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Characterization of colmated wine cork stoppers

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ABSTRACT

The objective of this work is to describe and compare colmated and non-colmated stoppers cork stoppers, regarding their differences in appearance (image analysis), structure (analysis with scanning electron microscopy- SEM), and mechanical behavior (compression test). For this study 75 natural cork stoppers were used and divided equally in 3 groups: (i) stoppers of superior class; (ii) stoppers of inferior class to be colmated; (iii) colmated stoppers.

Image analysis techniques were applied on the surfaces of superior and inferior (pre-colmated) class of stoppers, to analyze their porosity. Porosity features showed differences between two classes: higher values of all features in the inferior class and lower in the superior quality class. Water absorption test performed on colmated and pre-colmated group of stoppers showed small differences between them: colmated stoppers absorbed less water (92.1%) than pre-colmated class (98.8%) and the same trend was found with dimensional variations (swelling) (lower swelling of colmated stoppers was reported).

The behavior of the colmated and pre-colmated stoppers under compression performed in axial and radial direction was studied. Young's modulus for compression in axial direction were 21.2 MPa and 18.4 MPa for colmated and pre-colmated group respectively, while the compression in radial direction was characterized with the range of force for the given deformation, with mean values of 147 kN and 135 kN for 1 mm deformation.

Colmated stoppers were additionally analyzed by SEM, where the observations emphasis was given to the colmation material impregnation in the interior of the stoppers. Colmation material presence was mainly reported on the stoppers surface.

It can be concluded that colmation process primarily improves the appearance of the stopper, covering successfully the undesirable surface pores, which is the main objective of the colmation.

Key-words: wine cork stoppers, colmation, porosity, cellular structure, cork compression, swelling

RESUMO

O objetivo deste trabalho é a descrição e comparação entre rolhas de cortiça colmatadas e não colmatadas no que respeita às diferenças visuais (análise de imagem), estrutura (análise com microscópio electrónico de varrimento, SEM) e comportamento mecânico (testes de compressão). Para este estudo foram utilizadas 75 rolhas de cortiça, divididas igualmente em 3 grupos: (i) rolhas de classe superior; (ii) rolhas pré-colmatadas de classe inferior; (iii) rolhas colmatadas.

Foram analisadas rolhas colmatadas e os resultados obtidos correlacionados com o conhecimento atual sobre propriedades das rolhas de cortiça. Foram aplicadas técnicas de análise de imagem nas superfícies das rolhas pré-colmatadas de classe superior e inferior e efectuada a respectiva análise de porosidade. Os parâmetros de porosidade variaram conforme a classe: valores mais elevados para a classe de qualidade inferior e mais baixos para a classe de qualidade superior.

Realizaram-se testes de absorção de água com rolhas colmatada e pré-colmatadas. As rolhas colmatadas absorveram menos água (92,1%) do que as pré-colmatadas (98,8%) nas mesmas condições, apresentando variações de dimensão (expansão) correspondente a essa tendência (as rolhas colmatadas apresentaram valores mais baixos de inchaço).

Foi também estudado o comportamento das rolhas colmatadas e pré-colmatadas sob compressão no sentido axial e radial. O módulo de Young na compressão na direcção axial, apresentou valores de 21,2 MPa e 18,4 MPa para o grupo das rolhas colmatadas e pré-colmatadas, respectivamente. A compressão na direcção radial foi caracterizada através da variação da força para uma dada deformação, apresentando valores médios de 147 kN e 135 kN para deformações de 1 mm.

As rolhas colmatadas foram adicionalmente analisados por SEM, para observar a impregnação do material de colmatagem no interior das rolhas. A presença de material de colmatagem foi detectado principalmente na superfície de rolhas.

Pode-se concluir que o processo de colmatagem das rolhas de cortiça melhora o aspecto estético, cobrindo os poros de superfície sendo esse o principal objectivo desta técnica.

Palavras-chave: rolhas de cortiça, colmatagem, porosidade, estrutura celular, compressão

1. INTRODUCTION

Cork is a natural, renewable and sustainable material that has been known and appreciated for many centuries. Cork unique properties were known and used for various applications like fishing tools, floats and woman shoes. In Chinese and Roman civilizations, cork was first used as closure, such as those dated as 5th century BC from Greek amphora. Cork was first applied as a closure in the glass bottles of Champagne wine in the 17th century, as the legend says by Dom Pérignon, and remains still today as a symbol of wine bottles. Low density, low permeability to liquid and gas and high elasticity make cork the perfect sealant for liquids and the main closure for premium wines (Pereira 1988, Fortes et al. 2004).

Cork oak (*Quercus suber* L.) is an evergreen tree (leaves remain with dark green color throughout all year) with a porous outer bark from which the product named cork is obtained. Cork oak is specially found in the West Mediterranean coast and joining Atlantic coast. Cork oak is the only tree in the world with a bark – cork – that comprises such unique characteristics: in its bark, the cork layers are produced with appreciable thickness around stem and branches, and they may be stripped off from the stem without endangering the tree vitality, as the tree subsequently rebuilds new cork layers. In the cork production system in Portugal, this is done every 9 years, during cork oak 150-200 years long lifespan.

1.1 THE CORK OAK

Cork oaks characterize the landscapes in dry Mediterranean summers in Southern Europe. One of the advantages is that the tree is able to carry out photosynthesis for a longer period throughout the year, something that is not possible for deciduous trees, which loose their leaves during winter. The relatively dense and thick leaves are known as sclerophyllous (from the Greek, *skleros* = hard and *phyllon* = leaf). The cork oak leaves are, however, less dense and less tolerant to climatic extremes than the leaves of other evergreen trees, for i.e holm oak that frequently coexists with the cork oak (Pereira et al. 2008). The leaf duration is approximately 14 months (Oliveira et al. 1994, Fialho et al.2001), allowing photosynthesis activity from the beginning of the growth period in early spring till canopy renewal. Leaves are dark green, usually ovoid, 4-7 cm long and 2-3 cm wide, with sharp, uneven edges and dense white cuticle and numerous stomata on the lower side (Figure 1). Shape and size of the leaves vary among the trees, but also within the canopy (Pereira 2007). Tree height can reach up to 16 m, with short stem and thick branches. The crown dimensions on the other side can be very large, especially in open grown trees, i.e. 500 m^2 crown projection in mature trees with 150-200 years (Pereira, 2007). Dimensions depend on the favorable conditions during its growth (the tree requires a great deal of sunlight and a highly unusual combination of low rainfall and somewhat high humidity). The shape of the tree is influenced by competition - if the tree is growing in dense stands, crown is narrower and stems higher. Management practices such as early pruning result in a characteristic circular crown with flattened top (Figure 1). That tree form is nowadays symbol of cork oaks landscapes, and it can be found on different logos in Alentejo region, or in wine stoppers.

The root system is very well developed with strong and long tap root with thick lateral ramifications (Figure 1). The central root has the ability to penetrate several meters down in the soil and together with horizontal extensions extract water from the sub-soils. That explains the maintenance of leaf hydration in dry summer months and tree growth in high radiation periods with high water demand. During harsh summers more than 70% of the water transpired by cork oak may originate from the deepest soil and subsoil layers (Pereira et al. 2008). The presence of miccorhyza associated with the root system is common for this species (Pereira 2007).

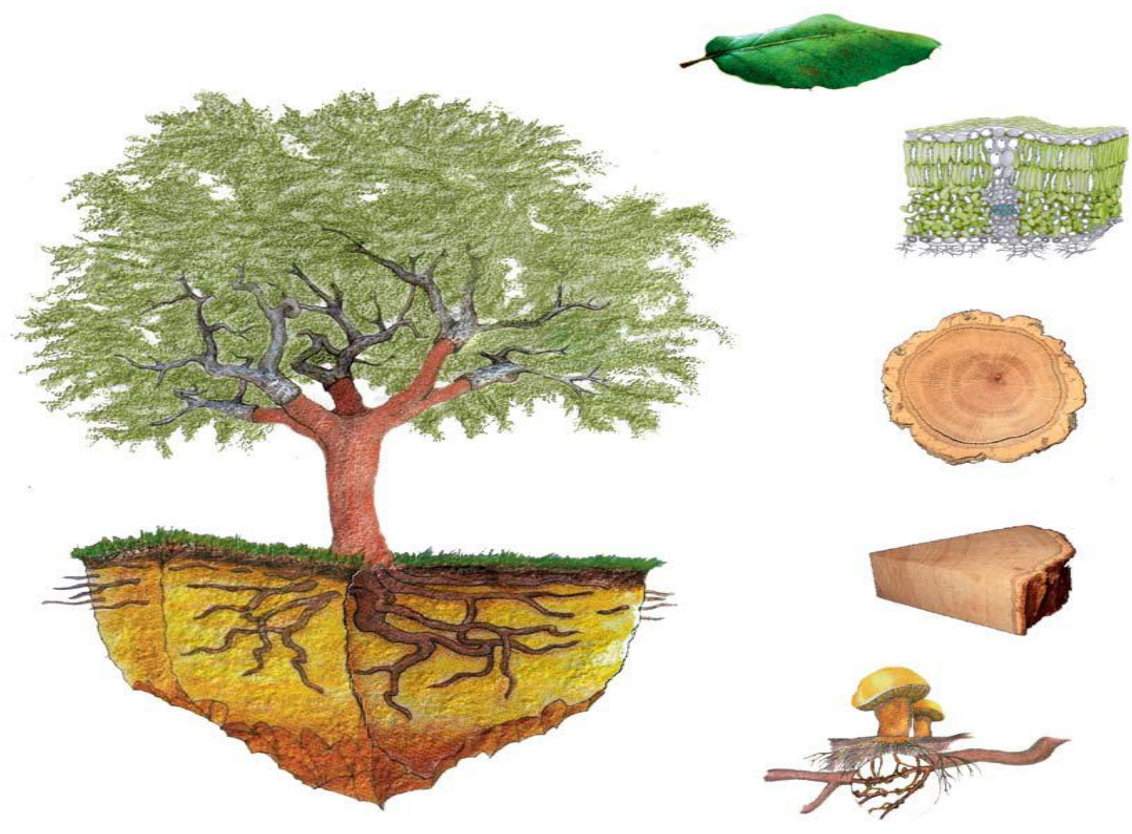


Figure 1. Cork oak: leaves, branch with cork, trunk 1 year after stripping, mycorrhiza
Source: APCOR, 2008

Cork oak tree is ecologically plastic, meaning that it can adapt its phenology and physiological activity to changing environmental conditions (Pereira 2007). It is well adapted to Mediterranean climate, with hot and dry summers and mild winters with mean precipitation of 600-800 mm concentrated mostly in late autumn and winter. The tree is well adapted to low fertility and shallow soils also characteristics of Mediterranean basin, with only restrictions of growth in calcareous soil. It grows spontaneously in western Mediterranean coast and adjoining Atlantic coast: Portugal and Spain, Morocco, Northern Algeria and Tunisia. In more restricted area it can be found in the South of France, and on the west coast of Italy, including Sicily, Corsica and Sardinia (Figure 2). The total cork oak area is currently around 1.43 million hectares in Europe and 0.85 million hectares in Northern Africa (APCOR 2010).

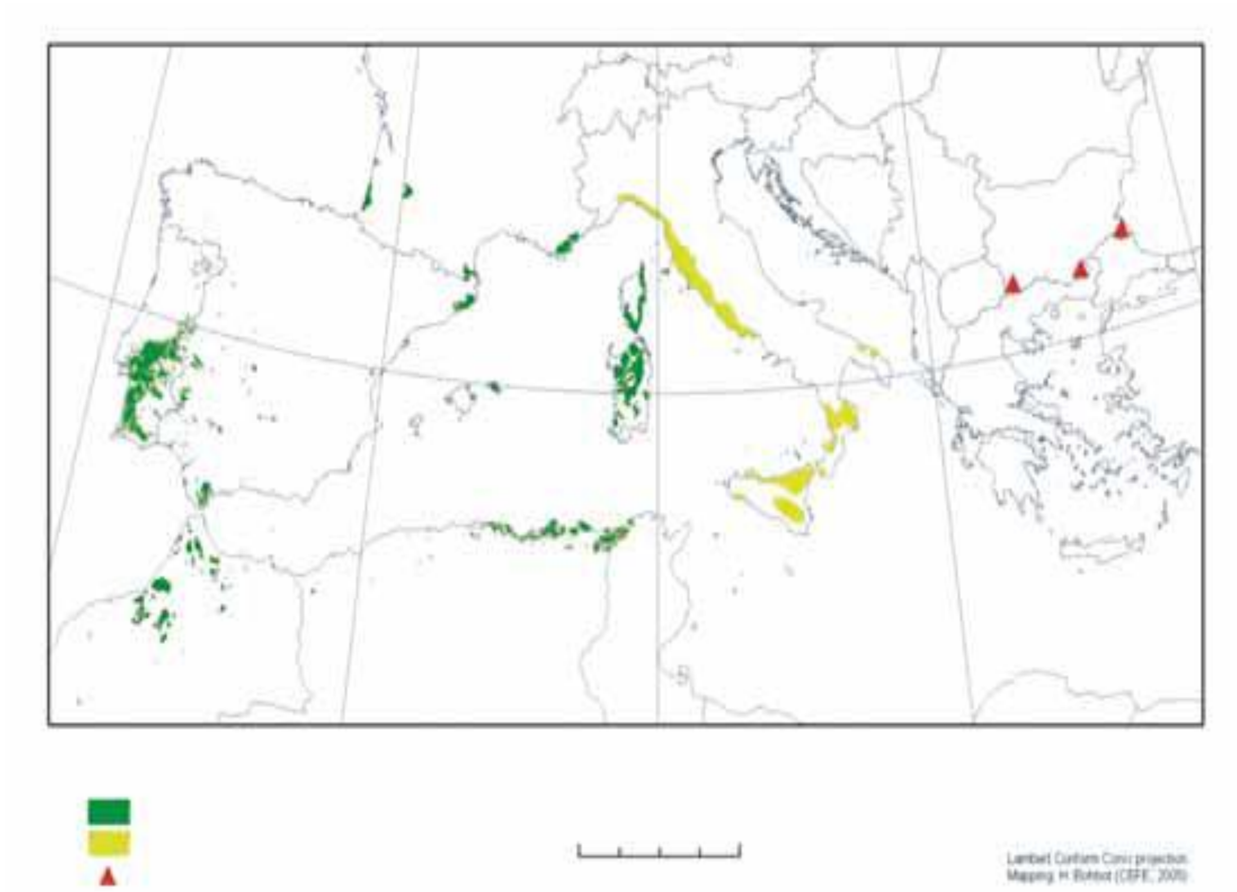


Figure 2. Approximate cork oak distribution. H Bohbot, J Aronson & C.Fontaine CEFE/CNRS, Montpellier, 2005.

Sources: Algeria (Alcaraz, 1977; Barry *et al.*, 1974; Gaussen, 1958, France (IFN, 1988-2003), Italy (Bellarosa & Schirone, 1997), Morocco (Sbay *et al.*, 2004), Portugal (DGF, 2001), Sardinia (Arigoni, 1968), Spain (Ceballos Fernandez de Córdoba, 1966), Tunisia (Khaldi, 2004, after IFPN-DGF, 1955) Bulgaria (Petrov & Genov, 2004).

The total area occupied worldwide is 2.277.700 hectares, more than half located on Iberian Peninsula. Based on geographic distribution, Portugal concentrates about 32% of the world's surface, which corresponds to an area of 736.700 hectares (Table 1)

Table.1 Montado world distribution area in hectares and corresponding percentage

Country	Area(hectares)	Percentage
Portugal	736.700	32
Spain	506.000	22
Algeria	414.000	18
Morroco	345.000	15
France	92.000	4
Tunisia	92.000	4
Italy	92.000	4
Total	**2.277.700**	**100**

Source: National Forestry Resources Department (DGRF), Year: 2006 and APCOR

At a global production level, cork production is close to 300 thousand tons annually, and 52% of cork originates from Portugal (more than 150 thousand tones a year), reinforcing the Portuguese sector’s leadership. Concerning national exports, approximately 90 percent of the cork transformed in Portugal is aimed for the international market. This is an important source of income for Portugal, with a rather stable annual production, i.e. after a minor decrease in 2009, production increased to 754.4 million euros in 2010, corresponding to 159 thousand tons of exported products (Instituto Nacional de Estatistica 2011). The value generated by cork exports is 2.2% of Portuguese total export’s value and about 30% of Portuguese forestry products exports (Instituto Nacional de Estatistica 2011).

Cork oak presents around 23% of the total area of forest in Portugal of 3186,8 thousands of hectares. The largest concentration of cork oak forestland can be found in the Alentejo (72%), whereas Lisbon and the Tagus Valley hold the second position at 21% (National Forestry Inventory, 2006)

Portuguese cork industry is distributed across ten districts. There are approximately 700 companies operating in the Portuguese cork sector, responsible for producing approximately 40 million cork stoppers a day (35 million coming from Northern Portugal) and employing about ten thousand workers (Portuguese State Department of Solidarity and Social Security, 2009). Wine industry using cork for bottle stoppers accounts for almost 70% of the total value of the cork market, followed by the building industry with more than 20%. Natural cork stoppers account for the greatest value of total market (Figure 3)

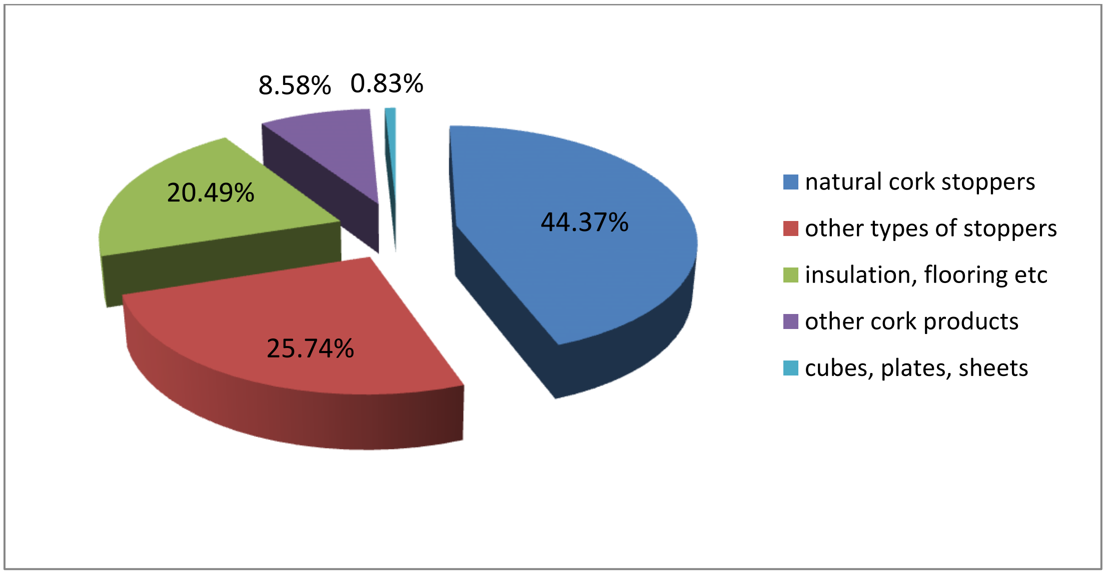


Figure 3. Structure of cork exports per product type in value - 2010

Source: Instituto National de Estatistica, 2011

Over 15 billion cork stoppers are produced every year and sold worldwide to the wine industry. Thus the wine industry plays a vital role in maintaining the economic value of cork and the cork oak forests. The wine industry today use cylindrical cork stoppers: solid natural stoppers (one piece); assembled natural stoppers (multi piece); technical stoppers with agglomerated body and discs glued to the tops; and agglomerated only stopper. Natural stoppers of inferior quality class can be submitted to the colmation process - filling the pores with a mixture of cork dust and resins (polyurethane or rubber binder), for improving their performance. This type of stoppers is called colmated stoppers.

The objective of this work is to describe and compare colmated and non-colmated stoppers cork stoppers, regarding their differences in appearance (by image analysis), structure (by SEM observations), and mechanical behavior (under compression).

1.2 FORMATION, STRUCTURE AND PROCESSING OF THE CORK

Cork is a cellular material made up of closed empty cellular elements with a regular structure (Silva et al. 2005). The regularity is interrupted namely by the presence of lenticular channels, but also of wooden inclusions and cracks. The cork oak's most interesting particularity is the outer bark production, formed by an elastic, impermeable and good thermal insulating tissue – cork. Cork is a tissue named phellem and it is a part of the periderm in the bark that surrounds the stem, branches and roots of dicotyledonous plants with secondary growth (Graca and Pereira 2004). It is composed of dead cells with walls that are impermeable due to a chemical compound named suberin. All the trees produce layers of suberized cells for protection, but only cork oak is able of "constructing" its outer bark by adding continuous and uniform annual rings resulting from activity of secondary meristem mother cells of the phellogen, as part of periderm (Pereira et al. 2008). Each phellogen mother-cell gives by cellular division cork cells (phellem cells in plant anatomy nomenclature) that grow unidirectionally outwards in the tree's radial direction (Figure 4).

The cellular division of the phellogen is linked to the physiological cycle of the tree and to factors that influence it, namely environmental conditions. The homogeneity of cork is the result of the cork oak's phellogen maintaining its activity throughout the tree's lifespan what contrasts with other tree species, where each phellogen has usually a short life span. A good example is its capability to naturally regenerate a new phellogen after extracting its cork layer. After the extraction of cork that leads to the death of the phellogen, there is a rapid formation of a traumatic phellogen that resumes the functions of the protective cork layer. The cork oak tree responds in that way whenever there is need for it. These characteristics make it sustainable producer of cork through its lifetime (Graca and Pereira 2004).

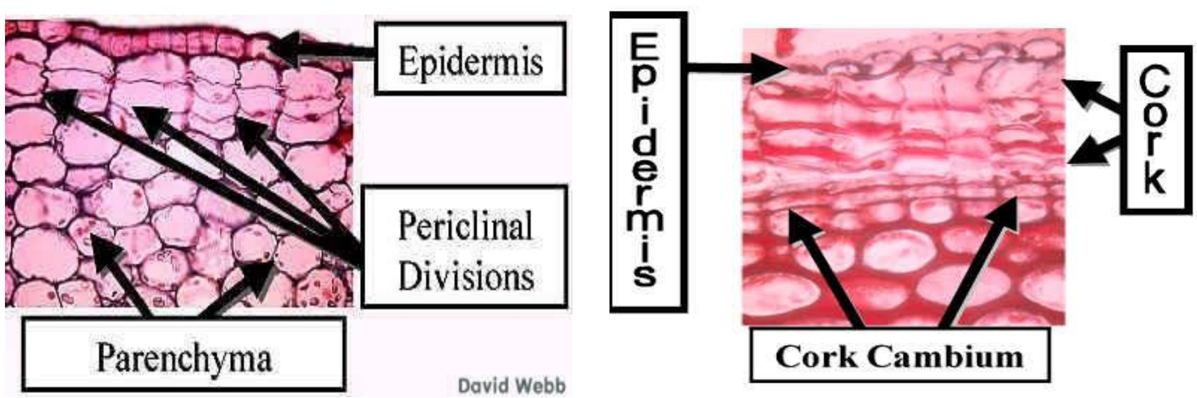


Figure 4. Phellogen cells division and cork formation
Source: http://www.biologie.uni-hamburg.de/b-online/library/webb/BOT311

In its life cycle of cork production, the cork oak produces three qualities of cork: virgin cork obtained from the first periderm, second cork after the stripping of virgin cork and obtained from the traumatic periderm, and reproduction cork from subsequent strippings (Silva et al. 2005). The first periderm is formed in the first year of the shoot, below the epidermis (Graca and Pereira 2004). Initiation of the phellogen starts with division of a few cells around the perimeter, and extends afterwards circumferentially and continue the meristematic activity dividing and forming polygonal phellem cells regularly arranged and pushed outwards towards epidermis. In the first year few layers of cork cells are formed, and in the second year they keep their radial flattened appearance, while epidermis stretches and fractures. The perimeter increases fast with growing, and tangential stress causes fractures of the first layers of cork cells. Thus virgin cork, formed in this first periderm will develop deep fractures and cracks with following years of radial enlargement (Figure 5) (Pereira 2007).

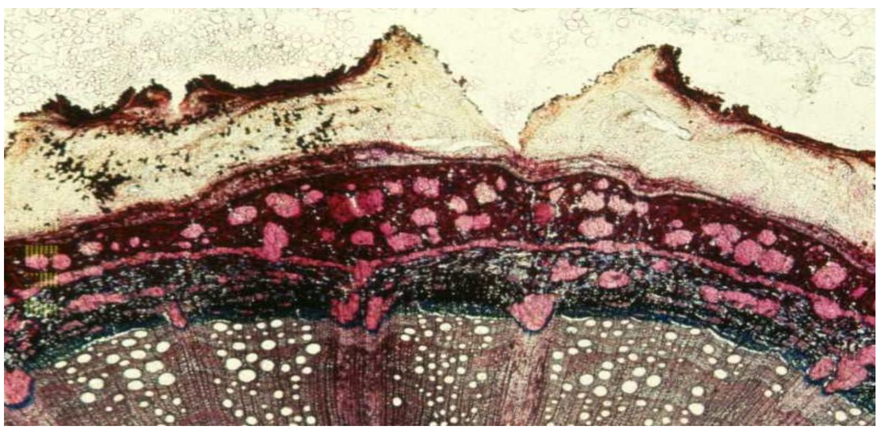


Figure 5. External cork layer with longitudinal cracks due to tangential growth stresses
Source: Pereira, 2007

Phellogen activity is maintained throughout all tree life, decreasing its intensity with age (Graca and Pereira 2004). After the removal of virgin cork, the phellogen exposed to the atmosphere dies, and it is replaced by a traumatic phellogen. The formation and activity of the traumatic phellogen follows the same pathway as in the first periderm, and cork produced by this periderm is called the second cork. Meristematic cell-dividing activity is higher in initial years after formation. With the radial growth, large tangential stress leads to fracturing in external layers of this cork.

The thickest cork layer is generally formed in the growing cycle following the second cork extraction. The process is repeated in a similar way, but now the cork tissue is called reproduction cork and has a perimeter big enough to resist the tangential growth stress, resulting in much less deep fractures and cracks on the external surface. The cork produced per year diminishes progressively from the first year of activity of the traumatic phellogen until the next extraction (Lopes and Pereira 2001).

Cork harvesting is an environmentally friendly process during which not a single tree is cut down. It is a delicate process regulated by laws which control the periods between each extraction and the intensity of the extraction. Extracting the cork, or cork stripping, is done manually by cutting large rectangular planks and pulling them out from the tree. In order to be able to tear out from the tree and not damage the inner bark and cambium, cork stripping is done in late spring and early summer when the phellogen is physiologically active (Pereira 2007). It is only undertaken by professional and experienced workers, avoiding harming the cork oak tree.

The tree responds to the removal of cork layer first with fast closing stomata to prevent increased transpiration and water loss, and then by forming the traumatic phellogen and some layers of cork to protect the active phloem from more water loss. It will return its normal functions in about 24 to 30 days after extraction (Santos 1940, Oliveira 1995). In the next two years, a small reduction in the tree`s radial growth is observed (Leal et al. 2006). Intervals between one extraction and the next one are minimum 9 years, the legal limit in Portugal and Spain. The tree perimeter must be a minimum of 0.7 m at a height of 1.2 m from the ground before bark can be extracted for the first time (ASECOR 2006). However, it is only after the third harvesting of the tree onwards, that cork grows with the required characteristics for its application in wine closures. The most important industrial requirements of raw material for the stoppers production are a thickness of the cork planks over 27 mm and absence of defects such as deep fractures (Pereira 2007). The average life time of a cork oak varies between 170 and 200 years; a cork oak can therefore generate cork which is adequate for wine closures about 17 times throughout its whole lifespan (ASECOR 2006).

From cork nowadays it is possible to get a variety of products through industrial processing, due to cork unique properties of high energy absorption, high resilience, excellent insulation properties, etc. Cork has a wide range of traditional applications, but still, natural cork stoppers remain the most important of cork applications, having the highest added-value and largest market. The impermeability of cork to liquids and gases and its high compressibility and flexibility, make it an ideal material for sealing bottles (Silva et al. 2005). However, the fact that the byproducts of stopper production are used in other applications should not be overlooked. Following what is said above, it is clear that industrial production is organized in two main directions: production of natural cork stoppers and discs, and production of agglomerates of cork particles including by-products of former transformations (Pereira 2007). The natural cork stoppers are made by a solid part as a single piece. They are punched from a corkboard with adequate quality, with a minimum transformation of the cork material apart of the changes that occur with the cork boiling operations. Agglomerated corks are made of cork granules that are bound together with or without adhesive and then pressed, or with surface activation.

1.3 PRODUCTION OF CORK STOPPERS

1.3.1 Cork stripping

In the chain from the cork oak to the final stoppers, the first step is cork stripping or extraction of the cork layer that covers the cork oak. This is commonly done manually, in late spring or early summer, when the periderm shows physiological activity. The phellogen mother cells and recent formed phellem cells are turgid and cell walls are fragile, so by applying a tensile force, it is possible to separate cork by pulling it out without damaging underlying layers phloem and cambium (Pereira 2007). Therefore, the timing of this operation is essential for its success, namely from mid-May to the beginning of August, when phellogen is in strong activity.

After removing of the cork layer, the cork oak responds by regenerating a new traumatic phelogen a few millimetres inside the phloem. This phellogen quickly starts its activity of forming new layers of cork to the exterior, thus restoring this protective barrier, so reproduction cork is formed. This process is repeated whenever the cork layer is removed. It is this characteristic of cork oak that allows the sustainable exploitation of cork during the tree's lifetime by the periodical removal of the cork layers when they have attained a thickness enough to make a wine stopper (Pereira and Tomé 2004). In the field numbers are painted on the trees stem after cork removal, to track the year of the stripping process.

The cork is cut away from the tree with precision. The forest workers (usually a team of two workers) first make a horizontal cut around a tree perimeter below the lowest branches (Barker

2010). Then the vertical cut is made with the sharp blade of an axe. The axe point should slip through the cork layer to the inner bark, but without penetrating in it. The first cut is followed by others in a descending line down to the ground. At this point, the bark can be ‘unzipped’ from the trunk. The wedge shaped end of the axe shaft is used to lever the cork plank off (Figure 6). The rectangular cork plank is then grabbed and pulled out with moderate force as it should be separated easily. The plank itself can have variable dimensions; for stopper production cork planks have at average 1.19m height and 0.47m width (Costa and Pereira 2004).

Figure 6. Cork stripping: 1.first incision; 2.axe used as a lever in separation of plank; 3.puling the cork plank; 4.cork oak tree harvested in 2005**.**
Source: APCOR, 2006

Cork extraction is carried out by a large group of workers, sometimes 100 persons with different assignments. It is this picturesque event that has its place in the local culture. After extraction, trees have a light brown color, that with time and oxidation becomes reddish, and give the unique appearance to the oak forests.

Intensity of the cork stripping is related with tree size, and in Portugal it is regulated by law and good practices. The cork cannot be removed before the tree has overall cork perimeter at breast height (1.3 m) of 70cm (22 cm of diameter) (Pereira 2007). The age at which cork becomes productive depends on radial growth, but commonly the required diameter is obtained at 20-25 years of age. At that age, the first cork which can be extracted is virgin cork, but it is not used in stoppers production due to its lower quality caused by deep fractures and cracks. For the stoppers production cork in its third crop is used, at the tree age of about 40 years.

Industrial requirements for the quality of cork suitable for the processing assume thickness of the plank at the first place, and absence of any defects and fractures. Thickness needs to be at least 27 mm to comply with the width of a stopper. The plank thickness from 3-3.5 cm, in most of the Portugal regions is attained in 9 years, which is the legal limit between two extractions. This can be seen in a cork section by counting the rings, with the year of extraction counting at two half years (Figure 7). Immediatly after separation, a first selection is done: bottom end of cork strip that is in contact with the ground is removed, and so a clean surface is obtained. Cork planks are transported to the field yard for the storage, or directly to industrial yard, to be proceeded in next step.

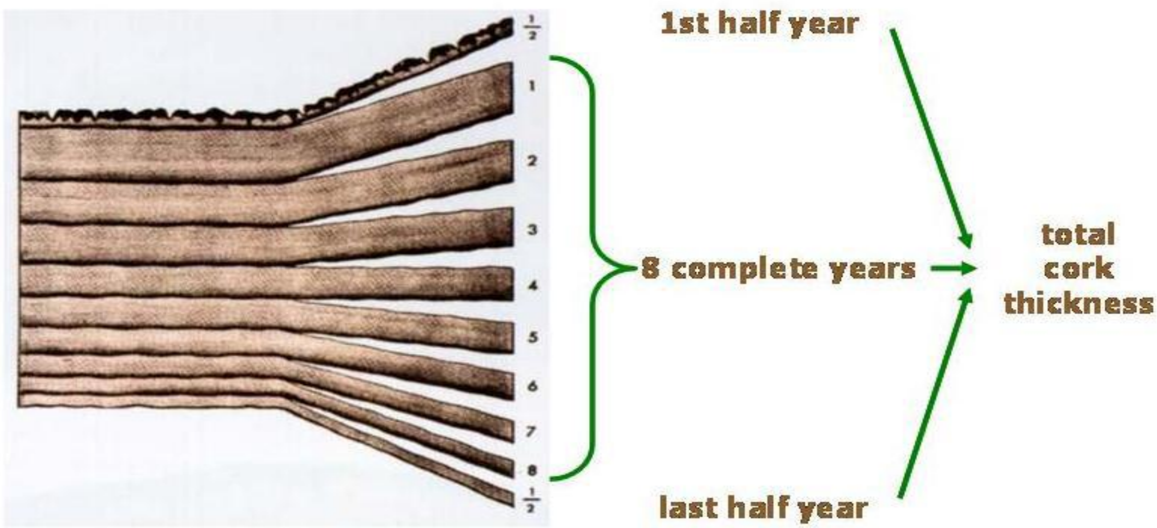


Figure 7. Scheme of counting rings for determination the age of cork

Source: Pereira, 2007

1.3.2 Post-harvest processing

In the field yard piles of cork planks are assembled. As for cork stripping, for this procedure experienced workers are needed, since very often visual appreciation of the pile is the first condition for the potential buyers. Location must be leveled and dry and approachable for transport, with enough air circulation to allow drying of inner layers. Cork barks are piled on each other with the cork bark facing up, around 2-2.2 m high and usually 8-10 m wide. Time of field storage of the planks is not determined by rule; it depends on buyers need and availability of industrial mill. The objective of this outdoor exposure (seasoning) is to oxidize polyphenols dry the inner layers and stabilize the cork texture (Silva 2005).

Recently, cork planks are being transported directly to the industrial yard, without field storage. In the yard storage, there are also procedures to be followed to avoid contamination, and assure preservation of the piles (Figure 8). Yards are normally a large area to maximize aeration and drainage of the planks, and with a small slope for preventing accumulation of rainwater. Piles are separated by geographic origin, tagged and recorded, as a first step of traceability within the process. After a period of storage of at least 6 months, planks are placed on pallets and prepared for the next phase of industrial processing, water boiling. During this operation, planks with lower quality, with eventual signs of moulds or yellow stains are separated and refused, and planks with thickness lower than it is necessary for stoppers are separated. Recently some producers such as Amorim use stainless steel pallets to reduce any microbiological spoilage.

Figure 8. Pile of cork planks and pallets with planks in the industrial yard, Amorim

1.3.3 Industrial processing

Industrial processing of cork raw material has as primer objective production of stoppers and discs from natural cork, so reproduction cork is aimed for during production. All the other types of raw material, wastes from production of natural cork stoppers and other by-products are used to make agglomerates (Figure 9). Natural cork products are made up by solid cork as a single piece punched from the cork plank, including stoppers and discs. Agglomerates are made up of cork granules bond together with or without adhesive, and they include three types:

a) cork agglomerates made up of granules glued together with adhesive and hot pressed. They are used for agglomerated cork stoppers, or the body of technical stoppers, production of boards and sheets

b) pure expanded agglomerates, or black agglomerates, made up of granules bounded without adhesive at high temperature. Common application of those is for insulation materials.

c) the cork and rubber composites, made up of granules of cork and rubber after surface activation. They are used as a shock absorbers in industrial and surfacing equipment

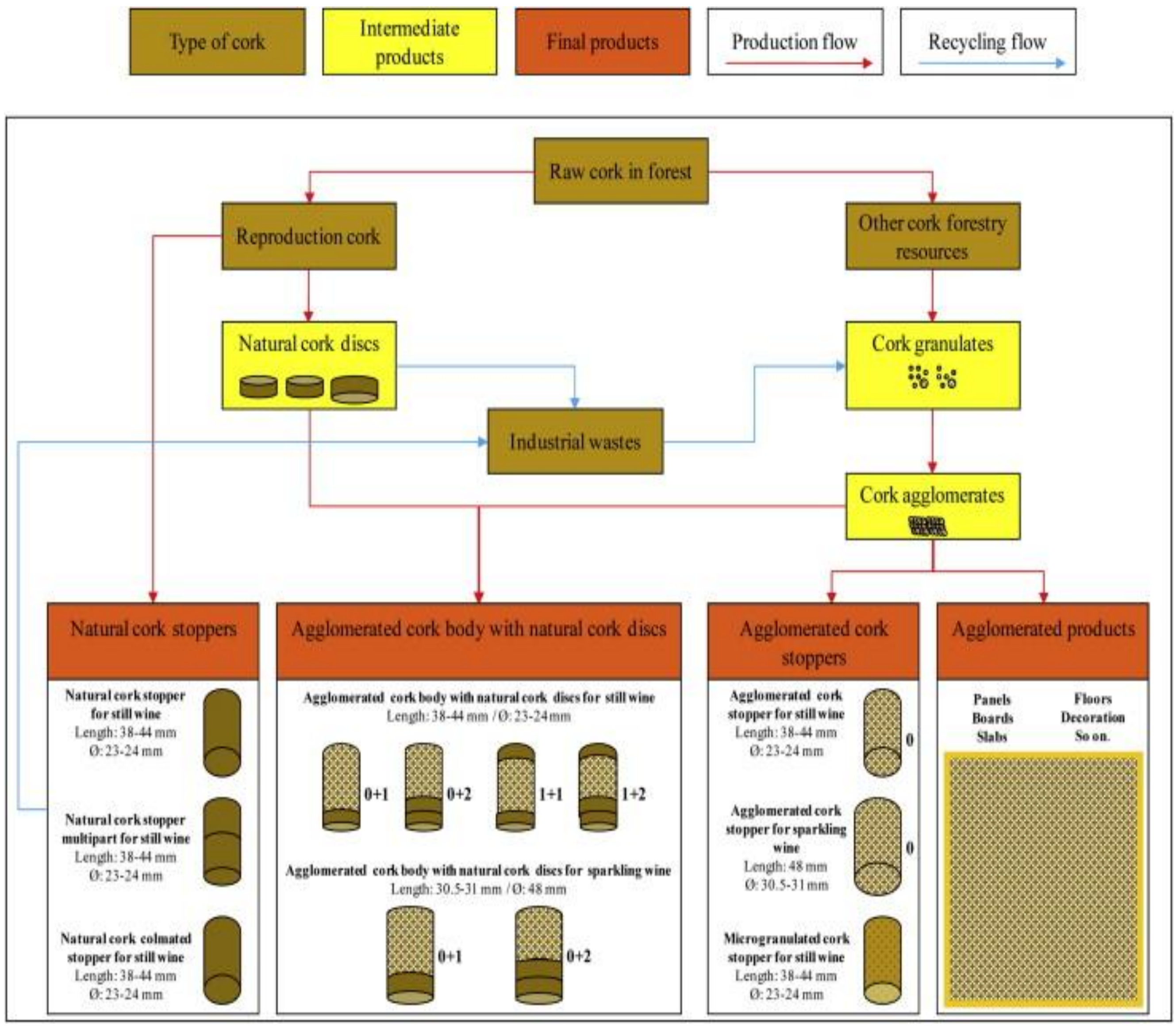


Figure 9. Scheme of flow of cork material in the industry
Source: Journal of Cleaner Production, 2012

During the production process of stoppers, cork goes through different stages:

1. boiling of cork planks,
2. stabilization,
3. selection and trimming,
4. punching of stoppers,
5. washing and drying,
6. classification,
7. surface treatment.

1.3.3.1 Boiling

Boiling is a process of immersion of cork planks placed on stainless steel pallets in autoclaves with the addition of clean, not-chlorine treated boiling water. The autoclaves are closed and treatment lasts for one hour (Figure 10). Water with constant temperature of 95°C is circulated within stainless steel autoclave with filters in order to remove suspended solids. After an hour, autoclave is emptied, and pallets taken out.

Traditionally, planks were boiled in tanks and allowed to dry, and then re-boiled if they were selected as wine stopper material. This step was subject to much criticism hence the water was not changed frequently enough and with batch after batch being boiled in the same water, the risk of microbiological cross-infection was high. Much research and development was undertaken and Amorim, for example, developed a new process which has been used on all corkwood since 1999. The planks are boiled in closed steel tanks fitted with a device known as a volatile compound trap. This process, referred to as the Convex process, continuously extracts volatile compounds, such as trichloroanisole (TCA) (Barker 2010).

This new process differs from the old one as the cork planks are boiled in smaller, two ton batches and the even temperature distribution and improved water circulation improves the extraction of contaminants. It is also a dynamic system where washwater is pumped through a tank and then filtered to remove suspended solids.

Figure 10. Boiling operation of planks in closed autoclaves: placing pallet with cork planks in the autoclave

Source: APCOR, 2006

The entire water volume is filtered every 20 minutes. Non-chlorinated, filtered water is used which is regularly tested to ensure absence of chemicals. The boiling process is not only undertaken to remove the micro flora within the bark. The aim of this procedure is at first place to change mechanical properties, thereby make cork planks softer, more elastic and flattening them, which will make easier later trimming process. Before boiling, the cork cells are compressed in irregular structure, but during the process, the gas contained in the cells expands, growth stress in cells relief and as a result, the cellular structure of the cork becomes more uniform.

Boiling increase plank thickness trough the straightening of the cell walls, approximately 15% in the radial directions (Rosa 1990). Porosity decrease with the decrease of lenticular chanels (Cumbre et al. 2001) and density is reduced. During the boiling process cork is cleaned and small amount of water-soluble substances are extracted, less than 2%, supporting the claim that extraction is not the objective of the procedure (Pereira 2007).

Boiling is one of the operations prescribed by the International Code of Cork Stopper Manufacturing Practices. It is an operation which, in addition to improving the internal structure of cork, also contributes substantially to reducing the microflora contained within it. A number of cork stopper manufacturers use additional processes to achieve improved disinfection. For example, some have implemented boiling processed in an enclosed environment.

1.3.3.2 Stabilisation

Stabilisation is the step after boiling, where planks are stacked on the top of each other on the pallets and left to air dry and stabilize for some time, i.e. several weeks (Silva et al. 2005) or a few days in new industrial practices (Pereira 2007). Planks are placed in well ventilated and humidity controlled warehouse. In this step, planks are flattened and dried. The moisture content decreases from 40% to 70% immediately after boiling, to values 14-18% after 2 days (Pereira 2007), what is considered an adequate moisture content in industry.

1.3.3.3 Selection and trimming

In this step, planks with major defects are separated from further production of natural stoppers. Parts with yellow stains, mouldy patches, insect galleries, large extent of failures, cracks as well as too thin parts are refused, and taken out for trituration. Planks are sorted by thickness and quality, where heterogeneous planks in terms of thickness or quality are cut in several small homogeneous parts and large planks are divided in sub planks that can be easily handled (Figure 11).

Figure 11. Trimming of the edge of the plank

With trimming good planks get the edges straightened and better looking cross sections and then planks are separated into quality categories based on their thickness, porosity and appearance. The thicker planks are used for the production of whole, natural corks while the thinner planks are used for cork discs. Common practice today is the separation in three thickness classes: 14-22, 22-27 and >27mm and two quality classes, first from 1st to 5th, and second 6th quality class with lower value (Silva et al. 2005).

1.3.3.4 Punching

After preparation of the planks with the thickness above 27mm, they are cut into parallel strips with a width slightly (1-2 mm) greater than the length of the corks to be manufactured, for instance 38 mm that is most common length dimension of wine stoppers (Figure 12). Vertical rotating blade discs make cutting lines horizontally in the plank, perpendicular to the axial direction of the plank.

Figure 12. Cutting cork strips with automatic functioning

Source: Pereira, 2007

Punching is the manual or semi-automatic process where the cork stopper is punched with cylinder axis in axial direction of the cork strip (Figure 13). This punching direction is the reason why two circular tops of the stopper correspond to the transverse sections. That is also the reason why the thickness of the cork plank needs to be more than 27mm, so it can be made a cork stopper with 24mm width which is the most common diameter of a wine stopper. The result is a cylindrical stopper of the required dimensions. The best seal is obtained when the axis of the stopper is parallel to the prism axis of the cork cells, so that the circular symmetry of the cork and its properties are used to best advantage (Cumbre et al., 2000)

Figure 13. Cork strip after punching out a stoppers using automated equipment

Source: Pereira, 2007

Each raw cork stopper is cut to size, polished and graded (Valverde et al. 2000). The corks are polished to ensure that the ends are regular and that the stoppers are with the required length and even in texture. This polishing is done using an abrasive stone.

The punched strips are by-products, used for trituration in granules and production of agglomerates.

1.3.3.5 Washing and drying

The selected stoppers undergo washing and disinfection, most commonly by washing in an aqueous solution of hydrogen peroxide called bleaching. Washing is the step with objective to clean the surface dust and disinfect the surface lenticular channels. It can be done with water, or with addition of oxidants such as hydrogen peroxide or paracetic acid, and then increase bleaching of the surface.

The process of washing corks began over a century ago. The cosmetic appeal of cork was certainly improved in the process but it was the deep cleaning into the thousands of pores which could introduce bacteria. The traditional wash involved washing of corks in a chlorinated lime and oxalic acid solution. The cork was disinfected and a residual layer of calcium oxalate created an acidic environment so as further to protect the cork. Safe and sound seals are produced in this way, however if done incorrectly washing can contribute to off flavours in a wine (Barker 2010). Laboratory tests are undertaken to check the quality throughout the process. In a quest for chlorine free washing processes, two such methods were developed in the1980's. One option is the use of a mild hydrogen peroxide solution. The other uses potassium metabisulfite. The washwater itself can also be treated with ozone to destroy contaminants. Amorim claims to have an innovative washing and extraction process known as INOS II, by which the interior of the cork is completely washed by pumping hot purified water into and out of the lenticels using pressure changes. After the bleaching, stoppers are dried at 40-60°C on air pressure or in microwaves, until the final moisture content 5%.

1.3.3.6 Classification

After the bleaching and drying, stoppers are graded in up to seven categories (Borges and Cunha 1985). The objective of classification is to separate the finished stoppers into different classes, according to macroscopic appearance. In the past, this was done manually with each stopper visually estimated and sorted. Nowadays, there are sorting machines based on machine vision, where cameras register each stopper lateral surface and top, and image analysis give porosity characteristics and allow classification regarding it (Figure 14). In some cases, selection is carried out visually and manually, relying on the human eye. During this phase, in addition to establishing quality classes, defective stoppers are eliminated. In standard selection processes, the following categories are usually used, defined according to visual criteria: Flor, Extra, Superior are premium classes, then lower qualities 1st-6st, and refused.

Figure 14. Automatic sorting machine based on vision technics
Source: Pereira, 2007

1.3.3.7. Surface treatment

Final operations are printing of the stoppers with client brand and surface treatment. Surface treatment is coating the stopper with a lubricant film with the aim to reduce the friction while cork placing in or out of the bottle neck. For that purpose the most common is the use of emulsified paraffin and silicon. They are then tumbled in industrial dryers, bagged and dosed with a small 35 parts per million of sulphur dioxide to prevent contamination en route to the winery or while being stored. Cork companies in all the world, receive the batches from Portugal, perform quality control checks, de-dust the corks and then print the relevant branding for their local clientele. Traceability codes are nowadays also being printed onto the cork. An invisible food grade and ultra-violet sensitive ink is used to ensure that each cork has an identity document of its own. The corks are then ozone sterilised, surface coated and packaged.

1.3.3.8. Colmation process

The stoppers with lower quality due to higher porosity coefficient, normally 5th and 6th but sometimes 4th class, are usually further processed with colmation of their surface. Colmation is a process of sealing the pores on the surface of cork stoppers (lenticels) with a mixture of cork powder obtained from the dimensional rectification of natural cork stoppers and a glue, based on natural reisin or a rubber binder. The purpose of the glue is to fix the cork dust in the pores. At the present, water-based glue is commonly used in this process.

In the first step, stoppers are well cleaned from the dust, or de-dusted. Cork powder is mixed with the water based glue, and applied on cork stoppers. Duration of the colmation process is one hour, and half of that time – 30 min is performed at temperature not lower than 50°C. This temperature is needed for polymerization of the glue. After that time, the stoppers can be submitted to further superficial, cosmetic treatment, to improve the visual appearance of the surface and increase uniformity.

After colmation and cosmetic coating, the stoppers are treated with silicon and paraffin emulsion as final superficial treatment.

Colmation has two main purposes, improving the appearance of the stopper and improving their performance.

2. CORK PROPERTIES

Despite the fact that cork has been known to men since ancient times for its distinctive characteristics and various applications, research of its properties from a material science point of view started in the 1980s, and important findings in chemical properties in late 1990s. Still, there are a lot of features of cork and its properties not fully exploited, and therefore further research is needed.

2.1. MACROSCOPIC APPEARANCE

The quality of cork raw material and final products is a key factor in industrial processing. Cork planks intended for natural stoppers are visually inspected and selected to guarantee the best appearance and properties. The stoppers are manually or automatically selected, where stoppers for top quality wines undergo another, finer selection. Selection is essentially based on external surface analysis (Lopes and Pereira 2000). Quality depends on the extent of natural porosity and existing defects such as cracks and insect galleries. The macroscopic porosity of cork, the main indicator of quality, corresponds to the prevalence of lenticular channels that cross cork planks radially, from outside to the inner tissues of phellogen. They appear in tangential section as pores with more or less circular form, whereas in radial and transversal section they appear as channels (Figure 15).

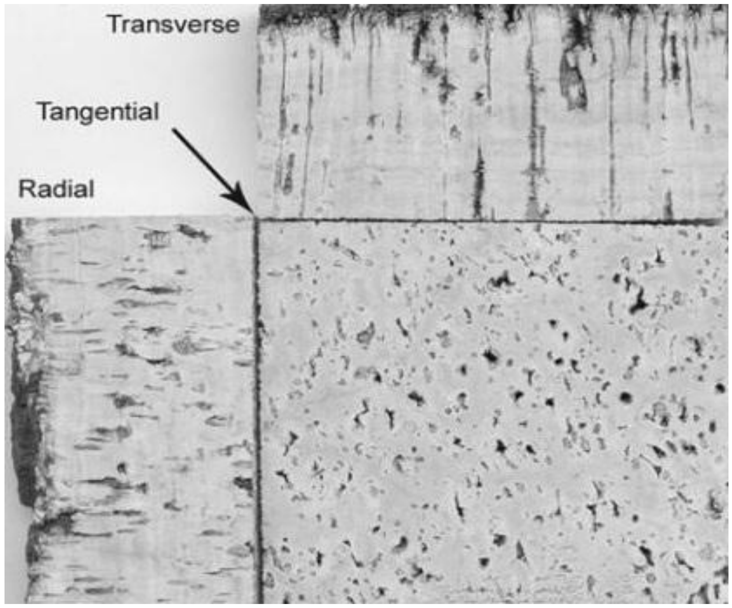


Figure 15. Lenticular channels in transversal, radial and tangential section

Source: Pereira,2007

Lenticular channels are filled with dark-colored, non-suberified material, occasionally lined by heavily lignified cells and such of their appearance actually represent distinctive macroscopic mark of the cork (Pereira et al. 1996, Pereira 2007). Their number, dimensions, concentration and distribution are the main factor for classification of cork into quality classes (Costa and Pereira 2007).

There is a large variation of porosity between different trees, as well as in early and late cork. The total porosity of the cork plank decreases by approximately half as a consequence of the boiling process, the expansion during boiling inducing the formation of larger pores (Cumbre et al. 2000).

Lenticular channels are the main factor for quality classification of raw cork and cork products. In cork closures, lenticular chanels or pores are found in small number and dimensions in best, extra and superior quality stoppers, and no defects are found (Figure 16). Lower quality stoppers are considered to have higher porosity, cracks and bigger areas of woody inclusions (Radeva et al. 2002).

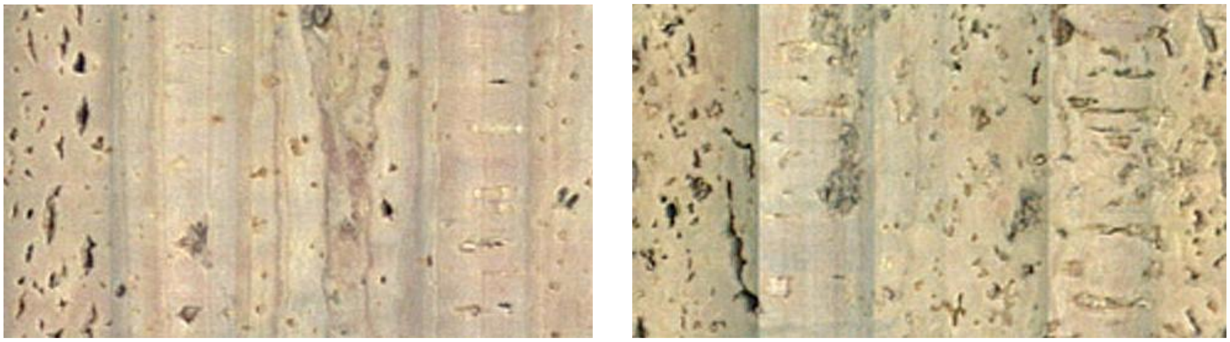


Figure 16. Cork stoppers body cylindrical surface for two quality classes, best quality (left) and lower quality (right)

Source: Costa and Pereira, 2010

Visual quality is determined according to the criterion of experienced operators who classify the cork planks by visual inspection bearing in mind factors of visual quality. In the past this classification method was completely manual and not standardized. Studies have shown that although it exists a certain degree of coincidence among skilled operators when classifying cork, it was not uncommon for various operators or even individual operators to differ in their classifications clearly suggesting that this system had lacks in scientific accuracy. Inspite of subjectivity of criteria, this system had very important role in the overall process (Pereira et al. 1994).

At present, the quantitative classification is done using image analysis: visually set references and image processing and automatic vision. Automatic visual equipment based on line scan cameras and computers embedded in industrial sorting machines are installed in all cork stopper industries. The system is capable of acquiring and processing in real time the surface image of cork stoppers, with high production rates and adopting quantitative sorting decision rules aimed at overcoming human subjectivity (Chang et al. 1997). Nevertheless, after the automated inspection, for a more correct classification of the stoppers with high quality demands, usually a final manual inspection is done (Costa and Pereira 2007).

Images of cork surfaces (tops and lateral surfaces) are taken by video or photographic equipment and then processed by image analysis techniques. The objects can be distinguished from the background by different color intensity or composition may be extracted from the image by adequate tresholding of the grey level. Image analysis techniques applied to cork are based on the measurement of the number of pixels with a grey level above a selected threshold value, thereby classifying the area observed into only two categories: cork and defects (pores and other defects read as pores) quantified by a porosity coefficient (Costa and Pereira 2007).

Lenticular channels have different color intensity and can be extracted from the image by tresholding of the grey level. Grey level scale goes from 0-254, corresponding to pure black and white respectively. The cork tissue has gray level between 100-120, while the filling of lenticular channels has between 170-200, and each color - red, green and blue, has their grey-level thresholds. The maximum and minimum gray-levels of pixel intensity for pores extraction from the cork mass in image tresholding are respectively Red 126-164, Green 114-158 and Blue 118-161 (Costa and Pereira 2009).

Image extracted pores can be quantitatively characterized like individual objects, with specific dimensional, shape or concentration type variables, and the defined observation area can be characterized by the average characteristics of the pores or by their concentration (Pereira 2007). Dimension type variables are: area, width, length, diameter (orthogonal distance between two parallel lines that completely include the pore). Shape type variables are shape factor (sf), measures roundness of the pores, esfericity (measures elongation of the pore, and has a value 1 for perfectly circular particle), aspect ratio that represent ratio between width and the length of the pore and orientation, angle of the longest chord linking the gravity center to the periphery. Concentration type variable is the next neighbor distance, or distance to the closest pore (nnd, mm). The number of pores per unit area and proportion of the area occupied by the pores are also very important variables to express porosity of the cork. Percentage of the area occupied by pores in total area of the sample is called coefficient of porosity.

For sample characterization, average and maximal values of these variables are used. Obtained data are filtered to exclude very small pores (bellow 0.5 – 0.8mm^2), hence they are functionally irrelevant and bring higher variance and variability to the sample (Gonzalez-Adrados and Pereira 1996, Lopes and Pereira 2000).

There are several studies that have investigated the use of image analysis techniques for quantification of porosity in cork planks (Molinas and Campos 1993, Gonzalez-Adrados and Pereira 1996, Gonzalez-Adrados 2000), in cork discs (Lopes and Pereira 2000), and in cork stoppers (Costa and Pereira 2005, 2006, 2009).

Studies on image analysis techniques also investigated computer vision systems in quality characterization and classification of natural cork stoppers (Costa and Pereira 2005, 2006). Different quality class stoppers have shown different values for the concentration variables like coefficient of porosity or number of pores per 100cm², dimensional variables like maximal pore area, or maximum length and width of pores, while shape variables stayed rather constant and showed no differences between quality classes (Costa and Pereira 2005).

Several studies have shown that coefficient of porosity can be used as a good indicator of cork quality. For example, Lopes and Pereira 2000 concluded that it could be applied for the quality grading of champagne cork stoppers.

The porosity expressed as porosity coefficient was mostly correlated with maximum pore area and with number of pores. The porosity was higher in lateral bodies than in tops, clearly because the area observed by image analysis is higher for the lateral surface than tops. The study had also shown that there were variations of the pores characteristics within the same quality class, and overlapping due to the stoppers variability in the same class (Costa and Pereira 2005).

2.2 CELLULAR STRUCTURE OF THE CORK

The cellular structure of cork is well known (Pereira et al. 1987, Gibson 2005) and cork tissue has retained a special place in the history of plant anatomy. Robert Hooke was the first to examine thin sections of cork under the microscope in 1665, and revealed its cellular structure (Pereira 1988). Cork structure was also observed and detailed by scanning electron microscopy (SEM) (Pereira et al. 1987).

For the description of the different directions and sections in cork structure, nomenclature used in plant (wood) anatomy is commonly used (system associated with the tree growth. Figure 17 displays section of cork tree with its layers and different directions.

There are three directions corresponding to three axes, x, y, z: tangential, radial and axial direction respectively. Following, there can be seen three sections: transversal, perpendicular to axial and containing radial and tangential direction; tangential, perpendicular to the radial direction and containing tangential and axial directions; radial section, containing axial and radial, and perpendicular to the tangential direction.

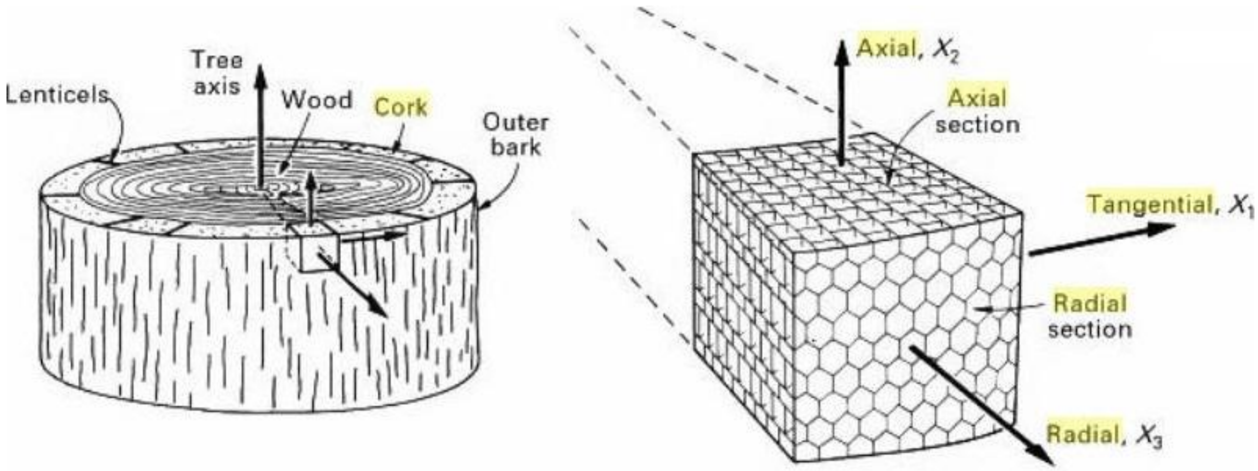


Figure 17. Sections of the cork structure

Source: Gibson et al. 1981

Because the lateral cell walls (parallel to the radial direction) are randomly oriented, cork can be considered, in a first approximation, as a transversally isotropic material, implying that all directions perpendicular to the radial direction (i.e. the axial and tangential directions) are nearly equivalent (Pereira 1992).

Cork is characterized by an alveolar structure, with a cells displayed as a honeycomb arrangement with no empty intercellular space between them (Gibson 2005). The cork cells can be described as rectangular prisms, packed base-to-base in columns parallel to the radial direction of the tree. SEM observations show that in a radial section cork cells appear as 4- to 9-sided polygons (Figure 18a). Axial and tangential sections show a structure that resembles a brick wall (Figure 18b).

The lateral faces of prismatic cork cells are corrugated (Figure 19), with two or three complete corrugations per cell (Gibson et al. 1981). Corrugations are irregular, from almost straight to almost collapsed cell walls, and they are result of compression during cell and bark growth (Cumbre et al. 2001).

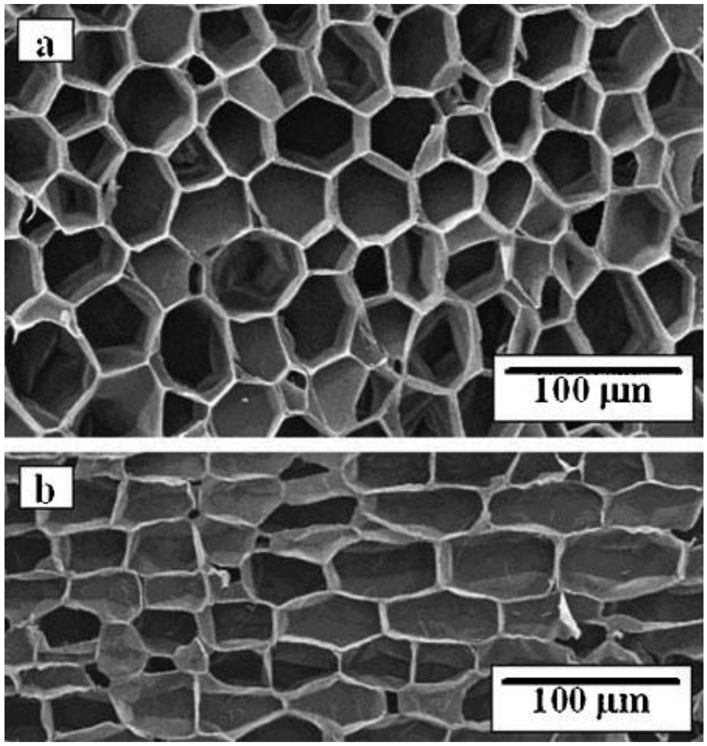


Figure 18. SEM micrograph of natural cork in a) radial and b) tangential section

Source: Silva et al., 2005

In different stages of the cork growth, they are varying between heavily corrugated cell walls at the beginning of growth when cork has thin cell walls and bigger prism height, and much less corrugated thick and rigid cell walls of late cork, with reduced size of prism. Therefore, cork cells have different dimensions in different stages of growth, and it said that cork has anisotropic cellular structure with anisotropic properties (Gibson et al.,1981).

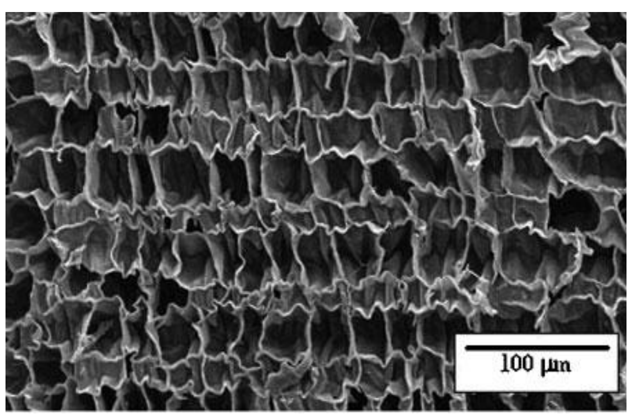


Figure 19. SEM micrograph of tangential section of cork with cells corrugation

Source: Silva et al., 2005

The cork structure with closed and hollow cells is the reason for cork specific properties, like specific mechanical properties: cork lengthens when it is under stress and shortens when it is compressed (Baptista and Vaz, 1993). Very low specific weight, with small solid fraction concentrated in thin cell walls and without any intercellular communication, makes cork floating on the water and absorbs water very slowly (Silva et al. 2005). The cork hydrophobic character and low permeability for the liquids are among the main reasons for cork domination as a sealant for bottles and other liquid containers.

Density in the cellular solids such as cork depends on the solids that make up the cell walls and solid fraction occupied by cell walls in total volume (Pereira 2007). Density of the air-dried cork is low, on average 150-160 kg/m^3 but values can go below 120 to over 200 kg/m^3 (Pereira 2007). It is expressed as mass of volume (kg/m^3), and specified at defined moisture content because of changing cork mass and volume with water absorption. If density is equilibrated under natural air conditions, it is called air-dried. Density of cork depend on its structural features: the size of the cells, proportion of earlycork and latecork in annual ring, corrugation of cells, extent of porosity and presence of woody inclusions and discontinuities. Corrugation degree is increasing, so as density, with agglomeration of cork granules, but also in cork in bottle neck, and decreasing with boiling process of planks. More lenticular channels and larger size give higher density values, and voids, like insect galleries or lung failure-lower (Pereira 2007).

Absorption of the water in the cork is going in three phases: faster initial phase where water is absorbed rapidly with constant rate, second with slowing of the rate and last phase, where absorption is very slow, and mass is almost not changing, showing there is almost no water uptake (mass variation is indicator of water absorption). Maximum absorption is achieved when mass increase is around 60% (Fortes et al. 2004). Structural anisotropy of the cork explains different absorption rate in different directions, higher in radial than in non-radial. Absorption rate is increasing with temperature: maximal water absorption is achieved after 8000h on 20°C or 100h on 90°C, when cell walls are saturated (Pereira 2007). From this can be concluded that absorption is a very slow process at the ambient temperature, depending on cork position, density and porosity.

When absorbing water, cork changes its dimensions, what is called swelling of the cork. The swelling is larger in non-radial than radial directions about twice (Pereira 2007). In the experiments at 20°C maximum swelling was attained after 70 h with radial expansion of 0.7%

and non-radial 1.8%, where maximum volume increase was 4.4% for water content of 58%. (Rosa and Fortes 1993). Swelling increase with the temperature increase: with immersion in water at 100°C, maximum volume increase is 7.8% (Pereira 2007).

2.3 MECHANICAL PROPERTIES

Mechanical performance of the cork is specific and differentiates it from other materials. Beside playing a positive role in the evolution of bottled wine, a suitable closure for wine should be easy for the consumer to extract from the bottle (Deves 1997). To fulfill this requirement, sufficient compression against the bottleneck must exist, so as contact between closure and bottle surface to avoid liquid percolation.

The mechanical properties of cork were studied mostly in compression, due to its relevance for the performance of cork stoppers in wine bottling and sealing (Rosa and Fortes 1988, Gibson et al. 1981, Gibson and Ashby 1997). Cork is elastic, allows large deformations under compression without fracture and dimensional recovery after stress is relieved. As result of application of large loads is compaction of its cellular structure and densification. Cork fracture happens only when it is stressed under tensile and torsion forces and deformation overcomes material strength (Pereira 2007).

The mechanical properties of the material present their resistance when subjected to an external force, and include resistance to deformations and distortions (elastic properties), and failure related (strength properties). Stress-strain curves are commonly used for describing mechanical behavior of the material (Gibson et al. 1981). Stress is a measure of internal forces resulted in material after application of external force. It is calculated as the force applied per unit area of the section perpendicular to its direction of application and it is measured in Pascal units (Pa.) Strain measures material deformation while under stress, and it is calculated as deformation per initial dimensional unit (%). Strength corresponds to the material`s ability to resist applied forces and represents the greatest unit stress material can stand without fracture.

It is said that material is elastic when after being submitted to external forces and deformed by a stress, it regains the original dimensions after stress is removed. When it does not recover its initial dimensions and stay with permanent distortion, material is plastic. Viscoelastic material behaves between these two ways, where dimension recovery is not complete and there are remains of residual deformation.

The compression (stress–strain) curves for stoppers are characterized by three regions: (i) the initial elastic region, corresponding to the reversible bending of the material; (ii) the second collapse region, corresponding to progressive buckling of the material which cause a decrease of the slope of the compression curve; and (iii) the final densification region, when a critical stress is reached and the curve increase rapidly with strain (Gibson 2005) (Figure 20). The elastic region (i) corresponds to the linear part of the curve where stress and strains are directly proporcional under Hooke's law: $\sigma = E(\varepsilon)$. This is happening in the first phase when apply force, when stresses are small, and elastic deformations are up to a strain of 5-7% approximately (Pereira 2007). The second region (ii) starts after yield point (elastic point) and forms almost horizontal large plateau, with curve small inclination for strains up to 50%. The third region (iii) corresponds to the sharp increase of stress, where strain starting about 70% and in the usual compression tests goes to 80-85% (Pereira 2007). In this phase densification of the material appears, with permanent crushing the cells.

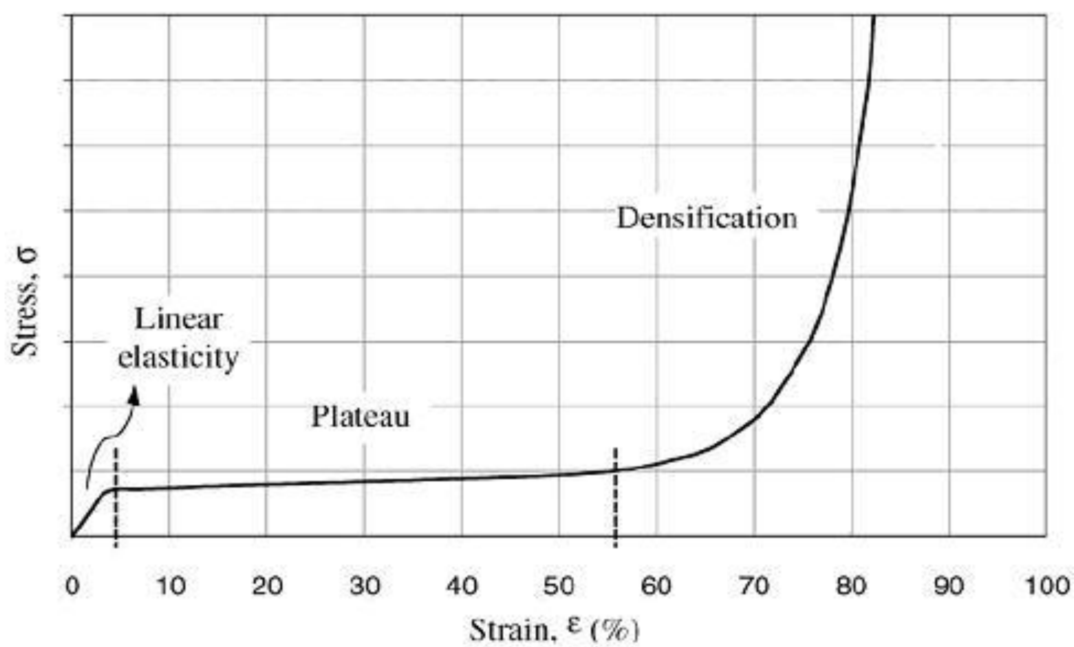


Figure 20. Example of typical stress-strain curve for the cellular foam

Source: Goga Vladimir, 2010

The elastic behavior of cork is described with the elasticity modulus, called Young's modulus. This modulus describes the relationship between stress and deformation strain. Young's modulus corresponds to the slope of the linear elastic region in the stress-strain curve, and it is usually calculated between two points corresponding to the small strains, for example between 1-2% (Gibson, 2005)

Cork is structurally anisotropic material, and shows the differences in stress/strain when the load is applied in radial, tangential or axial direction. Average values for the Young modulus are 18,3MPa; 16,9Mpa and 12,3Mpa for radial, axial and tangential direction respectively (Pereira, 2007).

Another mechanical property of cork is described with Poisson effect, corresponding to the variation of dimensions, usually an increase of dimensions in directions perpendicular to the direction of compression. Random arrangement of cork cell bases (Gibson et al. 1981, Pereira et al. 1987) and the corrugation of lateral cell walls influence the Poisson coefficient (n), which provides some of cork's most interesting properties that lead to its diverse applications (Fortes and Nogueira 1989). Poison coefficient is a negative ratio of strains in one perpendicular direction and in the compression direction. When cork is compressed in the radial direction, the cell walls fold and pack due to the corrugations, the amplitude of corrugations increases and the cell bases align perpendicular to radial direction. Both these effects cause a small expansion in the non-radial direction, which results in a small positive value for Poisson coefficient. When the compression is in the non-radial direction, the lateral cell walls bend, straighten and, at high strains leads to shrinkage in the radial direction and hence to a negative Poisson ratio at high strains (Fortes and Nogueira 1989).

During wine bottling the cork stopper is subjected to pressure of about the 30% that corresponds to collapse region. Materials that show the critical densification region at 30-35% strain are not suitable for wine bottling. The initial elastic region extends up to 7% and 10% in corks and synthetic closures respectively, whereas the collapse region begin up to 50% and 70% strain at synthetic closures (De Filippis et al. 2004) and corks (Silva et al. 2005). The natural cork, for example 24 mm diameter stopper, inserted in 18.5 mm bottleneck will have a strain of 23% and,a 26 mm stopper a stress of 29%. These values are in the plateau region on the stress – strain curves, corresponding the stress in range of 1 MPa, and buckling the cells of cork (Pereira 2007).

After insertion in the bottle, fast stress relaxation happens, from 1.2 MPa and 0.9 MPa for radial and tangential sections respectively, to 0.8 MPa in less than an hour (Fortes et al. 2004).

Extraction force increase with diameter and length of the stopper: larger diameter increase compressive stress and longer increase the contact surface. The ease of extraction depends on the structure of the closure which affects the adhesion (friction) to the glass bottle neck. With the surface treatments, adhesion of the surfaces, and therefore extraction force can be reduced. Natural cork stoppers should have extraction force above 200N and around 350N (Pereira 2007). The force of extraction should be >15 kg to guarantee a sufficient adhesion of the cork to the bottleneck. Values of extraction force >45 kg indicate that the closures cannot be easily removed (Silva et al. 2003, Chatonnet et al. 2005).

There are several studies on the mechanical properties of natural and synthetic cork stoppers. Giunchi et al. (2008) measured selected mechanical parameters for the characterization of wine closures (natural and technical corks, co-extruded and injected synthetic closures) in terms of compression force, extraction force and resilience. The results showed the presence of significant differences among the closures for the parameters tested. The force of compression was highest for corks (1006–1046 N), whereas lowest values were found for the synthetic closures (566–639 N).

3. MATERIAL AND METHODS

3.1. MATERIAL

The raw material was obtained directly from the world largest cork stoppers producer Amorim&Irmaos. For this study 75 natural cork stoppers were used (24mm x 45mm, diameter x length), already classified in different quality classes at the producer company.

The stoppers were divided in 3 groups, each with 25 stoppers: (i) stoppers of Superior class; (ii) stoppers of Inferior class to be colmated; (iii) colmated stoppers Classification was done automatically by sampling after inspection in the automated vision systems and followed by manual selection of skilled operators. Colmated stoppers were previously classified in the Inferior class of quality cork stoppers, and the colmation process was also done in Amorim.. For the purposes of the work, there was no application of surface treatments with paraffin and silicon on the stoppers, neither washing and bleaching.

Figure 21 displays an example of differences in appearance between the two groups of Superior and Inferior class. Cork stoppers. Each group is represented by one cylindrical body surface and top of the cork stopper.

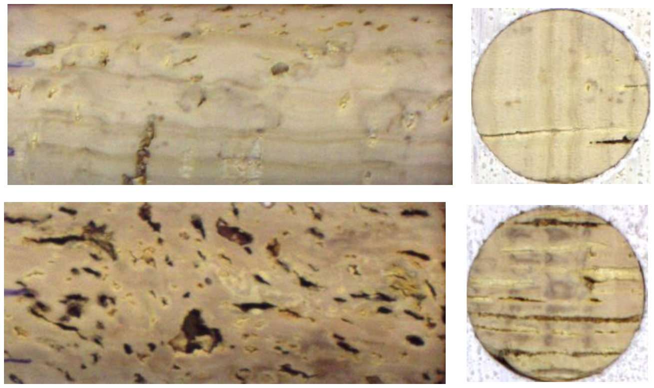


Figure 21. Cylindrical body and top for Superior (up) and Inferior (down) quality class stoppers

3.1.1. IMAGE ACQUISITION AND IMAGE ANALISYS

In order to obtain data regarding the quality of the cork stoppers based on their surface appearance, image processing was done. In this part of the work, two groups of stoppers, Superior and Inferior class with 25 stoppers each, were used. Colmated stoppers were not analyzed by image analasys, since the pores filled with the colmation mass are not differentiated from the cork mass. All the cork stoppers were proceeded in the same way, obtaining image surfaces of the body of cork stoppers (cylindrical lateral surfaces) and of the tops (circular bases).

The image of the cork surface was captured by photographic digital equipment and subsequently processed by image analysis techniques. Digital camera 7mega pixels ProgRes Capture Pro 2.7 with the lenses AF Nikkor 24mm was in an acquisition Kaiser RS1 Board with a column 89cm, with the high frequency illumination sistem and connected with the computer with Software AnalySIS® (Analysis Soft Imaging System Gmbh Münster, Germany, version 3.1)

Acquisition images were done with the same light intensity in form of RGB. In color RGB (red-green-blue) model, objects (defects in cork analysis) can be differentiate from the background by different color intensity, or by extracting from the image by tresholding the grey level.

Each cork stopper was fragmented at eight frames, named with capital letters A, B, C, D, E, F, G, H; therefore eight frames were acquired for the lateral surface (body) of each stopper. For each image, 12 stoppers were placed at the same time on the board, with the same marked frame-ROI captured in all of them (Figure 22).

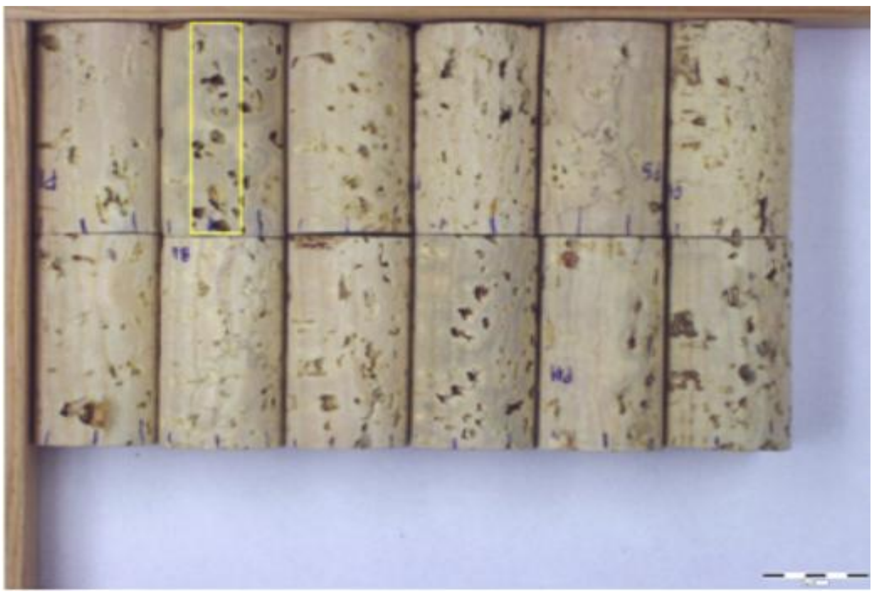


Figure 22. Cork stoppers in a frame during acquisition images with the marked ROI on the second stopper

The first frame (A) was perpendicular to the cork growth rings, what was observed on the cork top bases. The other frames were subsequently acquired rotating the stopper 45° in the right direction. Thus, frames A and E were tangential sections of the cork, knowing that stoppers are punched at cylinder axis of the strip in axial direction, frames C and G were radial while frames B, D, F and H were in between sections. The tops corresponded to the transversal sections of the cork.

For both, lateral body surface and circular cork tops, ROI (Region Of Interest) was predefined. For the body of cork stopper, rectangular frame of ROI covered the area of 425,39mm², and for the tops it was circular with area 406.25mm². Eight images were representing 100% of the lateral surface of the cork stoppers. Optimal conditions for visualization and tresholding were selected for the acquiring images of each cork stopper and optimizing tresholding and detecting the pores in the mass of stoppers (Figure 23). Therefore the same calibration and illumination conditions were used for all. Magnification used was 0.4705. The thresholds for defects (pores) extraction from the cork mass were adjusted for each image individually.

Figure 23. Frame with the stoppers, tresholding and detecting the pores in the second stopper

3.1.2. IMAGE DATA ANALYSIS

All the objects (pores) extracted from the obtained images can be measured and characterized as individual objects (Section 2.1). Each pore in the cork surfaces is characterized with a set of variables-dimension, shape and color type variables.

The dimension-type variables include: area, mean and maximum diameter, defined as the arithmetic mean and the maximum of all diameters (range angles between 0º and 179º, with step width of 1º), and mean and maximum rectangle, defined as the rectangle whose area is the average or the maximum of all rectangles.

The shape-type variables include: shape factor, defined as (area/perimeter^2)*4π, measuring the roundness of the pores; esfericity, that describes the elongation of the pore (value 1 for the perfect circular particle); convexity; aspect ratio, as the maximum ratio between width and length of a bounding rectangle of the pore; and orientation, measuring the angle of the longest chord linking the gravity centre to the periphery.

The color-type variables include the value of red, green and blue (RGB system) and hue, saturation and intensity (HIS system) for each pore.

In image analysis, each frame of each stopper was quantitavely described as one excel file, accordingly each excel file had the data from the pores of one frame. Therefore, for each stopper was obtained 10 excel files– eight for the lateral surfaces and two for the tops.

The first step was to filter obtained data, where only pores with area equal or superior to 0.1 mm^2 were considered for the analysis. Very small pores bellow the 0.1mm^2 are considered functionally and esthetically irrelevant and only bring higher variability to the sample (Gonzalez-Adrados and Pereira 1996, Pereira et al. 1996, Lopes and Pereira 2000, Costa and Pereira 2009).

After the pore data was filtered, calculations of the average values of variables for each frame were made as well as the maximum values (Section 2.1). Each ROI of each cork stopper was characterized by several calculated variables: the total area of pores (mm^2); total number of pores that representing sum of all the pores in frame area bigger than 0.1mm^2; largest pore area (mm^2); porosity coefficient (%), defined as the proportion of the area occupied by pores.

3.2. DENSITY AND WATER ABSORBTION TEST

3.2.1. DENSITY

Density is the mass of solid per unit volume, and it is expressed in kg/m^3 (detailed in section 2.2). It is calculated as $\rho=m/V$, where m is the mass in kg, and V is volume in m^3.

For the measurements of densitiy, 40 cork stoppers of two quality groups, Inferior and Colmated were used, with 20 stoppers of each group. Mass of the stoppers was weighed on a digital balance with two decimals. For calculating the volume the dimensions of the cork stoppers - cork length and cork diameter, were measured with the digital caliper. Volume was calculated knowing equation for the volume of the cylindar $V = r^2 \pi H$, where r is half of the cylindar (cork) base diameter, and H is cork height. Measurements were done on ambient temperature, in natural conditions. All data was recorded.

3.2.2 WATER ABSORPTION

For this test 16 corks of two different groups were used, 8 of Inferior and 8 of Colmated. Stoppers mass and dimensions were measured initially: mass on the digital balance with 1 decimal readout and dimensions with digital caliper with accuracy of 0.02 mm. The method used in this work is a common method used in cork industry as absorption test, for assesing the ammount of wine absorbed by stoppers.

Stoppers were verticaly placed in glass bottles filled to the top with 12% soluton of ethanol, two stoppers, one on the top of another, in each bottle. Solution of 12% ethanol was used to simulate conditions in the bottle of wine, where cork stoppers are eventually in contact with wine comonly having 12% alcohol content. Bottles were left in a hot chamber, at a temperature of 60°C for 72 h. After 72 h, they were taken out, excess of the water was gently cleaned with paper and cork mass and dimensions were measured in the same manner as before heating. Variations-increase in mass indicating absorbed ethanol solution, as well as volume variations indicating swelling, were calculated.

3.3. MECHANICAL TESTING

In this part of the work, two sets of 20 stoppes each, Inferior (Pre-colmated) and Colmated, were analized. The aim was to compare mechanical properties of these two groups of stoppers, and for that reason on each stopper was perfomed a compression test under the same conditions, at room temperature 20°C±2°C. For all stoppers, weight and dimensions (diameter and height) measurements were taken. The stoppers were almost the same size (length-diameter), hence the weight represented a good estimation of the density.

3.3.1 COMPRESSION TEST

The system for obtaining data about mechanical characteristics of stoppers included a universal testing machine Shimadzu AG-IS with 250 kN load cell capacity and TRAPEZiUM-X software based on a different testing styles. Equipment included also an air-conditioner, allowed a stable environment (20ºC±2ºC temperature and 65%±5% air relative humidity) in the room where the tests were carried out (Figure 24).

Figure 24. Universal test machine, equipment for mechanical tests of materials

Each stopper was separately positioned under the test machine compression plate for the applied load perpendicular to the tangential surface of the stopper. Compression was conducted with circular plate probe speed of 1 mm/min, what corresponding to constant rate strain of 0.17 mm/s. For each stopper two tests were done with different directions of applied load:, axial pressure was applied on the top surface (verticaly positioned stopper) and as perpendicular load to the stopper body lateral surface (horizontal position). For the second, pressure was applied in the radial direction of cork, accordingly lateral surface was tangential section of the cork and that was observed at the cork top: applied pressure was perpendicular to the cork growth rings. The specimen (stopper) was preloaded to 10 bs and then compressed, until 5% strain was achieved. The load at 5% strain was recorded.

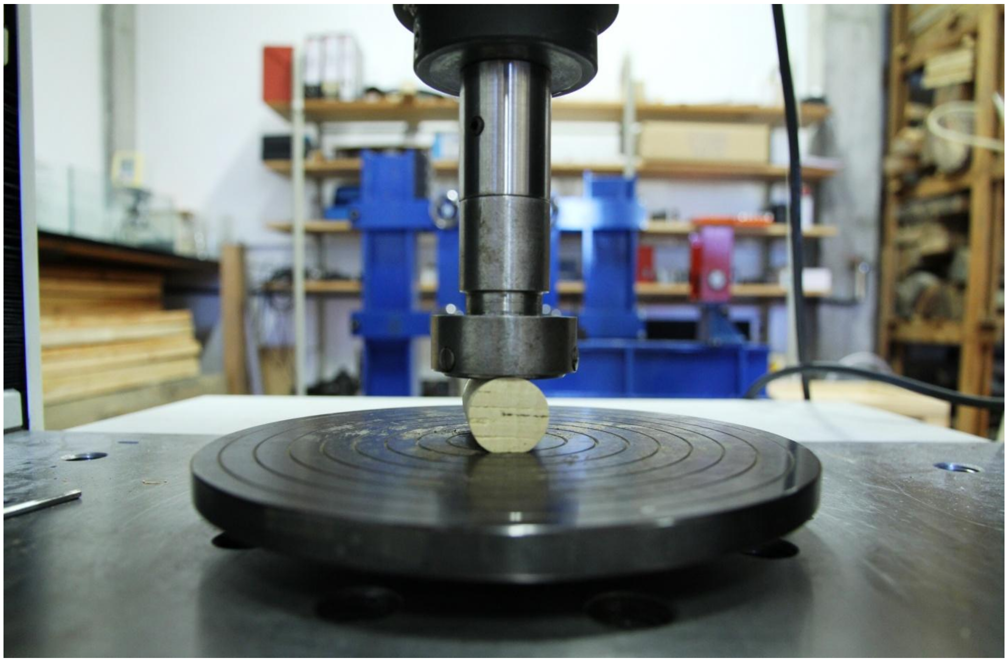


Figure 25. Transverzal ompression test conducted on cork body surface

3.3.2 Data processing

Data processing in the software used allowed direct calculations of Young's modulus. In each test, stress-strain curves and maximum force of compression were recorded (Figure 32). Young's modulus were calculated from the average slope of the curve, between loads of 10 N and 100 N, what corresponded to strains between 1% and 2.5%. Young's modulus were only calculated for compression in the axial direction of the stopper.

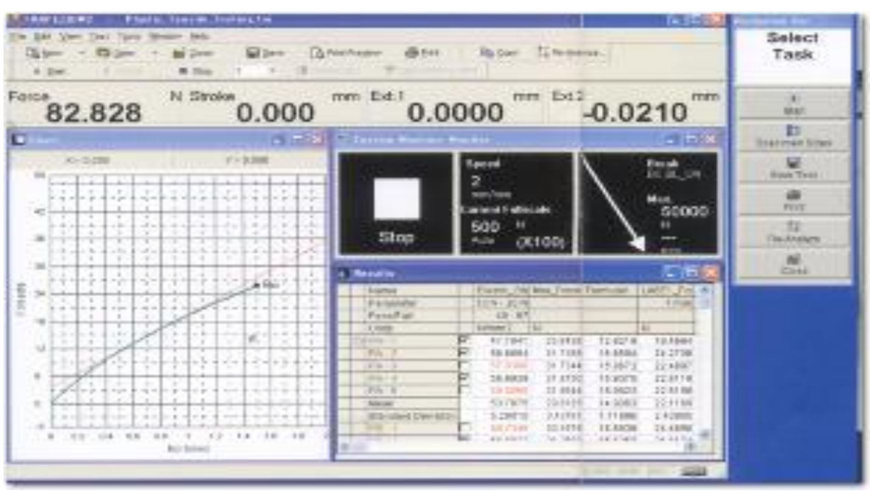


Figure 26. Image of software processing data obtained in compression test

Young's modulus, E is calculated by dividing the stress by the strain in the elastic (initial, linear) portion of the stress-strain curve:

$$E = \text{stress/strain} = \sigma/\varepsilon = (F/ A_0)/(\Delta L/ L_0)$$

$$E = (F*L_0)/ (A_0* \Delta L)$$

where

E is the Young's modulus (modulus of elasticity)
F is the force load on the stoppers under compression;
A_0 is the cross-sectional area on which the force is applied;
ΔL is the variation in stopper length after loading the force;
L_0 is the initial length of the stopper

3.4 SCANNING ELECTRONIC MICROSCOPE

The aim of this part of the work was to analyze the cellular structure of the Colmated cork stoppers and verify the presence of the colmation filling mass (cork dust mixed with resins) inside the cellular structure. Structure and cellular properties of the cork were detailed in Section 2.2. The structure of the cork was observed directly by Scanning Electron Microscopy. Cork samples were 3 different small size (less than 2 cm) pieces of Colmated cork stoppers, carefully sliced.

This analysis used Scanning Electron Microscope S-2400 Hitachi with Rontec standard EDS detector, with maximum voltage of 25 kV, diffusion-pumped, tungsten gun type, with maximum magnification 300.000x. Screened cork samples previously were prepared. Preparation called ‘spotering’ was done with gold/palladium in spotter coater, by bombarding the sample with Argon ions through plasma. Prepared 'piece parts' less than 2 cm on a side, were mounted on a specimen stub with conductive paste. After sample loading and evacuation, high voltage of 20kV was applied. Focusing was done with an automatic 'AUTO' mode which is usable up to 1000x. Minimum magnification was limited by the sample-to-objective lense working distance

(WD): 400x for TV mode @ 6 mm WD Images were 'photographed' with a Sony digitizer with printer. The images of the structure were taken in three sections of cork: tangential, transversal, and radial section, and were observed in real time. Recorded images were observed and described.

Figure 27. SEM equipment

4. RESULTS AND DISCUSSION

4.1. CHARACTERISATION OF CORK STOPPERS QUALITY FEATURES USING IMAGE ANALISYS

For each stopper of both quality classes (Inferior and Superior) the lateral (body) surface and top, pores were characterized with several independent variables with image analysis. Obtained data were filtered considering only pores bigger than 0.1 mm^2. Table 2 displays average values with standard deviation for dimension and concentration variables. It is noticeable that these values were different between the two quality classes: stoppers in the superior class showed less pores and smaller pores dimensions, whereas inferior class stoppers had higher values of all the porosity variables. This trend was observed both for the body surfaces and tops of stoppers. Apart of the differences between the two classes, variation between the stoppers was high in the same quality class too, which was represented by high values of standard deviation for the variables observed.

Table 2. Average porosity parameters and standard deviations for two quality classes stoppers, Superior and Inferior, bodies and tops

Cork stopper variable	Quality class	
	Superior	Inferior
Lateral surface (body)		
Total area of pores (mm²)	69,8 (22,4)	183,5 (72,7)
Nº of pores	114 (33)	229 (59)
Maximum pore area (mm²)	6,6 (4,2)	15,5 (6,5)
Porosity coefficient (%)	2,0 (1,1)	5,5 (3,1)
Top		
Total area of pores (mm²)	18,5 (9,8)	41,4 (17,5)
Nº of pores	23 (9)	27 (9)
Maximum pore area (mm²)	5,6 (3,6)	13,3 (6,9)
Porosity coefficient (%)	2,3 (1,0)	5,0 (2,1)

The porosity coefficient of the lateral surfaces was 2,0% and 5,5%, for the superior and inferior quality classes respectively. These values were in accordance with the results referred in the bibliography. Pereira et al. (1996) reported mean values for porosity coefficient between 3,3% and 6,7% from best to the worst quality class. Costa and Pereira (2005) presented values for the porosity coefficient of 1,6% and 6,2% for the Extra and 5th class respectively. The same authors referred similar values for the porosity coefficient of 1,4% for the Extra quality class; 2,1% and 2,3% for Superior and 1th class respectively and 4,2% and 4,5% for the second and third quality class respectively (Costa and Pereira, 2009).

The total number of pores on the lateral surface of the stoppers was 114 and 229 for the Superior and Inferior quality class respectively, and this number corresponded to the total area of pores of 69,8mm^2 and 183,5mm^2 for the same observed quality classes (Table2). Values referred in bibliography for tangential section of cork planks were 47 and 176 (Pereira et al.1996), corresponding to the pores larger than 0,8mm^2. Other referred values for the number of pores were 128 and 242 for the Extra and 5th class (Costa and Pereira, 2005).

For the lateral surface of the two quality classes, values found for the largest pore area were on average 6.6 mm^2 and 15.5 mm^2 for Superior and Inferior class respectively (Table 2). Costa and Pereira (2005) presented average values of 3.1 mm^2 and 26.5 mm^2 for the Extra and 5th class respectively. The same authors (2009) referred average values of the largest pore area between 3.5 mm^2 and 25.5 mm^2 of Extra and 5th class respectively, and average values for the Superior/1st class were 5.7 mm$^{2.}$ and for 2/3rd class 10.1mm$^{2.}$

For the tops, the observed porosity variables showed a similar trend, lower for the Superior quality class and higher for the Inferior. Porosity coefficient was 2.3% and 5.0% for those two classes respectively (Table 2). Referred values in the bibliography were between 2.5% and 8% for the transversal section of cork planks (Lopes and Pereira 2000), or a somewhat higher interval of variation, between 2.1% and 16.4% (Gonzalez-Adrados et al. 2000). The total number of pores was 23 and 27 for the Superior and Inferior class respectively, whereas maximum pore area had values of 5.6 mm^2 and 13.3 mm^2 for these two classes (Table 2).

Values of the porosity variables were similar to those referred earlier by Costa and Pereira (2005) and Gonzalez-Adrados et al. (2000). The differences could be explained with the fact that those works were considered pores with dimensions higher than 0.5 mm^2, while in this work pores bigger than 0.1 mm^2 were considered.

In the same quality class, the variation range of the variables was relatively similar for the bodies and tops. Table 3 and Table 4 present average, maximum and minimum values of the variables, for the Inferior and Superior quality class respectively. The average values for the porosity coefficient of the lateral surfaces and tops were 5.5% and 2.0% (Table 3) and 5.0% and 2.3% (Table 4), for the Inferior and Superior quality class respectively. Average values were similar in both quality classes, whereas from the maximum and minimum values it can be seen that the range was broader for the lateral surfaces when comparing with tops for both quality groups.

For the largest pore area, values were very similar between bodies and tops in the same class, 15.5 mm^2 and 13.3 mm^2 (Table 3) and 6.6 mm^2 and 5.6 mm^2 (Table 4), for the Inferior and Superior class respectively.

Table 3. Mean, maximum, minimum values and standard deviation for the porosity variables of the Inferior quality class

BODY SURFACE	mean	max	min	standard deviation
porosity coeficient (%)	5,5	10,8	1,9	3,1
number of pores	229	380	95	59
largest pore area(mm²)	15,5	27,6	6,3	6,5
TOP				
porosity coeficient (%)	5,0	6,5	3,3	3,0
number of pores	27	46	12	9
largest pore area(mm²)	13,3	27,4	2,5	6,9

The greater difference was in the number of pores, with higher variation range for bodies in relation to tops. On the other hand, number of pores was similar between Inferior and Superior class, 27 and 23 for these two classes respectively (Table 3 and Table 4). These differences can be explained with structural anisotropy of the lenticular chanels and the orientation of the stopper in the cork planks plank. (Pereira etal.1996, Fortes et al.2004)

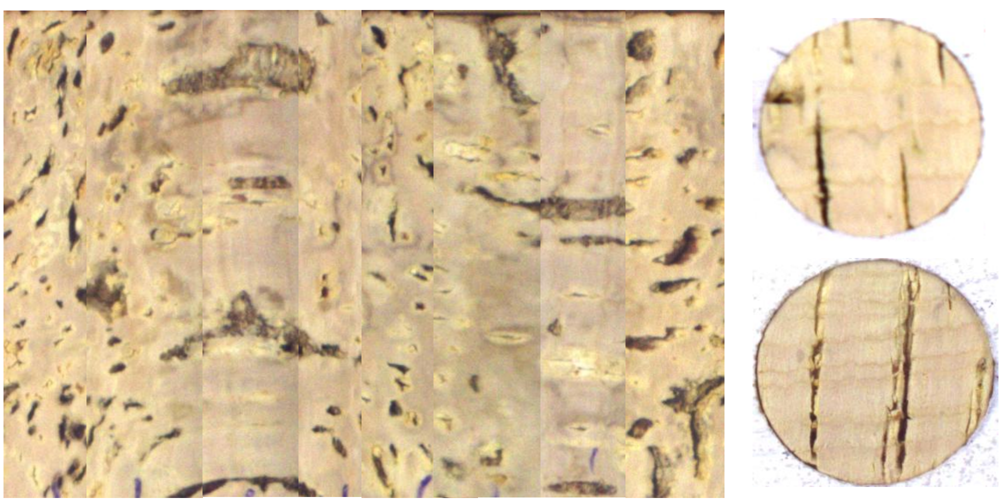
Table 4. Mean, maximum, minimum values and standard deviation for the porosity variables of the Superior quality class

BODY SURFACE	mean	max	min	standard deviation
porosity coeficient (%)	2,0	4,0	0,7	1,1
number of pores	114	174	33	54
largest pore area(mm²)	6,6	19,6	2,1	4,2
TOP				
porosity coeficient (%)	2,3	3,0	1,6	1,0
number of pores	23	41	5	9
largest pore area(mm²)	5,6	15,0	0,9	3,6

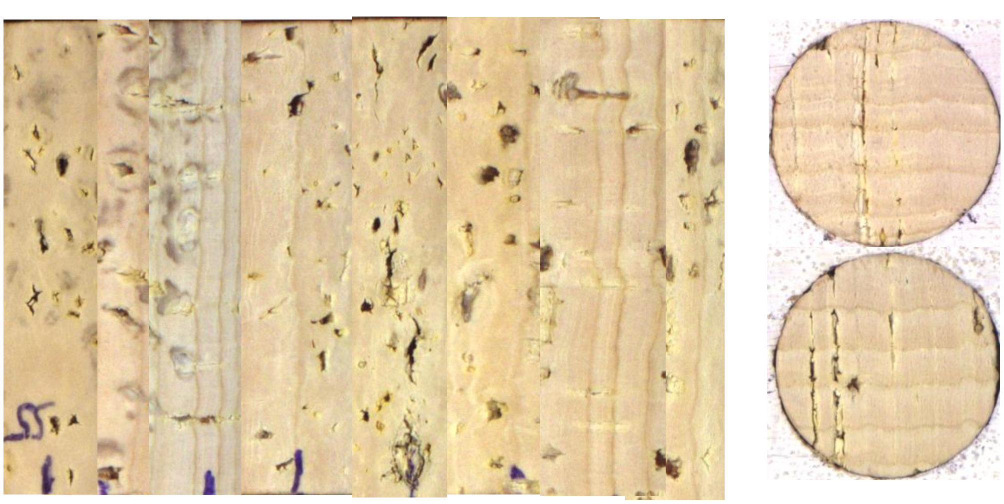
Stoppers are punched from the plank so that tops correspond to the transversal section of the cork, where the lenticular chanels appear as thin strips and longer than in other sections. This explains the lower number of pores in the tops with lower variation, and large pores area. Figure 28 presents visual appearance of the pores on the lateral surfaces and the tops for three quality classes: a) Inferior, b) Superior and c) Colmated class. In Figure 28a I 28b, it is observed that pores show variations in different sections of the bodies: in the tangential sections they are more circular and smaller, and in the radial sections they are horizontally elongated and larger. Higher porosity is observed in the lateral surfaces than in the tops, as stated before.

Higher porosity and higher variability of the bodies than tops can also be explained with difference in the size of observed area. Body or lateral surface has a larger observed area, with tangential but also axial variations of the pores, whereas area of the tops is smaller and only tangential variations are taking into account. In the bibliography, the importance of the observed area was previously stated for the cork planks by Pereira et al. (1996).

Figure 28c show body surfaces and tops where pores are not clearly differentiated from the stopper mass, due to colmation material pores are filled with. Pore structure and color is less visible and filling color similar to the cork color. Therefore, these stoppers we are not possible to analyze with image analysis techniques, as it was stated before.



a

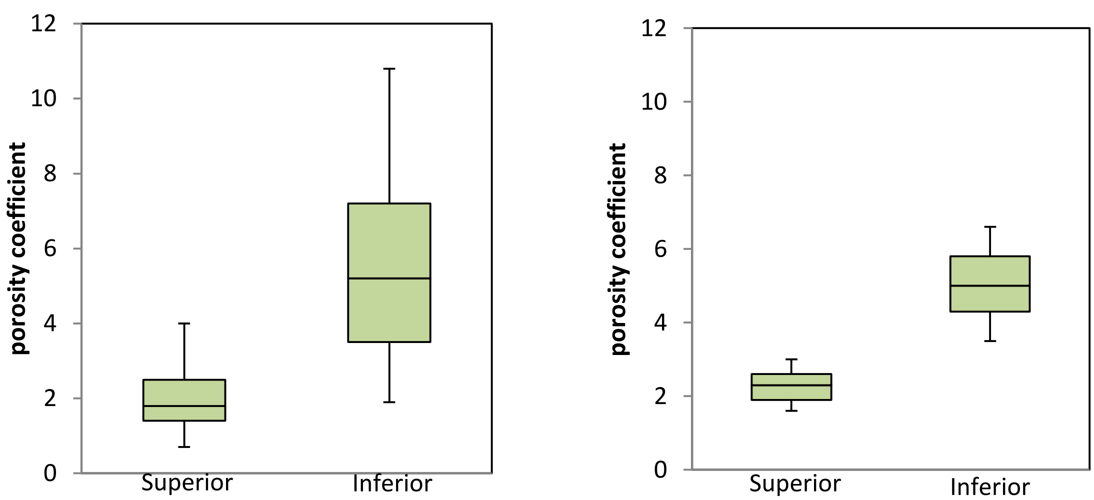


b

c

Figure 28. Surface of body and tops of the Inferior class a), Superior class b) and Colmated stoppers c)

Figure 29 displays the variations in the ranges of porosity variables and the large dispersion of individual values around mean values. The amplitude of variations was higher for the Inferior class than Superior, or in other words the Superior quality class of stoppers is characterized with more uniformity in macroscopic appearance.



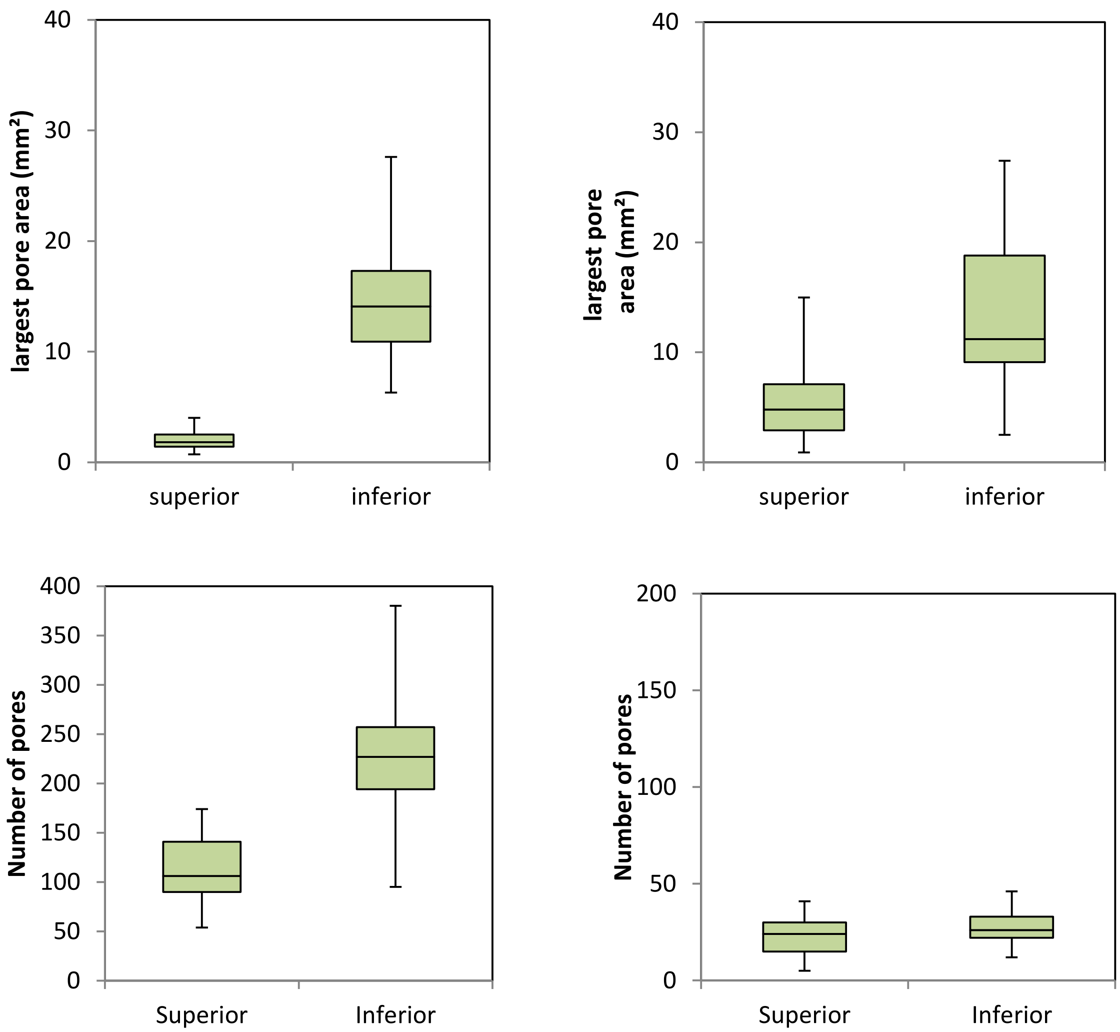


Figure 29. Box plots of porosity coefficient, largest pore area and number of pores for Superior and Inferior quality class. Left-cork stoppers bodies; Right-cork stoppers tops

4.2. DENSITY AND ABSORPTION TEST

4.2.1. DENSITY

Density of the two groups of stoppers, Inferior and Colmated, is presented in Table 5. Average density was 182,6kg/m^3 and 190,4kg/m^3 with variations of the mean 13,8% and 11,8% for the Inferior and Colmated class respectively. These values are similar to those referred in the bibliography: in average 160kg/m^3, but can go below 120 to over 200kg/ m^3 (Pereira, 2007), or 179 kg/ m^3 for the 4.class (Inferior class) of cork planks (Anjos et.al, 2010)

Table.5 Density of two classes of stoppers, Inferior and Colmated, with standard deviation

stoppers class	density (kg/m³)				mass (g)
	mean	max	min	standard deviation	
Inferior	182,6	244,8	153,5	25,5	3,7
Colmated	190,4	225,0	130,0	22,6	3,8

Average value of density was similar in both groups of stoppers, although somewhat higher for the Colmated stoppers. The average mass was similar in both groups, although slightly higher for the colmated stoppers (3,7g and 3,8g respectively). The inclusion of the colmating material in the pores of the stoppers should be the explanation for this small difference.

4.2.2 ABSORPTION TEST

Water absorption after 72h at 60°C, measured as percent of mass increase, was 92,1% and 98,8% for the Colmated and Inferior group of stoppers respectively (Table 6). In the bibliography, recorded values of the absorption expressed as mass increase vary regarding the conditions of the experimental method, mainly time and temperature of test duration. Furthermore, experiments about absorption were mainly done during the certain period of time, where kinetic of diffusion was recorded. There are indicative values for maximum absorption of 500% after 100h at 90°C or 8000h at 20°C (Pereira, 2007), around 170% after 72% on 22°C(Gil et al., 2000), around 70% after 20days at 20°C (Saramago et al.,1996). Gonzalez-Adrados et al. (2008), found 13,5% for wine absorption in the bottled wine closed with natural cork and storage at 16°C during three months.

Table 6. Increase of mass due to water absorption and volume swelling of the two groups of cork stoppers after 72h on 60°C

Variation (increase) in dimensions after treatment (%)	Quality class of stoppers	
	Colmated	**Inferior**
mass increase	92,1(12,8)	98,8(14,0)
radial expansion	1,2	1,9
non radial expansion	2,1	2,6
total volume swelling	4,5(0,8)	6,4(3,0)

Regarding the dimensional variations or swelling of cork, volume swelling after 72 h at 60°C was 4.5 and 6.4% for Colmated and Inferior group of samples respectively (Table 6). These values were in accordance with the bibliography: 4.4% for the treatment at 20°C and water content of 58% (Rosa and Fortes 1993), or higher values of 7.8% recorded for the experiment with immersion in water with higher temperature at 100°C during 28 h (Pereira 2007). Values for radial and non-radial expansion showed the same trend as it is referred in the bibliography: higher values for non-radial expansion than radial, what is explained with anisotropy of the cork cellular structure. Values for radial expansion were 1.2 and 1.9%, and for non-radial 2.1% and 2.9% for the Colmated and Inferior samples respectively. Values in the bibliography are 0.7% and 1.8% for radial and non-radial expansion at 20°C after 70h. It is known that with the temperature expansion increase in all directions, as well as volume swelling of the cork.

It can be concluded that Colmated stoppers present lower absorption and less dimensional variations caused by water absorption. Also, standard variations values were appreciably less for the Colmated stoppers changes, suggesting that this group has more uniformity.

4.3. MECHANICAL TEST

Mechanical testing was done by applying pressure in axial and radial directions. For the pressure in axial direction, on the top of the stoppers, the results are presented as the Young's modulus for both group of stoppers, Colmated and Inferior. For the compression in radial direction (transverse compression), the results present a comparison of the stress corresponding to the given deformation for two groups of stoppers.

Values of Young's modulus indicated in the bibliography vary between less than 10 MPa to more than 20 MPa, depending on the direction of the compression (Pereira 2007). Anjos et al. (2006) referred average values for the Young's modulus from 18.5 to 12.5 MPa, for radial and tangential direction respectively, while Fortes and Ferreira (2003) referred 20 MPa and 13.5 MPa in those two directions.

The values obtained in this work are in accordance with the bibliography. Average value of Young's modulus for the Inferior class of stoppers was 18.4 MPa and for the group of Colmated stoppers 21.2 MPa. The somewhat higher values for the Colmated group can be explained by the higher density of Colmated stoppers, knowing that mechanical properties depend on the structure of the cork, so as higher density influence on higher compression stress. Standard deviation was 5.2 and 4.9 for Colmated and Inferior group respectively, corresponding to the similar mean values of Young's modulus (Table 7).

Table 7. Young's modulus for the axial compression and standard deviation for the Colmated and Inferior group of stoppers

Compression parameters	**Quality class**	
	Colmated	**Inferior**
Young's modulus (MPa)	21,2	18,4
Standard deviation	5,2	4,9

Figure 30 displays kinetic of compression, similar for both groups of stoppers. Some curves in the Colmated group (right) showed fluctuations with sudden and short-term force change at certain deformation. A possible explanation for this occurrence would be variation in structure of these stoppers, eventual appearance of the voids that could cause pressure drop. It can also be speculated that colmation process of filling channels with the mixture with certain density, has some influence on this appearance, but there is not enough data for confirming this speculation.

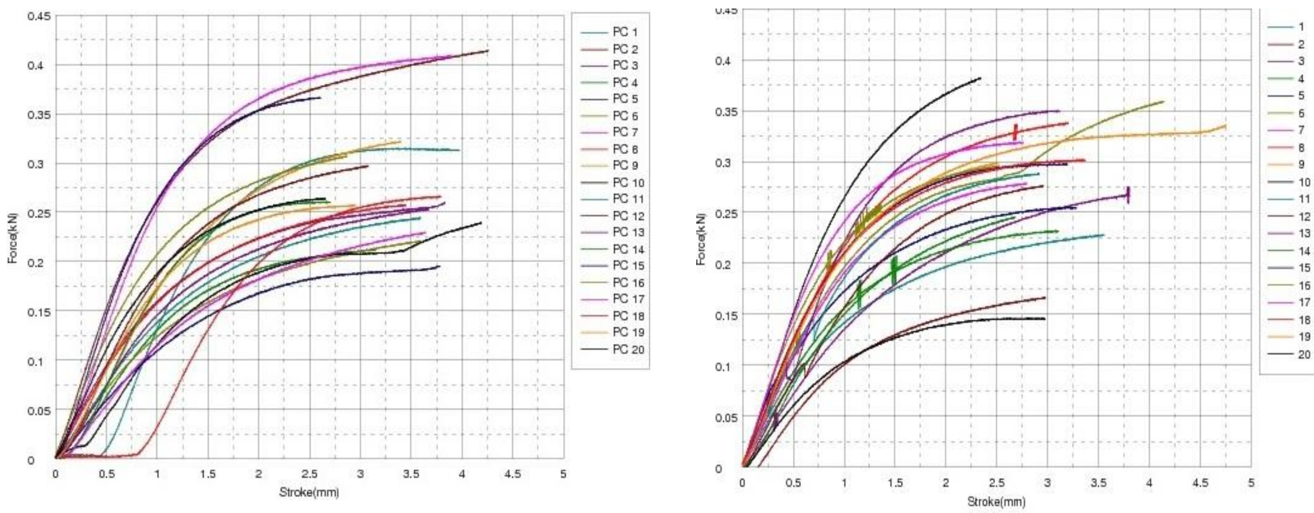


Figure 30. Force-stroke curves for Inferior (left) and Colmated (right) group of stoppers for Axial (vertical) compression

When compression was performed in the radial direction, for the given deformation of 1mm and 2mm, maximum, minimum and mean force were recorded. That was observed from the graphs (Figure 31), both for the for Inferior and Colmated group of stoppers.

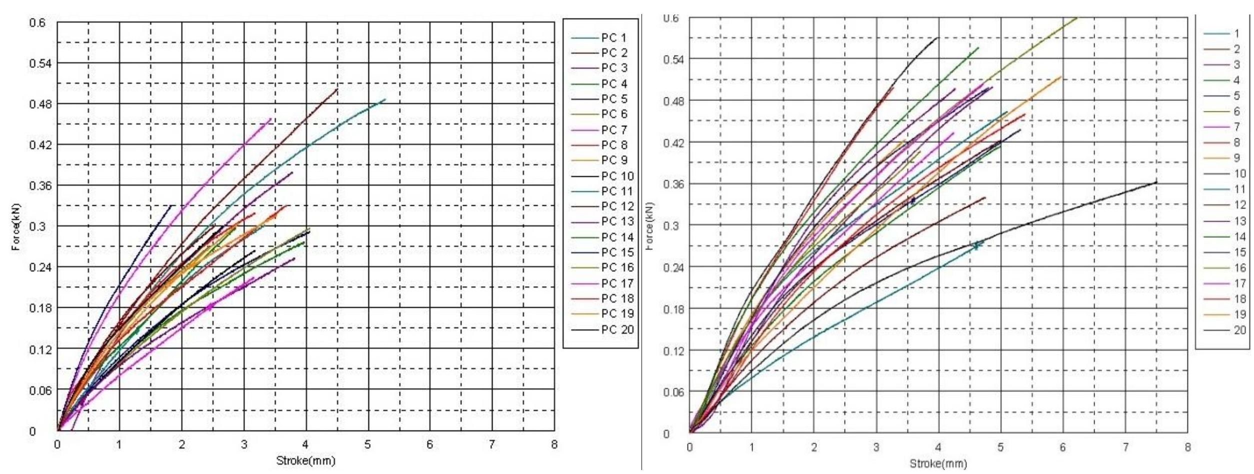


Figure 31. Force-stroke curves for Inferior (left) and Colmated (right) group of stoppers for Radial (horizontal) compression

From the graphs, it can be seen that the range of the force was similar for both group of stoppers in the same range of deformation. Results showed the same values of 80 N for the minimum force for the given deformation of 1 mm in both groups of stoppers, while maximum force was 215 N and 205 N for the Inferior and Colmated group respectively (Table 8). Mean curve values for the same deformation of 1 mm were 135 N and 147 N for Inferior and Colmated group.

Table 8. Range of the force - maximum, minimum and mean force and standard deviation for the given deformation of 1mm and 2mm, in radial compression for the Inferior and Colmated group of stoppers

Compression parameters	Quality class			
	Inferior	**Colmated**	**Inferior**	**Colmated**
given deformation	1mm		2mm	
Minimum force (N)	80	80	150	141
Maximum force (N)	215	205	340	343
Mean	135	147	228	256
Standard deviation	34	34	50	54

For the deformation of 2 mm, average recorded force was 228 N and 256 N for inferior and Colmated group respectively, while minimum force for that deformation was 150 N and 142 N and maximum 340 N and 343 N for the two groups.

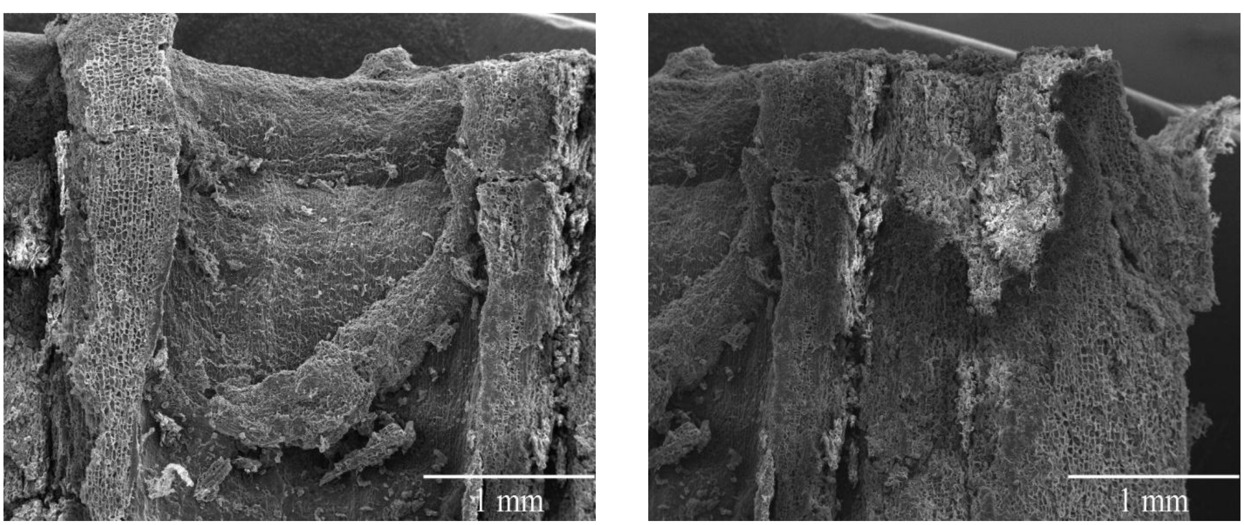
Both for axial and radial tests, results for Inferior and Colmated group of stoppers were similar. Colmated stoppers presented somewhat higher values for Young's modulus in axial and higher mean values of the force for a given deformation in the radial tests, which corresponded to their higher density.

4.4. SEM IMAGES ANALISYS

From the images recorded on SEM, following observation were made. The colmation material covers and fills the surface (outer part) of the pores. It penetrates somewhat in the interior of the channels although not completely filling them, as shown by Figure 32. Therefore the stopper still contains voids from lenticular channels or from occasional cracks in the interior. The external surface of the colmation filling material was also often concave i.e. there was a small depression in the place where the pore was located, with a slightly darker contour line of the pore.

Figure 32. A partial section of a colmated stopper

Figure 33 shows SEM images of the pores of a colmated cork stopper. It is possible to see the difference between the regular cellular structure of cork and the filling (colmation) material where aggregates can be seen containing cellular material of the cork powder used for the filling as well as the binding polymer. The colmation material shows the cellular structure of the cork granules with the random orientation, while places with polymer constitutes a solid mass but with the small dimensions.



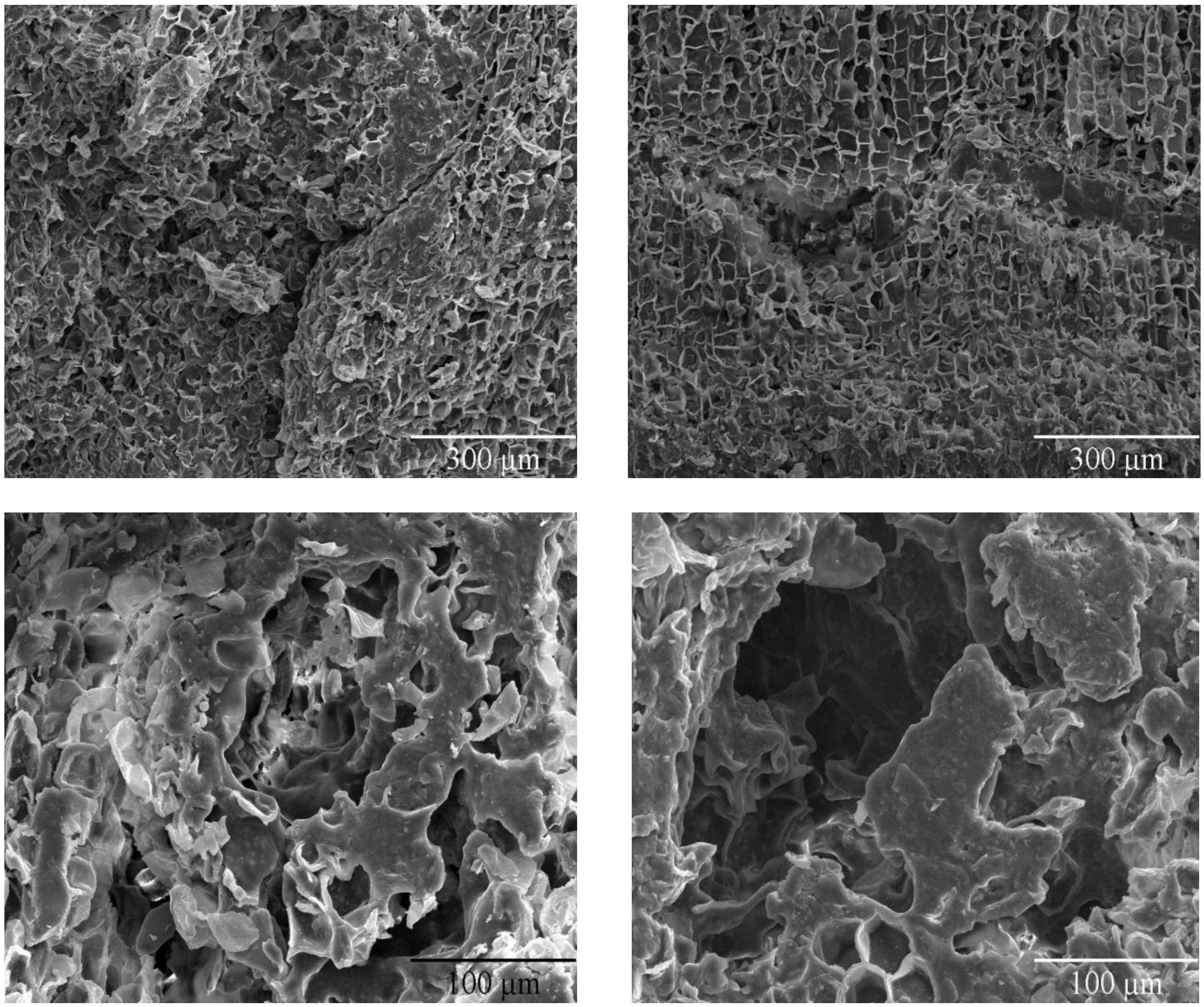


Figure 33. SEM images of colmated pores of a cork stopper showing the pore filling material (upper images), the irregular structure of the cork granules used in the filling (middle images) and the polymer binding material (bottom images)

5. CONCLUSION

The porosity of cork is the main quality parameter for grading cork stoppers in industry,. At present, seven quality classes are separated in production process, with considerable differences in the price between the best and the worst class. To improve performances, the worst quality classes (fifth, sixth and sometimes forth) are often colmated.

In this work, colmated stoppers were studied to verify the effects of the colmation process on performances of these stoppers. The mechanical characteristics, density and water absorption were compared with those characteristics in inferior quality group of stoppers (before colmation). Porosity was studied for superior and inferior group of stoppers and image analysis showed large variations of the pores characteristics between better quality class and the inferior quality stoppers, justifying the importance of reducing the pores appearance with the colmation filling. Colmated stoppers were not analyzed with image analisys, since the pores were no longer visible.

Density was similar for uncolmated and colmated stoppers, even though density of colmated stoppers was somewhat higher than density of the stoppers of inferior (pre-colmated) group, which was expected concerning filling addition in the stoppers mass. Following, colmated stoppers showed lower water absorption and lower dimensional swelling, than pre-colmated stoppers, but the differences were small. Mechanical properties also corresponded to the previous results: values were similar between the two groups, with slightly higher Young's modulus and compression force for a given deformation for the colmated stoppers comparing to the pre-colmated.

SEM images observation showed that colmation process was mostly superficial, covering the surface of the pores, with occasional penetration of the colmation filling in interior of the stopper. The structure of the filling itself is cellular, derived from the cork powder used, with appearance of solid parts of the polymer.

It can be concluded that colmation primarily improves the appearance of the stopper, covering successfully the undesirable surface pores, what in fact is the main objective of the colmation. Furthermore, the analyzed properties of colmated stoppers showed some advantages comparing to the pre-colmated stoppers, like less absorption and swelling and stronger elastic properties, all desirable in the wine bottling and storage. However, further analysis of colmated stoppers, with higher number of samples and testing in given conditions (time and temperature mainly), are necessary to verify their advantages and promote their use.

The colmated cork structure showed that the filling material was irregularly distributed and mostly located at the surface of the pores. Future studies of parameters of the colmation process, i.e. time of the process in the industry, could influence on a better distribution of the material and better performances. A higher inclusion of cork powder with its cellular structure may improve the performance of colmated stoppers, but further studies of the colmation filling and ratio of the material are recommended.

In this study, oxygen transfer of these stoppers during wine bottling and storage was not studied due to the time needed for this research, and that is also a potential advantageous aspect of those stoppers comparing to pre-colmated stoppers

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