New, sustainable fire retarded (FR) biopolymer systems – research for controlled preparation and mechanistic understanding

Content

1. Aims

The main aim of the project – according to the proposal - was to develop new environmental and bio-polymer systems with flame retardant function to be applied for engineering purposes. The structural, technological and methodological findings of the research work was planned to extend to further fields.

This plan included research work on
- synthesis/preparation/modification of new bio-based polymers, additives and nano-objects,
- interface modification aiming to develop controlled/active interlayers,
- innovative monitoring and control of production processes of FR-components/systems,
- investigation of specific properties determining the processability and performance,
- mechanism of action to be identified in the cases of new flame retarded systems,
- extension of the developed principles, materials and technologies to other industries.

The project was planned to be accomplished within 4 years.

2. Introduction

The first sentence of the project proposal: “the relationship between plastics and the environment is contradictory” became a key issue during the run of the project as it has been highlighted in Ref. 33 (the reference numbers bellow follow the order of the list of publications registered in the project's record). The environment and safety is more important nowadays than ever as it appears in the social and scientific media as well. Thus the simultanaeous consideration of the safety and sustainability aspects in the development of new polymer systems, proposed in the present project, proved to be a good idea. In fact no eco-efficient marketable flame retarded biopolymer is available for the industry. Thus we decided to realize a new approach by forming lightweight, fiber-reinforced, flame retarded (FR) and/or recyclable materials applying spectroscopically controlled gentle processing technologies. For this purpose we selected renewable resources (such as glucose), biopolimers (such as PLA), natural fibers and recyclable (self)reinforcing agents. Furthermore, we decided to use the most recent methods of process analytical technology (PAT) and industry 4.0 for developing platform technologies that are adaptable even to other - such as (bio)pharmaceutical - segments of industry. Focused research was strongly needed both on thermoplastic and thermosetting polymers. The increasing interest towards these research areas required more detailed investigation of certain scientific research subjects than planned at the beginning of the project. Thus the timeframe (without additional financial support) has been extended to 5 years (with agreement of the funding office). This report summarizes only the main outcomes of the far-reaching research work performed - the flow chart of which is presented in figure 1 - focusing especially on the most recent results. The future prospects, the relevant world-congess (FRPM) - to be organized by our research group - and the main industrial users of the achieved results (DS-Smith, Proform, Polifoam, PEMÜ, Richter, MOL) are highlighted in the conclusion of this final report.

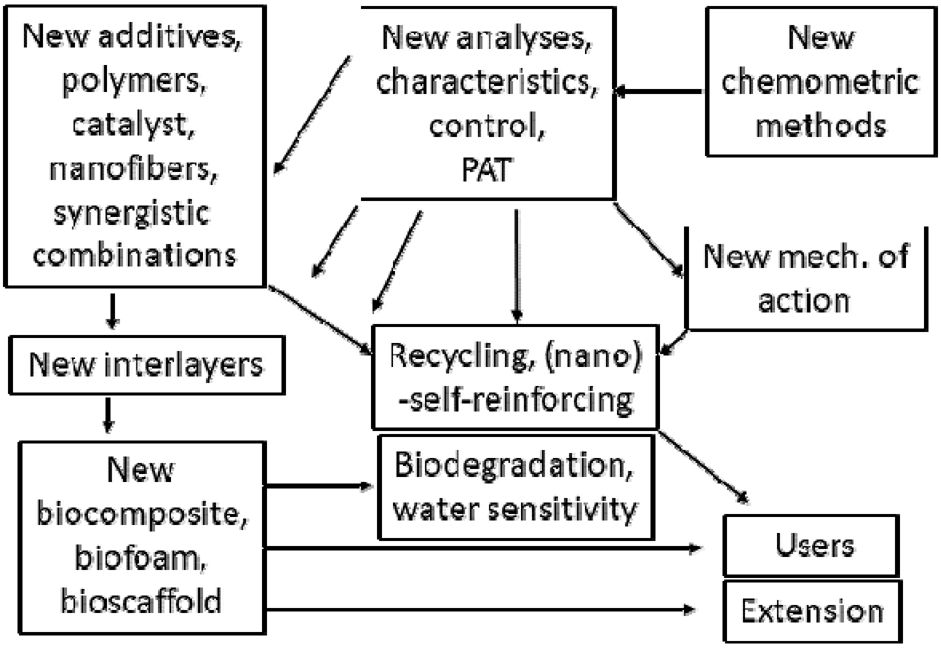


Figure 1 Flow chart of the results achieved within the project period

3. Results

3.1. Preparation of new components of FR biopolymer system

Synthesis and preparation of new components of fire-safe biopolymer systems has been performed several ways. New synthesis methods of bio-based epoxy monomers derived from d-glucose and flame-retarded precursors are described in Ref. 6 and 7. As examples, the scheme of formation of monomers can be seen in figures 2 and 3.

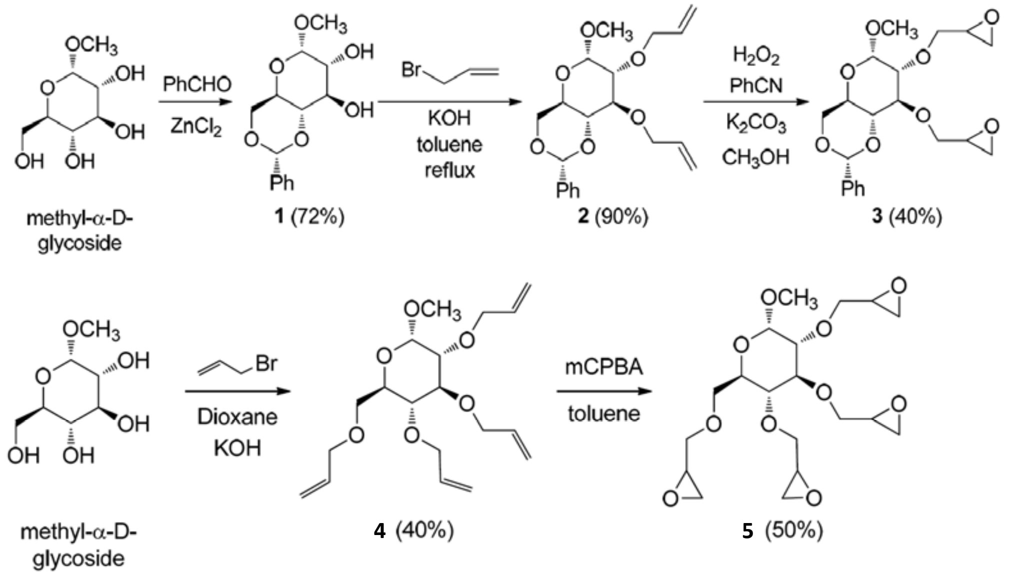


Figure 2 Synthesis of glucopyranoside-based bi- and tetrafunctional epoxy monomers

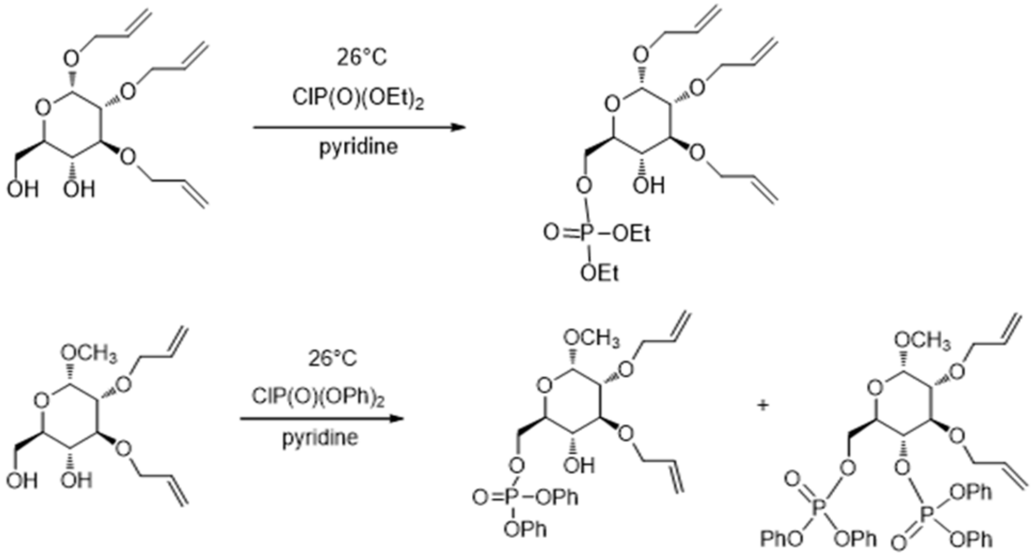


Figure 3 Synthesis of phosphorylated diallyl-glucopyranosides

Bioepoxy FR systems synthesized using selectively protected sugar-based monomers outperform the known non-flame retarded epoxy resins in respect of heat resistance, e.g. their

T_g is outstanding, allowing their application in aerospace industry according to the results in Ref. 24. Important reactions are the amine formation of monomers in order to enable their reactive and FR function (e.g. as epoxy crosslinker). After transforming methyl 4,6-O-isopropylidene-D-glucoopyranoside to dinitrile derivative a subsequent reduction allows the diamine formation. Catalysis of enamine reactions under pseudo-homogeneous circumstances using an immobilised organocatalyst, developed in an international cooperation, confirmed the recyclability of the new catalyst, as described in Ref. 21.

Parallel to the synthetic activities, development work on the technology of syntheses was carried out. Such example is described in Ref.3 demonstrating the applicability of in-line Raman spectroscopy for the control of (oxime-formation) model reaction of reactive functionalization. This approach of green chemistry was applied also when synthesis of sugar-based biopolymers were monitored with in-line Raman spectrometer and the real-time evaluation of the spectra was performed with methods of chemometrics (e.g. CLS, PLS) determining the current composition of the reaction media in each minutes.

Synergistic components such as (nano)-fibrous additives can enhance the activity of expensive FR components significantly. Preparation of nanofibers by means of electrospinning – in comparison with electrospraying and melt blowing – as well as their application in polylactic acid (PLA) self-reinforced composites is discussed in Ref. 9, 10 and 40. Multifunctionary combinations of flame retardants and fibers in self-reinforced PLA FR composites, published in Ref. 1, allowed parallel improvement of fire safety and impact resistance. Bio-fiber reinforcements modified with phosphorous compound acted also as multifunctionary additive according to the results published in Ref. 11.

Synergistic combination of resorcinol bis(diphenyl phosphate) (RDP) and ammonium polyphosphate (APP) allowed to reduce the P content to 3% in sorbitol polyglicidylether (SPE) crosslinked with cycloaliphatic amine. The resulting FR-bioepoxy products – presented in Ref. 13, 22 - reach the self-extinguishing (V0) grade and limiting oxygen index (LOI) value of 34 V/V%, while their heat release during combustion reduced with 60%.

A detailed review of the bio-based flame retarded polymer system compared our activities in this field with that of other researcher's in Ref. 20.

3.2. Formation of new FR-active interphase

Combinations of flame retardants and reinforcing agents required the application of such an adaptive interlayer that takes part in the increase of the mechanical strength and stability at ambient and elevated temperature respectively. For this purpose we applied the combination of RDP and APP. By compensating the too soft character of the RDP with APP the two components together absorbed the interfacial stresses and thus enhanced the Charpy impact strength. Regarding the flame retardancy the RDP ensured the protection in the gas phase, while the APP hindered the flame spread in the solid phase (see the identified mechanism in section 3.5). This way the self-extinguishing level of fire retardancy could be achieved. Detailed results are published in Ref. 23.

Investigating the effect of the size and type of surface area on the FR efficiency and mechanical properties we prepared modified APP particles with various particle size. Although the grinding - performed under green solvent-free circumstances - led to enhanced FR efficiency the aggregation of the particles hindered the formation of homogeneous dispersion. Surface modification by means of dispersing agent (e.g. FR-active P-containing surfactant) was required to improve the homogeneity. Details of these results are published in Ref. 2.

APP was microencapsulated with a biobased sorbitol polyglycidyl ether type epoxy resin too and used as flame retardant additive in polylactic acid (PLA) matrix. The thickness of the bioepoxy shell was optimized in terms of flammability and mechanical properties. Raman maps taken from the microcapsuled additives contribute to the visualization of the core-shell structure of the prepared bioresin-encapsulated APP particles. Figure 4 shows the maps of the calculated Raman scores (i.e., spectral concentrations) obtained from an MCAPP3 particle, which visualizes the compositions calculated at each point with a two-way image.

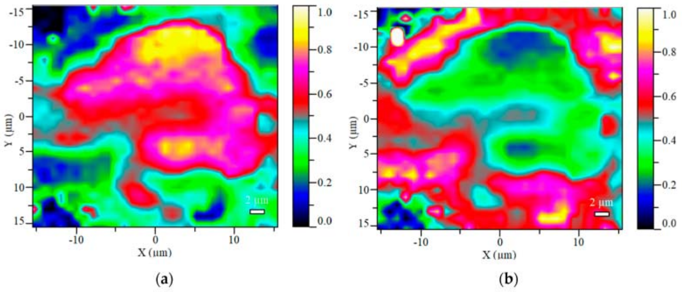


Figure 4 The visualized score maps of the distribution of the two major components in the MCAPP3 microcapsule (at 100× magnification): (a) the calculated APP content, (b) the calculated resin content.

Better interfacial interaction of the MCAPP with PLA was found at scanning electron microscopic (SEM) observation (figure 5).

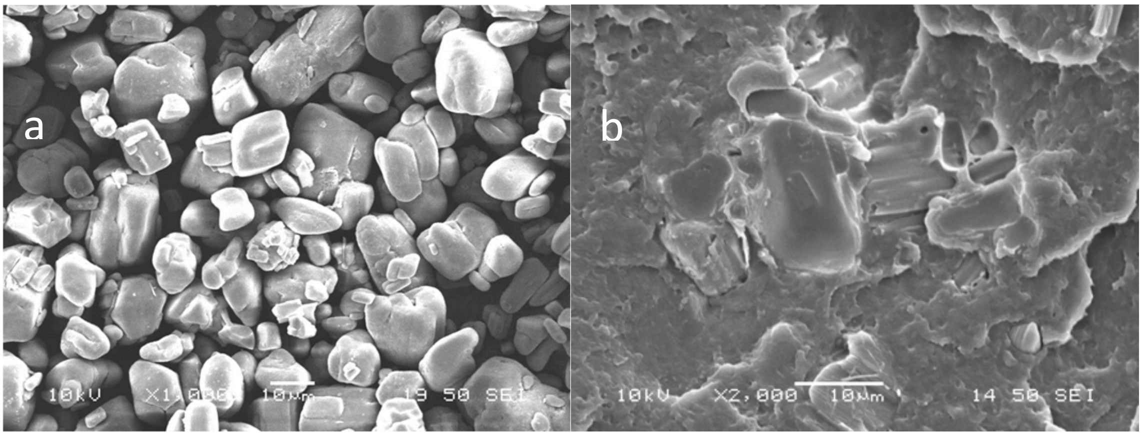
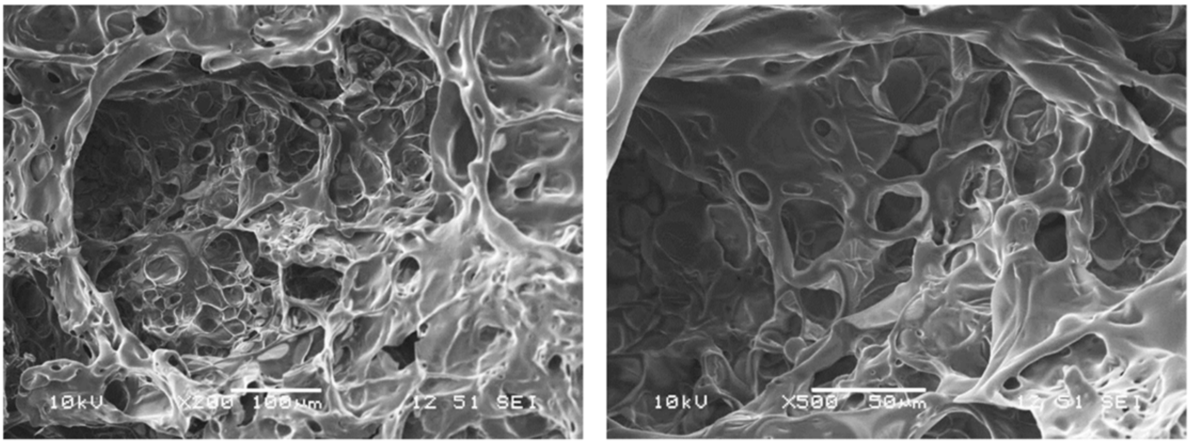


Figure 5 SEM image of FR microcapsules (a) and their embedding in PLA (b) magnification are 1000x and 2000x respectively

It was found that the bio-resin shell effectively promotes the charring of the APP loaded PLA composites, as found during thermogravimetric and SEM analyses (figure 6), and eliminates the flammable dripping of the specimens during UL-94 tests, thus V-0 rating becomes achievable.



(**a**) (**b**)

*Figure 6 The pore structure of the char residue formed during combustion observed by SEM imaging: (**a**) 200× magnification, (**b**) 500× magnification.*

With the optimized microcapsulated (MCAPP) additive increased limiting oxygen index, reduced peak of heat release rate (by 20%) and reduced total heat emission (15%) were reached compared to the effects of neat APP. The optimized interphase resulted in increased modulus of these composites. Water-resistance of FR-PLA composites were investigated by soaking the samples of 100 × 10 × 3 mm3 dimensions in distilled water for 96 h at 40 °C.

After the soaking the dried samples were measured and the results compared to the weights before soaking. The mass loss of the samples containing microencapsulated additives is noticeably lower than PLA + APP without interfacial layer. Even with the thinnest bioresin shell (MCAPP1), the mass loss is only 0.37% larger than that of the additive-free sample. It is supposed that other types of bio-based epoxy resins (such as sugar-based epoxy resins) could also be utilized in other polymer types/systems to provide a more effective and green fire retardancy solution.

Interface modification was performed also by plasma treatment around polycaprolactone (PCL), poly(lactic acid) (PLA), poly(lactide-co-glycolide) (PLGA), poly(lactide-co-caprolactone) (PLC), poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-co-hydroxy). Plasma surface treatment successfully modified the surface energy in the required way and the change in elemental composition of the surface was determined by means of X-ray photoelectron spectroscopy (XPS). The utilisation of the method was extended to the field of biomedicine in the Ref. 30.

3.3. Development of new FR biocomposites, biofoams, fibrous biosystems

Flame retarded biopolymers represent highest category of green and safe materials. ***Biocomposites*** suitable for airspace or other high-tech applications are, however, not available on the market. Therefore the new sugar-based bioepoxy types have been optimized to an airplane construction (e.g. glass transition temperature above 160 °C). Natural fibre reinforced full-bio composites could be developed in fire-safe form and the latter one processed to airplane furniture as shown in figure 7 (Ref. 34).

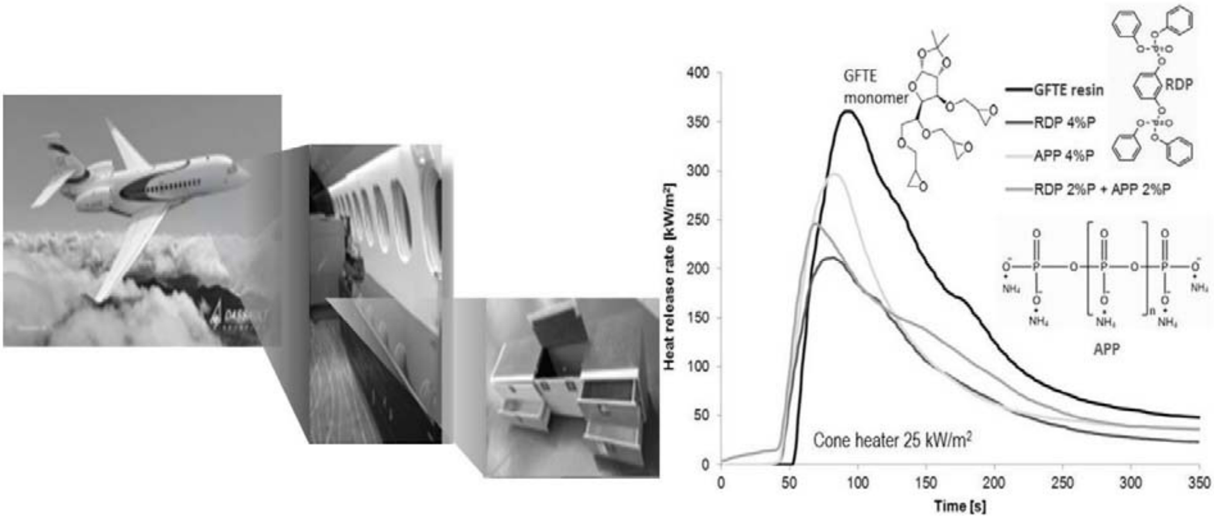


Figure 7 Airplane-furniture made of bioepoxy composite and its heat release rate results

Foams made of synthetic polymers are the materials causing the largest impact on the environment. On the other hand fire-safe foamed lightweight structures are badly needed for reducing the fuel consumption and thus cut the CO_2 emission of transportation. However FR-biofoams are not available on the market. Therefore we manufactured new PLA foams by means of supercritical carbon dioxide ($ScCO_2$) assisted extrusion, the method of which is described in Ref. 12. For this purpose setup of new foaming system was performed by our research group. The formulation of biomaterias for this purpose required their detailed rheological analysis. This way the morphology of the foams can be designed according to the need of a certain application area as described in Ref. 14. The low melt strength of PLA could be improved by the application of epoxy-functionalized chain extender. Introduction of fillers and natural fibers (talc, basalt and cellulose fibers) influenced the pore-sructure and crystallinity of the foams. Highly porous ($\varepsilon > 95\%$) mikro-cell PLA foams of controlled crystallizing kinetics could be prepared this way. The increased compression strength of PLA foams reached the 40 kPa level (Ref. 16). In the next step biofoams could be developed in flame retarded form and the results are published in Ref. 27 and 36. Electron microscopic analyses revealed the flame retardant additives concentrated at the cell wall joints, as shown in figure 8, which proved to be of key importance regarding expandability and charring ability. Such structure can compensate the enhanced flammability of foams ascribed to the large area of air/surface interface resulting in self-extinguishing (V0) biofoams with an LOI value of 31,5%.

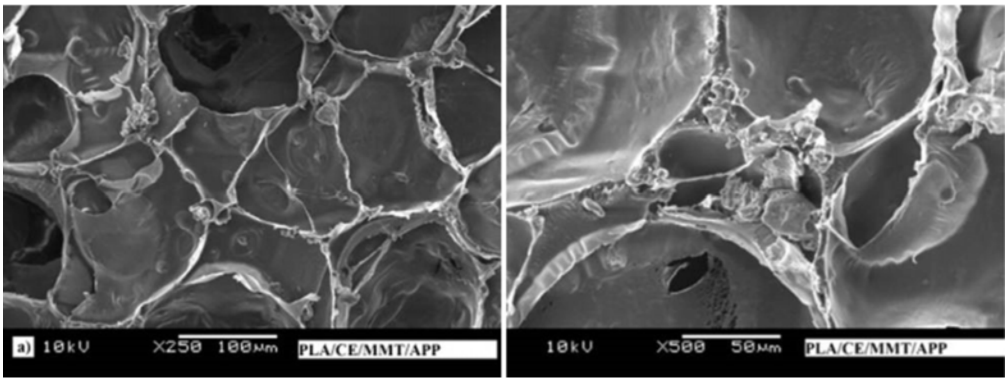


Figure 8 SEM images of flame retarded PLA foams for light-weight fire-safe structures

Thus we succeeded to develop the first FR-PLA biofoam with larger expansion coefficient and better performance than the relevant commercial flammable petrochemical foam (EPS-100).

Fibrous biosystems utilized the electrospun or melt blown micro/nanofibers - mentioned in section 3.1 - in the form of coating layer on packaging trays and self reinforced composites.

The first ever developed packaging trays covered with nanofibrous coating layer was manufactured by combining PLA extruded sheet and coating layers and subsequent vacuum forming. The nanofibrous coating provides as soft protecting layer against mechanical stresses and protects the packed food from fragments of packaging sheet in case of crash during transportation. For this purpose the technology for continuous formation of nanofibrous PLA had to be developed followed by continuous collection of fibers, exrtusion of PLA sheets and overly them with the fibers. Self-reinforced composites are extremely important in respect of recycling. In such systems the matrix and reinforcing phases are made of the same polymers. Fine tuning of the mechanical and functional properties of self-reinforced composites, containing melt-blown PLA fibres, was performed by heat treatment resulting in 47% enhancement of tensile strength as reported in Ref. 38 and 39. Other type of flame retarded self-reinforced PLA composites exhibited outstanding impact resistance as reported in Ref. 1.

Recycling of polymer wastes - which is “hardly economic” according to the project proposal - combined with FR modification has the advantage of upgrading feature. It is the most critical in case of PET used for bottle formation in large extent. Such an approach using additive-combination of reactive FR and nanoparticles resulted in an increase of molecular mass due to altered mechanism of degradation. Consequently the rheological and mechanical properties improved along with the reduction of the heat released during combustion and achievement of self-extinguishing V0 level of flame retardancy as described in Ref 7. Preparation of low-density microcellular foams from recycled PET required the modification of the macromolecular structure by means of solid state polymerization and chain extension. Further details are presented in Ref. 26 and 29.

3.4. Investigation of specific properties and control processes

Beyond the frequently used functional (e.g. FR, TGA, mechanical) and structural (e.g. SEM, XRD, XPS) and process-oriented (rheological) measurements some specific analytical techniques were applied/developed in order to promote better understanding and advanced monitoring or process-control. Realization of the potentials of these new information-sources required the strong mathematical support of chemometrics.

Modulated differential scanning calorimetry (MDSC), X-ray diffractometry (XRD) and ***localised thermomechanical analysis (LTMA)*** methods were applied for the analysis of the recrystallization processes in PLA microfibres produced by high speed electrospinning. An example of MDSC results is shown in figure 9.

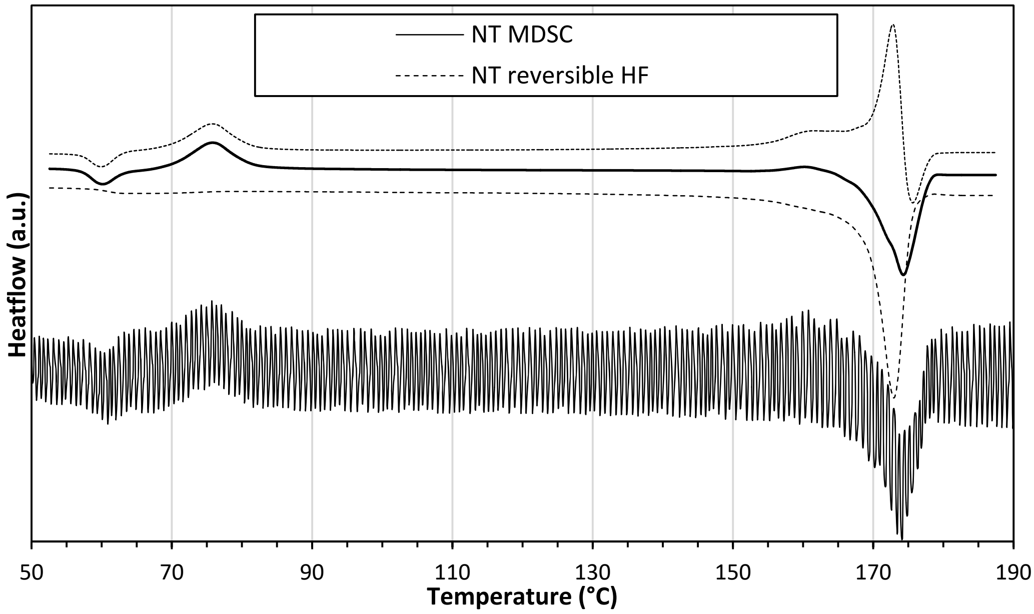


Figure 9 MDSC plot of a PLA nonwoven sample with the resulting reversible, non-reversible and total heat flow curves

It was published in Ref. 40 that only disordered α’ crystals are formed during the conventional heat treatment of the electrospun microfibers, however, ethanol-induced crystallization favours the formation of the ordered α polymorph. In connection with the differing crystalline structures, noticeable differences in the macroscopic properties such as heat resistance and mechanical properties were evinced.

The more stable α polymorph was detected in nanostructured FR-PLA foams prepared by scCO2 assisted extrusion as reported in Ref. 36. ***Pyrolysis combustion flow calorimetry (PCFC)*** highlighted excellent flame retardancy of the highly expanded foams forecasting good applicability as cushion packaging of electronics for airline transportation.

Laser pyrolysis – Fourier Transform Infrared (LP-FTIR) method – developed by our research group - was described in the final report of a former research period. We ued this novel technique for investigating the pyrolytic degradation products of FR thermoplastic and thermosetting samples the results of which are discussed in section 3.5 of this report. The system comprises of a CO_2 pyrolyser laser (10.6 nm, SYNRAD 48-1, Mukilteo, WA, USA) unit coupled with Bruker Tensor 37 type FTIR spectrometer (Billerica, MA, USA) (detector: deuterated triglycine sulphate (DTGS), gas cell: KRS5 type thallium bromo-iodide window, resolution: 4 cm-1). The pyrolysis of the samples was carried out with 1 W laser power for 1 min, and the formed gases were subjected to FTIR analysis.

Quantitative evaluation of the distribution of components in a multicomponent polymer system (e.g. in composites and pharmaceuticals) can be performed by means of ***Raman chemical mapping***, the improved evaluation of which is described in Ref. 31. The method was developed further by the assistance of silver nanoparticles that allows ***surface enhanced Raman spectrometry (SERS)***. Controlled product quality can be ensured this way even if the concentration of a component is very low. Such results are published in Ref. 4, 5. The accurate determination of the composition in a multicomponent system can be performed with MCR-ALS method of chemometrics only if the number of components is known. However, no method was available for the determination of the number of components thus we elaborated a new ***variable-clustering*** (VARCLUS) algorithm. This method makes possible cluster formation from data originating from Raman mapping and thus the exact determination of composition. The applicability was validated with "Spectral Angle Mapper-Orthogonal Projection (SAM-OP)" method. The combined VARCLUS and SAM-OP process proved to be optimal for rapid evaluation of spectral data and for the identification of components even at 1 % concentration. Details of this method are published in Ref. 25.

Non-destructive characterisation of all-polypropylene composites was elaborated using ***polarized Raman spectroscopy*** and validated by off-line ***small angle X-ray scattering (SAXS)*** measurements. Results, reported in Ref. 28, confirmed that polarized Raman spectrometry is suitable for rapid analysis of the structure of reinforcing fibers playing a key role in the FR mechanism of self-reinforced polymer composites. The crystallinity and molecular orientation of the reinforcing fibers could be determined with the aid of chemometrics by building (CLS-based) model from real reference-spectra. Strong correlation between the calculated degree of orientation and the Young modulus confirmed the suitability of the method published in Ref. 17 and 28.

The project proposal promised to use the methods of "process analytical technology" (PAT) „applying control strategy governed by product quality" for relyable production of the various products. A detailed review about PAT in Ref. 8 reports the ***first Raman-based closed-loop control*** developed by our research group for such purposes. More recent examples of the application of process-Raman are reported in Ref. 3 and 35. However, the characterization of multicomponent biopolymer systems is still based on off-line analytical methods even if the recycling of polymer wastes would require the application of advanced control methods in accordance with the industry 4.0 strategy. Use of spectroscopy and image-analysis for feedback control of twin screw mixing is feasible also for pharmaceutical purposes meeting the following aim of the project proposal: “extension of the developed principles, materials and technologies to … pharmaceutical industry”. Related results are published in Ref. 35, 32. Figure 10 – taken from Ref. 34 - shows our proposals for industrial application.

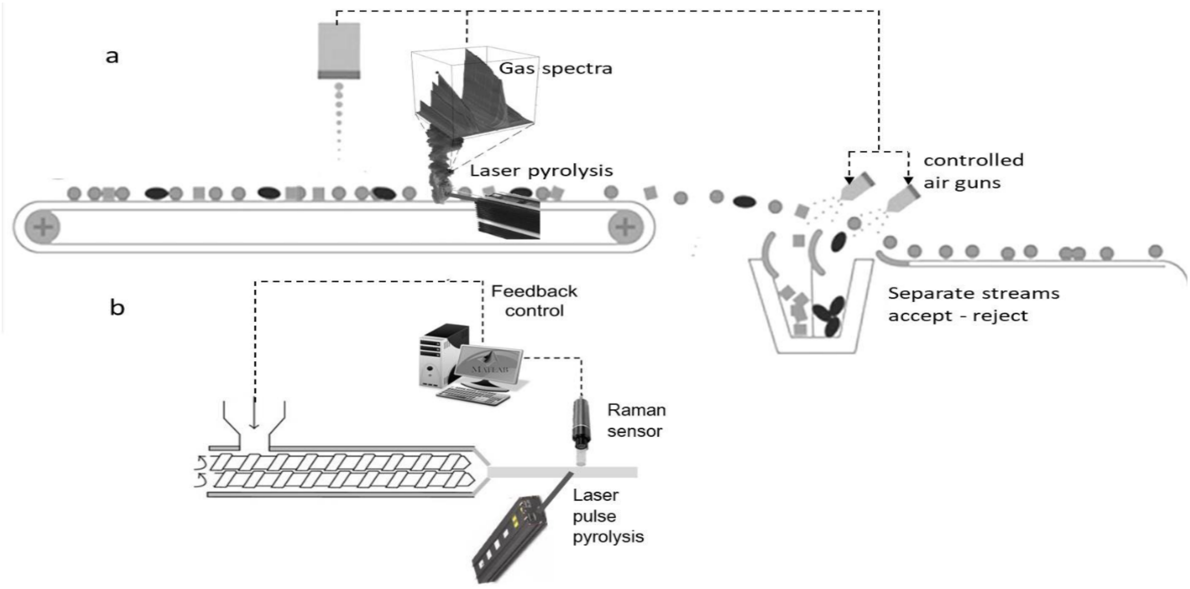


Figure 10 Use of LP-FTIR for chemical identification of black pieces at waste sorting technology (a), control of intumescent flame retardant content through feedback from laser pyrolysis assisted Raman spectrometry (b)

Fully recyclable self-reinforced FR-composites, in which both the matrix and reinforcing fibres are made of the same polymer family and consolidated through their interfacial layers. Such composites can be easily processed by simple thermoforming methods if the level of heat-induced relaxation of the reinforcing fibres can be controlled. In order to facilitate this precise processing of self-reinforced composites, novel Raman monitoring and control methods have been proposed by the authors in Ref 28. Scheme of the principle and Raman images visualizing the relaxation is shown in figure 11.

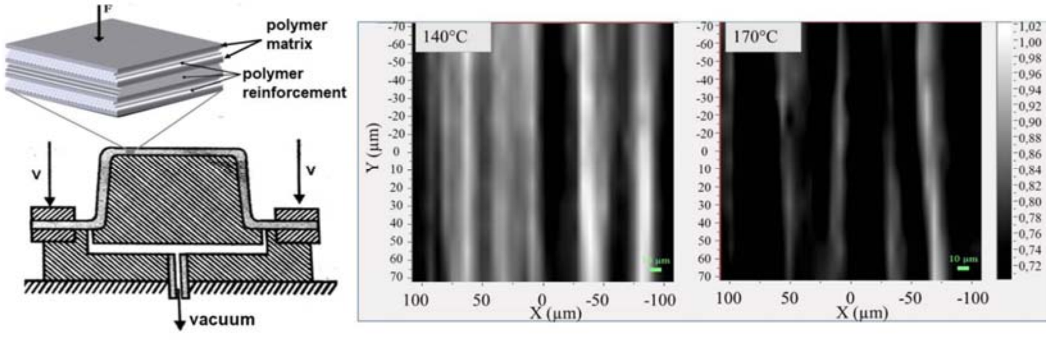
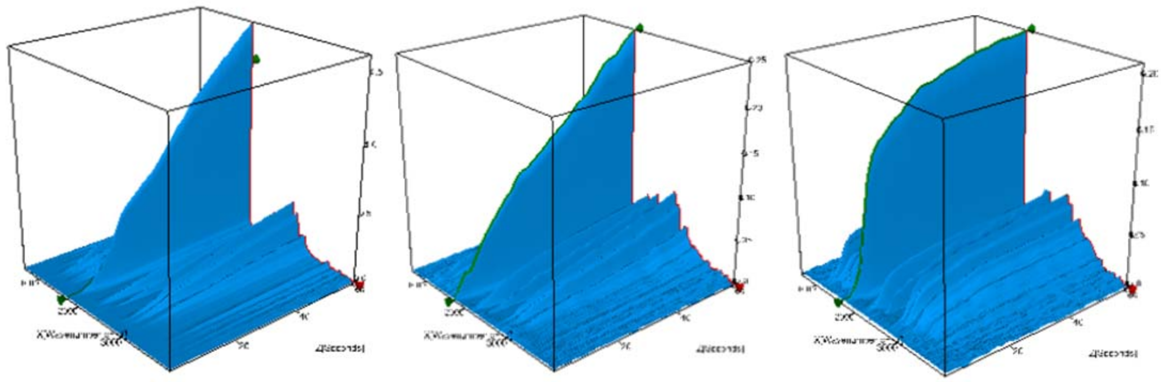


Figure 11 Thermoforming of self-reinforced polypropylene composite and demonstration of the heat-induced relaxation of reinforcing fibres by Raman mapping (bright bands represent the oriented fibres, while the dark bands the relaxed ones)

3.5. Identification of new mechanism of FR action and water-induced changes

The investigation of earlier not examined materials, such flame retarded self-reinforced and foamed polymers, led us as the conclusion that the orientation of polymer chains plays a role in the mechanism of fire retardancy. We found a close correlation between the structure of reinforcement (i.e. arrangement, orientation and waving-pattern of fibers) and the FR-efficiency achieved by an intumescent FR additive system. The amount of additives needed for achieving the self-extinguishing (V0) level could be reduced from 20-22% to as low as 7.2% when optimal (aligned) structure was applied. A ***new mechanism of fire-control*** has been identified this way, which is governed by shrinkage of reinforcing fibres and thus contribute to extinguishing of fire. Ref. 15 and 37 disclose further details of these new findings.

The mechanism of fire retardancy of an APP type (AP462) additive combined with montmorillonite (MMT) nanoparticles was analysed using LP-FTIR, according to the method described in 3.4 section of this report. The results of LP-FTIR analyses could be plotted in 3D diagrams – shown in figure 12 - with the aid of OPUS 5.5 software.



PLA PLA+10%AP462 PLA+10%AP462+1%MMT

Figure 12 Time dependent 3D spectra of evolved gas taken at LP-FTIR analyses of pure and FR-PLA samples

The amount of degradation products in the gas phase were compared through the time-dependent GramSchmidt intensity (frequency-independent total-chromatograms) curves shown in figure 13. Increasing amount of APP reduced the evolved gases comparing to the reference PLA. It suggests that the pyrolysis products of PLA are mostly gases, while the APP acts in solid phase promoting the charring of the polymer. If suitable amount and type of char is formed on the surface of the material it hinders the heat, oxygen and material transport effectively and thus improves the resistance of the material against fire.

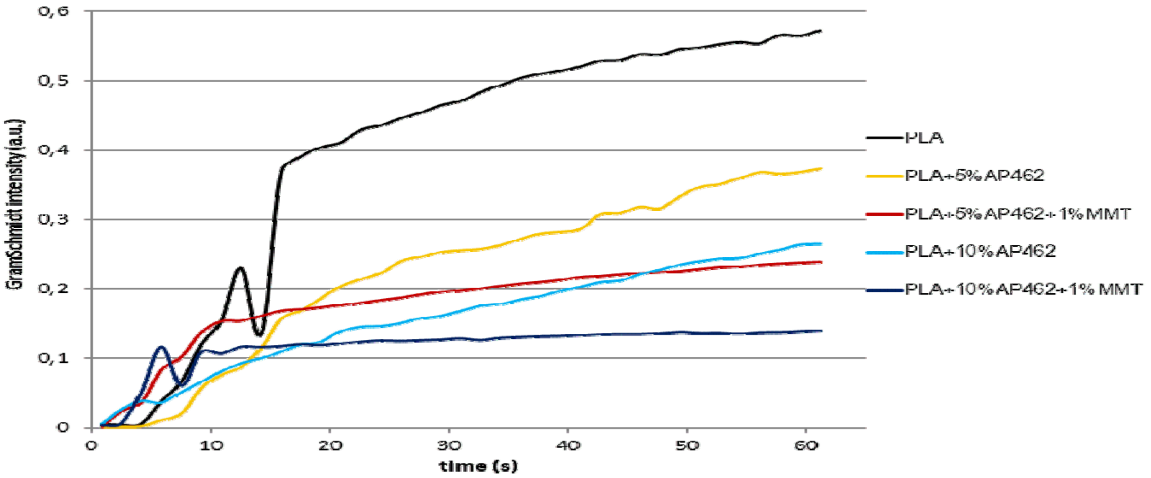


Figure 13 Time dependent GramSchmidt intensities of pure and FR-PLA samples

In the presence of 1% MMT synergist the evolution of degradation gases slowed down further by promoting the formation of the protecting char layer on the surface, which prevented the degradation of the underlying polymer layers.

Another synergistic effect was found between the inorganic APP and the organophosphorus RDP, when applied in combination. We explained it with the complex effect of optimal balance between the two types of mechanisms. This explanation derived from the results of LP-FTIR, ATR-IR, charring residue, and rheometric analyses. The FTIR spectra of the gases formed during the laser pyrolysis is shown in figure 14. The spectra indicated no gas-phase effect in the case of sample containing only APP, while increasing the RDP content led to increased amount of P species among the gas-phase degradation products. Thus the RDP ensured the blocking of the radical reactions in the gas phase, while APP prevented the spread of fire in the solid phase. The outstanding FR results published in Ref. 23 and 24 could be explained by this mechanism.

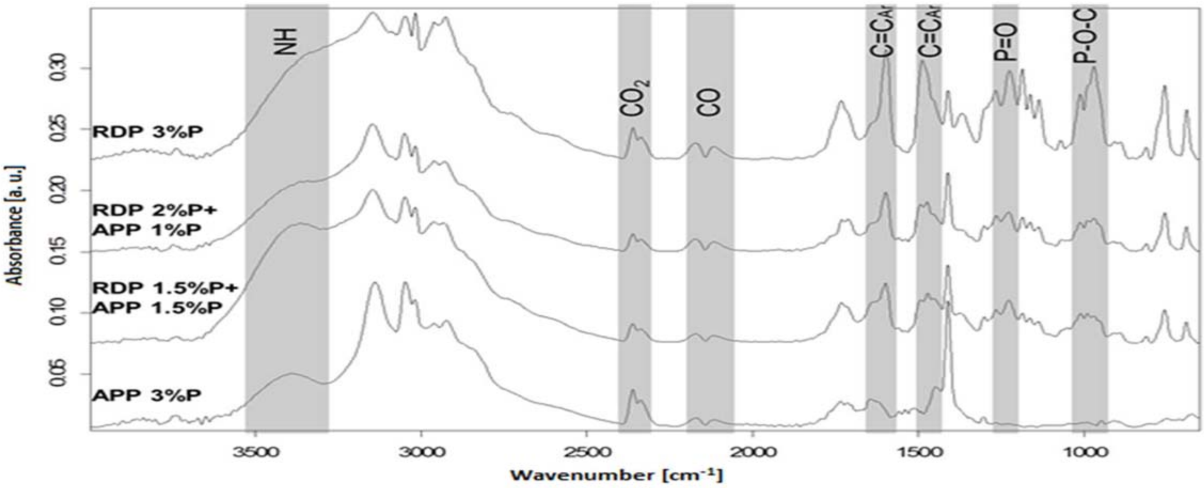
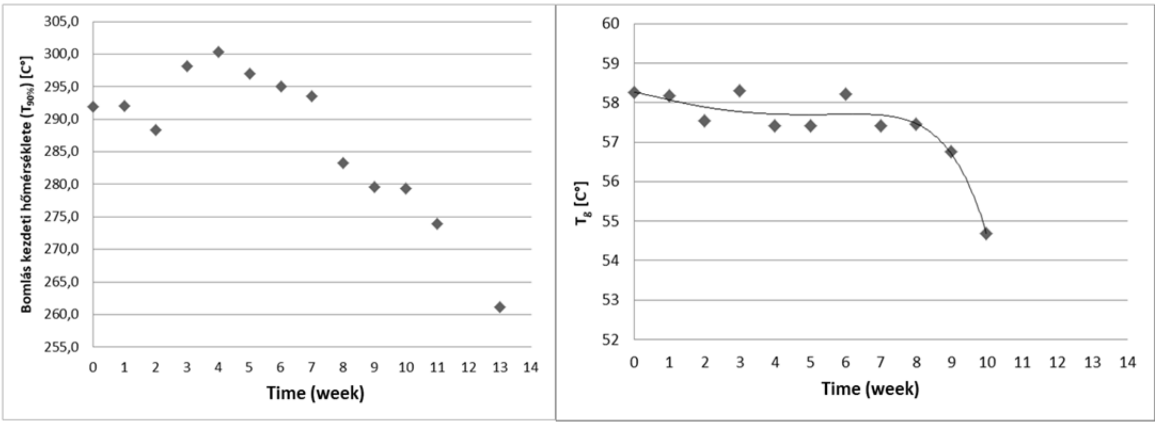


Figure 14 LP-FTIR spectra of the gas phase degradation products of samples containing 3% P

The mechanism of biodegradation was investigated by keeping FR-PLA foam samples in a climate test chamber at RH: 75% and T: 50°C, during which the level of degradation was checked weekly. Beyond measuring the strength of the foams, TGA, DSC, ATR-IR, XRD and SEM measurements were performed. The decrease of the strength and of the initial temperature of the thermal degradation (T90%) could be detected as a consequence of reduction of molecular mass caused by hydrolytic degradation (figure 15.a). DSC results indicated increase in the crystallinity with the aging of the foams. The newly formed crystalline phase consisted of less ordered α' crystallites melting at lower temperature than the original crystals. The increase of crystallinity can be explained with two parallel mechanisms. On the one hand the degradation of sensitive amorphous phase and on the other hand the increased mobility of the shortened macromolecules increases the relative and absolute crystallinity respectively. The sharp fall of the glass transition temperature (T_g) after the 8th week, shown in figure 15.b, is ascribed to the decrease of the molecular mass of PLA below the critical (Mc) value of 20.000 g/mol, which is accompanied with significant change of viscoelastic properties. The lack of the glass transition after the 11th week indicates the transformation of the product to useless rigid foam.



a b

Figure 15 The changes of the initial temperature of degradation (a) and the glass transition temperature (T_g) as a function of the temperature against the temperature (b)

The images show in figure 16 that the samples treated for longer time could hardly keep their microcellular structure after a compression test and their deformation is large (even 90%). The FTIR spectra in figure 16 indicate sudden decrease of the molecular mass (reduced peak belonging to carbonyl groups), while the XRD results confirm the continuous increase of the crystallinity during aging.

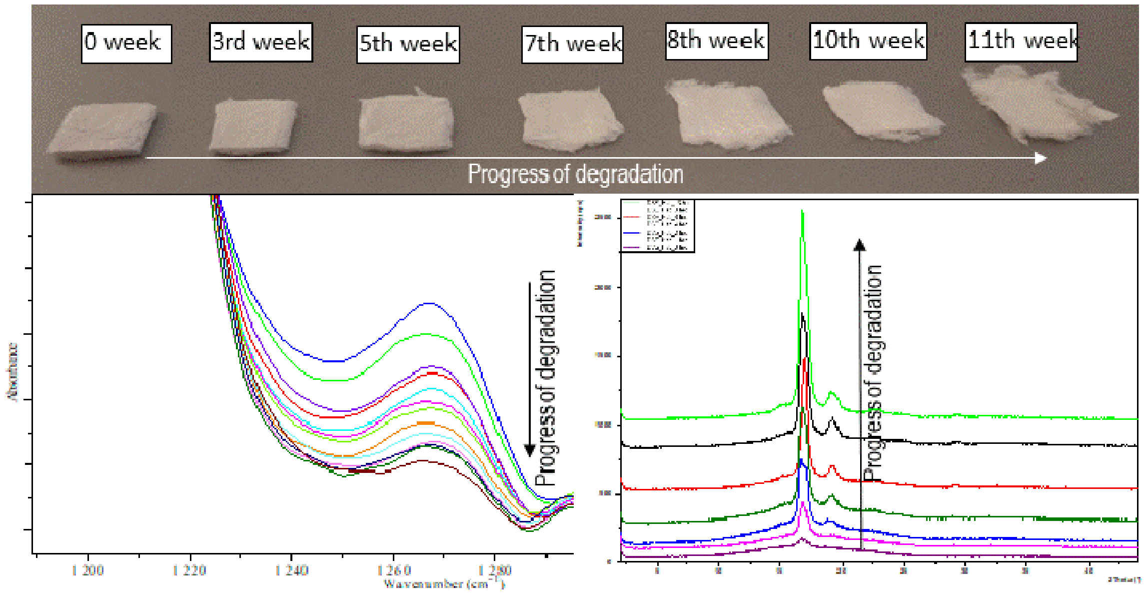


Figure 16 Residues of foams after aging of various duration after compression test (above), change of IR peak at 1265 cm-1 belonging to carbonyl groups of PLA with the temperature (left), X-ray diffractograms taken from the foams during aging

Based on the performed thermal, morphological, spectroscopic and mechanical measurements the rapid initial hydrolytic degradation of the investigated PLA foams reaches a critical level only after 8 week accelerated aging in climate test chamber, which corresponds to 1 year at normal circumstances.

3.6. Extension of the results to bio-pharmaceuticals

Most of the methods developed during the run of this project serve the innovative technologies in both the plastic and pharmaceutical industries. Especially the complex systems of biopharmaceuticals are related. Especially the Ref. 9,10, 18, 19, 30-32, 34, and 35 demonstrate the importance of knowledge-transfer among these fields.

4. Conclusions

The accomplishment of the project plans resulted in breakthrough regarding the understanding of the mechanism, the enhancement of the efficiency and the advanced processing of several fire retardant systems. As a consequence the safety and sustainability of polymeric materials could be improved significantly. The practical outcomes originating from the basic-research results of the project are about to be utilized by DS-Smith, Proform, Polifoam, PEMÜ, Richter and MOL companies. It seems to be reasonable to develop the new findings further in several fields especially in the biopharmaceuticals of high economic and social importance.

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