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PHYSICAL AND CHEMICAL CHARACTERIZATION OF COLORED POLY(ACID LACTIC) 3D PRINTING FILAMENTS

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RESUMO

ABSTRACT

This paper presents the rheological, chemical and thermal characterization of colored 3D printing filaments made of poly(acid lactic) (PLA). PLA is one of the most popular materials in Fused Filament Fabrication (FFF), but the lack of standardization with regard to the material properties often results in printing difficulties and limited quality. Characterization experiments were performed in order to investigate the causes of filament grinding observed with some colors of PLA during 3D printing. The analyses showed that the materials present different levels of viscosity, low content of inorganics and also diverse melting temperatures and crystallinity degrees. From the six colors tested, two exhibited very distinct properties, which may be related to the optical activity of PLA and thermomechanical degradation. No relation could be draw between the inorganic materials added to the polymers and the observed properties. Although the supplier of the filaments suggests the same range of temperature, the materials with higher viscosity should be extruded at higher temperatures.

INTRODUCTION

Additive manufacturing (AM), also known as 3D printing, encompasses a set of techniques that can generate physical objects directly from three-dimensional data, usually layer-by-layer, by joining volumetric elements of material. Most extrusion-based AM systems use the effects of temperature variations on thermoplastic polymers. The current market of such 3D printers is dominated by Fused Filament Fabrication (FFF) platforms, which use filament shaped feedstock and derive from the prescribed Stratasys' Fused Deposition Modeling (FDM®) patent [1-8].

In FFF, the solid portion of the filament acts as a piston, pushing the melt through a calibrated nozzle and thus depositing material onto the build platform, while the print head generally moves on the plane. After completion of the first layer, the build platform moves down so that a new layer can be deposited over the previous and so on, until the part is finished [2-10].

Poly(lactic acid) (PLA) can be considered one of the most popular materials in FFF due to its user-friendly properties. When compared to acrylonitrile butadiene styrene (ABS), for example, PLA requires lower print temperature, has less tendency to warp, and exhibits better mechanical performance and lower toxicity [3, 4, 8-15].

Many studies have been published about the influence of process parameters (*e.g.* temperature, raster angle, printing velocity) on the mechanical properties and surface quality of 3D printed parts made of PLA [7, 10-14, 18-22]. In contrast, few works focus on the material characterization, except for [10, 14] and [7] which observed that the addition of colorants in PLA affects the microstructure and the properties in flow, reflecting on the quality of the printed parts. Of these, only the latter authors characterized the PLA filaments before the printing process.

This research was motivated by a frequent problem experienced by the 3D printing community, shown in Figure 1, which is caused when the nozzle is clogged or the required pressure to extrude the material is too high. Filament grinding [23] was observed with natural, red and yellow PLA filaments when trying to print at 190ºC and 60 mm/s using a desktop FFF printer. On the other hand, white, black and blue PLA filaments bought at the same date and from a same retailer could be printed under the same conditions with no problem.

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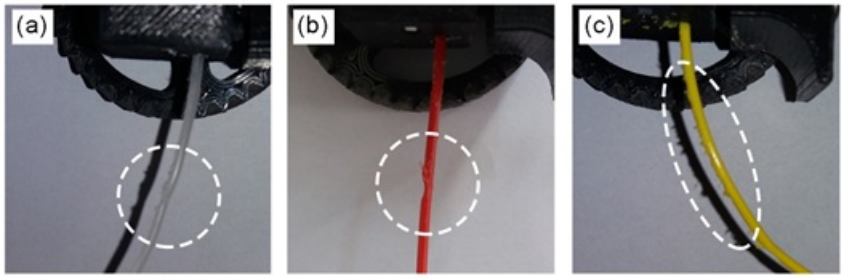

FIGURE 1 *(a) Natural, (b) red, and (c) yellow PLA filaments showing grounded surface when trying to print at 190ºC.*

The observed lack of standardization from feedstock suppliers reflects on expressive variation in the properties of PLA filaments, which limits its application to simpler products [10]. Certain PLA colors are usually perceived as worse than others, requiring often adjustments in process parameters (*e.g.* nozzle and bed temperature, printing speed) in order to be effectively used in FFF machines. However, the source of feedstock variability with respect to the rheological properties, chemical formulation and microstructure has not been thoroughly investigated. The next sections describe the materials and experiments performed to investigate the possible sources of the grinding problem observed with some colors of PLA filaments.

EXPERIMENTAL PROCEDURE

Materials

Natural, white, black, red, yellow and blue 3D printing filaments made of PLA were acquired from a local retailer. All material, consisting of 1 kg vacuum-packed spools of 1.75 mm diameter filaments, was purchased on the same date. The recommended print temperature for all the spools ranged from 190 ºC to 220 ºC. No further information about flow index, batch or date of manufacture was provided.

Rheological Measurements

Rotational rheometry was performed to analyze the behavior of the molten material subject to low shear rates using an ARES-G2 rheometer (TA Instruments, Newcastle, UK), equipped with 25 mm diameter parallel plates separated by 1 mm. The imposed shear rate ranged from 0.01 s^{-1} to 100 s^{-1} at 190 °C, with N_2 purge. Before starting the tests, the samples were kept at the set temperature for 5 minutes.

Chemical Analysis

The ash content in the filaments was determined by burning 10 g samples of each color in a muffle furnace at 600 ºC for 4 hours, using porcelain crucibles according to the procedure B from ASTM D5630. The ashes were analyzed by Energy-Dispersive X-Ray Spectroscopy (EDS) using an EDX Link Analytical equipment (Isis System Series 300), with ultra-thin window (ATW II) and SiLi Pentafet detector coupled to a scanning electron microscope Zeiss LEO 440 (Cambridge, England). The calibration was made with copper, and the analyses were performed using a 20 keV electron beam, focal distance of 25 mm, 30 % dead time, current of 2.82 A and I probe of 2.5 A.

Thermal Analysis

In order to destroy the filaments' thermal history, the samples (ca. 7 mg) were first heated from 25 ºC to 220 ºC at 10 ºC min^{-1}, then kept at 220 ºC for 5 minutes and cooled to 25 ºC at 10 ºC min^{-1}. After that, a second heating was performed at 10 ºC min^{-1} until the maximum temperature of 220 ºC was reached. The experiments were performed using a Q100 DSC (TA Instruments, Newcastle, UK), purged with N_2 at 50 mL min^{-1}. An empty aluminum pan was used as reference.

The crystallinity (%X_c) was calculated according to the Equation 1 [13], using the values of the enthalpy of cold crystallization (ΔH_{cc}) and melting (ΔH_m) for each sample as available on the resulting thermograms and considering the value of the enthalpy of melting of 100% crystalline PLA (ΔH^0_m) to be 93.0 J g^{-1} [13].

$$X_c(\%) = \frac{(\Delta H_m - \Delta H_{cc})}{\Delta H_m^0} \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Rheological Measurements

The rheological curves of viscosity versus shear rate are shown in Figure 2. In general, in the lowest shear rate regime (up to 0.02 s^{-1}) two trends can be observed: the natural, red and yellow filaments exhibit viscosity levels higher than 1000 Pa s, while the white, black and blue filaments show viscosity levels between 100 and 1000 Pa s. The group of filaments with higher zero shear rate viscosity at 190ºC are the same that exhibited filament grinding. The viscosity of the natural, red and yellow filaments was kept almost constant up to a shear rate of 5 s^{-1}. In contrast, for the white, black and yellow samples, constant viscosity is observed over a wider shear rate range.

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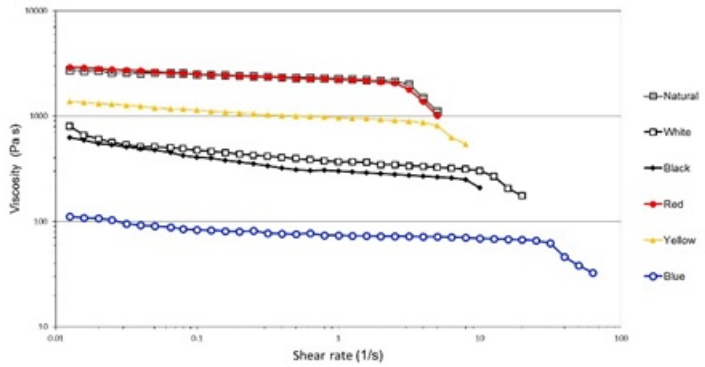

FIGURE 2 Rheological curves of the unprocessed PLA filaments at 190 ºC

According to the Mark-Houwink relation, the higher viscosity levels at zero shear rate indicate that the natural, red and yellow filaments have higher molecular weight, despite all being retailed under the same general denomination. Considering that the PLA spools were fabricated with similar resins of initially high molecular weight, the viscosity discrepancies can be attributed to different levels of degradation experienced by the filaments.

As a biopolymer, PLA is easily subject to thermomechanical degradation during processing, which is related to the moisture content of the resin, temperature and process residence time. In addition, the presence of residual amounts of catalysts can also trigger reverse depolymerization and hydrolysis reactions, all those factors leading to a significant drop in the molecular weight and deterioration of PLA properties [16, 17].

Polymer degradation reduces the length of the molecular chains leading ultimately to a narrower molecular weight distribution (MWD), which can be observed by a wider Newtonian plateau as in the case of the white, black and blue filaments. Especially in the case of the blue filament, the rheological curve can indicate an extensive degradation that affected most of the polymer chains, leaving a very narrow MWD of low molecular weight polymer chains.

Chemical Analysis

The content of inorganic compounds determined after burning the each filament sample is reported in Table 1. The white and yellow filaments exhibited the highest quantity of inorganics, in very similar values. Next, the black and blue filaments can be grouped as showing intermediary ash content, followed by the red with the smaller amount. As expected, no residue was left after burning the natural filament.

TABLE 1 Content of inorganic compounds after burning at 600ºC for 4 hours

Filament	**Inorganic content (wt %)**
Natural	0.0
White	1.5
Black	0.6
Red	0.2
Yellow	1.4
Blue	0.5

Table 2 shows the average weight percentage of the chemical elements detected by the SEM-EDS analysis in two regions of the ash samples. Although the values do not necessarily represent the chemical composition of the filaments, results can give clue of the main compounds that were added to the PLA resins to produce the filaments.

TABLE 2 Quantification of the elements found in the ashes of the PLA filaments through SEM-EDS analysis

Filament

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wt% of the element	O	Mg	Al	Si	Ca	Ti	Zn	Cu	Cl	S
White	45.3	1.7	0.5	0.7	27.2	23.6	1.1	0	0	0
Black	55.1	3.5	0	0.6	39.9	0	1.0	0	0	0
Red	46.7	0	0.6	0.4	3.3	46.4	0	0	0.5	1.5
Yellow	45.4									

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2.5

3.0

1.5

34.8

11.3

0

0

1.3

0

Blue

49.5

3.4

0.2

0.6

34.7

7.2

1.8

2.5

0

0

The proportion of calcium is high in all ash samples except that one derived from the red filament and can be attributed to calcium carbonate ($CaCO_3$), which is often used as low-cost processing aid in thermoplastics. The significant levels of titanium with exception of the black filament can be related to titanium dioxide (TiO_2), a common white pigment that can also be used as opacifier when applied in conjunction with other colorants [24,25].

Even in small amounts, some inorganic compounds can promote crystalline nucleation in PLA [24-26], modifying the mechanical properties of the filaments and the flow behavior of the materials during 3D printing. Thermal and chemical analyses were correlated to determine whether the different characteristics observed when using each filament could be attributed to any nucleation effect.

Thermal Analysis

The thermograms for the second heating cycle are reported in Figure 3, and represent inherent properties of the materials. The glass transition temperature (T_g), cold crystallization (T_{cc}) and melting temperatures (T_m), crystallization (ΔHc) and melting enthalpies (ΔHm), and crystallization degree (X_c) for the first and second heating cycles are summarized in Table 3.

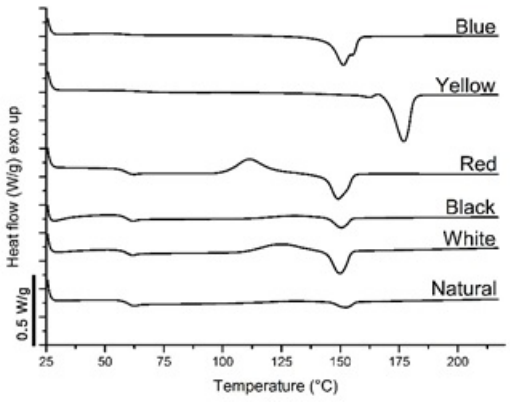

FIGURE 3 DSC curves for the PLA filaments, second heating

TABLE 3 Thermal and crystalline properties of the PLA filaments at 10 ºC min $^{-1}$, second heating

Filament

T_g (°C)

[1] EESC - USP, joaquim.netto@usp.br
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	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
Natural	60.0	129.7	4.0	152.7	3.8
0	White	59.6	125.7	16.5	149.9
15.8	0	Black	60.0	130.2	6.2
150.7	6.1	0	Red	59.5	112.0
22.2	149.2	23.2	1.1	Yellow	64.6
166.7	1.1	177.0	32.5	33.8	Blue
58.2	-	-	151.4	28.8	

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31.0

Glass transition of PLA polymers depends on several factors, including molecular weight, and optical purity. Most filaments showed similar glass transitions temperatures around 60ºC, with exception to the yellow and blue. Cold crystallization temperature was higher for the yellow filament, followed by the black, natural, white, and the red filament. The blue filament showed no cold crystallization, having achieved its maximum crystallizability under cooling after the first heating cycle. The melt temperature was also higher for the yellow filament, followed by the natural, black, white and red with similar values, and finally the blue with the lowest value. Crystallization was significant for the yellow and blue filaments only.

The discrepant values for the yellow filament could be related to the major presence of l-lactic acid and higher optical purity of its PLA resin. When in greater proportion, l-lactide favors crystallization and increases T_g and T_m. In addition, the presence of mesolactides (*i.e.* d,l-lactides) reduces T_m and increases the crystallization half-time, which usually results in lower crystallinity [9, 16, 17]. The peak temperatures and crystallinity level obtained for the yellow filament are similar to what is reported in literature for PLA with l-lactide content higher than 90% [9, 26-28].

Strong disparities were also found in the low thermal properties of the blue filament, which is another indication of the possible low molecular weight caused by extensive degradation. Indeed, the expressive melt crystallization in this case can be attributed to the higher molecular mobility, which enhances the crystallization rate by reducing the energy required for the chain folding process [25].

Due to the very small amount of inorganics found in the filaments and the lack of strong relation between the observed thermal properties and ash content, the variation of properties was considered to be more related to the degradation level, l-lactide proportion and optical purity of the base resins.

CONCLUSIONS

The rheological tests showed that the PLA filaments have distinct flow properties, which affect the printability of each color for a given set of 3D printing parameters. The differences of viscosity can be related to the molecular weight of the base resins used as well as to the degree of degradation resulting from preceding feedstock fabrication steps.

Except for the natural PLA, the chemical analyses revealed that the filaments have up to 1.5 wt % of inorganic additives, which can include mostly calcium carbonate, and titanium dioxide. Those compounds, however, are not necessarily related to the color of the filaments and were found to not affect the rheological and thermal properties expressively.

The DSC analyses demonstrated that the inherent thermal properties of the PLA filaments receive little influence from added inorganic compounds, being most likely a result from the average molecular size and sizes distribution together with the enantiomer proportion and optical purity.

Filament grinding of the yellow filament at the described printing conditions can be attributed to the combination of high viscosity and crystallinity degree. In fact, the yellow PLA might actually be composed of a base resin with more l-lactide content for its higher melting temperature and crystallizability. With regard to the natural and red filaments, the observed printing difficulty could be attributed to the high levels of low shear rate viscosity, which derive simply from its high molecular weight. Higher nozzle temperatures would be required to successfully extrude those materials.

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PALAVRAS-CHAVE: additive manufacturing, material extrusion, polymer characterization

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