Extrusion Foaming of Poly-(Lactic Acid) blends with additives as nucleating agent.

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ABSTRACT
Foamed polymers are used in many fields as insulation and packaging. Due to environmental constraints, biopolymer foams are becoming a viable alternative to petrochemical plastics while keeping the properties without drawbacks.
In this study, a biobased and biodegradable polymer, poly-(lactic acid) (PLA) was foamed with a green process based on hot-melt extrusion combined with supercritical CO_2. Furthermore, starch and thermoplastic starch (TPS) were used and blended with PLA. Different operating parameters (additive content, temperature, and CO_2 mass fraction) were studied. Finally, foams with a porosity over 95% were obtained. By varying the operating parameters, we were able to observe manufacture foams different morphologies. Blending with additives as starch allows to overcome the low melt strength and slow crystallization of PLA. Both PLA and additives are biodegradable after exposure to moisture and they can substitute petroleum synthetics polymers.

INTRODUCTION

Foamed polymers from petrochemical source are used in many fields as insulation and packaging. These products show excellent properties such as a low density and a low cost. Biopolymer foams are a viable alternative to petrochemical plastics while keeping the properties without drawbacks. In particular, PLA is a promising biobased, biodegradable and biocompatible thermoplastic obtained from lactic acid by the fermentation of renewable resource as starch corn. Several applications have been proposed for this polymer in the fields of agriculture, packaging but also medicine due to its biocompatible and bioresorbable properties with the human body [1,2,3,4,5].
To create porous structure, supercritical carbon dioxide ($scCO_2$) has been used as a physical blowing agent (PBA). CO_2 is a well-known green solvent with interesting properties: inert gas, not pollutant, non-flammable, high availability and low cost. Moreover, the CO_2 supercritical conditions are easily reachable (T_c=31 °C, P_c=7.38 MPa). Also CO_2 is known to have high solubility in a large number of polymers, depending on the temperature and the pressure.
Hot-melt extrusion combined with supercritical CO_2 is thus an effective way to produce foams with different morphologies. After its injection, the CO_2 is dissolved in the melted polymer under pressure, what modifies its rheological properties, then it acts as a blowing agent during the depressurization phase by flowing through the die and creating porosity [6, 7].
This paper reports the foaming of PLA using hot melt extrusion assisted by $scCO_2$. Native starch or TPS has been added to create different morphologies. Also different operating conditions (temperature, CO_2 mass fraction) has been used in order to determine their influences. The first part is dedicated to PLA foams properties and the second part is about the addition of starch and TPS.

MATERIALS & METHOD

Materials

PLA (PLE001) was purchased from NaturePlast. This is a semi-crystalline polymer, it has a glass transition temperature, T_g, at 58 °C and a melting temperature, T_m, at 148 °C.
Corn starch was purchased from Roquette with a powder size averaging 200 µm, thermoplastic starch (NPWS001) from NaturePlast and CO_2 from Air Liquide.

Extrusion assisted by supercritical CO_2

Hot-melt extrusion was performed using a single-screw extruder, which has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 37 (Rheoscam, Scamex, France). The set-up has already been described in details elsewhere [8, 9, 10, 11, 12] (Figure 1). The screw is divided into four parts. The first part is conical and has a length of 20L/D. It allows the solid polymer to be transported, melted and then plasticized. In the two following parts, the screw has a cylindrical geometry from the first gastight ring to the last part. Between the screw and the die, four static mixers with a diameter of 17 mm (SMB-H 17/4, Sulzer, Switzerland)have been added. This removable part improves the mixing quality and minimizes the plug flow effect. In this work, a cylindrical die of 3 mm diameter was used.
Barrel temperature was controlled separately in 6 zones: T_1 and T_2 before the CO_2 injection point, T_3 and T_4 after it, T_5 in the mixing zone and T_6 in the die. Four pressure sensors (P_1, P_2, P_3, P_4) and three temperature sensors (T_{mat1}, T_{mat2}, and T_{mat3}), positioned along the barrel, enable the monitoring of the state of the matter.
Carbon dioxide was injected in the extruder barrel using a syringe pump (260D, ISCO, USA) in a constant volumetric flow rate mode. The CO_2 pressure in the pump is kept higher than the pressure P_1.
During all foaming experiments T1, T2, T3 and T4 were fixed whereas T_5 and T_6 could be changed, also the volumetric flow rate went from 1.5 mL/min to 4.5 mL/min. The static mixer and die temperatures are lowered, and once steady state conditions are reached with the chosen operating conditions, samples are collected.
The experiments are stopped when the syringe pump is empty.

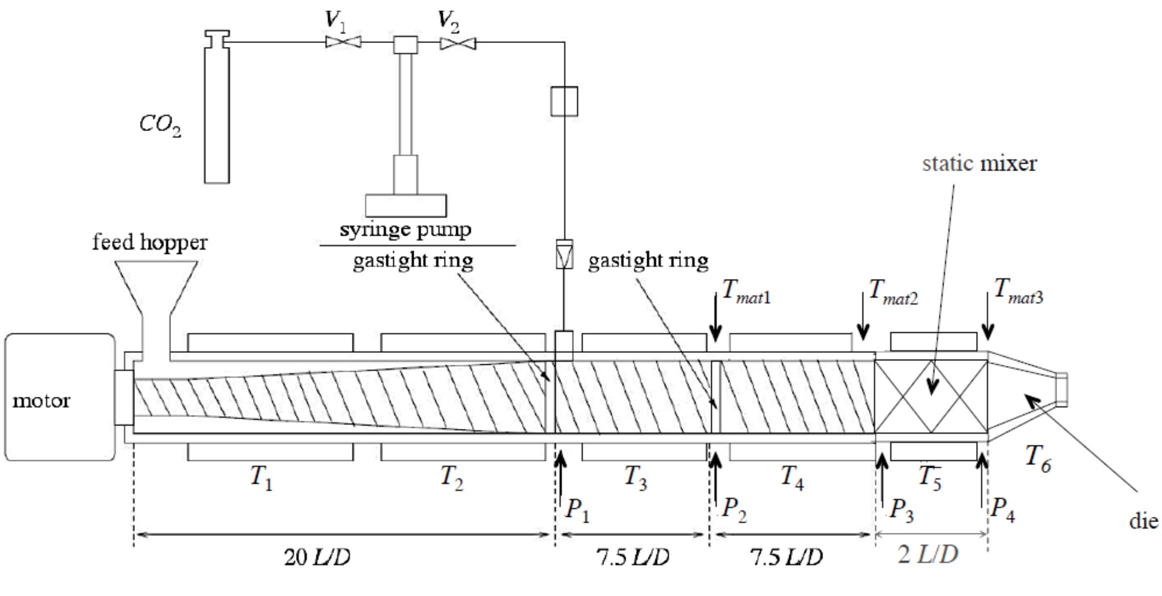

Figure 1: Experimental device

Characterization

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:

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

with ρ_{app} the apparent density of the foamed sample, ρ_p is the solid polymer density.

RESULTS

Effect of die temperature and $scCO_2$ on PLA foaming

The evolution of the porosity with the temperature is shown in Figure 2. The addition of $scCO_2$ brings the porosity of the polymer up to 50%. Also, decreasing the temperature to 110°C or below, increases the porosity to higher values over 95 %. During the foam generation, there is a limit to the volume expansion caused by the loss of CO_2. This occurs because the CO_2 escapes from the foam. Cooling the extrudate by controlling the die temperature is a way to prevent the CO_2 diffusion. With the temperature decrease, the foam will retain more gas, increasing its expansion [13, 14, 15].

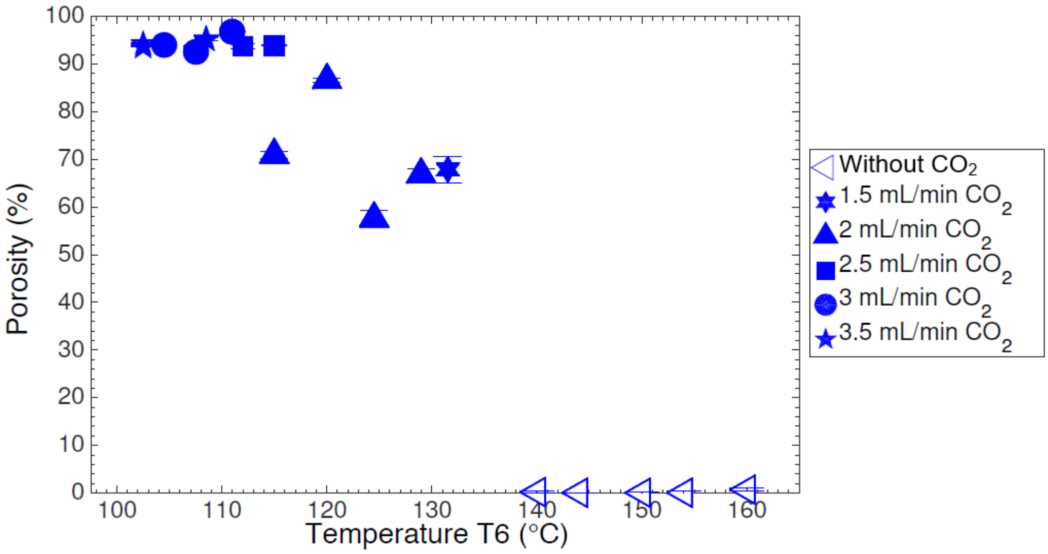

Figure 2: Evolution of porosity of PLA foams with temperature

Figure 3 shows the SEM pictures of PLA foams. At high temperature, there are few cells but they are big and inhomogeneous. At a lower temperature (111 °C), the number of cells increases causing a reduction of the cell size, also the porosity is open. At 109 °C and below, the foam has a closed porosity and the cell size is smaller.

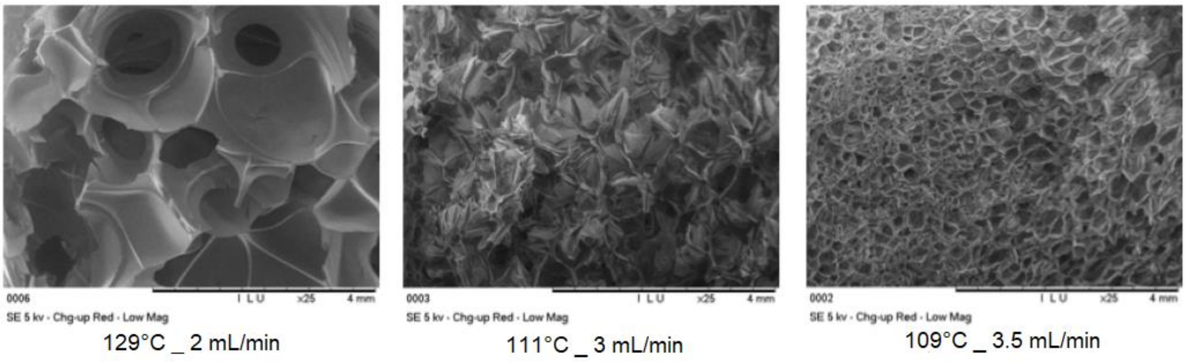

Figure 3: SEM images for PLA foams at different die temperature

Starch and TPS influences on PLA foaming

PLA was foamed with starch and thermoplastic starch as nucleating agent. Figure 4 shows the evolution of the porosity of PLA foams with starch. With the incorporation of starch, the foam porosity is the same as raw PLA but it was obtained at lower operating temperature. With 1 % of starch, a temperature of 111 °C or below is required to get a porosity at 90 %, but with 5 % of starch, 101 °C or below is necessary to keep values over 90%. The starch might have modified the viscosity of the PLA: in order to have foams with high porosity, a low operating temperature is needed. It can be an interesting property when thermolabile components are used during hot-melt extrusion.

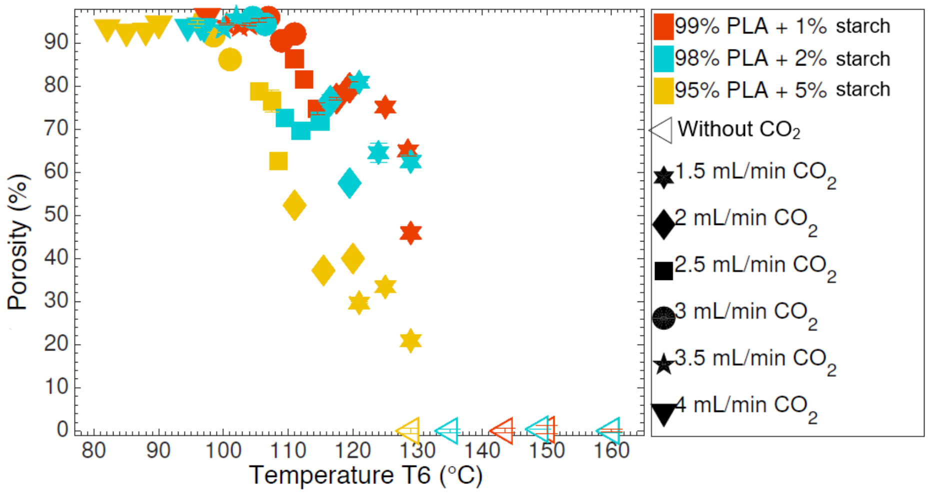

Figure 4: Evolution of porosity of PLA-starch foams with temperature

Figure 5 shows the morphology of PLA foams with 1 % of starch. As seen at 118 °C and 111 °C, the cell size is high whereas there were less nucleated cells. At lower temperature, the opposite can be observed. Indeed, as seen at 104 °C, the cells are more homogeneous with a closed porosity.

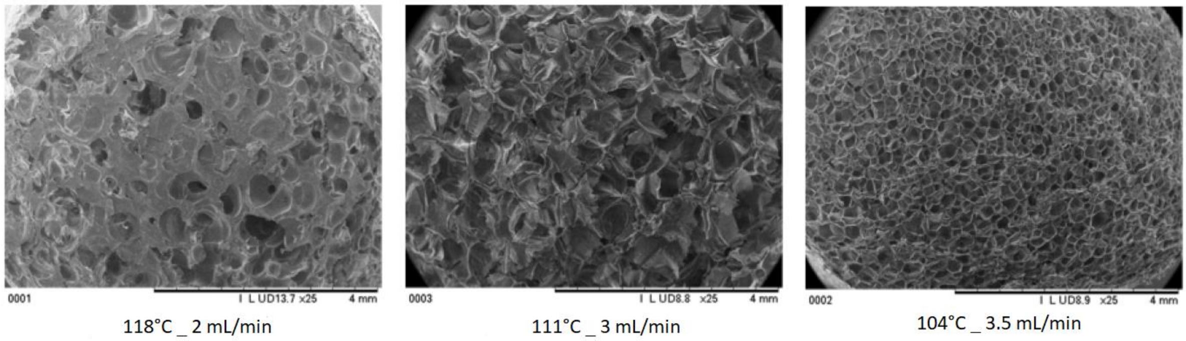

Figure 5: SEM images for PLA foams with 1% of starch at different die temperatures

As seen in figure 6, the morphology of PLA foams with 2 % of starch is coarse. Indeed, the cell nucleation was important but the cell size is not homogeneous. At 105 °C and higher temperatures, the porosity is open. Below 105 °C, the cell porosity is closed.

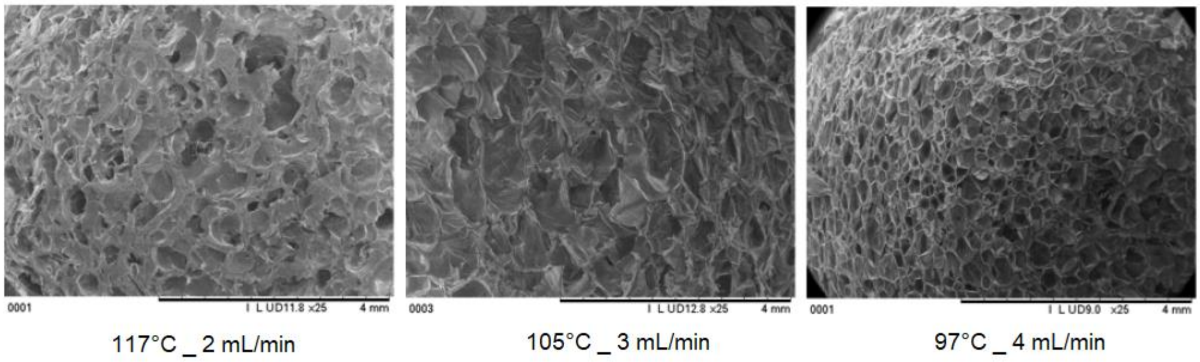

Figure 6: SEM images for PLA foams with 2% of starch at different die temperatures

PLA foams with 5 % of starch are shown in figure 7. The foam morphology is heterogeneous. The cell nucleation was important with an open porosity. With lower temperature, the cell shape is more regular.

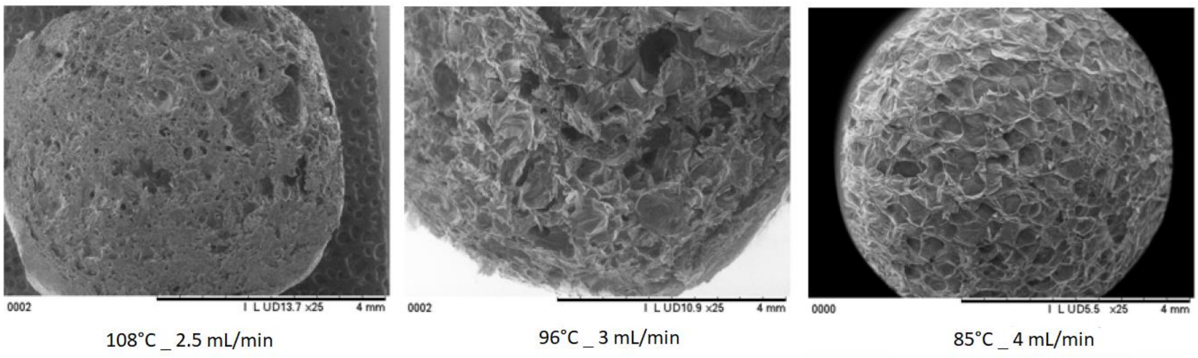

Figure 7: SEM images for PLA foams with 5% of starch at different die temperatures

Figure 8 shows the evolution of porosity with temperature of PLA foams with thermoplastic starch. With 20 % of TPS, the behavior is almost the same as raw PLA: with the temperature decrease, the porosity value increases. Below 109 °C, the porosity goes up to 91 %. A value of 96.3 % is reached at 95 °C. Besides, PLA foams with 50 % of TPS have a lower porosity value even at low temperature. The maximum value of porosity is 68 % for a temperature of 108 °C.

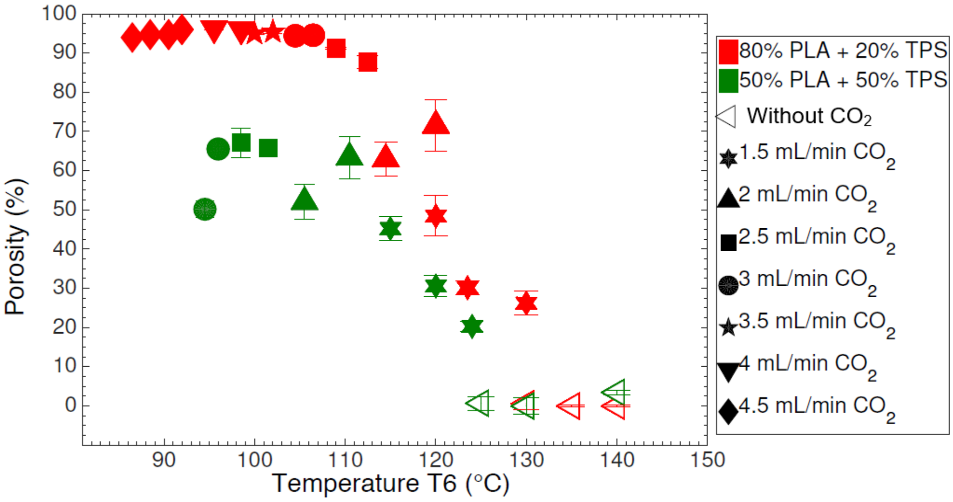

Figure 8: Evolution of porosity of PLA-TPS foams with temperature

The morphology of PLA foams with 20 % of TPS is shown in figure 9. Even though the decrease of the temperature brings a smaller cell size and a more significant cell nucleation, the porosity seems to be open and the structure is heterogeneous. For PLA foams with 50 % of TPS, the same behavior has been observed despite being more irregular. Those results show the weak compatibility between PLA and TPS.

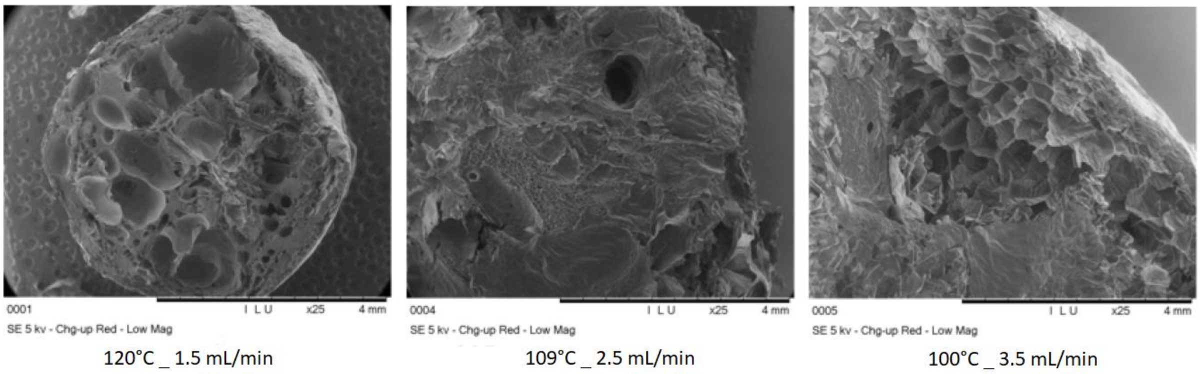

Figure 9: SEM images for PLA foams with 20% of TPS at different die temperature

CONCLUSION

Foams of PLA with a porosity over 95 % were obtained using hot-melt extrusion assisted by $scCO_2$. The die temperature has to be at 110 °C or below in order to reach high values of porosity. Two different structures were obtained at this high level of 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.

PLA was also foamed with starch as nucleating agent. The results show that the die temperature has to be lowered in order to reach high value of porosity. This can be an interesting property when thermolabile components are used during extrusion.

PLA was then foamed with thermoplastic starch. However the results were not conclusive: the morphology was coarse and the structure heterogeneous, showing a weak compatibility between PLA and TPS. Adding an agent which is able to improve the affinity between the two polymers can be a solution.

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