The goal of the project was to develop polymer foam structures and analyze their energy absorption mechanism. In order to achieve this, we focused on four different research areas, the results of which are detailed below.

1. Extensive analysis of the properties of traditional polymer foams

In the first phase of the project, we carried out comprehensive mechanical, microscopic and morphological studies on cross-linked polyethylene (XPE), ethylene-vinyl acetate (EVA), polyurethane (PU) and recycled polyurethane (rPU) foams of different densities and thicknesses.

Based on our measurements to investigate the compression set, we have shown the relationship between the recovery capability of the foams, the cell structure type, the average cell size and the average cell wall thickness. Our compression tests on the foams validated the previous results in the literature, which suggest that the compressive stress-strain curves can be divided into three distinct regions, which can be attributed to different cellular deformation mechanisms. In order to determine the static stiffness according to EN12503, we applied a new test method including an optical measurement system and digital image correlation, and showed that open-cell foams are less resistant to loading, while the stiffness of closed-cell structures decreases with cell size but increases with increasing cell wall thickness and cell density.

For cross-linked polyethylene (XPE) foams, we found that the relationship between foam density and mechanical properties (compressive strength, energy absorption, shock absorption, resilience) can be accurately approximated by the power law (see Figure 1).

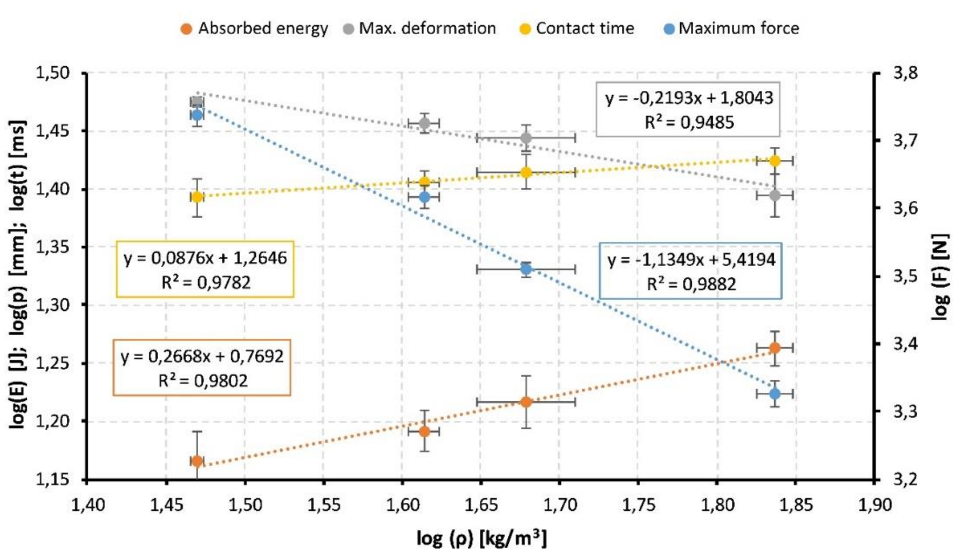

Figure 1 – Results of falling weight impact tests: density dependence of absorbed energy, maximum force, maximum deformation, and contact time in case of 30 mm thick XPE foam

In order to investigate the shock-absorbing capacity of the foam structures, we performed a large number of impact tests with different parameters (impact energy, javelin geometry, impact velocity). Based on these measurements, we have shown that repeated impacts impair the dynamic properties of foams but this deterioration of properties depends on foam type. Closed-cell foams are more resistant in terms of energy absorption, while open-cell foams are more resistant in terms of impact damping. The reduction in impact damping in the case of microcellular EVA foams comes from the viscoelastic, time-dependent properties of polymers and can be attributed to delayed elastic deformation, while the cell structure of macrocellular XPE foams suffers permanent, irreversible deformation.

After analyzing the measurement results, we identified the local cell compaction in the region underneath the impactor as the main underlying cause behind the deterioration of the shock absorption capacity, which can be eliminated by a better load distribution, i.e. by increasing the diameter of the deforming zone.

2. Producing syntactic biopolymer foams and extensive analysis of their properties

The second main objective of our research was the development of syntactic biopolymer foams, including the analysis of their producibility and the extensive morphological and mechanical characterization of the produced foams. Therefore, different amorphous and semi-crystalline polylactic acid (PLA) matrix materials with different D-lactide content were used, to which 0-8 wt% thermally expandable microspheres (EMS) were added. The foams were produced by flat film extrusion, and the effect of the processing parameters and the foaming agent content on the cell structure and mechanical properties was investigated. By measuring the density of the produced foams using the buoyancy principle, we found that the foam density as a function of the amount of added blowing agent can be estimated with high accuracy using an exponential relationship, and the foam structures produced have a normal cell size distribution.

Since the puncture impact tests on the produced PLA foams revealed the brittle nature of the PLA specimens, we aimed to soften the foam structures by adding other biopolymers (e.g. poly(butylene adipate terephthalate) (PBAT) and polybutylene succinate (PBS)). Blends were created using twin-screw extrusion, and then the foamability of the blends with EMS was investigated. Then, we performed impact tests and showed that the addition of PBAT is effective in increasing the energy absorption of the inherently brittle PLA, and that 50-50% blends are best, as the resulting co-continuous phase synergistically increases the mechanical properties of biopolymers. These claims have been verified by atomic force microscopy images, where we have shown that biopolymer blends form a co-continuous phase in the case of 50/50% blends (Figure 2) and a droplet structure in other blend ratios.

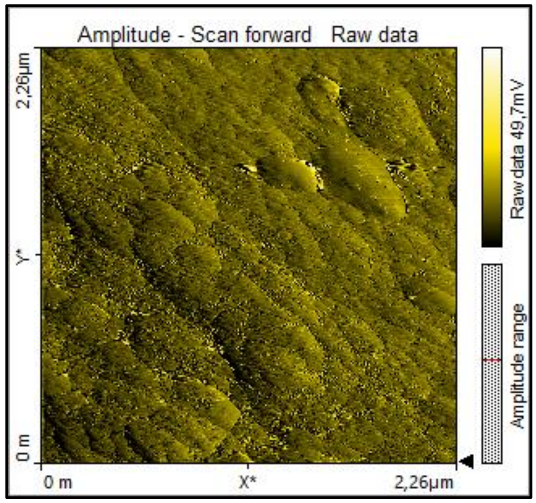

Figure 2 – Atomic force microscope image of the co-continuous system

We also investigated the damping properties of the produced biopolymer-based foams. With DMA tests, we found that the damping properties of a homogeneous, closed-cell foam structure produced with thermally expandable microspheres increase in the range of 0.1 20 000 Hz as a function of foaming agent content. In the case of PLA/PBAT blends, the results indicated that the presence of PBAT in the PLA system has a plasticizing effect. The storage modulus of the unfoamed reference samples showed a decreasing tendency as a function of frequency.

Finally, we applied targeted annealing to influence the crystallinity percentage of the produced PLA foams. Previously, increasing the heat deflection temperature (HDT) of biopolymer-based foams has not been addressed, and its potential has not been demonstrated. We found that D lactide content affects crystallinity in the same way as it does with bulk PLA. Lower D-lactide content results in a higher degree of crystallinity. Annealing proved to be an effective way to induce cold crystallization and therefore increase the HDT of the PLA-based foam structures. Heat deflection temperatures above 150 °C were achieved in the case of syntactic foams made with EMS.

3. The comparison of traditional and biopolymer foams, creating sandwich structures and determining their dynamic mechanical properties

In the third research period, one of our main objectives was to determine the cushioning curves of foamed polymer packaging materials using a novel approach. In our experiments, we carried out drop-weight tests on cross-linked polyethylene and ethylene-vinyl acetate foams of different densities and on 50/50 PLA/PBAT and PLA/PBS based biopolymer foam blends busing different drop heights. The investigated foam samples were chosen based on the results of the first two research aims. Our results have shown that the blend formation could positively modify the shock absorption of biopolymer foams, as the addition of PBS to the system significantly improved the resistance to repetitive impacts, while the PBAT/PLA blend showed advanced energy absorption even from the first impact. Furthermore, by investigating the EVA and XPE foams, we have shown that the cushioning curves of closed-cell foams can be described by a general equation that adequately describes the material behavior even under static loads outside the measurement range. We have also shown that implementing the equation in the estimation methods commonly used in the literature to predict the curves without impact testing, increases their accuracy.

As our results from the first and second research periods revealed that high-energy impacts above a certain load level lead to the complete compaction of the cells and cause irreversible deformation, we set up the goal to increase the shock absorption capacity of the foams by producing multi-layer structures by using three different approaches.

First, we bonded weakly cross-linked polyethylene and rebonded polyurethane foam layers of different densities with a special type of adhesive interlayer, which not only functioned as a glue but also had a breaking effect on the downward movement of the impactor. To investigate the homogeneity of the glue distribution in the interlayer, we took electron scanning microscopic images, which were analyzed using a special optical measurement method. Then, the response of the bonded foam structures to dynamic loading was evaluated by comparison with homogeneous polymer foams. We found that the adhesive interlayer reduces the cell structural compaction in the area under the impactor due to its damping effect, thus significantly increasing the shock-absorbing capacity of the foams. We also showed that the hardness of the adhesive significantly influences this increase. From the analysis of high-speed camera recordings, we also demonstrated that the special adhesion interlayer increases the volume involved in deformation due to its stress-dissipating effect.

In our second approach, we investigated functionally graded, three-layer, weakly cross-linked polyethylene foam structures with the same average density but different densities in each layer. Based on the results of drop weight impact tests in the 10–22 J impact energy range, we showed that increasing the impact energy decreases the energy absorption efficiency of the foam structures. We also showed that the shock absorption of the foams could be improved by modifying the density distribution along the thickness. We demonstrated that decreasing density from top to bottom causes the top layer to transfer the load to the layer below, which transmits it to the bottom layer so that the cells in all three layers start to compress at the same time. The high-density top layer is also more resistant to the impact and distributes the load over a larger area, so cellular deformation takes place over a wider zone. The wider impact zone and the simultaneous deformation of the layers significantly increase the energy absorption capacity in the initial stage of deformation. As more cells absorb the load, the structure becomes more resistant, and the plateau of the force–deformation curve is shifted upwards. This will increase the amount of energy absorbed by the end of the plateau zone, and the dart will have a lower velocity at the start of the densification zone. The downward movement of the dart stops sooner, thus reducing the degree of critical cell compaction, which would cause a significant increase in the reaction force.

Finally, in our third approach, we sprayed a two-component polyurea layer on the top surface of cross-linked polyethylene foams and investigated the energy-dissipating effect of the cover layer through impact testing. We performed drop tests on different impact energy levels, which were set by the modification of drop height and drop weight, and revealed that the application of the polyurea layer increased the energy required to reach the densification zone associated with irreversible deformation and high reaction forces. Based on the results of high-speed camera recordings, we revealed that the cover layer significantly modified the edge contour of the deforming zone and dissipated the load over a wider zone. The polyurea-coated and uncoated specimens were tested according to ASTM F1292 by using the Triax drop-weight device purchased for the project (see the test layout in Figure 3), and it was shown that the coating significantly reduces the head injury criterion and critical fall height, which reduces the probability of severe head injuries associated with permanent neurological damage from 42% to 9% when these structures are used as sports mats in combat sports (e.g., wrestling).

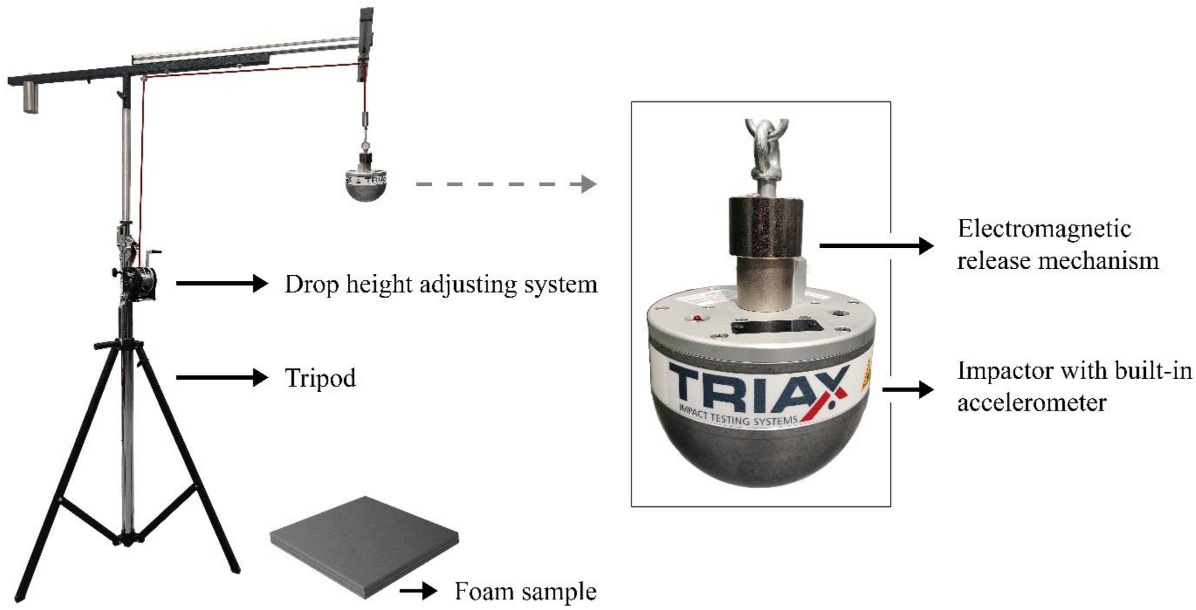

Figure 3 - Test layout for the impact tests performed according to the ASTM F1292 standard using the Triax impact tester device

4. Recycling and biodegradability tests (according to the standard)

Our last goal within the research project was to investigate the recyclability and the biodegradability of the developed biopolymer foams, as increasingly stringent environmental directives are pushing the industry towards the use of biopolymers, where the proper waste management will be a challenge

First, we investigated how the compostability of polymeric foam samples is influenced by the D-lactide content of poly(lactic acid) and the presence and dosage of an expandable microspheres-type foaming agent. Our results show that the poly(lactic acid)-based foam sheet with higher D-lactide content decomposed faster (49 days) than the foam sheet with lower d-lactide content (63 days), when 8 wt% foaming agent was applied (Figure 4.). As the degradation time is shorter for amorphous PLA due to the water diffusion through amorphous PLA. Furthermore, we found that in a poly(lactic acid)-based syntactic foam structures, thermally expandable microspheres decreased the rate of degradation, because not only matrix hydration should take place, but another mechanism like the hydration of the expandable microsphere and the polymer matrix interface as well. However, even the medium-density foams degraded before day 70. Thanks to the latest developments, microspheres that are bio-based and preferably biodegradable will be available. In this way, our results can be applied to such new types of environmentally friendly foaming agents as well.

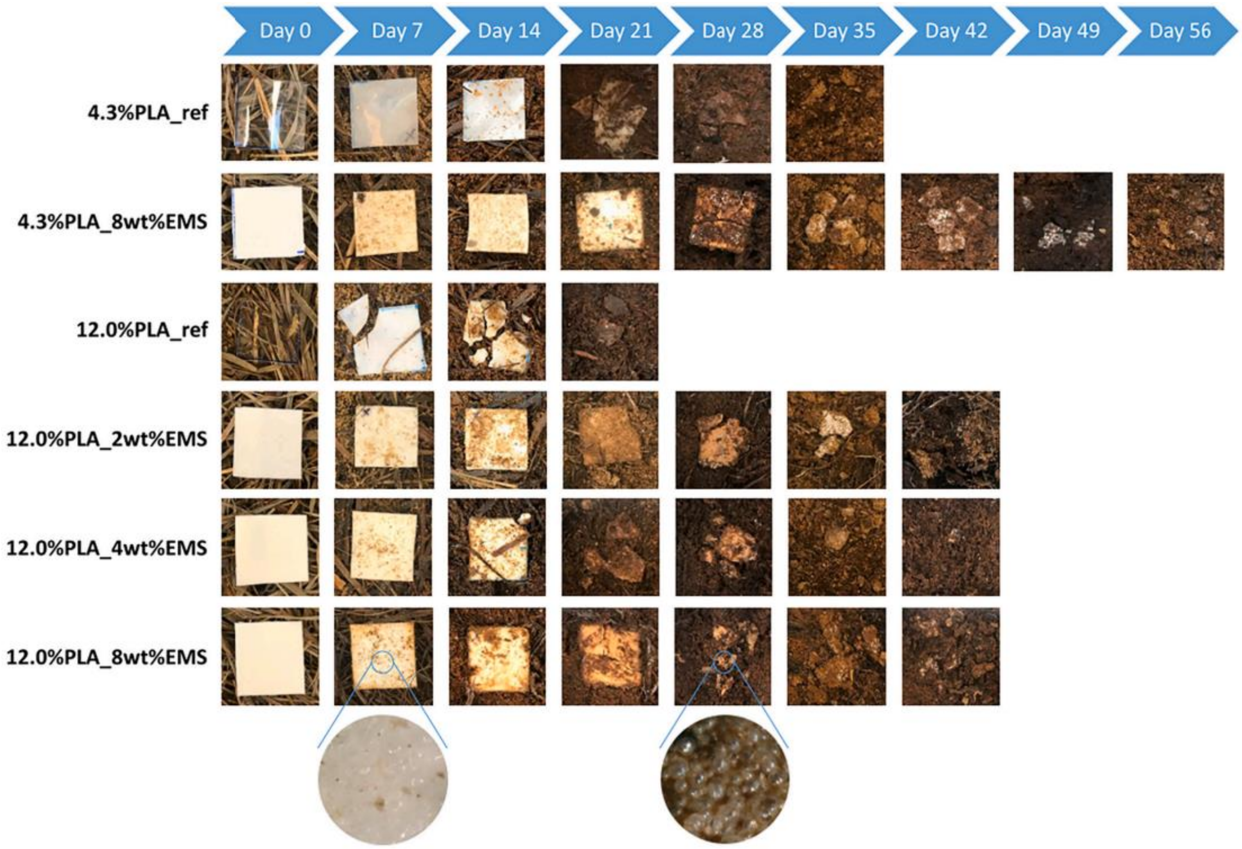

Figure 4 - Decomposition of sheet samples as a function of composting time
(the number at the beginning of each sample designation indicates its d-lactide content)

In addition to the compostability tests, we also investigated the end-of-life recycling potential of the produced biopolymer-based foams. For that, we conducted a detailed study on types of normal and mixed biopolymer foam systems, which also differed in the content and type of foaming agent Initially, these materials were milled, dried, and subsequently re-melted using a twin-screw extruder to create granules. We subjected these granules to MFI and TGA tests, and also used them to produce injection molded specimens for mechanical and optical evaluations.

With the MFI and TGA tests, we have demonstrated that the PLA-based biopolymer foams underwent molecular degradation, leading to increased melt flow rates and reduced thermal stability, and the addition of PBAT and PBS to the mixture further increased these effects. We observed by microscopy that the amorphous and partially crystalline EMS-foamed PLA samples exhibited slight porosity, while the PBAT and PBS-based samples did not. However, the latter two had inhomogeneous distributions. We also carried out tensile and impact tests, and revealed that the results of the biopolymer mixtures have a clearly higher variation than the samples containing only PLA and foaming agent. However, the decrease in the impact strength of the recycled samples can be compensated by the increase of the blowing agent content.

In summary, our study demonstrates that biopolymer-based foams are recyclable with minimal property degradation. However, associated polymers may show significant inhomogeneity in properties.