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ABSTRACT

A comprehensive study was carried out to investigate the critical role played by the interface between the stopper and the bottleneck on oxygen penetration into the bottle, as well as the effect of surface treatment of the stopper. First, the compression of micro-agglomerated cork, at close to 40% (similar to that of a cork stopper in a still wine bottleneck), had a very limited effect on the oxygen transfer. Second, once a cork was inserted into a glass bottleneck without any surface treatment, up to 99% of the total oxygen transfer took place at the stopper-bottleneck interface. Third, when the cork surface was coated with a paraffin-silicone mixture, there was almost no oxygen transfer at the interface. Although initially used as a slippery agent for easier uncorking, the surface coating of the stopper, as a thin layer of several hundred nanometers, had a remarkable and unexpected impact on the control of the oxygen transfer.

KEYWORDS gas transfer, oxygen, agglomerated cork, interface, surface treatment.

1. INTRODUCTION

During wine conservation in a bottle, the control of oxygen transfer from the outside environment to the wine inside the bottle is a key parameter that determines the wine quality. Many other factors can also influence the evolution of wine during postbottling aging, such as the composition of the wine itself (also related to the wine-making process), the temperature, the relative humidity, the storage position, as well as the amount of oxygen initially present in the bottle (Arapitsas et al., 2014; Lopes, Saucier, Teissedre & Glories, 2006; Lopes et al., 2012; Roullier-Gall et al., 2017; Venturi et al., 2016). However, the oxygen transfer is the most critical factor (Roullier-Gall et al., 2016). For this reason, the choice of the packaging and in particular of the stopper is crucial in providing the best conditions for wine aging (Caloghiris, Waters & Williams, 1997; Crouvisier-Urion, Bellat, Gougeon & Karbowiak, 2018; Karbowiak et al., 2010; Lopes, Saucier, Teissedre & Glories, 2007a; Lopes, Saucier, Teissedre & Glories, 2007b; Waters, Peng, Pocock & Williams, 1996).

The transfer of oxygen into the bottle occurs by diffusion through the stopper itself and also at the interface between the glass bottleneck and the cork stopper. The oxygen transfer at the interface between the glass bottleneck and the cork stopper was first investigated experimentally in two studies (Lopes, Saucier, Teissedre & Glories, 2007b; Waters et al., 2001). Lopes *et al.* and Waters *et al*. measured the oxygen transfer through cork stoppers compressed in a bottleneck with an epoxy glue applied to the stopper-bottleneck interface present on the external surface in contact with the air. Their setup prevented the entry of oxygen through this top part of the cork-glass interface but still allowed the transfer that can occur through the lower part of the stopper-bottleneck interface once it has passed through the outer surface. A preliminary study by Lagorce-Tachon *et al*., on natural cork stopper inserted in a bottleneck without surface treatment showed that the global diffusion coefficient through the cork-glass bottleneck system was fifty times higher (5×10^{-7} $m^2.s^{-1}$) than through the compressed cork stopper alone (8×10^{-9} $m^2.s^{-1}$) (Lagorce-Tachon et al., 2016).

Recently, Karbowiak *et al.* measured the oxygen transfer through corked bottlenecks and through cork stoppers alone for bottles containing oxidized and nonoxidized white wines(Karbowiak et al., 2019). Their results showed that the effective oxygen diffusion coefficient for the cork compressed in a bottleneck was considerably higher for oxidized wines than for nonoxidized wines, whereas the oxygen diffusion coefficient for the cork stopper alone remained similar in all cases. However, in the studies by Lagorce-Tachon *et al.* and Karbowiak *et al.*, the diffusion coefficient values were measured on dry cork without taking into account the possible effects of water and ethanol on barrier and mechanical properties of cork. These two studies highlight that the cork stopper-glass bottleneck interface is likely to play an important role in oxygen transfer.

With the various types cork stopper currently used (natural or agglomerated), an additional outer layer of a surface treatment product is always applied in the final step of the manufacturing process. The most common coating agents are food-grade paraffin wax, silicone, or emulsions of these two products in a mixture (Lefebvre et al., 2006). They are usually spread in a drum coater to cover the surface of the stoppers, but the method of application and the quantity applied depend on the cork supplier. The primary function of these surface treatments is to facilitate the introduction and especially the extraction of the stopper from the bottleneck at the opening as they reduce the adhesion between the glass and the cork acting as a slippery agent (Chatonnet & Labadie, 2003; Fortes, Rosa & Pereira, 2004; Gonzalez-Adrados et al., 2011). They also improve the tightness to liquids by reducing the risk of leakage and they reduce the kinetics of liquid sorption by the stopper during cork-wine interaction (Gonzalez-Adrados et al., 2008). However, only a few studies have reported the effect of the coating agents on the transfer of oxygen through the cork-bottleneck system (Keenan, Gozukara, Christie & Heyes, 1999; Waters, 1997). Keenan *et al.* determined the oxygen permeability of macrocrystalline paraffin wax coated on natural cork stoppers and calculated the theoretical ingress of oxygen diffusing through a 17 µm layer of macrocrystalline paraffin wax coated on these stoppers. The oxygen transfer through the paraffin layer was not sufficient to cause the wine oxidation. The calculation was made in the case of a continuous coating along the stopper compressed in a cylindrical tube (18.5 mm in diameter) and did not take into account the permeation of oxygen along the interface between the bottleneck and cork coating. Therefore, it is particularly relevant to investigate the oxygen transfer through the system composed of a cork stopper that has undergone a surface treatment prior to being inserted in a glass bottleneck.

The present work examines the oxygen transfer at the interface between the glass bottleneck and the cork stopper. In particular, we focus on the effect of surface treatment of the stopper on the oxygen transfer at the glass-stopper interface. First, permeation experiments were performed for uncompressed and compressed (40% in volume) micro-agglomerated stoppers to determine their intrinsic oxygen diffusion coefficients and the effect of compression. Then, permeation experiments were carried out on the system composed of the cork stopper without surface treatment inserted in a glass bottleneck. In the final step, the oxygen transfer was evaluated on the glass-stopper system with the stopper coated with a surface treatment product. This comprehensive approach aimed to quantify and differentiate between the two oxygen flows passing through the stopper and at the interface between the stopper and the glass.

2. MATERIALS AND METHODS

2.1. Cork stopper samples

Micro-agglomerated cork stoppers (of the type Diam 10) were produced by Diam Bouchage (Céret, France) by a molding process using cork particles associated with binding agents. The stoppers used for the experiments were 24.2 mm in diameter and 49 mm long and were either coated with an anionic emulsion of paraffin and silicone or were without a surface treatment agent. The different conditions used are summarized in figure 1.

2.1.1. Compressed cork stopper

Cork wafers 3 mm thick were cut in the middle of full-length cork stoppers. They were then inserted uncompressed in a metal ring and attached at the periphery with Araldite 2012 to avoid gas transfer at the interface. The experiments were carried out on 3 mm thick cork wafers to reduce the time of measurement.

2.1.2. Compressed cork stopper

Full-length cork stoppers were first compressed using a professional bottling machine comprising four stainless steel jaws (GAI 4040, France) and inserted in a metal ring of 18.5 mm diameter, corresponding to the diameter of the entry bore of a bottleneck (AFNOR, 2018). This operation leads to a 40% compression of the initial stopper volume. Similar to uncompressed cork stoppers, the interface between the cork wafer and the metal ring was glued to avoid gas transfer at the interface. Here, the cork samples were 6 mm thick to prevent buckling during compression.

2.1.3. Cork stopper inserted in a glass bottleneck

Uncoated full-length cork stoppers were inserted in empty glass bottles (Bourgogne Astre 37.5 cL, Verrerie de Bourgogne, France) using the same bottling machine. Prior to bottling, the bottleneck profile of each bottle was measured using a profilometer (Egitron PerfiLab PRF 2014 01) to ensure they complied with the corresponding standard (AFNOR, 2018). The bottles were then cut below the stopper with a diamond cutoff wheel and inserted in a metal ring (Figure 2). Here, only the part between the ring and the bottleneck was glued with Araldite 2012. Oxygen transfer measurements were performed on 49-mm-long closures inserted in a bottleneck having an inner diameter of 18.5 ± 0.5 mm.

2.1.4. Cork stopper with surface coating

The same procedure was applied for cork stoppers coated with a surface treatment product. A coating composed of an emulsion of paraffin wax and silicone was sprayed in a drum coater at an industrial scale. For these stoppers, only 6 mm wafers were inserted in the bottleneck (Figure 2). This allowed the time of permeation experiment to be reduced. Ten measurements were performed for each of the four conditions chosen for this comprehensive study.

2.2. Oxygen permeation

During storage, we can distinguish between two phenomena; the oxygen given out by the stopper expressed by the oxygen initial release (OIR), and the oxygen coming from the outside environment expressed by the oxygen transmission rate (OTR) (Chevalier, Pons & Loisel, 2019). In this study, the OTR was determined using a homemade apparatus based on a manometric method (Figure 2).

The equipment and protocol have been detailed previously (Lagorce-Tachon et al., 2014; Lequin et al., 2012). The oxygen flow was measured through a sample separating two chambers. First, an oxygen purge was performed in the measuring chamber C_1. The initial pressure was then set at around 900 hPa while the other compartment, C_2, was kept under dynamic vacuum (0.1 hPa).

The decrease in oxygen pressure in the measuring compartment, caused by the transfer of oxygen from compartment C_1 to, C_2 was monitored over time. The temperature was kept constant at 298 K (±1 K) by a water circulation surrounding compartment C_1 under thermostat control. The pressure sensitivity was ± 0.1 hPa.

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 with a 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 of the coating.

3. CALCULATION

3.1.Oxygen transfer in the cork stopper

Considering the gas as ideal, the surface molar flow of oxygen passing through the wafer, J_w ($mol.m^{-2}.s^{-1}$) is given by the equation:

$$J_w = -\frac{1}{S_w}\frac{dn}{dt} = -\frac{V}{S_w.R.T}\frac{dp}{dt} \qquad \text{(Equation 1)}$$

p is the pressure (Pa) in the compartment C_1 along time t (s), V is the volume of the compartment C_1 (m^3), S_w is the surface of the wafer (m^2), R is the ideal gas constant (8.314 $J.\ mol^{-1}.K^{-1}$) and T is the temperature (K).

According to the first Fick's law, the surface molar flow of oxygen passing through the cork wafer, once the steady state is established, is also given by the equation:

$$J_w = -D_w . \nabla C^a \approx -D_w . \frac{C^a}{e} \qquad \text{(Equation 2)}$$

With D_w the diffusion coefficient ($m^2.s^{-1}$) of oxygen inside the wafer, e the thickness of the wafer (m) and ∇C^a ($mol.m^{-4}$) the concentration gradient of oxygen adsorbed on both side of the wafer. C^a ($mol.m^{-3}$) is related to the concentration of the gas C^g ($mol.m^{-3}$) by the equation:

$$C^a = \psi . C^g \qquad \text{(Equation 3)}$$

With ψ, so called the separation factor. Ψ is obtained from the sorption isotherm of oxygen, on cork which has been determined on previous work(Lequin et al., 2012).

By combining the equations (1), (2) and (3), and after integration over time, we obtain:

$$\ln\left(\frac{p_{t=0}}{p_t}\right) = \frac{D_w . \psi . S_w}{e . V} . t \qquad \text{(Equation 4)}$$

Thus, the diffusion coefficient of oxygen through the cork wafer is determined from the slope of the straight-line of the plot $\ln(\frac{p_{t=0}}{p_t})$=f(t) obtained once the steady state is established.

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

As cork stoppers are not homogeneous materials, the diffusion coefficient measured through a cork wafer of thickness e is not representative of the diffusion coefficient through a full-length cork stopper of length L_s. 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 that end, the stopper was considered as a serial stack of *n* wafers, where each slice represents a local resistance to gas transfer, R_w. The sum of these resistances allowed us to calculate the total resistance R_s of the stopper, as defined by the following equations:

$$R_s = \frac{L_s}{D_s} = \sum_{i=1}^{n} R_{wi} = \sum_{i=1}^{n} \frac{e}{D_{wi}} \quad \text{(Equation 5)}$$

$$L_s = e.n \quad \text{(Equation 6)}$$

$$\frac{1}{D_s} = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{D_{wi}} \quad \text{(Equation 7)}$$

Where R_s is the overall resistance of the stopper, D_s is the extrapolated diffusion coefficient of the stopper, L_s is the total length of the stopper, *n* is the total number of wafers contained in a full-length stopper and D_{wi} is the diffusion coefficient of the wafer *i* drawn at random in the statistical distribution of diffusion coefficients determined experimentally.

3.3. Oxygen transfer at the glass-cork interface

The oxygen flow through the cork stopper-glass bottleneck interface, $J_{interface}$ (mol.m^{-2}.s^{-1}), is determined by subtracting from the total flow, J_{total}, going through the system comprising the cork stopper inserted in the glass bottleneck, the oxygen flow going through the cork stopper alone, J_s.

$$J_{interface} = J_{total} - J_s \quad \text{(Equation 8)}$$

The total flow of gas passing through the bottleneck-cork system is expressed by an equation similar to Equation 1:

$$J_{total} = -\frac{1}{S}\frac{dn}{dt} = -\frac{V}{S.R.T}\frac{dp}{dt} \simeq -\frac{V}{S.R.T}\frac{\Delta p}{\Delta t} \quad \text{(Equation 9)}$$

As we know the diffusion coefficient of oxygen through the full-length cork stopper, D_s, the flow passing only through the cork stopper is calculated with the relation:

$$J_s = -D_s.S.\frac{\Delta p}{L_s.R.T} \quad \text{(Equation 10)}$$

In the last two equations, S is the section area of the cork inserted in the bottleneck, and Δp is the pressure decrease in compartment C_1 during time, Δt.

4. RESULTS AND DISCUSSION

4.1. Role of the compression on the oxygen transfer

To determine the effect of compression on the gas transfer through the cork stopper, the effective diffusion coefficient of oxygen was first measured on uncompressed and compressed cork wafers, with the interface glued in both cases. The experimental and extrapolated oxygen diffusion coefficient values for the compressed and uncompressed samples are given in Figure 3 and in Table 1. The effective oxygen diffusion coefficient through uncompressed 3 mm cork wafers was between 10^{-12} $m^2.s^{-1}$ and 10^{-10} $m^2.s^{-1}$. For the compressed 6 mm cork wafers, the effective diffusion coefficient values ranged from 10^{-11} to 10^{-10} $m^2.s^{-1}$. These data were then extrapolated to a full-length cork stopper (48 mm) for comparison using the model of series resistances to mass transfer. From the statistical distribution, the oxygen diffusion coefficient value was reduced from 1.4 x 10^{-11} $m^2.s^{-1}$ for the uncompressed to 9.2 x 10^{-12} $m^2.s^{-1}$ for the compressed cork stoppers.

Thus, when compression corresponding to a reduction of 40% in volume is applied to the stopper, this leads to a slight decrease in the oxygen transfer through the stopper with a reduction of the oxygen diffusion coefficient by a factor of 1.5. With natural cork stoppers, Lagorce-Tachon *et al.* did not find a significant impact of compression on the diffusion coefficient of oxygen after a 40% reduction in volume (with a diameter reduction from 24 mm to 18.5 mm)(Lagorce-Tachon et al., 2016). Indeed, the effective diffusion coefficients measured after compression led to a relatively large distribution of oxygen diffusion coefficients of uncompressed cork ranging from 10^{-10} to 10^{-7} $m^2.s^{-1}$. In such a case, it is highly probable that the heterogeneity between samples of natural cork (which are much more heterogeneous than agglomerated cork) masked the effect of the compression. For agglomerated cork stoppers, the statistical distribution of the effective diffusion coefficients for full-length stoppers were narrowed to values around 10^{-11} $m^2.s^{-1}$, reflecting the homogeneity of the agglomerated cork stoppers and indicating the effect of compression on oxygen transfer. These results also accord with those reported by Rabiot *et al.* They measured oxygen permeability in dry condition for agglomerated cork wafers (10 mm thick) with the initial diameter of 24 mm compressed to final diameters of 21 mm and 18.5 mm, which represent the lower and upper bottleneck diameters, respectively (Rabiot, Sanchez & Aracil, 1999). Such differences in the compression of the stopper, corresponding to a reduction between 23% and 40% in volume, led to a decrease in oxygen permeability between 9.3 x 10^{-13} $mol.m.m^{-2}.Pa^{-1}.s^{-1}$ and 1.8 x 10^{-13} $mol.m.m^{-2}.Pa^{-1}.s^{-1}$, respectively, which represents a reduction in oxygen permeability by a factor of 5. This decrease in the oxygen transfer through an agglomerated cork stopper could be attributed to a reduction in the initial porosity between cork particles. This could vary according to the formulation of the agglomerated cork stopper, in particular with respect to the ratio of weight of adhesive to the weight of cork (Crouvisier-Urion et al., 2020).

4.2. Oxygen transfer at the stopper-bottleneck interface: role of the surface treatment

In the second step, the effective diffusion coefficient of oxygen through the whole stopper-bottleneck system was determined. First, this was calculated for stoppers with no surface treatment and then for stoppers coated with an emulsion of paraffin and silicone. This allowed us to evaluate the gas transfer at the stopper-bottleneck interface and to assess the impact of the surface treatment on the oxygen diffusion. The experimental and extrapolated distributions of the logarithm of the diffusion coefficient of oxygen of the different samples are reported in Figure 4 and the mean oxygen diffusion coefficients extrapolated to a full cork stopper are displayed in Table 1.

For the stopper without a surface treatment agent and inserted in the bottleneck, the mean effective diffusion coefficient appeared significantly higher than that of cork stoppers alone (i.e., outside the bottleneck) and with the same compression level. The mean value was 1.3×10^{-7} $m^2.s^{-1}$ for the former compared with 9.2×10^{-12} $m^2.s^{-1}$ for the latter. Such a stopper-bottleneck system is thus much more permeable than a compressed stopper outside the bottleneck (with the interface glued). The poor resistance to gas transfer of this system must therefore originate from the stopper-glass interface, which thus addresses the likely role of defects (macropores, scratches, roughness irregularities, etc.) formed on the cork surface during its processing or at the bottling stage, or of defects present on the surface of the bottleneck. Such defects might constitute preferential pathways for gas transfer.

The OTRs through the stopper-bottleneck systems and through the stoppers alone were also calculated to determine the OTR through the interface. These results are summarized in Table 1 and highlight that more than 99% of the total oxygen transfer occurs at the stopper-bottleneck interface. A similar result was previously found for natural cork with an effective diffusion coefficient 50 times higher for a natural whole cork stopper compressed in a bottleneck compared with a compressed stopper alone with the interface glued (Lagorce-Tachon et al., 2016).

Table 1. Mean oxygen diffusion coefficients and OTRs determined for uncompressed and compressed cork stoppers alone and for cork stoppers inserted in a bottleneck with and without a surface treatment agent (extrapolated to a full cork stopper, from 10 replicates in each case; see figure 4 for corresponding distributions). For practical reasons, OTR is expressed as $mg.year^{-1}$, referring to as mg of oxygen going through the stopper per year.

	Effective Diffusion Coefficient D_s ($\times 10^{-12}$ $m^2.s^{-1}$)	**OTR_{total} ($mg. year^{-1}$)**	**$OTR_{interface}$ ($mg. year^{-1}$)**	**$OTR_{stopper}/OTR_{total}$ (%)**
Agglomerated uncompressed stopper (interface glued)	14.4 ± 2	0.61 ± 0.11	/	/
Agglomerated compressed stopper (interface glued)	9.2 ± 2	0.38 ± 0.08	/	/
Agglomerated stopper compressed in a bottleneck without surface treatment	130 000 ± 90 000	17 313 ± 4432	17 313	0.003
Agglomerated stopper compressed in a bottleneck with surface treatment	7.9 ± 2	0.34 ± 0.08	0	100

When the stopper is coated with a surface treatment agent, the effective oxygen diffusion coefficients through 6 mm cork wafers compressed in a bottleneck were around 8.8 x 10^{-12} $m^2.s^{-1}$. When extrapolated to a 48 mm cork stopper, the mean effective oxygen diffusion coefficient is 7.9 x 10^{-12} $m^2.s^{-1}$. This value is similar to that obtained previously for a compressed cork without any transfer at the interface (9.2 x 10^{-12} $m^2.s^{-1}$). Moreover, the OTR at the interface between the stopper and the bottleneck is around 0.34 mg.year^{-1} compared with 17 313 mg.year^{-1} in the case of a cork stopper compressed in a bottleneck without surface treatment. When coated with a surface treatment product, the oxygen flow at the interface decreases significantly and the effective diffusion coefficient becomes 10 000 times lower. These results emphasize the crucial role played by the surface treatment agent present between the stopper and the glass bottleneck on oxygen transfer. This thin layer coating appears to provide an efficient barrier against the ingress of oxygen from the external environment into the bottle. In addition to its primary function of facilitating uncorking, it can act as well as lubricating agent at bottling (during the compression and insertion stages) by reducing the creation of defects on the outer stopper surface. It can also act as an additional barrier to oxygen transfer by masking defects at the interface between the stopper and the bottleneck, providing an oxygen permeability as low as the cork stopper itself.

It should be noted that all analyses of oxygen transfer were performed under conditions that differ from oenological conditions (i.e., a dry sample under vacuum and without partial pressure of water and ethanol vapors). In a bottleneck, the cork is in contact with the wine (if bottles are stored horizontally) or in contact with a vapor phase saturated with water and ethanol vapors (if the bottles are stored vertically). These conditions might also affect the barrier properties of stopper. Further experiments are clearly needed to fully understand how the global diffusion coefficient of oxygen through cork could change depending on hydration or the presence of ethanol.

4.3. Microscopic characterization of the surface coating

In addition to permeability measurements, SEM analysis was performed for agglomerated stoppers with and without coating. The corresponding microscopic images of the cork stopper surface are presented in Figure 5. First, the stopper surface without coating is shown in Figure 5A-B. The cork particles, as well as microspheres, are entrapped within the adhesive network that maintains the cohesion of the stopper. As the cork particles have no specific orientation, this confers more isotropy at the macroscopic scale, to the agglomerated stopper compared to the natural cork stopper having a strong anisotropy due to the specific orientation of cork cells (Gibson, Easterling & Ashby, 1981).

Surface treatment of the stopper, performed by drum coating with paraffin wax and silicone emulsion, results in a thin coating layer that can be observed on the stopper surface (Figures 5C-D). The deposited coating layer fully covers the surface of the stopper and does not tend to form aggregates (Fig 5C). It is also distributed in a very thin layer over the cork cells and does not fill the volume of the outer empty cells. Such SEM observation was performed at the scale of a 1 mm^2 surface and is representative of the whole coated stopper surface. However, only small-scale observations could be performed with SEM microscopy. This method unfortunately does not enable a full assessment of the homogeneity of the coating on the surface of the whole stopper. Nevertheless, even if qualitative, these results seem to indicate that the coating was homogeneously distributed on the stopper surface, at the scale of observation provided by SEM.

At a lower scale, the coating thickness could be estimated from cross-sectional images at around 0.5 µm (Fig 5d) and was quite thin in view of the coating process. This thickness was much lower than the 17 µm (paraffin wax layer) reported by Keenan *et al*. on natural cork stoppers (Keenan, Gozukara, Christie & Heyes, 1999). However, this last value was calculated from the weight and density of the paraffin. The weight value was obtained by solvent extraction of the wax layer from cork stoppers. This result could thus be overestimated because of the solvent extraction of other compounds from the cork in addition to those used for the surface treatment.

5. CONCLUSIONS

The transfer of oxygen in a cork/bottleneck system was assessed through a comprehensive study starting from the effective diffusion through the stopper alone and ending with a more complex system comprising the stopper covered by a surface treatment agent and compressed in the glass bottleneck. First, the effect of compression on agglomerated cork (with the interface glued) showed that a 40% reduction in the volume of the stopper (compression applied for still wines) reduced the effective oxygen diffusion of the stopper by 35%. Then, the oxygen transfer through a corked bottleneck was examined. Without coating, the oxygen effective diffusion coefficient through an agglomerated cork stopper compressed in a bottleneck was significantly higher than through the stopper alone (10^{-7} $m^2.s^{-1}$ vs 10^{-11} $m^2.s^{-1}$). However, when the stopper was coated with a silicone-paraffin emulsion, the effective oxygen diffusion coefficient through the cork-bottleneck gave a similar value to that of the compressed stopper (10^{-11} $m^2.s^{-1}$). These results clearly highlighted the crucial role of the surface treatment in oxygen transfer through a corked bottleneck. A coating with a thickness of less than 0.5 µm provided an efficient barrier for the stopper-bottleneck interface system to act against gas transfer at the interface. In addition to its initial role of ensuring easier uncorking, the surface coating therefore confers an additional and unexpected barrier efficiency to the wine sealing system.

AUTHOR CONTRIBUTIONS

T.K., J.C. and J.-P.B. designed research; T.K., R.D.G., J.C. and J.-P.B. performed research; T.K., J.C., R.D.G. and J.-P.B. analyzed data; and T.K., J.C., R.D.G., and J.-P.B. wrote the paper.

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COMPETING INTERESTS STATEMENT

The authors declare no competing interests.

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Figure 1. Conditions used for the measurement of oxygen transfer.

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

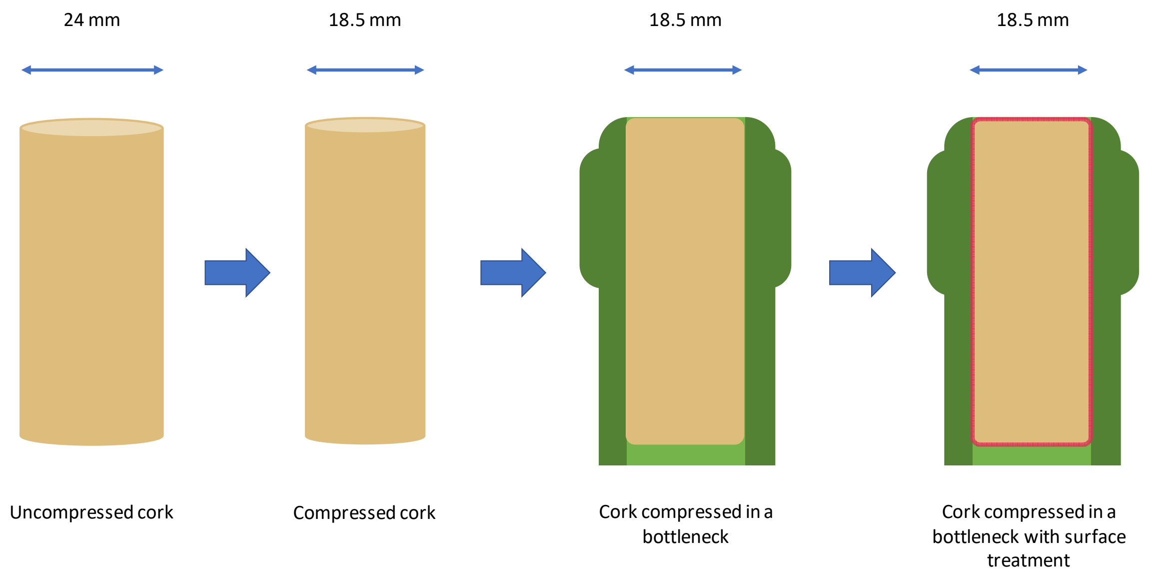
Figure 3. Experimental and extrapolated distributions of the logarithm of the diffusion coefficient of oxygen of uncompressed and compressed agglomerated cork stoppers at 298 K obtained from 10 replicates. Green dashed line (--): experimental distribution of a 3 mm uncompressed cork wafer. Blue dashed line (--): experimental distribution of a 6 mm compressed cork wafer (from 10 replicates). Green line (-): extrapolated distribution to a 48 mm stopper from the experimental data measured for 3 mm uncompressed cork wafers. Blue line (-): extrapolated distribution to a 48 mm stopper from the experimental data measured for 6 mm compressed cork wafers.

Figure 4. Distributions of the logarithm of the diffusion coefficient of oxygen at 298 K obtained from 10 replicates. Green (-): extrapolated distribution to a 48 mm stopper from the experimental data for 3 mm compressed cork wafers. Blue (-): extrapolated distribution to a 48 mm stopper from the experimental data for 6 mm compressed cork wafers. Red (-): experimental distribution of 48 mm stoppers compressed in a bottleneck without surface treatment. Yellow (-): extrapolated distribution to 48 mm stoppers from the experimental data measured for 6 mm cork wafers compressed in a bottleneck with surface treatment (emulsion of paraffin and silicone).

Figure 5. SEM observations of the surface of agglomerated stoppers observed at different magnifications factors. a) without surface treatment, b) cross section of agglomerated cork stopper without surface treatment c) with surface treatment, d) cross section of an agglomerated cork stopper with surface treatment.

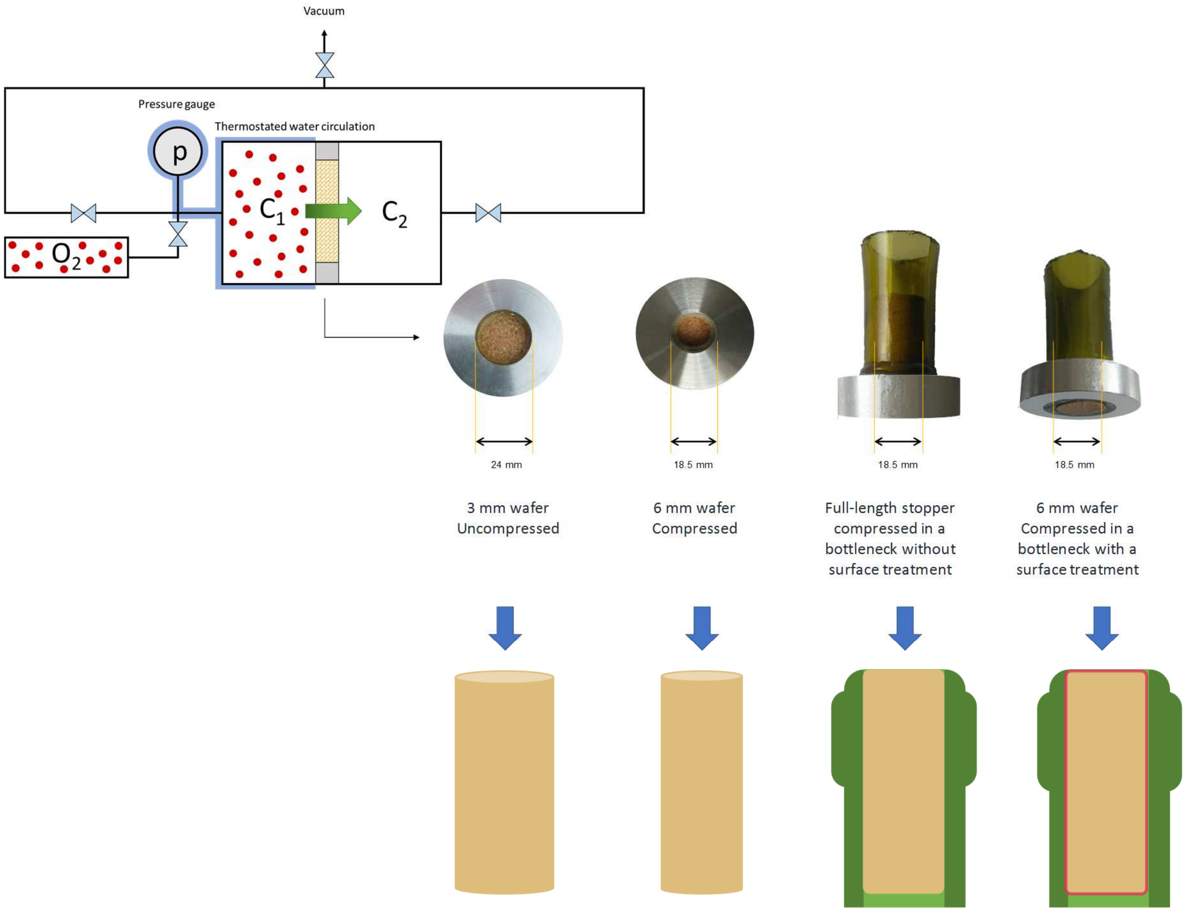
Table 1. Mean oxygen diffusion coefficients and OTRs determined for uncompressed and compressed cork stoppers alone and for cork stoppers inserted in a bottleneck with and without a surface treatment agent (extrapolated to a full cork stopper, from 10 replicates in each case; see figure 4 for corresponding distributions). For practical reasons, OTR is expressed as $mg.year^{-1}$, referring to as mg of oxygen going through the stopper per year.

Figure 1



24 mm
18.5 mm
18.5 mm
18.5 mm
Uncompressed cork
Compressed cork
Cork compressed in a bottleneck
Cork compressed in a bottleneck with surface treatment

Figure 2



Vacuum
Pressure gauge
Thermostated water circulation
p
C_1
C_2
O_2
24 mm
18.5 mm
18.5 mm
18.5 mm
3 mm wafer Uncompressed
6 mm wafer Compressed
Full-length stopper compressed in a bottleneck without surface treatment
6 mm wafer Compressed in a bottleneck with a surface treatment

Figure 3

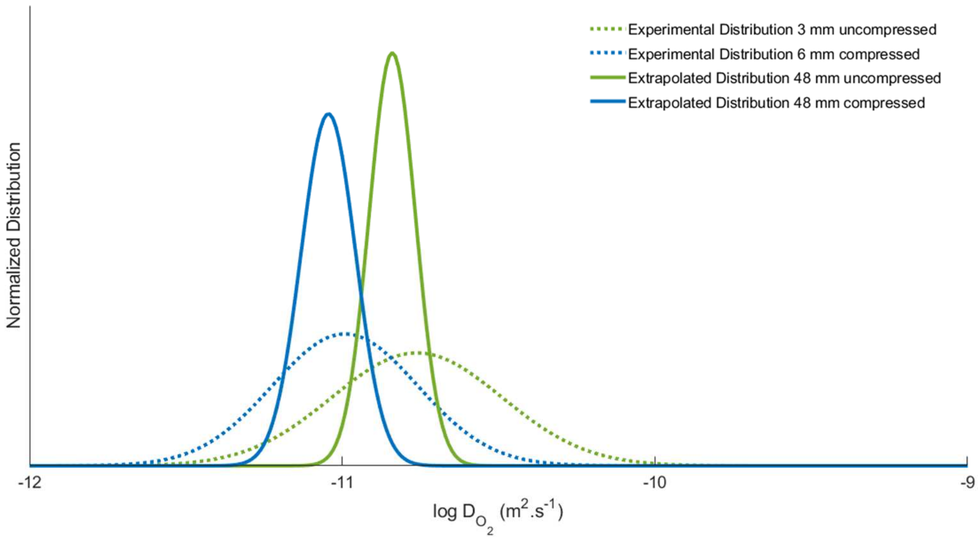
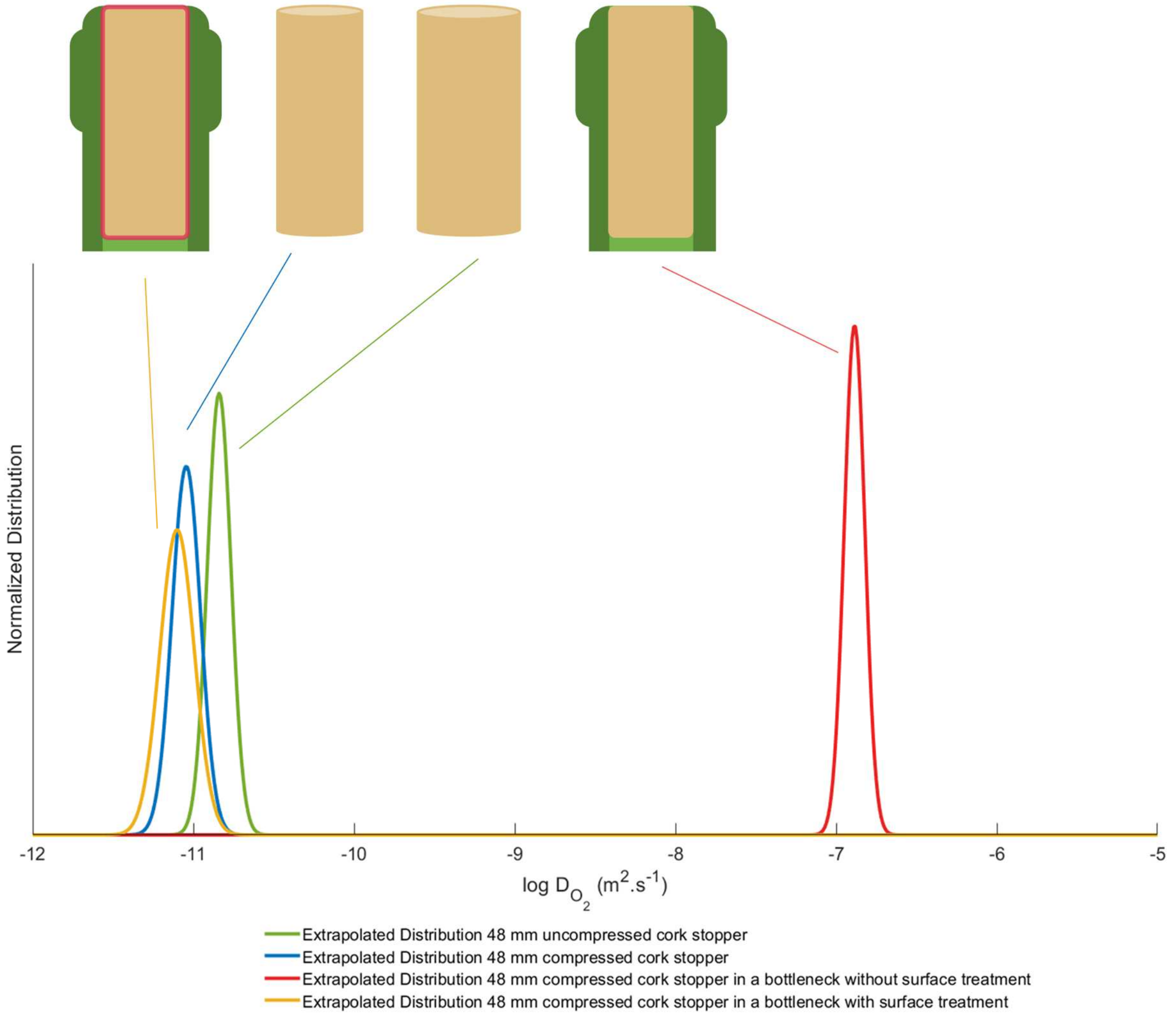
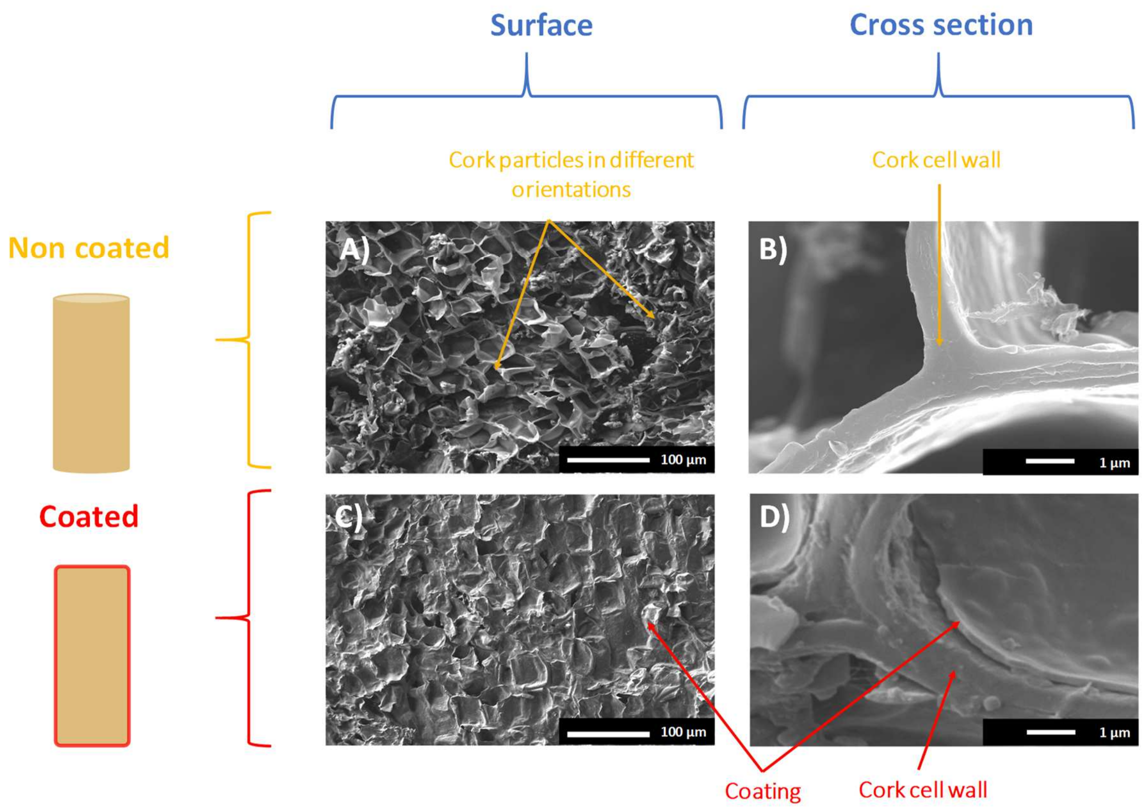

Experimental Distribution 3 mm uncompressed
Experimental Distribution 6 mm compressed
Extrapolated Distribution 48 mm uncompressed
Extrapolated Distribution 48 mm compressed
Normalized Distribution
-12
-11
-10
-9
log D_{O_2} ($m^2.s^{-1}$)

Figure 4



Normalized Distribution
-12
-11
-10
-9
-8
-7
-6
-5
log D_{O_2} ($m^2.s^{-1}$)
Extrapolated Distribution 48 mm uncompressed cork stopper
Extrapolated Distribution 48 mm compressed cork stopper
Extrapolated Distribution 48 mm compressed cork stopper in a bottleneck without surface treatment
Extrapolated Distribution 48 mm compressed cork stopper in a bottleneck with surface treatment

Figure 5


Surface
Cross section
Cork particles in different orientations
Cork cell wall
Non coated
A)
B)
100 µm
1 µm
Coated
C)
D)
100 µm
1 µm
Coating
Cork cell wall

Graphical abstract