

# CRYSTALS AND BUBBLES INTERACTION IN PLLA FOAMING



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Poly (L-lactic acid) (PLLA) is the most extensively studied and used biodegradable and renewable thermoplastic polyester, due to its potential to replace conventional petrochemical-based polymers. It is biocompatible, derived from annually renewable resources, and is used in a variety of industrial fields, which include films for packaging or agriculture, or biomedicine, as 3D printing, or for production of foams. Besides being used for tissue engineering and medical implants, PLLA foams have several additional applications such as thermal and sound insulation in construction and food packaging industry.

The aim of this PhD thesis is to exploit the deep knowledge on the crystallization mechanisms and crystal morphology to design PLLA graded foams.

PLLA has also few shortcomings. One of the most serious is its low crystallization kinetic, which limits a wider industrial application of this biopolymer. Common procedure to overcome this drawback, include blending with plasticizers or addition of nucleating agents. During the first year of this PhD thesis, in order to enhance crystallization rate of PLLA, a structural modification of the polymer chain has been attempted. The aim is to obtain a branched structure where fast-crystallizing short branches can favor overall crystallization. A PLLA branched copolymer, where branches are made of optically pure PLLA, has been synthesized. Its crystallization kinetic is much higher than the starting commercial PLLA grade. Comparison with a blend having the same nominal composition revealed a much faster crystallization rate of the branched copolymer. The influence of the varied chain structure and crystallization rate on foamability of PLLA is to be investigated.

Supercritical CO<sub>2</sub> is a commonly used physical blowing agent for production of PLLA foams. CO<sub>2</sub> influences thermal properties of PLLA since it acts as plasticizer, depressing the glass transition temperature ( $T_g$ ) of the polymer, increasing the chain mobility and thus resulting in a faster crystallization rate. At low temperature (around room temperature), CO<sub>2</sub> can induce formation of a metastable mesophase, named  $\alpha''$ -form, that upon further heating transforms to stable  $\alpha$ -crystals.

Not only CO<sub>2</sub> influences crystallization rate of PLLA, but also the degree of crystallinity influences the dissolution of CO<sub>2</sub> and so the foaming properties. CO<sub>2</sub> cannot dissolve within crystals and segregates at the interphase between crystalline and amorphous areas. This leads to an enhanced nucleation of bubbles on the surface of crystals. But at the same time an excessive degree of crystallization increase the stiffness of the polymer, resulting in a depression in the expansion ratio.

Literature data clarify how annealing glassy PLLA allows formation of homogeneous crystal nuclei which enhances/accelerates subsequent crystallization at temperatures above the glass transition by reducing the energy barrier needed to create new surfaces. The same enhancement in surface free energy is expected to apply also for nucleation of bubbles in foaming, where crystals, or any other solid surface, may promote bubble nucleation and their subsequent growth. The large advantage of homogeneous nuclei, compared to existing crystals, is the absence of initial crystallinity, which, coupled to their very high density per unit volume, should provide an enormous number of sites for bubble growth.

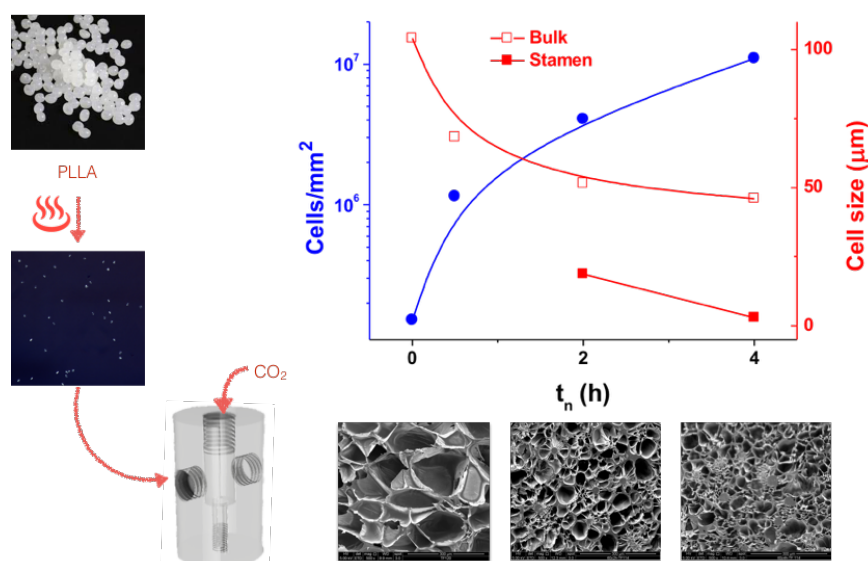
Despite the wide knowledge on the effect of crystalline phase of PLLA on foaming, the influence of homogeneous crystal nuclei on foam morphology has not been investigated to date. Due to this, in this PhD project it is attempted for the first time to foam amorphous PLLA containing homogeneous crystal nuclei.

Experiments of foaming glassy PLLA annealed for various times have been conducted. Results showed how increasing nucleation time, foam density decreases. This, together with a foam morphology showing clearly the presence of crystal nuclei surrounded by growing bubbles, confirms the role of homogeneous crystal nuclei in promoting nucleation of bubbles and thus increasing expansion ratio. Data have been compared to foaming of PLLA with initial low degree of crystallization, attained with different thermal treatments. Samples crystallized from the melt showed

less expansion ratio respect to cold crystallized samples, with crystallization enhanced from homogeneous nuclei, corroborating the role of homogeneous crystal nuclei in bubble nucleation.

Unfortunately such studies require precise temperature/pressure control during experiments, not attainable with the available instrumentation. Therefore part of the research work has been devoted to design and construction of a novel foaming reactor, with reduced temperature fluctuations upon variation of internal pressure. The reactor has the possibility to be equipped with two customized sapphire optical windows, which allow to perform studies on the effect of high pressures of CO<sub>2</sub> on the crystallization rate of PLLA and of spherulites growth rate. The optical system allows also to follow the ongoing foaming experiments with a camera to study the CO<sub>2</sub> sorption and foaming mechanism.

The gained knowledge on the effect of homogeneous nuclei and of CO<sub>2</sub> induced metastable crystals on foaming will be exploited to design graded foams, using a non-equilibrium gas concentration profile. Such foams are highly innovative materials, as they try to mimic natural porous materials, hence are expected to have a wide range of applications.



### References:

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