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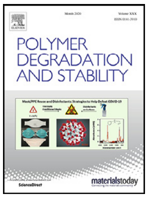

Improving the heat deflection temperature of poly(lactic acid) foams by annealing

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ABSTRACT

Poly(lactic acid) is a promising biopolymer but due to its low heat deflection temperature, the usage of PLA-based products is limited. In the case of bulk products, annealing is an effective way to increase the heat deflection temperature. Our aim was to improve the heat deflection temperature of poly(lactic acid) foams by annealing. In this study, we showed that D-lactide content affects the crystallinity of foam structures in the same way it affects the crystallinity of bulk PLA. Lower D-lactide content resulted in a higher degree of crystallinity. Annealing proved to be an effective way to induce cold crystallization. The heat deflection temperatures were calculated with the use of DMA, which produced more accurate results than the HDT device. Outstanding heat deflection temperature results were achieved (from 54°C to 131°C) with the use of annealing of chemically foamed PLA foams (1.4% D-lactide content) containing a nucleating agent. The excellent results can be explained with increased crystallinity, which exceeded 40%. Also, no signs of thermal degradation were found after successful annealing.

1. Introduction

As a result of increasing global environmental consciousness, biopolymers are more and more recognized and used [1]. They are produced from renewable resources and/or biodegradable. Biopolymers help reduce landfill waste and the polymer industry's dependance on the oil industry. In industrial composts, biodegradable polymer waste is broken down into water, humus, carbon dioxide and other, environmentally neutral compounds [2]. As biopolymer research has only accelerated in the past few decades, polymers that can be processed on traditional equipment with minimal modification are still preferred. One of the most promising biopolymers is poly(lactic acid) (PLA) [3], which has mechanical properties similar to traditional, mass-produced plastics [4]. Poly(lactic acid) can be produced from biomass and is biodegradable after use. Producing PLA from raw materials requires 25–55% less energy than traditional plastics made from crude oil [5]. The main disadvantages of PLA are its brittleness and low glass transition temperature of approx. 60°C. PLA parts lose their stiffness at temperatures above T_g, therefore they cannot be used at elevated temperatures (>60°C). Due to this drawback, improving the heat deflection temperature of PLA could make its use more widespread.

Poly(lactic acid) is semicrystalline, yet it rarely has a high degree of crystallinity after processing, due to its slow crystallization [6]. The ratio of the building block isomers of the molecule, D-lactide and L-lactide, determines its ability to crystallize [7]. Commercial processes overwhelmingly yield L-lactide, therefore PLA grades are usually characterised by their D-lactide content [5]. More than 10% D-lactide results in amorphous PLA [5]. A higher degree of crystallinity generally improves mechanical properties and increases the heat deflection temperature. Polymer processing usually includes fast cooling, which retards crystallization. Post-process annealing, a method for improving crystallinity, is being investigated by researchers [8-11]. Hajba [8] conducted isothermal annealing experiments (80–140°C, PLA grade: Ingeo 3001D, 1.4% D-lactide). His results indicate that annealing is an effective treatment to increase the heat deflection temperature. The improvement in heat deflection temperature (HDT) resembles a sigmoid curve as a function of the degree of crystallinity. Between 37% and 42% of crystallinity, heat deflection temperature increased from approx. 60°C to above 120°C. The cause of the sudden increase

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was found to be α'-/α-crystal polymorphism and the growth in spherulite size. Tang et al. [9] examined PLA crystallization from melt at an isothermic 105°C. Ethylenebishydroxystearamide was used as nucleating agent in 1 wt%, and annealing time varied from 0.5 to 120 minutes. They found that the use of nucleating agents resulted in a higher degree of crystallinity (40%) and faster crystallization kinetics. Neat PLA (Ingeo 2002D, 1.5–2% D-lactide) had a heat deflection temperature (HDT-B) of 51°C, which increased to 93°C as the nucleating agent was added. The nucleating properties of talcum and starch in annealed PLA (Ingeo 4032D, D-lactide: 1.4%) were examined by Kang et al. [10]. The initial 2.4% degree of crystallinity increased to 36% and 26% by 1 wt% talcum and starch, respectively. According to microscopic images, the effectiveness of the nucleating agent is determined by its shape, wettability, and effectiveness of dispersion. Experiments with different annealing parameters showed that crystallization kinetics has an optimum temperature, at which the process takes place the fastest. Multiple researchers [12,13] found that the addition of nucleating agents causes the enthalpy peak of cold crystallization to occur at lower temperatures, by as much as 14°C. The heterogeneous nuclei lower the free enthalpy needed for crystallization. Nascimento et al. [11] examined the recycling of PLA and conducted annealing experiments. It is important to measure whether multiple processing cycles (recycling) cause significant changes in the properties of PLA. The DSC curves of the annealed (6 hours, 120°C) samples showed no significant difference, therefore multiple processing resulted in no change in thermal properties in this case. Annealing increased the degree of crystallinity from 1% to above 33%, which resulted in a 10°C increase in the heat deflection temperature.

In many aspects, foams are an important segment of polymer products. Due to their structure, foams inherently have better dynamic properties and fracture toughness [14]. These properties have further benefits in the case of poly(lactic acid), for the bulk material is quite brittle. As polymer foams are difficult to recycle [15], biodegradable foams could help ease the load on landfills. Therefore biopolymer, especially PLA foaming is intensively reserached [16]. High-density foams can be produced with chemical blowing agents (CBA) or expandable microspheres (EMS). These agents, mixed into the polymer resin, can be processed with traditional extrusion equipment. This method does not require expensive gas-injection systems, making foaming more available. Chemical blowing agents usually produce high density ($>$0.5 g/cm^3) foams, where density as a function of CBA content has a minimum [4,17]. This point, after which density begins to increase, is the gas retention limit. Higher CBA content results in cell coarsening, the process of gas diffusing from a smaller cell into a neighbouring bigger cell, due to higher pressure. This results in macro cavities, the inhomogenous cell structure increases density and impairs mechanical properties [18]. Cell structure is also affected by extrusion speed, as the CBA may not have sufficient time to fully decompose [4].

To sum up, if the brittleness of PLA could be counteracted by foaming, and its low heat deflection temperature by annealing, the resulting material could be used for numerous purposes. In this present research, PLA is foamed with CBA and EMS. The foams are characterised by microscopic examination, and mechanical and morphological tests. Heat deflection temperatures are measured, and improved by annealing. The aforementioned studies were aimed at annealing bulk PLA, foams were not examined. We use three grades of PLA with significantly different D-lactide contents, so they have different crystallization behaviours. We present a characterisation method for heat deflection using dynamic mechanical analysis (DMA). The goal of this research is to reach the region of sudden increase in the heat deflection temperature of PLA foams, which is 40% crystallinity, according to the literature [8].

2. Materials and Methods

2.1. Materials

Three extrusion grade poly(lactic acids) were purchased from NatureWorks LLC. (Minnetonka, Minnesota, USA): Ingeo 4032D (1.4% D-lactide), Ingeo 2003D (4.3% D-lactide) and Ingeo 4060D (12.0% D-lactide). The density of neat PLA is 1.24 g/cm^3, as given by the distributor and verified by our measurements. The exothermic chemical blowing agent Tracel IM 3170 MS was produced by Tramaco GmbH (Tornesch, Germany). The foaming agent is azodicarbonamide, present in 30 wt%. The Tracel G 6800 MS expandable microspheres were produced by Tramaco GmbH as well. The material of the expandable microspheres shell is acrylonitrile/methyl methacrylate, the encapsulated physical blowing agent is isopentane [19]. The blowing agents were used at a fixed 2 wt% ratio, as we found in the literature [20]. The Ecopromote HD crystal nucleating agent was purchased from Nissan Chemical Co. (Tokyo, Japan). It is composed of zinc salts and zinc oxides, and was used in a ratio of 2 wt%.

2.2. PLA foaming

Prior to processing, PLA resins were dried in a hot air oven at 85°C for 6 hours (WGLL 45B, Huanghua Faithful Instrument Co.) to prevent hydrolysis. Foams were manufactured with a Labtech Scientific 25-30C single-screw extruder (screw diameter: 25 mm, L/D ratio: 30). Screw speed was 80 rpm. A 300 mm wide flat slit die was used with a 4 mm gap size. The temperature profile from hopper to die was 155°C–160°C–175°C–190°C. Die temperature was 190°C. The extruded foam sheet was solidified on a Labtech Scientific LCR300 flat film line. The temperature of the tempering roller was 55°C, its peripheral speed was 0.3 m/min. The peripheral speed of the traction roller was 0.9 m/min. Prior to extrusion, the resins were blended together by dry mixing, the ratios can be found in Table 1.

2.3. Compounding

For samples containing a nucleating agent, a compound was made from the agent and PLA in order to better distribute the nucleating powder. Compounding was done at a screw speed of 25 rpm on a Labtech LTE26-44 twin-screw extruder (screw diameter: 26 mm, L/D ratio: 44). The temperature profile from hopper to die was 180°C–180°C–185°C–185°C–190°C–190°C–195°C–195°C–200°C–200°C. Die temperature was 200°C. The extrudate was pelletized with a Labtech LZ-120/VS granulator.

2.4. Annealing

The samples were annealed in a WGLL 45B hot air oven. For sustained flatness of the bottom of the specimen, they were put on a steel plate that had been allowed to take on the ambient temperature of the oven. Specimens were cut from the middle of the extruded foam sheet, their longitudinal axes corresponding to the direction of extrusion. Annealing times were 5, 9, and 13 minutes at 90°C, 110°C, and 140°C [8]. Annealed samples were cooled to room temperature in open air. In the following, annealed samples are named according to annealing time and temperature.

2.5. Testing methods

Density

Density (ρ) was determined according to Eq. (1) with the use of a Sartorius Quintix (e=0.01 mg) analytical balance. The measurements were repeated 5 times and the results averaged. The ex-

Table 1
Manufactured samples (BA = blowing agent, NA = nucleating agent).

PLA grade	D-lactide content [%]	BA type	BA content [wt%]	NA type	NA content [wt%]
4060D	12.0	IM 3170 MS	2	-	0
2003D	4.3	IM 3170 MS	2	-	0
4032D	1.4	IM 3170 MS	2	-	0
4032D	1.4	IM 3170 MS	2	Ecopromote HD	2
4032D	1.4	G 6800 MS	2	-	0
4032D	1.4	G 6800 MS	2	Ecopromote HD	2

pansion rate and void fraction were calculated from the density of unfoamed PLA Eq. (2),(3).

$$\rho_{\mathrm{foam}} = \frac{m_{sa}}{m_{sa} - m_{sl}} * \rho_{\mathrm{dw}}, \tag{1}$$

$$\mathrm{ER} = \frac{\rho_{\mathrm{polymer}}}{\rho_{\mathrm{foam}}}, \tag{2}$$

$$V_f = 1 - \frac{\rho_{\mathrm{faom}}}{\rho_{\mathrm{polymer}}}, \tag{3}$$

where ρ_{foam} [g/cm^3] is the density of the foamed polymer, m_{sa} [g] is the mass derived from the weight of the specimen in air; m_{sl} [g] is the mass derived from the weight of the specimen measured in the measuring liquid, ρ_{dw} [g/cm^3] is the density of the measuring medium, ER [-] is the expansion rate, ρ_{polymer} [g/cm^3] is the desity of the unfoamed polymer, and V_f [-] is the void fraction.

Scanning electron microscopy

We examined the cryogenic fracture surfaces of the foams by scanning electron microscopy (SEM) (Jeol 6300LA, accelerating voltage 10 kV). The cross-sections of the foams were coated with a gold-palladium alloy.

Differential scanning calorimetry

Morphological properties were examined by differential scanning calorimetry (DSC) (TA Instruments Q2000). The temperature range was 0-200°C, the heating rate was 5°C/min, and the mass of the samples was 3–6 mg. The degree of crystallinity was calculated according to Eq. (4). In the case of syntactic foams made with EMS, the effect of the spherical cell shells was neglected.

$$X_{c'} = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{kr}} * 100, \tag{4}$$

where $X_{c'}$ [%] is the degree of crystallinity after manufacturing, ΔH_m [J/g] is the melting enthalpy, $\Delta H_{100\%}$ [J/g] is the theoretical melting enthalpy of 100% crystalline PLA (93 J/g [4]), and ΔH_{cc} [J/g] is the cold crystallization enthalpy.

Heat deflection temperature

The heat deflection temperature (HDT) was measured with a Ceast HV3 6911.000 device. The measurements were repeated 3 times and the results were averaged. The size of the specimens was 80 mm × 15 mm, span length was 64 mm in flatwise configuration. Loading stress was 1.8 MPa, and the final deflection was 0.68 mm according to the ISO 75 HDT-A standard. The heating rate of the silicone oil was 2°C/min, the starting temperature was 30°C, and initial soaking time was 5 minutes.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a TA Instruments Q800. Specimen size was 60 mm × 10 mm. Span length was 35 mm in dual cantilever configuration. The temperature range was 0–150°C, the heating rate was 2°C/min, and initial soaking time was 5 minutes. The amplitude was 20 μm, with a frequency of 1 Hz.

We calculated the storage modulus to characterise the heat deflection temperature according to Eq. (5).

$$E_{\mathrm{HDT-A}} = \frac{FL^3}{48\frac{bh^3}{12}f} = \frac{\sigma L^2}{6h^2 f} = 903\ \mathrm{MPa} \tag{5}$$

where F [N] is the force applied, σ [MPA] is the induced stress, b [mm] is the width of the specimen, h [mm] is the height of the specimen, L [mm] is the span length, $E_{\mathrm{HDT\text{-}A}}$ [MPa] is the storage modulus, and f [mm] is the deflection.

Thermogravimetric analysis

Thermal stability was characterised by thermogravimetric analysis (TGA) with a TA Instruments Q500. Sample mass was 3–6 mg, and the temperature range was T_{Room}–600°C. The heating rate was 10°C/min in a measuring medium of air.

Characterising cell structure

Cell structure was characterised with SEM images. We used the number of nucleated cells to calculate cell population density according to Eq. (6) [17].

$$N_c = \left(\frac{n \cdot M}{A}\right)^{\frac{3}{2}} \cdot \frac{1}{1 - V_f} \tag{6}$$

where N_c [cells/cm^3] is the cell population density, n [cells] is the number of cells counted in the recorded image, A [cm^2] is the cross-section area of the sample, M [-] is the magnification factor, and V_f [-] is the void fraction.

3. Results

3.1. Effect of D-lactide content on the cell structure of foamed PLA

We examined PLA foams made with the chemical blowing agent to determine the effect of D-lactide content to the cell structure, as syntactic foams are less sensitive in this regard to the type of PLA used. 2wt% CBA was used to create PLA foams with all three grades, and 2 wt% expandable microspheres with 4032D.

The densities of foamed polymers made with azodicarbonamide were in the range of 0.8–1.0 g/cm^3, which corresponds with literature data [4]. The correlation of density and D-lactide content can be seen in Fig. 1. We found that higher D-lactide content caused higher foam density. Molecules containing less D isomer are better suited to crystallize, which results in different melt and mechanical properties. The growing cells are less likely to rupture, causing the structure to hold more gas, thus resulting in lower density than in the case of amorphous PLA. A density above 1.0 g/cm^3 was achieved in the case of the syntactic foam, this kind of blowing agent is usually added in higher ratios to achieve lower density. Density values can be seen in Table 2.

The present foaming method resulted in high-density, closed-cell foams. Using SEM images, we found that the semicrystalline PLA grades had larger average cell size than the amorphous 4060D (0.116 mm and 0.096 mm). The standard deviation of cell size was quite high, which suggests a heterogenous structure, which can be clearly seen in Fig. 3. A rudimentary core–skin structure was also

Table 2
Density-related properties of poly(lactic acid) foams.

Sample name	D-lactide [%]	BA content [wt%]	Density [g/cm^3]	Expansion rate [-]	Void fraction [-]	Cell density [cells/cm^3]
Neat PLA	-	0	1.24	1	0	0
4060D_2_IM3170	12.0	2	0.991±0.003	1.25	0.20	$5.1 \bullet 10^5$
2003D_2_IM3170	4.3	2	0.899±0.009	1.38	0.28	$8.5 \bullet 10^5$
4032D_2_IM3170	1.4	2	0.818±0.004	1.52	0.34	$6.3 \bullet 10^5$
4032D_2_G6800	1.4	2	1.147±0.018	1.08	0.08	$3.7 \bullet 10^5$

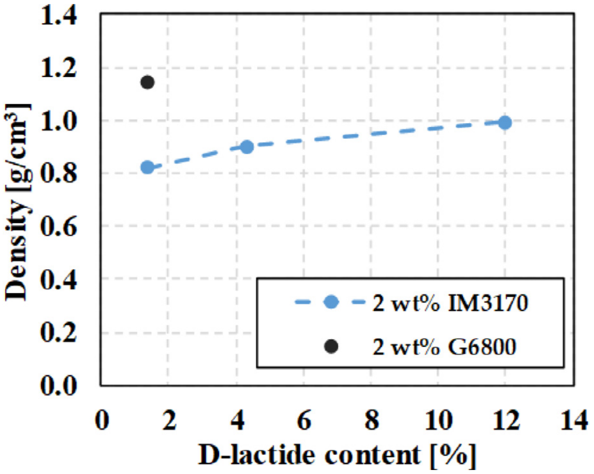


Fig. 1. Densities of PLA foams with varying D-lactide content.

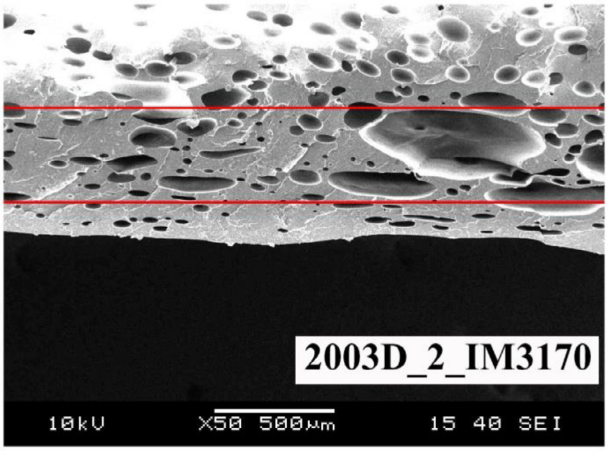


Fig. 2. Core–skin structure of the cross-section of a PLA foam.

Table 3
Crystalline portion of as-manufactured foams.

PLA grade	D-lactide content [%]	ΔH_{cc} [J/g]	ΔH_m [J/g]	$X_{c'}$ [%]
4060D_2_IM3170	12.0	0	0	0
2003D_2_IM3170	4.3	24.4	27.6	3.4
4032D_2_IM3170	1.4	30.4	35.9	6.0
4032D_2_G6800	1.4	23.7	29.4	6.2

Table 4
Results of differential scanning calorimetry of PLA foams.

Sample name	D-lactide [%]	T_g [°C]	T_{cc} [°C]	$X_{c'}$ [%]
4060D_2_IM3170	12.0	57	-	0
4060D_2_IM3170_13min_140C	12.0	53	-	0
2003D_2_IM3170	4.3	59	107	3.4
2003D_2_IM3170_13min_140C	4.3	56	-	32.9
4032D_2_IM3170	1.4	60	95	6.0
4032D_2_IM3170_13min_140C	1.4	59	-	38.4
4032D_2_IM3170_30min_140C	1.4	59	-	37.5
4032D_2_IM3170_60min_140C	1.4	60	-	38.2
4032D_2_G6800	1.4	55	101	6.2
4032D_2_G6800_13min_140C	1.4	59	-	41.3

revealed by the SEM images. The outer area of the cross-section, which was contacted and cooled the most by the tempering roll, had smaller cells. Here, the developing gas pressure was not able to overcome the increasing melt strength of the solidifying skin. An inhomogeneous layer, containing ruptured and coarsened cells, could be found below the skin, due to the fact that gas was not able to diffuse into the solid skin, thus it became locally more concentrated. Spherical cells with even size and homogenous distribution were formed in the core area of the cross-section. The core–skin structure can be seen in Fig. 2.

As expected, fairly uniform, spherical cells were formed when expandable microspheres were used (Fig. 3). In the case of this blowing agent, the cells are predefined, hence the orderly structure. Cell distribution was normal, a core–skin structure was not formed.

Less than 7% crystallinity was achieved in each case after manufacturing. Differential scanning calorimetry results are shown in Table 3. Cold crystallization and melting enthalpies are nearly equal, therefore crystallization almost entirely took place in the DSC device during the analysis.

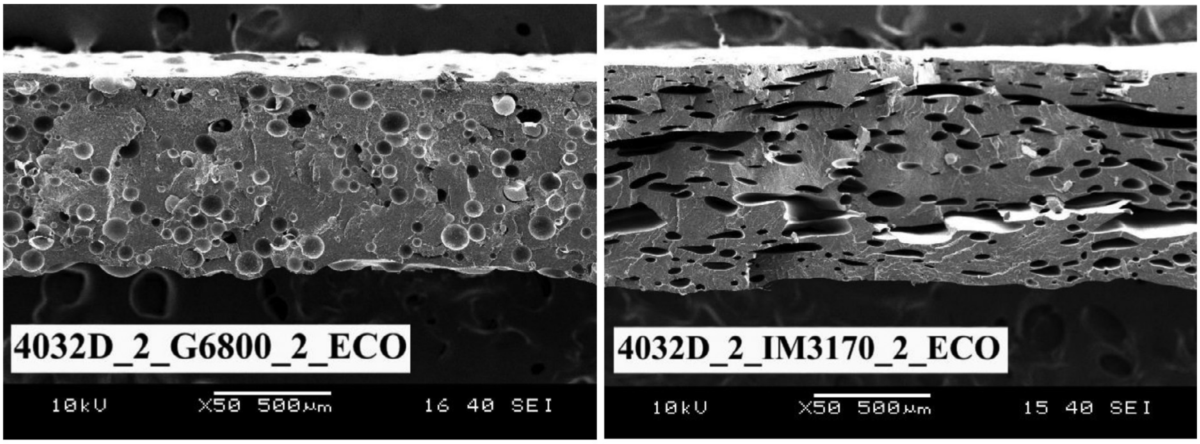
3.2. Improving crystallinity by annealing

Significant crystalline portion did not form during manufacturing, due to the slow crystallization of poly(lactic acid). Therefore, we used post-manufacturing annealing to increase the degree of crystallinity. It was performed in a hot air oven for 5, 9, and 13 minutes, at 90, 110, and 140°C according to the literature. Afterward, the samples were cooled to room temperature in open air.

3.2.1. Measuring the heat deflection temperature

The heat deflection temperature of PLA foams produced with the chemical blowing agent was measured with an HDT device. Tendencies were best shown by 4032D, containing the lowest amount of D-lactide Fig. 4. The heat deflection temperature increased with longer and higher temperature annealing. The tendency can be clearly seen, but the improvement itself is not satisfactory. The maximum heat deflection temperature was 59.1°C. These results led us to believe that the degree of crystallinity required for the sudden increase of heat deflection temperature was not achieved. A maximum crystallinity of 38.4% was shown by DSC (Table 4). We experimented with annealing at 140°C for 30 and 60 minutes to further increase the heat deflection temperature, but the HDT value reached a plateau at 60°C. However, due to the longer annealing times, we had to take thermal degradation into consideration. Thermogravimetric analysis was carried out on as-manufactured and annealed (13, 30, and 60 minutes at 140°C) 4032D foam samples made with CBA (Fig. 5).

TGA showed that at 140°C, annealing had not caused thermal degradation up to 30 minutes annealing time. On the contrary, thermal stability slightly increased due to more perfect crys-



a) b)

Fig. 3. Differences in the cell structure of PLA foams made with expandable microspheres (a) and an exothermic chemical blowing agent (b).

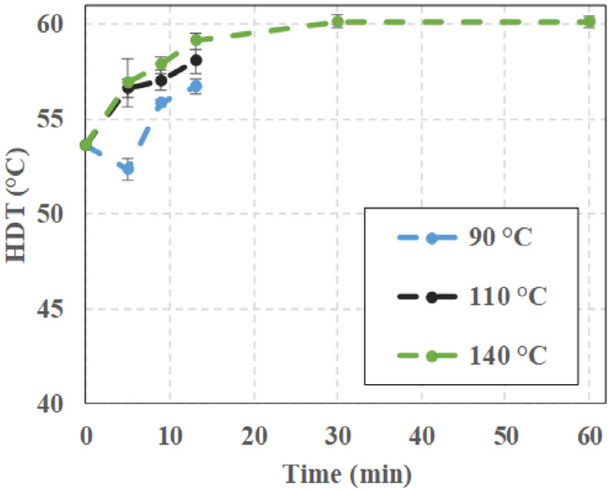


Fig. 4. HDT results of annealed 4032D foams made with 2m% IM3170 CBA.

tal variants [8]. Degradation can be seen in the sample annealed for 60 minutes, as its weight loss shifted to lower temperatures. Therefore, 13 minutes annealing at 140°C was sufficient for cold crystallization to fully take place, whilst the foamed polymer did not suffer thermal degradation. No notable change can be seen on the TGA curves in the decomposition temperature range of the chemical blowing agent, proving that the CBA was fully decomposed during extrusion and no active residue remained in the samples.

3.2.2. The effect of annealing on crystallinity

Differential scanning calorimetry was used to give insight into the HDT results. The glass transition temperature was measured, and cold crystallization and melting were characterised. The degree of crystallinity was calculated for as-manufactured and post-annealed samples. The effect of annealing was examined on samples heated for 13 minutes at 140°C, as heat deflection temperature did not increase at longer annealing times. A mostly amorphous ($X_{c'} < 7\%$) structure was found in the case of as-manufactured samples made with a chemical blowing agent. The crystalline portion of the low D-lactide 4032D foam was only 6.0% (Table 4). Samples produced from 4060D, containing 12.0% D-lactide, were fully amorphous even after annealing (Fig. 6). Annealing caused significant cold crystallization in the case of 2003D and 4032D, resulting in 32.9% and 38.4% crystallinity, respectively. These results are consistent with that of Nascimento et al. [11], who annealed PLA with a D-lactide content similar to that of 2003D, and achieved 33% crystallinity. We evaluated the sam-

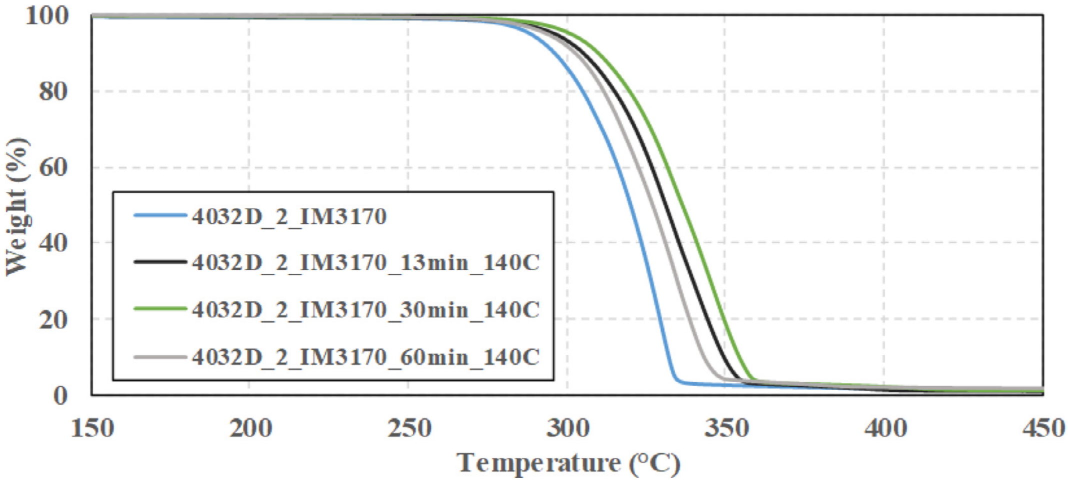


Fig. 5. Thermogravimetric results of annealed PLA foams.

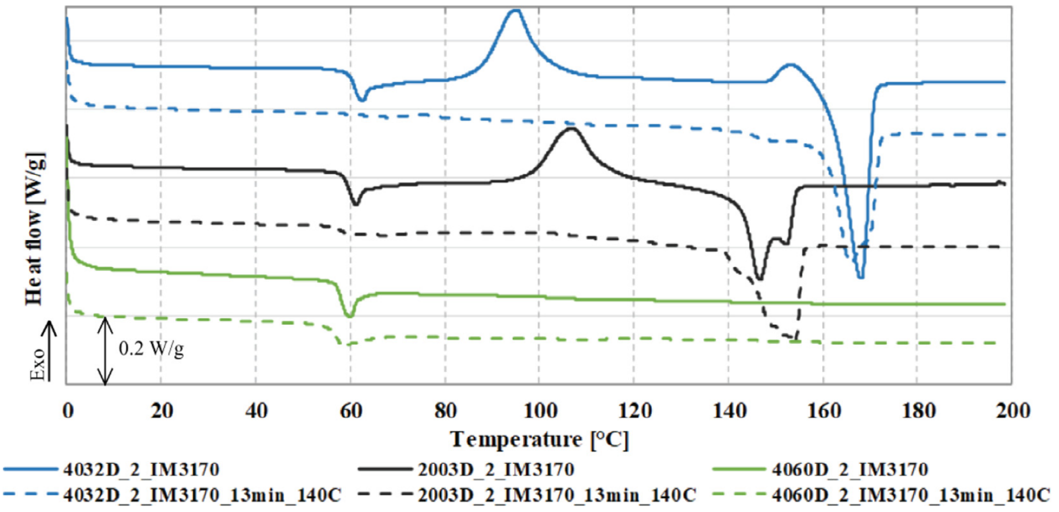
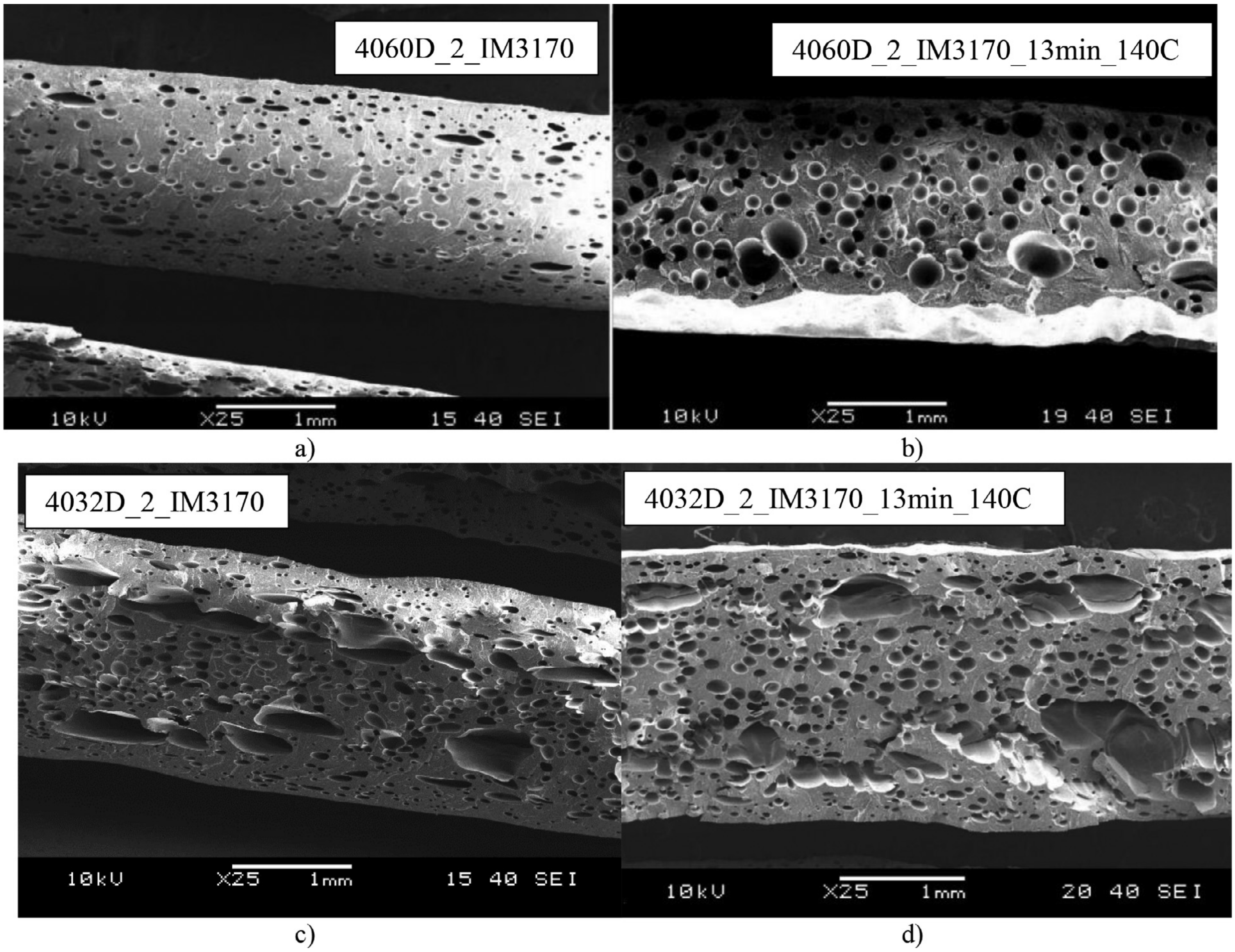


Fig. 6. DSC curves of as-manufactured and annealed PLA foams made with CBA.



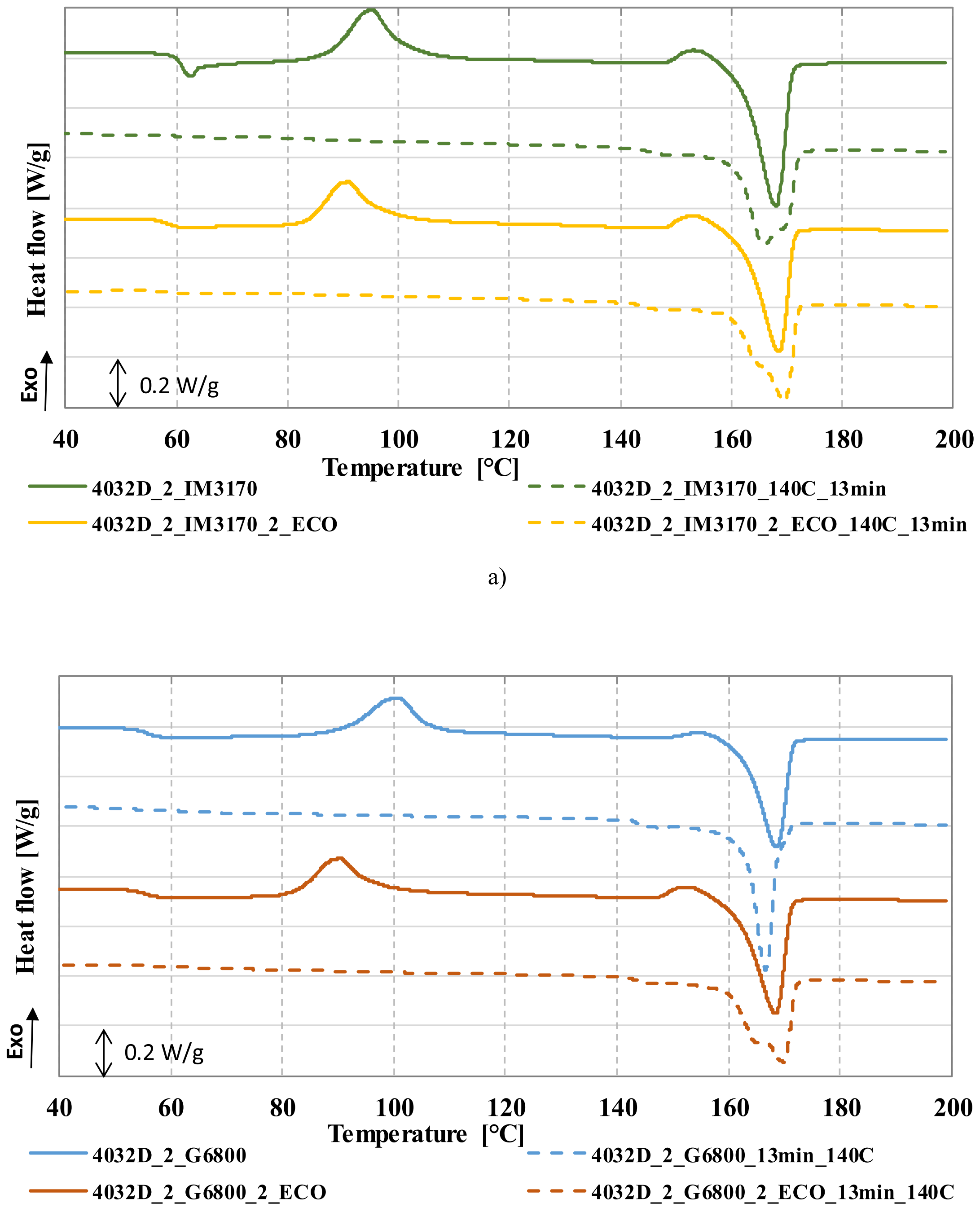
a) b) c) d)

Fig. 7. Changes in cell shape of annealed PLA foams made with CBA a) 4060D_2_IM3170, b) 4060D_2_IM3170_13min_140C, c) 4032D_2_IM3170 and d) 4032D_2_IM3170_13min_140C.

ples annealed for 30 and 60 minutes to find out whether crystallinity had increased even more, but found only marginal improvement. 13 minutes at 140°C was the optimum, as the lack of the cold crystallization peak suggests that crystallization was fully completed.

3.2.4. Effect of annealing on cell structure

No changes in cell structure were found in the case of semicrystalline PLA foams after annealing. The shape of the cells was altered in the case of the amorphous 4060D as well as in the case of 4032D. Without the stiffening effect of crystalline structures, the flattened, ellipsoid cells, seeking minimal surface energy, were able



a)

b)

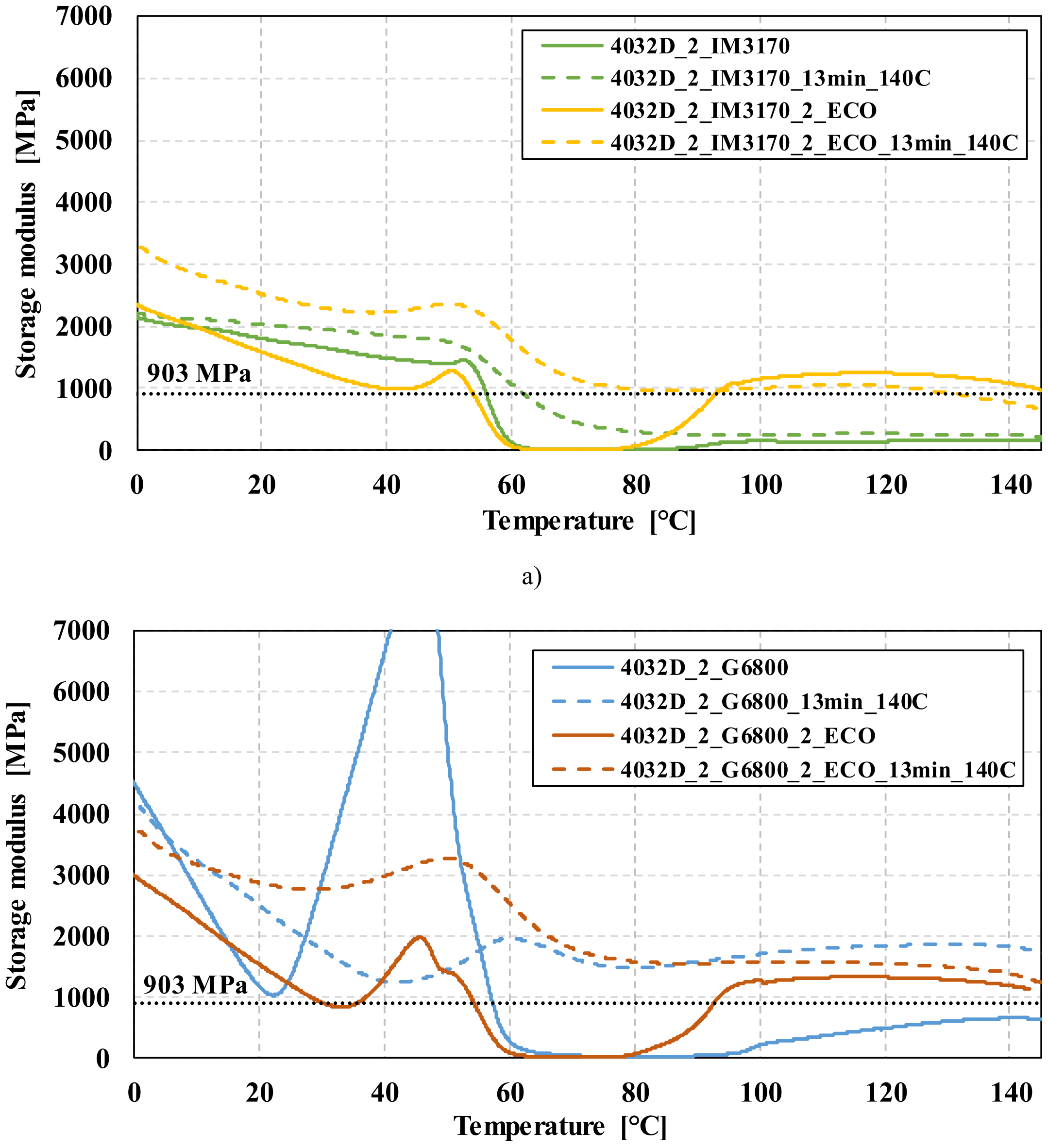
Fig. 8. DSC curves of 4032D PLA foams made with chemical blowing agent (a) and expandable microspheres (b).

to take on a spherical shape (Fig. 7). Thus the thickness of the rubbery foam had also increased.

To sum up, the annealing process was most promising in the case of 4032D PLA foams, wich contain a low amount of the D-lactide isomer. The improvement in HDT, however, was not satisfactory. Hereinafter, we continued our experiments using a crystal nucleating agent to further improve crystallinity and increase the heat deflection temperature of poly(lactic acid) foams.

3.3. Improving HDT with a crystal nucleating agent

The previously discussed results show that annealing can effectively increase the degree of crystallinity of PLA foams. However, the crystallinity needed for the sudden increase of the heat deflection temperature was not reached [8,9]. Therefore, we added 2 wt% crystal nucleating agent (NA) to reach that threshold. The effect of the addition of the nucleating agent on the density of the foamed polymers can be seen in Table 5.



a)

b)

Fig. 9. DMA results of chemical (a) and syntactic (b) PLA foams (903 MPa represents the storage modulus in the HDT-A test).

Table 5
Density of PLA foams with a nucleating agent.

Sample name	BA content [wt%]	NA content [wt%]	Density [g/cm^3]	Expansion rate [-]	Void fraction [-]	Cell density [cells/cm^3]
Neat PLA	0	0	1.24	1	0	0
4032D_2_IM3170	2	0	0.818±0.004	1.52	0.34	$6.3 \bullet 10^5$
4032D_2_IM3170_2_ECO	2	2	0.925±0.004	1.34	0.25	$1.6 \bullet 10^6$
4032D_2_G6800	2	0	1.147±0.018	1.08	0.08	$3.7 \bullet 10^5$
4032D_2_G6800_2_ECO	2	2	1.070±0.004	1.16	0.14	$1.1 \bullet 10^6$

In the case of syntactic foams, an increase of 10 μm in average cell diameter was found (53→63 μm) in the samples containing NA. This resulted in a lower density foam, but density increased in the case of foams made with CBA. This can be explained with the difference in viscosity and melt pressure in the extruder die.

3.3.1. Effect of the nucleating agent on crystallinity

As expected, a higher degree of crystallinity was achieved with the nucleating agent, exceeding our goal of 40% (Table 6). 40% is the threshold for the sudden increase of heat deflection temperature in this case. The cold crystallization peak of the samples shifted to temperatures 10°C lower (Fig. 8), which is a phenomenon well documented by literature. This can be explained by the increased ability to crystallize in the presence of heterogeneous nuclei. The annealed samples show no cold crystallization peak, once again proving that the process had been completed.

Table 6
DSC results of annealed PLA foams with a nucleating agent.

Sample name	D-lactide [%]	T_g [°C]	T_{cc} [°C]	X_c' [%]
4032D_2_IM3170	1.4	60	95	6.0
4032D_2_IM3170_13min_140C	1.4	59	-	38.4
4032D_2_IM3170_2_ECO	1.4	59	91	10.7
4032D_2_IM3170_2_ECO_13min_140C	1.4	58	-	41.7
4032D_2_G6800	1.4	55	101	6.2
4032D_2_G6800_13min_140C	1.4	59	-	41.3
4032D_2_G6800_2_ECO	1.4	56	90	11.3
4032D_2_G6800_2_ECO_13min_140C	1.4	61	-	40.0

Table 7
DMA results of PLA foams, where HDT-A* represents the heat deflection temperature calculated from the storage moduli (150+ results were above the upper limit of the measurement).

Sample name	Storage modulus at 25°C [MPa]	Storage modulus at T_g+10°C [MPa]	Calculated HDT-A* [°C]
4032D_2_IM3170	1724	11	56
4032D_2_IM3170_13min_140C	1980	544	62
4032D_2_IM3170_2_ECO	1410	4	54
4032D_2_IM3170_2_ECO_13min_140C	2392	1797	131
4032D_2_G6800	1324	77	57
4032D_2_G6800_13min_140C	2123	1682	150+
4032D_2_G6800_2_ECO	1201	19	54
4032D_2_G6800_2_ECO_13min_140C	2788	1751	150+

3.3.2. Measuring the heat deflection temperature by DMA

The HDT device could not measure the heat deflection temperature accurately enough in our case. The samples containing nucleating agent were characterised by dynamic mechanical analysis, also used by Hajba [8]. The thin, uneven foam samples produced unreliable results, as the HDT device is designed to be used with standard, injection moulded specimens, not with extruded foams. Due to the varying thickness, each specimen had to be measured manually, which introduced error, as opposed to injection moulded specimens, which have set dimensions. Furthermore, due to the foam structure, the actual load-bearing cross-section cannot be accurately defined, introducing error to the bending results. Also, the HDT test only yields a singular, arbitrary temperature value, while DMA shows the behaviour of the material on a wide temperature spectrum [21].

HDT-A* was introduced to represent the HDT calculated from the DMA results. It can be calculated from the storage modulus according to Eq. (5). HDT-A* was defined as the following: The temperature value in the $T \in [T_g - 10, +\infty)$ interval of the temperature–storage modulus DMA graph, at which the storage modulus is 903 MPa for the first time, and it has a negative slope. The unit is °C. The temperature interval is necessary to exclude false results around room temperature (e.g. 4032D_2_G6800_2_ECO, Fig. 9); the measurement of the HDT normally starts at 30°C.

Foams made from 4032D PLA were analysed in this way, both made with CBA and EMS (Fig. 9). We examined regular samples and recipes containing the nucleating agent, and evaluated the dependency of storage modulus on temperature. The storage modulus ultimately determines the stiffness of the structure and its heat deflection temperature. We also characterized the effect of the crystal nucleating agent.

Without annealing, overwhelmingly amorphous foams were produced by extrusion, with either blowing agent. In the sub-T_g region, slow descent of the storage modulus was registered with increasing temperature. This phenomenon can be originated from secondary relaxation [22]. Approaching the glass transition temperature of the PLA causes the storage modulus to plummet, rendering the material unusable at elevated temperature applications. Storage modulus began to increase at around 90°C, as cold crystallization took place, as the DSC results show (Fig. 8). The annealed samples did not show any sign of cold crystallization; the storage moduli stayed roughly constant above T_g, as the crystalline portion of about 40% was responsible for load-bearing. This, once again, proves that crystallization fully took place during annealing. In the case of foams made with Tracel IM 3170 MS, the residual storage modulus above T_g was around 250 MPa, which increased to above 1000 MPa when the nucleating agent were added—a four-fold improvement. The storage modulus of 1000 MPa is on par with that of some common plastics (polyethylene, polypropylene).

The results of foams made with the expandable microspheres were less consistent, although the same tendencies can be seen: the storage modulus drops at the glass transition temperature and begins to increase at the threshold of cold crystallization. Annealed samples retained a storage modulus of 1.5-1.8 GPa at temperatures above T_g. The higher moduli can be explained with the spherical shells introduced by the blowing agent.

HDT-A* values can be seen in Table 7. Annealing the foamed polymers made with CBA resulted in a modest increase in the heat deflection temperature. The measured HDT was 59.1°C, while the calculated value was 61°C. The relative error of less than 5% can be attributed to the previously discussed causes. In the case of annealing, the HDT-A* value rose from 54°C to 131°C when 2 wt% Ecopromote HD crystal nucleating agent was added—an improvement of 240%.

Annealing also proved to be successful in the case of foams made with EMS. In this case, both recipes—with and without a nucleating agent—achieved heat deflection temperatures above 150°C, the upper limit of the measuring range. As DSC results show (Fig. 8), crystal melting begins at such temperature.

4. Conclusion

In this study, the effect of D-lactide content was investigated in the case of PLA foams. Annealing was used to increase the heat deflection temperature of the foams. We found that D-lactide content affects crystallinity in the same way it does with bulk PLA, as lower D-lactide content resulted in a higher degree of crystallinity. Annealing proved to be an effective way to induce cold crystallization, which was characterised by DSC and DMA. The heat deflection temperature was found to increase suddenly above 40% crystallinity. The nucleating agent was found effective to aid in reaching such crystallinity. Both unannealed and annealed samples benefited from the addition of the nucleating agent, the latter exceeding 40% crystallinity in the case of 4032D PLA (1.4% D-lactide). The heat deflection temperatures were calculated using DMA, which produced more accurate results than the HDT device. The HDT rose from 54°C to 131°C in the case of foams made with CBA (nucleating agent+annealing). Temperatures above 150°C were achieved in the case of syntactic foams made with EMS. We could not determine the exact value, as it exceeded the upper limit of the measuring range. No signs of thermal degradation were found after annealing (13 minutes at 140°C).

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Credits author statement

Conceptualization, Ákos Kmetty and Katalin Litauszki; methodology, Ákos Kmetty and Katalin Litauszki; validation, Tamás Péter; formal analysis, Tamás Péter; investigation, Tamás Péter; resources: Ákos Kmetty; writing—original draft preparation, Tamás Péter; writing—review and editing, Ákos Kmetty and Katalin Litauszki; visualization, Tamás Péter; supervision, Ákos Kmetty; project administration, Ákos Kmetty; funding acquisition, Ákos Kmetty.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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