**Final report on the 2013-2015 Hungarian Scientific Research Fund project named "Development of advanced polymer composites from renewable resources (OTKA K105257)"**

In the research period of 2013-2015 our first task was to review the literature of biodegradable polymers and reinforced biodegradable polymer composites or so called biocomposites. It was found that the most promising renewable resource based and inherently biodegradable polymer nowadays is the Poly(Lactic Acid) (PLA), while its mainly used reinforcements to make biocomposites are renewable resource based plant fibres (e.g. cellulose, flax, cotton, hemp, jute). In few cases basalt fibres were also used as an efficient reinforcement for PLA, since basalt is also considered as a natural, volcanic rock based mineral fibre with bioinert features and capable of increasing the mineral content of soil during its weathering. Finally, PLA was also found suitable for foaming based on literature data.
After reviewing the literature, materials were selected for purchasing. Injection moulding grade PLA was purchased as matrix material, while silane treated basalt fibres with various length and basalt fabrics, as well as cellulose fibres with various length and cellulose based plant fibre fabrics were purchased as reinforcements for biocomposite preparation.
In accordance with the OTKA project proposal, the selection and purchasing of the heat deflection temperature (HDT) measuring unit type CEAST HV3 6911.000 and the side-feeder type LSF 26 for the already available twin screw extruder were also performed (Fig. 1).


Fig. 1. The purchased CEAST HV3 6911.000 type heat deflection temperature measuring equipment (left) and the LSF 26 type side-feeder (right)

According to the physical foaming unit, unfortunately much higher quotations arrived than expected due to changed EUR/HUF rate, and thus it was decided not purchase it, but to collaborate with other departments, who already have a physical foaming unit for an extruder and perform the necessary measurements there.
According to the research plan of the 2013-2015 period of OTKA project (K105257) all the main research plan aims were successfully achieved including the development and analysis of short as well as long basalt and cellulose fibre reinforced PLA based biocomposites and the physical foaming of PLA and PLA based biocomposites. Additional research was also performed strictly related to PLA and PLA based biocomposites including nucleation to achieve high heat deflection temperature, increasing fire retarding and incorporating PLA to new melt processing technologies like fused deposition modelling (FDM) based rapid prototyping (RPT) or as nowadays called, additive manufacturing.

**According to the research based on basalt fibre reinforcement**, it was found that by incorporating 30wt% silane treated short (chopped) basalt fibres into PLA, an injection moulded composite with excellent mechanical properties could be fabricated namely with a tensile and flexural strength of 120 and 180 MPa, a tensile and flexural modulus of more than 7.6 and 10.4 GPa as well as a Charpy impact strength of 9.3 kJ/m$^2$ (notched) and 38.3 kJ/m$^2$ (unnotched) respectively (Fig. 2).

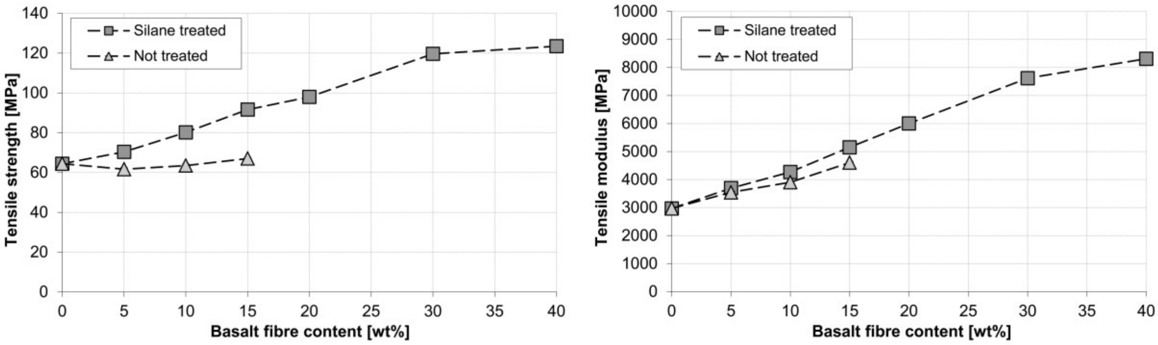


Fig. 2. Tensile strength (left) and tensile modulus (right) of the short basalt fibre reinforced PLA biocomposites

By using scanning electron microscopy (SEM) strong adhesion was observed between the phases, and excellent wetting of the silane treated basalt fibres was seen (Fig. 3).

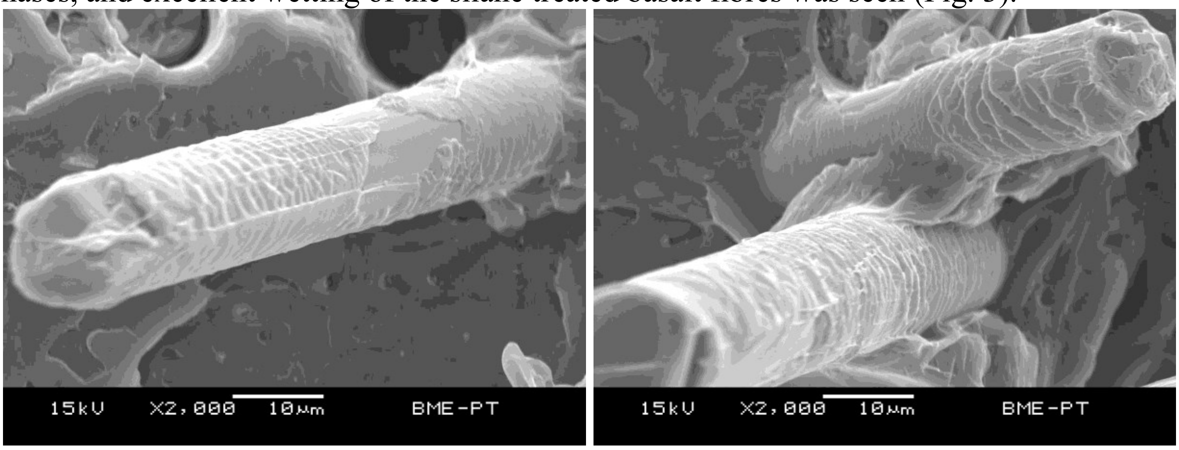


Fig. 3. Fracture surface of the short basalt fibre reinforced PLA biocomposites in two different locations

Long basalt fibre reinforced PLA composites were also prepared by using continuous basalt roving extrusion coated with PLA and chopped into 10 mm length rod like pellets as pre-products ready to be injection moulded (Fig. 4).

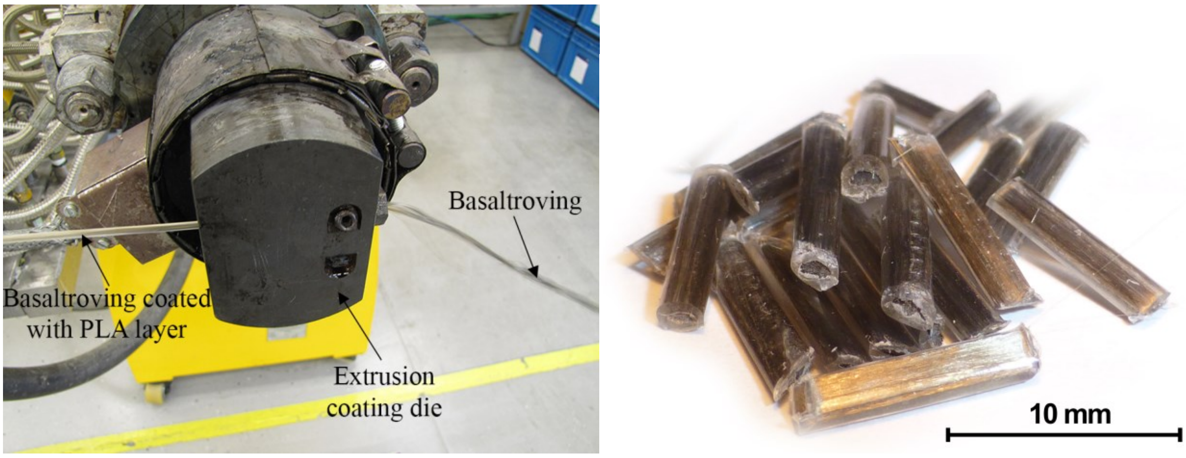


Fig. 4. The extrusion coating of basalt roving with PLA by using the coating die (left) and the coated basalt roving chopped for injection moulding (right)

For the extrusion coating technology it was possible to set the fibre ratio between 14.8 and 25.8wt% by controlling the pulling speed of the basalt roving and thus the thickness of the coating. The investigated mechanical properties of the long basalt fibre reinforced PLA composites were superior compared to the short basalt fibre reinforced composites, which was caused by the increased remaining average fibre length from 159 µm to 658 µm in case of the 20wt% of short and long basalt fibre reinforced composites respectively. Accordingly, the 20wt% long basalt fibre reinforced composites had practically the same tensile and flexural strength, than the 30wt% short basalt fibre reinforced composites, thus 10wt% less basalt fibre content was enough to obtain same mechanical properties in case of long basalt fibre reinforcement. Moreover, in case of 20wt% short and long basalt fibre composites impact strength increased enormously from 5.8 kJ/m$^2$ to 18.3 kJ/m$^2$ (notched) and from 29.9 kJ/m$^2$ to 70.1 kJ/m$^2$ (unnotched) respectively (Fig. 5).

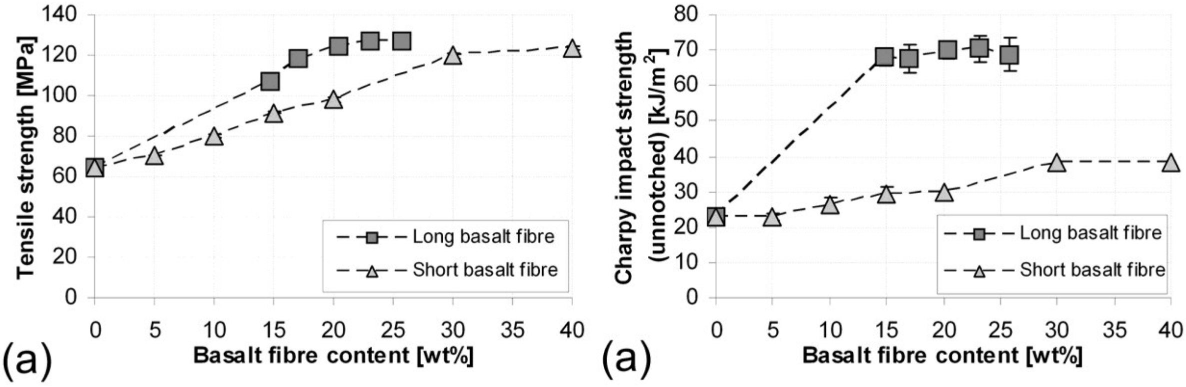


Fig. 5. Tensile strength (left) and Charpy impact strength (right) of short and long basalt fibre reinforced PLA biocomposites

In the case, when the basalt fibre reinforced biocomposites were prepared by the side-feeder, the mechanical properties were found to be between the short and long basalt fibre composites. Compression moulding was also used to produce basalt fabric reinforced PLA biocomposites. By optimizing the processing parameters (temperature and pressure) 437 MPa of tensile strength and 25.4 GPa of tensile modulus could be reached with a fibre ratio of 75% (Fig. 6).

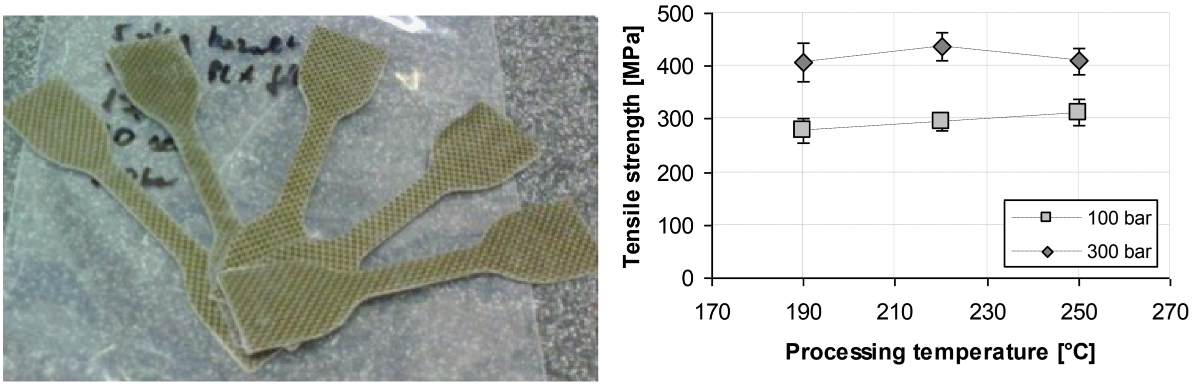

Fig. 6. Basalt fabric reinforced compression moulded PLA biocomposite (left) and its tensile strength as a function of processing temperature and pressure (right)

Since not only the quasistatic mechanical properties are in the line of focus in case of an engineering composite, thus the long-term creep properties of the developed short and long basalt fibre reinforced injection moulded PLA biocomposites were investigated. It was proved that even the short basalt fibres highly retard the creep of PLA under constant load, but naturally, the creep of basalt fibre reinforced PLA could be further decreased even at the same fibre reinforcement ratio by using the above mentioned extrusion coating technology to produce long basalt fibre reinforced PLA composites and thus to increase average fibre length in the composites (Fig. 7).

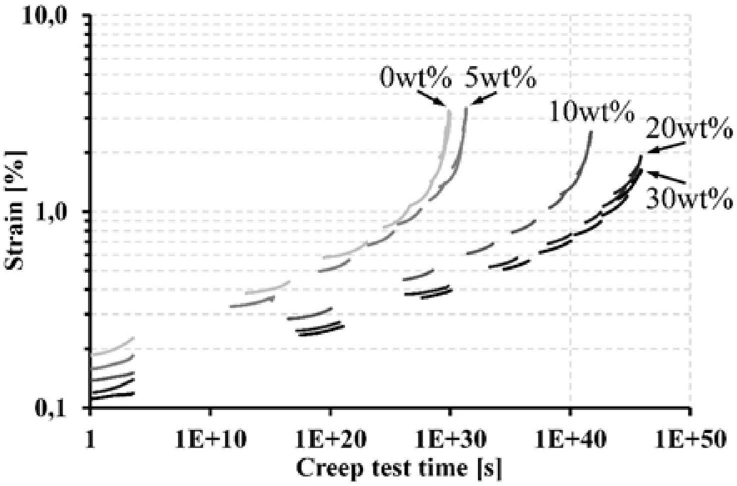

Fig. 7. Creep of short basalt fibre reinforced PLA biocomposite as a function of basalt fibre content

Finally, since as the maximum applicable temperature of an engineering composite is also important, thus additional natural additive, namely talc was added to the short basalt fibre reinforced PLA biocomposites to increase crystallization during processing and thus heat deflection temperature (HDT). By using 30wt% of short basalt fibres as well as 15wt% of talc and by injection moulding this compound into 90°C hot mould to achieve lower cooling rate (compared to the conventional 20°C mould temperature typically used to injection mould PLA), the HDT of pristine PLA of 55°C could be enhanced enormously up to 144°C. This was caused by the positive cross-effect of the stiffness increasing effect of basalt fibres and the developed crystalline structure. Latter is, in turn caused by the lower cooling rate of the 90°C hot mould as well as the nucleating ability of talc and basalt fibres (Fig. 8).

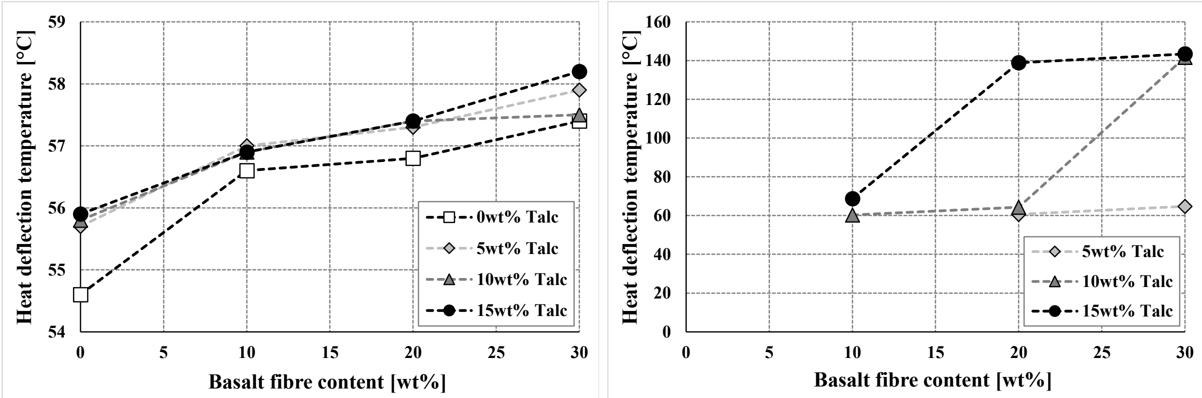


Fig. 8. Heat deflection temperature of basalt fibre reinforced and talc filled PLA biocomposites injection moulded into 20°C (left) and 90°C (right) temperature mould

From these results 2 papers with impact factor [1, 2], 1 paper without impact factor in national journal [3], 2 conference proceedings [4, 5] and 2 diploma thesis [6, 7] were published. Another paper is currently being submitted to a high impact factor journal [8] as well as another conference proceeding [9].

**According to the research based on cellulose fibre reinforcement** it was demonstrated that it is crucial to use the adequate pre-process drying temperature and time for both the PLA and for the cellulose based fibres. The investigation of the mechanical properties of the PLA based, flax, jute and cotton fabric reinforced biocomposites made by film-stacking (compression moulding) method revealed that pre-process drying temperature of PLA and the fabrics has significant effect, since 20-40 MPa improvements were found in the tensile strength of the biocomposites only by increasing the pre-process drying temperature from 80 to 120°C. The tensile strength and modulus of the pristine PLA increased from 62 MPa and 2.7 GPa to 99 MPa and 5.7 GPa respectively, by using flax fabric as reinforcement. Also, flexural strength and modulus of the neat PLA increased from 58 MPa and 3.4 GPa to 110 MPa and 8.0 GPa respectively, by using jute fabric as reinforcement. Finally, the impact strength of neat PLA of around 15 kJ/m$^2$ could be mostly increased with Cotton fabric reinforcement up to 60 kJ/m$^2$ (Fig. 9).

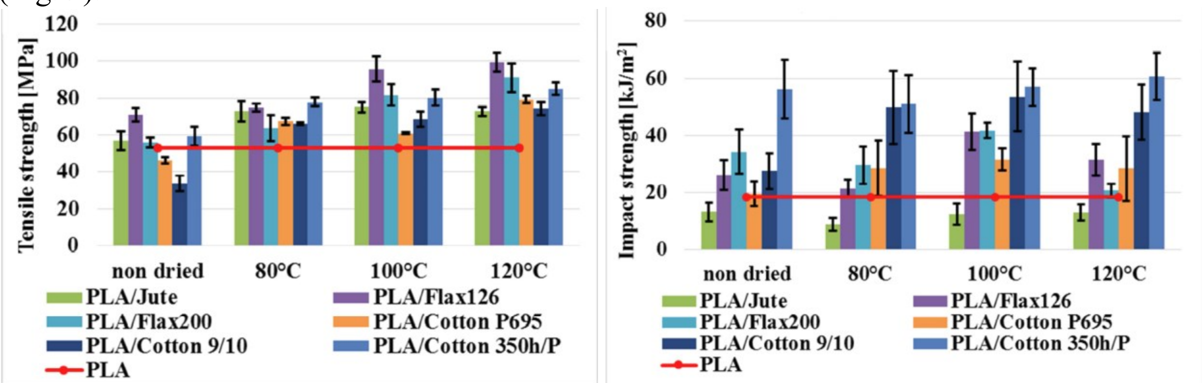


Fig. 9. Tensile strength (left) and Charpy impact strength (right) of the flax, jute and cotton fabric reinforced PLA biocomposites

It was also demonstrated that it is possible not only to develop high impact strength compression moulded, but also injection moulded biocomposites by preparing long cellulose fibre reinforced injection moulded PLA biocomposites by using extrusion coated pellets as it was already proved for basalt fibres. In this case, the long cellulose fibre reinforced PLA biocomposites reached a Charpy unnotched impact strength of 69.3 kJ/m$^2$ (Fig. 10).

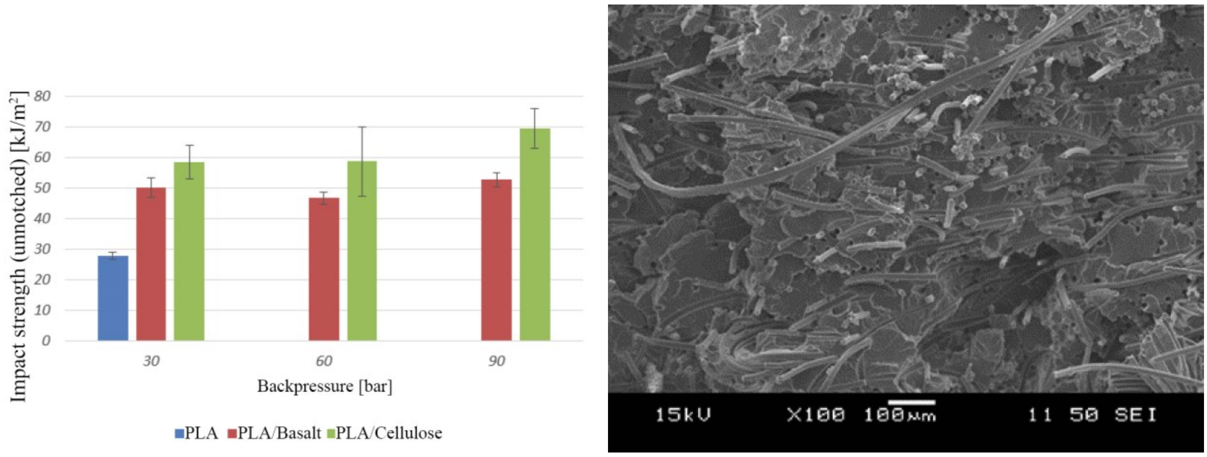

Fig. 10. Charpy impact strength (left) and the fracture surface (right) of the long cellulose fibre reinforced PLA biocomposite

Moreover, HDT was also significantly improved from 55°C (pristine PLA) up to 83°C. Finally, the hybrid reinforcing effect of basalt and cellulose fibres on PLA was investigated, but unfortunately it could only be found that there is no or negative cross-effect between these two reinforcing fibres.

From these results 5 conference proceedings [10-14] and 3 diploma thesis [15-17] were published.

**According to the research based on foamed PLA** it was demonstrated that chemical foaming agents can be effectively used to prepare foamed PLA structure. For injection moulded and foamed PLA parts, a skin-core structure developed due to the intensive cooling in the skin layer of the part as investigated by SEM (Fig. 11).

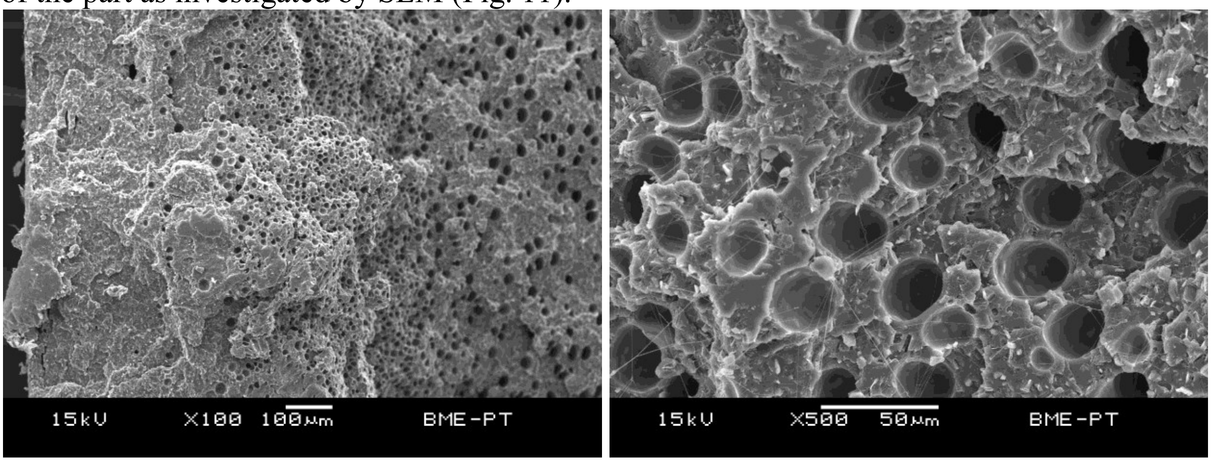

Fig. 11. Skin (left) and core structure (right) of chemically foamed PLA biofoams

When the chemical foaming agents decomposed into $CO_2$, the nucleating property of $CO_2$ on PLA was demonstrated by differential scanning calorimetry (DSC) analysis measuring significant crystallinity in the PLA. However, only minor improvements were found in the HDT values most probably due to the decreased effective cross-section of the foamed structure.
In the continuation of the research the physical foaming process of PLA was intensively studied by using supercritical state $CO_2$. First, a PLA compound with 2wt% chain extender and 2wt% talc content were prepared in a twin screw extruder to make it suitable for physical foaming by enhancing the melt strength and crystallisation of the PLA matrix respectively. To this compound 5wt% of cellulose and 5wt% of basalt fibres were added to create foamed

biocomposites and the foaming technology including the porosity of the developed foams was investigated as a function of extrusion temperature. It was found that it is possible to produce PLA based biofoams with high porosity, namely over 95% by using $CO_2$ (Fig. 12).

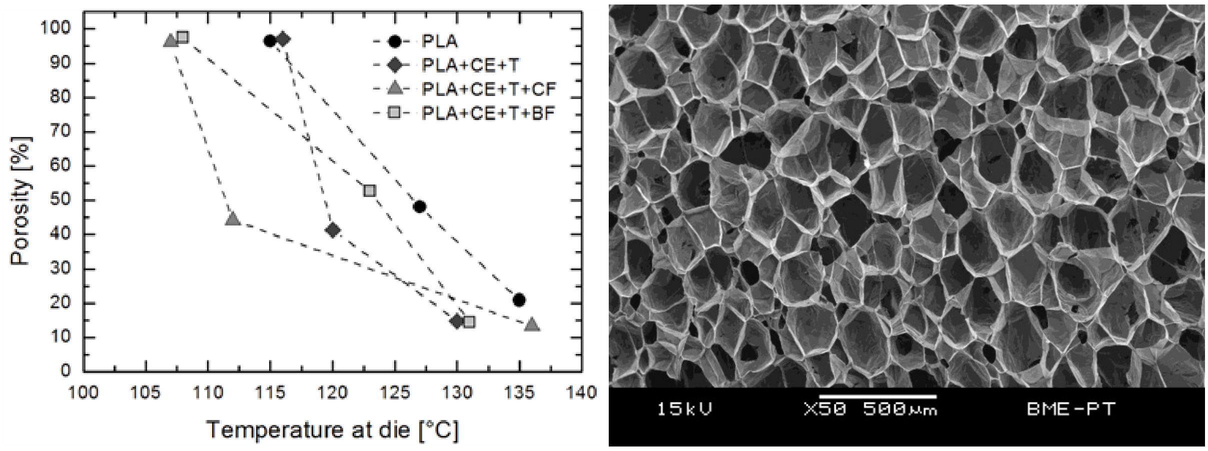

Fig. 12. Porosity of the physically foamed PLA based biofoams (left) and fracture surface of PLA biofoams with 96% porosity (right)

In case of PLA with 2wt% chain extender and 2wt% talc content it was found that the porosity could be widely controlled from 15% to 95% by setting the extrusion temperature from 115°C to 135°C respectively. Besides the nucleating effect of cellulose and basalt fibre on PLA, it was found that also $CO_2$ effectively nucleates PLA during foaming, which could lead to high HDT, high porosity biofoams with sufficient compression strength possibly suitable for applying in packaging industry to substitute expanded Polystyrene (EPS) foams. Finally, an extrusion die was designed, manufactured and used for the experiments to be able to produce physically foamed, highly porous PLA biocomposite tubes and sheets (Fig. 13).

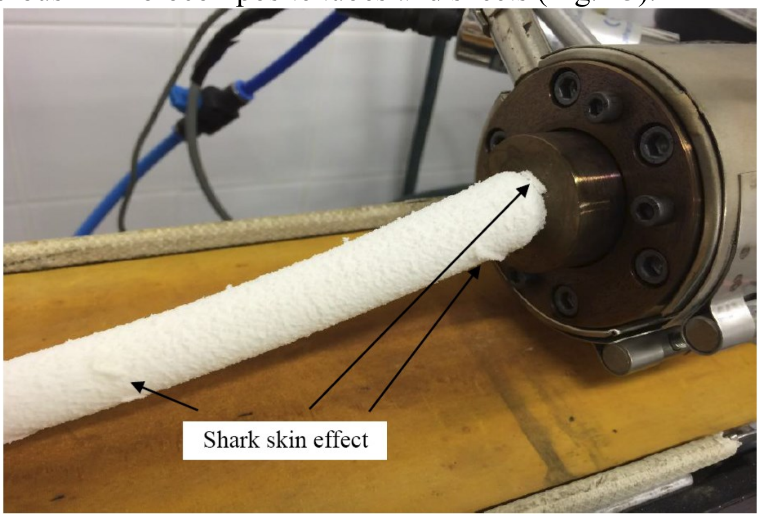

Fig. 13. Physically foamed PLA biofoams tube

From these results 1 paper without impact factor in national journal [18] and 2 diploma thesis [19-20] were published. Another paper is currently being submitted to a high impact factor journal [21].

**According to the research based on nucleation** of PLA it was demonstrated that talc and Poly(Ethylene Glycol) (PEG) is a highly effective nucleating agent and plasticizer for PLA respectively to significantly improve HDT. By using 20wt% small particle size (0.65 μm average particle size) talc and 10wt% PEG filled PLA, it was possible to increase HDT significantly from 37.9°C to 108.6°C by using hot (90°C) mould temperature. In this case, due to the highly effective nucleating agent, the increased molecular chain mobility caused by the plasticizer, and the low cooling rate caused by the hot mould, all together induced high crystallinity in the PLA, which finally resulted in the high HDT value (Fig. 14).

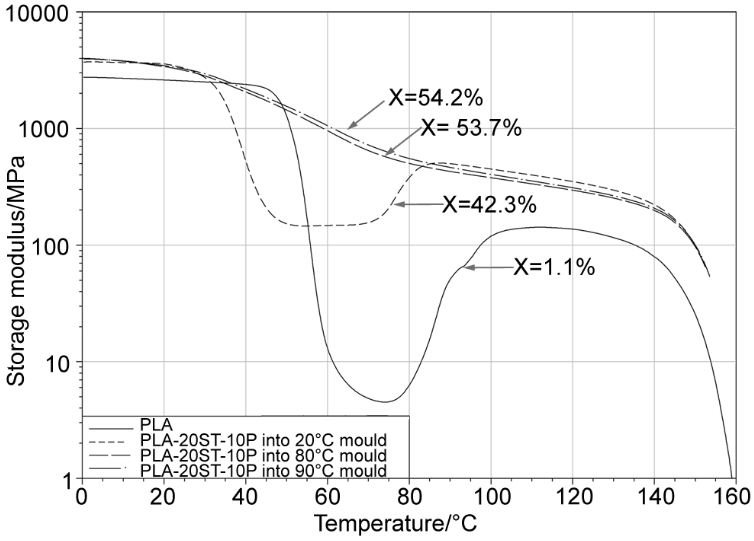


Fig. 14. Storage modulus of 20wt% talc and 10wt% PEG filled PLA injection moulded into 20, 80 and 90°C

Moreover, the same compound was also injection moulded into a special mould made by using the PolyJet (Objet) rapid prototyping technology as a rapid mould. As this mould is polymer based, its heat transfer (0.28 W/mK) and conduction is much lower than of the conventional steel moulds (20-25 W/mK). This heat transfer from the part to the mould was also simulated by using injection moulding simulation software. As the result of the low heat transfer caused low cooling rate, the PLA based compound had more time to crystallise in the mould even though the initial temperature of the mould was room temperature (23°C). This led to an increased Vicat softening temperature of 124°C, which is again considered as significant result since the Vicat softening temperature of pristine PLA is around 63°C (Fig. 15).

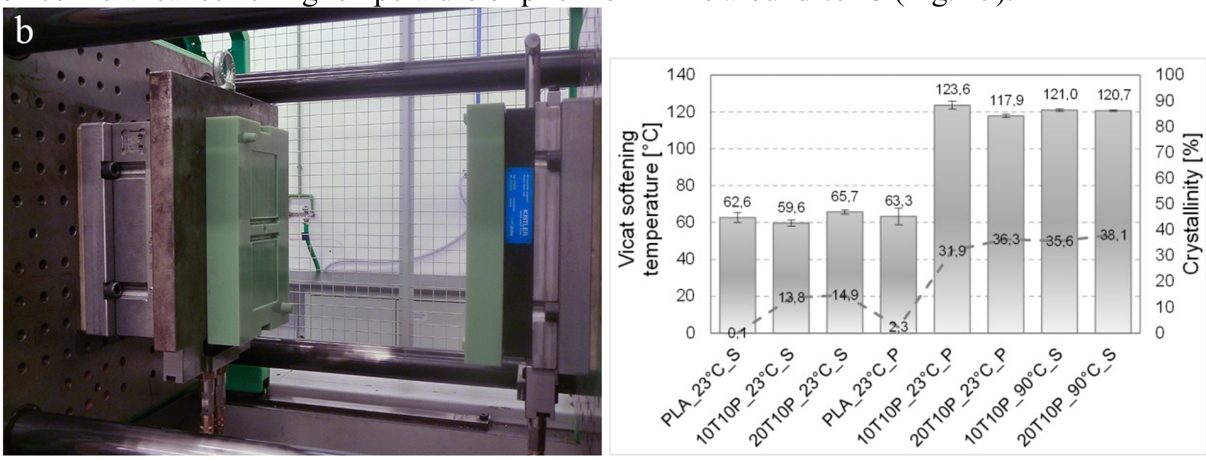


Fig. 15. The rapid prototyped (PolyJet) mould (left) and the Vicat softening temperature of PLA based, talc and PEG filled compounds injection moulded into steel (S) and PolyJet (P) moulds (right)

From these results 3 papers with impact factor [22-24], 1 conference proceeding [25] and 1 diploma thesis [26] were published.

**According to the research based on fire retarded PLA** novel phosphorus-containing multifunctional additives were synthesized in order to provide improved flame retarding capability to natural fibre reinforced PLA/Thermoplastic Starch (TPS) biocomposites in an economical way. The synthesized phosphorus-containing polyol, glycerol phosphate, was used as plasticizer to obtain thermoplastic starch of reduced flammability. This modified starch proved to have enhanced char promoting capability when applied in PLA, and thus provided improved flame retarding property to PLA/TPS blends. 10wt% of the developed flame retardant proved to be sufficient to achieve V_0 rating, and a LOI (Limiting Oxygen Index) value as high as 33vol% was reached this way (Table 1).

| | UL-94 classification | LOI (vol%) |
|---|---|---|
| PLA/TPS | HB | 21 |
| PLA/TPS-GP | HB | 23 |
| PLA/TPS/flax | HB | 20 |
| PLA/TPS-GP/flax | HB | 21 |
| PLA/TPS/flax-PSil | HB | 23 |
| PLA/TPS-GP/flax-PSil | HB | 24 |
| PLA/TPS-GP/flax-PSil + APP | V−0 | 33 |

Table 1. UL94 classification and LOI values of the PLA/TPS biocomposites with Glycerol Phosphate (GP) and Phosphorous Silane treated flax (PSil)

In case of PLA based, flax reinforced biocomposites, the phosphorus containing species, being present both on the surface of the reinforcing flax fibres and in the biodegradable matrix material resulted in adequate strength and stiffness and proved to have effective flame retarding property. The mechanical performance of the prepared flame retarded biocomposites was comparable with that of a common Polypropylene (PP), regarding to tensile and flexural properties.

From these results 2 papers with impact factor [27, 28] and 1 paper without impact factor in national journal [29] were published.

**According to the research based on the incorporation of PLA into fused deposition modelling** based rapid prototyping it was demonstrated that it is possible to use PLA as renewable resource and biodegradable polymer in this field instead of the conventional and in most cases not recyclable thermoset plastics used in order to be able to easily recycle rapid prototyped parts by melt reprocessing or composting into humus, water and $CO_2$. It was demonstrated that the processing temperature, the filling pattern and the layer thickness all had significant role on the mechanical properties of the final product. By optimizing the processing parameters the mechanical properties (including tensile, flexural and impact properties) of the PLA based rapid prototyped parts could reach around 80-90% compared to the homogenous injection moulded PLA products. The best mechanical properties were achieved by using small layer thickness, high melt temperature to allow sufficient cohesion between the layers and by using rectangular filling pattern to have the most number of layers in the direction of the load analogously to composite design guidelines (Fig. 16).

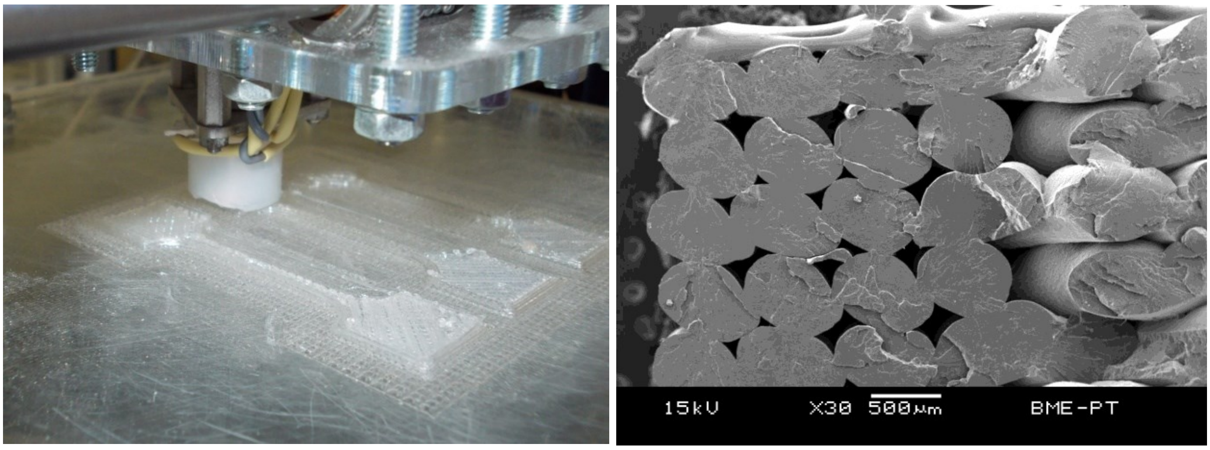

Fig. 16. PLA specimens and being prototyped by Fused Deposition Modelling (left) and its fracture surface (right)

From these results 1 paper without impact factor in national journal [30] was published.

All of our results were published in (or currently submitted to) impact factor journals, international conferences and in diploma thesis's. Altogether 7 papers with impact factor, 4 papers without impact factor in national journal, 8 conference proceedings and 8 diploma thesis were published, while 2 papers are currently being submitted to high impact factor journals as well as 1 conference proceeding. These publications prove the appropriate utilization of OTKA funds related to the purchased new equipments, without this research could not have been performed. All the publications were deposited (or in the case of submitted and being published papers, will be deposited) in the Repository of the Academy's Library (REAL).

**List of published papers supported by this OTKA project**

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Budapest, 2016.01.22.

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