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# BIOPOLYMER FOAM PRODUCTION USING A (SC CO<sub>2</sub>)-ASSISTED EXTRUSION PROCESS

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A process based on extrusion coupled with supercritical carbon dioxide (scCO<sub>2</sub>) was implemented. ScCO<sub>2</sub> modifies the rheological properties of the material in the barrel of the extruder and acts as a blowing agent during the relaxation at the passage through the die. An experimental device based on a single-screw extruder allows the injection of scCO<sub>2</sub> into the melt, the mixing of both components and the creation of porosity into the extruded polymer. In this work, it was used to produce foams of polyhydroxybutyrate-hydroxyvalerate (PHB-HV), a semi-crystalline biodegradable and biocompatible copolymer. The effects on material porosity of the melt temperature before the die and the die temperature were studied.

## INTRODUCTION

Polymers are widely used in several areas. However, due to their slow degradation and the predicted exhaustion of the world petroleum reserves, significant environmental problems have arisen. Therefore, it is necessary to replace them with bioplastics that degrade in a short time when exposed to a biologically active environment [1]. Biopolymers like PHAs (polyhydroxyalkanoates) are marketed as the natural substitutes for common polymers, as they are 100% biodegradable polymers. PHAs are polyesters of various HAs which are synthesised by numerous microorganisms as energy reserve materials in the presence of excess carbon source. Poly(3-hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate (PHB-HV) are the most widely found members of this biopolymer group and were also the first to be discovered, and most widely studied PHA [2]. They possess properties similar to various synthetic thermoplastics like polypropylene and hence can be used alternatively. Specifically, PHB exhibits properties such as melting point, a degree of crystallinity and glass transition temperature, similar to polypropylene (PP). Although, PHB is stiffer and more brittle than PP, the copolymerization of PHB with 3-hydroxyvalerate (PHB-HV) produces copolymers which are less stiff and tougher. That is to say that there is a wide range of applications for these copolymers [3]. The properties of this copolymer depend on the HV content, which determines the polymer crystallinity [4].

Extrusion is a process converting a raw material into a product of uniform shape and density by forcing it through a die under controlled conditions [5]. It has extensively been applied in the plastic and rubber industries, where it is the most important manufacturing process. A particular application concerns the generation of polymeric foams. Polymeric foams are expanded materials with large applications in the packaging, insulating, pharmaceutical and car industries because of their high strength/weight ratio or their controlled release properties.

Conventional foams are produced using either chemical or physical blowing agents. Various chemical blowing agents, which are generally low molecular weight organic compounds, are mixed with a polymer matrix and decompose when heated beyond a

threshold temperature. This results in the release of a gas, and thus the nucleation of bubbles. This implies however the presence of residues in the porous material and the need for an additional stage to eliminate them.

Injection of  $\text{scCO}_2$  in extrusion process modifies the rheological properties of the polymer in the barrel of the extruder and  $\text{scCO}_2$  acts as a blowing agent during the relaxation when flowing through the die [6]. The pressure drop induces a thermodynamic instability in the polymer matrix, generating a large number of bubbles. The growth of cells continues until the foam is rigidified (when  $T < T_g$ ). Moreover, its relatively high solubilisation in the polymer results in extensive expansion at the die. The reduction of viscosity decreases the mechanical constraints and the operating temperature within the extruder. Thus, coupling extrusion and  $\text{scCO}_2$  would allow the use of fragile or thermolabile molecules, like pharmaceutical molecules. The absence of residues in the final material is also an advantage for a pharmaceutical application.

Our lab has developed a  $\text{scCO}_2$ -assisted extrusion process that leads to the manufacturing of microcellular polymeric foams and already elaborated microcellular foams using a biocompatible amorphous polymer [7, 8, 9]. In this work, this process has been applied to PHB-HV. Foam production of semi-crystalline polymer is less frequent in the literature. Crystallinity hinders the solubility and diffusion of  $\text{CO}_2$  into the polymer and leads consequently to less uniform porous structure [10]. Moreover, it has been shown that a large volume expansion ratio could be achieved by freezing the extrudate surface of the polymer melt at a reasonably low temperature [11]. Thus, in this work, in order to control and improve the porous structure of the PHB-HV, the influence of melt and die temperatures have been studied.

## MATERIALS AND METHODS

PHB-HV ( $M_w=600$  kDa), with a HV content of 13 % and plasticized with 10 % of a copolyester was purchased from Biomer (Germany). Melting temperature was measured at  $159^\circ\text{C}$  by DSC (ATG DSC 111, Setaram). The solid density  $\rho_p$ , determined by helium pycnometry (Micromeritics, AccuPYC 1330) is about  $1216 \text{ kg.m}^{-3}$ . A rheological study at atmospheric pressure has been performed in oscillatory mode (MARS, Thermo Scientific). The polymer viscosity decreases when temperature and shear rate increase, which is a characteristic behaviour of a pseudoplastic fluid (Figure 1). This characterization step helped in choosing the operating conditions to process PHB-HV by extrusion. These conditions have to ensure that the polymer flows well enough through the barrel without being thermally degraded.

Figure 2 shows the experimental set up, which has previously been detailed elsewhere [8, 9]. The single-screw extruder has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 35 (Rheoscam, SCAMEX). A great L/D ratio generally indicates a good capacity of mixing and melting but important energy consumption. The screw is divided into three parts. The first one has a length to diameter ratio of 20 and the two others have a length to diameter ratio of 7.5. Between each part, a restriction ring has been fitted out in order to obtain a dynamic gastight which prevents  $\text{scCO}_2$  from backflowing. The first conical part allows the transport of solid polymers and then, their melting and plasticizing. Then, the screw has a cylindrical geometry from the first gastight ring to the die. This die has a diameter of 1 mm and a length of 11.5 mm. The temperature inside the barrel is regulated at five locations:  $T_a$  and  $T_b$  before the  $\text{CO}_2$  injection,  $T_c$  and  $T_d$  after the injection and  $T_e$  in the die.

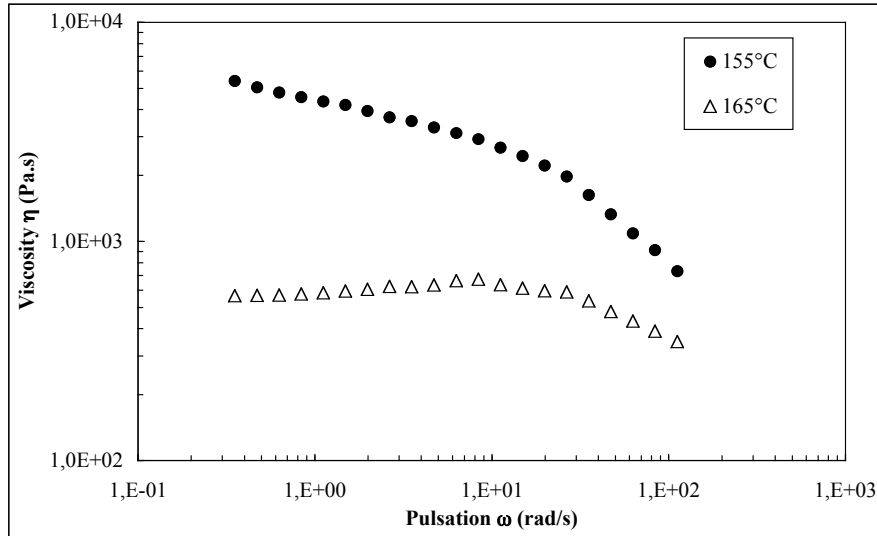


Figure 1: Evolution of viscosity with pulsation

There are three pressure and two temperature sensors:  $P_1$  after the  $\text{CO}_2$  injector,  $P_2$  and  $T_1$  before the second gastight ring and  $P_3$  and  $T_2$  by the die. This allows measuring the temperature and the pressure of the polymer inside the extruder. Errors associated to pressure and temperature sensors were about 0.2 MPa and 3.3°C respectively.

$\text{CO}_2$  (N45, Air liquide) is pumped from a cylinder by a syringe pump (260D, ISCO) and then introduced at constant volumetric flow rate. The pressure in the  $\text{CO}_2$  pump is kept slightly higher than the pressure  $P_1$ . The  $\text{CO}_2$  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. The pressure, the temperature and the volumetric  $\text{CO}_2$  flow rate are measured within the syringe pump.  $\text{CO}_2$  density, obtained on NIST website by Span and Wagner equation of state [12], is used to calculate mass flow rate and thus the  $\text{CO}_2$  mass fraction  $w_{\text{CO}_2}$ .

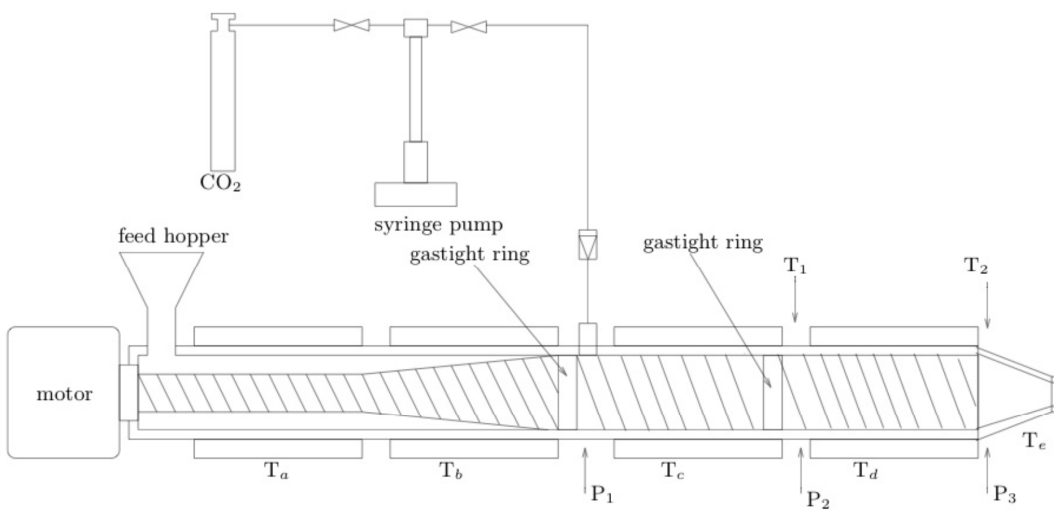


Figure 2: Experimental device

For each experiment, only the temperature of the metering zone  $T_d$  and of the die  $T_e$  were changed. The three other temperatures  $T_a$ ,  $T_b$  and  $T_c$  were kept constant at 160°C. CO<sub>2</sub> mass fraction  $w_{CO_2}$  was also kept constant at 1 %, which is much less than solubility [13]. Three series of experiments were carried out.  $T_d$  was fixed at 140°C, 135°C and 130°C respectively and  $T_e$  varied from 140 down to 110°C. At lower values of  $T_e$ , the extruder stopped due to too high a pressure  $P_3$  according to the established alarm value.

Once steady state conditions are reached, extrudates were collected and water-cooled at ambient temperature in order to freeze the extrudate structure. Several samples were collected during the experiment in order to check the homogeneity of the extrudates. To calculate the apparent porosity  $\rho_{app}$ , samples were weighed and their volumes were evaluated by measuring their diameter and length with a vernier (Facom). To obtain this apparent density with a good enough precision, the mean of 6 measurements was carried out. Porosity, defined as the ratio of the pore volume to total volume is calculated by equation 1:

$$\varepsilon = 1 - \frac{\rho_{app}}{\rho_P} \quad (1)$$

$\rho_P$  is the PHB-HV density and  $\rho_{app}$  the apparent density of the extrudates.

The theoretical maximum porosity  $\varepsilon_{max}$  is obtained if all the dissolved CO<sub>2</sub> would become gaseous inside the extrudate at ambient conditions and would thus create porosity. It could be calculated by the following equation:

$$\varepsilon_{max} = \frac{w_{CO_2} \rho_P}{w_{CO_2} \rho_P + \rho_{CO_2}(atm)} \quad (2)$$

$w_{CO_2}$  is the CO<sub>2</sub> mass fraction and  $\rho_{CO_2}(atm)$  is the CO<sub>2</sub> density at ambient conditions.

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

## RESULTS

The results of porosity are presented in Figure 3. It is noticeable that, for all experiments, the obtained porosity is lower than the theoretical maximal porosity  $\varepsilon_{max}$ , which is estimated at about 90 %. The higher porosity, obtained at the lowest  $T_d$  and  $T_e$ , 130 and 110°C respectively, is about 70 %.

The porosity increases with decreasing temperature  $T_d$ . The evolution of porosity with the temperature  $T_e$  depends on the value of  $T_d$ . At  $T_d$  equal to 140°C, the porosity is constant, whereas at  $T_d$  lower than 140°C, the porosity decreases with increasing die temperature. It was previously observed for polystyrene that, at a reasonably low temperature of polymer melt, there exists an optimal die temperature for which large volume expansion ratio are achieved by freezing the extrudate surface [11]. This effect is explained because more gas is retained in the foam at lower temperature and used for cell nucleation and growth. However, when the nozzle temperature was further decreased, the volume expansion ratio decreased because of the increased stiffness of the frozen skin layer. Our experiments might be explained in the same way. Thus  $T_e$  would be still too high to obtain higher porosity.

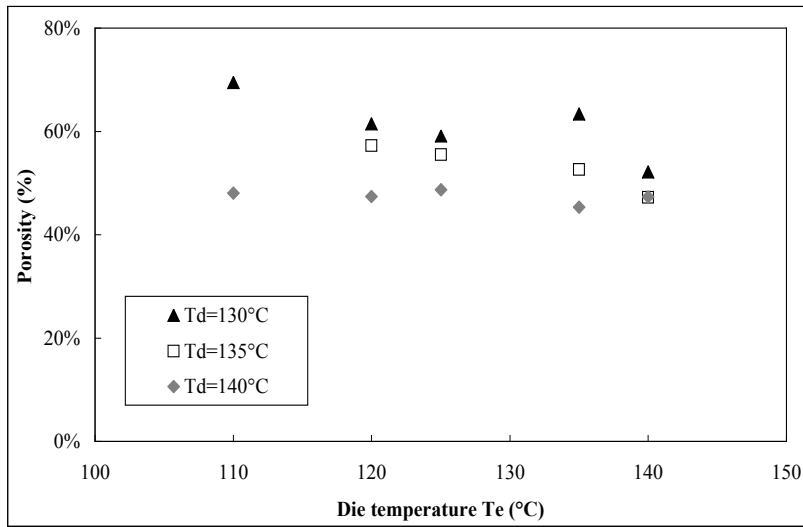


Figure 1: Porosity evolution

Figure 2 presents pictures at two different values of  $T_d$ . It could be observed that the pores are large (more than 200  $\mu\text{m}$ ) and that they become fewer and larger when  $T_d$  decreases. As porosity increases, it seems thus that growth phenomena occur at lower temperature. This evolution is opposite to previous results in which coalescence and growth phenomena occurred when temperature increased and led to larger porosity [7, 11]. Indeed, it was believed that the polymer melt should be cooled substantially in order to increased melt strength and thus prevent cell coalescence.

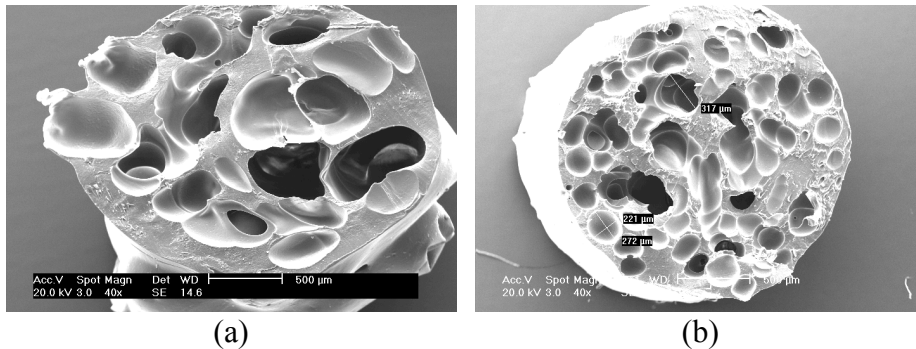


Figure 2: SEM pictures (a)  $T_d=130^\circ\text{C}$  (b)  $T_d=140^\circ\text{C}$

## CONCLUSION

PHB-HV foaming by extrusion assisted by supercritical fluid is thus feasible according to the temperature profile established. Porosity up to 70% was obtained. However, this foaming must be improved by lowering the operating temperature. The experimental device should be thus modified in order to optimize the cooling of the foamed samples.

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