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The bottleneck/cork interface: A key parameter for wine aging in bottle

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Abstract. This study investigated the impact of the stopper / bottleneck interface on oxygen ingress in wine bottles, emphasizing the role of the surface treatment on the stopper. Considering first the corkstopper alone, compressing the microagglomerated cork by 40 % by volume had minimal impact on oxygen transfer. When examining the entire sealing system, without surface treatment, 99 % of oxygentransfer occurred at the stopper / bottleneck interface. However, when the stopper was coated with a paraffin-silicone mixture, oxygen transfer was almost entirely prevented at the interface. Initially intended to ease uncorking, this coating also significantly improved oxygen control. The second part ofthe work focused on examining the effect of aging on the properties of the sealing system under conditions that simulate wine storage in the bottle, using a 6 mm thick cork. Over a 24-month period simulating wine aging, the cork's intrinsic oxygen diffusion properties remained stable. At 20 °C, the presence of model wine increased oxygen transfer at the glass / cork interface, accounting for 75 % ofthe total transfer. The position of the bottle during storage, whether vertical or horizontal, did not influence oxygen transfer. At higher temperatures, 35 °C and 50 °C, the sealing system's barrier properties remained stable for 9 and 3 months, respectively, before degrading, which resulted in increased oxygen transfer at the interface.

1. Introduction

The shelf life of wine is a major concern for the wine industry. This is particularly true for wines intended for long cellaring, which are supposed to reach their peak after an ageing period ranging from a few months to several years, or even decades. Low, controlled oxygen inputs through the sealing system are generally necessary for the wine to evolve towards its optimum organoleptic characteristics. Understanding and quantifying these oxygen transfer phenomena is therefore a major challenge in controlling oxygen transfer to optimize wine aging and ensure oxidative stability. Although often described as a single process, the transfer of oxygen into the wine actually results from three simultaneous phenomena : an initial transfer, corresponding to the oxygen released by the cork after its compression into the bottleneck, and a progressive transfer from the external environment into the wine, occurring both through the cork stopper and at the interface between the bottleneck and the cork stopper.

Regardless of the different types of cork stoppers currently in use, an additional outer layer of a surface treatment product is consistently applied as the final step in the manufacturing process. The most commonly used coating agents include food-grade paraffin wax, silicone, or emulsions combining these two products [1]. Although the specific application method and quantity used vary by cork supplier, these coating agents are typically applied using a drum coater to cover the surface of the stoppers. The primary purpose of these surface treatments is to facilitate both the insertion and, especially, the extraction of the stopper from the bottleneck, as they reduce adhesion between the glass and the cork by acting as a lubricant [2, 3]. Additionally, they enhance the liquid-tightness by minimizing leakage risks and slow down the liquid absorption by the stopper in contact with wine [4]. However, only a few studies have examined how these coating agents affect oxygen transfer through the cork / bottleneck system [5, 6].

In this work, an in-depth investigation was carried out to determine the role played by the interface between the stopper and the glass bottleneck. How much oxygen enters the bottle via the bottleneck / cork interface? What role does the cork's surface treatment play in transfer at the bottleneck / cork interface? How does this transfer of oxygen through the sealing system evolve over time? How it is influenced by environmental storage parameters ? First, oxygen transfer at the glass / cork interface and the role of surface treatment were considered. To this end, the intrinsic oxygen diffusion coefficient of agglomerated corks was measured. Then, the oxygen diffusion coefficient of the entire sealing system (cork compressed in a bottleneck) was determined in the presence or absence of surface treatment. This step-by-step approach enabled us to quantify and differentiate between the two oxygen flows passing through the stopper and at the interface between the cork stopper and the glass bottleneck. The second part of the work was devoted to studying the aging of the sealing system, under conditions simulating wine storage in the bottle. The evolution of the oxygen barrier properties under aging conditions were followed in presence of a model wine solution on oxygen transfer, paying particular attention on the role of the glass / cork interface.

2. Materials and methods

2.1. Experimental plan to determine the oxygen transfer occurring at the interface between the cork stopper and the bottleneck

2.1.1. Cork stopper samples

The stoppers used for the experiments were microagglomerated stoppers with a diameter of 24.2 mm and initial length of 49 mm. The first experiments on cork stopper alone, uncompressed (Figure 1, ①), were carried out on 3 mm thick cork wafers to reduce the time of measurement. In the case of compressed stopper (Figure 1, ②), cork samples were 6 mm thick to prevent buckling during compression. In both cases, cork wafer (compressed or uncompressed), was placed in a metal ring and the interface between the cork and the metal was glued to avoid any gas transfer at the interface. For cork compressed in a bottleneck, non-coated full-length cork stoppers were inserted in empty glass bottles (Figure 1, ③). The bottleneck was cut and inserted in a metal ring with the part between the ring and the bottleneck glued. The same procedure was applied for cork stoppers coated with a surface treatment product (Figure 1, ④). They were coated with a monolayer surface treatment product composed of an emulsion of paraffin and silicone. For these stoppers, only 6 mm wafers were inserted in the bottleneck to reduce the time of permeation experiments.

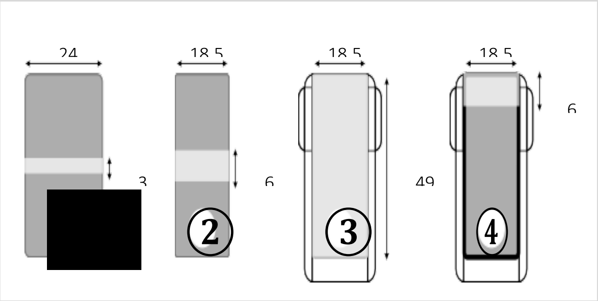

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Figure 1. The different sealing systems studied, comprising.

①: uncompressed microagglomerated cork, ②: compressed microagglomerated cork, ③: compressed microagglomerated cork in a bottleneck without surface treatment and ④: compressed microagglomerated cork in a bottleneck with surface treatment.

2.1.2. Measuring oxygen permeability through corkstoppers

The oxygen diffusion coefficient of microagglomerated cork stoppers was determined using a manometric system developed in the laboratory [7-9]. This experimental set-up consists of two chambers separated by the sample (Figure 2). Firstly, after an oxygen flush in the C_1 measuring chamber, an initial oxygen pressure is set, while the second chamber C_2 is placed under a dynamic primary vacuum (0.1 hPa). The temperature is kept constant at 20 °C, throughout the experiment, by circulating thermostated water around the measurement chamber. The decrease in oxygen pressure in measurement chamber C_1 is monitored over time. This corresponds to the transfer of oxygen from C_1 to C_2 through the sample. For the measurements, the full-length cork was replaced by a wafer a few millimeters thick (3 or 6 mm, depending on the cork analyzed), thusreducing the experimental time from several weeks to a few days.

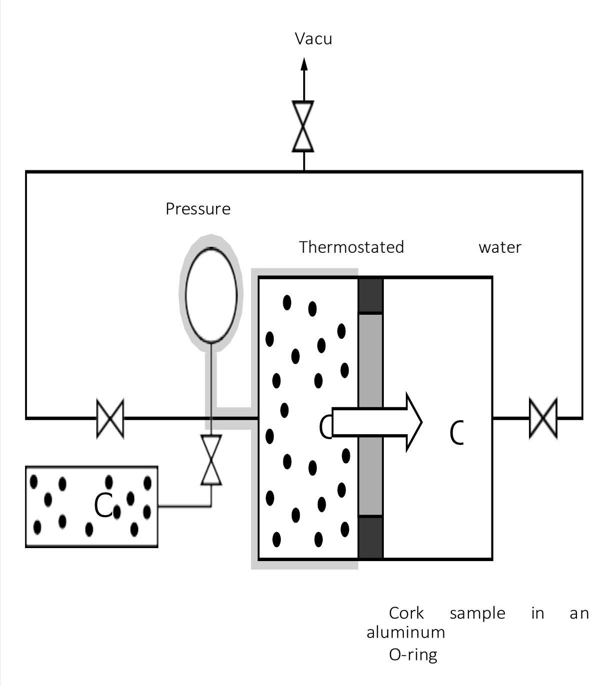

Figure 2. Scheme of the homemade manometric device for theoxygen transfer measurement of the different cork samples.

The phenomenon of permeation is classically described as a three-step mechanism: (*i*) firstly, sorption of gas molecules on the surface of the material; (*ii*) secondly, diffusion through the material according to the concentration gradient; and (*iii*) lastly, instantaneous desorption from the other surface of the material.

2.1.3. Calculation of oxygen diffusion through thecork stopper alone

Considering the gas as ideal, the surface molar flow of oxygen passing through the cork wafer, J_{wafer} (mol·m^{-2}·s^{-1}) is given by Equation 1:

$$J_{wafer} = \frac{1}{S_{wafer}}\frac{dn}{dt} = -\frac{V}{S_{wafer}.R.T}\frac{dp}{dt} \quad (1)$$

with n the amount of oxygen (mol), p the pressure (Pa) in the measuring chamber along time t (s), V the volumeof the measurement compartment (m^3), S_{wafer} the surface of the wafer (m^2), R the ideal gas constant (8.314 J·mol^{-1}·K^{-1}), and T the temperature (K). According tothe first Fick law, the surface molar flow of oxygen passing through the cork wafer, once the steady state isestablished, is also given by Equation 2:

$$J_{wafer} = -D_{wafer}.\nabla C^a \approx D_{wafer}\frac{C^a}{L_{wafer}} \quad (2)$$

with D_{wafer} the diffusion coefficient (m^2·s^{-1}) of oxygen inside the wafer, L_{wafer} the thickness of the wafer (m), and ∇C^a (mol·m^{-4}) the concentration gradient of oxygen adsorbed on both sides of the wafer. C^a (mol·m^{-3}) is also related to the concentration of the gas Cg (mol·m^{-3}) by Equation 3:

$$C^a = \psi.C^g = \psi.P.R.T \quad (3)$$

with ψ, the separation factor or partitioning coefficient.

ψ is obtained from the sorption isotherm of oxygen on cork, which has been determined in previous work on natural cork [8]. For the measurements carried out on the cork wafer alone, the partition coefficient used for the calculation is 0.9, which corresponds to the pressure gradient applied of 900 hPa.

By combining Equations 1-3, and after integration over time, the following Equation 4 is obtained. The diffusion coefficient of oxygen through a cork wafer D_{wafer} (m^2·s^{-1}), is then determined once steady state is reached.

$$\ln\left(\frac{p_{t=0}}{p_t}\right) = \frac{D_{wafer}.\psi.S_{wafer}}{L_{wafer}.V}.t \quad (4)$$

2.1.4. Calculation of oxygen diffusion through the cork stopper compressed in the bottleneck

The total flow J_{total}, going through the system comprising the cork wafer inserted in the glass bottleneck, is expressed by the following:

$$J_{total} = \frac{}{S_{wafer}+S_{interface}}\frac{an}{dt} - \frac{V}{S_{wafer}.R.T}\frac{ap}{dt} \quad (5)$$

Here, we assume that the surface section defined by the glass / cork wafer interface, $S_{interface}$, is negligible compared with the one of the cork wafer, S_{wafer}. Moreover, it is supposed that oxygen sorption can occurat the interface between the cork wafer and the glass bottleneck. Thus, ψ is also considered in the determination of the total effective diffusion coefficient :

$$J_{total} = -D_{total}.\square C^a = D_{total}.\psi.P.R.T \quad (6)$$

For the measurements carried out on the cork wafer compressed in a bottleneck, the partition coefficient ψ used for the calculations is 0.7, corresponding to the pressure gradient applied of 600 hPa. As mentioned above, by combining Equations 5 and 6, we obtain thefollowing, once steady state is reached :

$$\ln\left(\frac{p_{t=0}}{p_t}\right) = \frac{D_{total}.\psi.S_{wafer}}{L_{wafer}.V}\ t \quad (7)$$

2.1.5. Extrapolation of the diffusion coefficient for a *full-length cork stopper*

However, as the cork is not a homogeneous material, the diffusion coefficient measured through a wafer is not representative of the diffusion coefficient through a whole cork. For the measurements made on wafers 3 or 6 mm thick, it was thus necessary to extrapolate the experimental results to a full-length cork stopper. To thatend, by analogy with an electrical circuit, the stopper wasconsidered as a serial stack of n wafers, where each slicerepresents a local resistance to gas transfer, R_{wafer}. The sum of these resistances allowed us to calculate the total resistance $R_{stopper}$ of the stopper and thus $D_{stopper}$ which is the extrapolated diffusion coefficient of the stopper. This model therefore makes it possible to compare samples of different thicknesses (3 or 6 mm), by extrapolating experimental values to an extrapolated distribution for a full-length cork stopper [7, 8].

2.2. Parameters influencing wine aging inbottle

For the second part of the work, more oxygen-permeable microagglomerated corks stoppers were selected in orderto facilitate the detection of any potential changes in permeability during aging. For these tests, a miniaturized bottle system was designed (Figure 3a). Surface-treated microagglomerated corks were compressed into bottlenecks cut 70 mm from the top. After corking, only6 mm of the cork remained in the bottleneck. To assess the effect of the presence of wine on the oxygen barrier properties of the cork, the samples were stored in the absence or presence a model wine solution and sealed inan inert atmosphere (argon). Samples without model wine were directly sealed with a glass disc glued with epoxy glue to prevent gas transfer between the lower edge of the bottleneck and the glass disc. For samples in contact with model wine, 10 mL of solution was added before closing the bottleneck with the glass disc [10]. In this closed system, the residual oxygen pressure in the bottleneck was initially between 5 and 7 hPa. Samples were positioned either in contact with the vapor phase ofthe model wine, or directly in contact with the liquid phase, thus reproducing vertical or horizontal bottle storage. For samples stored horizontally, three temperatures were studied : 20 °C, 35 °C and 50 °C. The50 °C temperature was chosen to simulate accelerated aging of the samples. The latter storage conditions were applied only to samples in the “horizontal” position.

An external relative humidity of 50 % was selected for aging under conditions of controlled hygrometry (corresponding to storage under ambient conditions for temperate countries). Although high-temperature conditions deviate from a typical cellar storage environment, they do accelerate processes that may occur during the bottle aging of wines. Additionally, such temperatures can be encountered during thetransportation of bottles. The different storage conditions, with the corresponding diagram, are shown in figure 3a.

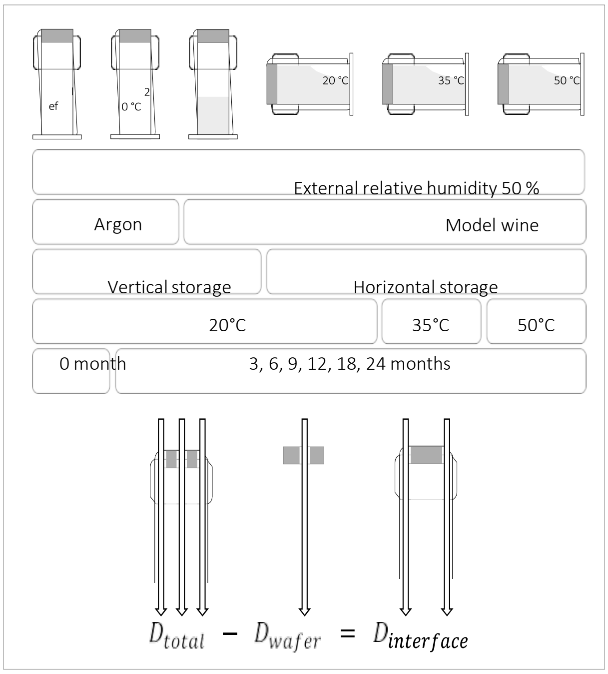

Figure 3. a) Overview of the different conditions investigated for the aging study and corresponding classification used for the five types of samples compared with the initial reference. B) Representation of the different oxygen transfers occurring through the entire sealing system and the stopper (6 mm thick stopper wafer), giving access to the transfer at the interface.

Oxygen permeation measurements were conducted using manometry in two consecutive stages (Figure 3b). First, measurements were performed on the entire sealing system, including the cork wafer compressed in the bottleneck, to determine D_{total} . Second, measurements were carried out on the wafer alone to determine D_{wafer}.The oxygen transfer at the interface, $D_{interface}$, was then calculated by subtracting D_{wafer} from D_{total} (Figure 3b). Samples were monitored for 24 months, withmeasurements taken at 3, 6, 9, 12, 18 and 24 months. Measurements were conducted on at least 4 samples for each storage condition and analysis time.

It is important to note that, unlike the previous section, in this part of the study, the results are presented as the oxygen diffusion coefficient through a 6 mm thick cork wafer, without extrapolating to a full-length cork stopper.Such an extrapolation would require developing a more complex multiparametric model that considers thehydration state of the stopper.

2.3. Scanning electron microscopy

Prior to bottling, agglomerated cork stoppers without and with surface treatment were observed by SEM using a Jeol JSM 7600F apparatus (3.5 kV). Before imaging cork samples were cut with a razor blade, and coated witha carbon film (15–20 nm). The obtained images allowed us to visualize the distribution of the surface treatment product on the stopper surface as well as the thickness ofthe coating.

2.4. Characterization of the surface treatment product

The evolution of the thermal properties of the stoppers' surface treatment product after evaporation of the solvent was studied using Q20 calorimeter (TA instruments, New Castle, DE, United States). The samples were weighed and sealed in aluminum capsules (T-Zero, TA instruments, New Castle, DE, United States) before being subjected to a double heating–cooling cycle at 10 °C·min^{-1} under nitrogen atmosphere. The temperature range was from −20 °C to 120 °C.

3. Highlighting oxygen transfer at the glass / cork interface and the role of surface treatment

A comprehensive study was carried out to determine the role played by the interface between the cork and the glass bottleneck. Particular attention has been paid to theeffect of cork compression (leading to 40 % of the cork volume for still wines) and to the surface treatmentapplied on the cork surface [11]. To assess the effect of cork compression on oxygen transfer through the cork, the oxygen diffusion coefficient was first determined onuncompressed and then, on compressed microagglomerated cork wafers with the interface glued.The mean value of the oxygen diffusion coefficient, $D_{stopper}$, determined from the extrapolated distribution, was 1.4 × 10^{-11} m^{2}·s^{-1} for uncompressed corks (Figure 4a, ① solid line) and 0.9 × 10^{-11} m^{2}·s^{-1} for compressed corks (Figure 4a, ② dashed line). Thus, when the cork stopperundergoes a 40 % volume reduction, only a slight reduction in oxygen transfer through the cork isobserved, with a reduction of a factor of 1.5. This reduction in oxygen transfer through a microagglomerated cork stopper can be attributed to a reduction in the initial porosity between the cork particles composing the stopper. This initial porosity can vary according to the formulation of the stopper and the size of the cork particles.

The oxygen diffusion coefficient was then determined on the bottleneck / cork system, in the presence or absence of surface treatment. In the case of the cork compressed in a bottleneck without surface treatment, the oxygen diffusion coefficient is extremely high (Figure 4a, ③ dashed-dotted line), with an average value of 1.3 × 10^{-7} m^{2}·s^{-1}, compared with 0.9 × 10^{-11} m^{2}·s^{-1} for the cork alone compressed (with the interface glued). This means 10 000 times more permeable than the compressed stopper alone. Such low resistance to gas transfer is due to the bottleneck / cork interface. More than 99 % of oxygen transfer in the bottle takes place at this interface. This phenomenon is probably due to defects formed on the surface of the stopper during corking (macropores, roughness, etc.), or to defects present on the surface of the glass bottleneck. They can act as preferential pathways for gas transfer. Nevertheless, when the stopper is surface-treated, the oxygen diffusion coefficient returns to a level similar to that obtained for the compressed stopper with the interface glued. Its average value is 7.5 x 10^{-12} m^{2}·s^{-1} (Figure 4a, ④ dotted line). When coated with a surface treatment product, theoxygen flow at the interface decreases significantly with a diffusion coefficient 10 000 times lower.

In addition to permeability measurements, scanning electron microscopy (SEM) analysis was carried out on microagglomerated corks without and with surface treatment (Figure 4b). The surface treatment of the cork, carried out by drum coating, results in a thin layer that can be observed on the surface of the cork. Its thickness can be estimated from cross-sectional images at around 300 nm (Figure 4b.*iii*).

This methodical approach enabled us to quantify and differentiate between the two oxygen flows : one throughthe cork and the other at the bottleneck / cork interface. The results clearly demonstrated the crucial role of surface treatment in the transfer of oxygen of the wine sealing system. The surface treatment therefore provides an effective barrier to oxygen transfer at the glass / cork interface, in addition to its initial role of facilitating uncorking.Effect of aging on the barrier properties of the stopper in operating conditions

In the following of this work, a more detailed study was conducted on the evolution of the oxygen barrier properties of the sealing system, over a 24-month aging period, under controlled conditions simulating the conservation of wine in bottle.

3.1. Intrinsic barrier properties of cork stopper

The oxygen diffusion coefficient through the cork stopper was determined for the different storage conditions at 3, 6, 9, 12, 18 and 24 months. The averagevalues of the oxygen diffusion coefficient are shown in Figure 5, and refer to oxygen transfer through a cork wafer with glued interface. Whatever the storage conditions, the oxygen diffusion coefficient values for the cork alone remained similar throughout the 24-monthperiod, with an average value of 1.3 × 10^{-11} m^{2}·s^{-1}.Neither the presence of model wine, nor position or temperature have a significant effect on the oxygen diffusion coefficient, highlighting the remarkable stability of the corks over time, at least in terms of their oxygen barrier properties under these storage conditions. However, for samples stored at 50 °C, the measurements were stopped after six months' storage, as the model wine contained in the bottleneck had completely evaporated and therefore no longer reflected the initial storage conditions.

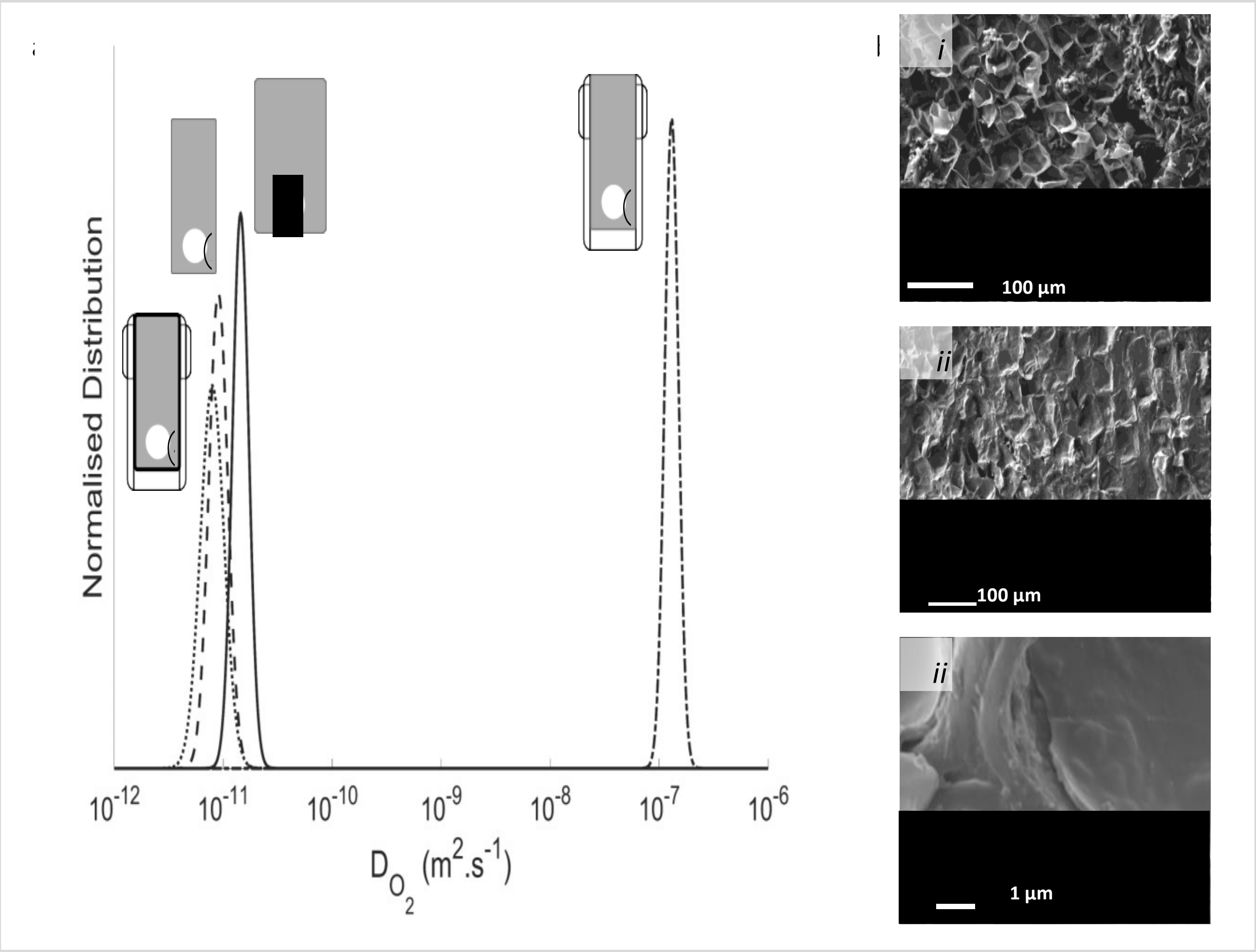

Figure 4. a. Distributions of the logarithm of the diffusion coefficient of oxygen. ① (-) : extrapolated distribution to a 48 mm stopper from the experimental data of 3 mm uncompressed cork wafers. ② (--) : extrapolated distribution to a 48 mm stopper from the experimental data of 6 mm compressed cork wafers. ③ (:): experimental distribution of 48 mm stoppers without surface treatment andcompressed in a bottleneck. ④ (.-): extrapolated distribution to a 48 mm stopper from the experimental data of 6 mm cork wafers witha surface treatment (emulsion of paraffin and silicon) and compressed in a bottleneck. b. Scanning electron microscopy observations ofthe surface of microagglomerated stoppers. *i*) stopper without surface treatment, *ii*) stopper with surface treatment, *iii*) cross-section at higher magnification showing cell walls covered with a thin layer of paraffin and silicone deposited on the surface.

3.2. Impact of aging on the oxygen transfer at the glass–cork interface

3.2.1. Evolution of the barrier properties in theabsence of wine

The effect of aging was then assessed on the entire sealing system, comprising the compressed cork wafer ina bottleneck. Oxygen transfer occurs both through the cork and at the interface between cork and bottleneck. The initial diffusion coefficient of oxygen through the stopper and through the bottleneck / stopper system wasdetermined with a value of 2.3 × 10^{-11} $m^2 \cdot s^{-1}$ (Figure 6, indicated as “ref.”). The oxygen diffusion coefficient of the compressed cork in the glass bottleneck is slightly higher than that of the compressed cork alone, suggesting that part of the oxygen transfer initially takes place at theinterface between cork stopper and bottleneck. This oxygen transfer at the glass / cork interface accounts forover 30 % of total oxygen transfer.

The effect of aging was then evaluated focusing on the cork compressed in a bottleneck without model wine Oxygen transfers occurring both through the cork and atthe glass / cork interface were considered. After 3, 6, 9, 12, 18, and 24 months of storage, the corresponding global oxygen diffusion coefficients for the cork compressed in the bottleneck were similar to that of the initial reference (Figure 6). The observed variations weremostly related to the variability of the raw material itselfrather than to aging. An average value of all the diffusioncoefficients in a single distribution over the period of 24months was thus used thereafter as the reference for the condition without model wine, both for the intrinsic cork value and for the total value (cork + glass / cork interface). This gave an oxygen diffusion coefficient for the stopper alone and for the cork stopper compressed in the bottleneck of 1.9 × 10^{-11} $m^2 \cdot s^{-1}$ and 3.0 × 10^{-11} $m^2 \cdot s^{-1}$, respectively. These values remained in the same range as that of the reference at time 0. Moreover, the oxygen diffusion coefficient measured on the stopper compressed in the glass bottleneck was higher than that of the compressed stopper alone (without considering the transfer occurring at the interface with the glass bottleneck). This indicates, again, that part of the oxygen transfer occurred at the glass / cork interface.

3.2.2. Influence of the presence of wine and ofstorage position

The effect of model wine presence and wine bottle storage position (vertical or horizontal) on gas transfer through the bottleneck was then determined at a storage temperature of 20 °C over 24 months. In the presence ofthe model wine, the total oxygen diffusion coefficient forthe bottleneck / cork system is significantly higher after 3 months' storage. The values obtained for vertical and horizontal storage with model wine (6.7 × 10^{-11} $m^2 \cdot s^{-1}$ and 4.6 × 10^{-11} $m^2 \cdot s^{-1}$, respectively) are higher than thosefor the condition without model wine (3.0 × 10^{-11} $m^2 \cdot s^{-1}$). Thus, between 0 and 3 months' storage, the presence of model wine favors oxygen transfer at the interface between cork stopper and bottleneck. However, after 3 months, this oxygen diffusion coefficient remains stablefor samples stored for 6, 9, 12, 18 and 24 months. Although samples stored vertically for 24 months appear to show a higher value of total oxygen diffusion coefficient.

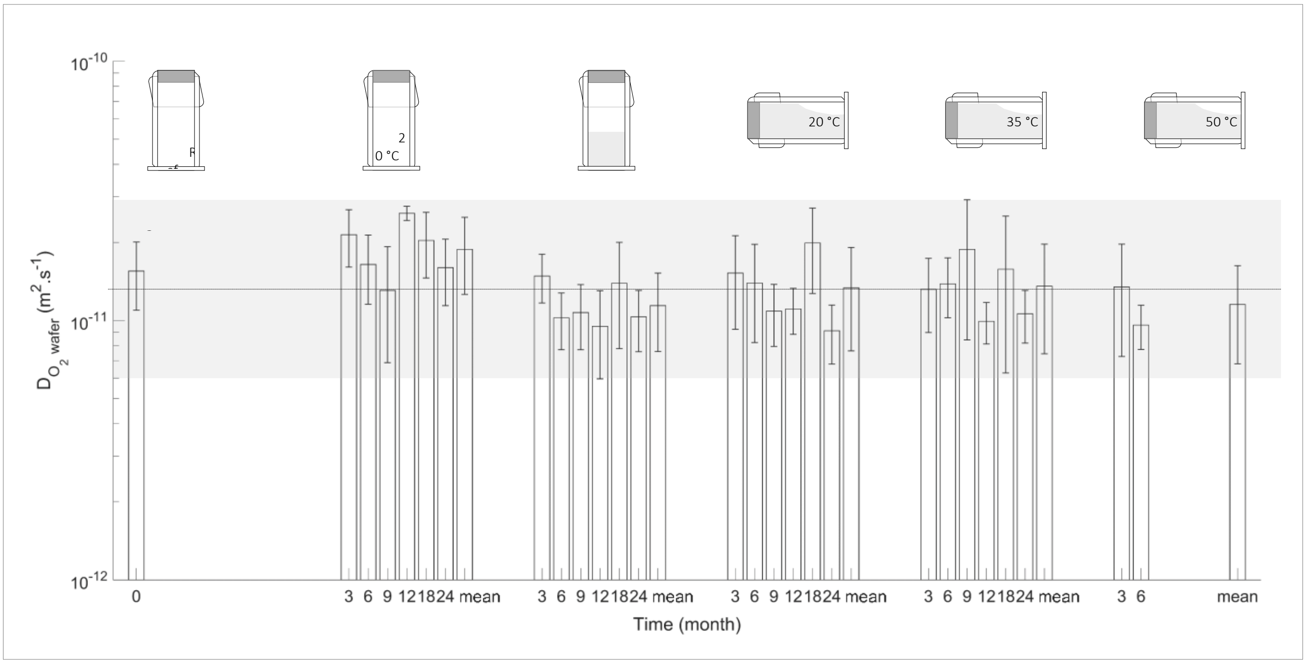

Figure 5. Evolution of the oxygen diffusion coefficient through compressed cork alone after storage in the different conditions over 24 months determined by experimental data measured on 6 mm compressed cork wafers. From left to right : Reference without model wine,storage at 20 °C without model wine, storage at 20 °C with model wine and vertical position, storage at 20 °C with model wine and horizontal position, storage at 35 °C with model wine and horizontal position and storage at 50 °C with model wine and horizontal position. Shaded area: 95 % distribution corresponding to all conditions. One-way ANOVA test was carried out on the average values for each condition. Significant differences ($P < 0.05$) are indicated with different letters (a, b).

It is important to note that the values remain in the same order of magnitude Such an increase in the oxygen diffusion coefficient after 3 months in the presence of model wine could be due to the presence of water and ethanol sorbed by the cork, which would promote surface diffusion between the polymeric chains composing the cork [12, 13]. This increase could also be due to a changein the cork's mechanical properties. Indeed, work by Lagorce *et al.* has shown that cork hydration affects the mechanical properties of stoppers, with a significant reduction in Young's modulus by half its initial value between 50 % and 100 % relative humidity [14, 15]. At higher levels of adsorbed water, water molecules aggregate around hydrophilic sites to form clusters that tend to plasticize the material. Consequently, we can assume that the force applied by the closure to the glass walls of the bottleneck decreases as the material hydrates, leading to increased oxygen transfer at theinterface. Once equilibrium has been reached in the sorption of water and ethanol on the cork, a relatively stable diffusion coefficient is observed over the following months

Additionally, two storage positions were studied: a "vertical storage" position, where the cork is in contact with the vapor phase, and a "horizontal storage" position, where the cork is in contact with the liquid phase. The values for the total oxygen diffusion coefficient for these two different storage positions are similar. These observations hold true for all durations (3 to 24 months) measured under these conditions. Therefore, the study established that the storage position of wine bottles during a 24-month aging period at 20 °C does not impact the oxygen transfer through the bottleneck / cork system, whether through the cork itself or at the interface with the glass bottleneck.

3.2.3. Effect of temperature

Finally, the effect of storage temperature was evaluated with samples where the model wine was in contact with the cork (horizontal position). At 20 °C, oxygen diffusion coefficients remained unchanged from 3 months to 24 months of storage (Figure 6). At 35 °C, diffusion coefficients were similar to those measured at 20 °C, but only up to 9 months' storage. At 12 months, a sharp increase in the total oxygen diffusion coefficient was observed (from 5.2×10^{-11} $m^2 \cdot s^{-1}$ to 3.5×10^{-8} $m^2 \cdot s^{-1}$), while the diffusion coefficient through the stopper remained unchanged (Figure 6). Such an increase istherefore due to significant transfer taking place at the bottleneck / cork interface. Finally, for samples stored at50 °C, significant oxygen transfer at the interface was visible from 3 months onwards, with a total diffusion coefficient value of 1.8×10^{-7} $m^2 \cdot s^{-1}$. This phenomenon was accentuated after 6 months, with a value of 7.2×10^{-6} $m^2 \cdot s^{-1}$, close to the diffusion coefficient of oxygen in air(2.0×10^{-5} $m^2 \cdot s^{-1}$), indicating the presence of a leak at the cork / glass interface. The appearance of leaks can be attributed, as previously, to a change in the mechanical properties of the stopper, leading to a weaker force applied by the closure on the glass of the bottleneck. Another hypothesis is linked to the temperature stability of the surface treatment product. Indeed, a high storage temperature of 50 °C could induce partial melting of the surface treatment product applied to the external surfaceof the cork.

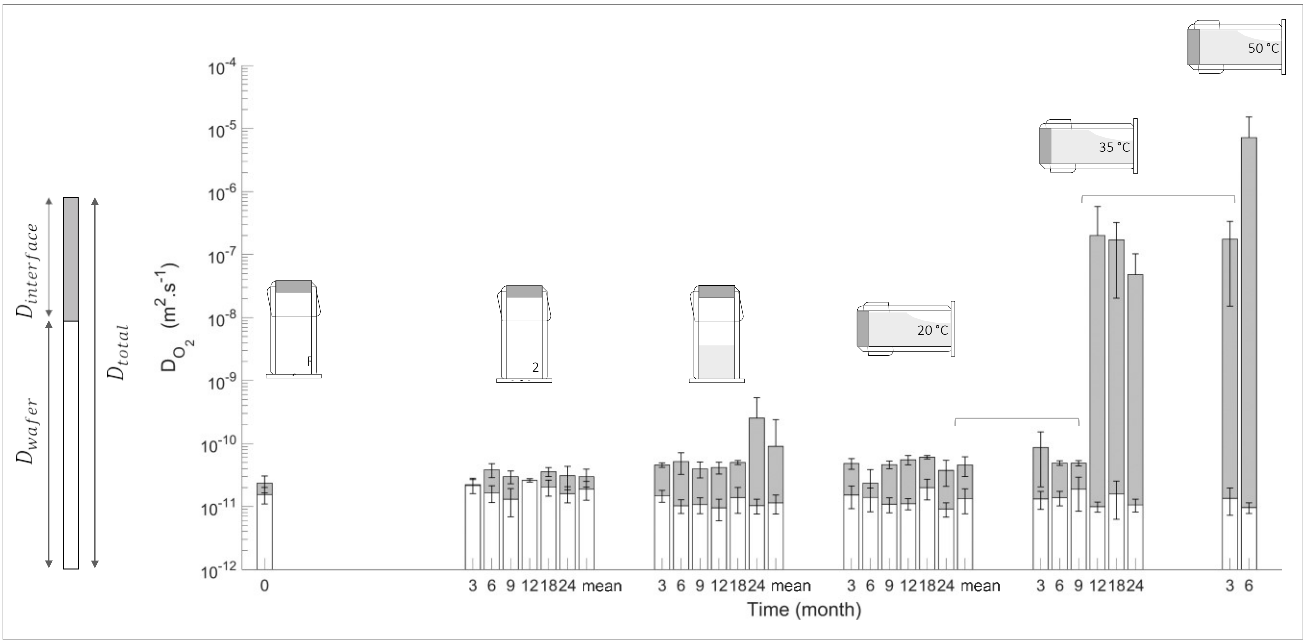

Figure 6. Evolution of the oxygen diffusion coefficient through compressed cork alone (D_{wafer}) and through cork compressed in a bottleneck (D_{total}) over 24 months, determined by experimental data measured on 6 mm compressed cork wafers alone and compressedin the glass bottleneck. From left to right : Reference without model wine, storage at 20 °C without model wine, storage at 20 °C with model wine and vertical position, storage at 20 °C with model wine and horizontal position, storage at 35 °C with model wine and horizontal position and storage at 50 °C with model wine and horizontal position. Data are displayed as the sum of the diffusion coefficient through the cork alone (light color) and the diffusion coefficient at the interface (dark color). Statistical test was carried out on the average values of D_{total} for each condition, and significant differences ($P < 0.05$) are indicated with different letters (a, b).

Additional measurements carried out by differential scanning calorimetry showed, during the first heating cycle, a significant endothermic peak beginning at around 20 °C and ending at around 70 °C (Figure 7). Thisthermal event consists of a first peak at around 45 °C anda second peak with a maximum at 64 °C [19], corresponding to the melting of the various paraffins contained in the product. The partial melting of thetreatment product could therefore promote oxygen transfer at the interface between the stopper and the bottleneck.

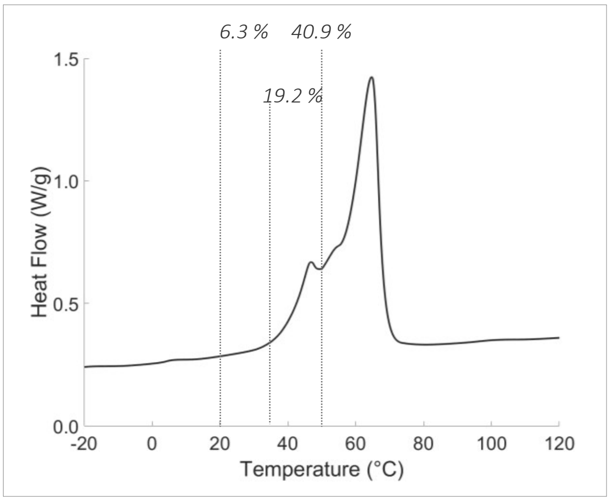

Figure 7. DSC curve of the surface treatment agent from -20 °Cto 120 °C, with the liquid / solid ratio reported in percentage for20 °C, 35 °C and 50 °C.

This study highlighted the preponderance of oxygen transfer occurring at the interface as a function of different storage conditions. The data obtained showunambiguously that oxygen transfer at the glass / cork interface does not depend on whether the bottle is stored vertically or horizontally at 20 °C, but is strongly influenced by the presence of wine in contact with the cork, as well as by temperature.

4. Conclusion

In this work, several crucial aspects relating to the use of cork-based microagglomerated oenological stopperswere studied: (*i*) oxygen transfer at the glass / stopper interface and the role of stopper surface treatment on thistransfer and (*ii*) aging of the bottleneck / stopper system under conditions simulating wine storage in the bottle.

Firstly, oxygen transfer through different microagglomerated cork was quantified using the manometric method. Complex systems were studied for microagglomerated corks, in order to differentiate the flow of oxygen through the sealing system (cork compressed in a bottleneck) from that through the cork alone. The compression of a cork in the bottleneck of a still wine bottle has little impact on oxygen transfer. On the entire sealing system, when a cork is inserted into a glass bottleneck without any surface treatment, the oxygen diffusion coefficient through the compressed cork in a bottleneck is 10 000 times greater than through the compressed cork alone with the glued interface. However, when the stopper surface is coated with asurface treatment product, oxygen transfer through the cork / bottleneck system is similar to that measuredthrough a compressed stopper alone with the glued interface. This work has demonstrated that the surface treatment, in addition to its lubricating role, acts as an additional barrier to oxygen transfer by masking defects at the interface between the stopper and the bottleneck, enabling oxygen permeability to be as low as that of the stopper.

Secondly, we focused on the evolution over time of the transfer properties of the sealing system under conditions simulating wine storage in the bottle. The results obtained using the manometric method indicate that the intrinsic oxygen diffusion coefficient of the cork remains unchanged, whatever the storage conditions after 24 months of aging. In the case of the entire sealing system (cork compressed in a bottleneck), the presence of model wine favors oxygen transfer at the interface, which accounts for nearly 70 % of total oxygen transfer. Storage position (bottle kept upright or lying down) does not affect oxygen transfer, at least for the 24-month period investigated. Once water and ethanol sorption equilibrium has been reached after three months' storage (corresponding to the first time step analyzed), the barrier properties of the sealing system do not change over the following months. Finally, temperature also has an impact on oxygen permeability in the sealing system, with very significant oxygen transfer at the interface after 12 months' storage at 35 °C. This period is reduced to 3 months for samples stored at 50 °C for the studied system. The present work thus paves the way for future research on this interesting topic.

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