THIS IS THE PEER REVIEWED VERSION OF THE FOLLOWING ARTICLE:

Volpe, V., De Filitto, M., Klofacova, V., De Santis, F., Pantani, R.
"EFFECT OF MOLD OPENING ON THE PROPERTIES OF PLA SAMPLES OBTAINED BY FOAM INJECTION MOLDING"
Polymer Engineering and Science
Volume 58, Issue 4, April 2018, Pages 475-484
DOI: 10.1002/pen.24730

WHICH HAS BEEN PUBLISHED IN FINAL FORM AT
https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.24730

THIS ARTICLE MAY BE USED ONLY FOR NON-COMMERCIAL PURPOSES

Effect of mold opening on the properties of PLA samples obtained by foam injection molding

Valentina Volpe[a]*, Martina De Filitto[a], Vera Klofacova[b],
Felice De Santis[a], Roberto Pantani[a]

[a]*Department of Industrial Engineering. University of Salerno*
Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy

[b]*Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin,*
Trida Tomase Bati 5678, 760 01 Zlin, Czech Republic

CORRESPONDING AUTHOR FOOTNOTE:
* To whom correspondence should be addressed. E-mail: vavolpe@unisa.it

Effect mold opening on the properties of poly(lactic acid) samples obtained by foam injection molding

Valentina Volpe[a*], Martina De Filitto[a], Vera Klofacova[b],
Felice De Santis[a], Roberto Pantani[a]

[a]*University of Salerno - Italy*
[b]*Tomas Bata University in Zlin, Czech Republic*

ABSTRACT

Foam injection molding is a process by which complex, thick parts with a cellular core and a compact solid skin can be manufactured. The addition of a physical blowing agent under high pressure allows the decrease of the viscosity and the glass transition temperature of the gas/polymer melt. These features of the foam injection molding are very beneficial for biodegradable polymers, in which the processability window is very narrow. In this study, morphology, rheological and mechanical properties of parts with a complex shape, obtained by foam injection molding, were analyzed. In particular, two commercial grades of poly(lactic acid) having different rheological behavior were adopted to obtain foamed parts by injection molding process with nitrogen as a physical blowing agent. For both resins, the effect of the mold opening on morphology and mechanical properties was assessed.

Keywords

Foam injection molding, poly(lactic) acid, mold opening

INTRODUCTION

Foam injection molding is a very advantageous process to make parts having better dimensional stability with less material and a faster production cycle with respect to the conventional injection molding process [1-5]. A physical blowing agent mixed with the polymer melt allows the reduction of the processing temperatures due to its plasticization effect that reduces the melt viscosity [6, 7]. This is a great advantage for the processing of biodegradable polymers, well-known for their limited thermal sensibility and very narrow processing window [8, 9]. One of the most promising biodegradable polymers is the poly(lactic) acid, PLA, satisfying the increasing requirements in a wide variety of applications [10-14]. PLA is an aliphatic polyester obtained by the polymerization of the lactic acid (LA). Lactic acid presents two optically active configurations known as D-LA and L-LA [15]. Commercial PLA resins usually are random L-isomer rich copolymers, containing a low amount of D-isomer co-units. The D-LA percentage can influence the maximum crystallinity of the material: on increasing the D-LA percentage, the crystallization kinetics becomes slower and the maximum attainable crystalline content reduces [16, 17]. Minor amounts of the D-LA form are typically used to tune mechanical properties and melting temperature that also increases with the decreasing of D-LA percentage [18-21]. Mihai et al. in 2009 [22] investigated the relation between crystallization and the foaming properties of three semi-crystalline PLA with different D-LA content processed by extrusion. In particular, the effect of gas concentrations, melt flow rates, and die diameters on crystallinity development in relation to foam properties was observed. They observed that the crystallinity of the PLAs with low D-LA content was enhanced by dissolved gas, with resulting more uniform morphology. A crucial step in order to obtain the desired finished product is the selection of the raw material with its properties. Dorgan et al. [23] assessed that a wide spectrum of flow properties are available through simple modification of PLA thus allowing the use of this important degradable thermoplastic in a variety of processing. Foam injection molding is a process capable of producing complex, thick parts sink free, with a low level of

internal stress [24-26]. In 2004 Chien et al. [27] studied the effect of the processing parameters on foaming degree and mechanical properties of parts with different geometric shapes obtained by conventional injection molding and foam injection molding. They showed that the part thickness is a dominant factor determining the degree of foaming, that can reach weight reduction of 50% in parts with 15 mm thickness. In this work, besides studying the behavior of two different materials, the mold-opening technology was coupled with the foam injection molding process. During the filling stage, the polymer/gas solution is injected into the mold cavity. The low-temperature mold surfaces allow the fast solidification of the material in contact with them, with the formation of a compact skin thin layer. After a delay time step, the movable mold is commanded to retract for a set distance in order to partially open the mold cavity. The foamed part is allowed to cool further in between the two mold surfaces before demolding. Several researchers studied the influence of process control on the structure and the correlating mechanical properties [28-31]. Chu et al. [32] in 2016 presented a numerical approach to simulate the cooling of the polymer/gas mixture inside the mold cavity, and thereby, estimating the foaming temperature of this manufacturing process. Ameli et al. [11] characterized microcellular structure and crystallization of PLA composite foams obtained by conventional foam injection molding and foam injection molding with mold opening.

In this study, the effect of the mold opening on morphology and mechanical properties of two PLA grades obtained by foam injection molding was investigated.

MATERIALS AND METHODS

Materials

Two different commercial grades of poly(lactic) acid (PLA) produced by NatureWorks were adopted in this work: PLA 4032D and PLA 3251D. The main properties of these two PLA grades as provided by the supplier are reported in Table 1. Before any test or processing, the materials

were dried for 24 h under vacuum at a temperature of 60 °C. The physical blowing agent adopted for the foaming process was nitrogen.

Injection molding

A 70-ton Negri-Bossi injection molding machine with a screw diameter of 25 mm and L/D=22, modified to carry out the microcellular injection molding process, was utilized in this work. In particular, the cylinder of the injection molding machine is connected to a system for controlling the quantity of gas injected during the batching step. The screw was modified introducing a mixing section in order to enhance the dissolution of the gas inside the melt. A nozzle with a needle valve was adopted to avoid premature foaming. A hot runner system was used, to avoid solidification inside the channels. Furthermore, the mold temperature was controlled by a combined system of cooling channels and electrical heaters. The injection molding process was coupled with the mold opening technique. In particular, for some of the tests, after 2 s from the end of injection phase (mold opening delay time) the mold was opened of a distance equal to 1 mm or 3 mm (length of the mold opening) at a speed of 2 mm/s, in order to allow the foaming of the material in a larger volume with respect to the cavity volume (Fig. 1). In this work, samples molded without mold opening, i.e. foamed in standard condition, are indicated with the abbreviation “STD”, while the samples obtained with mold opening at the two different distances are named “MO 1 mm” and “MO 3 mm”. The microcellular injection molding process does not need a packing step after the filling as the system expands with time rather than shrinking.

The sample geometry is shown in Fig. 2. The total volume of the cavity, when the mold is closed, is 5.1 cm^3.

The particular geometry of the sample, which reminds the Mexican wide-brimmed hat, “sombrero”, allows observing different features of the foam injection molding. The lower part of the sample, which in this work will be referred to as “brim”, is characterized by a radial shear flow, due to the position of the injection point at the center of the bottom part of the brim. The top of the sample,

which will be named “crown”, is characterized by a larger thickness (in the cross-flow direction) than the one adopted in conventional injection molding. This last feature allows appreciating the potential of the foam injection molding process. In fact, when produced by conventional injection molding, the “sombrero” presents large voids in the crown due to shrinkage. By using the foam injection molding process instead, the polymer/gas solution allows for a complete the part.

The experimental parameters were chosen in order to obtain the optimal molding conditions of the foamed parts. In particular, the set temperature profile of the PLA 4032D was 20 °C higher than that of the PLA 3251D, due to the different rheological properties of the two PLA grades: 4032D could not be injected at lower temperatures due to its excessive viscosity, whereas 3251D could not be foamed at injection temperatures higher than the one chosen. The injected volume of both resins was the same that allowed a complete foamed part without mold opening. The experimental conditions adopted for both PLA grades are reported in Table 2. It can be noticed that the nominal injected volume (shot) for the two materials is significantly different, being much smaller for 3251D, which presents a lower viscosity. This difference can be partly explained with the compressibility of the polymer-gas mixture, which induces a difference between the nominal and the real injected volume [33]: the larger viscosity of 4032D induces larger pressures inside the injection chamber and thus a larger compression of the shot.

Moldflow simulations

The 3D model of the part, shown in Fig. 2, was imported into Autodesk Moldflow for the simulation of thermoplastics injection molding process. This analysis was intended to understand in which way the cavity was filled and to evaluate the cooling times. Obviously these fundamental issues are significant in order to comprehend the subsequent differences in morphology between brim and crown. The simulations were carried out on both materials. In particular, while the PLA 3251D was already present in Moldflow database, the PLA 4032D was added by changing the material properties of a Natureworks PLA grade. The presence of gas inside the melt was neglected

in the Moldflow simulation. The processing parameters were set as those adopted during the experimental campaign.

Rheological tests

A rheological characterization of the two PLA grades was carried out by a Haake Mars II (Thermo scientific) rotational rheometer in an oscillatory dynamic mode with parallel plates configuration under a nitrogen atmosphere. The experiments were performed both on the neat material in form of pellet and on the processed samples in the temperature range 140 °C-200 °C for PLA 3251D and 160 °C-220 °C in the case of PLA 4032D. Master curves of the neat and processed materials were then built at the injection temperatures (200 °C for PLA 3251D and 220 °C for PLA 4032D).

Gel Permeation Chromatography (GPC)

The measurements of molecular weight distribution were carried out by a Waters Breeze 2 HPLC system. The samples were dissolved in tetrahydrofuran (THF) at 58 °C and then the solution was filtered by means of a Chromafil PTFE 0.45 mm filter.

Density measurements

Density measurements of samples were made on the basis of Archimedes principle applied to molded samples immersed in water at 25 °C. Subsequently, the density reduction was calculated as:

$$\text{density reduction } [\%] = \left(\frac{\rho_0 - \rho_f}{\rho_0} \right) \cdot 100 \tag{1}$$

Where ρ_0 is the unfoamed sample density and ρ_f is the foamed sample density.

Volumetric Shrinkage

In order to check the ability of the materials to completely fill the cavity, for both the parts of the sample the volumetric shrinkage was calculated as:

$$\text{Shrinkage } [\%] = \left(\frac{V_n - V_m}{V_n} \right) \cdot 100 \tag{2}$$

where V_n is the nominal volume (namely the volume of the cavity for the specific part, also considering the length of the mold opening) and V_m is the measured volume.

Tomography

All samples obtained by injection molding were subjected to tomographic analysis thanks to the use of a SkyScan1174 compact micro-CT (voltage 28 kW, current 800 μA), in order to observe the morphology of the samples obtained by injection molding. This tomography procedure utilizes computer-processed X-rays to produce tomographic images or slices of the specific part by means of a SkyScan1174 compact micro-CT. Scanning was carried out without using any filter; the pixel size was 11.66 μm.

X-Ray Diffractometry

Samples molded in standard conditions were subjected to X-Ray Diffractometry by an Advance D8 Brucker diffractometer (equipped with a continuous scan attachment and a proportional counter) with Ni-filtered Cu-Kα radiation. In particular, the crystallinity content was assessed in two different positions of the molded samples: in the middle section of the crown and at half-thickness of the brim, in both cases far from the part surface (Fig. 2).

Morphological analysis

The micrographs acquired during the tomography were analyzed by an image analysis software, ImageJ. On each analyzed section the voids percentage, i.e. the area occupied by cells with radius R included in the range $R_{i\text{-}1}$-R_i, was calculated as:

$$V_i = \frac{A_i}{A_{tot}} \cdot 100 \tag{3}$$

Where A_i represents the area of each cell whose radius is within the chosen range and A_{tot} is the sum of the areas of the cells of any size.

Compression tests

The crowns of the samples were subjected to compression tests in the axial (flow) direction by using a universal testing machine mod ATSFAAR TC1000 with a load cell of 10 kN and a speed of 1 mm/min, in order to evaluate the mechanical behavior of this portion of the sample.

Flexural tests

Flexural tests were carried out on the brim of the samples by using a universal testing machine mod ATSFAAR TC1000, with a load cell of 2 kN. The specimen was placed on a testing apparatus composed of a three-point support regularly distributed along its periphery, shown in Fig. 3. The load was applied at the center of the sample using a crosshead speed of 1 mm/min [34].

RESULTS

Moldflow simulations

Before studying the properties and the morphology of the molded samples, the filling and cooling stages of the injection molding process were explored by Moldflow simulations. The process simulations carried out by the software Moldflow on both materials show that the crown is filled before the brim (Fig. 4a). The filling mechanism was confirmed also for foamed samples, by molding foamed samples with increasing injected volumes (short shots), as shown in Fig. 4b. On the basis of this observation, it can be assumed that the main path of the foaming process is from the crown toward the brim. The cooling of the brim is faster with respect to the crown because of the lower thickness (Fig. 4a).

In Fig. 5 the temperature distribution inside the sample at the mold-opening is reported, as evaluated by Moldflow simulations for 4032D. It is worth recalling that the Moldflow analysis was carried out neglecting the presence of the gas and thus the whole foaming phenomenon. Nevertheless, the indications provided by the simulations show that the solid skin layer (assuming that the material is solid when the temperature is below 70 °C, namely about 5-10 °C above T_g) is

thinner than 0.4 mm at the mold opening. This means that a significant part of the brim can still expand at mold opening.

Rheological measurements

The results of rheological measurements, as a master curve at the injection temperature (200 °C for PLA 3251D and 220 °C for PLA 4032D), are shown in Fig. 6. The values of the thermal shift factor αT of the neat and processed materials are reported in Table 3. PLA 3251D, namely the grade with the higher melt flow rate, has a viscosity significantly lower than that of the PLA 4032D and a longer Newtonian plateau, in spite of the different temperature at which the two materials are processed. The elastic and loss moduli of both materials are reported in Fig. 7. The inverse of the frequency at which the two moduli assume the same value (the so-called crossover point) provides an indication of the characteristic relaxation time of the material, which is, therefore, longer for 4032D with respect to 3251D. Longer relaxation times indicate higher melt elasticity and normally a better foamability, and thus the rheological measurements suggest that 4032D should provide better foams than 3251D [35].

The effect of processing on the rheological properties should never be neglected for biodegradable materials like PLA. Indeed, due to thermos-mechanical degradation during processing, the materials from the injection molded parts have a viscosity significantly lower than the neat pellet. This is confirmed by the rheological measurements carried out on the material taken from the injection molded parts, namely after processing, shows in Figs. 6 and 7. For both materials, the crossover point moves to higher frequencies and thus the relaxation time decreases, as expected.

In order to complete the information obtained by the rheological experiments, the molecular weight distribution is evaluated through the gel permeation chromatography (GPC). Fig. 8 shows the molecular weight distribution of the neat and processed PLA for both grades. From this plot, it is possible to observe that the processing of the materials causes the distribution to moves towards lower values of molecular weight. Furthermore, neat and processed PLA 3251D are characterized

by lower values of molecular weight with respect to the values of the PLA 4032D. Values of M_w and M_n of the neat and processed materials for both resins are shown in Table 4.

Density measurements

Density measurements were carried out on all the molded samples, obtained without mold opening (STD) and with mold opening at two different lengths (MO 1 mm and MO 3 mm). Fig. 9 shows the density reduction of the foamed samples with respect to the density of the unformed material. For both PLA grades, the density reduction increases with the length of mold opening. This was expected since with the mold opening the same amount of material used during the foaming in standard conditions is injected in an increased volume. The values reached were significantly high, from 30% to more than 50%, and no particular differences were found between the two materials.

The samples were cut into two parts in order to study separately the properties and the morphology of the crown and the brim. The differences in terms of density reduction for both parts were within the experimental uncertainty.

Fig. 10 shows the volume reduction for both grades of PLA in the three different molding conditions. In the case of the crown, it is possible to observe that the volume reduction in the samples with mold opening was almost the same of that obtained in the samples in standard conditions. The values are always about 5%, which is consistent with a volumetric thermal shrinkage. In the case of the brim, the volume reduction increases dramatically for the mold opening of 3 mm: in this case, for both grades of PLA, the polymer/gas solution fails to fill the whole brim volume during foaming. The fact that the mold opening influences essentially just the brim is consistent with the foaming mechanism indicated above: the material completely fills the crown, and then the brim; if the brim increases the volume due to mold opening, foaming can be not enough to completely fill the part.

In general, PLA 3251D presents a volumetric shrinkage smaller than PLA 4032D (except at the largest MO span) which is a clue toward a better foaming capability of this grade.

Tomography

In order to observe the morphology of the molded samples, a tomographic analysis was conducted. Fig. 11 shows the tomographic images of the PLA 3251D and PLA 4032D samples. The images confirm the trend obtained by the density measurements, i.e. the increases of the voids percentage with the mold opening. Moreover, PLA 4032D shows greater cells with respect to the PLA 3251D. The difference in morphology between the two PLA grades is more visible in the cross-section taken along the axis of the crown (on the left of each image) that in the brim section (right). It is interesting to notice that the cells in the crown of the samples of 3251D are nearly circular, whereas for 4032D the cells are elongated toward the brim. This is surprising since on the basis of the rheological properties of the materials the opposite was expected. The presence of elongated cells is demonstrated by the fact that, if the crown is observed on a plane normal to the flow direction (Fig. 12 bottom), the cells appear to be circular.

A detailed analysis of the distribution of the dimension of the cells in the midplane of the crown is reported in Fig. 13. The largest part of the samples is characterized by cells having a dimension below 1 mm. It is interesting to notice that for 3251D the mold opening tends to reduce the number of the cells having dimensions larger than 1.2 mm, whereas the opposite is found for 4032D.

As for the crown, the tomographic images corresponding to the midplane of the brim were analyzed by the image analysis software. Fig. 14 shows the voids percentage versus cell equivalent diameter for both grades of PLA obtained with mold opening and in standard conditions. It was observed for both the PLA grades that increasing the thickness of the mold opening the voids percentage composed of large cells increases.

The crown of the samples was subjected to compression tests. From the linear elastic region, it is possible to evaluate the Young modulus as the slope of the stress-strain curve. Fig. 15 shows the normalized Young modulus of foamed PLA samples obtained without mold opening and with mold opening at 1 mm and 3 mm. The normalized Young modulus is calculated as:

$$E_N = \frac{E}{E_0} \cdot \frac{\rho_0}{\rho} \tag{4}$$

where E is the Young modulus, ρ is the density of the foamed sample, E_0 and ρ_0 are modulus and density of an unfoamed sample. It was observed that for 4032D the normalized modulus is about the same for all the samples, namely the reduction of modulus is nearly completely compensated by the reduction of density. Vice-versa, for 3251D the measured modulus is about the same for all the samples and thus the normalized modulus increases significantly for the samples obtained with mold opening.

The three-point support was used to analyze the flexural behavior of the brim of the molded samples. The slope of each stress-strain curve, S_0, was used to evaluate the parameter S_P, defined as corrected slope in Eq. 5 [34]:

$$S_P = S_0 \Big/ \left[0.59 \left(1 - \exp\left(-4.1 \frac{\Delta R}{2R} \right) \right) + 1 \right] \tag{5}$$

where R is the radius of the circumference where the supports are located and ΔR is the radial extension of the sample outside the supports. The corrected slope S_p was normalized as follows:

$$S_{PN} = \frac{S_P}{S_{P0}} \cdot \frac{\rho_0}{\rho} \tag{6}$$

where S_{P0} is the corrected slope of the unfoamed sample and S_p is the corrected slope of the foamed sample. The Fig. 16 shows the normalized slope (S_{PN}) of foamed PLA samples without mold opening (STD) and with mold opening at 1 mm and 3 mm. The effect of mold opening on the brim morphology of the foamed PLA samples is confirmed by the mechanical properties. In fact, the normalized slope increases with the brim thickness for both the PLA grades. Furthermore, the higher crystallinity of the PLA 3251D, and then the more regular morphology, involves in a better flexural strength with respect to the PLA 4032D.

Crystallinity

The crystallinity degree of the samples was evaluated by means of wide X-ray diffraction spectra and reported in Table 5. PLA 3251D presents a higher crystallinity than PLA 4032D, as expected because of the lower molecular weight. Somewhat surprising is the fact that in both materials the brim is more crystalline than the crown, in spite of the much faster cooling rate experienced by that portion of the sample. The crystallinity degree in the brim could be influenced by the effect of flow-induced crystallization: indeed, the molecular stretch in the brim is much higher than in the crown due to the thinner section and the lower temperature. It should be mentioned that a crystallinity of 10% is quite significant for PLA since the maximum crystallinity degree for this material is normally about 40%. Furthermore, PLA presents a slow crystallization kinetics [17, 36] if compared to other thermoplastic materials and results normally amorphous after injection molding due to fast cooling rates imposed by this process.

The presence of a significant degree of crystallization can explain the fact that PLA 3251D presents nearly circular cells: when crystallization takes place, the material hardens [37] thus limiting the elongation of the cells. For 4032D this effect is surely less evident and thus, in spite of the larger viscosity, the cells are elongated toward the brim.

CONCLUSIONS

In this study, morphological, rheological and mechanical properties of parts with a complex shape obtained by foam injection molding with two different PLA grades were compared. The mold-opening technology was coupled with the foam injection molding process studying the behavior of these two different resins. Moldflow simulations of the process show that the filling takes place from the crown, which cools more slowly than the brim because of the larger thickness. PLA 3251D, namely the grade with the higher melt flow rate, has a viscosity significantly lower than that of the PLA 4032D and a longer Newtonian plateau. Furthermore, the characteristic relaxation time of the 4032D is longer than that of the 3251D. For both PLA grades, the processed materials have

viscosity significantly lower than the neat material, because of thermal and hydrolytic degradation during processing.

The density reduction increases with the length of mold opening, as expected, since with the mold opening the same amount of material utilized during the foaming in standard conditions is injected in a bigger volume. If the brim volume increases excessively because of mold opening, foaming cannot completely compensate the filling of the part and the sample is smaller than the cavity.

Morphological analysis showed that the largest part of the crown is characterized by cells having a dimension below 1 mm. In the case of the brim, by increasing the thickness of the mold opening the voids percentage composed of large cells increases. Furthermore, the cells in the crown of the samples of 3251D are about circular, whereas for 4032D the cells are elongated toward the brim. This behavior, unexpected on the basis of the rheological properties of the materials, was justified by the presence of a considerable flow-induced crystallization for 3251D: crystallinity can surely harden the material and limit the cell expansion.

Mechanical tests on the crown have shown that for 4032D the normalized modulus is about the same for all the samples, namely the reduction of modulus is nearly completely compensated by the reduction of density. Vice-versa, for 3251D the normalized modulus increases significantly for the samples obtained with mold opening. Furthermore, the higher crystallinity of the PLA 3251D, and the more regular morphology, implicates a better flexural strength with respect to the PLA 4032D.

REFERENCES

1. Pantani, R., V. Volpe, and G. Titomanlio, *Foam injection molding of poly (lactic acid) with environmentally friendly physical blowing agents.* Journal of Materials Processing Technology, 2014. **214**(12): p. 3098-3107.
2. Volpe, V. and R. Pantani, *Foam injection molding of poly (lactic) acid: Effect of back pressure on morphology and mechanical properties.* Journal of Applied Polymer Science, 2015. **132**(48).
3. Hikita, K., *Development of weight reduction technology for door trim using foamed PP.* JSAE review, 2002. **23**(2): p. 239-244.
4. Lee, J.W., et al., *Strategies to achieve a uniform cell structure with a high void fraction in advanced structural foam molding.* Industrial & Engineering Chemistry Research, 2008. **47**(23): p. 9457-9464.

5. Kramschuster, A., et al., *Quantitative study of shrinkage and warpage behavior for microcellular and conventional injection molding.* Polymer Engineering & Science, 2005. **45**(10): p. 1408-1418.
6. Stevenson, J.F., *Innovation in polymer processing: molding*. 1996: Hanser.
7. Pantani, R., et al. *Foam injection molding of poly (lactic acid) with physical blowing agents*. in *American Institute of Physics Conference Series*. 2014.
8. Speranza, V., A. De Meo, and R. Pantani, *Thermal and hydrolytic degradation kinetics of PLA in the molten state.* Polymer Degradation and Stability, 2014. **100**: p. 37-41.
9. Lim, L.-T., R. Auras, and M. Rubino, *Processing technologies for poly (lactic acid).* Progress in polymer science, 2008. **33**(8): p. 820-852.
10. De Santis, F., V. Volpe, and R. Pantani, *Effect of molding conditions on crystallization kinetics and mechanical properties of poly (lactic acid).* Polymer Engineering & Science, 2016.
11. Ameli, A., et al., *Development of high void fraction polylactide composite foams using injection molding: Crystallization and foaming behaviors.* Chemical Engineering Journal, 2015. **262**: p. 78-87.
12. Auras, R., B. Harte, and S. Selke, *An overview of polylactides as packaging materials.* Macromolecular bioscience, 2004. **4**(9): p. 835-864.
13. Ouchi, T., S. Ichimura, and Y. Ohya, *Synthesis of branched poly (lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film.* Polymer, 2006. **47**(1): p. 429-434.
14. Suyatma, N.E., et al., *Mechanical and barrier properties of biodegradable films made from chitosan and poly (lactic acid) blends.* Journal of Polymers and the Environment, 2004. **12**(1): p. 1-6.
15. Henton, D.E., et al., *Polylactic acid technology.* Natural fibers, biopolymers, and biocomposites, 2005. **16**: p. 527-577.
16. Gorrasi, G. and R. Pantani, *Effect of PLA grades and morphologies on hydrolytic degradation at composting temperature: assessment of structural modification and kinetic parameters.* Polymer Degradation and Stability, 2013. **98**(5): p. 1006-1014.
17. De Santis, F., R. Pantani, and G. Titomanlio, *Nucleation and crystallization kinetics of poly (lactic acid).* Thermochimica acta, 2011. **522**(1): p. 128-134.
18. Bigg, D., *Polylactide copolymers: effect of copolymer ratio and end capping on their properties.* Advances in Polymer Technology, 2005. **24**(2): p. 69-82.
19. Kale, G., et al., *Compostability of bioplastic packaging materials: an overview.* Macromolecular bioscience, 2007. **7**(3): p. 255-277.
20. Auras, R.A., et al., *Poly (lactic acid): synthesis, structures, properties, processing, and applications*. Vol. 10. 2011: John Wiley & Sons.
21. Dorgan, J.R., *Rheology of poly (lactic acid).* Poly (Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications, 2010: p. 125-139.
22. Mihai, M., M.A. Huneault, and B.D. Favis, *Crystallinity development in cellular poly (lactic acid) in the presence of supercritical carbon dioxide.* Journal of Applied Polymer Science, 2009. **113**(5): p. 2920-2932.
23. Dorgan, J.R., H. Lehermeier, and M. Mang, *Thermal and rheological properties of commercial-grade poly (lactic acid) s.* Journal of Polymers and the Environment, 2000. **8**(1): p. 1-9.
24. Klempner, D., V. Sendijarevi′c, and R.M. Aseeva, *Handbook of Polymeric Foams and Foam Technology*. 2004: Hanser Publishers.
25. Lee, S.T., C.B. Park, and N.S. Ramesh, *Polymeric Foams: Science and Technology*. 2006: CRC Press.
26. Eaves, D., *Handbook of Polymer Foams*. 2004: Rapra Technology.

27. Chien, R.D., et al., *Study on the molding characteristics and mechanical properties of injection-molded foaming polypropylene parts.* Journal of reinforced plastics and composites, 2004. **23**(4): p. 429-444.
28. Bledzki, A.K., et al., *Microcellular injection molding of PP and PC/ABS with precision mold opening and gas counterpressure.* Cellular Polymers, 2008. **27**(2): p. 91.
29. Jahani, D., et al., *Open-cell cavity-integrated injection-molded acoustic polypropylene foams.* Materials & Design, 2014. **53**: p. 20-28.
30. Heim, H.-P. and M. Tromm, *General aspects of foam injection molding using local precision mold opening technology.* Polymer, 2015. **56**: p. 111-118.
31. De Santis, F. and R. Pantani, *Melt compounding of poly (Lactic Acid) and talc: assessment of material behavior during processing and resulting crystallization.* Journal of Polymer Research, 2015. **22**(12): p. 242.
32. Chu, R.K., et al., *Estimation of the foaming temperature of mold-opening foam injection molding process.* Journal of Cellular Plastics, 2016. **52**(6): p. 619-641.
33. Volpe, V. and R. Pantani, *Effect of processing condition on properties of polylactic acid parts obtained by foam injection molding.* Journal of Cellular Plastics, 2016: p. 0021955X16670589.
34. Esteves, F.R., et al., *The Influence of Processing on the Aesthetic, Morphological and Mechanical Properties of Structural Foam Mouldings of High-Impact Polystyrene.* Strojniški vestnik-Journal of Mechanical Engineering, 2013. **59**(11): p. 637-645.
35. Oliviero, M., et al., *Foaming behavior of bio-based blends based on thermoplastic gelatin and poly(butylene succinate).* Journal of Applied Polymer Science, 2015. **132**(48).
36. Refaa, Z., et al., *Thermophysical analysis and modeling of the crystallization and melting behavior of PLA with talc.* Journal of Thermal Analysis and Calorimetry, 2016: p. 1-12.
37. Pantani, R., V. Speranza, and G. Titomanlio, *Simultaneous morphological and rheological measurements on polypropylene: Effect of crystallinity on viscoelastic parameters.* Journal of Rheology, 2015. **59**(2): p. 377-390.