Effect of processing condition on properties of poly(lactic) acid parts obtained by foam injection molding

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Abstract
Foam injection molding is a processing technology particularly interesting for biodegradable polymers, which present a very narrow processing window, with the suitable processing temperatures close to the degradation conditions. The addition of a physical blowing agent, besides decreasing the final part weight, reduces both the viscosity and the glass transition temperature of the polymer melt, allowing the processability of these materials at lower temperatures. In this work, structural foams of PLA with nitrogen as physical blowing agent were obtained by foam injection molding. In particular, the effects of back pressure, namely the pressure imposed inside of the cylinder when the screw is returning back to prepare a new amount of material to be injected, and of the injection flow rate on foaming and mechanical properties of the molded parts was assessed.
It was found that the samples molded adopting a higher injection flow rate are shorter than those injected at lower flow rate, and this result was ascribed to the large compressibility of the injected shot. As far as the mechanical properties of the foamed parts, it was found that the modulus decreases with decreasing density. However, the density reduction is not the only significant parameter, but also the morphology of the foams should be taken into account in order to justify the differences between tensile and flexural modulus.

Keywords: Foam injection molding, poly(lactic) acid, mechanical properties, injection flow rate, physical foaming/blowing agent.

Introduction

Foam injection molding is a processing technology in which an environmental friendly blowing agent under high pressure and temperature allows to produce structural foams[1]. This technology is particularly interesting for biodegradable polymers and in particular for Poly(lactic) Acid (PLA), which presents a very narrow processing window, with the suitable processing temperatures close to the degradation conditions[2]**.** The addition of a physical blowing agent, besides decreasing the final part weight, reduces both the viscosity and the glass transition temperature of the polymer melt, allowing the processability of those materials at lower temperatures[3-5].

The optimization of the various processing parameters involved in the foam injection molding process is essential in order to produce parts with good foaming and optimal properties[6].

One of the most important variables in foam injection molding process is the back pressure, namely the pressure imposed inside of the cylinder when the screw is returning back to prepare a new amount of material to be injected. Since the physical blowing agent is injected in form of gas into the cylinder simultaneously with the polymer, the back pressure is fundamental in order to control the batching time and then the gas dispersion into the

polymer. Rizvi et al.[7] demonstrated that a higher back pressure allows a better gas dispersion inside the polymer melt. In a previous paper[8], the effect of the back pressure on the foaming of molded PLA was analyzed. It was found that on increasing the back pressure, a higher amount of polymer and a smaller percentage of foaming agent is injected, and thus foaming is less effective. Another critical variable is the flow rate. It is indeed well accepted that a high flow rate allows more homogeneous foams due to the fact that the temperature is more homogeneous when foaming starts[1, 6]. This is due to the fact that less time is given to the injected shot to cool down before foaming. In this work, the effect of the injection flow rate on foamed parts molded with different back pressures is analyzed.

Materials and methods

In this work, a commercial grade of PLA produced by Natureworks with the trade name of 4032D was adopted. This PLA grade has a D-enantiomer content of approximately 2 % and a maximum degree of crystallinity of about 45 %[9]. PLA 4032D has a molecular weight distribution characterized by Mn=120 kg/mole, Mw=210 kg/mole, a melt temperature of 168 °C and a glass transition temperature of 58 °C. Rheological measurements were performed at three different temperatures (160 °C, 180 °C and 200 °C) by means of a Haake Mars II (Thermo scientific) rotational rheometer in a plate-plate configuration under dry nitrogen atmosphere. During the frequency sweep experiments, constant stress of 100 Pa and frequency variable between 0.1 and 150 rad/s were applied. Figure 1 shows the results of the rheological measurements in terms of master curves at T=200 °C. The thermal shift factors αT are reported in Table 1.

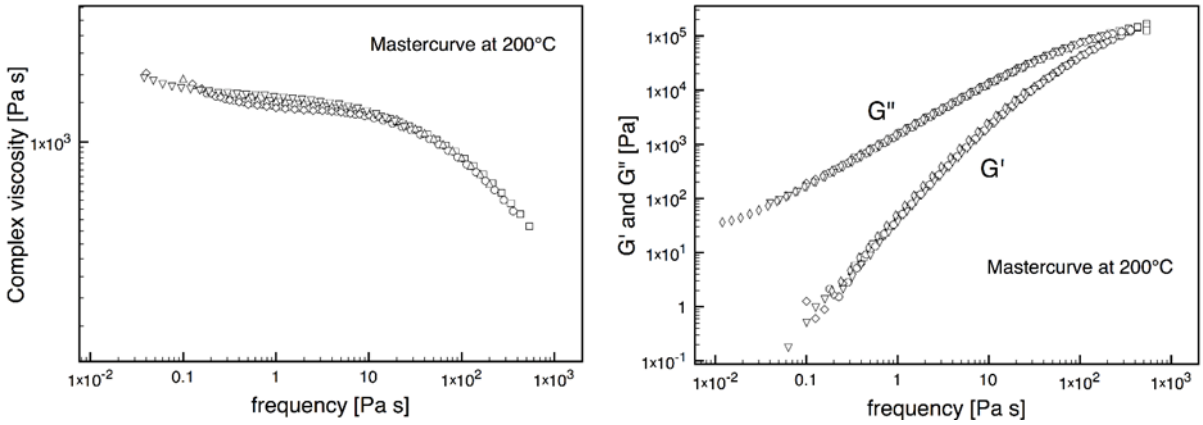

Figure 1. Rheological measurements on PLA Natureworks 4032D.

Table 1. Thermal shift factors αT.

Temperature [°C]	*αT*
200	1.0
180	1.8
160	4.7

A traditional injection molding machine (a 70 ton Negri-Bossi press) with a screw diameter of 25 mm and L/D = 22 was adapted to carry out the microcellular injection molding process using a home-made design. In particular, the cylinder of the injection molding machine was modified to host a system for controlling the quantity of gas injected during the batching step. The screw was modified introducing a section for improving the mixing between the physical blowing agent and the polymer melt. Finally, a nozzle with a needle valve was adopted to avoid premature foaming. A complete description of cavity geometry is reported in Figure 2.

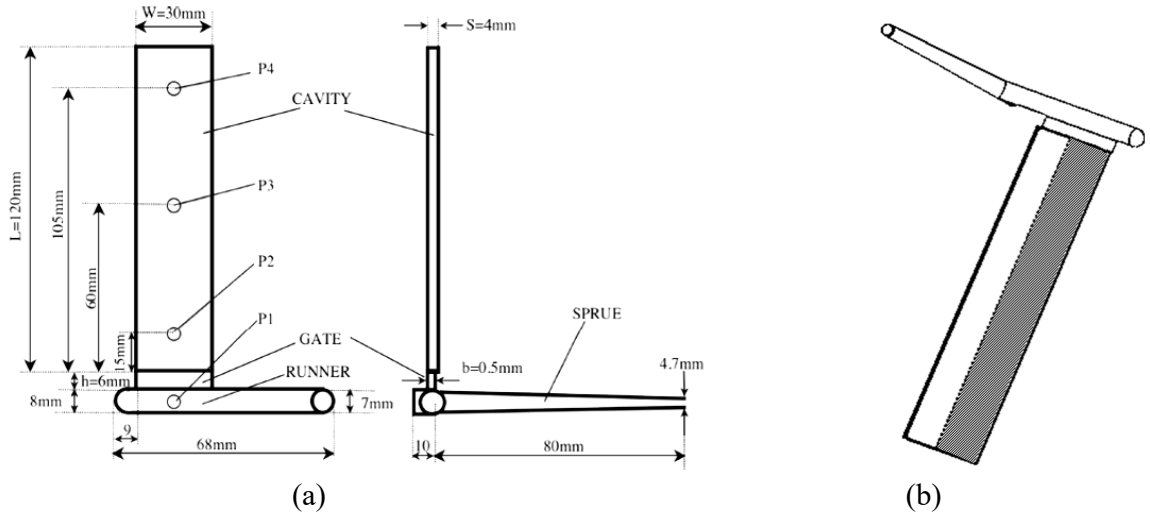

Figure 2. (a) Schematic view of the cavity. (b) Gray part of the sample represents the specimen used for mechanical tests

Table 2. Experimental conditions.

Injection Temperature	*[°C]*	*200*
Gas Pressure	[bar]	0, 100
Injection Flow Rate	[cm^3/s]	18, 36
Mold Temperature	[°C]	25
Rotation speed	[rpm]	200
Shot volume supplied	[cm^3]	27
Back pressure, bp	[bar]	2-5
Mold Temperature	[°C]	25

The mold cavity is equipped with pressure transducers in the runner (P1) and at increasing distances from the gate (P2 - P4).

The very narrow processing window of the PLA, due to the sensitivity to thermal degradation, restricts the injection temperature range at 180-220 °C, while the relatively low glass transition temperature limits the mold temperature below 55-60 °C[10]. Table 2 reports the experimental conditions adopted in this work.

The physical blowing agent used in this work is nitrogen. A volumetric pump connected by an injector to the cylinder of the injection molding machine allows monitoring the amount of gas injected during the batching step. Knowing the values of pressures and volumes before and after the injection of gas, the molar volume of nitrogen allows to obtain the number of moles injected and the corresponding amount in grams.

In this work, the effect of back pressure, bp, on the foamed parts obtained by imposing two different injection flow rates was investigated. In particular, the volume of batching and the pressure of the gas injected were kept constant and tuned so to obtain a complete part with a bp=5 bar, whereas the bp was changed in the range from 2 bar to 5 bar. These bp values in the hydraulic system correspond to pressure values about 18 times larger on the melt[11]. Since the maximum bp adopted (5 bar) corresponds to about 90 bar on the melt and since the gas pressure is 100 bar, it was not possible to inject gas with back pressures higher than 5 bar.

Results and discussion

It was demonstrated that the amount of polymer conveyed toward the injection chamber during the batching phase is strongly dependent on the back pressure[8]. This happens because at higher values of back pressure a lower amount of N_2 is injected, due to a smaller difference between the pressure into the cylinder during the gas injection and the gas pressure. It was also demonstrated that on decreasing the back pressure, a lower amount of polymer is injected due to the fact that the gas pushes back the screw reducing the conveying of polymer toward the injection chamber.

Figure 3 shows the ratio between the amount of nitrogen and the amount of polymer injected for the test conditions adopted in this work.

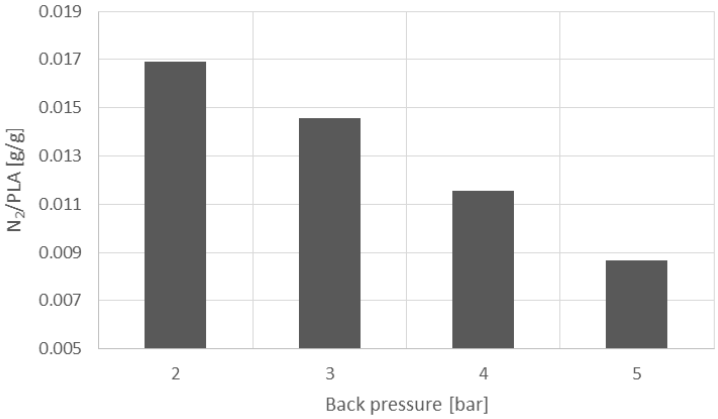

Figure 3. Ratio between amount of nitrogen injected in grams and amount of polymer injected in grams.

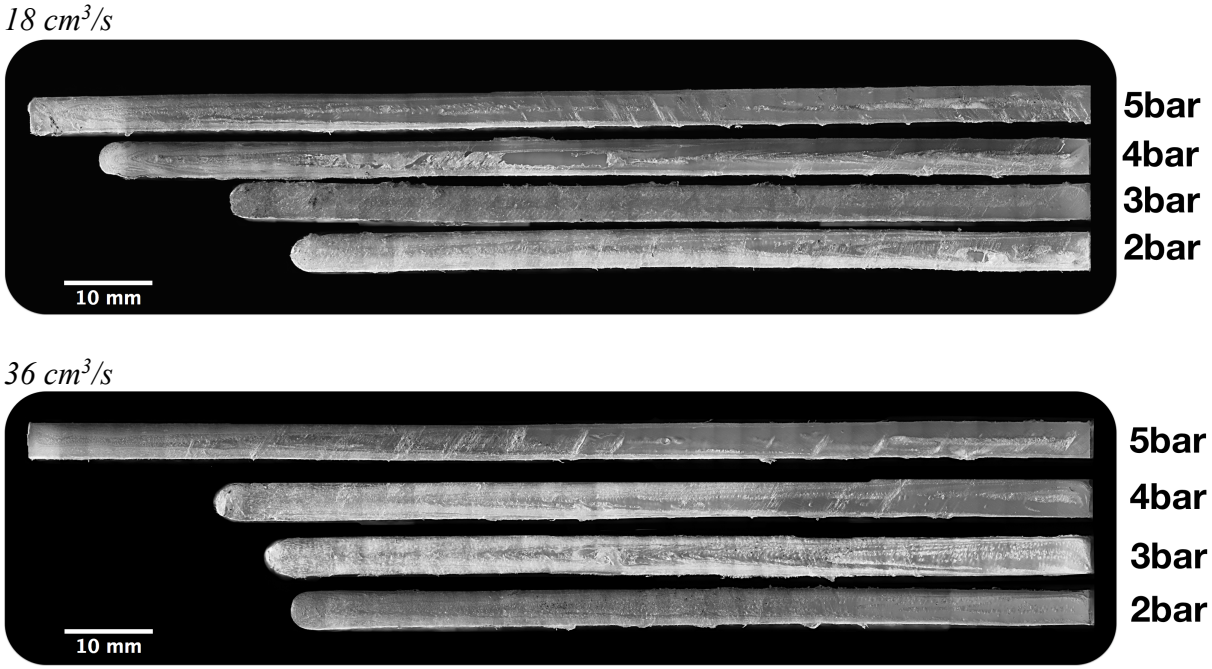

Figure 4. Vertical section of the foamed samples at different back pressures. The material flow direction is from right to left.

Figure 4 shows a length-thickness section of foamed samples with injection flow rates of 18 cm^3/s and 36 cm^3/s at increasing bp from the bottom upwards.

For both injection flow rates, the sample length increases with increasing back pressure. Only the sample obtained with the higher back pressure (5 bar) results to be complete. At higher injection flow rate, the incomplete samples (bp 2, 3, and 4 bar) obtained at 36 cm^3/s are

shorter than those obtained with the lower flow rate. This is due to the large compressibility of the polymer-gas mixture. Indeed, assuming isothermal conditions during filling, the mass flow rate entering the cavity, $\dot{m}$, depends on the compressibility according to the following equation

$$\dot{m} = \dot{m}_i - V(t)\rho\beta\frac{dP}{dt} \quad (1)$$

where $\dot{m}_i$ is the nominal flow rate (i.e. the product between the density, ρ, and the flow rate imposed by the screw), *V(t)* is the volume between the tip of the screw and the cavity entrance, *P* is the (average) pressure in the volume *V* and β is the compressibility ($\beta = 1/\rho\ \partial\rho/\partial P$). It is clear from eq. 1 that if the pressure increases the flow rate entering the cavity is smaller than the nominal one and the difference is larger for large shot volumes and cushions, and for large compressibility. The reverse happens when the pressure decreases, for instance when the screw stops. If the gate solidifies before the pressure P goes back to the value it had before injection, the mass injected into the cavity is lower than expected by an amount which can be estimated as:

$$\Delta m = V_{gf}\beta\rho_r\left(P_{gf} - P_r\right) \quad (2)$$

In eq. 2, the subscript "gf" indicates the gate freezing point and the subscript "r" the conditions before injection. As reported in Fig. 3, on decreasing the back pressure, for the same shot volume supplied, a lower mass of polymer is injected into the cavity. This completely changes the compressibility and the viscosity of the injected mixture. At low values of back pressures, the relative amount of gas inside the melt is large and thus the compressibility is high and the viscosity is low. A low viscosity means a low pressure needed to inject the shot. This means that the effect of increasing the flow rate on the mass of material injected into the cavity is not significant. On increasing the back pressure, the relative amount of gas reduces and thus the compressibility decreases but the viscosity increases. In these conditions, the increase of flow rate can surely induce a lower mass of material injected. When the back pressure is so high that the amount of gas is negligible, the compressibility reduces so that the increase of flow rate is again not effective on the mass of material injected into the cavity.

In Figure 5, the measured pressure profiles in position P1 (runner) and P2 (15 mm from the gate) are reported versus the injected volume calculated by the screw position for some of the tests conducted in this work. The pressure at a given position starts to increase when the material reaches that position. In a previous work[8] it was demonstrates that the volume to be injected in order to reach a given position increases on decreasing the back pressure. Furthermore, from Figure 5 it is possible to assert that it increases on increasing the injection flow rate. This confirms that the compressibility of the shot injected is more significant at higher flow rates. Density measurements were performed at 25 °C by weighing the samples immersed in water on the basis of Archimedes' principle. Values of samples density are reported in Table 3. The density of the unfoamed PLA 4032D is 1.24 g/ccm. Figure 6 shows the comparison in terms of length and density reduction of samples obtained at 18 and 36 cm^3/s. Density reduction, R, with respect to the unfoamed part, is evaluated as:

$$R = \frac{(\rho_0 - \rho_f)}{\rho_0} \quad (3)$$

where ρ_0 is the density of the unfoamed PLA and ρ_f is the density of the foamed part.

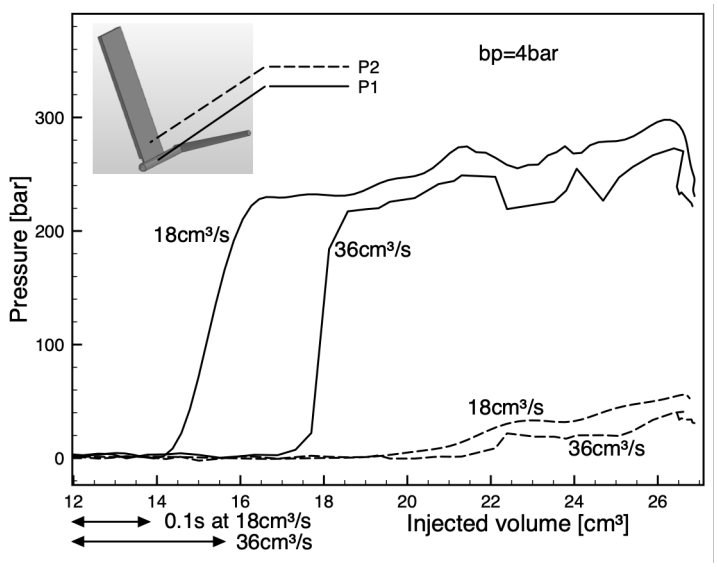

Figure 5. Pressure evolution in two positions versus the injected volume. "bp" stands for back pressure. The double arrows indicate the volume injected in 0.1s for each flow rate

Table 3. Density values of foamed samples.

Back pressure [bar]	*Density [g/ccm]*	
	18 ccm/s	*36 ccm/s*
2	0.93	0.91
3	0.91	0.90
4	1.06	0.92
5	1.09	1.09

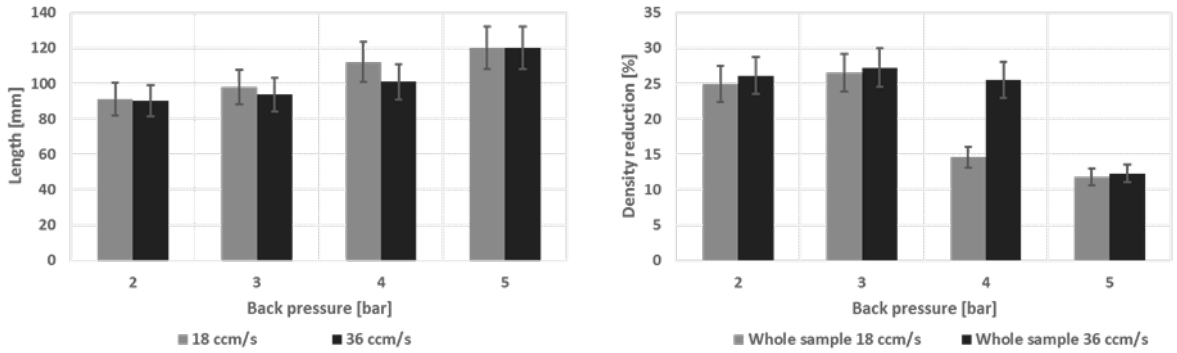

Figure 6. Sample length and density reduction of PLA 4032D at two different injection flow rates.

The higher temperature of the material injected at high injection flow rate results in a larger foaming, that allows a higher density reduction with respect to the samples injected at lower flow rate[3, 6]. The lower density reduction of the samples molded at high back pressure can be also explained by the samples morphology. As observed in a previous work[8], samples molded at lower back pressure have a more homogeneous foaming both in the transition layer and in the core, while those molded at high back pressure have a thin foamed zone in the transition layer and a core with compact zones and large cells.

Mechanical properties

Mechanical tests were carried out by means of a universal testing machine mod ATSFAAR TC1000. Flexural tests were performed by a load cell of 10kN. The specimen (Figure 2) was placed on two supports with a distance of 60 mm and loaded midway between the supports with a speed of 5 mm/min. Tensile tests were performed by placing the test specimens in the grips with a gage length of 60 mm and loaded at a speed of 10 mm/min until breaking. A normalized modulus E_n was calculated as:

$$E_n = \frac{E_f}{E_0} \cdot \frac{\rho_0}{\rho_f} \tag{4}$$

where E_f is the Young's modulus of the foamed sample, E_0 is the Young's modulus of the unfoamed sample, ρ_0 is the density of the pure PLA and ρ_f the density of the foamed PLA sample. The normalized modulus allows to keep into account the density reduction and the change of modulus.

Figure 7 shows the normalized modulus of elasticity obtained by flexural tests (a) and by tensile tests (b) measured on the analyzed specimens.

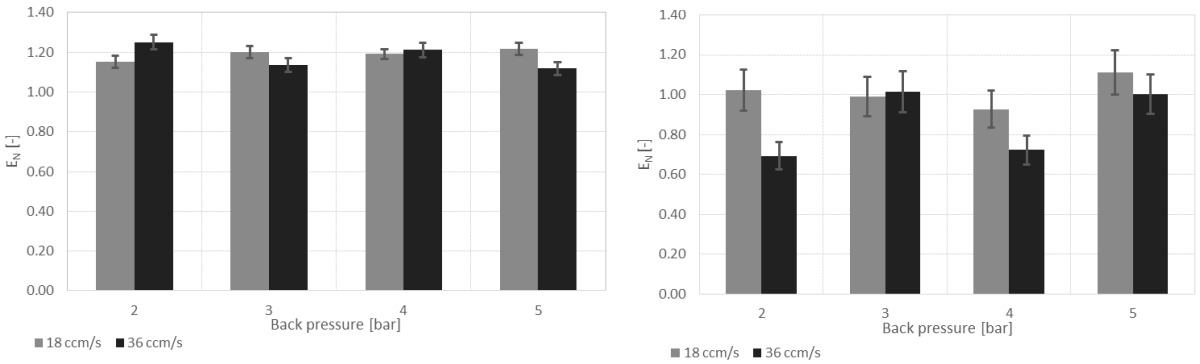

Figure 7. a) Normalized modulus of elasticity obtained by flexural tests at 5 mm/min samples foamed with different back pressures and injection flow rates. b) Normalized modulus of elasticity obtained by tensile tests at different back pressures and injection flow rates.

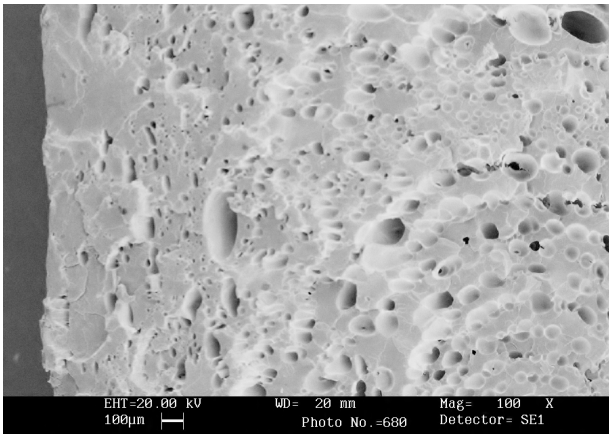

Figure 8. Cross-section of a PLA 4032D sample foamed at 18 ccm/s with bp = 3 bar. The flow/expansion direction toward the reader.

Values of flexural modulus larger than 1 are found for all analyzed specimens, indicating that the decrease in modulus is less significant than the decrease in density.

From tensile tests, values of normalized modulus smaller or close to 1 are obtained. The difference in behavior between tensile and flexural moduli are due to the inhomogeneous foaming of the samples along the thickness direction[1, 12]. The flexural modulus is essentially determined by the unfoamed skin layer, mostly solicited in this kind of test, while the core region, more foamed, has much less influence on such properties because is located close to the neutral axis (Figure 8). On the other hand, tensile tests solicit the whole section of the specimen and thus the measured properties are more influenced by the foamed core of the specimen[8, 13, 14].

In Figure 8, showing the cross-section of a foamed sample obtained at 18 ccm/s with a back pressure of 3 bar, moving from the wall towards the center of the sample it is possible to observe a layer of unfoamed skin, a first foamed zone (transition layer) and a foamed core.

In Figure 7 it is possible to observe that the flexural modulus is not so much dependent on the injection flow rate, inasmuch as the compact skin layer does not vary substantially with the injection flow rate. The tensile modulus, instead, seems to be slightly lower for samples obtained at higher injection flow rate, which also present (as shown in fig. 6) a lower density. Evidently, the reduction in tensile modulus is not entirely compensated by the reduction of density.

Conclusions

In this work, the effect of injection flow rate and back pressure on properties of poly(lactic) acid parts obtained by foam injection molding was studied. On the basis of the experimental observation carried out, it could be concluded that a larger compressibility of the shot due to the presence of gas can change the amount of material injected into the cavity. For this reason, the samples molded at high injection flow rate are shorter than those injected at low flow rate. However, the higher temperature of the material injected at high injection flow rate results in a greater foaming, that induces a higher density reduction with respect to the samples injected at lower flow rate.

Flexural modulus values larger than 1 are found for all analyzed specimens, meaning that the decrease in modulus is less relevant than the decrease in density. The flexural modulus is not so much dependent from the injection flow rate, inasmuch as the compact skin layer, which deforms more during flexural tests, does not substantially vary with the injection flow rate. Values of normalized tensile modulus smaller than or close to 1 are obtained. The difference in behavior between tensile and flexural moduli are due to the inhomogeneous foaming of the samples along the thickness direction. The tensile modulus, moreover, is lower for samples obtained at higher injection flow rate. Those samples, in fact, are more foamed because of the high temperature of the material established by the higher injection speed.

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