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Foaming PLA with Thermoplastic Starch by Extrusion Assisted by Supercritical CO₂

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ABSTRACT

The manufacture of biopolymers foams with poly-lactic acid (PLA) and thermoplastic starch (TPS) using the green process of extrusion assisted by supercritical CO₂ is a promising way towards new applications. A parametric study evidenced that the porosity is strongly correlated with the die temperature, CO₂ content and TPS load. To get a high porosity, die temperature has to be diminished to block the gas escape from the extrudate sample. This reduction in temperature was only feasible when it was associated to an increase in CO₂ content to lower melt viscosity in the extruder. Higher TPS content led to foam samples with lower porosity, due to a weaker melt strength which in turn favoured the CO₂ escape instead of forming pores. Finally, for the 80 % PLA-20 % TPS blend, porosity as high as 96 % has been obtained.

INTRODUCTION

In the field of packaging, expanded thermoplastics from petrochemical origin are often used. These products show excellent mechanical properties, in addition to low density and cost. The main issues are the manufacture impact on the environment and the management of waste. With the goal of retaining these properties without the drawbacks, the use of biobased and biodegradable polymers to make foams with a green technology is highly recommended.

Extrusion assisted by supercritical CO₂ (sc-CO₂) is considered as a green process for the manufacturing of foam [1]. In this process, sc-CO₂ is injected in the heating barrel of an extruder. Not only it modifies the melt properties inside the extruder by dissolving in the polymer under pressure, but also it acts as an expansion agent during the return to atmospheric pressure through the die and creates porosity. This process has shown great interest and is frequently investigated with biopolymers as recently reviewed by Chauvet *et al.* [2].

In this study, a blend of poly-(lactic acid) (PLA) and thermoplastic starch (TPS) was used. These two biopolymers are obtained from renewable resources and both are biodegradable after exposure to moisture. They can substitute synthetic polymers, especially in the packaging area. The literature has shown that blending TPS with PLA improves the biodegradability of PLA [3,4]. Even if Martin and Averous have reported the lack of affinity between these two biopolymers [5], Mihai *et al.* [6] have shown that for a blend consisting of 33 % TPS and 67 % PLA, a foam density as low as 34 kg.m⁻³ was obtained without any coupling agent.

The aim of this study is to observe the influence of the operating conditions (temperature and sc-CO₂ mass fraction) on the foams porosity without coupling agent on blend with TPS content varying between 0 and 50 %.

MATERIALS AND METHODS

Materials

PLA (PLE 001 extrusion grade) and TPS (NPWS 001 grade) were purchased from NaturePlast (France). The first polymer is semicrystalline with a glass transition temperature

(T_g) around 58 °C and a melting temperature (T_m) around 148 °C. The thermoplastic starch used is an amorphous polymer with a glass transition temperature (T_g) around -45 °C.

In this work, pure PLA and two different blends will be extruded: 80 % PLA-20 % TPS (referred to as 80PLA-20TPS) and 50 % PLA-50 % TPS (referred to as 50PLA/50TPS) in mass fraction.

Extrusion assisted by sc-CO₂

The equipment have already been used and described in recent publications [7–10]. It consists of a single-screw extruder (Rheoscam, SCAMEX) with a 30 mm screw diameter with a length to diameter ratio (L/D) of 37 as illustrated on **Figure I**. This extruder is divided into four parts: the first zone ($L/D=20$) allows the transport of solid polymer pellets and their melting and plasticizing, the next two zones ($L/D=7.5$ each) corresponds to the location where the CO₂ is injected, the last zone ($L/D=2$) being a removable static mixer (consisting of four static mixer elements with a diameter of 17 mm (SMB-H 17/4, Sulzer)) to favour the CO₂ dissolution in the polymer melt. Between each part, a restriction ring has been fitted out in order to obtain a dynamic gastight, which prevents sc-CO₂ from back-flowing.

The temperature inside the barrel is regulated at six locations: T_1 and T_2 before the CO₂ injection, T_3 and T_4 after the injection, T_5 in the static mixer and T_6 in the die. There are four pressure and three temperature sensors: P_1 after the CO₂ injector, P_2 and T_{mat1} before the second gastight ring, P_3 and T_{mat2} before the static mixer and P_4 and T_{mat3} by the die.

CO₂ is pumped from a cylinder by a syringe pump (260D, ISCO). 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, i.e. the part where the channel depth is constant and equal to 1.5 mm.

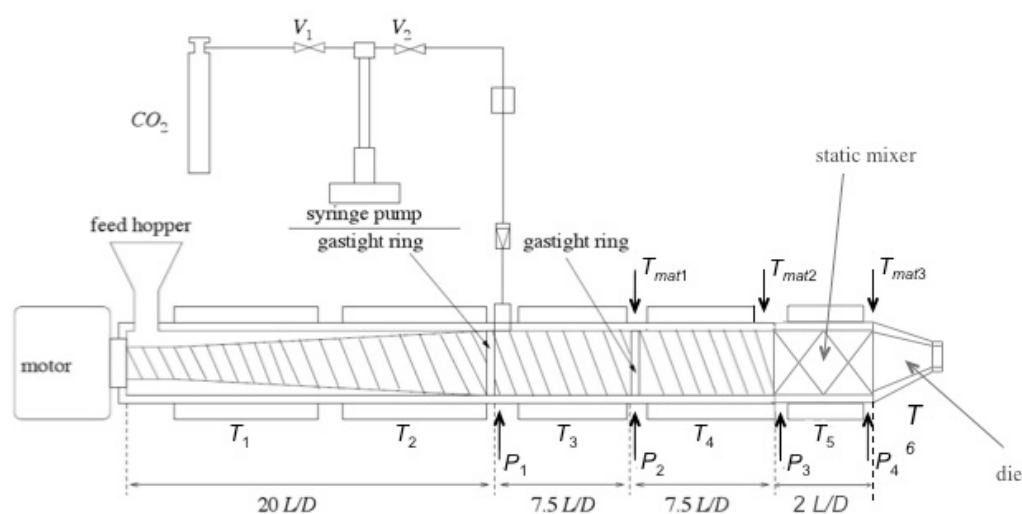


Figure I. Experimental device

Foaming experiments began with a constant volumetric flow rate of 1.5 mL/min and with $T_5=T_6$. The static mixer and die temperature are lowered together and samples are collected once the system has reached a steady state. This temperature will be called die temperature. When the pressure upstream the die becomes too high, the volumetric flow rate of sc-CO₂ is increased to have an enhanced plasticization, and by consequence a lower viscosity. The experiments are stopped when the syringe pump is empty.

Characterization of the foams

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

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

ρ_{app} is the apparent density of the foamed sample, determined by water pycnometry and ρ_p the polymer density determined after extrusion with water pycnometry at 1231 kg.m⁻³.

RESULTS

In the literature about polymer foaming with sc-CO₂, it has been shown that the temperature was the predominant parameter to obtain high porosity. Park *et al.* [11] have shown that, for promotion of large volume expansion ratio, the gas lost must be prevented. The solution is to stiffen the extrudate surface by a decrease of the melt temperature obtained by lowering the die temperature. They also shown that, in order to prevent cell coalescence, a uniform cooling of the polymer is required, hence the temperature before the die must be decreased too. Authors demonstrated that, with further decreased temperature, extrudate was too stiff, preventing the CO₂ to achieve its total blowing agent effect. It was also demonstrated that the temperature and CO₂ content were strongly correlated [12]. With low temperature, viscosity of the polymer, as well as pressure inside the extruder, will increase, hence more CO₂ has to be injected in order to plasticize the polymer. This principle has been applied with a lot of different polymer (polycarbonate [12], polypropylene [13–15], polyethylene [16]) and more particularly with the poly-(lactic acid) [17–23].

Figure II shows the evolution of porosity with temperature and sc-CO₂ content.

For the pure PLA, the previously described behaviour is observed. As soon as CO₂ is injected, 65 % of porosity is created. Then, porosity increases with decreasing temperature, to finally reach a maximum of 96.8 % at 111 °C. Beyond this maximum, porosity starts to decrease with further decrease in temperature.

The PLA-TPS blends show a similar trend: porosity increases with decreasing temperature, reaches a maximum, and finally decreases with further temperature decrease. However, it can be observed that, for a given porosity, there is a shift in temperature between the PLA and the two blends. In other word, the same porosity is obtained at lower temperature than for pure PLA. For instance, to get a porosity of at least 60 %, the temperature of the die must be lower than 130 °C for the pure PLA, against 120 °C for the 80PLA-20TPS blend and 112 °C for the 50PLA-50TPS one. Moreover, the maximum porosity is 96.3 % and is obtained at 99 °C while it is only 67.1 % at the same temperature of 99 °C for the 50PLA-50TPS.

These differences are mostly due to the inherent properties of the TPS. As explained in the Materials and Methods section, TPS is an amorphous polymer with a very low glass transition temperature (-45 °C) in comparison with operating temperatures. In consequence, at the die exit, the TPS is still amorphous lowering the global melt strength and cannot prevent the CO₂ from escaping and giving its total blowing effect. A lower operating temperature would be probably necessary to obtain a better expansion of TPS (Alavi and Rizvi [24]). Moreover, the solubility of sc-CO₂ is lower in TPS than in PLA (see reference [25] for the TPS and reference [26] for the PLA), what limits also the expansion level. This effect is not observable for a TPS mass fraction of 20 %, as the TPS volume fraction remains low in the final foam. But it becomes largely significant for the 50PLA-50TPS blend.

A similar result was published by Mihai *et al.* [6] for a blend with 33 % TPS: a density of 34 kg.m⁻³ representing a porosity of approximately 97 % considering the PLA density at 1267 kg.m⁻³. However, these authors observed that the addition of a coupling agent was necessary to obtain a large foaming and a fine cell structure.

In consequence, the effect of blend composition on the foam morphologies needs to be further investigated, in particular by carrying out microscopic observations of foam samples.

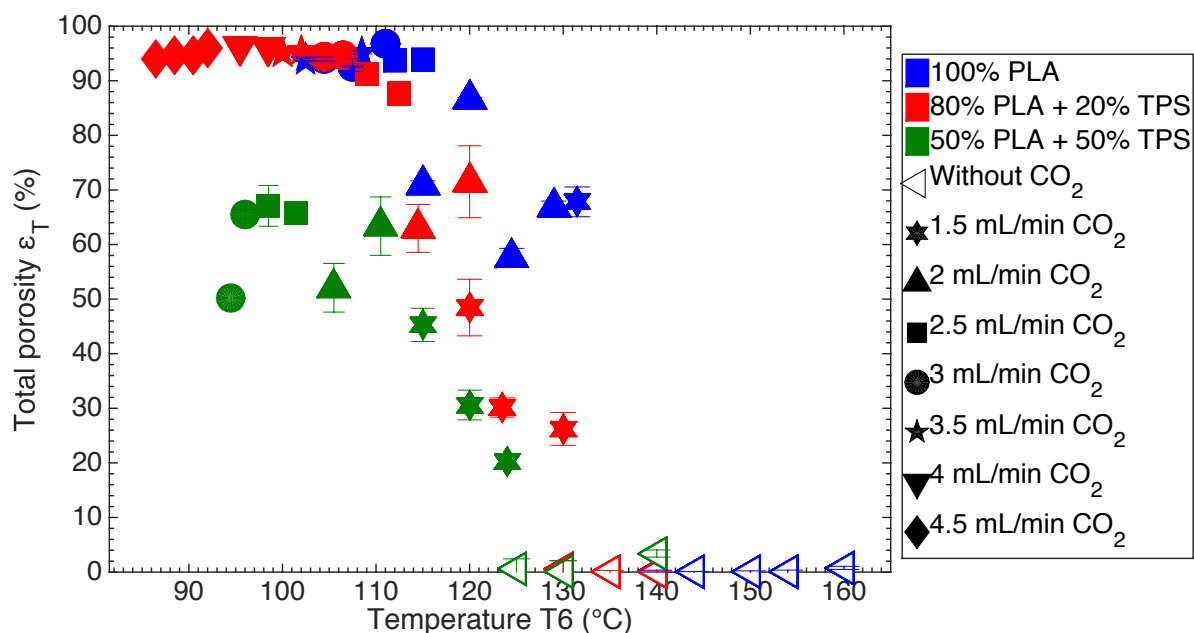


Figure II. Evolution of porosity with temperature and sc-CO₂ content

CONCLUSION

Foams of biopolymers blend were successfully manufactured by the process of extrusion assisted by supercritical CO₂. A maximum porosity of 96.8 % was obtained for the pure PLA at an optimal temperature of 111 °C.

The addition of TPS shifts the operating temperature towards lower values and decreases the maximum porosity. Indeed, TPS exhibits a low glass transition temperature and a lower sc-CO₂ solubility, what decreases the operating temperature and the expansion. This effect is limited for the blend with 80 %PLA and 20 % TPS as the volume fraction of TPS is low in the final foam. However, it becomes significant for the blend with 50 % PLA and 50 % TPS. The effect of blend composition on the foam morphologies needs to be further investigated to confirm these observations.

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