A Continuous Foaming Process of Low-Density PLA by Supercritical CO_2 Assisted Extrusion

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ABSTRACT

Polylactic acid (PLA) represents probably one the most viable environmentally-sustainable alternative to petrochemical-based plastics. This paper reports the continuous processing of PLA foams with CO_2 as the blowing agent. Different operating conditions were tested for a commercial linear PLA and the obtained foams were characterized on the basis of porosity and thermal properties. Finally, foams with expansion ratio up to 95% were obtained. The importance of the operating temperatures was emphasized, what requires the use of high CO_2 fractions. Higher crystalline contents than the raw material can be obtained, this content being linked to the process conditions and thus to the porosity.

INTRODUCTION

The Polylactic Acid (PLA) is a promising biobased and biodegradable thermoplastic material usually obtained by the fermentation of renewable resource as starch corn. Several applications have been proposed for this polymer in the fields of medicine, agriculture, and packaging [1, 2, 3, 4]. In order to further improve the toughness and widen the application of PLA, research works have continuously been made in PLA foaming technology, which is a well-known process to enhance the ductility and impact resistance by providing a significant expansion ratio and weight reduction [5, 6]. The high expansion ratio induced by foaming generally could reduce the material cost and consumption in mass-produced plastic parts without significantly impairing its other properties.

In this context, a great deal of attention has been given to supercritical carbon dioxide ($scCO_2$), due to its ability to solubilise in large quantities into many polymers. Recently, efforts have been made to produce PLA foams from $scCO_2$-assisted extrusion [7, 8, 9, 10, 11, 12]. The injection of $scCO_2$ into the barrel of an extruder modifies the rheological properties of the polymer melt and $scCO_2$ acts as a blowing agent upon depressurisation when flowing through the die [7].

Our laboratory has developed such an extrusion process [13, 14]. In the present work, it has been used to prepare PLA foams.

MATERIALS AND METHODS

Materials

PLA used in this study was purchased from Natureplast (PLE 001). According to the manufactures, it is semi-crystal-linear with a low D-lactide molar content.

ScCO_2 assisted extrusion

Hot-melt extrusion was performed using a single-screw Rheoscam extruder, which has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 35 (Scamex, France) already described in details elsewhere [13] (Figure 1). The screw speed was kept constant at 20 rpm.

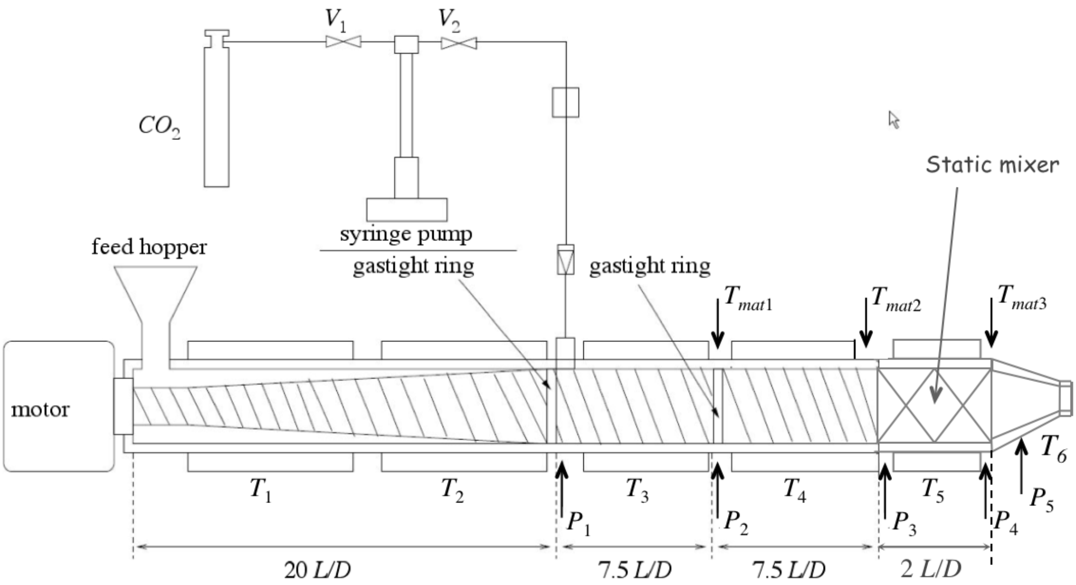

Figure 1: experimental device.

Four static mixer elements (Sulzer, SMB-H, 17/4), with a diameter of 17 mm and a whole L/D of 2, were added between the screw and the die to improve the mixing quality and thus minimising the plug flow effect [14].

The die used in these trials was a home made one, with an annular shape. It allowed controlling the backflow pressure inside the extruder by means of a pin controlled by an air counter-pressure.

Hopper temperature was fixed at 50 °C. Barrel temperature was controlled separately in 5 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. T_1 to T_4 were fixed for all experiments at respectively 160, 180, 180 and 160°C, while T_5 and T_6 were varied.

The state of the matter was controlled by five pressure sensors (P_1, P_2, P_3, P_4, and P_5) and three temperature sensors (T_{mat1}, T_{mat2}, and T_{mat3}) positioned along the path of the polymer.

Carbon dioxide was injected in the extruder barrel, at a L/D of 20 from the feed hopper at the same pressure as that of the extruder, using a syringe pump in a constant volumetric flow rate mode (260D, ISCO). CO_2 density obtained from the website of NIST [15] and calculated with the Span and Wagner equation of state [16] was used to determine the CO_2 mass flow rate and the CO_2 mass percentage in the melt.

Once steady state conditions reached with the chosen operating conditions, extrudates were cooled at ambient conditions, collected and then characterised.

Characterisation

Thermal analyses were carried out by differential scanning calorimetry (DSC Q200, TA Instrument). Two cycles of heating-cooling from 20 to 200 °C have been applied with a heating rate of 5 °C/min. The crystalline content was determined during the first heating by the following formula [17]:

$$\chi = \frac{\Delta H_m - \Delta H_c}{\Delta H_f} \qquad (1)$$

ΔH_m is the heat of melting, ΔH_c the heat of cold crystallisation and ΔH_f the theoretical heat of fusion of 100 % crystalline PLA. A value of 93.1 J/g was taken as PLA theoretical heat of fusion [17].

Porosity ε, defined as the ratio of void volume to the total volume of the sample, was calculated by Equation (1):

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

ρ_{app} is the apparent density calculated from the weight of the samples and their volumes evaluated by measuring their diameter and length with a vernier (Facom, France). ρ_p is the solid polymer density, determined by helium pycnometry (Micromeretics, AccuPYC 1330), which is about 1270 $kg.m^{-3}$.

To complete the characterization of the porosity structure, samples were examined by scanning electron microscopy (ESEM, FEG, Philips).

RESULTS

The evolution of the porosity is shown on Figure 2. The porosity usually reaches a maximum when the melt strength balances the diffusion of the blowing agent, such that cells grow to their maximum without rupturing [18]. For a screw rotation speed equal to 20 rpm, the porosity increase as the temperature T_6 decreases, whatever the temperature T_5. No decay below a certain temperature can be observed, which is already known for most thermoplastics because of excessive melt strength [10, 18]. At a lower temperature T_5, higher porosity can be reached, with values up to 95 %, for a higher range of the die temperature T_6. As already observed, a compromise should be obtained between this two temperatures [7].

If the screw rotation speed is increased to 30 rpm (and thus the polymer mass flow rate) at a constant CO_2 mass fraction, a maximal porosity can be observed for T_6=112 °C at about 90 %, what is lower than the one at 20 rpm.

However, it has to be noted that the operating window for producing high porosity PLA foams is very narrow. Indeed, to reach the interesting range of temperatures, the polymer has to be plasticized with a sufficiently high quantity of CO_2 [17].

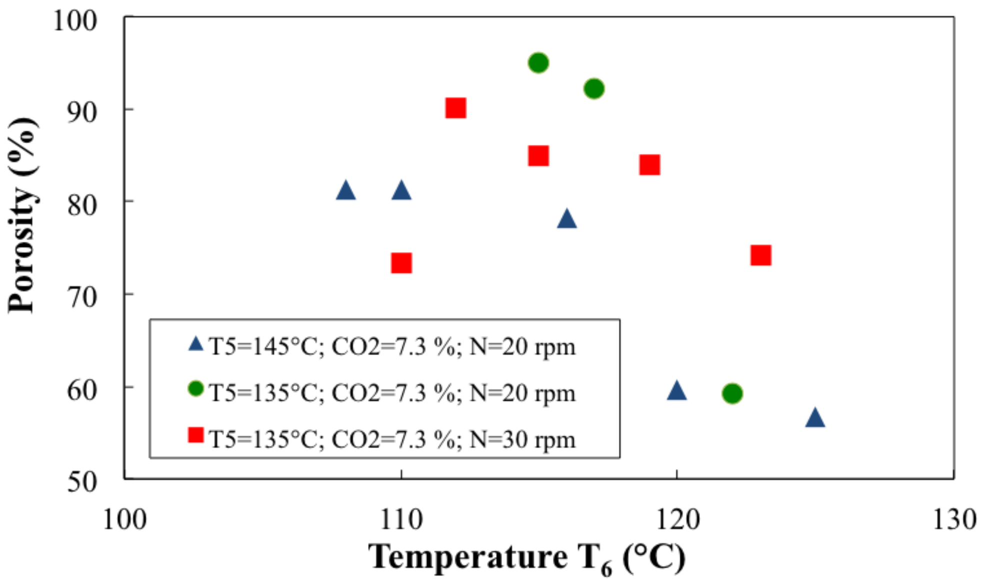

Figure 2: evolution of the porosity for different die temperatures and screw rotation speed.

The morphology of the highly expanded foams can be observed on Figure 3. The structure is uniform with well-formed cells, which are rather closed one.

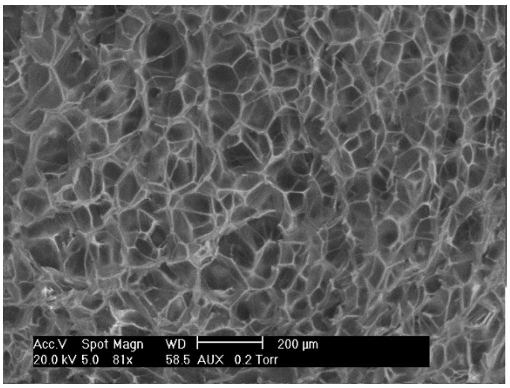

Figure 3: SEM images of samples at T_5=135 °C, T_6=115 °C, CO_2=7.3 %, N=20 rpm.

The results of the thermal analyses are presented in Table 1. As previously reminded, upon initial heating, the glass transition temperature T_g and enthalpic relaxation peak of the PLA

are followed by an exothermic cold crystallization (temperature T_c and heat of crystallisation ΔH_c) and by a well defined endothermic melting (temperature T_m and heat of melting ΔH_m).
For the raw PLA, T_g is about 59 °C, the crystallisation temperature 101 °C and the melting temperature 152 °C. Based on the different enthalpies, the crystalline content is estimated to 0.5%.
For the two foams analysed, the characteristic temperatures remain more or less the same. However, the crystalline content X_c is increased by foaming, the highest cristallinity corresponding to the highest porosity. Crystallinity seems to be determined by processing conditions and is known to be linked to the expansion ratio [8]. *In situ* formed crystal domains seems to supply nucleating sites to enhance cell nucleation and cell structure [12].

Sample	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
raw	59	101	152	21.5	21.6	0.5
foam (T_5=145 °C)	57	102	155	22.3	27.0	5.0
foam (T_5=135 °C)	59	107	155	20.3	27.0	7.3

Table 1: thermal results of the raw PLA and two foamed samples (T_6=117±1 °C, CO_2=7.3 %, N=20 rpm)

CONCLUSION

The extrusion foaming behaviour of a linear PLA was investigated using CO_2 as the physical blowing agent. Highly expanded foams with porosity up to 95% were obtained. Thermal analysis allowed to show that increased crystallinity can be obtained, this crystallinity being linked to the operating conditions. However, it has to be noted that low processing temperatures were necessary, what required high CO_2 mass fraction.

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