Materials Research Proceedings **3** (2017) 11-18 doi: http://dx.doi.org/10.21741/9781945291401-2

Revaluation of Catalan Low Quality Cork as Feedstock for the Additive 3D Printing Technology

M. Verdum[1a*], C. Sánchez[2b], J. Castro[1c], J. Lladó[1d] and P. Jové[1e]

[1] Catalan Cork Institute, R+D Department, Miquel Vincke i Meyer, 13 – 17200 Palafrugell, Spain

[2] 3D Spider Print, Pol. Ind . La Bòvila Nau1 - 08232 Viladecavalls, Spain

[a]mverdum@icsuro.com, [b]csanchez@3dspiderprint.com, [c]jcastro@icsuro.com, [d]jllado@icsuro.com, [e]pjove@icsuro.com

Keywords: Cork, Coil, 3D Printing, Plastic Biopolymer

Abstract. Recently 3D printing polymeric coils have been introduced to the market combined by a plastic base and vegetal support. These dual coils own the features of biopolymer and physicochemical characteristics of the plant which it has been mixed with, resulting in a new material with a high added value. Cork properties are able to provide versatility in terms of 3D printing technology and directly compete with other plastic-based products, which have a greater environmental impact. Low quality cork is not suitable for the manufacturing of cork stoppers: byproducts, first harvesting cork, dust or even burnt cork. The use of low quality cork will increase the economic value of cork encouraging forest owners to manage their forests, which are unmanaged in Catalonia at 50%. The new material will be ecosostenible because it is PLA based and the cork percentage is greater than 20%. This study compares the physical, chemical and mechanical properties of pellets, the studied cork coil and the commercial cork coil. In general, pellets and the studied cork coil showed a higher percentage of cork than the commercial cork coil. The presence of cork material in a 3D filament can be evaluated using a chemical composition assays and scanning electron microscopy. The percentage of suberin is related to the filament cork content and allows us to compare different commercial products.

Introduction

According to Allied Market Research, 3D printing is referred as additive printing technology that enables manufacturers to develop objects using a digital file and variety of printing materials. The global market for 3D printing material includes polymers, metals and ceramics. In addition, 3D printing offers a wide array of applications in various industries, namely consumer products, industrial products, defense and aerospace, automotive, healthcare, education and research.

The plastic coils have been combined with wood, coconut fiber or carbon named as dual coils. In these three cases polylactic acid (PLA) has been used as a binding polymer. Those interesting materials have different properties according to the natural material added to and its proportion. These dual coils own the versatility of the biopolymer and the physicochemical characteristics of the plant which it has been mixed with, causing a new material with a high added value. For example, coconut and wood coil are a mixture of 40% coconut and wood particles respectively crushed together by the plastic polymer. The prints actually look and smell like wood and post-processing presents various options, as the prints can be sanded, grinded and painted like standard wooden products. In the case of carbon fiber coils have 15% of this compound and have been used in the automation industry to make less heavy prototypes.

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3D Printing Market Report, published by Allied Market Research, forecasts that the global market is expected to garner $8.6 billion by 2020, registering a CAGR of 21% during the period 2015-2020. This surge in growth is primarily attributed to the rising demand for faster and efficient ways to manufacture complex design objects using a wide array of materials.

Cork is a natural material, renewable and biodegradable with a combination of properties that make it unique and versatile. These properties include its low density, high mechanical strength and fire, low thermal and electrical conductivity, as well as being a good thermal insulation, acoustic insulation and possess a high elasticity. These properties can provide a lot of versatility and possibilities in terms of 3D printing technology and directly compete with other plastic-based products, which have a greater environmental impact. Low quality cork is not suitable for manufacturing cork stoppers: byproducts, first harvesting cork, dust or even burnt cork. The use of low quality cork will increase the economic value of cork encouraging forest owners to manage their forests, which are unmanaged in Catalonia at 50%.

3D Spider Print and Catalan Cork Institute are working to find a new duel cork-coin. The study aims to create a new product with cork base additive usable for printing, extrusion, injection and other manufacturing processes. This product corresponds to a mixture of granulated cork and plastic biopolymer (as used in 3D printing). The new material will be ecosostenible because of being PLA based and having a cork percentage greater than 20%.

3D filament manufactures are looking for innovative means expanding sales into the industrial prototyping and additive manufacturing market [1]. 3D printing is a new technology for making objects by building up layers of a given material, usually plastic or metal. The material is fed into 3D printers in the form of a filament, which is heated so that it liquefies and then solidifies one layer at a time. Cork oak forests have to be managed for about 60 years before they produce high-quality cork. During this time large amounts of low quality cork is produced, and there is little demand for it as a product. In Catalonia, lacking of economic incentive means forests are left unmanaged and this has led to large forest fires. These fires left behind huge amounts of burnt cork oak groves [2]. Catalan Cork Institute research had shown that the burnt cork can be used in new applications, such as 3D printing, therefore, offering a new opportunity for forest managers to still make a profit from these areas and to manage them again in following years. The plastic coils have been combined with wood, coconut fiber, carbon and even cork. Thus, the results exposes above are a comparative between cork, commercial filament and a new dual cork coil (studied cork coil).

The aim of this study is to reevaluate Catalan low-quality cork, introducing it to the 3D technology and thus giving it a new application.

Material and methods

Samples

Cork granules were prepared by cutting planks of natural cork from the North East of Spain (Catalonia). The cork particle size lower than 250 µm is considered cork dust, thus cork dust is a by-product [3]. In this study, we used cork dust generated during the preparation and cutting cork planks intended for sparkling wine. The chemical mix with PLA and cork dust was studied by 3DSpider Print. A dual bis machine was needed due to the low density of granulate cork. A sieve has been used to strain cork dust at 250µm. Then cork dust lower than 250 µm particle size were introduced in a turbo-mixer and acid polilactid was added too. After this process, pellets were made that can be stretched to obtain coils (filaments).

Polylactic acid or polylactide (PLA) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca roots, chips or starch or sugarcane. Pellets and the studied cork coil are lightweight cork-filled PLA-based filament which are gravimetrically filled with approximately 25% cork dust. Different proportions of cork dust (10-20-30%) were tested. This study compares the physical, chemical and mechanical properties of pellets, the studied cork coil and a commercial cork coil (Easy Cork of Form Future).

Chemical & physico-mechanical characterization
The summative chemical analyses included the determination of extractives, suberin, lignin and holocellulose content. The studied pellets and cork filaments were cut by an Ultra centrifugal Mill ZM 200 at 0,75mm.

The methodology used is an adaptation of chemical composition of Jové P. et al. 2011 [4], and is described above. Extractives were removed by successive Soxhlet extractions with dichloromethane (6h), ethanol (8h) and hot water (17h). After each extraction step the solution was evaporated and the solid residue was weighed with an analytical balance. The suberin content was analyzed in extractive-free material by methanolysis for depolymeritzation. The desuberized fraction was used for subsequent analyses. Klason lignin or acid-insoluble lignin were determined by acid hydrolysis. The residue was washed with hot water, dried and boiling. The filtrate was used to determine acid soluble lignin by measuring the absorbance. Klason lignin and acid-soluble lignin were combined to give the total lignin content [5]. Holocellulose was isolated from the desuberized fraction by delignification for 2h using the acid chloride method [11].

The dual cork coil morphology and structure was revealed by scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The SEM samples have been placed on a stub and evaporated carbon (Emitech, German, K950 turbo evaporator). Examinations were carried out with a scanning electron microscopy FE-SEM Hitachi, Japan, S-4100. Digital images was collected and processed by Quarz PCI program. The results were compared with the commercial cork filament.

The FTIR test was carried out using a Cary 630 FTIR equipment to study the vibration and rotation of the molecules in the infrared region of the electromagnetic spectrum.

Print characteristics
Print characteristics were also done. The filaments were tested with a Delta printer WASP 20 40 with software Cura 14.07.

Results and discussion

Chemical & physico-mechanical characterization
The chemical analysis that were used for the chemical composition evaluation is the methodology used for chemical composition of bark layers of *Quercus suber* L. Results for chemical analysis of the commercial coil, the pellets and the studied coil are shown in table 1.

Table 1 Chemical composition of commercial cork coil, pellets and studied cork coil.

	Commercial coil	Pellets	Studied coils	Cork [4]
DCM extractives	91,6%	19,2%	74,2%	9-20%
Et-OH extractives	0,3%	1%	0,8%	
H_2O extractives	1%	2,9%	2,4%	
Suberin content	3,6%	25,4%	5,8%	30-60%
Lignin and holocellulose content	3,5%	51,5%	16,8%	12-22%

These results were different than previously described cork samples [4]. Cork, the outer bark of *Quercus suber* L., is a plant tissue composed of suberin (30-60%), lignin (19-22%), polysaccharides (12-20%) and extractives (9-20%) [6].

The chemical composition of the commercial coil showed higher percentages of dichloromethane extractives than the pellets and the studied coil. The commercial coil also had a lower percentages of ethanol and water extractives than the pellets or the studied coil. This could be explained because PLA (the majority compound) being an aliphatic polyester. It seems that it should be solubilised with a low-polarity solvent, like dichloromethane. According to these results, the commercial coil would seem to contain more PLA than the studied coil (Fig.1 A and B).

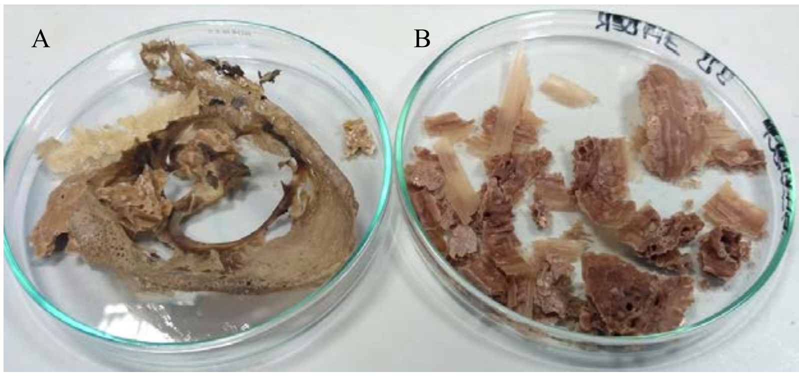

Fig. 1 Dichloromethane extractives content in commercial (A) and studied coil (B).

The commercial and studied coil have a higher extractives fraction than cork due to the presence of PLA. In the case of cork, extractives only include n-alkanes, n-alkanols, waxes, triterpenes, fatty acids, glycerids, sterols, phenols and polyphenols. They are classified into two groups: aliphatics or commonly named cork waxes that are solubilised with low-polarity solvent (e.g. hexane, dichloromethane, chloroform) and phenolics extracted by polar solvents (e.g. ethanol and water) [4; 6].

Nevertheless, in the chemical composition it has been observed that the suberin content of pellets is 25,4%, higher than the commercial (3.6%) and the studied coil (5.8%), respectively. Although lower than cork (30-60%), it is consistent with the percentage of cork in the chemical mix.

The suberin content of the commercial and the studied coil were slightly smaller than expected. Although it was thought that previously extractions were not enough to remove all the PLA, further investigations need to be done. Another extraction in low-polarity solvent might have been necessary to facilitate the extraction of suberin. The lignin and holocellulose content of the pellets (51.5%) was higher than the studied (16.8%) and commercial coil (3.5%), respectively.

According to these results, the pellets chemical composition is similar to cork. Obtaining the pellets was the first step to make the coil, so it could explain that its chemical composition was similar to the cork ones. Following our interest in the development of the cork coil, the commercial coil and the studied cork coil were compared. The amount of cork is an important parameter to take into account in this type of products. According to this, the percentage of suberin is a value related to the cork content: the higher percentage of suberin, the higher the content of cork. In spite of the content of suberin in the studied cork coil being less than expected, the commercial coil had an even lower percentage. Knowing this, the chemical composition suggests that the commercial coil has also a lower content of cork.

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The comparison of the FTIR spectra of the PLA coil, the studied cork coil, the commercial cork coil and the pellets did not show obvious differences between them. Although cork spectra seemed divergence between pellets and cork coils, some characteristic bands appeared (Fig 2).

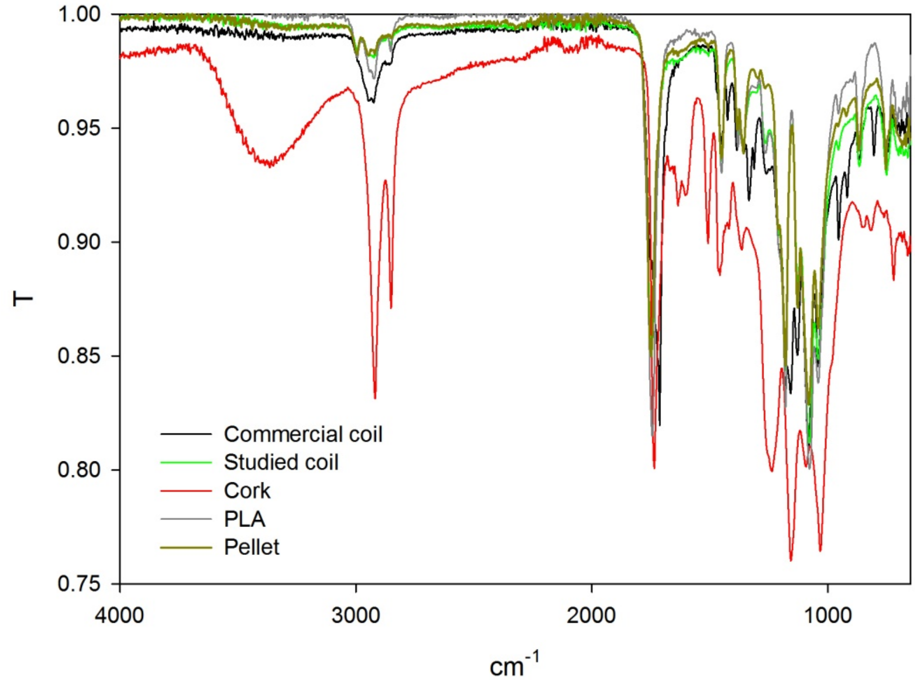

Fig. 2 FTIR spectra of cork, PLA, studied cork coil and commercial cork coil.

In the case of a cork sample, the band 3425cm^{-1} indicates the presence of holocellulose and two major peaks of approximately 2919 cm^{-1} and 2854 cm^{-1} correspond to symmetric and asymmetric vibrations respective link characteristic CH_3 aliphatic suberin. Other bands also characteristic of cork are at 1607cm^{-1} and 1513cm^{-1} corresponding to C = C bond of suberin and lignin and 1162cm^{-1} corresponding C-O-C the bond and 1263cm^{-1} corresponding C = O the bond of suberin, respectively (Fig. 2). [6-9].

According to figure 2, it would appear that FTIR methodology would allow observing lignin and suberin corresponding peaks (1162cm^{-1} and 1263cm^{-1}) in commercial and studied coil but these peaks are also characteristics of PLA. Nevertheless, FTIR methodology could not discriminate properly peaks corresponding to cork and PLA. This fact could be explained because the major compound of them is PLA and their principal components may mask the characteristic components of cork.

In order to go in depth, SEM analysis of the PLA coil, the studied cork coil and the commercial cork coil were performed (Fig. 3).

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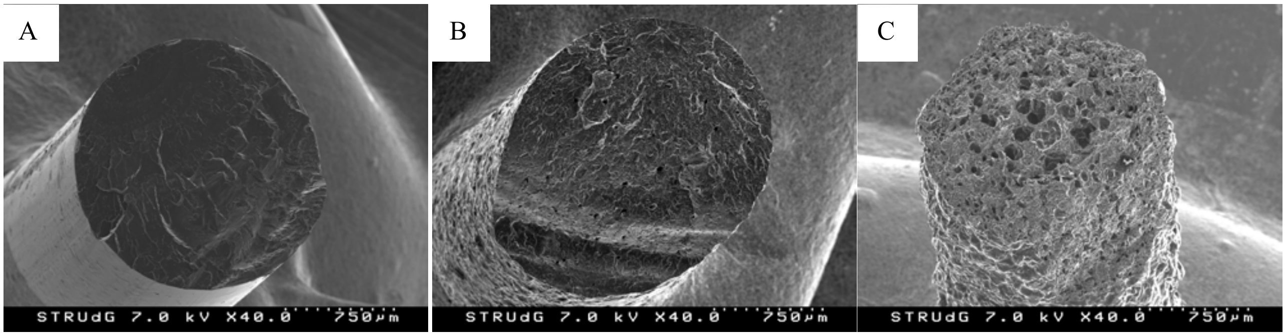

Fig. 3 SEM micrographs of PLA coil (A), cork commercial coil (B) and cork studied coil (C).

According to the micrographs shown in Fig. 3, the morphology of the filaments seems apparently different between them even though PLA (Fig 3 A) is the major component of both the commercial and the studied coil (Fig 3 B and C). The Commercial and the studied cork coil show a more rugged structure compared to PLA. This is probably caused by the presence of vegetal material in its composition.

In the case of commercial and studied coil, it was expected that the typical cellular morphology of cork (tiny hollow hexagonal prismatic cells stacked) [8] were generally preserved. Although, according to figure 3, the typical structure of cork was not observed in either. It could be explained by two hypotheses. On the one hand, most of the cells may be broken during the grinding phase. It should be noted that for the manufacture of the filaments cork powder has been used and therefore cork material had undergone an aggressive mechanical process. On the other hand, during the grinding phase most of the final cork granules had a diameter size of less than the diameter of the cork cell. It should be taken into account that cork powder comprises all cork particles with less than 250 µm. Each cork cell is surrounded by a cell wall and is hollow inside. It is estimated that each cm^3 of cork has 15 to 40 million cells, each measuring approximately 40µm on average [9]. Therefore, some cork particles used in the coils could be smaller than the cork cell.

In addition, differences have been observed between the commercial and the studied coils (Fig 3 B and C). The studied coil presented a rougher morphology than the commercial one probably caused by the different chemical composition and the higher content of cork components (lignin and suberin).

The chemical composition results revealed that the studied coil has higher proportion of cork components than the commercial coil. This fact would be related to the content of cork. An increase of SEM magnifications, allowed to see *some cork particles* dispersed in the PLA matrix in the studied coil (Fig 5B) which were not evident in the commercial coil (Fig 5C).

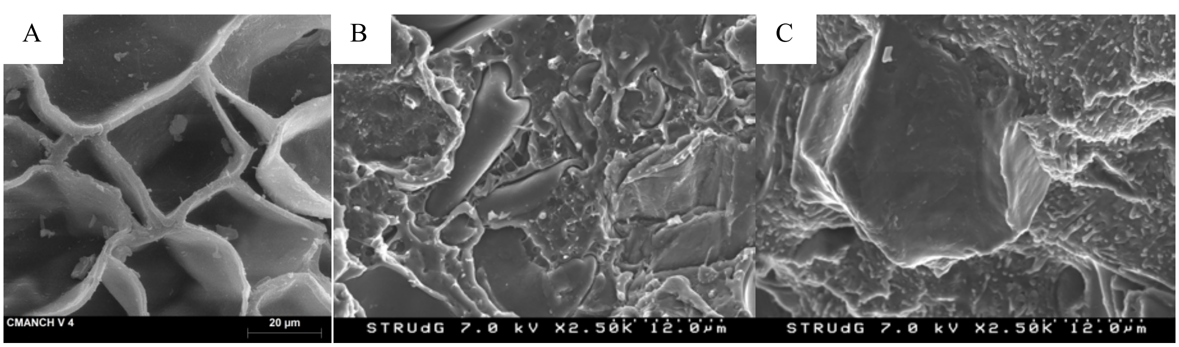

Fig. 5 SEM micrographs of cork (A), cork studied (B) and cork commercial (C).

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Print characteristics or features

Both the cork studied coil and the cork commercial coil have about the same thermal durability as PLA and it is actually quite easy to print with both. In the commercial coil, the manufacturer's recommended printing temperature range between 175°C to 250°C [10]. However, we used 165°C as printing temperature and 40°C on a heated print bed. As an interesting side effect, by playing with the temperature settings it could be avoid that a higher temperature will create a darker color and burnt smelt. Another aspect to consider is the printing speed as it is recommended not to use very high speeds with such filaments "experimental material status". So we used 130m/s intend of 160m/s (height print speed recommend in PLA). In this case we have also obtained exceptional results (Figure 5) preserving the high level of detail of the original model. Notwithstanding that the commercial coil presented more flexibility than the studied coil, the material has a greater flexibility than the PLA in both impression for both cork coils.

Other physico-mechanical characterization of the coil will be done according to international code.

Fig. 5 Model of printing a cork studied coil.

Conclusions

Novel duel coil base in cork was successfully obtained. In general, the cork studied coil showed more content of cork than the cork commercial coil. The presence of cork material in a 3D filament can be evaluated using a chemical composition assays and SEM. The percentage of suberin is related to the cork content and allows us to compare the differences of these cork products. FTIR is not a good methodology to assay PLA based products.

This work represents, therefore, very interesting material for the up-grading of an important industrial residue and simultaneous for the development of a new class of sustainable material with potential application in areas such as in the automotive and decoration industries. Work is in progress to further evaluate other features of this novel sustainable material and future biocomposites should be explored.

Acknowledgments

The authors thank the Department of Territory and Sustainability of the Catalan Goverment and the Waste Agency of Catalonia for the grant of the project in the framework of the Circular Economy TES/1275/2016. The authors especially thank 3D Spider Print (http://3dspiderprint.com/index.php) for the production and development of the studied cork filament.

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