Thermo-Mechanical Evaluation of Novel Plant Resin Filaments Intended for 3D Printing

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Abstract— **With the development of three-dimensional printing technologies (3D) for rapid prototyping, new materials are being constantly researched, but not all have the necessary characteristics to be used for this purpose. The cost of materials commonly used for this application and their reuse limitations are aspects that must be taken into account and involve the search for low-cost and more environmentally friendly new replacement materials. The aim of this study is to evaluate some properties and the application of natural plant resins as possible materials for 3D printing by using the technique fused deposition modeling (FDM). The filaments were manufactured via hot melted extrusion (HME). The tests made include the determination of density, mechanical evaluation of materials (tensile and compressive strength) and also the analysis of their thermal behavior by differential scanning calorimetry (DSC). According to the results, materials showed lowest tensile and compressive strength when compared to other plastics commercially available, nevertheless the resins present excellent molding to be extruded in the manufacturing of filaments and successfully 3D printed, using relative lower temperatures.**

Keywords— Biopolymer, Filament, Production Engineering, Renewable Materials, Thermoplastics.

INTRODUCTION

Three-dimensional printing (3D) is an additive manufacturing technology which enables the creation of a 3D object from a digital model. In recent years, 3D printing technologies have evolved very rapidly beyond its traditional application field [1]. In fact, 3D printing is routinely used in a variety of manufacturing industries ranging from aerospace and automotive sector as well as bioengineering [2-3] among other sectors. The various 3D printing technologies differ in terms of cost, maximum spatial resolution, and type of materials used. However, there still are concerns about the relatively high costs of materials and equipment and the need for specialized personnel to operate them [4-5].

The development of new materials, resins and polymers including the use of fillers in composites could be one way to improve the mechanical properties of the components printed by fused deposition modeling (FDM) which commonly utilizes filaments produced via hot melt extrusion (HME) [6-7-8]. In sum, FDM is a technique that recently has become quite popular, especially among the unskilled personnel, since it represents a very effective low-cost approach for the production of 3D objects with relatively good resolution. The FDM basically consists in the deposition of the material to be printed by layers, through heating, typically by using this technique, the raw material is found in the form of a filament, which may be polymeric, metallic, ceramic, wood or even [9]. However, there are some limitations, since FDM requires a thermal conduction process of a particular thermoplastic filament before the additive deposition of the extruded material occurs, a determining factor which presents some limitations to the materials to be used, since only a relatively small number of polymers have the thermal and rheological properties suitable to be easily processable using this technology [10].

On the one hand, the plastics most commonly used in 3D printing are derived from polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate glycol (PETG), nylon (polyamide), polyethylene terephthalate (PET), polyvinyl acetate (PVA), and polycarbonates, additionally new materials come out every time such as bamboo derivates and composites. On the other hand, several studies evidences that during the 3D printing of synthetic plastics, besides materials being environmentally unfriendly, there is the releasing of diverse volatile harmful compounds such as aldehydes, phthalates, benzene, toluene, and ethylbenzene, among other particulates [11-12-13-14].

Within this context the aim of study is to investigate the thermal-mechanical properties of novel sustainable materials, from renewable sources, intended for use in 3D printing fused deposition modeling, in attempt to contribute to a decreasing on the utilization of synthetic plastics for this purpose.

I. MATERIALS AND METHODS

A. Plant Materials

Natural oleo-gum resins from benzoin (*Stirax benzoim*) originally harvested from Singapure, myrrh (*Commiphora myrrha*) from Somalia and olibanum (*Boswellia papyrifera*) from Ethiopia were purchased from Mountain Rose Herbs (Eugene, Oregon, USA). These resins had not undergone any kind of treatment such as purification or distillation.

B. Preparation of Materials

Resins in powder form were added to the feed hopper of HME equipment (Filastruder, USA) thereby forming 1.75 printable filaments, the temperature of extrusion was maintained at 65-90 °C and the screw speed was maintained at 20 rpm, the materials were cooled at ambient temperature (21 °C). In sequence, filaments were 3D printed using a FDM machine (Prusa Mendel–I3, USA) the temperature was maintained at 80-100 °C and the heating of the deposition table was maintained at 40 °C, with feeding speed set at 10 mm/min.

C. Mechanical Evaluations

Evaluations of the tensile and compressive strength of materials were performed in a universal testing machine (EMIC DL-5000) the tests were conducted at the Laboratory of Mechanics from the Federal Institute of Santa Catarina (IFSC) Brazil. Tensile test was performed according to ISO standard 527:1 (2012) and ISO-1926 (2009) and compression test was performed consulting ISO-604 (2002); ASTM D3410 (2016); and ASTM D1621 (2010). The Figure 1 shows the schematic view of test specimens used in different orientations: (a) traction and (d) horizontal compression; (b) traction and (e) vertical compression; (C) traction and (f) compression perpendicular view.
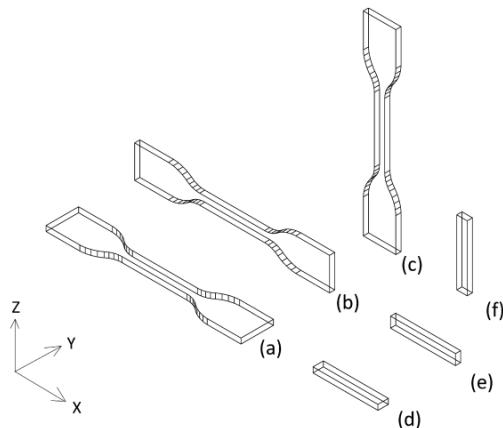

Fig. 1.   Schematic view of the test specimens

D. Determination of Materials Density

In density test, 1-2 g of each material was analyzed using a digital densitometer (DSL-910 Gehaka) with an accuracy of 0 g / cm^3 to 3 g / cm^3. Tests were performed in according to ASTM D792 (2013) specific for plastics.

E. Determination of Melting Point and Glass Transition

For the determination of the melting point, the raw materials were weighted and (2.0 ± 0.5 mg) placed into a Becker (1L capacity) and consequently placed into laboratorial water bath equipment (Solab, Brazil) with internal water circulation pump and temperature control. So the melting point was determined by visual check the softening of resins with transition from solid state to viscous state (liquid). Tests were carried out at the Laboratory of Chemistry from Federal University of Santa Catarina State (UDESC) Brazil, consulting ASTM E-1142-07. The glass transition temperatures were defined by DSC, procedures are better explained below.

F. Differential Scanning Calorimetry

Samples were weighed (2.0 ± 0.5 mg) and hermetically sealed in porcelain crucibles and then placed into the sample holder of a Shimadzu calorimeter (DSC-60 model), using a nitrogen atmosphere with a flow of 50 mL min^{-1} at a heating rate of 20 °C min^{-1} set up to the maximum temperature of 550 °C. The equipment was calibrated with indium standard for temperature (156.6 ± 0.3 °C) through their melting peak. The enthalpy and heat flow was calibrated using indium fusion heat (28.59 J / g ± 0.30) using the same conditions as the samples. The correction factor was calculated in accordance with the procedures and specifications of Shimadzu. Tests were carried out at the Laboratory of Materials from Federal University of São Paulo (UNIFESP) Brazil.

II.   RESULTS AND DISCUSSION

Table 1 shows the results of the mechanical evaluations. The resins are identified as follows: *Boswellia papyrifera* (resin P), *Commiphora myrrha* (resin M) and *Stirax benzoin* (resin B). According to the results the resin from *Stirax benzoin* reached the highest values of tensile as well as compressive strength, reaching a maximum value of 3.67 and 6.56 kgf/cm^2, followed by the resin of *Commiphora myrrha* 2.11 and 3.35 kgf/cm^2 and *Boswellia papyrifera* 1.65 and 4.24 kgf/cm^2, respectively.

TABLE I.   TENSILE AND COMPRESIVE STRENGH OF SAMPLES

Test/Sample	Traction (kgf/cm^2)	Compression (kgf/cm^2)	Standard Deviation
P1	1.412	3.020	1.13
P2	1.316	4.241	2.06
P3	1.835	3.169	0.94
P4	1.744	2.640	0.63
P5	1.658	3.165	1.06
B1	2.624	4.646	1.42
B2	2.212	5.572	2.37
B3	2.652	6.561	2.76
B4	3.679	5.963	1.61
B5	2.241	4.860	1.85
M1	1.933	3.244	0.92
M2	1.143	2.495	0.95
M3	2.116	2.373	1.18
M4	1.749	3.171	1.00
M5	1.763	3.352	1.12

During the realization of mechanical essays, the fragility of the solidified materials is an aspect which should be taken into consideration, resulting in complications in the performance of tests. After solidification of the resin, materials present a glassy behavior (with rigid and brittle characteristics).

The values obtained were considered low when compared to the mechanical strength that other commercial plastics can tolerate, such as PLA, ABS, PET, and nylon, but these numbers are likely to increase with the addition of loads, additives and plasticizers, or even by changing the temperatures used in the manufacturing of specimens,

seeking to reduce the crystallinity of the specimens. The addition of fibers and nanoparticles of carbon for reinforcement is also suggested to improve the materials resistance and performance [15-16-17-18-19-20-21].

With respect to the temperature of extrusion for the preparation of filaments and injection of specimens, the resins can be processed at similar temperature ranges. The Figure 2 shows an image of a specimen manufactured using the resin of *Commiphora myrrha* during tensile strength assay

Fig. 2.   Failure of sample during test

Table 2 shows the temperature ranges considered ideal for the extrusion of filament and 3D printing of materials.

TABLE II.   TEMPERATURES INDICATED FOR THE EXTRUSION OF FILAMENTS AND 3D PRINTING OF RESINS

Material	HME (°C)	FDM (°C)
Resin P (*Boswellia papyrifera*)	65-78	80-90
Resin B (*Stirax benzoin*)	70-95	80-90
Resin M (*Commiphora myrrha*)	70-90	80-100

In view of the temperatures shown in Table 2, considered suitable for the materials analyzed, it can be noted that those are just few Celsius degrees below the temperatures used for other materials commonly used in 3D printing technology. According to the manufacturer of filaments Sigma-Aldrich [22] the ideal temperature for printing PLA 1.75 mm is around 190-220 ° C and the heating table (in which material is deposited) must be maintained at 23-60 °C. For example, the optimum temperature for printing ABS 1.75 mm is 230 °C and the heating table must be maintained at least at 100-110 °C throughout the whole printing process to ensure the adhesion of the piece, and to avoid that the piece doesn´t split or crack. Still following the recommendations of the same manufacturer, in general, when printing materials such as polycarbonate and nylon, it is necessary to use

temperatures around 260 °C, so it is important to check the printer features and limitations, to avoid permanent damage of the printing head (hot end) which normally cannot withstand temperatures above 250 °C (depending on the printer brand).

According to the manufacturer of filaments and printers M3D [23] and Ragan (2013) [24], plastics such as PLA and ABS are very resistant to mechanical stress, but the same present high shrinkage coefficients (1-4 mm) which makes it very difficult printing larger pieces which have a tendency to deform (warp effect) crack and peel off the table during the process.

Regarding the resins evaluated in this study, it is still necessary to perform more tests in order to define the thermal coefficients of contraction and expansion the best way as possible. Additionally, during the extrusion and printing essays, it was found that the cooling of the materials can be conducted at room temperature (20 °C) without needing of heating table and artificial cooling, because the materials solidify naturally, without the tendency to crack due to inherent characteristics. In this study, parameters such as temperature and speed used for extrusion and injection of samples also should be optimized in order to obtain better results. It is worth mentioning that the filaments were not wrapped in reels due its brittle and fragile behavior, thus, filaments used for printing were manufactured in the form of sticks (1 m x 1.75 mm). Table 3 presents the results of density and melting point of materials, results are exposed as mean value of 5 tests.

TABLE III.   DETERMINATION OF MELTING POINT AND DENSITY OF MATERIALS

Material	Melting point (C°)	Density (g/cm³)
PLA	60	1.24
ABS	105	1.03
PETG	88	1.27
PVA	85	1.18
Resin P	78	1.25
Resin B	95	1.31
Resin M	89	1.02
Nylon	47	1.13
Policarbonate	145	1.20

According to Table 3, the resins showed results approximate to other commercial filaments, in the same table, the melting point and density values exposed for the plastics were adapted from Daniels (1999) and McMillan (1996) [25-26]. The Figure 3 shows the differential scanning calorimetry curve for the resin of *Stirax benzoin.*
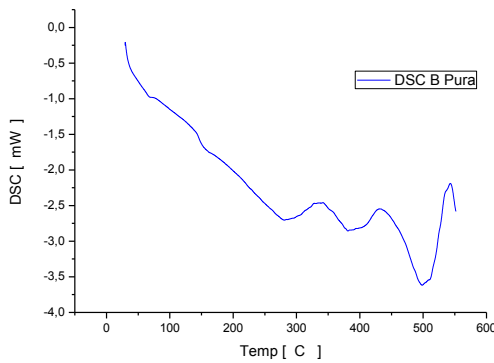
Fig. 3.   DSC phase diagram of *Stirax benzoin*

According to Figure 3, the weak base line change showing an endothermic peak at around 95 °C, followed by a subsequent mass loss of the material after reaching 95 °C denotes that the glass transition temperature of this resin actually occurs from 95 °C to 270 °C, so at this temperature range the material is still a mobile liquid, the resin behavior is rigid and fragile because the polymeric chains do not have enough energy to provide mobility, elastically responding to the requests. Around 280 °C it's noted through the phase shift and strong exothermic peak the occurrence of an initial crystallization range. Around 400 °C there's the occurrence of a secondary crystallization peak; at this stage the material exhibits a rubbery behavior, the energy level is already sufficient to give mobility to the amorphous phase only, while still maintaining the crystalline phase rigid. At around 500 °C the material present viscous behavior and a third exothermic peak at around 510 °C indicates when it reaches his final melting temperature; at this point the resin has a molten behavior. This energy level is characterized by highly mobile polymeric chains. By analyzing this chart as a whole, it was realized that this polymer has semi-crystalline behavior indicating that has moderate molecular weight, and the resin has similar characteristics to commercial polyurea. The Figure 5 shows the DSC curve for the resin of *Commiphora myrrha*.
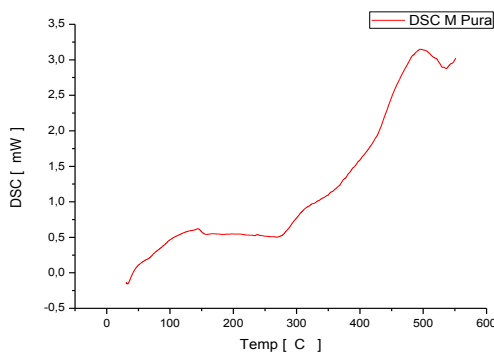

Fig. 4.   DSC phase diagram of *Commiphora myrrha*

Fig. 5.

According to Figure 4, the phase diagram shows a change of phase with mass gain until reach an exothermic peak at around 150 °C, this phenomenon is related to a primary crystallization of the resin in question, and at this

stage the biopolymer exhibits glassy behavior. The baseline without changing peaks found around 150 °C to approximately 280 °C indicates that at this temperature range the material presents rubbery behavior (between Tg and Tm). The sharp exothermic peak detected after the 300 °C to 500 °C with a consequent mass gain indicates the occurrence of a secondary crystallization; hence, at this temperature range the resin has rubbery behavior. Finally, when reaching 500 °C the material reaches its final melting temperature. Analyzing the curve as a whole, the material exhibits a semicrystalline with characteristics approximate to those of commercial polyester. The Figure 6 shows the DSC curve for the resin of *Boswellia papyrifera*.
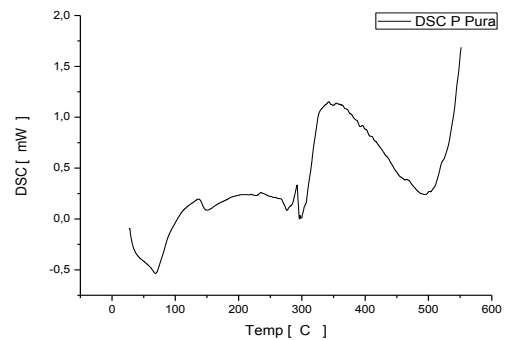

Fig. 6.   DSC phase diagram of *Boswellia papyrifera*

According to Figure 5, due to the remarkable mass loss starting from initial heating until reaches 90 °C with a strong endothermic peak, shows that at this temperature range the polymer exhibits a glassy behavior. After 90 °C due to the phase shift with a consequent mass gain and the presence of various exothermic peaks, denotes the occurrence of a primary crystallization extending to 300 ° C, at this temperature range the resin exhibits rubbery behavior. Furthermore, after 300 °C there is another mass gain with new baseline change, indicating the occurrence of secondary crystallization, the presence of an exothermic peak until reaches at 500 °C shows that at this stage the material has rubbery behavior. Finally, reaching 500 ° C it is observed the presence of another endothermic peak, and a new baseline change, indicating that the material reached its final melting temperature. Analyzing the diagram as a whole, it was noted that this resin also presents semi-crystalline behavior with similar characteristics to commercial polyurea.

III.   CONCLUSIONS

The materials tested showed similar characteristics between each other, with the possibility to be extruded for the preparation of filaments and 3D printed using fused deposition modeling. From mechanical evaluations, the materials showed lower values of resistance if compared to other commercial plastics, but these are still considered adequate for the desired application. From thermal analysis, the resins showed similar behaviors passing from the glassy state to the rubbery and finally reaching the molten state, characteristic of semi-crystalline thermoplastic polymers such as polyurea, and polyester, although its amorphous structure consists of a mix of organic compounds.

For future studies it is suggested to investigate the thermal expansion and contraction of these materials in order to improve the resolution of printing, and also to evaluate their reuse features, biodegradability and emissions released when subjected to heating processes. Furthermore, this study opens the way for new research in regarding to identify the properties of renewable materials intended for use in additive manufacturing.

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