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Development and Functionalisation of Lightweight Poly(lactic acid) Composites

Summary of PhD thesis

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1 INTRODUCTION, OBJECTIVES

As society and decision-makers tend to become more environmentally conscious, technical terms like *sustainable development* and *circular economy* are becoming more and more embedded in common parlance as increasingly fashionable terms. Fortunately, research has already been going on for decades in academia and amongst market players to develop raw materials and manufacturing methods with low environmental impact and high efficiency. Inexpensive, easily manufactured, durable polymers and their composites increase the standard of living of humanity and reduce energy consumption year by year, thanks in part to their key role in food safety, transportation & logistics, automotive, and construction industries. To facilitate reprocessing, self-reinforced composites (SRCs) are being developed in which the reinforcing fibres and the matrix material are made of the same polymer type. Thus, SRCs are much lighter than conventional composites (reinforced with glass, basalt, or carbon fibre) and can be fully recycled, as there is no need to separate the reinforcing fibres from the matrix. Lightweight articles can also be achieved by foaming the polymeric base material, in which case up to 90-97% of the product consists of air-filled pores. Polymer foams, as thermal insulation, save more than 140 times the energy needed for their production, and as packaging, they can protect valuable products from physical impacts.

However, the advantageous properties of plastics (cheap, durable, lightweight) also led to their potential to cause serious environmental damage. Notorious example of this is the excessive plastic pollution in the oceans, 98% of which is the result of problematic (or non-existent) waste management practices in low- or middle-income countries outside the European Union (EU) and the United States of America (USA) [1]. Although this is primarily a waste treatment issue, there has also been an increasing focus on biodegradable polymers over the past decade. Among these, poly(lactic acid) (PLA) has been produced commercially in the largest quantities, in addition, PLA is obtained from renewable resources.

The aim of my research was to develop composite systems that, due to their lower density, could offer an environmentally friendly alternative for product designers in the future, thus providing the opportunity to gradually replace the conventional solutions and petrol-based raw materials currently in use. My goal was to effectuate the value-adding modification of PLA, which is an intensively researched, promising raw material with properties similar to polyethylene terephthalate (PET). Besides its high tensile strength and modulus, nevertheless, it is characterised by low elongation at break and poor impact resistance, so it is essential to improve these properties. By developing self-reinforced composites and highly porous foams, these drawbacks can be offset, while also serving the objective of weight reduction. The relatively low melt strength and slow crystallisation of PLA have a negative effect on the foamability; therefore, these characteristics must also be improved. In addition, foamed PLA is even more flammable than the raw material, so a suitable flame-retardant (FR) additive system is required to produce a safe product. Since, according to the literature, FR PLA foams have not yet been produced by continuous technology (e.g., extrusion), the way of implementation abounds in open questions.

It is important to consider the raw material of the end-of-life product as a valuable resource, therefore the recycling of biopolymer products is also an issue to be addressed. Prior to the production of SRCs, design for recycling is already taken into account. In the case of PLA the main challenge is to prevent hydrolytic degradation during the series of hot processing steps (extrusion, injection moulding). Since the reinforcing and matrix materials of SRCs are

¹ J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan, K. L. Law: *Plastic waste inputs from land into the ocean*. *Science*, 347(6223), (2015) 768–771.

made of similar (or identical) polymers, there is also a small difference (i.e. processing window) between their melting temperatures (T_m). Accordingly, the manufacturing parameters must be adjusted so that proper fibre-matrix adhesion is achieved, but fibres are not damaged. In some cases, the processing window can only be increased by crystallisation of the fibres, so the crystalline structure formed during the production and annealing of PLA fibres have a major influence on the properties of the final product.

In my doctoral work, the production, testing and application-oriented development of lightweight biopolymer composite systems were carried out, requiring synthetic, technological, analytical, and methodological developments at the same time. The topicality of the research is given by the fact that reducing the weight of products, thus the amount of raw material used, is one of the most obvious directions of development towards the sustainability of many industries. When creating composites, the advantageous properties of different raw materials are combined, and high value-added, high-performance products can be manufactured by the appropriate choice of composition and structure. Both SRCs and polymer foams meet these criteria, so the objective of my research was to characterise and improve the functional properties of such heterogeneous systems, and to further develop their production technology.

2 LITERATURE REVIEW

2.1 Supercritical CO₂-aided extrusion foaming

During physical foaming, certain gases, or liquids (e.g., nitrogen, pentane, hexane) are mixed in the polymer melt under pressure as physical blowing agents (PBAs), and then by reducing the pressure, the gases are released within the melt, their volume expanding, thereby causing the polymer to foam [2]. Carbon dioxide (CO₂) is also used as PBA because it is non-toxic, non-flammable, chemically inert [3]. During extrusion foaming, the polymer melt is usually processed at high pressure and high temperature, under which conditions CO₂ is in a supercritical state. The critical pressure of CO₂ is 7.38 MPa and its critical temperature is 31.1°C, if the processing parameters exceed these values, diffusion coefficient and viscosity of supercritical CO₂ (sc-CO₂) are similar to those of gases, but their density and solubility is more comparable to that of liquids.

2.2 Effects of natural fibres on PLA foams

Relatively poor thermal resistance and low toughness are the two most significant drawbacks of PLA. Hence, natural fibres are frequently blended with PLA as reinforcement with aspiration to improve these mechanical properties. For instance, aiming to obtain crystalline PLA composites of high HDTs, the outstanding nucleating ability of basalt fibres has been employed by Tábi et al. [4]. Cellulose micro- and nanofibres, due to their large surface area, high modulus of elasticity and high aspect ratio, were investigated as reinforcements for PLA foams, most particularly for foams made via the sc-CO₂-assisted batch process [5]. When natural fibres are added to a lightweight foam structure, achieving simultaneous improvement in mechanical performance along with other desirable properties might be quite complex. This

² A. Praller: *Foaming Plastics with Inert Gases*. *Kunststoffe*, 95(6) (2005) 96–99.

³ M. Sauceau, J. Fages, A. Common, C. Nikitine, E. Rodier: *New challenges in polymer foaming: A review of extrusion processes assisted by supercritical carbon dioxide*. *Progress in Polymer Science*, 36(6) (2011) 749–766.

⁴ Tábi T., Tamás P., Kovács J. G.: *Chopped basalt fibres: A new perspective in reinforcing poly(lactic acid) to produce injection moulded engineering composites from renewable and natural resources*. *Express Polymer Letters*, 7 (2013) 107–119.

⁵ Matuana L. M., Faruk O.: *Effect of gas saturation conditions on the expansion ratio of microcellular poly(lactic acid)/wood-flour composites*. *Express Polymer Letters*, 4, 621–631 (2010).

is because the final properties of the foams are directly controlled by several factors including dispersion of filler in the polymer matrix, fibre orientation, voids and porosity, pore structure, adhesion, interfacial interactions between filler and polymer matrix, and the percentage weight concentration of filler used [6]. Accordingly, Ding et al. showed that cell density increases and expansion ratio decreases with increasing cellulose nanofibre content [7]. However, cellulose-containing highly porous PLA foams produced by the continuous extrusion foaming method is rarely found in the literature. The field of sc-CO₂-assisted continuous foaming of cellulose fibre reinforced PLA is of scientific interest, also considering the favourable flame-retardant attributes of this multifunctional additive.

2.3 Flame retardancy of PLA foams

Today, high-tech applications demand polymers to have not only excellent mechanical properties but also increased fire safety in order to satisfy various regulatory standards. Ensuring fire safety is a prerequisite to deliver the maximum benefits of polymer products with regard to performance and sustainability [8]. Foams made from highly combustible polymers are much more flammable than the base material; due to the excellent thermal insulation of the cells, the high local temperature required for combustion develops faster after ignition, and the matrix material does not dissipate heat. High porosity foams have a high specific surface area, which also increases flammability.

In the literature, intumescent flame-retardant (IFR) systems are favourably used to reduce the flammability of PLA [9]. It was also found that the efficiency of the IFR system can be noticeably increased by combining it with nanoparticles such as montmorillonite [10]. Furthermore, the charring ability of the IFR system has also been investigated with renewable carbonizing agents such as cellulose.

Nevertheless, flame retardancy of PLA foams is a special, new field of research, therefore only limited sources of literature exist, which, moreover, exclusively deal with batch foaming technologies. These pioneering works have been carried out by Zhai et al. [11, 12], who prepared phosphorous flame-retardant PLA foams by solid state foaming, and by using starch and graphene as coactive additives, respectively. The produced foams showed non-uniform cell structure, which they explained by the poor cell nucleation ability of the used flame-retardant particles, and their weak interfacial bonding with the matrix. Therefore, it is still an actual challenge of research to produce microcellular PLA foams in flame-retarded form, preferably by means of the industrially more relevant extrusion technology.

⁶ K. Oluwabunmi, N.A. D'Souza, W. Zhao, T.-Y. Choi T. Theyson: *Compostable, fully biobased foams using PLA and micro cellulose for zero energy buildings*. Scientific Reports, 10 (2020) 17771.

⁷ W. D. Ding, T. Kuboki, A. Wong, C. B. Park, M. Sain: *Rheology, thermal properties, and foaming behavior of high D-content polylactic acid/ cellulose nanofiber composites*. RSC Advances, 5 (2015) 91544–91557.

⁸ Q. de Hults, M. El Houssami: *A European framework to ensure fire safety in taller buildings*. 3rd International Symposium on Fire Safety of Facades, (2019)

⁹ G. Fontaine, S. Bourbigot: *Intumescent poly (lactic acid): a nonflammable material*. Journal of Applied Polymer Science, 127 (2013) 4967–4973.

¹⁰ S. Li, H. Yuan, T. Yu, W. Yuan, J. Ren: *Flame-retardancy and anti-dripping effects of intumescent flame retardant incorporating montmorillonite on poly (lactic acid)*. Polymers for Advanced Technologies, 20 (2009) 1114–1120.

¹¹ J. Wang, Q. Ren, W. Zheng, W. Zhai: *Improved Flame-Retardant Properties of Poly(lactic acid) Foams Using Starch as a Natural Charring Agent*. Industrial & Engineering Chemistry Research, 53 (2014) 1422–1430.

¹² K. Wang, J. Wang, D. Zhao, W. Zhai: *Preparation of microcellular poly(lactic acid) composites foams with improved flame retardancy*. Journal of Cellular Plastics, 22 (2016) 1–19.

2.4 Self-reinforced polymer composites

The concept of *self-reinforced composites* (SRCs) is based on the combination of thermoplastic fibres as a reinforcement phase within an isotropic thermoplastic matrix of the same (or a similar) chemical composition. In a broader sense, both the reinforcing and matrix materials belong to the same polymer family [13]. The advantages of SRC systems include the ability to achieve outstanding interfacial adhesion between the chemically similar components [14]. The ease of recycling also has to be emphasised as they represent likely the best recycling option when reprocessing via remelting is targeted. Self-reinforcement is a promising means of producing impact resistant and lightweight composites from biopolymers without compromising their reprocessability or biodegradability.

The literature shows that the reinforcement of PLA SRCs was mostly manufactured via conventional fibre production technologies, i.e. melt spinning and drawing [15]. Popular manufacturing method to obtain micro- or nanofibrous PLA mats are electrospinning (ES) and melt-blowing (MB). Electrospun stereocomplex nanofibres were produced by *Tsuji et al.* thus increasing the T_m to about 222°C, in contrast to the T_m (178°C) of PLLA fibres [16]. *Kurokawa et al.* compiled highly transparent SRCs using compression moulded PLLA sheets and electrospun stereocomplex PLA fibres by applying a compaction pressure of 8 MPa at 180°C [17]. *Somord et al.* used the electrospinning technique as well to produce reinforcement for their PLA SRCs [18]. Both *Kurokawa et al.* and *Somord et al.* took advantage of a heat treatment step, characterisations on the products were conducted after the drying process at 100°C, 2 h [17] or 50°C, in the presence of ethanol solvent [18]. While *Somord et al.* failed to mention that an annealing process could also occur during heat treatment, *Kurokawa et al.* acknowledged the annealing effect of the drying process on the completely amorphous electrospun fibres proven by WAXS analysis. The composites were manufactured via hot compaction of the PLA fibres, applying 165°C, 6 MPa and a compression timeframe of 10–60 s.

Recently, high-speed electrospinning (HSES) technique has been developed to increase the productivity of this process [19]. To the best of our knowledge, the HSES concept has not yet been utilised to produce PLA fibres and melt-blown PLA fibres were not studied either as reinforcements of SRCs. It was found crucial to comprehensively examine the crystalline structure of the reinforcing fibres, as different crystalline forms or even stereocomplex crystal domains may be key factors in SR PLA composites [17].

¹³ B. Alcock, T. Peijs: *Technology and Development of Self-Reinforced Polymer Composites*. In: A. Abe, H. H. Kausch, M. Möller, H. Pasch (Eds.) *Polymer Composites – Polyolefin Fractionation – Polymeric Peptidomimetics – Collagens*, Advances in Polymer Science, vol. 251 Springer, Berlin, Heidelberg (2011) 1–76.

¹⁴ C. Gao, L. Yu, H. Liu, L. Chen: *Development of self-reinforced polymer composites*. *Progress in Polymer Science*, 37(6) (2012) 767–780.

¹⁵ K. Bocz, M. Domonkos, T. Igricz, Á. Kmetty, T. Bárány, G. Marosi: *Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance*. *Composites Part A: Applied Science and Manufacturing*, 70 (2015) 27–34.

¹⁶ H. Tsuji, M. Nakano, M. Hashimoto, K. Takashima, S. Katsura, A. Mizuno: *Electrospinning of poly(lactic acid) stereocomplex nanofibers*. *Biomacromolecules*, 7(12) (2006) 3316–3320.

¹⁷ N. Kurokawa, A. Hotta: *Thermomechanical properties of highly transparent self-reinforced polylactide composites with electrospun stereocomplex polylactide nanofibers*. *Polymer*, 153 (2018) 214–222.

¹⁸ K. Somord, O. Suwantong, N. Tawichai, T. Peijs, N. Soykeabkaew: *Self-reinforced poly(lactic acid) nanocomposites of high toughness*. *Polymer*, 103 (2016) 347–352.

¹⁹ Z. K. Nagy, A. Balogh, B. Démuth, et al.: *High speed electrospinning for scaled-up production of amorphous solid dispersion of itraconazole*. *International Journal of Pharmaceutics*, 480 (2015) 137–142.

3 METHODS

3.1 Equipment used for sample preparation

Melt compounding

Labtech Scientific LTE 26-44 modular twin-screw extruder with a screw diameter of 26 mm and a length to diameter (L/D) ratio of 44.

Supercritical CO₂-aided melt extrusion foaming of PLA foams with natural fibres

Rheoscam, SCAMEX single-screw extruder with a screw diameter of 30 mm and a length to diameter ratio (L/D) of 35 equipped with a Teledyne Isco 260D syringe pump.

Supercritical CO₂-aided melt extrusion foaming of flame retarded PLA-foams

Collin Teach-Line ZK 25T type co-rotating twin-screw extruder with a screw diameter of 25 mm and a L/D ratio of 24 equipped with a Teledyne Isco 260D syringe pump.

Melt-blowing

Quick Extruder QE TS16 02/2016A type twin-screw pharmaceutical extruder with an L/D ratio of 25.

High-speed electrospinning (HSES)

A Quick2000 Ltd. HSES setup consisting of a stainless steel spinneret equipped with orifices ($d = 330 \mu\text{m}$) connected to a high-speed motor, a high voltage generator (45 kV) and a peristaltic pump.

Annealing - thermally-induced crystallisation

Nonwoven mats were placed in a conventional oven for annealing at 85°C. The sample temperature was precisely measured using a thermocouple and a digital multimeter.

Annealing - solvent-induced crystallisation

PLA nonwoven mats were placed in a covered Petri dish containing 99.5% ethanol. The solvent was previously heated and held at 40°C.

Compression moulding

Collin GmbH Teach-Line Platen Press 200E hydraulic press equipped with a square mould.

3.2 Characterisation methods

Rheological measurements

TA Instruments AR 2000 type rotational rheometer, with 25 mm diameter parallel-plate geometry.

Scanning electron microscopy (SEM)

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

Porosity measurements

The void fraction and expansion ratio of the foams were determined by water displacement method (Archimedes method).

Differential scanning calorimetry (DSC) of foamed samples and melt-blown fibres

TA Instruments Q2000 type instrument.

DSC analysis of high-speed electrospun fibres

Mettler Toledo DSC3+ type instrument

Modulated differential scanning calorimetry (MDSC)

Mettler Toledo DSC3+ type instrument using TOPEM® mode.

Thermogravimetry

TA Instruments Q5000 type instrument.

UL-94 flammability tests

UL-94 flammability tests were performed according to the ASTM D 635 and ASTM D 3801 standards.

Determination of limiting oxygen index (LOI)

Limiting oxygen index (LOI) measurements were performed according to the ASTM D 2863 standard.

Pyrolysis combustion flow calorimetry (PCFC)

Fire Testing Technology FAA Micro Calorimeter, according to ASTM D-7309.

Fourier transform infrared spectrometry (FTIR)

Bruker Tensor 37 type FTIR Spectrometer equipped with DTGS detector.

X-ray diffraction (XRD)

PANalytical X'pert Pro MDP diffractometer using Cu-K α radiation (1.541 Å) and Ni filter, a current of 30 mA, and a voltage of 40 kV. The samples were placed on a Si sheet and analysed between 2 θ angles of 4° and 44°.

Raman micro-spectroscopy

Horiba Jobin-Yvon LabRAM system coupled with an Olympus BX41 optical microscope and an external 532 nm frequency-doubled Nd-YAG laser source.

Localised thermomechanical analysis (LTMA)

TA Instruments μ TA 2990 Micro-Thermal Analyzer equipped with a thermal probe.

Compression tests

TA Instruments AR2000 Rheometer with plate-plate adjustment.

Tensile tests

ZWICK Z005 universal testing machine equipped with a 20 N and a 5 kN load cell.

4 RESULTS AND DISCUSSION

4.1 Continuous manufacturing of PLA biocomposite foams and characterisation thereof

In this work, natural fibre-containing PLA foams, as potential green replacements for petroleum-based polymer foams, were investigated. High porosity, microcellular biocomposite foams (Figure 1) were manufactured by continuous, sc-CO₂ assisted extrusion process, the same method that could be easily scaled-up even towards industrial-scale applications. To obtain uniform cell structures with increased cell density, epoxy-functionalised chain extender (CE) and talc were applied. The effect of cellulose and basalt fibres was investigated on the morphology and mechanical properties of the PLA foams.

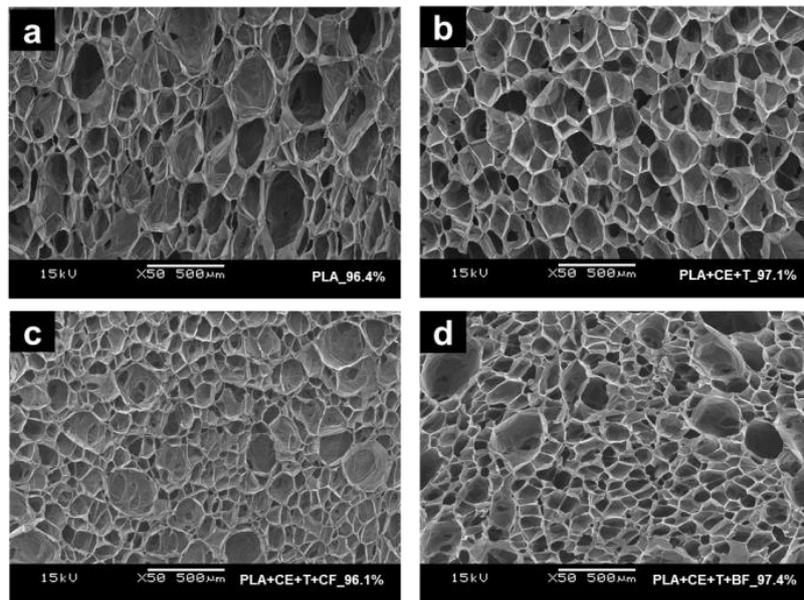


Figure 1 SEM micrographs of the cell morphologies obtained for highly expanded ($V_f > 95\%$) PLA foams.

It was found that the addition of 5 wt% cellulose or basalt fibres provides lower processing temperature profiles for PLA foam production (Figure 2 a). In accordance with the literature, it was evinced that natural fibres increase the melt viscosity and promote the heterogeneous cell nucleation. As a result, composite foam structures with smaller cell diameters and porosity higher than 95% could be obtained. However, due to the fibre distribution and the weak fibre-matrix adhesion, the fibre-containing foams have wider cell diameter distribution and increased open cell ratio compared to the fibre-free CE and talc containing foam (Figure 1). In the case of cellulose fibres, it is supposed that the increased dynamic viscosity and thus the hindrance of molecular chain mobility decreased the crystallisation. Basalt fibres can serve as reinforcement providing improved compression strength comparing to PLA foams (Figure 2 b). However, the best mechanical performance was achieved without natural fibres, by applying only the combination of CE and talc. The compression strength of this foam reaches 100 kPa. It is believed that further chemical or physical modifications, such as reinforcement and flame retardancy, could promote the market penetration of PLA foams in technical application fields as well. Due to their pronounced charring activity combined with intumescent flame-retardant systems, the multifunctional cellulose fibres could not only play the role of reinforcement in PLA foams, but also act as charring agent ensuring the fire safety of the product.

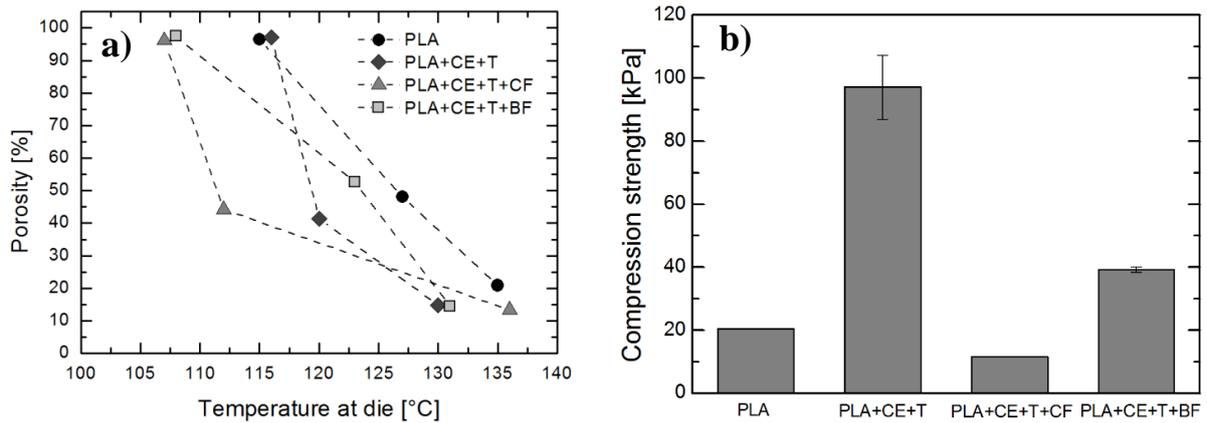


Figure 2 a) Effect of die temperatures on the porosity of PLA foams extruded at 8% of CO₂
 b) Compression strength of highly expanded (V_f > 95%) PLA foams

Related publications: I, VI, XVI

4.2 Development of flame retarded PLA foams

In this study, flame-retarded (FR) microcellular PLA foams were successfully manufactured by sc-CO₂-assisted extrusion foaming technology. During production, CE was used to improve the rheological behaviour and montmorillonite (MMT) was applied as nucleating agent for better foamability and as potential FR synergist at the same time. In spite of the fact that polymer foams are more flammable than their solid counterparts, significant flame retardancy was achieved by incorporating ammonium polyphosphate (APP) based intumescent flame-retardant (IFR) additive in the cellular structure. The efficiency of the IFR was enhanced by combining it with FR-treated cellulose fibres, which noticeably increased the charring ability of the system, as revealed by the thermogravimetric analysis (TGA) results and pyrolysis combustion flow calorimetry (PCFC) measurements.

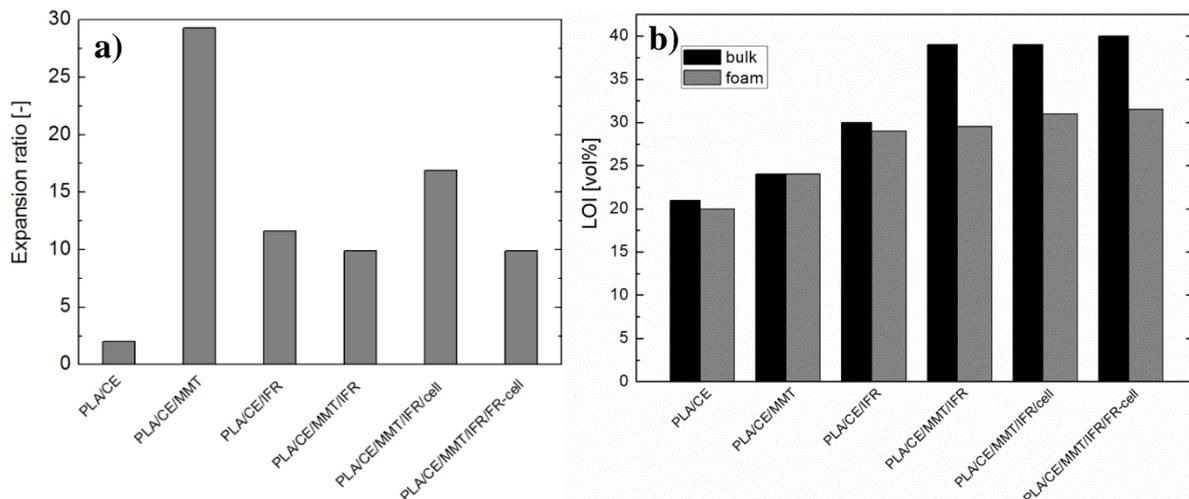


Figure 3 a) expansion ratio of the PLA foams
 b) LOI values of the prepared flame-retarded bulk and foamed samples

Supercritical CO₂-aided extrusion resulted in low-density foams having void fractions higher than 90% accompanied with expansion ratios of 10-20 (Figure 3 a), depending on the filler-matrix compatibility even at relatively high (15.0% APP, 1.5% MMT, 3.0% cellulose) additive contents. As a result, 40% reduction in specific peak of heat release rate, UL94 V-0 rating accompanied with LOI value as high as 31.5 vol% were reached for the FR-cell and IFR

containing PLA foam (Figure 3 b). Also, among the examined foams, the highest degree of crystallinity reached 19%, composed of the more stable α form, indicating nucleating effect of the used bio-based charring agent. In addition to cushion packaging, the prepared flame-retarded biocomposite foams could potentially find applications in the higher value-added E&E or transportation industries. SEM images revealed that the effectively flame-retarded PLA foams have uniform cellular structure with characteristic cell diameters of 100-150 μm . Major part of the FR particles was found to be embedded in the cell wall joints, which is of key importance regarding expandability and charring ability. From this respect, extrusion foaming was found to be favourable compared to the batch technologies due to the continuous mixing of the components and the typically higher temperature applied during foam forming, which allows the active fillers to allocate in the polymer melt simultaneously with the cell growth. As a result, fewer microholes will be induced at the filler-matrix interfaces in the thin cell walls, and thus lower open-cell ratios and higher expansion ratios can be obtained. Considering the flame-retardant properties, more polymer is available for the well-embedded active fillers, located in the cell wall joints, to be affected and thus enhanced char forming and improved flame-retardant properties can be obtained.

Related publications: II, VII, XVII, XXIII, XXIV, XXV, XXVI

4.3 Application of melt-blown PLA fibres in self-reinforced composites

The present study demonstrates the manufacturing method of one-component microfibrinous PLA mats by the solvent-free melt-blowing technique, focusing on the effect of the D-lactide content and thermal annealing on the morphological, thermal, and mechanical properties of the produced PLA fibres. The obtained nonwoven mats were further processed by hot compaction to form PLA SRCs, the corresponding properties of which were investigated as well.

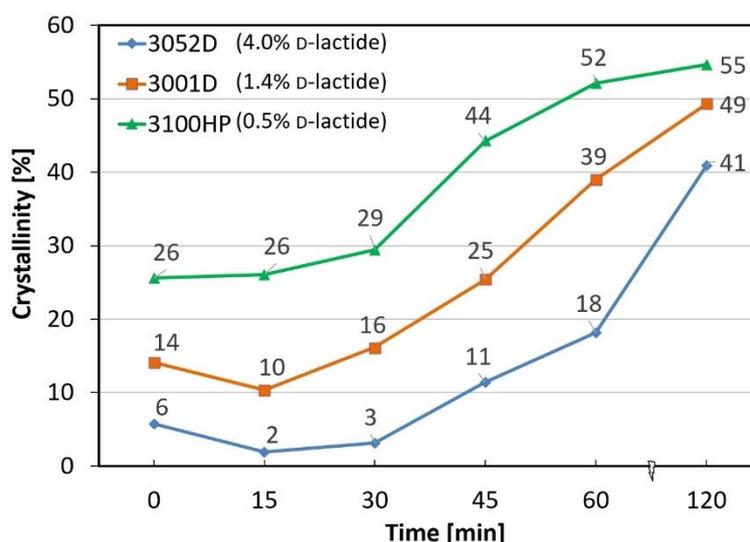


Figure 4 Crystallinity of PLA fibres as a function of annealing time

PLA microfibrinous nonwoven mats, serving as precursors for self-reinforced composite preparation, were prepared by melt-blowing technology. Fibres with diameters ranging between 2–14 μm were obtained with a productivity rate of 36 g/h from three types of PLA grades differing in D-lactide content. The crystalline fractions of the obtained fibres were significantly increased by thermal annealing at 85°C for 2 h with the aim of improving their thermal resistance (Figure 4). The heat treatment induced, however, relaxation of the molecular

orientation in the fibres, and thus decreased modulus values were measured for the annealed fibres. Nevertheless, self-reinforced composites with improved mechanical performance and adequate morphology could only be obtained from thermally pre-treated fibres. The improved thermal resistance of the highly crystalline PLA microfibrils proved to be of key importance regarding the ability of partial melting, i.e., matrix formation, and to obtain adequate consolidation quality by hot compaction. As a conclusion for the sake of future advancements in the field, PLA grades of low D-lactide content should be considered as reinforcement. Annealing conditions must be selected carefully, ensuring minimal fibre relaxation and maximal crystallinity. In an effort to prevent thermal degradation of the PLA during processing, and consequently the severe deterioration of molecular weight and mechanical properties, milder fibre production techniques such as solvent spinning methods might be considered. For further optimisation of SRC manufacturing, a more profound analysis of the thermomechanical properties and crystalline forms of the PLA fibres is recommended.

Related publications: III, VIII, XXII, XVIII, XIX, XX

4.4 Effects of thermal annealing and solvent-induced crystallisation on the structure and properties of PLA microfibrils produced by high-speed electrospinning

This research concentrates on the marked discrepancies in the crystalline structure of PLA nano- and microfibrils, achieved by different annealing strategies (Figure 5). Microfibrillar PLA nonwoven mats were successfully manufactured by high-speed electrospinning, reaching a remarkable productivity of 40 g/h, even higher than that of the melt-blowing technique used in the previous study. The effects of conventional thermal annealing and ethanol-induced crystallisation were investigated on the thermal and mechanical properties of low D-lactide-containing fibres, as well as on the morphology and the crystal structure of the microfibrils. SEM images revealed a more noticeable relaxation of the samples treated at 85°C; on the other hand, ethanol-treated fibres mostly preserved their original shape. The fibre diameters were in the range of 0.25–8.5 µm and were found to increase by 0.3 and 0.6 µm as a result of solvent and heat treatment, respectively.

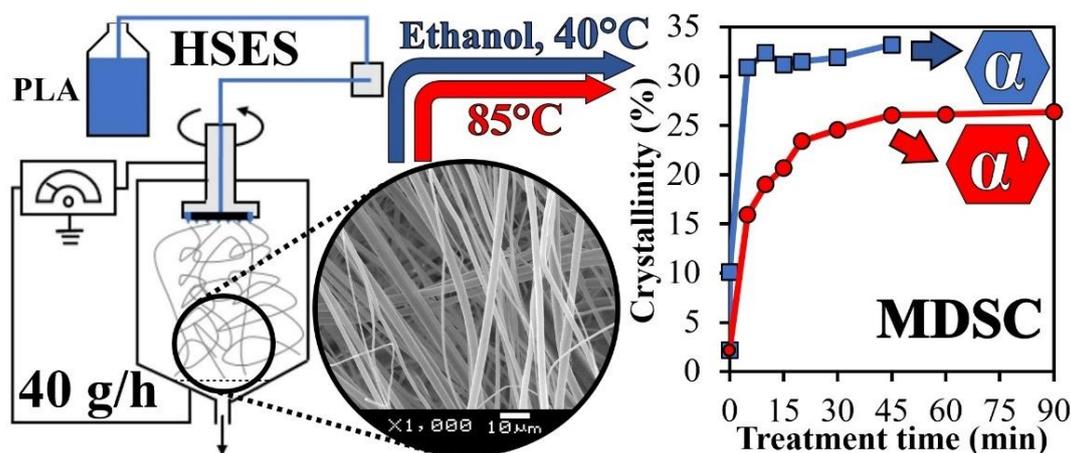


Figure 5 Graphical outline of the topic (HSES fibre production, effect of annealing)

Conventional DSC showed that solvent-induced crystallisation progresses 2-3 times more rapidly, besides, the large surface area to volume ratio further increases the efficiency of the methods. By using cold crystallisation, recrystallisation and melting enthalpy values of different crystalline forms, a novel formula developed for the estimation of crystalline fraction provided more accurate results compared to the previously used equation. Differentiation

between the melting of α' form and recrystallisation to α form within a single sample was accomplished using temperature-modulated DSC method (Figure 6). As this effect was absent from the MDSC curves of ethanol-treated fibres, it was evinced that this technique exclusively induces the formation of the more stable α polymorph. Raman micro-spectroscopy and XRD measurements confirmed this phenomenon, allowing in-line observation of the shift between α and α' crystalline structure. Based on the results of the LTMA measurements applied for single fibres, superior heat resistance of both recrystallised samples was verified when compared to non-treated microfibrils. Ethanol treatment resulted in fibres with a slightly higher melting temperature range due to their high α content. Tensile tests showed that annealing increased the tensile strength of the ethanol- and heat-treated nonwoven mats by 50–120% and 120–200%, respectively. We also found that better structural integrity plays a key role in improved mechanical properties of the heat-treated PLA nonwovens.

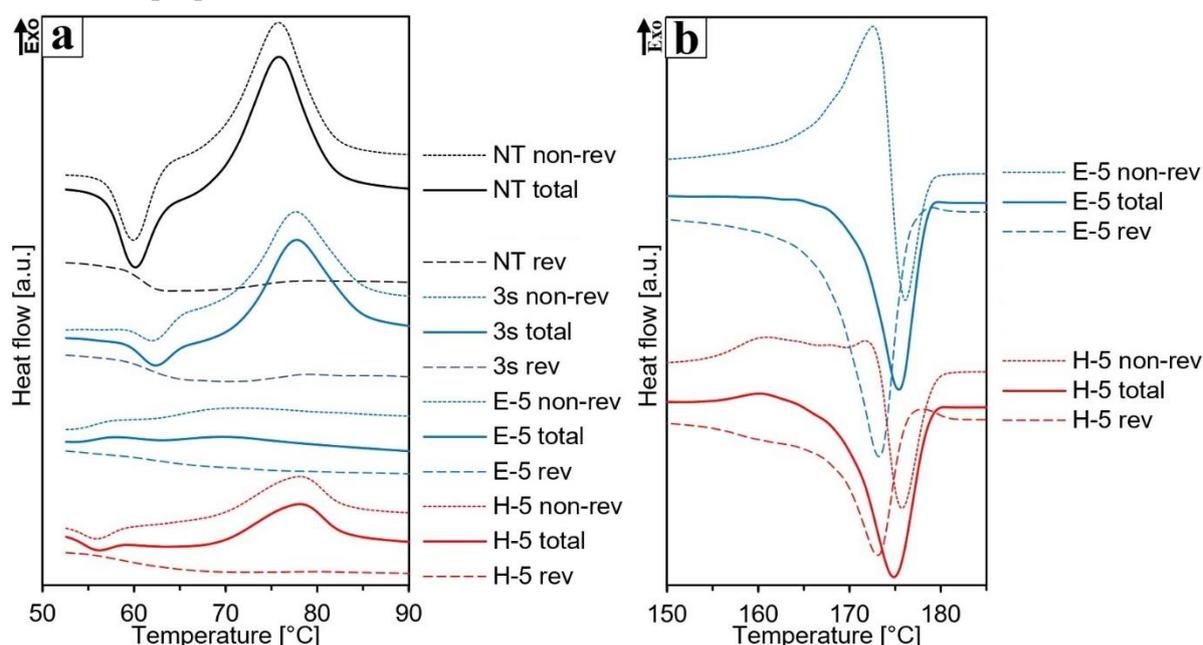


Figure 6 MDSC curves in the temperature ranges of (a) 50–90°C and (b) 150–185°C

The results might contribute to further research of lightweight PLA SRCs; the use of multiple layers of differently treated, thin nonwovens could be considered. Improvement in the fibre manufacturing method is also possible, high-speed coaxial or dual electrospinning of different PLA grades would widen the processing temperature window of SRC production. Recrystallised PLA nonwovens, due to their increased thermal stability and mechanical properties, are expected to find application in even wider fields such as medical aids, packaging or clothing.

Related publications: IV, XX, XXI

5 THESIS FINDINGS

1. Low-density ($\rho < 0.05 \text{ g/cm}^3$), natural fibre-containing polylactic acid (PLA) composite foams were firstly manufactured by supercritical carbon dioxide-assisted extrusion. It was found that compared to the fibre-free material the addition of 5% cellulose or basalt fibre allows the formation of foam cells at significantly lower processing temperatures. As a result of this advantage and the increased dynamic viscosity of the biocomposite blends, smaller cell diameters were obtained compared to fibre-free PLA foams. [I, VI, XVI]
2. Low-density ($0.05\text{--}0.13 \text{ g/cm}^3$), flame retarded microcellular PLA foams were firstly manufactured by supercritical carbon dioxide-assisted extrusion. Although PLA foams without flame-retardants are more flammable than their bulk counterparts, significant flame retardancy was achieved using a novel intumescent flame-retardant additive system, including cellulose treated with phosphorus and boron-containing compounds. 40% reduction in peak of heat release rate, UL-94 V-0 (i.e. self-extinguishing) rating accompanied with limiting oxygen index value as high as 31.5 vol% were reached for the developed flame-retarded PLA foam. [II, VII, XVII, XXIII, XXIV, XXV, XXVI]
3. PLA fibres with a diameter of 2-14 μm were produced by melt-blowing and used for self-reinforced composite preparation for the first time. The environmentally friendly, solvent-free fibre production technology allowed the manufacturing of nonwoven webs, the processability and thermomechanical properties of which were improved by annealing. The composites prepared by hot compaction of PLA microfibrils with 2–7 times higher crystalline proportions (compared to the original webs) have 47% higher tensile strength than the self-reinforced composites manufactured without the post-crystallisation step. [III, VIII, XXII, XVIII, XIX, XX]
4. Annealing methods of PLA nonwoven webs, produced by high-speed electrospinning (HSES) technique with a productivity higher than conventional single-needle electrospinning (40 g/h), were compared. It was evinced that the heat treatment promotes the formation of the less stable α' crystal modification, while ethanol treatment facilitates the formation of a more stable α crystalline form. Besides, higher crystallinity of the webs was obtained considerably faster by ethanol-assisted annealing than by conventional heat treatment. [IV, XX, XXI]
5. A new formula was proposed and applied for the calculation of complex crystalline compositions of poly(lactic acid), which, by using cold crystallisation, recrystallisation and melting enthalpy values of different crystalline forms based on temperature-modulated differential scanning calorimetry (MDSC) data, provides more accurate crystallinity results compared to the previously used methods. [IV, XX, XXI]

6 APPLICABILITY OF THE RESULTS

1. During the NVKP 16-1-2016-0012 project implemented in the consortium of BME, DS Smith Packaging Hungary Kft. and Polifoam Műanyagfeldolgozó Kft, a PLA cushioning material with extremely low density ($\sim 0.04 \text{ kg/m}^3$) and outstanding compressive strength ($111 \pm 20 \text{ kPa}$) was developed. The development of the twin-screw extruder used for physical foaming was realised within the framework of the project; the L/D ratio was increased to 30 by addition of a 5th zone (Figure 7). The extruder was also equipped with a gear melt pump to provide consistent flow rates, which are independent of temperature and pressure. A static mixer with robust air cooling was also inserted between the gear pump and the die to subserve heat dissipation from the melt. These additional parts eventually improved the manageability of the continuous foaming process. Due to a request from the partners, flat PLA foams were also produced using a $0.5 \times 25 \text{ mm}$ sheet die.

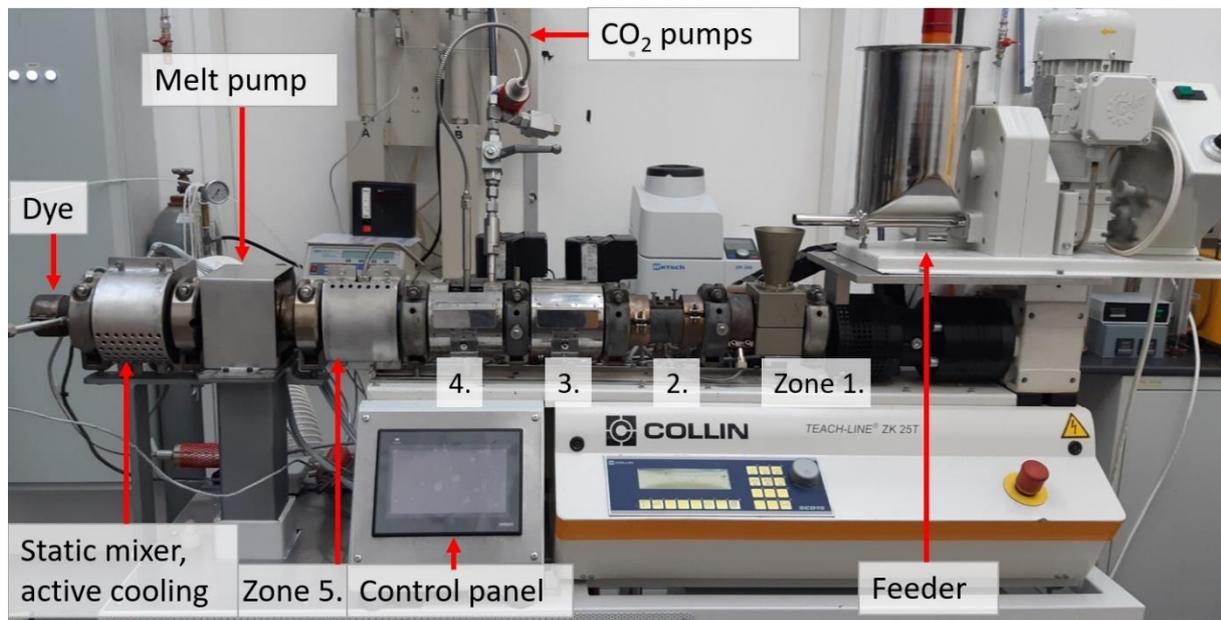


Figure 7 Twin-screw foaming extruder with additional parts

The flat PLA foams were applied on cardboard pallets, on which testing packages were located. Using a PDT-56 Precision Drop Tester, our partner conducted packaging performance drop tests from 610 mm height. Due to the prominent microcellular structure of the manufactured PLA foam, it showed better energy absorption than the polystyrene cushioning material widely used in the industry. Based on our accelerated aging tests, stability of the cushioning material is adequate, and they can be completely degraded in compost.

2. Based on new recognitions and the experience gained during this research, elastic and piezoelectric PLA foams were developed. The invention has been the subject of a priority patent application submitted by the Budapest University of Technology and Economics (SZTNH case number: P2000412). [V]

3. PLA cases were manufactured by vacuum forming using annealed PLA fibres. The micro- and nanofibrous mats produced by HSES did not deteriorate during heating at 100°C for 80 sec. Boxes modified by PLA mats can be used e.g. as an absorbent, or as a carrier for antioxidants and preservatives in a multifunctional packaging system.

7 PUBLICATIONS

7.1 Publications on which thesis findings are based

- [I] K. Bocz, T. Tábi, D. Vadas, M. Sauceau, J. Fages, G. Marosi: *Characterisation of natural fibre reinforced PLA foams prepared by supercritical CO₂ assisted extrusion*. Express Polymer Letters, 10(9), **2016**, 771–779.
<https://doi.org/10.3144/expresspolymlett.2016.71>
IF: 2.983, C: 31
- [II] D. Vadas, T. Igricz, G. Marosi, K. Bocz: *Flame retardancy of microcellular poly(lactic acid) foams prepared by supercritical CO₂-assisted extrusion*. Polymer Degradation and Stability, 153, **2018**, 100–108.
<https://doi.org/10.1016/j.polymdegradstab.2018.04.021>
IF: 3.780, C: 12
- [III] D. Vadas, D. Kmetykó, G. Marosi, K. Bocz: *Application of Melt-Blown Poly(Lactic Acid) Fibres in Self-Reinforced Composites*. Polymers, 10(7), **2018**, 766.
<https://doi.org/10.3390/polym10070766>
IF: 3.164, C: 4
- [IV] D. Vadas, Z. K. Nagy, I. Csontos, G. Marosi, K. Bocz: *Effects of thermal annealing and solvent-induced crystallisation on the structure and properties of poly(lactic acid) microfibrils produced by high-speed electrospinning*. Journal of Thermal Analysis and Calorimetry, 25. January **2020**
<https://doi.org/10.1007/s10973-019-09191-8>
IF: 2.731, C: 2

7.2 Further related articles

- [V] D. Vadas (70%), T. Igricz (15%), K. Bocz (10%), G. Marosi (5%): *Politejsav alapú hab és ennek előállítására szolgáló eljárás (Poly(lactic acid)-based foam and manufacturing the same)*, Szellemi Tulajdon Nemzeti Hivatala (Hungarian Intellectual Property Office) case number: P2000412 (priority patent application submitted by Budapest University of Technology and Economics on December 4th **2020**, 13:42)
- [VI] K. Bocz, T. Igricz, Á. Kmetty, T. Tábi, B. Szabó, D. Vadas, L. Kiss, T. Vigh, G. Marosi: *Funkcionalizált biopolimer habok fejlesztése szuperkritikus széndioxiddal segített extrúzióval*. Polimerek, 2(2), **2016**, 46–49.
- [VII] D. Vadas, K. Bocz, T. Igricz, T. Tábi, B. Szabó, G. Marosi: *Égésgátolt politejsav habok előállítása szuperkritikus szén-dioxiddal segített extrúzióval*. Polimerek, 3(5), **2017**, 156–160.
- [VIII] D. Vadas, D. Kmetykó, B. Szabó, G. Marosi, K. Bocz: *Ömledékfúvással gyártott mikroszálak felhasználása önerősített politejsav kompozitok előállítására*. Polimerek, 4(7-8), **2018**, 245–250.

7.3 Further articles

- [IX] D. Vadas, Á. Kmetty, T. Bárány, G. Marosi, K. Bocz: *Flame retarded self-reinforced polypropylene composites prepared by injection moulding*. Polymers for Advanced Technologies, 29(1), **2018**, 433–441.
<https://doi.org/10.1002/pat.4132>
IF: 2.162, C: 4

- [X] K. Bocz, K. E. Decsov, A. Farkas, D. Vadas, T. Bárány, A. Wacha, A. Bóta, G. Marosi: *Non-destructive characterisation of all-polypropylene composites using small angle X-ray scattering and polarized Raman spectroscopy*. *Composites: Part A: Applied Science and Manufacturing*, 114, **2018**, 250–257.
<https://doi.org/10.1016/j.compositesa.2018.08.020>
IF: 6.282, C: 1
- [XI] K. E. Decsov, K. Bocz, B. Szolnoki, S. Bourbigot, G. Fontaine, D. Vadas, G. Marosi: *Development of Bioepoxy Resin Microencapsulated Ammonium-Polyphosphate for Flame Retardancy of Polylactic Acid*. *Molecules*, 24(22), **2019**, 4123.
<https://doi.org/10.3390/molecules24224123>
IF: 3.267, C: 2
- [XII] K. Bocz, B. Szolnoki, A. Farkas, E. Verret, D. Vadas, K. Decsov, G. Marosi: *Optimal distribution of phosphorus compounds in multi-layered natural fabric reinforced biocomposites*. *Express Polymer Letters*, 14(7), **2020**, 606–618.
<https://doi.org/10.3144/expresspolymlett.2020.50>
IF: 3.083, C: 2
- [XIII] K. Bocz, F. Ronkay, B. Molnár, D. Vadas, M. Gyürkés, D. Gere, G. Marosi, T. Czigany: *Recycled PET foaming: supercritical carbon dioxide assisted extrusion with real-time quality monitoring*. *Advanced Industrial and Engineering Polymer Research* (accepted: 2nd March **2021**.)

7.4 Oral presentations

- [XIV] D. Vadas, K. Bocz, G. Marosi: *Flame retardancy of injection moulded, self-reinforced polypropylene composites*. 12th International Conference Students for Students, (22–25 April **2015**), Cluj-Napoca, Romania
- [XVI] D. Vadas, K. Bocz, G. Marosi: *Supercritical carbon dioxide aided extrusion foaming of biodegradable polymers*. 13th International Conference Students for Students, (13–17 April **2016**), Cluj-Napoca, Romania
- [XVII] D. Vadas, K. Bocz, G. Marosi: *Supercritical carbon dioxide aided extrusion foaming of biodegradable polymers*. 3rd International Conference on Bio-based Polymers and Composites, (28 August – 1 Sept. **2016**), Szeged, Hungary
- [XVIII] D. Vadas, D. Kmetykó, G. Marosi, Bocz K: *Application of melt-blown poly(lactic acid) filaments in self-reinforced composites*. *Polymers 2018: Design, Function and Application*, (21–23 March **2018**) Barcelona, Spain
- [XIX] D. Vadas, D. Kmetykó, K. Bocz, G. Marosi: *Preparation of self-reinforced poly(lactic acid) composites using melt-blown microfibrinous mats*. 18th European Conference on Composite Materials, (24–28 June **2018**) Athens, Greece
- [XX] D. Vadas, D. Kmetykó, K. Bocz, G. Marosi: *Comparison of fibre production methods for preparation of self-reinforced poly(lactic acid) composites*. 4th International Conference on Bio-based Polymers and Composites, (2–6 September **2018**), Balatonfüred, Hungary
- [XXI] G. Marosi, B. Démuth, D. Vadas: *Thermal and spectroscopic evaluation of the applicability of biopolymers for pharmaceutical and engineering purposes*. 2nd Journal of Thermal Analysis and Calorimetry Conference, (18–21 June **2019**) Budapest, Hungary

7.5 Poster presentations

- [XXII] D. Vadas, K. Bocz, M. Domonkos, T. Igricz, T. Bárány, G. Marosi: *Development of flame retarded self-reinforced composites from renewable resources*. International Conference on Bio-friendly Polymers and Polymer Additives, (19–21 May **2014**) Budapest, Hungary
- [XXIII] D. Vadas, K. Bocz, T. Igricz, B. Szabó, G. Marosi: *Green flame retardancy of microcellular poly(lactic acid) foams*. 16th European Meeting on Fire Retardant Polymeric Materials, (3–6 July **2017**) Manchester, United Kingdom
- [XXIV] D. Vadas, D. Kmetykó, K. Bocz, G. Marosi: *Phosphorus-based flame retardancy of microcellular poly(lactic acid) foams*. 22nd International Conference on Phosphorus Chemistry, (8-13 July **2018**) Budapest, Hungary
- [XXV] D. Vadas, D. Kmetykó, K. Bocz, G. Marosi: *Physical and Chemical Foaming of Flame Retarded Poly(lactic acid)*. 17th European Meeting on Fire Retardant Polymeric Materials, (26-28 June **2019**) Turku, Finland
- [XXVI] D. Vadas, D. Kmetykó, K. Bocz, G. Marosi: *Physical and Chemical Foaming of Flame Retarded Poly(lactic acid)*. XVII Conference of the George Olah Doctoral School - "Innovative research at the BME Faculty of Chemical Technology and Biotechnology" (23 September **2019**) Budapest, Hungary
- [XXVII] K. Bocz, B.Szolnoki, A. Farkas, E. Verret, D. Vadas, G. Marosi: *Flame retardancy of flax fabric reinforced polylactic acid composites*. XVIII Conference of the George Olah Doctoral School (28 September **2020**) Budapest, Hungary