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Processing and Characterization of thin wall and biodegradable injected pots

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Abstract

Currently, the industry of molds seeks new markets with diversified products and added value. The concept associated with the production by injection of biodegradable pots is therefore of particular significance. Furthermore, environmental factors are increasingly decisive in choosing a product by the consumer, either because of imposed legislation or by the growth of a global awareness of the harmful effects than conventional polymers induce in our quality of life present and future. The general goal of this work was the design, the development and characterization of a thin walled pot for germination of plants made of biodegradable material. In this paper the processing and characterization of the bioplastic selected, the Bioplast GS 2189, is presented. Experimental results confirmed that the biodegradable material undergoes changes during its processing, which is attested by the QIS difference as well as in the reduction of the glass transition temperature, which in the post-processed (injected pot) is lower than the pre-processed material (Bioplast GS 2189). From these results it can be concluded that the injection processing of the Bioplast GS 2189 material affects its properties inducing its degradation process. This behavior can be due to the shear forces and thermal variations to which the material is submitted during the injection process. It was demonstrated that the development of future products in very thin-walled and biodegradable materials obtained by thermoplastic injection process is a competitive and effective solution for molds industries.

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Keywords: Thin walled injected parts; Biodegradable polymers; Bioplastic; Injection molding; Pots plants.

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1. Introduction

The rising price of oil in recent years has led to the intensification of research projects, in order to obtaining alternative products to conventional plastics. Currently, biodegradable polymers begun to be produced for industrial and commercial use, leaving be just used for research purposes. Shen and coauthors [1] estimated the global production of bioplastics in 2020, they pointed out that from the most optimistic point of view an increase in worldwide production capacity of bioplastics from 0.36 million tons (in 2007) to 4.40 million tons (in 2020) is expectable. But even for a worst scenario, the world bioplastics production in 2020 will be 1.47 million tons. The most important products in terms of production volumes in 2007 were starch plastics (0.15 million tons) and polylactic acid (PLA) (0.15 million tons). In 2020 the most common bioplastics will be starch plastic (1.3 million tons), PLA (0.8 million tons), bio-based polyethylene (PE) (0.6 million tons) and polyhydroxyalkanoate (PHA) (0. 4 million tons).

The selling price of bioplastics is still the main obstacle to the penetration of these materials on the market, in average the price of granulate biodegradable plastic is 50% higher than conventional plastic such as polypropylene (PP), PE or Polyethylene terephthalate (PET). However, between 1990 and 2002 there was a great increase in bioplastics consumption as reported by [2, 3] due, in part, to higher oil prices, lower production costs and environmental policies.

Pots used in plant germination are currently produced in polyolefins such as PP. This is a low cost container in which the amount of material used is reduced to the maximum in order to reduce the production cost and an attempt to minimize the environmental impact. Nevertheless, to minimize the risk of plant roots damage containers are placed in the soil. Nowadays hundreds of thousands of these containers are used contributing to global pollution. Common thermoplastics, e.g. PP, are resistant to chemical and biological attack in order to delay and prevent attack by fungi, bacteria and other living organisms that is great for the plants germination and growth. These properties together with the good mechanical properties that characterize this kind of polymers represent advantages for most applications, but in the case of plant pots these properties represent a significant environmental problem. There is still a large-scale production of this type of formulations because the accessibility to proper selection of biodegradable polymers is not common, since they have to be selected and adapted to each case and biological environment. Biodegradable polymers are, in general, comprised of a synthetic polymer, such as polyester, and a natural polymer such as starch.

The general goal of this research aims to solve the ecologic problem related with the use of common thermoplastics to produce potted plants. The strategy involves an integrated solution for the injection of thin walled pots, manufactured using biodegradable materials, for plants germination. This integrated solution was divided basically into four phases as represented in the flowchart of Figure 1 and includes the design and manufacture processes of the mold as well as to find the optimum values for the injection parameters in order to become the process effective and competitive. The Phase I was dedicated to the pot design and rheological simulations and the Phase II devoted to the project and mold manufacturing. The Phase III corresponding to the selection and characterization of the pre-processed biodegradable material (bioplastic, synthetic/starch polymer) for the pot conception. Among the biodegradable thermoplastics commercially available the Bioplast GS 2189 of European origin from BIOTEC was chosen to produce the injected thin walled pots because it is particularly suited to inject food products and nonfood fully biodegradables. The Bioplast GS 2189 is classified as a mixture of PLA with starch and presents a stiffness comparable to those exhibited by the polystyrene (PS). Finally, the Phase IV, presented in this work, regards to the processing and characterization of the processed pots. After obtaining the mold, the pots were injected and their chemical and thermal characterization performed to check the possible influence of parameters processing on the material properties changes.

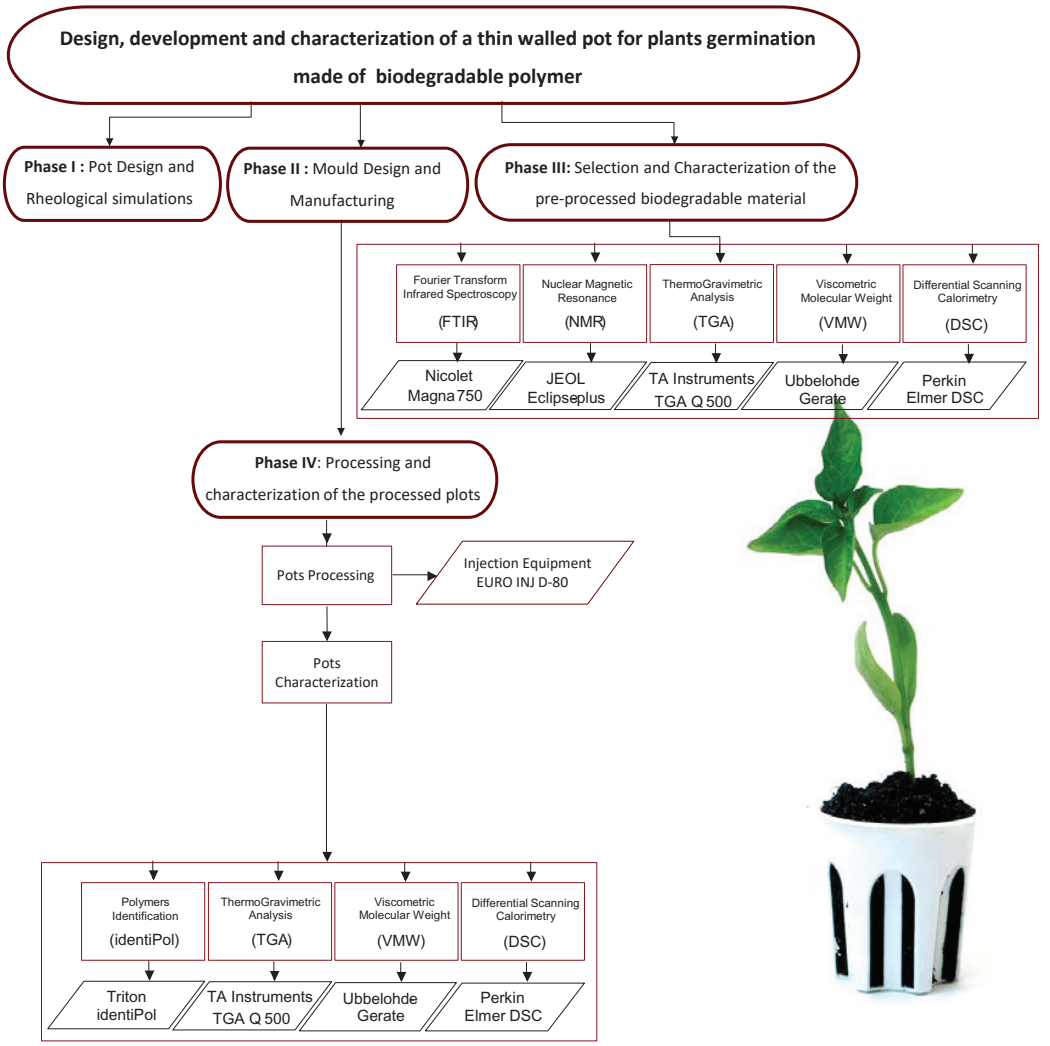


Fig.1. Flowchart for the design, development and characterization of a thin walled biodegradable plastic pot.

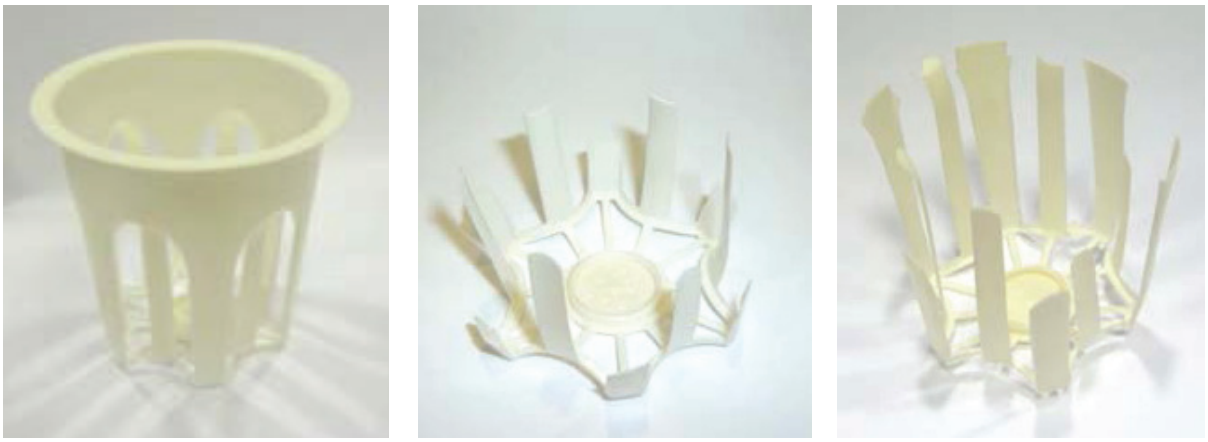
2. Processing by injection of thin walls and biodegradable pots

The required performance of an injection mold is directly related with the design and manufacture processes of the mold itself. In the mold development design features such as the injection molding machine characteristics, namely the distance between the columns, the closing and opening force of the mold as well as the injection capacity were taken into account. Additionally, the mold structure must be strong enough to withstand the efforts arising during injection process. For the particular case of components characterized by thin walls and manufactured using biodegradable materials, such the one here presented, special careful is required in the mold design and manufacture processes. Therefore, after manufacturing, the mold was tested. The mold test consisted in the assembly of the mold in EURO Inj D-80 injection machine, and in the mold cavity filling with the biodegradable plastic Bioplast GS 2189, checking the quality of the resulting part. In addition, at this stage, it was still verified if all mold components worked properly. The injection parameters considered are summarized in Table 1.

Table 1: Injection processing parameters.

Injection parameters	Value
Injection time [s]	0,3
Maintenance time [s]	3
Injection cycle time [s]	10
Injection pressure [MPa]	150
Maintenance pressure [MPa]	85
Injection velocity [%]	99
Maintenance velocity [%]	40
Processing temperature [°C]	210
Mold temperature [°C]	25
Injection time [s]	0,3

After a few injections the first fully filled pots and flawless, with the expected thickness of 0.5 mm, were obtained, as can be seen in Figure 2a). Through visual perception of the pot it was found that it showed good mechanical resistance, so it was decided therefore try a thickness of 0.2 mm for the pot walls. Unfortunately, the injection was unsuccessful because it was not complete for the thickness of 0.2 mm as can be seen in Figure 2b). Based on the previous failure, the thickness was changed to 0.35 mm. But once again, with the new thickness the results were likewise ineffective, as shown in Figure 2c), since a no complete injection is observed. Thus, it was assumed that the thickness of 0.5 mm is the proper value for the biodegradable pots injection.



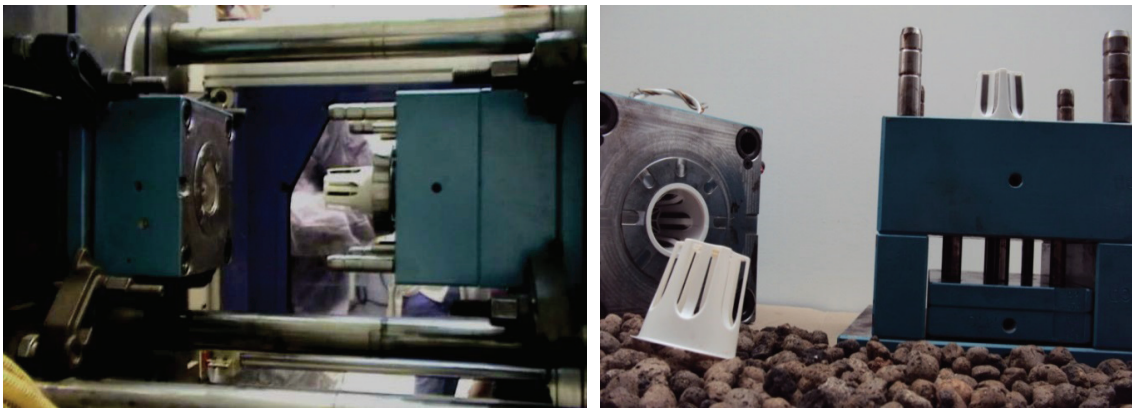
a b c

Fig.2. Results of the mold testing for a: (a) 0.5mm; (b) 0.2mm; and (c) 0.35mm thickness of the wall pot.

Further to the mold testing procedure small changes in the polishing faces and some other minor adjustments were made before began the production of thin walls biodegradable vessels. Thereafter, and with the aid of the crane of the injection molding machine, the mold was centered with the machine fixed plate, through the centering ring, and the four moorings tightened to the clamping plate of the injection mold. The movable plate of the injection machine was advanced, snuggling up to the clamping plate of the extraction of mold and the other four moorings clamped, thus ensuring the correct fixation and setting of the mold to the machine. Due to the mold complexity, related with their thin walls, and to facilitate the injection process, and as referred before, a hot nozzle was used. To

this purpose, it was necessary to couple a temperature controller for heating the nozzle and controlling its temperature.

Prior to beginning the injection of the biodegradable material, was still tested the correct operation of the extraction, opening and closing the mold. With the pre-processed material (in grain), in the hopper and the molten material inside the spindle, has been started the first injections of the material inside the mold. Each injection cycle took approximately 10 seconds and it was carried out essentially in the following steps: i) filling, ii) compacting, iii) opening the mold, iv) extraction part and v) closing the mold. Figure 3 illustrates the steps corresponding to the opening the mold and the thin walls biodegradable pot extraction, respectively. Due to the injected material properties and to the small injection cycles done (500 parts), the mold does not heat up too. The mold was therefore no refrigerated, because it always maintained a constant temperature along the injections made.



a b

Fig.3. Images corresponding to: (a) the opening the mold and (b) the thin walls biodegradable pot extraction.

3. Pre-processed (Bioplast GS 2189) and post-processed material (biodegradable pots) characterization

3.1. Thermogravimetric Analysis (TGA)

It is well known that thermal analysis allows for the understanding and characterization of the thermal degradation occurred on the structures and other important thermal properties of polymers and polymer blends. Moreover, these assays are very useful in terms of verifying the possible changes in blend characteristics compared with the characteristics of the initial materials. In this case the TGA results of the thermogravimetric analysis characterize the pre-processed material (Bioplast GS 2189) concerning to the thermal stability and the starch percentage (%) dispersed phase as displayed in Figure 4.

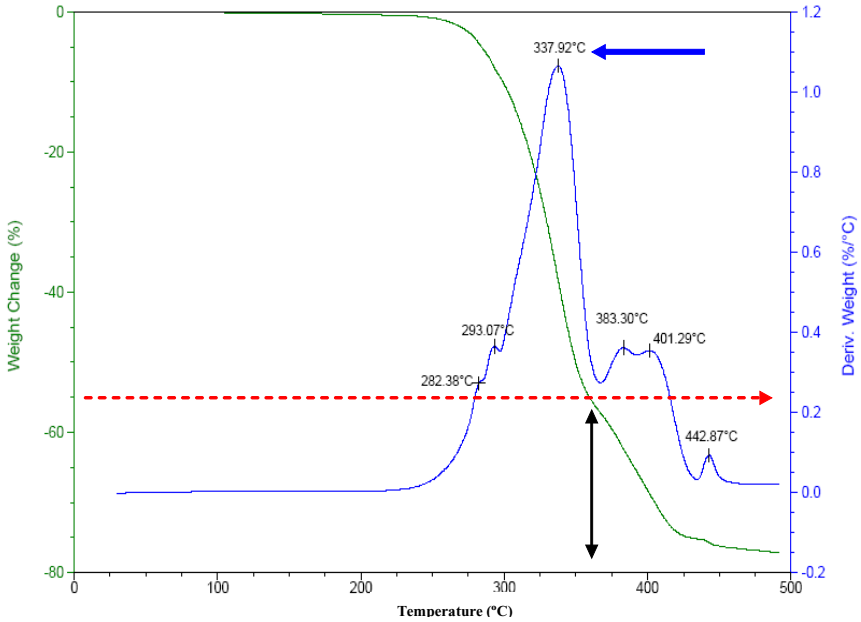


Fig.4. TGA Thermogram of the pre-processed material (Bioplast GS 2189).

The initial decomposition temperature and the weight loss at 500 °C were considered as comparison parameters of thermal stabilities. The thermal degradation of PLA is almost completely at 337.92 °C while for starch, depending on its molecular weight, the degradation begins to 383.30 °C and seems to be more thermally stable. This resistance to high temperatures can be attributed to the possible mineral waste present in the starch. The load content in the mixture that composes the pre-processed material (Bioplast GS 2189) is approximately between 40 to 45% of starch. This value coincides with those recorded during the Soxhlet extraction process. Although this is not a quantitative analysis when performed Soxhlet extraction PLA polymer dispersed phases, and placed 2g of material, it was found that almost 0.9g corresponded to load (starch).

The temperatures of 282 e 293 ºC correspond to the PLA thermal decomposition, since the PLA depolymerisation process starts around of 300ºC. This thermal stability result indicates that PLA is sensitive to temperatures. This fact together with the shear forces induced by the injection process lead to the decreasing of the molecular weight of the post-processed material (biodegradable pots). This conclusion is corroborated by both the molecular weight determination as well as by DSC analysis.

3.2. Molecular Weight determination

It is common some polymers undergo degradation during their processing, primarily in the molten state, as a result of a series of combined actions that include factors such as the residence time, moisture present, processing temperatures, shear rate in the melt, the presence of fillers, etc. These factors become particularly important when it comes PLA because of their high sensitivity to degradation during the processing phase in the molten state. The thermal stability of PLA depends largely on the residual traces of monomer, water and organometallic compounds used in the polymerization reaction. These factors are responsible for reducing the length of the polymer chains [4].

During its processing, the Bioplast GS 2189 was cumulatively subject: i) at a temperature of 210 ° C, ii) the residence time in the hopper of the injection molding machine, iii) the secondary shear effect of the spindle iv) the passage of melt at the nozzle, among others. These factors can induce a possible thermal degradation of the polymer

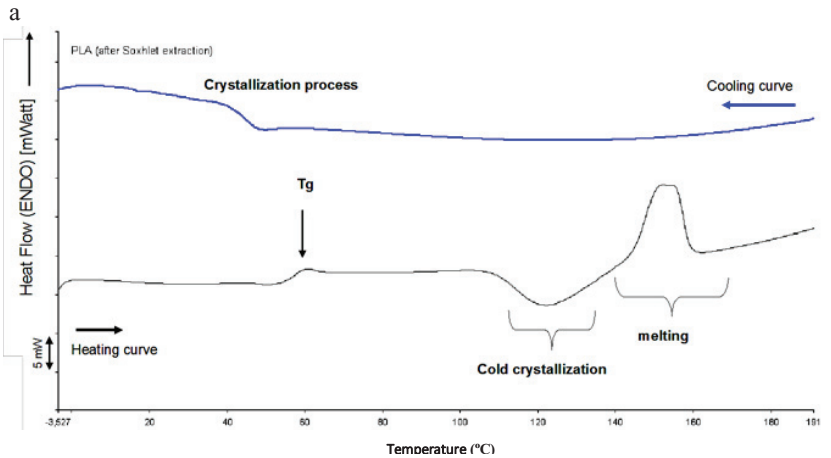
and consequently a reduction of its molecular weight. To investigate this question the molecular weight (Mw) of the PLA phase of the pre-processed (Bioplast GS 2189) and the post-processed material (biodegradable pot) was determined using a capillary viscometer. Before processing the PLA phase of the Bioplast GS 2189 had a molecular weight of 55000 g/mol. After processing, in the pot form, the molecular weight decreased to46300 g/mol. To ensure an effective biodegradative depolymerisation when subjected to chemical hydrolysis action (water) and/or enzyme (microorganisms) in composting facilities, biodegradable polymers have in general molecular weight values lower when compared with other polymers. Thus, the reduction of the molecular weight of the processed material is an additional advantage for the application in question.

3.3. Differential Scanning Calorimetry analysis (DSC)

The semicrystalline PLA has a glass transition temperature (Tg) of 60-65 °C and a melting temperature (Tm) in the range of 160 and 170 °C [5, 6]. Therefore and in order to observe these two thermal transitions, a range of temperatures between the 0°C and the 200 ° C were considered to perform the DSC analysis. A first heating ramp, to cancel the thermal history of the material, a controlled cooling and second heating ramp at a rate of 20 °C/min was the procedure followed. In this study the DSC thermograms from the second heating melting were preferably analyzed since these directly provide the morphological information indicating the changes permanent material. The starch contained in the pre-processed material (Bioplast GS 2189) does not show a melting point visible in the temperature range used. This means that it is an amorphous material therefore only the thermal properties of PLA in the compound were considered. Due to the differences in chemical structures, also the miscibility between the components is not favored.

The results of the DSC thermograms of the PLA sample (after PLA extraction in Soxhlet), PLA Bioplast GS 2189 (PLA extracted from Bioplast GS 2189 pre-processed) and the biodegradable vessel (after injection process) are shown in Figures 5a), 5b) and 5c), respectively and summarized in Table 2. In all thermogramas of Figure 5 the polymer exhibits an exothermic peak in a range of temperatures between 100°C to 145°C, which corresponds to the process of cold crystallization (Tcf).This behavior, typical of polyesters, occurs due to the incomplete polymer crystallization during the controlled cooling process (cooling curve) and therefore uses the thermal energy supplied during the second heating ramp to complete its crystal structure what happens just before the melting. The melting enthalpy (□Hf) provides the same behavior as the degree of crystallinity (Xc), since this is nothing more than the relation between the melting enthalpy obtained from the enthalpy of fusion of 100% crystalline PLA, which it is constant and equal to 93 J/g [7].

For PLA the crystallization process during the cooling is too weak, there is a small change in the region around of the 50 °C. This change is associated with the glass transition, which is more defined in the second heating thermogram showing clearly a thermal transition occurrence (Tg) between 58 and 60 °C as shown in Figure 5a).



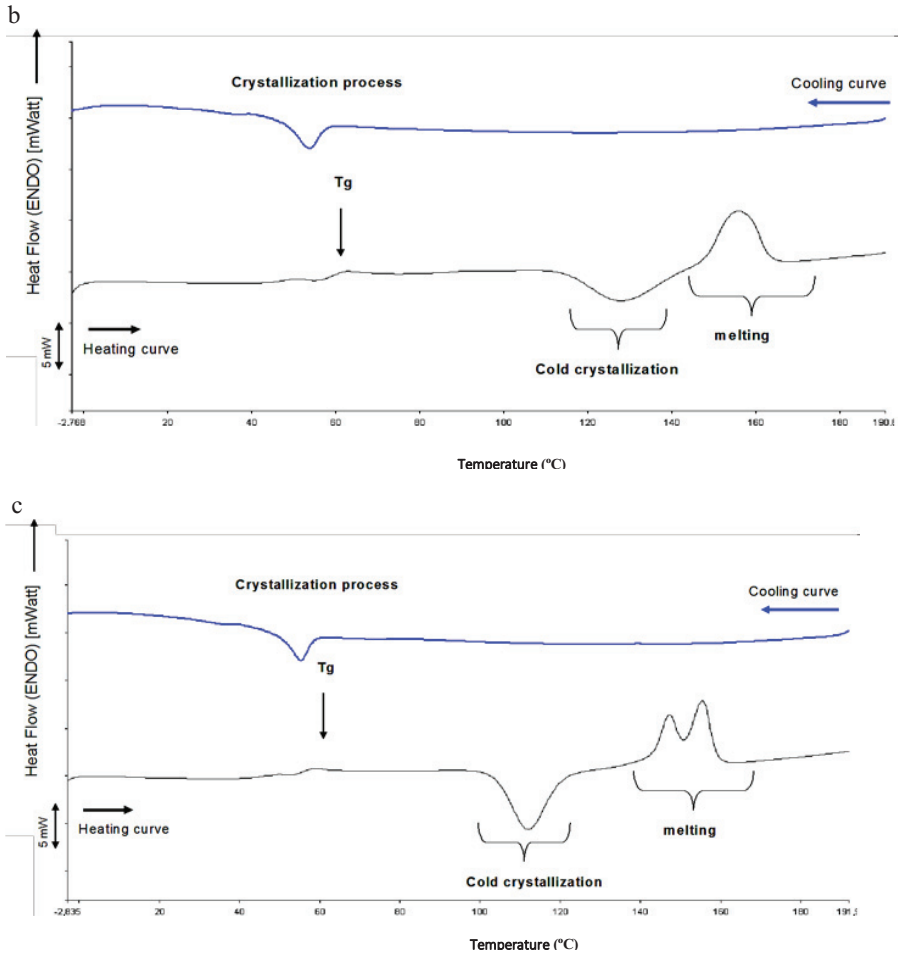


Fig. 5 .DSC Thermograms of the: (a) PLA, (b) PLA Bioplast GS2189 and (c) Biodegradable pot after injection process.

To the PLA extracted from the Bioplast GS 2189 pre-processed material, there are some changes in the thermal behavior of the polymer due to the starch presence as shown in Figure 5b). In the cooling process it is verified that the polymer crystallizes slightly and at the second heating the Tg is slightly displaced to a higher value, in the range of 60-62ºC, than those recorded for PLA (Figure 5a)). This is because the presence of starch induces to molecular stiffness in the system leading to a slightly delaying in the glass transition process. However, the starchy phase, provides a better cold crystallization process than that observed for PLA, delays the melting process and increases the endothermic reaction displacing the melting temperature to the 157 °C. The presence of the starch allows the PLA to crystallize during the controlled cooling process and to complete this organization process during the cold crystallization. The Xc value increases significantly, from 50.5 °C to 62.4 °C, at the starch presence.

Table 2: Thermal transitions (Tg, Tcf and Tm), enthalpies of fusion (ΔHf) and crystallinity degree (Xc) for PLA, PLA Bioplast GS2189 and biodegradable pot after injection process.

Sample	Tg (ºC)	Tcf (ºC)	Tf (ºC)	ΔHf (J/g)	Xc (%)
PLA	58-60	110-140	~ 154	47	50.5
PLA Bioplast GS2189	60-62	112-145	~ 157	58	62.4
Biodegradable pot	58-60	105-120	~ 148 and 157	65	69.9

Regarding to DSC thremogram of the biodegradable pot, Figure 5c) shows the appearing of a Tg below 60 °C (as verified for PLA) and a exothermic crystallization, which are a typical occurrences of a degradation process. In addition, two endothermic fusions for the polymer, which shows the possibility of the crystal clusters formation, are also observed. Become now evident, from both by the decreasing of the Mw value, previously obtained, as by thermal analysis (DSC) that the injection process used to obtain the biodegradable thin-walled pots induces a degradation process. This degradation may be due either to the presence of shear forces typical in the injection process and to the thermal sensitivity of the PLA. The decreasing on the Mw value gives to the PLA chains mobility enough so they can be organized increasing their degree of crystallinity [8]. The endothermic melting are observed are observed probably due to this phenomenon. However, the increase of crystallinity (69.9%) verified can also be the result of the annealing crystals during the heating scan, i.e. can be due to the incorporation of the chains in the amorphous phase to the crystalline phase, which it is only possible if there is a decrease in the molecular weight.

3.4. IdentiPol results

Based on the Quality Index Score (QIS) the identiPol results allow in a quickly and reliably way the comparison between the pre-processed and the post-processed polymer. The QIS is a value between 0 and 10 indicating the similarity between the sample that is analyzed with a set of reference, the 0 indicates a sample that is not similar to the reference, and 10 represents a sample which is equal to the reference. A QIS greater than 6 validates the tested sample relatively to the reference set. In order to create reference set - base line - 10 samples of the Bioplast GS 2189 material were subjected to analysis. Established the base line for the Bioplast GS 2189 a QIS of 9.0 was obtained. In addition, a Tg between 60-62 °C was recorded, as shown in Figure 6, which agrees with the observed in DSC analysis. Compared to the base line of the Bioplast GS 2189 pre-processed a QIS of 2.4 and a Tg value between 58-60 °C were obtained for the Bioplast GS 2189 post-processed, i.e. for the injected biodegradable pot. These results confirm that in fact the injection process leads to the Bioplast GS 2189 degradation.

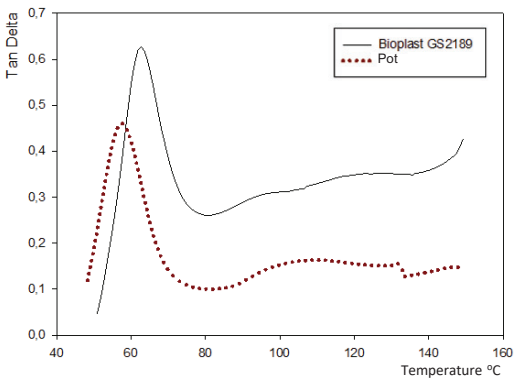


Fig.6. IdentiPol equipment results.

4. Conclusion

It was demonstrated that the Bioplast GS 2189 is composed of approximately 55% PLA and 45% of starch. From TGA results it was observed that the PLA degrades completely at the temperature of 338°C and the starch, in turn, begins to degrade at a temperature of 383°C. A reducing of molecular weight, from 55000 g/mol to 46300 g/mol, is clearly observed after biodegradable material processing. In addition, an increase of crystallinity, from 62.4% to 69.9%, as well as a decrease of glass transition temperature, from 60-62°C to 58-60°C are observed through the DSC analysis. The identiPol test results confirmed that the material undergoes changes during processing, which is attested by the QIS difference as well as in the reduction of the glass transition temperature, which in the post-processed (pot) is lower than the pre-processed material (Bioplast GS 2189). From these results it can be concluded that the injection processing of the Bioplast GS 2189 material affects its properties by inducing its degradation process. This behavior can be due to the shear forces and thermal variations to which the material is submitted during the injection process.

In this work a technical support for the development of biodegradable plastic products with thin walls manufactured using injection process was provided. The strategy presented, after implemented, will surely have a major impact on economic sectors as agriculture, packaging, etc., contributing significantly to the dynamics, growth and strengthening the technological image and of the quality of these economic sectors.

5. Acknowledgements

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