

Bio-Based Polymer Alternatives for Bead Foams

Blends of PLA and PHBV as Replacement for Expanded Polystyrene

Interest in the use of biopolymers is also growing in bead foams. Different kinds of methods are available for the processing of bead foams. Common to all processes is the welding of the single expanded beads, which can be challenging. A research project shows that the process can also be carried out with blends of polylactide (PLA) and polyhydroxybutyrate-co-valerate (PHBV).

Expanded beads can be welded to produce three-dimensionally shaped components with low densities. Bead foams generally have similar mechanical properties, comparable low thermal conductivity and acoustic insulation like extruded foams of the same density range [1]. The major advantage of them over extruded foams is the ability to produce components with complex geometries and high dimensional accuracy. This offers new application possibilities. For example, packaging material, electronic devices, insulation, furniture and in the automotive industry. Bead foams made of polystyrene (PS), polyethylene (PE), polypropylene (PP) and thermoplastic polyurethane (TPU) have become established in recent years [1].

Currently, expanded polystyrene (EPS) is one of the most important representatives of bead foams worldwide [1]. However, in some countries, e.g. in parts of the USA, there are restrictions for non-degradable single use food plastic packages. There is a risk of the styrene monomer remaining in the environment and may be in contact with the food. This should be prevented as the monomer is suspected of being carcinogenic [2–4]. Therefore, alternatives to bead foams made of PS are coming into focus. One such alternative is PLA, a bio-based polyester that is biodegradable under certain conditions, approved for use in the food industry, and available at competitive prices. In addition, PLA has comparable mechanical properties to PS [5, 6].

underwater pelletizing. PLA is a polymer that can be processed in all three production routes [1, 6].

The sintering or welding of the single expanded beads to a final part can be very challenging. These expanded beads are usually heated with steam and welded together. In the case of semi-crystalline thermoplastics such as PP, the process in the stirred autoclave results in a second melting point, due to different crystal sizes caused by rearrangement. The processing conditions are selected so that the steam temperature is between the two melting peaks (Fig. 1). Due to this, a part of the polymer melts and acts like a glue to merge the expanded beads together. Since the polymer only partially melts at the first melting peak, the structure can be stabilized by the crystallites of the second melting peak [1, 6].

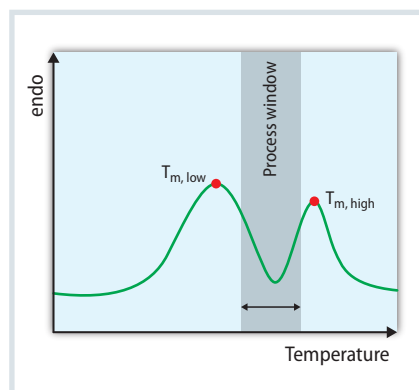


Fig. 1. Sintering of the foamed beads takes place between the two melting points of the used polymer, which can be seen from the DSC curve (schematic diagram) Source: [6]; graphic:

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Three Processes for the Production of Expanded Beads

Several processes have become established for the production of bead foams. Depending on the properties of the used material, the various processes are more or less suitable. For the production of expanded beads by means of stirred autoclaves, usually only semi-crystalline materials such as PP are used. Amorphous polymers such as PS are saturated with gas as micro-granules and then pre-foamed. The third possibility is to produce expanded beads in a continuous process combining extrusion with

Requirements for the Use of PLA

Conditions for the production of bead foams from PLA are sufficient melt strength for cell formation, weldability of the expanded beads and thermal stability of the polymer in every single process step. In the patent literature and in scientific publications, very different approaches to generate PLA bead foams can be found. Expanded PLA can be produced in the laboratory by impregnating PLA pellets in an autoclave followed by pre-foaming in a water bath [7]. To enable the weldability of individual expanded

beads to a molded part, coatings or so-called sticking agents can be used [8]. However, these are expensive and not always biodegradable.

Different Approaches for the Production of PLA Bead Foams

A completely different approach is the generation of multiple melting peaks by isothermal treatment of single expanded beads [9, 10]. During CO₂ saturation close to the polymer's melting point, unmolten crystals are able to rearrange into a higher order (crystal perfection) leading to an additional, higher melting peak. These perfected crystals contribute to heterogeneous nucleation during foaming, resulting in a particularly fine-cell foam structure.

Creating the Double Melting Peak

Another possibility to create a double melting peak is the use of two immiscible polymers. Due to the lack of miscibility, such a blend has two melting peaks [11] and thus fulfills the conditions for weldability of the expanded beads. However, it must be ensured that the two melting peaks are still present after foaming. In a project of the Institut für Kunststofftechnik (IKT) at the University of Stuttgart, Germany, and the chair of Polymer Engineering at the University of Bayreuth, Germany, such a blend system was tested for its suitability for bead foaming. The bio-based and biodegradable polymer PHBV was selected as a blend partner. PLA and PHBV showed two melting peaks in preliminary tests, fulfilling the condition for sintering. In addition, the two plastics can be processed on conventional equipment and no further additives such as compatibilizer are required, which might have affected biodegradability or are not available in biobased form.

PLA Ingeo biopolymer 7001D from NatureWorks, Minnetonka, MN/USA, as well as PHBV Enmat Y1000P from TianAn

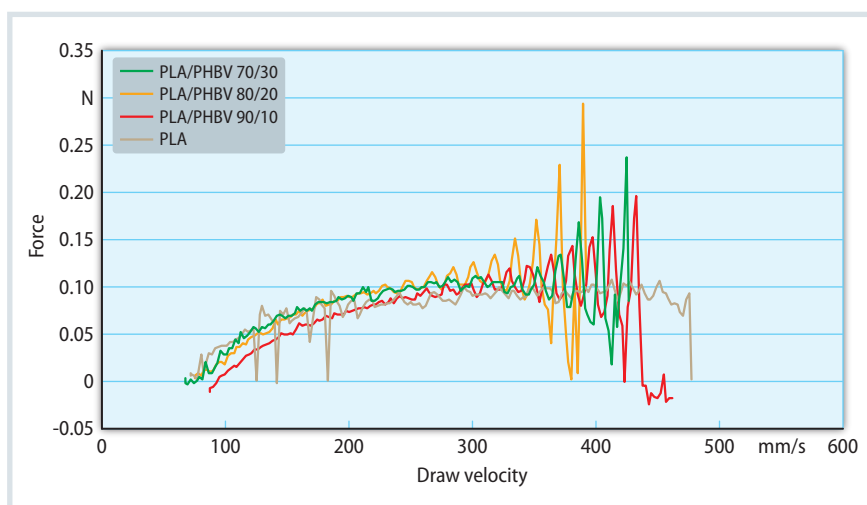


Fig. 2. Rheotens curves of PLA and PLA/PHBV compounds: the similar curves suggest that the PHBV content has no negative influence on the melt strength Source: IKT; graphic: © Hanser

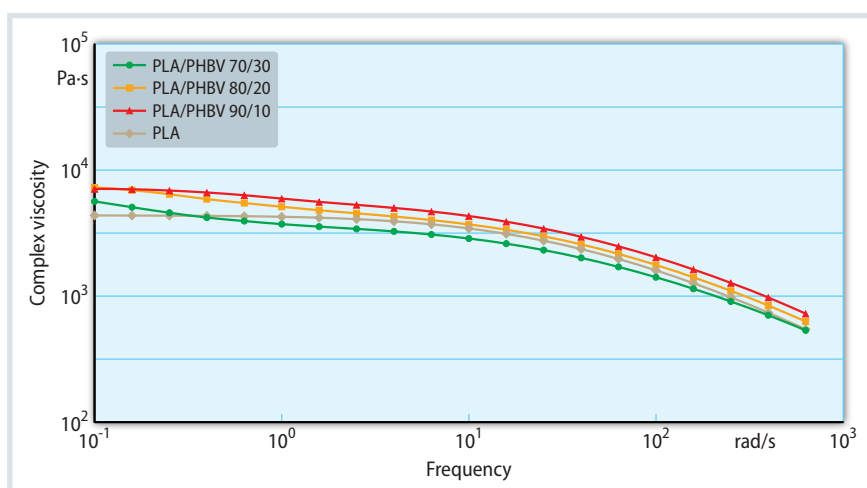


Fig. 3. Viscosity curves of PLA and PLA/PHBV compounds: the viscosity is not reduced by PHBV Source: IKT; graphic: © Hanser

Biologic Materials, Ningbo, China, were used. The compounds were produced on a ZSK26 twin-screw extruder (Coperion GmbH, Stuttgart, Germany). The melt strength of the compounds was determined using a Rheotens 71.97 extensional rheometer (Göttfert GmbH, Buchen, Germany) at a temperature of 180°C. A Discovery HR2 hybrid plate-plate rheometer (TA Instruments, New Castle, UK) was used to investigate the rheological properties of the com-

pounds. The compounds were tested at a temperature of 180°C. The melting behavior was analyzed by Differential Scanning Calorimetry (DSC) using a DSC204 instrument from Netzsch GmbH, Selb, Germany. The compounds were saturated with CO₂ as blowing agent in a self-designed and built autoclave at the University of Bayreuth for 30 min (150 bar and 135°C) before foaming. The morphology of the foams was examined with a scanning electron microscope (SEM) of »

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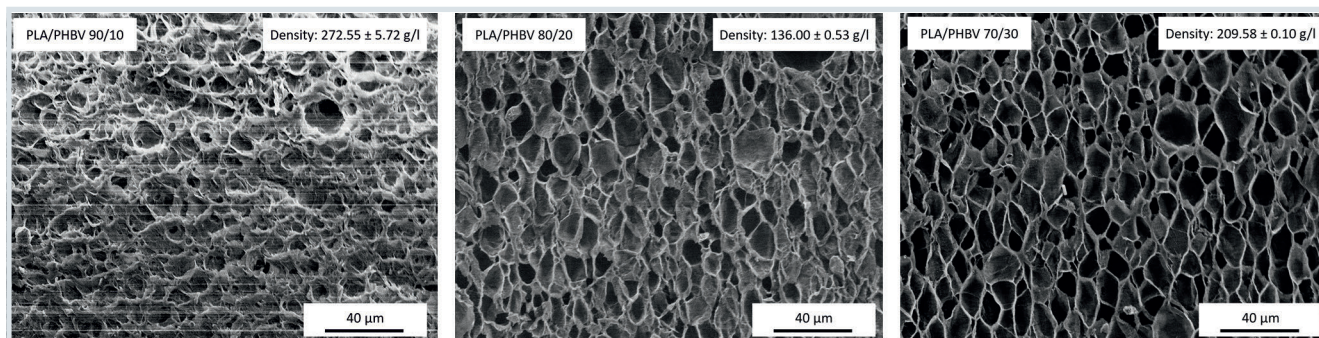


Fig. 4. SEM images of the foamed particles with different blend compositions: increasing the PHBV content provides a more homogeneous cell morphology © IKT

type JSM6300F from Jeol GmbH, Freising, Germany, and the density was determined according to the ISO1183 standard with an AG245 density scale from Mettler Toledo, Columbus, OH/USA.

Are PLA+PHBV Blends Suitable?

Without the addition of compatibilizers or other additives, it was possible to produce a homogeneous compound based on the two polymers. An important property for foaming is the melt strength. Is it too low, coalescence or collapse of the foam cells can occur and no homogeneous fine-cell foam structure is formed. **Figure 2** shows the Rheotens curves of the produced blends in comparison to pure PLA. No significant differences can be discerned in the individual curves. Thus, the low viscosity of PHBV has no negative influence on the melt strength. Since pure PHBV is very susceptible to thermal degradation, additional measurements

were made with a plate-plate rheometer to check whether the viscosity decreases due to PHBV. **Figure 3** shows the results of the measurements. The zero shear viscosity of the blends is higher than for pure PLA and the plateau at low angular frequencies, which is common for thermoplastics, is formed. The blends were foamed and examined morphologically.

More Homogeneous Foam due to PHBV

Figure 4 shows the SEM images of the foamed beads. It can be seen that the cell morphology becomes more homogeneous with increasing PHBV content. The blend with a composition of mass fractions of PLA to PHBV of 90/10 exhibits the highest density. It is also easy to see that the foam has compact areas and could not be completely foamed. The other two blends have similar average cell sizes around 7 µm. Although a lower density is

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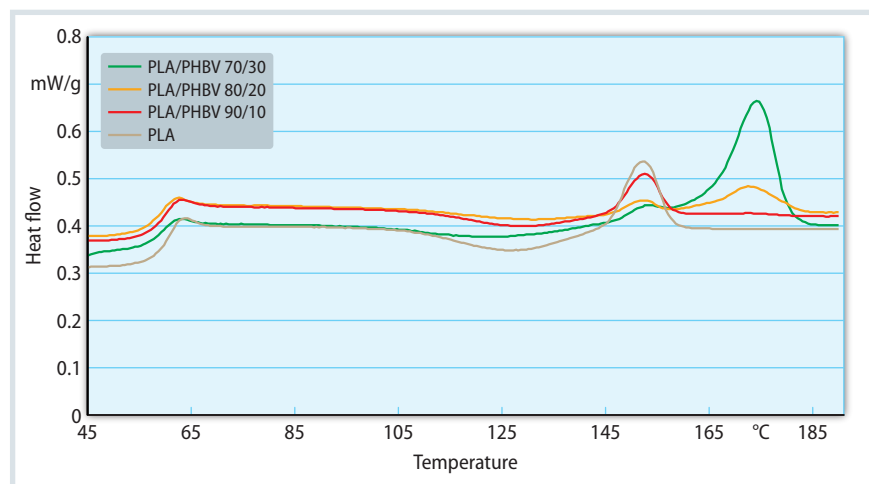


Fig. 5. Second heating curves of the blends before foaming: in the DSC thermograms, the two melting peaks of PLA and PHBV can be clearly seen Source: IKT; graphic: © Hanser

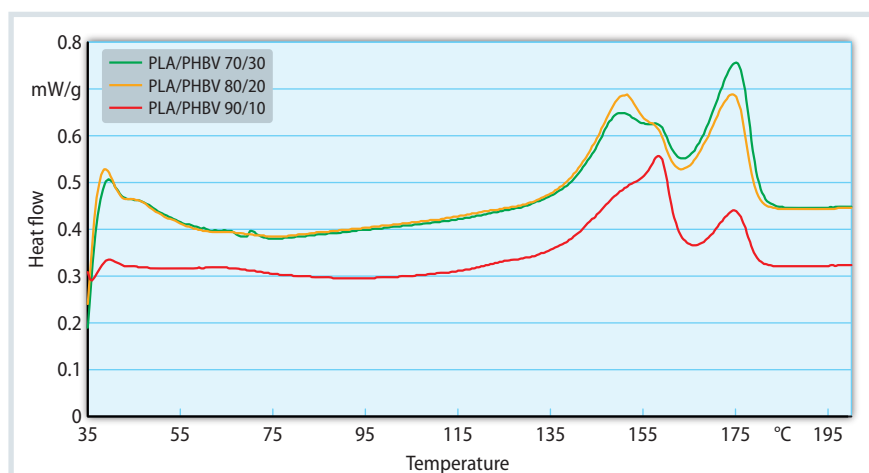


Fig. 6. Initial heating curves of the foamed PLA+PHBV blends: even after foaming, the blends still exhibit the two melting peaks Source: IKT; graphic: © Hanser

achieved with 20% PHBV than with 30%, the foam morphology shows some larger cells that were formed by coalescence or cell collapse. These would negatively affect the mechanical properties of the foam. The foam with 30% PHBV has the most homogeneous cell morphology.

As mentioned, welding or sintering of the foamed beads into the final part is a demanding process. Usually, the processing window is between the two melting peaks. Whether welding of the foam particles is theoretically possible was investigated using DSC. Since PLA and PHBV are not miscible with each

other, they should have two melting peaks. **Figures 5 and 6** show the DSC results before and after foaming. Both before and after foaming, the thermograms show the melting peak of PLA at about 160°C and that of PHBV at about 175°C. Thus, the foamed beads are potentially suitable for use as bead foam.

PLA is made of renewable raw materials and therefore a good candidate to replace fossil-based bead foams. In order to meet the required properties for bead foaming, especially for sintering of the foamed beads, blends of PLA and PHBV can be considered. The investigations have shown that the blend with 30% PHBV has a homogeneous cell morphology and the required double melting peak in DSC. In further investigations, a continuous production of the expanded beads with a combination of extrusion and underwater pelletizing and a subsequent welding of the foamed beads will take place. The resulting parts will be investigated for their mechanical properties and an evaluation of the welding. ■

Bio-Based Compounds

PLA Alternatives for Packaging

The European Green Deal is a concept presented by the European Commission in December 2019 with the aim of reducing net greenhouse gas emissions to zero in the EU by 2050 and thus becoming the first continent to be climate neutral. A 55% reduction in CO₂ is to be implemented already in 2030. With its predominantly fossil-free and sustainable PLA-based products, **Bio-Fed**, Cologne, Germany, a branch of Akro-Plastic GmbH, can offer an alternative material for a large part of packaging applications, for example.

The relevant M-Vera grades can be processed both in the injection molding process and in the extrusion process, e.g. thermoforming. As a 100% bio-based and industrially compostable polymer, PLA is versatile. Possible applications include packaging for food and cosmetics as well as consumer items, such as office supplies or household goods.

PLA compounds are characterized by variable stiffness and typically low shrinkage.



Application example of environment-friendly cosmetics packaging © Bio-Fed

The material properties can be individually adjusted by adding different fillers or reinforcing agents and additives. According to the manufacturer, transparent compounds are also possible. The compounds can also be colored with the bio-based AF-Eco master-

batches from the sister company AF-Color. These are developed and manufactured in close cooperation by the two companies.

To the product presentation:
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