A review about polylactic acid filament recycling to 3D printing process

Uma revisão sobre a reciclagem de filamentos de ácido poliláctico ao processo de impressão 3D

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ABSTRACT
Additive manufacturing, specifically 3D printing (3DP), is a trend of great relevance in industry 4.0. The objective of this work is presented as a systematic review of the available literature to define the main methods and standards towards analyzing the material properties, 3D printing filament extrusion variables, and polylactic acid (PLA) recycling. The research used the methodology of a mixed explanatory sequential review based on studies already published in books and journals. These data have relevant information to serve as a guide for the recycling, extrusion, and 3D printing of the PLA.

Keywords: 3d printing, recycling, pla, extrusion.
RESUMO
O fabrico de aditivos, especificamente a impressão 3D (3DP), é uma tendência de grande relevância na indústria 4.0. O objectivo deste trabalho é apresentado como uma revisão sistemática da literatura disponível para definir os principais métodos e normas para a análise das propriedades dos materiais, variáveis de extrusão de filamentos de impressão 3D, e reciclagem de ácido poliláctico (PLA). A investigação utilizou a metodologia de uma revisão sequencial explicativa mista, baseada em estudos já publicados em livros e revistas. Estes dados têm informação relevante para servir de guia para a reciclagem, extrusão, e impressão em 3D do PLA.

Palavras-chave: impressão em 3d, reciclagem, pla, extrusão.

1 INTRODUCTION
Additive Manufacturing (AM) has grown at a rate of USD 5 billion per year \[1\]. The main advantage is the possibility to create complex shapes quickly using Computer Aided Design (CAD) with very low costs \[1–3\]. A role-player in AM \[4,5\], polylactic acid (PLA) is a synthetic polyester derived from lactic acid, mainly found in plants, with non-toxic and biodegradable characteristics \[6,7\]. Between the advantages of choosing PLA, it is emphasized that the mechanical strength is about 2 times greater than the Acrylonitrile Butadiene (ABS) polymer \[3,8\].

However, biopolymers usually have a reduced life cycle (LC), limiting their application in the short term \[2\]. Still, the study on the LC of PLA shows that recycling also helps to reduce environmental impacts \[9\]. Nevertheless, there are few studies that demonstrate the effects of recycling and multiple reprocessing on its characteristics \[1\].

According to Pakkanen et al. \[2\] the recycling must maintain properties close to virgin material. Thus, the present study aims to review the available literature to define the main methods and standards towards analyzing the material, 3D printing and filament extrusion variables, and PLA recycling.

2 METHODOLOGY
The databases used were Emerald Insight, Science Direct, Springer and Wiley available through CAFE \(^1\) with the keywords: Extrusion; PLA; 3D printing and Recycling combined through the Boolean AND. The period of publications considered was defined between 2014 and 2019 for a greater wealth of publications. Initially, the articles were classified regarding their contribution to both theme and objectives of this literature.

\(^{1}\) Academic Federated Community
review. After reading, the main ideas were discussed towards interpreting their results. For better understanding, the present study is divided in standards and methods, extrusion process to produce filament, 3D printing process and recycling pipeline.

3 RESULTS AND DISCUSSIONS

3.1 COMMON METHODS OF EVALUATION AND STANDARDS

The ASTM D638 and ISO 527 are the standards regarding polymer tensile testing. In a similar way, the ASTM D790 comprehend the metrics for flexural testing. Mechanical tryouts ensure that the material has characteristics attractive for use. Concerning the characterization of the PLA, it is possible to find in rich details about the microscopy of the samples, especially utilizing scanning electron microscopy (SEM). Badia et al demonstrate the importance of comparing the microscopic surface between the virgin PLA and its 5 times recycled version through injection molding, concluding that there is a loss of orientation of the structural lines. Cruz Sanches also uses microscopy to evaluate the samples of recycled and printed PLA for 5 consecutive cycles, defining that a reduction of the molar mass, namely chain scissoring, results in a greater melt flow index and in a greater uniformity of printed species.

Among other techniques, it is possible to list differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy with Fourier transform (FTIR) and X-ray diffraction (XRD). Monitoring the chemical and structural nature of the polymer allows to track changes in these characteristics during recycling. Beltrán et al make the combined use of DSC, FTIR, TGA and XRD. The changes analyzed by DSC and XRD point to a reduction in polymeric chains and a greater crystallinity for recycled material, corroborating with the findings of Badia et al. From the results of the FTIR, it is possible to state that changes in polymer chains due to mechanical recycling are limited and may indicate the potential use of recycled material. Using TGA, it’s observed that mechanical recycling has little effect on its thermal stability.

3.2 COMMON CHARACTERISTICS OF VIRGIN POLYMER, PREPARATION, AND EXTRUSION PARAMETERS

Visually, PLA is transparent in its amorphous state and tends to become opaque as its crystallinity increases and its characteristics depend on the isomers provided by...
the lactic acid enantiomers, the most commonly used being Poly-L-Lactide (PLLA) [14]. The main characteristics of the PLA polymer are shown in Table 1.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Value (units)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>37 (%)</td>
<td>[8]</td>
</tr>
<tr>
<td>Density</td>
<td>1,21 – 1,26 (g·cm³)</td>
<td>[12,14–19]</td>
</tr>
<tr>
<td>Elongation</td>
<td>0,5 - 9,8 (%)</td>
<td>[7,8,12,14,17,19,20]</td>
</tr>
<tr>
<td>Enthalpy of 100% crystalline polymer</td>
<td>93 (J·g⁻¹)</td>
<td>[10,13,21]</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>2,392 - 4,930 (GPa)</td>
<td>[17]</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>48 -110 (MPa)</td>
<td>[8,17,19]</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>48 – 65 (°C)</td>
<td>[7,12,16,18]</td>
</tr>
<tr>
<td>Izod hardness</td>
<td>13 – 195 (J·m⁻³)</td>
<td>[8,14,19]</td>
</tr>
<tr>
<td>Melt flow index</td>
<td>5-8 (g·10min⁻¹ at 210°C)</td>
<td>[10,12,14,15,17,18]</td>
</tr>
<tr>
<td>Melt temperature</td>
<td>130 – 230 (°C)</td>
<td>[7,8,15,16,18,19]</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>80,000-380,000 (Dalton)</td>
<td>[22]</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>14-73 (MPa)</td>
<td>[1,8,14,19,20,23]</td>
</tr>
<tr>
<td>Young modulus</td>
<td>0,35 - 3,6 (GPa)</td>
<td>[1,8,12,17,19,20]</td>
</tr>
</tbody>
</table>

Due to its polymerization process, the structure ends up as a hydrophilic polymer, meaning that it absorbs water [24]. Wypych defines that the absorption of water by submerged PLA is 0.5% at 23°C [22], what implicates on important structural changes due to hydrolytic degradation and a consequent increase in its crystallinity [13]. Thus, reducing significantly its mechanical strength [25].

Adding to that Castro-Aguirré et al brings that, in general, for industrial processes the PLA is dried at humidity levels below 250 ppm [15], which meets the same information presented by Sin and Tueen [24]. Common temperatures of drying were found at 80°C for 4 hours [12,26] with emphasis on the study of Zhao et al, who, when analyzing the closed recycling cycle for PLA, carried out the drying process for both samples raw and recycled [26].

The processing of PLA can occur through extrusion. The feedstock is placed on the funnel and, using heat and a general-purpose screw, it is crushed onto the internal surface of the barrel [27]. The extrusion temperature recommended is 210°C to allow the melt of all crystalline phases of the polylactide and to achieve higher melt flow [24]. The screw length to diameter ratio is advised to be between 24 and 30 [24] and its speed was found between the ranges of 20 – 150 rpm [12,15,26].
3.3 THREE-DIMENSIONAL PRINTING PARAMETERS, CHARACTERISTICS OF FILAMENT AND PRINTED SAMPLES

Few authors test filaments prior to the execution of their experiments, relying several times on general data from PLA granules or even on technical data from the manufacturer. Casavola et al found that the Tensile strength and the Young Modulus are, respectively, in the range of 32-45 MPa and 1,8-2,6 GPa [28].

Fused deposition modelling (FDM) is a technique that consists of depositing layer upon layer of extruded material through a mobile nozzle on the Cartesian coordinate axes: x, y and z; allowing the creation of complex shapes through computerized 3D models [3,29]. The wide range of parameters available for the production of parts leads operators to base their selection on empirical knowledge [29]. Table 2 shows the main variables available in the literature.

Table 2. Variables of the 3D printing process. Ref.: Author compilation.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Value (units)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle diameter</td>
<td>0,3 – 1,5 (mm)</td>
<td>[1,4,12,16,26,29-31]</td>
</tr>
<tr>
<td>Layer Thickness</td>
<td>0,06 – 0,35 (mm)</td>
<td>[4,8,25-27]</td>
</tr>
<tr>
<td>Layer height</td>
<td>0,2 – 6 (mm)</td>
<td>[12,27,29,31]</td>
</tr>
<tr>
<td>Print bed temperature</td>
<td>0-100 (°C)</td>
<td>[8,10,11,20,21,24,26,28,31,32]</td>
</tr>
<tr>
<td>Nozzle Temperature</td>
<td>180 – 240 (°C)</td>
<td>[1,4,25,26,28,30-36,3,27,31,12,16,17,18,20,23,24]</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>1-150 (mm/s)</td>
<td>[8,25,30]</td>
</tr>
<tr>
<td>Print Rate</td>
<td>10 – 3600 (mm/s)</td>
<td>[4,12,19,21,24,33-35,39]</td>
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</table>

The three-dimensionality of the process implies the adoption of a naming convention for a better specimen evaluation. It’s used, for instance, in the nomenclature presented by Torres et al [19], as shown in Figure 1.

Figure 1: Possibilities of specimen’s orientation. Ref.: Torres et al [19].
The samples printed in the L1-S format tend to present the transposed fracture format and the best combination of mechanical characteristics of ductility, resistance and stiffness \[19,20,24,30,31,38\]. Another benefit of this position is the greater accuracy of the sample dimensions \[34\], due to the orientation of the overlapping layers in 3D printing.

There are several filling formats available e.g., 90/180° or 45/135° \[17,19\]. Rajpurohit and Dave go further and define that, when the filling is parallel to loading, better mechanical properties are obtained \[20\], meeting the same finding made by Lanzotti et al \[17\]. It is also observed that when there are more shell layers, the sample tends to have a greater mechanical resistance, for example, with 2 layers it presents 42.5 MPa, while with 6 edges, 52.0 MPa \[17\]. Still it is noted that the maximum tensile stress for the rectilinear filling of 53.6 MPa \[17\] is greater than the general obtained by grid formats in the studies by Torres et al with 32.0 MPa \[19\].

The layer thickness is an important parameter that affects the values obtained in the mechanical tests \[16,17,32,35\]. Jo et al concludes that it has origin in the reduction of air failures generated by a lower layer thickness \[32\]. Khatwani and Srivastava corroborate with these results, through SEM analysis evaluating likewise that a larger diameter of the printhead provides a wider line and, consequently, reduce the dimensions of these flaws \[16\]. Yang et al also concluded that there is a greater tensile strength and a greater surface hardness when the diameter of the extrusion nozzle is increased \[23\]. The biggest highlight is that this parameter also reduces the printing time \[23\]. The printing speed, in addition to defining the time of manufacture of the part, can promote a better adhesion of the layers due to the pressure exerted by the material that leaves the nozzle \[23\].

A longer residence time close to the heated nozzle can cause annealing with the crystallization of the material, especially at low printing speeds \[21\]. The crystallization of the polymer promoted by the permanence of the temperature in levels close to its melting increases the modulus of elasticity; however it promotes a greater rigidity without the gain in other mechanical properties \[5,12,21\].

Regarding the printing base, the best results are obtained closer to the Glass Transition (\(T_g\)) \[16,33\]. Analyzes of the nozzle printing temperature indicate that whenever closer to 240°C, better the diffusion and adhesion of the layers \[4,23,36\]. However, it should be noted that it has negative effects, as it is the point where degradation starts, resulting in a reduction up to 15 times the viscosity of the polymer \[4,5\]. Also, as pointed by Grasso et al, the increase in the ambient temperature from 20 to 30°C implies a 20% reduction in the maximum tensile strength \[40\].
3.4 CHARACTERISTICS OF THE RECYCLED PLA

Studies on the production of recycled filaments are sparse [1]. However, as the number of recycling cycles increases, a great loss in material properties is noted [11,12,18]. The chain scissoring due to the degradation of the polymer is the main reason responsible for this loss [11,12,18]. The proportion of molecular weight loss based on the studies of Zhao et al [26] indicates a reduction of 40% in two cycles. The tensile modulus, the flexural modulus, and the $T_g$ stay stable [1,26] but there is a huge lost in tensile strength, about 50% on 5 cycles [12].

4 CONCLUSIONS

In this review of the literature regarding the extrusion process, 3D printing, and recycling of polylactic acid (PLA), it was possible to analyze parameters and data of virgin and recycled PLA. Mechanical tryouts were verified by tensile and flexion tests, in addition to thermal tests, such as DSC and SEM microscopy. Satisfactory properties guarantee finesse of functionality and attractiveness for the use of the material. The evaluation of the chemical, thermal and mechanical properties of the PLA polymer allow identifying the changes during the recycling process. The present literature review is also a guide for future research to create a recycling line, with process control, for 3D printer feedstock.
REFERENCES


