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Cork and Cork Stoppers: Quality and Performance

Vanda Oliveira and Helena Pereira

Abstract

Cork is a world-renowned material used for sealing wine bottles. Cork is a cellular material with chemical inertia and a set of physical and mechanical properties that provide an outstanding performance for in-bottle wine aging, by combining minute oxygen transfer with sealing, durability, and chemical stability, for example, inertness toward the liquid content and along storage, preventing sensory deterioration. Cork is a natural material, one of the most important nontimber forest products, that is associated with sustainability and ecosystem preservation. The cork industry has steadily improved production processes and adopted innovative technologies, quality control measures, and certification, regarding prevention of potential wine taints and off-flavors. This chapter makes a review of cork stoppers, their properties, and quality and role for wine bottle aging, tackling their importance for wine aroma and off-flavors while presenting the latest advances in cork research.

Keywords: cork quality, chemical composition, permeability, oxygen ingress, off-flavors, phenolic compounds

1. Introduction

The cork oak (*Quercus suber* L.) forest is a unique production system developed by men that has a substantial ecological role, for example, against desertification and in maintaining animal and plant biodiversity in their restricted area of occurrence in the Western Mediterranean countries, covering a total of 2.1 million hectares. Portugal has 34% of the world's area, which corresponds to about 720,000 hectares and 22% of the national forest [1]. Cork is obtained from the bark of the cork oak, and the production is made in a sustainable process carried out during the tree's lifetime. It is one of the world's important nontimber forest products, supporting a dedicated industry of cork products directed toward global markets.

World cork production reached 201,000 tons annually. Portugal is the leader, concentrating 49.6% of the cork production, acting also as an importer of cork raw material, therefore increasing its share on the world production of cork products. In 2017, Portugal exported 197,000 tons of cork products representing 986.3 million euros [2]. Cork stoppers lead the exports, accounting for 72% of the total value (710.7 million euros). Within the cork stopper segment, natural corks come first with 60% of the total (428.6 million euros), followed by other types of stoppers with 21%, including technical stoppers, microstoppers, and others (149.8 million euros), and champagne stoppers with 19% [2].

Cork is a world-renowned material used for sealing wine bottles. Cork is a cellular material with chemical inertia and a set of specific physical and mechanical properties that provide an outstanding performance when in-bottle wine aging is wanted, by combining the required minute oxygen transfer with mechanical sealing of the bottle, durability, and chemical stability [3, 4]. Cork is the closure material preferred by wine consumers, and a bottle corked with a natural cork stopper is indicative of high-quality or very high-quality wine, as shown by recent surveys (Wine Opinions, CTR, Iniciativa Cork, Gfk, Opinion Way).

2. The sustainable management of cork production

Cork oak forests are often a part of a multifunctional agroforestry-pastoral system called "montado" that is considered a high nature value farming system, according to the European classification proposed by the European Environmental Agency [5]. These ecosystems are also recognized as habitats of conservation value listed in the Habitats Directive [6].

In this nonwood forest production system, cork harvesting is the major economic activity, and cork is the most valuable product. The entire cork chain from the forest to the consumer relies on the regular and sustainable production of cork. To maintain cork production capacity and provide the mentioned environmental services, it is necessary that cork oak forests are adequately managed, being the sustainability a matter of general concern [3].

The exploitation of the cork oak tree for cork production needs its periodical removal from the stem and branches in a degree that is considered well suited with the maintenance of the tree in good physiological conditions [3]. Cork production yields depend on the tree and cork growth, as well as on management variables such as the intensity of cork extraction and the interval between strippings that are regulated with strict rules by the Portuguese legislation (Decreto-Lei nr. 155/2004).

The production of cork relies on specific forest management and silvicultural model, often called subericulture that is based on the biological characteristics of the cork oak bark development [7]. The extraction of cork, or cork stripping, is done manually by cutting large rectangular planks and pulling them out of the tree when the cork oak is physiologically active in late spring and early summer. By law, young trees can only be stripped when they reach at least 70 cm of the perimeter at 1.3 m of height, corresponding to about 25 years of age. Moreover, cork cannot be stripped above a stem height equal to twice the perimeter of the stem in the first stripping, or not more than three times, for a mature tree in full production, the so-called stripping coefficient. The trees are then debarked every 9 years (the legal minimum allowed in Portugal and Spain) or more, called the production cycle [8]. The decision of longer production cycles is often related to an adjustment to cork growth and productivity in order to achieve the cork plank thickness required by the industry.

This means that cork growth is the main criteria to consider in cork management planning since it determines the thickness of the cork plank that is available for industrial processing, which is primarily oriented toward the production of wine stoppers (requiring a minimum thickness of 27 mm after the cork postharvest boiling operation).

The annual cork growth along the production cycle varies with the number of years in the cork growth sequence (growth is usually higher in the first years of the cycle) and is influenced by environmental and tree conditions [9, 10]. A recent study encompassing a large time span (24 years) and sampling (1584 cork samples), reported an average annual cork ring width ranging from 1.2 to 7.3 mm with an average value of 3.3 mm [11].

Cork oaks show high resiliency to interannual precipitation variability, with rapid and complete recovery from extreme dry years or from rainfall exclusion, but have a high sensitivity to the amount and timing of late spring precipitation [12]. In Mediterranean conditions, access to water resources and the relationship to soil-site conditions are key factors for cork oak development [13]. Soils with low depth and high compactness have a negative influence on the development of the cork oak deep root system, thereby diminishing the access to direct groundwater resources, namely, during summer drought [14–16].

It is foreseen that in the Iberian Peninsula, spring precipitation will be reduced and more severe droughts will occur as predicted by the Intergovernmental Panel on Climate Changes (IPCC). In such a scenario, cork growth will be slower resulting in narrower annual rings that will decrease the overall thickness of the cork layer at the end of the production cycle. Given the importance of the cork plank thickness for the industrial processing into cork stoppers, it is foreseeable that the silvicultural cork management will require an adjustment to mitigate the effects of drought by postponing the cork striping (i.e., increasing the duration of the cork production cycle) [17].

3. The cork formation

Cork is a protective tissue located in the outer bark of the cork oaks as part of the periderm. The formation of cork in the periderm results from the activity of a secondary meristem, the phellogen: each phellogen mother cell originates by cellular division cork cells that grow unidirectionally outward in the tree's radial direction and phelloderm cells to the inside [18]. In the cork oak, the first phellogen maintains its activity year after year, producing successive layers of cork. The phellogen may be functional for many years, probably during the tree's life, although the intensity of its activity decreases with age [3].

If the cork layer of the initial periderm (virgin cork) formed in the young cork oaks is removed (by an operation called cork stripping), a new phellogen is formed inside the phloem and rebuilds a traumatic periderm and its subsequent cork layer (second cork). At this time of life in the young cork oaks, the radial growth of the stem is still important, and the second cork external regions are subject to large tangential stress that may result into deep fractures of the cork [19]. If the second cork is removed, the process is repeated with the formation of a new phellogen and the production of a new cork layer (reproduction cork) that will endure few fractures due to the low tangential stress caused by the radial growth of the mature tree. Upon removal of this reproduction cork, the process is repeated, therefore allowing exploitation during the tree's lifetime by successive removals of the reproduction cork. The second and reproduction corks are covered at the outside by a thin lignocellulosic layer of phloem, corresponding to the part of the phloem that remained to the outside when the traumatic phellogen was regenerated inside the phloem (**Figure 1**).

The cork oak periderm has lenticels that originate from the activity of particular regions of the phellogen, called lenticular phellogen, and differ from the surrounding cork tissue. The activity of lenticular phellogen is maintained year after year, and therefore, the lenticels prolong radially from the phellogen to the external surface of the periderm forming approximate cylinders named lenticular channels [3]. The lenticular channels are loosely filled with a lenticular filling tissue of rigid unsuberified cells with thick walls and show ruptures and intercellular voids to a great extent [3]. The region bordering the lenticular channels has often higher density than the surrounding material due to the presence of lignified and thick-walled cells at their borders.
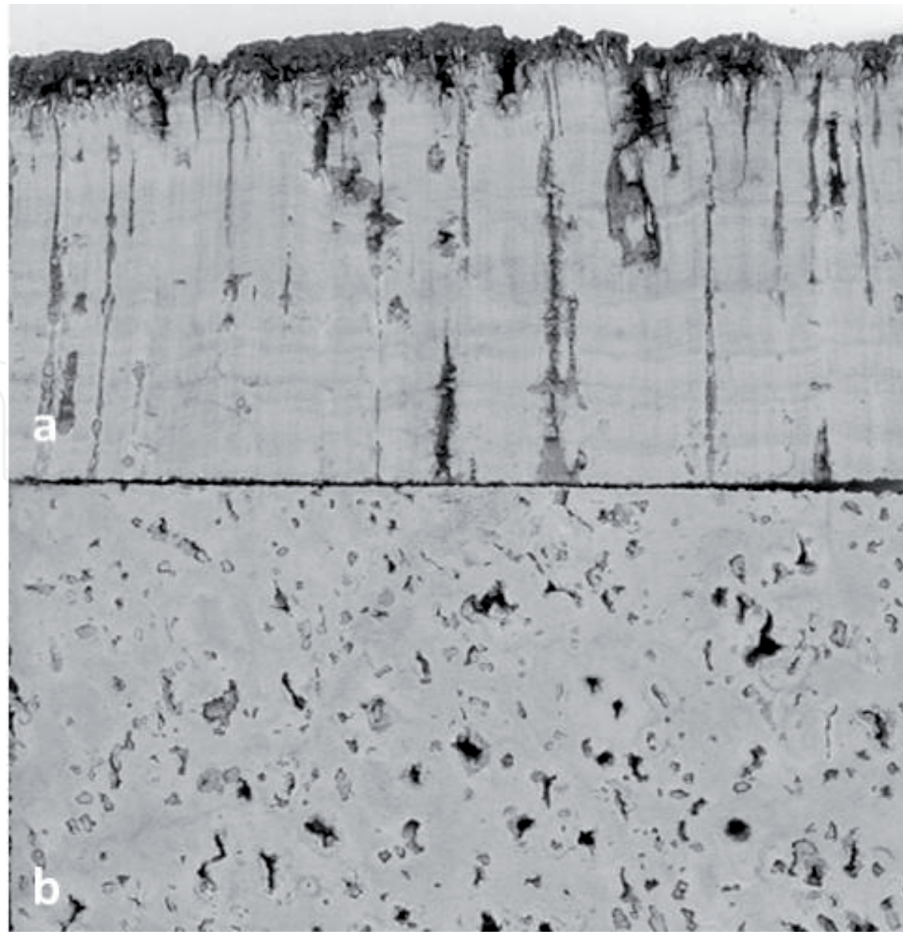
Figure 1.
Lenticular channels crossing the cork layer: (a) in cross section and (b) in the tangential section of the belly (inner part of the cork layer). The thin layer of phloemic lignocellulosic tissue can be observed in the outer side of the cross section (adapted from Ref. [3]).

The lenticular channels (**Figure 1**) are the most important and characteristic features of cork visual heterogeneity, variable in number and dimension between trees, and related directly to the quality and value of the cork material accounting for the so-called cork porosity [3, 8, 10].

4. What matters for corking

The most valuable products in the cork industry are the natural cork stoppers, and therefore, the value of the cork planks as raw material is related to their suitability to produce cork stoppers. Only the cork obtained after the second stripping is used, but the plank thickness that is related to the cork annual growth is a major parameter to establish the technological quality required to produce natural cork stoppers [9, 10]. Given its importance, the cork plank thickness is normalized by caliper classes (NP 298:1993 and ISO 1219:1998). Having the suitable thickness, the plank quality is given mostly by the cork porosity [20, 21] that also determines the suitability and quality yields of the products [22–24]. Porosity quantification by surface image analysis is the basis of cork stoppers classification into quality grades [24, 25].

4.1 Structure

Cork is a cellular material with a compact three-dimensional structure of closed prismatic, on average hexagonal, cells that are assembled base to base creating

rows that are aligned in the radial direction in the tree and disposed of in parallel, forming a honeycomb-type structure [19, 26]. The structure of cork observed by scanning electron microscopy in the three principal sections is shown in **Figure 2**. In adjacent rows, the prism bases of neighbor cells most often lay in staggered positions. **Table 1** summarizes the main structural features of cork. The individual cell volume is on average 1.7×10^{-5} mm^3, and the solid cell wall content is 10% of the total volume. The cork cell walls, especially those that constitute the lateral prism faces, show ab initio some bending and undulations of varying intensity that can attain strong corrugation derived from constraints during cork growth in the tree [19, 26].

The formation of cork rings (**Figure 1a**) that give cork a layered structure is the consequence of the biological annual growth rhythm: in the main growth period from April to July, the cells formed are bigger (i.e., with a larger prism height) and have thinner walls than those formed in high summer and autumn, at the end of the growth period, which are smaller and thicker walled (earlycork and latecork cells, respectively) [26].

Cork cell walls are composed of a suberinic secondary wall and are flexible enough to undulate or corrugate with variable intensity under compression without fracture. The latecork cells are more rigid and less compressible than the earlycork cells due to their thick walls and small size (**Figure 3**). When the meristematic activity starts in spring, usually in early April, the initial cork cells formed are compressed against the existing cork layers causing the undulation of the cell walls [3].

As referred previously, the cork tissue is not completely homogeneous, and the cellular structure contains discontinuities that influence several properties of the material and the in-use performance of cork products and are thereby closely associated with the commercial value of raw cork and of cork products [3].

The occurrence of lenticular channels crossing radially the cork tissue is one of the most important features of cork heterogeneity: they cross the cork layers
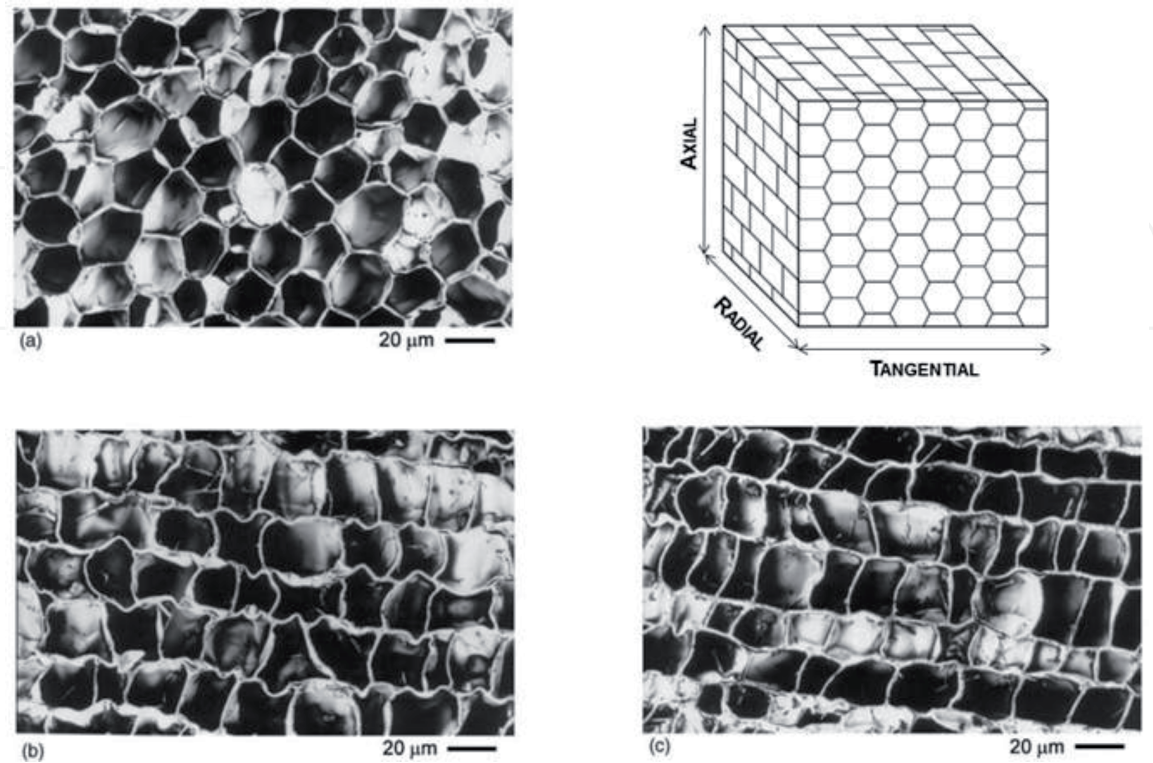

Figure 2.
Schematic representation of the cellular structure of cork with scanning electron micrographs of sections of reproduction cork: (a) tangential, (b) radial, and (c) transverse sections (adapted from Ref. [3]).

Material	Natural suberized lignocellulosic composite
Density	120–170 kg m^{-3}
Type of cells	Closed
Mean edges/face	$n = 6$
Mean faces/cell	$f = 14$
Individual cell shape	Hexagonal prism
Symmetry of structure	Axisymmetric
Cell thickness	1–1.5 μm
Fraction of solid material	10%
Largest principal cell dimension	40 μm
Smallest principal cell dimension	20 μm
Intermediate principal cell dimension	30 μm
Shape anisotropy ratios	$R_{13} = 1.5–1.7$, $R_{12} = 1–1.1$
Other specific features	Growth rings, lenticular channels

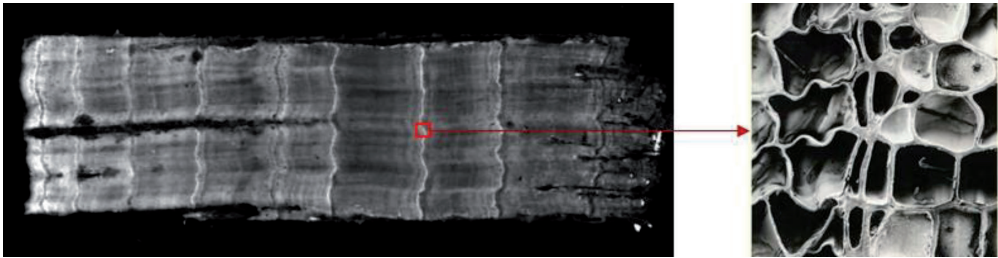**Table 1.**
Main characteristics of cork structure [3].

Figure 3.
Fluorescence image of the transverse section of a cork piece showing the different cork rings and a scanning electron micrograph detailing the transition between latecork and earlycork.

from the outside to the inner tissue and are loosely filled with a dark brown colored, unsuberified material, usually conspicuous to visual observation [20]. The lenticular channels appear differently shaped in the three sections of cork (**Figure 1**): (a) in the transverse and radial sections, they are thin elongated rectangular channels oriented radially, and (b) in the tangential section, they present circular to elliptical form. This feature contributes to increase the structural anisotropy of cork.

4.2 Chemical composition

Cork performance depends on structure and chemistry [27], although the impacts of variation are far from being well established, for example, it is believed that the cell wall chemical variation is related to contents in suberin (23.1–54.2%) and lignin (17.1–36.4%) and the suberin-to-lignin ratio plays a determining role in properties, namely, in compression [28–30].

Table 2 summarizes the chemical composition of cork and the range of its natural variability [29]. Cork is mainly composed of suberin, representing on average 43% of the total dry mass. Suberin is a polyester macromolecule obtained by polymerization of linear long-chain fatty acids and hydroxy acids and glycerol, which are assembled and develop spatially as flexible ribbon-like structures. Suberin is, therefore, the component responsible for the elastic properties of cork and allows the bending and compression of cell walls [3, 27].

Chemical parameter (% o.d. cork)	Mean	Std.
Extractives, total	16.2	3.9
Dichloromethane	5.8	0.8
Ethanol	5.9	3.0
Water	4.5	1.6
Suberin, total	42.8	6.2
Long-chain lipids	41.0	5.2
Glycerol	3.8	0.6
Lignin, total	22.0	3.3
Klason lignin	21.1	3.3
Acid soluble lignin	0.9	0.2
Monosaccharide composition, % of neutral sugars		
Glucose	46.1	3.6
Xylose	25.1	3.7
Arabinose	18.0	3.0
Mannose	3.0	2.8
Galactose	7.3	1.2
Rhamnose	0.5	0.5

Table 2.
Chemical composition of cork, in % of oven-dried initial material (mean of 58 samples and standard deviation) [29].

Lignin is an aromatic cross-linked polymer that represents on average 22% of the cork dry mass and is responsible for the structural rigidity of the cells and their resistance to compression [29]. Cork lignin is mostly constituted of G units (guaiacyl units) with an important proportion of H units (hydroxyphenyl units) and minor contents of S units (syringyl units) (H:G:S 1:2.5:0.3, S/G 0.12) [31].

The cellulose and hemicelluloses are less representative and amount up to 16.2% of the cell wall structural components [31]. Hemicelluloses are mainly composed of arabinoxylans with a significant proportion of galactose including uronic acids. The suberin-to-lignin ratio is 2.0, and the cellulose-to-hemicellulose ratio, determined by the ratio of glucose to other sugars, is 1:1.2 [27, 29, 31].

Cork contains a substantial proportion of nonstructural compounds that may be removed by solubilization with suitable solvents without impairing the core properties of cork. These so-called extractives represent on average 16.2% of cork: 5.8% are nonpolar compounds (e.g., lipids and terpenes), and 10.4% are polar compounds of phenolic and polyphenolic nature [29].

4.3 Looking at the surface and inside of a cork stopper

The stoppers are punched out from cork strips so that their cylindrical axis is parallel to the axial direction of cork. Therefore, the surface of the cork stoppers is not homogeneous relative to the section of cork: (a) the circular tops correspond to transverse sections with the lenticular channels crossing the surface as thin rectangular channels perpendicular to the growth rings and (b) the lateral surface of the body ranges from regions corresponding to tangential and radial sections of cork (**Figure 4**). The lenticular channels appear differently shaped in these two sections: in the radial section, they look like elongated rectangular channels, and in the tangential section, they have an approximately circular to elliptical form [3].
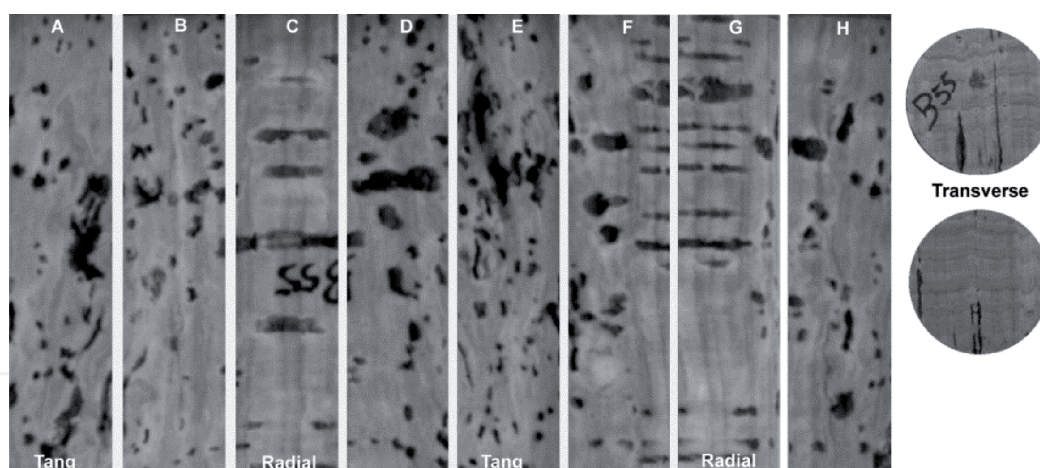
Figure 4.
Image analysis frames (eight frames in the lateral surface and two tops) and the corresponding cork sections ranging from tangential (A and E) to radial (C and G) sections, with in-between sections (B, D, F, and H).

The lenticular channels, woody inclusions, and other defects that give the cork surface its typical visual heterogeneity are together considered as the porosity of cork [20, 32]. Nowadays the evaluation of cork quality is made by visual analysis of the outer surface (lateral body surface and tops) using automated image-based inspection systems with high throughput rates based on line-scan cameras and a computer embedded in an industrial sorting machine capable of acquiring and processing in real time the surface image of the stoppers [33].

The comparison of porosity between the two tops of a cork stopper confirms the existence of axial variation in the tree, for example, one top may have significantly lower porosity than the other top. This fact can be used in practical terms in the production of capsulated natural cork stoppers for spirits by selecting the top with the lowest porosity as the visible one [21].

X-ray tomography was used as a nondestructive technique to acquire knowledge on the internal structure of natural cork stoppers and quantify the lenticular channels present in different classes of cork stoppers [34, 35]. Due to the relationship between X-ray absorption and material density, this technique allowed the visualization and identification of some defects within the cork stopper.

The image resolution with a voxel size of 50 μm achieved by Oliveira et al. [34] allowed the observation of lenticular channel development and geometry (**Figure 5**). The channels are loosely filled with a tissue of rigid unsuberified cells with thick walls, showing ruptures and intercellular voids to a great extent [3]. The region bordering the lenticular channels showed a higher density than the surrounding material due to the presence of lignified and thick-walled cells at their borders.

4.4 Cork properties as closures

Cork has an unusual combination of properties: low density, very low permeability to liquids and gases, low conductivity, chemical stability and durability, and high compressibility with dimensional recovery.

These are properties that are fundamental for the application of cork as a sealing closure in bottles. To a cork stopper, it is requested that (a) it does not allow any leakage from the liquid content either through the stopper itself or at the interface between stopper and bottle; (b) it does not negatively alter the liquid chemical and sensory features; (c) it is durable and preserves its physical and chemical characteristics during storage; and (d) it can be removed from the bottle for consumption easily. To satisfy these requirements, namely, the first requirement of liquid sealing,
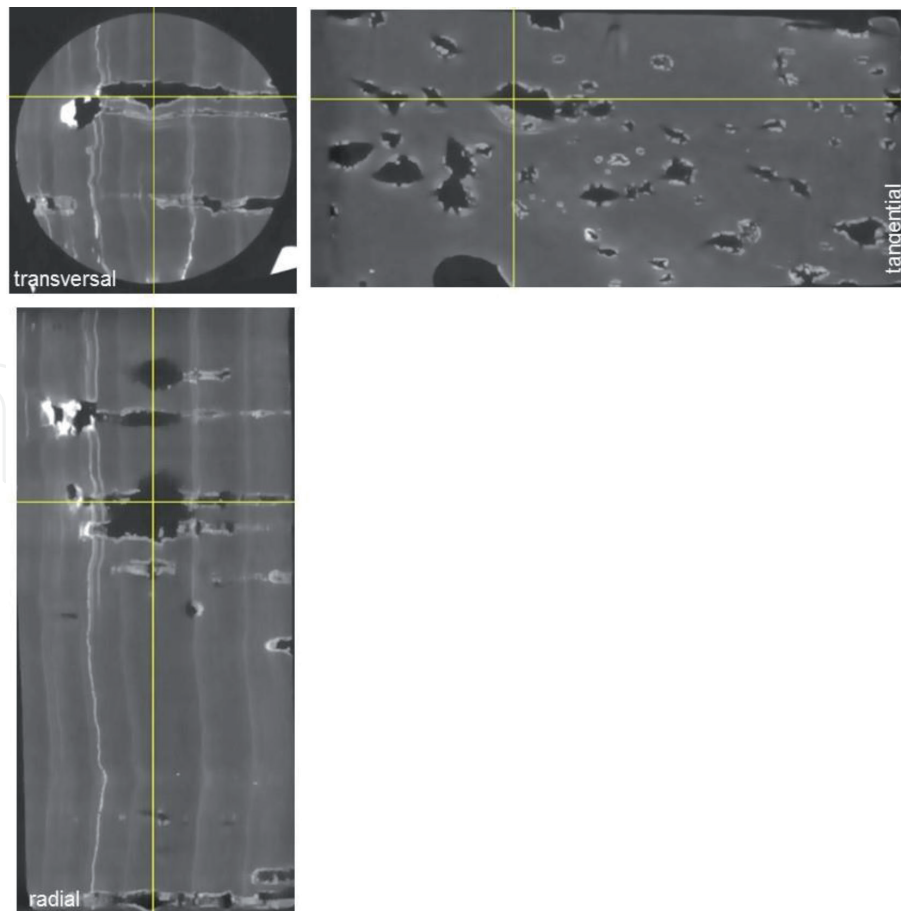
Figure 5.
Typical 2D "slices" from a 3D grayscale image of a cork stopper scanned at 50 μm resolution. Different sections through the cork stopper in three orthogonal planes: Transversal, radial, and tangential. Crossing lines represent the same point in the three images.

it is necessary to have an appropriate compression against the bottleneck and close contact between the stopper and the bottle surface to avoid liquid percolation as well as material's impermeability to avoid diffusion through the stopper.

Cork is a viscoelastic material which allows large deformations under compression without fracture, with substantial dimensional recovery when stress is relieved [36]. The stress-strain compression curve of cork is characteristic of a cellular material: it shows an elastic region up to 5% strain, followed by a wide plateau where strong dimensional reductions occur for small stress increases due to the undulation of cells and their collapse, until a densification phase with a strong stress increase but without cell or cell wall fractures.

The compressive behavior of cork is anisotropic although the differences between directions are not very large: the strength in the radial direction is only slightly higher than in axial and tangential directions, which are more similar (**Figure 6**) [30]. This anisotropy in the stress distribution is also noticed in the compression of a stopper with the radial direction corresponding to the maximal stress and the tangential direction to the minimum value [3].

The cork stoppers have a diameter well above the inside diameter of the bottleneck, and when inserted in the bottle, they will be compressed exerting pressure against the bottle glass. The strains in bottled cork average 30%, a value that is in the plateau region of the stress-strain curve corresponding to the physical phenomenon of the buckling of the cells and to stress values in the range of 1 MPa (**Figure 6**). Industry technical guides refer that cork stopper compression must never be more than 33% of their diameter, as there is a risk that this could compromise its elasticity, with loss of part of the recovery and consequent difficulty in the correct sealing of the wine in the bottle.
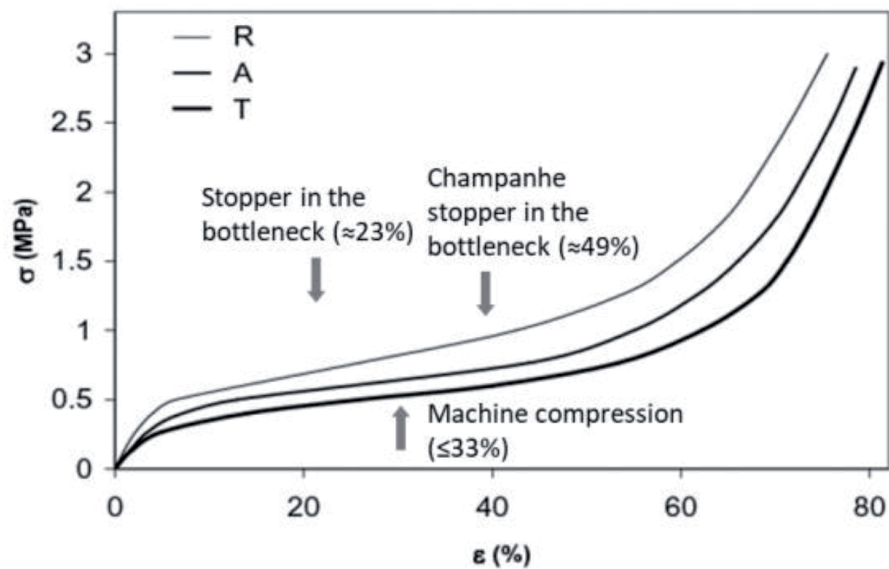
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Figure 6.
Average stress-strain curves for the compression of cork in the radial (R) and nonradial (A, T) directions (adapted from [3]). The arrows indicate the compression region of a stopper in different conditions: in the bottling machine, in the bottleneck of a still wine, and a champagne stopper inserted in the bottle neck.

After insertion in the bottle, there will be a quick stress relaxation [3]. Following compression to 30%, recovery is almost total after approximately 20 days; however, the recovery rate decreases appreciably with time and increases with the degree of deformation previously imposed [37]. The standard (ISO 9727-4:2007) specifies a test method for determining the percentage of diameter recovery of cylindrical cork stoppers, after compression, and specifies that this recovery after 5 minutes shall be greater than 90%.

The extraction force applied in the longitudinal direction of the bottleneck after fixing the cork to a pulling device (usually a corkscrew) depends on the compressive stress against the bottle and on the sliding friction between cork and glass. The extraction force increases with the increase of dimensions of the stopper: a longer stopper will increase the contact surface while a larger diameter stopper will increase the compressive stress [3]. The surface treatments (silicon and paraffin coatings) can reduce the extraction force. It is considered that the extraction force of natural cork stoppers should be 20–40 decanewtons (daN). The test method for the determination of maximum extraction force is specified in ISO 9727-5:2007.

The sealing performance of a cork stopper involves two possibilities for liquid passages: leakage between the stopper and the bottleneck and diffusion through the cork material. In the first possibility, the sealing capacity is evaluated by the penetration of the liquid in the interface, and it is usually measured by applying liquid pressures over the atmospheric pressure and observing the depth of penetration of the liquid [3]. The standard (ISO 9727-6:2007) specifies a test method for determining the liquid tightness of a cylindrical cork stopper: the liquid seal capability is expressed as the maximum internal pressure that the stopper can support in a bottle (at 1.2 bar internal pressure).

On the other hand, a cork stopper absorbs water/wine, and this liquid penetration through the cork is governed by the diffusion of the liquid in contact with the surface of the stopper [3]. González-Adrados et al. [38] evaluated the magnitude and evolution in time of absorption phenomena under conditions as close to reality as possible and described the transport of liquid as a combination of liquid progression by the cork-glass interface and diffusion through cell walls.

5. Oxygen transmission rate (OTR) properties of cork stoppers during bottled wine aging

The oxygen transmission rate (OTR) into the closed bottle is one important parameter for the wine cellars given its relation to the quality development of the wines [4, 39–43]. Therefore, the OTR properties of cork stoppers will define their ability as a quality sealant, also in comparison with other types of wine closures [41, 44, 45]. The OTR behavior depends on the type of wine closure. As shown by Lopes et al. [41] and presented in **Figure 7**, technical stoppers allow the lowest value of OTR into the closed bottle (1.0–1.2 mg of oxygen over 36 months), while synthetic closures present the highest value with an average oxygen ingress of 1.6 mg of oxygen in the first month. The path of oxygen ingress into the bottle was also experimentally studied by Lopes et al. [46]: the oxygen coming into the bottle and the wine during the storage period originates from the cork stopper itself, that is, from its macroscopic and cellular structure and not from an interface flow. In fact, the closed cells of cork contain air-filled lumens while lenticular channels or other tissue voids may provide additional air-filled pockets [26]. The cork itself has very low permeability to oxygen [47, 48], and correspondingly, the cork stoppers are essentially impermeable to atmospheric oxygen [46].

The kinetics of oxygen ingress into the bottle could be adjusted to logarithmic models, with an initial high ingress rate, followed by a decreasing ingress rates during the 1st month and further on, until stabilizing a low and rather constant ingress rate from the 3rd to the 12th month and thereafter (**Figure 7**) [49].

As primarily suggested by Ribéreau-Gayon [50], oxygen ingress into bottles occurs mainly out of the cork structure due to the high internal pressure in the cork cells created when the cork stoppers are compressed into the bottleneck. Natural cork stoppers with 24 mm diameter and 45 mm length have a volume of 20.4 mL of which 80–85% is air contained in the cell lumen, implying the existence of 4.9–5.2 mg of oxygen within their structure [3]. Oliveira et al. [49] showed that, in average, 1.88 and 2.35 mg of oxygen diffuses from the natural cork stoppers that
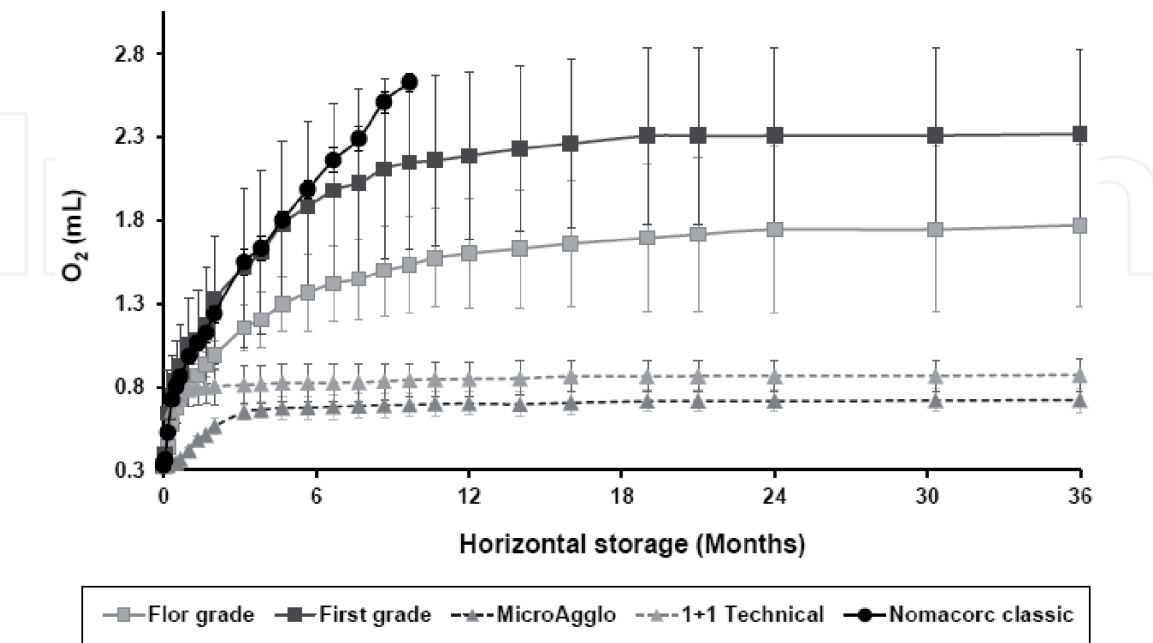

Figure 7.
Kinetics of oxygen ingress through different closures (natural cork stoppers of "flor" and extra quality grade, microagglomerated cork stoppers, 1 + 1 technical stoppers, and Nomacorc synthetic stoppers) into commercial bottles stored horizontally over 36 months. Error bars represent the standard deviation of four replicates (adapted from [41]).

were bored out of cork planks with 27–32 and 45–54 mm calipers, respectively, representing 36–38 and 47–50% of the theoretically total oxygen present in the cell structure. Moreover, Oliveira et al. [34] suggested that the high oxygen ingress rates immediately after bottling are due to the transfer of the air trapped in the voids in the bottom part of the cork stopper. After this first period, gas transport through the cork cells occurs with very low diffusion rates through small channels (i.e., through the plasmodesmata) present in the cork cell walls [47].

6. Off-flavors and beneficial compounds

One of the most important taints in wine is a moldy taste and aroma due to the presence of haloanisoles, namely, of 2,4,6-trichloroanisole (TCA), traditionally named as corkiness or cork taint. The olfactory detection threshold (ODT) of TCA is very low (1–4 ng/L) although variable depending on the consumer, the type of wine, and the occasion at which it is consumed, among other factors.

TCA is a nonpolar compound that has a large affinity for lipids such as those found in cork (monomeric extractives and polymeric suberin) that therefore can absorb TCA as well as other chloroanisoles [3]. The accumulation of chloroanisoles and chlorophenols in cork could be related to the use of polychlorinated phenolic biocides in forest, the chlorine bleaching of cork, the hypochlorite washing of wine barrels, the use of chlorinated phenolic biocides in packaging material, and the environmental contamination of wine cellars [3]. Therefore, the contamination sources have been eliminated in the cork industry in the last years. The International Code of Cork Stopper Manufacturing Practices prohibits nowadays the use of chlorine and other materials containing this compound at any stage of stopper production in order to reduce the possibility of chlorophenol development. Stoppers are currently washed with hydrogen peroxide as means of disinfecting and whitening.

Once the TCA can have origin in microbial sources (such as yellow stain), cork industry implemented new and changed old procedures aiming at the elimination of microbial contamination: the cork planks are screened before processing and during the process line for the elimination of those that contain signs of microbial activity; the industrial yards are nowadays cemented to avoid the contact of cork planks with soil in the preprocessing storage; and the time was decreased and the conditions controlled for the storage between the boiling of cork planks and their processing into stoppers.

In addition to the recognized standards in the International Code of Cork Stopper Manufacturing Practices, other processes to eradicate TCA have been implemented by companies in the sector: new boiling systems, controlled steam distillation, volatilization by dragging a controlled temperature and humidity, volatilization by dragging in the gaseous phase of adjusted polarity, under controlled temperature and humidity, and supercritical extraction with CO_2 [51].

Quality control of cork stoppers also increased, with procedures given by standard protocols, for example, ISO 20752:2014 specifies a test method to determine releasable TCA from cork stoppers, and ISO/PRF 22308 specifies a method for detecting and quantifying by sensory analysis several aromas including mold. The Cork Quality Council in the USA developed a research project using SPME-GC/MS analysis which allows technologically complex and very sensitive equipment to be used in the quantification of TCA in cork lots. Recently, Amorim launched NDtech, a natural cork that they guarantee with a nondetectable TCA (releasable TCA content at or below the 0.5 ng/L quantification limit; analysis performed in accordance to ISO 20752), based on the deployment of fast and unitary cork stopper chromatography.

In addition, research studies demonstrated that TCA does not permeate through cork showing that cork stoppers can act as an effective barrier against environmental TCA contamination [52].

Wine is, from a chemical point of view, a very complex fluid composed of a mixture of water, alcohols, organic acids, phenolic compounds, sugars, amino acids, and various minerals [53]. Several phenolic compounds present in wine, especially red wine, have gathered scientific interest in medical applications, including nonflavonoid phenolic acids (coumaric, cinnamic, caffeic, ferulic, and vanillic acids), trihydroxy stilbenes (resveratrol and polydatin), and flavonoids (catechin, epicatechin, and quercetin) [54].

Extrinsic sources of phenolic compounds found in wine include the barrels used in oak aging and cork stoppers, where small molecules are susceptible to migration from oak wood or cork into the wine.

Cork polyphenols were reported to migrate into wine after bottling, which may benefit the aging of wine through the release of phenolics and volatiles from the structure of the closure. In recent years, various studies have been carried out to analyze the intrinsic chemical features of cork regarding its advantages to health. The phenolic composition of cork has been studied, and several polyphenols were identified in cork: low molecular weight polyphenols such as acids, aldehydes, flavanones, and coumarins; hydrolysable tannins; and highly antioxidant molecules, such as gallotannins and ellagitannins and condensed tannins [55, 56]. Hydrolysable tannins are not naturally present in grapes, and their presence in wine stems from enological practices such as oak aging and natural wood extraction or the addition of extrinsic tannins in commercial products [57].

Polyphenols are easily extracted by a hydroalcoholic solution [55] and may react with the main components of wine [58], impacting on color and sensory properties of a bottled wine such as odor, flavor, and astringency. Azevedo et al. [59] identified and quantified the phenolic compounds from cork that were able to migrate from different cork stoppers to wine model solutions during 27 months. The phenolic compounds that solubilized in higher amounts were gallic acid, protocatechuic acid and aldehyde, and vanillin, while in lesser amounts, more complex structures have migrated such as valoneic acid, ellagic acid pentose, and castalagin/vescalagin. Mislata et al. [60] characterized the aromatic composition of different wine cork stoppers and granulates, reporting that vanillins are by far the most important aromatic family in cork extracts (**Table 3**).

Aromatic compound	Aromatic descriptor	Content (µg/g)
Vanillins		
Vanillin	Vanilla	9–170
Acetovanillone	Vanilla	0.6–14
Volatile phenols		
Guaiacol	Wood, smoked, sweet, medicine	0.03–5.0
4-Vinylguaiacol	Wood, spice cloves, curry	0.5–23
Eugenol	Spice cloves, honey	0.01–0.3
Isoeugenol	Carmination	0.06–2.4
Cerulignol	Spicy	0.04–2.2
Aldehydes		
Benzaldehyde	Almonds, sweet, caramel	0.02–0.21
Nonenal	Wax, citrus	0.03–0.47
Phenylacetaldehyde	Green, grass, honey	0.05–4.5

Aromatic compound	Aromatic descriptor	Content (µg/g)
Alcohols		
Phenylethyl alcohol	Flowers, honey, pollen	0.01–2.26
Benzyl alcohol	Roses, almond	0.05–0.13
Terpenols		
Camphor	Mint	0–0.23
Borneol	Pine tree	0–0.2
4-Terpineol	Spices, wood, soil	0.02–0.14
α-Terpineol	Flowers, lilac, sweet	0–0.2
Lactones		
γ-Nonalactone	Coconut, peach	0.03–0.11
Fatty acids		
Nonanoic acid	Wax, dry, fatty	0.12–0.67
Vanillic acid	Vanilla	0.07–0.86
Octanoic acid	Coconut, lactic, rancid, Cheese, sweet	0.14–3.38
Dodecanoic acid	Coconut, fatty, metallic	0–6.3
Benzeneacetic acid	Honey, fruity, sour	0–3.0
Furans		
Furfural	Caramel, candy	0–0.19

Table 3.
Aromatic compounds, families, descriptors, and minimum and maximum content found in the studied granulates and cork macerates [60].

7. Conclusion

The natural cork stoppers are world known, to many years, as closures for high-quality wines. The cork is a natural and sustainable material that provides an outstanding performance for in-bottle wine during aging, by combining minute oxygen transfer with sealing, durability, and chemical stability, for example, inertness toward the liquid content and along storage, preventing its sensory deterioration. Both the cellular structure features and the chemical composition of cork are at the base of a set of physical and mechanical properties that are important for bottle sealing, namely, the very low permeability to liquids and gases and the behavior under compression with an outstanding recovery upon stress relief, which is absolutely essential for the sealing in the bottle neck preventing liquid leakage.

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Figure 7 was adapted with permission from Lopes P, Saucier C, Teissedre P-L, and Glories Y. Impact of storage position on oxygen ingress through different closures into wine bottles. Journal of Agricultural and Food Chemistry. Copyright 2006 American Chemical Society.

Conflict of interest

The authors declare no conflict of interest.

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