POLY(L-LACTIC ACID) FOAMING WITH SCCO$_2$: THE INFLUENCE OF HOMOGENEOUS NUCLEI ON FOAM MORPHOLOGY

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Abstract

In this technical paper, homogeneous crystal nuclei are exploited as heterogeneous nucleation sites for bubbles in poly (l-lactic acid) (PLLA) physical foaming to improve expansion ratios. PLLA slabs are thermally annealed to form homogeneous crystal nuclei and then foamed using super critical CO$_2$ as physical blowing agent. Crystal population density and thermal properties of the polymer were studied before foaming and resulting foams were then observed via Scanning Electron Microscopy, and cell number density and average diameter were calculated. The density of homogeneous crystal nuclei influences foam morphology with the effect of increase cell density and reduce average cell diameter with the formation of smaller stamen-like cells surrounding growing spherulites.

Introduction

In the recent decades, many research efforts have been made to substitute petroleum derived plastics with biobased and biodegradable polymers [1]–[3]. PLLA is one of the most produced biodegradable polyesters [4], widely used in industrial applications [5] thanks to its favorable cost-property balance [6].

Among being interesting for sensing applications, or as material in packaging and disposable items, PLLA is attracting attention for foam production due to the several applications that PLLA foams can potentially have, as packaging industry, sound insulating element, construction and tissue engineering with a range of application consistently growing thanks to the biodegradability of the material.

The assortment of uses for PLLA foams depend on the morphology of the foams that can be obtained both in the dimension and the distribution of cells within the material. Morphology can vary from nanofoams to microfoams depending on the dimension of the cells. One of the methodology to control the foam morphology is to add nucleating agents which reduce the Gibbs free energy for the nucleation process [7].

Many nucleating agents have been tested giving a favorable effect on foaming by reducing cells average diameter and enhancing cell density. As example, a PLLA composite containing the 3 wt% of halloysite nucleates $2\times10^5$ cells/cm$^3$ [8], talc increases cell density by an order of magnitude and improves the uniformity of cell size [9] while and addition of 5 wt% of modified silica nanoparticles increases the cell density by 77 times respect to neat PLLA foams [10].

Despite the positive effects of the heterogeneous bubble nucleation conveyed by nucleating agents, the compounding with different polymers or the inclusion of particles of a different material can make the biodegradation process harder. To overcome this problem, several studies on foaming pre-crystallized PLLA are reported in literature. Existing crystals act as heterogeneous nucleation sites enhancing cell nucleation during foaming [11] and the number of cells increases with spherulite density and surface area [12]. Unfortunately, an increase in the crystal fraction, favored by dissolution of the foaming agent at high pressure, can interfere with foam formation [13][14][12] reducing the sorption of scCO$_2$ and increasing the stiffness of the polymer which hinders expansion [15].

Thus, a faultless situation implies a high number of very small crystals with the lowest possible crystal fraction. At low temperatures, polymer crystallization generally proceeds via homogeneous crystal nucleation [16] and recent studies are available on the formation kinetic and thermal stability of homogeneous nuclei, and their effect on crystallization [17][18]. Homogeneous nuclei are small parallel chain aggregates which grow when a semi-crystalline polymer is annealed at a temperature around its glass transition temperature ($T_g$) and act as nucleation sites for crystal growth, by reducing the energy barrier needed to create new surfaces [19], generating a high number of crystals with a high surface/volume ratio. The most important characteristic of homogeneous crystal nuclei is a negligible initial crystallinity since the maxima of nucleation and crystal growth rates are located at different temperatures [20], implying that at nucleation temperature crystal growth is almost negligible and the developed crystal fraction is not measurable [21]. Hence homogeneous crystal nuclei represent the ideal candidates for a better nucleating agent.

Starting from this knowledge, after an evaluation of nuclei density and on their influence on crystal fraction of the polymer, homogeneous crystal nuclei as enhancers in PLLA physical foaming are studied in this paper with the aim to offer a novel methodology to the production of mono material PLLA foams with tunable morphology.

Materials and methodology
A commercial PLLA grade with L-isomer content of 96% and melt-flow index of 6g/10min (210 °C/2.16 kg), grade name PLA Lx175 [22] was provided by Total Corbion (The Netherlands). Before processing, PLLA was dried in an oven at 60°C under vacuum overnight. To have a uniform sample size, PLLA pellets were compression molded with a Carver Laboratory Press at a temperature of 190°C for 2 min. Then, a pressure of about 20 bar was applied for 2 min and the slabs with thickness of 0.7 mm were quenched to room temperature. Slabs were then cut into disks of a diameter of 5mm with a hollow punch.

A Perkin-Elmer Pyris Diamond DSC, equipped with an Intracooler II was used to grow homogeneous nuclei, as well as for the thermal analysis of foamed and un-foamed samples.

Foaming process was conducted in a batch autoclave using CO₂ as blowing agent. The temperature of the autoclave was set to 120°C and the sample was placed in the chamber after pre-set temperature was reached, to limit possible crystallization before foaming. CO₂ was injected into the reactor to reach a pressure of 100 bar. Samples were saturated for 3 minutes and finally the pressure was released to atmospheric pressure to obtain foamed samples. The thermal and pressure protocol used for PLLA foaming is sketched in Figure 1.

Figure 1. Scheme of the employed thermal and pressure protocol for PLLA foaming.

The efficiency of nuclei formation was evaluated using Tamman’s two stage crystal nuclei development method, which consists in monitoring formation of homogeneous nuclei after their growth to crystals at higher temperature, upon detection of change of the overall crystallization rate [23], [24].

Foam morphology was evaluated using a FEI Quanta 200 FEG Scanning Electron Microscope. SEM micrographs were used to calculate the crystal number density ($N_0$) by [33]:

$$N_0 = \left(\frac{n}{A}\right)^{3/2} \varphi$$  \hspace{1cm} (1)

where $n$ is the number of cells, $A$ is the area of micrograph (in cm²), $\varphi$ is expansion ratio calculated as

$$\varphi = \frac{\rho_{PLLA}}{\rho_{Foam}}$$  \hspace{1cm} (2)

where $\rho_{PLLA}$ and $\rho_{Foam}$ are bulk densities of pure PLLA and of foamed sample respectively.

**Discussion**

Before foaming experiments, the nucleation step has been conducted in a power compensated DSC. Based on literature data [18], three different durations have been selected, and samples were thermal annealed at 60°C for 0.5, 2 and 4 hours to allow the growth of homogeneous crystal nuclei.

The influence of homogeneous nuclei on crystal fraction of the polymer has been studied by the analysis of heat flow curves after an isothermal crystallization of a duration of 3 minutes at 120°C. The crystal fraction ($w_c$) is determined interpolating the crystallization endothermic peaks and comparing the enthalpy with that of completely crystalline PLLA. Results are showed in Table 1.

The efficiency of nucleation step has been evaluated by Tamman’s method [23], [24], monitoring the growth of homogeneous nuclei via Polarized Electron Microscopy, with samples maintained at 120 °C for 3 min to allow spherulite growth after nuclei formation.

Results of Tamman’s evaluation in terms of number of spherulites/mm², compared with $N_0$ are reported in Figure 2.

Figure 2. Spherulite number as a function of annealing time at 60°C, determined from optical micrographs, compared with $N_0$ measured by SEM micrographs.

<table>
<thead>
<tr>
<th>$t_n$ (min)</th>
<th>$w_c$</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.07</td>
</tr>
<tr>
<td>30</td>
<td>0.14</td>
</tr>
<tr>
<td>120</td>
<td>0.21</td>
</tr>
<tr>
<td>270</td>
<td>0.28</td>
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Table 1. Crystal fraction determined from DSC plots.
$W_c$ increases from 0.07 for neat PLLA to 0.28 after a 4h nucleation step and a comparable tendency is displayed in the crystal population density which increases of about one order of magnitude from neat PLLA to the 4h nucleated sample. This is related to a higher number of homogeneous nuclei grown during the nucleation step.

In Figure 2, is interesting to observe how crystal population density and $N_0$ as functions of $t_n$ display the same trend and $N_0$ is about 3-4 orders of magnitude higher than crystal density, indicating how each homogeneous crystal nucleus is able to promote the nucleation of an enormous amount of bubbles.

These results suggest that progressive increase of $t_n$ leads to a corresponding increase of the density of crystal nuclei confirming that the designed experimental conditions lead to a sizable increase of the density of homogeneous nuclei and represents the achievement of the first goal of the present paper.

Foaming experiments were hence designed with the same thermal protocol. Nucleated samples were batch foamed with scCO$_2$ at a pressure of 100 bar and a short sorption time of 3 minutes to avoid the development of a high crystal fraction which could hinder the expansion.

Figure 3 reports the SEM micrographs of foams obtained.

![Figure 3. SEM micrographs of: a) neat PLLA foam and PLLA foams after $t_n$ of b) 0.5h; c) 2h; d) 4h.](image)

As shown in Figure 3, the presence of homogeneous crystal nuclei influences the foam morphology.

An increase in the nucleation time, leads to cells with smaller size and higher density and to the formation of two types of cells. The bulk region is characterized from larger bubbles, while some round entities which are crystal spherulites generated by preexisting homogeneous nuclei are surrounded by smaller stamen-like cells.

Figure 4 reports average cell diameters as a function of $t_n$, thus of the number of homogeneous crystal nuclei. Values increase monotonically with nucleation time.

![Figure 4. Average cells diameter](image)

In particular, from neat PLLA to PLLA nucleated for 4h before foaming, cell size decreases of about two orders of magnitude.

These results demonstrate how homogeneous crystal nuclei can act as nucleation sites for bubbles, overcoming the risk of excessive initial crystal fraction which, as stated above, could hamper expansion.

The advantages of this method are represented primarily from the easiness in waste disposal, improving foaming of PLLA without affecting its biodegradability. Moreover, the variation in foam morphology with number of homogeneous nuclei, results an easy way to tune the foam properties only by changing the thermal pre-treatment.

Conclusions

PLLA was homogeneous nucleated by thermal treatment at low temperature, with nuclei density that increases with nucleation time. Nucleated samples were then physical foamed with scCO$_2$ and morphology were observed. Samples nucleated for 2 and 4 hours show the formation of two different types of cells, bigger in the bulk and smaller stamen-like cells surrounding growing crystals and the average cell size decreases and the cell density increases of two orders of magnitude together with nucleation time.

This paper describes a successful method to enhance foaming of PLLA with no need of compounding with different polymers or additives.

References

22. Luminy LX175 Product Data Sheet, revised 1 Sept 2017.