LARISSA CAROLINA DA SILVA VIANA GONÇALVES

PREPARAÇÃO E CARACTERIZAÇÃO DE FILMES PLÁSTICOS BIODEGRADÁVEIS A BASE DE POLY (LACTIC) ACID E BORRA DE CAFÉ

(“PREPARATION AND CHARACTERIZATION OF
BIO-BASED DEGRADABLE PLASTIC FILMES
OF POLY (LACTIC) ACID AND COFFEE SPENT”)

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PREPARATION AND CHARACTERIZATION OF BIO-BASED DEGRADABLE PLASTIC FILMES OF POLY (LACTIC) ACID AND COFFEE SPENT

Monografia apresentada ao colegiado do
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ABSTRACT

Coffee is one of the most favourite beverages in Canada due to personal, social and cultural habits. It is estimated that more than 150 thousand metric tons of spent coffee ground is generated in Canada per year, creating a considerable amount of solid waste. Currently, spent coffee grounds are disposed off in the landfill, being composted, or used as fuel in boiler, all of these can be considered as waste economy opportunity. The purpose of this project is to utilize the high quality waste product, specifically to develop biodegradable composite based on poly (lactic) acid – an emerging biobased thermoplastic polymer that has gained increasing acceptance by the food industry in Ontario, Canada. The hypothesize that the coffee waste product can be processed and incorporated into poly(lactic acid) to produce composite materials with enhanced material properties. The envisaged "green" materials may be suitable for replacing some of the existing petroleum-based plastic packages in food and consumer products. By diverting the spent coffee grounds away from the landfill and developing novel applications for the waste product, the value of coffee bean can be upgraded, which is beneficial for coffee processors and end-users in Ontario. Furthermore, the disposal issues of spent coffee can be partially addressed.

Keywords: Spent coffee - Biobased thermoplastic polymer - poly (lactic acid)

RESUMO

Café é uma das bebidas mais apreciadas do Canadá devido a hábitos pessoais, sociais e culturais. Estima-se que mais de 50 mil toneladas de borra de café são geradas no país por ano, o que gera considerável quantidade de resíduo sólido. Atualmente, esta borra de café é descartada em aterros sanitários, para ser degradada, ou usada como combustível em caldeiras, sendo que todos estes destinos caracterizam desperdício de oportunidade econômica. O objetivo deste trabalho é utilizar a grande quantidade de resíduo gerado, especificamente para desenvolver um composto biodegradável maioritariamente constituído por poly (lactic) acid - um polímero biodegradável termoplástico emergente que vem conquistando uma aceitabilidade cada vez maior das indústrias da província de Ontario, Canadá. A hipótese é de que este resíduo gerado pelo café possa ser processado e incorporado no poly (lactic) acid a fim de produzir materiais compostos com propriedades mecânicas melhores. A consideração de um material "verde" pode ser aplicável para substituição de algumas embalagens plásticas já existentes, a base de petróleo, e que são utilizadas em alimentos e outros produtos. Desviando o resíduo de borra de café dos aterros sanitários e desenvolvendo uma inovadora aplicação para este resíduo, o valor agregado ao café poderá ser aumentado, o que é beneficial para os produtores de café e consumidores finais de Ontario. Além disso, o descarte deste resíduo pode ser parcialmente solucionado.

Palavras-chave: borra de café, polímero termoplástico biodegradável, poly (lactic) acid

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1 INTRODUCTION

The current watchword is sustentability. People, in general, are more aware of the environmental issues and concerned about the alternatives to take a better care of the nature.

This scenario reflects directly on industry behaviour, once industries are one of the most harmful players related to the safety of ecosystems. Of course that humans still are responsible for polluting water and wasting it to much, producing to much wast at home, driving cars that do not have appropriate maintenance and release lots of carbon monoxide and so on.

However, concerning about the amount of trash produced at homes, most industries are tremendously responsible for it. Most packages that are available at stores are not bio-based and take years to decompose. Glass bottles take more than four thousand years to decompose, PET bottles take around four hundred years, plastic cups take fifty years.

Thinking of that many actions have been made to, at least, make consumers thing about what they are buying and how it can affect the environment. Some supermarkets in Toronto, Canada, are not offering plastic bags for the groceries anymore, and the ones that sill offer it charge twenty cent per bag. This kind of action came with advertisements mostly on TV about how these bags can damage the aquatic animals life because they eat the bags or can get trapped for them and die, can damage the manholes causing floods in rainy days, increase the solid wast that can not be composted in landfills with the aim of educate people and make them fell responsible of changes.

Another important concern is about the organic food wast that are underused and take two to twelve months to decompose. It seems very good compared to the other examples given before, but actually it means that a lot of economical opportunity has been lost based on this wast. These problem could be partially solved if consumers have a greater concern about how to peel fruits and vegetables, how to use part of the wast to do different recipes and condiments, and industries could use organic waste to incorporate at packaging producing materials to improve its biodegradability.

The objective of this project is to try to find and alternative for all these problems in order to offer to industries an option of plastic packaging that does not damage the environment as much as the current one available.

In Canada tons of coffee spent are produced per year once Canadians are increasing the consumption of coffee year after year. Thinking of that, Tim Hortons franchise of coffee shops of Guelph city, decided to provide their coffee spent to encourage the scientific search at University of Guelph.

The attitude of this company revels how important it is to develop new materials in order to create new polymers that are more environmental friendly and for the process of packaging to become more sustainable.

The concern of the new generation of consumers causes that companies sponsoring projects tat enable “green” ideas have a prominent place in the community and at the midia. In this way companies will boost their selling and cut short the waste of production, optimizing the whole production chain becoming more competitive to sell products and leveraging greater profits.

It is noticeable that in many areas of the market this atitudes are been taken as a tool for a better living and consuming consciously and respecting the environment.

2 THEORETICAL FOUNDATION

2.1 Coffe in Canada

Coffee is one of the most popular beverages in Canada, where it is deeply rooted in the cultural and consumption habits of Canadian. Coffee is one of the major sources of antioxidant in Canadian diet. It has been implicated in reducing the risk of several diseases, including cardiovascular disorders, type 2 diabetes, Alzheimer's disease, Parkinson's disease, and other diseases (Taylor & Deming,2007). Coffee beverages are prepared by extracting roasted, milled coffee beans with hot water. The resulting byproduct is spent coffee grounds (SCG). On per capital basis, Canadian consumed about 100 litres of coffee per year (Statistics Canada,2011). Based on the typical brewing requirement (10 g of ground per 180 mL of coffee) and a population of 34 million (Wintgens,2004; Statistics Canada,2011), the total amount of SCG produced is estimated at 189,000 tonnes. Considering that about 17% of coffee is prepared from instant coffee which does not contribute to the generation of coffee waste (Coffee Association of Canada, 2011), and assuming that all instant coffees are produced outside of Canada, the total amount of SCG generated in Canada is estimated at 157,000 tonnes - a significant amount of solid waste. Spent coffee is not optimal for use as ruminant feed due to poor digestability, low gross energy, and lack of essential amino acids in the proteins (Girens & Barber,1986; Silva,1998). Currently, spent coffee is discarded in the landfill or composted, both of which can be considered as lost economic opportunity. Another disposal avenue of spent coffee is using it as fuel in boiler (Silva 1998).

2.2 Utilization of coffee byproducts

For economic and environmental reasons, attempts have been made to utilize coffee byproducts. For instance, using alcohol, hexane or super critical carbon dioxide as solvents, the residual lipid in SCG (at ~15% level) has been extracted to produce high quality biodiesel (Kodamodi,2008; Oliveira,2008; Couto,2009). Residual phenolic compounds, mainly chlorogenic and hydroxycinnamate-quinic acid derivatives, have been extracted from SCG for dietary antioxidant supplement (Clifford,2000; Pinelo et al,2007). Several studies reported that SCG can be converted into adsorbent materials by pyrolysis and microwave treatments that are effective for the removal of dye contaminants in wastewater discharge from the textile industry, such as methylene blue and gentian violet (Hirata et al,2002; Franca,2009). Kaikake et al. investigated the feasibility of using degreased spent coffee as an adsorbent for cadmium (II) and other base metals ions. They concluded that the material can be used as an effectively adsorbent for removing base metal ions from wastewater and it may be useful for cation exchange applications (Kaikake et al,2007). Another study showed that activated carbon prepared from SCG impregnated with $ZnCl_2$ exhibited strong activities towards formaldehyde adsorption, suggesting that the material may be useful for air purification applications (Boonamnuayvitava, 2005). One plastic recycling company, Axion Polymers (Manchester, UK) developed moulded plastic composite sheeting containing SCG fillers (Axion Recyclihg,2011).

2.3 Poly(lactic)acid

There are three main polymer groups: thermoplastics, thermosets and elastomers. Thermoplastic ones are soft when heated and solid when cooled and can be reground and recycled; thermosets undergo a cross linking reaction when the temperature is raised above a certain temperature forming a 3-D network that do not change after cooling and ca not be recycled as thermoplastics; elastomers are capable of deformations with the material behaving in a largely elastic manner (Rauwendaal).

Poly(lactide) (PLA) is a biodegradable/compostable polymer derived from renewable sources which possess properties similar to some of the existing petroleum-based thermoplastics. The monomer of PLA is lactic acid which is produced by fermentation of starch, mainly from corn (Vink,2003; Lim,2008).

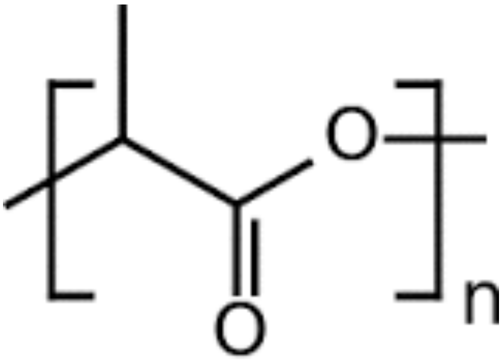


Fig 1: PLA chemical structure
Source: wikipedia

It is an aliphatic polyester derived from corn and sugar beets, and degrades into nontoxic compounds in landfill. It can be synthesized from direct condensation of lactic acid of ringing-opening polymerization of cyclic lactide, a solvent free process where lactic acid is first transferred to a low-molecular weight PLA, followed by depolymeriation to lactide, and then polymerized continuously to a controlled high-molecular weight polymer through a catalytic ring-opening process (Lunt,1998).

Due to its sustainable feedstock and biodegradable properties, PLA has been viewed as a promising material for addressing solid waste disposal problem of packaging (Auras,2004; Garlotta,2001). However, PLA has relatively lower heat reflection, weaker barrier properties, and lower impact strength than thermoplastics commonly used in packaging application, such as poly(ethylene terephthalate) (Auras,2003). To improve the material properties of PLA, fillers have been incorporated into PLA matrix, including organically modified layered clay mineral, wood pulp, flax fibers, glass fiber, cellulose, and so on (Oksman,2003; Huda,2006; Mathew,2006; Mathew,2005; Ouchi,2006; Ray & Okamoto,2003; Chang,2003). Besides material properties enhancement, this approach also reduces cost since PLA resin is more expensive than other commodity polymers.

The conversion of PLA resin into packaging is mainly based on melt extrusion technology wherein the polymer is heated above its melting point and plasticized within an extruder. The molten polymer is then shaped into films/sheet with a slit die or 3-dimensional articles in a mold cavity. While highly efficient in terms of production throughput, this process has an inherent drawback in that the polymer has a tendency to undergo thermo-oxidative degradation, (Taubner,2001). In view of the anti-oxidative properties of SCG, incorporation it into PLA may be useful to reduce the thermal degradation of PLA during melt processing. Moreover, its surface activities can potentially improve barrier and mechanical properties of PLA. The envisaged PLA-SCG composite may be used in food packaging. For instance, plastic lids for coffee and soft drink beverages commonly used today are made of non-biodegradable polystyrene. The biodegradable PLA-SCG composite may be a “greener” substitute. Many plastic components used in agricultural applications, such as mulch films, seed mats, and plant pots are not biodegradable. The retrieval of these materials from the field at their end-of-life can be both labor-intensive and costly. By manipulating the properties of SCG fillers, the composite can be designed to undergo controlled biodegradation, thereby addressing the disposal issues.

The production of roasted coffee ground involves careful harvesting and processing of coffee beans to ensure that the brewed coffee has consistent organoleptic properties (Wintgens,2004). This implies that SCG is quite consistent in quality, which is ideal when it is further processed into filler for thermoplastic polymers. Moreover, coffee spent is microbiologically stable due to its significant residual phenolic compounds, as well as the thermal treatment it received during roasting and brewing processes. These characteristics will confer short-term stability to SCG during transportation. By and large coffee beans are distributed to coffee shop franchises by fleets of trucks dispatched from distribution centers. By using the same truck that delivers the coffee (and other merchandize) to collect SCG from the coffee shop, and transport it back to the distribution center, the byproduct can be centralized for further processing. By leveraging the existing distribution network, the logistic and cost of collection can be partially addressed.

2.4 Extrusion

2.4.1 History of polymer extrusion

Many items are made by extrusion, noodles, sausages, snacks, cereals, pipes, window frames, adhesive tapes, wire insulation can be made by this process; however, in the packaging industry many materials can be produced by this process too as metals, clays, ceramics, foodstuffs and processed polymers.

The polymer processing industry has many important elements that are essential for its functioning, but the extruder is indisputably the most important of them followed by molding. The meaning of “to extrude” is to push or to force out (dictionary.com). This means that the material is extruded when it is pushed through an opening.

The process of extrusion is now new, in 1953 was built the first extrusion machine for thermoplastic materials by Paul Troester in Germany. Before that, just rubber was produced by extrusion that were steam-heated ram extruders and screw extruders with short length to diameter (Kaufman 1969).

After the invention of Troester, extruders were evolved into electrically heated screw extruders with length increased which an Italian Roberto Colombo conceived the principles of the twin screw thermoplastic extruders. Colombo worked with Carlo Pasquetti to develop two types of extruder, Colombo created an intermeshing co-rotating twin screw extruder and Pasquetti created the intermeshing counter-rotating twin crew extruder. Both of these inventions were patented in several countries and are used by many industries (Rauwendaal).

Around 1950, some scientific studies about the process of extrusion started to appear with increasing frequency. In the mid-fifties, the first quantitative study on solids conveying was published by Darnell and Mol (1956).

However, not until around 1965 that the entire extrusion process, from the feed to hooper to the die, could be described quantitatively. The theoretical work since this time has concentrated on generalizing and extending the extrusion theory and the development of numerical techniques and computer methods to solve equations that can not no longer be solved by analytical methods.

Another interesting development in practical extrusion technology was the concept of feed-controlled extrusion. In this type of extrusion, the performance is determined by the solids conveying zone of the extruder. In this type of extrusion it is possible to develop very high pressure and positive conveying characteristics using grooves in the first portion. However, this new concept was not well accepted among all companies specially in the blow film industry that uses very high molecule weight polyethylene.

In the early 2000’s, a new generation of mixing devices was developed to generate strong elongating flow to improve mixing, particularly dispersive mixing. This knowledge was not translated into practice until nowadays, but it was known at this time that this new technique would improve mixing better than dispersive mixing.

The invention of effective new mixers for single screw extruders had improved the capabilities of conventional single screw extruders. Very high speed single screw extruder have been commercially since 2005-2010. This is one of the most importante developments in single screw extrusion over the past several decades. These small extruders (50 - 75 mm) can run at screw speeds as high as 1,000 to 5,000 rpm and achieve output rate about an order of magnitude above the rate of conventional extruders.

2.4.2 Types of extrusion

The are many types of extrusion such as screw molding, die molding, calendaring, injection moulding, blow moulding, compression moulding, thermoforming, and rotational moulding. The screw extruder is the workhorse of the plastics industry. Screw extruders are polymer pumps with the capacity to melt the material which they are fed.

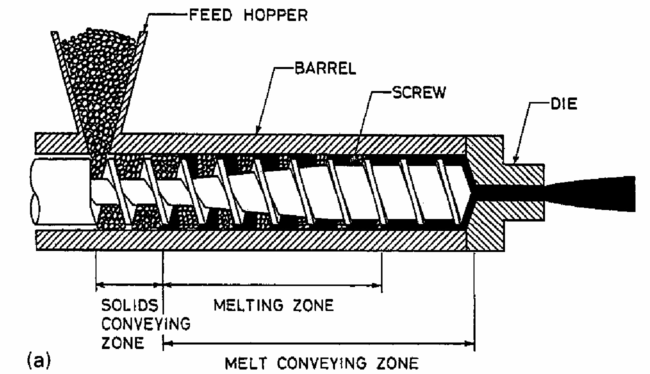


Fig 2: Single screw extruder

In the first zone (Fig.2), solids conveying zone, the solid polymer particles are compacted together in the screw channel by the rotating action of the screw to form a solid bed of material. At the plastication (melting) zone, barrel heaters cause the a thin filme of molten polymer to form in the gap between the solid bed and the barrel wall. The melt filme is subjected to intense shearing in the thin gap, and because of the extremely high viscosities of molten polymers, high rates of viscous dissipation result. The generated heat melts the solid bed within a short distance os the star of melting. In the last zone of the extruder, the metering section, the polymer melt flow is stabilized in the shallow screw channels, and finally the material passes out through the die at the end of the machine (Vlachopoulos & Shutt, 2003).

The twin screw extruders are extruders with two screws of the same diameter, which turn side by side within the extruder barrel at the same speed. Recently, these extruders are becoming more used in application as mixing, blending, compounding of thermoplastic polymers with additives, devolatilisation and reactive extrusion. This extruder have greater control over residence time distribution and mixing than the single screw extruder and have superior heat and mass transfer capabilities. The disadvantage is the higher capital cost.

Die extrusion is used to produce pipe, tubing, coating of wire, plastic bottles, plastic films and sheets, plastic bags, coating for paper and foil, fibres, filaments, yarns, and tapes. It is responsible for the continuous foaming (after cooling and solidification) into a final product (Doyle,1985).

Calendering is used for the production of continuous sheet or films of uniform thickness, by squeezing the molten material between a pair of heated driven rolls (Vlachopoulos,1992).

Injection moulding has to ciclic processes that include, melt generation by a rotating screw and filling of the mould with molten polymer by te forward ramming of the screw, followed by a very short packing stage. The material is held in the mould under high pressure until it has solidified to allow ejection (Doyle,1985).

Blow moulding is the process by which articles are formed by inflation of a molten resin to fill a mould cavity having the shape and dimensions desired. Products as soft drinks bottles are blow moulded (Rosato,1988)

Compression moulding is the oldest technique for the production of polymer products, and is mainly used for thermosets. In this process the material is pressed in the mould by the heated platens of a hydraulic press. Injection moulding has replaced this process for some polymers because of the advantages in materials handling and automation. Compression moulding is better for reinforced polymers (Isayev,1987).

Thermoforming techniques involve the softening of thermoplastic sheets by heat, followed by forming by the application of vacuum, pressure, or a moving plug. The sheet may be stretched over male mould or into a female mould. On contact with the mould, heat is lost and the material regains stiffness as it cools. Usually for simple geometric forms as boxes, food trays, containers refrigerator liners, and computer cases (Trone,1996).

In rotational moulding, a charge of plastic powder is placed in one half of a medal mould. The mould halves are then clamped together and heated while the mould rotates biaxially. The powder particles melt and coalesce to form a homogeneous layer on the surface of the mould. Then the mould is cooled and the polymer layer dandifies and solidifies (Crawford,2002).

2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is an efficient analytical tool for characterizing the physical properties of a polymer. It enables the determination of melting, crystallization, and mesomorphic transition temperatures, the corresponding enthalpy and entropy changes, and characterization of the class transition and other effects which show either changes in heat capacity or a latent heat.

The machine has two sample positions, one sample is the reference sample and the other one is the sample under studies. The reference sample is often an empty pan or filled with inert material. Both of samples will be heated and cooled at the same rate determined by the program. These samples have their own pans and heaters because they have different composition, so the heat given to each pan to guarantee that they heat at the same rate is different.

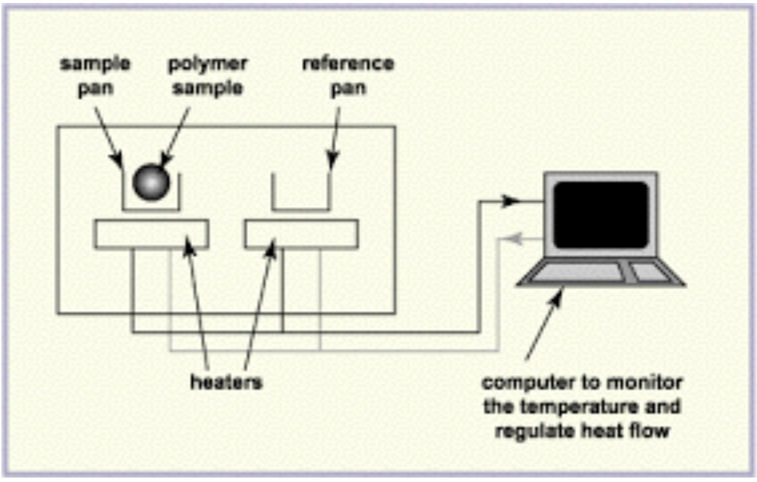


Fig 3: DSC equipment diagram
Source: Wikipedia

The most used operation mode of DSC is heating or cooling at constant rates. The first outcome of this experiment is heat flow rate as a function of time. It is possible to have a graph of heat flow versus temperature if the temperature of the sample is known (Fig.4).

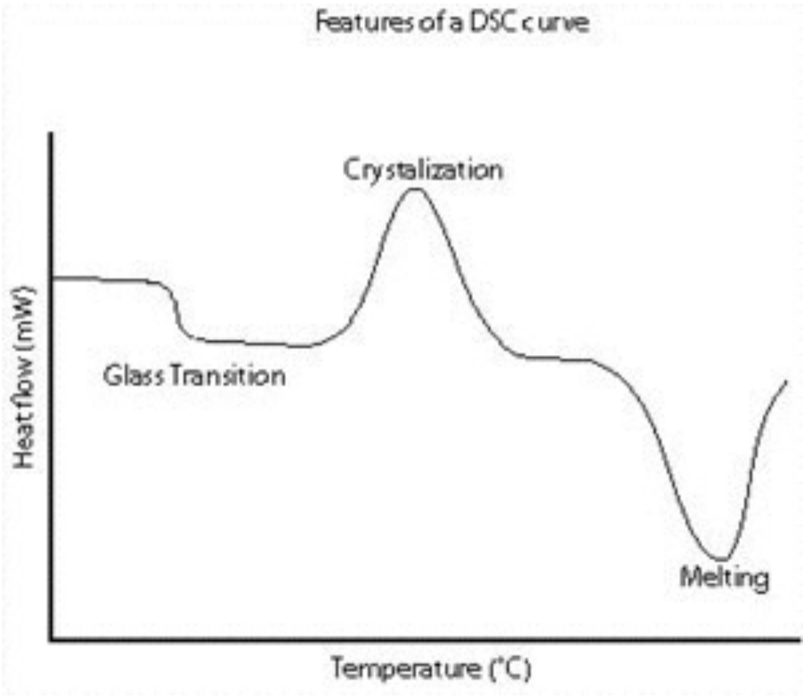


Fig 4: Generic DSC graph
Source: Wikipedia

From the heat flow curve it is possible to obtain heat capacity (Cp), and with known sample mass specific heat capacity (cp), can be obtained using the Eq.1

$$c_p(T) = c_{p\ saphire}(T)\,\frac{m_{saphire}\cdot\beta}{m_{sample}\cdot\beta}\cdot\frac{\Phi_{sample}(T)-\Phi_{empty}(T)}{\Phi_{sapphire}(T)-\Phi_{empty}(T)}$$

$$= K(T)*\frac{\Phi_{sample}(T)-\Phi_{empty}(T)}{m_{sample}\cdot\beta}$$

$$K(T) = c_{p\ saphire}(T)\,\frac{m_{saphire}\cdot\beta}{\Phi_{sapphire}(T)-\Phi_{empty}(T)}$$

Eq.1: Calculus of specific heat capacity
Source: Schick,2009

The most useful given by DSC is the specific heat capacity because it is directly related to sample properties and linked to stability and order.

In order to obtain the degree of crystallinity of the polymer using DSC it is necessary to calculate the area (Eq.2) of the melting peak and the crystallization peak and using the sample mass calculate the total heat at melting and at crystallization (Eq. 3-4). After this, it is needed to subtract these two numbers and divide it per specific heat of melting of the material under studies (Eq. 5-6). The final step is to obtain crystalline fraction subtracting the mass found by the sample mass (Eq.7).

Eq.2. area = $\frac{\text{heat x temperature}}{\text{time x mass}} = \frac{\text{J K}}{\text{s g}}$

Eq.3. $\frac{\text{area}}{\text{heating rate}} = \frac{\text{J}}{\text{g}}$

Eq.4. Total heat (H) = $\frac{\text{J}}{\text{g}}$ x g = J

Eq.5. H (melting) - H (crystallization) = H

Eq.6. $\frac{\text{H}}{\text{H* (specific heat of melting)}}$ = mc

Eq.7. $$\text{Crystallization fraction} = \frac{mc}{m \text{ (of the sample)}}$$

Source of the equations 2-7: http://pslc.ws/macrog.dsc.htm

3 MATERIALS AND METHODS

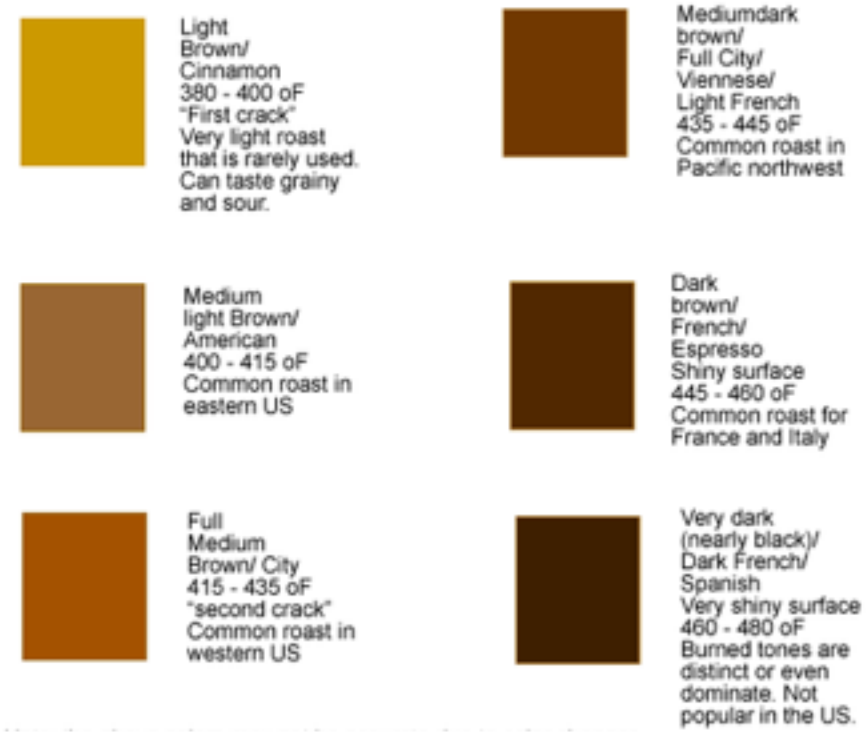
3.1 Preparation of the films

3.1.1 Roasting

The roasting used was the "Hottop coffee roaster - KN8828P-2". This machine is appropriate for small amounts of coffee beans. It has manual programs, which you can custom the temperatures and times, and it has 10 custom programs that are already customized for different types of roasting. It is also possible to reset these customized programs to have them saved for future roastings.

Fig. 5: Hottop coffee roaster
Source: www.roastermasters.com

The first step was to turn on the machine and set the manual program. This specific chosen temperatures and times were chosen after some experimental trials to provide the best light, medium and dark coffee beans compared to the image color samples of coffee roasting that came with the machine.



Light
Brown/
Cinnamon
380 - 400 oF
"First crack"
Very light roast
that is rarely used.
Can taste grainy
and sour.

Mediumdark
brown/
Full City/
Viennese/
Light French
435 - 445 oF
Common roast in
Pacific northwest

Medium
light Brown/
American
400 - 415 oF
Common roast in
eastern US

Dark
brown/
French/
Espresso
Shiny surface
445 - 460 oF
Common roast for
France and Italy

Full
Medium
Brown/ City
415 - 435 oF
"second crack"
Common roast in
western US

Very dark
(nearly black)/
Dark French/
Spanish
Very shiny surface
460 - 480 oF
Burned tones are
distinct or even
dominate. Not
popular in the US.

Fig 6: Samples of standard colour of coffee roasting

Source: Hottop coffee roaster manual of instructions

In this case the best combination of temperature and time was the STD manual program specified below:

- stage 1: heating until 79 degrees celsius.
- stage 2: heating until 190 degrees celsius.
- stage 3: heating until 210 degrees celsius.
- stage 4: heating until 219 degrees celsius.

The raw beans were added at 79 degrees, after the heating of the machine, and as the temperature increased, samples of the grains were periodically taken to check their colour and guarantee that all the repetitions had the same colour pattern. The standard for light roasting set at 205 degrees celsius and for the dark roasting at 219 degrees celsius.

At each batch were roasted 250 grams of green coffee beans of Robusta and Arabica varieties per time to have more information about how the characteristics of them can influence the mechanical properties of the polymer.

3.1.2 Grinding I

The second step is grinding and brewing the previous roasted coffee beans.The grinder used was the “Bistro bodum grinder”, which is a common home grinder. Because of that, small quantities of beans were ground at a time and the machine was stopped periodically to prevent it to over heat. As the beans were ground they released oils that added to the heat of the machine caused the still non grind beans to be stucked in the engine and damage the machine.

Fig 7: Bodum coffee grinder
Source: www.bodum.com

3.1.3 Brewing

The brewer machine was a home coffee maker and for 60g of coffee powder was added 1 L of distilled water.

Fig 8: Home coffee maker
Source: google images

3.1.4 Oven drying

After brewing, the coffee spent was dried. The dry process involved two steps. As the spent was too wet after the brewing, it was heated using a micro oven for ten minutes stopping this procedure every three minutes to sieve the spent in order to prevent burning and to promote homogenization of the sample. Then the dried material was spread in trays and placed in an oven at 80 degrees celsius for one day to finish the process of drying.

3.1.5 Grinding II

The fourth step is to dramatically reduce the particle size of the dried coffee spent using the "Planetary Ball Mill PM100".

Fig 9: Ball Mill PM100
Source: University of Guelph packaging lab

The machine has one grinding station with one jar three big balls and eight small ones. The different ball sizes that come inside with the sample can be combined to achieve a final particle size of 1 micrometer. Another factor that can be used to achieve the final goal is to use reverse spinning or conventional spinning. The best combination of balls is due to experimental trials.

The standard that best reduced the coffee ground size was made utilizing a sample of 40 g of spent and 7 g of distilled water in three steps specified below:

- step 1: 15 minutes, 2 big balls, 450 rpm, reverse spinning

- step 2: 15 min, 8 medium balls, 500 rpm, reverse spinning
- step 3: 10 min, 8 medium balls, 500 rpm, reverse spinning

Between each step the jar was removed and its walls were scraped to unglued the retained particles and to homogenize the sample.

3.1.6 Sieving

Next step was to sieve all the material in order to guarantee that all the particles have the same size. The equipment utilized for these process was a sieve shaker with a sieve of 0.0029 inches (U.S.A. Standard test sieve N0.200).

Fig 10: U.S.A standard sieve N0.200
Source: University of Guelph packaging lab

Each sample of 10 g was sieved for an average of two hours with an interval of thirty minutes to homogenize the sample and avoid the excessive heating of the machine. Also, to optimize the sieving, several stoppers of different sizes were used to prevent the agglomeration of the particles as the absorption of the air moisture increases during sieving.

3.1.7 Vacuum drying

After sieving all the coffee spent was placed in trays in a “Isotemp Vacuum Oven model 285A” at 80 degrees Celsius and -20 inHg for 24 hours and then mixed to the PLA pellets for the extrusion.

Fig 11: Isotemp vaccum oven
Source: University of Guelph packaging lab

3.1.8 Extrusion

The spent coffee grains master batch was prepared by dispersing them in PLA using a counter-rotating twin-screw compounder and further converted into pellets a pelletizer. The pellets were mixed with PLA resin and extruded into films using a Randcastle extruder equipped with a 6” slit die and a film cast line. Microstructures of the films were examined using electron microscopy to evaluate the compatibility between the SCG and PLA phases. The dispersed phase may act as nucleates for crystallization. A modifier from Dupont (Biomax) was incorporate during compounding to optimize the toughness of the resulting composite structures. Thicker composite sheets were extruded to evaluate the feasibility of thermoforming them into packaging containers.

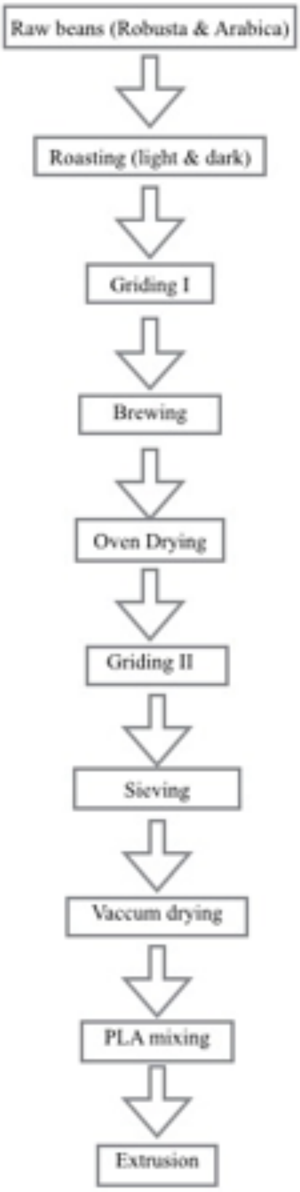


Fig 12: Process Fluxogram

3.2 Characterization of the films

3.2.1 Differential Scanning Calorimetry (DSC)

The “Differential scanning calorimeter Q2000” from TA Instruments was used to find the melting point, class transition temperature, and the temperature of crystallization during heating, cooling and re-heating.

The procedure is specified below:

- equilibrate at 0.00 degrees celsius
- isotherm 1 min
- ramp 10.00 degrees celsius/min to 200.00 degrees celsius (we also did it at 3.00 degrees/min)
- isotherm 1 min
- ramp 10.00 degrees celsius/min to 0.00 degrees celsius (we also did it at 3 degrees/min)
- isotherm 1 min
- ramp 10.00 degrees celsius/min to 200.00 degrees celsius/min (we also did it at 3 degrees/min)
- isotherm 1 min

The pan used was the “standard aluminum flat pan” and the average sample size was 0.00636 mg.

3.2.2 Fourier transform infrared spectrophotometer (FTIR)

This equipment was used to determine the chemical composition of the polymer and its functional groups.

The sample was prepared using a “Diamond EX’Press 2.0mm, which has a diamond to compress the sample in order to make it as thin as possible.

4 RESULTS AND DISCUSSION

4.1 Differential Scanning Calorimetry (DSC) ramp 5 °C/min

As a semi-crystalline polymer under the conditions specified above, PLA's thermograms show the glass transition, melting exotherm and crystallization endoderm peaks of each sample (Fig.13-16).

The glass temperature (Tg) of pure PLA is 60.62°C according to Fig. 13 and this value compares well with Tg of 61°C reported by Witzke; this validates the data obtained as reliable.

As evident by the flat line at the cooling, there is no crystallization at cooling. Pure PLA just present crystallization during heating at 109.82°C (Fig.13).

Looking at Fig.14-16 it is evident that the PLA polymers treated with 5%, 7.5% and 10% present crystallization during cooling and during heating; however, the crystallization during cooling is less expressed than during heating. Comparing the 3 treatments of PLA it is also noticeable that the crystallization peak during cooling in increasing as the amount of coffee spent increases.

The temperature of crystallization during heating is decreasing as the amount of coffee spent is increased and there is a huge difference drop at the temperature of pure PLA compared with the treated ones. All the treated samples have a very small difference between their temperatures of crystallization. This shows that the addition of coffee spent affects effectively the crystallinity of the PLA.

Polymer	Crystallization temperature
PLA	109.07
PLA + 5% coffee	93.49
PLA + 7.5% coffee	93.12
PLA + 10% coffee	92.42

Table 1: Relation between polymer sample and temperature of crystallization.

The degree of crystallization of each sample including pure PLA was calculated using the data obtained at theoretical foundation.

Polymer	% of crystallization
PLA	12.87%
PLA + 5% coffee	13.27%
PLA + 7.5% coffee	13.52%
PLA + 10% coffee	13.64%

Table 2: Percentage of crystallization of PLA and treated samples.

It is evident an increasing at the crystallization rate as the percentage of coffee spent increases. This is expect once that PLA is more likely and amorphous polymer, it is semi-crystalline and the characteristics of this kind of polymer are, transparency and poor barrier. As the crystallinity increases, as showed by Table2, the barrier properties are improved, and the opacity is increased.

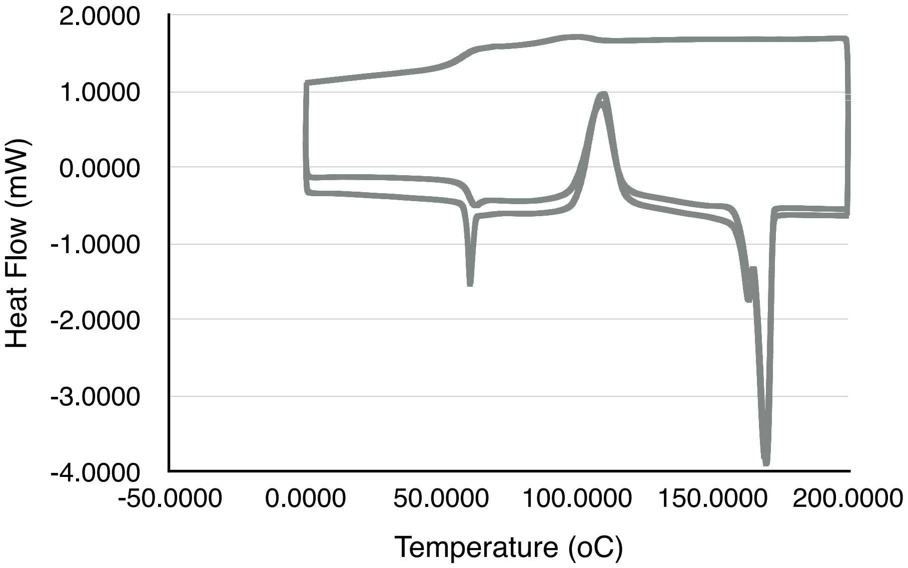


Fig.13: DSC of Pure PLA (no treatment) at ramp 5 °C/min.

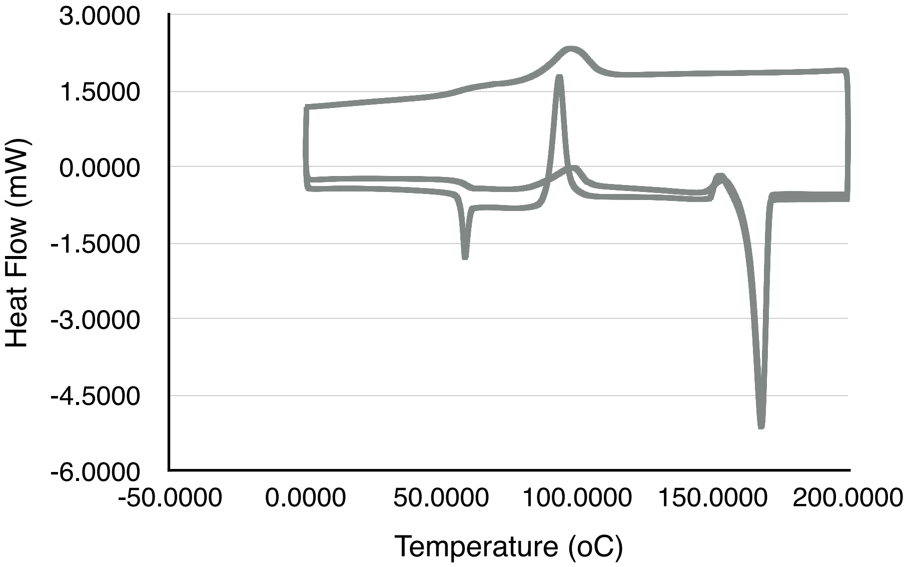


Fig.14: DSC of PLA with addition of 5% coffee spent at ramp 5 °C/min.

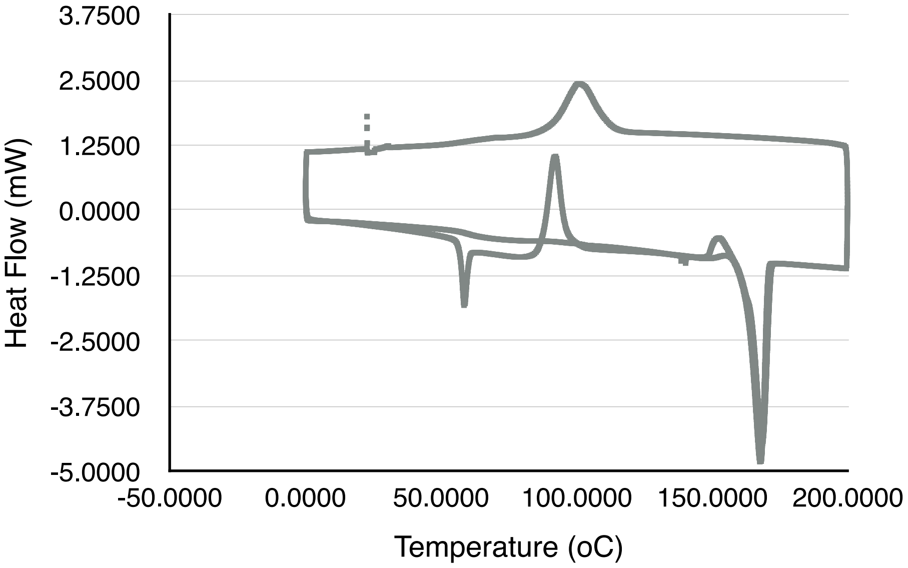


Fig.15: DSC of PLA with addition of 7.5% coffee spent at ramp 5 °C/min.

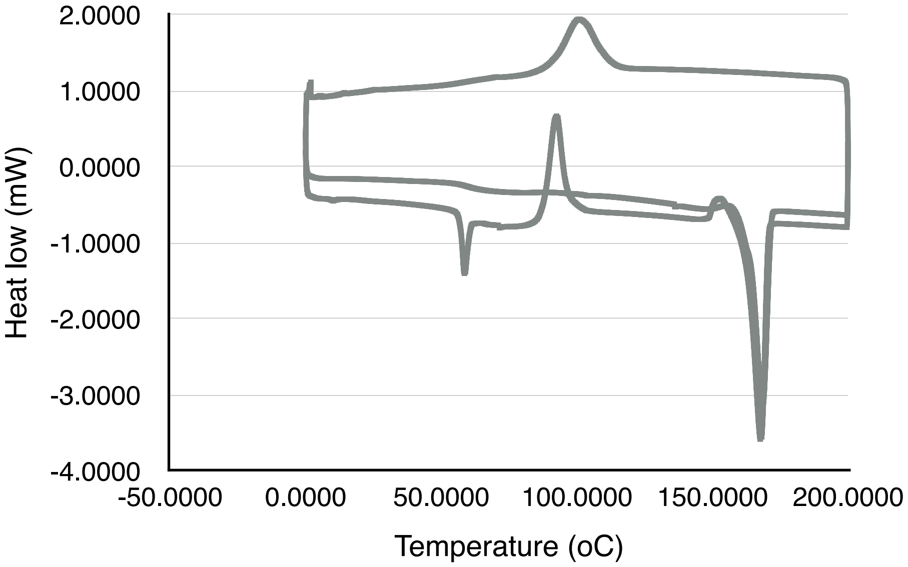


Fig.16: DSC of PLA with addition of 10% coffee spent at ramp 5 °C/min.

4.2 Differential Scanning Calorimetry (DSC) ramp 10 ^{o}C/min

The glass transition of pure PLA is 59.98 ^{o}C (Fig.18) as reported by Witzke and even with the modification or ramp, there is no difference of glass transition temperature between pure PLA, but there is a difference of less than one degree Celsius from Tg of the samples at ramp 5 ^{o}C/min compared to ramp 10 ^{o}C/min (Table 3).

Polymer	Tg (ramp 10	Tg (ramp 5
PLA	59.98	60.62
PLA + 5% coffee	59.97	58.78
PLA + 7.5% coffee	59.17	58.91
PLA + 10% coffee	59.18	58.60

Table 3: Glass transition temperature of samples at different heating rates.

As expected for a semi-crystalline polymer as PLA, the flat line appears on cooling again, indicating that there is no crystallization during the decreasing temperatures. However, in this case that the rate of heating was increased, there is no crystallization at cooling for none of the samples.

Besides, there was crystallization during heating and its temperature was higher compared to the samples at ramp 5 ^{o}C/min (Table 4).

Polymer	Crystallinization temperature (ramp 5	Crystallinization temperature (ramp 10
PLA	109.07	122.18
PLA + 5% coffee	93.49	99.68
PLA + 7.5% coffee	93.65	98.16
PLA + 10% coffee	92.42	95.93

Table 4: Temperature of crystallization of the polymer samples for different rates of heating.

It is known that crystallization depends on stereochemical regularity, placement of comonomers, branching and orientation, so it is possible to induce that the heating rate also influence the crystallinity of the polymer because at different heating rates in the same samples, there was different results.

At the rate of 5 °C/min the heating is slowly, therefore, the molecules have more time to rearrange and crystallize and reorganize their structure after melting. At the faster rate of 10 °C/min, the molecules agitation are more intense and rapid, causing the polymer to not form well organized crystallized structures after the "damage" caused by melting. These explains why there is no crystallization at cooling for ramp 10 °C/min as there is for ramp 5 °C/min.

The degree of crystallization was calculated using the theoretical foundation (Table 5).

Polymer	% of crystallization
PLA	5.3%
PLA + 5% coffee	13.27%
PLA + 7.5% coffee	16.52%
PLA + 10% coffee	19.29%

Table 5: Percentage of crystallization of PLA and treated samples.

The degree of crystallization of this treatment was higher than for the lower heating rate (Table 2).

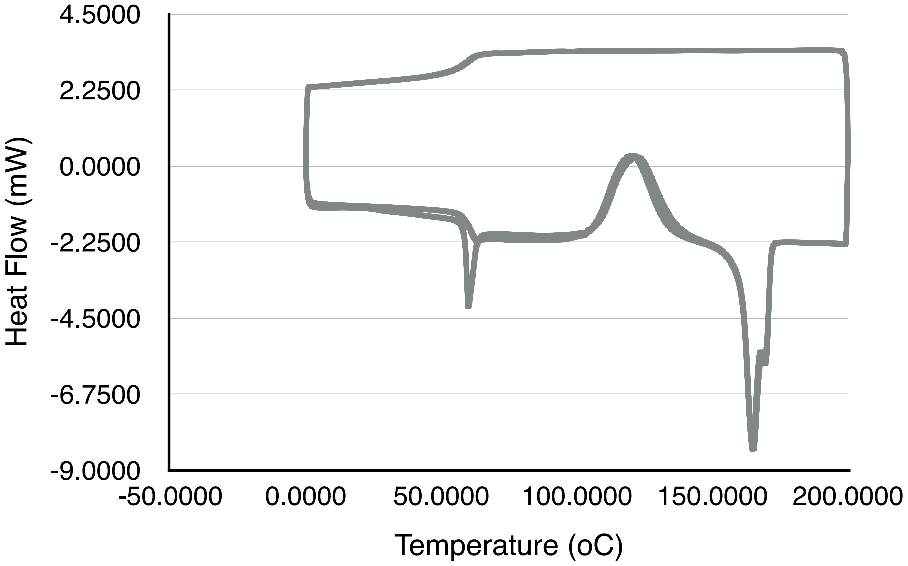


Fig 17: DSC of Pure PLA at ramp 10 °C/min.

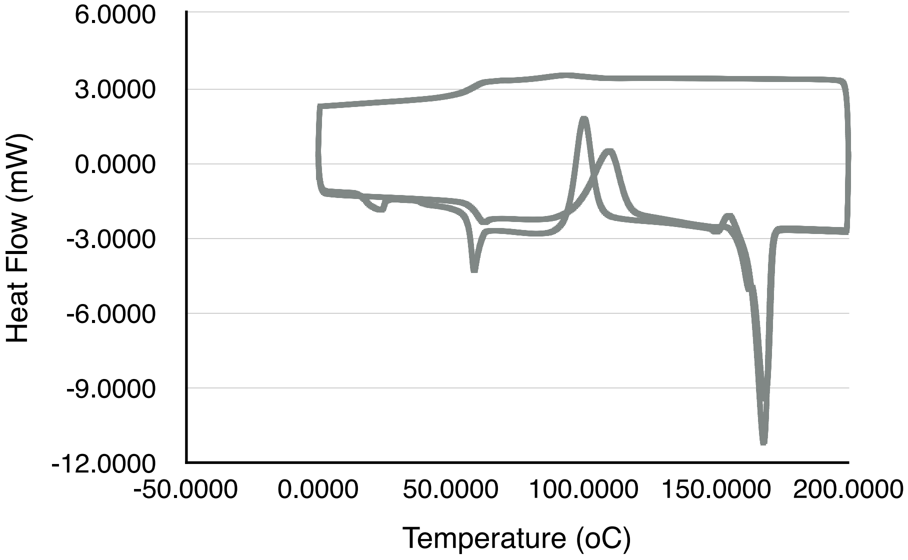


Fig 18: DSC of PLA with addition of 5% coffee spent at ramp 10 °C/min.

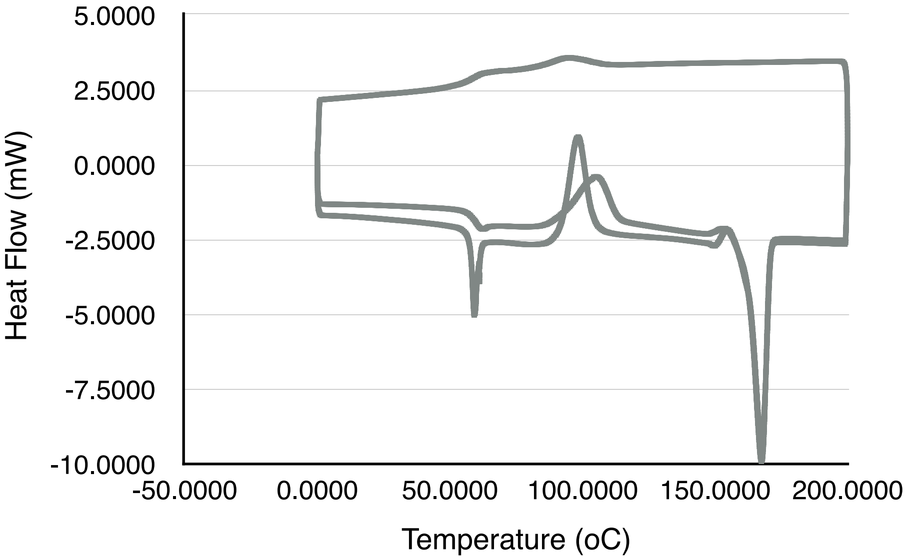


Fig 19: DSC of PLA with addition of 7.5% coffee spent at ramp 10 °C/min.

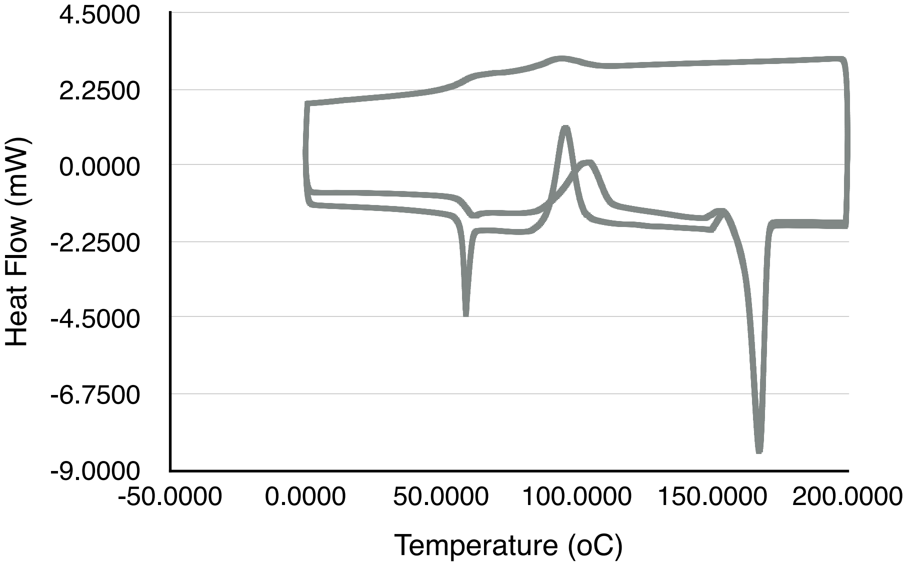


Fig 20: DSC of PLA with addition of 10% coffee spent at ramp 10 °C/min.

5 CONCLUSION

The addition of different amounts of coffee spent in poly(lactic)acid presented noticeable results related to the crystallinity of the material. It is possible to conclude that as the samples are more crystalline than pure PLA, their barrier properties were enhanced, their opacity was increased gradually with the amount of coffee added, the tensile strength was increased too.

More tests need to be done to learn about the biodegradability of these material, but certainly it will be less than the pretroleum-based polymer current available.

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