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DETERIORATION OF CORK STOPPERS IN VINTAGE PORT WINE BOTTLES

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Deterioration of cork stoppers in vintage Port wine bottles

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held in

Symington Family Estates

Supervisor at FEUP: **Professor Adélio Mendes**

Coordinator at Symington Family Estates: **Engineer Cláudia Santos**

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ABSTRACT

This dissertation was developed along with Symington Family Estates to study the deterioration of natural cork stoppers in bottles of vintage Port wine. The main goal is the identification of the parameters responsible for the rupture and crumbling of the stoppers which are bound to endure numerous physical and chemical processes, as they are compelled to durably remain in bottle in account of the vintage wines' ageing taking several years.

Provided it is stored in ideal conditions (of temperature, pressure, and humidity) and with an adequate type of cork stopper, a perfect seal can last for decades. This time lasting property is crucial in the case of vintage wines (age-worthy wines), as they undertake a long ageing stage in bottle. That is only attainable through the use of a natural cork stopper for sealing since it can adapt to the bottleneck's internal irregularities, ensuring flawless sealing even in the event of the glass's expansion or contraction caused by changes in room temperature during shipment or storage.

To achieve the proposed goal, some analyses were performed on the batch of collected samples, from which a few presented the identified problem. A morphological analysis, through SEM, was carried out to check the constitution of the various samples. A chemical analysis, through FTIR tests, served to establish and compare possible differences in the composition of the cork, or rather some inconsistencies in treatment amongst the samples. Finally, a mechanical analysis, through DMA tests, was performed to evaluate and compare the mechanical properties between the various samples. All these tests were performed to compliant and non-compliant stoppers to better identify and compare the differences between them. The results achieved were not conclusive, since none of the performed tests revealed a pattern from which one could consistently infer on the existence of a link between certain inadequacies presented by the stoppers and their compliance or non-compliance, thus rendering impossible the drawing of a solution for the proposed problem.

Keywords: Cork; Natural cork stoppers; Suberin; Lignin; Morphology; Chemical composition; Mechanical behaviour.

RESUMO

O trabalho subjacente a esta dissertação foi realizado em conjunto com a empresa *Symington Family Estates* e teve como intuito estudar a deterioração de rolhas de cortiça natural usadas em garrafas de vinho do Porto vintage. O principal objetivo deste estudo é a identificação de parâmetros que possam ser responsáveis ou agravar a deterioração das rolhas quando são removidas da garrafa, rolhas estas que são concebidas para resistirem aos exigentes processos químicos e físicos a que estão sujeitas durante a longa vida útil dos vinhos vintage.

Quando armazenadas as garrafas nas condições ideais de temperatura, pressão e humidade, e com o tipo de rolha mais adequado, a selagem criada é quase perfeita e pode durar décadas sem se alterar. Para os vinhos vintage esta durabilidade é crucial, pois terão de estagiar em garrafa por longos períodos de tempo, o que só é possível recorrendo a rolhas de cortiça natural, uma vez que estas se adaptam à forma interna da garrafa e às suas irregularidades, assegurando, então, uma selagem quase perfeita, mesmo quando a garrafa se expande ou retrai devido a alterações de temperatura que podem eventualmente ocorrer durante os processos de transporte ou armazenamento.

De forma a atingir o objetivo proposto foram realizadas algumas análises a um conjunto de rolhas retiradas de garrafas com o mesmo vinho, nomeadamente, uma análise morfológica com recurso a SEM, para avaliar variações na constituição celular da cortiça, uma análise química usando FTIR, com o objetivo de averiguar diferenças na composição da cortiça ou mesmo identificar inconsistências no tratamento de superfície aplicado às diferentes rolhas, e uma análise mecânica através de testes de DMA, realizados para avaliar e comparar as propriedades mecânicas das várias amostras. Todos os testes elencados anteriormente foram feitos tanto em rolhas conformes como em rolhas não conformes, isto é, em rolhas sem defeito e em rolhas que se desintegraram aquando da remoção da garrafa, por forma a identificar e concluir acerca das diferenças entre elas. Os resultados obtidos foram inconclusivos, uma vez que nenhum dos testes realizados revelou um padrão que permitisse inferir sobre a possível relação causa efeito entre certas características e a desintegração das rolhas. Foi assim impossível determinar causas que respondessem ao problema em estudo

DECLARATION

I hereby declare, under word of honour, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source

Maria João Sousa

Monday, 15th of March of 2021

INDEX

LIST OF FIGURES

LIST OF TABLES

NOTATION AND GLOSSARY

E'	Storage modulus	MPa
E''	Loss modulus	MPa
tan*(δ)*	Damping factor	

List of Acronyms

DOC	*Denominação de Origem Controlada*
SEM	Scanning Electron Microscopy
TCA	2,4,6-trichloroanisole
ROSA	Rate of Optimal Steam Application
BwoST	Blank without Surface Treatment
BwST	Blank with Surface Treatment
BUb	Blank Unbottled
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
DLaTGS	Deuterated Lanthanum α Alanine doped TriGlycene Sulphate
ATR	Attenuated Total Reflectance
ST	Surface Treatment
DMA	Dynamic Mechanical Analysis

1 INTRODUCTION

1.1 FRAMING AND PRESENTATION OF THE WORK

Cork has been used as a wine sealer in glass recipients for several centuries. This material is recognized as the only truly reliable option for sealing wine bottles, due to its cellular structure, compressibility and elasticity. These are the foundations of cork's indispensable hermetic quality that allows the excellent conservation of the wine, while preventing any interference in its composition.

Vintage wines are the very best wines of a harvest, displaying the finest and most complete aromas, as well as the necessary depth and endurance to mature over several years in a bottle. Before being bottled, this type of wine spends a complete year stored in oak vats, ageing in direct contact with the wood. Only then will it undergo a taste test to assess if the wine produced is worthy of being bottled as a vintage, assuring the intense flavour that will continue to reveal its layers of complex aromas over many years.

Provided it is stored in ideal conditions (of temperature, pressure, and humidity) and with an adequate type of cork stopper, a perfect seal can last for decades. This time lasting property is crucial in the case of vintage wines (age-worthy wines), as they undertake a long ageing stage in bottle and must thus endure the numerous physical and chemical processes that go down between their components. That is only attainable through the use of a natural cork stopper for sealing since it can adapt to the bottleneck's internal irregularities, ensuring flawless sealing even if the glass expands or contracts due to changes in room temperature during shipment or storage. Moreover, when compared to other types of cork stoppers, the natural cork stopper is the only one that can provide the optimal chemical balance, allowing the proper evolution of the wine and the production of a *bouquet* of pleasant aromas during the maturation phase of bottled wine, a highly prized quality.

Symington Family Estates has been producing vintage Port wines for the last centuries, being one of the lead producers in the field. Product development was always a priority for the company, as well as the assurance of the utmost quality in their wine production. Thus, when faced with a problem or a defect whatsoever in the production, they intend to act quickly and decisively, working closely with engineering faculties and providing internship programmes for master students, which allows them to tackle a real-world issue. Hence, this project was carried out with an internship at Symington Family Estates.

This dissertation studies the deterioration of the natural cork stoppers used to seal vintage Port wine bottles. These stoppers are under compression for more than 10 years, causing the problem of their degradation to be much clearer and more complex in this type of wine. This was

identified by the company along the ageing stage, at the moment of the stoppers' removal from the vintage wine bottles for the wine tasting phase. The main goal is identifying which parameters cause the rupture and crumbling of the stoppers that are bound to endure numerous physical and chemical processes, being in a bottle for several years.

1.2 PRESENTATION OF THE COMPANY

The Symington Family Estates is a Portuguese wine company that owns and operates several vineyards and wineries, producing a variety of wine such as Port and Douro DOC wines. It is considered one of the world's leading producers of premium Port and one of the top Portuguese wine producers.

The company was founded as a family business in 1882 by Andrew James Symington, who arrived in Porto from Scotland. Since then, the business has expanded, having acquired new estates, coming to own 26 *Quintas* covering a total of 2255 ha of which 1024 ha are under vine. This expansion comprises the acquisition of the vineyards of *Quinta do Zimbro*, *Quinta da Senhora da Ribeira*, and the legendary Douro estate, *Quinta do Vesúvio*, as well as the buying in 1970 of the W & J Graham & Co. Nowadays, there are still ten family members, from the 4th and 5th generation, working across the business.

The Symingtons, always preserving their company values to produce exceptional Ports and wines that celebrate and preserve the uniqueness of Portugal and contribute to a positive future for the regions where they work, have thus become the biggest and most influent vineyard owners in the Douro Valley and holders of brands such as Cockburn's, Quinta do Vesúvio, Gould Campbell, Dow's, Warre's and Graham's. In 2020, the net sales volume was 19 million litres of wine, which translates to 98 million euros in sales. Their wine empire is appreciated and cherished globally registering a percentage of exportation of 85 %, the United Kingdom being the lead importer (27 %), followed by the Netherlands (14 %) and the USA (12 %).

Also, Symington runs three award-winning visitor centres with highly professional teams of guides: the Graham's 1890 Lodge, the Cockburn's Port Cellars, and Quinta do Bomfim. In 2014, the *Wine Spectator* ranked Dow's 2011 Vintage Port as no. 1 Wine of the Year in its annual Top 100 Wines of the World, which confirms the prestige of the wines produced by this company.

1.3 CONTRIBUTION OF THE AUTHOR TO THE WORK

For the correct development of the planned project, the author of this document performed a rigorous literature review on cork and its composition, on the mechanical and physical properties of cork, on the complete production process of cork stoppers, as well as on surface treatment and the specific experimental procedures of FTIR and DMA.

The experimental procedures were planned by the author, with some advice from Professor Adélio Mendes. The performance of all the experiments, excluding SEM, was also carried out by the author, as was the entire writing of this document, integrating the comments and advice of Professor Adélio Mendes, at FEUP.

1.4 ORGANIZATION OF THE DISSERTATION

The present dissertation is structured in four chapters and begins with an examination of the context into which it will be inserted, both as a project that concludes five years of study and as a first encounter with the corporate and industrial environment. The description of the four chapters is as follows:

- Context and State of the Art: This first section encompasses an important basis of knowledge obtained through an extensive literature review on specific content relevant to the project. Starting from the very foundations of the understanding of cork, its composition and its mechanical and physical properties, it comprises the complete description of the cork stoppers production process, as well as the relation between bottle, cork and wine;

- Materials and Methods: This section contemplates all the cork stoppers and bottle samples used during the development of this project. In addition, the testing methods are also presented and explained;

- Results and Discussion: The experimental findings are discussed and analysed in-depth in this dissertation main section, with some of them serving as crucial factors in achieving the dissertation objectives;

- Conclusions: The project's main goal is achieved in the final chapter. The reported findings will be used to draw the final conclusions.

2 CONTEXT AND STATE OF THE ART

In order to understand the mechanisms that lead to the degradation of cork stoppers, it is important to know the raw material, cork, and its composition and properties.

2.1 CORK

Cork is a natural and sustainable material sourced from the bark of cork oak (*Quercus suber* L.). The inner bark of the cork oak takes a minimum of 25 years to start producing the suberose tissue (formed by the phellogen of the cork oak), after which is harvested periodically from the tree, usually every 9 - 12 years, during the phase of most active growth (between the middle of May or the beginning of June until the middle or end of August) and all throughout the tree's lifetime. Due to the tree's specific requirements, such as abundant sunlight and a singular combination of low rainfall and high humidity, it thrives only in specific regions, namely in Portugal. [1] Portugal is the world's largest producer and processor of cork, being responsible for 50 % of the global production. [2], [3]

2.1.1 HARVESTING

During the tree's life cycle, three types of cork are produced. The first stripping, known as *desboia*, takes place when the cork oak is 25 years old, and the trunk has reached 70 centimetres in diameter when measured 1.30 metres from the ground. It gives structurally irregular and hard-to-handle cork – virgin cork (Figure 1) [4]; the following one yields a much more regular and not so hard material – *secundeira* or reproduction cork from the second stripping (Figure 1); from the third and successive strippings, a structurally smoother and more regular cork inside and out is obtained – *amadia* or reproduction cork from subsequent strippings (Figure 1). The latter flaunts the tree's finest qualities, being the only one used to produce natural cork stoppers. [5]

After stripping, the planks are stacked and exposed to the sun, rain, and wind for never less than six months, to oxidise the polyphenols and to stabilise the cork's texture. In the growing cycle following cork extraction, the thickest cork layer is typically formed. After this layer, a progressive decrease in cork production takes place every year until the following extraction. [1], [6]

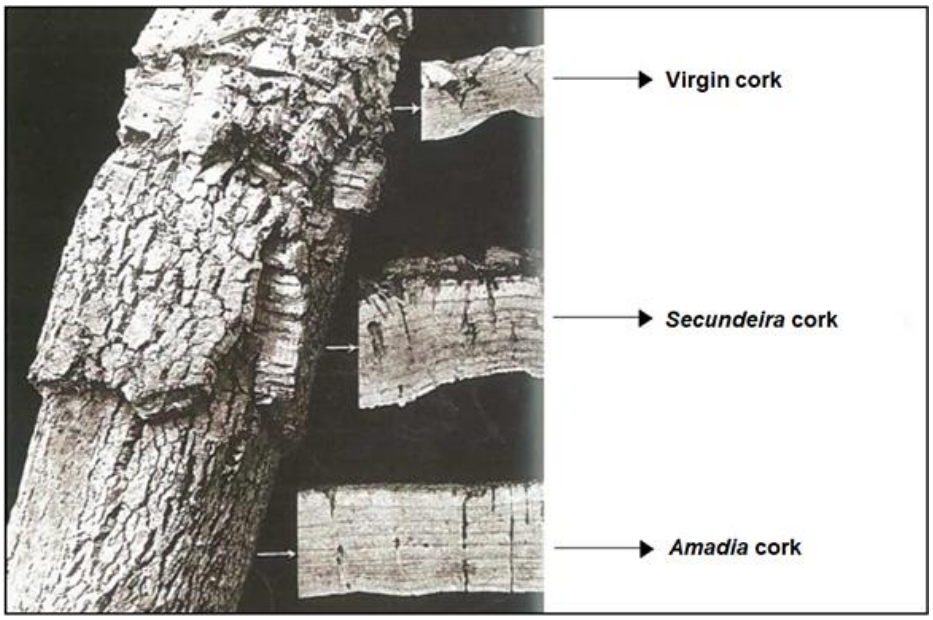


Figure 1 - Types of cork obtained from the various strippings.

2.1.2 CHEMICAL COMPOSITION

Although broadly studied, the chemical constitution of cork is hard to precise as it can be rather variable. It is highly dependent on factors such as tree dimensions, growth conditions, soil type, climate conditions, genetic background and whether it is virgin or reproduction cork. [1]

There are four main components present in different amounts due to the above-mentioned factors: suberin, lignin, polysaccharides, and waxes and phenols (extractives). Nevertheless, suberin is the most abundant component in the structure, representing on average 40 % of the total dry mass, followed by lignin corresponding to 22 %, polysaccharides to 18 %, and finally extractives to 15 %. The remaining 5 % are inorganic components. [1] The variation of suberin and lignin, as well as the suberin-to-lignin ratio, are known to affect the properties of cork. [6]

On Table 1 [1], it is possible to see the variation of composition between the different cork formations. On average, virgin cork contains more suberin and extractives than cork regenerated after the original extraction.

Table 1. Cork's chemical composition by different authors.

	Virgin cork composition (%)		***Amadia* cork composition (%)**			
Component	CALDAS (1986)	PEREIRA (1981)	GIL (1998)	CALDAS (1986)	PEREIRA (1981)	CARVALHO (1968)
SUBERIN	45	45	42	48	33.5	50
LIGNIN	27	21	21.5	29	26	19
POLYSACCHARIDES	12	13	16	12	25	13
EXTRACTIVES	10	19	13	8.5	13	15
OTHERS	5	2	7	2.1	2.5	3

- *SUBERIN*

Suberin is a structurally complex macromolecule with ester bonds between ester-type monomers, including an aromatic and an aliphatic part, as can be seen in Figure 2 [1]. It is responsible for the low permeability of cork and its elastic properties, allowing the bending and compression of cell walls, and its removal destroys cell integrity. [1], [7]

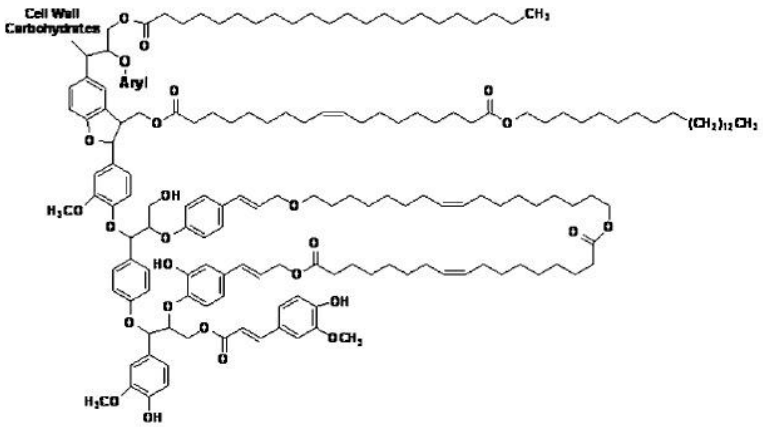


Figure 2 – Schematic structure of suberin.

- *LIGNIN*

Lignin is the second most important structural cell wall component in cork. However, it is not specific to cork, being present in most plants' secondary cellular tissue. It is an aromatic cross-linked polymer, produced by the monomers of coniferyl, sinapyl and *p*-coumaryl alcohols. This component is responsible for the structural rigidity of the cells and their resistance to compression and its structure is presented in Figure 3 [8]. [1], [7]

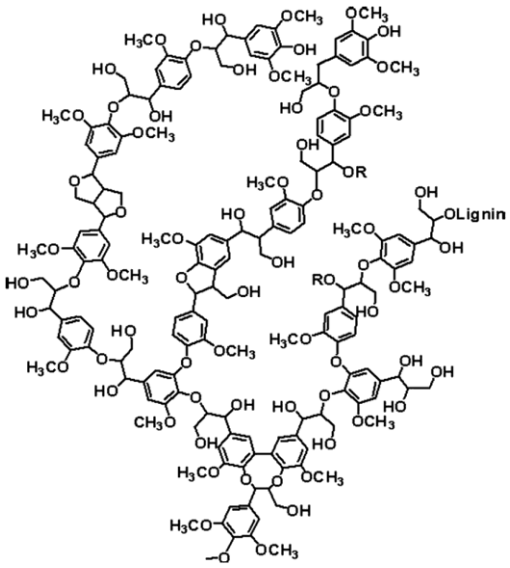


Figure 3 – Schematic structure of lignin.

- *POLYSACCHARIDES*

The polysaccharides present in cork are cellulose (homopolymer) and hemicellulose (heteropolymer). They grant structural rigidity to the cork cell, preventing the cells from collapsing, and consist of a sequence of low molecular weight chains of monomers connected by glycoside bonds. [1], [7]

- *EXTRACTIVES*

Cork contains a significant yield of non-structural components, such as waxes (also responsible for low permeability) and tannins (phenolic compounds). These may be removed by solubilization with suitable solvents, without compromising the core properties of cork. [1], [7]

2.1.3 MACROSCOPIC STRUCTURE

When the cork is removed from the tree, the outer part of the *entrecasco* is revealed and then pushed by the successive layers of new cells developing from within, originating the *costa,* which is the outer part of the cork that dries, contracts and hardens, ultimately cracking due to the increase in the outer perimeter caused by growth. Similarly, the inner part of the suberose tissue, which corresponds to the last layer of annual growth, is called *barriga*. It has less elasticity than the other layers and presents pores all throughout its area: lenticular channels. Porosity is closely linked to the quality of cork. [9] The various phases of cork growth are represented in Figure 4 [10].

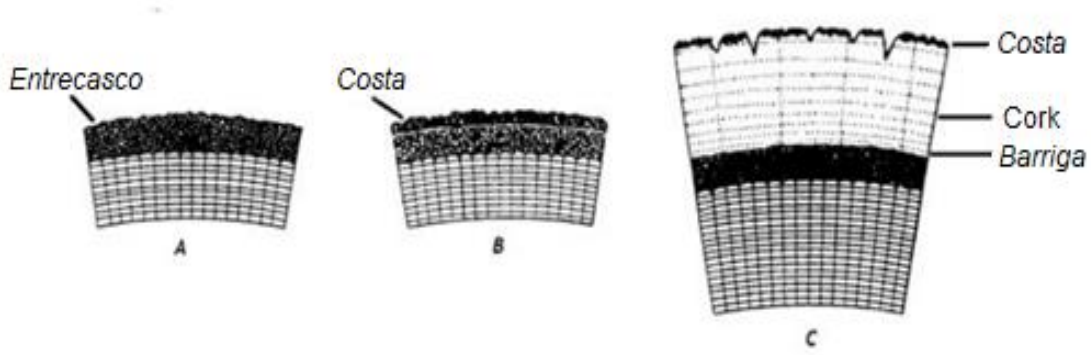


Figure 4 – Schematic representation of cork's formation: A) After stripping; B) Formation of the costa; C) End of cork's growth.

2.1.4 MICROSCOPIC STRUCTURE

By performing scanning electron microscopy (SEM) on cork, it is possible to determine its structure and cellular arrangement. Cork is constituted by an alveolar structure formed by suberised dead cells, *i.e.*, closed and hollow cells containing a gas mixture identical to air. These cells are arranged without empty spaces in-between them, as evidenced in Figure 5 [6], and, in a radial section, cork cells resemble 4-to-9-sided polygons (heptagonal, hexagonal and pentagonal cells being the most common), while on tangential and axial directions they present a rather rectangular conformation. [6], [7]

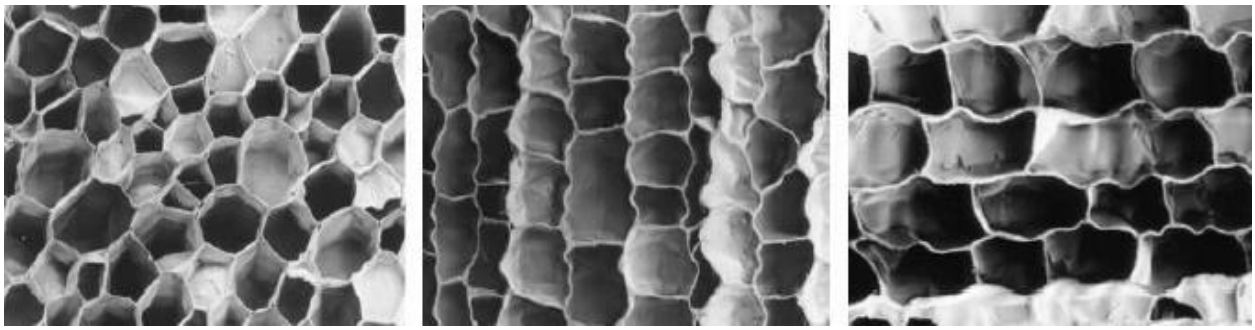


Figure 5 - Structure of cork as observed by SEM.

Cork cell walls are displaced as a three-layer structure as represented in Figure 6 [1], [6]. The primary and tertiary layers are essentially composed of lignin and cellulose, respectively, which provide structure and rigidity to the cells. The secondary wall is formed by alternating layers of suberin and waxes. [1]

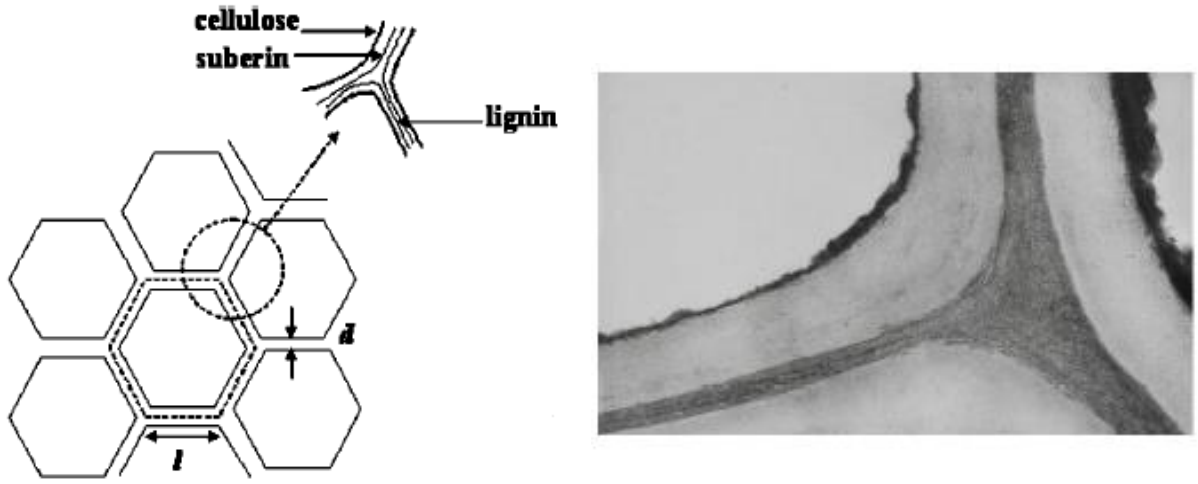


Figure 6 - Cork's cell wall: A) Schematic representation; B) Transmission electronic micrograph.

This secondary layer is flexible enough to undulate or corrugate under compression without fracturing, during the bark growth. Corrugation occurs massively during the different stages of cork tree growth. At the beginning of the growth layer, cells collapse against the last cells produced in the previous growing season. Therefore, late cork cells show much less corrugation, having thicker walls and being more rigid compared with early cork. Cork cells' lateral faces present an irregular corrugation, ranging in the same cell tissue from straight cell walls to heavily corrugated or even collapsed ones. [6]

Cork thermal decomposition starts at temperatures around 150 ℃, with the first significant mass loss at 200 ℃, where polysaccharides decompose to a great extent. Suberin degradation will start at 250 ℃ and above that cellular structure will be severely affected due to acute thermal chemical degradation. At last, reaching 450 ℃, the cellular structure is lost and the material turns to ash. [11]

2.1.5 PHYSICAL PROPERTIES

Since the gas mixture occupies a large fraction of cork's volume, the latter is a very light material, and thus has low density (between 120 and 240 $kg \cdot m^{-3}$). Its low density, along with the fact that the cells in cork are closed, without open connections to one another at a microscopic level, gives cork poor heat transfer properties and makes it buoyant. Its acoustic insulating capacity, low electrical conductivity and high resistance to wear, corrosion and fire are other properties appreciated in this material. Suberin is the most abundant component in cork and its insolubility in water and alcohol allows it to have low permeability to gases and liquids. This feature endows cork with wet strength, providing it with high stability. [6]

2.1.6 MECHANICAL PROPERTIES

In general, cork presents excellent elastic properties, being able to be compressed to half of its initial volume and then decompressed, recovering its initial shape and volume. This feature enables cork to withstand high variations in temperature and pressure. [6]

Compression, when applied in the radial direction, will make cell walls fold, increasing the amplitude of corrugations. In the non-radial directions, however, it will create a small expansion. Accordingly, when compression is applied in the non-radial directions, the lateral cell walls will bend, inverting the undulation pattern and leading to a shrinkage in the radial direction. [6]

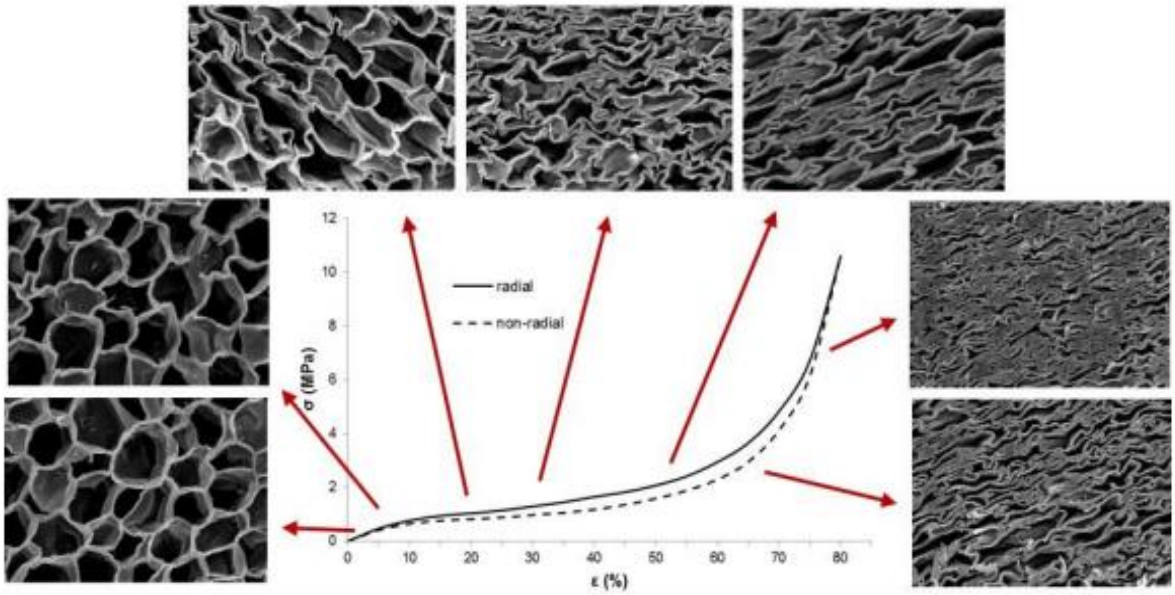


Figure 7 – Stress-strain curves for cork's compression.

The stress-strain curves, in Figure 7 [6], show three regions associated with distinct deformation processes. The first area refers to the elastic bending of the cell walls, up to about a 7 % strain. The second starts after the yield stress point, forming a large and almost horizontal *plateau*, which rises to strains up to about 70 %. The last region shows a sharp increase in stress and a steep slope, caused by the crushing and collapsing of cells – densification. [6]

Heat treatment with air affects the compression properties of reproduction cork. The longer the treatment, at constant temperature, the lower the compression resistance becomes. Heat treatment with water also affects the mechanical properties of cork. The boiling process softens the cell walls and, due to tensile stresses between adjacent cells, eventually leads to their straightening. [1]

2.2 CORK STOPPERS

Despite cork's vast range of applications, such as in construction, transportation and fashion, cork stoppers persist as the producing focus of cork companies due to the wine industry's high demand. [1] A cork stopper is able to preserve its chemical and physical characteristics during storage, is durable and can be easily removed from the bottle; it does not allow any leakage of the liquid content, either at the interface between the bottle and the stopper or through the stopper itself, nor does it negatively alter the liquid's chemical and sensory features. [7] This material has the highest added-value and widest market. According to a survey conducted by *Wine Spectator* magazine, 89 % of the world's best wines use cork as a sealant. [12] The perceived value of cork stoppers is highly significant with 98 % of Chinese and American consumers associating cork to wine quality. [13]In 2018, Portugal exported the equivalent to 752.8 million euros in cork stoppers. [14]

Cork stoppers can be sorted into seven categories considering the way they were produced:

- Natural stoppers, which are fabricated by punching of a single strip of cork; [15]
- Colmated stoppers, achieved by the penetration of an approved adhesive and of cork powder into the pores of natural cork stoppers of lower quality; [16]
- Multi-piece stoppers, that are manufactured from two or more halves of natural cork glued together with an approved adhesive; [17]
- Agglomerated stoppers, which are made entirely from cork granules derived from by-products resulting from the production of natural stoppers or virgin cork or *secundeira*; [18]
- Technical stoppers, obtained from a very dense agglomerated cork body with discs of natural cork glued to its top, end or both; [19]
- Champagne stoppers, which are considered a technical cork stopper with a larger diameter in order to contain the high pressures in gasified wine bottles; [20]
- Capsulated stoppers, that are assembled from natural or colmated stoppers attached to a capsule made out of several materials. [21]

Their overall quality depends strongly on the raw material and the processes adopted by the manufacturer.

2.2.1 NATURAL STOPPERS

Natural cork stoppers have been the method of choice to seal wine bottles of various types since the beginning of this industry and they still reign, presenting some characteristics that simply cannot be achieved with artificial materials. Given cork's structure, compressibility and elasticity

that result in a perfect fit to the interior of the neck of the bottles, the establishment of a thus hermetic environment thoroughly and completely seals the bottle, as cork is able to adapt to the imperfections of the surface and to the expansions and contractions of the glass. Furthermore, these characteristics can be maintained for decades if high-quality cork is employed. [15]

These stoppers provide the ageing wines with an environment where the oxygen is present in a minimal, yet necessary and sufficient, content for a gradual evolution of wine. In doing so, the perfect balance needed for these complex chemical and physical processes is delivered, allowing the formation of some important and highly appreciated characteristics of the wine, namely the set of aromas developed, in part, during the ageing period of bottled wine - the *bouquet* - that characterizes it, working as a mirror of the conditions under which the wine aged and was conserved. [7], [15]

Cork stoppers can vary in length and diameter and their size should be carefully chosen depending on the type of bottle, the bottling process and the ageing period intended for the wine. [15]

2.2.2 PRODUCTION OF NATURAL CORK STOPPERS

After the stabilisation period in the forest or in the yards at a factory, the cork planks undergo additional steps before natural cork stoppers are obtained. These stabilised planks are boiled in clean water for no less than one hour to make them softer and more elastic and to completely expand the lenticels. As the gas enclosed in the cells expands on account of boiling, a tighter and more homogeneous cell structure is achieved. This process also allows the cork to be cleaned, removing water-soluble substances, and ensuring a meaningful reduction of the microflora population. [22], [23]

These planks, now smoother and less dense, are stored for about three weeks – rest period – in an area with good ventilation so they can reach both the required consistency to be transformed into stoppers and the ideal moisture content for further processing. A second boiling followed by another rest period is optional. After this stage, the planks are sorted into quality classes based on key characteristics (cork stoppers are only produced using good quality, thick planks - *cheios*) and cut and trimmed into smaller strips facilitating the punching process, where cylindrical stoppers are obtained. Later, these are graded, enabling the separation of the finished stoppers into industrial categories according to visual criteria. In addition, defective stoppers are eliminated. Before being cut to the desired size and polished (rectification), the stoppers are pre-dried so the said latter process can be performed. They are then washed and disinfected using an aqueous solution of either hydrogen peroxide or peracetic acid. Subsequently, the stoppers are fully dried. This procedure eliminates internal moisture without compromising the cells' structure, minimising microbial contamination, and maximizing stopper performance. Later, the stoppers are branded with approved ink or laser for the food industry. [22]–[24]

- *SURFACE TREATMENT*

To facilitate their insertion into and extraction from the bottle, the stoppers are covered with paraffin or silicone. Paraffin treatments aim at waterproofing as well as improving sealing. Treatments with silicone mainly aim at lubricating the stopper. The type of treatment to be applied and its dosage depend on the type of wine, bottle, maturation period and bottling machine type. For wines that require an ageing period of over 18 months, a previous paraffin coating should be applied and then followed by a silicone one. [23], [24] [25]

Finally, the stoppers are again sorted into commercial classes (*Flor, Extra, Superior, 1º, 2º, 3º, 4º and 5º*. In vintage wines, only *Flor* is used), sterilised with sulphur dioxide (SO_2) gas, sealed in gas-barrier bags and prepared for transport. [1], [23] The whole process is depicted in Figure 8. All the cork shavings, powder and rejects are then put to other uses such as the production of cork granules, cork flooring and cork insulation boards.

The quality and price of natural cork stoppers are established according to their apparent porosity, *i.e.*, the level of overall porosity one can deduce from the observation of the stopper's surface.

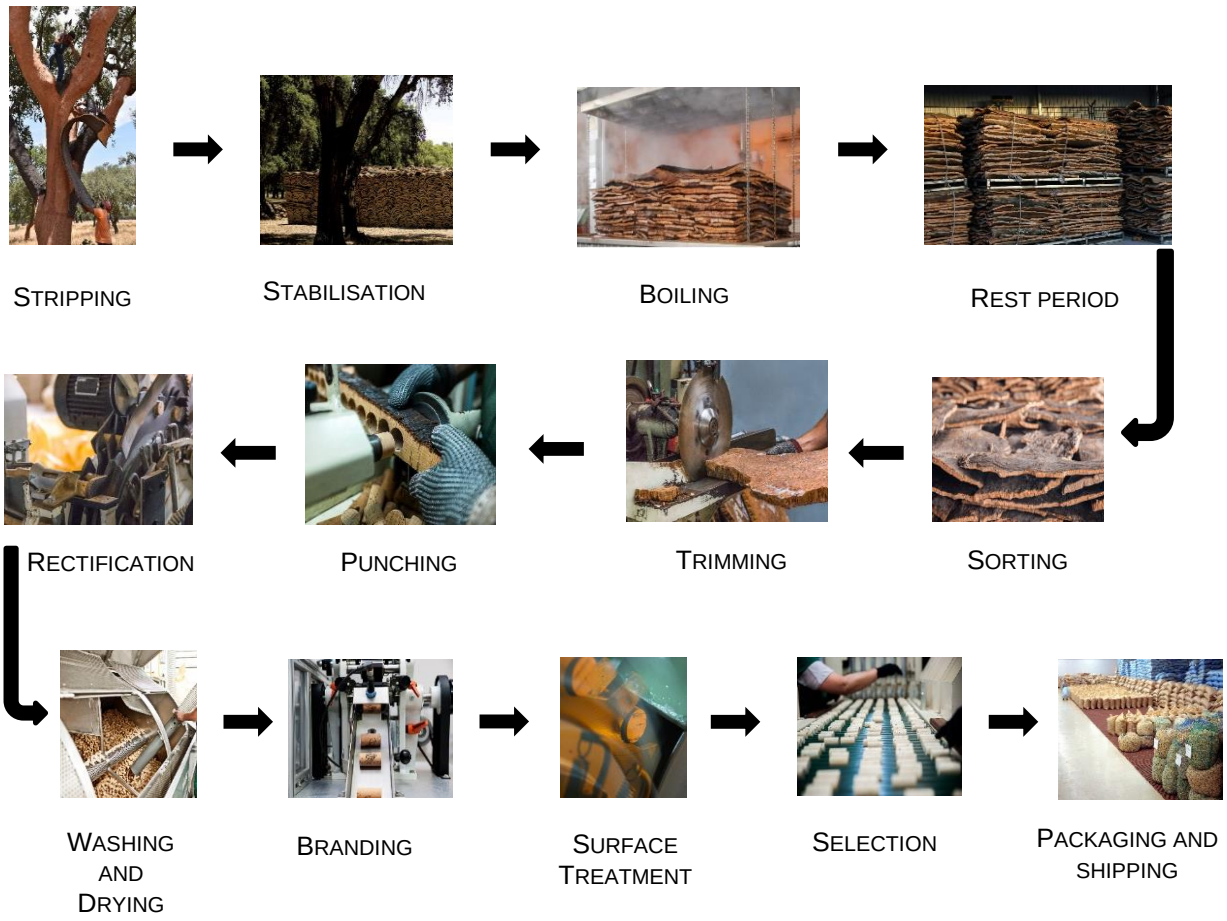


Figure 8 – Diagram of the natural cork stoppers production process.

- *TCA REMOVAL*

Cork taint refers to the mouldy taste and aroma of the wine on account of the presence of haloanisoles, namely the 2,4,6-trichloroanisole (TCA) produced by the activity of undesirable fungal strains. Several approaches to avert undesired aromas and off-flavours, *i.e.*, to significantly diminish the microbial load in stoppers have been adopted. [7], [26] These processes tend to be specific to each company and thus have become their trade secret.

Several methods aiming at the eradication of TCA have been developed and implemented by different companies in the sector, such as:

- improved boiling systems that increase the removal of the aforementioned molecule;
- controlled steam distillation, which allows the TCA to be drifted away in a stream of vapor during the distillation process thanks to its volatility;
- volatilization by dragging under controlled temperature and humidity, which takes in consideration the TCA's volatility temperature of 60 ˚C to extract it from the stoppers;
- volatilization by dragging in the gaseous phase of adjusted polarity, under controlled temperature and humidity, that simulates the yielding of cork molecules to bottled wine using the dissolving effect of ethanol;
- super-critical extraction with CO_2 that drags TCA and other volatile compounds present in granulated cork using a CO_2 stream in a super-critical state. [25]

The most known one, the Rate of Optimal Steam Application (ROSA) system, developed by *Amorim & Irmãos, S.A.*, consists of a steam extraction that removes volatile components. [1] [27]

2.3 THE TRINOMIAL BOTTLE – WINE – CORK STOPPER

As mentioned above, the type of bottle, the bottling process and the ageing period of the wine dictate the specifications of the stopper used. [25]

When selecting the stopper, the internal profile of the bottles is studied thoroughly. It is after this analysis that a recommendation for the dimensions of the stopper for a certain bottle is made, ensuring the best possible performance of the duo bottle/stopper. For most wines, the diameter of the stopper should be at least 6 mm larger than the smallest diameter of the bottleneck. For lengthy periods in a bottle, it is advisable to use a stopper with a diameter larger than 6 mm but not over 8 mm. [25]

Regarding the length of the stopper, the necessary space between its bottom and the surface of the wine should be respected to save an expansion chamber that makes up for any thermal expansions of wine. This space should be of at least 15 mm and longer in wines that age for a longer period. [25]

The humidity in the cork stoppers should fall between 4 % and 8 % to maintain suitable elasticity and to reduce the possible risk of microbial development. [25]

When it comes to bottling, for the compression to be withstandable it should not shrink the stopper to a size more than 2 mm smaller than the bottleneck's diameter at its narrowest point. In addition, the shrinking should never be greater than 30 % of the stopper’s diameter as its elasticity may be compromised, thereby hindering the correct sealing of the wine in the bottle. [25]

After being bottled, the stopper recovers its volume in the first 5 to 10 minutes, adjusting itself to the irregularities of the bottleneck. Within an hour, a uniform force is exercised over the surface of the glass. [25]

The bottling machine should be calibrated to allow a gap of at least 15 millimeters between the wine surface and the stopper, with the correct selection of the length of the stopper (values for 750 mL bottles). This vacant chamber is necessary to allow and contain the expansion of the wine in case the temperature increases during shipment or storage. [25]

The cellar, where the bottles are stored, should follow these guidelines: [25]

- Room temperature between 15 ℃ and 20 ℃, with no great variation either during the day or throughout the year;
- Humidity between 50 and 70 %;
- Absence of insects and rodents;
- Absence of chemically treated wood;
- Odour-free;
- Absence of chemical products, such as paints or cleaning products;

The bottles should be stored horizontally.to prevent the stoppers from drying.

3 MATERIALS AND METHODS

The proposed problem is to understand the reason behind the crumbling of a significant percentage of the stoppers used in vintage Port wines as they are removed from the bottle. To tackle this issue, several experiments have been conducted on the following samples:

- three cork stoppers from the same batch, that were never inserted in a bottle, without surface treatment, and produced in 2020 – blank without surface treatment (**BwoST1 to BwoST3**);
- three cork stoppers from the same batch, that were never inserted in a bottle, with surface treatment, and produced in 2020 – blank with surface treatment (**BwST1 to BwST3**);
- five cork stoppers from the same batch, that were never inserted in a bottle, with surface treatment, and produced in 2020 – blank unbottled (**BUb1 to BUb5**);
- twelve cork stoppers inserted in a bottle in 2005 and removed in 2020, with the respective bottles; out of the twelve cork stoppers, only ten were subjected to experiments due to the complete disintegration of the other two during their extraction from the bottles (**cork stoppers: S1 to S10; bottles: B1 to B12**);
- fourteen cork stoppers inserted in a bottle in 2005 and removed in 2020 (**S11 to S24**).

3.1 QUALITY CONTROL OF CORK STOPPERS AND BOTTLES

Upon reception of the wine bottles and cork stoppers by the company, a range of tests are conducted *in loco* to assess the quality of these materials. Concerning the bottles, their internal profile is analysed and compared to the datasheet. For the purpose of this work, the internal profile of B1 to B12 will be examined. As for the stoppers, these tests follow the internal company's practices which are based on the *International Code of Cork Stoppers Practices* [24] and make use of the *International Organization for Standardization* norms. They can be either dimensional, physical, mechanical, chemical, visual or sensorial. From this work's perspective, only a few of them will be performed on the stoppers S1 to S10.

3.1.1 EXTRACTION FORCES

The aim of this test is to ascertain the value of the force required to extract the stopper from the bottle, taking into consideration that it is highly linked to the cork's properties, the corking process, and the surface treatment. According to *ISO 16420:2013*, the values for the extraction force should fall somewhere between 15 and 45 daN. A prior test was carried out in 2005 at room temperature and one hour after corking, having as guideline *ISO 9727-5:2007, Cylindrical cork*

stoppers – Physical tests – Part 5: Determination of extraction force. The test was repeated in 2020 at the removal of the stopper. The analysis of the extraction force was conducted by the means of a dynamometric test press (METALOMECÂNICA JAV® Mod. TC 2000), at a steady speed of 300 $mm \cdot min^{-1}$. In the performance of this test, a standard helical stem corkscrew was used.

The measured values were then compared with the ones obtained in 2005 when five stoppers from the same batch were tested.

3.1.2 DENSITY

To infer on density, an intensive property of the materials, and on its variances amid the cork stoppers, their masses were measured, and their volumes calculated loosely resorting to the volume formula of a cylinder. To do so, the wholly extracted stoppers were cut by the edge where some wine had been absorbed so that the measured mass of the stoppers did not comprise that of the wine. Furthermore, the stoppers that suffered crumbling when extracted were cut in order to obtain regular surfaces so that their heights would not be wrongly measured.

3.1.3 MOISTURE CONTENT

The tests were carried out following the *ISO 9727-3:2007, Cylindrical cork stoppers – Physical tests – Part 3: Determination of moisture content*. An analogic moisture meter for solid products (AQUA-BOY®) was used to determine the relative water content in the mass of the stoppers by conductimetry. The *ISO 16420:2013* establishes that the average value of water content in the stoppers before corking should be (6 ± 2) % since low values compromise the cork's mechanical properties and high ones stimulate microbiological growth.

Three readings were performed for each stopper. The results thus collected were compared to the ones obtained by sampling before their insertion into the bottle, in 2005, when 50 stoppers were tested. This measurement was done at the stoppers' top (facing outwards), far from the wine's influence.

3.1.4 INTERNAL PROFILE OF THE BOTTLES

The inspection of the bottleneck profile is an important control parameter for wineries since it can affect the cork's performance and therefore potentially jeopardise its sealing capacity. For that purpose, an automatic system (Perfilab EGITRON®) was used. This process procures a variation in the values retrieved from the measuring of two perpendicular diameters (diameter at 0º, aligned with the *disparado*r, and diameter at 90º), all the way down the bottle's neck. The degree of ovalization, corresponding to the difference between the two diameters, can thus be gauged. Having obtained these values, one can compare them with the product datasheet (see ANNEX A) to infer about irregularities.

3.2 SCANNING ELECTRON MICROSCOPY

This technique uses the behaviour of electrons to create a 3D-image. The electrons that are reflected or knocked off the near-surface region of a sample create an image.

Due to the electrical insulant properties of cork, it was necessary to sputter coat them. The cork's nonconductive nature renders the surface of these materials an electron trap. The resulting accumulation of electrons on the surface is called charging and produces extra-white regions on the sample that can affect the information on the obtained image. When the sputter coating technique is used, the conductive coating layer serves as a way for the charging electrons to be eliminated.

The stoppers S1 to S10 were analysed through this method for the recording of the morphology of their interior. Three sections were selected (base, middle and top), all equally spaced along the central axis of the stoppers, and cross-sectioned samples from the interior were extracted. To allow clear observation surfaces, the cuts were done with a sharp razor blade.

The samples were sputter-coated (Leica EM ACE200®) in diffuse mode with gold for 20 s at 60 mA. The surfaces were then observed in an electron scanning microscope PHENOM XL® at different magnifications, in high vacuum, 15 kV map and SED detector, and the images were recorded in digital format. With the same equipment, an elemental analysis of the surface was performed, using energy dispersive spectroscopy (EDS), where the mass weight percentage of the elements present in the surface sample was obtained.

3.3 INFRARED SPECTROSCOPY

The Fourier transform infrared (FTIR) spectroscopy works by measuring how much light is absorbed by the bonds of vibrating molecules to establish a molecular fingerprint. This technique was employed with the purpose of searching for staggering potential differences in the cork spectra given by the samples and that could be the reason for the crumbling.

The lateral surface of cork stoppers BwST1 to BwST3, BwoST1 to BwoST3, and S1 to S10 were examined under FTIR; the interior of stoppers S1 to S10 was also studied.

For the completion of the analysis, small fragments of both the surface and interior of the cork stoppers were removed using a sharp razor blade, a procedure followed by their attachment to the crystal window of the ATR accessory. After exposing the fragments to infrared radiation, it was possible to obtain the characteristic absorption wavenumbers for the composition of the cork stoppers' surface and interior, as well as the corresponding absorption intensities.

The infrared spectra were registered using a VERTEX 70 FTIR spectrometer (BRUKER®) in transmittance mode with a high sensitivity DLaTGS detector at room temperature. The samples were measured in ATR mode, with a A225/Q PLATINUM ATR Diamond crystal with a single

reflection accessory. The spectra were recorded from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}, and 64 scans were averaged to compute one spectrum.

In an attempt to infer on the homogeneity of the surface treatment (ST) from one stopper to another, it was necessary to calculate the ratio between the peaks corresponding to the integration (A) of the -CH3 and -CH2 in aliphatic compounds (3000 – 2800 cm^{-1}) to the one identified as the C=O stretching (around 1740 cm^{-1}). This analysis was performed for both the surface and the interior of S1 to S10 so that these two ratios could be compared, using the equation (1):

$$\mathrm{ST} = \frac{\left(\frac{A_{-\mathrm{CH2}}}{A_{C=O}}\right)_{Surface}}{\left(\frac{A_{-\mathrm{CH2}}}{A_{C=O}}\right)_{Interior}} \quad (1)$$

These integrations were executed employing the trapezoidal rule.

3.4 Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) is a powerful tool to study materials, as well as their properties and behaviour. The quality of a cork stopper is highly dependent on its mechanical and physical properties. Its ability to seal wine can be translated into four important factors: flexibility, insulation, resistance, and impermeability to gas and liquids. By performing DMA, the cork stopper's flexibility and resistance properties can be determined with a quantifiable method.

To carry out these analyses, samples S11 to S14 were used.

Tensile dynamic mechanical measurements were performed using a DMA 242 E Artemis (Netzsch®) in a temperature range of − 100 to 150 °C. The temperature increased at a rate of 2 $K \cdot min^{-1}$ and gaseous nitrogen was used to keep a controlled atmosphere inside of sample container during the cooling and heating steps. For tensile experiments, all specimens had a rectangular shape with typical dimensions of 8.5 × 2.5 × 5.2 mm^3 (length x thickness x width) and were tested at the frequency of 1 Hz. Experiments were carried out in mixed control with a maximum dynamic force of 4 N and a maximum sample amplitude of 50 µm. Despite being an influential factor, the direction of the cork stopper (either radial, axial or tangential) was not taken into account.

Through this procedure, the storage modulus (*E'*) and the damping factor (tan*(δ)*) of S11 to S14 can be studied. The *E'* corresponds to the measurement of the elastic response, *i.e.*, the energy stored in the material, whereas the tan*(δ)* is the measure of how well a material can get rid of energy. The loss modulus (*E''*) represents the measurement of the viscous response, *i.e.*, the energy lost due to heat. The ratio between these two moduli gives the tan*(δ)*.

3.5 COMPRESSIBILITY TEST

During the wine bottling process, the cork stopper is subjected to pressure. By measuring the necessary force to compress the cork stopper, one can infer about its mechanical properties, a procedure done to S15 to S24 and BUb1 to BUb5.

The force required to compress each closure from its initial diameter to 30 % of its value was determined using the MECMESIN®-MULTITEST 1-d equipment. Each sample was individually positioned on a plug device and compressed at a constant rate of 5 mm·min^{-1} using a 1000 N load cell with a 0.01 N resolution compression gauge sensor. The test starts with an initial measurement of the diameter of the stopper followed by its compression in up to 30 %. Once its diameter is thus reduced to 30 % of its previous dimension, the stopper is yet subjected to a now constant compressing force for precisely one minute. After this compression, it is necessary to wait three minutes to measure the stopper's diameter again, at the same points of the previous measurement. The recovery rate is established by checking the stopper's capacity to return to its initial diameter after being compressed and is calculated by equation (2):

$$\text{Recovery rate (\%)} = \frac{Final\ diameter}{Initial\ diameter} \times 100 \quad (2)$$

4 RESULTS AND DISCUSSION

The cork stoppers used to bottle the Gould Campbell Vintage 2003 Port wine were validated in 2005, which ascertains their compliance to the norms in force at that time and their suitability to be inserted into the bottles.

When removed from the bottle, S1, S6, S10, S11, S12, and S15 to S19 were fully extracted and, therefore, considered compliant. The extraction of the remaining samples, on the other hand, resulted in crumbling, hindering the complete removal of the stoppers and resulting in their bottom part needing to be pushed into the bottle, as it was the only way to remove them, and the stoppers were thus considered non-compliant. The tests were performed on the part that was able to be extricated.

In Table 2, the mechanical integrity of each sample is stated. To render easier the reading of this document, in the following sections any reference to the compliant samples will be underlined.

Table 2. Extracted cork stoppers and their mechanical integrity: compliant or non-compliant.

Cork stopper	Condition	Cork stopper	Condition
S1	COMPLIANT	S13	NON-COMPLIANT
S2	NON-COMPLIANT	S14	NON-COMPLIANT
S3	NON-COMPLIANT	S15	COMPLIANT
S4	NON-COMPLIANT	S16	COMPLIANT
S5	NON-COMPLIANT	S17	COMPLIANT
S6	COMPLIANT	S18	COMPLIANT
S7	NON-COMPLIANT	S19	COMPLIANT
S8	NON-COMPLIANT	S20	NON-COMPLIANT
S9	NON-COMPLIANT	S21	NON-COMPLIANT
S10	COMPLIANT	S22	NON-COMPLIANT
S11	COMPLIANT	S23	NON-COMPLIANT
S12	COMPLIANT	S24	NON-COMPLIANT

4.1 PHYSICAL AND MECHANICAL TESTS

To assess the correct evolution of the characteristics of the stoppers through time, a few of the commonly performed physical and mechanical tests for the validation of a batch of cork stoppers were carried out. The extraction forces, the moisture content, the diameters at 0º and 90º, the height and the mass were measured.

4.1.1 EXTRACTION FORCES

In Table 3, the values of the extraction force that was required to remove the stoppers are presented.

Table 3. Extraction forces of samples S1 to S10 removed from the bottle.

Cork stopper	Extraction force (daN)
S1	57.6
S2	70.9
S3	58.3
S4	51.8
S5	52.5
S6	46.3
S7	43.5
S8	47.8
S9	67.3
S10	53.3

It is possible to verify the abnormally high values of the extraction force applied to each of the stoppers, given most of the samples outstripped the range for this normative specification, having just as well exceeded 50 daN (it should be noted that the extraction force should not be superior to 45 daN).

When comparing the average of the values for the compliant samples, (52.4 ± 4.7) daN, and the average value for the non-compliant samples, (56.0 ± 9.3) daN, it is possible to observe that the difference is not significant, even more taking into consideration the error of these values. Therefore, the obtained results appear to not show any relation between the non-compliance of the stoppers and the variation in extraction forces.

The data recovered from 2005, when the average extraction force was 65.4 daN, is not too different from the values from 2020. As there is no particular trend in the variation of extraction forces with time, no blatant differences could be pointed out in the establishment of a probable link between a change in the stoppers' structure, leading to a more difficult or easier extraction, and their observed crumbling.

4.1.2 DENSITY

The calculated density for each stopper is presented below, along with diameters and mass, in Table 4.

Table 4. Density of samples S1 to S10 removed from the bottle.

Cork stopper	Diameter 0º (mm)	Diameter 90º (mm)	Average diameter (mm)	Mass (g)	Density (kg·m^{-3})
S1	18.03	17.79	17.91	3.8174	297
S2	17.95	17.68	17.82	2.4481	335
S3	17.85	17.43	17.64	2.0951	358
S4	17.52	17.86	17.69	2.8448	387
S5	18.25	17.88	18.07	2.0613	272
S6	17.53	17.42	17.48	4.2865	350
S7	17.81	17.85	17.83	1.8627	254
S8	17.22	17.85	17.54	2.1375	276
S9	17.73	17.64	17.69	2.6542	364
S10	17.60	17.75	17.68	3.2341	311

As expected, these stoppers' density is higher than that of unbottled stoppers (between 120 and 240 kg·m^{-3} - cork's density as retrieved from the literature).

Since the density of the cell wall materials is believed to be fairly constant, the global density variations must be related to the cell dimensions (height and wall thickness), cell wall corrugation, and/or the volume fraction of lenticular channels. High densities correspond to thick and heavily corrugated walls and a low incidence of lenticular channels.

These samples were under great pressure in the bottleneck, leading to a significant compression of the cork cells that entails the diminishing of their size and an ensuing decrease in the stopper's volume. In some extreme cases, if the bottling pressure is well above the recommended, there can be a densification of the cork, causing the stopper to be brittle and to disintegrate as it is removed, as observed in the non-compliant samples. Furthermore, the difference between the average value for compliant stoppers, (319 ± 22) kg·m^{-3}, and the average for the non-compliant stoppers, (321 ±49) kg·m^{-3}, is considered insignificant. Therefore, there is no evident difference between the compliant and the non-compliant stoppers that could justify this behaviour.

4.1.3 MOISTURE CONTENT

The data collected in 2021 regarding this property, after the ageing of the bottled wine for fifteen years, is compiled in Table 5.

Table 5. Moisture content of samples S1 to S10 removed from the bottle.

Cork stopper	Moisture content (%)			
	Reading #1	Reading #2	Reading #3	Average
S1	8.2	7.8	7.6	7.9
S2	6.2	6.3	6.4	6.3
S3	8.0	7.8	7.8	7.9
S4	7.3	7.1	7.2	7.2
S5	9.0	8.7	9.0	8.9
S6	9.2	8.9	8.7	8.9
S7	6.8	6.9	6.5	6.7
S8	9.3	9.1	8.9	9.1
S9	8.2	7.8	7.8	7.9
S10	7.2	7.8	7.7	7.6

The results obtained show that moisture tends to be slightly higher at the end of the ageing period than before bottling, when it was on average 5.5 %. This behaviour was expected due to the prolonged contact period of the cork with the wine and the humidity of the cellar where the bottles are stored.

On one hand, low levels of humidity could cause the material to turn more brittle and disintegrate more easily upon removal, while on the other, high levels of humidity could lead to the flourishing of bacteria or of microbial activity. However, given the negligible difference between the average for the compliant samples, (8.1 ± 0.7) %, and the average for the non-compliant ones, (7.7 ± 1.1) %, the data does not disclose any evident pattern that could correlate the level of humidity with the compliance or non-compliance of the samples.

4.2 INTERNAL PROFILE OF THE BOTTLES

The internal profile of the bottles B1 to B12 were analysed. These bottles were obtained using five moulds (# 2, 4, 5, 7 and 8), that were made to be similar and present a bottle's normal construction, and to have the nozzle diameter be the smallest diameter, ensuring that the stopper is never subjected to compression levels higher than the ones that assisted its insertion into the bottle. The measurements done to the internal profiles in 2020 are congruent with the ones performed in 2005. The fact that the bottles obtained from the same mould (mould #5) integrated different bottle-stopper duos with stoppers coming from both groups (a compliant stopper: bottle #1; a non-compliant stopper: bottle #3; and a stopper that crumbled completely: bottle #12), allows us to establish that there is no link between the internal profile of the bottle and the type of mould

it is made from with the deterioration of the stopper (see Internal profile of the bottlesAPPENDIX A).

4.3 MORPHOLOGICAL ANALYSIS

Due to the observed crumbling of the non-compliant stoppers, it was not possible to examine all three sections of these stoppers. In such cases the cuts were then performed immediately above the fracturing surface.

The differences arisen in brightness are due to the uneven levelling of the samples, despite the effort to cut them to the same height. Moreover, some dragging of the material was also evidenced in some of the images.

The studied sections are cross sections, as can be seen from the rectangular shape of the cells, packed base-to-base in columns aligned with the tree's radial direction. The top refers to the part facing outwards and the bottom to the part facing the wine.

The structure observed on the BwST (Figure 9) was that of the typical cellular structure of fresh cork. It is possible to see the cellular arrangement as described in subsection 2.1.4. The minuscule alveoli are compactly arranged, and their dimensions are so minute that the number of cells can vary significantly from cork to cork.

The corrugation effect on the lateral faces of each cell, a direct consequence of the compression suffered during cork's growth, is rather clear to observation. This phenomenon is highly irregular, ranging from no corrugated cells to heavily corrugated ones.

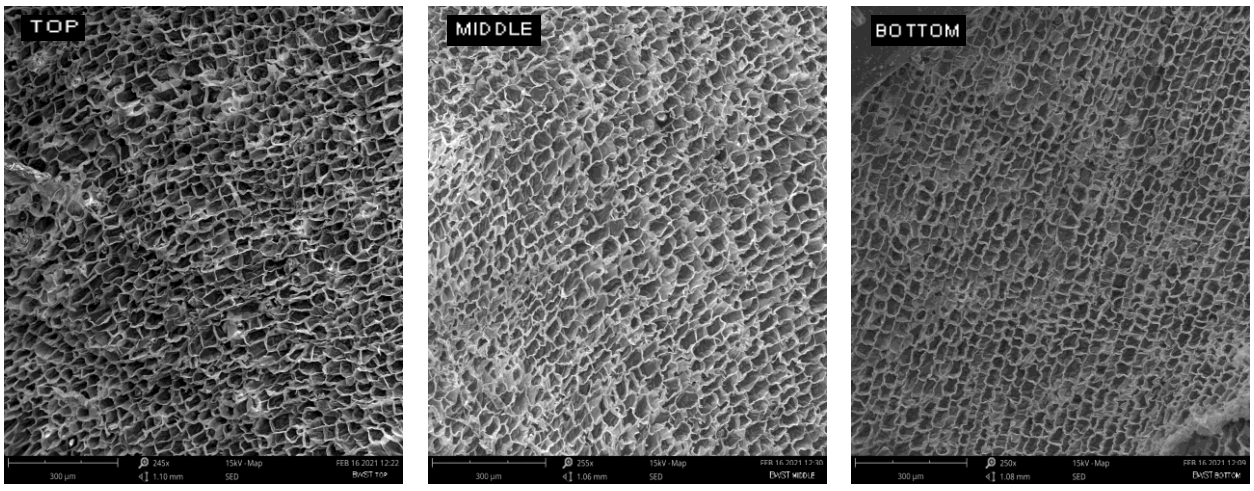


Figure 9 – SEM images of sample BwST.

From S1 to S10, all the samples reveal the typical cellular structure of cork when under compression, due to the previous insertion of the stoppers into the bottles, which translates in a more shrunk appearance when in comparison to the BwST. There are different levels of observable corrugation of the cell walls among the samples, which is the result of the cellular

materials' variable responses to compression, making their ensuing corrugation ununiform and occurring in bands.

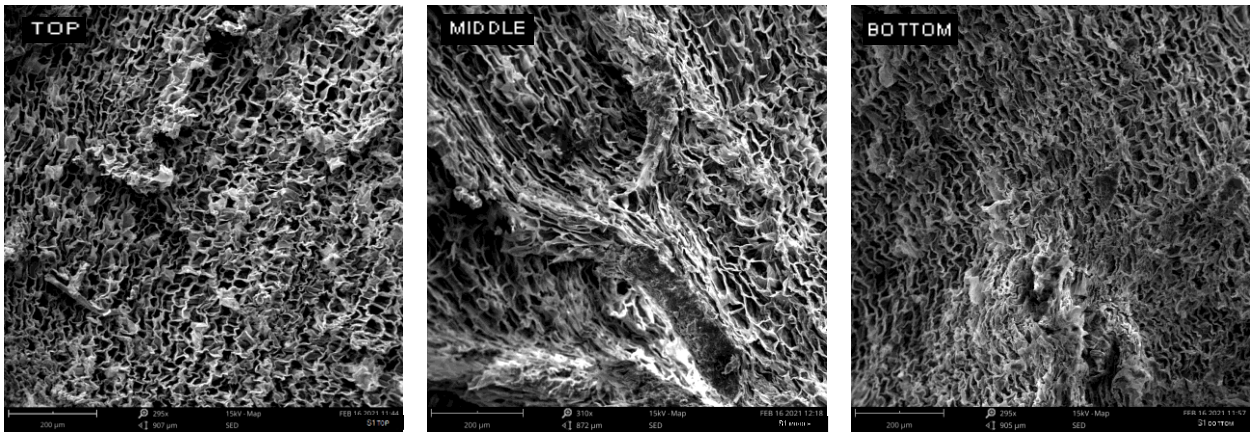


Figure 10 - SEM images of sample S1 at the top, middle and bottom.

The samples S1, S6 and S10, of which both the top and bottom were observed, presented a noticeably different pattern of corrugation. In fact, the top appears to be less corrugated than the bottom. This can be explained by the bottom's higher moisture content, on account of its direct contact with the wine, when compared to the stopper's top that remains in equilibrium with the external environment. It is known that the cork's response to compression varies according to water content and, in fact, a damp cork will offer less mechanical resistance when facing compression, such that its subjection to the same compression force (in this case determined by the bottleneck's width) will result in a greater corrugation of its cells than of those of dry or less damp cork. [28]

When inside the bottleneck, the compression upon the stopper is exercised in all directions of the transversal plane. Accordingly, the corrugation of the cell walls can be of many types: along the cells disposed tangentially, the corrugation procures their narrowing.

The analysis of the top section of the ten stoppers revealed no differences in terms of their microstructure (see APPENDIX B). Also, observing the images taken from samples S2 and S4 (Figure 11 and Figure 12), respectively the ones with highest extraction force and highest density, there seems to be no difference between them and the other bottled stoppers.

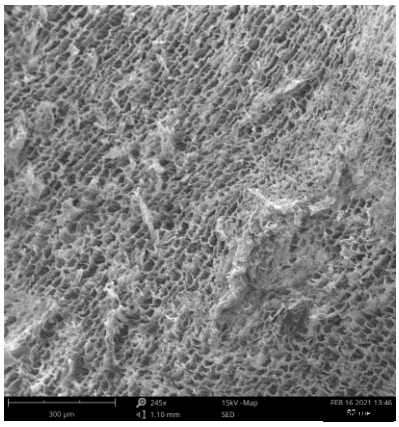


Figure 11 - SEM image of sample S2 at the top.

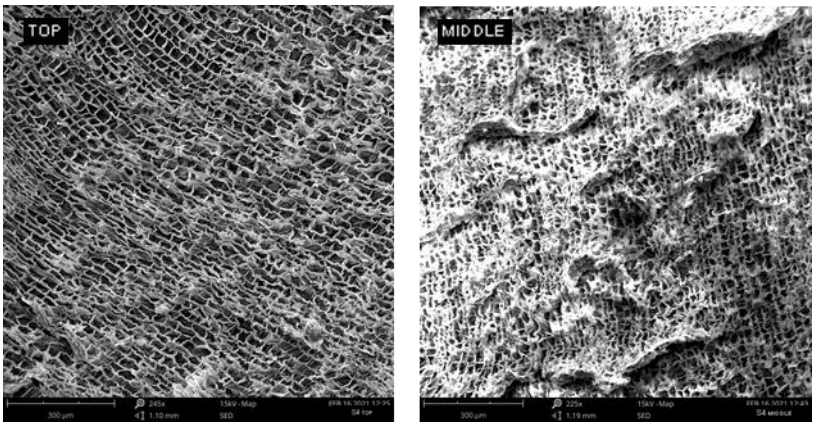


Figure 12 - SEM images of sample S4 at the top and middle.

Through the EDS analysis, the elements carbon, oxygen and gold were identified in similar values in all samples. The first two, along with hydrogen and nitrogen, are present in the molecules that make up cork, even though these last two cannot be identified through this test. The gold detected was due to the coating.

4.4 CHEMICAL ANALYSIS

The spectra of the BwoST1 makes it possible to identify the peaks from the cork material, considering the spectra of the BwoST1 similar to the one of untreated cork.

The extensive overlap of bands in the FTIR spectrum of cork, in Figure 13, reflects the complex nature of the material. At 3356 cm^{-1}, the broad O-H stretching band is from water, the carbohydrate hydroxyls (cellulose and hemicellulose), and from the suberin and lignin; the two sharp peaks at 2920 and 2851 cm^{-1} retrace to all of the cork's components (suberin, lignin, polysaccharides, and the extractives) and correspond to an C-H aliphatic stretch. [29], [30]

The strong peak at 1736 cm^{-1}, particular of the C=O stretching in ester groups, arises primarily from suberin, and the interval of peaks from 1635 to 1500 cm^{-1} matches the aromatic

region: 1633, 1602 and 1510 cm^{-1} correspond to the C=C stretching and accommodate signals from suberin, lignin and the extractives. The peaks at 1463 and 1371 cm^{-1} respectively refer to the C-H antisymmetric and symmetric deformation, with contributions from all of the components. [29], [30]

When it comes to the fingerprint region (1300 to 900 cm^{-1}), suberin ester groups support the transmittances at 1235 and 1159 cm^{-1} on account of its C=O stretching. The contribution of lignin methoxy groups, and of cellulose and hemicellulose is included in this last band, as these components absorb strongly in this area. Finally, the bands at 1091 and 1029 cm^{-1} are related to the C-H and C=O deformation and are attributed to lignin and polysaccharides. [29], [30]

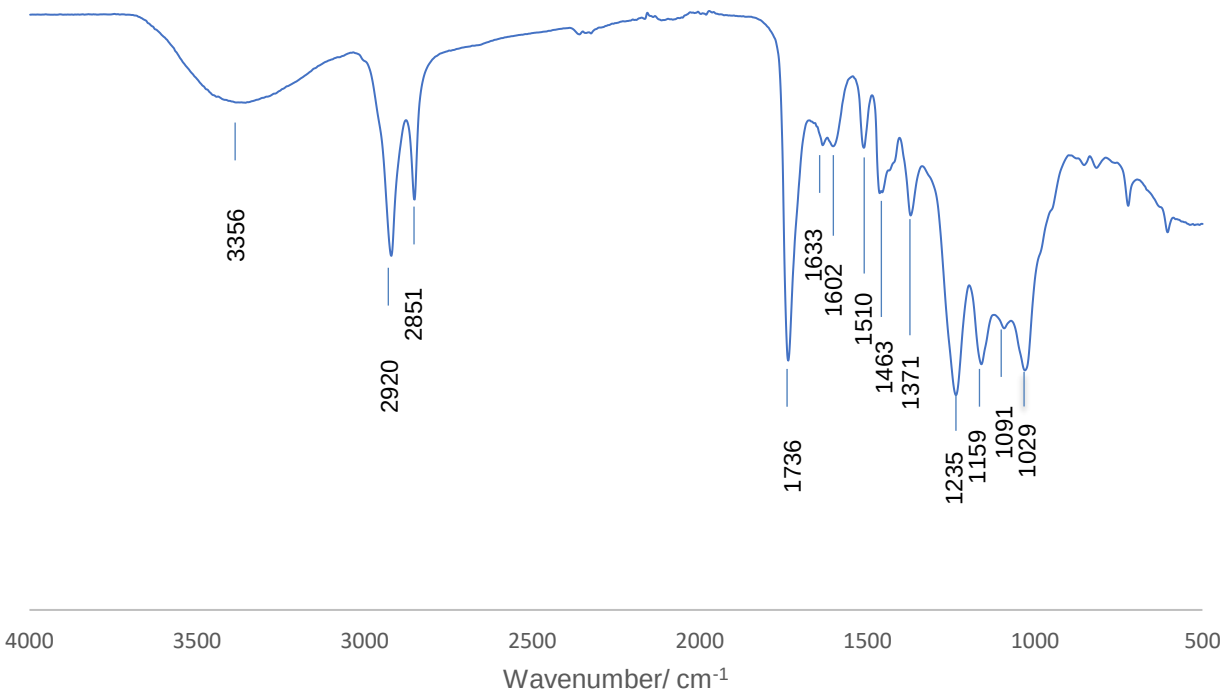


Figure 13 – FTIR spectrum of BwoST1.

The FTIR spectra retrieved from the BwST2 and the BwoST1 are displayed below (Figure 14). There, the peaks pertaining to both the cork and the surface treatment can be identified if one follows the rationale establishing that the much more intense or, for that matter, at all existing peaks of the BwST2, when compared to those of the BwoST1, should allow us to identify the former as the surface treatment.

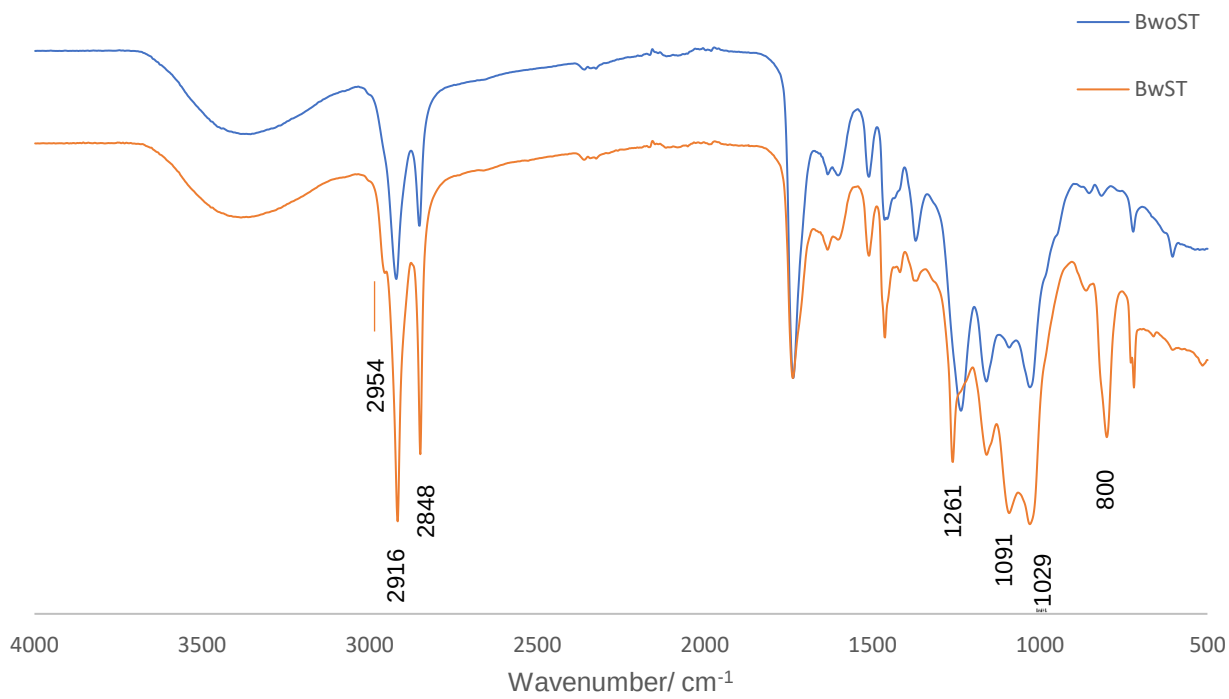


Figure 14 - FTIR spectra of BwoST1 and BwST2.

By comparison, the peaks between 3000 and 2800 $cm^{-1}$and between 1120 and 740 cm^{-1} are from the surface treatment. The bands seen in the first interval are less specific, corresponding to C-H bonds. The 2954 cm^{-1} shoulder is due to the CH_3 attachment to O, and is, therefore, exclusive to silicones as the only methyl group. It also occurs as a terminal CH_3 group in paraffins, although as a minor feature. The 2916 and 2848 cm^{-1} bands are due to the stretching of the CH_2 functional group in aliphatic compounds. These groups prevail in paraffins and are non-existent in silicones. As they are also present in the cork material, there may have been some overlap between the CH_2 groups from paraffin and the underlying cork. The peaks from the second interval are specific to silicone. The 1091 and 1029 cm^{-1} bands are the result of the Si-O-Si bond's symmetric stretching**,** whereas the band from 800 cm^{-1} refers to the rocking of the Si-CH_3 bond.

The literature on the subject suggests one should expect a particular spectrum from FTIR performed on paraffin and silicone, as can be seen on Table 6. [31]

Table 6. Assignments of selected bands from the paraffin and silicone FTIR spectra.

Wavenumber (cm^{-1})	Assignment
2963	C-H Stretch CH_3 Antisymmetric
2916	C-H Stretch CH_2 Antisymmetric
2850	C-H Stretch CH_2 Symmetric
1258	Si$(CH_3)_n$O Stretch Symmetric
1079	Si-O-Si Stretch Symmetric
1010	Si-O Stretch
787	Si-C Bonding

The peak concerning the Si-CH_3 bond is near to the wavenumber of the C=O stretching of the cork material. For this reason, this peak was not considered dissonant when compared to the BwoST1.

For the extracted corks stoppers, S1 to S10, FTIR was performed on both their surface and interior, following the same logic mentioned above. This being said, the rise of spectra similar to the BwoST1 was expected when examining their interior, as was the emergence of spectra akin to the BwST2 after the analysis of their surface.

Regarding the ten analysed cork stoppers, their interior spectra (Figure 15) are fairly identical between them, not showing any staggering differences. Moreover, the arisen peaks present are the same as the ones seen on the BwoST1 spectrum for all ten samples. The stronger peaks at 2919 and 2850 $cm^{-1}$of the sample S6 might be due to the permeation of paraffin into the pores of cork. This occurrence might be more notorious for this sample but happens in all cork stoppers. The current analysis, with its disclosing of a great similarity between the fresh cork and the interior of used cork, does not show any clear evidence of a relationship between the composition of their interior and the crumbling of the stoppers.

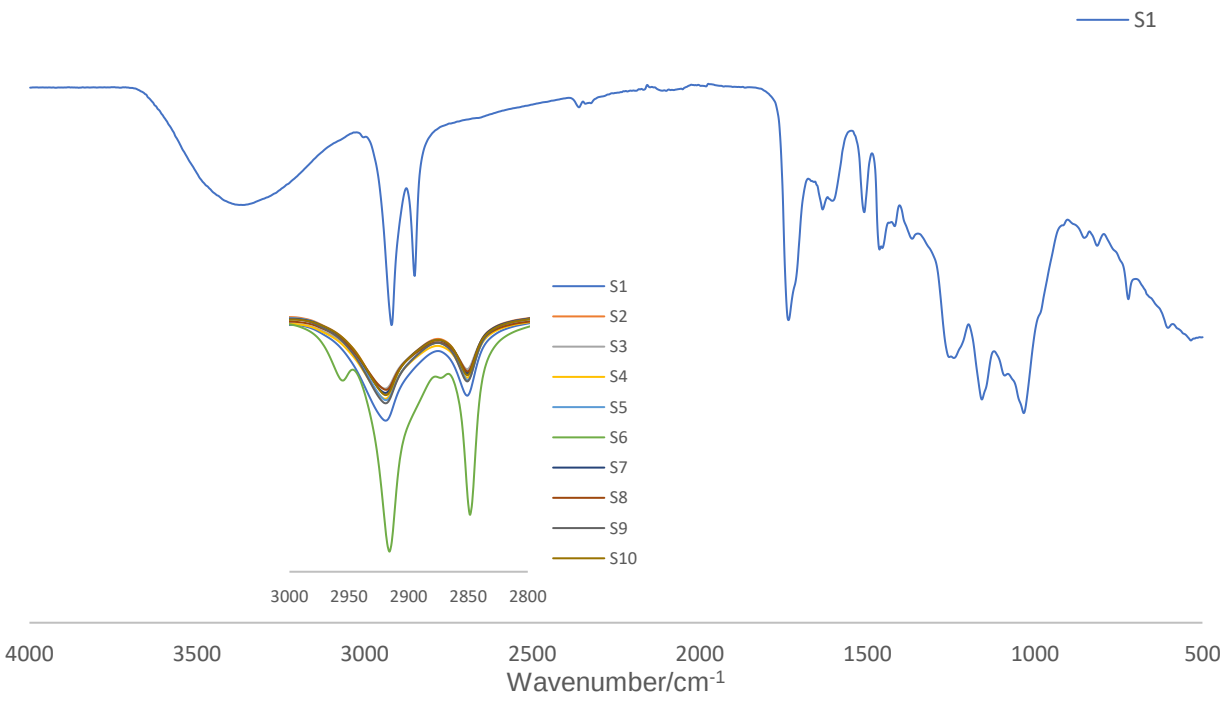


Figure 15 –FTIR spectrum of the interior of sample S1 with a detail of the peaks between 3000 and 2800 cm^{-1} for all samples.

When it comes to their lateral surface spectra (Figure 16), two conclusions can be drawn. First off, they lack the characteristic peaks of silicone; secondly, they are noticeably alike with the exception of the peak between 1050 and 1000 cm^{-1}.

In fact, S2, S3, S4, S5, S7, S8 and S9 display a more intense peak at around 1020 cm^{-1} than the one displayed by S1, S6 and S10. Given the region where this peak appears, this difference could be attributed to the irregular application of silicone, since its spectrum has a peak at that wavenumber, as mentioned above. Nevertheless, there is no peak around 1090 nor 800 cm^{-1}, making these stoppers silicone-free and their surface treatment consisting solely of paraffin. Under such conditions and given the absence of any lubricant agents (such as silicone compounds), it is clear that the cork stoppers under study were subjected to a particularly high frictional force regime, both during their insertion into the bottles and at the moment of their mechanical extraction. To verify this, it suffices to pay attention to the extraction force values shown on the Table 3 which are superior than the limit established on *ISO 16420:2013,* since this is for stoppers with surface treatment containing silicone.

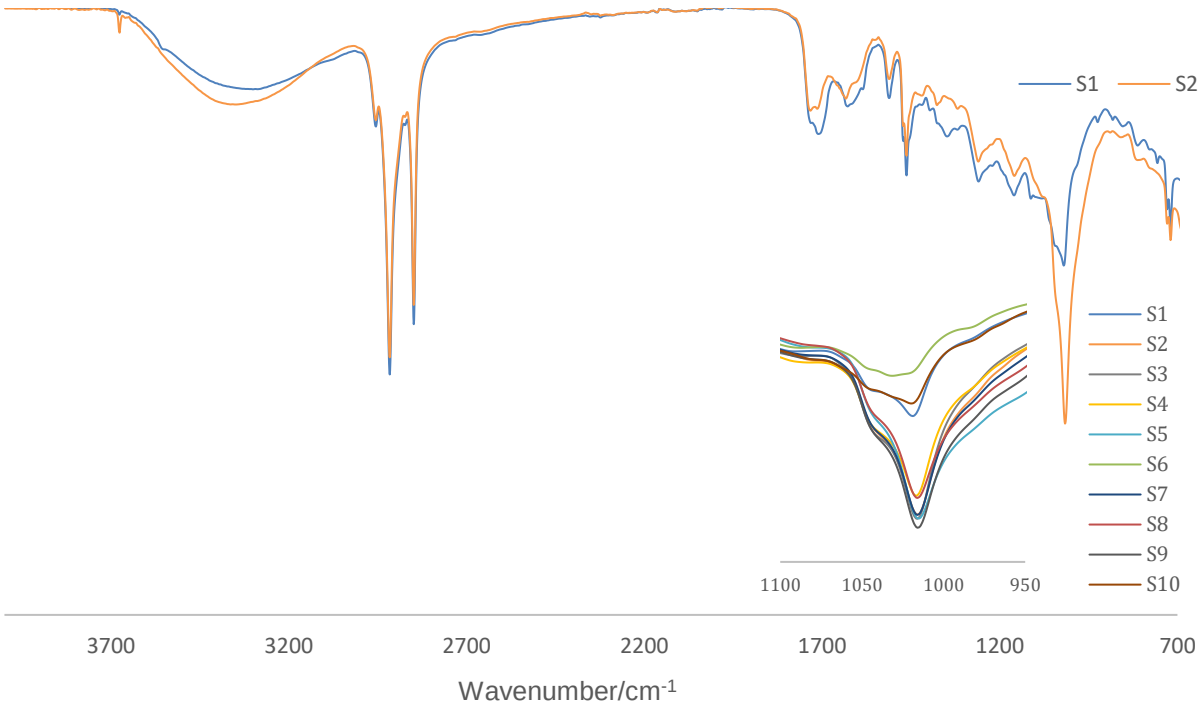


Figure 16 – FTIR spectra of samples S1 and S2 of the lateral surface and detail of the peaks between 1050 and 1000 cm^{-1} for all samples.

One possible explication for this disparity is the adsorption of SO_2 by the flanks off the cork stoppers since the latter are transported in bags containing SO_2. The fact that this compound's spectrum shows a peak around that wavenumber (between 1060 and 1045 cm^{-1} [32]) seems to strongly corroborate this assumption. Additionally, the absence of this phenomenon in the spectra of the interior of the cork stoppers further suggests the validity of this hypothesis.

To loosely infer on the homogeneity of the surface treatment between stoppers, the surface treatment ratio was calculated for all ten stoppers. The peak at around 1740 cm^{-1} was considered to be the most representative of cork since it has contributions from all of the cork's components and is fairly isolated. The bands between 2990 and 2800 cm^{-1} present contributions from cork and paraffin.

Table 7. Surface treatment ratio.

Cork stopper	Surface treatment ratio
S1	2.55
S2	2.46
S3	1.97
S4	1.71
S5	2.42
S6	1.13
S7	1.80
S8	2.70
S9	1.92
S10	1.59

As can be seen, the variability is immense and there is also no pattern differentiating the compliant stoppers from the non-compliant ones.

This variability in results is an indicator of the non-uniformity of the application of the surface treatment between stoppers. Nonetheless, it should be noted that this process is not always to be held as generally precise, due to the variability and complexity of the molecules that compose cork. The obtained results are thus sheerly indicative and a more precise technique should be resorted to in order to properly study the surface treatment.

All six samples BwST and BwoST were analysed, and they retrieved very similar results, therefore only the most representative one is analysed from each group (see APPENDIX C). The same rationale was used for the groups of compliant and non-compliant samples (see APPENDIX C).

4.5 MECHANICAL ANALYSIS

The tensile DMA thermograms obtained for each stopper are presented below, displaying *E*' and *tan (δ)* as a function of temperature.

For all samples (S11 and S12; S13 and S14), the *E'* decreases with increasing temperature, as can be seen in Figure 17, due to the softening of the material, although at different rates, until reaching a *plateau*. This ultimate decrease of *E'* is connected to the occurrence of different relaxational processes. The glass transition temperature was determined by the onset given by the *E*' curve, when the modulus presents the highest decrease. From analysing Figure 17, it is correct to say the compliant ones have a lower glass transition temperature than the non-compliant ones.

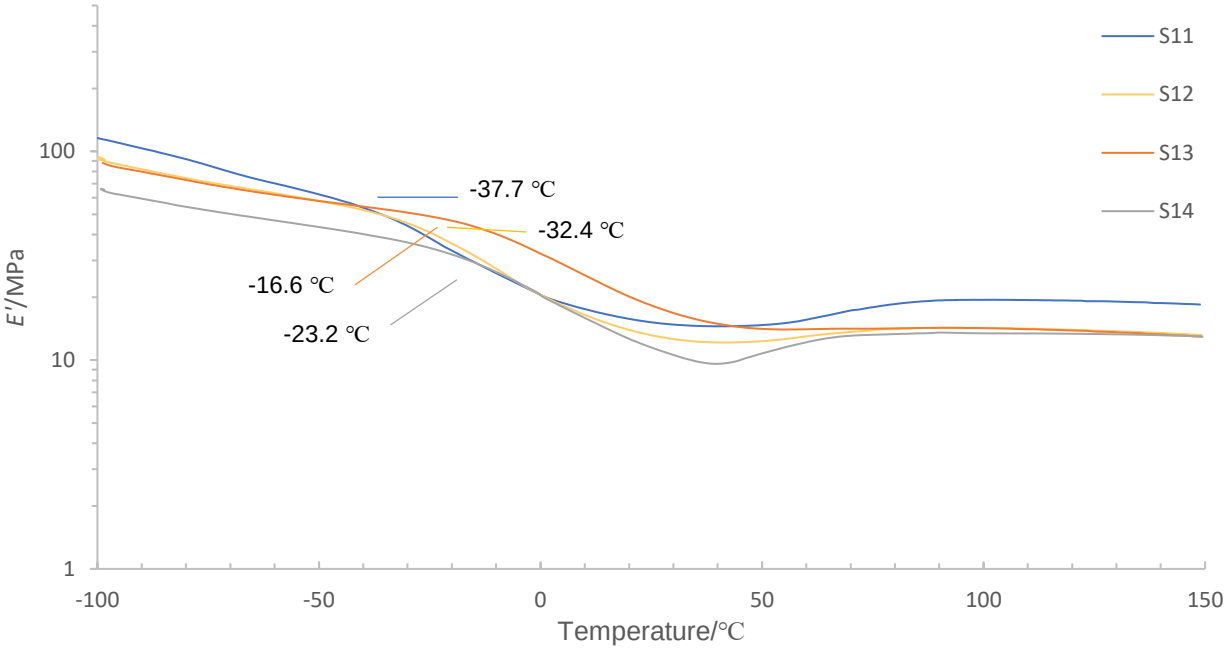


Figure 17 - Storage modulus of samples S11 to S14 against the temperature and respective glass transition temperatures.

The thermograms yielded by either compliant and non-compliant stoppers were extremely akin to one another and disclosed the stoppers' same comprehensive behaviour.

As can be seen on Figure 18 and Figure 19, both samples (S12 and S14) (see APPENDIX D for remaining thermograms) present a transition between - 25 and 20 ℃. This can be corroborated by the tan *(δ)* plot, where a broad peak appears at this interval for the two stoppers. The melting of suberin can be the reason behind this large transition and consequent loss of elasticity. At around - 70 ℃, another transition can be observed, one resulting from the localized rotation of polar groups present on the cell walls of cork. Another peak can be seen at around 40 ℃, possibly due to the melting of the wax's components. A slight increase in the modulus observed above 50 ℃ is possibly related to some water loss, contributing to the hardening of the material. For higher temperatures, around 120 ℃, there is a decrease in *E'* and an increase in tan *(δ)* that can be explained by the thermal transition of lignin, although the analysis is in the temperature limit.

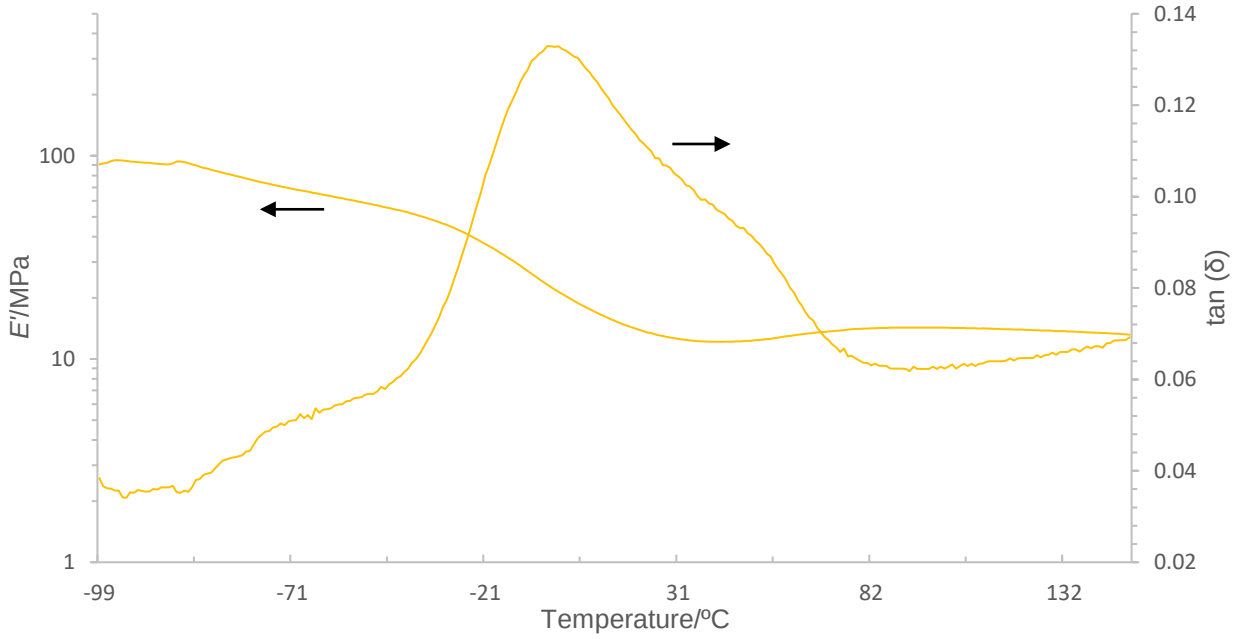


Figure 18 - Tensile DMA thermograms of sample S12.

There is no way to distinguish the compliant stoppers from the non-compliant ones solely based on their mechanical properties, as no major difference between the two groups was retrieved by this analysis.

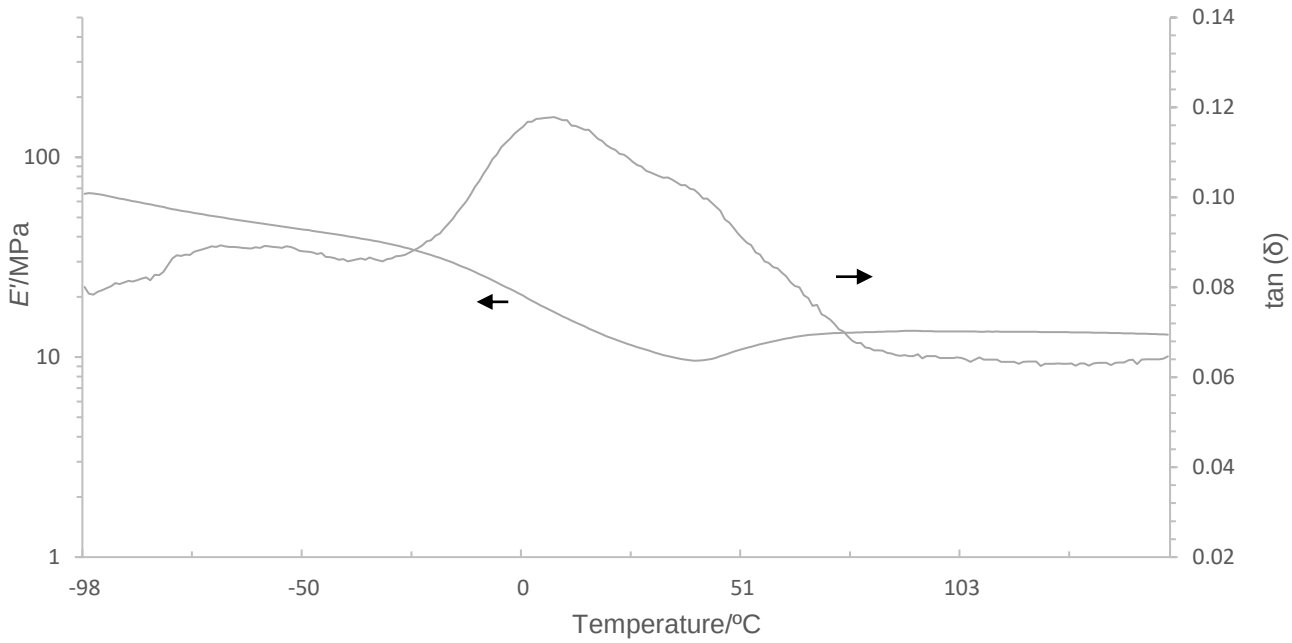


Figure 19 – Tensile DMA thermograms of sample S14.

Considering the results indicated by the literature regarding the characteristics of fresh cork [33], a comparison to the ones obtained in this study bespeaks a loss of mechanical properties

that renders used cork stoppers less elastic. Also, the glass transition temperatures for the non-compliant samples are more similar to those of the fresh cork than to those of the compliant ones.

The ageing of the cork stopper inside the bottle seems to affect the mechanical behaviour of the cork, not only in its surface, more often subjected to stronger forces, but also in the centre of the cork stopper, from where the samples for DMA were collected. To better understand the ageing process and its influence on cork's properties, some cork stoppers from the batch of those used in bottling should be kept so that future testing can be run on them after a period of 5, 10 or 15 years.

4.6 COMPRESSIBILITY TEST

According to the results obtained in Figure 20, the BUb type required a much higher force (320 N) to achieve the same deformation. The compliant stoppers demanded the application of a mean force of 216.6 N, whereas the non-compliant only needed a force of 187.5 N for their 30 % deformation to be attained. This staggering difference in the force applied indicates a loss of mechanical properties, which allowed a much easier compression of the compliant and non-compliant stoppers.

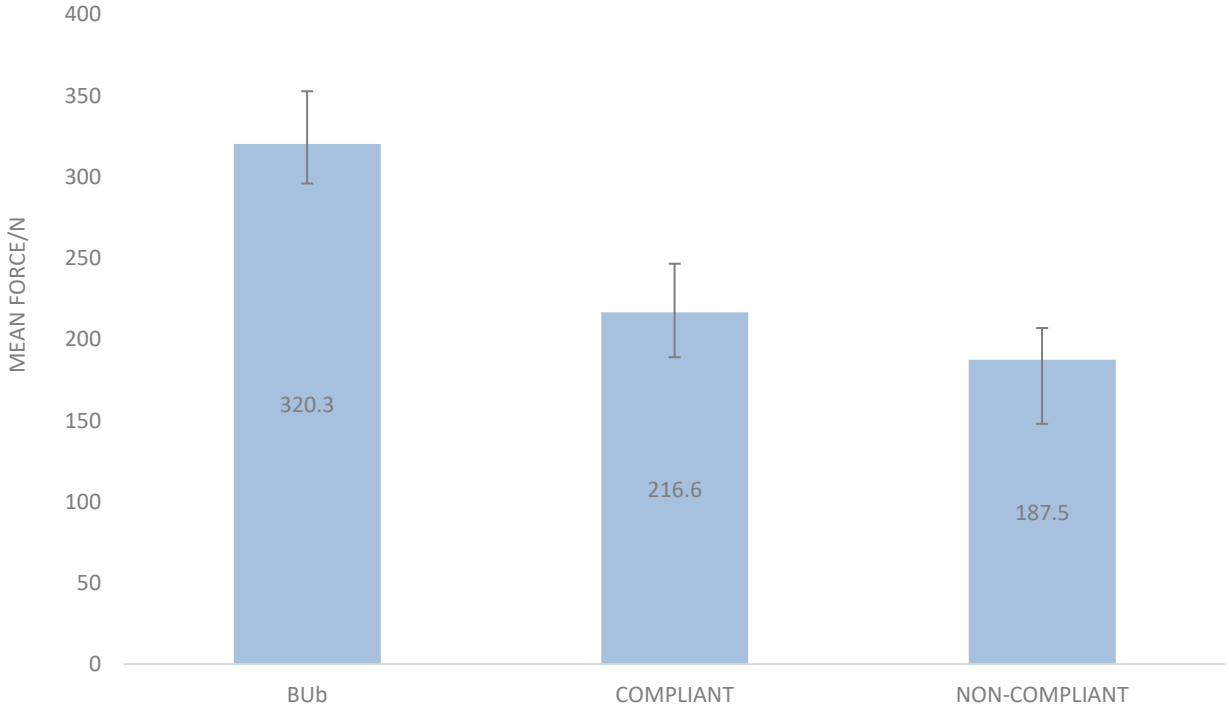


Figure 20 - Mean force for the different groups of cork stoppers.

From these stoppers, the compliant type proved to have the highest mean recovery rate, having registered a 97.2 % recovery, followed by the non-compliant, with a score of 96.8 % and then the BUb one, registering 95.7%. Accordingly, the diametrical recovery is higher in the used

types than in the unbottled one. Nevertheless, this difference in results is not significant, since the associated error of the calculations is superior to the difference itself, as can be seen in Figure 21.

Regarding the stoppers' behaviour after compression, it is important to note that the halt in the application of the compression force resulted in the quick restoring of the used stoppers' initial shape, an occurrence that was fairly noticeable to the naked eye, whilst the recovery of the unbottled stoppers was comprehensively more subtle.

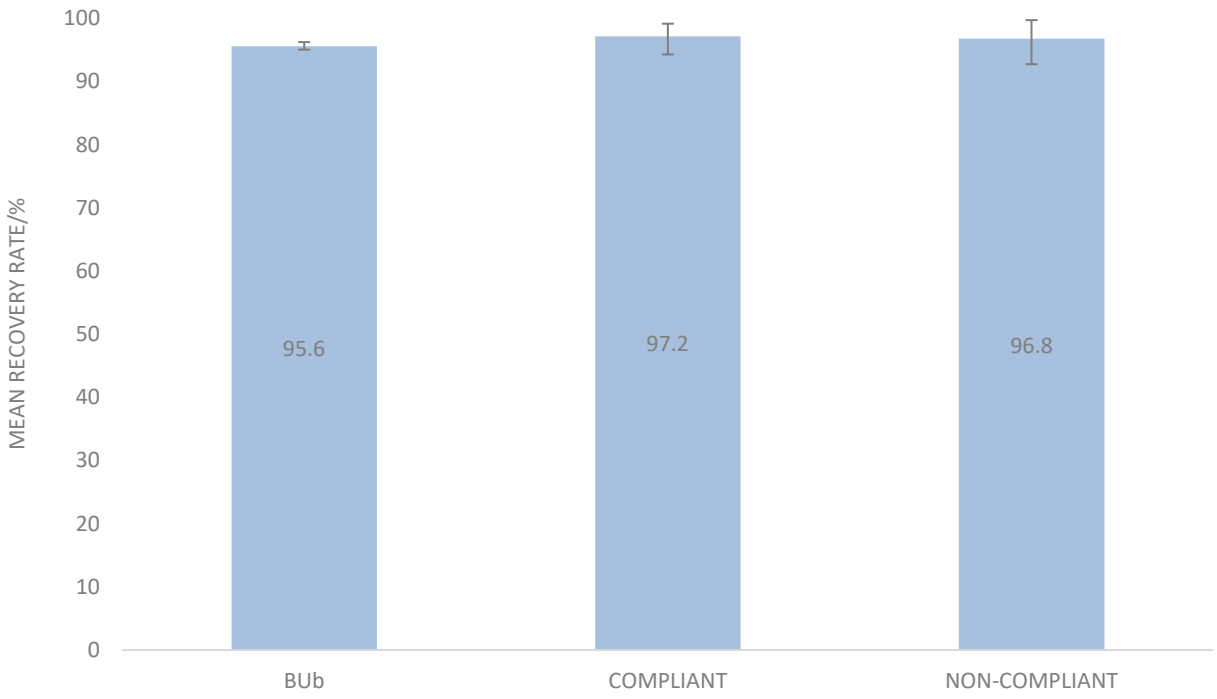


Figure 21 - Mean recovery rate for the different groups of cork stoppers.

5 CONCLUSION

To understand the reason for the crumbling of the stoppers, several analyses were carried out. These were performed to assess physical, mechanical, chemical and morphological differences between blank samples and bottled samples, either compliant or non-compliant.

After the measurement of the extraction forces, the mean extraction force for the compliant stoppers was found lower than for non-compliant ones. The difference between them was not considered significant and hinders the drawing of a concrete conclusion. When comparing the values measured in 2020 with the ones from 2005, the values do not vary enough to be able to observe a pattern.

The values obtained in the evaluation of the stoppers' density were higher for the used stoppers than for the unbottled ones, as it was expected. These samples were under great pressure in the bottleneck, leading to a significant compression of the cork cells that entailed the diminishing of their size and the ensuing decrease in the stoppers' volume. In some extreme cases, if the bottling pressure is well above the standard values, the possible following densification of the cork can be as significant as to cause the stopper to become brittle and to crumble as removed, as observed in the non-compliant samples. However, none of these differences in density seem to play any part in the stoppers' compliance.

The results of the gauging of the moisture content show that the humidity tends to higher after the ageing period. This was expected given the long period of time in which the cork is in contact with the wine, and the humidity of the cellar where the bottles are stored. On one hand, low levels of humidity could cause the material to turn more brittle and disintegrate more easily upon removal, while on the other, high levels could lead to the appearance of bacteria or microbial activity. However, the data shows no evident pattern that could correlate the level of humidity to the degree of compliance of these stoppers and these values are in the interval considered for moisture content before insertion into the bottle.

The morphological analysis, using SEM, showed that there are more signs of compression in the cells of the used stoppers, both compliant and non, than in the unused stoppers, as expected due to the compression exercised by the bottle's neck. Also, a different degree of corrugation is noticeable on the bottom of the stopper, that may be caused by the higher humidity procured by direct contact with the wine. This contact deprives cork of its mechanical resistance.

The chemical analysis, carried out through FTIR tests, showed that the analysed samples present characteristic FTIR peaks of cork and that the surface treatment, consisting only of paraffin, is not uniform from one stopper to another. Under such conditions and given the absence of any lubricant agents (such as silicone compounds), it is clear that the cork stoppers under study

were subjected to a particularly high frictional force regime, both during their insertion into the bottles and at the moment of their mechanical extraction. The results also show that the surface samples are noticeably alike with the exception of the peak between 1050 and 1000 cm^{-1}, that could be attributed to the irregular surface treatment and to the adsorption of SO_2 by the flanks of the cork stoppers since these are transported in bags containing this compound.

As for the mechanical analysis, the thermograms yielded by either compliant or non-compliant stoppers disclosed the stoppers same comprehensive behaviour. Throughout the temperature range, there is a loss of elasticity that occurs in account of different relaxational processes. The comparison between the results obtained in this study and the results for fresh cork as indicated in the literature bespeaks a loss of mechanical properties that renders used cork stoppers less elastic. This is confirmed by the compressibility test, where a higher force is needed to obtain the same deformation in unbottled than in used cork.

The achieved results were not conclusive, since none of the performed tests revealed a pattern from which one could consistently infer on the existence of a link between certain inadequacies presented by the stoppers and their compliance, thus rendering impossible the drawing of a solution for the proposed problem.

Based on the work developed and results obtained, further suggestions can be made. Firstly, the method used for evaluating the chemical composition of the stopper (FTIR) was found insufficient and imprecise for such a complex material. Therefore, a more accurate method should be used in the future to quantify more precisely the composition of cork, enabling the detection of possible differences. Nonetheless, to achieve such goal it is necessary to separate the components of cork, which is a rather complex task.

Another path that can be pursued is the study of the ageing of cork given that time is a very relevant variable when it comes to stoppers used in vintage Port wine. Additional batches of stoppers from different years could be submitted to the same analyses and a statistical study performed to infer on the stoppers quality evolution with time.

6 ASSESSMENT OF THE WORK DONE

6.1 OBJECTIVES ACHIEVED

The main goal of this project was the identification of the parameters responsible for the rupture and crumbling of the stoppers in vintage Port wines. However, it was not possible to achieve it.

The results of the analyses performed to the non-compliant stoppers did not present enough differences when compared to the compliant ones to clearly identify the cause of the deterioration. Nevertheless, the main conclusion of this work is that the parameters that were analysed, being them morphological, physical, mechanical, and chemical properties of the stoppers, are not likely to be cause of the problem.

6.2 FINAL ASSESSMENT

This project provided an opportunity to have a real-world experience, enlightening the daily challenges of a non-stopping industry. For five months the development of a structured work that could provide the best answer possible to the proposed problem was my solely focus. It was a very rewarding experience but that also came with its challenges. The current pandemic situation created some unexpected setbacks which created some delays and required fast acclimation.

7 REFERENCES

[1] S. P. Silva, M. A. Sabino, E. M. Fernandas, V. M. Correlo, L. F. Boesel, and R. L. Reis, "Cork: Properties, capabilities and applications," *Int. Mater. Rev.*, vol. 50, no. 6, pp. 345–365, Dec. 2005.

[2] "Realcork – Statistics." [Online]. Available: https://www.apcor.pt/en/media-center/statistics/. [Accessed: 12-Jan-2021].

[3] "Industry Statistics | Cork Quality Council." [Online]. Available: https://www.corkqc.com/pages/industry-statistics. [Accessed: 12-Jan-2021].

[4] V. Constantino, M. Rocha, D. António, P. Oliveira, C. Co-Orientador, and F. J. C. Xavier De Carvalho, "DESENVOLVIMENTO DE PAVIMENTO FLUTUANTE COM AGLOMERADO DE CORTIÇA, DE DESEMPENHO ACÚSTICO OTIMIZADO Dissertação submetida para satisfação parcial dos requisitos do grau de MESTRE EM ENGENHARIA CIVIL-ESPECIALIZAÇÃO EM CONSTRUÇÕES."

[5] "About Oak Tree | Facts and Curiosities | Amorim Cork Composites | Facts and Curiosities > Why Cork > Amorim Cork Composites." [Online]. Available: https://amorimcorkcomposites.com/en/why-cork/facts-and-curiosities/about-cork-oak-tree/. [Accessed: 12-Jan-2021].

[6] H. Pereira, "The Rationale behind Cork Properties: A Review of Structure and Chemistry."

[7] V. Oliveira and H. Pereira, "Cork and Cork Stoppers: Quality and Performance."

[8] B. Prieur *et al.*, "Phosphorylation of lignin: characterization and investigation of the thermal decomposition," *RSC Adv.*, vol. 7, no. 27, pp. 16866–16877, 2017.

[9] L. Gil, "Cortiça," *Ciência e Eng. Mater. Construção*, pp. 663–715, 2012.

[10] "APONTAMENTOS DE TECNOLOGIA DOS PRODUTOS FLORESTAIS A CORTIÇA-SUAS CARACTERÍSTICAS E PROPRIEDADES MARIA EMÍLIA CALVÃO MOREIRA DA SILVA UTAD 2010."

[11] H. Pereira, "The thermochemical degradation of cork," *Wood Sci. Technol.*, vol. 26, no. 4, pp. 259–269, May 1992.

[12] "Wine Spectator's Top 100 List Reveals 89% Of World's Top Wines Have Cork Closures - 100% Cork | Produced by Nature. Preferred by Winemakers." [Online]. Available: http://100percentcork.org/wine-spectators-top-100-list-reveals-89-of-worlds-top-wines-have-cork-closures/. [Accessed: 04-Feb-2021].

[13] “How many stoppers are produced annually?, Myths and Facts, Why Cork - Corticeira Amorim, Cork Sector World Leader.” [Online]. Available: https://www.amorim.com/en/why-cork/myths-and-facts/How-many-stoppers-are-produced-annually/109/392/#collapse415. [Accessed: 04-Feb-2021].

[14] “• Cork stoppers exports Portugal 2006-2018 Statistic | Statista.” [Online]. Available: https://www.statista.com/statistics/445756/cork-stoppers-export-portugal/. [Accessed: 04-Feb-2021].

[15] “Realcork – Natural Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/cork/processing/industrial-path/natural-cork-stoppers/. [Accessed: 02-Feb-2021].

[16] “Realcork – Colmated Natural Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/colmated-natural-cork-stoppers/. [Accessed: 13-Feb-2021].

[17] “Realcork – Multi-Piece Natural Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/multi-piece-natural-cork-stoppers/. [Accessed: 13-Feb-2021].

[18] “Realcork – Agglomerated Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/agglomerated-cork-stoppers/. [Accessed: 13-Feb-2021].

[19] “Realcork – Technical Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/technical-cork-stoppers/. [Accessed: 13-Feb-2021].

[20] “Realcork – Champagne and Sparkling Wine Cork Stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/champagne-and-sparkling-wine-cork-stoppers/. [Accessed: 13-Feb-2021].

[21] “Realcork – Capsulated cork stoppers.” [Online]. Available: https://www.apcor.pt/en/products/cork-stoppers/capsulated-cork-stoppers/. [Accessed: 13-Feb-2021].

[22] “Realcork – Industrial Path.” [Online]. Available: https://www.apcor.pt/en/cork/processing/industrial-path/. [Accessed: 13-Feb-2021].

[23] “Matéria-Prima E Processo Produtivo - A Cortiça e o Vinho - Amorim Cork.” [Online]. Available: https://www.amorimcork.com/pt/a-cortica-e-o-vinho/materia-prima-e-processo-produtivo/. [Accessed: 02-Feb-2021].

[24] “ICSMP2014-EN.”

[25] “CULTURA, NATUREZA, FUTURO. MANUAL TÉCNICO ROLHAS.”

[26] “Realcork – Fight against TCA.” [Online]. Available: https://www.apcor.pt/en/fight-against-tca/#1439896006087-2-5. [Accessed: 07-Feb-2021].

[27] “Qualidade e I&D - A Cortiça e o Vinho - Amorim Cork.” [Online]. Available: https://www.amorimcork.com/pt/a-cortica-e-o-vinho/qualidade-e-i&d/. [Accessed: 07-Feb-2021].

[28] A. Lagorce-Tachon, T. Karbowiak, D. Champion, R. D. Gougeon, and J. P. Bellat, “Mechanical properties of cork: Effect of hydration,” *Mater. Des.*, vol. 82, pp. 148–154, Oct. 2015.

[29] C. Pascoal Neto *et al.*, “SOLID STATE Nuclear Magnetic Resonance Solid State Nuclear Magnetic Resonance 4 (1995) 143-151 13C Solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork.”

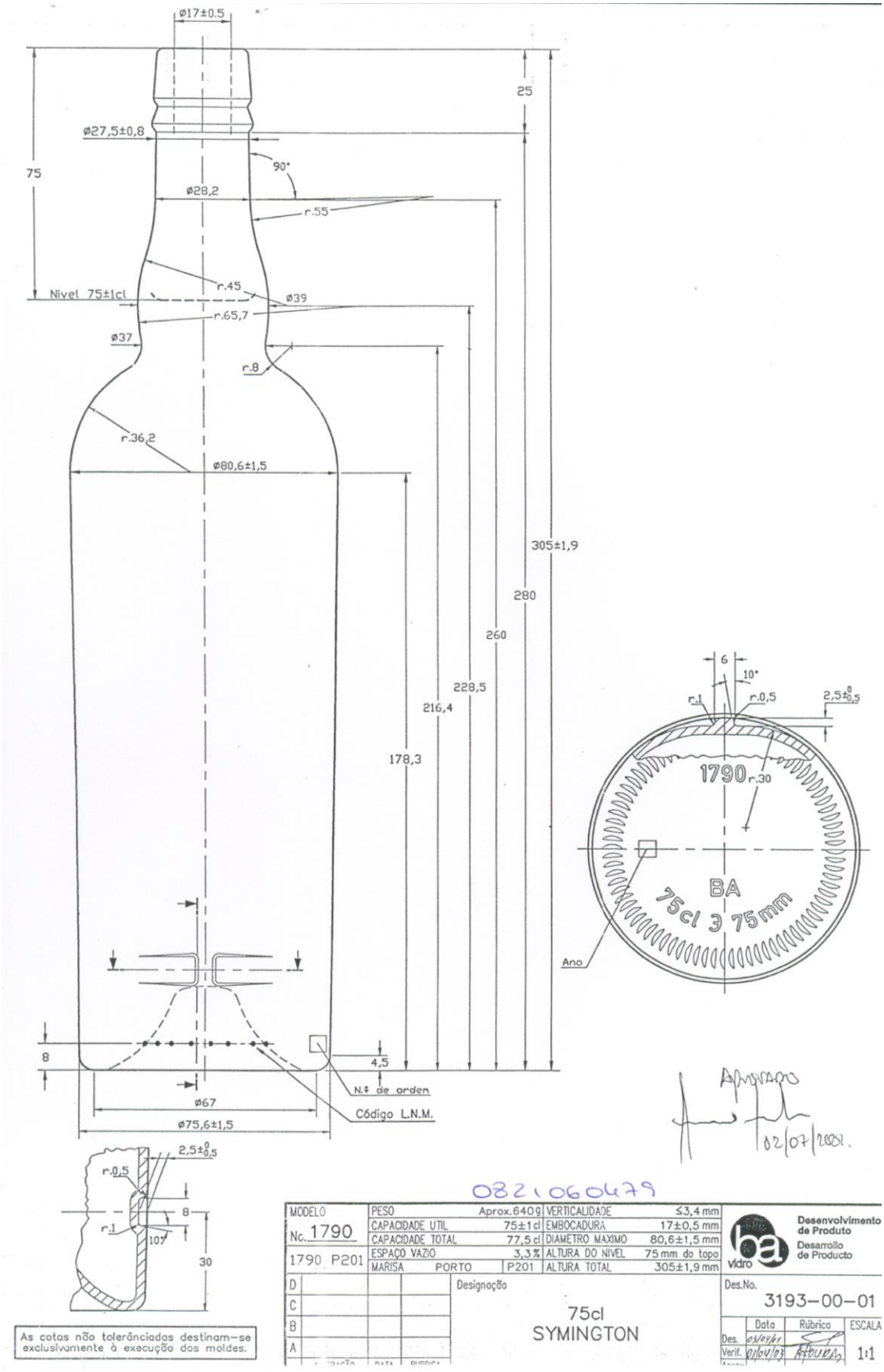
[30] A. Şen, A. V. Marques, J. Gominho, and H. Pereira, “Study of thermochemical treatments of cork in the 150-400°C range using colour analysis and FTIR spectroscopy,” *Ind. Crops Prod.*, vol. 38, no. 1, pp. 132–138, Jul. 2012.

[31] C. Ortega-Fernández, J. R. González-Adrados, M. C. García-Vallejo, R. Calvo-Haro, and M. J. Cáceres-Esteban, “Characterization of surface treatments of cork stoppers by FTIR-ATR,” *J. Agric. Food Chem.*, vol. 54, no. 14, pp. 4932–4936, Jul. 2006.

[32] “Sulfur dioxide.” [Online]. Available: https://webbook.nist.gov/cgi/cbook.cgi?ID=C7446095&Index=0&Type=IR-SPEC#IR-SPEC. [Accessed: 05-Mar-2021].

[33] D. Paiva and F. D. Magalhães, “Dynamic mechanical analysis and creep-recovery behavior of agglomerated cork,” *Eur. J. Wood Wood Prod.*, vol. 76, no. 1, pp. 133–141, Jan. 2018.

ANNEX A. DATASHEET OF THE BOTTLE



APPENDIX A. INTERNAL PROFILE OF THE BOTTLES

In this section are presented the measurements retrieved by the Perfilab equipment

Table 8. Internal profile of the bottles B1 to B12.

Valores Médios e de Ovalidade (mm)

	Garrafa # 1 *Molde 5*		Garrafa # 2 *Molde 8*		Garrafa # 3 *Molde 5*		Garrafa # 4 *Molde 4*		Garrafa # 5 *Molde 8*		Garrafa # 6 *Molde 4*		Garrafa # 7 *Molde 8*		Garrafa # 8 *Molde 7*	
Prof.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.
2,0	17,18	0,07	17,30	0,03	17,19	0,05	17,16	0,06	17,27	0,10	17,15	0,08	17,16	0,06	17,15	0,02
4,0	17,36	0,08	17,54	0,01	17,37	0,02	17,33	0,09	17,50	0,13	17,33	0,13	17,40	0,10	17,35	0,04
6,0	17,53	0,10	17,72	0,03	17,53	0,01	17,48	0,15	17,66	0,18	17,49	0,18	17,59	0,14	17,51	0,07
8,0	17,73	0,12	17,90	0,06	17,70	0,02	17,67	0,21	17,83	0,26	17,71	0,25	17,77	0,21	17,68	0,11
10,0	18,01	0,15	18,11	0,10	17,92	0,02	17,92	0,31	18,03	0,36	17,98	0,34	17,97	0,30	17,92	0,16
12,0	18,26	0,17	18,30	0,16	18,12	0,03	18,17	0,43	18,24	0,49	18,23	0,46	18,16	0,42	18,17	0,23
14,0	18,37	0,23	18,42	0,21	18,22	0,03	18,29	0,56	18,38	0,65	18,37	0,59	18,26	0,56	18,28	0,30
16,0	18,37	0,30	18,46	0,22	18,26	0,02	18,32	0,64	18,45	0,78	18,39	0,66	18,29	0,67	18,32	0,36
18,0	18,33	0,34	18,48	0,18	18,28	0,02	18,34	0,65	18,49	0,84	18,39	0,66	18,30	0,69	18,37	0,37
20,0	18,21	0,37	18,40	0,15	18,24	0,04	18,29	0,63	18,47	0,91	18,34	0,63	18,25	0,68	18,39	0,39
22,0	17,97	0,38	18,19	0,15	18,08	0,09	18,14	0,60	18,33	1,01	18,20	0,62	18,10	0,68	18,34	0,42
24,0	17,80	0,33	18,02	0,18	17,92	0,17	18,03	0,59	18,19	1,10	18,12	0,63	17,97	0,68	18,33	0,45
26,0	17,77	0,33	18,00	0,21	17,89	0,21	18,04	0,55	18,16	1,14	18,14	0,57	17,97	0,67	18,43	0,41
28,0	17,83	0,38	17,98	0,18	17,95	0,21	18,10	0,40	18,12	1,10	18,19	0,41	18,04	0,64	18,54	0,28
30,0	17,90	0,44	17,89	0,10	18,00	0,19	18,11	0,23	18,03	1,01	18,17	0,25	18,08	0,61	18,56	0,10
32,0	17,97	0,44	17,81	0,08	18,04	0,17	18,10	0,12	17,94	0,93	18,14	0,17	18,09	0,57	18,54	0,01
34,0	18,06	0,38	17,76	0,10	18,09	0,18	18,12	0,08	17,89	0,85	18,14	0,13	18,11	0,55	18,53	0,05
36,0	18,16	0,29	17,76	0,16	18,16	0,20	18,15	0,10	17,87	0,82	18,16	0,14	18,13	0,54	18,53	0,06
38,0	18,27	0,17	17,81	0,25	18,24	0,22	18,20	0,16	17,89	0,83	18,21	0,22	18,16	0,54	18,54	0,03
40,0	18,39	0,05	17,91	0,34	18,35	0,25	18,28	0,24	17,97	0,84	18,30	0,32	18,22	0,53	18,57	0,01
42,0	18,57	0,07	18,10	0,43	18,51	0,29	18,42	0,32	18,14	0,87	18,44	0,40	18,31	0,52	18,64	0,02
44,0	18,83	0,17	18,39	0,50	18,75	0,32	18,65	0,37	18,41	0,91	18,67	0,47	18,49	0,52	18,80	0,04
46,0	19,19	0,27	18,81	0,53	19,10	0,35	18,97	0,40	18,82	0,95	19,00	0,52	18,79	0,53	19,07	0,04
48,0	19,68	0,34	19,36	0,57	19,57	0,38	19,45	0,43	19,37	0,99	19,46	0,56	19,21	0,52	19,50	0,02
50,0	20,32	0,41	20,07	0,57	20,20	0,43	20,09	0,45	20,07	1,02	20,08	0,60	19,79	0,52	20,10	0,00

	Garrafa # 9 *Molde 8*		Garrafa # 10 *Molde 3*		Garrafa # 11 *Molde 2*		Garrafa # 12 *Molde 5*	
Prof.	Média	Oval.	Média	Oval.	Média	Oval.	Média	Oval.
2,0	17,18	0,08	17,19	0,10	17,16	0,01	17,19	0,03
4,0	17,41	0,12	17,42	0,14	17,40	0,02	17,36	0,05
6,0	17,59	0,18	17,61	0,17	17,58	0,00	17,51	0,05
8,0	17,77	0,25	17,79	0,25	17,77	0,02	17,68	0,08
10,0	17,97	0,34	18,00	0,34	18,02	0,04	17,91	0,09
12,0	18,16	0,46	18,19	0,48	18,28	0,08	18,11	0,14
14,0	18,25	0,59	18,28	0,62	18,42	0,12	18,22	0,18
16,0	18,27	0,70	18,31	0,74	18,46	0,16	18,27	0,23
18,0	18,29	0,72	18,34	0,77	18,49	0,20	18,29	0,26
20,0	18,25	0,71	18,30	0,76	18,46	0,22	18,26	0,25
22,0	18,09	0,68	18,15	0,73	18,33	0,17	18,11	0,21
24,0	17,97	0,67	18,02	0,68	18,20	0,10	17,96	0,16
26,0	17,98	0,64	18,02	0,61	18,22	0,04	17,95	0,13
28,0	18,09	0,58	18,08	0,55	18,34	0,07	18,02	0,14
30,0	18,16	0,50	18,10	0,51	18,40	0,13	18,09	0,17
32,0	18,19	0,42	18,10	0,48	18,41	0,15	18,14	0,13
34,0	18,22	0,38	18,12	0,48	18,40	0,12	18,21	0,09
36,0	18,25	0,36	18,15	0,49	18,40	0,09	18,29	0,02
38,0	18,29	0,35	18,19	0,53	18,41	0,06	18,38	0,06
40,0	18,34	0,37	18,25	0,56	18,44	0,02	18,50	0,13
42,0	18,44	0,39	18,37	0,60	18,52	0,01	18,68	0,21
44,0	18,62	0,40	18,58	0,63	18,68	0,06	18,93	0,27
46,0	18,93	0,41	18,91	0,69	18,96	0,10	19,28	0,34
48,0	19,37	0,42	19,37	0,72	19,38	0,14	19,77	0,39
50,0	19,97	0,43	19,99	0,76	19,93	0,18	20,41	0,45

APPENDIX B. SEM IMAGES

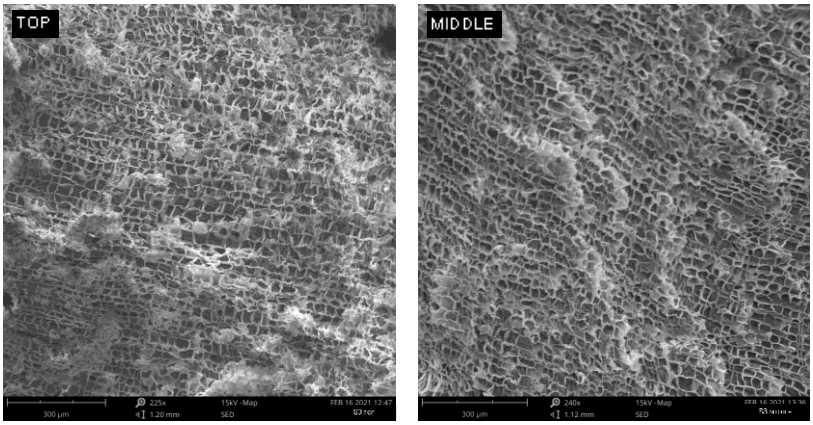


Figure 22 - SEM images of sample S3 at the top and middle.

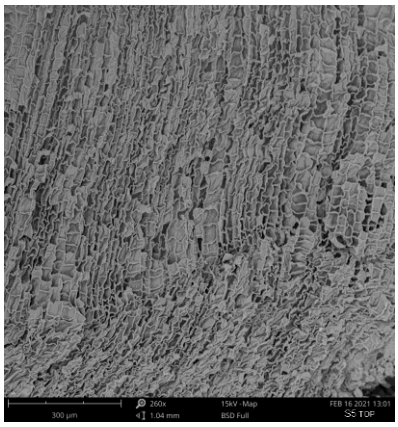


Figure 23 - SEM images of sample S5 at the top.

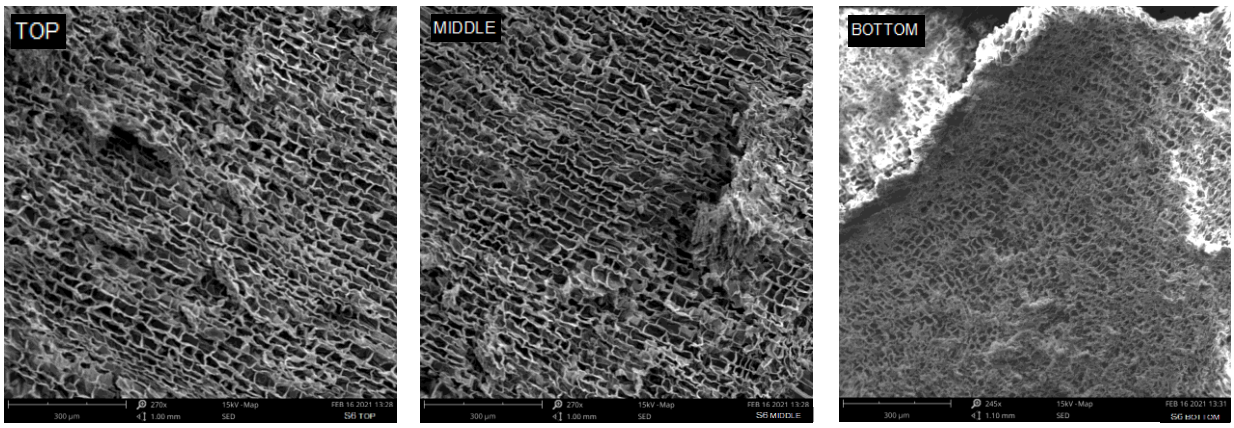


Figure 24 - SEM images of sample S6 at the top, middle and bottom.

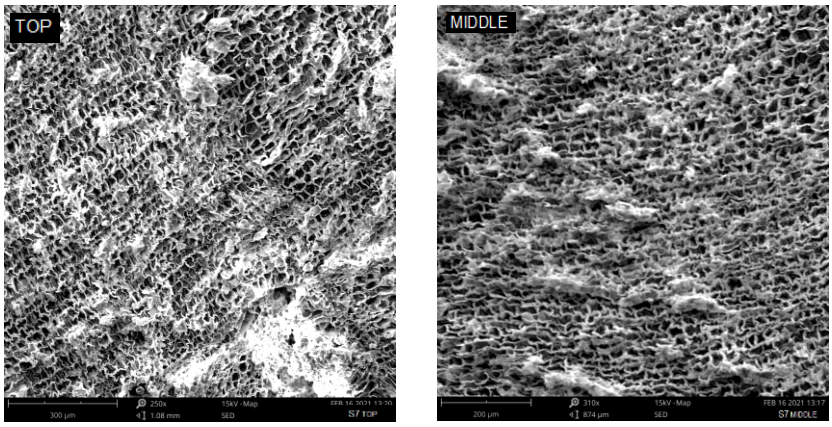


Figure 25 - SEM images of sample S7 at the top and middle.

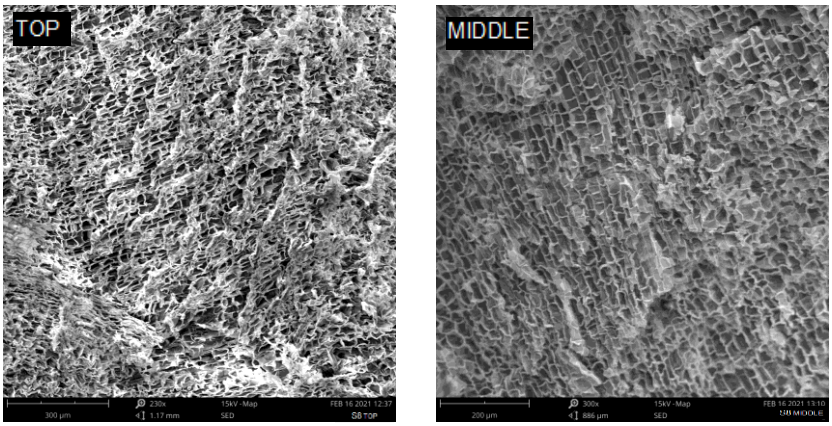


Figure 26 - SEM images of sample S8 at the top and middle.

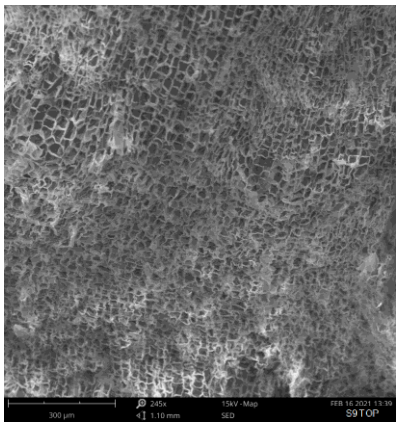


Figure 27 - SEM images of sample S9 at the top.

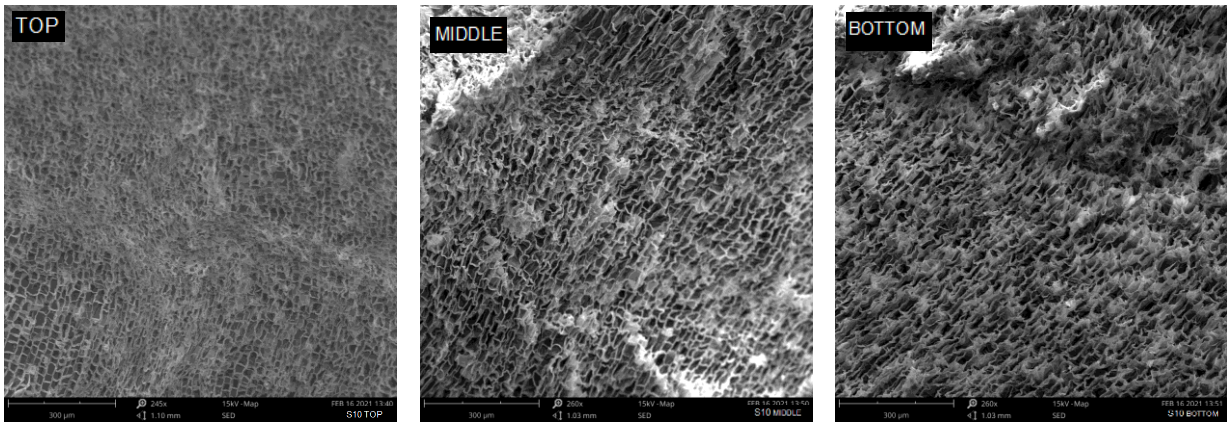


Figure 28 - SEM images of the centre of sample S10 at the top, middle and bottom.

APPENDIX C. FTIR SPECTRA

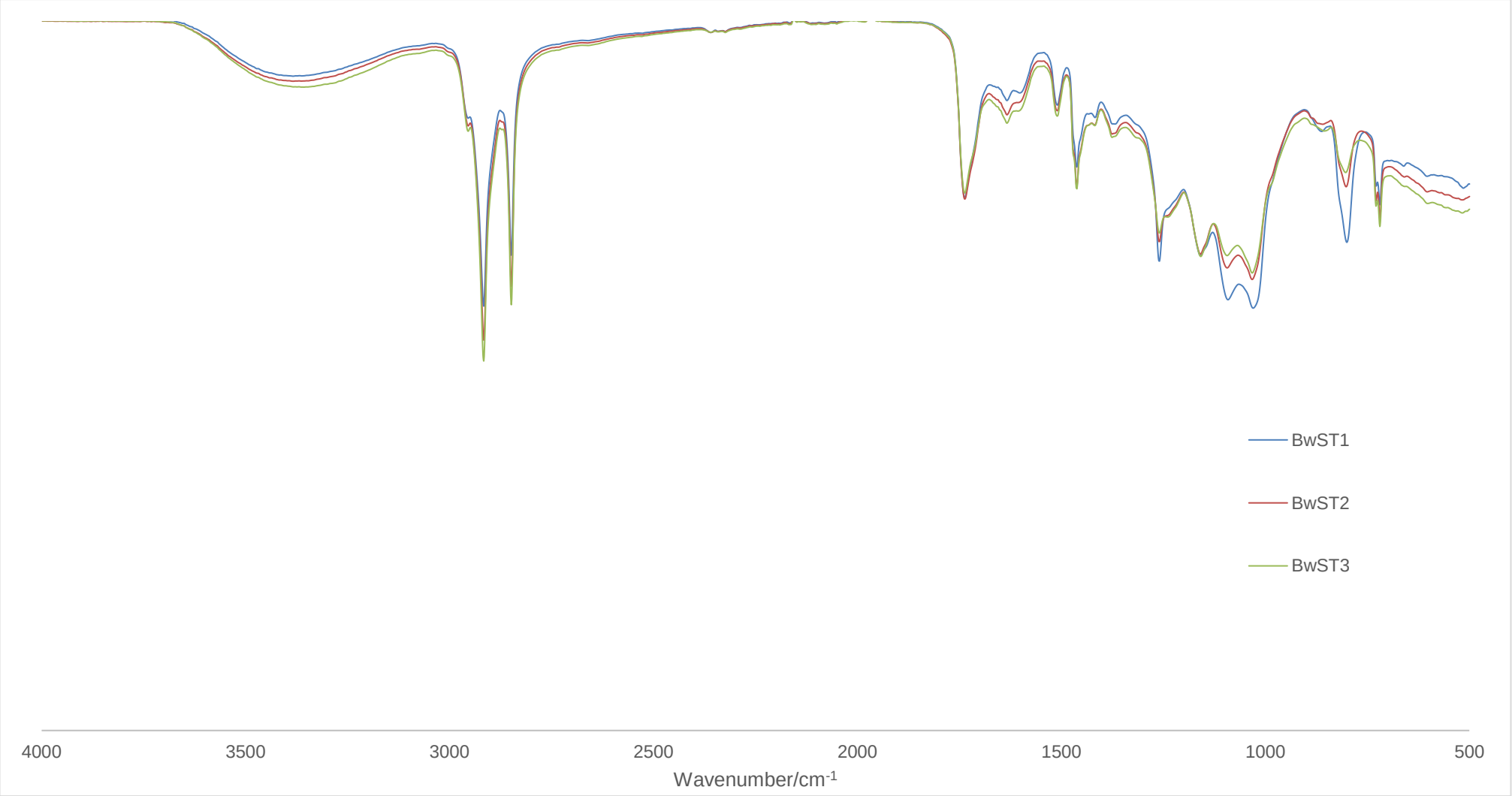


Figure 29 - FTIR spectra of samples BwST1, BwST2 and BwST3.

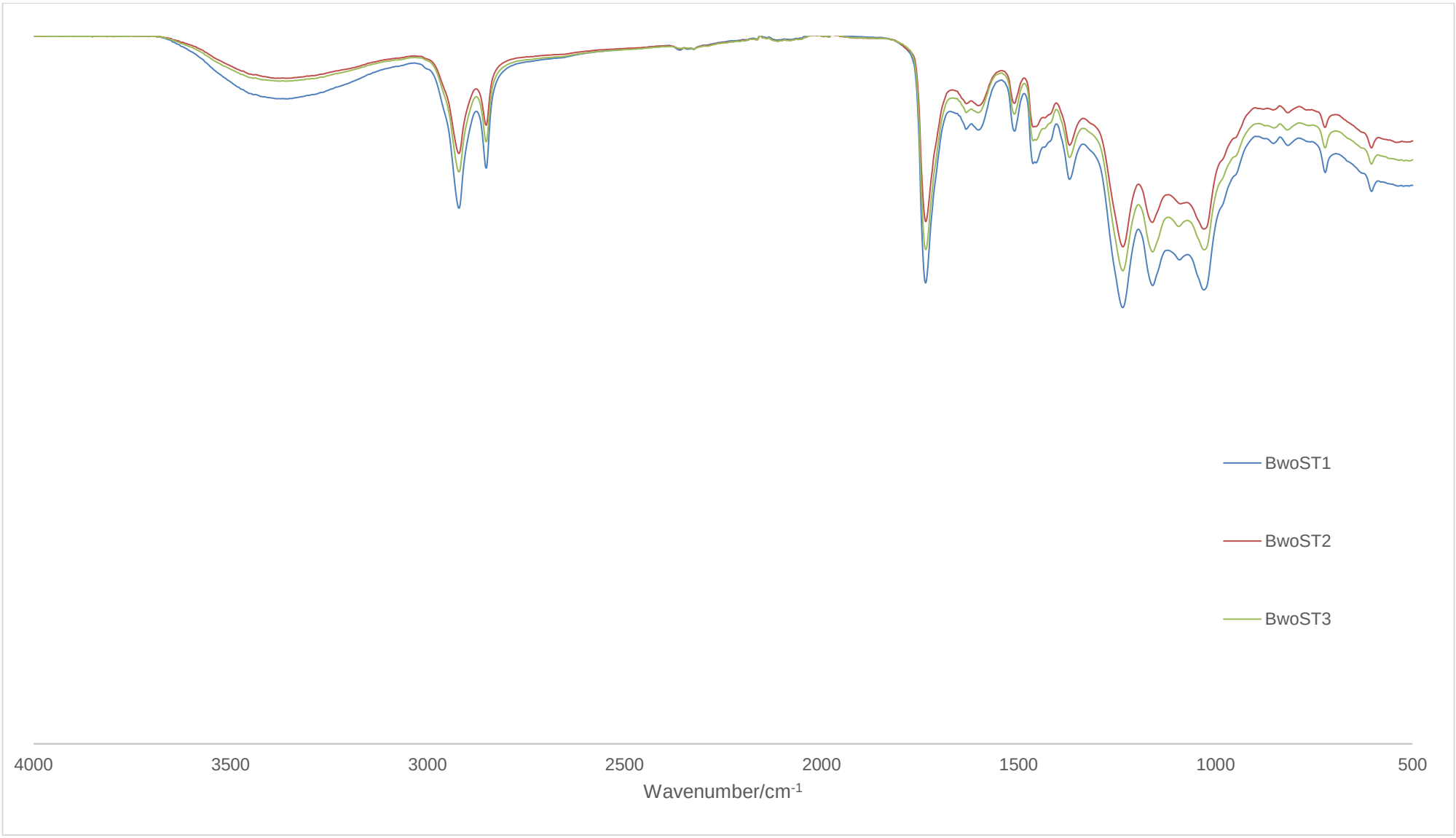


Figure 30 - FTIR spectra of samples BwoST1, BwoST2 and BwoST3.

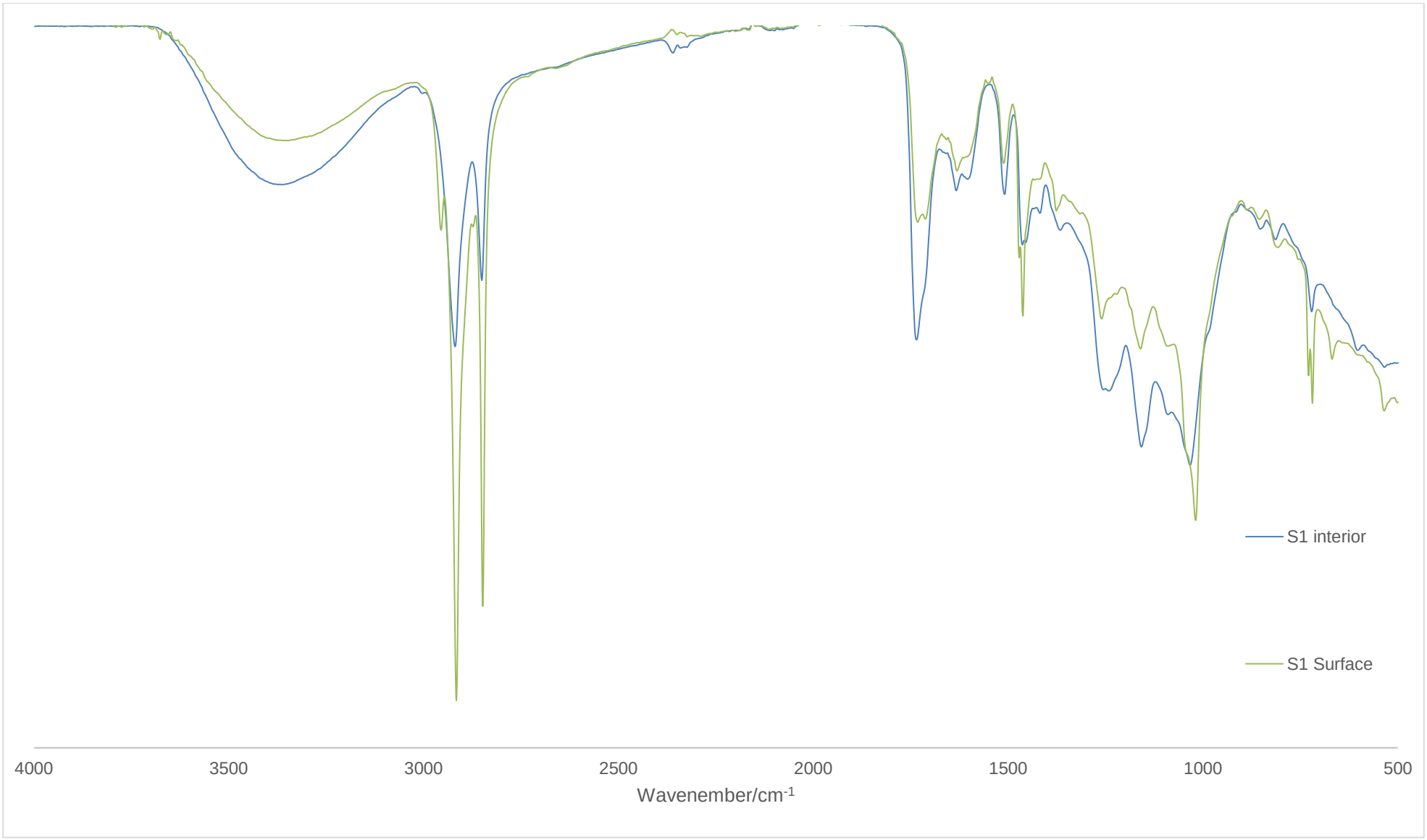


Figure 31 - FTIR spectra of sample S1 at the surface and interior.

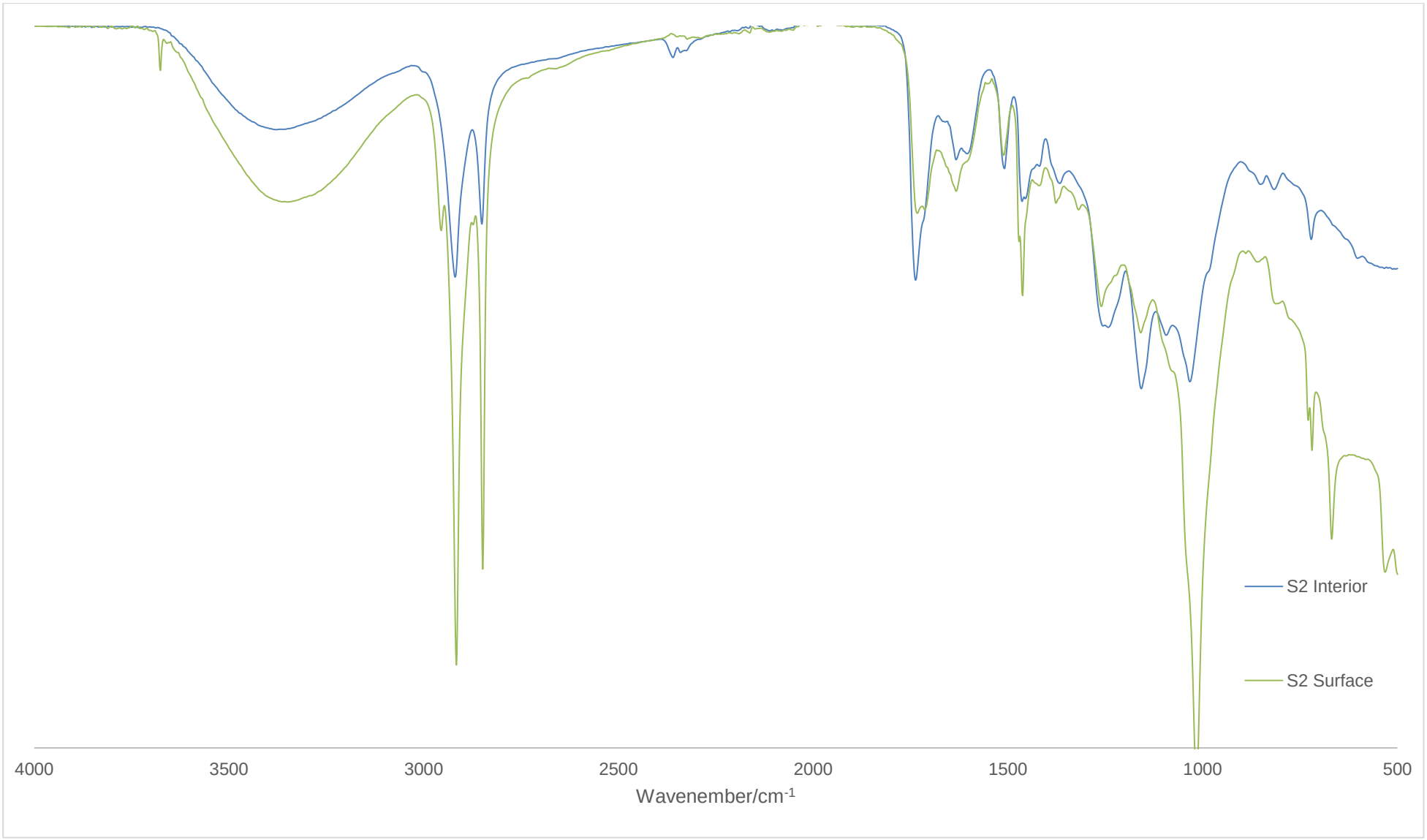


Figure 32 - FTIR spectra of sample S2 at the surface and interior.

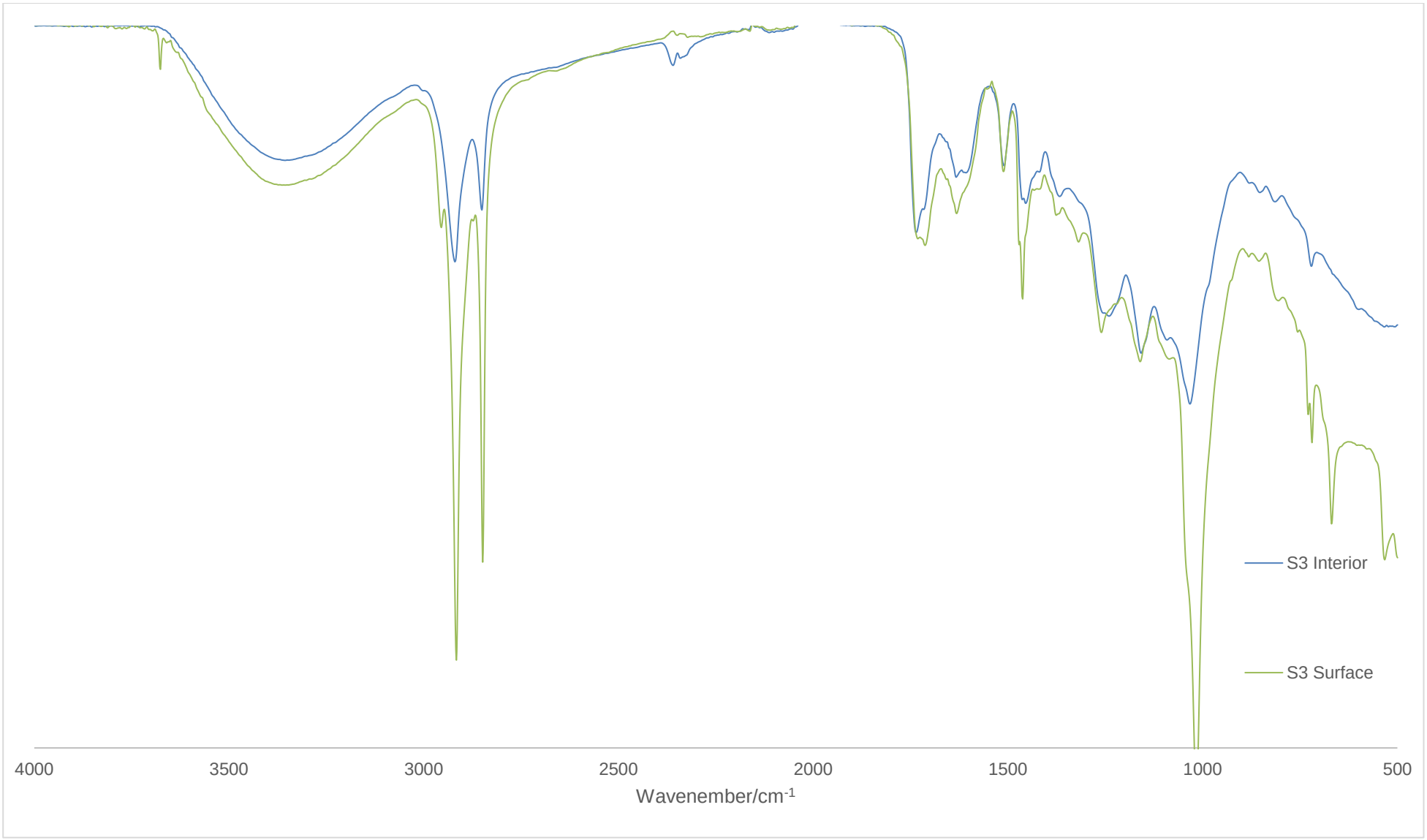


Figure 33 - FTIR spectra of sample S3 at the surface and interior.

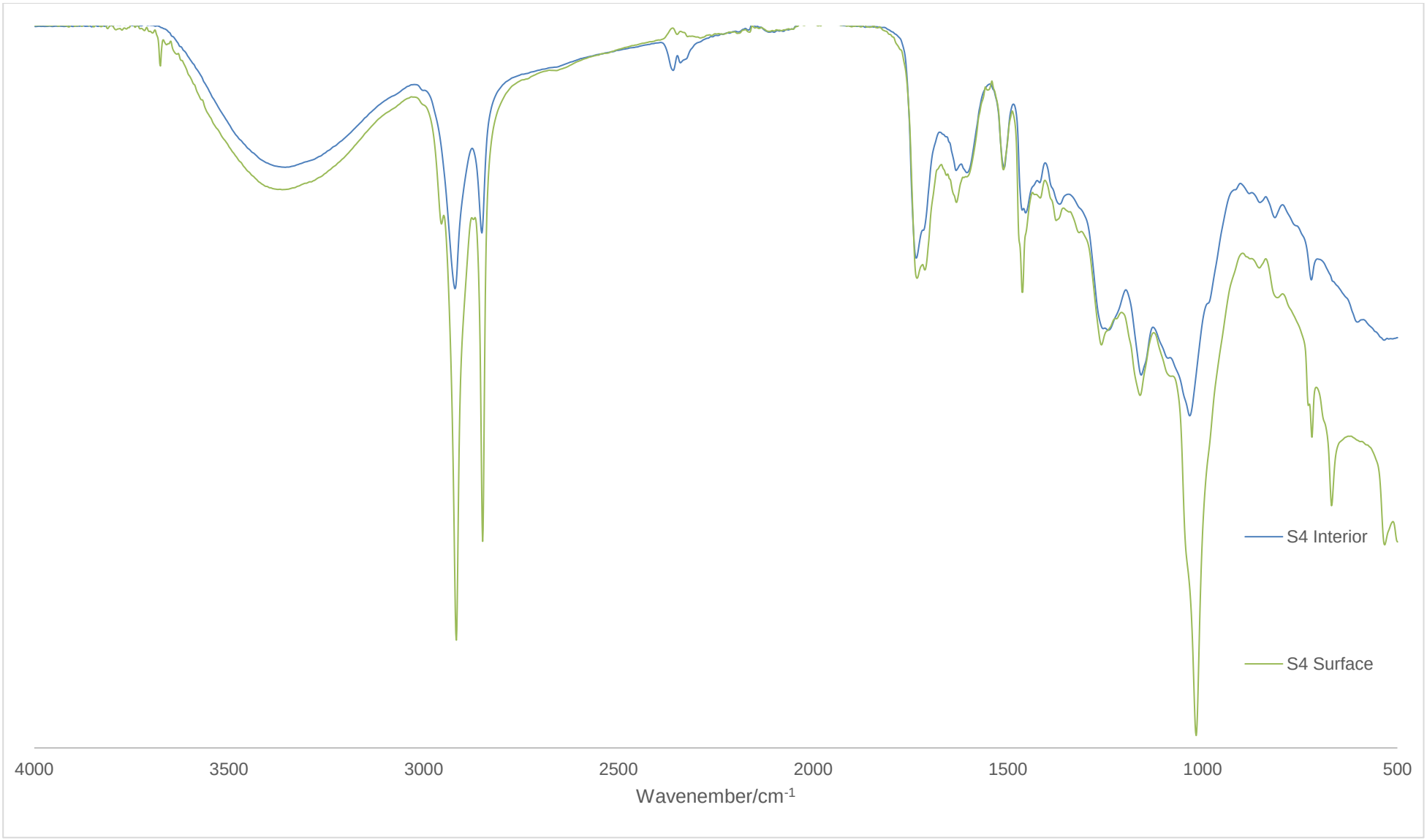


Figure 34 - FTIR spectra of sample S4 at the surface and interior.

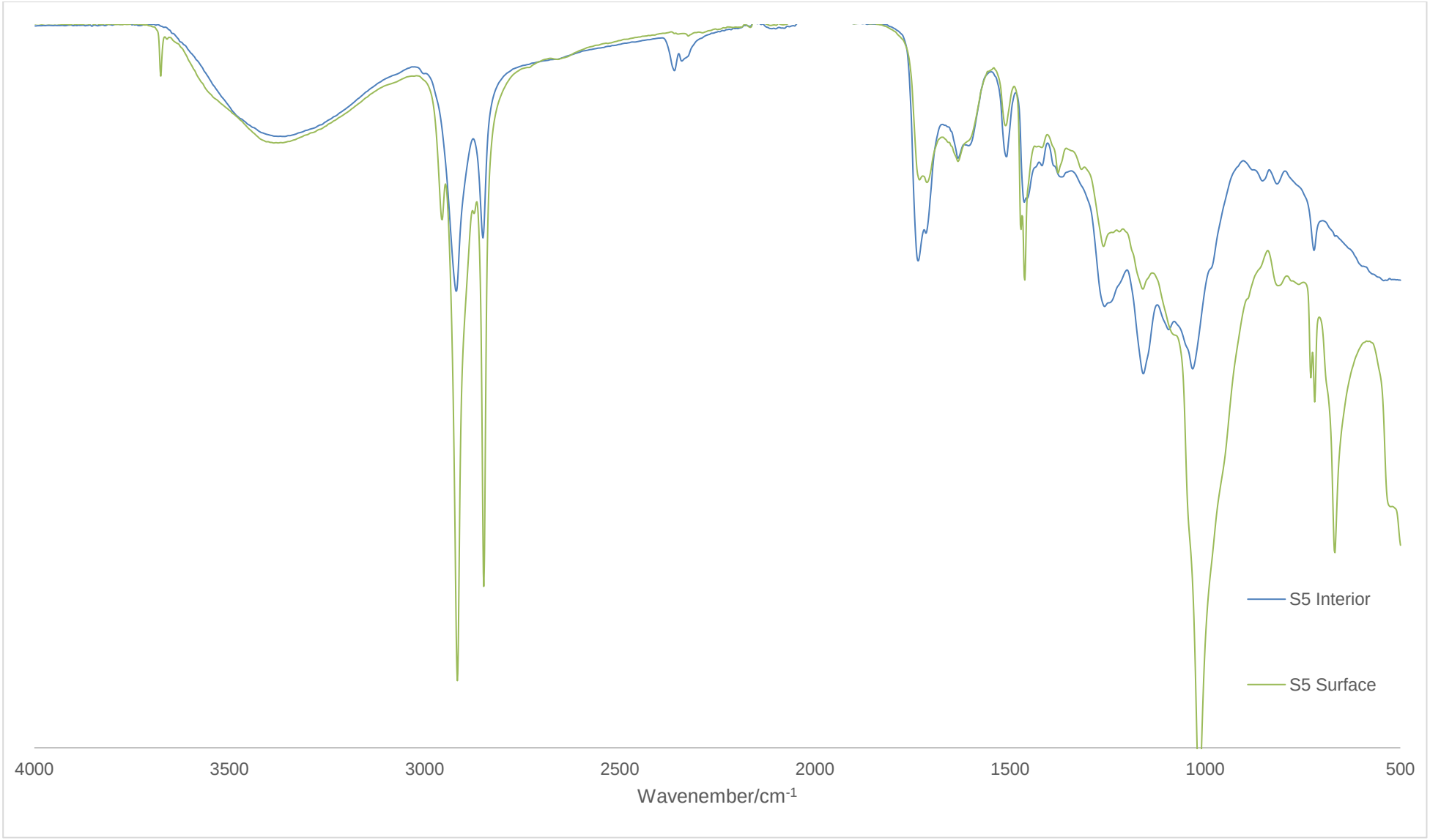


Figure 35 - FTIR spectra of sample S5 at the surface and interior.

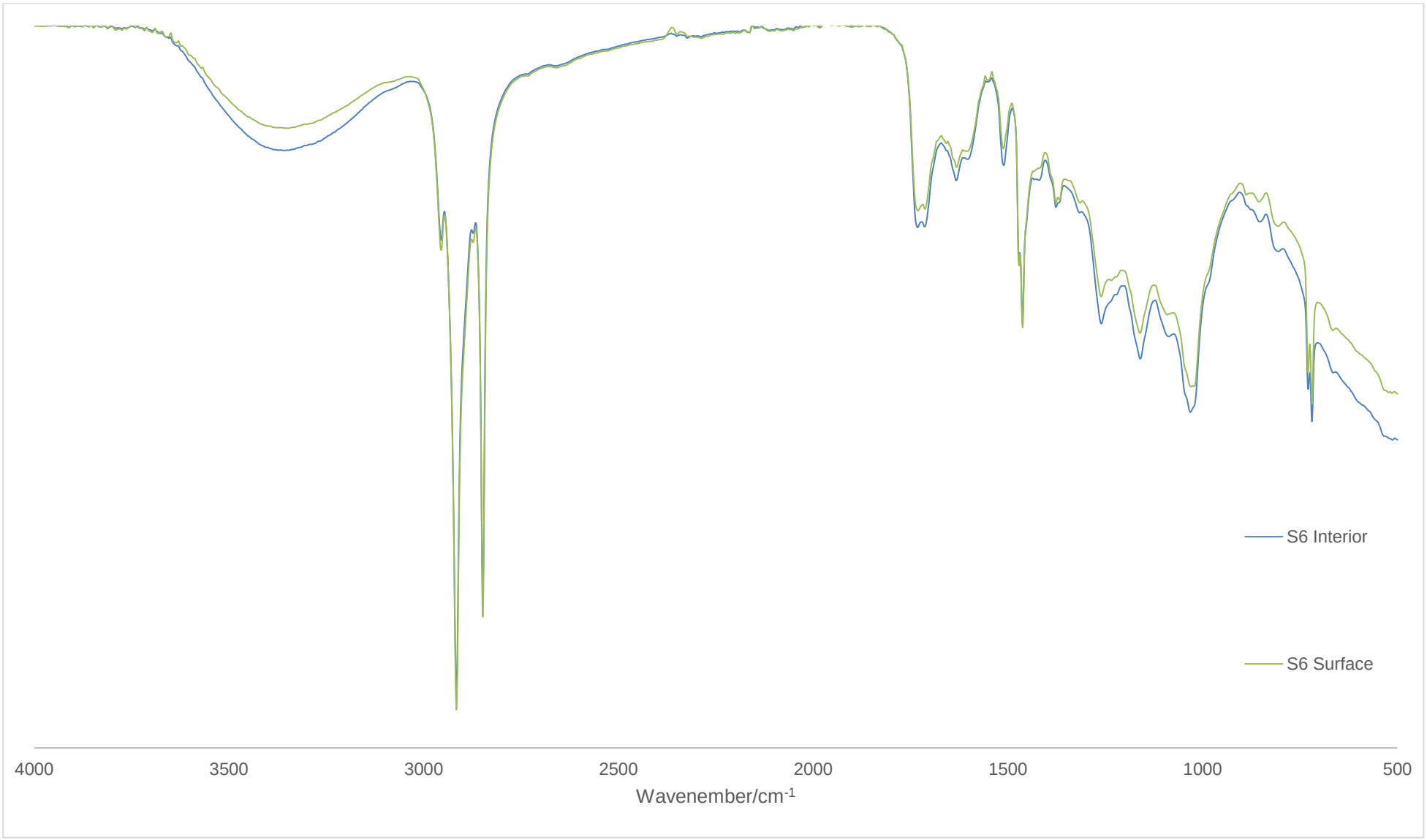


Figure 36 - FTIR spectra of sample S6 at the surface and interior.

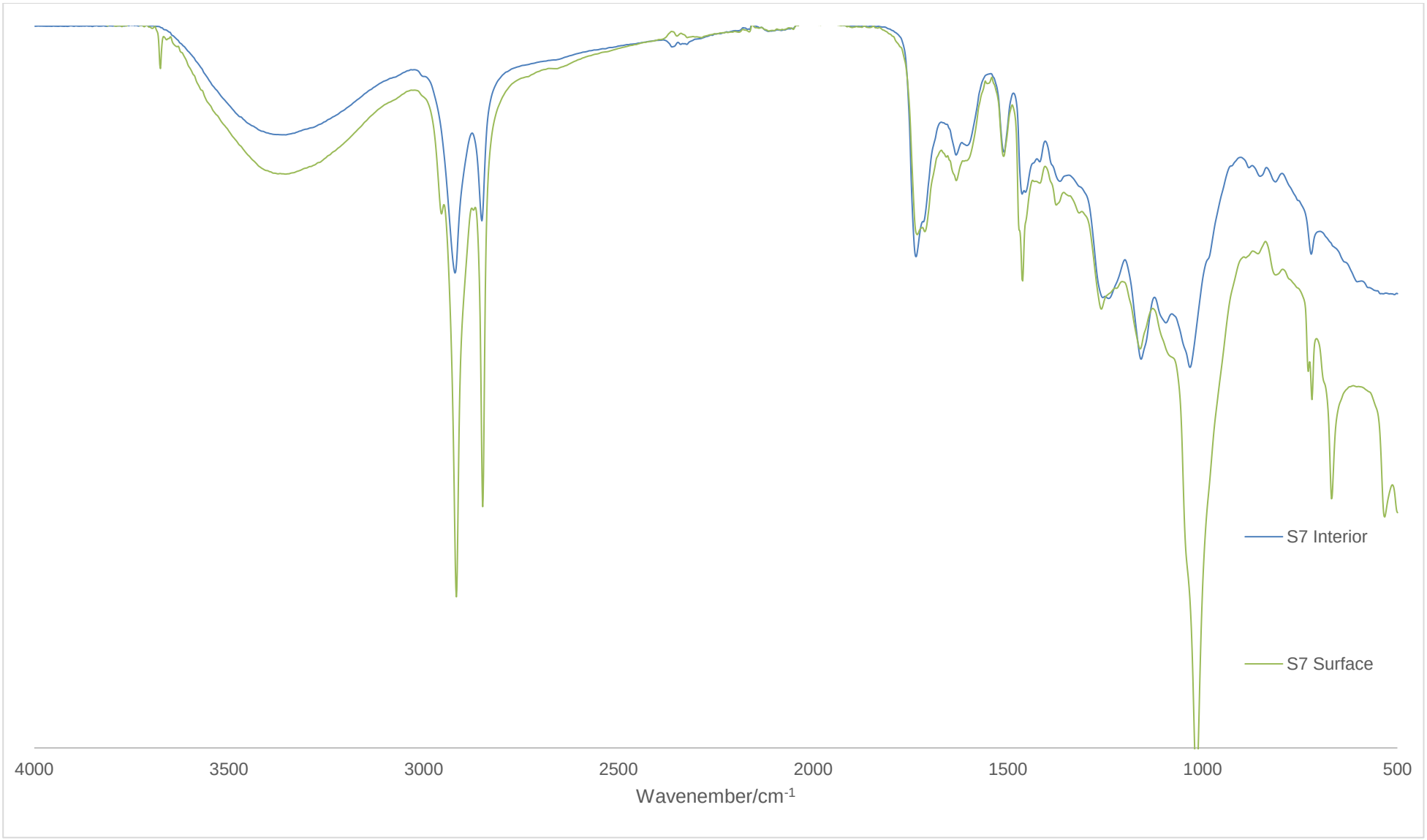


Figure 37 - FTIR spectra of sample S7 at the surface and interior.

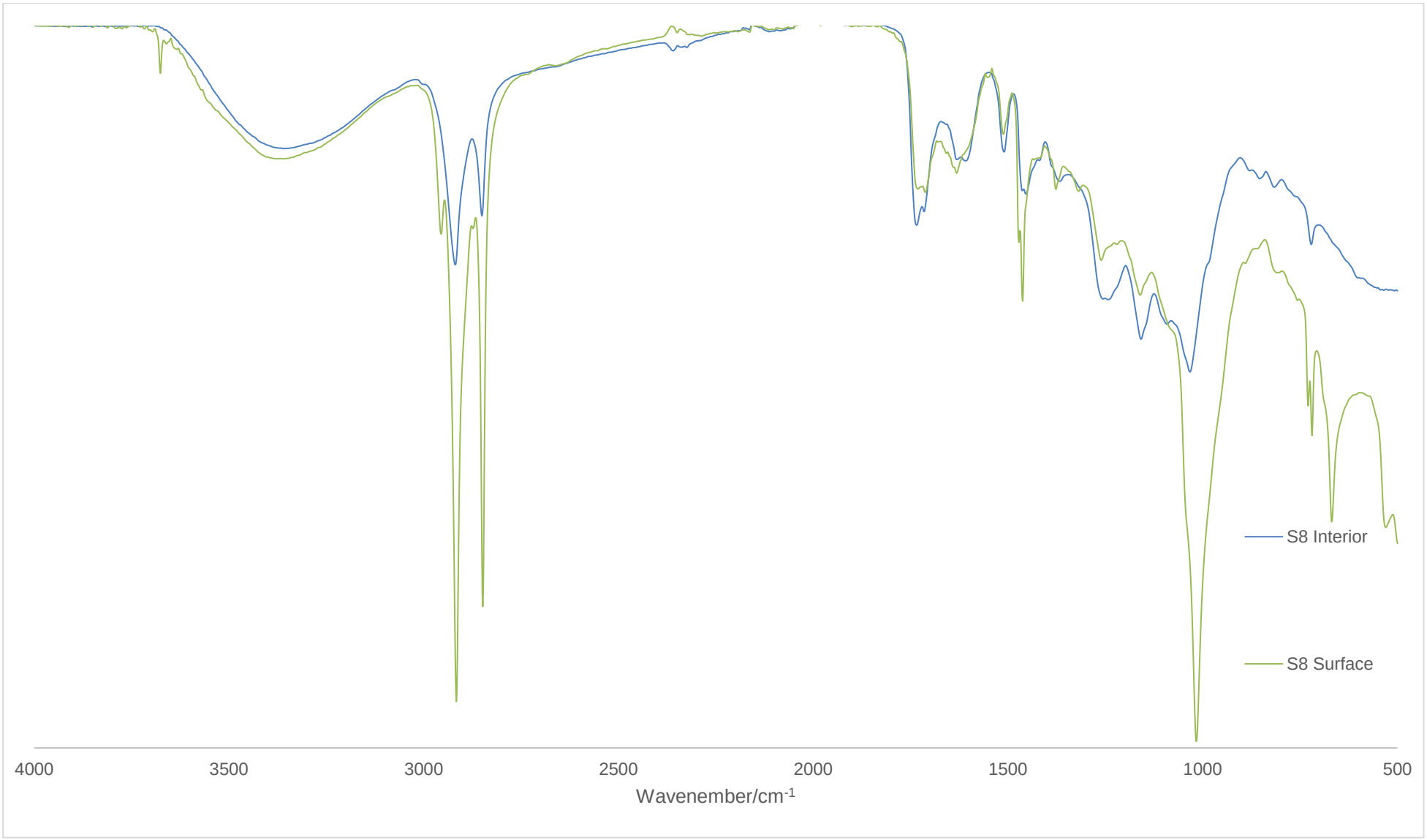


Figure 38 - FTIR spectra of sample S8 at the surface and interior.

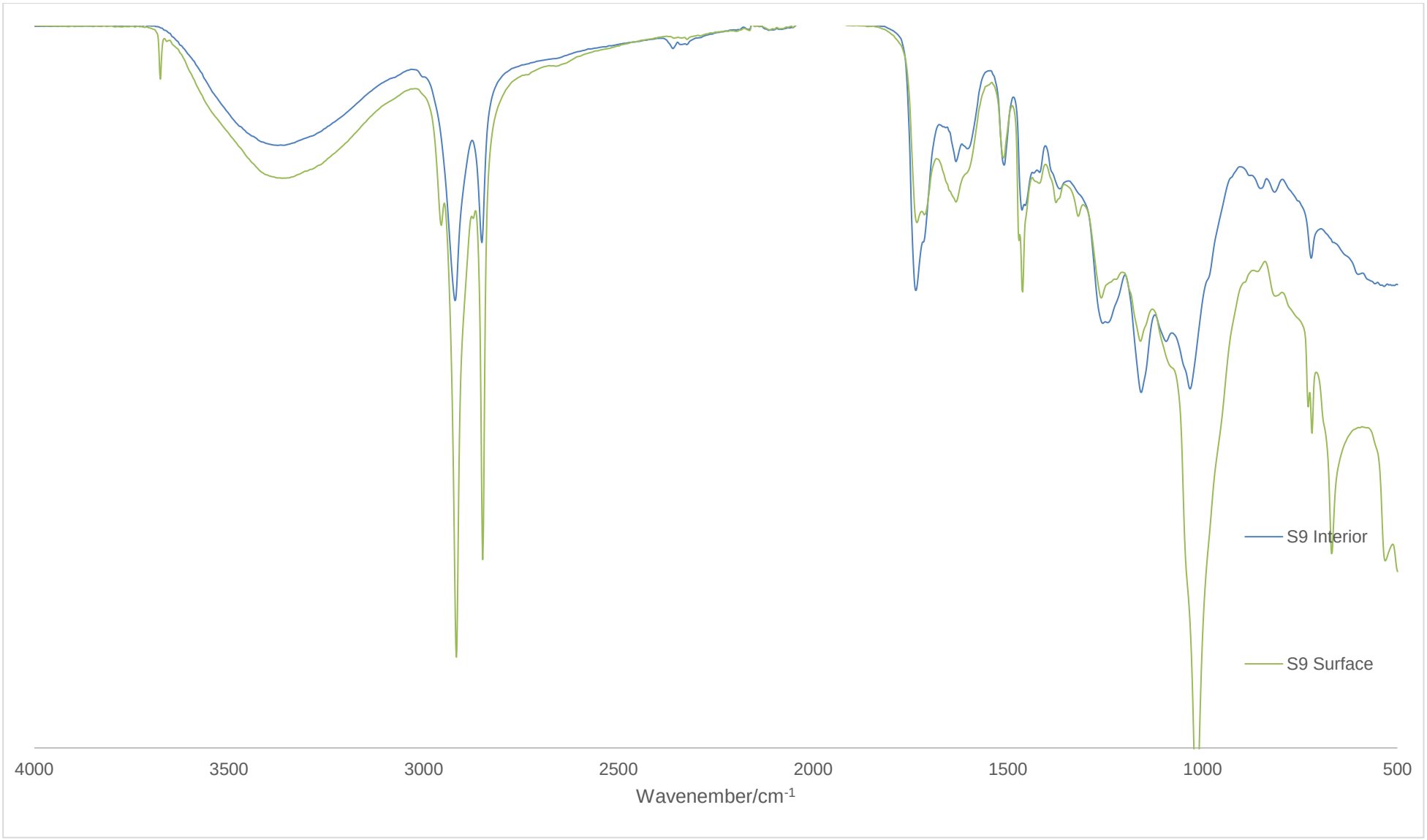


Figure 39 - FTIR spectra of sample S9 at the surface and interior.

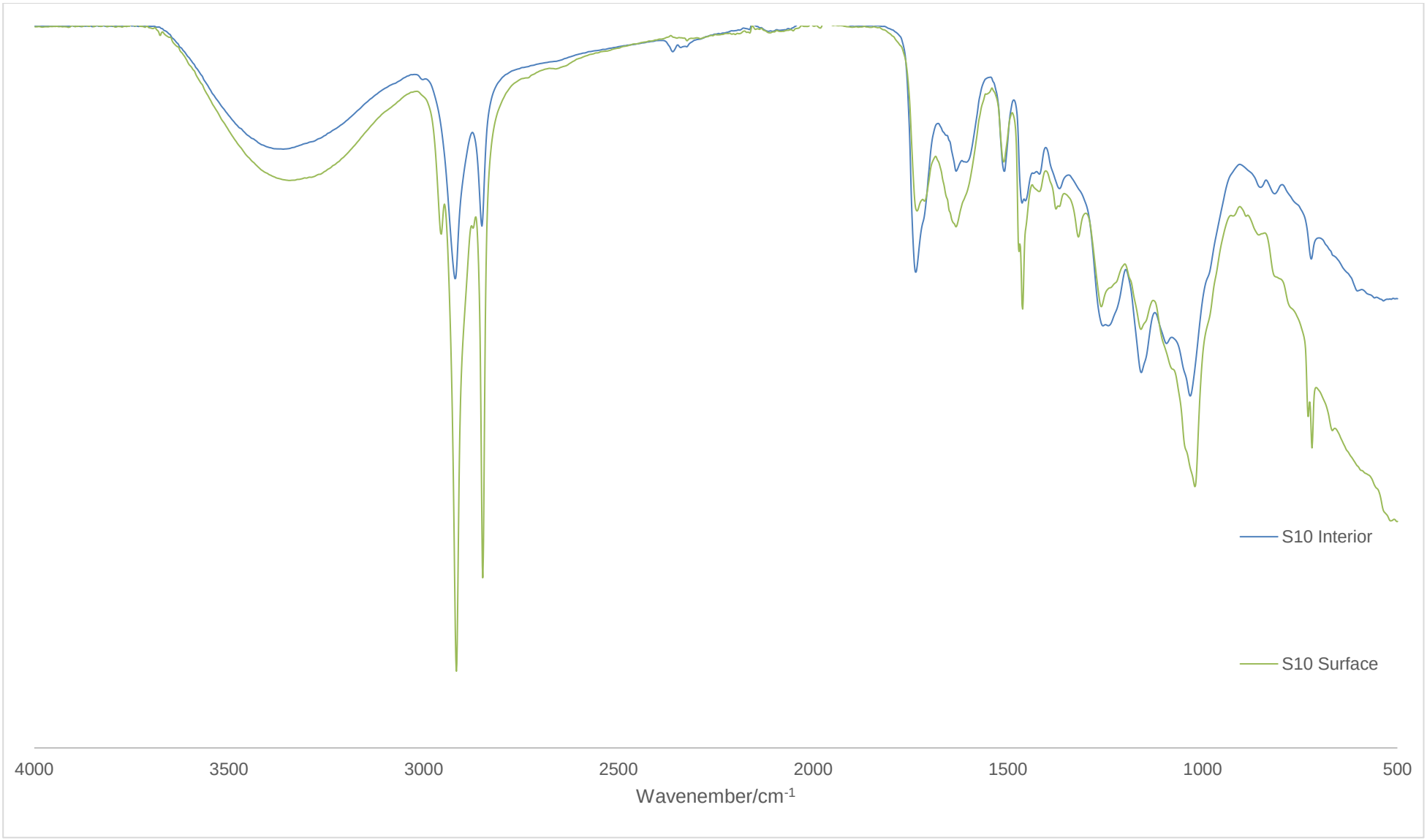


Figure 40 - FTIR spectra of sample S10 at the surface and interior.

APPENDIX D. DMA THERMOGRAMS

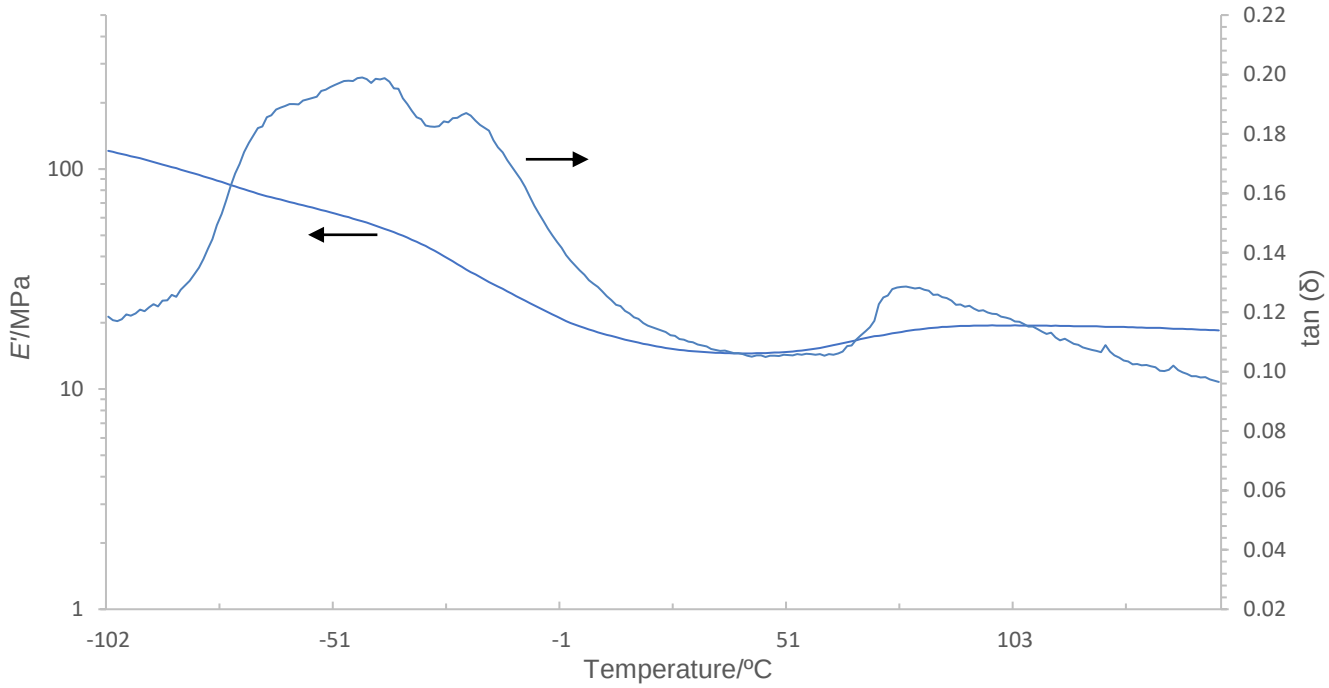


Figure 41 - Tensile DMA thermograms of sample S11.

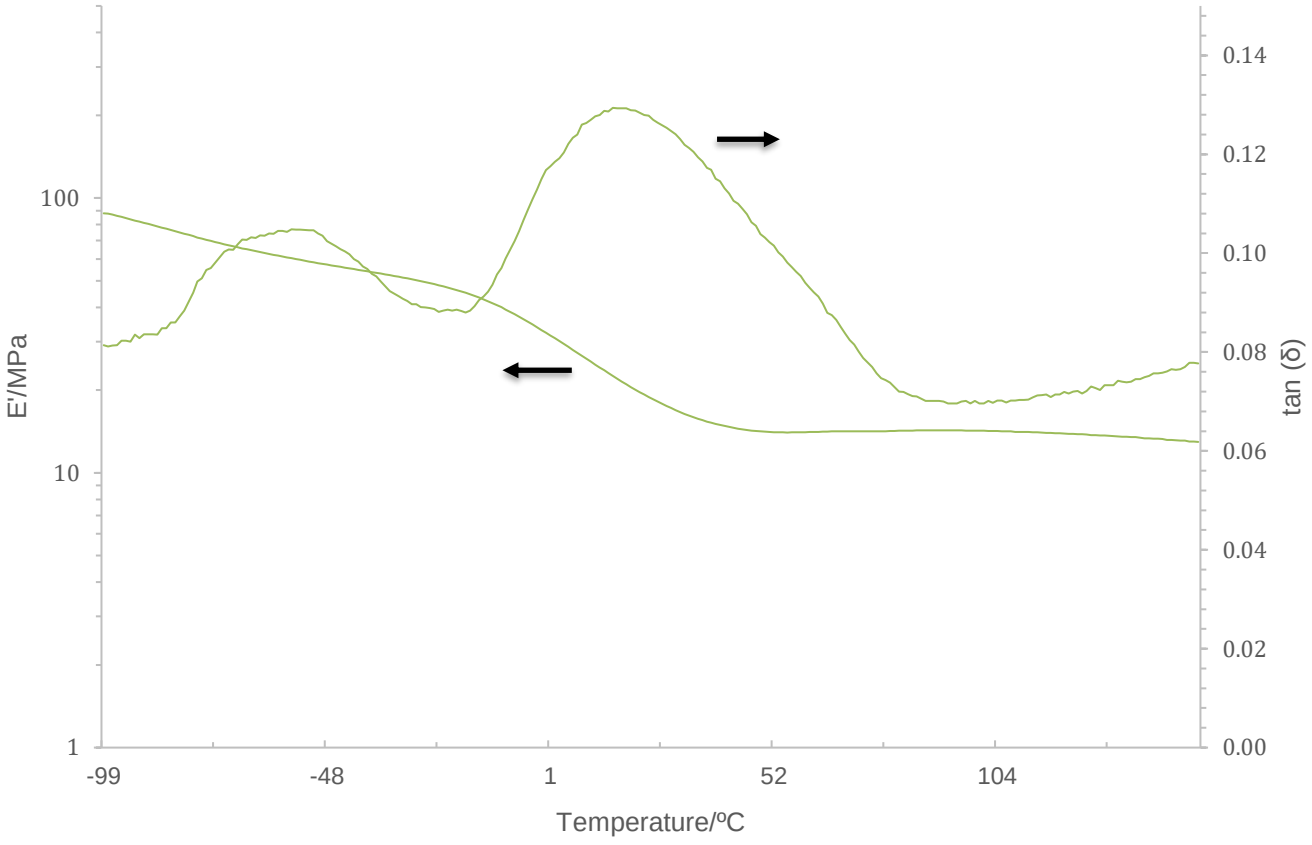


Figure 42 - Tensile DMA thermograms of sample S13.