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Final research report

2017. 10. 01. – 2021. 09. 30.

Summary of results

During the research project, we focused on the production of light-weight - such as natural fibre-reinforced, self-reinforced and foamed - polymer composites, as well as the development of innovative flame retardant methods for these highly flammable material associations. In the course of our research, we placed special emphasis on the fact that the newly produced polymer composites, the new flame retardant solutions and the applied production technologies follow the guidelines of green chemistry and the circular economy as much as possible. For this purpose, composite components of renewable (such as polylactic acid, natural fibers, sorbitol, glucose, cyclodextrin) or recycled (recycled PET) origin were used, from which recyclable (self-reinforced) and / or biodegradable (natural fiber-reinforced, biopolymer-based) composites were manufactured. In the development of new flame retardant additive systems, also biobased starting materials (such as sorbitol, glucose, cyclodextrin, etc.) were processed, by-product-free addition chemical reactions (e.g. phosphorus-silane production) were preferred, and instead of organic solvents, where possible, water was used (electrospinning of cyclodextrin, flame retardant treatment of natural fibres). We have discovered new methods and mechanisms (synergistic effects) that can be exploited to achieve the desired property (eg. flame retardancy level) with significantly less additives (and cost) (eg. combined intumescent flame retardant additive systems, toughening of recycled PET, flame retardancy of natural fiber-reinforced composites). By monitoring of the applied continuous manufacturing technologies (eg extrusion foaming) using in-line applicable spectroscopic methods (NIR, Raman), by reducing by-product/waste formation, reducing off-line testing costs and saving human resources, we also demonstrated the possibility of more economical production of environmentally friendly polymer composites.

The main results of the three-year research work are classified by topic below:

Development and flame retardancy of environmentally friendly polymer foams

Low density ($\rho < 50$ kg / m^3) microcellular polylactic acid (PLA) foams were successfully produced in flame retardant form with environmentally friendly technology (supercritical carbon dioxide (sc-CO_2) assisted extrusion). The foamability of PLA was improved by the appropriate addition of reactive chain-extender and nano-sized clay mineral particles, while a new intumescent flame retardant additive system, containing cellulose treated with phosphorus and boron-containing compounds, was developed to reduce flammability of the biofoams [4,22].

With the further development of the extrusion foaming technology, we have also been able to produce PLA foam products with uniquely structured, lens-shaped cells, which have several advantageous properties: they are elastically deformable, as well as adjustable modulus of elasticity (0.1-5.0 MPa) and piezoelectric charge. We have filed a patent application for the invention which, due to its biocompatibility, could be used in, inter alia, medical devices (drug pumps, artificial tissues) or disposable energy harvesting products [2].

Value-adding recycling and flame retardancy of recycled raw materials

The recycling of significant amounts and varying qualities of poly(ethylene-terephthalate) (PET) waste, whether significantly degraded (selective municipal waste, industrial waste, or even marine waste) is a major challenge today. Recycling usually results in significant embrittlement of the material, which limits its potential uses. The production of high-performance plastics from recycled PET is therefore a particularly important and topical goal, which is further encouraged not only by increasingly stringent legal requirements but also by the ever-increasing price of the original polymeric raw materials.

As a first step, the change in the crystalline structure of PET, which is particularly sensitive to hydrolytic degradation, as a function of its molecular weight has been comprehensively investigated [14]. Subsequently, a new process has been developed, in which the waste PET fraction contributes to the outstanding increase of the impact resistance of the plastic product - exceeding the performance of ABS, HDPE and PA6 (30–50 kJ / m^2). At the same time, as lower amount of reactive additive is necessitated, a cost reduction of about 20% can be realised. The key to this solution is that the efficiency of the reactive impact-modifier additive can be increased through the increased mobility and reactivity of the reduced-molecular-weight polymer chains characteristic for degraded PET waste [17,19]. In this way, the technology provides a solution for the economical recycling of even highly degraded, non-marketable PET waste in a productive, continuous way (eg injection molding or 3D printing) that was not previously typical for this material. We filed a patent application for this technological process [1].

Our experience in the production and flame retardancy of microcellular PLA foams [27] has also been transferred to secondary polyethylene-terephthalate (RPET); low-density (ρ <350 kg / m3) microcellular foams were successfully produced from the recycled raw material by continuous extrusion technology. The molecular weight of the degraded recyclate was effectively increased by two methods, solid phase polymerisation and the use of a reactive chain extender, to obtain a raw material suitable for foaming [9].

In our sc-CO_2 dioxide assisted foaming experiments, if the intrinsic viscosity (IV) of the recycled material was increased from 0.62 dl / g to 0.87 dl / g using an epoxy-functional chain extender, and the addition of talc effectively aided nucleation and stabilisation of the cells, RPET foam products with a density of even less than 150 kg / m^3 were obtained. We found a strong correlation between the apparent density of the foams and the near-infrared (NIR) spectrum of the foamed RPET samples, which allowed the in-line, rapid, and non-destructive characterisation of product quality. Accordingly, NIR spectroscopy has been found to be a suitable method for in-line monitoring of product quality during extrusion foaming of recycled PET, which is particularly prone to quality fluctuations [16].

The flame retardancy possibilities of RPET were also investigated. By combining aluminium-alkyl-phosphinate and montmorillonite clay mineral, nanocomposites with reduced flammability and excellent mechanical properties were produced. The applicability of the value-added recycled material in the electric or electronic fields was demonstrated by injection moulding of television housings [10]. Using the optimised formulation, flame retardant RPET foam products have also been successfully produced [28], which are promising to be used primarily in construction as lightweight heat insulator or sandwich core materials.

Flame retardancy of biocomposites – development of new additives and exploring new mechanisms

Multifunctional additives have been developed which – in addition to their flame retarding effect - have reinforcing, heat stabilising and / or compatibilising effects as well. These additives can be used to reduce the amount (and cost) of additives required for flame retardant biocomposites.

New phosphorus-containing silane (PSil) adducts were prepared by addition reactions of phosphorus-containing polyols (such as ethylene-glycol-phosphate, glycerol-phosphate, Exolit OP560) and 3- (triethoxysilyl)-propyl-isocyanate. The products were used as reactive surface treating agents for the flame retardancy of cut flax fibres as well as cyclodextrin microfibres. Thermogravimetric studies have shown that treatment with new PSils greatly promotes carbonisation of biofibres without reducing their thermal stability [29,30].

Environmentally friendly flame retardant additives, mainly produced from renewable resources, have been also developed. Sorbitol and glucose-based bioepoxy resins were synthesized and then tested for their use as flame retardant components (such as efficiency, compatibility with biopolymer matrices, water sensitivity, stability, price). Processes for microencapsulation of ammonium-polyphosphate and melamine-polyphosphate with bioepoxy resins have been elaborated. The microencapsulated additives with the optimized composition have proven to be easy to handle (combined), waterproof, and effective flame retardants in PLA matrix. In addition to significantly improving flame retardant properties, they provided better filler-matrix interaction, increased modulus, and better water resistance compared to the neat additives [11,24].

The role of the physical form of a polysaccharide-type carbonising component on its effectiveness in an intumescent flame retardant system has been firstly investigated. Microfibrous structures were prepared from the aqueous solution of (2-hydroxypropyl)-β-cyclodextrin (HPBCD) by electrospinning process. It was shown that the polymer-like supramolecular structure can greatly increase the flame retardant efficiency of the cyclodextrin in the intumescent flame retardant systems. It was found that the advantage of the special microfibrous structure of the oligosaccharide type carbonising agent lies in the effective interaction with APP and the formation of a carbonaceous protective layer with increased thermal and mechanical resistance. The fact that only by changing the aspect ratio of HPBCD significant improvement can be achieved in both the flame retardant effect and the mechanical properties is a new finding [15].

The structure-property relationships of flame retardant multilayer biocomposites with phosphorus- and nitrogen-containing compounds were analysed by experimental design and multivariate evaluation methods. Positive interactions have been shown between the flame-retardant-treated phases in terms of several flammability (eg oxygen index, ignition time, maximum of heat release rate) and even mechanical characteristics (tensile strength). Our results demonstrate that the combined flame retardancy approach of multilayer biocomposites, i.e. the balanced distribution of phosphorus-containing additives between the matrix and reinforcement phases, results in increased mechanical performance and economic advantage as well [8,23,25].

Our new insights into the manufacturing technology of biocomposites (compression versus injection moulding) and our results in the field of Raman signal-based monitoring and control of composition and structure have been reported in further impact factor journals [12,13].

Development and functionalization of self-reinforced composites

Self-reinforced PLA composite sheets with special nanofibrous structure were manufactured [5,18,20,21]. The production of PLA microfibers, serving as a reinforcing phase, was achieved with the uniquely high yield of 40 g / h using the high-speed electrospinning process (HSES) developed by our research group. We have shown that the two methods, i.e. heat treatment and ethanol treatment, that are used to increase the crystallinity of inherently amorphous PLA microfibers result in different crystalline structures. We also pointed out that these differences in the crystalline structure also cause significant changes in the macroscopic characteristics, e.g. heat resistance, mechanical properties [7,26].

We were the first to produce flame-retarded (FR) SR composites by injection moulding. In this way, we proved that in addition to 2D sheets that can be manufactured with traditional technologies, it is also possible to produce 3D products. These products meet the increasingly stringent safety standards, both in terms of mechanical and flammability characteristics, and can be easily recycled once they have become waste. However, we found that in the case of short-fiber reinforced injection-moulded sheets, the synergism previously shown between the infinite, highly stretched and oriented fibres and the intumescent flame retardant additive system, is only moderate. From this, we concluded that the length, direction, and arrangement (structure) of reinforcing fibres are key parameters for the flammability properties of flame retardant self-reinforced composites [3].

We showed a strong correlation between the tensile modulus of multilayer self-reinforced (SR) polypropylene composites and the degrees of molecular orientation estimated from the Raman spectra recorded from the composites. Based on our results, both SAXS and Raman spectroscopy are suitable methods for non-destructive estimation of the mechanical properties of SR composites that are particularly sensitive to manufacturing and application conditions. In our opinion, process control based on polarized Raman spectrometry may find application in the production and quality control of self-reinforced composites, as well as in all areas where the ordering of macromolecules is of paramount importance [6].

Related publications:

patent applications:

[1] Mihályfi Á, Helmajer L, Lovas Z, **Bordácsné Bocz K**, Ronkay F, Molnár B, Marosi G
Thermoplastic polyester and production process thereof patent filed at: Hungarian Intellectual Property Office, application number: P2000393, filing date: 24 Nov 2020 (Pending Patent)
PCT filing in progress

[2] Vadas D, Igricz T, **Bocz K**, Marosi G Poly(lactic acid)-based foam and manufacturing the same patent filed at: Hungarian Intellectual Property Office, application number: P2000412, filing date: 04 Dec 2020 (Pending Patent)
PCT filing in progress

International journal articles

[3] Vadas D., Kmetty Á., Bárány T., Marosi G., **Bocz K.**
Flame retarded self-reinforced polypropylene composites prepared by injection moulding
Polymers for Advanced Technologies 29(1): 433-441. (2018)
Q1, IF= 2,162

[4] Vadas D., Igricz T., Sarazin J., Bourbigot S., Marosi G., **Bocz K.**
Flame retardancy of microcellular poly(lactic acid) foams prepared by supercritical CO2-assisted extrusion

Polymer Degradation and Stability 153: 100-108. (2018)
Q1, IF= 3,78

[5] Vadas D., Kmetykó D., Marosi G., **Bocz K.**
Application of melt-blown poly(lactic acid) fibres in self-reinforced composites
Polymers 10(7): 1-12. (2018)
Q1, IF= 3,164

[6] **Bocz K**., Decsov K.E., Farkas A., Vadas D., Bárány T., Wacha A.F., Bóta A., Marosi G.
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D1, IF= 6,282

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Journal of Thermal Analysis and Calorimetry 1-14 (2020)
Q1, IF = 4,626

[8] **Bocz K.,** Szolnoki B., Farkas A., Verret E., Vadas D., Decsov K., Marosi G.
Optimal distribution of phosphorus compounds in multi-layered natural fabric reinforced biocomposites
Express Polymer Letters 14 (7): 606-618. (2020)
Q1, IF = 4,161

[9] **Bocz K.,** Molnár B., Marosi G., Ronkay F.
Preparation of low-density microcellular foams from recycled PET modified by solid state polymerization and chain extension
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Q2, IF = 2,572

[10] Ronkay F., Molnár B., Szalay F., Nagy D., Bodzay B., Sajó I. E., **Bocz K**.
Development of flame-retarded nanocomposites from recycled PET bottles for the electronics industry
Polymers 11 (2): 233 (2019)
Q1, IF = 3,426

[11] Decsov K., **Bocz K**., Szolnoki B., Bourbigot S., Fontaine G., Vadas D., Marosi G.
Development of bioepoxy resin microencapsulated ammonium-polyphosphate for flame retardancy of polylactic acid
Molecules 24 (22): 4123 (2019)
Q2, IF = 3,267

[12] Marosi G., Hirsch E., **Bocz K**., Toldy A., Szolnoki B., Bodzay B., Csontos I., Farkas A., Balogh A., Démuth B., Nagy Z. K., Pataki H.
Pharmaceutical and macromolecular technologies in the spirit of industry 4.0
Periodica Polytechnica – Chemical Engineering 62 (4): 457-466 (2018)
Q3, IF = 1,382

[13] Jozo M., Cui L., **Bocz K.,** Pukanszky B.
Processing induced segregation in PLA/TPS blends: Factors and consequences
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Journal of Polymer Research 27 (12): paper 372 (2020)
Q2, IF = 2,426

[15] Decsov K.; Takács V.; Marosi G.; **Bocz K**.:
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Q1, IF = 5,03

[16] **Bocz K**.; Ronkay F.; Molnár B.; Vadas D.; Gyürkés M.; Gere D.; Marosi G.; Czigany T.:
Recycled PET foaming: supercritical carbon dioxide assisted extrusion with real-time quality monitoring
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Application of low-grade recyclate to enhance reactive toughening of poly(ethylene terephthalate)
Polymer Degradation and Stability 185: paper 109505 (2021)
Q1, IF = 5,03

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[20] Vadas D., Kmetykó D., Marosi G., **Bocz K.**
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Polymers 2018: Design, Function and Application
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Athén, Görögország, 2018. június 24-28.

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22nd International Conference on Phosphorus Chemistry
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[23] Szabó L., **Bocz K.,** Szolnoki B., Marosi G.
Flax fibre reinforced PLA/TPS biocomposites flame retarded with phosphorus-based multifunctional additive system
22nd International Conference on Phosphorus Chemistry
Budapest, Magyarország, 2018. július 8-13.

[24] Decsov K. E., **Bocz K.,** Baranyi B., Bourbigot S., Szolnoki B., Fontaine G., Vadas D., G.
Development of bioepoxy resin microencapsulated ammonium-polyphosphate for flame retardancy of polylactic acid
European Meeting on Fire Retardant Polymeric Materials
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[25] **Bocz K**., Szolnoki B., Farkas A., Verret E., Dániel Vadas D., Marosi G.
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[26] Vadas D., Kmetykó D., **Bocz K.,** Marosi G.
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Physical and chemical foaming of flame retarded poly(lactic acid)
17th European Meeting on Fire Retardant Polymeric Materials,
Turku, Finnország, 2019. június 26-28.

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[29] Decsov K. E.; Ötvös B.; Marosi G.; **K. Bocz.:**
Phosphorus-treated microfibrous cyclodextrin boosts flame retardancy of poly(lactic acid)
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Winner of the Best Poster Award

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Phosphorus-treated microfibrous cyclodextrin boosts flame retardancy of poly(lactic acid)
23rd International Conference on Phosphorus Chemistry
Czestochowa, Lengyelország, 2021. július 5-9. (online)

Main scientific indicators:

- ***patent applications: 2***
- ***international journal articles: 15***
  - highlighted (first or last) author **: 12**
  - Q1: **10**
  - summa impact factor: **51,469**
- ***national journal article: 2***
- ***international conference presentations: 11***
- ***PhD supervision: 2***
  - PhD degree: **1** (Dániel Vadas, 2021)