Measurement of Oxygen Transmission Rate through Foamed Materials for Bottle Closures

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SUMMARY

The determination of the oxygen transmission rate (OTR) through closures in glass bottles is becoming increasingly important for quality control of different batches and for development purposes. The Mocon method for measuring OTR is globally accepted and used in different applications. However, one of the major drawbacks this method presents when applied to bottle/closures systems is the long time required to obtain stable measurements when 40 mm long closures are tested. This paper describes a method to obtain OTR values with samples of reduced thickness with much shorter measurements time, since the condition of steady state during measurements is achieved faster and compares the estimated full-length commercial closure OTR with experimental values.

KEY WORDS: oxygen transmission rate; synthetic closures; foamed plastics

INTRODUCTION

Oxygen plays a crucial role in wine properties at all stages of production and storage of all styles of wine. The effects of exposure can be both positive and negative, depending on the style of wine in question, the phase of production at which the oxygen exposure occurs and the amount of oxygen introduced, together with the rate of introduction.[1] In the case of finished, packaged, still-wine, it is recognized that wine quality is generally diminished by excessive oxygen exposure,[1] but slow and continuous oxygenation may be beneficial for wine aging.[2] In the case of wine packaged in glass bottles, oxygen ingress depends on the sealing effectiveness of the closure.[2]

Cork stoppers have been used for many years and still are the preferred bottle closure for high-value wines. Cork is a natural product derived form the bark of *Quercus Suber* L., a tree that only thrives in certain geographically limited regions. As a natural product, cork demonstrates considerable variability in many of its properties relevant to its functions as a bottle closure.[3] This, along with the possibility of taint arising from trichloroanisols (TCA), has led to a search for alternative solutions within the glass bottle/closure binomial. This search has been particularly driven by demand from newer wine-producing countries such as the USA and Australia, but is now more widespread.

A range of synthetic closures is currently commercially available, produced in different plastics by either injection or extrusion (single or co-extrusion) processes. Synthetic closures are generally

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referred as offering a lower barrier to oxygen ingress,[2,4,5] and although clear improvements have been achieved, recent wine closure surveys still reflect this idea.[6] Although not giving the potential problems of TCA, synthetic closures can cede components and additives from the plastic into the wine.[4]

The screw cap represents a distinct closure system. Normally made in aluminium, the screw cap has a liner that provides an airtight seal around the bottle rim. The liner is commonly composed of a Polyvinylidene chloride (PVDC) film (which is the surface in contact with the wine), a layer of tin or aluminium foil and a polyethylene foam layer. The screw cap is generally considered the closure that offers the greatest barrier to oxygen,[2] although at least one author has reported that after a period of storage, the barrier offered to gas transfer is the same as of natural corks.[4]

The sealing effectiveness of the closure system is a function of both the permeability of the material of the closure and of the tightness/adherence of the closure to the bottle wall. This latter consideration may affect, depending on the type of closure, the possibility of oxygen ingress through the interface between the closure and the glass. For both corks and synthetic stoppers, in addition to the nature of the material itself, the ratio between the diameters of the closure and the bottle neck and the nature of the closure surface are obvious factors in determining the barrier to oxygen ingress which the whole system represents. Storage position, upright or horizontal, is another variable that can influence oxygen ingress rate into the bottle.[2] Additionally, air trapped within the cork or foam cells can be a relevant source of oxygen that is transferred into the head-space during storage.[5]

Oxygen ingress through the closure system into the bottle and its importance in the evolution of wine properties has been discussed intensively, although it is recognized that other factors are as much, or more, relevant in this respect. Included in the latter group would certainly be the filling height and head space volume, pre-filling with inert gas and other bottling conditions. It has been argued that insufficient independent research is yet available to draw clear conclusions on this matter, particularly peer-reviewed and published research.[7]

Several methods have been referred to measure the oxygen ingress rates through closures using oxygen gas sensors or indirect measurements, such as colorimetric methods.[8] Standard, or at least standardized, methods are advisable to enable the traceability of the results and permit comparison between samples. However, given the complexity of the wine matrix and of the chemical reactions oxygen is involved in, once it passes through the closure/bottle system, it is always very difficult to mimic the real conditions when measuring the oxygen transmission rate through the closure. The method usually called ‘Mocon’ is a globally accepted standard method for the measurement of permeability in packaging applications that uses a patented coulometric sensor to detect oxygen. When applied to the bottle/closure system, it cannot mimic exactly the configuration of storage because the closure is not ‘wet’ with wine – although it is not certain that the wetting is significant in any case. Despite this potential limitation, this standard method can be validly applied to measuring oxygen passage through closure/bottle systems. A commonly cited drawback of the Mocon system is the long time required to obtain stable measurements when 40 mm long closures are tested. This work analyses the influence of thickness on the oxygen transmission rate (OTR) in order to estimate the barrier provided by a full-length closure based on faster measurements obtained with thinner samples.

Mathematical models that describe physical processes of practical interest are of great use as replacement for, or auxiliaries to, the experimental study of the actual process. Processes of mass transfer from and through packaging materials are commonly assumed to be diffusional and described by Fick’s law.[9] In the case of oxygen permeability, this may be expressed, for steady flow, as:

$$OTR = P_{eff} \cdot A \cdot \frac{\Delta p}{L} \tag{1}$$

where: OTR is the oxygen transmission rate in O_2 cc/day; P_{eff} is the effective permeability coefficient in O_2 cc.mm/day.mm^2.atm; A is the surface area available for oxygen transfer in mm^2; Δp is the oxygen partial pressure difference between the material’s faces in atm; and L is the material thickness in mm.

The coefficient of permeability (P) is usually defined for non-cellular materials and it relates the diffusion coefficient of oxygen in the material with its solubility enabling to use oxygen partial pressure as a measure of its concentration in Equation 1, which is more convenient for gases.[10] When there is no interaction between the polymer and the permeant, like it happens with oxygen through polyethylene (PE), P is independent of the pressure of the diffusion gas.[11] P rapidly increases with temperature, following an Arrhenius-type relationship, and is independent of thickness.[11]

Mass transfer through cellular materials has not been studied to the same extent as for non-cellular ones, most probably because with the exception of more recent use in closures, their major application as cushioning materials does not imply relevant barrier properties. The oxygen pathway through cellular materials involves diffusion in air entrapped in the foam, as well as adsorption and diffusion through the several polymeric cell walls. The system can be regarded as a disperse phase (air bubbles) in a continuous phase (PE), and factors such as the density and cell structure of the foam may influence the permeability coefficient. Therefore, a P_{eff} is defined as the permeability coefficient of the foamed material in Equation 1.

If the closure made of foamed plastic presents an homogeneous structure and a constant permeability coefficient along its length is assumed, the oxygen transmission rate at steady state would increase linearly with the inverse of closure thickness.

A simplified solution of the unsteady state Fick's second law describing the total amount of mass diffusing through the material up to time t, assuming initial concentration in the material equal to zero and assuming constant concentrations in both faces of the material, one of which equals to zero, is given by Crank[12]:

$$M = C_1 \cdot A \cdot L \cdot \left(\frac{D_t}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{1}^{\infty} \left[\frac{(-1)^n}{n^2} \exp\left(-\frac{D n^2 \pi^2 t}{L^2} \right) \right] \right) \tag{2}$$

where M is the total amount of oxygen diffusing up to time t in g; D is the diffusion coefficient in cm^2/s; C_1 is the oxygen concentration on one face of the material in g/cm^3; A is the surface area available for oxygen transfer in cm^2; and L is the material thickness in cm.

This equation becomes asymptotic to the straight line as described by Equation 3 as time tends to infinite[12]:

$$M = \frac{C_1 \cdot A \cdot D}{L} \left(t - \frac{L^2}{6D} \right) \tag{3}$$

The intercept of this straight line with the t-axis at location Θ is:

$$\Theta = \frac{L^2}{6D} \tag{4}$$

usually used to determine the diffusion coefficient using permeation measurements. Equation 4 indicates that the time required to achieve steady state (Θ) is proportional to the square thickness of the material. Thus, a reduction in measuring time should then be obtained by reducing sample thickness under test.

In this paper, the linear relationship between the oxygen transmission rate and the inverse of closure thickness is confirmed by performing experimental measurements of oxygen transmission rate on samples with different thickness. A tailor-made sample holder connected to the Mocon equipment was used in the tests. The method was tested in extruded foamed rod and in commercially available closures. The result estimated by the linear model for the commercial closure was compared with the experimental value obtained with the full-length closure inserted in glass bottles.

MATERIALS AND METHODS

Extruded foamed rod: cylindrical rod, 21.6 ± 0.2 mm diameter, foam density 340 ± 5 kg/m^3 and average cell size 240 μm. A catalyst, modified polyethylene resin (LDPE), is extruded using CO_2 as foaming agent and a chemical nucleating agent, in a commercial single-screw extruder of L/D = 51 : 1 and screw diameter of 65 mm. The samples were supplied by Epoli – Espumas de Polietileno, S.A. (Trofa, Portugal).

Synthetic closures: commercially available Normacorc® Classic, 22 mm diameter and 45 mm length.

The samples were sliced in pieces with thickness ranging from 5 to 22 mm. The closures were also tested without slicing and inserted in glass bottles. All measurements were made in replicate.

Glass bottles: with the internal neck diameter at different distances from the top shown in Table 1.

Measurement of OTR: Ox-Tran 2/20 (Mocon, Inc.) was used (ASTM F1307). Mocon operating conditions are presented in Table 2.

Sample holder: Figure 1 presents a sample holder tailor-made to support the sliced samples. The barrier that the holder and fixing material represent was previously tested with a metal disc in place of the plastic test material. This sample holder was replaced by the glass bottle neck in the case of measurements in whole closures.

Table 1. Bottle neck internal diameter (ϕ) at different distances from the top (H).

H (mm)	ϕ (mm)
0	17.70
15	18.28
40	19.17
45	19.01

Table 2. Operating conditions of the OTR measuring equipment.

Cell examination time	60 min
Carrier gas flow	10 ml/min
Converge testing	18 h
Minimum flushing time before starting test	24 h
Compensation to barometric pressure 760 mmHg	Yes

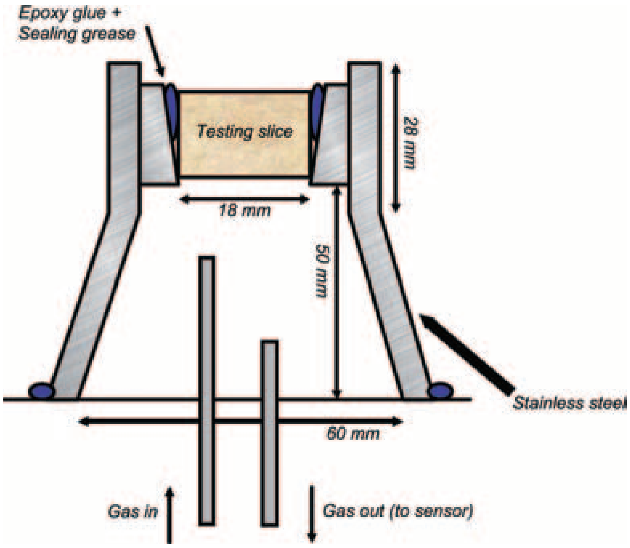

Figure 1. Sample holder to be connected to Oxtran.

The equipment (and sample holder) was kept under controlled conditions of temperature (23 ± 1°C) and relative humidity (50 ± 5%) and normal air gas composition. The lower chamber of the sample holder is continuously flushed with oxygen-free carrier gas. Molecules of oxygen diffusing through the sample to the lower chamber of the holder are conveyed to the sensor by the carrier gas and quantified. Therefore, an oxygen partial pressure difference between the faces of the sample equal to 0.21 atm is maintained during the tests.

RESULTS AND DISCUSSION

Figure 2 presents the results obtained for the OTR for the slices of different thicknesses. The OTR is expressed in O_2 cc/day and plotted against the inverse of thickness in mm. The data is relatively well represented by the linear model in both samples. The model parameters estimated are presented in Table 3.

The OTR of a full-size closure inserted in a glass bottle neck was also measured for comparison with the value estimated by extrapolation of the data obtained with sliced closures. Figure 2 presents the OTR predicted by the model for the whole (full-size) closure (■ = 0.016 O_2 cc/day) and the value obtained experimentally (▲ = 0.018 O_2 cc/day). A considerable good agreement between the two values was found, indicating that the technique of using the sliced closures can be used to predict the OTR of the full-size closure. The difference between the two is ca. 11% (the predicted value is lower than the experimental one). This difference is of the same order found in other studies, where the potential contribution for oxygen ingress through the interface between the bottle and the closure was studied.[13] In our study, the sliced samples were obviously glued to the sample holder, and therefore, the rim was protected; however, in the tests with the closures inserted in the bottles, the rim was not covered. In a parallel experiment, OTR values for bottles with and without the rim

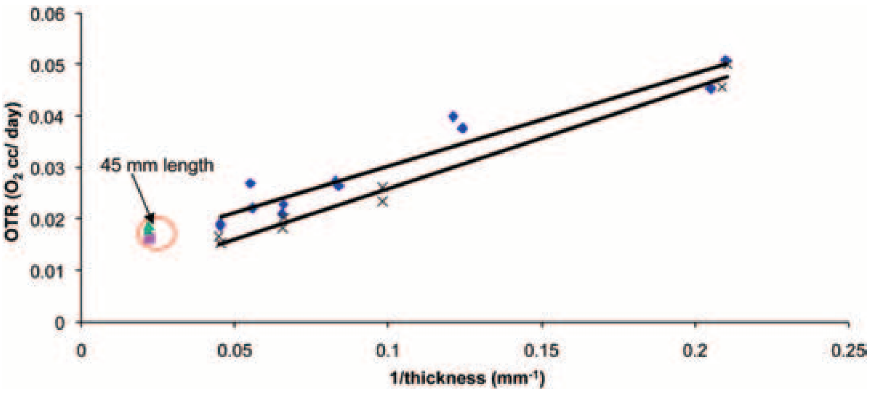

Figure 2. Oxygen transmission rate at 23°C through samples of 22 mm diameter and different thicknesses exposed to a difference of oxygen partial pressure of 0.21 atm: ◆ – Nomacorc® slices, × – PE rod slices, — – linear model, ▲ – experimental Nomacorc® full-length closure, ■ – predicted Nomacorc® full-length closure.

Table 3. Statistics of linear model parameters estimation.

		Estimate	Standard error	*t*-value df = 10	*p* level	Lo. conf limit	Up. conf Limit	R^2
Nomacorc®	Slope	0.180	0.016	11.1733	0.000001	0.144	1.216	0.926
	Intercept	0.012	0.002	6.7983	0.000048	0.008	0.016	
PE rod	Slope	0.196	0.010	20.4542	0.000001	0.173	0.220	0.985
	Intercept	0.006	0.001	5.3084	0.001815	0.003	0.009	

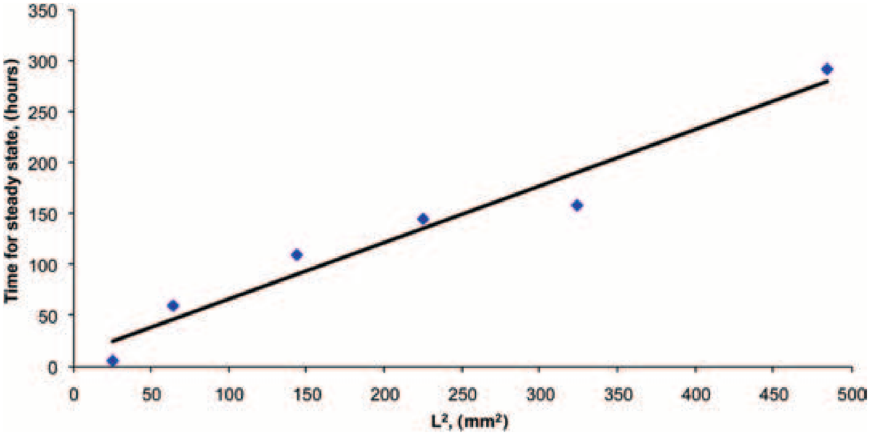

Figure 3. Estimated time required to achieve steady state for samples of different thicknesses.

protected differed ca. 10%. However, other factors may also contribute for the higher experimental value as compared to the predicted by the linear correlation: when the closure is inserted in the bottle neck it is compressed, the global dimensions and the density change and, most importantly, the geometry of the foam cells also change. The cells with an original circular shape tend to become oblong in the longitudinal direction. The analysis of the mass transfer in heterogeneous media showed that when the ratio of the diffusion coefficients of the two phases (polymer and air) is high, and the continuous phase (PE) has the lower diffusion coefficient, a noticeable effect of the shape of the disperse phase (air bubbles) on the global diffusion coefficient is expected.[12] In the present case, the change in the shape of the foam cells by lateral compression exerted by the bottle yield an increase of the diffusion coefficient as compared to the same foam with the circular regular shape cells. Additional experiments are required to verify this hypothesis.

The values obtained for the Nomacorc® Classic were also compared with values found in the literature for this type of closures. The value specified by the manufacturer is 0.03 O_2 cc/day; for closures with a thickness range between 37 mm and 47 mm, a higher value than the experimental value is found.[14] However, the temperature and the oxygen differential pressure of the tests in the specifications are not referred. SupremeCorq®, another synthetic stoppers manufacturer, presents a comparison of OTR for several closures, including Natural cork and Nomacorc® Classic, referring to this latter one a value of 0.011 O_2 cc/day for a 45 mm length stopper.[15] This value is lower than the value found experimentally in the present work. Since the testing conditions are not exactly known, no other conclusions can be drawn. This is a problem frequently found in literature where low care is taken when presenting the conditions and measurement units of oxygen transmission rate through closures.

A considerable reduction of the time required to get the results is achieved with this method. Although the experiments were not designed to determine the time for steady state, it can be anticipated from Equation 4 that the time for achieving constant OTR increases with the square thickness of the sample under test. Figure 3 shows the time required for the Oxtran system to give constant readings in the OTR measurement of samples with different thicknesses. A trend to a linear behaviour is confirmed for the range of measurements considered. While OTR measurements on a 5 mm thickness piece are completed in 1 day, an extrapolation of the data indicates that to achieve constant OTR values with a full-length closure of 40 mm, it would take 38 days. This is in agreement with values reported in technical literature, where more than 30 days are commonly referred as the time required to stabilize measurements in closures.[13,16]

CONCLUSIONS

The results obtained indicate that there is a linear relationship between OTR and the inverse of the thickness that can be used to estimate the barrier performance of thicker samples with considerable measuring time saving. The method presented is a useful tool to rapidly access the oxygen transmission rate of different closures, particularly in development stages of new stoppers or when comparison between batches or suppliers is the objective. However, the extrapolation to the full-length closure barrier in the bottleneck final environment requires a better understanding on the factors influencing the mass transfer through foamed plastics under compression forces and/or through glass closure interface.

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