

Wood-biopolymers composites

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Abstract

This Master's thesis aimed at bringing a new use to sawdust. Sawdust is an inherent residue of the wood industry in its most varied branches, being that, to invest in its recycling is an advantage to be combating the waste of raw material, in other words, looking for sustaining the "Zero Waste" policy, the reuse and reutilization of waste. As a way of providing a new application to sawdust, two new composite materials were created containing wood in the form of sawdust in its constitution. Besides the addition of sawdust, it was also sought that these composites, of the polymeric matrix, constitute a more environmentally friendly option than the existing options until then. These composites are derived from the polymers polyglycerol citrate and glycerine with corn starch. They were chosen because they use natural products or products from eco-friendly processes. As the main purpose of this thesis is the use of sawdust, it was also established as an objective of this work the attempt of increasing the mass of wood inserted in the polymer that serves as a matrix to the composite concerning the already existing commercial solutions, namely the ones that use PLA mixed with wood. An attempt was made to produce filament for FDM 3D printing using the composite glycerine/corn starch/ sawdust in which, in turn, there was also a focus on increasing the mass of wood present in the filament when compared to commercial samples of PLA mixed with wood. Finally, mechanical and physical-chemical tests were carried out on the glycerine/corn starch/ sawdust composite.

Keywords: Biopolymers; Biocomposites; Sawdust; Wood; Sustainability

1. Introduction

This work addresses the process of obtaining 2 new composites of biopolymer origin, from its idealization, through its conception, to its characterization using physicochemical and mechanical tests and an attempt to produce filament for 3d printing. The starting point of this work was the search for raw materials from natural sources or eco-friendly manufacturing processes, which could be applied in the development of new composites with wood. From the research originally done, it was not possible to find much information about the polymers used in the development of the composites. So, the objectives of this thesis were to meet the following requirements

- The biopolymer matrices of the composites should be bio-based and use raw materials that are products or by-products of low-polluting or eco-friendly processes.
- Promote the use of residues resulting from the wood industry, i. e., sawdust.
- They must be biodegradable bioplastics.
- Have a similar visual appearance to wood.

In this way, besides the development of these new products, it was also sought to study their properties

in order to be able to characterise them. They may also be used in 3D printing, in Fused Deposition Modelling (FDM).

Considering all these factors, these materials were sought to be a more ecological and sustainable alternative to the polymeric composites with wood already existing in the market, as well as applicable in an additive printing technology.

To be matrix of these composites were chosen 2 biopolymers: polyglycerol citrate and glycerine/corn starch.

Biopolymers are considered advanced materials, which are materials with ground-breaking features reinforcing new manufacturing technologies and processes, such as FDM printing, and the opportunities to fabricate entirely new technologies and products based on raw materials (Mitchell, 2018). Bioplastics or biopolymers, according to European Bioplastics Organization, is a really wide concept. These words include bio-based and biodegradable polymers, which are 2 kinds of materials (Verma & Fortunati, 2018). If bio-based materials are the ones that are bio-products made from living organisms like trees and plants, biodegradable materials are the ones that can be degraded naturally (Yang et al., 2018). To be a

bioplastic does not necessarily mean that it is biodegradable, because, according to the official definition of this word, fossil-based polymers are in this category (Verma & Fortunati, 2018). Because of these facts, biopolymers can be divided into 3 distinct groups: biodegradable biobased, biodegradable fossil-based, and nonbiodegradable biobased.

The composites developed were polyglycerol citrate/sawdust and Glycerine/ Corn starch/ Sawdust.

These composites can be considered WPCs. Wood composites are defined as materials that bond together small pieces of wood, usually waste resulting from wood manufacturing operations, to produce products with specific and definable physical and mechanical qualities. Wood composites are the class of materials most abundantly used in construction at present (Matuana & A. Heiden, 2005).

As a general rule, WPCs (Wood-Plastic Composites) result from the by-products from two different industries, which in itself represents an environmental and economic advantage (Horta et al., 2017). These composites, mainly used in the form of decking boards, pavements and railing systems, are mostly based on polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) (Klyosov, 2007). In smaller quantities, WPCs are also used as cladding, fencing, pallets, roofing tiles, and window frame liners. Other uses such as pilings, railroad ties, marinas, shutters, and noise barriers are rather experimental, not yet marketed, or sold at a very small fraction compared to the main WPC products. Automotive products also often make use of this solution (Klyosov, 2007).

2. Materials

2.1. Sawdust

The sawdust samples used in this work were collected from two carpentries in the district of Aveiro, Portugal, which are referenced for only using solid wood in their production. The aim was to avoid particles resulting from wood by-products, such as particleboard, as they may contain chemical contamination. The samples collected are mainly of mixed oak and pine. These two types of wood can be visually distinguished by their colour, where pine has a lighter brown colour than oak.

These particles may show different shapes depending on the process that originated them. One sample was obtained from woodcutting with circular saw blades, in sliding table saws and toothed cutting strips, in band saw blades and the other sample from sanding, in a wide belt sanding machine with a roller-roller configuration. The

particles resulting from sanding have a more elongated profile, while those resulting from cutting have a more rounded shape as can be seen in the figure below.

From the sawdust collected in the sawing processes, a sample was taken to be sieved. The sample selected was used to analyse the particle size distribution of the sawdust. All the work presented hereafter was done using the sawdust resulting from the sawing. The sieving process results are presented in table 1.

Table 1- Wood particle size distribution resulting from the cutting processes.

Sieve (µm)	Dp (µm)	Mass (g)	Mass (%)
710	855	39.4	18.8
500	605	40.0	19.1
355	427.5	41.7	19.9
250	302.5	34.4	16.5
125	187.5	39.5	18.9
63	94	9.68	4.6
0	31.5	4.39	2.1
Total:	-	209	-

To do this work, the sawdust with a granulometry of 125-250µm was used. The choice of this size was due to the fact that not being the coarsest sawdust, it was the one that presented the highest abundance among the smaller sizes. It was decided not to mix the sizes smaller than 125µm in this work, in order to have a narrower range of wood particle sizes.

2.2. Corn starch

The starch chosen for this work is the most abundant commercially in Portugal, as well as the most accessible to the common citizen, corn starch. This starch is extracted from corn kernels and, according to information provided by the manufacturer Espiga®, characteristically dissolves easily in cold liquids (Espiga, n.d.). For this reason, it seemed suitable for the production of the polymer.

2.3. Glycerine

Purified glycerine, also known as pharmaceutical glycerine, was chosen for the development of this work. Non-purified glycerine is cheaper than pharmaceutical glycerine, however, the impurities in the first one could introduce large variability in the results, so purified glycerine was used. Therefore, pharmaceutical glycerine of LABCHEM® was used.

2.4. Citric Acid

For the preparation of the experimental processes used in this work, citric acid from the manufacturer Riedel-de Haën was used.

3. Experimental

3.1. Preparation of Sawdust/ Polyglycerol Citrate

First, the pre-polymer, polyglycerol citrate, was prepared, either with the stoichiometric proportion 1:1 or with 2:1, glycerine and citric acid, respectively. With the pre-polymer already prepared, sawdust was added in different amounts. Figure 1a shows the final appearance resulting from the addition of wood to the polymer in a 2:1 ratio. In the same figure 1, there are four numbered samples. In sample 1 no sawdust was added, presenting only 7g of polymer; in sample 2 there are 7g of polymer and 3g of sawdust (30% wood); in sample 3 there are 7g of polymer and 1g of wood (12.5% wood) and, finally, in sample 4 there are 7g of polymer and 2g of wood (22.2% wood).

The polymer composites were cured in the oven at 180°C for 20 hours. The final result is visible in figure 1b. The procedure was repeated in the same way for the 1:1 ratio.

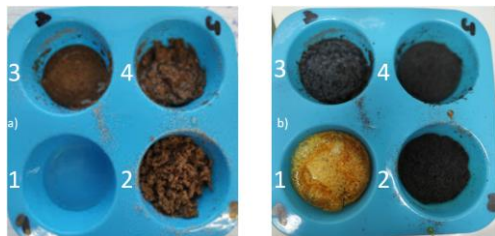


Figure 1 - Polyglycerol Citrate/sawdust a) before curing in the oven; b) after curing in the oven.

1:1 and 2:1 samples containing 7g prepolymer and 3g sawdust, like the one shown in figure 2, were cured in the microwave at 700W power for 10min.



Figure 2 - 2:1 Polymer with sawdust, microwave cured.

The preparation of the pre-polymer polyglycerol citrate was carried out. Then, the wood was mixed in the pre-polymer and homogenisation was carried out. Samples were prepared with a mass of wood above 10% of the total mass of the composite. The maximum value of wood that could be added was for the pre-polymer with 2:1 stoichiometry, where the sawdust mass was 42% of the total mass of the composite, cured in the oven. Other samples were made with smaller amounts of wood, namely 15, 20

and 30% of the total mass of the composite. The results obtained when using oven curing were interesting, regardless of the polymer stoichiometry. It was noted that the greater the amount of wood inserted in the composite, the more fragile the material became. However, some qualitative characteristics were kept, such as its behaviour as a rigid foam, without compromising the goal of having a large amount of wood. Given the impossibility of studying other characteristics of this composite, such as its mechanical properties and its stiffness/density ratio, these studies are projected for future works.

In addition to the curing process in an oven, the composite was also cured in a microwave. It was found that the result of the samples cured in the microwave was different from those samples cured in the oven. Although the composite was completely polymerised, the sawdust, previously homogeneously mixed by the polymer matrix, partially migrated to the surface (figure 3).



Figure 3 - Microwave-cured polyglycerol citrate/sawdust.

3.2. Preparation of Sawdust/ Corn Starch/ Glycerine composite

The preparation of the pre-polymer began with the addition of the three components that form the composite, in a beaker. The corn starch and glycerine were used in equal proportion, being only varied the amount of sawdust. Samples containing 7g, 10g or 15g of wood were made, as a way of progressively increase the amount of wood in the composite. Therefore, for 10 g of corn starch and 10 g of glycerine, the 3 different amounts of wood previously mentioned were used.

Once the components were added in the appropriate amounts, they were mixed until there was some cohesion and homogeneity between them. Distilled water was added in 5 grams amounts until a 55g quantity of water was pre-filled, to make mixing easier.

Afterwards, the solution was placed on the hot plate and, using a stirring rod, the solution was stirred while it was heated. Due to the high viscosity of the solution, even with the addition of distilled water, it was not possible to use the magnetic stirrer. The solution was heated to temperatures between

60°C and 70°C so that the prepolymer could be boiled and the chemical bonds to form the prepolymer could be established; at this point, the excess distilled water in the mixture was evaporated. When the distilled water had evaporated or reacted mainly with the other components and the prepolymer had a viscosity that made stirring difficult, it was removed from the hot plate (figure 4). The operation of creating the prepolymer requires approximately 30 minutes.



Figure 4 - Pre-polymer with wood, before drying in the oven. In the first image, the viscous solution is fresh off the hotplate and in the next one after 1 hour in ambient air.

Once the processes described above were duly concluded, the pre-polymer composite was taken to the oven. It remained there for 12 hours at a temperature of 125°C. When the composite was removed from the oven, the result obtained was the one shown in figure 5.



Figure 5 - Glycerine/ corn starch/ sawdust after curing in the oven.

The polymer that was later used to create the mechanical test specimens was prepared differently. The glycerine was first heated to reduce its viscosity, at a temperature between 30 and 40°C, so that there was no great degradation of its chemical properties. While stirring the heated glycerine, corn starch was added. The mass proportion of that components was 1:1. The solution was stirred continuously, its viscosity increasing until it became a solution that could not be further stirred. At this point, sawdust was added to the pre-polymer, in quantities representing 16.67% and 28.57% of the total mass of the composite. After mixing and homogenizing the mixture in a mortar (figure 6), the composite was placed in the oven at 150°C for 12 hours.



Figure 6 - Corn-starch/ glycerine/ sawdust composite prepared in the mortar, before being deposited in the dies.

In the first iteration, the composite constituents were all added at once. Then, they were stirred in the beaker in an attempt to have some homogeneity before being heated. This was not possible, regardless of the amount of wood that was added, so distilled water was added. This was done not only to favour the homogenisation of the solution but also to improve the miscibility during the composite cooking. Different masses of wood were used, representing 26%, 33.3% and 43% of the total mass of the samples. There were no major differences in the preparation of the composite before curing, and their colour and viscosity were similar. The composite baking process took place on the hot plate until the excess water was evaporated. Since it was not possible at this point to determine the amount of free water remaining in the solution, it was removed from the heating plate when it began to resist being stirred.

Then, the composite was placed in the oven, initially in an aluminium bowl and later in the moulds for the specimens for the mechanical tests. As both the samples in the moulds and in the bowl were exposed to the same curing time and temperature conditions, similar results could be expected. This was not verified. The composite in the bowl dried, verifying only the mass variation corresponding to the evaporated water. On the other hand, the composite that was inserted in the mould through the syringe was expelled from its curing place. This distinct behaviour was due to the fact that the mould composite was in a practically closed environment and, with the evaporation of the water present there, air bubbles were created. For the air bubbles to be released, they forced the polymer to leave the moulds. It was thus concluded that the polymer should already be inserted in the moulds without water. It was also possible to verify that varying the amount of wood in the composite did not cause relevant changes in its qualitative behaviour, since only a slightly more brittle behaviour was observed with the increase in wood content.

In the second iteration, an attempt was made to solve the problem of the presence of water in the composite before its curing. Now, the glycerine was preheated before the addition of the corn-starch, water was not added, and the sawdust was added after the pre-polymer was prepared. The mixing of the pre-polymer with the wood was done using a mortar and pestle. The specimens were made using the composite with only 16.67% of the wood mass. The mould was filled with the composite, it was pressed and placed in the oven for 12 hours at a temperature of 145°C. An attempt was made to cure the polymer in 8 hours, however, it was found that this wasn't time enough to polymerise the matrix. Figure 8 shows a specimen still in the mould. The specimens looked flexible and weak. Specimens with 28.6% of wood mass were made, however, they easily crumbled.



Figure 7 - Specimen for tensile test after curing in the oven for 12 hours at 140/150°C. Composite with 16.67% of sawdust by mass was used.

3.3. Physical-Chemical Characterization

3.3.1. Thermogravimetry

Samples of glycerine/corn-starch/sawdust were characterized by thermogravimetry (Netzsch® STA 409 PC equipment), under air flow, to evaluate their thermal stability and degradation temperature. The samples were heated from 30°C to 1100°C at 25°C/min using alumina crucibles. The DTG profiles, the weight losses and the degradation temperatures were computed using the equipment software

Thermogravimetries were performed, according to the conditions mentioned to the glycerine/corn starch/ sawdust composite. For these analyses were used samples obtained in the 3d filament extruder using the 4mm and 2mm nozzles. The results of this characterisation are visible in the graph in figure 8, in which in the left y-axis we can see the sample mass (TG) and in the right y-axis the thermal degradation speed (DTG).

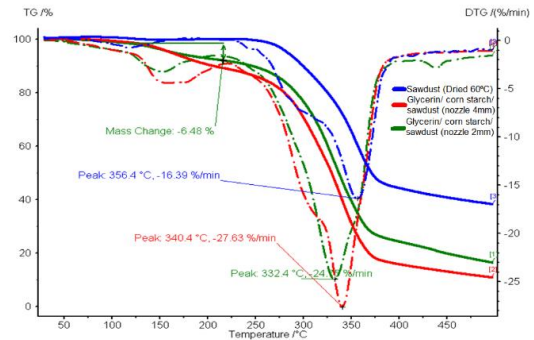


Figure 8 - Thermogravimetry graph for glycerine/corn starch/ sawdust composite.

By analysing the results obtained, it is possible to note that the initial section of the TG curves show that the composites do not adsorb a great quantity of water, which means that it is not a hygroscopic polymer. It can also be observed that the maximum degradation speed temperature of the wood that is used in the preparation of these composites (356.4°C) is higher than that of the composite (<345°C). This behaviour from the composites may show that there is an interaction between the wood and the polymeric matrix.

3.3.2. Tomography

To perform this characterisation, a 3D X-ray microscope (XRM) combined with micro-computed tomography (micro-ct) was used.

The images obtained in the topography performed to the composite glycerine, corn starch and sawdust are presented in figure 9. Analysing the monochrome image it is possible to see, in white, the wood particles dispersed throughout the composite. It was possible to identify 2 types of heterogeneity. It is visible that the particles are not equally dispersed throughout the sample since there are areas with a higher wood flour concentration than others (heterogeneity in the wood particle dispersion); heterogeneity can also be seen in the wood particle orientation in the polymer matrix.

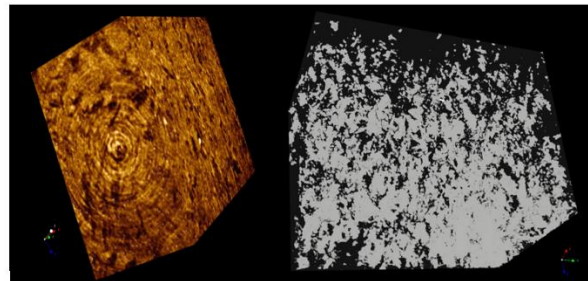


Figure 9 - Images obtained in the tomography.

3.3.3. Assessment Thermoplastic/ Thermoset behaviour

Polyglycerol Citrate/ Sawdust composite was characterized regarding its type. For this, a device designed to identify if it is either thermoplastic or thermosetting was used. Thus, it was placed the composite, in powder form, inside the container and compressed at a temperature of 380°C, for 24h. When the polymer was removed from the device, it was found that there was no difference in the appearance of the composite, except that the wood had carbonised. Given that the composite did not change its state at a temperature very near its degradation temperature, it may be assumed as a thermoset. The initial and final phases of the process can be observed in figures 10a and 10b, respectively.

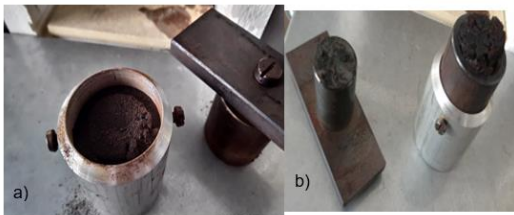


Figure 10 - a) Polyglycerol citrate shredded before putting in the oven; b) Polyglycerol citrate shredded after having been in the oven at 380°C.

The glycerine/ corn-starch/ sawdust composite was also submitted to the polymer type characterization test. After shredded, the composite was placed in the device, compressed and taken to the oven at 380°C for one day. It was verified a complete change of the composite aspect because it changed its state from solid to liquid, at the same time that it overflowed of the container where it was placed (figure 11). Analysing its behaviour and comparing it with that of polyglycerol citrate/ sawdust it is possible to verify that it is a thermoplastic.



Figure 11 - Sawdust/ Corn Starch/ Glycerine composite after the test in which it was found to be a thermoplastic.

3.4. Mechanical Tests

The Instron® 5566 universal testing machine, in figure 12, present in the LEM2 laboratory, was used to perform the mechanical tests, duly equipped with the 500N load cell, as well as the specific ties for each

type of test. The technical specifications and user manual of the equipment can be consulted in (Instron, 2005b). The software used for the test and data processing was the Bluehill 2, developed by Instron and its datasheet can be found in (Instron, 2005a).



Figure 12 - The Instron 5566 Universal Testing Machine, used to perform all of the mechanical tests.

ASTM D638-14 (ASTM, 2014) for tensile tests, ASTM D695-15 (ASTM D695, 2015) for compression tests were the standards used.

3.4.1. Tensile Tests

The tensile tests were performed using, as previously mentioned, a 500N load cell. The ties for the tensile tests were installed and properly aligned and calibrated. To measure the strain of the specimens, a video extensometer was used, which, in turn, was also duly calibrated to correctly measure the extension values in each test. The specimens, due to their dark colour, were also marked with white spots representing the test area of each one. In the test program, a test speed of 1.2 mm/min was used.

3.4.2. Compressive Tests

The compressive tests were performed using a load cell of 500N. In this test compression plates were used. A test speed of 5 mm/min was used.

3.5. Filament Extrusion

The filament extrusion process had several stages of research, and several parameters were modified throughout it. It should be noted that although different preparations of the composite were made to be used in the production of the filament, they all had the same amount of glycerine, corn-starch and sawdust, 33.3% of each.

The process started by using the largest extrusion nozzle, 4mm. It began by using a constant

temperature along with the 4 temperature control points, 160°C, with a worm gear speed of 3.5rpm. A uniform filament was obtained, with good elasticity, which favoured its winding, however, the diameter obtained was higher than 4mm. It was decided to increase the temperature to 180°C, keeping the linear temperature profile. There was a change in the composite behaviour since it became less compliant. The filament diameter decreased to a size between 3.5 and 3.7 mm. The filament came out with the wood carbonised (figure 13). Keeping the same temperature, the worm gear speed was increased to 7.5rpm. it was verified that the wood started to come out lighter than in the previous configuration, however, the filament diameter increased again to 4mm. Then, the worm gear speed was maintained, and a step temperature profile was chosen, with temperature steps of 10°C. The highest temperature was near the nozzle, to ensure the fluidity of the composite and, consequently, a smaller diameter. The filament obtained kept the flexibility, but this time with a colour that was neither as clear as with the linear temperature profile of 160°C, nor as dark as when the temperatures were all 180°C. However, the lowest diameter obtained was 3.2mm, which is far from the 2.85mm that was aimed at. Therefore, it was concluded that a smaller extrusion nozzle should be used.



Figure 13 - Filament obtained using the 4-mm nozzle.

The tests proceeded with a 3mm extrusion nozzle. From the experience previously acquired, it was decided to maintain the rest of the machine configuration. The filament obtained under these conditions had a diameter of 3.4mm. The filament diameter was larger than the nozzle diameter presumably because the worm gear speed was not enough, allowing the material to accumulate at the nozzle exit. The worm gear speed was increased to 10 rpm and a reduction of the filament thickness to values around 3mm was verified. Besides still not being the diameter targeted in this study, the filament was brittle, which made its winding impossible. It was decided to go back to linear

temperature profiles, having set the temperature at 160°C, to avoid dark colour and the worm speed at 3.5rpm, to increase the dwell time inside the extruder. Due to the temperature being too low, the extruder started to present difficulties in expelling the filament from the heating zone, so it started to auto shut down, for the safety of its components. The temperature was increased to 170°C, maintaining the extrusion speed. It was found out that wood carbonised again. In the last iteration performed, in figure 14, a temperature of 180°C and a worm gear speed of 10rpm were used. The problem of the material being too brittle before the winding and the sawdust carbonisation was significantly reduced, although its diameter was irregular, varying between 2.70 mm and 2.95 mm in the same strand.



Figure 14 - Filament obtained using the 3-mm nozzle.

The iteration process occurred in the same way with the nozzle of 2mm, however, it was not obtained filament with a diameter inferior to 2mm nor superior to 2.5mm, therefore, far from the desired values. The filament was very brittle. A sample of filament extruded with this nozzle can be seen in figure 15.



Figure 15 - Filament achieved using the 2-mm nozzle.

4. Results and Discussion

From the tensile tests performed to characterise the glycerine/corn starch/ sawdust composite, the following results in figure 16 were obtained.

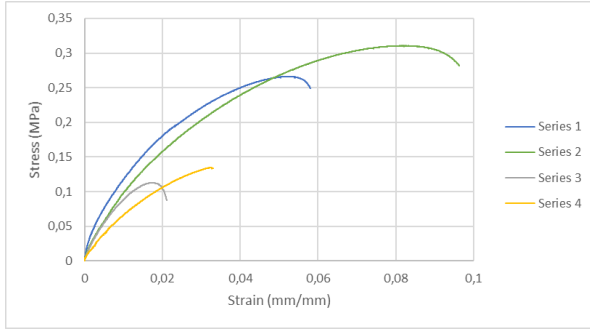


Figure 16- Stress-strain curves of the various tensile tests performed on glycerine/corn-starch/sawdust.

As can be seen in the same figure, the results obtained in each of the tensile tests were very disparate. Although the behaviour of the curves was similar in all tests, the stress-strain values obtained were quite different from each other. For the determination of a Young Modulus (E) only tests 2 and 3 showed some similarity. This difference of results between tests, taking into account that the test conditions were the same, was ascribed to the difficulty of obtaining repeatability between preparations of the composite under study. The preparation of the pre-polymer and the addition of wood was done manually and could not be ensured a completely uniform distribution of sawdust through the polymeric matrix. This problem may be responsible for the high variability in the results of the mechanical tests. With the research development of this composite and its progressive approximation to a commercial version, it may be possible to obtain more homogeneous tensile test results.

It is also noticeable nowhere tests shows a linear behaviour. This behaviour of the material makes it more complex to obtain the Young Modulus of the material. To obtain these values an iterative process was used. Knowing that the Young Modulus is determined according to equation 1, the derivative definition was used to obtain the Young Modulus for each test.

Equation 1 - Hooke's Law, where σ represents stress, E represents Young Modulus and ϵ represents strain.

$$\sigma = E * \epsilon$$

Considering that the test curves correspond, through an interpolation, to functions of the type $y=f(x)$, the derivative of the functions $f(x)$ in relation to the variable x is the function f' whose value at x is:

Equation 2- Derivative definition (adapted from Bastos & Bravo, 2010)

$$f'(x) = \lim_{h \rightarrow 0} \frac{f(x+h) - f(x)}{h}$$

Thus, Young's Modulus (E) can be calculated as the derivative of $\sigma(\epsilon)$ at the origin, i.e., by applying the definition of derivative at the origin:

Equation 3 - Definition of derivative applied to obtain the Young modulus, where E represents the Young Modulus, σ the stress and ϵ the strain.

$$E = \lim_{\epsilon \rightarrow 0} \frac{\sigma(\epsilon) - \sigma(0)}{\epsilon}$$

By applying this equation to the various stress values obtained in the tests and extrapolating these values to the origin, the graph in figure 17 is obtained. Making the average of the obtained results, it was determined a Young Modulus of 20.317 MPa. Note that this value is only indicative, given the disparity of the results obtained.

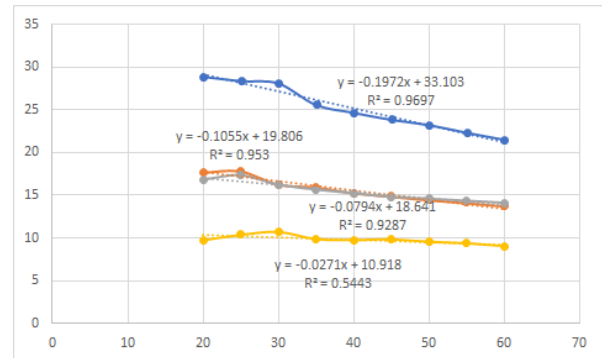


Figure 17 - Graph used to obtain Young Modulus for each of the tensile tests.

Compressive tests were also performed to characterise this composite. The following results shown in figure 18 were obtained.

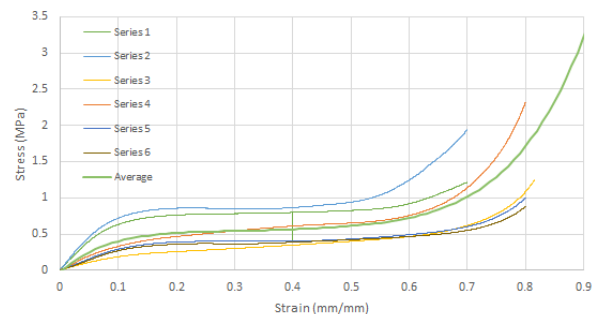


Figure 18 - Stress-strain curves of the various compression tests performed with glycerine/corn starch/sawdust, including the average of the results obtained.

Similarly to what happened in the tensile tests, there were visible variations in the experimental

results. Although the stress-strain curves presented a similar shape in all tests, the stress-strain results varied significantly from test to test. Then, to facilitate the obtention of a representative Young Modulus, interpolations were made to the stress-strain-curves. After obtaining the approximate equations of the curves, their analytical average was calculated.

Then, the stress-strain curve corresponding to the average equation was graphically represented. In figure 19, the derivative at the origin was obtained, as a way to determine the young modulus representative of the compressive strength of this material. The Young Modulus obtained was 6.9MPa. These values should be considered a rough estimate, given the dispersion of the results obtained between tests.

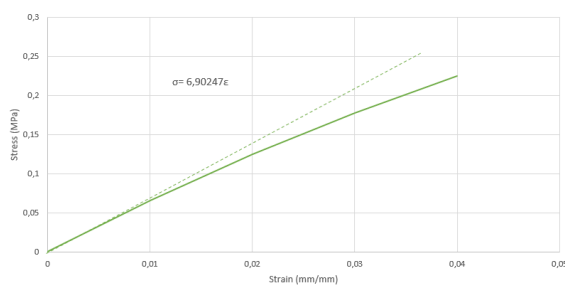


Figure 19 - Graph representing the calculation of Young Modulus to compressive strength.

5. Conclusions

5.1. Original Contributions

The following points are considered as original contributions in this work:

- Development and preliminary study of 2 new composites: polyglycerol citrate/sawdust and glycerine/corn starch/sawdust.
- Creation of a device to characterize the type of polymers regarding their behaviour under temperature variation.
- It was verified that polyglycerol citrate behaves as a thermoset and glycerine/corn starch as a thermoplastic.
- Creation of moulds for specimens for tensile, compression and bending tests of polymers.
- Mechanical and physical-Chemical characterization of glycerine/corn starch/ sawdust.
- Exploratory study of filament production for FDM 3D Printing using glycerine/corn starch/ sawdust.

5.2. Future Works

There is still a lot of work ahead in the development and application of these materials. Each of which can be improved in different ways.

Thus, for polyglycerol citrate and its composite with wood the following explorations can be made:

- Application of glycerine without any kind of treatment, as it is obtained as a by-product from biodiesel transesterification.
 - Exploration of different stoichiometries of citric acid and glycerine, and their conjugation with wood.
 - To investigate the importance of wood particle sizes in the preparation of the composite.
 - Increase the amount of wood inserted in the composite.
 - Explore the use of sawdust produced from sanding in the preparation of the composite.
 - To search for processes of curing the polymer and the composite in a way that it is possible to obtain a given form.
 - Discover methods of controlling the number and size of gas bubbles formed in the polymer elaboration.
 - To explore in more detail the curing of the polymer and of the composite using microwaves, trying to solve the dispersion of the wood particles and the polymerisation deficit inside the samples.
 - To discover ways of demoulding for the polymer and the composite given its high adherence to the walls of other materials
 - Perform the mechanical and physical-chemical characterisation of the polymer and the composite.
 - To develop methods of surface protection for the polymer and the composite to avoid their too early degradation.
- In the development of the polymer glycerine/corn starch and its composite with wood, the following improvements can be made:
- Use of glycerine without any kind of treatment, as it is obtained as a by-product of biodiesel.
 - To investigate the importance of wood particle sizes in the preparation of the composite.
 - Increase the wood volume inserted in the composite.
 - Explore the use of sawdust produced from sanding in the preparation of the composite.
 - Carry out a more refined study of the preparation of the pre-polymer, studying more intensely the need of adding distilled water in the pre-polymer, the moment in which the addition of sawdust is made and, finally, the whole curing process of the same.
 - To research a bio-filler that can be applied on the polymer and the composite to reduce the water absorption due to its hygroscopicity, as well as to increase its longevity without degradation.
 - To study the longevity of these materials.

- Characterize the polymer regarding its mechanical and physical-chemical properties.
- To proceed with the development of filament for 3d printing using the polymer and the composite, studying the mechanical and physical-chemical properties after printing.

5.3. Final Remarks

It may be concluded that all these materials show remarkable potential and applicability, either at the insulation level or merely for aesthetic application or non-structural functionalities. All these materials are biocompatible and, therefore, can be used, for example, in the creation of spoons to stir coffee, cups, among other applications.

It is considered that the process of development of these materials is still in an embryonic state, as tests and characterisations have only been carried out on them in their purest state, but they may still be improved on several fronts, such as using additives.

It is considered that the goal of creating new composites that would allow the reuse of sawdust, while still being bio, was successfully concluded, although it is necessary to improve the work carried out so far.

The glycerine/corn starch and the glycerine/corn starch/ sawdust have a high potential of applicability in FDM, and in this work, several tests were already developed aiming to achieve this goal. Given the increasing use of rapid prototyping (RP), it would be interesting to introduce these materials, which are environmentally friendly and promote the reduction of raw material waste.

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