Investigation of CO_2-blown Polylactide Foams by Experimental Characterization and Theoretical Modeling

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ABSTRACT

Supercritical CO_2 is used as physical blowing agent to process the biopolymer Polylactide (PLA) into a microcellular foam. The continuous foam extrusion is carried out by a tandem-line extrusion unit consisting of a single-screw melt extruder and a planetary roller extruder as a downstream mixing and cooling device. The effects of the operating temperature and pressure on the foam characteristics are analyzed. In order to characterize the foam morphology, a MATLAB script based on SEM micrographs is developed to detect the cellular structure automatically. Furthermore, a three-dimensional cell size distribution of the specimens is calculated by theoretical modeling. Experimental studies confirm that expansion ratios of over 55 are achieved with mean cell sizes of about 50 μm.

INTRODUCTION

In times of increasing awareness of sustainability, biopolymers are discussed as an eco-friendly alternative to replace conventional, petroleum-based polymers. Based on fermented cornstarch or sugarcane, the biopolymer Polylactide (PLA) can be synthesized by the ring-opening polymerization of lactic acid. Due to its properties, PLA fits into a broad field of applications, such as films or molded parts for packaging or construction. Especially in the packaging industry, PLA is a promising material for manufacturing eco-friendly polymeric foams. [1–3]

Extrusion enables a continuous processing of foamed polymer products. Therefore, the polymer resins are melted inside an extruder and mixed with a blowing agent. Due to a pressure drop at the extrusion die, supercritical CO_2 as physical blowing agent causes cell nucleation and growth. In contrast to using chemical blowing agents, CO_2 as blowing agent guarantees a foam product that is free from harmful residues. [4–6]

In this work, CO_2-blown PLA foam extrusion at various operating temperatures and pressures is carried out to show the effects on the foam properties. Besides an experimental characterization of the foam expansion ratios, the formation of the cellular structure is of particular significance. Based on microscopic images, such as SEM micrographs, large numbers of cells are counted and the cell dimensions are evaluated in order to get information about the cell density and the cell size distribution. Due to the fact that this is a time-consuming procedure, there is a high demand for automated and user-independent methods to describe cellular structures of porous media [7]. Therefore, an approach is introduced which is performing image editing and cell detection using an in-house developed MATLAB script. This method makes a fast and automated evaluation of the foam morphology possible.

MATERIALS AND METHODS

The PLA grade Ingeo 2003D from NatureWorks LLC (USA) is used for the foam extrusion. In table 1, the material parameters of the PLA resin is listed. Carbon dioxide is used as physical blowing agent with a purity of 99.9 % supplied by YARA GmbH & Co. KG (Germany).

Table 1. The material parameters of PLA 2003D [8]

Property	Value
Density	1.24 g/cm^3
MFR (210 °C, 2.16 kg)	6 g/10min
M_W	210000 g/mol
D-lactide content	4.25 %

The foaming experiments are carried out using a tandem-line extrusion system, consisting of a single-screw extruder (SSE) and a planetary roller extruder (PRE) whose schematic is shown in figure 1. The single-screw extruder supplied by EXTRUDEX Kunststoffmaschinen GmbH (Germany) with a screw diameter of 45 mm and a screw length of 25 D comprises six barrel zones. In order to melt the PLA resin, these barrel zones are heated with the temperature profile 200 °C/ 220 °C/ 220 °C/ 220 °C/ 220 °C/ 220 °C from the feed throat to the outlet die.

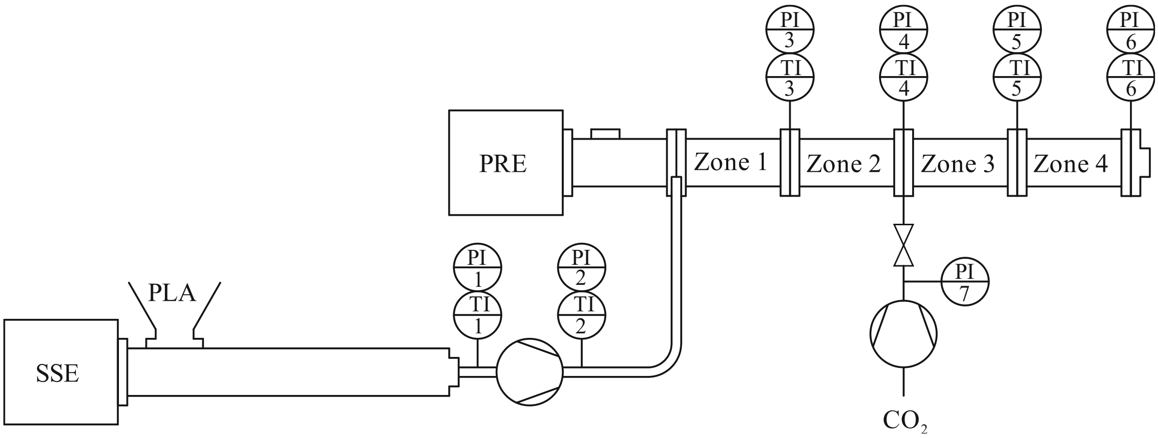

Figure 1. Tandem-line extrusion unit

Further process steps are taking place inside the planetary roller extruder, which is provided by Entex Rust & Mitschke GmbH (Germany). Each of the four rolling cylinders (see also figure 1, zone 1 to 4) has an inner diameter of 70 mm and a length of 430 mm, which results in an effective process length of 1720 mm. In each of the rolling cylinders, six 24 mm planetary spindles are revolving around the 45 mm central spindle. The temperature profile of the planetary roller extruder, as shown in table 2, is varied in order to analyze the effect on the foaming process. For each process setting, the measured values for temperature and pressure are recorded.

The PLA melt is conveyed by a gear pump from the single-screw extruder into the planetary roller extruder. Compressed CO_2 is injected by a three head positive displacement pump between the second and third rolling cylinder. The CO_2 saturated polymer melt is homogenized and cooled down within the third and fourth zone. Subsequently, the mixture is conveyed through a 2.5 mm filamentary die, where nucleation and foam expansion occurs.

Table 2. Temperature profiles of the planetary roller extruder

Profile \#	Central spindle °C	Zone 1 °C	Zone 2 °C	Zone 3 °C	Zone 4/ Die °C
1	160	160	160	140	130
2	160	160	160	140	125
3	160	160	160	140	115
4	160	160	160	140	110
5	160	160	160	130	110

The expansion ratio *ER*, as well as the cellular structure of the foamed PLA samples are analyzed. The expansion ratio results from the foam volume in comparison to the initial volume of the non-foamed PLA by using equation 1.

$$ER = \frac{V_{\text{foam}}}{V_{\text{PLA}}} = \frac{\rho_{\text{PLA}}}{\rho_{\text{foam}}} \quad (1)$$

For this calculation, the water displacement method (ASTM 792-08) is applied to measure the foam density. The relation between the expansion ratio and the porosity ε is described by equation 2.

$$\varepsilon = 1 - \frac{V_{\text{PLA}}}{V_{\text{foam}}} = 1 - \frac{1}{ER} \quad (2)$$

The cellular structure of the PLA foams is visualized by scanning electron microscopy. Therefore, the foams are cut perpendicular to the direction of extrusion and coated with a thin layer of gold. Then, the prepared specimens are scanned by a LEO Gemini 1530 (Carl Zeiss Microscopy GmbH, Germany) with a voltage between 0.2 kV and 30 kV. For each SEM micrograph, an automated image analysis is carried out to detect the foam morphology quickly and user-independently. The whole image editing and the further calculations are implemented as a MATLAB script.

The flow diagram of the operations is shown in figure 1. For an accurate identification of the cell walls, the image has to be edited. The contrast is adjusted, followed by an adaptive image binarization. Furthermore, the connection of single pixels and closing of gaps enables the cell detection and labeling. The cell dimensions are exported for the further modeling of the cell structure.

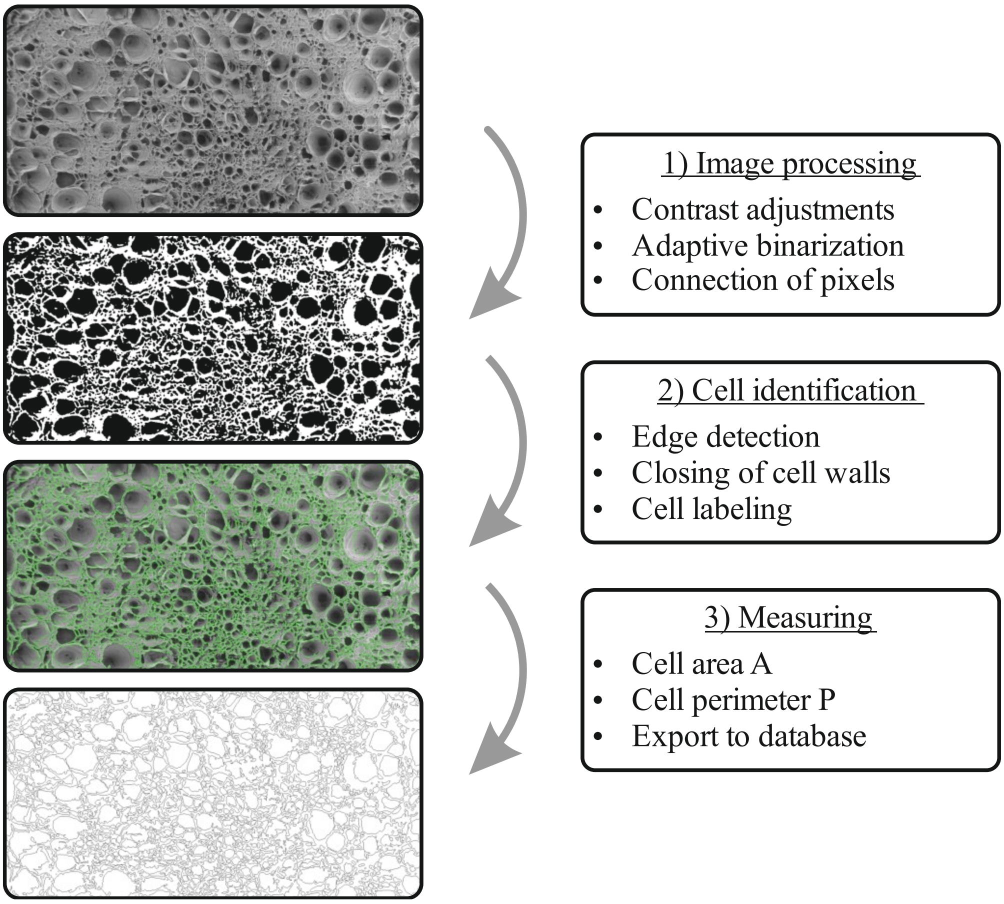

Figure 2. Operation flow diagram for the foam morphology analysis

Measuring both, the area A and the perimeter P for each cell gives information about the cell irregularity ratio by equation 3. In fact, the irregularity ratio IR is defined as the ratio of the cell perimeter to the perimeter of an ideal circle, having exactly the same area as the cell.

$$IR = \frac{P_{circle}}{P_{cell}} = \frac{2\sqrt{A\pi}}{P} \quad (3)$$

Subsequently, the model of Bach is applied to calculate a three-dimensional cell size distribution based on the cell sizes, detected at the two-dimensional plane sections of the SEM micrograph [9]. So, the cell radii r_i are divided into classes and the associated frequencies p_i are counted. Then, the number of spheres per unit volume is calculated by equation 4.

$$N_V = \frac{1}{\pi}\sum_{i=0}^{n}\frac{p_i}{r_i} \quad (4)$$

With the number of cells per unit area N_A, the mean spherical radius $\bar{R}$ is described by equation 5.

$$\bar{R} = \frac{N_A}{2N_V} \quad (5)$$

Additionally, the variance according to equation 6 provides information about the shape of the cell size distribution.

$$\sigma_R{}^2 = \frac{2}{\pi}\left(\frac{N_A}{N_V}\bar{r}\right) - \bar{R}^2 \tag{6}$$

With the mean radius for the two-dimensional plane sections of the cells $\bar{r}$.

RESULTS

The foaming process using a planetary roller extruder as a mixing and cooling device is brought into operation successfully. Initially, it is examined how the pressure within the planetary roller extruder is built up. For a constant CO_2 injection pressure of 7.5 MPa, the temperature of the planetary roller extruder is varied on the basis of table 2. Figure 3 exemplifies that the die pressure increases slightly with lower die temperatures due to a higher melt viscosity. Furthermore, additional experiments with CO_2 pressures of 8.2 MPa and 10.2 MPa are conducted to analyze the effect on the die pressure. Although both process settings are carried out with the same temperature profile (table 2, profile 5), the die pressure at 10.2 MPa CO_2 pressure is higher than at 8.2 MPa. Obviously, the pressure caused by the PLA melt viscosity is overlaid by the CO_2 pressure.

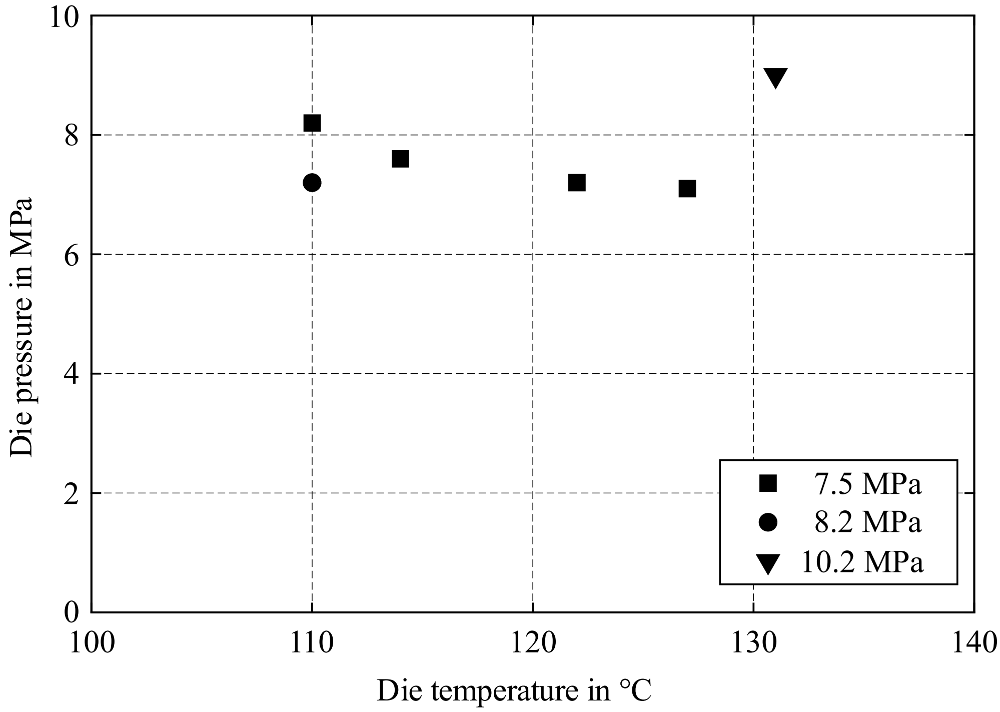

Figure 3. Die pressure depending on the CO_2 injection pressure and the operating temperature measured at the die

Figure 4 shows the expansion ratios of the foamed PLA samples at various CO_2 injection pressures and die temperatures. Keeping the CO_2 injection pressure constant at 7.5 MPa, expansion ratios between 20 and 32 are achieved depending on the die temperature. Higher expansion ratios occur at higher CO_2 pressures. An expansion ratio of 51 is achieved at 8.2 MPa, supplemented by an expansion ratio of 59 at 10.2 MPa.

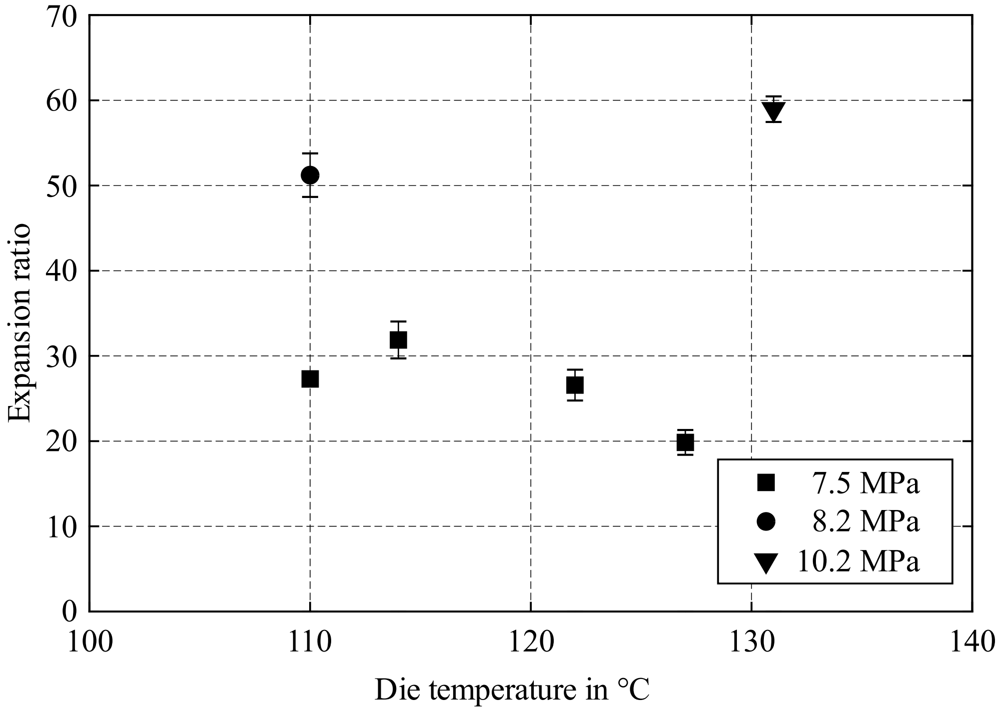

Figure 4. Expansion ratios of PLA foams depending on the CO_2 injection pressure and the operating temperature measured at the die

The cellular structure of various foamed samples is visualized in figure 5. The four samples are processed with a CO_2 injection pressure of 7.5 MPa at various die temperatures. These SEM micrographs are also used for the automated morphology analysis. The magnification factor is selected in a way that each micrograph comprises at least 1000 cells to guarantee an adequate sample size.

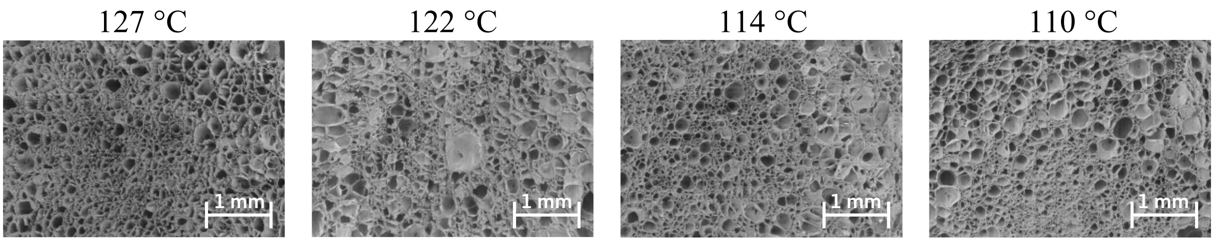

Figure 5. SEM micrographs of PLA foams at various die temperatures and a CO_2 injection pressure of 7.5 MPa

Figure 6 compares the cell size distribution of the plane sections from figure 5. While the shape of the distributions is similar, the samples at lower die temperatures comprise a higher number of cells.

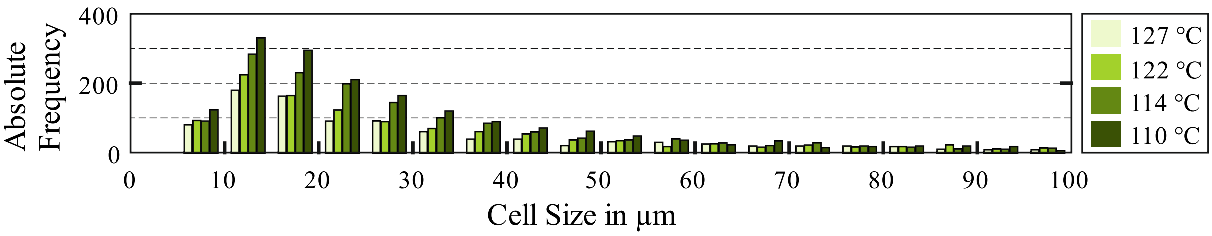

Figure 6. Cell size distribution of PLA foams depending on the die temperature at 7.5 MPa CO_2 injection pressure

Finally, the three-dimensional cell size distribution is calculated based on the histogram for the plane sections (figure 6) and shown in table 3. The model for the three-dimensional cell size distribution confirms the correlation between the die temperature and the cell density. As seen in the table, the number of spheres is increasing with declining die temperatures.

Table 3. Modeled three-dimensional cell size distribution at various die temperatures and a CO_2 injection pressure of 7.5 MPa

Die temperature	N_V	$\bar{R}$	${\sigma_R}^2$
°C	-	µm	µm^2
127	15	31.8	466
122	18	32.3	535
114	23	32.7	417
110	28	31.4	337

CONCLUSION

With the described foam extrusion process, PLA expansion ratios of up to 59 are achieved, which represents a porosity of 98.3 %. The operating temperature affects the die pressure and thus also the foam expansion. Furthermore, it is shown that the CO_2 injection pressure can be used as a regulator for the whole pressure build-up within the planetary roller extruder.

The developed MATLAB script for the automated morphology analysis gives a quick and user-independent overview of the cellular foam structure. Modeling a three-dimensional cell size distribution based on two-dimensional SEM micrographs offers a potential alternative to expensive and time-consuming micro-CT scans. Thus, this approach will be pursued and further optimized.

REFERENCES

[1] PARKER, K., GARANCHER, J.-P., SHAH, S., FERNYHOUGH, A., Expanded polylactic acid - an eco-friendly alternative to polystyrene foam, Journal of Cellular Plastics, Vol. 47, 2011, p. 233-243.

[2] FRERICH, S., Biopolymer foaming with supercritical CO_2 - Thermodynamics, foaming behaviour and mechanical characteristics, The Journal of Supercritical Fluids, Vol. 96, 2015, p. 349-358.

[3] KUSKA, R., MILOVANOVIC, S., JANOWSKI, J., FRERICH, S., ZIZOVIC, I., IVANOVIC, J., Supercritical foaming and impregnation processes design based on thermodynamic measurements of PLA under high pressure CO_2, 15th European Meeting on Supercritical Fluids, 11-14 October 2015.

[4] SAUCEAU, M., FAGES, J., COMMON, A., NIKITINE, C., RODIER, E., New challenges in polymer foaming: A review of extrusion processes assisted by supercritical carbon dioxide, Progress in Polymer Science, Vol. 36, 2011, p. 749-766.

[5] CHAUVET, M., SAUCEAU, M., FAGES, J., Extrusion assisted by supercritical CO_2: A review on its application to biopolymers, The Journal of Supercritical Fluids, Vol. 120, 2017, p. 408-420.

[6] NOFAR, M., PARK, C.B., Poly (lactic acid) foaming, Progress in Polymer Science, Vol. 39, 2014, p. 1721-1741.

[7] PINTO, J, SOLORZANO, E., RODRIGUEZ-PEREZ, M.A., DE SAJA, J.A., Characterization of the cellular structure based on user-interactive image analysis procedures, Journal of Cellular Plastics, Vol. 49, 2013, p. 555-575.

[8] NATUREWORKS, Ingeo Biopolymer 2003D Technical Data Sheet.

[9] BACH, G., Kugelgrößenverteilung und Verteilung der Schnittkreise; ihre wechselseitigen Beziehungen und Verfahren zur Bestimmung der einen aus der anderen, Quantitative Methoden in der Morphologie, 1967, p. 23-45.