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Trabajo Fin de Grado

Estudio del reciclaje de polímeros para la impresión 3 D – Caracterización del PLA

Study of polymers recycling for 3D printing PLA characterization

Para acceder al Titulo de

Graduado/a en Ingeniería Química

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Abstract

Additive Manufacturing has been studied for more than 20 years. The technology creates new object adding the material layer by layer. Usually, plastics as PLA or ABS are used as raw material to feed 3D printers. However, environmental pollution made by plastics is a real problem to solve. For that reason, PLA is used more and more. It is biodegradable, thermoplastic, semi-crystalline and aliphatic. This research focus on PLA recycling. After the 3D printing, a mechanical treatment and re-extrusion are used in order to refeed the machine with PLA. This project explain how the processes affect PLA main properties. Degradation is visible after 3rd recycling cycle with 30% reduction of molecular weight and 50% reduction of viscosity. Beside it is a real problem after 5th cycle with 50% reduction of molecular weight and 80% reduction of viscosity. Because of time, there is not information of properties reduction for printing samples. Finally, we can affirm that main thermoplastics temperatures and working range temperature are the same in each sample no matter degradation in recycling and printing samples.

Keys words

Additive Manufacturing (AM), AM processes, Polylactic acid (PLA), polymers recycling, polymers test characterization.

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1. Introduction – Main issue

Nowadays, the used of 3 D printings (Additive Manufacturing) is expanding more and more. As the use increased, the quantity of polymer used as raw material step up (ABS, PLA, PVA and PC). Usually polymers for Additive Manufacturing are non-biodegradable or degrade slowly. They release toxic fumes when they are burned and they can contaminate food with dangerous chemical compounds. Thus, plastics are being an important environmental problem which concerns the whole world. The synthesis and the use of new biodegradables materials are so important in order to solve some environmental problems such as pollution or waste. PLA is a biodegradable polymer used in 3D printing. As the next goal is PLA recycling. The main problem is that there isn't any evidence of non-degradation during this process. This project is an analysis of polymers degradation during recycling processes, especially PLA characterization. In order to realise the research, the project is reacted to Mr. Fabio's A. Cruz thesis of PLA recycling. This thesis propose a way to recycle PLA for 3 D printing uses:

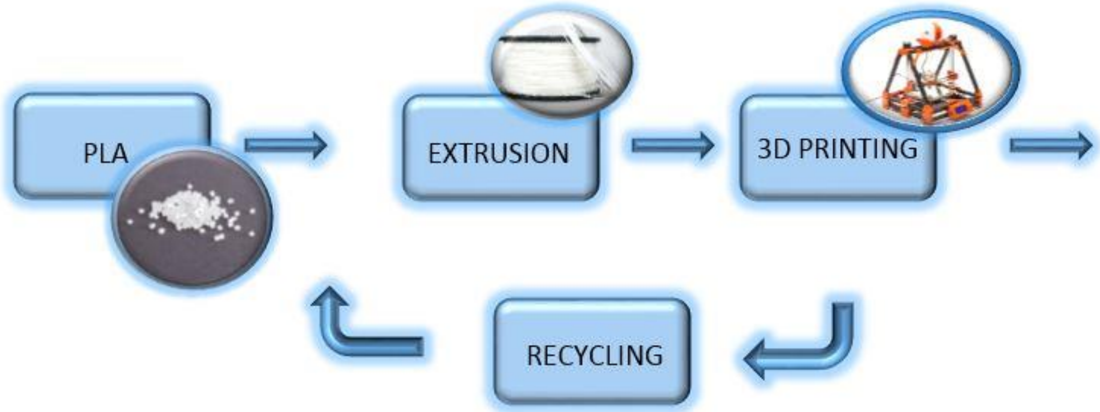


Figure 1. Scheme of PLA recycling for 3D printing.

The process stars with a drying in order to avoid degradation (water quantity less than 100 ppm) as we will explain later (Lim et al. 2008). Then the polymer is extruded so as to get a filament of PLA (temperature around the fusion temperature, 180ºC). This filament is used to feed 3D printer. Finally, the mechanical recycling consists in PLA breaking and drying in order to perform the re-extrusion and re-printing.

The document begins with a state of art where we introduce AM history and main properties, polymers definition, PLA characterization and recycling processes. Then, some typical analysis are proposed to test polymers degradation. We also exposed an experimental case where real PLA samples are tested. Finally, the protocol explain all required steps to follow the tests.

2. Objectives

The main objectives of this research are to characterize the degradation of PLA in Additive Manufacturing (3D printing) and mechanical recycling, and propose a standard protocol for polymers degradation evaluation. In order to achieve these goals, we are going to test some PLA samples to get the value of each properties related with degradation at each step.

3. State of the art

a. What is Additive Manufacturing

Additive Manufacturing Technology (AM), included all the processes of making 3D objects joining materials layer by layer (ASTM International F2792-12a 2010). It is known as three dimension printing, additive processes, additive techniques, additive layer manufacturing, layer manufacturing, rapid prototyping, and solid freeform fabrication (Zhai et al. 2014). Additive Manufacturing gets the information from a CAD file that is converted into STL format. The object is divided in slices in order to print it layer by layer (Guo & Leu 2013). It is the opposed process of subtractive manufacturing technology whose objective is remove undesired materials to achieve desired forms.

The technology has been improved and developed for three decades (Guo & Leu 2013). Additive Manufacturing principles are from photosculpture and topography. In 19th century photosculpture was born to create exact three-dimensional replicas of any object. In 1860 Frenchman François Willème photographed a subject placed in the middle of a circular room using 24 cameras around it. Then, he carved 24 cylindrical portions using each photography. All the portions together made the 3D photograph (Bourell et al. 2009). In 1890, topography was developed by Blanther. He suggested a new method to describe relief maps by using layers. The contour lines were printed and cut on a series of wax plates. Then, the wax plate were stacked (J.E. Blanther 1892). The actual process of stereolithography (it will be explained later) is based on the system proposed by Munz in 1951. In Munz's system, the object is scanned and a layer of transparent photopolymer is selectively exposed. The piston adds the fixing agent to create the next the next layer (Munz 1956). In 1968, Swainson proposed the use of two laser beams to polymerize a photosensitive polymer and produce a plastic pattern (W.K. Swainson 1977). In 1979, the first description of a power laser sintering is presented by Housholder (R.F. Housholder 1981). Between 1980 and 1990 the studies of additive manufacturing increased and new additive manufacturing processes appeared (Zhai et al. 2014).

AM technology allows a huge range of designs with complex geometries, reduce raw materials quantity used up to 75 %, and minimised the carbon footprint compared to conventional manufacturing technologies (Zhai et al. 2014). Besides, Additive Manufacturing follows the **Mass Customization Concept** that gives the facility to individualize and customize goods manufacturing (Fogliatto 2010). Mass Customization means produce and commercialize affordable goods and services with enough variety and customization that almost everybody could find what they need or want (Ii 2005). It includes two business practices: mass production which objective is manufacture low cost products by standardization of the processes; and craft production that assumes a high level of individualization in order to satisfice customer requirements (Blecker & Abdelkafi 2006).

Nowadays, AM technology is applied in different areas such as **aeroespacial design** (Thomas C L, Gaffney T M, Kaza S 1996), its objects are usually made of advanced materials (titanium alloys, nickel super alloys, special steels or ultrahigh-temperature ceramics) which are pretty difficult to manipulate, Additive Manufacturing processes reduce 80 % de cost and 70% de time needed to produce most of aeroespacial components [2]; **automobile industry,** to design and develop new products like F1 special gearboxes (Song Y, Yan Y, Zhang R, Xu D 2002); and **biomedicine**, personal medical implants made of biomaterials using AM technologies (Giannatsis J 2009).

Most of the time, Additive Manufacturing processes use **polymers** (ABS, PLA, PVA, PC) as raw material. Nevertheless, after intense developments Additive Manufacturing works with **metals** (steel, stainless steel, titanium, gold, silver)**, ceramics and composites** (materials made of two or more constituent materials with different physical or chemical properties) (Guo & Leu 2013). Even more, new application of Additive Manufacturing uses food as raw material such as chocolate (Last n.d.).

b. Types of Additive Manufacturing

Additive manufacturing processes are divided into four groups: **liquid**, **powder, solid sheet** and **filament** (ASTM International F2792-12a 2010) .

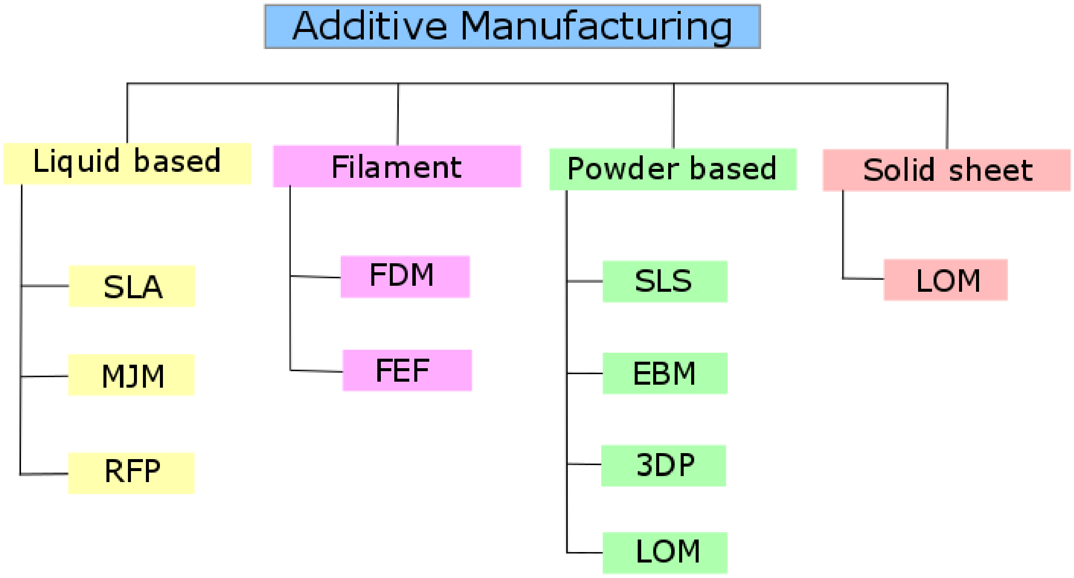


Figure 2. Three-dimensional printing processes (Guo & Leu 2013)

As shown in Figure 2, there are several different processes of additive manufacturing available, each appropriate for different materials and requirements, the most important techniques are:

Stereolithography (SLA) is a liquid layer deposition(J.-P. et al. 1998). Liquid photosensible resin becomes into solid state using ultraviolet light. The photopolymer is disposed layer-by-layer while the platform of the system descends. Between layers, the object is scanned by the UV light (Brady A G 1997).

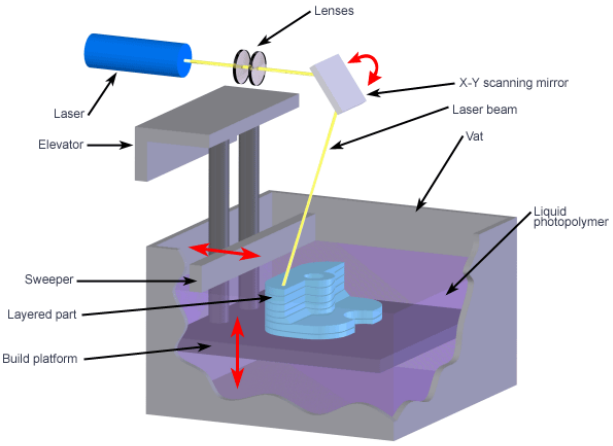


Figure 3. SLA machine example (CustomPartNet n.d.).

Multi-Jet Modeling (MJM) is classified as liquid process. MJM uses several nozzles disposed on an array to inject ultraviolet curable polymer. After each layer, platform descends to continue with the next layer (Chua C K, Leong K F 2010).

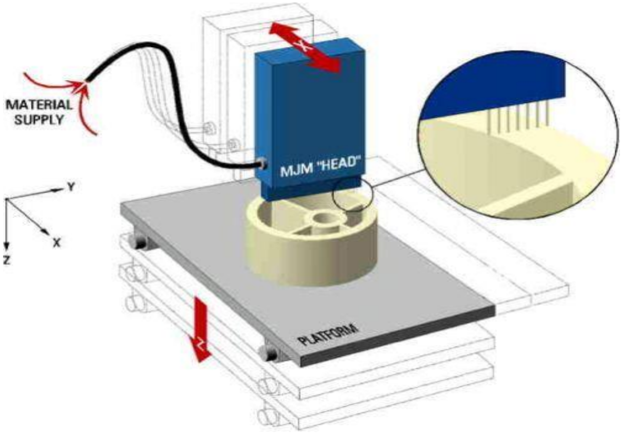


Figure 4. MJM machine example (CustomPartNet n.d.).

Rapid Freeze Prototyping (RFP) is a liquid additive manufacturing process. It is based on keeping the temperature level of the system below the water's freezing point. The water is injected by the nozzle on the surface. Once the water becomes ice, the nozzle starts with the next layer (Liu Q, Sui G 2002).

Selective Laser Sintering (SLS) is in the powder category. The process is focused on the application of material in powder form and selective formation of the part by using a heat source to make each layer. In this case, the heat source is a laser beam. The laser beam scans the cross-sections on the surface to produce the desired object designed before on CAD (Pham D T, Dimov S 1999).

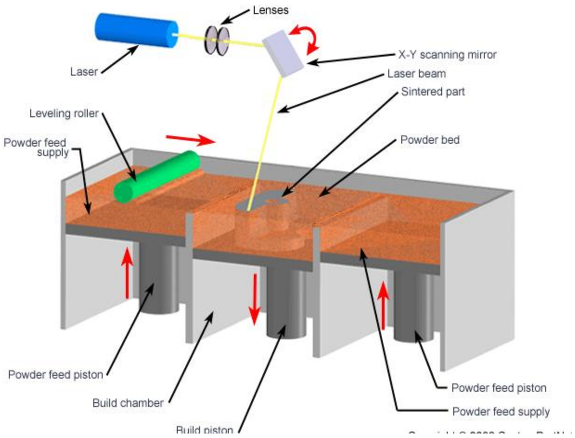


Figure 5. SLS machine example (CustomPartNet n.d.).

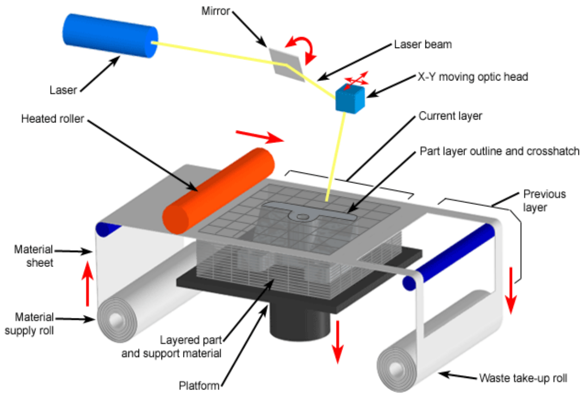


Figure 6. LOM machine example (CustomPartNet n.d.).

Laminated Object Manufacturing (LOM) is a process that includes additive and subtractive techniques to produce 3D objects. The process uses solid material sheets. A carbon dioxide laser cut the layer according to the CAD and the STL file. Then, hot roller compresses the sheet and activates a heat sensitive adhesive to continue with the next layer (Prechtl M, Otto A 2005).

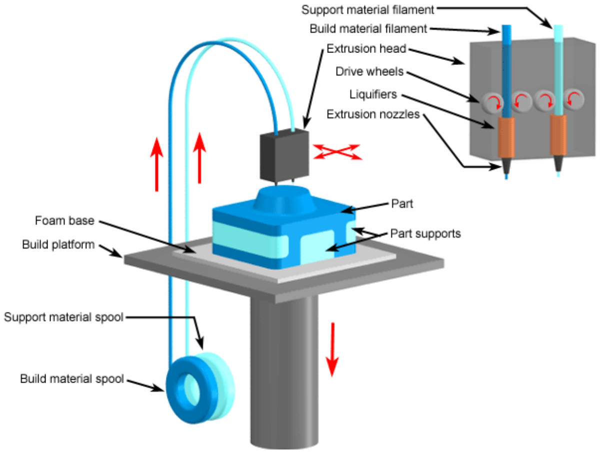


Figure 7. FDM machine example (CustomPartNet n.d.).

Fused Deposition Modeling (FDM) inside filament category is based on solidification by cooling. The polymer in filament form is heated in order to be melted and extruded. Then, the nozzle injects the exact quantity on the surface where the material is cooling until it solidifies. The newest system uses several nozzles with different material (Crump S S 1991).

i. Case of RepRap

RepRap means Self-Replicating Rapid-prototyping. **A RepRap machine is designed to be able to manufacture most of its own parts required to build a copy of itself**. Conventional rapid prototypers use Fused Deposition Modeling (FDM) , it utilises a filament of thermoplastics polymers to print de 3D objects (Jones et al. 2011).

There are some statements about RepRap:

- RepRap machines can produce its own parts to conform a new machine who will works as good as the original. Otherwise, the machine needs help to be assembled. **Self-Replicating is different from self-assembly** (Bailard et al. 2007)**.**

- **RepRap is an Open Source project** (Bailard et al. 2007). Usually, patent protects technologies and processes; anyone who desire to use techniques must pay a license. However, open source means that documentation of the project can be accessed, utilised, modified and redistributed by everyone (Holland, D, O'Donnell, G., Bennett 2010). Every detail of technical information is on Internet, thus everyone can download the information and build their own Rep Rap machine using the require parts from anywhere they prefer. There is not restriction to modify the technology, and anyone with a RepRap can produce another RepRap. Nevertheless, everything designed or created from a RepRap machine should be licensed in the same way (open course license), so many design improvements will be upload on the web and owners of old version machines will be able to upgrade it (A. Bowyer 2006).

c. Polymers

i. Definition and classification of polymers

Polymers are macromolecules made of many repeating subunits called monomers. These monomers are matched by covalent bonds where atoms share electrons being a strong union. The process to produce a polymer is known as polymerization reaction (Beltrán & Marcilla 2012). There are many types of polymers that we can classify as we can see in Figure 8.

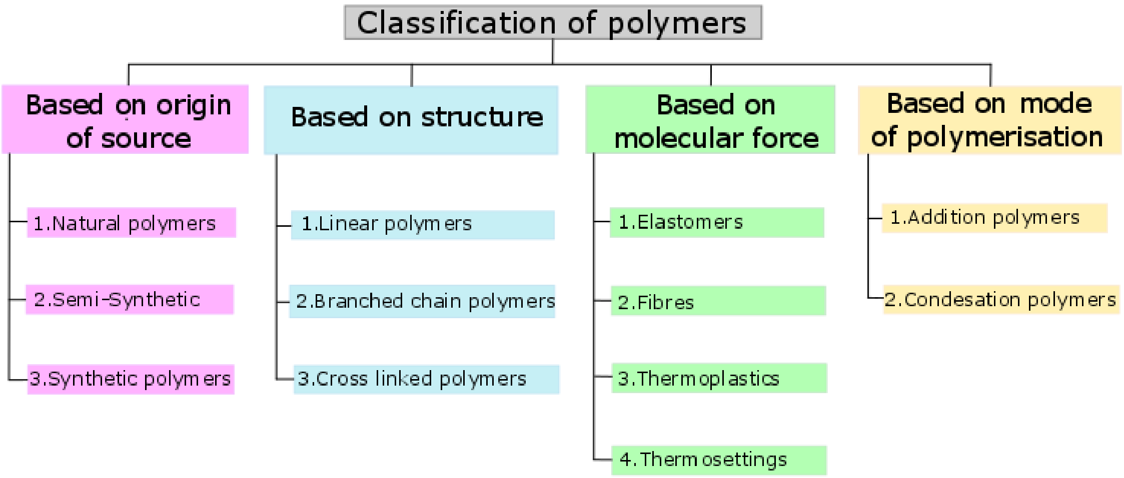


Figure 8. Classification of polymers according to American Chemistry council.

According with Figure 8, the description of each polymer are the following.

Some polymers can be found in the environment (called **natural polymers** or biopolymers). Besides polymers can be modified in order to get different properties (**semi- synthetic or synthetic polymers**) (B. Ramos 2007).

If we attend to the way of monomers are held we can difference: **linear polymers, branched chain polymers, and cross linked polymers**. Their shapes are shown in figure 9.

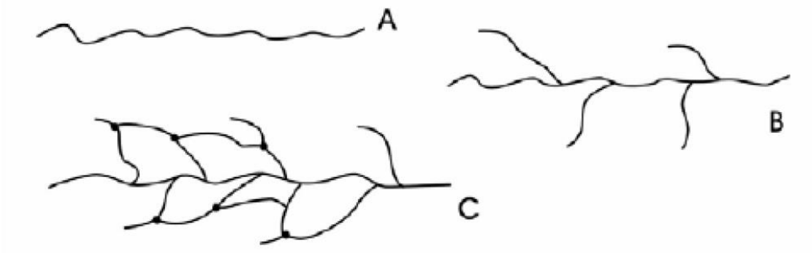


Figure 9. Polymers classified by their structure.
A: linear polymer; B: branched polymer; C: cross linked polymer (B. Ramos 2007).

Thermoplastic polymers are really important in Additive Manufacturing. The reason is that thermoplastic monomers are held together by weaker intermolecular force that other polymers. Thus they **are sensitive to temperature**, when thermoplastic polymers are heated they become viscous liquid, and when they are cooled become hard**. They can be formed and deformed in so many shapes** (Muzzy 2000). Some thermoplastics examples are Polyethylene, Polypropylene, or Polyvinyl Chloride (PVC). However, **thermosetting polymers solidifies irreversibly when they are heated**. It happens because there is a high degree of cross-linking between polymer chains that restricts the movement of the chains (Theriault et al. 1997). Polyurethanes, Epoxies, Unsaturated Polyester and Phenol Formaldehyde are some thermosetting polymers examples**. Elastomers**, known as rubber**, have flexible chains with weak intermolecular forces that produce a reversible and immediately response to a deformation** (Gananou 2013). An elastomer will undergo an immediate, linear and reversible response to high strain to an applied force. it is important their mechanical response, not their chemical structure (Shanks & Kong 2012). **Fibre polymers are important in textile sector.** Their chain is disposed in a straight line and they have a crystal structure. Thus it is easy to make threads (Carrasquero 2004). The most important fibre polymer is nylon.

Finally, polymers can be classified according their synthesis reaction. When monomers are joined together without losing atoms they produce an **addition polymers**. In **condensation polymerization**, a small portion of the monomer molecule is not incorporated in the final polymer (Roberts, John D. and Caserio 1977).

ii. Biopolymers

1. Definition

Biopolymers are a long molecules of repeating chemical blocks found in nature. They are produced by organisms and are biodegradables (low environment footprint). It exist three main groups: polysaccharides (made of sugars), proteins of amino acids, and nucleic acids of nucleotides. Its importance is due to environmental benefits which increase the interest in composite manufacturing made of natural fibers (Van De Velde & Kiekens 2002). Nowadays, plastics are used for a wide range of applications, increasing problems of waste and toxic emissions. Biopolymers have similar properties than plastics and they are eco-friendly (Visch 2001).

2. Importance of polylactic acid (PLA)

Polylactic acid (PLA) is a biodegradable polymer made of renewable raw material (such as corn and sugar beets) and it is an alternative to petrochemical plastics (Drumright et al. 2000). PLA is colorless, semi-crystalline, glossy, **aliphatic** (non-aromatic compound), rigid **thermoplastic** and it has got similar properties than polyethylene (PET) (Xiao et al. 2006). It has got several applications such as biomedicine, pharmaceutical solutions, fibers, paper coating and conventional large scale polymer uses (PLA is also used in 3D printing instead of ABS) (D. Garlotta 2002).

PLA is a homopolymer made of lactic acid monomers. It is a simple chiral molecule. That means there is another molecule which composition is identical but its space disposition is different. There are two enantiomers (two mirror images of a chiral molecule), also known as two stereoisomers. They are named L-Lactic acid and D-Lactic acid, and they rotate polarized light in opposite directions (Lasprilla et al. 2010). Figure 10 shows the optical differences between L-Lactic acid and D-Lactic Acid.

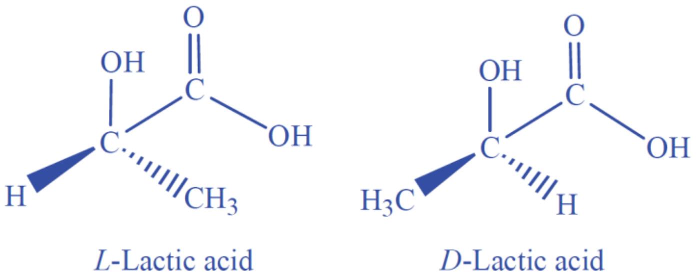


Figure 10. Lactic Acid enantiomers (Lasprilla et al. 2010).

The synthesis of PLA has two steps, it stars with lactic acid production, and it finishes with the polymerization (Avérous 2011). Lactic acid can be produced commercially by fermentative (sugars and starches become into lactic acid or chemical synthesis after a bacteria fermentation) or chemical synthesis (Lasprilla et al. 2010). Then, there are two reaction mechanisms to produce PLA: direct polymerization of lactic acid and ring opening polymerization (ROP) of the cycle lactide dimmer (D. Garlotta 2002).

Direct polymerization is based on continuous condensation. Lactic acid has the two necessary groups for polymerization: hydroxyl group (-OH) and carboxyl group (-OOH). During the condensation the molecule will lose some atoms to produce water (figure 11).

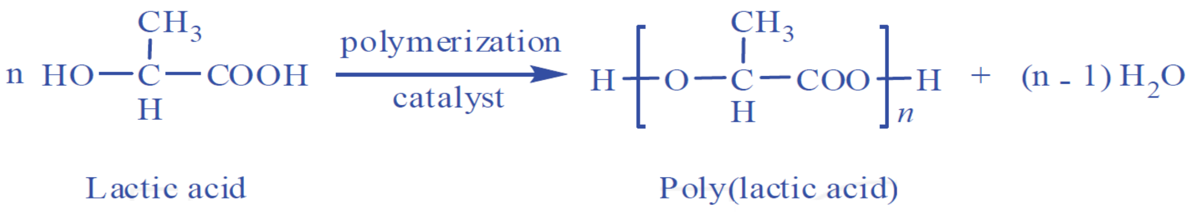


Figure 11. Direct polymerization reaction (Xiao et al. 2006).

In order to keep producing PLA is important to remove continuously the water formed during the polymerization because it is equilibrium reaction (Marques et al. 2010). It involves solvents under high vacuum and temperatures (Gupta et al. 2007). Higher reaction time is required and **the PLA produced is a polymer of low molecular weight** (Lasprilla et al. 2010).

Ring opening polymerization is not a condensation polymerization thus there is no need to remove water (Porter 2006). Cargill Dow LLC has capitalized on the ROP of lactide to produce about 300 x 106 lbs/year of PLA. The process stars with a condensation of lactic acid to produce a low molecular weight pre-polymer, then lactide is produced by catalyst with tin **(**selective cyclization). The mixture is purified by vacuum distillation. Finally, PLA is produced by catalyst. **Ring opening polymerization produce PLA with controller molecular weight** but It needs a strict purity of lactic monomer (Gupta et al. 2007).

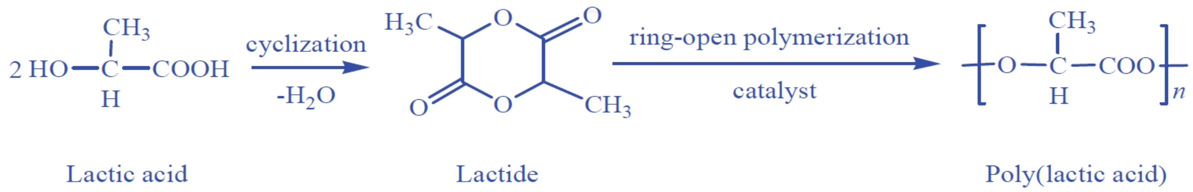


Figure 12. Ring opening polymerization reaction (Xiao et al. 2006).

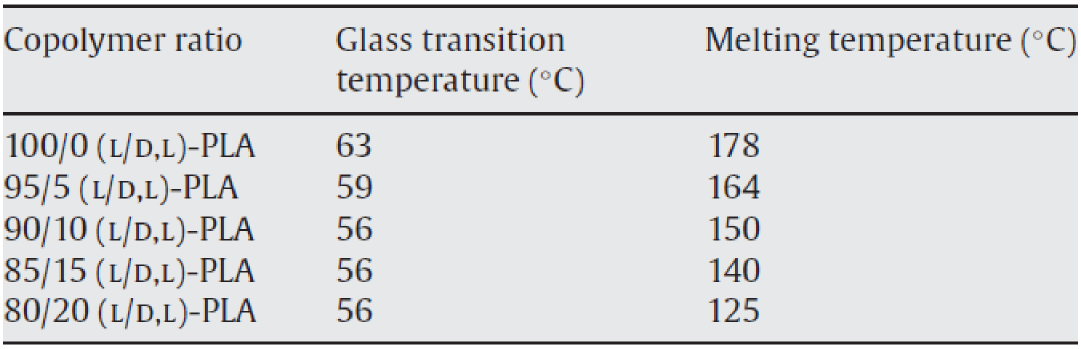
Physical, chemical, mechanical and rheological properties of PLA depend of optical purity and molecular weight (Drumright et al. 2000). Enantiomerically pure PLA is semi-crystalline with glass transition temperature (Tg) of about 55ºC (Södergård & Stolt 2002). When polymer is heated at more than 55ºC, it becomes softer, decreases density, hardness and rigidity. It is an intermediate state between the molten and rigid states. Glass transition temperature value increase with the molecular weight (until 60ºC). Besides, PLA monomers affect the glass transition temperatures. Higher quantity of L-lactic acid increase Tg, PLA with 100, 80, 50% of L-lactic acid, it glass transition temperature is 60.2, 56.4, and 54.6 ºC respectively. Moreover, PLA made of L-lactic acid has higher Tg than PLA made of d-lactic acid (Lim et al. 2008). Each glass transition temperature can be estimate with equation 1:

Equation 1. Glass transition temperature formula where T∞g is the Tg at the infinite molecular weight (58 ◦C) , K is a constant representing the excess free volume of the end groups for polymer chains ((5.5–7.3)×104), and Mn is the number average molecular weight (Jamshidi K, Hyon S-H 1988).

$$T_g = T_g^{\infty} - \frac{K}{Mn}$$

Melting point is also affected by optical composition. Melting point for enantiomerically pure PLA is 180ºC (Lim et al. 2008), over this temperature the polymer becomes a viscous liquid. Table 1 shows how temperatures value change with the optical composition of PLA:

Table 1. Glass transition temperature and melting point values for different optical composition (Lim et al. 2008)



Copolymer ratio	Glass transition temperature (°C)	Melting temperature (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (L/D,L)-PLA	59	164
90/10 (L/D,L)-PLA	56	150
85/15 (L/D,L)-PLA	56	140
80/20 (L/D,L)-PLA	56	125

Tg and Tm fix the working range temperature for each PLA. Knowing glass transition temperatures and melting point it is possible to identify the optimal application of each type of PLA. The problem is that high temperatures produces a thermal degradation (an important change of initial thermal properties) of polymers (Grupo de Polímeros y Reactores de Polimerización del INTEC (UNL-CONICET) 2010). Thermal degradation is due to: hydrolysis, oxidative (random main-chain scission) and intermolecular and intramolecular transesterification (process of exchanging the organic group of an ester with the organic group of an alcohol) (Södergård & Stolt 2002). The most important thermal degradation cause is hydrolysis. The water molecules in touch with the polymer gets into the PLA structure. It swells the polymer and finally it breaks the hydrogen bonds (attractive force between electronegative atoms and hydrogen atoms). Thermal degradation starts over 200ºC (Kopinke FD, Remmler M, Mackenzie K, Moder M 1996). Thus polymer must be dried (temperatures between 50-100ºC) to prevent the hydrolysis (less than 100ppm) (Lim et al. 2008).

PLA specific heat capacity is 1800 J/Kg K (J. A. Brydson 1999). Pure PLA density is 1.25 g/cm^3 (D.R. Witzke 1997). But density is function of temperature, and it can be approximate with Witzke formula (equation 2):

Equation 2. Witzke formula for PLA density where thermal coefficient of expansion is $\alpha = 7.4 \times 10^{-4}$ ºC^{-1} *and* $\rho_{(150°C)} = 1.1452$ g/cm^3 (D.R. Witzke 1997).

$$\rho\ \left(\frac{g}{cm^3}\right) = \frac{\rho_{150ºC}\ \left(\frac{g}{cm^3}\right)}{1+\propto_1\ \ (T\ (ºC)-150)}$$

PLA rheological properties are also dependent on temperature, molecular weight and shear rate (Lim et al. 2008). The viscosity is around 500-100 Pa s to high molecular weight PLA, and it has a non-Newtonian behavior (pseudoplastic). However, low molecular weight PLA shows Newtonian behavior (Cooper-White JJ 1999).

It shows a good mechanical strength (40 kN-m/kg) (J. A. Brydson 1999), high Young's modulus (3.5 GPa) (J. A. Brydson 1999), thermal plasticity and has good processability (Xiao et al. 2006).

During the project, the polymer used is “ingeo Biopolymer 4043D” from “Nature Works LLC” which properties are shown in table 2.

Table 2. . Main properties of PLA from Nature Works LLC (Nature Works 2014).

Properties	Value		ASTM Method
Density	1,24 g/cm^3		D1505
Tensile Strength	MD	16 kpsi	D882
	TD	21 kpsi	D882
Tensile Modulus	MD	480 kpsi	D882
	TD	560 kpsi	D882
Elongation a Break	MD	160 %	D882
	TD	100 %	D882
Elmendorf Tear	MD	15 g/mil	D1922
	TD	13 g/mil	D1922
Spencer Impact		2,5 joules	
Melting Point		145-160 °C	D3418

Note: MD (polymer orientation in machine direction); TD (polymer orientation in transvers direction).

d. Recycling of Polymer

Since the first industrial scale production of polymers appeared in the 1940s (Al-Salem et al. 2009), the consumption of polymers increased drastically (Hamad et al. 2013). The current society uses plastics in their daily lives (over 50% of all Europe’s goods are packaged in plastics, and the global plastic production increased 500% over the last 30 years (Kreiger et al. 2014)) in many applications (mulches, greenhouse, films, cover, bags, …) (Europe & (APME). 2004). Furthermore, polymers are substituting other materials because they are lightweight, flexible and easy to process. However, plastic production implies a substantial environmental burden on land, water pollution (10-450 years to decompose in a landfill) (Rees 1980) and an important energy consumption (Rydberg 1995). Thus, this increase amount of waste plastic motivated the interest in plastic recycling and reusing.

There are two main ways to treat plastic solid waste: chemical and mechanical recycling (Mastellone 1999).

i. Chemical recycling

The term is used to call all advanced technology processes that change the chemical structure of materials (Al-Salem et al. 2009). In case of polymers, chemical recycling is a depolymerization process that recovers synthesis monomers or feedstock chemicals (Brandrup, J., Bittner, M., Michaeli, W. & G. 1996). It converts plastic materials into smaller molecules to reuse it as raw material of new petrochemicals and plastics (Mastellone 1999).

The main advantage of chemical recycling is the possibility of treating heterogeneous and contaminated polymers with limited use of pre-treatment (Scheirs 1998). Nowadays chemical recycling is important as a method of producing fuel fraction from plastic solid waste (Al-Salem et al. 2009).

Some typical chemical recycling processes are: pyrolysis (thermal cracking of polymers in inert atmospheres), gasification (thermal cracking in the sub-stoichiometric presence of air usually leading to CO and CO2 production), and hydrogenation (hydrocracking) (Ahrenfeldt 2007).

ii. Mechanical Recycling

It is known as physical recycling because it does not modify chemical properties of polymers (Hamad et al. 2013). It recovers clean plastics: polymers are shredded and then processed and compounded to reuse it (Hamad et al. 2013). It is the recycling technique most used in Europe (used for the 50,1% of total plastic recycled in Western Europe in 2002), and it is an economic and viable route for plastic recovery, especially for foams and rigid plastics (Europe & (APME). 2004). The main problems are the degradation of polymers (chemical reaction of polymerization is reversible) and the need of heterogeneity (separation, washing and preparation of plastic solid waste are essential)(Al-Salem et al. 2009). The polymer contamination, the degradation or the separation difficulties make easier use plastics in energy recovery in instead of recycle them (Scheirs 1998).

There are some typical steps involved in mechanical recycling. The first step in mechanical recycling is a size reduction of the polymer to an easy manipulated form (pellets, powder or flakes) called cutting/shredding step. Then, impurities and different types of polymers are separated, sometimes based on density differences. The polymer should be washed and dried. Finally, the plastic is extruded and pelletized if it is necessary (Aznar, M.P., Caballero, M.A., Sancho, J.A., Francs 2006).

3. Methodology – Protocol of characterization of degradation

a. Definition of degradation

Degradations (known as ageing) means a change of initial properties of polymers (chemical, physical or thermal properties) because of external factors such as the weather, the light or some acids. Most of the changes are physics and the reason is a chemical reaction who brakes the main carbon chain decreasing the molecular weight and the chain length (Gabriel Jaime Pelaez Arroyave 2012). Biodegradation is the only desired change however, PLA is sensitive to moisture and heat because of the presence of weak hydrolysable blonds. Thus its properties (especially mechanical and rheological) are extremely sensitive to stocking, processing, and use conditions (V. Speranza, A. de Meo 2014). In order to check the degradation of PLA during de impression 3D and mechanical recycling in this project, different test are used (TGA, DSC, GPC, MFI and Rheometry).

b. Tests of characterization

The following test are used to know the main properties of polymers in order to relate it with degradation.

- **Differential Scanning Calorimetry (DSC)** is the thermal analysis **which goals are get the melt point of polymers, the glass transition temperature and the heat capacity** (study what happens to polymers when they are heated) (Iqbal 2013). It consists in two pans, the first one with a polymer sample (10 mg of material) and the second one empty (reference pan), situated on the top of heaters. The system should increase the temperature at the same velocity (usually 20º C per minute). However, to get the same temperature the heat needed will be different in each pan because one pan is empty and the other one has a sample. Thus it is connected to a computer to monitor the experiment in order to plot the values (x-axis temperatures are plot, y-axis the heat flow difference are plot which is the heat absorbed by the polymer). During the experiment, a flow of nitrogen gas is maintained over the samples to create a dry atmosphere who eliminates are oxidation of samples (Colby College 2007). Figure 13 resumes DSC systems.

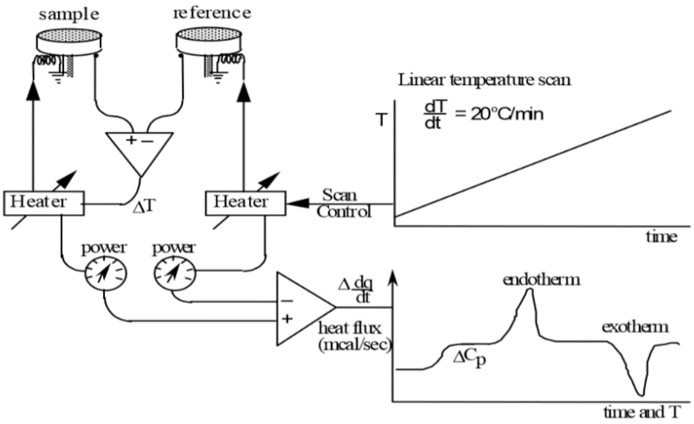


Figure 13. Differential Scanning Calorimetry diagram (Colby College 2007).

The typical DSC plot looks like figure 14:

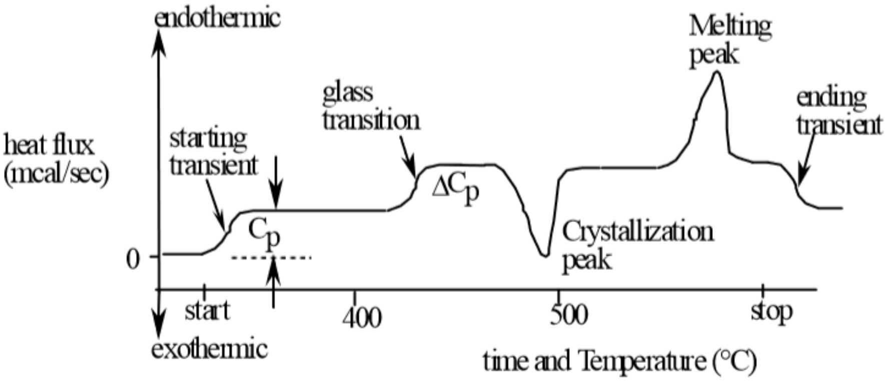


Figure 14. Typical DSC scan (Colby College 2007) *where important temperatures point for thermoplastics are shown.*

The working temperatures of this analysis should be selected according to the material properties.

- **Gel Permeation Chromatography (GPC) is a molecular weight analysis**. It is also known as Size Exclusion Chromatography (SEC). The test separates the molecules depending on the size to study the molecular weight and distribution (Cegarra 2009).

  There is a packed column made of porous material which acts as a sieve. The mixture of polymers cross the packing. Then, little molecules will be fixed in the tiny holes, while intermediate molecules will be half captured, and the bigger ones will be excluded (Cegarra 2009). A correlation can be made between size and molecular weight. Figure 15 shows a plot typical of logM against retention volume. Thus, knowing a calibration plot and retention volume of the sample, its molecular weight can be determined (Aglient.Technologies 2000).

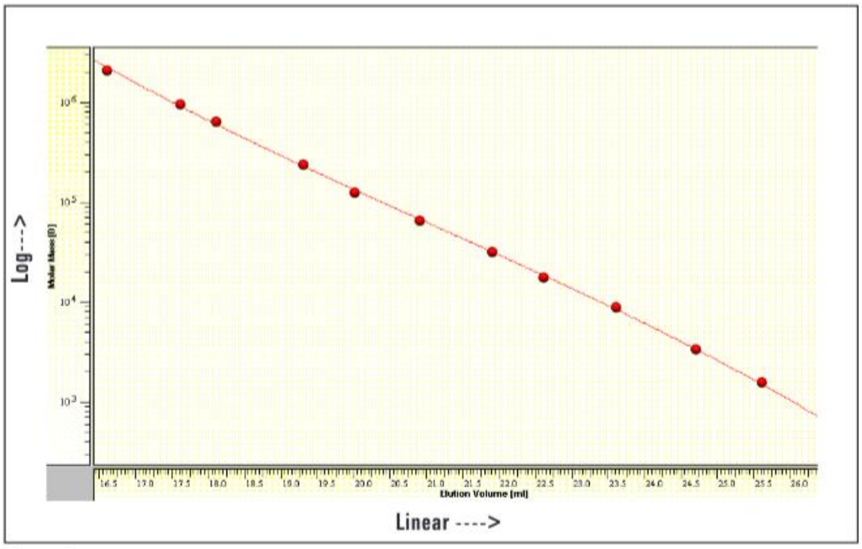


Figure 15. Typical GPC calibration plot.

At the end of the experiment, we obtain a graph (concentration vs time) where polymer distribution is shown. The first peak will represent the number of biggest molecules in the sample (total exclusion, they are too big to rest in the porous material) while the last peak will represent the smallest molecules (total permeation, small enough to get into the porous material) (Holding et al. 2011). The important results of GPC are number average molecular weight (Mn, statistics weight of all the chain in the polymer sample) and weight average molecular weight (Mw, it takes into account the molecular weight of a chain in determining contributions to the molecular weight average) and polydispersity (the measure of the broadness of a molecular weight distribution) (Cegarra 2009). The parameters can be calculate with the following formulas:

Equation 3. Formula to calculate weight average molecular weight where Ni is the number of molecules of fraction i, and Mi is the molecular weight of molecules of fraction i.

$$Mw = \frac{\sum NiMi^2}{\sum NiMi}$$

Equation 4. Formula to calculate the number average molecular weight where Ni is the number of molecules of fraction i, and Mi is the molecular weight of molecules of fraction i.

$$M_N = \frac{\sum NiMi}{\sum Ni}$$

Equation 5. Formula to calculate polydispersity index with molecular weight parameters.

$$\text{Polydispersity index} = \frac{\text{Mw}}{\text{Mn}}$$

- **Thermogravimetric Analysis (TGA) is a technique used to know the degradation of a material related with the increase or decrease of it mass.** It consists in a pan made of Alumina in order to tolerate high temperatures. The pan is supported by a precision balance. The machine heats or cools the sample during de experiment. Furthermore, a computer monitors the mass of a substance as a function of temperature or time in at controlled atmosphere (nitrogen or helium). It is important to control the gas purge. During each experiment, it is necessary select a range of temperatures and the heating rate (Widmann 2001).

Typical TGA thermal curve looks like Figure 16. The abscissa (X-axis) can be displayed as time or temperature and the ordinate (Y-axis) can be displayed as weight (mg) or weight percent (%). The decrease on TGA thermal curves indicate a weight loss and the onset temperature denotes the temperature at which the weight loss begins. However, it is important to repeat the experiment several times to denote and difference the experimental errors and extraordinary behaviour (PerkinElmer 1960). In each experiment it is important to specify the atmosphere used, the temperature program selected, the initial weight of the sample, the material, and the machine used (Widmann 2001).

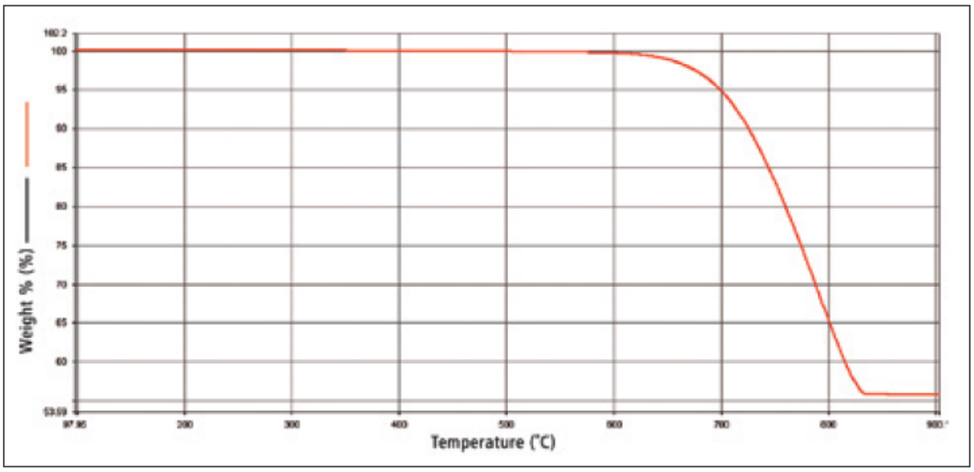


Figure 16. Typical TGA plot (PerkinElmer 1960). *The degradation temperature is the point where the step begins. Thus the work temperature for each material should be lower than this point.*

The first derivate of weight loss curve is useful to know the point of greatest rate of change on the weight loss curve as shown in Figure 17.

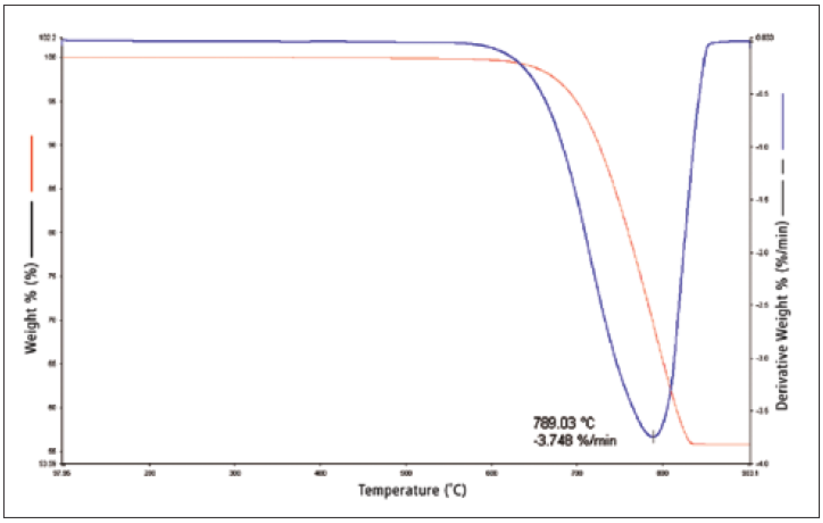


Figure 17. TGA thermal curve and first derivate plots. The minimum of the first derivate is the temperature of the maximum degradation.

- **Spectroscopy (NMR)** is known as nuclear magnetic resonance. **The test gives information to study the microstructure and the chain configuration of polymers.** It is important to know that many nucleus has spin and all nuclei are electrically charged. During the test, an external magnetic field is applied, so an energy transfer is possible between the base energy to a higher energy level inside the atoms. This energy transfer takes place at a wavelength that corresponds to radio frequency. When the spin returns to its base level, energy is emitted at the same frequency (Juan J. Iruin 1996). The signal is measured in order to get the NMR spectrum for the nucleus concerned. The technics is valid to know easily 20 different nucleus such as ^{1}H, ^{7}LI, ^{11}B, ^{13}C, ^{15}N, ^{19}F, ^{23}Na, ^{27}Al, ^{29}Si, ^{31}P, ^{195}Pt and ^{199}Hg (Belmonte 2004).

- **Melt Flow Index (MFI)** know as melt mass flow rate **is an analysis to measure how easy thermoplastic polymers flow**. It is used as indirect technique to know polymers viscosity because viscosity is inversely proportional of MFI.

  The procedure is explained in ASTM D-1238 and ISO 1333 standards. A thermoplastic sample is made fluid by a heater. Then, it is forced to flow out of a capillary die. The machine measures the quantity of material that flows out in 10 minutes through the capillary (g/10min) (Olsen n.d.). The index is function of pressure, capillary die diameter (the standard die is 2.0955 mm diameter and 8.000 mm in length) and viscosity. The larger the melt index value, the lower is its viscosity, and therefore, the average molecular weight of the polymer is lower. Higher molecular weight polymers will be more viscous and less will flow under the same conditions so the melt index will be a smaller number (Ken Anderson 2012).

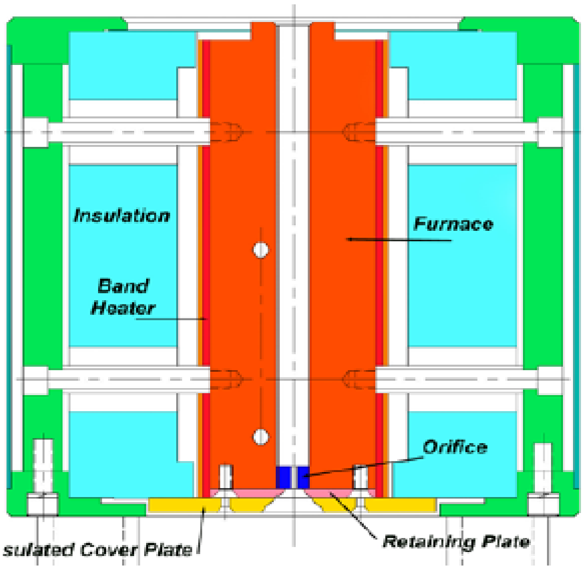


Figure 18. Melt flow index machine cross section.

Assuming that the polymer behave as Newtonian fluid, volumetric throughput follows Poiseuille's law:

Equation 6. Formula of Poiseuille's law where R is the radio of the die, L is the length of the die, µ is polymer's viscosity and P is the pressure.

$$Q = \frac{\pi R^4 \Delta P}{8 \mu L}$$

Equation 7. Polymer's mass formula where ρ is the density.

$$Mass = \rho Qt = \rho \frac{\pi R^4 \Delta P}{8 \mu L} t$$

Reorganizing:

Equation 8. MFI formula related with density, machine's parameters and molecular weight.

$$MFI = \rho \frac{\pi R^4 \Delta P}{8L \times KM^{3,4}} t$$

Thus we can confirm that MFI is also an indirect measure of molecular weight. That's the reason that MFI and GPC results should be explained at the same time.

- **Rheometer is a laboratory device to measure materials behaviour when a force is applied**. It is used with complex materials who cannot be defined by a single value of viscosity. Polymers behaviour has a viscosity and elastic component (Couarraze 2014).

  Samples are placed between two solid plates. One of them is immobile, while the other makes a rotatory shear movement. There is an oven around the sample and the plates in order to keep the fusion temperature of polymers. The force needed to make the rotation movement is the shear stress, while rotation velocity is the shear rate. Rheometer is connected to a computer to monitor the process. Besides, the software has some essential formulas to relate viscosity with known stress parameters. To sum up, molten materials are subjected to various deformation forces and stress is measured (GFR 2013).

  The software produce some graph to analysis how viscosity changes with shear rate in dynamics and steady experiment. It is important compare Rheometer results with GPC results in order to complete each other. The reason is that if the average molecular weight (results from GPC tests) increase, Newtonian viscosity raises (results from GPC). Thus if there is degradation, it will be shown as less average molecular weight and viscosity.

5. Experimental Case

Assuming that mechanical recycling does not affect chemical properties of PLA (the goal is to break PLA in small portions in order to feed the extrusion machine), the experiment is divided in two steps. The first part is about PLA recycling (green line in figure 19). It includes extrusion and mechanical recycling. The task is to take two samples of PLA in the first cycle (PLA virgin and PLA after the extrusion) and one sample of PLA in the following cycles (PLA after extrusion). The second part is about PLA printing (red line in figure 19). The task is to take one sample of PLA in each cycle (after 3D printing). In order to get a better idea of PLA degradation, the experiment includes five printing-recycling cycles.

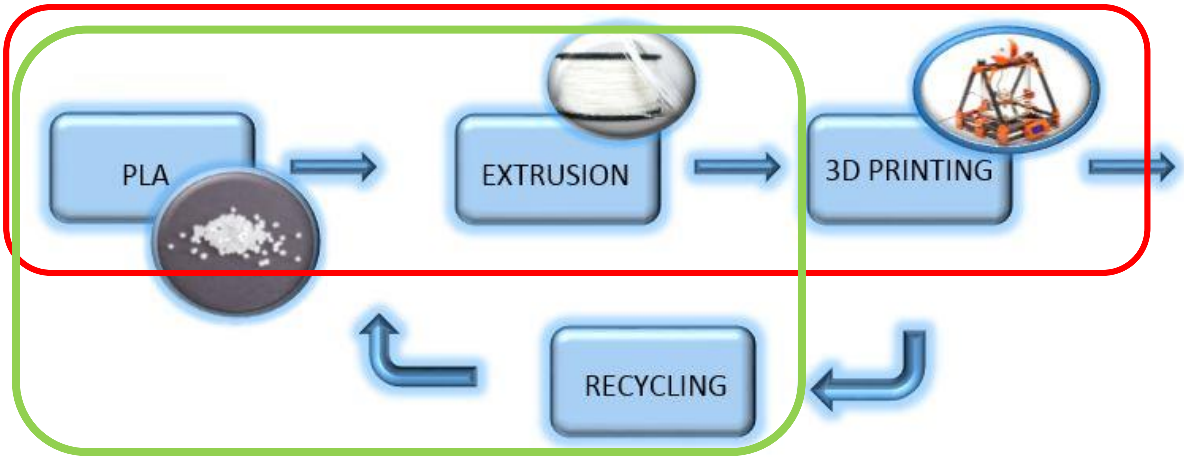


Figure 19. Process diagram divided in experimental steps. The red line belongs to the first part of the experiment where the test are used to know the main properties of PLA without recycling degradation. The green line belongs to the second part of the experiment where the test are used to know the degradation after some recycling cycles.

Once in the laboratory all the samples are analysed with the tests (DSC, TGA, PGC and MFI) explained before. At the beginning, it is necessary to do a simulation just to estimate the best operation conditions for PLA. We estimated that DSC should works from 25ºC (atmosphere normal temperature) to 225 ºC (higher that fusion temperature, 160ºC, but less than degradation temperature, 300ºC). In DSC analysis there are three segments. The first one it is to heat the PLA in order to clean the thermal historical (we will see the glass transition and the fusion). The second, which goal is to make PLA recrystallization and the last one which it is goal is to heat the PLA in order to get the real values of temperatures. The temperature range of TGA analysis estimated is from 30ºC to 500 ºC (typical range to estimate polymers degradation temperature). The working temperature of MFI is 180ºC (temperature closes to PLA fusion temperature). Finally, tetrahydrofuran solution is used for GPC, and rheometer is programed at 180ºC (temperature closes to PLA fusion temperature) with dynamic analysis at the beginning, and steady analysis at the end. It is important to notice that each sample is analysed 2-3 times in order to reduce the experimental error at the laboratory.

6. Results

At the beginning of the research, the steps was fixed: 5 samples of 5 PLA extrusion-recycling cycles and 5 samples of 5 PLA printing cycles. Five analysis for each sample should be realise (TGA, DSC, MFI, GPC and Rheology). However, due to several problems (TGA machines was broken, DSC capsules weren't enough, technician delayed and not enough time), we analysed less data than we would like to do. All the samples of printing were tested, but there wasn't enough time to make the analysis so they are added in appendix B in order to make the analysis later.

Without further delay and based on the hypothesis that printing and extrusion modify PLA properties the result of each test are the following.

a. Reference values

First of all, PLA virgin was checked in order to know the main properties. These values will be the reference to compare all the next results.

The TGA is important to verify that all the processes works in a well range of temperatures in order to avoid the thermal degradation. The range used to test PLA was 30ºC – 600ºC (typical temperature range to estimate polymers degradation). A pan made of alumina was used in order to support high temperatures, and a gas extractor was used so as to eliminate gases produced into the machine. Figure 20 shows the degradation graph achieved in the process (mass vs temperature). Degradation starts at 300ºC when PLA mass begins to decrease. Nevertheless, the most degradation point is at 370ºC (minimum of the first derivate of the curve). From 300ºC to 400ºC, we can see how the mass decrease with temperature incensement. We can conclude that **Additive Manufacturing, extrusion and drying temperatures rang (200ºC, 180ºC and 50-100ºC respectively) is under 300ºC so there is no risk of degradation because of work temperatures range.**

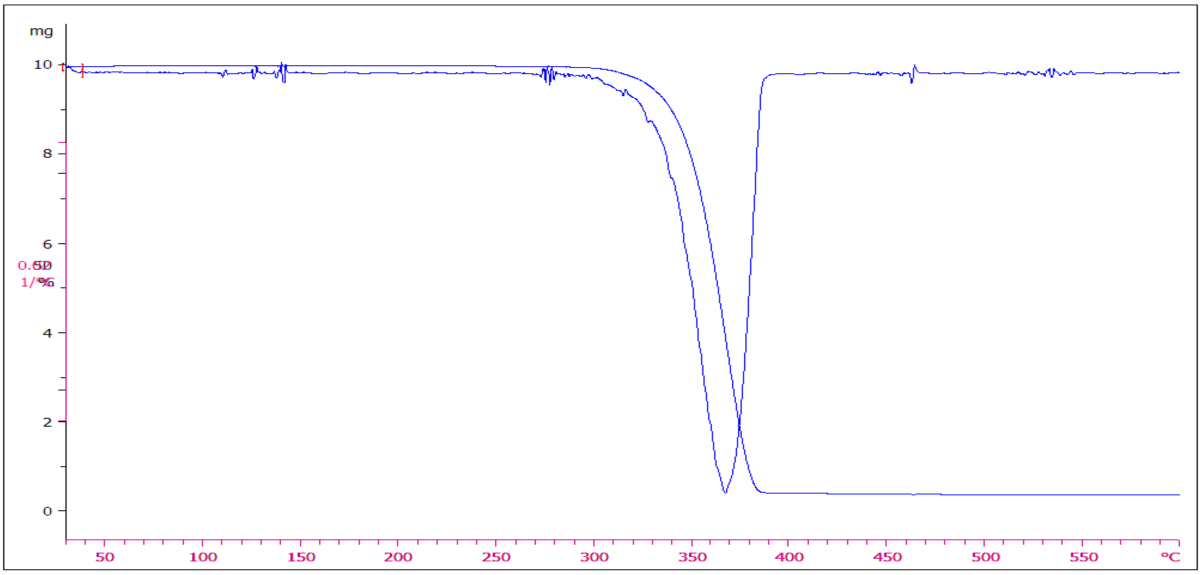


Figure 20. The graph shows the degradation of PLA virgin depending on temperature. From 30ºC to 300ºC there is not degradation (100% of sample is in the pan), and from 300ºC de degradation starts (reduce of sample mass in the pan).

Next test was **DSC**. The analysis is important to know the typical temperatures of thermoplastics. At the first time, the software was programed with **three segments: warming segment in order to clean the thermal history** (red line in Figure 23, from 25ºC to 225ºC with 10ºC/min) where glass transition and fusion should appear; **cooling segment to recrystallize the polymer** (from 225ºC to 25ºC with -10ºC/min), and finally the **warming segment in order to get the main information** (green line in Figure 23, from 25ºC to 225ºC with 10ºC/min).

As we can see in Figure 21, **in the last cooling segment it was impossible to discern the fusion of the polymer**. The reason is that there is not any crystal to make the fusion of. **Recrystallization didn't happen.**

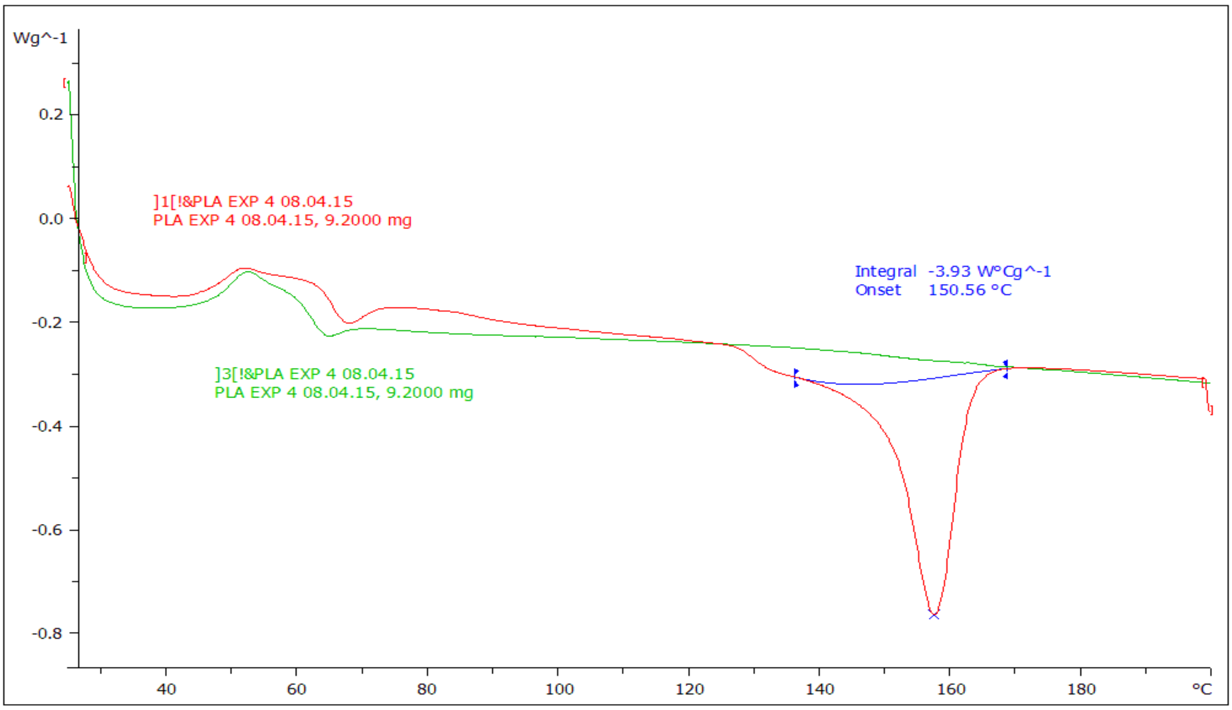


Figure 21. DSC diagram for PLA virgin: the red line is the first warming segment, and the green line is the second warming segment.

Therefore, knowing that typical PLA crystalize at 110ºC, **the software was reprogramed with four segments: warming segment** (from 25ºC to 225ºC with 10ºC/min), **cooling segment** (from 225ºC to 110ºC with -10ºC/min), **isothermal segment at 110ºC for half hour in order to make sure that polymer recrystallize, and finally warming segment** (from 25ºC to 225ºC with 10ºC/min).

Figure 22 shows the results of four segments. As we can see in the picture, the energy of crystal fusion in last warming segment (green line) is lower than energy in first segment (red line). If crystallization had occurred and thermal history hadn't been important, the energy would have been similar. Thus, we affirm that there is not recrystallization. The main reason is that during recrystallization, molecules should reorganize themselves into a regular structure; however, it is not easy to move PLA carbon chain, consequently PLA recrystallization is really slowly. **To sum up, it is not possible to observe recrystallization in the graph because there is not enough time to reorganize PLA molecules into regular structure, thus there is not recrystallization.**

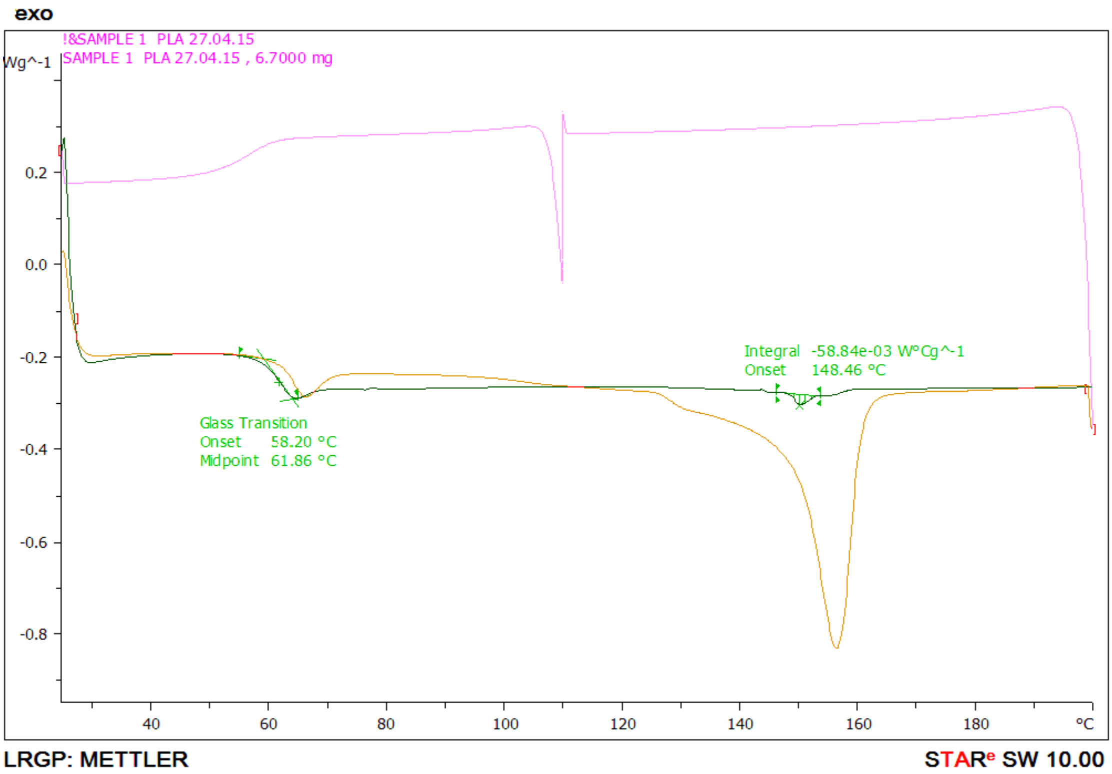


Figure 22. DSC diagram for PLA virgin with isothermal segment. The red line is the first warming, the pink line is the cooling and isothermal segments, and the green line is the last warming segment.

For that reason the following DSC test will be make with one warming segment. **Finally, according with DSC we can conclude that PLA virgin glass transition is at 58ºC (error $^{+}_{-}$1 ºC), crystallization is at 110ºCand fusion temperature is 148ºC (error $^{+}_{-}$1 ºC).**

MFI test was made in order to get a viscosity change idea over the processes. The machine was programed at 180ºC so as to make sure that fusion happens (according with DSC fusion temperature is 148ºC). The results of PLA virgin are englobed in table 3.

Table 3. Values of MFI measures for PLA.

Extrusion cycle	Measures (g)					Time (s)	Media (g)	MFI (g/10min)
0	0,357	0,373	0,373	0,393	0,38	60	0,3752	3,752

This value doesn't explain anything by themselves. However, it is important to compare this references values with MFI values for the next cycles in order to know how the degradation affects PLA viscosity (as it was explained before, MFI is inversely related with viscosity). Besides, MFI results are connected with GPC results.

With GPC analysis we obtained graph (concentration vs time) where we can see the concentration of molecules going out the column. The important thing is the first and the last peak. As we explained before, first peak is connected with bigger molecules that don't rest in the column, and the last peak is related with smallest molecules. It is really important the values of molecular weights (two of them: number and weight) and polydispersity of PLA virgin. The reason is that if there is any degradation after processes PLA chain will be break, so molecules will be smaller, thus the last peak on GPC will be increased and the first peak will be decreased. Speaking about parameters, molecular weight average will be decrease. Finally, if polymer is homogeneous polydispersity will be closer than 1 (1,00 – 1,20). After processing all the data, the main information is in table 4:

Table 4. Molecular weight and polydispersity for PLA virgin (Nature Works 2014).

PLA virgin	
Mn (g/mol)	85 000
Mw (g/mol)	110 000
I = Mw/ Mn	1,29

The results of steady rheology of virgin PLA were plotted in Figure 23 (apparent viscosity vs shear rate). Based in literature polymers used to shows a non Newtonian behavior so viscosity is not a unique value, it is should be a curve depending on shear rate. In the Figure 23 it is easy to see two different behavior of viscosity. The first part of the curve, it is almost a constant value which means a Newtonian behavior. However, in the last part of the curve there is a notable diminution of viscosity which means pseudoplastic behavior (Brazel 2012).

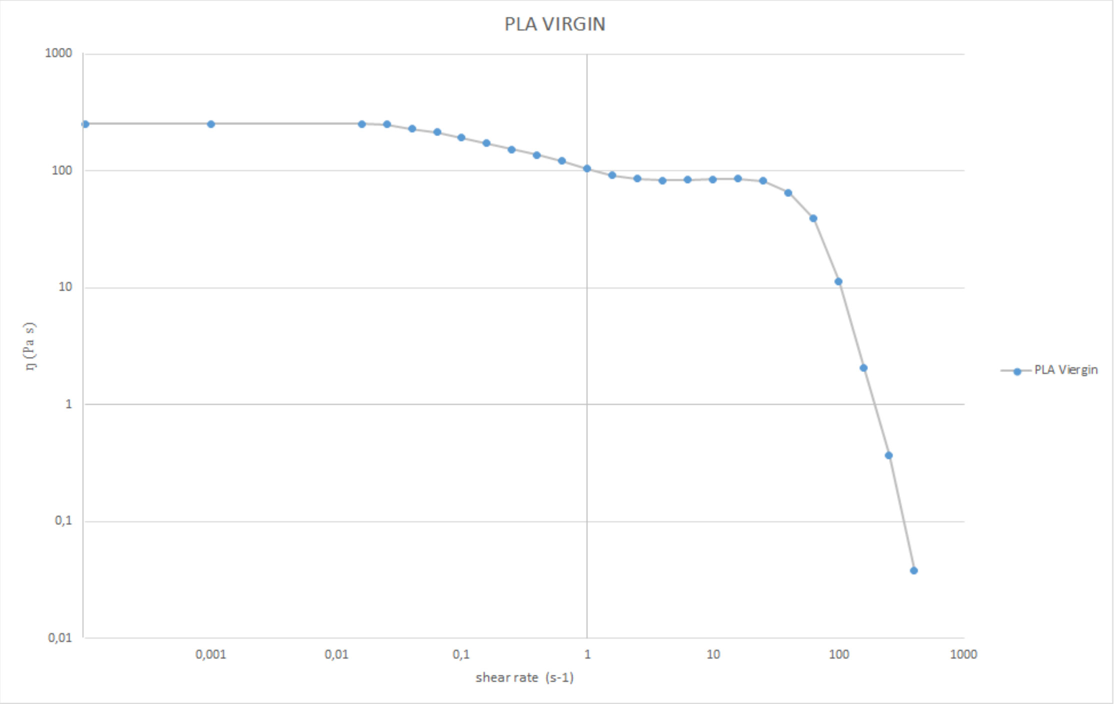


Figure 23. Rheological results for PLA virgin made at 180ºC.

Finally rheological dynamic results was obtained but because of time there weren't treatment, the main graph obtained are in Appendix B.

b. Recycling – Printing test values

We completed PLA recycling-printing cycle 5 times. As we explained before, we assume that mechanical recycling (the goal is to break PLA before extrusion process) does not affect PLA main properties. So we only took PLA samples after each extrusion process and after printing process. We tested all the samples (3 times each sample to reduce experimental error) and we compared the results with PLA reference values.

Checking literature, it is known that TGA is not an important test to analyze degradation in polymers. Nevertheless, samples of recycling and printing from the 1st cycle were tested. **As we can see in Figure 24, the result was exactly the same for all the samples. The degradation still starts at 300ºC, and as Figure 25 shows, maximum degradation temperature is at 370ºC for all the samples (PLA virgin, 1st printing and recycling).**

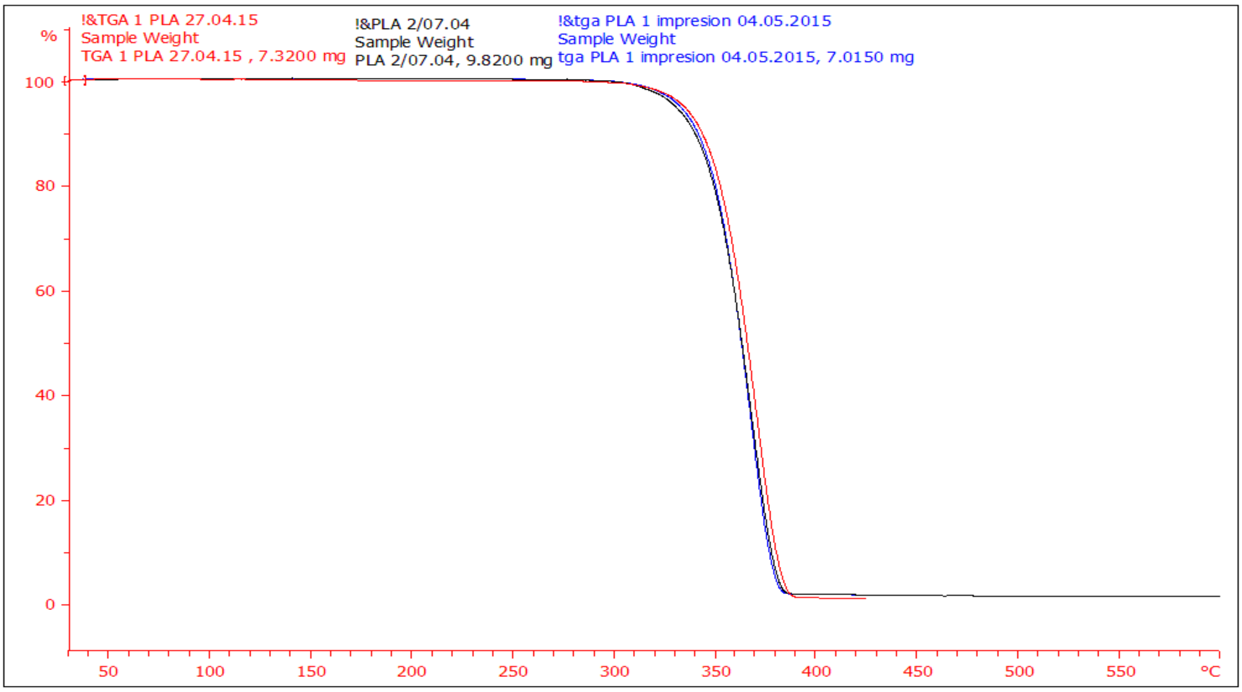


Figure 24. TGA diagram (% mass vs temperature) where data from PLA virgin (red line), first printing (black line) and recycling (blue line).

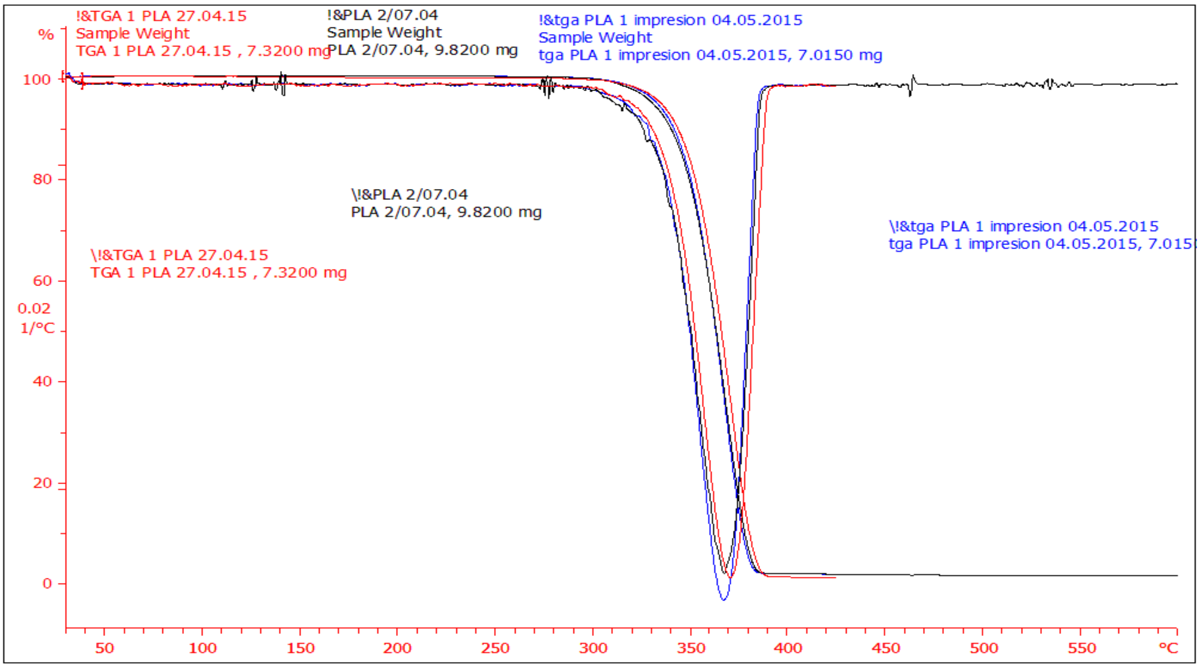


Figure 25. TGA diagram with maximum degradation point for PLA virgin (red line), first printing (black line) and recycling (blue line).

In the same way, DSC was checked just for samples of 1st cycle. The results are shown in Figure 26 where each curve was exactly the same. **There is any change. For all the samples, glass transition temperature is 47ºC, and fusion temperature is 147ºC. Thus there is not hermal degradation who produce a change in main temperatures.**

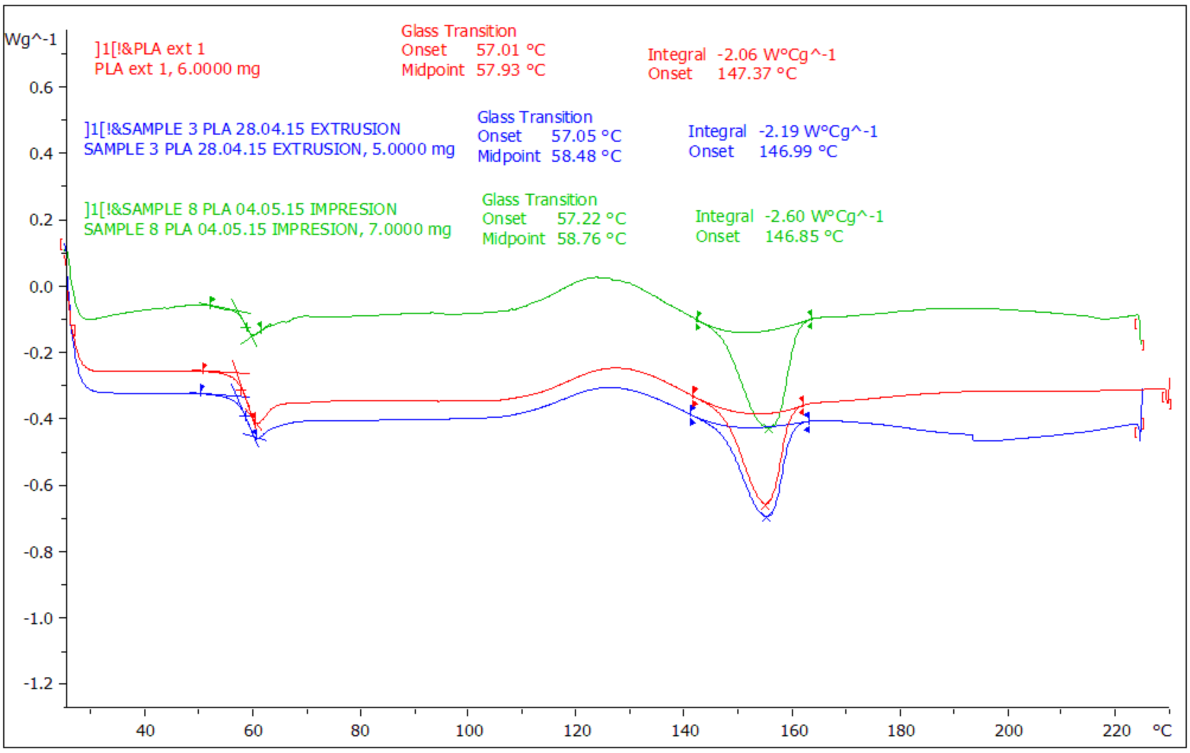


Figure 26. DEC diagram for PLA virgin (red curve), 1st recycling (blue curve) and 1st printing (green curve).

Figure 27 shows all the results of PLA extrusion samples of MFI test (there is not value for 5th recycling process; the test was made, but we are waiting for the results from laboratory technician). As we can see in the graph, the results follow a polymeric tendency. **MFI decreases with each recycling cycle of PLA**. Knowing that MFI is related with viscosity, **it means that viscosity decreases with the process**. Viscosity diminution is an evidence of molecular weight diminution, **and therefore degradation** because lower viscosity slow down polymer crystallization losing the main mechanical properties such as strength. The reason is the hydrolytic degradation during PLA fusion, as we explained before, water inside the polymer structure destroy the polymer.

However, for a better degradation analysis MFI data will be compare at the same time with GPC data (Table 5) in order to be sure that the reason is that molecular weight decrease and quantify molecular reduction, and rheological analysis so as to quantify viscosity decrease.

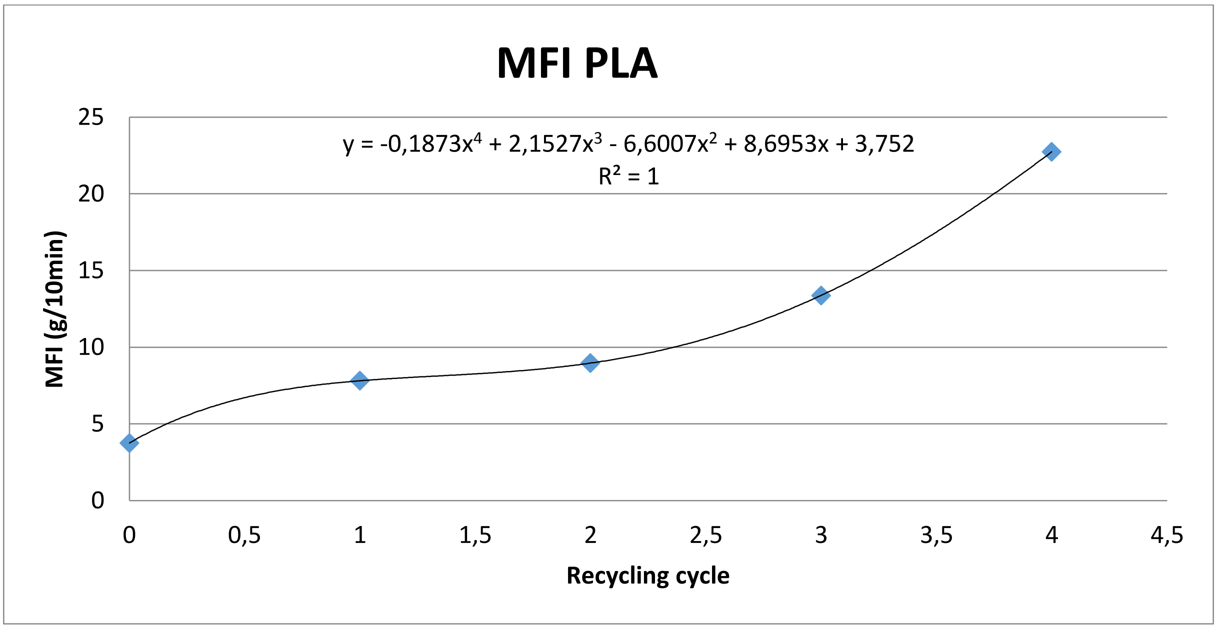


Figure 27. MFI results graph for PLA virgin and PLA from recycling cycles.

GPC analysis was made for five recycling cycles (Table 5) and five printing cycles, nevertheless printing results are no available now, we will receive them next week.

Table 5. GPC results for recycling cycles.

PLA	Virgin	Rec 1	Rec 2	Rec 3	Rec 4	Rec 5
Mn (g/mol)	85 000	75 000	66 600	57 500	45 800	37 300
Mw (g/mol)	110 000	104 000	88 200	80 600	68 600	58 400
I = Mw/Mn	1,29	1,39	1,32	1,402	1,50	1,55

As we expected with MFI values, with each recycling test the average molecular weights decrease with each recycling cycle as a proof of degradation. **It is really important to notice that after the 3rd recycling cycle**

the molecular weight is reduced a 30%, but after 5th recycling cycle it is reduced a 50% what it is problem. To quantify how it reduction affects viscosity parameters rheology results are used.

Finally, the rheometer was used in steady state to test all the samples for recycling and printing. Recycling data is analysis in Figure 28, however printing data are added in appendix B. As we can see, all the samples follow the same behavior, Newtonian behavior at the begging, and pseudoplastic behavior at the end. It easy to see that degradation is shown as less viscosity each recycling cycle. **The main problem is that PLA virgin should be on the top of figure 28. But it is not. Its viscosity is lower than the other samples. The reason is that this samples of PLA virgin was degraded**. The samples was prepared in February and it were kept in a plastic bag (it supposed to be tested in February). However the laboratory wasn't available until July, obviously, the moisture degraded the PLA virgin sample during 5 month and a half. To demonstrate it, we would like to repeat the test with a new sample.

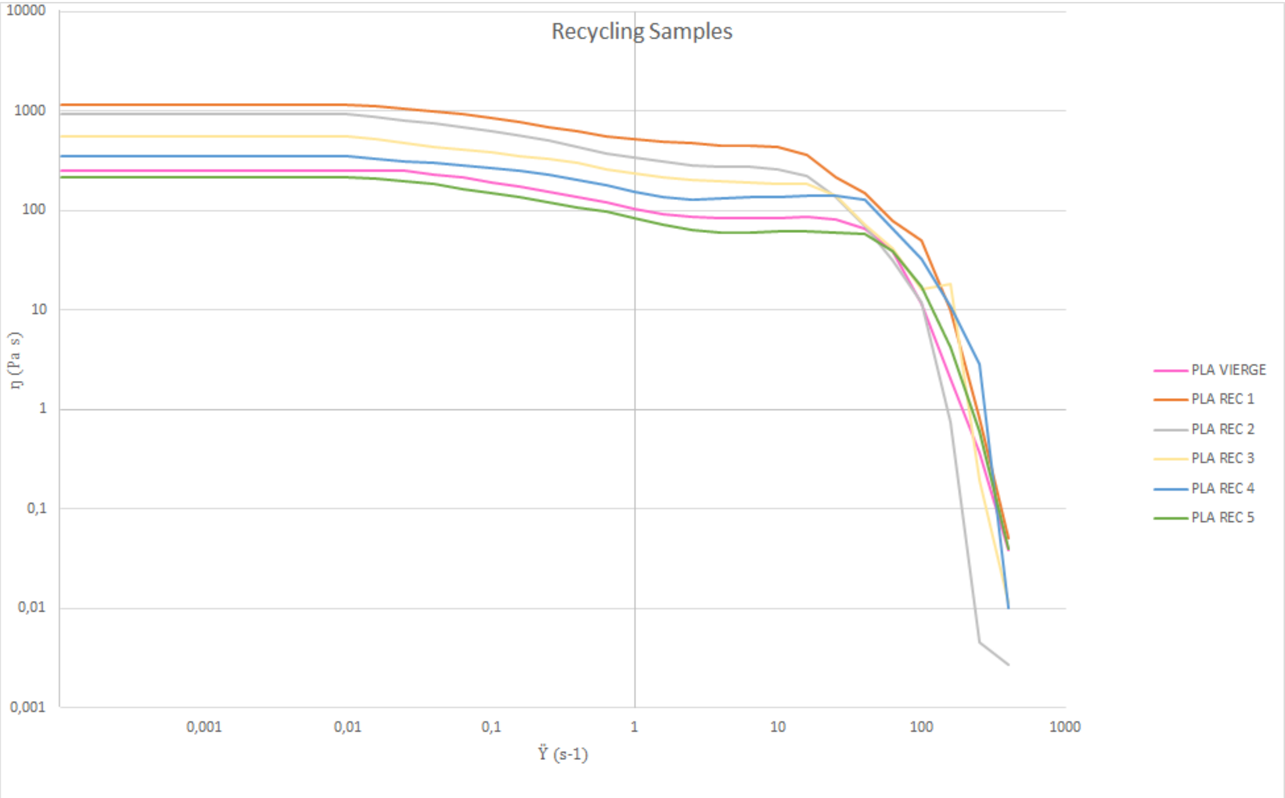


Figure 28. Rheological results for recycling samples (viscosity vs shear rate).

In order to show easy how the viscosity decrease with recycling process, Figure 29 represents viscosity vs recycling cycles. **It is important to realize that after 3rd recycling cycle the viscosity decrease a 50% while after the 5th cycle decrease an 80%.**

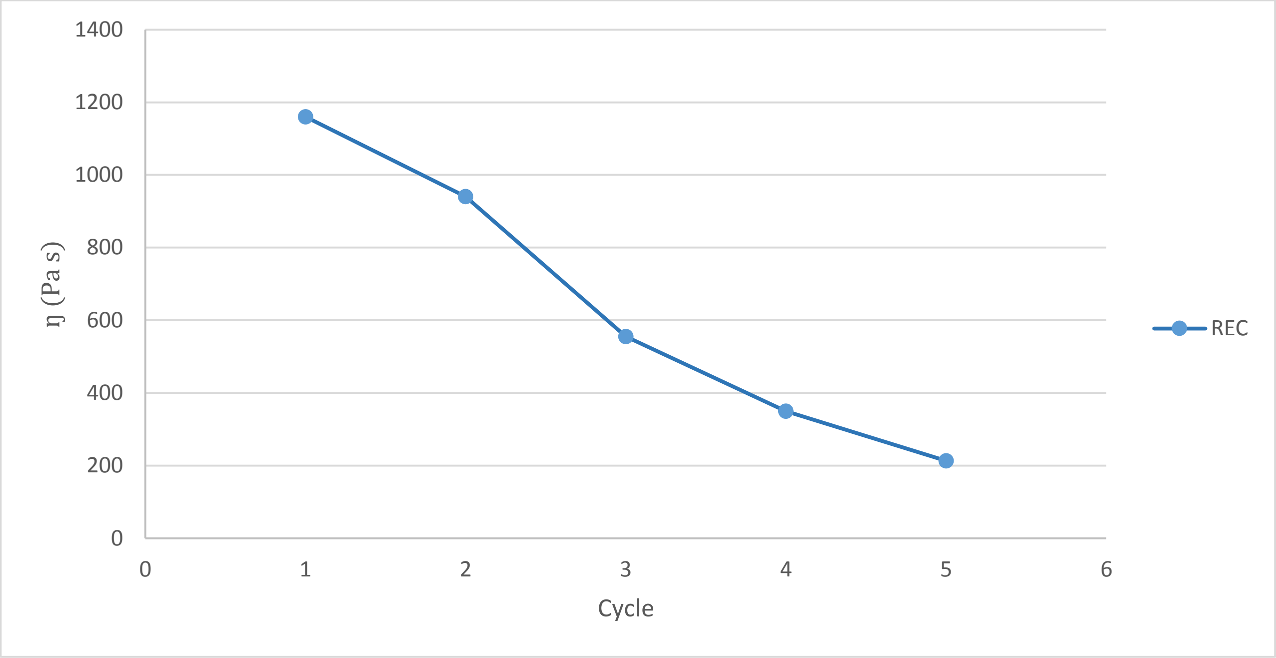


Figure 29. Diagram viscosity vs recycling cycle.

7. Conclusions

According to all the results and explanations collected in this rapport, we can conclude that:

- Main PLA virgin properties are:

VIRGIN PLA	
Glass transition temperature	57 ºC
Fusion temperature	147 ºC
Crystallization temperature	110 ºC
Degradation temperature	300 ºC - 370 ºC (max degr.)
Density	1,24 g/cm^3
Molecular weight average	110 000 g/mol

- The first hypothesis is true: PLA recycling damage the main properties. As it was demonstrated:
    - after 3rd recycling cycle the viscosity decrease a 50%, while after the 5th cycle decrease an 80%
    - after 3rd recycling cycle the molecular weight is reduced a 30%, but after 5th recycling cycle it is reduced a 50% what it is problem.

- The optimal working temperature for PLA is under 280ºC in order to avoid completely the thermal degradation temperature range. It stars at 300ºC and at 400ºC the degradation is total (nothing resist).

- Additive Manufacturing, extrusion and drying temperatures rang (200ºC, 180ºC and 50-100ºC respectively) is under 300ºC so there is no risk of degradation because of work temperatures range.

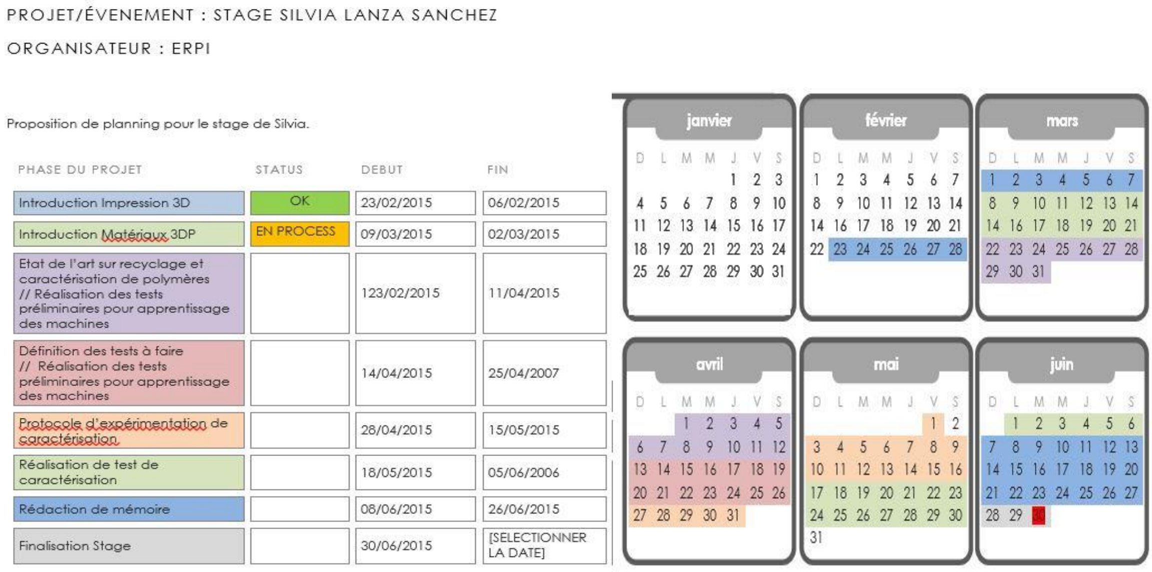
- TGA and DSC tests are the less important analysis to check the degradation of polymers. It is important just to decide the working temperature and main temperatures. However, as we see the results for all the samples are the same, thus, it is not an indicative data of degradation.

Perspectives

Biggest problems of this project were time and laboratory availability. As we planned at the begging of March, characterization test should had made in May. However I get the printing samples Thursday 2nd July and rheology laboratory was available (to test recycling and printing samples) on Friday 3rd July and Monday 6th July. All the data were obtained on Tuesday 7th July. Knowing that report should be sent Friday 10th July and no enough professor availability during July to support the analysis it was impossible to analyse all the data that I get. If I would have more time I would like to repeat rheological test to verify samples data. Finally, the next goal it to understand and explain PLA printing behaviour with the data obtained and placed on Appendix B.

Experience feedback

First of all, we should speak about the project evolution. At the beginning a plan was made with approximate dates of each step in the research. A priori, most of them was achieved. The work stared with a deep investigation of Additive Manufacturing and polymers. Around one month later, the research continued with and extensive and detailed study of PLA and PLA degradation. Finally, the first step finish with the understood of each test of characterization. The, as we planned, first tests were made in order to know how everything works. The problems appeared with real characterization test. When rheometer was available as we planned, and some results wasn't as we expected. Only recycling samples was ready to test and we continued the plan but just for these samples not for printing samples. The report was prepared with all the data that we had. Finally, at the end of the research we could made rheological test and we had printing samples ready. However, it was one week before research ending, and around one month later than we planned. Not enough time to complete the process described before.



PROJET/ÉVENEMENT : STAGE SILVIA LANZA SANCHEZ

ORGANISATEUR : ERPI

Proposition de planning pour le stage de Silvia.

PHASE DU PROJET	STATUS	DEBUT	FIN
Introduction Impression 3D	OK	23/02/2015	06/02/2015
Introduction Matériaux 3DP	EN PROCESS	09/03/2015	02/03/2015
Etat de l'art sur recyclage et caractérisation de polymères // Réalisation des tests préliminaires pour apprentissage des machines		123/02/2015	11/04/2015
Définition des tests à faire // Réalisation des tests préliminaires pour apprentissage des machines		14/04/2015	25/04/2007
Protocole d'expérimentation de caractérisation		28/04/2015	15/05/2015
Réalisation de test de caractérisation		18/05/2015	05/06/2006
Rédaction de mémoire		08/06/2015	26/06/2015
Finalisation Stage		30/06/2015	[SELECTIONNER LA DATE]

janvier

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février

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During all the research I think my roll was fine. I followed the steps informing my tutors frequently in order to explain what I did and improve the research. While I was investigating based principles of printing and polymers I was guided by Fabio A Cruz in order to facilitate the work. Beside, during the laboratory part I was guide by Sandrine Hoppe in order to get a better and easier performance.

Speaking about my skills in this project I am glad to say that they are improved. It is really difficult to manage a research and I had to learn how to do it by myself. It was difficult but I did it. In my opinion some knowledge of the subject before starting was really important. Some subject studied during academically years as basic polymerization, and mechanical and dynamical of fluids. Besides, I could say that my level of comprehension in this field have been improved. On the other hand, to follow a research I realised that it is really important keep the sequence and being tidy. The same test is performed several times with different samples producing similar results. It is really important keep a logical order to an easy realization and understanding.

Consider the work realised we have to speak about troubles, good performing, and some improvement. During all the month in Erpi some troubles appeared. A pretty important one was the language. I followed the research in three languages: English for understanding papers, information data sheet, standard protocols and report writing; French was used to understand laboratory personal, library books, meetings, to divulge the project in front of a jury and teachers exchange opinion; finally Spanish was used to communicate with some laboratory technicians and teachers. It was really confuse understood all the technical information in three different languages. The most hard and delicate thing was write and explain the same project in dissimilar languages.

As we explained before the time was the challenge. It wasn’t enough to realise all points that we expected to. However, just data analysis was missed. Not too much time would be needed to finish the project. However, we have to explain that more time that we expected was needed to understand PLA behaviour and to remake test after unexpected mistakes or problems as no recrystallization of PLA shown in DSC diagrams. It makes me repeat the same analysis for the same sample more than ten times in order to understand what happens and how to avoid it.

Some hard obstacles cannot be expected or prevented. I am talking about TGA machine damaged or not enough DSC capsule and delayed capsule delivery.

The last point should be the improvement items. If I repeat the research I would improve rheological basic information to better understand PLA behaviour. I would like to repeat DSC and TGA analysis for all the samples in order to really demonstrate that it is not necessary getting similar results for all the samples not just samples from 1st cycle.

Appendix A: Protocol of polymer degradation evaluation

This protocol shows the standard steps to evaluate physic and chemical degradation of polymers.

a. Reference values

References values are getting from the polymer virgin or the first row material used in the process. Before starting, it is important to dry the polymer with a heater (water level should be under 40 ppm). To characterize the polymer the following test will be used: TGA, DSC, MFI, GPC and Rheometry. The steps to execute the analysis are explained in section c “protocol”.

b. Polymer samples

Before each process, polymer should be dry with a heater. After the dry step, polymer should be introduce in special bags in order to not to add humidity. Each analysis should be repeated three times for each sample in order to reduce the experimental error. In the same way, it is important to take some samples of the same polymer. The analysis are the following: MFI, GPC and Rheometry. The steps to execute the analysis are explained in section c “protocol”.

The results of each test should be compare with reference values in order to understand polymer behaviours and polymer degradation.

c. Protocol

1) TGA analysis should be the first test in order to determine working temperature range:

- Open nitrogen gas valve to TGA machine (40 ml/min)
- Make sure that refrigeration works properly
- Switch on gases extractor
- Switch on TGA machines
- Start TGA software
- Select the method
- Introduce the temperature range (not less than 30º in order to accelerate the test; highest temperature around 600ºC is usually enough)
- Select new sample
- Name the sample as “white” (this first test will be used to verify that the machine is calibrated)
- Open the oven with “open button” on the machine screen
- Place carefully (it is really sensitive) an alumina pan of 70 µl on the precision balance inside the oven (it is really important make sure that the pan is made of alumina in order to handle high temperatures inside the oven)
- Close the oven pressing “close button” on the screen
- Press “cero” on the screen (pan weight is going to be the cero in precision balance)

- Start the test
- Once it is finish, measure 10 mg of dry polymer in a precision balance (note the weight of the sample if it is no exactly 10mg)
- Open the oven pressing the "open button" on the screen
- Insert the sample in alumina pan of 70 µl
- Close the oven pressing "close button" on the screen (the weight shown in the screen should be the same as we noted)
- Select "new sample" in TGA software
- Name the sample
- Start the test

Note: TGA result is a graph (%mass vs temperature) where the important information is degradation temperature (the step on the graph).

2) DSC should be the second analysis in order to get the main temperature parameters.

- Open nitrogen gas valve (40ml/min)
- Switch on DSC machine
- Start DSC software
- Select method "Start"
- Introduce the minimum weight possible, 0.00001 mg
- Select "Send the experiment"
- Before start the test it is important to verify that DSC oven is empty, to open and close the oven is mandatory use laboratory tweezers
- Start the analyze calibration
- Select "New method"
- Introduce segment temperatures for the analysis as the example:

    Segment 1: from 25ºC to 225ºC, + 10ºC/min
    Segment 2: from 225ºC to 110ºC, - 10ºC/min
    Segment 3: 110ºC, isothermal
    Segment 4: from 110ºC to 25ºC, - 10ºC/min
    Segment 5: from 25ºC to 225ºC, + 10ºC/min

- Select new sample
- Measure 10 mg of polymer in a precision balance
- Place the sample in an aluminum pan of 100 µl and cover it
- Open the oven with the laboratory tweezers
- Place carefully the aluminum pan with the sample and an aluminum pan empty in the oven
- Close the oven with the laboratory tweezers
- Name the sample
- Introduce the weight of the sample
- Select "Send the experiment"

- Start the analyze

Note: DSC result is a graph (heat flux vs Temperature) where the important information and main temperatures are (glass transition temperature, crystallization temperature, and fusion temperature). All the graph should be place together in order to compare the data.

3) MFI will be the third analyze

- Switch on MFI machine
- Introduce the set point as the polymer fusion temperature
- Place the polymer inside the machine
- Introduce the piston in order to cause the extrusion
- When the polymer starts to fluidize on the bottom of the machine, cut it
- Start the chronometer
- Cut the polymer when the chronometer shows 30 seconds
- Measure the polymer sample and note it

Take care about the units, MFI should be shown as g/10 min, however, after this test the units will be g/30sec. The analysis should be made six times in order to reduce the experimental error.

Note: MFI result is a number with g/10min units. Data tendency is important in order to compare all the results.

4) GPC should be the fourth test

- Measure 10 mg of polymer in a precision balance
- Introduce it in a volumetric flask of 50 ml
- Full the volumetric flask with tetrahydrofuran solution
- Turn on the software
- Turn on all the detectors
- Introduce the solution inside the chromatographic column
- Start the analysis

Note: main GPC results are average molecular weight and number, and polydispersity index. It is recommended resume all the data in the same table to show de degradation.

5) Rheometry

- Make circle pieces of polymers (25mm diameter, 1.5mm thickness)
- Turn on the rheometer
- Turn on rheometer software
- Fix oven temperature as the fusion temperature of the polymer
- Open the oven
- Separate the plates inside the oven
- Place one polymer piece between rheometer plates
- Move the plates in order to be in touch with the piece

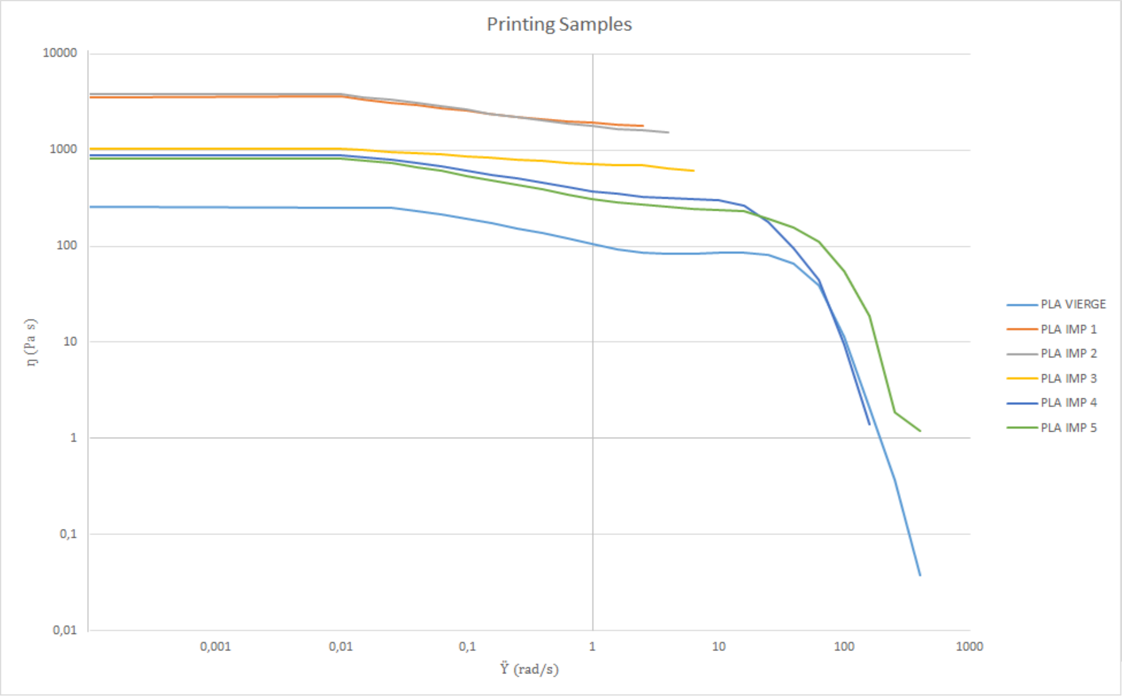
- Close oven
- Wait until fusion stars
- Open the oven
- Clean polymer residue out of the plates
- Close the oven
- Introduce gap value (it is shown on the top of the machine) in the software
- Select method (dynamic or steady)
- Start the analysis
- When the light becomes green, open de oven
- Separate the plate as much as you can
- Clean the polymer between the plates with a putty knife, a brush and some paper
- Turn off the software
- Turn off the machine

Note: rheology result is a graph (viscosity vs shear rate usually) where it is important to notice polymer behaviour (Newtonian, pseudoplastic …).

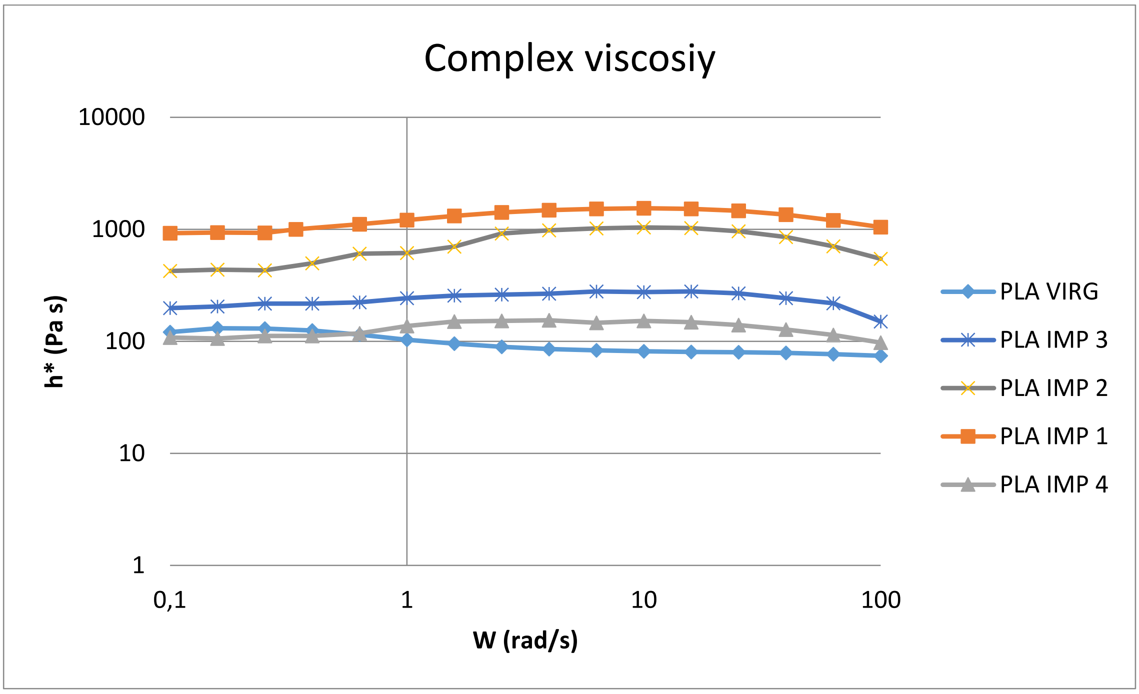
Appendix B: PLA data not analysed

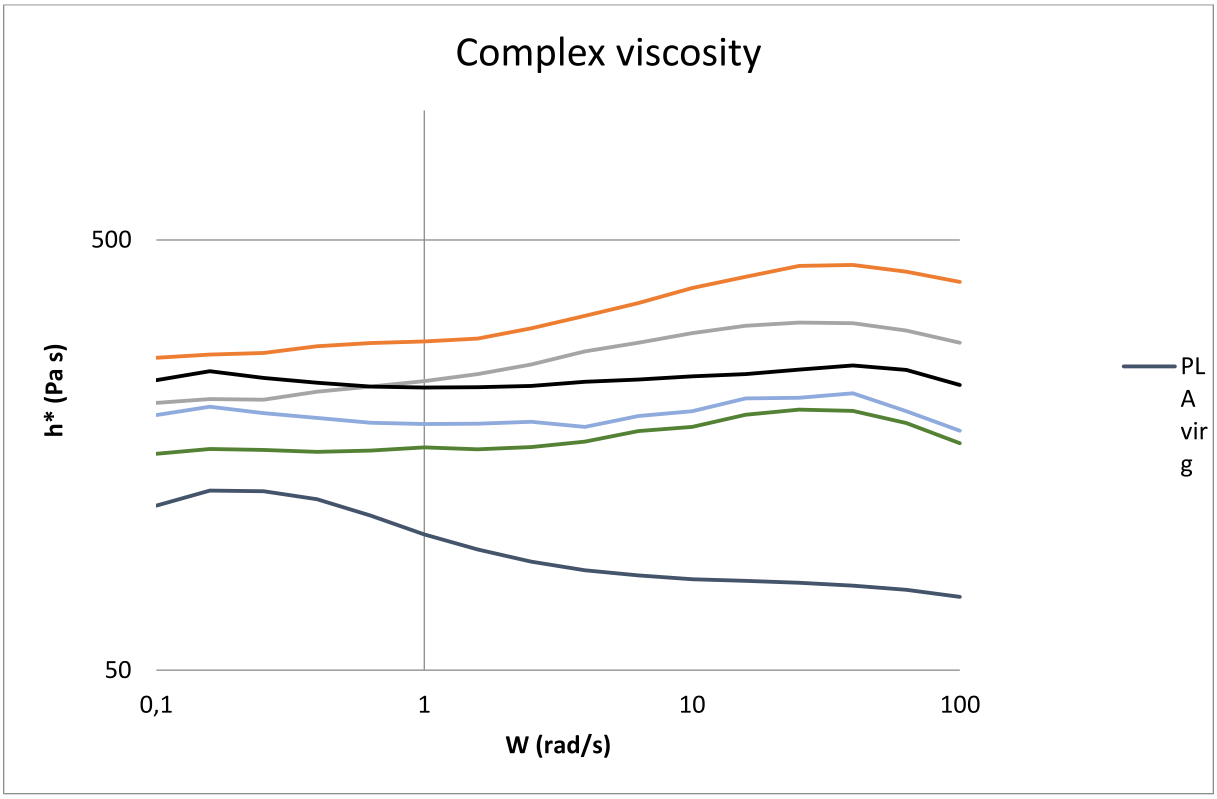
Some results of PLA were tested but not analysed. The reason is that there wasn't enough time to make it. These data are englobed in this appendix.

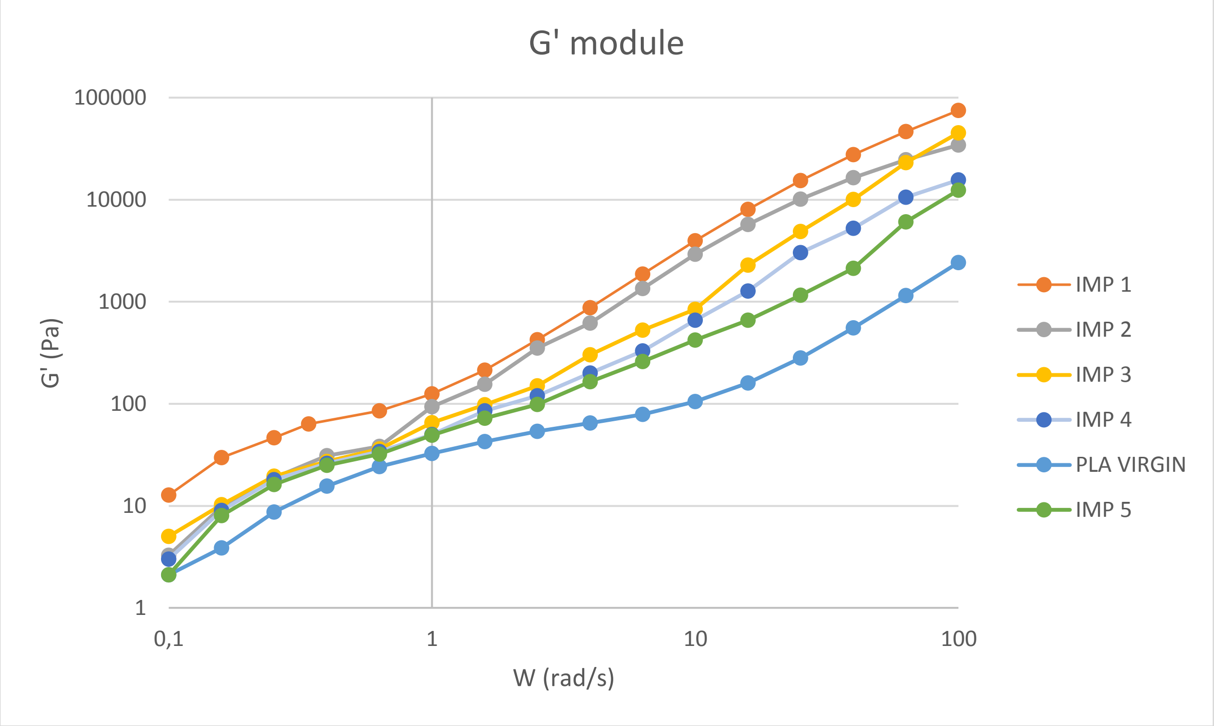
1. Steady rheology for PLA printing samples



2. Dynamic rheology for PLA samples




Complex viscosity
500
50
h* (Pa s)
0,1
1
10
100
W (rad/s)
PL
A
vir
g


G' module
100000
10000
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100
10
1
G' (Pa)
0,1
1
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W (rad/s)
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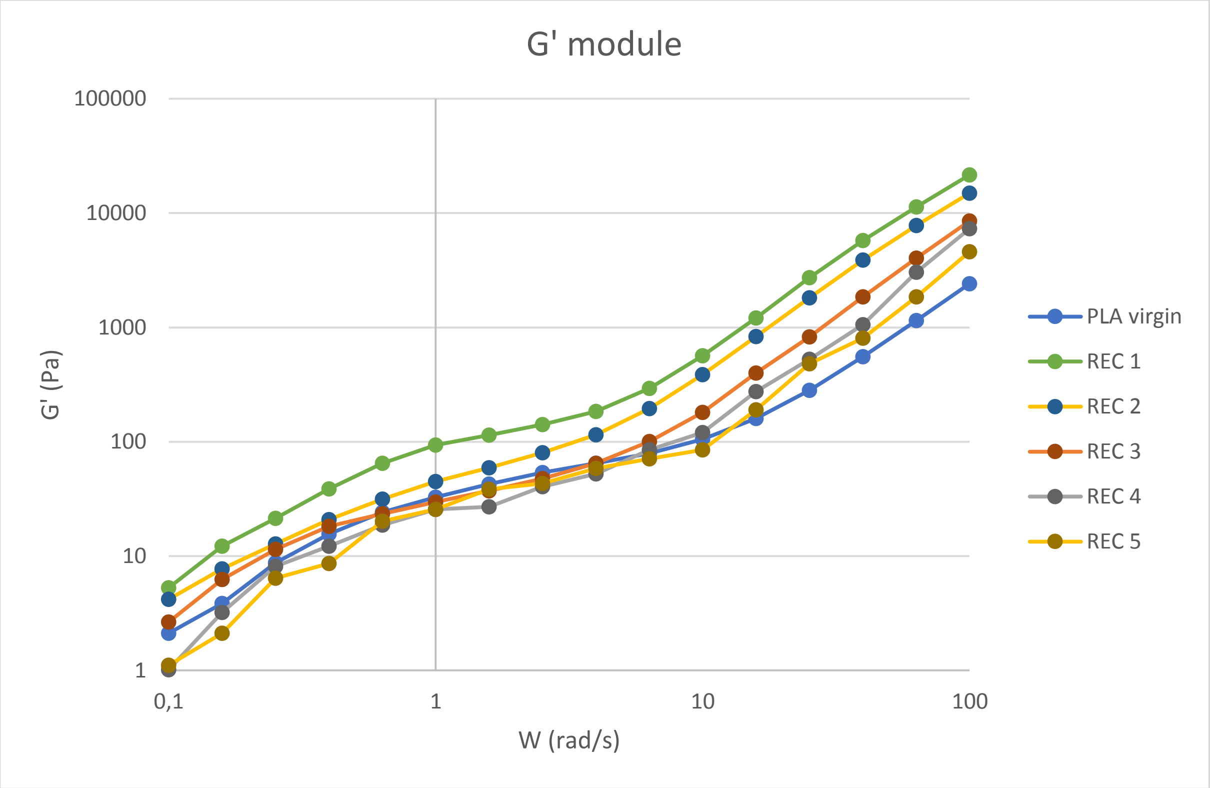
IMP 2
IMP 3
IMP 4
PLA VIRGIN
IMP 5


G' module
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G'' module
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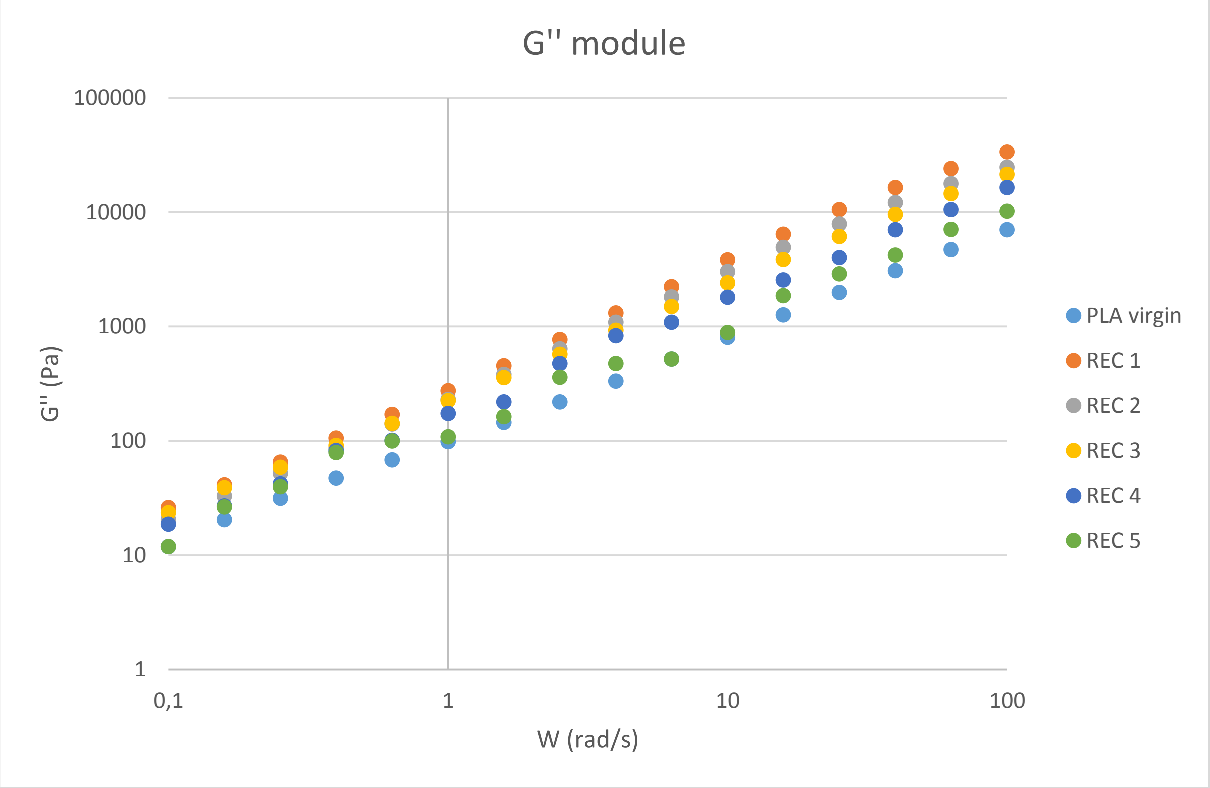
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Reporter summary

Additive Manufacturing is the technology to cretes new object joining material layer by layer, improved and rdeveloped duing three decades. It is allows a huge range of desings with complex geometries, reducing raw materials wuantity up to 75% and minimizating carbon footprint compared to conventional manufacturing technologies. Nowadays, the used of 3 D printings (Additive Manufacturing) is expanding more and more (aeroespacial deigns, automobile industry, biomedice …). As the use increased, the quantity of polymer used as row material step up (ABS, PLA, PVA and PC). Usually polymers for Additive Manufacturing are non-biodegradable or degrade slow. They release toxic fumes when they are burned and they can contaminate food with dangerous chemical compounds. Thus, plastics being an important environmental problem who concern the whole world. The synthesis, the use and recylcling of new materials biodegradables are so important in order to solve some environmental problems such as pollution or waste. PLA is a biodegradable polymer used in 3D printing. The next goal is PLA recycling. However, the main problem is that there isn't any evidence of non-degradation during this process. This project is an analysis of polymers degradation during recycling processes, especially PLA characterization. In order to realise the research, the project is connected to Fabio's A. Cruz thesis of PLA recycling. This thesis propose a way to recycle PLA for 3 D printing uses: staring with a drying step in order to avoid degradation (water quantity less than 100 ppm); then extrusing the polymer so as to get a filament of PLA (temperature around fusion temperature, 180ºC); using the polymer to feed 3D printer; and finally, recycling PLA breaking and drying in order to perform the re-extrusion and re-printing.

The main objetives of the research "Study of polymers recycling for 3D printing – PLA characterization" are: carachterize PLA virgin and PLA degradation during recycling process and make a standard protocol to evaluate recycling degradation in thermoplastics materials.

To achieve these goals some test are described and used: DSC (in order to get main temperature properties of thermoplastics), TGA (so as to get safe working temperature range), MFI (to estimate how fluidity change with degradation), GPC (to connect degradation with average molecular weight, and reology (to connect degradation with viscosity values).

Samples for 5 recycling cycles were tested and analysed their data in order to understand PLA behavior. Samples for 5 printing sycles were tested but not data analysis which will be the next step to continue with the research.

To conclude, PLA virgin main properties are 57ºC for glass transition temperature, 147ºC for fusion temperature, 300ºC for initial thermal degradation temperature, 25-280ºC working temperature to avoid it and 110000 g/mol for average molecular weight. Comparing this data with recycling information, we can conclude that after 3rd recycling cyecle molecular weight is reduced 30% and 50% reduction of viscosity; while after 5th cycle molecular weight reduction is around 50 %, and viscosity reduction is around 80%.

References

A. Bowyer, 2006. Distributing and copying RepRap. Available at: http://reprap.org/bin/view/Main/RepRapGPLLicence [Accessed January 19, 2010].

Aglient.Technologies, 2000. Polymer analysis by GPC-SEC Technical Note. , pp.1–8.

Ahrenfeldt, J., 2007. *Ph.D. Thesis: Characterization of biomass producer gas as fuel for stationary gas engines in combined heat and power production*. Technical University of Denmark.

Al-Salem, S.M., Lettieri, P. & Baeyens, J., 2009. Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Management*, 29(10), pp.2625–2643. Available at: http://dx.doi.org/10.1016/j.wasman.2009.06.004.

ASTM International F2792-12a, 2010. Standard Terminology for Additive Manufacturing Technologies. , 10.05.

Avérous, L., 2011. Polylactic Acid : Synthesis , Properties and Applications. In *Monomers, Polymers and Composites from Renewable Resources*. Elsevier.

Aznar, M.P., Caballero, M.A., Sancho, J.A., Francs, E., 2006. Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. *Fuel Processing Technology*, 87(5), pp.40–50.

B. Ramos, U.P.C., 2007. Síntesis y caracterizacion de polímeros. *Revista Iberoamericana de Polímeros*, 8(3), pp.21–41.

Bailard, S., Fabrication, S. & Smith, Z., 2007. RepRap: The Replicating Rapid Prototyper. Maximizing Customizability by Breeding the Means. In M. M. Piller, F. T.and Tseng, ed. *The 2007 World Conference on Mass Customization & Personalization (MCP)*.

Belmonte, A.E., 2004. Resonancia Magnética Nuclear aplicaciones al estado sólido. *Anales de la Real Sociedad Española de Química*, Abril - Ju, pp.27 – 36.

Beltrán, M. & Marcilla, A., 2012. Estructura y propiedades de los polímeros. In *Tecnología de polímeros: procesado y propiedades*. Alicante: Universitat d' Alacant, pp. 1–54.

Blecker, T. & Abdelkafi, N., 2006. Mass Customization: State-of-the-Art and Challenges. In *Mass Customization: Challenges and Solutions*. Springer US, pp. 1–25.

Bourell, D.L.D. et al., 2009. A brief history of additive manufacturing and the 2009 roadmap for additive manufacturing: looking back and looking ahead. *RapidTech2009*, (2), pp.80–88. Available at: http://iweb.tntech.edu/rrpl/rapidtech2009/bourell.pdf.

Brady A G, H.J.W., 1997. Stereolithography of ceramic suspensions. *Rapid Prototyping Journal*, 3(2), pp.61 – 65.

Brandrup, J., Bittner, M., Michaeli, W., M. & G., 1996. *Recycling and recovery of plastics* 10th ed., Hanser Publisher.

Brazel, C. and S.R., 2012. *Fundamentals principles of polymeric materials* 3th ed., Wiley.

Carrasquero, F.L., 2004. Fundamentos de polímeros. In *VI Escuela Venezolana para la Enseñanza de la Química*. Venezuela: Universidad de los Andes, pp. 11–63. Available at: http://www.saber.ula.ve/bitstream/123456789/16700/1/polimeros.pdf.

Cegarra, J., 2009. La cromatografía de extrusion: análisis de la distribucion de pesos. *Boletin Intexter*, (135), pp.33–40.

Chua C K, Leong K F, L.C.S., 2010. *Rapid Prototyping: Principles and Applications* 3rd ed., Singapur: World Scientific Publishing Company.

Colby College, 2007. Differential Scanning Calorimetry; First and Second OrderTransitions in Polymers. Available at: http://www.colby.edu/chemistry/PChem/lab/DiffScanningCal.pdf [Accessed May 15, 2015].

Cooper-White JJ, M.M., 1999. Rheological properties of poly(lactides). Effect of molecular weight and temperature on the viscoelasticity of poly(l-lactic acid). *Journal of Polymer Science*, 37(15), pp.1803–1814.

Couarraze, G., 2014. *Initiation à la rhéologie* 4th ed., Lavoisier.

Crump S S, 1991. Fused deposition modeling (FDM): putting rapid back into prototyping. In *The 2nd International Conference on Rapid Prototyping. Dayton, Ohio*. pp. 354–357.

CustomPartNet, Additive Manufacturing. *24.03.2015*. Available at: http://www.custompartnet.com/wu/additive-fabrication [Accessed January 1, 2001].

D. Garlotta, 2002. A Literature Review of Poly(Lactic Acid). *Journal of Polymers and the Environment*, 9(2), pp.63–84.

D.R. Witzke, 1997. Introduction to Properties, Engineering, and Prospects of Polylactide Polymer. *Ph.D. thesis, Chemical Engineering, Michigan State University*.

Drumright, R.E., Gruber, P.R. & Henton, D.E., 2000. Polylactic acid technology. *Advanced Materials*, 12(23), pp.1841–1846.

Europe, A. of P.M. in & (APME)., 2004. An analysis of plastics consumption and recovery in Europe. *Plastics in Europe*, 1, pp.1–18.

Fogliatto, F., 2010. *Mass Customization: Engineering and Managing Global Operations* 1st ed., UK Springer.

Gabriel Jaime Pelaez Arroyave, 2012. Ddegradación de polímeros. Available at: http://es.scribd.com/doc/92280093/Degradacion-de-polimeros-Completo#scribd [Accessed April 10, 2015].

Gananou, Y., 2013. *Chimie et physico-chimie des polymères* 3rd ed., Dunod.

GFR, 2013. *La mesure en rheologie* 1st ed., France: EDP sciences.

Giannatsis J, D.V.D., 2009. Additive fabrication technologies applied to medicine and health care: a review. *International Journal of Advanced Manufacturing Technology*, 40(1-2), pp.116–127.

Grupo de Polímeros y Reactores de Polimerización del INTEC (UNL-CONICET), 2010. *Cambio de estado, transición vítrea y cristalización* 3rd ed., Argentina: Universidad Nacional del Litoral.

Guo, N. & Leu, M.C., 2013. Additive manufacturing: Technology, applications and research needs. *Frontiers of Mechanical Engineering*, 8, pp.215–243.

Gupta, B., Revagade, N. & Hilborn, J., 2007. Poly(lactic acid) fiber: An overview. *Progress in Polymer Science (Oxford)*, 32, pp.455–482.

Hamad, K., Kaseem, M. & Deri, F., 2013. Recycling of waste from polymer materials: An overview of the recent works. *Polymer Degradation and Stability*, 98(12), pp.2801–2812. Available at: http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.025.

Holding, S. et al., 2011. Characterisation of Polymers Using Gel Permeation Chromatography and Associated Techniques. , (December), pp.4–8.

Holland, D, O'Donnell, G., Bennett, G., 2010. Open Design and the RepRap Project. In and G. M. M. V. Butler, K. Kelly, P. Delassus, ed. *27th International Manufacturing Conference*. Galway, pp. 97 – 106. Available at: http://hdl.handle.net/2262/41053.

Ii, B.J.P., 2005. Mass Customization. *Horizons*, 1(1993), pp.23–41.

Iqbal, S., 2013. *Thesis: Characterization of Viscoelastic Properties of a Material Used for an Additive Manufacturing Method*. University North Texas.

J. A. Brydson, 1999. *Plastics Materials* 7th ed., Elsevier.

J.E. Blanther, 1892. Manufacture of contour relief maps.

J.-P. et al., 1998. Progress in Additive Manufacturing and Rapid Prototyping. *CIRP Annals - Manufacturing Technology*, 47(2), pp.525–540.

Jamshidi K, Hyon S-H, O.Y., 1988. Thermal characterization of polylactides. *Polymer*, 29(12), pp.2229–2234.

Jones, R. et al., 2011. RepRap – the replicating rapid prototyper. , 29(1), pp.177–191. Available at: http://dx.doi.org/10.1017/S026357471000069X.

Juan J. Iruin, M.J.F.-B., 1996. *Fundamentos de Ciencia de Polimeros: Un Texto Introductorio* 1st ed., CRC Press.

Ken Anderson, 2012. What is the melt index? Available at: http://www.vitaldose.com/blog/what-is-melt-index/ [Accessed April 24, 2015].

Kopinke FD, Remmler M, Mackenzie K, Moder M, W.O., 1996. Thermal decomposition of biodegradable polyesters. *II. Poly(lactic acid). Polym Degrad Stab*, 53, pp.329–42.

Kreiger, M. a. et al., 2014. Life cycle analysis of distributed recycling of post-consumer high density polyethylene for 3-D printing filament. *Journal of Cleaner Production*, 70, pp.90–96. Available at: http://dx.doi.org/10.1016/j.jclepro.2014.02.009.

Lasprilla, A.J.R. et al., 2010. Synthesis and Characterization of Poly (Lactic Acid) for Use in Biomedical Field. *Chemical Engineering Transactions*, 24, pp.985–990.

Last, P., 3D Printing for Chocolate Molds Guide Contents Overview Customize & Design 3D Printing. Available at: https://learn.adafruit.com/downloads/pdf/3d-printed-chocolate-castings.pdf [Accessed March 20, 2015].

Lim, L.-T., Auras, R. & Rubino, M., 2008. Processing technologies for poly(lactic acid). *Progress in Polymer Science*, 33, pp.820–852.

Liu Q, Sui G, L.M.C., 2002. Experimental study on the ice pattern fabrication for the investment casting by rapid freeze prototyping. *Computers in Industry*, 48(3), pp.181–197.

Marques, D. a S. et al., 2010. Poly(lactic acid) synthesis in solution polymerization. *Macromolecular Symposia*, 296, pp.63–71.

Mastellone, M.L., 1999. Thermal treatments of plastic wastes by means of fluidized bed reactors. *Ph.D. Thesis, Department of Chemical Engineering, Second University of Naples, Italy*.

Munz, O.J., 1956. Photo-glyph recording.

Muzzy, J.D., 2000. Thermoplastics - Properties. *Comprehensive Composite Materials*, 2, pp.55–57.

Nature Works, 2014. Ingeo Biopolymer 4043D Technical Data Sheet.

Olsen, T., An introduction to melt index testing user manual.

PerkinElmer, 1960. Thermogravimetric Analysis (TGA) A Beginner ' s Guide. *Analysis*, pp.1–19. Available at: www.perkinelmer.com.

Pham D T, Dimov S, L.F., 1999. Selective laser sintering: applications and technological capabilities. *Journal of Engineering Manufacture*, 213(5), pp.435–449.

Porter, K.A., 2006. lactic acid, 1 and 2. Lactic acid forms PLA. *Scanning*, 16(March), pp.25–32. Available at: http://dx.doi.org/10.1016/j.cub.2006.05.063.

Prechtl M, Otto A, G.M., 2005. Rapid tooling by laminated object manufacturing of metal foil. *Advanced Materials Research*, 6–8, pp.303–312.

R.F. Housholder, 1981. Molding Process.

Rees, J.F., 1980. The fate of carbon compounds in the landfill disposal of organic matter. *Chem. Technol. Biotechnol*, 30(1), pp.161–175.

Roberts, John D. and Caserio, M.C., 1977. Polymers. In *Basic Principles of Organic Chemistry*. Menlo park: W. A. Benjamin.

Rydberg, T., 1995. Cascade accounting in life cycle assessment applied to polymer recycling. *Polymer Recycling*, 1(4), pp.233–241.

Scheirs, J., 1998. *Polymer recycling science, technology, and applications* 4th ed., Wiley.

Shanks, R. & Kong, I., 2012. *Thermoplastic Elastomers* 4th ed. A. Z. El-Sonbati, ed., Rijeka, Croatia: InTech. Available at: http://www.intechopen.com/books/thermoplastic-elastomers.

Södergård, A. & Stolt, M., 2002. Properties of lactic acid based polymers and their correlation with composition. *Progress in Polymer Science (Oxford)*, 27, pp.1123–1163.

Song Y, Yan Y, Zhang R, Xu D, W.F., 2002. Manufacturing of the die of an automobile deck part based on rapid prototyping and rapid tooling technology. *Journal of Materials Processing Technology*, 120(1-3), pp.237–242.

V. Speranza, A. de Meo, R.P., 2014. Thermal and hydrolytic degradation kinetics of PLA in the molten state. *Polymer Degradation and Stability*, 100, pp.37–41.

Theriault, R., Osswald, T. a. & Stradins, L., 1997. Properties of thermosetting polymers during cure. In *Technical papers of the anual technical conference-society of plastics engineers incorporated*. Wisconsin, pp. 766–773.

Thomas C L, Gaffney T M, Kaza S, L.C.H., 1996. Rapid prototyping of large scale aerospace structures. In *Proceedings of Aerospace Applications Conference IEEE*. pp. 219–230.

Van De Velde, K. & Kiekens, P., 2002. Biopolymers: Overview of several properties and consequences on their applications. *Polymer Testing*, 21, pp.433–442.

Visch, S., 2001. Biopolymers ; what is their place in future society in relation with sustainable design ? *Sustainable Design*, 201, pp.1–9. Available at: http://www.angelfire.com/freak/rat_xxx/default.html.

W.K. Swainson, 1977. Method, medium and apparatus for producing three-dimensional figure product.

Widmann, G., 2001. Interpreting TGA curves. *UserCom*, 13, pp.1–20.

Xiao, L. et al., 2006. Poly (Lactic Acid) -Based Biomaterials : Synthesis , Modification and Applications. *Biomedical Science, Engineering and Technology*, 11, pp.247–302.

Zhai, Y., Lados, D. a. & LaGoy, J.L., 2014. Additive Manufacturing: Making Imagination the Major Limitation. *Jom*, 66(5), pp.1–9.