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Characterization of chemically foamed poly(lactic acid)

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Abstract. This paper presents the characterization of poly(lactic acid)-based chemically foamed foam structures. We used extrusion grade, high molecular weight poly(lactic acid) as matrix material and azodicarbonamide as foaming agent. The resulting foams were characterized by foam density, cell population density, scanning electron microscopy, and based on the fracture surface of the foam cross-section, we calculated cell size distribution. The obtained distributions were fitted with the use of log-normal distribution in each case. We presented the effect of chemical blowing agent content (0.5 wt%, 1 wt%, 2 wt%, 4 wt% and 8 wt%) on the PLA-based foam structure and the effect of processing temperature (190 °C, 210 °C and 230 °C) on cell size distribution.

1. Introduction

The characterization of foam structures at a microstructural level can be approached from four aspects. The first approach is based on the amount of material in the foam structure (density, relative density and void fraction). The foam structure can be characterized (2) by the ratio of open and closed cells, (3) cell size distribution and (4) cell structure anisotropy. Nowadays, cell size distribution is typically investigated along a surface, such as a cross-section (2D). The surface can be examined with a digital optical microscope or a scanning electron microscope (SEM). The cross-sectional surfaces used for observation are typically produced with a microtome or are cryogenic fracture surfaces. The number of cells, their size, their distribution and the degree of anisotropy can be determined from these images [1]. Based on the literature, cell size distribution is typically described with a log-normal distribution [2-5].

The applicability of chemical blowing agents is very different from the usage of thermally expandable microspheres (EMSs). Depending on the chemical blowing agent (CBA) content, different phenomena can be observed in the foamed polymer structures. Effective gases evolved during the decomposition of CBA affect the number of cells formed and their size [6]. The number of cells formed is affected by the amount and type of dissolved effective gas [7]. We determined how the resulting cell size distribution changes when foaming agent content and processing temperature are increased, using PLA, a promising biopolymer, as matrix [8, 9].

2. Experimental

2.1. *Materials*

The polymer matrix material was selected from the NatureWorks LLC (Minnetonka, MN, USA) Ingeo PLA product line. We selected extrusion type Ingeo 2003D. The D-lactide content of this PLA is 4.3 mol% [8], its melting temperature is 150.9 °C (determined by DSC), its Melt Flow Index is 2.0 g/10 min (CEAST 7027.000, 2.16 kg, 190 °C). We determined its number average molecular weight (100,422 g/mol), its weight average molecular weight (180,477 g/mol), and its polydispersity index (1.79) [10].

We used a chemical blowing agent (CBA) for the extrusion foaming of PLA. The CBA was Tracel IM 3170 MS, provided by Tramaco GmbH (Tornesch, Germany). Tracel IM 3170 is an azodicarbonamide-based, exothermic foaming agent. The effective gases are mainly carbon dioxide, but some carbon monoxide is also generated, cyanic acid is formed as well, but it will further decompose to nitrogen and ammonia. The maximum intensity of gas generation measured by thermogravimetric analysis is at 183 °C, and the decomposition range is 147-212 °C, according to the dTG curve (measured in air) [10].

2.2. *Foaming process*

Foaming was carried out in a Teach-line ZK25T (Collin GmbH, Ebersberg, Germany) twin-screw extruder, which has an L/D ratio of 24 and a screw diameter of 25 mm. The processing parameters were 155 °C at the feed section (Z1), 160 °C (Z2), 175 °C (Z3), 190 °C (Z4) and 190 °C at the rod die (rod diameter: 3 mm). The rotation speed of the screw was 10 rpm. Before dosing, the PLA and CBA were dry mixed, the amounts of CBA were 0.5 wt%, 1 wt%, 2 wt%, 4 wt% and 8 wt%. Prior to extrusion, the PLA was dried in a drying oven for 6 hours at 80 °C.

We also investigated the effects of higher processing temperature. The foaming process was also carried out at 175/180/195/210/210 °C, and 195/200/205/230/230 °C. The rotation speed of the screw was also 10 rpm, and all the other parameters were the same. The amounts of CBA that we used were also 0.5 wt%, 1 wt%, 2 wt%, 4 wt% and 8 wt%.

3. Methods and analysis

3.1. *Density measurement*

Density was calculated according to Equation 1. The weight of the specimens was measured with an Ohaus Explorer (Nänikon, Switzerland) balance (accuracy 0.0001 g). The medium was distilled water.

$$\rho = \frac{m_{sa}}{m_{sa} - m_{sl}} \cdot \rho_{dw} \tag{1}$$

where ρ (g/cm^3) is the density of the sample, m_{sa} (g) is the mass of the specimen measured in air, m_{sl} (g) is the mass the sample measured in distilled water and ρ_{dw} (g/cm^3) is the density of distilled water at room temperature.

3.2. *Scanning electron microscopy*

The cell structures were investigated by scanning electron microscopy (SEM). The microscope was a JEOL (Japan) JSM 6380LA. The samples were coated with a gold-palladium alloy with a JEOL 1200 device. The accelerating voltage was 10 kV. We determined cell sizes using the ImageJ software.

3.3. *Foam characterization*

Cell size distribution can be described as the density function of the log-normal distribution (2.) [11]:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \cdot e^{-\frac{(lnx-\mu)^2}{2\sigma^2}} \tag{2}$$

where x is the random variable, μ is the mean value of the normally distributed probability variable, σ is the standard deviation of the normally distributed variable.

3.4. *Calculation of cell population density*

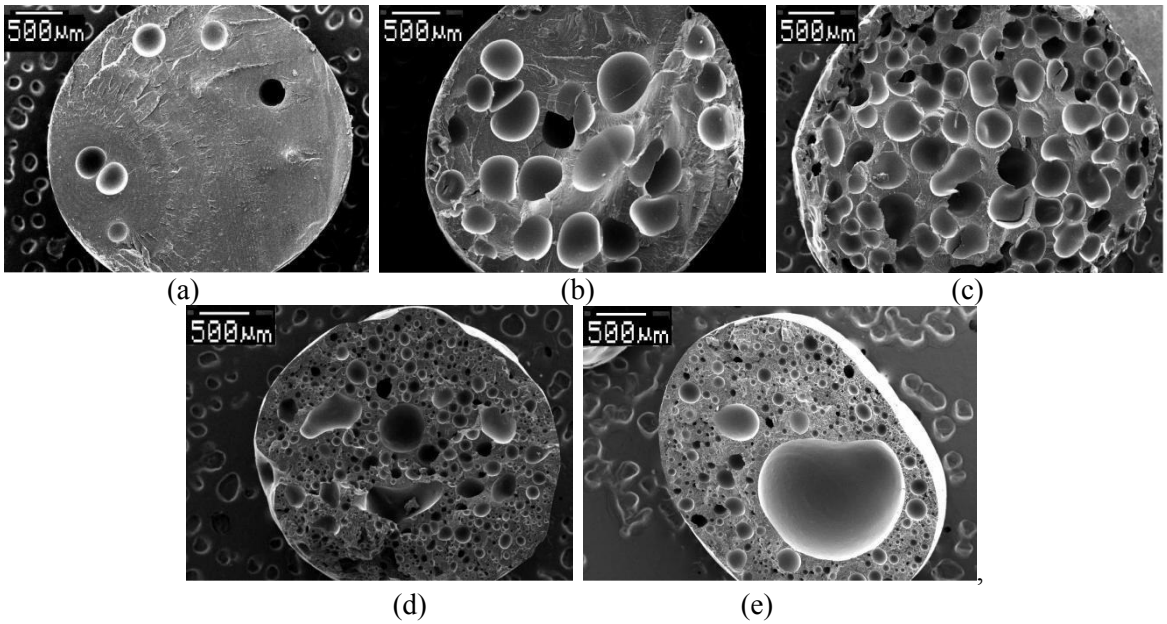
Cell population density was calculated according to Equation 3, where n is the number of cells, A [cm^2] is the area of the sample, M [-] is the magnification factor, and V_f [-] is the void fraction [12].

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

4. Results and discussion

4.1. *The effect of the chemical blowing agent content on the PLA-based foam structure*

Scanning electron microscope images of foam structures produced with different amounts of the chemical blowing agent are shown in Figure 1. A small number of cells nucleated at small content (0.5 wt% and 1 wt%) and the size of the cells was in the order of 300 μm. At medium dosing, the number of nucleated cells increased dramatically and the cells typically had a smaller size. That results in a more favourable, homogeneous, lower density PLA foam, thus providing greater porosity than lower content. At a high content of exothermic chemical blowing agent (4 wt% and 8 wt%), the number of nucleated cells is still high, but the phenomenon of cell collapse appears (Figure 1. e). This is unfavourable—although large cells reduce density, they also decrease mechanical and insulating properties [13, 14].



(a) (b) (c)

(d) (e)

Figure 1. SEM images of PLA foams produced with a) 0.5 wt%, b) 1 wt%, c) 2 wt%, d) 4 wt%, e) 8 wt% exothermic chemical blowing agent at the same manufacturing temperature (190 °C); magnification is 30x

The phenomenon that we described based on the SEM images earlier were characterized by measuring cell sizes and cell size distribution was calculated according to Chapter 3.3. Figure 2. a) shows the resulting density function as a function of cell size in the case of 8 wt% CBA. Cell size distributions were plotted against foaming agent content for Ingeo 2003D polylactic acid (Figure 2. b). In the case of chemical foaming, cell size distribution is shifted towards smaller cells as the content of the chemical blowing agent was increased. Larger cells formed by the collapse of the cell walls appear

in the case of higher (4 wt% and 8 wt%) CBA content. By performing the χ^2 test, we found that the observed cell size differences are significant (Table 1.).

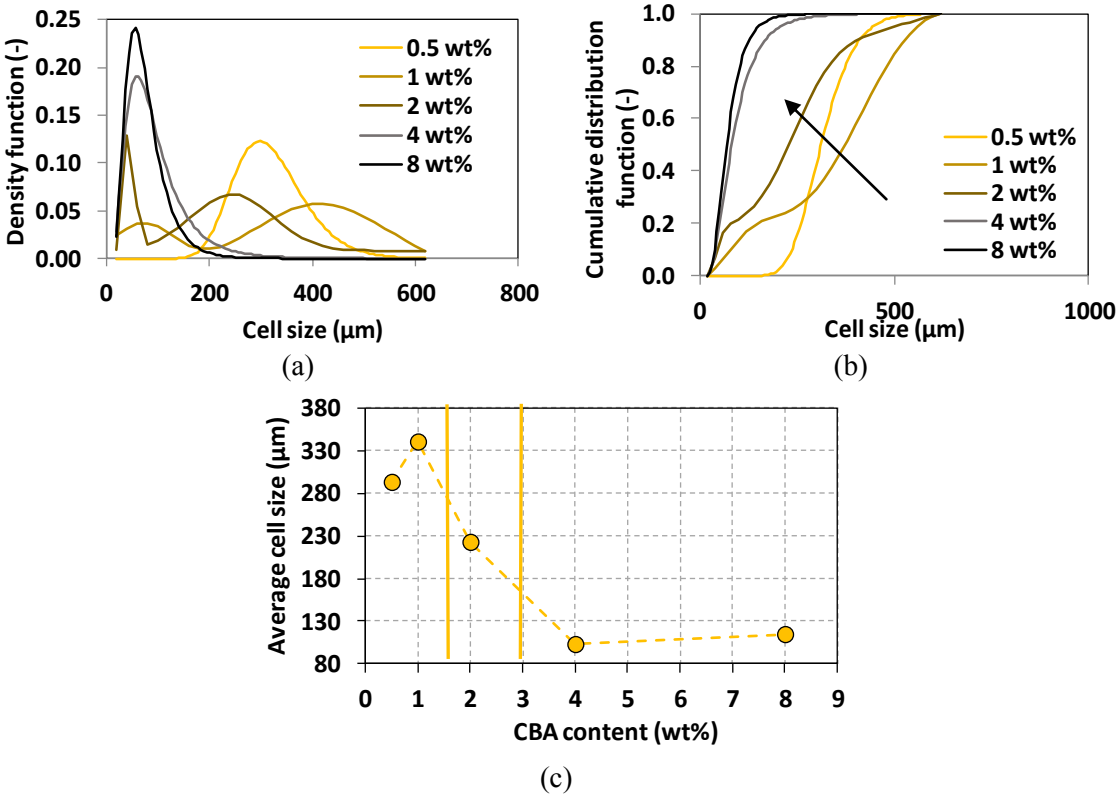


Figure 2. Calculated values of foam structures containing exothermic CBA a) density function as a function of cell size (8 wt% CBA), b) Cumulative distribution function and c) average cell size as a function of CBA content

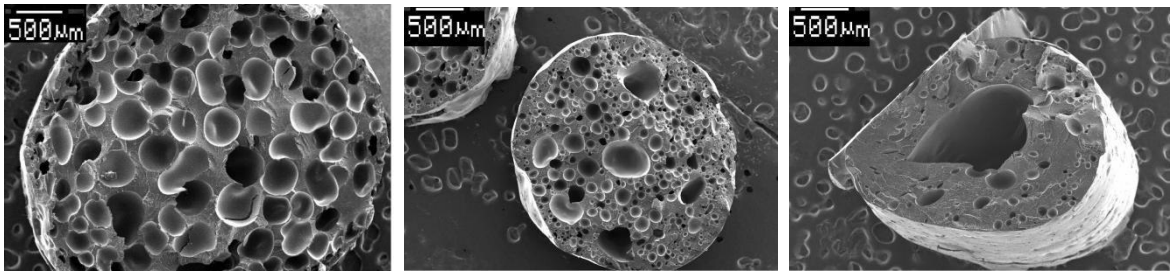
Table 1. P-values of the χ^2 test for the exothermic chemical blowing agent; the different concentrations compared to each other

CBA content	PLA_CBA$_{exo}$
	p-value
0.5 (wt%)-1 (wt%)	0.00024
1 (wt%)-2 (wt%)	0.00000
2 (wt%)-4 (wt%)	0.00000
4 (wt%)-8 (wt%)	0.00001
8 (wt%)-0.5 (wt%)	0.00000

The results indicate that the number of cells formed in the case of small amounts (0.5 wt% and 1 wt%) of chemical blowing agent is low, typically less than 10 cells. In this case, the gases evolved in the polymer matrix are not used for cell nucleation, but typically the growth of the nucleated cells. At 2 wt% CBA, cell population density increased to 1.32 x 10^9 cells/cm^3 and the distribution is bimodal. The reasons of the bimodal cell size distribution is the phenomenon of secondary nucleation [15]. At higher contents of CBA (4 wt% and 8 wt%), the phenomenon of cell collapse occurs, due to cell roughening [13, 16], therefore the large number of nucleated cells cannot grow further.

4.2. *The effect of processing temperature on the foam structures produced*

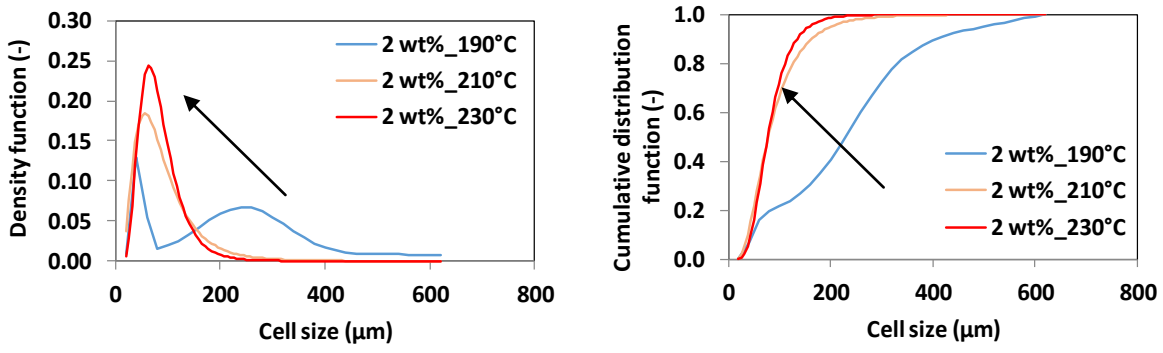
Not only the CBA content, but production temperature also has paramount importance in the case of polymer foam processing [2, 16]. Both the amount of effective gases produced during the decomposition of CBA and the solubility of the gases depend on the temperature and pressure of the polymer melt. Therefore, processing temperature parameters are important [13]. In the case of chemical foaming, low viscosity of the polymer melt typically adversely affects the resulting foam structure. We described the cell size distribution of the cells at increasing production temperatures (die temperatures were 190 °C, 210 °C and 230 °C). SEM images of the produced PLA-based foams are shown in Figure 3. The foam structures show that fewer cells were nucleated at 190 °C at the same CBA content (2 wt%) than at 210 °C. At a higher processing temperature the number of nucleated cells is higher (at 210 °C 3.96 x 10^{10} cells/cm^3), but the phenomenon of cell collapse appears (Figure 3. a) and b). This is also unfavourable in accordance with the decreasing mechanical and insulating properties [13, 14].



(a) (b) (c)

Figure3. SEM images of PLA foams with 2 wt% exothermic CBA at different processing temperatures a) 190°C, b) 210 °C, c) 230 °C; magnification 30x

Based on the images in Figure 3., we also evaluated cell size distribution according to Chapter 3.3. Cell size distribution (Figure 4.) is shifted towards smaller cell sizes as processing temperature is increased. As chemical blowing agent content is increased, larger cells are produced from the collapse of cell walls.



(a) (b)

Figure 4. The cell size distribution of PLA foams produced with an exothermic chemical blowing agent at different processing temperatures (190 °C, 210 °C and 230 °C)

There were significant differences in cell size distribution, which was confirmed by the χ^2 test (Table 2.). The increasing addition of chemical blowing agent reduced the gas retention capacity of the polymer. Therefore, more than 2 wt% CBA addition will not decrease further the density (Figure 5.). The foam production limit at 190 °C it is 8 wt%, means that the pressure inside the extruder die decreased to a level, where continuous product can not be extruded, With the increasing

temperature, the foam production limit is reduced from 8 wt% to 4 wt% at 210 °C, and 1 wt% at 230 °C. Expansion and density reduction are more favourable for samples made at a lower (190 °C) temperature.

Table 2. P-values of the χ^2 test for the exothermic chemical blowing agent at 2 wt% CBA for samples produced at different processing temperatures (190 °C, 210 °C, 230 °C)

Processing temp.	PLA_2wt%_CBA$_{exo}$
	p-value
190 (°C)–210 (°C)	0.00000
210 (°C)–230 (°C)	0.00000
230 (°C)–190 (°C)	0.00000

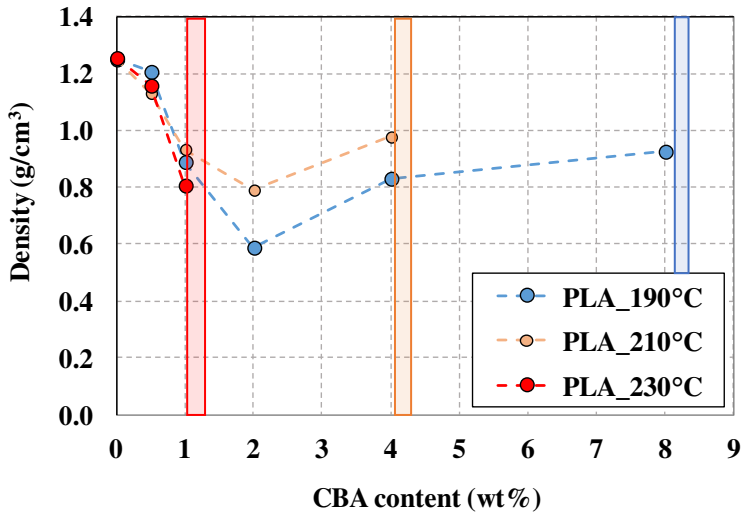


Figure 5. The density of foams as a function of CBA content at different production temperatures (190 °C, 210 °C and 230 °C); blue line: production limit at 190 °C; orange line: production limit at 210 °C; red line: production limit at 230 °C

5. Conclusions

In this study, we characterized chemically foamed poly(lactic acid)-based foam structures. We measured the density of foam samples calculated their cell population density, examined them by SEM and calculated the log-normal cell size distribution. First, we investigated the effect of chemical blowing agent content (0.5 wt%, 1 wt%, 2 wt%, 4 wt% and 8 wt%). The SEM images show that a small amount of cells nucleated at low CBA content (0.5 wt% and 1 wt%), and cell size is around 300 µm. At medium dosing, the number of nucleated cells increased considerably, and the cells are typically smaller. At high contents (4 wt% and 8 wt%) of CBA, the number of nucleated cells is still high, but cell collapse sets in. Cell size distributions were plotted against foaming agent content. Cell size distribution shifted towards smaller cells as CBA content was increased. We found that the observed cell size differences are significant. Second, presented the effect of processing temperature (190 °C, 210 °C and 230 °C). The cell size distribution of PLA foams shifted towards smaller cells when processing temperature was increased. With an increase in chemical blowing agent content, fewer larger cells were produced due to the collapse of cell walls—we found that there were significant differences in cell size distributions. With the increasing temperature, the foam production limit is reduced from 8 wt% to 4 wt% at 210 °C, and 1 wt% at 230 °C. To achieve the largest density loss in the case of examined processing temperatures and CBA content, we recommend the use of 190 °C and 2 wt% CBA.

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