Effect of annealing on mechanical properties of 3D alternated printed layers of PLLA and PDLA

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Abstract. In recent years, additive manufacturing, particularly 3D Printing via Fused Deposition Modeling (FDM), has seen remarkable growth. FDM, characterized by melting thermoplastic filament through a metallic nozzle to build objects layer by layer, offers unique advantages in creating complex geometries at low costs. However, this technology faces challenges regarding the poor adhesion between layers, resulting in weaker mechanical properties along the Z-axis. Among the most used materials, Polylactic Acid (PLA) stands out due to its biodegradability and high strength. However, this material has limitations related to high brittleness. This paper explores the feasibility of producing tougher PLA using the stereocomplexation process in the alternated printing of PLLA and PDLA, followed by annealing thermal treatment.

Keywords. 3D Printing, PLA, Polylactic Acid, Stereocomplexation, Annealing

1. Introduction

In recent years, there has been significant growth in the adoption of additive manufacturing technologies, with 3D Printing leading the charge, particularly through the Fused Deposition Modeling (FDM) technique. FDM involves melting a thermoplastic filament and extruding it through a metallic nozzle, enabling the creation of physical objects layer by layer. This method offers the unique advantage of producing unique geometries at a low equipment cost, distinguishing it from conventional manufacturing processes [1].

Although 3D printing technology has great potential for use, this technique faces challenges related to adhesion between the printed layers. As the deposition time of printed layers is short, the printed material ends up being cooled quickly, which does not allow good adhesion between the printed layers. This fact culminates in weaker mechanical properties in the construction Z axis, perpendicular to the printing bed.

Among the materials applied to the 3D printing technique, Polylactic Acid (PLA) emerges as a prominent option. PLA is a biodegradable material derived from renewable resources, like corn and rice, with easy processability, In terms os mechanical properties, PLA has a high strength and high modulus of elasticity. However, this material also has some limiting characteristics, such as high brittleness [2]. This fact stimulated research using thermal treatment techniques, such as annealing, to optimize such characteristics, seeking to make the material more ductile.

In view of the limitations of 3D printed parts, the stereocomplexation process was studied as an alternative to reinforce the connection between 3D printed layers. This process consists of the formation of a stereocomplex polymer by combining two complementary stereoregular polymers, PLLA and PDLA, in solution, which enhances the thermal properties of PLA-based materials through the robust interaction between L-lactide and D-lactide monomers [3].

This research aims to analyze the possibility of producing a 3D printed tougher PLA from alternating printing between PLLA and PDLA, with subsequent annealing thermal treatment.

2. Theoretical Background

2.1 3D Printing

The use of 3D printing technology has grown significantly in recent years due to the possibility of exploring the construction of complex parts quickly, at low cost and in different materials, making it a very useful resource for prototyping. This process occurs through the extrusion of melted material and the deposition of layers upon layers, allowing the creation of complex geometries. However, this method has process limitations, such as poor adhesion between layers, which affects the mechanical properties of the printed part.

2.2 Polylactic Acid

PLA, or Polylactic Acid, stands out for characteristics such as biodegradability, high strenght and wide natural availability. These attributes make it highly attractive and promising for various industrial areas, thus driving increasing studies and tests with this material. In the context of 3D printing, this material is widely applied due to its ease of processing, wide availability and low cost. Its mechanical properties are related to its molar mass and thermal history, but in general this material has a tensile strength of approximately 59 MPa and an elongation at break of approximately 7% [2]

Recently, there has been an expansion of studies aimed at optimizing the mechanical properties of PLA (polylactic acid), exploring the production of Poly-L-lactide (PLLA) and poly-D-lactide (PDLA) through the polymerization of L-lactide. and D-lactide monomers. These monomers are distinguished only by their 3D rotation, a factor that influences their physical properties [4].

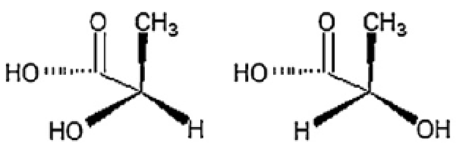

Fig. 1 – D-Lactic Acid and L-Lactic Acid chemical structure.

2.3 Stereocomplexation

The use of PLLA and PDLA in solution promotes the occurrence of stereocomplexation, which is a process related to the formation of a stereocomplex polymer from specific intermolecular interactions, arising from the strong interaction of the L-lactide and D-lactide monomers. Therefore, this stereocomplex polymer promotes an improvement in the mechanical and thermal properties of PLA-based materials [4].

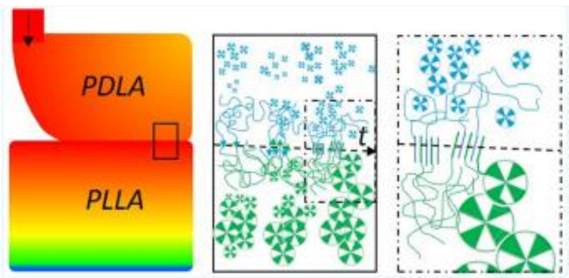

Fig. 2 – Alternating deposition between PLLA and PDLA.

Therefore, stereocomplexation appears as a resource for improving connections between layers of parts printed alternately between PDLA and PLLA. Previous research has shown an increase in Storage Modulus and improved tensile performance in the Z direction of printed parts [3].

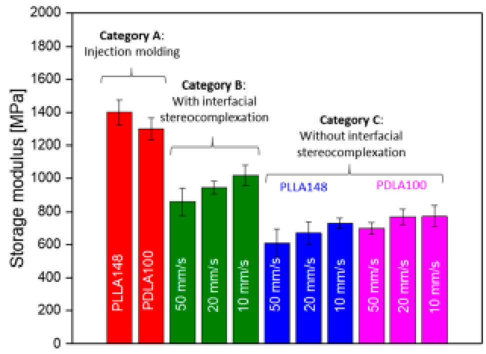

Fig. 3 - the Storage Modulus at 40°C for three categories: Injecting molding, 3D printing with interfacial stereocomplexation and 3D printing without interfacial stereocomplexation.

Figure 3 allows us to compare the Storage Modulus at 40°C for three categories: Injecting molding, 3D printing with interfacial stereocomplexation and 3D printing without interfacial stereocomplexation. It is possible to see a greater stiffness between the 3D printed layers in cases where stereocomplexation is present. In these cases, the interaction between PLLA and PDLA caused a better connection between the layers, which impacted the tensile test results.

Furthermore, it is also observed that parts printed at lower printing speeds have higher Storage Modulus, which is related to the longer time that the nozzle is close to the printed layers. This allows a longer heating time for the printed layer, contributing to the occurrence of stereocomplexation.

2.4 Annealing

The annealing process is a thermal treatment to change the mechanical properties of a material. This process, initially applied to metals, consists of keeping a material at a high temperature for a period of time, followed by slow and controlled cooling. This process increases the ductility and reduces the hardness of the material, in addition to relieving internal stresses. These properties are fully related to thermal treatment process data, such as temperature, time and cooling rate. [7]

This type of thermal treatment also has an important effect when applied to polymers, causing significant changes in the mechanical properties of these materials. During the annealing of polymeric materials, the polymer chains have the opportunity to rearrange themselves, reducing internal tensions, increasing crystallinity and improving the homogeneity of the material. This can result in improvements in the mechanical, thermal and optical properties of the polymer, such as increased strength, stiffness and dimensional stability [5].

In this context, annealing can be an important alternative for 3D printing of polymers. With this thermal treatment, it is possible to make the printed material more ductile, as annealing induces the formation of finer crystals, which affects the flexibility of the printed material [6]. Furthermore, annealing also contributes to improve the connection between the printed layers, which can affect the tensile performance of the printed part [5].

Fig. 4 - Gaps between layers before annealing.

Fig. 5 - Gaps between layers after annealing.

From figures 4 and 5 it is possible to see a reduction in the gaps between the printed layers in the printed bed that has undergone annealing. Reducing these gaps can be an important factor in the performance of this printed part.

3. Methodology

The research methodology was carried out in different stages, seeking to collect information about each process analyzed in the article. The first step consisted of understanding the 3D printing process and its application with PLA. For this, Google Scholar was used as a tool, using the following keywords: "3D printing", "PLA", "Mechanical Properties", "Tensile test", "Fused Deposition Modeling".

Then, still using Google Scholar, research was performed towards understanding the stereocomplexation process. For this, the following keywords were used: "3d printing", "Stereocomplexation", "Alternated 3D Printing", "PLLA", "PDLA".

Finally, research was performed to understand how annealing thermal treatment could affect 3D printed polymeric parts. In this case, the following keywords were used for search: "Annealing", "Polymer thermal treatment", "3D printing". The searches were also carried out on Google Scholar.

In addition, the references of the articles found were also checked, aiming to find more materials for analysis and study.

4. Results and Discussion

The research carried out returned, firstly, a great potential for using PLA in the scope of additive manufacturing, mainly due to its availability, sustainability and properties [2]. However, on the other hand, it is necessary to deal with the challenges of this use. The first, the weak connection between the 3D printed layers, culminates in worse mechanical properties in the Z direction of construction, causing the part to have poorer tensile performance.

Therefore, studies related to the use of stereocomplexation showed the possibility of printing PLLA and PDLA alternately, using two printing nozzles. In this case, there is an increase in the strength of the connection due to stronger molecular interactions, therefore increasing the mechanical strenght of the material [3].

However, despite this improvement, the printed part still presents high brittleness and low ductility. In view this, it was sought to understand whether annealing would be a viable alternative for this purpose. Research has shown an efficiency in increasing the ductility of printed PLA after being annealed, which is related to the reduction of gaps between layers and the formation of finer crystals [5].

Therefore, the use of the stereocomplexation process between alternately printed parts between PLLA and PDLA, added to the subsequent occurrence of annealing, can be a viable alternative for the production of tougher 3D printed parts.

5. Conclusion and recommendations

The results obtained showed great potential for producing a tougher PLA, based on alternating 3D printing of PLLA and PDLA, followed by annealing.

Therefore, it is suggested that practical tests be carried out to validate the results. Firstly, tests related to alternating printing between PLLA and PDLA of specimens can be carried out, in the Z direction of construction. Once this is done, these materials can be annealed using different temperatures and heating times, which will influence the mechanical properties of the materials. With these data, it is possible to analyze the data obtained and conclude more assertively about the effect of annealing on parts printed alternately between PLLA and PDLA.

6. References

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