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MECHANICAL PROPERTIES OF RECYCLED POLYMERS AFTER 3D PRINTING

Dissertação no âmbito do Mestrado Integrado em Engenharia Mecânica Especialidade de Produção e Projeto orientada pela Professora Doutora Ana Paula da Fonseca Piedade e apresentada ao Departamento de Engenharia Mecânica.

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Mechanical Properties of 3D Printed Recycled Polymers

Submitted in Partial Fulfilment of the Requirements for the Degree of Master's in Mechanical Engineering in the Speciality of Production and Project

Propriedades Mecânicas de Polímeros Reciclados Processados por Impressão 3D

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Abstract

The main objective of the work presented is to study a sustainable processing solution using a circular economy approach from the raw material to the processing technique. The intention is to contribute to the global effort to reduce the use of non-renewable sources for polymer/plastics manufacturing, and, consequently, decrease the plastic pollution and CO_2 release. Sustainability would be also improved using 3D printing as the processing technology, since it is optimized for almost no residue production.

Recycled Poly(lactic acid) (PLA) from food packaging and Acrylonitrile-Butadiene-Styrene copolymer (ABS) from the car's dashboard with and without additive were used as recycled materials. Their mechanical properties, after 3D printing, were compared to those of the virgin material.

The studied recycled materials fulfilled the mechanical properties requirements for the applications used before recycling. This study enabled to conclude that it is possible to recycle ABS and PLA from car dashboard's and food packaging, respectively, and re-use it, by 3D printing processing for the same purpose. By adopting this procedure, fewer resources will be consumed, less waste will be created, and less CO_2 will be produced, decreasing the impact on global warming. Moreover, 3D printing has shown to be a suitable, efficient and sustainable solution.

Keywords 3D Printing, Recycled Polymers, PLA, ABS, Mechanical Properties.

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Resumo

O principal objetivo do trabalho apresentado é estudar uma solução de processamento sustentável através do uso de uma abordagem de economia circular, desde a matéria-prima até à técnica de processamento. O intuito é contribuir para o esforço global de redução do uso de fontes não renováveis na fabricação de polímeros/plásticos e, consequentemente, diminuir a poluição plástica e a liberação de CO_2. A impressão 3D, enquanto tecnologia de processamento, otimiza a sustentabilidade da fabricação pela sua reduzida produção de resíduos.

Os materiais utilizados neste trabalho foram: o Poli(ácido lático) (PLA) virgem e PLA reciclado de embalagens de alimentos e o copolímero de acrilonitrilo-butadieno-estireno (ABS) natural, aditivado de cor preta e reciclado a partir de painéis de carro, também de cor preta. As suas propriedades mecânicas, após a impressão 3D, foram avaliadas e comparadas.

Os materiais reciclados estudados cumpriram os requisitos de propriedades mecânicas para as aplicações utilizadas antes da reciclagem. Este estudo permitiu concluir que é possível reciclar o ABS e o PLA de painéis de carro e de embalagens de alimentos, respetivamente, e reutilizá-los, através do processamento de impressão em 3D para o mesmo objetivo. Ao adotar esse procedimento, menos recursos serão consumidos, menos desperdício será criado e menos CO_2 será produzido, diminuindo o impacto no aquecimento global. Além disso, a impressão 3D mostrou ser uma solução adequada, eficiente e sustentável como método de processamento para a utilização de materiais poliméricos reciclados.

Palavras-chave: Impressão 3D, Polímeros Reciclados, PLA, ABS, Propriedades Mecânicas.

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LIST OF SIMBOLS AND ACRONYMS

List of Symbols

E – Elastic Modulus

Ra - Arithmetic Mean Deviation of The Assessed Profile

Rq – Root Mean Square Deviation of The Assessed Profile

Rz – Maximum Height of Roughness Profile

Sa – Average height of selected area

Sq – Root-Mean-Square height of selected area

Sz – Maximum height of selected area

Tc- Crystallization Temperature

Tdeg- Degradation Temperature

Tg- Glass Transition Temperature

Tm- Melting Temperature

δ- Deflection

ε - Strain

σ – Stress

List of Acronyms

ABS- Acrylonitrile-Butadiene-Styrene copolymer

AM - Additive Manufacturing

ASTM – American Society for Testing and Materials

DEM – Departamento de Engenharia Mecânica

DMTA – Dynamic Mechanical Thermal Analysis

DSC - Differential Scanning Calorimetry

EBM - Electron Beam Melting

FCTUC – Faculdade de Ciências e Tecnologia da Universidade de Coimbra

FDM - Fused-Deposition Modelling

PET – Poly(ethylene terephthalate)

PLA - Poly(lactic acid)

REACH – Registration, Evaluation, Authorization and Restriction of Chemicals

RoHS - Restriction of Hazardous Substances

SLA- Stereolithography

SLM - Selective Laser Melting

SLS - Selective Laser Sintering

TGA - Thermogravimetric Analysis

UAVs - Unmanned Aerial Vehicles

INTRODUCTION

The main market sector that plastic covers in European countries (in this work Europe and European country consis of Eu28 + Norway + Switzerland -EU28+NO/CH) according to the demand by segment in 2017 is given in Figure 1:

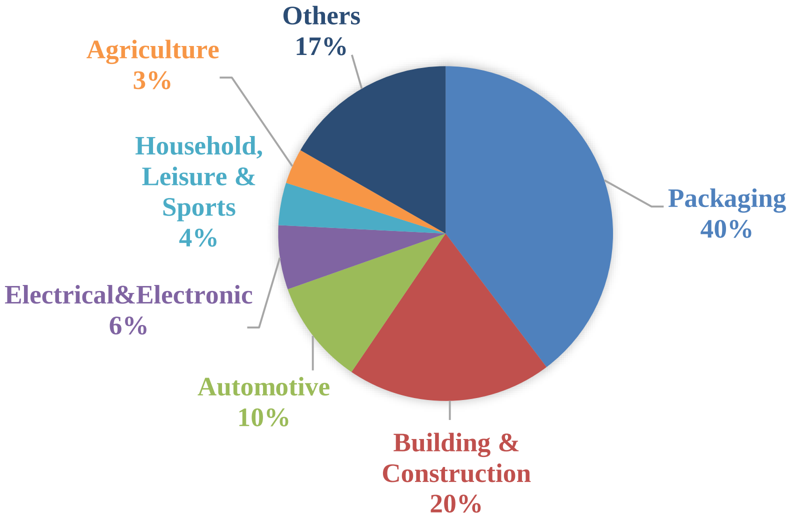

Figure 1: Distribution of European Plastic Converter Demand by Segment in 2017 (PlasticsEurope, 2017).

The world plastic production reached almost 350 million tonnes in 2017, which represents the largest field of application for crude oil (PlasticsEurope, 2017). Most of the existing polymer materials are made of non-renewable petrochemical resources. Using only non-renewable resources is not a long-term solution as these sources will eventually be exhausted, and its manufacturing process and disposal by incineration produces CO_2 that is a threat to global warming.

This widespread use of plastic materials has given rise to large quantities of waste, meaning that recycling of plastics is important to reduce both the number of plastics sent to landfills and the continuous use of raw material. Direct use of post-consumer polymers is the most efficient way to treat plastic waste (Chen et al., 2011).

Plastics are still very valuable resources at the end of life. They can be transformed into new feedstock or energy. In 2016, from the collected waste, 31.1% went to recycling, 41.6% to energy recovery and 27.3% to landfill. And, for the first time, more plastic waste was recycled than landfilled. From 2006 to 2016 the volumes of plastic waste collected for recycling increased by almost 80% (PlasticEurope, 2016). The numbers are optimistic and now the recycled material should be used not only in plastic bags but also in functional components. Recycling is not a single solution but is one of the drivers for a more sustainable planet.

In order to contribute the global effort to reduce the processing of virgin material and, consequently, decrease the plastic pollution, the focus of this thesis will be on evaluating the effect of using recycled polymers on the mechanical properties of 3D-printed materials. 3D printing, specially of polymeric materials, is nowadays an established technology and is one of the main drivers of innovation in smart manufacturing technologies. 3D printing is uprising as the chosen technology in the production of functional components to be applied in several fields: agriculture, biomedical, unmanned aerial vehicles (UAVs), bioprinting, membrane (selective barriers) technology, aerospace, civil engineering, metal matrix composites, multi-material components and food production (Ferreira, R., et al., 2017).

The polymeric materials required to be used in 3D printers are generally thermoplastics that, unlike thermosetting, can be processed at relatively moderate temperature and pressure. Numerous thermoplastics are currently available for 3D printing, including acrylonitrile butadiene styrene copolymer (ABS), Nylon®, polycarbonate (PC), high-density polyethylene (HDPE), high-impact polystyrene (PS), and poly(lactic acid) (PLA). Among these ABS and PLA are the most used materials for the 3D printing of components/parts (Zhao et al., 2018).

An alternative to fossil-fuel based polymers that have attracted great interest over the past years are the bioplastics. PLA present some interesting properties, such as its biodegradability, good processability, low-cost production, low environmental impact and optical and mechanical properties similar to those of PS or poly(ethylene terephthalate) (PET) (Auras et al., 2010). These good properties have caused a growing interest in PLA, making it one of the most important bioplastics in the market, specifically in packaging applications, with a global production capacity of 0.21 million tons in 2016. Furthermore, it is projected a sustained growth of the production of PLA, reaching 0.5 million tons in 2020 (Aeschelmann and Carus, 2016).

This expected growth of the production and consumption of PLA could lead to some social and environmental problems in the coming years. Firstly, the sustenance and health of poor countries might be threatened, as farmers could exchange the cheap food production for the high-value crops used in the manufacture of PLA and other biopolymers, such as corn (Mülhaupt, 2013). Secondly, there is concern about the management of the wastes derived from the massive use of PLA, since the commercial grades used in packaging applications degrade at a low rate when compared with the large volume of accumulated wastes (Niaounakis, 2013). These problems highlight the need to study the potential of extending the life of PLA based products, to reduce the consumption of essential raw materials and the generation of wastes. Piemonte (2011) carried out Life Cycle Analysis for PLA, evaluating four different final scenarios: incineration, composting, anaerobic digestion and mechanical recycling. The results showed that, from an environmental point of view, the best alternative for the valorisation of PLA wastes is mechanical recycling.

In order to frame the specific application of ABS in the automotive industry, it must be stated that the global figure of dismantled cars was around 24 million in 1995, generating 2.2 million tons of plastics scrap (Balart, R., et al., 2005). The steady growth in the use of plastic materials in automotive applications has promoted the leading industries to search for solutions for reducing the environmental impact of cars at the end of their life cycle. Completely recover of the materials present in the car is a challenge for automobile manufacturers. For metallic components, which presently constitute 75% of the car, the problem has been already solved. However, for plastic components, which represent 12.5%, a number that is expected to grow further in the near future, the problem is still being studied (Ragosta, G., el al., 2000).

This dissertation starts, in chapter 1, with a literature review with a description of the historical framework and technologies used in additive manufacturing, followed by an introduction of mechanical recycling and ending with previous studies on mechanical properties of PLA and ABS including the impact of mechanical recycling. The second chapter defines the materials and techniques used during the experiments. In the last chapter the results obtained are presented and discussed. Lastly, the conclusions and bibliography are listed.

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CHAPTER 1- LITERATURE REVIEW

1.1. Historical Framework of Additive Manufacturing

According to American Society for Testing and Materials (ASTM), and in accordance with its F2792 Standard Terminology for Additive Manufacturing Technologies (Withdrawn, 2015), the term additive manufacturing (AM-Additive Manufacturing) is "*the process of bonding materials to make objects from 3D model data, usually layer by layer, as opposed to subtractive manufacturing methodologies*". The same standard defines AM as synonymous with the following designations: additive processes, additive techniques, additive layer manufacturing, layer manufacturing and free form manufacturing.

There are several technologies that are used in AM and which are currently generically referred to as 3D printing. The emergence and use of these technologies has not been simultaneous but phased over time. It is quite common in the literature to refer that the beginning of additive manufacturing occurred in the 80's of the last century. However, as can be seen from Table 1, the findings that enabled AM to appear as known today occurred well before that date. (https://www.digitaltrends.com/cool-tech/history-of-3d-printing-milestones). Table 1 highlights the dates on which: (i) findings were made; (ii) patent applications have been submitted; (iii) companies were created; and (iv) patents expired. These dates are recorded in the history of additive manufacturing as being responsible for today's technology, its success as well as contributing to the success of Industry in the 21st century.

Table 1: Historical Landmarks of Additive Manufacturing (adapted from Oliveira, Rúben (2019)).

Year	Occurrence
1859	French photo sculptor François Willème used 24 cameras to simultaneously photograph objects from different angles. This was the first demonstration of 3D scanning technology.
1892	The inventor Joseph E. Blanther filed a patent for the creation of 3D topographic maps using a layered method that is similar to the concept currently used in 3D printers.
1980	Hideo Kodama develops a functional rapid prototyping technique based on light curing. It was the first to describe the concept of layer by layer deposition.

1984	Charles Hull invents and registers the patent for SLA (Stereolithography Apparatus). He used as a photopolymer an acrylic-based material.
1986	Charles Hull is the co-founder of the world's first 3D printing company, 3D Systems.
1987	3D Systems creates the first SLA equipment that has made it possible to manufacture complex parts layer by layer in a short time.
1988	Carl Deckard patents SLS (Selective Laser Sintering) technology. This 3D printing technology uses the principle of localized powder fusion by the action of a laser.
1989	Scott Crump, the co-founder of Strasays Inc., has registered the patent for Fused Deposition Modeling (FDM). This is the third principal 3D printing technology.
1992	DTM produces the first SLS equipment. The MDF patent is granted to Strasays. The development of professional printers begins with the introduction of conventional 3D printing.
1993	CAD tools are developed specifically for 3D printing and Soliscape is founded.
1999	The year of birth of Medical 3D Bioprinting - the first organ (bladder) is successfully transplanted into a patient.
2004	Adrien Bowyer founds the open-source RepRap project to build a 3D printer that prints its own components.
2005	ZCorp launches the first high-resolution 3D colour printer - the Spectrum Z510.
2006	The first SLS equipment becomes commercially viable. The industrialization of custom components by 3D printing is starting to make sense. Start-up Objet develops the first multi-material 3D printer.
2008	3D printing gains even more recognition in the medical community when applying the first prosthetic limb. Darwin is the first 3D printer released by RepRap.
2009	Scott Crump's FDM patent expires. The price of printers drops drastically. MakerBot creates Thingiverse, the largest 3D printing online community where was possible to submit and download files for 3D printing.
2011	The first aircraft and car prototypes are developed, achieving the expanding potential of 3D printing.
2014	Carl Deckard's SLS patent expires. The low cost of this high-resolution technology now enables companies to expand. NASA takes the first 3D printer into space.
2015	Swedish company Cellink launches the first commercial bio-ink for cartilage printing.
2016	3D printing covers many more areas: houses are built to solve the global housing crisis; The fashion industry adopts 3D printing to create complex designs; The sports industry uses 3D printing to improve athletes' performance, and the medical industry continues to evolve with cell and organ printing.

1.2. 3D Printing Technologies

There are currently several 3D Printing technologies available at the market, being the more important ones presented in table 2.

Table 2: Technologies used for AM (adapted from Oliveira, Rúben (2019)).

Technology Method Group	Shared Characteristics	Method
Power Bed Methods	- Materials in powder form between 15-100 µm in size; - Use of metallic materials, some ceramics and some polymers but difficulty using multi-materials; - Minimum spot size of ~ 100 µm;	Eletron Beam Melting (EBM)
Photopolymerization Methods	- Use of photopolymerizable resins - Minimum spot size of ~ 50 µm - Excellent surface finish - Weak mechanical properties - Inkjet method is suitable for multi-color printing and, with some restrictions, multi-material printing.	Selective Laser Melting (SLM)
		Selective Laser Sintering (SLS)
		Stereolithography (SLA)
		Brinder Jet powder bed
Extrusion Methods	- The thermoplastic or viscoelastic material is extruded through a thin nozzle mounted on a 3-axis mobility platform. - When extruding composite materials the extrusion aligns the reinforcement fibers and the nozzle path defines the fiber orientation - Suitable for multi-material deposition - Allows 3D printing of a wide range of essentially polymeric materials.	Fused-deposition modelling (FDM)
		Direct-write extrusion

In this dissertation, the method used was FDM and is described in figure 2.

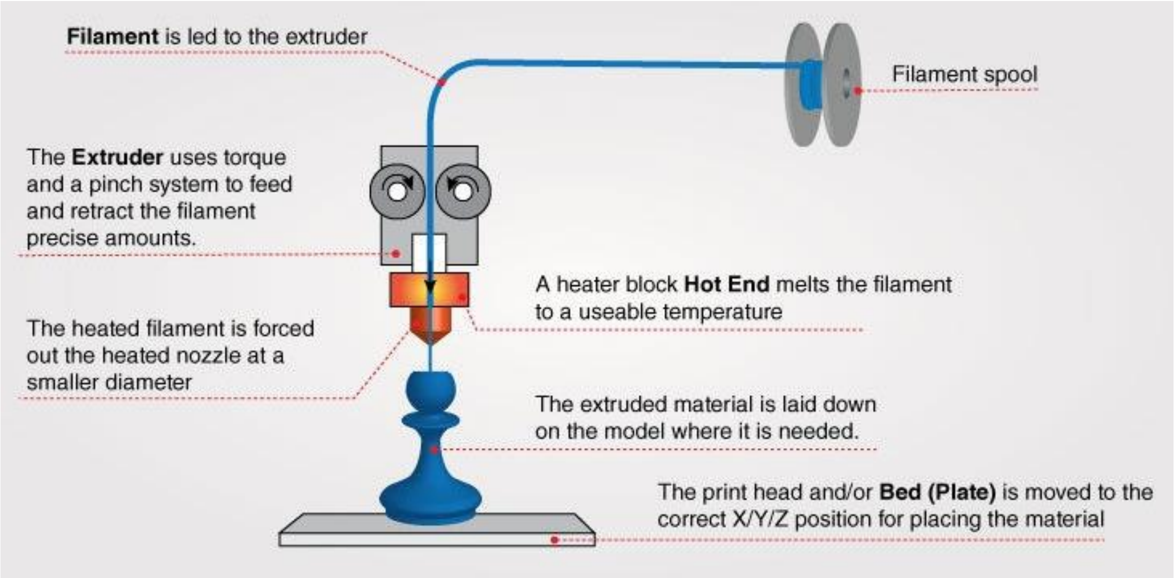

Figure 2: FDM Method Description (adapted from Filter S., (2017))

The filament is extruded and deposited by the 3D printer on top or next to the previous extruded material, in order to create a bond by heat and/or adhesion. The material is carefully positioned into layer upon layer, working from the bottom up. As the material is extruded through the nozzle, the extruder moves horizontally (X, Y axis) while the bed moves vertically (Z axe) producing the desired component/part.

1.3. Mechanical Recycling Process of Polymers

Mechanical recycling of polymers and plastics is the process of recovering the solid waste for the re-use in manufacturing plastic products via mechanical means (Mastellone, 1999). Collecting, sorting, washing and preparation of plastic solid waste are all essential steps to produce high quality, clear, clean and homogenous end-products. The steps involved in mechanical recycling are schematically represented in figure 3 (Aznar et al., 2006):

1. Cutting/shredding: Large plastic parts are cut by shear into chopped small flakes.
2. Contaminant separation: Paper, dust and other forms of impurities are separate from plastic.
3. Floating: Different types of plastic flakes are separate in a floating tank according to their density.
4. Milling: Single-polymer plastics are mill together.

5. Washing and drying: Washing stages are performed with water. Chemical washing, with caustic soda and surfactants, is also employed in certain cases, mainly for glue removal from plastic
6. Agglutination: The product is gathered and collected.
7. Extrusion: The plastic is extruded to strands and then pelletized to produce a single-polymer plastic.
8. Quenching: Water-cooling the plastic by water to be granulated and sold as a final product.

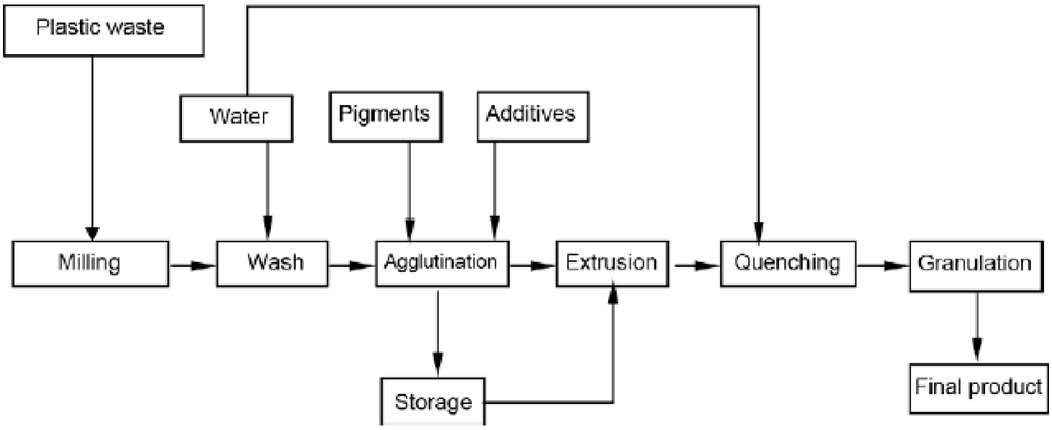

Figure 3: Mechanical Recycling Steps as described by Aznar et al. (2006).

Physical processing and sorting technologies have reached a high standard during the last decades (Serranti et al., 2015) which also allows sorting polymer waste by colour (Safavi et al., 2010). Unfortunately, each time a polymer is heated and extruded the mechanical properties are susceptible to degradation. This effectively limits the recycling process to 5 cycles without the use of blending virgin materials or adding materials with the purpose of reinforcing the mechanical properties (Woern, A. et al., 2018).

1.4. Properties of Recycled PLA

PLA is an aliphatic polyester produced, at industrial scale, by ring-opening polymerization of lactide, a cyclic oligomer of lactic acid. The lactic acid is obtained from the fermentation of glucose, derived from agricultural sources such as corn, potato or sugar beet (Reddy et al., 2013). PLA is produced from renewable resources and is completely biodegradable.

Structurally, PLA is a semi-crystalline thermoplastic with a glass transition temperature (Tg) in the range of 50 to 80 ºC, and melting point (Tm) at 130 ºC to 175 ºC. PLA present some interesting properties, such as its biodegradability, good processability, low cost production, low environmental impact and optical and mechanical properties similar to those of PS or PET (Auras et al., 2010). PLA may have numerous applications in packaging, consumer goods, fibres and biomedicine because of its biosafety, as well as adjustable hydrolyzability (Garlotta, 2001; Henton et al., 2005; Maharana et al., 2009; Pilati and Toselli, 2009 and Harshe et al. 2007).

Because PLA is biocompatible and bioresorbable, it can be used in a number of biomedical applications, provided the properties for each specific applications are present, such as sutures, implants, fracture fixation, drug delivery, and tissue engineering. It can also be employed in the preparation of bioplastics, useful for producing loose-fill packaging, compost bags, food packaging, disposable tableware, upholstery, disposable garments, awnings, feminine hygiene products, and nappies. As the depletion of petrochemical feedstock draws near, PLA is becoming an environmentally sustainable alternative to petrochemical derived products because of its biodegradable characteristics and the renewable nature of its feedstock (Pang et al., 2010).

PLA is susceptible to thermo-mechanical and hydrolytic degradation during the melting process (Scaffaro et al., 2014). The polymer, when subjected to high temperatures and shear stresses, can suffer chain scission processes, which cause a decrease in the molecular weight, and in the intrinsic viscosity. Besides the degradation during melt processing, PLA can also suffer degradation processes during its use. These processes can be thermal, photochemical and hydrolytic, and can also cause a reduction in the molecular weight of the polymer (Le Marec et al., 2014; Tuna and Ozkoc, 2016). The degradation of the polymer during its use and/or during the recycling process can have an impact on the structure and on some properties, such as thermal, mechanical and, optical properties.

Pillin et al. (2008) studied the reprocessing of PLA and concluded that up to seven injection mouldings cycles, the stress and strain at break, the Young modulus, hardness and rheological properties decreased. They attributed this effect of repeated processing cycles in the degradation of PLA to chain scission during processing, which yields to a significant decrease in the molecular weight.

Beltrás et al. (2018) studied the effects of different simulated mechanical recycling processes on the structure and properties of PLA. They observed that the recycling process does not have a significant effect on the glass transition temperature (Tg) but it decreased the cold crystallization temperature (Tcc) in about 5 ºC. This Tcc reduction is attributed to a higher mobility of the polymeric chains, as a consequence of molecular weight reduction during the reprocessing (Pillin et al., 2008; Brüster et al., 2016; Yarahmadi et al., 2016; Scaffaro et al., 2011). Consequently, the recycled materials were stiffer, with reduced deformability, impact resistance and water absorption when compared to the reference one. These results agree with those found by intrinsic viscosity measurements, where the recycled PLA showed a decrease in the molecular weight, as a consequence of the mechanical recycling process.

Zenkiewicz et al. (2009) extruded PLA up to ten times using a double-screw extruder, from granulated PLA, followed by laboratory injection moulding press. They found that the tensile strain and the impact strength decreased with the number of extrusion cycles. The thermal events showed a slight decrease of the thermal stability of PLA, such as lower Tcc and a slight reduction of the Tm with increasing number of cycles. However, no effect on the glass transition temperature was observed.

Badia et al. (2012) showed that during the multiple mechanical recycling of amorphous PLA, chain scission occurs as a result of thermomechanical degradation. In fact, although PLA remained amorphous throughout the reprocessing cycles, a Tcc was observed during differential scanning calorimetry (DSC) and dynamical mechanical thermos analysis (DMTA) characterizations, with the cold crystallization enthalpy increasing with each reprocessing step.

Nascimento et al. (2010) studied the effect of an extrusion process followed by an injection process in the structure and thermal and mechanical properties of PLA, concluding that a single reprocessing step does not have a significant impact on the performance of the polymer.

Considering the processing through 3D printing, Anderson (2017) evaluated the tensile, shear, and hardness properties of test specimens printed with virgin PLA filament. They compare the results to those obtained from specimens made from PLA filament produced from the recycling of the original 3D printed test specimens. The recycled specimens demonstrated similar properties to the virgin material. The tensile yield strength, the tensile modulus, and hardness decreased, but shear yield strength increased. The study demonstrated that recycling 3D printed scrap materials into usable filament can yield parts with similar properties to parts produced with virgin filament.

1.5. Properties of Recycled ABS

ABS is one of the most used industrial polymeric material and among the five most highly consumed in the word. High levels of strength, rigidity, toughness and impact strength of ABS has led to its good mechanical properties (Bakerand Mead, 2000). ABS is a 100% amorphous copolymer and is a common component in consumer electronic housing, automobiles and motorcycles. (Chen et al. 2011)

Brennan et al. (2002) studied the impact on the mechanical properties of recycling ABS after blending it with high impact polystyrene. They found that changes in glass-transition temperature, tensile strength, and tensile modulus in reprocessed ABS were negligible, but elongation at break and impact strength were considerably reduced.

Boldizar and Möller (2003) studied the properties of ABS exposed to a series of seven combined cycles of extrusion and ageing in air at 90ºC for 72h. They reported that from the second to the sixth cycle, the elongation at break decreased noticeably and attributed this result to thermo-oxidative ageing of the polybutadiene chains.

Bai et al. (2007) reprocessed ABS up to four cycles. They found that, after reprocessing, impact strength was much more significantly affected than the tensile properties. They reported that two of the most important factors affecting the properties of reprocessed ABS were: loss of the smaller and more volatile molecules, and degradation induced by chain scission and, particularly, due to the crosslinking of its chains.

Karahaliou and Tarantili (2009) reported that mechanical recycling up to five repeated extrusion cycles of ABS, in a twin screw extruder, did not affect the processing characteristics and the mechanical properties of the material. The mechanical and rheological properties showed that ABS had good stability during all the processing cycles

Perez at al. (2010) studied the effects of the reprocessing on the mechanical, thermal and rheological properties of ABS. They found that neither the flow index nor the tensile strength were affected by up to 10 reprocessing cycles, although the impact strength slightly decreased.

Salari and Ranjbar (2008), simulated the reprocessing and thermo-oxidation of ABS resins. They showed that the impact strength, the stress at yield point and the elongation at break decreased critically. Nevertheless, Young’s modulus slightly increased at first reprocessing cycle and then remained constant.

Chen et. al (2011) studied the influence of mixing recycled with virgin ABS on the mechanical properties and moulding characteristics of the obtained blends. They found that the recycled ABS weight percentage did not affect the tensile and flexural strengths. Concomitantly, a significantly reduction of the impact strength was observed, together with the improvement of the hardness and of the processing behaviour due to higher melting flow index. The Tg value of the blends increased with the increase of the weight percentage of the recycled ABS. The same study showed that there was no significant effect of recycled ABS weight percentage on the tensile strength, elongation, flexural strength, and flexural modulus. The hardness increased with increasing weight percentage of recycled ABS. The impact strength was found to vary with the recycled ABS ratio.

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CHAPTER 2- MATERIALS AND METHODS

Polymer architecture plays an important role on the mechanical properties, and consequently on the process utilized to modelling the final product (Auras et al., 2005). Therefore, the polymer architecture was studied through thermal analysis and the mechanical properties evaluated with hardness, tensile and three-point flexural tests. In addition, the material roughness was measured due to appearance and production factor and because it is an indication of the polymer viscosity.

2.1. Materials

The recycled materials used in this study (recycled PLA and ABS) were acquired from the Refil Company (https://www.re-filament.com/). The filaments were produced via mechanical recycling of waste from different sources. PLA was recycled from food packaging and copolymer ABS from car dashboards. After collecting, the material is shredded into tiny plastic flakes. Then, these flakes are filtered from all contaminants, melted, and extruded into a clean, 1.75 or 2.85 mm diameter filament. The recycled filaments are then winded onto biodegradable, cardboard spools. The recycled filaments used in this work had a diameter is 1.75 mm with a tolerance of 0.05 mm.

All the materials are REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) and RoHS (Restriction of Hazardous Substances) compliant.

The virgin materials for this thesis (white PLA, black ABS and natural ABS) were acquired from the company DoWire (http://dowire.pt/). Figures 4 and 5 show the macro aspect of the studied filaments.

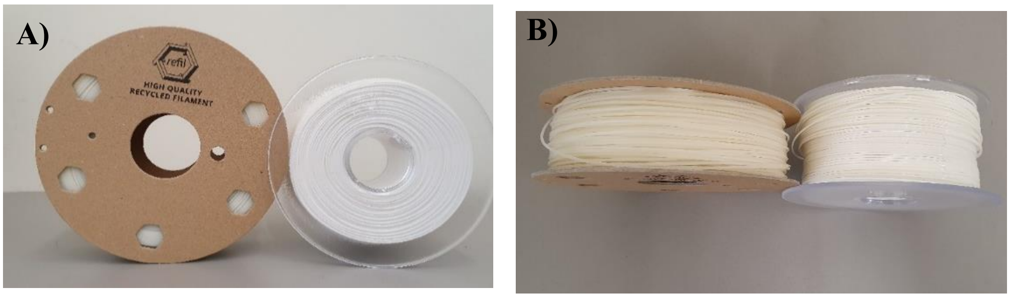

Figure 4: Filament spools optical macrographs. Recycled PLA on the left and Virgin PLA on the right. A) front view, B) top view.

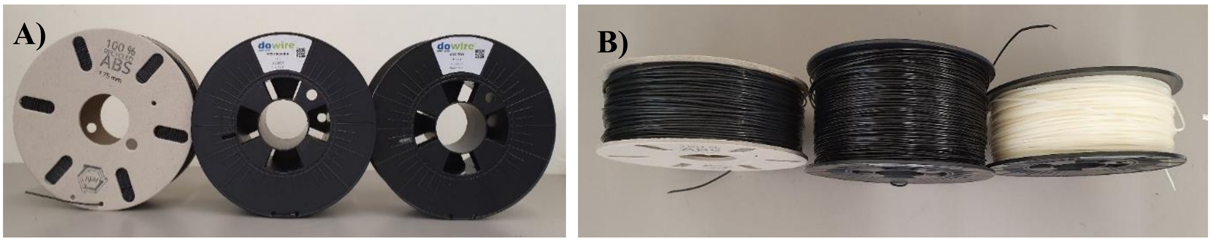

Figure 5: Filament spools optical macrographs. Recycled ABS on the left, virgin black PLA on the middle, and virgin natural ABS on the right. A) front view, B) top view.

In order to facilitate the presentation and discussion of the results, the several types of filaments were designated according to what is summarized in table 3.

Table 3: Material's Designation.

Material	Designation
Recycled ABS	ABSR
Virgin Black ABS	ABSB
Virgin Natural ABS	ABSN
Recycled PLA	PLAR
Virgin PLA	PLA

2.2. Experimental Methods

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2.2.1. 3D Printing

All testing specimens were 3D printed with a Robo R2 equipment with a printing velocity of 50 mm/s and a 100 % infill. The equipment had a nozzle diameter of 0.4 mm and all layers were printed with 0.2 mm diameter. The first printed layer has 45º angle in relation with the sample wall, and the subsequent layers have 90º related to the previous one. The 3D printed samples' processing temperatures and the dimensions of the tested specimens in the mechanical characterization techniques of three-point flexural test (3PB) and tensile tests are summarized in table 4.

Table 4: Samples' Processing Temperatures and Dimensions of the Printed Specimens for the Mechanical Tests.

Material/Testing		Extruder Nozzle Temperature (ºC)	Printing Platform Temperature (ºC)	Length (mm)	Width (mm)	Thickness (mm)
PLA	3PB	205	60	60	9.8	2.3
	Tensile	205	60	180	15.0	2.2
PLAR	3PB	205	60	60	9.7	2.4
	Tensile	205	60	180	14.5	2.6
ABSN	3PB	230	70	60	9.7	2.0
	Tensile	230	70	180	14.8	2.3
ABSB	3PB	230	70	60	9.8	2.3
	Tensile	230	70	180	14.8	2.2
ABSR	3PB	230	70	60	10.0	2.3
	Tensile	230	70	180	14.9	2.3

2.2.2. Thermal Properties

2.2.2.1. Thermal Gravimetric Analysis – TGA

The degradation measured has the loss of weight with increasing temperature, of the different materials were investigated by thermal gravimetric analysis (TGA). TGA measurements were performed in a TGA Q500 V20.13 equipment, at a heating rate of 10ºC/min, from 25 to 600ºC, under a nitrogen flow of 50 mL/min. Sample's weight was between 6 and 7 mg.

2.2.2.2. Differential Scanning Calorimetry - DSC

The thermal events suffered by the polymeric materials due to increasing temperature were studied by Differential Scanning Calorimetry (DSC). Measurements were carried out on a DSC Q100 V9.9 equipment, with a scan rate of 10ºC/min, from -80 to 400ºC, under a nitrogen flow of 50 mL/min. The samples' weight was between 6 and 7 mg.

2.2.3 Surface Roughness

3D optical microscopy by focus variation combines the small depth of focus of an optical system with a vertical scan in order to provide topographic information. This technique evaluates surface roughness and can be used as a complement to other techniques. It allows the use of lenses with different amplifications and different light sources (ring light) that enable the measurement of tilt angles greater than 87° and a maximum vertical resolution of about 10 μm.

The equipment used was the Alicona-InfiniteFocus, equipped with a fixation system of the materials to be analyzed, which allowed the acquisition of a three-dimensional image of the specimens after printing and the evaluation of different surface roughness parameters.

The main parameters were the average surface roughness, both in line mode (Ra) and in area mode (Sa), the average square roughness (Rq and Sq), and the evaluation of the maximal valley-to-peak distance (Rz and Sz). The roughness parameters in line mode determined longitudinally and transversely, being the designation used “-L” and “-T” respectively.

2.2.4 Mechanical Properties

2.2.4.1. **Hardness**

Material hardness was measured on a Shore D durometer. Five measurements per sample arbitrarily distributed were done at a temperature of 23 ± 2°C. The values presented are a result the measurements’ average value.

2.2.4.2. Tensile Test

The mechanical properties of the different materials were evaluated by tensile test performed in an Autograph AGS-X, from Shimadzu, with 100 kN maximum load and a MFA25/12 mechanical extensometer (Figure 6).

In these measurements, gauge length was 50 mm and the displacement rate 3 mm/min. The software used for results analysis was Trapezium X.

Figure 6: Autograph AGS-X, from Shimadzu, during the tensile test.

2.2.4.3. Three-Point Flexural Test

The mechanical properties were also evaluated by a three-point flexural test (Figure 7). The equipment used was an Autograph AGS-X from Shimadzu, with a 5 kN cell, and the displacement rate 3 mm/min. Results were analysed using the Trapezium X software.

Figure 7: Shimadzu Autograpgh AGS-X during three-point flexural test.

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CHAPTER 3 - RESULTS AND DISCUSSION

3.1. Thermal Properties

As important as analysing the mechanical properties of the material, is to understand the filament behaviour, specially the thermal properties. Table 5 presents the characteristic temperature values of the filaments calculated from the DSC analysis. ABS samples do not show any melting neither crystallization temperatures, which was expected due the amorphous structure of the copolymer. Glass transition temperature for recycled, black and natural ABS were all within the same range. However, the degradation temperature for the recycled ABS was higher than black and natural, according to both DSC and TGA analysis (Table 6). ABSB has lower degradation temperature than ABSN, indicating that the use of additives (at least a colorant was added to ABSB) influences the thermal properties.

Considering the PLA polymers, glass transition temperature was similar to both virgin and recycled material (table 5). However, the DSC values in table 5 also show a higher melting temperature and lower crystallization temperature for recycled PLA. The higher melting temperature for the recycled material indicates that the additives present in the virgin material (at least a white colorant was used) prevent the same degree of structural order when compared to PLAR. On the other hand, the lower crystallization temperature for recycled PLA can be due to the recycling process that induce chain scission (Badia et al. 2012), and, consequently, the smaller chains are able to re-organize at lower temperatures than longer macromolecules.

Table 5: Temperature values for the five samples calculated from DSC curves.

	Temperature (ºC)			
Sample	**Tg**	**Tm**	**Tc**	**Tdeg**
ABSR	111.9	-	-	314.9
ABSB	111.1	-	-	277.6
ABSN	110.7	-	-	289.6
PLAR	59.9	171.2	98.4	-
PLA	60.8	151.6	117.4	-

The results from the TGA characterization also enables to determine the amount of residue left after the tests at the used temperatures (table 6). The decomposition of non-recycled PLA happens in higher extension, with higher mass loss, resulting in fewer residues percentage than in recycled PLA with lower mass loss. ABS samples have similar weight loss percentages. However, ABSB and ABSR had also shown slightly higher mass loss percentage values when compared to ASBN, being ABSR the ABS sample with the highest mass loss percentage. Even though that materials with additives are the ones that usually present the highest percentage of residues, the only additive information known is the presence of a colourant/pigment in ABSB, ABSR and PLA and, its degradation temperature is lower than ABS and PLA, thus, not ending as residue in the TGA test.

Table 6: Total mass loss and degradation temperature values for the five samples calculated from TGA.

Sample	Total mass loss (%)	Tdeg (ºC)
ABSR	93.7	427.3; 402.7; 378.0
ABSB	93.3	419.0
ABSN	93.0	420.0
PLAR	95.3	347.4; 313.9; 275.9
PLA	98.5	355.0

3.2. Surface Roughness

The values obtained from linear and area surface roughness measurements are despite in figures 8 and 9, respectively. Recycled ABS shows a less rough profile compared to natural and black ABS. In figures 10 and 11, the same parameters are summarized for PLA. Again, the PLAR is less rough than PLA, being this difference even more obvious with PLA than ABS.

Roughness values can be an indication of material viscosity and molecular weight. A material with higher molecular weight normally present higher viscosity. In the 3D printing process, a higher viscosity of a material, at the printing temperature, correspond to a higher surface roughness. In fact, in this case the material tends to maintain the shape acquired during extrusion, which implies that will not “spread” onto the printed surface. Therefore, the lower roughness of the recycled materials (ABSR, PLAR) can be an indication of a lower molecular weight, due to the chain scission provoked by the mechanical recycling process as already explained.

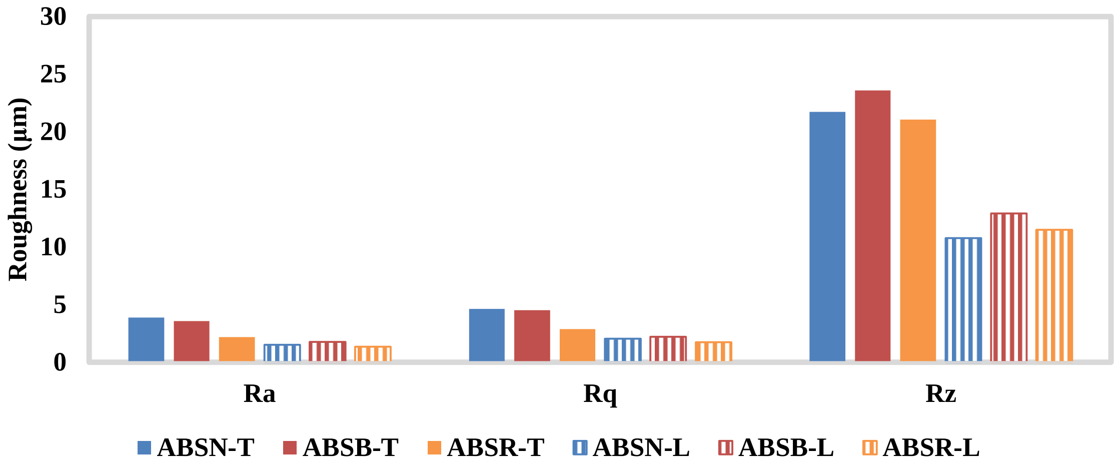

Figure 8: Profile surface roughness values for ABS samples calculated from 3D optical microscopy.

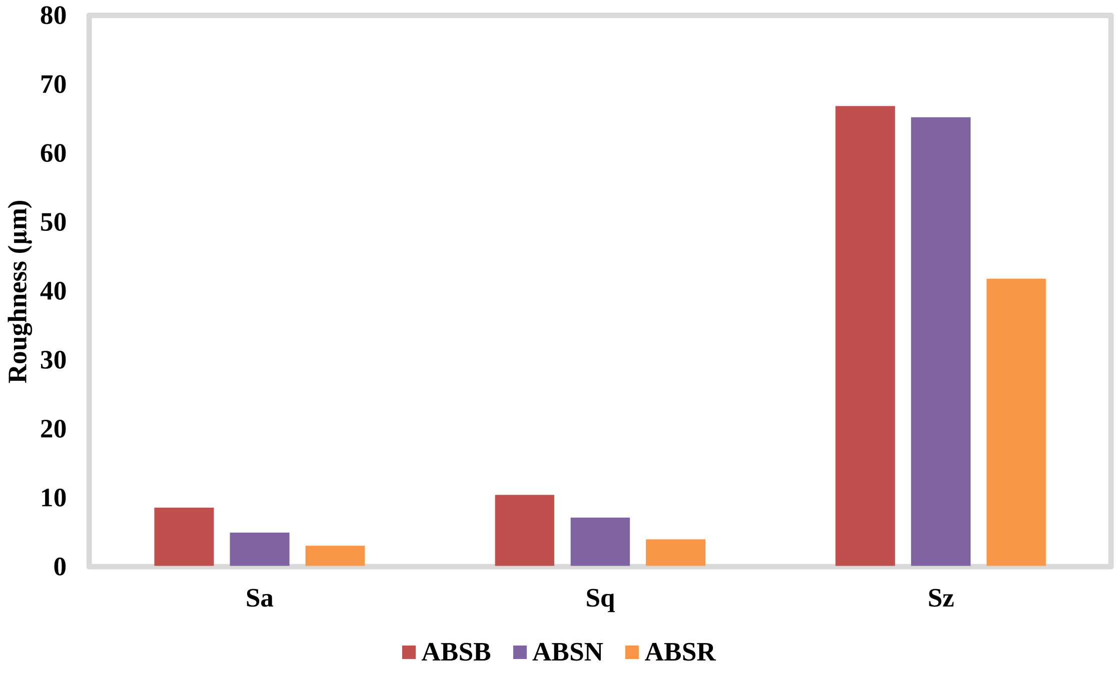

Figure 9: Area surface roughness values for ABS samples calculated from 3D optical microscopy.

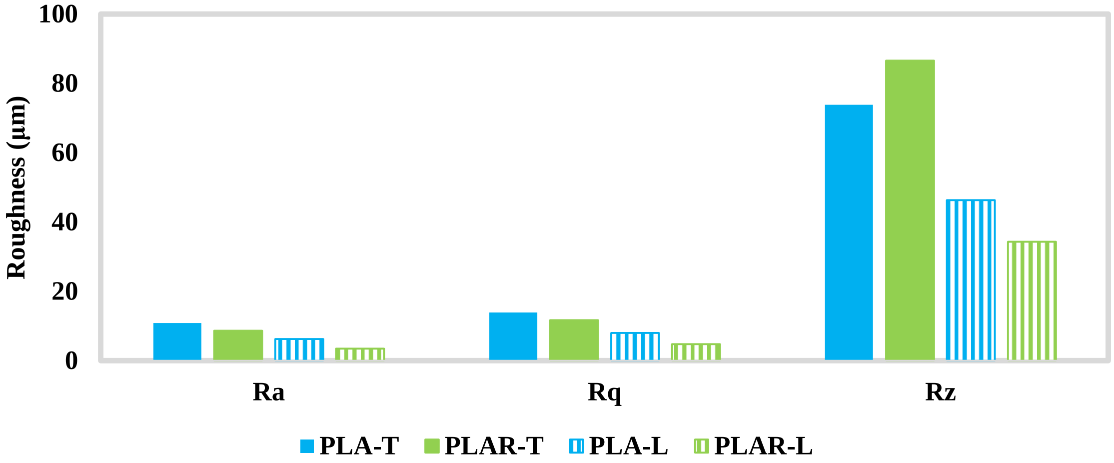

Figure 10: Profile surface roughness values for PLA samples calculated from 3D optical microscopy.

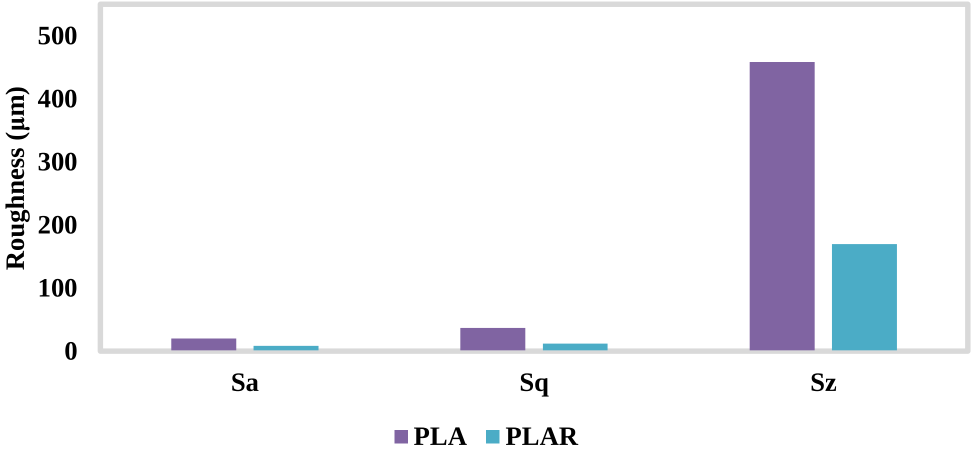

Figure 11: Area surface roughness values for PLA samples calculated from 3D optical microscopy.

3.3. Mechanical Properties

Hardness values are presented in figure 12, showing no significant difference for all the studied samples. This was an expected result as thermoplastic materials tend to present very similar resistance to plastic deformation when subject to indentation.

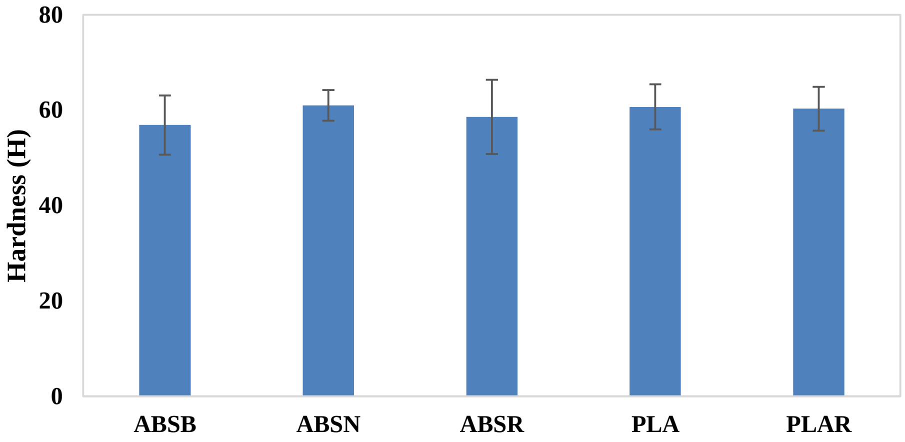

Figure 12: Hardness values for the five samples from the hardness test.

Figure 13 present the maximum tensile stress calculated from the tensile test characterizations. The three ABS samples are within the same range relative to the maximum tensile stress value. A slight lower value is observed for ABSB which can be due to the presence of additives. Although, these chemical compounds are also present in ABSR due to the recycling process and additional thermal history of the material (consequence of the process to obtain the filament) some of the additives could have been removed. However, for PLA, the recycling process reduces the maximum tensile stress. This can be attributed to a lower molecular weight, as previously reported, which correspond to lower chain length. Therefore, upon solicitation the resistance offered by the number of secondary bounds per chain will be, in average, lower.

The same trend was seen for the elastic modulus (Figure 14). The three ABS materials have an elastic modulus within the same range, and recycled PLA has lower elastic modulus than non-recycled PLA. Figures 15 and 16 show representative stress-strain curves of the tensile test for ABS and PLA materials, respectively.

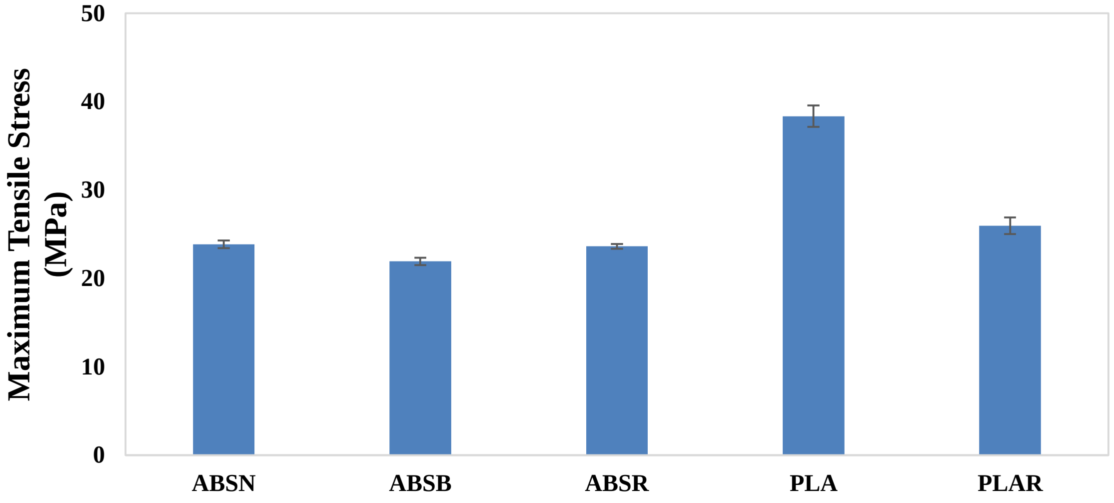

Figure 13: Maximum tensile stress values for the five samples calculated from the tensile tests.

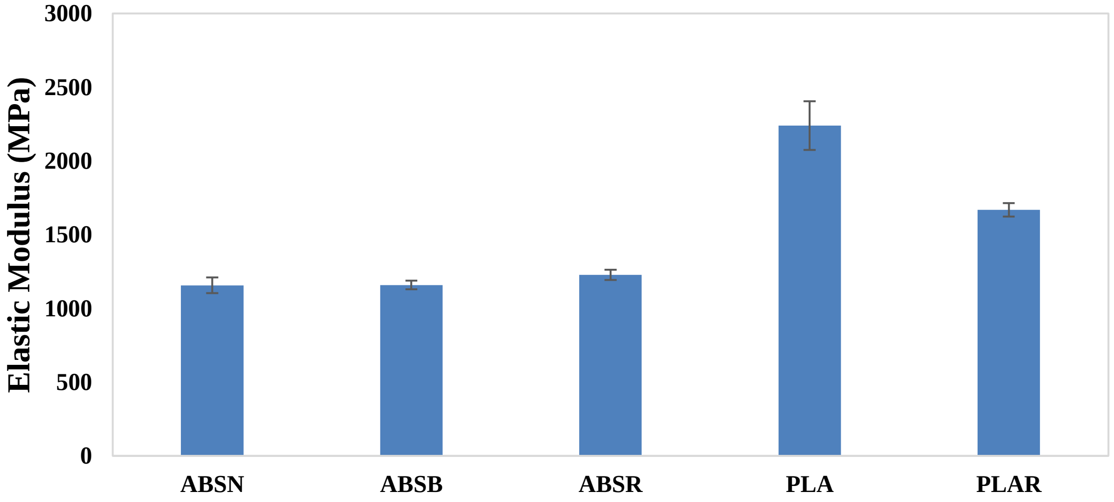

Figure 14: Elastic modulus values for the five samples calculated from the tensile tests.

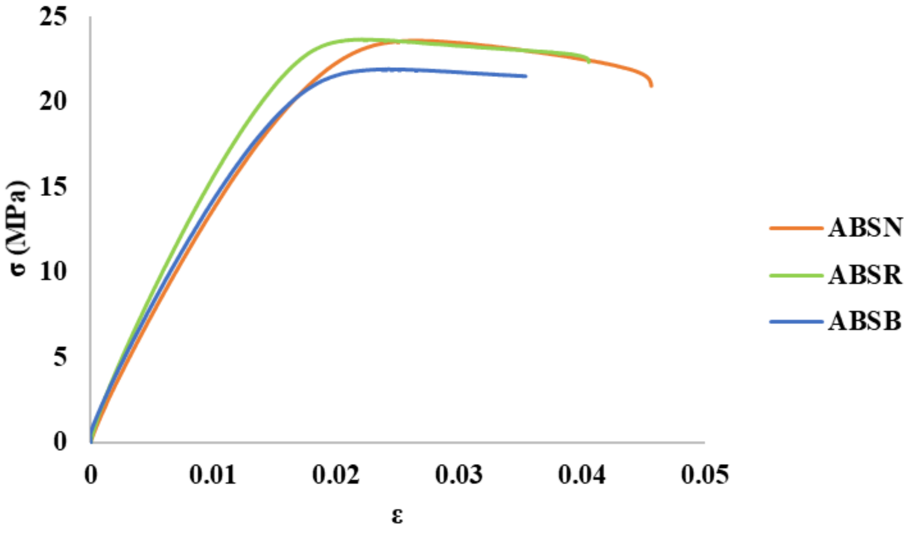

Figure 15: Representative stress-strain curves of the tensile test for ABS samples.

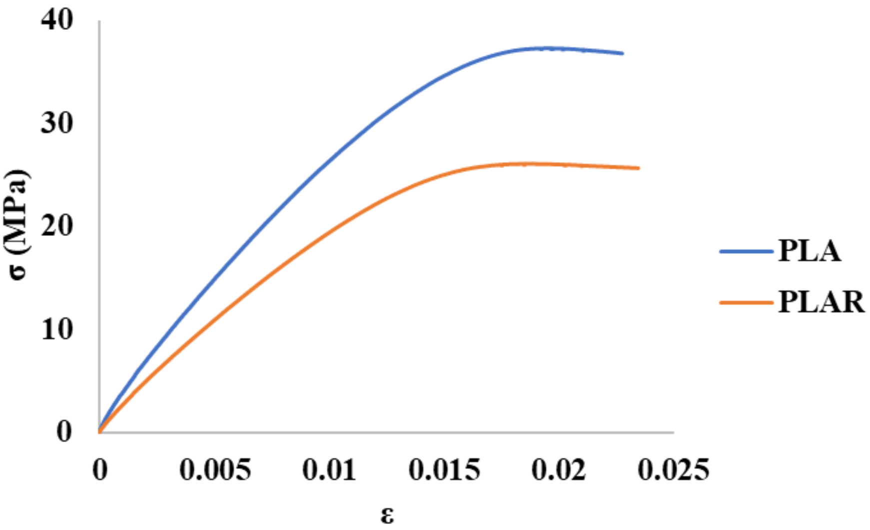

Figure 16: Representative stress-strain curves of the tensile test for PLA samples.

Considering some possible applications for the recycled material, namely the reutilization of ABS in the car’s dashboard, it is important to evaluate the mechanical properties in flexure mode. In fact, this type of mechanical solicitation will be the most important when airbags deploy. In the three-point flexural test the maximum flexural strain was calculated, and results are presented in figure 17.

The presence of additives induces a decrease of the maximum flexural stress of ABS, as it is visible when comparing ABSN and ABSB. ABSR maximum flexural stress present a mean value between ABSN and ANSB. When compared with the virgin black material this can be due to the elimination of some of the additives, as explained before. The suppliers of FDM polymeric filaments give no information on the type or number of additives in each material formulation. The conclusions need to be carefully considered when comparing ABSB and ABSR as different additives and different concentrations of the same compound will produce differentiated properties/characteristics in the polymer and, consequently, in the mechanical properties.

The recycling process reduces the maximum flexural stress for PLA, an equivalent behaviour to the tensile mode. This behaviour is attributed to lower molecular weight, as explained before.

Figure 18 and 19 show representative curves of the three-point flexural test for ABS and PLA, respectively.

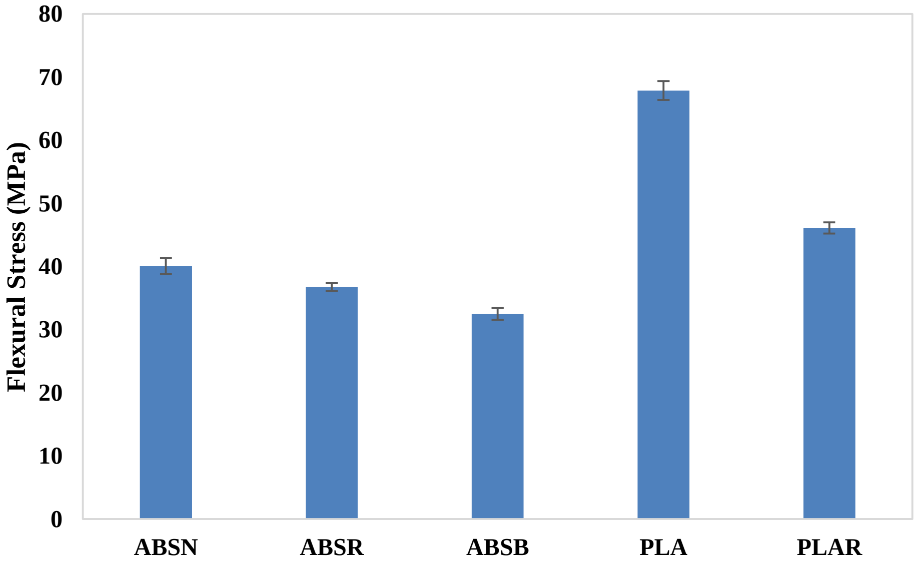

Figure 17: Maximum flexural stress values for the five samples calculated from their stress-deflection curves of the three-point flexural test.

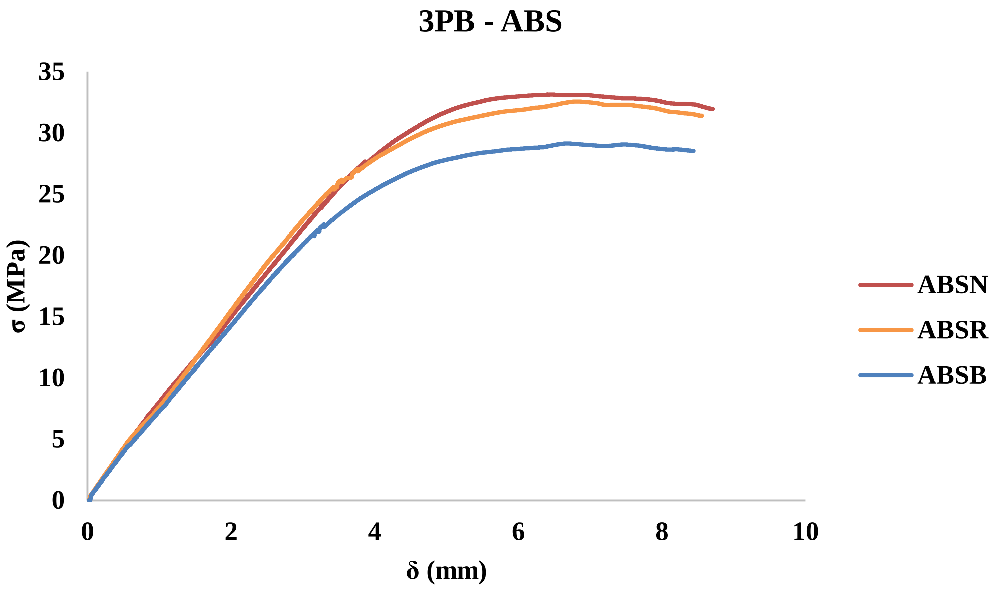

Figure 18: Representative stress-deflection curves of the three-point flexural test for ABS samples.

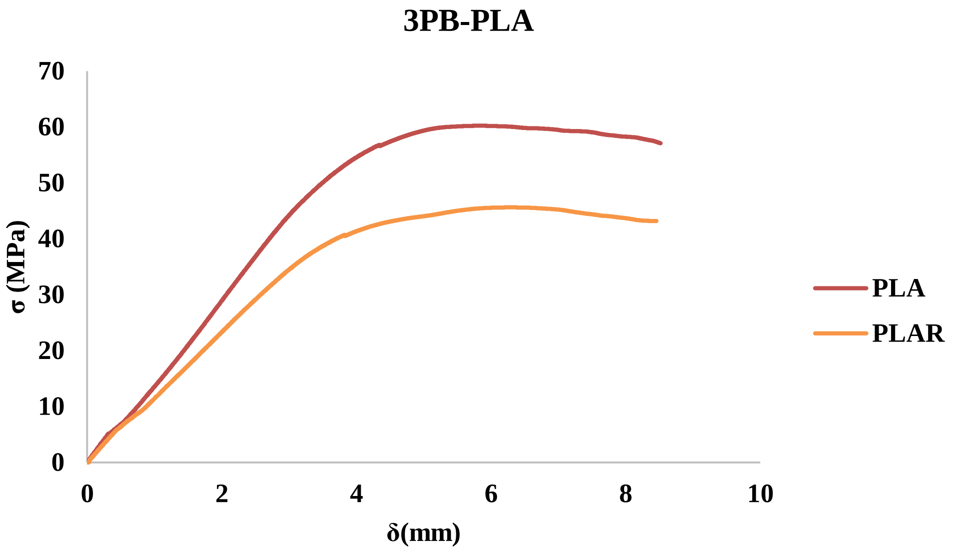

Figure 19: Representative stress-deflection curves of the three-point flexural test for PLA samples.

An overview of the mechanical properties of various PLA and ABS suitable for food packaging and car dashboards, respectively, collected from several companies, was made (table 7). Table 7 shows that the studied materials cover the requested mechanical characteristics for the selected applications.

Table 7: Mechanical properties of commercial PLA and ABS (https://omnexus.specialchem.com/).

	PLA	**ABS**
Tensile Stress (MPa)	16-78	12-75
Elastic Modulus (MPa)	340-5800	975-4100
Flexural Stress (MPa)	21-108	18-150
Hardness (H)	47-83	35-73

CONCLUSIONS

The most limitation factor within this study was the lack of information regarding the polymeric filaments' properties. The thermal and mechanical analysis of this dissertation enabled the creation of some hypothesis. However, in-depth characterization is fundamental for mechanical behaviour understanding. This in-depth characterization should be made from a chemical approach, which is not in the scientific area of mechanical engineering.

The lower crystallization temperature from PLAR, the lower roughness values for both PLAR and ABSR are an indicator that, most probably, the principal cause of degradation from the mechanical recycling process is chain scission and therefore, the recycled material show lower molecular weight and viscosity.

The additives present in PLAR, ABSR and ABSB (at least colourants/pigments were added) had a notorious impact on the thermal and mechanical properties. ABSB had closer properties to ABSR than ABSN, meaning that the additives bring more impact to the polymer morphology than the recycling process.

The virgin and recycled materials had, in general, similar mechanical properties when processed with the same parameters. The lower roughness from the recycled material can be beneficial for some applications, namely those that include better surface finishes.

The studied recycled materials fulfil the mechanical properties requirements for the same application of the polymeric materials before recycling. In conclusion, it is possible to recycle ABS and PLA from car dashboard's and food packaging, respectively, and re-use it, by 3D printing processing for the same purpose. This way, fewer resources will be consumed, less waste will be created, and less will be produced, decreasing the impact on global warming. Moreover, 3D printing has shown to be a suitable, efficient and sustainable solution as it works with almost no waste/residues production.

The results from this dissertation were particularly optimistic since the samples were produced with the least favourable 3D printing parameters to work as a proof of principle. As future work, parameters can be optimized for better productivity and, different designs should be tested to analyse different material behaviour.

Since a material loses its properties after reprocessing more than six times, blends of the virgin with recycled material could safeguard long-term quality. Thus, the optimization study and the ratio of virgin material to blend with the recycled one, should also be considered in a future work.

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APPENDIX – DSC THERMOGRAMS

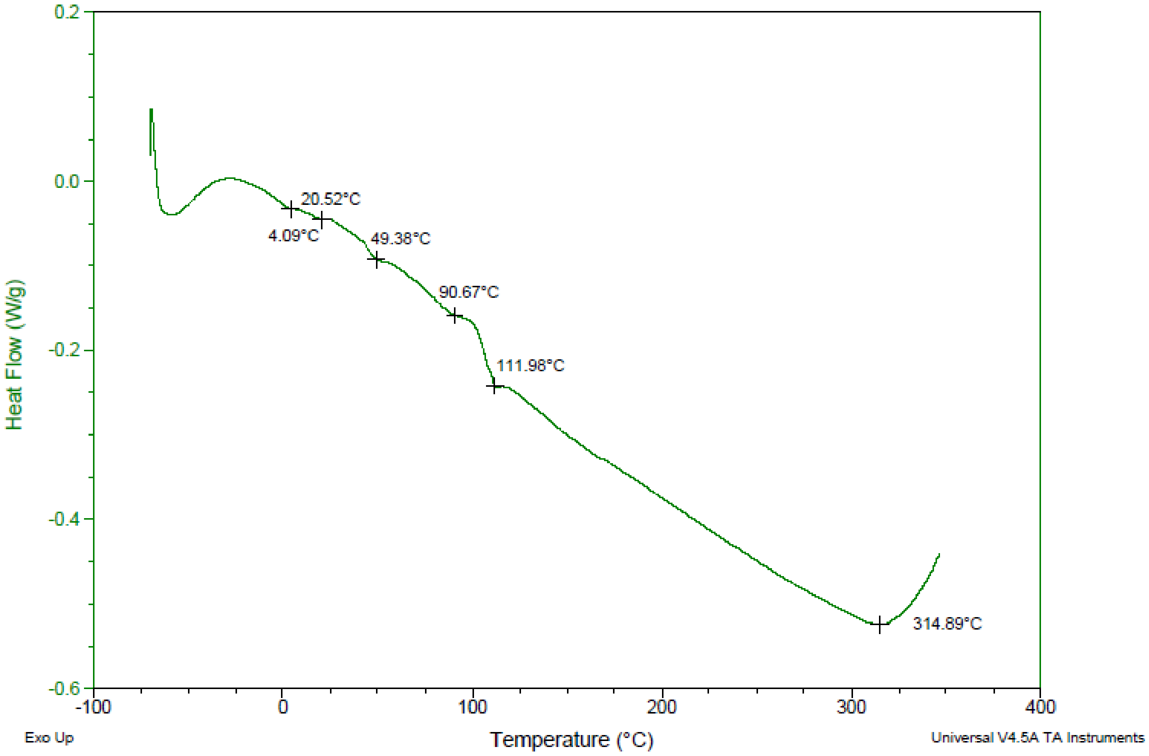

Figure 20: DSC thermogram of ABSR.

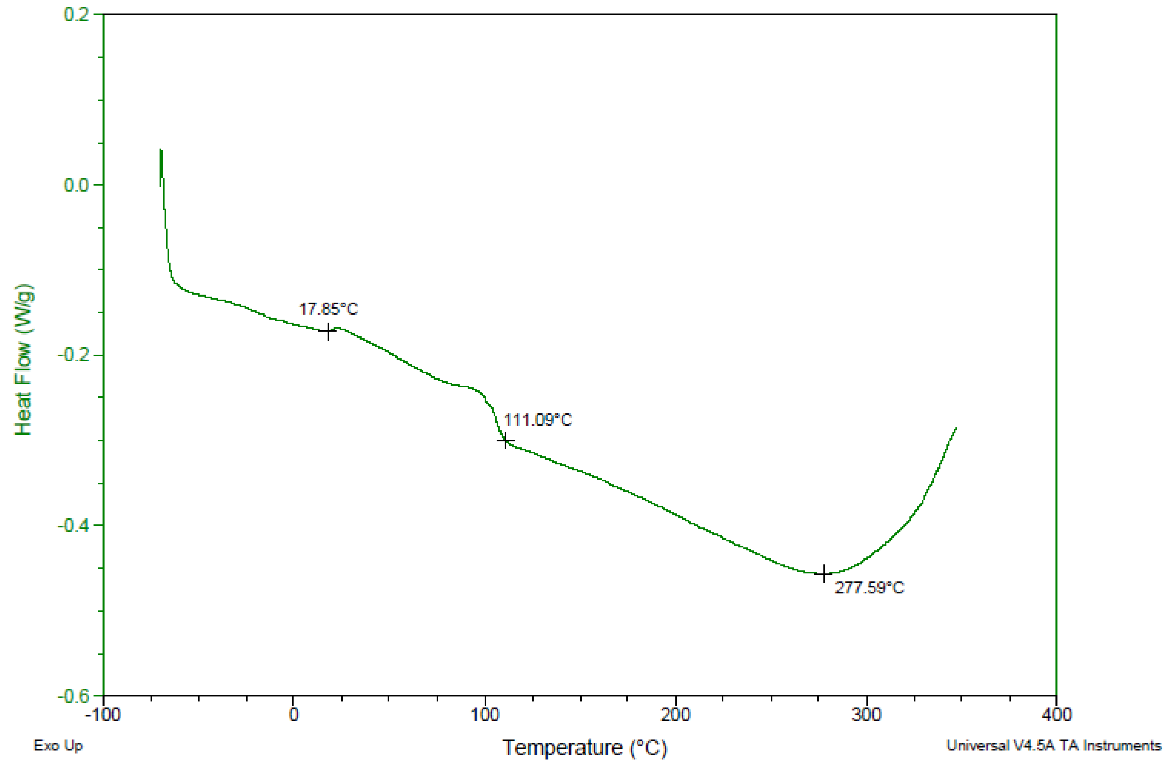

Figure 21: DSC thermogram of ABSB.

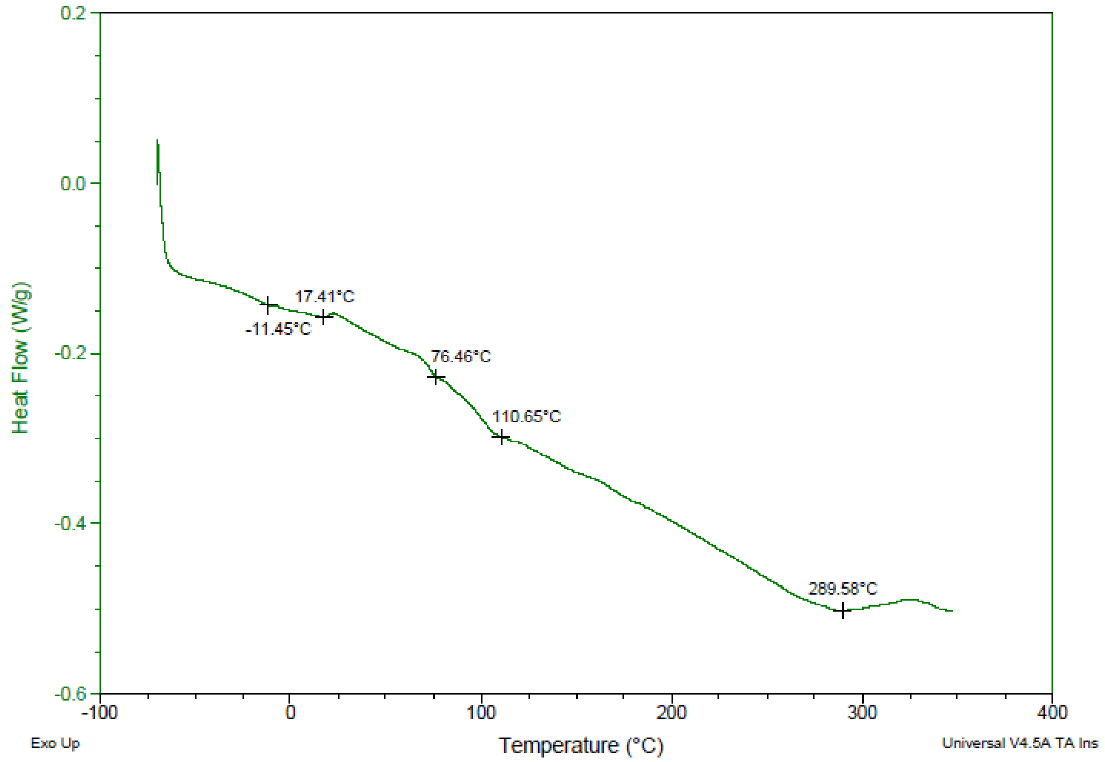

Figure 22: DSC thermogram of ABSN.

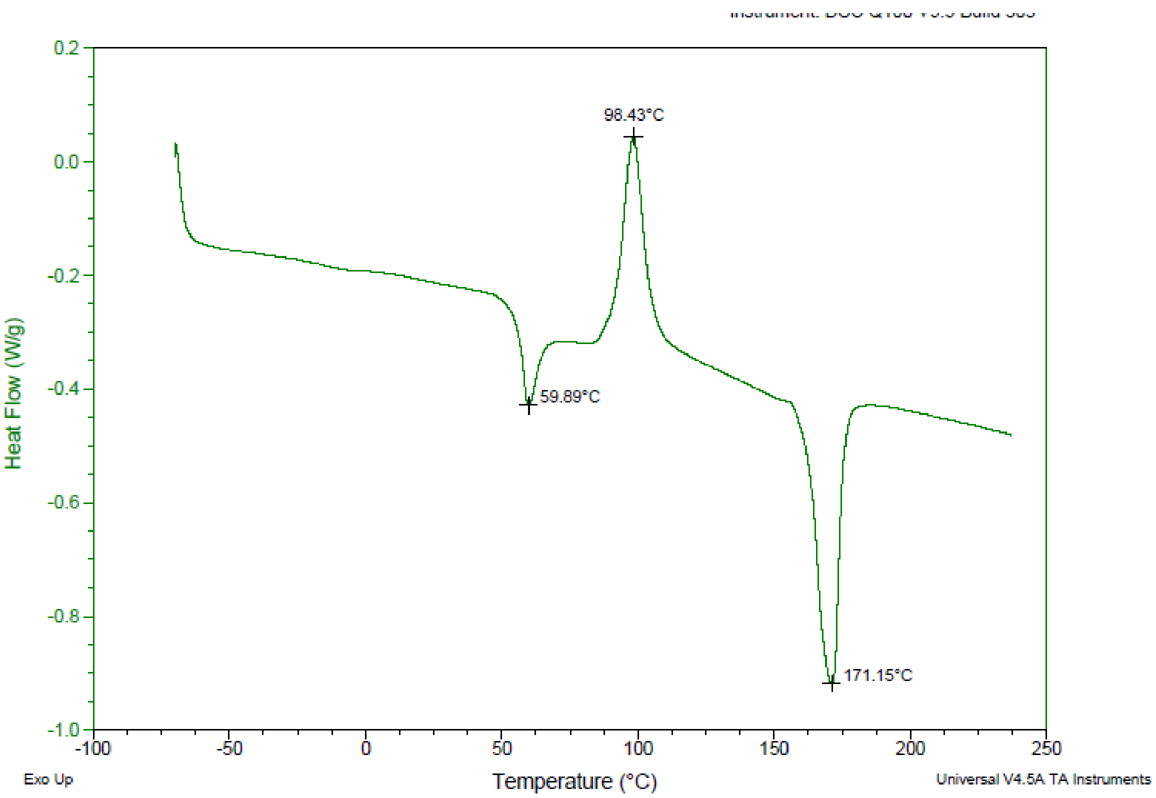

Figure 23: DSC thermogram of PLAR.

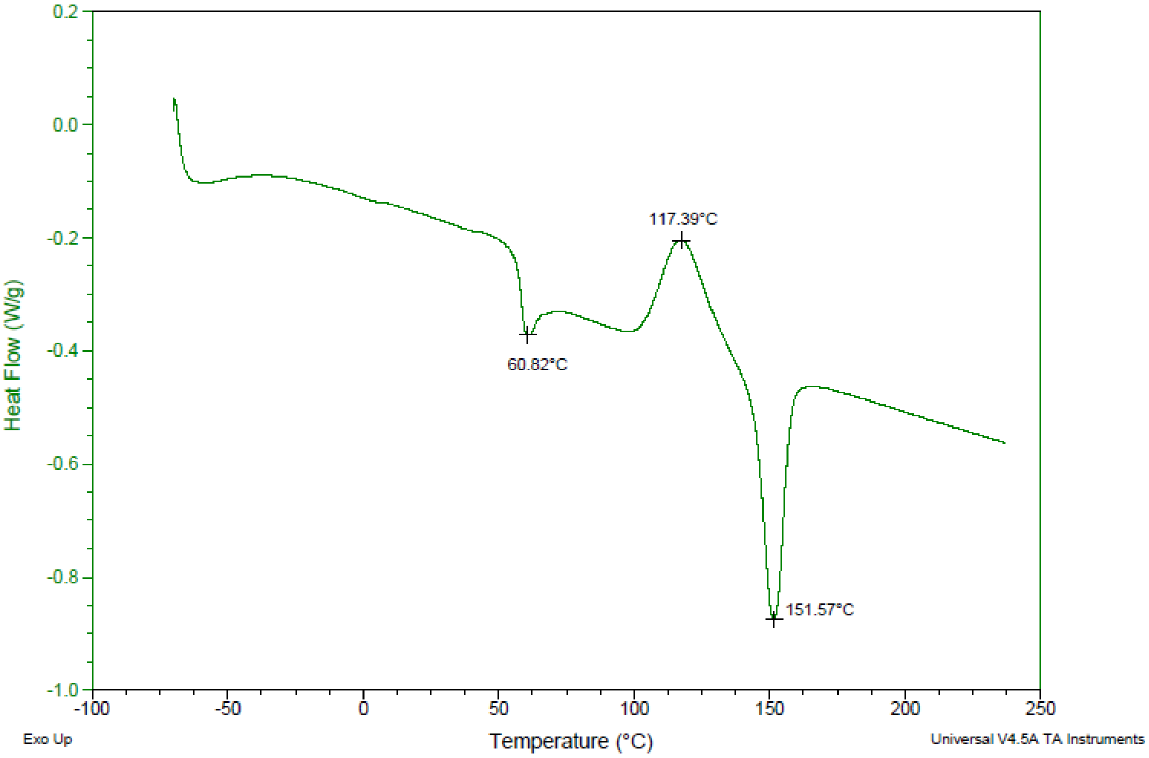

Figure 24: DSC thermogram of PLA.