ARTICLE

Amorphous Polylactide Bead Foam–Effect of Talc and Chain Extension on Foaming Behavior and Compression Properties

Christian Brütting[1], Julia Dreier[2], Christian Bonten[2], Volker Altstädt[1] and Holger Ruckdäschel[1,*]

[1]Department of Polymer Engineering, University Bayreuth, Bayreuth, 95447, Germany

[2]Institut für Kunststofftechnik, University of Stuttgart, Stuttgart, 70569, Germany

[*]Corresponding Author: Holger Ruckdäschel. Email: ruckdaeschel@uni-bayreuth.de

ABSTRACT

Polylactide (PLA) bead foams show a high potential regarding their applicability in packaging or consumer products. Concerning the comparable properties of PLA to Polystyrene (PS) and the good CO_2 footprint it represents a potential alternative to petroleum-based polymer foams. However, foaming of PLA is challenging, due to its low melt strength, therefore chemical modifiers are often used. Concerning the bead foam technology regarding PLA, the available literature is limited so far. Within this study, the bead foaming behavior of neat and modified amorphous PLA was investigated. The material was modified by talc and an epoxy-based chain extender. These compounds have been investigated regarding their sorption behavior in CO_2 atmosphere and their foaming behavior. Foaming was conducted by using the batch foaming method based on a rapid temperature increase after saturation with CO_2. In order to achieve welded bead foams, a one-step processing for foaming and welding has been established. Finally, the compression properties of the PLA bead foams have been investigated. Densities below 50 kg/m^3 for single bead foams and 80 kg/m^3 for molded foams were achieved, respectively.

1 Introduction

Bead foaming has gained more and more interest in the recent years due to the combination of low densities and complex shape geometries. Expandable polystyrene (EPS) is the most commonly used bead foam on the market [1]. However, a biobased alternative is desirable for polystyrene bead foams [2]. The most researched biopolymer is Polylactide (PLA) which is bio-based as well as biodegradable. It should be noted here that PLA has a glass transition at about 60°C which might limit its application. PLA is composed out of D- and L-lactide, whose ratio influences its properties. Low D-lactide contents lead to a high crystallization rate whereas high D contents (~12%) lead to a completely amorphous PLA [3]. By changing the D to L ratio, the foaming behavior is changed due to the varied crystallization behaviors [4,5]. In general, foaming of polylactide is challenging due to its low melt strength. In order to overcome this drawback, different methodologies, such as branching by using chain extender (CE) [6–8], using additives [9] as heterogeneous nucleation or controlling the crystallization behavior have been shown to be efficient methods to improve the foaming behavior of PLA [2].

A widely used method for producing foams is batch foaming. Here, it is distinguished between pressure and temperature induced batch foaming [4]. The temperature induced batch foaming which is similar to the industrial process for EPS, has been rarely used in scientific research for PLA. For instance Wang et al. [10] used semi-crystalline PLA and CO_2 as blowing agent in temperature induced batch foaming. They saturated their PLA grade with the blowing agent (50 bar and 25°C) and used a water bath in combination with ultrasonic irradiation to induce a rapid temperature increase up to 85°C. As result, they reached expansion ratios up to 8.4 with cell sizes below 139 μm. By applying ultrasonic irradiation, the expansion ratio could be enhanced to approx. 12 with cell sizes below 30 μm. Another study by Richards et al. [11] dealt with the foaming of PLA-PHBV composites by the temperature induced batch foaming. They showed that the blending of semi-crystalline PLA with PHBV leads to higher foam densities but finer cell morphologies. They showed that the blend composition, the sorption pressure and the foaming temperature have a huge influence on the foaming behavior. Within their study, an increasing temperature led to higher expansion ratios while the saturation pressure showed a minor impact. These researches show the potential for high quality foams by using the temperature induced foaming. However, the foaming behavior of amorphous PLA has not been investigated by a temperature induced batch foaming process.

Next to the foaming, the welding of particle foams is a challenging processing step. Established welding mechanisms are based on diffusion of polymer chains across the interfaces for amorphous polymers [12,13] or crystallization in the interbead area which is known from expanded Polypropylene (EPP) [14]. For PLA bead foams only a few publications [15–19] and patents [20] are available and the processing similar to EPP has been established by Nofar et al. [15–17]. Additionally, In line with this, patents regarding PLA based bead foams are based on the same mechanism [21–24]. However, the processing of amorphous PLA based on the welding mechanism of polystyrene which is only based on diffusion across the bead borders has been investigated.

Within this study, it is aimed to prove, that foaming, and welding of amorphous PLA is similar to EPS. This means, the sorption and foaming by using the temperature induced batch foaming is expected to lead to low density foams below 100 kg/m^3. Furthermore, it is addressed to investigate the sorption and foaming behavior of neat and modified amorphous PLA. Finally, welded amorphous bead will be investigated regarding their morphological and compressive properties.

2 Materials and Methods

2.1 Materials

For this study, an amorphous polylactide (4060D) with a D-content of 12% from Natureworks Ltd., (Minnetonka, USA) and a compact density of 1.240 kg/m^3 was used. The molecular weight (M_w) is 217.000 g/mol with a polydispersity index (PDI) of 1.84. The polylactide was modified with Joncryl ADR 4468 (BASF, Ludwigshafen, Germany) to enhance the melt strength and Finntalc M30 (Mondo Minerals B.V., Amsterdam, Netherlands) as nucleating agent. The materials have been compounded at a Dr. Collin tandem line (Collin Lab & Pilot Solutions GmbH, Maitenbeth, Germany).

2.2 Methods

DSC

The Mettler Toledo DSC 1 (Columbus/OH, USA) was used to determine the thermal properties. All experiments were conducted of about 10 mg samples from 25°C to 200°C at a heating rate of 10 °K/min in nitrogen atmosphere. The heat flow curves have been analyzed by Star-Software.

Foaming

The samples were saturated in a lab autoclave (HR-700, Berghof Products + Instruments GmbH, Eningen unter Achalm, Germany). After sorption, they were foamed by raising the temperature by placing them in a temperature-controlled oven from room temperature to 100°C. From literature it is

known, that the decomposition temperature of PLA is above 300°C which means, that the material is stable during the processing temperatures [25,26].

One-Step Process of Foaming and Welding

Welding of the beads could not be achieved after foaming. For this reason, the saturated beads have been put in a self-made mold to calibrate the foam to the dimensions. Afterwards this mold has been put in temperature-controlled glycerin bath that led to a foaming and simultaneously welding of the bead foams. The foaming is induced by a temperature drop. The most promising welding parameters were 80°C for a time of three minutes. (Lower times lead to insufficient welding, higher ones to shrinkage–similar for the temperature profile).

Foam Properties

Scanning Electron Microscopy

Cutted foam samples were investigated by SEM JEOL JSM-6510 (Akishima, Japan).

Density

The density was determined according to the Archimedes principle with a balance from Mettler Toledo AG245 (Columbus/OH, USA).

Mechanical Characterization

For determining the mechanical properties of the bead foam parts, a universal testing machine from Zwick (Ulm, Germany) was used. The samples had a geometry of approx. 30 mm × 30 mm × 1.1 mm and have been measured according to DIN EN ISO 844. The preforce was set to 5 N and the testing speed to 1.1 mm/min.

3 Results and Discussion

DSC

From literature it is known that the D-content determines the crystallization behavior of PLA [5]. The used PLA has a high D content why it should remain amorphous. Modifiers can induce or increase the crystallization behavior. For this reason, the materials have been investigated in the DSC to proof that the selected PLA-grade stays amorphous. The measurements are shown in Fig. 1.
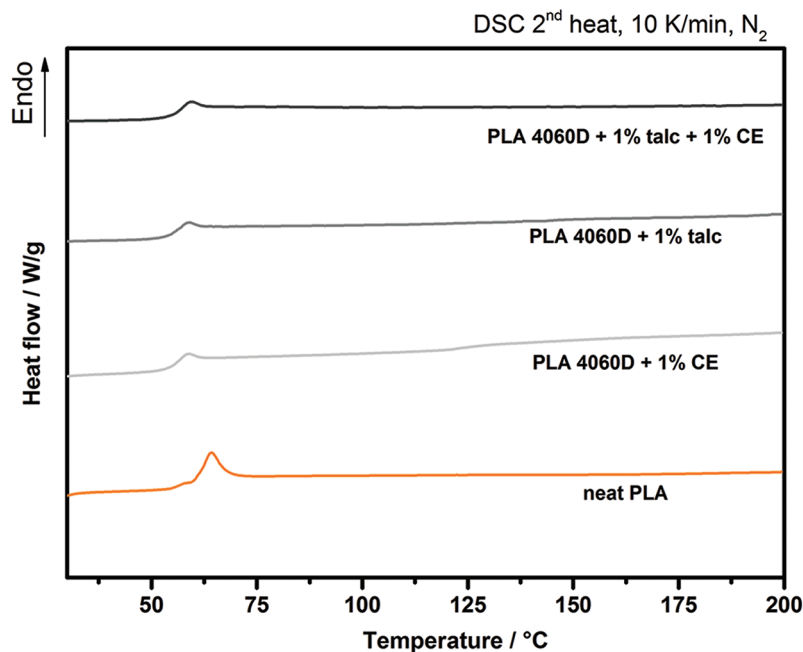

Figure 1: DSC curves of neat and modified PLA grades (second heating run)

The heat flow curves for all used materials show no sign of cold crystallization or melting of present crystals and agree well with the literature [27]. In this case, the sorption, foaming and welding behavior is not influenced by crystallization effects.

Sorption

In order to identify appropriate foaming conditions, the sorption behavior with CO_2 as blowing agent was determined. Interestingly after sorption was conducted at certain pressures after certain saturation times, the PLA was foaming after depressurization at room atmosphere. The results for the sorption results and the resulted foams are shown in Fig. 2.
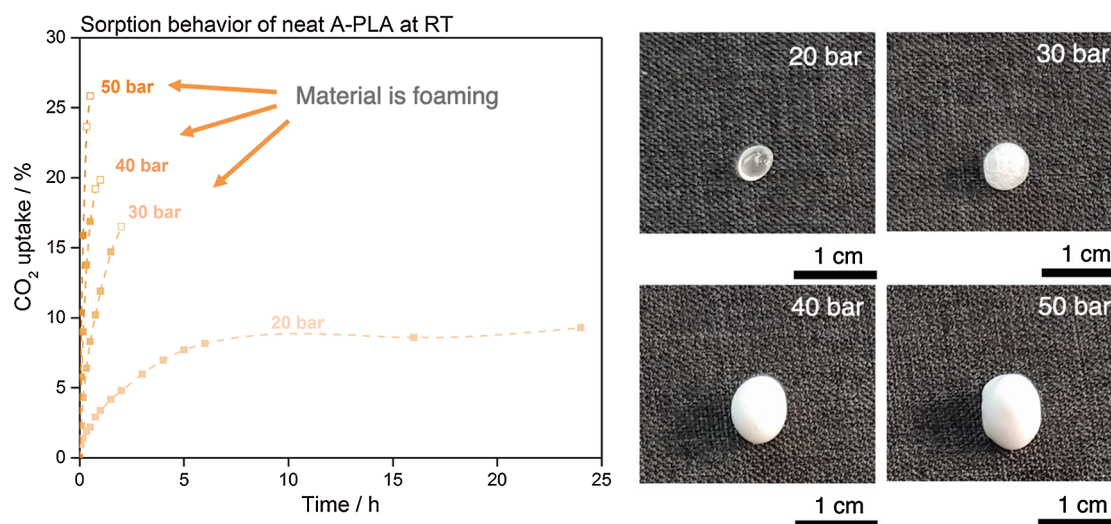

Figure 2: (left) Sorption behavior of amorphous PLA for different CO_2 pressures; (right) resulting foams after sorption measurements

The sorption measurements were conducted between 20 and 50 bar of CO_2 pressure. It can be seen that an increasing saturation pressure and saturation time lead to higher sorption levels. As it was expected, the diffusion rate for higher pressures is much faster than for low pressures leading to a higher sorption for higher pressures. This can be seen by the slope of the measurements which indicates the diffusion rate. In other publications similar effects have been found [28]. During the measurements for 30, 40 and 50 bar, foaming of the material took place at atmospheric pressure which is indicated by hollow symbols. The foaming in room temperature might be due to the plasticization effect of CO_2 which reduced the T_g below room temperature. The resulted materials after the sorption for various pressures at room temperature are given in the left part of Fig. 2. Within this study, different modifiers have been investigated. How these additives influence the sorption at equilibrium state is shown in Fig. 3.
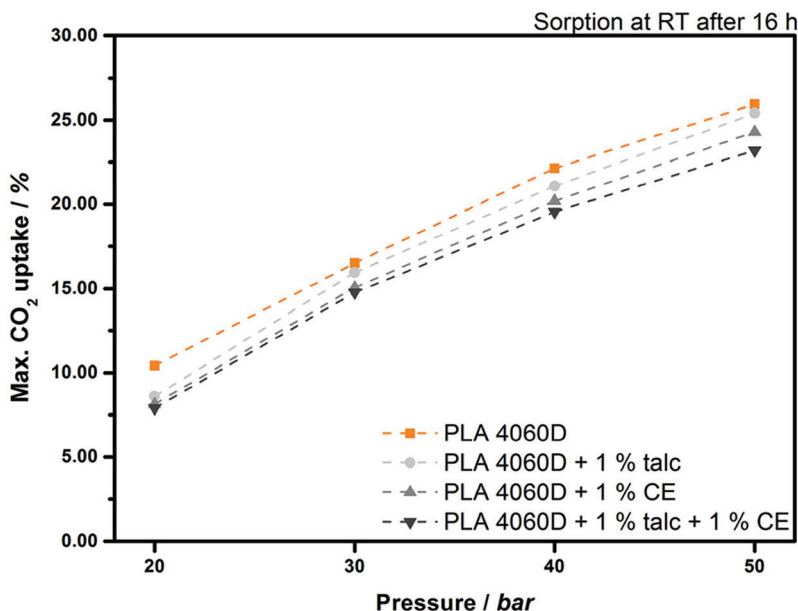
Figure 3: Effect of saturation pressure and modification on sorption

The sorption in equilibrium state (after 16 h) for different modifiers in amorphous PLA is shown. Here, the neat material shows the highest sorption while adding of 1% of talc, 1% of an epoxy-based chain extender, and 1% of talc in combination with 1% of chain extender leads to a slight decrease in the sorption values. These effects can be caused by the reduction of free volume. The addition of talc showed a minor influence than the addition of chain extender. The combination of talc and chain extender affected the sorption to even lower values for all sorption measurements. This can be explained by a more pronounced decrease in the free volume. By comparing Figs. 2 and 3, it can be seen, that 30 min at a pressure of 50 bar are sufficient to reach high sorption values, indicating a high potential to reach low density foams. For this reason, these parameters have been used for the following foaming procedures.

Bead Foaming

The saturated particles have been foamed by the temperature drop method. Usually, hot steam is used for blowing agent loaded polymers. However, the T_g of the materials is far below 100°C (Fig. 1), which would lead to a contraction of the gas loaded samples. In order to avoid contraction, the saturated beads have been foamed in a temperature-controlled oven.

All materials have been foamed at 25, 50, 65, 80 and 100°C. It is interesting to see that even at very low temperatures of about 25°C densities of 200 kg/m^3 can be achieved. With increasing temperature, the density is reduced for all materials. However, for the neat material, the achieved density starts to increase at a temperature of 80°C. For the modified materials, temperatures above 80°C led to an increase in the density. This "U-Shape" in foaming conditions is well known [27]. The increase in temperature lead to a more and more pronounced blowing effect while the modulus of the material is decreasing. At a certain temperature the modulus decreases so much that the material is shrinking or collapsing during foaming. This turnover is represented by the lowest achievable foam density. The SEM images of these foams can be seen in Fig. 4. As expected, the use of talc lead to a more homogeneous cell structure compared to the neat and the chain extender modified materials. Usually, after foaming, bead foams are processes in a steam chest molding unit to a bead foam part. In this case, the welding could not be done, due to shrinking of the samples at elevated temperatures. This can be traced back to the lower T_g of approx. 60°C in comparison to Polystyrene (~100°C). For this reason, the saturated materials have been welded by an one-step process. The results of the welding trials are shown in the following section.
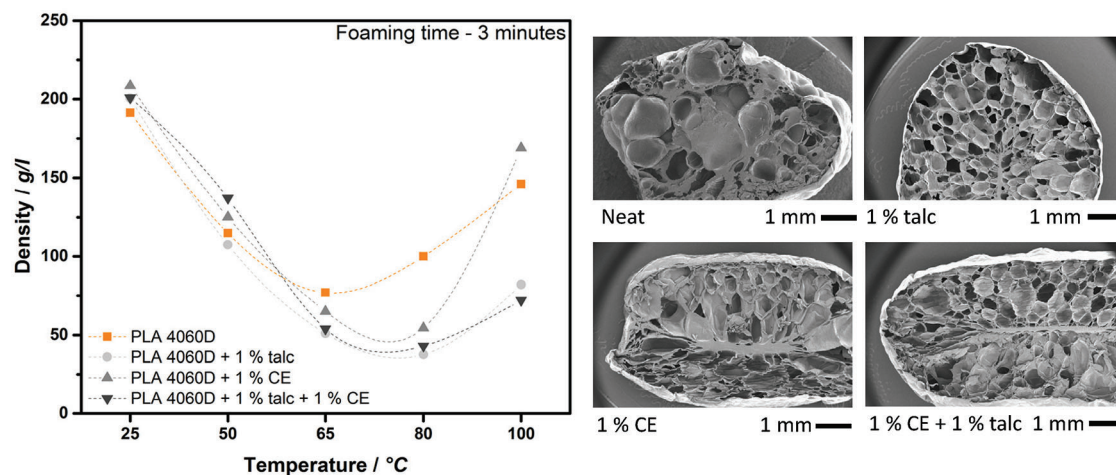
Figure 4: (left) Foaming behavior of amorphous PLA depending on temperature and modification; (right) SEM images of bead foams (lowest achieved densities)

In One-Step-Foaming and Welding

The one-step process led to solid bead foam parts with mean densities of 80 ± 5 kg/m^3 of all modified grades. Lower densities could not be achieved due to weak welding and an insufficient expansion behavior. The neat material could not be welded due to a shrinkage (to high temperature) of the beads or unwelded (too low temperature) bead foams. Nevertheless, three kinds of amorphous PLA bead foams could be welded. SEM Images of the cut parts are shown in Fig. 5.
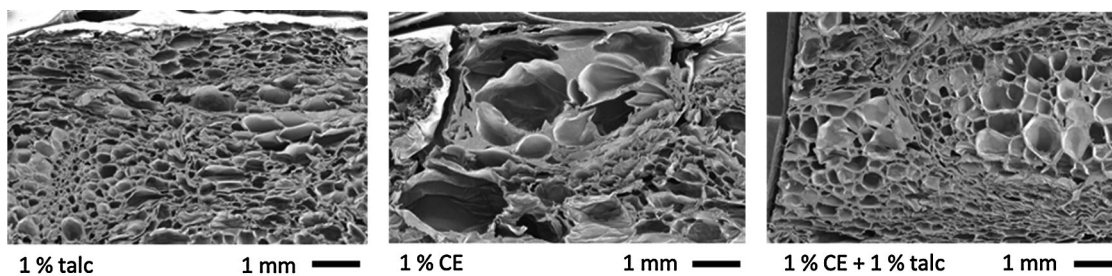

Figure 5: SEM images of the morphology of cut, welded parts

From the SEM images it can be seen that talc showed a homogeneous and fine celled morphology in comparison to the chain extender modified material. This can be traced back to the heterogeneous nucleation of talc, which lead to a higher number of cell nuclei resulting in a finer morphology. These results are in good agreement to the SEM pictures of the single bead foams from Fig. 4. The additives have similar effects on the morphology. Additionally, for talc as modifier, a homogeneous morphology without the indications of bead borders are visible, indicating a good welding. However, foam structure between the beads and the molded parts differ which is based on the foaming and welding inside the mold. On one side, the use of the mold restricts the bead expansion leading to slight deformations and on the other side the heat transfer is different to the oven foaming which influences the cell formation and growth. These differences in processing lead to a variation in foam structure. Furthermore, the molded parts have been investigated regarding their compressive properties.

Compressive Properties

The mechanical properties of polymeric foams are influenced by various factors, such as the type of the polymer [13,29], the foam density [29,30], cell morphology [29,31,32], or additives [32,33]. Fig. 6 shows the compression curves of all molded samples of the modified EPLA including the standard deviation for each strain. The mean densities of all EPLA parts have been about 80 +/− 5 kg/m^3.
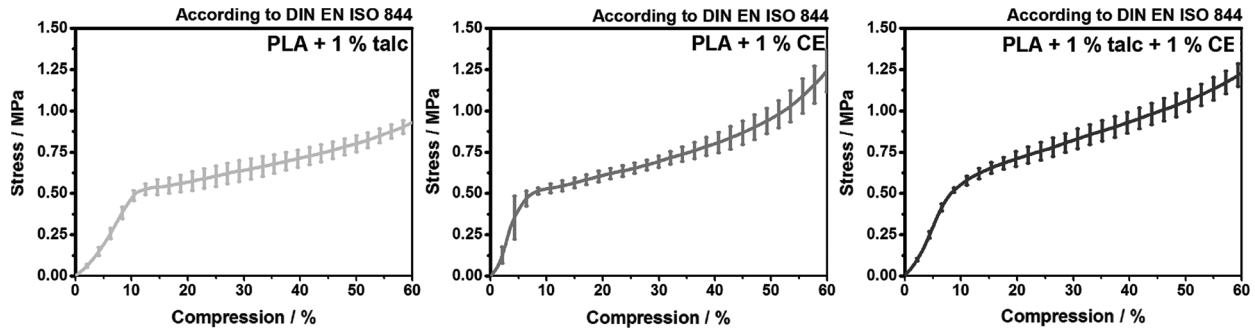

Figure 6: Stress strain curves for all welded bead foam parts at densities of approx. 80 kg/m^3

The compression curves for all welded parts show a similar behavior, which can be classified in three sections. In the beginning, the behavior is determined by the elastic deformation of the cells. Within this linear range, the compression modulus is determined. In the following sections, the plastic deformations and the cell rupture take place. Finally, after the plastic deformations, the third section is classified as densification, where the materials become more and more a compact material.

In general, for all measured bead foams the behavior looks similar with an elastic, a plastic and an indication of the densification regime. However, the materials show different mechanical behavior. First of all, the talc modified materials shows a compressive modulus of 5.5 ± 0.3 MPa and a very slight standard deviation in the elastic regime. During the plastic deformation, the mean curve shows some slight indentations, representing the rupture of cell walls. The low standard deviation over the whole measurement period indicates a homogeneous cell distribution, which confirms to the SEM images in Fig. 5. The chain extender modified PLA, showed a compressive modulus of 12.7 ± 4.0 MPa. This one is more than 100% increased in comparison to the talc modified material. Nevertheless, the standard deviation is ten times higher, which results out of the inhomogeneous cell structure, consisting of large as well as small cells and unfoamed parts (Fig. 5). These compact volume elements lead to locally higher densities implementing higher compression forces, because they absorb the force. Though, the higher mean compression modulus showing the influence of the modifier. The PLA bead foam, which was modified with 1% talc as well as 1% of chain extender has a modulus of 7.8 ± 0.5 MPa, which is about 40% higher compared to the talc modified PLA and approx. 38% less with lower standard deviations compared to the chain extender modified bead foam. In contrast to the chain extender modified material, the mean value is decreased, which might be traced back to the inhomogeneous foaming behavior, respectively.

All in all, it was shown, that the talc led to low standard deviations, resulting out of the nucleation effect which caused a more homogeneous cell morphology. Only the chain extender as modifier arises in an inhomogeneous morphology which has a negative impact on the standard deviation of the compression modulus.

4 Conclusion

In this work, PLA has been modified and investigated regarding the sorption, foaming and mechanical behavior of welded bead foams. The saturation behavior of PLA has been evaluated for different pressures and various times. Herby, the modifications resulted in slightly lower sorption levels and higher pressures

lead to higher diffusion rates. Saturated PLA granules have been used for analyzing the foaming behavior by a rapid temperature increase.

The influence of the modifications on the foaming behavior has been shown. Specifically, it was worked out that the modifications resulted in lower foam densities compared to unmodified PLA. It was shown that talc significantly affected the nucleation leading to lower cell sizes and a more homogeneous cells size distribution. The addition of chain extender lead to a low foam density of approx. 50 kg/m^3 but to inhomogeneous cell structure while the combination of chain extender and talc lead to similar foam densities with a homogeneous cell size distribution. The bead foams could not be welded directly why they saturated pellets have been foamed and welded in a one-step process. After the one-step processing, welded EPLA parts have been analyzed via SEM and a compression test.

In SEM it was found that talc lead to a nucleation effect which resulted into a homogeneous cell morphology and was confirmed by low standard deviations in the compression test. The addition of chain extender, without talc as nucleating agent led to inhomogeneous cell morphology. This inhomogeneity caused a higher modulus with higher standard deviation.

In a nutshell, amorphous PLA was modified and successfully foamed to densities below 50 kg/m^3. Additionally, a one-step processing for foaming and welding of saturated particles was used to manufacture a bead foam part with a density of approx. 80 kg/m^3. Finally, the influence of the modifications on the morphology and the compression properties have been evaluated, whereby, the used chain extender led to an inhomogeneous cell structure, but higher compression values and the talc resulted in a homogeneous cell structure with low standard deviations.

Author Contributions: Christian Brütting: conceptualization, writing–review and editing sections "1. Introduction", "2. Materials and Methods", "3. Results and Discussion", abstract and conclusions, review, editing and preparation of original draft. Julia Dreier: review and editing section "1. Introduction, "2. Materials and Methods", "3. Results and Discussion". Prof. Dr.-Ing Holger Ruckdäschel review and editing section "1. Introduction", "2. Materials and Methods", "3. Results and Discussion", Prof. Dr.-Ing. Christian Bonten, Prof. Dr.-Ing. Volker Altstädt, supervision, reviewing and funding acquisition.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

1. Raps, D., Hossieny, N., Park, C. B., Altstädt, V. (2015). Past and present developments in polymer bead foams and bead foaming technology. *Polymer, 56,* 5–19. DOI 10.1016/j.polymer.2014.10.078.

2. Nofar, M., Park, C. B. (2014). Poly(lactic acid) foaming. *Progress in Polymer Science.* DOI 10.1016/j. progpolymsci.2014.04.001.

3. Garancher, J. P., Fernyhough, A. (2012). Crystallinity effects in polylactic acid-based foams. *Journal of Cellular Plastics, 48(5),* 387–397. DOI 10.1177/0021955X12448804.

4. Standau, T., Zhao, C., Castellón, S. M., Bonten, C., Altstädt, V. (2019). Chemical modification and foam processing of polylactide (PLA). *Polymers, 11(2),* 306. DOI 10.3390/polym11020306.

5. Saeidlou, S., Huneault, M. A., Li, H., Park, C. B. (2012). Poly(lactic acid) crystallization. *Progress in Polymer Science, 37(12),* 1657–1677. DOI 10.1016/j.progpolymsci.2012.07.005.

6. Di, Y., Iannace, S., Di Maio, E., Nicolais, L. (2005). Reactively modified poly(lactic acid): Properties and foam processing. *Macromolecular Materials and Engineering, 290(11),* 1083–1090. DOI 10.1002/(ISSN)1439-2054.

7. Mihai, M., Huneault, M. A., Favis, B. D. (2010). Rheology and extrusion foaming of chain-branched poly(lactic acid). *Polymer Engineering and Science, 50(3),* 629–642. DOI 10.1002/pen.21561.

8. Göttermann, S., Standau, T., Weinmann, S., Altstädt, V., Bonten, C. (2017). Effect of chemical modification on the thermal and rheological properties of polylactide. *Polymer Engineering and Science, 57(11),* 1242–1251. DOI 10.1002/pen.24505.

9. Nofar, M., Tabatabaei, A., Park, C. B. (2013). Effects of nano-/micro-sized additives on the crystallization behaviors of PLA and PLA/CO_2 mixtures. *Polymer, 54(9),* 2382–2391. DOI 10.1016/j.polymer.2013.02.049.

10. Wang, J., Zhai, W., Ling, J., Shen, B., Zheng, W. et al. (2011). Ultrasonic irradiation enhanced cell nucleation in microcellular poly(lactic acid): A novel approach to reduce cell size distribution and increase foam expansion. *Industrial and Engineering Chemistry Research, 50(24),* 13840–13847. DOI 10.1021/ie201643j.

11. Richards, E., Rizvi, R., Chow, A., Naguib, H. (2008). Biodegradable composite foams of PLA and PHBV using subcritical CO_2. *Journal of Polymers and the Environment, 16(4),* 258–266. DOI 10.1007/s10924-008-0110-y.

12. Köppl, T., Raps, D., Altstädt, V. (2014). E-PBT-bead foaming of poly(butylene terephthalate) by underwater pelletizing. *Journal of Cellular Plastics, 50(5),* 475–487. DOI 10.1177/0021955X14528524.

13. Weingart, N., Raps, D., Kuhnigk, J., Klein, A., Altstädt, V. (2020). Expanded polycarbonate (EPC)—A new generation of high-temperature engineering bead foams. *Polymers, 12(10),* 2314. DOI 10.3390/polym12102314.

14. Zhai, W., Kim, Y. W., Jung, D. W., Park, C. B. (2011). Steam-chest molding of expanded polypropylene foams. 2. Mechanism of interbead bonding. *Industrial and Engineering Chemistry Research, 50(9),* 5523–5531. DOI 10.1021/ie101753w.

15. Nofar, M., Ameli, A., Park, C. B. (2015). Development of polylactide bead foams with double crystal melting peaks. *Polymer, 69(1),* 83–94. DOI 10.1016/j.polymer.2015.05.048.

16. Nofar, M., Ameli, A., Park, C. B. (2015). Expanded polylactide bead foaming-a new technology. *AIP Conference Proceedings,* vol. 1664, *Cleveland, Ohio, USA*.

17. Nofar, M., Ameli, A., Park, C. B. (2015). A novel technology to manufacture biodegradable polylactide bead foam products. *Materials and Design, 83,* 413–421. DOI 10.1016/j.matdes.2015.06.052.

18. Parker, K., Garancher, J. P., Shah, S., Fernyhough, A. (2011). Expanded polylactic acid-an eco-friendly alternative to polystyrene foam. *Journal of Cellular Plastics, 47(3),* 233–243. DOI 10.1177/0021955X11404833.

19. Liu, W., He, S., Yang, Y. (2019). Effect of stereocomplex crystal on foaming behavior and sintering of poly(lactic acid) bead foams. *Polymer International, 68(3),* 516–526. DOI 10.1002/pi.5742.

20. Witt, M. R. J., Shah, S. (2012). *Methods of Manufacture of Polylactidc Acid Foams*, US Patent, US8, 283, B2.

21. Lohmann, J., Sampath, B. D. S., Gutmann, P., Künkel, A., Hahn, K. et al. (2013). *Method for Producing Expandable Granulates Containing Polylactic Acid,* WO Patent 2014/001119 AI.

22. Haraguchi, K., Ohta, H. (2006). *Expandable Polylactic Acid Resin Particles, European Patent EP, 1683828,* B1.

23. Gebraad, M., Kuijstermans, F. P. A., Noordegraaf, J. (2014). *Particulate, Expandable Polymer, A Method for Preparing the Same as Well as the Use Thereof, U.S. Patent No. 8, 901,181*. Washington DC: U.S. Patent and Trademark Office.

24. Britton, R. N., Hendrikus, F. A., Van doormalen, C., Noordegraaf, J., Molenveld, K. et al. (2012). *Coated Particulate Expandable Polylactid Acid, U.S. Patent No. 8, 268, 901*. Washington DC: U.S. Patent and Trademark Office.

25. Pluta, M., Galeski, A., Alexandre, M., Paul, M. A., Dubois, P. (2002). Polylactide/montmorillonite nanocomposites and microcomposites prepared by melt blending: Structure and some physical properties. *Journal of Applied Polymer Science, 86(6),* 1497–1506. DOI 10.1002/(ISSN)1097-4628.

26. Hapuarachchi, T. D., Peijs, T. (2010). Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for polylactide and its natural fibre reinforced composites. *Composites Part A: Applied Science and Manufacturing, 41(8),* 954–963. DOI 10.1016/j.compositesa.2010.03.004.

27. Standau, T., Long, H., Murillo Castellón, S., Brütting, C., Bonten, C. et al. (2020). Evaluation of the zero shear viscosity, the D-content and processing conditions as foam relevant parameters for autoclave foaming of standard polylactide (PLA). *Materials, 13(6),* 1371. DOI 10.3390/ma13061371.

28. Mahmood, S. H., Ameli, A., Hossieny, N., Park, C. B. (2014). The interfacial tension of molten polylactide in supercritical carbon dioxide. *Journal of Chemical Thermodynamics, 75,* 69–76. DOI 10.1016/j.jct.2014.02.017.

29. Saha, M. C., Mahfuz, H., Chakravarty, U. K., Uddin, M., Kabir, E. et al. (2005). Effect of density, microstructure, and strain rate on compression behavior of polymeric foams. *Materials Science and Engineering A, 406,* 328–336. DOI 10.1016/j.msea.2005.07.006.

30. Saint-Michel, F., Chazeau, L., Cavaillé, J. Y., Chabert, E. (2006). Mechanical properties of high density polyurethane foams: I. Effect of the density. *Composites Science and Technology, 66(15),* 2700–2708. DOI 10.1016/j.compscitech.2006.03.009.

31. Chen, Y., Das, R., Battley, M. (2017). Effects of cell size and cell wall thickness variations on the strength of closed-cell foams. *International Journal of Engineering Science, 120,* 220–240. DOI 10.1016/j.ijengsci.2017.08.006.

32. Okolieocha, C., Köppl, T., Kerling, S., Tölle, F. J., Fathi, A. et al. (2015). Influence of graphene on the cell morphology and mechanical properties of extruded polystyrene foam. *Journal of Cellular Plastics, 51(4),* 413–426. DOI 10.1177/0021955X14566084.

33. Aksit, M., Zhao, C., Klose, B., Kreger, K., Schmidt, H. W. et al. (2019). Extruded polystyrene foams with enhanced insulation and mechanical properties by a benzene-trisamide-based additive. *Polymers, 11(2),* 268. DOI 10.3390/polym11020268.