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SUPERCritical CO₂ ASSISTED FOAM EXTRUSION FOR AERONAUTICAL SANDWICH STRUCTURE MANUFACTURING

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Abstract: *Sandwich structures represent a very interesting approach for the development of new multifunctional and lightweight materials for aerospace and space applications. Nomex[®] or aluminum honeycomb is at this date the most widely used core materials for sandwich structures, given their extraordinary strength-to-weight-ratio. However, these materials exhibit some important drawbacks as a poor vibrational and acoustic damping [1], along with a limited impact energy absorption capability. Several studies are in progress in order to develop new composite materials with enhanced acoustic and vibrational damping properties [2-8]. A very promising solution to overcome these issues is represented by thermoplastic foams, having several advantages as ease of processing, good impact energy absorption, recyclability and enhanced properties in terms of thermal and acoustic isolation [9-12], along with the possibility to modify their intrinsic properties through micro and nano-particles addition.*

A relatively new and promising technique to develop thermoplastic foams is represented by supercritical CO₂ (sc-CO₂) assisted foam extrusion [13,14], with sc-CO₂ acting as Physical Blowing Agent (PBA). Sc-CO₂ has limited environmental impact, given its low toxicity and energetic requirements to attain its supercritical conditions (31 C, 74 bars), making this process economic, sustainable and totally green. In the frame of this work, a continuous process has been used to produce PLA foams with different microstructures depending on the operating conditions. Typical densities range from 20 to 60 kg/m³, crystallinity from 10 to 30 % and cell size from 90 to 500 μm.

Keywords: Supercritical CO₂, PLA polymer, extrusion foaming, sandwich structures, aeronautical materials

1. Introduction

Classic sandwich structures are widely used in several industrial sectors but have significant shortcomings such as low damping and sound insulation rates [1], as well as low impact resistance. In aeronautical structures, noise can have significant effects on the health of passengers and aircrew [15] and several studies are in progress with the aim of developing new solutions with enhanced sound insulation [2-6, 16]. Through its potentially nonlinear viscoelastic properties, the intrinsic damping of the core material influences the amplitude of the vibration and acoustic response of the structure. Thus, the study of the vibro-acoustic behavior of the core material is fundamental.

A promising solution is to use cellular core materials such as thermoplastic polymer foams. Poly lactic acid (PLA) is a biopolymer that has been extensively studied in recent years, due to its promising potential in reducing waste by replacing petroleum-based polymers. Indeed, PLA monomers can be derived from renewable sources such as corn starch [17,18]. Furthermore, PLA has been considered as a non-toxic/eco-friendly polymer, with a good combination of mechanical properties and ease of processing. This family of materials has in fact several advantages, such as ease of implementation, the ability to absorb energy during an impact (resilience), recyclability and increased properties in terms of thermal and acoustic insulation [19,22]. Moreover, their intrinsic properties can be easily optimized by the dispersion of nano or micro particles.

In this context, the development of alveolar composites shows significant scientific and industrial interest. A certain number of technologies allow the realization of alveolar structures, most conventional using physical blowing agents (PBA) and chemical blowing agents (CBA) which are incorporated into the molten polymer. The gas formed in situ by chemical reaction (CBA) or injected into the polymer (PBA) will create pores or cells and will thus generate porosity in the polymer. However, the use of these compounds poses several problems: (i) CBAs, which are generally carbonated salts that decompose into gases under the action of heat, leave residues in the polymer after formation of the porous network and their decomposition often requires high temperatures; (ii) PBAs, such as freons (CFCs, HCFCs, etc.), are harmful to the environment by attacking the ozone layer or, like hydrocarbons such as pentane or butane, pose safety issues due to their flammability.

Supercritical fluid technology, and more particularly supercritical CO₂ (sc-CO₂), could respond to these problems by offering an alternative free of the aforementioned defects [14]. It is widely described in the literature and, in recent years, has been extensively studied with biopolymers in order to manufacture "green" foams with a clean process. The process has also been applied to technical thermoplastics such as polyphenylene sulphide and polyamide [23-26], but only with batch foaming processes which involve long implementation times, in particular for the saturation of the polymer by the fluid under pressure. It is possible to overcome these very long saturation times and thus increase the production rate by carrying out the polymer-supercritical fluid mixture continuously in an extruder [27-30]. In this continuous process, the polymer is melted, then sc-CO₂ is injected and the mixing actions of the extrusion screw allow to obtain a single-phase mixture. Nucleation then takes place at the injection point. However, the injection process remains a semi-discontinuous process and it seems relevant to think about a totally continuous implementation to reach the highest production rates.

The purpose of the study concentrated in the manufacturing of polymer foams and tested their properties in order to come to a stage that could be integrated in aeronautical structures. At a first stage, an extrusion foaming process of PLA polymer was examined at different operating conditions. Samples with a range of porosity were managed to be fabricated.

2. Materials and methods

2.1. Materials

The basic raw materials used in this study are PLE 005-A from NaturePlast supplied in the form of granules and a sc-CO₂ fluid used as physical blowing agent.

2.2. Extrusion foaming process

Experiments of extrusion foaming are performed on a single-screw extruder, described in details in previous publications [14]. A schematic representation of the equipment is shown in Figure 1. The single-screw extruder has a 30 mm screw diameter and a length-to-diameter ratio (L/D) of 37 (Rheoscam, Scamex). PLA is inserted into the hopper, while the screw drives the transportation of the solid granulated polymer to the end of the extruder where a die is placed. Along the way towards the exit, the polymer is melted and subsequently mixed with sc-CO₂. The foaming process of the polymer takes place when it flows out from a homemade die.

The extruder is thermo-regulated at six locations: T₁ and T₂ before the CO₂ injection port, T₃ and T₄ after the injection port, T₅ in the static mixer and T₆ at the die. There are three temperature and four pressure sensors: P₁ after the CO₂ injector, P₂ and T_{mat1} before the second gastight ring, P₃ and T_{mat2} before the static mixer and P₄ and T_{mat3} close to the die.

The sc-CO₂ is injected into the extruder using a syringe pump (260D, ISCO) between the second and the third temperature control device at the same pressure as that of the polymer (P₁). The screw rotation speed is kept constant at 30 rpm during the whole experiment and a constant volume flow rate of sc-CO₂ (Q_{CO2}) is used. Temperatures T₁ to T₄ are kept constant, while T₅ and T₆ are progressively decreased while keeping them equal. Samples are collected once a steady state is established [27-30].

The mass fraction of CO₂ ω_{CO2} in the CO₂-polymer mixture is calculated as follows:

$$\omega_{CO2} = \frac{Q_{CO2} \rho_{CO2}^{pump}}{Q_{CO2} \rho_{CO2} + \dot{m}_p} \quad (1)$$

\dot{m}_p is the mass flow rate of the polymer measured by weighing outside of the die and ρ_{CO2}^{pump} is the density of CO₂, in the pump. This density is obtained from NIST website [31].

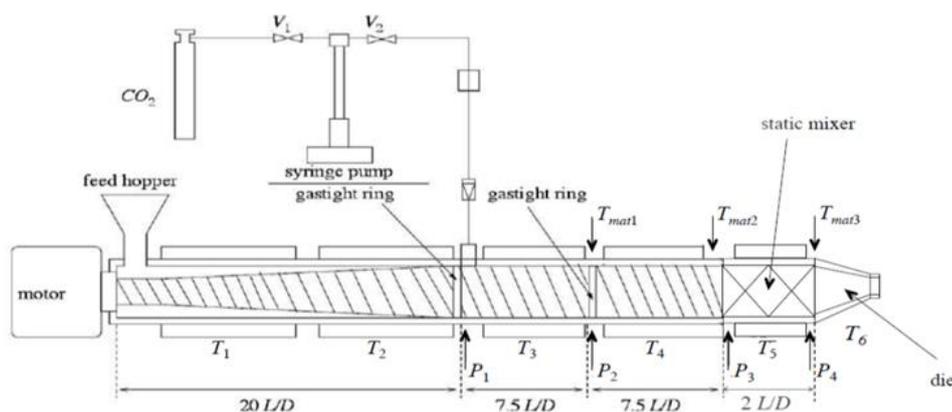


Figure 1. The experimental system used [25].

2.3. Influence of operating conditions on porosity

The supercritical CO₂ assisted extrusion process has shown that the expansion rate or the type of porosity were dependent on temperature. Indeed, with a die temperature too high, a loss of CO₂ is present which limits the expansion of the foam. Decreasing the temperature of the die, the surface of the foam is more quickly solidified and retains CO₂. Moreover, with the decrease in temperature, the diffusion of gas at the surface of the polymer decreases and therefore more gas remains in the foam to contribute to its expansion. However, an excessive die temperature

decrease penalizes the expansion, the surface of the extruded sample becoming too rigid and therefore limiting expansion. In the case of a semi-crystalline polymer, this surface stiffening is often related to crystallization. Furthermore, it was observed that the temperature upstream of the die also had an influence while it reduces the coalescence of cells thanks to an increase in the melt strength. The CO₂ content also plays a key role. With decreasing temperature, the viscosity polymer increases which can lead to pressure increases within the extruder. Adding more CO₂ in the extruder plasticizes the polymer and therefore reduces viscosity and pressure, which allows working at lower temperatures [14].

2.4. Foam characterization

Porosity (ε_{sample}) is defined as the ratio of void volume to total volume and is calculated as follows:

$$\varepsilon_{sample} = \frac{v_{porosity}}{v_{Total}} = 1 - \frac{\rho_m^{H_2O}}{\rho_p^{H_2O}} \quad (2)$$

$\rho_m^{H_2O}$, is the apparent density of the foamed sample determined by water pycnometry, while $\rho_p^{H_2O}$ is the density of the solid polymer determined on a sample after extrusion by water pycnometry.

The samples obtained by extrusion foaming process are characterized by Scanning Electron Microscopy (SEM) in order to define the cells microstructure and diameter. Cells diameters (d_i) and surfaces (S_i) are measured using ImajeJ open source software for image analysis. The average cell size of the foamed samples is calculated according to the following equation:

$$d_{sample} = \sum_{i=1}^n \frac{S_i d_i}{S_i} \quad (3)$$

Sample crystallinity of the extruded foams is measured using Differential Scanning Calorimetry (DSC), applying a constant heating rate of 10 °C/min from 20 to 200°C to samples obtained directly after the extrusion. For each grade of material five samples of 10-15 mg were tested using sealed aluminum pans. The defined thermal cycle allows evaluating the cold crystallization enthalpy (ΔH_c) and the enthalpy of fusion (ΔH_m). These parameters are necessary to compute the degree of crystallinity (X_c) of the PLA foam, determined according to Equation (4) [13, 14]:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_\infty} \quad (4)$$

Where ΔH_∞ is the theoretical enthalpy of fusion of the material equal to 93 J/g [14].

3. Results and discussion

3.1. Porosity of PLA foamed samples

Five samples were taken at the extruder outlet and are listed in table 1. This table indicates the temperature T_{5-6} of the static mixer and die, the pressure P_4 before the die, the mass fraction of CO₂ ω_{CO_2} , porosity ε_{sample} , density $\rho_m^{H_2O}$, diameter d_{sample} and crystallinity X_c .

Figure 2 represents the pressure before the die P_4 , and the final material porosity $\rho_m^{H_2O}$, both measured as a function of the final temperature T_{5-6} . The two variables follow a similar tendency,

inversely proportional to temperature. Indeed, when the temperature decreases, an increase of the porosity can be observed. This increase is small as the porosity level is already high. The pressure also increases due to the increase of the polymer viscosity, despite the plasticizing effect of the increasing mass fraction of the CO₂.

Table 1: Overview of PLA foamed samples.

N°	T ₅₋₆ (°C)	P ₄ (bar)	ω _{CO2} (%)	ε _{sample} (%)	ρ _{sample} (g/cm ³)	d _{sample} (μm)	χ _c (%)
1	110	122	2.5	97.5	0,037	500	7
2	105	135	3	97.6	0,032	380	14
3	100	137	3.5	97.6	0,029	290	12
4	95	145	4	97.9	0,025	220	23
5	90	160	4.5	98.1	0,023	140	24

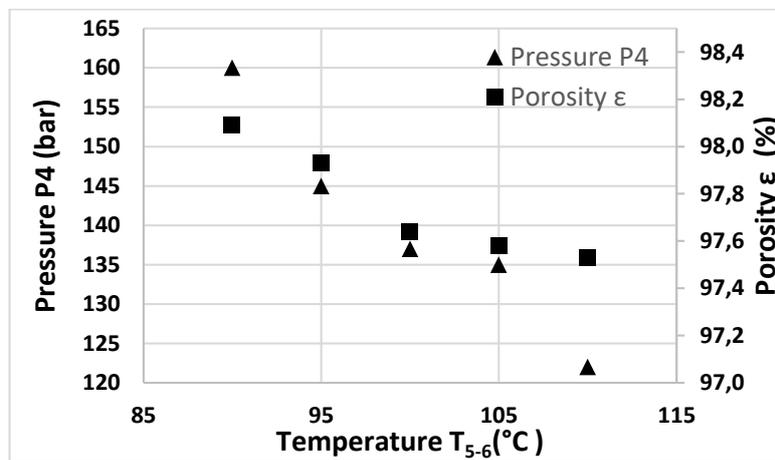


Figure 2. Behavior of porosity in temperature and pressure

3.2. Scanning electron microscope SEM

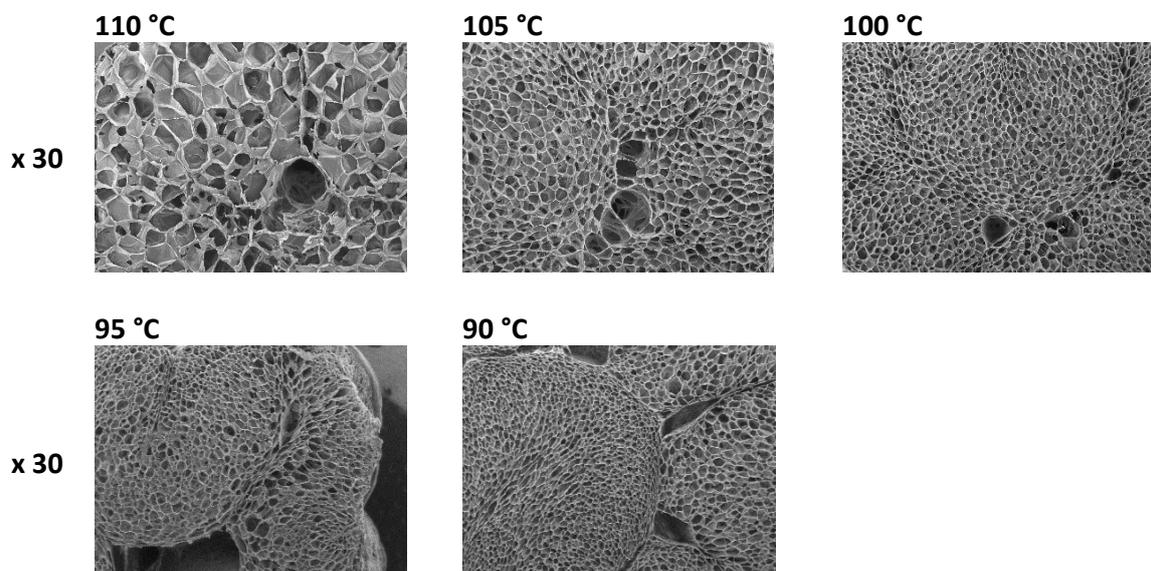


Figure 3. Microstructure of PLA foamed samples

The SEM photomicrographs of the different foams are shown in Figure 3. The images indicate the influence of temperature on the size and number of cells. The first image shows that, at high die temperature, few pores are present, they are very large and the structure is very coarse. All the other images represent that the pores are smaller at lower temperatures. In addition, the pore walls are slightly torn, confirming that the porosity is closed at the same time. The big cell in the middle is due to the annular shape of the die. The average cell diameters are presented in Table 1 (equation 3). It confirms that the mean diameter decreases with the temperature from 500 μm at 110°C to 140 μm at 90°C. This variation with temperature is obtained at a high level of total porosity which is more or less constant and it shows that it is possible to tune the porous structure by means of the temperature.

3.3. Crystallization properties of PLA foamed samples

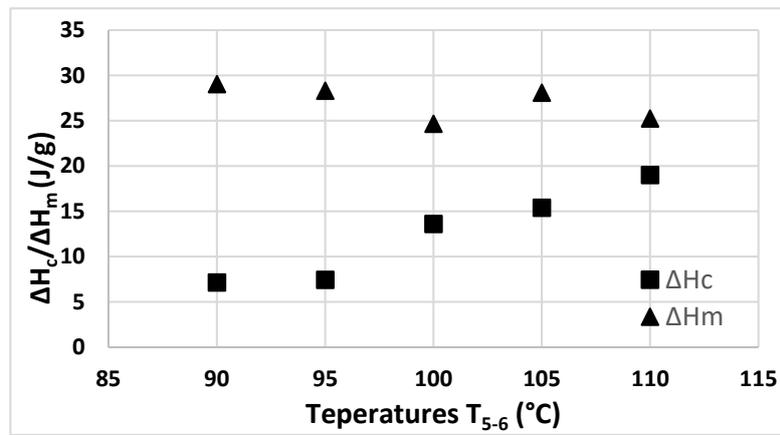


Figure 3. Behavior of crystallinity with temperature

After completing a first heating cycle for all five samples, the crystallinity of the samples was calculated using equation 4. The results are summarized in Table 1 and plotted in Figure 3, where the evolution with temperature of the two enthalpies is presented: the melting enthalpy (ΔH_m) and the cold crystallization enthalpy (ΔH_c). It has to be noticed that the crystallinity X_c is proportional to the difference between these two enthalpies. As the die temperature decreases, the melting enthalpy seems to slightly increase, while a more important evolution is observed for the cold crystallization, which decreases. It results in an increase of the sample crystallinity with decreasing temperature, the sample at the lower temperature (90 °C) having a crystallization degree of 24 %, while the sample at the higher temperature (110 °C) presenting a level of only 7 %.

A possible explanation arises from the viscosity of the polymer, which increases with the temperature decrease. Indeed, this viscosity increase provokes a decrease of the Reynold number (the flowrate being more or less constant) and thus the obtention of a more laminar flow inside the die. This flow evolution is favorable to the organization of the polymer chains and thus to the increase of the degree of crystallinity of the final material.

4. Conclusions

PLA polymer was the principal material used in this study for the foam's fabrication by continuous extrusion foaming. A series of characterization techniques were implemented including water pycnometry in order to determine the apparent density, scanning electron microscopy to reveal the inner structure of cells and differential scanning calorimetric to

measure the crystallization properties of the foam. All these parameters are strongly influenced by the processing temperature and thus to CO₂ mass fraction which has to be increased to reach the lower temperatures. Finally, it is possible to tune the cellular structure of the foam at a high level of porosity (97-98 %) by means of the operating temperatures: a more crystalline porous structure (24 %) with a smaller cell mean diameter (140 μm) can be obtained while a more amorphous one (7 %) with higher cell mean diameter (400 μm) is obtained at higher temperatures. These materials will be further investigated in the following, in order to integrate them in composite sandwich structures and a full study of the acoustic and damping mechanical properties is planned.

5. Acknowledgement

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