the fluctuation around the characteristic average normal force is considerably larger, and the compaction phase starts at significantly lower stage of deformation than those of the corresponding counterparts at both examined additive content.

For characterization of the strength of the foam structures by a general index, the foam strength values at the first maximum of the normal force were calculated and compared in Table 4.4. The calculated indices could be interpreted as the characteristic resistance of char layers or cell structures of the formed foams against deformation. The chars corresponding
to the SRCs proved to be much more rigid and resistant to deformations than those of the compounded samples (in accordance with the SEM images). The more dense character of these chars is also demonstrated by the much lower deformation percentages corresponding to the starting point of compaction (Figure 4.12). These observations are also in accordance with the measured higher amount of charred residues obtained after cone calorimeter tests in the case of the SRCs (Table 4.3).

Figure 4.12 Compression test of the charred residues obtained after combustion under cone heater

Table 4.4 Calculated specific foam strength of the charred residues

<table>
<thead>
<tr>
<th>FR content [%]</th>
<th>Sample type</th>
<th>Foam strength [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>mixture</td>
<td>300</td>
</tr>
<tr>
<td>13</td>
<td>SRC</td>
<td>930</td>
</tr>
<tr>
<td>9</td>
<td>mixture</td>
<td>704</td>
</tr>
<tr>
<td>13</td>
<td>SRC</td>
<td>1264</td>
</tr>
</tbody>
</table>

According to the flammability test results, the flame retardancy of multilayered SRCs proved to be significantly superior to compounded PP mixtures. The improvement in flame retardancy cannot be ascribed to the crystallinity and orientation of reinforcing PP tapes. The observed char-promoting behaviour of originally non-charring PP fabrics required further explanation. As in our system the chemical composition of the two types of flame retarded samples was the same, it was concluded that a physical phenomenon must play the key role behind the observed mechanism, which is a completely novel concept in the field of flame retardancy. Therefore, the effect of the high-strength PP fibres on the flame retardant action of the IFR system was investigated hereinafter.

4.2.1.2 Investigation of the Effect of Fibre Molecular Orientation on the Flame Retardant Performance of the Intumescent System

SRCs with identical chemical compositions (9 and 13 wt% flame retardant contents) but with different degrees of orientation were prepared and examined; the one type contained heat-treated (relaxed) reinforcing PP layers while the other type had the original (highly-
stretched) reinforcements. The degree of molecular orientation of the used highly stretched PP fabrics was reduced by heat-treating them at 164°C. The molecular relaxation was confirmed by Raman spectroscopic analysis and by comparing the tensile strength and impact resistance of the two types of prepared SRCs.

Reference Raman spectra were collected from the tapes of the used iPP fabric in its original, highly stretched form, representing the 100% relative orientation state, and from its completely heat relaxed form, representing the 0% relative orientation state. Then, the average relative orientation degree of the heat treated (relaxed) iPP fabrics were estimated by applying the multivariate evaluation method (CLS modelling), introduced in chapter 4.1., on the Raman spectra collected from the heat-treated (relaxed) iPP tapes. Accordingly, a relative orientation degree of 87.6 ± 2.5% was estimated for the heat-treated (relaxed) iPP fabric, indicating that significant molecular relaxation occurred during the 10 min heat-treatment at 164°C under a pressure of 0.4 MPa.

![Raman spectra](image)

**Figure 4.13 Raman spectra collected from original, heat treated and fully relaxed iPP fabric**

The tensile strength and perforation energy values of the simple PP mixtures and the two types of SRCs with IFR content of 9 and 13 wt% are demonstrated in Figure 4.14. Additional mechanical test results are summarized in Table 4.5. As shown in Figure 4.14 a, the tensile strength of PP in the form of SRCs containing high-strength PP fabrics is 4 times higher than that of the simple PP mixtures. Also, the impact resistance (expressed by the perforation energy) of the un-treated SRCs exceeds considerably the performance of the PP reference (see Figure 4.14 b). It is visible that an 8-fold increase in perforation energy was achieved with SRCs, even when flame retarded. While the FR additive content of the compounded PP mixtures negatively affected the properties of the samples (it decreased the tensile strength, reduced the elongation at break significantly and also the perforation energy of the samples), no remarkable influence on the mechanical properties of the SRCs was caused by their IFR additive content (Table 4.5).
The molecular relaxation of the reinforcing fabrics reduced the tensile strength of the SRC_RLX composites by 20% compared to the original SRCs (Figure 4.14 a), and also the perforation energy was reduced by approximately 35% (Figure 4.14 b). The ductility factor (Table 4.5) of both fabric reinforced composites is considerably higher than that of PP mixtures, indicating that large amount of energy is absorbed in the damage growth (debonding) among the fibre/matrix interface during impact failure. This indicates that both types of SRCs could be characterized with adequate consolidation quality and the difference in the mechanical performance of SRC and SRC_RLX composites is mainly due to the difference in the degree of orientation of the reinforcing tapes. Thus, it was proven by mechanical tests that the relaxed composites represent a kind of transition, regarding the degree of molecular orientation, between the high performance SRCs and the non-reinforced compounded mixtures.

![Figure 4.14 (a) Tensile strength and (b) perforation energy of PP compounded mixtures, SRCs and heat-treated SRCs with identical IFR contents](image)

**Table 4.5** Tensile modulus, elongation at break and ductility factor values determined from the tensile and IFWI tests, respectively

<table>
<thead>
<tr>
<th>FR content [%]</th>
<th>Sample type</th>
<th>Tensile modulus [Gpa]</th>
<th>Elongation at break [%]</th>
<th>Ductility factor [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>mixture</td>
<td>0.79 ± 0.04</td>
<td>41.7 ± 2.2</td>
<td>27.6 ± 9.4</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>0.72 ± 0.05</td>
<td>25.9 ± 1.0</td>
<td>40.3 ± 6.1</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>1.01 ± 0.07</td>
<td>23.9 ± 1.2</td>
<td>37.7 ± 4.7</td>
</tr>
<tr>
<td>9</td>
<td>mixture</td>
<td>0.89 ± 0.01</td>
<td>22.4 ± 1.4</td>
<td>28.1 ± 6.9</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>0.98 ± 0.03</td>
<td>25.5 ± 0.1</td>
<td>35.0 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>1.01 ± 0.05</td>
<td>24.2 ± 0.7</td>
<td>35.7 ± 5.1</td>
</tr>
<tr>
<td>13</td>
<td>mixture</td>
<td>0.93 ± 0.01</td>
<td>12.4 ± 1.6</td>
<td>33.1 ± 6.5</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>0.99 ± 0.03</td>
<td>23.7 ± 0.8</td>
<td>41.4 ± 6.2</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>1.16 ± 0.06</td>
<td>22.6 ± 0.8</td>
<td>37.9 ± 3.1</td>
</tr>
</tbody>
</table>
The flammability characteristics of these samples, with different degrees of orientation and IFR contents of 0, 9 and 13 wt%, were also examined and compared. The results of the UL-94 flammability tests and LOI measurements are summarized in Table 4.6. As shown, in the case of flame retarded high performance SRCs an IFR content of 9 wt% proved to be adequate for self-extinguishment, in contrast, when heat-treated PP fabrics were used for preparation of multilayered SRCs (relaxed SRCs), 9 wt% IFR was no longer sufficient to reach V-0 classification. Although the SRC-IFR9_RLX marked specimens did not burn horizontally, they burned completely in the vertical direction after 10 second ignition, as did the simple flame retarded PP mixture with the same additive content. The relaxed SRCs reached the V-0 rating at an additive level of 13 wt% - still much lower than the amount needed for the simple PP mixtures. Analysing the results in Table 4.6, it seems that, as the degree of molecular orientation of the relaxed composites means an intermediate state between the unreinforced PP samples and the high-performance SRCs, their LOI values also represent an intermediate position. This proves that the degree of molecular orientation of the embedded PP fibres is the key factor for the extraordinary flame retardant performance observed.

<table>
<thead>
<tr>
<th>FR content [%]</th>
<th>Sample type</th>
<th>UL-94 classification</th>
<th>burning rate [mm/min]</th>
<th>LOI [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mixture</td>
<td>HB (30.5)</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC_RLX</td>
<td>HB (33.6)</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC</td>
<td>HB (33.5)</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 mixture</td>
<td>HB (22.8)</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC_RLX</td>
<td>HB (-)</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC</td>
<td>V-0</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 mixture</td>
<td>HB (19.4)</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC_RLX</td>
<td>V-0</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRC</td>
<td>V-0</td>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of the UL-94 and LOI flammability tests on the SRCs, reinforced with PP fabrics of different degrees of orientation, prove that the highly stretched tapes of the fabrics contribute to the FR effect of the IFR additives. This beneficial effect is attributed to a balanced physical interaction between the mechanism of intumescence and the shrinking of the highly oriented tapes. In this system, if exposed to an ignition source from the edges of samples, parallel to the direction of stretching (UL-94 and LOI test), all the layers of PP fabrics start to shrink in coincidence with the development of the intumescent process, thus a special compact char develops on the surface of the specimen. In this case, higher concentration of FR active compounds retains in the solid phase and in the pyrolysis zone resulting in more effective fire extinguishing action.

In a cone calorimeter, where the heat flux is applied perpendicular to the layers of stretched tapes, the mechanism of enhancement of flame retardant efficiency and the influence of the degree of orientation differ from the above described ones. The obtained heat release rate curves in Figure 4.15 and the results summarized in Table 4.7 confirm the synergism
between the stretched PP tapes and the IFR system as the combustion of both types of flame retarded SRCs was accompanied with significantly lower $pkHRR$ and $tHR$ values and greater char masses (compared to simple PP mixtures). Although the almost identical $TTI$ values of the two types of SRCs suggest that the relaxation of fabrics do not influence the ignitibility of the multilayer composites, the embedding of heat-treated fabrics into the flame retardant matrix layers (relaxed SRCs) resulted in even lower but earlier appearance of $pkHRR$ than in the case of original fabric reinforcement (normal SRCs) (Figure 4.15 b and c). Furthermore, in presence of the relaxed fabrics the formed charred layer was the most compact and consequently also the highest residual masses remained after combustion. The more effective char modifying influence of the relaxed fabrics could be ascribed to its more effective barrier performance. Under the heated cone only a few upper fabric layers participate in the control of the IFR mechanism, which are denser after relaxation as shown Figure 4.16. The relaxed composites (Figure 4.16 b) show plainer and more uniform distribution of tapes as a consequence of the pressure of 0.4 MPa applied during the heat-treatment (in order to avoid shrinkage).

Figure 4.15 Heat release rate curves recorded during the burning of flame retarded simple compounds, high-performance and relaxed SRCs with IFR content of 0, 9 and 13 wt%, respectively
Table 4.7 Summary of the Mass Loss Calorimetric test results

<table>
<thead>
<tr>
<th>FR content [%]</th>
<th>Sample type</th>
<th>TTI [s]</th>
<th>pkHRR [kW/m²]</th>
<th>pkHRRtime [s]</th>
<th>Residue [%]</th>
<th>tHR [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>mixture</td>
<td>38</td>
<td>880</td>
<td>171</td>
<td>0.5</td>
<td>128.0</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>30</td>
<td>781</td>
<td>184</td>
<td>0.6</td>
<td>131.1</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>30</td>
<td>751</td>
<td>180</td>
<td>0.6</td>
<td>120.7</td>
</tr>
<tr>
<td>9</td>
<td>mixture</td>
<td>34</td>
<td>587</td>
<td>416</td>
<td>2.6</td>
<td>126.1</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>23</td>
<td>307</td>
<td>261</td>
<td>5.1</td>
<td>90.6</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>24</td>
<td>413</td>
<td>351</td>
<td>3.6</td>
<td>102.7</td>
</tr>
<tr>
<td>13</td>
<td>mixture</td>
<td>33</td>
<td>514</td>
<td>513</td>
<td>2.9</td>
<td>117.3</td>
</tr>
<tr>
<td></td>
<td>SRC_RLX</td>
<td>22</td>
<td>234</td>
<td>359</td>
<td>7.3</td>
<td>88.9</td>
</tr>
<tr>
<td></td>
<td>SRC</td>
<td>22</td>
<td>295</td>
<td>464</td>
<td>4.3</td>
<td>89.7</td>
</tr>
</tbody>
</table>

Figure 4.16 Light microscopic photographs of the cross section of multilayer SRCs reinforced with (a) non-treated and (b) heat treated PP fabrics

The significantly reduced rates of heat release observed in the case of multilayer SRCs can be explained by the reduced oxygen permeability and enhanced heat barrier effect of the compact char layer formed, which is similar to the “char bonded” structure [187,188] reported in case of fibre-intumescent interaction earlier. It seems that the shrinkage of the highly-stretched tapes promotes the formation of a coherent network of expanding and interlinked domains by increasing the specific concentration within the surrounding matrix, as predicted by the models proposed by Zhang [101] and Bourbigot [105]. The effectiveness of the observed synergism obviously depends on the ratio of the expanding domains and the shrinking ability, which need to be optimized in order to fully utilize the interaction.

Conclusions

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, 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. 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 the two types of examined samples. In the case of the compounded flame retarded PP samples the observed loose foam structures could be attributed to the intensive gas release and instantaneous foaming process occurring at the initial stage of burning, while in the case of the multilayered SRCs the abrupt gas escape and expansion is also 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.

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. All the characteristics of SRCs outperformed the PP mixture of same composition excepting the time to ignition, which decreased due to earlier appearance of decomposition products in the gas phase. The advantageous interaction is observable with all the applied measurements but the values and mechanisms are different. When the heat comes from the edges of the specimens (UL-94, LOI) all the stretched layers start to shrink and the compact char formed this way stops the propagation of the flame. When, however, the heat radiates perpendicularly to the layers of reinforcing fabrics (cone) only the upper layers influence the mechanism of intumescence. Their effect in this case is realized in hindering the escape of active FR species and the development of a compact charred layer. 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 self-reinforced composites). It is prospected that high amount of flame retardant additives could be spared this way and by this means a more cost-effective flame retardancy of polymers could be realized in the near future.

As a next step of the development, secondary raw materials were used for manufacturing flame retarded self-reinforced composites. The possibility of synergism was also investigated in flame retarded, injection moulded (i.e short fibre reinforced) all-polypropylene composites.

**RELATED PUBLICATIONS:** [III, IV, VIII, X, XIV, XVIII, XXVI, XXVIII, XXIX]

### 4.2.2 DEVELOPMENT OF FLAME RETARDED ALL-POLYPROPYLENE COMPOSITES FROM PLASTIC WASTE

**Rationale and aims**

The worldwide increasing plastic usage, owing to the achievable outstanding strength/density balance, processing flexibility and cost-effectiveness, produces enormous amount of end-of-life (EOL) plastic products. Their current treatment, due to the low volume/weight ratio and shortage of recycling, greatly burdens the landfills. The European legislation, in accordance with the waste treatment hierarchy (2008/98/EC Directive), aims to reduce the waste disposal and supports more environmentally friendly waste treatment technologies such as recycling.

In the case of mixed EOL plastics the conventional thermo-mechanical recycling is accompanied by property damage (downcycling) [189]. The main causes of downgrading (poorer quality and reduced functionality) of the reprocessed plastic mixture are the impurity (metals and dirt), inhomogeneity (large number of polymers with different molecular structure, melt behaviour, rheology and thermal stability) and incompatibility (different components form discrete phases with weak adherence) [190]. Additionally, there are economic constraints hindering the recycling of mixed plastic waste; the products obtained by conventional mechanical reprocessing do not meet the requirements of the market (neither in terms of mechanical properties nor in aesthetic aspects). Those products are almost unmarketable, which negatively affects the motivation for plastic recycling [191]. The solution for this negative tendency could be the transformation of the low-cost plastic waste into valuable composites or products that have special functions or properties, such as outstanding strength, impact resistance, and heat and/or fire resistance.

Among the mixed plastic waste the polyolefin fraction is the most suitable for thermo-mechanical recycling. Recyclable polyolefin fractions can be mostly obtained from automotive, electric and electronic components and packaging waste. To achieve economically effective recycling rates and high quality products, the mixed polyolefin
fractions must be sorted by polymer types (polyethylene (PE) and polypropylene (PP)), and according to Bakker et al. [192] the fraction purity should be better than 97%. These requirements can only be ensured by new, effective separation techniques. Nevertheless, the compensation of the negative effects of impurity and inhomogeneity is indispensable to achieve mechanically suitable materials.

In order to enhance the mechanical properties of polyolefins, glass fibre reinforcement is generally used due to their stiffness, high strength, heat resistance, or natural fibres [193] due to their renewability, low-cost and light weight. For further improvement in strength, longer (continuous) reinforcing fibres or fabrics can be applied. However, the glass or natural fibre reinforced composites are multi-component systems, where the use of dissimilar materials does not provide good adhesion. Furthermore, it encumbers the reprocessing and application of other waste treatment technologies. Whereas, their novel alternatives, the self-reinforced (SR) polymer composites [13], are easy to recycle [194].

It was assumed that the development of flame retarded polymer composites, capable of replacing more expensive metallic structural units, could acquire market benefit of recycled materials. However, the simultaneous reinforcement and reduction of flammability (with the commonly used ammonium-polyphosphate based intumescent flame retardants) are apparently antagonistic requirements, as the imperfect dispersion and the pure interfacial interaction between the IFR and the polymer considerably deteriorate the mechanical properties of the materials [195, 196]. This fact is even more apparent when fibre reinforcement is applied [122,197]. We planned to eliminate this contradiction by preparing multilayer composites including reinforcing and flame retarded sheets separately but well consolidated.

Our work aimed at developing environmentally advantageous composites from secondary raw materials accompanied with improved mechanical properties and reduced flammability at the same time. To reach this goal multilayered composites were prepared from the polyolefin fraction of automotive shredder waste. Polypropylene fabrics were applied as reinforcement, supporting the possibility of multiple recycling, while the flammability was reduced by modifying the recycled matrix layers with APP based flame retardant additive. Also, the possible synergistic effect, evinced in flame retarded primary all-polypropylene composites as a result of the beneficial cooperation of an intumescent flame retardant and highly oriented fibres, was planned to be investigated in the recycled system.

Experiments with real polymer wastes (i.e. not only mixtures of virgin polymers modelling polymer waste) and results for reprocessing of mixed plastic waste are quite rarely discussed in the literature, therefore our results regarding the recycling of automotive shredder light fraction could not rely on antecedents. Flame retarded self-reinforced composites were prepared by lamination and hot-pressing of polypropylene reinforcing fabrics and matrix layers made of secondary polyolefins. In order to reduce the flammability of the fabric reinforced composites, the recycled matrix layers have been modified by adding 34 wt% IFR additive. The properties of easily recyclable self-reinforced composites (SRREC) were
compared to common glass fabric reinforced composites (GF-REC) (prepared by the same technological parameters) and to reference samples without reinforcement (REC).

**Composite preparation**

Density-separated polyolefin fraction ($\rho < 0.92 \text{ g/cm}^3$) of automotive shredder waste, obtained from Alcufer Ltd. (Hungary), was used as secondary matrix material for the prepared multilayered composites. On the basis of comprehensive analyses [198,199] (TGA, DSC, IR- and Raman spectroscopic measurements) the main polymer component of the chosen fraction is polypropylene (but far from the advantageous purity of 97%, the PP content was 78 wt%), its inorganic filler (mainly silicates and calcium-carbonate) content, determined by heating at 900°C, is lower than 0.75 wt%.

Three types of flame retarded recycled samples: compounds without reinforcement (REC-FR18), glass fabric reinforced (GF-REC-FR18) and self-reinforced (SR-REC-FR18) composites were prepared with the same IFR (Exolit AP766) content of 18 wt%, the properties of which were compared to additive-free references: REC, GF-REC and SR-REC, respectively. In the case of compounds without reinforcement the specimens (REC-FR18) were prepared by simple mixing 18 wt% APP with the recycled matrix (REC) in a Brabender Plasticorder PL 2000 type internal-mixer at 190°C, with a rotor speed of 30 rpm, for 10 min and then hot-pressed to form 4 mm thick specimens in a Collin P200E type laboratory hot press. In the case of the multilayered composites (GF-REC-FR18 and SRREC-FR18) first a higher amount (34 wt%) of IFR was introduced into the recycled matrix, then from the obtained compounds 180 mm thick matrix layers were compression moulded at 190°C in a Schwabenthan Polystat 300 S laboratory hot press. The multilayered fabric reinforced composites were manufactured by lamination of 11 recycled matrix layers and 10 woven glass (HexForce 01717 1050 Z6224) or PP fabrics (T-PPT-181) according to the film-stacking method. The film-stacked packages were hot-pressed to composites in the same hot press at 162°C with a pressure of 6 MPa, for 2 min. The thickness of the prepared self-reinforced (SR) and glass fabric reinforced (GF) composites was 3.78 mm and 2.78 mm, respectively. For the sake of better comparison between the GF and SR composites, the composition (number of layers) and the nominal reinforcement content (i.e. glass or PP fabric) of ca. 48 wt% were also kept constant for each reinforced composite.

**Results and discussion**

The tensile and bending tests results of SR and GF composited are compared by column charts presented in Figure 4.17. a-d. It can be noticed that despite the relatively low purity of the polyolefin waste applied as matrix material in both glass fabric and self-reinforced composites (GF-REC and SR-REC), the tensile and flexural strength were remarkably increased compared to the non-reinforced recycled polyolefin blend (REC-REF). Although the original strip tensile strengths of the reinforcing fabrics are comparable, the load bearing capacity of the highly oriented PP tapes decreased during the heat treatment of the composite preparation (162°C for 2 min) leading to approx. 50% inferior tensile and flexural strength values in the case of SR composites compared to GF composites (Figure 4.17 a and
b). Still, 5 times higher tensile strength and 2 times higher flexural strength were achieved using reinforcing PP fabrics than those of the unreinforced reference (allowing multi-fold recycling as well in this case). It can also be observed that due to the FR content of the matrix layers the prominent tensile and flexural strength of the reinforced composites only slightly decreased. Consequently, also the prepared flame retarded recycled composites are proposed to be suitable for several technical applications. Considering the tensile and flexural moduli of the fabric reinforced composites (Figure 4.17 c and d), it can be seen that the self-reinforced composites’ moduli are almost as low as that of the reference matrix (REC-REF); meanwhile, the stiffness was significantly increased by glass fabric reinforcement. This is the expected consequence of the difference between the specific properties (stiffness, flexibility, etc.) of the applied reinforcing materials. Their selection and utilization depends on the application requirements. The different effect of the applied FR additive on the tensile and flexural moduli (Figure 4.17 c and d) of the composites can be explained by the dissimilarity of the two stress profiles i.e. bending involves some compression as well (Figure 4.17 d).

![Figure 4.17 Tensile and bending test results of the prepared recycled composites: (a) tensile strength, (b) flexural strength, (c) tensile modulus, (d) flexural modulus](image-url)
In order to investigate the adhesion between the layers of the prepared reinforced composites, their interlaminar shear strength was determined (Figure 4.18 a). The harmful effect of the FR additive on the adhesion between the recycled matrix and the glass fabrics has been manifested by the decrease of their interlaminar shear strength. In the case of the self-reinforced composites it was concluded that the transcrystalline layer, which is the key factor of the improved adhesion and consequently of the good mechanical performance [200,201], was not noticeably influenced by the added flame retardant. The lower initial interlaminar shear strength in the case of the self-reinforced composites can be ascribed to the lower specific surface and thus lower contact area of the PP fabric than that of the used glass fabric.

![Graph showing interlaminar shear strength and perforation energy](image)

**Figure 4.18 (a) Interlaminar shear strength and (b) perforation energy of the prepared recycled composites.**

Photographs taken of the tensile and IFWI test specimens are shown in Figure 4.19 and Figure 4.20, respectively. In the case of the self-reinforced composites (Figure 4.19 b,d and Figure 4.20 b,d) imperfect consolidation quality is reflected by slight delamination and tape pullout, in contrast to the photographs showing instantaneous breakage of the GF systems (Figure 4.19 a,b and Figure 4.20 a,b). The observed failure behaviours are in close connection with the different interlaminar shear strengths characteristic for the two types of composites [201], and which also strongly influences their creep resistance [202]. The delamination process absorbs high energy [121,201], resulting in noticeable impact resistance (perforation energy), as shown in Figure 4.18 b. In the case of the glass fabric reinforced composites just the opposite tendencies (less delamination, higher tensile-, flexural- and interlaminar shear strength) can be observed. However, these well consolidated GF composites are not superior considering the IFWI test (Figure 4.18 b), their perforation energy is about the same as that of the SR composites. The obtained high perforation energy (more than 4-times higher than that of the recycled reference matrix (REC-REF)) of the prepared multi-layered recycled composites can be advantageous in many fields of application where shock-resistant protection (covers, equipment housing, etc.) is required. The applied film-stacking method can be easily implemented in industrial scales by double belt press technology.
All the prepared flame retarded samples (multi-layered composites and compounds without reinforcement) contain 18 wt% FR additive (considering their total mass), thus relevant conclusions could be drawn on the bases of comparative flammability tests. The results of the performed LOI and UL-94 flammability tests are summarized in Table 4.8. With 18 wt% IFR content V-1 rating could be achieved in the case of REC-FR18 compound, which is in accordance with the fact that at least 20-22 m/m% IFR is required to achieve V-0 classification in PP [101]. In contrast, 18 wt% IFR content proved to be sufficient for the V-0 rating when incorporated into multilayered composites (GF-REC-FR18 and SRREC-FR18). It is also shown, that in spite of the same IFR content 7 vol% and 4 vol% higher LOI was reached by preparing fabric reinforced composites. The lower flammability of GF-REC-FR18 can be explained by its high (ca. 48 wt%) incombustible material (glass) content, which is also manifested by the low burning rate (19.9 mm/min) and relatively high LOI (21 vol%) of the additive-free GF reference composite (GF-REC). Nevertheless, the favourable behaviour of the self-reinforced composite (SR-REC-FR18), which is entirely composed of combustible materials, is much more remarkable. This beneficial effect is assumed to be attributed to the physical interaction between the intumescent i.e. expanding structure and the highly oriented, consequently shrinking tapes, as also found in flame retarded primary SRPPCs (see in section 4.2.1). So, the new synergism was successfully evinced and confirmed in an other matrix material, namely in secondary polyolefin matrix.
The combustibility of the prepared recycled samples was characterized under the conditions of a Mass Loss type Cone Calorimeter. The heat release rate (HRR) and the mass loss (ML) curves of the examined specimens are given in Figure 4.21. Compared to the recycled matrix material (REC) significant reduction of the heat release rates was observed in the cases of flame retardant and glass fabric containing samples; the measured pkHRR values were lowered with 71% in the case of the flame retarded matrix material (REC-FR18), with 63% in the case of the glass fabric reinforced composite (GF-REC-FR18), and with 77% in the case of the self-reinforced composite (SR-REC-FR18). The quantitative experimental results are summarized in Table 4.9. The remarkably lower heat release rate values (pkHRR and tHR) of the GF composites (GF-REC and GF-REC-FR18) compared to reference materials cannot be explained only by their significantly lower (52%) combustible content. The enhanced horizontal heat conductivity of the glass fabrics containing composites has to be taken into account as well. As for the SR composite containing 18 wt% IFR additive (SR-REC-FR18), the 16% reduction of the pkHRR can be ascribed to the compact surface structure of enhanced protective efficiency achieved by the shrinkage of the surface layer (see also in section 4.2.1). The mass loss data recorded in the case of glass fabric reinforced composites (GF-REC and GF-REC-FR18) have been corrected for providing better comparison. Thus, only the mass loss of the combustible content are presented in Figure 4.21 b. (The real masses of the residues are shown in Table 4.9). It can be seen that the combustible part of the flame retarded GF composite (GF-REC-FR18) burns out, due to the candlewick effect, faster than that of the SR-REC-FR18 sample i.e. glass fibres accelerate the transport of flammable mass to the burning area [121,197]. On the other hand, the charred residue that was detected in the case of flame retarded self-reinforced composite confirms the assumption that the shrinkage of the surface layer improves the protection capability of the of the IFR system. Comparing the released total heat (tHR) of the two materials with exactly the same composition even more remarkable difference can be found: the self-reinforced recycled sample (SR-REC-FR18) released 28% less total heat (tHR) than the compound without reinforcement (REC-FR18).
Figure 4.21 (a) Heat release rate and (b) mass loss (of the combustible content) measured during the burning of flame retarded recycled samples

Table 4.9 Results of mass loss type cone calorimeter measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI [s]</th>
<th>pkHRR [kW/m²]</th>
<th>pkHRR_time [s]</th>
<th>Burning time [s]</th>
<th>Residue [mass%]</th>
<th>tHR [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>REC</td>
<td>34.1</td>
<td>23</td>
<td>875.0</td>
<td>182</td>
<td>194</td>
<td>0.3</td>
</tr>
<tr>
<td>GF-REC</td>
<td>36.5</td>
<td>33</td>
<td>243.6</td>
<td>213</td>
<td>266</td>
<td>53.9</td>
</tr>
<tr>
<td>SR-REC</td>
<td>34.1</td>
<td>27</td>
<td>922.4</td>
<td>190</td>
<td>225</td>
<td>0.1</td>
</tr>
<tr>
<td>REC-FR18</td>
<td>39.8</td>
<td>24</td>
<td>253.6</td>
<td>728</td>
<td>841</td>
<td>3.7</td>
</tr>
<tr>
<td>GF-REC-FR18</td>
<td>35.8</td>
<td>26</td>
<td>90.9</td>
<td>435</td>
<td>515</td>
<td>59.3</td>
</tr>
<tr>
<td>SR-REC-FR18</td>
<td>36.9</td>
<td>25</td>
<td>213.1</td>
<td>613</td>
<td>740</td>
<td>8.1</td>
</tr>
</tbody>
</table>

The difference is quite obvious when the photographs taken of the charred residues after combustion are compared (Figure 4.22). Based on the flammability test results of the flame retarded SR composite, the special synergistic effect between the APP based intumescent flame retardant additive and the highly oriented PP fabrics could be evinced in the recycled matrix as well. This interaction resulted in improved flame retardancy such as 4 vol% higher LOI value, significantly lower intensity of burning and better UL-94 classification (V-0) than expected. Consequently, smaller amount of flame retardants are needed in order to achieve acceptable levels of flame retardancy, resulting in cost-effectiveness and higher market value of such flame retarded secondary products. In addition, it has to be highlighted that excellent mechanical properties can be guaranteed in the case of the recycled multi-layered composites with reduced flammability as well, thus the preparation of such composites can be a solution for the upgrading recycling of plastic waste.

Figure 4.22 Photographs taken of the charred residues of flame retarded samples obtained after combustion in Mass Loss type Cone Calorimeter.
Conclusions

In accordance with the increasingly strict European legislation, environmental and safety aspects of material development became relevant besides the economic efficiency. As a consequence the potential of those plastic industrial applications, where reduced flammability combined with reinforcement and recyclability are essential requirements, is continually increasing.

The present investigation aimed at upgrading automotive shredder plastic waste by the development of flame retarded self-reinforced composites from density separated secondary polyolefin fraction. The mechanical and flammability properties of the prepared self-reinforced composites were compared to conventional glass fabric reinforced composites and to the secondary polymers.

The mechanical properties of the 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%) pkHRR during combustion.

Based on the described results it can be concluded that products of high technical value can be obtained from secondary raw materials with the preparation of self-reinforced composites upgraded with flame retardancy. Considering that the scaling-up of fabric reinforced composite preparation can be easily implemented, it is assumed that the safe, recyclable, self-reinforced polyolefin composites made of low-cost recycled materials could become especially attractive for the industry.

Related publications: [I, II, IV, VI, VII, XVI, XVII, XVIII, XXV].
4.2.3 STUDY ON THE FLAMMABILITY PROPERTIES OF INJECTION MOULDED ALL-POLYPROPYLENE COMPOSITES

Rationale and aims

Nowadays, self-reinforced products are produced by three main processing methods; hot-compaction, consolidation of coextruded tapes and film-stacking. All of these methods yield in sheet-like (pre)products, these ways three-dimensional parts with complex geometry cannot be directly produced. Therefore, intensive efforts are being made to produce self-reinforced composites by the more versatile injection moulding method [203,204].

Our aim was to manufacture injection mouldable all-PPCs in flame retarded form and to investigate the presence of synergism, evinced both in primary and recycled film-stacked all-PPCs. In contrast to the bidirectional plain-woven fabric reinforcement (used in multi-layered composite structures), the injection moulded composites comprise the reinforcing polymer fibres in short and peculiarly aligned form. This difference was expected to have significant influence on the cooperation of the expanding (intumescent flame retardant) and the shrinking (oriented fibres) domains.

Composite preparation

In the first step, reference and flame retarded rPP (Versify 4200) based compounds were produced by melt-compounding using a Labtech Scientific LTE-26-44 twin-screw extruder (with temperature profile from feed zone to die of 200, 205, 210, 210, 210 and 215°C, and screw rotation speed of 70 1/min) and then injection moulded to form non-reinforced elastomer sheets with FR (Exolit AP766) contents of 0, 10 and 15 w%.

The fibre reinforced composites sheets were manufactured according to a multi-step procedure. The fibre containing granules, suitable for injection moulding, were obtained by cutting and granulating the unidirectionally reinforced all-polypropylene composites prepared by film-stacking of flame retarded matrix foils and reinforcing polypropylene fibres. For this purpose, first 0, 20 and 30 wt% FR additive (Exolit AP 766) was melt-compounded with the neat rPP matrix. The extruded materials were cooled down by air cooling method and granulated to 3 mm length (Labtech LZ-120/VS). Then, from the granulates 50 μm thick films were manufactured by Labtech LCR300 cast-film extrusion (screw rotation speed: 22 1/min; extruder temperature profile from feed zone to die: 215, 215, 205, 205 and 205°C, temperature of coat-hanger die: 235, 230 and 235°C; winding speed: 10 1/min). Reference and flame retarded consolidated SR-PPCs sheets with 50 wt% nominal reinforcement content and unidirectional (UD) fibre direction were manufactured by filament winding process using film-stacking method and compression moulding technique. Actually, the processing window was 90°C. The filament-wound, film-stacked packages were inserted in between the preheated moulds to 140°C and held for 240 s without pressure, then compressed for 480 s under a pressure of 5.26 MPa and finally cooled to 45°C (under pressure). The thickness of the produced sheets was 1.6 mm. The consolidated plates were then cut into 5 (wide) x 5 (length) mm² sections (as pre-impregnated pellets) suitable for
injection moulding. The length dimension of these cut pieces determined the length of the reinforcing fibres.

Plaque specimens measuring 80 × 80 × 2 mm in dimensions and with flame retardant contents of 0, 10 and 15 wt% were injection moulded both from the non-reinforced and reinforced (50 wt% fibre containing) granulates with fan gate. The process parameters are listed in Table 4.10.

<table>
<thead>
<tr>
<th>Injection moulding parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection volume [cm³]</td>
<td>44</td>
</tr>
<tr>
<td>Injection rate [cm³/s]</td>
<td>50</td>
</tr>
<tr>
<td>Switch over point [cm³]</td>
<td>10</td>
</tr>
<tr>
<td>Holding pressure [bar]</td>
<td>400</td>
</tr>
<tr>
<td>Holding time [s]</td>
<td>10</td>
</tr>
<tr>
<td>Residual cooling time [s]</td>
<td>15</td>
</tr>
<tr>
<td>Screw rotational speed [m/min]</td>
<td>15</td>
</tr>
<tr>
<td>Back pressure [bar]</td>
<td>20</td>
</tr>
<tr>
<td>Decompression volume [cm³/s]</td>
<td>5</td>
</tr>
<tr>
<td>Decompression rate [cm³/s]</td>
<td>5</td>
</tr>
<tr>
<td>Temperature of the zones:</td>
<td></td>
</tr>
<tr>
<td>120, 125, 130, 135, 140°C</td>
<td></td>
</tr>
<tr>
<td>Temperature of the mould:</td>
<td>20°C</td>
</tr>
</tbody>
</table>

**Results and discussion**

The 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 4.23). The skin-core formation, typical for injection moulded products, is also observable; the fibres are aligned in the flow direction. Density measurements confirmed that the composites are well consolidated; the measured density values were higher than 95% of the theoretical density in all cases, also indicating that the fibres are properly impregnated by the matrix material.

![Figure 4.23 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)

As the present investigation focuses on the flammability behaviour of the flame retarded injection moulded all-PPCs, the mechanical properties of the manufactured all-PPCs are presented as supplementary material. The UL94 and LOI flammability test results of the two types of flame retarded injection moulded sheets are compared in Table 4.11. Accordingly,
no significant difference could be evinced between the flammability behaviour of the non-reinforced and the self-reinforced specimens of identical FR contents. Slightly better flame retardant performance was observed for the composites during vertical burning tests; some of the 15 wt% FR containing specimens showed self-extinguishing behaviour ever after the second (10 s) ignition, which could be ascribed to the beneficial effect of the presence of highly oriented iPP fibres, as proposed earlier. However, it has to be declared that the contribution of the short iPP fibres to the synergism with the IFR system is almost negligible compared to the plain-woven iPP fabrics composed of highly stretched tapes.

Table 4.11 Comparison of the UL-94 classifications and LOI values of injection moulded rPP sheets and all-PPCs

<table>
<thead>
<tr>
<th>Sample</th>
<th>UL-94 classification*</th>
<th>LOI vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPP</td>
<td>HB (4.8)</td>
<td>18</td>
</tr>
<tr>
<td>SR-PP</td>
<td>HB (3.9)</td>
<td>18</td>
</tr>
<tr>
<td>rPP_FR10</td>
<td>HB (3.1)</td>
<td>24</td>
</tr>
<tr>
<td>SR-PP_FR10</td>
<td>HB (3.1)</td>
<td>24</td>
</tr>
<tr>
<td>rPP_FR15</td>
<td>V-2</td>
<td>29.5</td>
</tr>
<tr>
<td>SR-PP_FR15</td>
<td>V-2</td>
<td>29.5</td>
</tr>
</tbody>
</table>

*in parenthesis the horizontal burning rates [mm/min], if measurable, are indicated

The burning behaviour of the injection moulded all-PPCs was compared to non-reinforced rPP sheets also using cone calorimeter tests. The obtained HRR curves are presented in Figure 4.24. As it can be seen, the HRR curves of the two types of samples are very similar. When considering the pkHRR values, each SRPPC outperformed its non-reinforced counterpart of same FR content; however the degrees of pkHRR reductions are not remarkable. Based on these results it was concluded that, in contrast to plain-woven iPP fabrics, peculiarly oriented, short iPP fibres do not noticeably influence the combustion behaviour of an intumescent flame retarded PP system.

Figure 4.24 Heat release rate curves of injection moulded non-reinforced and self-reinforced PP sheets
Conclusions

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. 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.

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.

Related Publications: [XXIX, XXXI].
4.3 FLAME RETARDANCY OF BIODEGRADABLE COMPOSITES

The enormous plastic usage worldwide is accompanied with several serious environmental and sustainability issues. Therefore, besides striving towards higher recycling rates for plastic products, in recent years increasing attention arose to biodegradable and renewable materials as well. However, even until recently, these are widely used only in the packaging industry and in the medical field. Extension of biopolymers to engineering applications would serve the realization of sustainable development; however, these new types of polymers require various modifications, including reinforcement and flame retardancy, in order to offer a reasonable green alternative the conventional petroleum-based plastics in all aspects.

4.3.1 DEVELOPMENT OF FLAME RETARDED THERMOPLASTIC STARCH BASED COMPOSITES

Rationale and aims

In the recent decades, the need for application of environmentally favourable biodegradable polymers, especially when originating from renewable resources, is increasingly coming to the forefront. In the market many biobased and degradable polymers, such as polylactic acid (PLA), polycaprolactone (PCL), polyhydroxyalkanoate (PHA), etc., are already available; however these are generally more expensive than their traditional petrochemical based counterparts (PP, PE, PET, etc.). In this sense, starch-based thermoplastic biopolymers have a potential for a wider range of application [59] due to their availability and low cost.

The most commonly used plasticizers for starch are water and glycerol, but also several low molecular weight polyols (such as glycerol, glycol, xylitol, malitol, sorbitol, etc.) have been already employed. However, the use of a heteroatom (such as P of flame retarding effect) containing functionalized polyol as plasticizer seems to be a novel idea.

In order to increase the originally weak mechanical performance of the thermoplastic starch (TPS) matrix by a way that preserves the environmental friendly character of the final material the usage of natural lignocellulosic reinforcements is a logical choice [205]. The availability, renewability, low density, and price as well as satisfactory mechanical properties make the biofibres an attractive and ecological alternative to glass, carbon and other man-made fibres [206,207]. The combination of TPS matrix with different type of natural fibres is increasingly investigated by researchers, and has also been reviewed recently by Faruk et al. [56].

Biocomposites, comprising of biodegradable matrix materials and reinforcing biofibres, are presumed to be increasingly used in industries (such as transportation and construction) where the development of safe and environmental friendly flame retardant composites is of great importance. Still, the flame retardancy of starch-based biopolymers was barely studied until recently, only a few papers have been published in this field [129,153,154]. On the other hand, according to earlier reports, reinforcing biofibres (without flame retardants in the polymer matrix) increase the heat conductivity and decrease the apparent stability of
the composite, and thus ignition becomes easier [125]. Candlewick effect of natural fibres represents a big challenge for flame retardation thus its suppression is required for improving the flame retardancy of the natural fibre reinforced biocomposites [123,131]. Inorganic phosphorous compounds (such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), monoammonium phosphate (MAP) and diammonium phosphate (DAP) [130,140,141,142] proved to be adequate to effectively flame retard cellulose based fibres.

In our work, the flame retardancy of fully biodegradable, natural fibre reinforced TPS composites of increased mechanical performance was further investigated. To overcome the candlewick effect of biofibres and effectively reduce the flammability of the biocomposites phosphorous-based chemical substances were used both on the surface of the reinforcing biofibres and in the TPS matrix.

**4.3.1.1 USE OF PLASTICIZER WITH FLAME RETARDANT EFFECT IN STARCH**

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

**Sample preparation**

Commercially available corn-starch of 19% amylose content was modified. Two types of TPS matrices were prepared. One of them was plasticized with 30 wt% glycerol by itself (marked as TPS-G) that served as TPS reference; while the other (marked as TPS-GOP) was plasticized with the combination of 11 wt% glycerol and 15 wt% phosphorus-containing polyol, Exolit OP 560. The chemical structure of OP560 is presented in Figure 4.25. The applied phosphorous polyol, owing to its high phosphorus content (10-13 wt%) was expected to exhibit high flame retardant performance besides its plasticizing functionality.

![Figure 4.25 Chemical structure of Exolit OP 560 type phosphorous-polyol](image)

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

**Results and discussion**

The plasticizing effect of the applied chemical substances was followed by recording the torque during mixing. It can be seen in Figure 4.26 that the two types of polyols acted differently as plasticizers. In the case of glycerol, when used by itself, the torque increases continually right after starting the mixing indicating the continual decrease of hydrogen bonding between the polymer chains and the continuous increase in molecular space. The
maximum of torque demand appeared typically at 380 ± 30 s, when the gelatinization begins, i.e. starch molecules start getting released from the granule structure, and behave similarly to thermoplastic synthetic polymers [208]. On the contrary, the incorporation of the long-chain phosphorous polyol (Exolit OP560) between the starch chains proved to be more time-consuming. Significant increase in torque demand could not be measured until 1060 ± 60 s, when in all cases a sharp peak of torque indicated the beginning of plasticization process. The observed different plasticizing phenomenon of a short-chain and a long-chain polyol can be explained by the kinetically controlled interaction process between starch and plasticizers; the smaller molecule (in this case glycerol) penetrates the starch chains more easily [209]. It is visible that the energy necessary for plasticizing corn starch is about the same for the two types of plasticizer. However, after reaching the plateau, the equilibrium torque for P-polyol plasticized starch is considerably lower than that of the glycerol plasticized starch, which indicates that the mobility of starch chains has been increased significantly when OP560 was used as plasticizer causing remarkable change in the viscosity and resulting in somewhat sticky specimen comprising of TPS-GOP matrix.

![Figure 4.26 Torque curves recorded during plasticizing starch with 30% glycerol (black) and with the mixture of 11% glycerol and 15% OP560 (gray)](image)

The obtained two types of TPS blends were compared through thermal analyses. The DSC, TG and DTG curves are shown in Figure 4.27. The onset temperatures of the decomposition steps of glycerol plasticized starch (TPS-G) can be seen, both in DSC and TG curves, at 155°C and 250°C. These correspond to the endothermic decomposition of glycerol and corn starch, respectively. It is visible that the addition of OP560 has remarkable influence on the thermal degradation of the obtained TPS. The TPS plasticized with addition of OP560 (TPS-GOP) decomposes at lower temperature than the glycerol-plasticized TPS, namely the temperatures of maximum mass loss for TPS-G and TPS-GOP are 314.5°C and 264.5°C, respectively. However, beyond the temperature of 318°C, TPS-GOP is more stable than TPS-G, moreover, the residue left at 500°C for TPS-GOP is 38.7% which is much higher than that of TPS-G reference (21.7%).
LP-FTIR method was used to analyse the gaseous products during the pyrolytic degradation of TPS matrices. The FTIR spectra of the pyrolysis products of the two types of plasticized starch are shown in Figure 4.28. The LP-FTIR spectrum of TPS-G fits well to the published TG-FTIR features (and degradation products) of PLA/glycerol-plasticized TPS [153]. Furthermore, besides the characteristic degradation products of starch such as $\text{H}_2\text{O}$ (3400-4000 cm$^{-1}$ and 1200-2200 cm$^{-1}$), hydrocarbons (2800-3000 cm$^{-1}$), $\text{CH}_3\text{O}$ (C-H stretching, 2780 cm$^{-1}$; C-O stretching, 1745 cm$^{-1}$), CO (2173 cm$^{-1}$), $\text{CO}_2$ (2280-2400 cm$^{-1}$), and $\text{CH}_3\text{OH}$ (C-O stretching, 1050 cm$^{-1}$; O-H deformation, 669 cm$^{-1}$) using LP-FTIR method the vapours of glycerol (such as at 861, 923, 1111 and 1418 cm$^{-1}$ wavenumbers) could be also unambiguously detected. When compared with the TG-FTIR coupled method, where the glycerol can condense between the TG and FTIR instruments [153], in the case of LP-FTIR the direct connection between the pyrolysis zone and the analyzing unit allows the immediate and in situ analysis of the degradation products without loss of any components [166]. It has to be also highlighted that, in contrast to the much more time-consuming TG-FTIR method, the presented LP-FTIR experiments took only 45 seconds per samples.
It is well-known that dehydration and depolymerization are the two main processes associated with the thermal degradation of polysaccharides [137]. In the process of dehydration, the sample may release water, and in the process of depolymerization, the main decomposition products are CO₂, CO, CH₃OH, and hydrocarbons, etc. As the TG measurements reveal (Figure 4.27), also the LP-FTIR analysis confirmed that the P-containing OP560 additive catalyze the thermal decomposition of TPS at the beginning. The amount of selected gas components could be compared through the integrated traces of FTIR peaks. The Gram-Schmidt thermogram (Figure 4.29 a) shows the overall absorption intensity and thus is proportional to the quantity of the evolved gases during pyrolysis. Comparing the quantity (Figure 4.29 a) and ratio of the pyrolytic degradation products presented in Figure 4.29 b, c and d, it can be established that in the first 20-25 seconds of laser pyrolysis the OP560 containing TPS release more CO₂ (2361 cm⁻¹), hydrocarbons (2928 cm⁻¹) and CH₃OH (669 cm⁻¹), etc. compared with the glycerol-plasticized starch (see also in Figure 4.28). However, after 25 seconds of pyrolysis the char promoting effect of the P-polylol prevails and the rapid decomposition of the TPS-GOP sample ceases, meanwhile the thermal decomposition of the glycerol-plasticized starch (TPS-G) increases furthermore exponentially in time. Consequently, the solid-state flame retarding action of the P-containing plasticizer could be confirmed by the LP-FTIR method.
4.3.1.2 THERMOTEX TREATMENT OF FLAX FIBRES WITH PHOSPHOROUS COMPOUNDS

Chopped flax fibres (BFibre) and plain woven linen-hemp fabrics (BFabric) were used for reinforcing TPS. In order to reduce the flammability and diminish the candlewick effect [123,131,210,211] of the fibrous substances, the natural fibres were treated with ammonium phosphate (AP) model surface treating agent according to the so-called thermotex procedure, elaborated by Rusznák [212].

Fibre treatment

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

**Results and discussion**

It is presumed that AP is mainly physically adsorbed on the surface and in the capillaries of the biofibres, however, also chemical interaction could be confirmed by FTIR spectrometry between phosphoric acid and the hydroxyl groups of cellulose and lignin containing fibres. The spectra of the untreated and AP-treated flax fibres shown in Figure 4.30 are in accordance with the results published by Suardana et al. [130]. The untreated fibres show sharp peaks at 2919 cm⁻¹, 1377 cm⁻¹ and 895 cm⁻¹ corresponding to the absorption peaks of cellulose. The peak at 3413 cm⁻¹ is due to the stretching vibration of hydroxyl (O–H) group of lignin. The presence of AP on the surface of fibres resulted in decrease in transmittance. It can be noticed that the primary and secondary hydroxyl groups of cellulose and lignin in the fibre have been partially replaced by phosphate groups by phosphorylation from phosphoric acid forming phosphorus ester (899 cm⁻¹) [140]. The FTIR spectrum of the AP-treated fibre also showed the vibration of N–H group at 3270 cm⁻¹.

![Figure 4.30 FTIR spectra of untreated and AP-treated flax fibres](image)

The thermal degradation of the untreated and AP-treated flax fibres were analyzed by TGA measurements. The TG and DTG curves are presented in Figure 4.31. As expected [145], AP significantly lowered the initial decomposition temperature of flax, and also the peak temperature of the DTG curve corresponding to the maximum weight loss rate of AP-treated biofibre, which is 262°C (90°C lower than that of untreated flax fibres). These shifts to lower temperatures cause an earlier liberation and dissipation of flammable gases, before their ignition temperature is reached [213]. On the other hand, AP promoted the formation of solid residues and char. The char amount at 500°C for AP-treated fibres was 41.1%, one and a half times higher than that of untreated flax fibres. The phosphorylation reaction of AP with cellulose, which is accompanied with release of water and ammonia, can also be recognized as a shoulder peak at 235°C in the DTG curve [214]. This phosphorylation inhibits the formation of flammable levoglucosan, and consequently reduces the fuel supply necessary for combustion [215].
The flammability of untreated and AP-treated biofibres was compared in mass loss type cone calorimeter which test models fairly well the real burning conditions. The heat release rates curves are presented in Figure 4.32. As it is visible, the AP-treatment contributed to high level of flame retardancy of natural fibres. After ignition the flame of the AP-treated flax extinguished almost immediately, thus also the sharp peak of heat release rate ($pkHRR$) of untreated biofibres was completely diminished. After burning both type of flax fibres glowed for a long time, however, while the untreated fibres disintegrated completely and formed grey ash, the AP-treated fibres turned black, formed char and maintained their fibrous form even after combustion (Figure 4.33). The enhanced flame retardancy of AP-treated biofibres can be explained by the esterification of phosphoric acid and primary hydroxyl groups of the cellulosic fibres when exposed to heat, which promotes the char formation [140].
4.3.1.3 Flax fibre reinforced thermoplastic starch composite flame retarded with multifunctional additive system

The fire retardancy of biofibre reinforced thermoplastic starch composites was accomplished with the combination of P-containing plasticizer and surface treatment of biofibres.

Sample preparation

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

Results and discussion

The microstructure of the two forms of biocomposites can be seen in Figure 4.34. The chopped fibres (Figure 4.34 a) are well distributed in the TPS matrix and the adhesion between the phases is fairly good. The fabric layers (Figure 4.34 b) are also well embedded into the matrix but, as expected, the wetting of individual fibres was not achieved in this case.
Figure 4.34 SEM images of TPS composites prepared with a) chopped cellulosic fibres and b) with cellulosic fabrics

The influence of the flame retardant modifications on the mechanical properties of the biocomposites was investigated by tensile and IFWI tests (Figure 4.35). It is visible, that the use of OP560 as plasticizer reduced both the tensile strength and modulus, but increased the perforation energy of the TPS matrix. It is presumed that the P-containing plasticizer improves the mobility of the polymer chains (in accordance with the lower torque shown in Figure 4.26).

It can be noticed, that the same (27%) percent of reinforcing fibres in form of woven fabrics, proved to be much more efficient in increasing the tensile strength of the TPS composites because, compared to short and randomly orientated flax fibres, the long continuous fibres are aligned in the direction of loads carry and transfer it better (Figure 4.35 a). As a consequence, also a 7-fold increase in perforation energy was achieved when woven fabrics were embedded into the TPS matrix, while the chopped flax fibres had no significant effect on the impact resistance (Figure 4.35 c). Nevertheless, the failure of both types of natural fibre reinforced composites can be characterized with fairly high ductility factor (Figure 4.35 d), i.e. these natural fibre reinforced TPS composites have high ability to withstand plastic deformation, which could be very advantageous from application aspects. On the other hand, the tensile modulus values (Figure 4.35 b) of the chopped fibre reinforced composites are superior to those of the fabric reinforced TPS samples. Probably the wetting and thus the immobile-interface formation is more general in the case, when the chopped fibres are thoroughly dispersed in the matrix.

Considering the tensile and IFWI test results, it can be concluded that the surface treatment of the natural fibres with AP, in contrast to the reasonable anticipation [216], slightly increased the tensile strength, the stiffness, the impact resistance (expressed in perforation energy) and the ductility of biofibre reinforced composites. It was concluded that the degradation of the cellulosic fibres at the low processing temperature is not significant, while the phosphorous compounds in both phases likely improve their interaction and mechanical cooperation. Suardana et al. [130] also observed that PLA composites reinforced with DAP-treated fibres show higher flexural modulus than those with untreated natural
fibres and ascribed this increase in stiffness to the biofibre-DAP-PLA interaction. In our case, similar interaction can occur, which can result in good compatibility among AP-treated fibres and the embedding starch matrix.

Figure 4.35 a) Tensile strength, b) tensile modulus, c) perforation energy and d) ductility factor of biofibre reinforced TPS composites

The results of the UL-94 and LOI flammability tests are given in Table 4.12. It is visible that the flame retardancy of TPS-G reference was significantly increased by the partial replacement of its conventional glycerol plasticizer with a P-polyol. As a result of using OP560 as plasticizer, the horizontal burning of the highly flammable (UL-94: HB) TPS-G sample completely ceased, thus V-2 rating according to the UL-94 test and LOI as high as 31 vol% were achieved in the case of the TPS-GOP sample. However, when neat natural fibres or fabrics were used as reinforcement, the UL-94 classification remained still HB and also the LOI values decreased noticeably compared to the unreinforced TPS-GOP matrix. The moderate flammability characteristics of these TPS composites could be attributed to the observed long-term glow of fibres during and after burning in the specimens ascribed to the candlewick effect [123,131,217,218]. However, when additional FR active components were used on the surface of the cellulosic fibres (AP-treatment) the heat and flame propagation
along the fibres were effectively suppressed, thus the extinction of the candlewick effect was possible. As a consequence, the TPS composites reinforced with both AP-treated natural fibres and fabrics (TPS-GOP_BFibre-AP and TPS-GOP_BFabric-AP) reached LOI of 32 vol% accompanied with the best UL-94 V-0 classification. Similar flammability properties (V-0 and 33 vol% LOI) of TPS composites were achieved by Matkó et al. [129] with the addition of 10% of ammonium polyphosphate, which acts, however, neither as plasticizer nor as reinforcing agent in contrast to the present formulation.

<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 (19.6)</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>

*in parenthesis the horizontal burning rates [mm/min], if measurable, are indicated

![Figure 4.36 a) Heat release rate curves and b) mass loss curves recorded during the burning of biofibre reinforced TPS composites](image)

The flame retarded natural fibre reinforced composites have also been characterized under the conditions of a Mass Loss type Cone Calorimeter. The recorded heat release rate (HRR) and mass loss (ML) curves are shown in Figure 4.36 a and b, respectively, and additional combustion characteristics are presented in Table 4.13. When comparing the burning behaviour of the prepared TPS matrices (TPS-G and TPS-GOP) significant difference can be observed between the time to ignition (TTI) values. The early inflammation in the case of the OP560 plasticized TPS can be ascribed to the initial char layer formation that is accompanied with fast volatilization of flammable substances at the initial stage of heating, as also observed when evaluating the TG curves in Figure 4.27. The charring of TPS-GOP sample resulted also in higher amount of residual mass after combustion than that of the glycerol-plasticized TPS. With the partial substitution of glycerol by P-polyol for plasticizing starch 10% reduction of both pkHRR and total heat release (tHR) was observed.
Further considerable reduction of both the \( pkHRR \) and the \( tHR \) of TPS-GOP matrix were visible when biofibres were introduced. The FR-treatment of both the biofibres and fabrics resulted in higher amount of residual mass, furthermore in the case of AP-treated fabrics additional significant reduction of \( pkHRR \) and \( tHR \) was achieved at the same time. Considering the \( TTI \) values, the multilayered composites act similarly to the unreinforced matrices, while in the case of the TPS samples filled with AP-treated chopped flax fibres, the \( TTI \) increased significantly. Also the \( HRR \) and \( ML \) curves of fabric reinforced samples are wavy as the single layers get into the burning zone one by one, while the homogenously dispersed chopped fibres modify the burning behaviour, thus also the \( ML \) and \( TTI \) values, of the entire sample. Because the well dispersed short fibres can influence the burning behaviour of the embedding TPS matrix more effectively, they can also contribute to the increase of burning residue of the flax fibre reinforced samples after combustion in higher extent.

As a consequence, with the preparation of TPS composite plasticized by OP560 and reinforced by AP-treated fibres (TPS-GOP_BFabric-AP), beside the considerable increase in mechanical properties, the best UL-94 classification accompanied with LOI of 32% were achieved, furthermore \( pkHRR \) and \( tHR \) were reduced by 45% and 27%, respectively, and with 11.3% more solid residue remained after combustion when compared to conventional glycerol plasticized TPS (TPS-G).

**Table 4.13 Results combustion tests executed on biofibre Reinforced TPS composites**

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>( pkHRR ) (kW/m(^2))</th>
<th>( pkHRR_{time} ) (s)</th>
<th>Residue (mass%)</th>
<th>( tHR ) (MJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-G</td>
<td>36</td>
<td>446</td>
<td>161</td>
<td>0.8</td>
<td>84.1</td>
</tr>
<tr>
<td>TPS-GOP</td>
<td>23</td>
<td>402</td>
<td>170</td>
<td>3.3</td>
<td>76.2</td>
</tr>
<tr>
<td>TPS-GOP_BFibre</td>
<td>36</td>
<td>287</td>
<td>200</td>
<td>14.9</td>
<td>63.7</td>
</tr>
<tr>
<td>TPS-GOP_BFibre-AP</td>
<td>37</td>
<td>302</td>
<td>192</td>
<td>19.3</td>
<td>64.1</td>
</tr>
<tr>
<td>TPS-GOP_BFabric</td>
<td>26</td>
<td>314</td>
<td>187</td>
<td>7.6</td>
<td>68.4</td>
</tr>
<tr>
<td>TPS-GOP_BFabric-AP</td>
<td>22</td>
<td>242</td>
<td>174</td>
<td>12.1</td>
<td>61.4</td>
</tr>
</tbody>
</table>
Conclusions

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.

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, therefore before embedding into the matrix the biofibres were surface treated with ammonium phosphate model compound. The flame retardant treatment of flax resulted in lowered initial decomposition temperature, but with approx. 14% higher amount of residual char, as measured by TGA. The AP-treated 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%, 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.

RELATED PUBLICATIONS: [II, V, IX, XVII, XIX, XXVII]
4.3.2 FLAME RETARDANCY OF POLYLACTIC ACID BASED COMPOSITES WITH MULTIFUNCTIONAL ADDITIVE SYSTEM

Rationale and aims

Among biopolymers, polylactic acid (PLA) is one of the most promising candidates for wide-range future applications due to its multiple benefits, such as biodegradability, prominent mechanical performance and comparable processing properties to commonly used thermoplastics [73]. However, the most severe limitation of the replacement of common polymers by PLA in greater amounts is its noticeably higher cost. For this reason PLA is often blended with cheaper biopolymers or biofillers. According to the paper published by Huneault and Li, blending of PLA with thermoplastic starch (TPS) not only reduces the overall cost of the final product, but it also results in decrease of the inherent brittleness and rigidity of PLA as well as in improvement of the material ductility [61]. Furthermore, as revealed by Reti et al., starch can effectively contribute to the flame retardant action of an intumescent additive system acting as a biobased charring agent [67]. Several lignocellulosic fibres (jute, flax, sisal etc.) are also used in PLA to ensure better properties, such as enhanced biodegradability, lower density, higher strength and modulus, at lower cost and without compromising biodegradability [56,219].

The flame retardancy of biopolymers is of great importance when applications in electronics, construction and transportation are considered. To achieve the desired levels of flame retardancy is, however, quite challenging in the case of the most promising raw material, PLA, due to its easy flammability and intensive dripping during burning [156,164,220]. Although a few options were already proposed to form flame retarded PLA [67,158,221], these methods, applying mostly a high load of expensive flame retardants in the expensive matrix, may not be implementable for industrial use. Consequently, the need for the elaboration of new cost-effective approaches for flame retardancy of biopolymers is very urgent.

In this work, our hypothesis was that the flammability of PLA can be cost-effectively reduced by applying multifunctional active ingredients, which, besides their essential functions (such as reinforcement, filler, plasticizer, compatibilizer, stabilizer, pigment, coating, etc.), display also flame retardant activity. Hence, in this chapter two innovative approaches were studied aiming at the production of a PLA-based biocomposite of reduced flammability and adequate mechanical performance in an economical way:

- replacement of glycerol, the most commonly used plasticizer of starch, by glycerol phosphate (GP) possessing flame retardant effect, and
- elaboration of a novel one-step reactive flame-retardant treatment for natural fibres, which can provide considerable flame retardant activity to the cheap cellulosic reinforcements used in PLA/TPS biopolymer blends.
Our strategy relating to the use of a P-containing plasticizer in TPS relied on our recent study on a commercial P-containing polyol (OP560) applied successfully in TPS both as plasticizer and as flame retardant agent, as reported in Section 4.3.1.

It is quite common to render cellulosic fibres or fabrics flame retardant by using P-containing compounds, such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), monoammonium phosphate (MAP) and diammonium phosphate (DAP) [130,140,141,142]. The non-toxic phosphorus-based compounds can effectively initiate the charring of fibres [140], however, due to the application of these treatments the initial decomposition temperature of natural fibres significantly decreases (even by 90°C) [145]. The reduced thermal stability 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 140°C (such as PP, PA, PET and also PLA) are considered. It is well known from the literature that the surface treatment with different silanes can result in increased thermal stability of cellulosic fibres [150,222].

Therefore, the application of a combined treatment, by utilizing P and Si synergism, was selected in this work for the flame retardant modification of reinforcing natural fibres. Then, the effects of the flame retardant plasticizer and the flame-retardant-treated flax fibres on the thermal, flammability and mechanical properties of the obtained biocomposites were investigated.

### 4.3.2.1 SYNTHESIS OF GLYCEROL-PHOSPHATES AND THEIR APPLICATION AS FLAME RETARDING EFFECT PLASTICIZER IN STARCH

*Synthesis and structure elucidation of glycerol-phosphates*

As atomic efficiency (AE), the conversion efficiency of a chemical process, is one of the most important criteria of green chemistry [223], glycerol phosphate was synthesized through the green, addition-type reaction between glycerol and phosphorus pentoxide (see in Figure 4.37).

The anhydrous glycerol (92.1 g, 1 mol) was cooled to 0°C in an ice bath under continuous mechanical stirring at 200 rpm. Phosphorus pentoxide (23.66 g, 0.166 mol, glycerol to P-atom ratio: 3:1) was added in 2-g fractions to the cold glycerol under more intense stirring (500 rpm). After each feeding step, temperature of the reaction mixture increased to 10–15 °C, therefore it had to be cooled back to 0°C before the next step. After the addition of the last portion of P2O5, the reaction mixture was allowed to warm up to room temperature and then the mixture was stirred for 24 h to ensure complete conversion. For neutralizing the formed acidic P-bonded hydroxyl groups, ammonia gas has been passed through the reaction mixture until the increase of the pH stopped at pH 4.5.
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 4.38. 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 2 h reaction; however, overnight intense stirring was necessary to ensure complete conversion.

The synthesized glycerol phosphate structures were identified by \(^{31}\)P NMR and MS measurements. According to the MS and NMR results, mainly diglycerol phosphate was formed during the reaction (MS positive ionization: 247 m/z; \(\delta\): –0.09 ppm, molar ratio reference: 1). Monoglycerol phosphate (MS positive ionization: 173 m/z; \(\delta\): 0.19 ppm) and phosphoric acid (MS positive ionization: 99 m/z; \(\delta\): 0.14 ppm) were formed in quasi-equal amounts, with molar ratios (relative to diglycerol phosphate) of 0.5. Triglycerol phosphate (MS positive ionization: 321 m/z; \(\delta\): -0.54 ppm) was also present in the product, with a relative molar ratio of 0.2. Some other minor by-products, with an overall relative molar ratio of 0.3, were also identified using the MS spectra, i.e. a product formed by the condensation of mono- and diglycerol phosphate (MS: 401 m/z) as well as pyrophosphoric acid (MS: 179 m/z).
Application of glycerol-phosphates as plasticizer with flame retarding effect

Corn starch of 19% amylose content was plasticized in the one case with 25 wt% commercial glycerol and in the other case by combining glycerol (12.5 wt%) with the newly synthesized glycerol-phosphate-based plasticizer (GP) (12.5 wt%) to obtain a reference common thermoplastic starch (TPS) and a flame retardant thermoplastic starch (TPS-GP) batch, respectively. In both cases, the starch and the plasticizer were mixed together in a mortar at least one day before processing. The two types of thermoplastic starch batches have been processed in a Brabender Plasti Corder PL 2000 type internal mixer at 135°C with addition of 0.6 wt% stearic acid and with a rotor speed of 60 rpm, until a decreased, close-to-constant torque demand was measured during mixing.

Glycerol phosphate was synthesized with an aim to study a multifunctional model plasticizer that can also display flame retardant activity in the polymer matrix. At first, the plasticizing effect exerted by the prepared glycerol phosphate on starch was investigated by continuous recording of the torque during mixing. The torque curves recorded for plasticization of starch with glycerol-phosphate (TPS-GP) and with pure glycerol (TPS) as a reference are compared in Figure 4.39. The sharp peak of torque demand indicates the stage when starch molecules start getting released from their granule structure followed by gelation [208]. As expected, the smaller molecule (glycerol) could penetrate the starch chains more easily [209] consequently the gelation began already after 60 ± 15 s of mixing. In the case of the glycerol phosphate this phenomenon was shifted in time and appeared only after 220 ± 20 s of processing. Typically 15% greater torque was needed for glycerol phosphate to decrease the number of hydrogen bonds between the polymer chains; however, the equilibrium torque for processing the TPS-GP batch was found to be about half of that measured for the conventional glycerol plasticized TPS. This decrease in viscosity can be explained by the increased molecular space and mobility of starch chains when glycerol-phosphate is incorporated. Similar plasticizing behaviour was observed previously, when a longer-chain phosphorus-containing polyol (Exolit OP560) was studied as a flame retardant plasticizer in starch (see in section 4.3.1).
The two types of plasticized starch blends (TPS and TPS-GP) were compared by TGA measurement. The analysis provided evidence for the significant char-promoting effect of the synthesized glycerol-phosphate-based plasticizer. It is shown in Figure 4.40 that the onset temperature of starch decomposition was shifted from 253 °C (TPS reference) to 200 °C in the case of the TPS-GP indicating the acid (of GP origin) induced dehydration and decomposition of starch. This is accompanied by a decreased amount of volatile combustive products and consequently increased char yield. The charred residue at 400 °C was 16.5% higher when TPS-GP sample was measured than in the case of the TPS reference.
The flammability characteristics of the prepared thermoplastic starch blends were studied by UL-94, LOI and mass loss calorimetric methods. The UL94 ratings, the LOI values and the total heat released (tHR) data for the two types of TPS are compared in Table 4.14. The use of glycerol phosphate plasticizer resulted in significant improvement of flame retardancy. The approximately 1 wt% of P introduced through the plasticizer into the TPS-GP resulted in V-1 rating, high LOI value and 44% reduction of the tHR.

### Table 4.14 Comparison of the flammability characteristics of TPS and TPS-GP

<table>
<thead>
<tr>
<th></th>
<th>UL-94 classification</th>
<th>LOI [vol%]</th>
<th>tHR [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS</td>
<td>HB</td>
<td>22</td>
<td>119</td>
</tr>
<tr>
<td>TPS-GP</td>
<td>V-1</td>
<td>34</td>
<td>67</td>
</tr>
</tbody>
</table>

4.3.2.2 Synthesis of a new phosphorous silane and its application as reactive treating agent for flax fibres

**Synthesis and corresponding analysis of PSil**

A novel reactive modifying agent for cellulose-based biofibres 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, Figure 4.41) was obtained after stirring of 5 ml of OP560 with 11.9 ml of TESPI vigorously at 90°C for 4 h under anhydrous conditions. The completion of the reaction was confirmed by FTIR spectrometry. As shown in Figure 4.42, the significant reduction of the intensities of both the OH groups of OP560 (at 3380 cm⁻¹) and the NCO groups of TESPI (at 2283 cm⁻¹) revealed that the reaction between the two components had taken place. Accordingly, signals indicating the formation of the PSil adduct appeared at 3334 cm⁻¹ (stretching vibration of the N-H bond), at 1534 cm⁻¹ (assigned to the C–N stretching and N–H bending vibrations), and also at 1721 cm⁻¹ (the characteristic peak for C=O stretching of carbamate linkage).

![Figure 4.41 Synthesis of the reactive phosphorous surface modifier (PSil)](image-url)
The successful linkage, associated with the consumption of the isocyanate group and creation of a linker carbamate group (see reaction in Figure 4.41), was also confirmed by NMR spectrometry.

**Application of PSil as flame retarding effect surface treating agent for flax fibres**

Flax fibres were treated with the new flame retardant according to the following procedure: at first, 8 g of dried fibres was stirred in 320 ml of absolute toluene for 20 minutes, and then 16 ml of PSil was added dropwise to the suspension. This toluenic mixture was refluxed at 111°C for 8 h. The flax fibres were then filtered and washed with pure toluene in order to remove PSil excess. The obtained fibres were heated in an oven at 130°C for 8 h in order to promote the hydrolysis of the alkoxy (triethoxysilane) groups of PSil to silanol moieties. The latter then would subsequently form new covalent bonds with the hydroxyl groups of the cellulosic fibres (Figure 4.43) [222].
Figure 4.43 Interaction of PSil with flax fibres through hydrolytic process

After the described procedure, an average 35% weight increase of the flax fibre indicated the immobilization of a noticeable amount of the modifier on the surface of the biofibres. Thus, approximately 2 wt% P content was introduced to the flax fibres through the PSil-treatment (a higher concentration would have caused adherence of fibres to each other and limited their dispersibility). The presence of PSil on the surface of flax fibres was also confirmed by SEM (Figure 4.44). It was observed that the modifier covered the surface of the fibres in a relatively thick but smooth layer.
The chemical reaction between PSiI and flax was also confirmed by comparing the FTIR spectra of the neat and PSiI-treated flax fibres, as presented in Figure 4.45. The characteristic peaks of PSiI are easily observable in the spectrum of the PSiI-treated flax fibres, such as the intensive bands at 1721 cm\(^{-1}\) and 1534 cm\(^{-1}\) corresponding to the carbamate linkage between the two starting components (TESPI and P-polyol) and the presence of other characteristic peaks assigned to P=O bonds (at 1250 cm\(^{-1}\)), and to C–H stretching of the additional CH\(_2\) groups (at 2974 cm\(^{-1}\)). The band around 790 cm\(^{-1}\) can be assigned to the overlap of P–O–C and Si–C stretching vibrations. It can be seen in the spectra that the intensity of the broad peak around 3380 cm\(^{-1}\), corresponding to the free OH groups of cellulose, has decreased as the result of the treatment. In the case of the spectrum of PSiI-treated flax fibres, the sharp peaks between 1000 and 1200 cm\(^{-1}\) are assigned to the Si–O–C and –Si–O–Si– bonds. The Si–O–C band confirm the chemical linkage between the hydrolysed silane and the hydroxyl groups of cellulose [224,225], and the chemisorption of the modifier onto the fibre surface by stable covalent bonds. The band at 708 cm\(^{-1}\) is also assigned to the –Si–O–Si– symmetric stretching vibrations and indicates that polysiloxanes were formed and deposited on the treated fibres, which explains the measured considerable weight increase as well as the SEM observations.
In Figure 4.46, the TG and DTG curves of neat flax fibres are compared with those of conventional diammonium-phosphate (DAP)-treated and the PSil-treated fibres prepared in the present work. For comparison, the DAP-treatment of flax fibres was carried out according to the termotex procedure [212]. At first, the flax fibres were heated to 120°C which temperature was maintained for 2 h, followed by a 5-minutes-immersion into a cold 5 wt% DAP solution. The ratio of fibre to solution was 1 g/10 ml. The fibres were then separated by centrifuging and dried at 80°C for 4 h. The amount of the absorbed phosphorus (P) was determined as 1.75 wt% of P, calculated from the mass increase.

As expected based on the literature [145], the thermal decomposition began at a significantly lower temperature in the case of the DAP-treated fibres and accordingly, the peak temperature of the corresponding DTG curve, indicating the maximum weight loss rate, was 89°C lower than that of the untreated flax fibres. On the contrary, PSil, synthesized by coupling a P-polyol with a silane, did not degrade earlier than the cellulosic substrate; the initial temperature of thermal degradation of neat and PSil-treated fibres was about the same. The maximal rate of degradation of PSil-treated fibres occurred at a slightly (~23°C) lower temperature; however, its rate (7.6%/°C) decreased notably compared to the case of untreated flax fibres (12.8%/°C). Considering the residual masses obtained after heating the flax fibres up to 500°C, it can be noticed that the highest amount (47%) of residual char belonged to the PSil-treated fibres. These observations can be attributed to the well-known synergistic effect of P and Si atoms [226,227]. Based on the observed significant char promoting effect of PSil, advantageous influence was expected on the flame retardant properties of PSil-treated fibres and their composites as well.
4.3.2.3  **FLAX FIBRE REINFORCED POLYLACTIC ACID COMPOSITE FLAME RETARDED WITH MULTIFUNCTIONAL ADDITIVE SYSTEM**

**Sample preparation**

PLA/TPS biopolymer blends were prepared with 80% PLA and 20% TPS contents. Ingeo™ Biopolymer 3052D type PLA was used. The biopolymer blends were prepared in the same internal mixer as the plasticized starch, heated to 160°C. TPS was added once PLA was molten. After 5 minutes of homogenization at a rate of 50 rpm, 25 wt% chopped flax fibres were added to the blends. The fibres were 2–3 mm long with diameters ranging from 20 μm to 60 μm. In the case of the samples marked as “flax_PSil”, the flax fibres were flame retardant-treated with a newly synthesized phosphorous-silane (PSil), prior to their addition to the blend. The obtained compositions of the prepared biocomposites are summarized in Table 4.15. In the case of one sample (PLA/TPS-GP/flax-PSil+APP), 10 wt% ammonium polyphosphate (APP, Exolit AP 422) was also introduced into the biocomposite as additional flame retardant agent.

The specimens for mechanical and flammability tests were manufactured from 4 mm thick plates prepared by hot pressing of the blends in a Collin P200E type laboratory hot press set to 160°C.
Results and discussion

Several advantages of blending of PLA with TPS have already been described, such as reduced cost, decreased rigidity and brittleness, as well as improved ductility [61], moreover TPS can serve as an effective charring agent during combustion [67]. In this work, seven types of PLA/TPS biocomposites were prepared, for all the samples the PLA to TPS ratio was kept constant at 4 to 1. PLA/TPS blends were prepared either with or without flame retarded plasticizer (glycerol phosphate, GP). The obtained two types of PLA/TPS blends were reinforced either with untreated or with treated flax fibres (see Table 4.15). Thus, one of the obtained biocomposites contained flame retardant agents both in the matrix material (in the form of GP based plasticizer) and on the surface of the reinforcing biofibres (i.e. the newly synthesized phosphorous-silane, PSil). Additional 10 wt% APP was introduced in the case of the sample marked with the code PLA/TPS-GP/flax-PSil+APP. The manufactured flame retarded biocomposites were then evaluated in terms of their flammability and mechanical properties.

The UL-94 classifications and the LOI values measured for the manufactured biocomposites, flame retarded through different ways, are summarized in Table 4.16. It can be seen that the best (V-O) rating according to the UL-94 standard was achieved only when additional APP was applied. This is not surprising considering that the P content introduced through the GP plasticizer adds up only to approximately 0.15 wt%, while that through the PSil treatment of the flax fibres only to about 0.5 wt% of P in respect of the total mass of the composite, which is certainly not sufficient to achieve higher levels of flame retardancy. However, when the LOI values of the biocomposites are compared, the effect of each approach of flame retardancy (FR plasticizer, FR fibre treatment and FR additive) can be evaluated one by one. The blending of PLA with glycerol phosphate plasticized starch (TPS-GP) resulted by itself in a 2 vol% higher LOI (23 vol%) than that measured for the conventional PLA/TPS blend (LOI = 21 vol%). Due to the embedding of neat flax fibres in the biopolymer blends, even when a P-containing plasticizer was applied, the flammability of the obtained composites increased noticeably, and thus the measured LOI values decreased to 20 and 21 vol%, respectively. The observed candlewick effect [123,125,131] of flax fibres was effectively counterbalanced by their flame retardant treatment with PSil prior to embedding, thus the corresponding LOI...
values increased by 3 vol% both in the presence or without FR plasticizer. The addition of only 10 wt% of APP to the thus obtained biocomposites resulted in a notable increase in LOI, and ensured self-extinguishing behaviour at ambient conditions (UL-94 test), which demonstrate the prominent charring capability of both starch and cellulosic fibres. This is a new example that in the presence of sufficient P atoms, biomaterials, which are rich in hydroxyl groups, can serve as adequate charring agents [67] in intumescent flame retardant systems. Moreover, their application is environmentally preferable, especially when flame retardancy of biopolymers is targeted.

Table 4.16 UL94 classification and LOI values measured for PLA/TPS based composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>UL-94 classification</th>
<th>LOI [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/TPS</td>
<td>HB</td>
<td>21</td>
</tr>
<tr>
<td>PLA/TPS-GP</td>
<td>HB</td>
<td>23</td>
</tr>
<tr>
<td>PLA/TPS/flax</td>
<td>HB</td>
<td>20</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax</td>
<td>HB</td>
<td>21</td>
</tr>
<tr>
<td>PLA/TPS/flax-PSil</td>
<td>HB</td>
<td>23</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil+APP</td>
<td>V-0</td>
<td>33</td>
</tr>
</tbody>
</table>

The flame retardant properties of the manufactured biocomposites were also characterized and compared under a cone heater applying 50 kW/m² heat flux. The obtained heat release rate (HRR) curves are presented in Figure 4.47. Additional experimental results are shown in Table 4.17. It can be seen that the application of GP as plasticizer of PLA/TPS blend by itself moderates the peak of heat release rate (pkHRR) by 20%. The embedding of flax fibres resulted in the change of shape of the HRR curves (plain running and prolonged HRR data were recorded compared to the sharp pkHRR characteristic for the unreinforced matrix materials). Both the use of GP plasticizer and the flame retardant treatment of the flax fibres slightly shortened the times to ignition (TTI) of the biocomposites, but resulted in a noticeable decrease in the measured HRR and tHR values. Indeed, in the case of their combination (PLA/TPS-GP/flax-PSil), pkHRR decreased by 30% and tHR by 17% compared to the FR-free composite, which is referred to as PLA/TPS/flax. The TPS content of the biopolymer blend certainly contributed to the charring capability of the manufactured composites. When further reduction of flammability is required, the addition of 10 wt% APP to the system (PLA/TPS-GP/flax-PSil+APP) provides prominent fire retardancy to the composite. HRRs lower than 150 kW/m², by 40% reduced tHR (compared to PLA/TPS/flax) and charred residue as much as 24% were obtained in this case (Table 4.17). It should be noted that owing to the presence of the beneficial multifunctional agents (plasticizer, surface treating agent) applied, the total amount of FR additives needed in this case (10 wt% APP) is significantly lower than applied commonly in similar PLA based systems [158,159,160,221].
Table 4.17 Experimental results of the mass loss calorimetric tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI [s]</th>
<th>pkHRR [kW/m²]</th>
<th>THR [MJ/m²]</th>
<th>residual mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/TPS</td>
<td>33</td>
<td>774</td>
<td>105.4</td>
<td>0</td>
</tr>
<tr>
<td>PLA/TPS-GP</td>
<td>29</td>
<td>623</td>
<td>100.0</td>
<td>4</td>
</tr>
<tr>
<td>PLA/TPS/flax</td>
<td>34</td>
<td>410</td>
<td>98.1</td>
<td>5</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax</td>
<td>28</td>
<td>270</td>
<td>90.3</td>
<td>6</td>
</tr>
<tr>
<td>PLA/TPS/flax-PSil</td>
<td>29</td>
<td>310</td>
<td>91.0</td>
<td>9</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil</td>
<td>29</td>
<td>285</td>
<td>81.0</td>
<td>10</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil+APP</td>
<td>34</td>
<td>149</td>
<td>57.5</td>
<td>24</td>
</tr>
</tbody>
</table>

The mechanical performance of the manufactured flame retardant biocomposites was characterized by static tensile- and bending tests. The measured strength and modulus values are compared in Figure 4.48, while the elongations measured at break during tensile tests are presented in Table 4.18. The blending of PLA with GP-plasticized starch (PLA/TPS-GP) resulted in noticeably better tensile and flexural properties than those of the reference PLA/TPS blend. The strain to failure of 2.63% measured for the GP-containing blend was also noticeably greater than the elongation measured for the reference blend (Table 4.18). These results can be (at least partially) attributed to the decreased viscosity of TPS-GP, which improved the dispersion between the two, originally immiscible biopolymers as shown in the SEM images of Figure 4.49. As a consequence, the mechanical performance of the obtained flame retarded blend (PLA/TPS-GP) mostly surpasses those of the PLA/TPS blends of similar compositions reported in the literature [81,83,228].

The addition of 25 wt% neat flax fibres increased the flexural strength (shown in Figure 4.48 b) and stiffness (see in Figure 4.48 c and d) of the biopolymer blends, however it caused significant (30%) reduction of the tensile strength and a considerable decrease in the
elongation at break (Table 4.18) of the PLA/TPS-GP blend, indicating that the presence of GP had reduced the compatibility between the cellulosic fibres and the embedding biopolymer matrix. Similar conclusions were drawn when P-containing species were used on the surface of the flax fibres embedded into the reference PLA/TPS matrix (without GP). All the studied mechanical characteristics of the latter prepared composite (PLA/TPS/flax_PSil) deteriorated due to the PSil treatment of flax fibres, compared to the composite reinforced with untreated flax fibres (PLA/TPS/flax). However, when P-containing species were applied in both phases, i.e. both in the matrix and on the surface of reinforcing fibres (PLA/TPS_GP/flax_PSil), increase of both the tensile- and flexural strength was observed (see Figure 4.48 a and b), as well as increased elongation at break (Table 4.18). Aiming at even better flame retardant properties, APP was added to the system, which, as expected, decreased the tensile strength, but increased the stiffness. The mechanical performance of this effectively flame retarded composite can still outperform their current counterparts [229].

Figure 4.48 (a) Tensile strength, (b) flexural strength, (c) tensile modulus and (d) flexural modulus of the flax fibre reinforced PLA/TPS biocomposites
Table 4.18 Elongation at break measured for the flax fibre reinforced PLA/TPS biocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/TPS</td>
<td>2.05 ± 0.14</td>
</tr>
<tr>
<td>PLA/TPS-GP</td>
<td>2.63 ± 0.08</td>
</tr>
<tr>
<td>PLA/TPS/flax</td>
<td>1.25 ± 0.06</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax</td>
<td>1.10 ± 0.10</td>
</tr>
<tr>
<td>PLA/TPS/flax-PSil</td>
<td>1.44 ± 0.04</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil</td>
<td>1.89 ± 0.08</td>
</tr>
<tr>
<td>PLA/TPS-GP/flax-PSil+APP</td>
<td>1.32 ± 0.08</td>
</tr>
</tbody>
</table>

Figure 4.49 SEM images of (a) PLA/TPS and (b) PLA/TPS-GP blends

Conclusions

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. 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.
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.

*RELATED PUBLICATIONS:* [IV, XI, XIII, XXXII].
4.4 DEVELOPMENT OF RECYCLABLE AND BIODEGRADABLE ALL-POLYLACTIC ACID COMPOSITES IN FLAME RETARDED FORM

Rationale and aims

Polylactic acid (PLA), being made from renewable resources, is one of the most extensively researched thermoplastic biopolymers. Thanks to its numerous advantageous properties, such as biodegradability, high degree of transparency, good strength and easy processability, PLA has significant potential to replace the conventional petrol-based thermoplastics in a wide range of applications.

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 [230,231] needs to be significantly improved in order to render PLA or its composites resistant to dynamic or impact stresses as well. Many studies have been conducted to overcome the brittleness of PLA by several approaches, such as chemical modification [76], blending with tougher resins or plasticizers [77,78], preparation of multi-layered film structures [232], fibre reinforcement [86,92] and use of woven structures [93,233]. However, these modifications generally affect the strength, stiffness, or degradability of PLA.

Self-reinforcement is a possible way to provide high impact resistance to polymers without compromising their inherent advantageous characteristics [13] or recyclability, still, this approach has not been employed to the brittle PLA substrate yet. Node et al. proposed the textile insert moulding technique, whereby PLA fabrics were attached to the surface of PLA resin by injection-compression moulding, and in the case of double textile insert mouldings recorded up to 400% improvement in impact resistance compared to the neat PLA resin [44]. For this method, however, both the (surface) position of the load bearing fabrics and the achievable maximum reinforcement content are limited, which encumbers the further enhancement of the impact resistance by this way. Although a few studies have already been published on the preparation of self-reinforced PLA composites (PLA-SRCs) by other techniques (such as compression moulding (film-stacking) [9,39,234] and hot compaction [43]), by which higher reinforcement contents are also achievable, the impact resistance of these all-PLA composite sheets have not yet been investigated.

Nevertheless, PLA is an easily flammable polymer, its heavy dripping implies increased fire danger during its burning [164,220]. Therefore, the flame retardancy of PLA based composites is indispensable when applications in electronics, transportation or construction are targeted. In our previous works, self-reinforced polypropylene composites (PP-SRCs) were successfully flame retarded by applying intumescent flame retardant (IFR) additive system in the matrix films of multi-layered composite plates manufactured by film-stacking method (see in sections 4.2.1). The effectively flame retarded PP-SRCs proved to have competitive mechanical performance with their additive-free reference composites even
when prepared from secondary raw materials (see in Section 4.2.2). Based on these encouraging experiences, the preparation of PLA-SRCs in flame retarded form was also targeted in this work to provide increased fire safety to the manufactured all-PLA sheets.

According to Bourbigot and Fontaine the best flame retardancy performance can be provided through intumescence [156], however, the melt dripping is often still an issue. As for a solution, Li et al. reported the anti-dripping effect of montmorillonite (MMT) clays in PLA when combined with IFR system [162].

In this study, the preparation of recyclable and biodegradable all-PLA composites of high-impact-strength was the aim. Film-stacking and subsequent hot pressing of fully amorphous PLA films and cross-plied reinforcing layers (composed of highly crystalline PLA multifilament yarns) was the selected method. The PLA-SRCs were flame retarded by incorporating IFR additive system in combination with MMT clays into the matrix films. The effect of the used FR additives was comprehensively studied on the morphology, flammability characteristics, and on the static- and dynamic mechanical properties of the manufactured PLA-SRCs.

Composite preparation

Reference and flame retarded PLA-SRCs were manufactured by the film-stacking of cross-plied reinforcing PLA fibre layers with neat and FR additive containing matrix films, respectively.

For the reference (FR additive-free) composites, 65 ± 5 μm thick matrix films were produced from the amorphous PLA granules (Ingeo™ 6302D) by film extrusion technique using a Labtech LCR 300 laboratory flat film at a winding speed of 13 1/min. The temperature profile from feed zone to die of the extruder was 195, 195, 200, 200 and 200°C, while that of the coat-hanger die was 210, 205 and 210°C. In order to determine the processing temperature window for preparing self-reinforced composites, the obtained PLA film and the PLA multifilament yarn were examined by differential scanning calorimetry (DSC). The measured thermograms, taken from the first heating cycle, are compared in Figure 4.50. As the matrix film proved to be fully amorphous (Tg ~ 62°C) even after processing, it was concluded that, below the initial melting temperature of the crystalline phase of the reinforcing PLA yarn (152°C), the composite processing temperature need to be determined principally with respect to the temperature dependent viscosity (fluidity) of the matrix material. The melt flow rate (MFI) values of PLA granules measured at 130, 140, 150 and 160°C, respectively, are presented in Table 4.19. Accordingly, the processing temperature of 140°C was selected for composite preparation. (Higher temperatures can result in (partial) melting of the reinforcing PLA yarns and thus in decreased mechanical performance of PLA-SRCs.)
Table 4.19 MFI values as a function of temperature measured for Ingeo 6302D type PLA

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>MFI [g/10 min] (2.16 kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>2.57 ± 0.06</td>
</tr>
<tr>
<td>150</td>
<td>1.38 ± 0.02</td>
</tr>
<tr>
<td>140</td>
<td>0.73 ± 0.02</td>
</tr>
<tr>
<td>130</td>
<td>~0 (not measurable)</td>
</tr>
</tbody>
</table>

11 plies of 65 ± 5 μm thick matrix films and 10 PLA filament layers were laminated onto a 6 mm thick aluminium core (300 x 300 mm) in a filament winding process to obtain cross-ply configuration, as shown in Figure 4.51. The filament-wound, laminated packages were consolidated by compression moulding in a laboratory hot press. The processing conditions such as temperature, pressure and time were optimized in terms of morphological and tensile mechanical properties; accordingly the following steps were found to be optimal; at first the packages were held for 180 s between the preheated press plates set to 140°C, then compressed for 180 s under a pressure of 1.8 MPa and finally cooled to 45°C under pressure. 2.20 ± 0.15 mm thick SR-PLA composite sheets with a nominal reinforcement of 53.5 ± 1.5 wt% were manufactured.
Flame retarded, self-reinforced PLA composites were manufactured by the film-stacking of cross-plied reinforcing PLA fibre layers with flame retardant additive containing matrix films. The flame retardant composition of the matrix films was determined based on preliminary experiments executed on PLA mixtures of different flame retardant compositions. Favourable performance/load balance was found in the case of combined application of APP (Exolit AP462) and MMT in a weight ratio of 10 to 1, thus this formulation was selected for preparation of flame retarded films. As the weight percentage of the matrix films adds up 46.5 ± 1.5 wt% considering the total weight of the self-reinforced composites, approximately double portion of flame retardant additives needed to be incorporated in the matrix films to ensure adequate flame retardancy to the SR composites.

In the case of the FR containing films, in order to ensure adequate dispersion, APP and MMT were compounded with the PLA granules using a Labtech Scientific LTE 26-44 modular twin screw extruder (the temperature profile from feed zone to die was 185, 190, 195, 195, 200, and 205°C) and then granulated prior film extrusion. Matrix films were extruded with two loading levels of FRs, 33 wt% (i.e. 30 wt% APP + 3 wt% MMT) and 22 wt% (i.e. 20 wt% APP + 2 wt% MMT), respectively (the temperature profile from feed zone to die of the extruder was 175, 185, 190, 200 and 195°C, while that of the coat-hanger die was 205, 210 and 180°C). Accordingly, the FR contents of the manufactured flame retarded composites (PLA-SRC_FR10 and PLA-SRC_FR16), calculated by the actually measured fibre contents, added up 9.9 wt% (~10 wt%) and 15.8 wt% (~16 wt%), respectively. The codes and composition of the prepared composite sheets are summarized in Table 4.20.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Reinforcement content [wt%]</th>
<th>FR content of the matrix films [wt%]</th>
<th>MFI of the matrix films (140°C/2.16kg) [g/10 min]</th>
<th>Overall FR content of the composite [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-SRC</td>
<td>54</td>
<td>0</td>
<td>0.73 ± 0.02</td>
<td>0</td>
</tr>
<tr>
<td>PLA-SRC_FR10</td>
<td>55</td>
<td>22.0</td>
<td>2.81 ± 0.22</td>
<td>9.9 (~10)</td>
</tr>
<tr>
<td>PLA-SRC_FR16</td>
<td>52</td>
<td>33.0</td>
<td>5.52 ± 0.64</td>
<td>15.8 (~16)</td>
</tr>
</tbody>
</table>
Results and discussion

The morphology of the consolidated PLA-SRCs was investigated by optical microscopy. Images of the cross sections of the multilayer composites are shown in Figure 4.52. Apparently, all the composites are well consolidated. This was also confirmed by density measurements; accordingly, the density of all the prepared PLA-SRCs is above 93% of the theoretical maximum, indicating that the optimized processing parameters are adequate to obtain well-consolidated self-reinforced PLA composites.

![Figure 4.52 Optical microscopic images of the polished cross-sections of the developed PLA-SRCs](image)

The flammability characteristics of the manufactured PLA-SRCs were examined by UL-94 tests, LOI measurements and mass loss calorimetric analyses. The obtained flammability test results are summarized in Table 4.21. The dripping of non-reinforced PLA specimens of 2 mm thickness is so intensive that no horizontal burning rates can be determined. The UL-94 rating of the FR-free PLA-SRC is HB, in horizontal position the PLA-SRC specimens burn with fairly high flame spreading rate ($v_{\text{flame}}=43.5$ mm/min) accompanied with intensive dripping until reaching the second mark. The use of FR matrix films with 22 wt% additive (APP + MMT) content proved to be sufficient to hinder the PLA-SRC’s ability to burn horizontally. Although the flaming combustion of the PLA-SRC_FR10 specimens holds only for a couple of seconds also in vertical position (UL-94V), due to some drips of flaming particles the UL-94 rating remains V-2. In contrast, the dripping is fully suppressed when matrix films with 33 wt% FR content are applied to form flame retarded PLA-SRC (PLA-SRC_FR16). Self-extinguishing behaviour can be observed after ignition both in horizontal and vertical position; the PLA-SRC_FR16 composite meets the requirements of the V-0 rating of the standard UL-94 flammability test. Furthermore, for this composite a LOI value as high as 34 vol% was measured. In the previous literature, at the same additive level (16 wt% IFR system) noticeably lower LOI values were reported [221], or in other words, to reach the LOI
value of 34 vol% in PLA matrix, higher loadings of IFR additives were needed [160]. Considering the results obtained from the cone calorimeter tests (Table 4.21), it can be seen that already 10 wt% FR content reduces the pkHRR by 45% compared to the additive-free reference composites, however, in order to achieve significant reduction of tHR and to obtain noticeable amount of charred residue after combustion, the higher, 16 wt% FR loading was needed. Shorter TTI values were measured for all the composites than for the non-reinforced PLA reference, which is the consequence of the faster volatization of the thin upper layers of the multi-layered structures compared to that of the thick bulk polymer.

Table 4.21 Flammability characteristics of PLA and the developed PLA-SRCs

<table>
<thead>
<tr>
<th>Codes</th>
<th>UL-94 [rating]</th>
<th>LOI [vol%]</th>
<th>pkHRR [kW/m²]</th>
<th>tHR [MJ/m²]</th>
<th>residue [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>no rating</td>
<td>21</td>
<td>401</td>
<td>44.4</td>
<td>0.3</td>
</tr>
<tr>
<td>PLA-SRC</td>
<td>HB</td>
<td>23</td>
<td>425</td>
<td>49.5</td>
<td>1.3</td>
</tr>
<tr>
<td>PLA-SRC_FR10</td>
<td>V-2</td>
<td>30</td>
<td>233</td>
<td>47.8</td>
<td>4.85</td>
</tr>
<tr>
<td>PLA-SRC_FR16</td>
<td>V-0</td>
<td>34</td>
<td>207</td>
<td>29.4</td>
<td>16.5</td>
</tr>
</tbody>
</table>

The tensile behaviour of the reference (non-reinforced) PLA sheet and the prepared (FR-free) PLA-SRC are compared in Figure 4.53 a. It can be seen that the stress-strain curves of the two materials are of different character: rigid failure is characteristic to PLA, while its self-reinforced composite shows ductile behaviour. The tensile yield stress (46.4 ± 1.7 MPa) of the PLA-SRC is by 23% lower than that of the unreinforced PLA sheet, but the measured value is in good agreement with the performance of other PLA-SRCs reported in the literature [9,39]. This can be explained by the cross-ply configuration of the PLA-SRC (only 50% of the yarns, i.e. about 26 wt% of the composite are involved in the load transfer) and by the fact that the reinforcing PLA fibres with a failure strain of about 45% are much more ductile than the embedding matrix. As a consequence, the fibres become detached from the matrix before reaching their maximum yield stress and deform freely. This fibre debonding from the matrix occurs when the applied stress overcomes the interfacial bond strength between the matrix and the fibre, as also found by Li and Yao in the case of all-PLA composites [9]. Considering the stress-strain curves recorded during three-point bending up to 10% deflection (Figure 4.53 b), the manufactured PLA-SRC shows better performance than the non-reinforced PLA reference; in respect to the flexural strength a characteristic 14% increase, while in respect to the flexural modulus a 6% increase was measured.
Figure 4.53 Characteristic stress-strain curves recorded during a) tensile and b) flexural test of non-reinforced PLA and PLA-SRC

The tensile and flexural strength and initial moduli of the prepared PLA-SRCs are presented in Figure 4.54. As it can be seen from the results, the tensile properties being fibre dependent are less affected by FR presence in the matrix, whereas the flexural properties being matrix dependent are lowered with FR additives. The experimental results plotted in Figure 4.54 a (Young’s modulus values of 10 specimens of each composite type) have been statistically tested, and the null hypothesis that the slope of the regression line for the Young’s modulus values of the composites of increasing FR contents is zero (H0: β1=0) has been rejected (p = 0.007), so it was concluded that there is an increase in initial tensile modulus with increasing FR addition. The decreasing yield stress values (Figure 4.54 a) measured for the flame retarded SRCs can be also connected to the increasing Young’s modulus i.e. stiffness of the embedding matrix layers as a function of their FR contents, which results in somewhat earlier slip of the ductile PLA fibres from the rigid flame retarded matrices. Nevertheless, the altogether 15% reduction of yield stress, measured for PLA-SRC_FR16 compared to the additive-free reference composite (PLA-SRC), can be considered as a fairly slight loss in mechanical performance for such an effectively flame retarded polymeric composite. The use of FRs resulted in more noticeable reduction of the flexural strength of the composites (shown in Figure 4.54 b), still at 16 wt% loading of additives the flexural strength of the manufactured self-reinforced composite (56 MPa) is comparable with that of the non-reinforced PLA sheet (60 MPa, see in Figure 4.53 b).
The observed trends in the mechanical characteristics of the prepared PLA-SRCs are supported by the visual observations of the failed specimens. Photographs taken of the composites after tensile testing are shown in Figure 4.55. In the case of the FR-free PLA-SRC significant fibre pull-out reveals that the matrix and the reinforcement broke at different strains, about 3% and 23%, respectively. Similarly, in the case of the 10 wt% FR containing composite also the matrix broke first, than the fibres were pulled out and continued to elongate until failure occurred, in this case, however, the noticeable vertical crack propagation indicates somewhat increased fibre-matrix adhesion. On the contrary, in the case of the PLA-SRC_FR16 sample the matrix and the fibres undergo about the same strain (35%) during deformation, their concurrent failure indicates strong bonding [9,235]. These observations can be explained by the balance of two competing phenomena. On the one hand, the FR particles decrease the fibre-matrix adhesion, and thus the interlaminar shear strength between them. On the other hand, the noticeably lower viscosity of the FR-containing matrix films at the composite processing temperature (see in Table 4.20) can result in better impregnation and thus in superior interfacial bonding in the case of the flame retarded PLA-SRCs. It is presumed that in the case of the 10 wt% FR containing PLA-SRC the former effect dominates, while at 16 wt% FR content, the latter one prevails.
The impact strength of the PLA-SRCs was evaluated based on IFWI tests performed on square composite specimens with thicknesses ranging from 2.05 to 2.35 mm at room temperature. Typical thickness-related fractograms are shown in Figure 4.56 a, while the corresponding thickness-related perforation energy values and ductility factors are plotted in Figure 4.56 b, respectively. Significantly increased impact resistance is expressed by the flame retarded PLA-SRCs compared to the very low impact absorption capacity (0.5±0.1 J/mm) of the inherently very brittle non-reinforced PLA (not shown in Figures). The outstanding perforation energy values of the self-reinforced PLA composites reveal prominent (more than one order of magnitude) improvement in impact resistance. The IFWI fractograms, shown in Figure 4.56 a, help the main impact damping mechanisms of the PLA-SRCs to be understood. In the case of FR-free PLA-SRC, after reaching the maximum load a great amount of energy is absorbed progressively, as also indicated by the corresponding relatively high ductility factor of about 50%. In correlation with the tensile failure behaviour, such impact fracture character can mainly be attributed to noticeable interfacial delaminations (debonding) indicating insufficient interlaminar adhesion between the layers. In contrast, as shown in Figure 4.56 a, with increasing FR contents increasing amount of energy was required to initiate fracture in the composites specimens and almost instantaneous impact failures (accompanied with decreased ductility factors) were recorded for the flame retarded PLA-SRCs. It is suggested that in these cases the fibre fracture occurs almost simultaneously with the matrix fracture, and thus the impact energy is mainly dissipated by fibre stretching, effective dispersion of impact loading and fibre rapture. The ability of PLA fibres to stretch under tension can provide substantial support to the composites during impact loading [44], and thus the increased fibre-matrix bonding obtained for the flame retarded PLA-SRCs largely contributes to the effective energy dissipation in the multi-layered composites.
The visual observation of the failed specimens fairly supports these establishments. Considering the photograph in Figure 4.57 a, noticeable crack propagation along the fibre/matrix interface (debonding) occurred during the impact failure of the reference PLA-SRC. In contrast, in the case of the PLA-SRC of 10 wt% FR content (PLA_SRC_FR10), improved consolidation quality is represented by the smaller delaminated areas and increased filament fracture surfaces, as it can be seen in Figure 4.57 b. Based on the fracture surface of the PLA-SRC_FR16 specimen (Figure 4.57 c) it can be suggested that the fibre fracture occurs almost simultaneously with the matrix fracture, and the impact energy is mainly dissipated by the fibre stretching, effective dispersion of impact loading and fibre rapture. These observations are in good agreement with the conclusions of Nodo et al. drawn for PLA textile insert mouldings of improved interfacial adhesion [44]. As a consequence of the improved consolidation state, the achieved outstanding perforation energy value of 16 J/mm renders the effectively flame retarded PLA composite (PLA_SRC_FR16) competitive with other shock-resistant polymeric composites, such as SR-PP composites [14].
In order to investigate the thermo-mechanical stability, an important applicability issue, the PLA-SRCs were examined by DMA (and compared with the performance of unreinforced PLA). The effect of temperature on the storage moduli is plotted in Figure 4.58a. The storage moduli of the PLA-SRCs were measurable until ~152°C, which is the starting temperature of crystalline melt of the reinforcing fibres. All the PLA-SRCs exhibit higher maximum storage modulus than the non-reinforced PLA reference (2940 MPa). It can be also noticed that the stiffness of PLA-SRCs consistently increased with their FR content. In the case of the PLA-SRC_FR16 composite a 27% improvement in maximum storage modulus was measured when compared to the additive-free PLA-SRC, which can also be in connection with its better consolidation quality [14]. The unusual simultaneous improvement in stiffness and impact resistance is the result of the significant difference between the physical characteristics of PLA as a bulk material and PLA fibres. While the former one is a rigid and brittle material, after drawing the obtained PLA fibres become ductile besides that their strength and stiffness also increase in the direction of orientation. Consequently, PLA fibres can act both as reinforcing and toughening agents in the embedding brittle matrix.

The PLA-SRCs showed also superior mechanical performance as a function of temperature. While above its $T_g$ (about 55°C) the storage modulus of the non-reinforced PLA decreased below 10 MPa, in the case of the effectively flame-retarded PLA-SRC (PLA-SRC_FR16) the storage modulus remained above 400 MPa even up to 110°C. Based on these results, it can be established that the thermo-mechanical stability of the manufactured PLA-SRCs, especially when flame retarded, is comparable [236] or even overcomes that of PP-SRCs [203].

The corresponding loss modulus results in the temperature range of 30 to 80°C are shown in Figure 4.58b. The peaks of loss modulus curves, i.e. the glass transition temperatures ($T_g$), of PLA-SRCs shifted to higher temperatures comparing to that of unmodified PLA. The lower $T_g$ of PLA-SRC_FR16 compared to the other composites is in connection with the decreased molecular mass of the APP containing PLA film, as also proposed based on its increased MFI value (see Table 4.20).

The increased storage moduli accompanied with decreased loss modulus values and the less ductile fracture behaviour observed during both tensile and IFWI tests all indicate enhanced fibre-matrix interaction, and thus better reinforcing efficiency imparted by the PLA fibres to FR containing matrices [237]. This increased interfacial adhesion provides elastic character and toughness for the flame retarded PLA-SRCs.
Conclusions

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. A review on inorganic polyphosphates by Kulakovskaya et al. [133] claims that APP is a nontoxic and biodegradable compound, therefore, it is supposed that the used APP based FR additive may influence but not hinder the biodegradation of the all-PLA composites.

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 lowered viscosity 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.

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.

**RELATED PUBLICATIONS:** [IV, XII, XVIII, XX, XXX, XXXIII]
5 SUMMARY

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.

Raman spectrometry is proposed as a new, non-destructive method for the quality assessment of self-reinforced polymer composites. Raman spectrometry is believed to be a suitable technique for in-line quality control during manufacturing as well as for post-mortem failure inspections. Introduction of well-controlled, high-throughput processing techniques in the manufacturing of self-reinforced composites could be a key issue to reduce the production costs and increase the competitiveness of these environmentally favoured polymer composites.

In order to widen the application field of recyclable self-reinforced polymer composites, their flame retardancy was investigated. It was found that owing to a previously unknown flame retardant mechanism, namely the synergistic interaction between highly oriented polymer fibres and intumescent flame retardant system, for self-reinforced polypropylene composites high level of flame retardancy can be achieved at significantly lower loading level than required in non-reinforced polypropylene matrix. Utilizing this phenomenon, cost-effective flame retardancy can be realised in self-reinforced polymer systems, providing market benefit to these composites.

It was shown that high-performance self-reinforced composites can be obtained by using secondary raw materials. This way, besides contributing to the upgrading recycling of secondary plastics, material costs of self-reinforced composite manufacturing can be significantly reduced.

On the example of preparation of flame retarded self-reinforced composites by injection moulding technique, an alternative, industrially relevant, production possibility was demonstrated. Multifunctional additives, having plasticizing, thermal stabilizing and/or compatibilising effect besides flame retardant action, were synthesized and applied with the aim to reduce the amount (and cost) of flame retardants required in bio-based polymer composites. Integrated approach was needed to successfully utilize the benefits of bio-based components by their innovative combination. As for an example, thermoplastic starch was used as cheap bio-based charring agent in polylactic acid, and its functionality could be further enhanced when a multifunctional phosphorus-polyol was used for plasticizing starch.
In order to support the integrated approach not only the matrices but also the reinforcing biofibres were flame retarded. A new additive was synthesized for this purpose, which made the parallel improvement of fire retardancy and thermal stability possible, which were thought to be two antagonistic requirements earlier.

In addition, the complex requirement of recyclability and fire retardancy of a biocomposite could be met by developing self-reinforced polylactic acid composites. The new method proved to be suitable to overcome two serious drawbacks, brittleness and flammability, of polylactic acid, simultaneously. Besides the indisputable environmental and safety benefits, competitive mechanical characteristics with conventional petrol-based composites, both in respect to static (tensile and flexural strength and stiffness) and dynamic mechanical properties (impact resistance and temperature dependent storage modulus), could be achieved.

Significant parts of the research work described in this PhD thesis was performed on the request of industrial partners (including the aircraft manufacturer Dassault Aviation company) thus there is a good chance for direct utilization of the results in various segments of the industry.
PUBLICATIONS

Related scientific book chapters

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

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

Development of flame retarded self-reinforced composite from automotive shredder plastic waste
Polymer Degradation and Stability 97 221-227 (2012)
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SUPPLEMENTARY APPENDIX

MECHANICAL PROPERTIES OF FLAME RETARDED INJECTION MOULDED ALL-PPCS

Dynamic mechanical analysis

Dynamic mechanical analyses were performed using a Q800 dynamic mechanical analyser (DMA, TA Instruments Inc., USA). Three-point bending mode was applied with a span length of 50 mm. The width and length of the specimens were approximately 10 mm and 60 mm (cut by water jet), respectively. The scanning range of temperature was -100°C - 70°C, and a heating rate of 5°C/min and a frequency of 1 Hz with a 0.08% deformation were selected.

Figure S1 a) Storage modulus and b) loss modulus of the injection moulded flame retarded non-reinforced and self-reinforced rPP samples

Figure S2 Tan delta of the injection moulded flame retarded non-reinforced and self-reinforced rPP samples
**Tensile test**

Static tensile tests were performed according to the EN ISO 8256 standard using a Zwick Z2020 universal testing machine (Zwick GmbH., Germany) with a crosshead speed of 5 mm/min.

![Stress-strain curves](image1.png)

**Figure S3** Comparison of the stress-strain curves of injection moulded flame retarded non-reinforced and self-reinforced rPP samples

![Tensile strength and modulus](image2.png)

**Figure S4** Comparison of the a) tensile strength and b) tensile modulus of injection moulded flame retarded non-reinforced and self-reinforced rPP samples
**Instrumented falling weight impact test**

IFWI tests were performed on Fractovis 6785 type equipment (Ceast SpA (Instron), Italy) using the following settings: maximal energy: 228.64 J; diameter of the dart: 20 mm; diameter of the support rig: 40 mm; weight of the dart: 23.62 kg and drop height: 1 m. 80 mm × 80 mm square specimens were subjected to IFWI tests.

![Figure S5 Comparison of the impact load-time curves of injection moulded flame retarded non-reinforced and self-reinforced rPP samples](image)

**Figure S5 Comparison of the impact load-time curves of injection moulded flame retarded non-reinforced and self-reinforced rPP samples**

![Figure S6 Comparison of perforation energy and ductility factor of injection moulded flame retarded non-reinforced and self-reinforced rPP samples](image)

**Figure S6 Comparison of a) perforation energy and b) ductility factor of injection moulded flame retarded non-reinforced and self-reinforced rPP samples**
Tensile impact test

Instrumented tensile impact tests were run on rectangular notched specimens of 10 x 80 mm dimensions and having standard 45° 2 mm deep notch with an instrument type Resil Impactor Junior (Ceast, Pianezza, Italy) using a 15 J hammer. The speed at impact was 3.7 m/s.

Figure S7 Comparison of the tensile impact strength (notched) of injection moulded flame retarded non-reinforced and self-reinforced rPP samples
NYILATKOZAT

Alulírott Bordácsné Bocz Katalin kijelentem, hogy ezt a doktori értekezést magam készítettem, és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelöltem.


Bordácsné Bocz Katalin

\[\text{Signature}\]