



HAL
open science

Use of Starch as Nucleating Agent for the Extrusion Foaming of Poly-(Lactic Acid)

Margot Chauvet, Jacques Fages, Martial Sauceau, Fabien Baillon

► **To cite this version:**

Margot Chauvet, Jacques Fages, Martial Sauceau, Fabien Baillon. Use of Starch as Nucleating Agent for the Extrusion Foaming of Poly-(Lactic Acid). 15th European Meeting on Supercritical Fluids, EMSF 2016, ISASF, May 2016, Essen, Germany. <hal-01318257>

HAL Id: hal-01318257

<https://imt-mines-albi.hal.science/hal-01318257v1>

Submitted on 19 May 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Use of Starch as Nucleating Agent for the Extrusion Foaming of Poly-(Lactic Acid)

Margot CHAUVET, Jacques FAGES^{*}, Martial SAUCEAU and Fabien BAILLON

Université de Toulouse; Ecole des Mines d'Albi; UMR CNRS 5302; Centre RAPSODEE,
81013 Albi, France

* jacques.fages@mines-albi.fr

Polymeric foams are used in many fields because they have a low density and they present insulation properties. Depending on the cell morphology of the foam, the applications are multiple. A closed-cell morphology foam is generally used for the packaging, construction or heat insulation whereas an open-cell morphology foam is preferably used for shock absorption, sound attenuation and tissue engineering.

Combining extrusion with supercritical CO₂ is an effective way to obtain foams with different morphologies. Indeed, depending on the operating conditions (T, P) and the CO₂ solubility in the polymer, its injection into the barrel of an extruder will modify the rheological properties of the polymer melt. In addition, CO₂ will act as a blowing agent upon depressurisation when flowing through the die. In our laboratory, this technology has shown great potential for the production of highly porous materials with different morphologies.

In this study, we chose to work with a biobased and biodegradable polymer: the poly-(lactic acid). It is a thermoplastic biopolyester obtained by polymerisation of lactic acid, a molecule obtained by fermentation of renewable resource like corn starch that can substitute traditional petroleum based plastics. To promote foam with heterogeneous nucleation, starch was used as nucleation agent, giving a final product entirely made of a blend of biopolymers.

The influence of several operating parameters on the foam properties has been studied: starch content, temperature and CO₂ mass fraction. Foams with an expansion ratio greater than 20, that is a porosity over 95 %, have been obtained. Two different behaviours were observed for this high porosity: high open cell content with small cell size or low open-cell content with large cell size. The die temperature and the nucleating agent content have been identified as the most important parameters to tune the open cell content.

INTRODUCTION

The poly-(lactic acid) (PLA) is a promising biopolymer fulfilling the three following requirements: biobased, biodegradable and biocompatible. It is derived from lactic acid (obtained from renewable agricultural source like corn), it is biodegradable under moisture, recyclable and compostable and moreover it shows bioresorbable and biocompatible properties in the human body [1]. The creation of porous structure with this material could replace synthetic and non-degradable polymer in many applications (packaging, medical, ...).

To create a porous structure, chemical blowing agent (CBA) or physical blowing agent (PBA) can be used. CBA are chemicals, which produce a gas upon thermal decomposition. The main issue with CBA, such as azodicarbonamide (AZ), is that they leave some residues in the polymer phase. In addition, they are expensive and their decomposition requires high temperatures. PBA, which are already gases, are known to produce better cell morphology and are generally cheaper. However, most of these gases can exhibit deleterious effects like the depletion of the ozone layer as well as some hazardous properties [2]. An alternative is to use supercritical fluids as PBAs. The most promising is carbon dioxide because of its inert nature, environmental friendliness, non-flammability, low cost, and mild supercritical

conditions ($T_c=31^\circ\text{C}$, $P_c=7.38\text{ MPa}$). Moreover, CO_2 is well known for its compatibility with several polymers in which its solubility can be relatively high depending however on the temperature and pressure conditions.

The supercritical CO_2 (sc- CO_2) can be coupled with extrusion to create porous structure. Its injection in a barrel of an extruder will change the rheological properties of the polymer and will act as an expansion agent at die exit due to pressure drop [3]. This work is dedicated to the foaming of PLA with this green process of extrusion assisted by sc- CO_2 . We have added native starch as nucleating agent to observe different morphologies. Besides the starch content, several operating conditions have been tested: temperature and CO_2 mass fraction.

In the first part, we are going to investigate the process on the PLA foams properties. In the second part we are going to observe the effect of starch addition.

MATERIALS AND METHODS

Materials

PLA (PLE001 extrusion grade) was purchased from NaturePlast (France). It is a semi-crystalline polymer with a glass transition temperature (T_g) around 58°C and a melting temperature (T_m) around 148°C (measured by DSC Q200 TA Instrument, see Figure 1). The apparent density of the solid polymer ρ_p was measured by helium pycnometry (AccuPYC 1330, Micromeritics). The mean of 25 measurements is 1.2679 g/cm^3 .

The native corn starch was purchased from Roquette (France). The average powder size is around $200\ \mu\text{m}$. Two different starch contents of 1 and 2 %wt were used in this study.

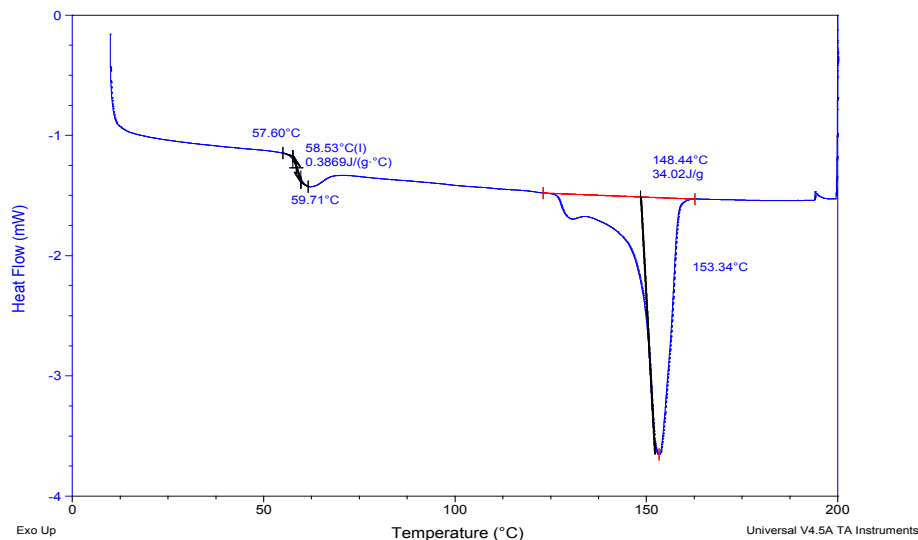


Figure 1: DSC spectra of neat PLA

Extrusion assisted by sc- CO_2

The experimental set-up has previously been detailed elsewhere [4–8] and is shown on Figure 2. The single-screw extruder has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 37 (Rheoscam, SCAMEX, France). The screw is divided into four parts. The length to diameter ratio is 20 for the first one, 7.5 for the two following zones and 2 for the last one. Between each part, a restriction ring has been fitted out in order to obtain a dynamic gastight, which prevents sc- CO_2 from backflowing. The first conical part of the screw allows the transport of solid polymer pellets and then, their melting and plasticizing. Then, in the two following parts, the screw has a cylindrical geometry from the first gastight ring to the last

part. The fourth part, which is removable, contains four static mixer elements with a diameter of 17 mm (SMB-H 17/4, Sulzer, Switzerland). In this work, a cylindrical die of 3 mm diameter was used. The temperature inside the barrel is regulated at six locations: T_a and T_b before the CO₂ injection, T_c and T_d after the injection, T_e in the static mixer and T_f in the die.

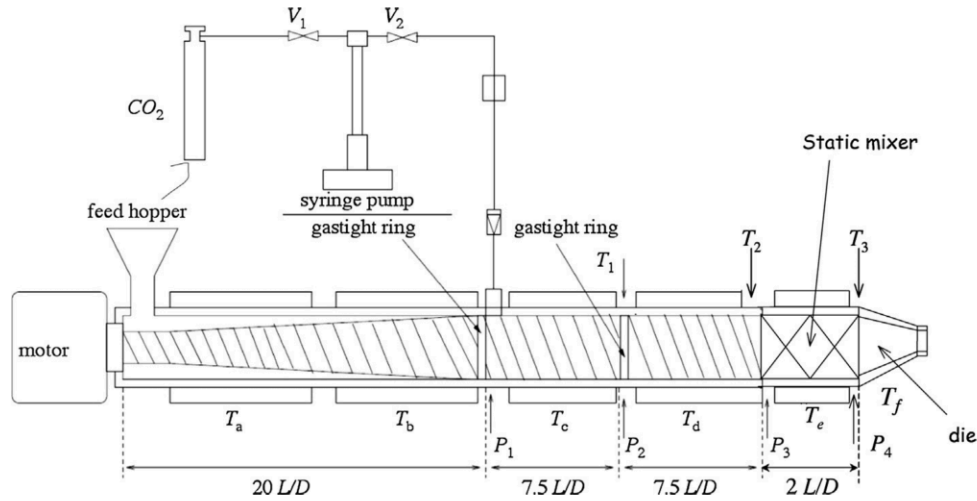


Figure 2 : Experimental device

There are four pressure and three temperature sensors: P_1 after the CO₂ injector, P_2 and T_1 before the second gastight ring, P_3 and T_2 before the static mixer and P_4 and T_3 by the die. This allows measuring the temperature and the pressure of the polymer inside the extruder.

CO₂ (N45, Air Liquide) is pumped from a cylinder by a syringe pump (260D, ISCO, USA) and then introduced at constant volumetric flow rate. The pressure in the CO₂ pump is kept slightly higher than the pressure P_1 . The CO₂ injector is positioned at a length to diameter ratio of 20 from the feed hopper. It corresponds to the beginning of the metering zone, that is to say the part where the channel depth is constant and equal to 1.5 mm.

All foaming experiments began with T_e and T_f fixed at 140°C and a constant volumetric flow rate of 1.5 mL/min. The static mixer and die temperature are lowered together and samples are collected when the system has reached a steady state. When the die pressure become too high (above 160 bars), the volumetric flow rate of sc-CO₂ is increased. The experiments are stopped when the syringe pump is empty.

Characterization morphological of the foam

The samples were observed with an Environmental Scanning Electronic Microscope XL30 ESEM FEG (Philips, Netherlands).

The foam porosity (ϵ), representing the ratio of void volume to the total volume of the sample, can be calculated by the following equation:

$$\epsilon = 1 - \frac{\rho_{app}}{\rho_p}$$

with ρ_{app} the apparent density of the foamed sample, determined by water pycnometry.

RESULTS

Effect of the die temperature and sc-CO₂ content

It has been shown in the literature, for PLA and other polymers, that the foam expansion is mainly controlled by the temperature [9–12]. Indeed, during the microcellular foam generation through and after the die, there is a loss of CO₂, which limits the volume expansion because the CO₂ easily escapes through the exterior skin of the foam sample. One

way to prevent gas escape from the foam is to “freeze” the skin of the extrudate by controlling the die temperature. Indeed, the decrease of the die temperature can limit the gas diffusion at the surface and finally, more gas remains in the foam and can contribute to the volume expansion [12]. Moreover, in order to prevent cell coalescence and to preserve the high cell density, the polymer melt should be cooled substantially to increase its strength to preserve the high cell density, while keeping a sufficient fluidity for bubble to grow.

Figure 3 shows the evolution of the porosity with the temperature. As soon as sc-CO₂ is injected, about 50% porosity is created. With further diminution of temperature, the porosity increases and finally reaches values over 95% at 110°C and below. At the end of the trial, the sc-CO₂ content is about 8 %wt with a volumetric flow rate of 4 mL/min.

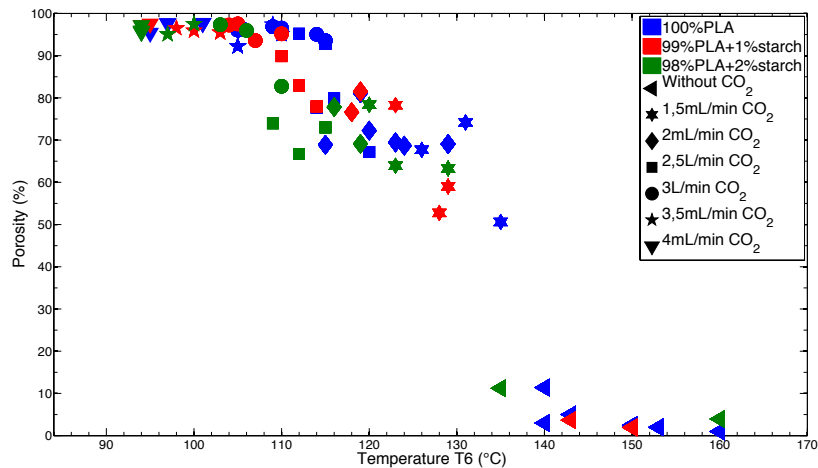


Figure 3: Evolution of porosity with temperature and sc-CO₂ content

Figure 4 shows the morphology of the foams. At high temperature (129 and 120°C), only a few cells are present with inhomogeneous and coarse porosity. With the decrease of temperature (between 107 and 112°C), the number of cell increases concomitantly to a diminution of cell size. The structure remains coarse with open cell walls. A significant difference is observable at 103°C. Indeed, the cells become closed with a thin cell wall and a low cell size. Again, the cell density has increased.

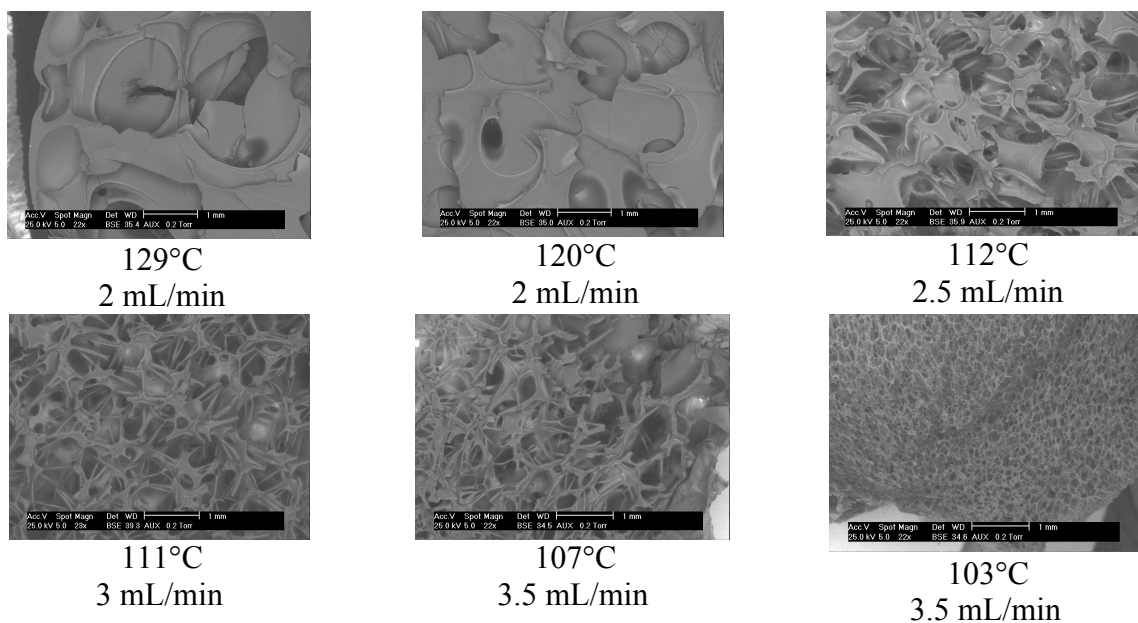


Figure 4: SEM images for pure PLA at different die temperature

Influence of the starch content

PLA was foamed with starch as nucleating agent. As seen on Figure 3, at a given temperature, porosity of the sample with starch is lower than the sample with neat PLA. There is a shift towards lower temperatures with the addition of starch. Indeed, for the raw PLA, at 110°C and below, the porosity is 95% and above. For the blend at 1% starch, the temperature needed to obtain this porosity is below 108°C. The starch seems to modify the matrix properties (kinetics of crystallization, cooling...). It is interesting from an operative point of view, since the extrusion at low temperature is accompanied by a diminution of energetic consumption. Moreover, it could be beneficial to operate at lower temperature if a third sensitive temperature component is added.

Figure 5 shows the SEM picture of the foam with PLA and 1% starch at different die temperatures. Here again, the observations are similar to pure PLA. At high temperature, the structure presents few and inhomogeneous cells. By decreasing the temperature, the cell size decreases and the cell density increases. At the end of the trial, closed-cell morphology can be observed with low cell size. Here also, the shift towards lower temperatures is observable (about 3°C for 1 % starch and 4°C for 2 % starch). The SEM image at 107°C with PLA+1% starch is really similar to the picture with raw PLA at 111°C and illustrates this shift towards lower temperatures. The SEM images do not show the presence of a heterogeneous nucleation.

The SEM images for PLA+2% starch are not shown here but presented similar morphology.

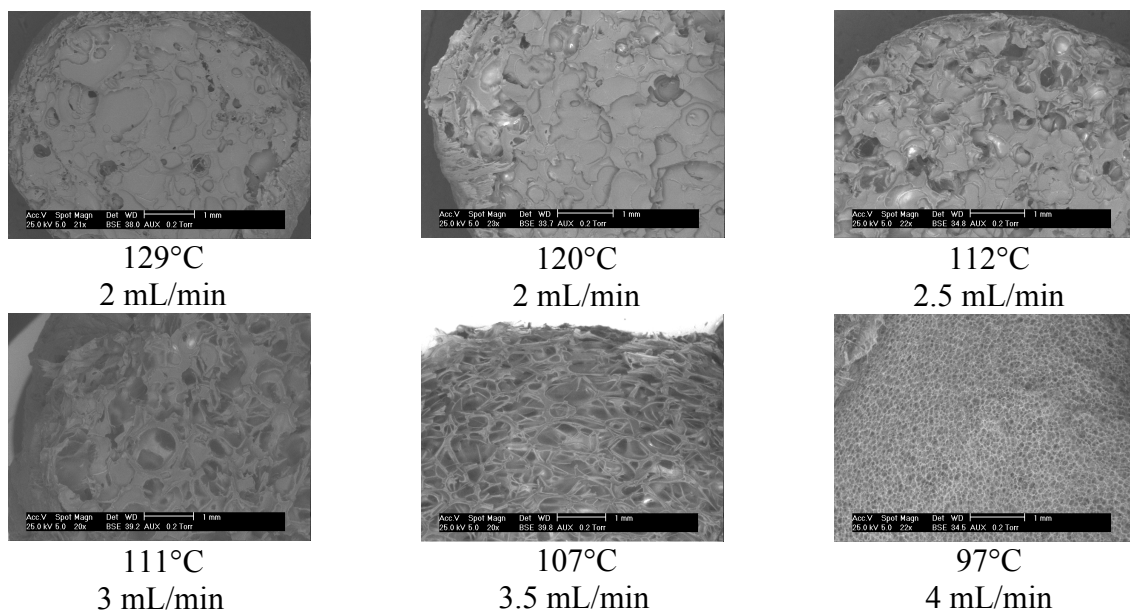


Figure 5 : SEM images for PLA+1% starch at different die temperature

CONCLUSION

Foams of PLA with porosity over 95% were obtained with the method of extrusion assisted by sc-CO₂. To obtain such a porosity, the die temperature has to be lowered below 110°C, what implies the increase of the CO₂ content up to 8 %wt. Two different structures were obtained at this high porosity: a closed-cell morphology with low cell size and high cell density or an open-cell morphology with bigger cell size and lower cell density.

Starch was added to see its capacities to promote heterogeneous nucleation and to create foam made entirely by means of biopolymers. The results show a shift towards lower temperatures with starch addition. To obtain similar results with blends of both biopolymers as those obtained with raw PLA, the die temperature has to be lowered. This is advantageous from an operating point of view. The SEM images did not show heterogeneous nucleation.

REFERENCES

- [1] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, *Macromolecular Bioscience*, Vol 4, (2004), p.835.
- [2] J. Zhang, G.M. Rizvi, C.B. Park, M.M. Hasan, Study on cell nucleation behavior of HDPE-wood composites/supercritical CO₂ solution based on rheological properties, *Journal of Materials Science*, Vol 46, (2011), p.3777.
- [3] M. Sauceau, J. Fages, A. Common, C. Nikitine, E. Rodier, New challenges in polymer foaming: A review of extrusion processes assisted by supercritical carbon dioxide, *Progress in Polymer Science*, Vol 36, (2011), p.749.
- [4] A. Common, M. Sauceau, E. Rodier, J.-J. Letourneau, J. Fages, Capillary rheometry of a binary mixture polymer/CO₂ in a single screw extruder, *Chemical Engineering and Processing: Process Intensification*, Vol 93, (2015), p.21.
- [5] N. Le Moigne, M. Sauceau, M. Benyakhlef, R. Jemai, J.-C. Benezet, E. Rodier, J.-M. Lopez-Cuesta, J. Fages, Foaming of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organo-clays nano-biocomposites by a continuous supercritical CO₂ assisted extrusion process, *European Polymer Journal*, Vol 61, (2014), p.157.
- [6] C. Nikitine, E. Rodier, M. Sauceau, J. Letourneau, J. Fages, Controlling the Structure of a Porous Polymer by Coupling Supercritical CO₂ and Single Screw Extrusion Process, *Journal of Applied Polymer Science*, Vol 115, (2010), p.981.
- [7] Z.K. Nagy, M. Sauceau, K. Nyúl, E. Rodier, B. Vajna, G. Marosi, J. Fages, Use of supercritical CO₂-aided and conventional melt extrusion for enhancing the dissolution rate of an active pharmaceutical ingredient, *Polymers for Advanced Technologies*, Vol 23, (2012), p.909.
- [8] C. Nikitine, E. Rodier, M. Sauceau, J. Fages, Residence time distribution of a pharmaceutical grade polymer melt in a single screw extrusion process, *Chemical Engineering Research and Design*, Vol 87, (2009), p.809.
- [9] S. Pilla, S.G. Kim, G.K. Auer, S. Gong, C.B. Park, Microcellular Extrusion-Foaming of Polylactide with Chain-Extender, *Polymer Engineering & Science*, Vol 49, (2009), p.1653.
- [10] J. Wang, W. Zhu, H. Zhang, C.B. Park, Continuous processing of low-density, microcellular poly(lactic acid) foams with controlled cell morphology and crystallinity, *Chemical Engineering Science*, Vol 75, (2012), p.390.
- [11] M. Keshtkar, M. Nofar, C.B. Park, P.J. Carreau, Extruded PLA/clay nanocomposite foams blown with supercritical CO₂, *Polymer*, Vol 55, (2014), p.4077.
- [12] C.B. Park, A.H. Behraves, R.D. Venter, Low density microcellular foam processing in extrusion using CO₂, *Polymer Engineering and Science*, Vol 38, (1998), p.1812.