K. Müller

Oxygen Permeability of Plastic Bottles for Oxygen Sensitive Beverages

Notation

A	area	m^2
b	hole affinity constant	bar^{-1}
c	concentration (e.g. oxygen)	$m^3(STP)/m^3$
c_D	concentration of dissolved species according to Henry's law	$m^3(STP)/m^3$
c_H	concentration of sorbate in "holes" (Langmuir term)	$m^3(STP)/m^3$
c'_H	saturation concentration of sorbate in "holes"	$m^3(STP)/m^3$
D	diffusivity	$m^2 \cdot s^{-1}$
D_0	diffusivity at $T \rightarrow \infty$	$m^2 \cdot s^{-1}$
E_D	activation energy of diffusion	$(N \cdot m) / mol$
F_x, F_y, F_z	flux in x-, y- and z-directions	$m \cdot s^{-1}$
k_D	solubility according to Henry's law	$m^3(STP)/(m^3 \cdot bar)$
k_{O2}	reaction kinetics constant	s^{-1}
l	layer thickness	m
P	permeability	$(m^3(STP) \cdot m)/(m^2 \cdot s^{-1} \cdot bar)$
p	partial pressure	bar
R	gas constant	$(N \cdot m) / (mol \cdot K)$
S	solubility	$m^3(STP)/(m^3 \cdot bar)$
S_0	solubility at $T \rightarrow \infty$	$m^3(STP)/(m^3 \cdot bar)$
	flow rate	$m^3(STP) \cdot s^{-1}$
x, y, z	coordinates	m
ΔH_S	heat of solution	$(N \cdot m) / mol$
EVA	ethylene-vinyl acetate	
EVOH	ethylene-vinyl alcohol	
PA	polyamide	
PC	polycarbonate	
PE	polyethylene	
PEN	polyethylene naphthalate	
PET	polyethylene terephthalate	
PP	polypropylene	
PVC	polyvinyl chloride	
STP	Standard temperature and pressure	

Oxygen is one factor which causes beverages to deteriorate after filling. In particular, the replacement of glass bottles by plastic bottles has implications for the shelf life. As a consequence, packaging manufacturers and food technologists must have precise knowledge about the composition of packaging materials, oxygen permeation and the interaction between oxygen, the packaging and the foodstuffs. This article discusses the theory of permeation and factors influencing permeation. Results of oxygen permeation through plastic bottles and closures are presented. The results show that the three main methods for barrier improvement are internal coating of PET bottles, the use of PEN bottles and the incorporation of oxygen scavengers into bottles and closures. Finally, numerical simulations indicate that although oxygen scavengers are useful for reducing the oxygen ingress, their potential for reducing dissolved oxygen and pre-existing oxygen in the headspace is limited.

Descriptors: permeability, oxygen ingress, PET bottle, beer, scavenger, imulation

1 Introduction

One of the main purposes of the packaging materials used in food industry is to prolong the shelf life. In this context, the barrier properties against gases, vapors and flavors play an important role. Plastics are permeable to small molecules such as gases, vapors and some flavors. In general, molecular mass transfer through a pore free membrane is called permeation. Over the last decades a set of books and reviews have been published covering the main topics of permeation of small molecules through polymers (1, 2,

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Dr.-Ing. Kajetan Müller, Fraunhofer-Institut fuer Verfahrenstechnik und Verpackung, Giggenhauser Str. 35, D-85354 Freising, Tel. +49 (0) 8161 491-509, Fax. +49 (0) 8161 491-555, Kajetan.Mueller@ivv.fraunhofer.de

Figures see Appendix

3, 4, 5, 6, 7, 8). Permeation through plastic bottles and closures has, however, not been considered in detail. This article, therefore, deals with gas permeation – and especially oxygen permeation – through plastic bottles and the corresponding closures.

2 Theoretical Background

Packaging materials

Glass is the most commonly used packaging material for beverages, especially in the form of bottles. After World War II cans made of aluminum or tin plate became established for beverages. Metals are used, furthermore, for bottle closures such as aluminum caps, crown corks and twist-off closures. When dealing with permeation or migration, only plastics have to be considered because glass and metals prevent gases and vapors from permeating. As a result, permeation takes place through the walls of plastic bottles and plastic closures as well as through the sealing disc of metal caps. Bottles and closures are studied separately due to their different compositions and geometries.

Plastic bottles

Different types of plastics are used for manufacturing beverage bottles. Polycarbonate is mainly used for milk bottles because of its thermal stability. Polycarbonate can withstand temperatures of 121 °C and this is important for sterilization (9). Polycarbonate is, however, not suitable for carbonated or oxygen sensitive beverages due to its high gas permeability. Carbonated and oxygen sensitive beverages are bottled in PET or PEN because these materials have better barrier properties compared to polycarbonate (10, 11, 12).

Polyethylene terephthalate, often called PET, is a polyester which was first developed in 1941 for synthetic fibers. The growth of the PET market for beverage packaging began in the early 1970s (13). Primarily PET is an important food packaging material because it combines excellent mechanical properties with inertness to food. It is one of the few packaging plastics which are approved by the FDA for contact with food at elevated temperatures (14). A typical 0.5 liter PET bottle weighs only 28 grams in contrast to an equivalent glass bottle which weighs about 350 grams. The use of plastic bottles also eliminates the problem of breakage associated with glass (15). Methods for recycling PET are available (16, 17, 18, 19).

Polyethylene naphthalate (PEN) is also a polyester. The starting substances are ethylene glycol and dimethyl-2,6-naphthalene dicarboxylate. These starting materials are polycondensed in the same way as the base materials for producing PET (20, 21). PEN has significantly better barrier properties than PET and is more temperature resistant, durable to chemicals and impermeable to UV light (22, 23).

Closures

The closures currently used for bottles are crown corks, aluminum roll-on caps and plastic screw caps. Twist-off closures are commonly used for milk, recently also for beer bottles.

Crown corks

Crown beverage caps are often used for carbonated beverages and beer. They are made of tin-free steel or tin-plate with a sheet thickness of 0.235 ± 0.02 mm and are standardized according to DIN 1616 in Germany (24). Sealing discs are nowadays made exclusively of plastics. Foamed or non-foamed polyvinyl chloride (PVC), non-foamed ethylene-vinyl acetate (EVA) or EVA free blends are used. PVC free compounds without plasticizer are composed of polyethylene (PE), polypropylene (PP), EVA copolymers and elastomers (25). The compound containing PVC weighs between 200 and 250 mg, whilst the PVC free compound weighs only between 170 and 230 mg.

Aluminum roll-on caps

The design of the sealing discs is similar to crown corks. The compound containing PVC weighs between 350 and 450 mg, otherwise from 230 to 250 mg. During capping an unthreaded shell is placed on the bottle neck and a capping head exerts downward pressure, which creates a seal as the sealing disc is pressed against the bottle finish. Finally rollers in the capping head shape the aluminum shell to the contour of the neck ring. The aluminum roll-on caps have a sheet thickness of 0.21 ± 0.02 mm. Further specifications regarding requirements, practice and test methods can be found in the literature (13, 14, 26).

Plastic screw caps

The plastic closures used for beverages are made of thermoplastics. In contrast to aluminum roll-on caps, the plastic screw caps have prefabricated threads. They are produced either as one piece or as two parts. The area of contact between the bottle neck and closure is crucial for the barrier properties. One-piece plastic closures seal with a trumpet-shaped element or with the help of a horizontal surface. A horizontal seal on the top edge and on the outside of the bottle neck can mostly be found on multipart closures (25). One-piece screw caps are made of PE or PP and thus have poor barrier properties. Consequently, they cannot be used for oxygen sensitive products. Multipart closures for oxygen sensitive foods comprise a sealing disc having low oxygen and CO_2 permeability. Finally, active material with an oxygen scavenger is often incorporated into the seal to absorb any permeating oxygen and oxygen in the headspace.

Permeation through plastics

In principle there are two different processes by which gases and vapors can permeate through polymers (27):

- a pore effect by which gases and vapors pass through microscopic pores, pinholes or cracks into the polymeric material and
- a solubility-diffusion effect by which gases and vapors dissolve at one surface of the polymer, diffuse through the polymer via a concentration gradient and evaporate on the other surface of the polymer.

The pore effect can be eliminated if the polymer is sufficiently thick. Hence only the solubility-diffusion effect causes permeation through plastic bottles.

The permeation of gases and vapors through plastics is characterized by the solution-diffusion effect and involves three steps (28):

- adsorption of penetrants on one side of the film, depending on the solubility,
- diffusion through the polymer towards the lower concentration as a result of random molecular motions,
- desorption on the side of lower concentration.

Mass transport through the polymer is characterized by Fick's laws. Fick's first law of diffusion describes the mass transport of a permeant through an area A in direction x under steady state conditions:

$$F_x = \frac{\dot{V}_x}{A} = -D \cdot \frac{dc}{dx} \qquad (1)$$

At constant partial pressure and temperature, the flux F_x is the gas volume permeating through a polymer of area A normal to the direction of flow. D and c are the diffusivity and the concentration of penetrant respectively.

Equation 1 only holds for homogeneous polymers having constant diffusion properties within the polymer. Assuming homogeneity and a steady state with constant concentrations on both sides of the polymer then:

$$\frac{d^2c}{dx^2} = 0 \qquad (2)$$

On one side of the polymer ($x = 0$) the concentration is c_1, whilst on the other side ($x = 1$) the concentration is c_2. From equations 1 and 2, there is the following relation:

$$F_x = D \cdot \frac{c_1 - c_2}{l} \qquad (3)$$

The surface concentrations c_1 and c_2 are often unknown. The diffusing concentration is related to the ambient penetrant concentration in contact with the polymer surface by Nernst's distribution function. For practical purposes the penetrant concentration is usually assumed to be proportional to the partial pressure. Assuming Henry's law:

$$c = S \cdot p \qquad (4)$$

and steady state conditions the permeation flux equation (3) can be written as:

$$F = \frac{\dot{V}}{A} = D \cdot S \cdot \frac{p_1 - p_2}{l} = P \cdot \frac{p_1 - p_2}{l} \qquad (5)$$

where p_1 and p_2 are the upstream and downstream pressures, l is the thickness of the film and S is the Henry's law solubility coefficient. The permeability constant is defined as the product of the solubility and diffusivity:

$$P = D \cdot S \qquad (6)$$

Equation 5 only holds if there is no reaction between the permeant and polymer, so that diffusivity and solubility can be regarded as constant. The methods to determine permeability, diffusivity and solubility in planar sheets have been described in the literature (29, 30, 31, 32, 33, 34, 35, 36, 37, 38).

Influence of temperature:

The change in solubility, diffusivity and permeability as a function of temperature can in most cases be described by the classical Arrhenius equation (7, 27). For the solubility S, this means:

$$S = S_0 \cdot exp\left(\frac{-\Delta H_S}{R \cdot T}\right) \qquad (7)$$

where ΔH_S is the heat of solution. ΔH_S is positive for permanent gases and therefore the solubility S increases slightly with temperature. For easily condensable vapors ΔH_S is negative because of the heat of solution and thus the solubility decreases with increasing temperature. The temperature dependence of the diffusion coefficient D can also be represented by an Arrhenius-type relation:

$$D = D_0 \cdot exp\left(\frac{-E_D}{R \cdot T}\right) \qquad (8)$$

where E_D is the activation energy for diffusion. E_D is always positive so that the diffusivity always rises with increasing temperature. From the above two equations one obtains the apparent activation energy for permeation:

$$P = D \cdot S = P_0 \cdot \exp\left(\frac{-(E_D + \Delta H_S)}{R \cdot T}\right) \quad where\ P_0 = D_0 \cdot S_0 \qquad (9)$$

Influence of pressure

In the case of gases such as oxygen or nitrogen the pressure dependence of solubility is given by Henry's law. This is also often appropriate for other gases or vapors when there is no interaction between the diffusing molecule and polymer (27). The situation is more complex for organic vapors and water vapor because the solved vapor plasticizes the polymer matrix. The diffusivity can therefore increase or decrease (39).

Polymers in the glassy state contain a distribution of micro-voids which become frozen into the polymer matrix when the temperature falls below the glass transition temperature. Polymer chains have restricted movement in the glass state, so that these micro-voids are present throughout the polymer. Adsorption in these micro-voids is exothermic. The mobility of the gas absorbed in the micro-voids is lower than the mobility of the diffusing molecules solved in the polymer (39). This model is called the "Dual Sorption Theory" due to the two simultaneous solution processes.

The influence of dual sorption at or beneath atmospheric pressure is relative small (39). The total solubility consists of two terms: the Henry term and the Langmuir term. The gas molecules immobilized in micro-voids are characterized by the Langmuir term. The Henry term is related to the fraction of gas which is solved according to the simple solution diffusion model. The magnitude of the Langmuir term relative to the Henry term increases at higher gas concentrations (40). Examples of the application and experimental verification of the dual sorption theory are given by *Vieth* (41).

$$c = c_D + c_H = k_D \cdot p + \frac{c'_H \cdot b \cdot p}{1 + b \cdot p} \qquad (10)$$

The parameter k_D is the Henry's law solubility coefficient, c'_H is the Langmuir capacity constant and b is an affinity constant.

Oxygen sorption and diffusion in PET bottle material is well described by Henry's law and Fick's law. For carbonated beverages such as beer or mineral water the CO_2 permeation is of interest. Below the glass transition temperature the sorption of CO_2 in PET bottles can be described by the dual sorption model. The influence of the Langmuir term depends on the ambient temperature. The closer the ambient temperature is to the critical temperature (31 °C), the faster the solubility of CO_2 increases with partial pressure. At and below atmospheric pressure the solubility as well as the permeability are independent of pressure even below the critical temperature (40, 42, 43). Carbonated beverages sometimes have a pressure above atmospheric pressure. Mineral water nowadays contains up to 7.5 g CO_2/l. The effect of temperature on CO_2

solubility in mineral water has been described (44):

$$S_{CO2} = 10 \cdot exp\left(-11.073 + \frac{2725}{T}\right) \qquad (11)$$

whereas S_{CO2} is the solubility of CO_2 in mineral water in g/(l · bar) and T is the absolute temperature in K.

Thus at 25 °C mineral water with 7.5 g CO_2/l holds a pressure of about 5 bar. At 5 bar the CO_2 solubility in PET as a function of pressure is shown in Figure 1. CO_2 diffusion in PET is independent of pressure in contrast to solubility. In order to characterize the diffusion in PET the correct concentration gradient is problematic. It is proposed that the driving force for diffusion is the concentration gradient of dissolved CO_2 molecules in the amorphous regions. The molecules bound in the holes are assumed to be in local equilibrium with the dissolved species. Then the material balance on a volume element may be written as follows (45):

$$\frac{(\partial c_D + \partial c_H)}{\partial t} = D \cdot \frac{\partial^2 c_D}{\partial x^2} \qquad (12)$$

Equation 12 looks similar to Fick's first law, except for ∂c_H. As the CO_2 immobilized in the holes is in local equilibrium with the dissolved species, only the dissolved CO_2 molecules contribute to diffusion. The temperature dependence of CO_2 diffusivity in PET (40 % crystalline fraction) follows an Arrhenius-type relation as derived from measurements given by *Michaels* (45).

$$D = 3.56 \cdot 10^{-5}\,\frac{m^2}{s} \cdot exp\left(-\frac{5.02 \cdot 10^4\,\frac{J}{mol}}{R \cdot T}\right) \qquad (13)$$

Multilayer effect

The multilayer effect on permeability can generally be derived from electric circuit analogy. Each layer in the membrane presents its own resistance to mass transport. Under steady state conditions the overall permeation is defined by the permeation flux equation (eq. 14). The flux F_i is the same for all layers i.

$$F = F_i \Rightarrow P \cdot \frac{\Delta p}{l} = P_i \cdot \frac{\Delta p_i}{l_i} \qquad (14)$$

With $\Delta p = {}_{i=1}^{n} \Delta p_i$ the total resistance to permeation is calculated as the sum of the resistances of the different layers (46):

$$\frac{l}{P} = {}_{i=1}^{n} \frac{l_i}{P_i} \qquad (15)$$

Water content of the polymer

Oxygen ingress is approximately independent of the relative humidity for most of the plastics used in food packaging. There are, however, some plastics, for example polyamides (PA) and ethylene-vinyl alcohol (EVOH), which show a strong dependence of oxygen permeability on relative humidity. The oxygen barrier properties of hydrophilic polymers change depending on the amount of water in the polymeric matrix. Dissolved water molecules, which diffuse within the polymeric matrix, interact with the polymer chains. Thus they act as a lubricant improving chain segment mobility and therefore the transport properties of other small molecules are changed. This has practical consequences for food packaging since the relative humidity of the surroundings and filled product will have an influence on the oxygen permeation through packaging (47, 48, 49, 50).

Influence of the fill good

The barrier properties needed are defined by the requirements of the fill good. Analyses regarding suitability of PET bottles for beer were performed at TU München-Weihenstephan [51, 52] and VLB Berlin [53]. The results show that it is not possible to fix one limit for the oxygen ingress and CO_2 loss for all beer types. However, it can be stated that beer is the most oxygen sensitive food and 1 mg/l oxygen uptake in six month is a practical benchmark for beer.

One weak point of the permeation measurement (see below in materials and methods) is that the measurement is performed not with a bottle filled with a carbonated liquid. Firstly the direct liquid contact may have an influence on the oxygen ingress. Secondly the literature reports about the so called creep effect in CO_2-containing bottles. The CO_2 overpressure may lead to expansion of the PET bottle and different permeability [54].

3 Materials and methods

Permeation measurement

The gas flux through the packaging wall can be calculated from the pressure increase with time and from the volume between the inner side of the cylinder and the outer side of the bottle. Due to the fact that a pressure sensor is used, gases are measured non-specifically.

The measurement via the isostatic method is similar to the above mentioned total pressure method. The difference is that only a partial pressure difference between outside and inside the bottle is maintained whereas the total pressure on both sides is the same. A gas stream of known oxygen partial pressure is pumped through the cylinder. It is also possible to remove the cylinder for oxygen measurements and to measure at the oxygen partial pressure of 21 % in the ambient air. Oxygen-free carrier gas is pumped through the bottle. The partial pressure increases until a constant partial pressure of oxygen in the carrier gas signal is achieved. This oxygen partial pressure is proportional to the oxygen permeability. Electrochemical sensors are often used for oxygen detection.

The Mocon Oxtran instrument is in widespread commercial use for measurement of oxygen permeability by the isostatic method (Modern Controls, Inc., Minneapolis, USA; Internet: www.mocon.com). An advantage of this measurement system is that the permeability of bottles and containers can be easily determined. It is specified in ASTM D 3985 (55) and DIN 53380 (56). The test bottles or closures are connected to the nitrogen inlet and outlet connections in the lower cell half. Most testing is performed under ambient laboratory conditions (23 °C and 50 % relative humidity) with the packaging surrounded by air (21 % oxygen). If the rate of permeation is small the sensitivity and accuracy of the measurement can be increased by immersing the package in 100 % oxygen (57). For moisture triggered oxygen scavengers, the relative humidity must be increased to 95 % because the scavengers only act at higher humidity.

Numerical permeation simulation

The permeation of gases through plastics with a complex geometry is described by Fick`s second law and cannot be calculated analytically because only few analytical solutions exist. Generally numeric methods are used for solving Fick`s second law in the case of complicated geometries and boundary conditions, for example permeation through plastic closures. In the case of plastic closures having an integrated scavenger, the permeation of oxygen through the closure with simultaneous oxygen scavenging is calculated according to equation 16.

$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) - k_{O2} \cdot c^n \qquad (16)$$

Commercial computer software was used to solve equation 16, namely FEMLAB version 2.3 from COMSOL, Stockholm. FEMLAB uses MATLAB from MathWorks GmbH, Munich, as a computation tool. This is interactive software for modeling and solving scientific objectives based on partial differential equations.

The basic principle of FEM is the breakdown of expanded elements into finite elements interlinked by intersections. Figure 4 shows a finite element image of a plastic closure.

Knowing the boundary conditions, the concentration distribution of oxygen in the plastic material can be approximated for every intersection. Finally, the permeation of oxygen through the boundaries is calculated via a post processing tool.

4 Results and discussion

Bottles

The standard conditions employed for permeation measurements are 23 °C and 50 % relative humidity. Oxygen permeation through PET, PEN or coated bottles is virtually independent of the relative humidity. As mentioned above, the relative humidity has a major influence on oxygen permeation through EVOH and PA. When filling liquids into multilayer bottles containing EVOH or PA as an intermediate layer, this layer has to be placed in a position close to the outside because the relative humidity of the ambient air is typically about 50 %.

In the majority of current studies on barrier properties, the migration of oxygen solved in the polymer before filling is disregarded. Usually, migration means the transfer of plastic components from the plastic into the product or the transfer of flavor components from the product into the plastic. In this context, oxygen migration means the transfer of oxygen, solved in the polymer, into the filled product. Oxygen migration can be estimated since the oxygen solubility and diffusivity of the polymer are well known. In the case of PET, Michaels (43, 45) found that both the solubility and the diffusivity of oxygen depend on the amorphous and the crystalline fractions of the polymer. At 25 °C the oxygen solubility is 0.100 ml (STP) /(ml·bar) for amorphous PET and 0.073 ml (STP) /(ml · bar) for PET with a crystalline fraction of 42 %.

PET bottles are partly crystalline with a crystalline fraction of about 20 to 30 %. A value of 0.073 ml (STP)/(ml·bar) has, therefore, to be applied for calculations. This value means that 0.073 ml (STP) oxygen is solved in 1 ml plastic at 1 bar. Under ambient conditions (23 °C; p_{O2}=0.21 bar), 0.45 ml (STP) oxygen is solubilized in a 40 g PET bottle with a density of 1.37 g/l which under standard conditions represents 0.64 mg oxygen/bottle.

For monolayer bottles without a coating, the concentration gradient in the bottle wall is linear under steady state conditions (see Fig. 5). A portion of the oxygen migrates from the plastic into the filled product in a transient state because the oxygen partial pressure is initially virtually 0 bar inside the bottle and 0.21 bar in ambient air. Thus, shortly after filling both permeation and migration occur. The steady state is reached within a few days.

Figure 5 shows the oxygen gradient inside a PET bottle with a wall thickness of 0.5 mm at 23 °C and a diffusivity of $2.9 \cdot 10^{-13}$ m²/s (45). The migrated oxygen corresponds to the area between the straight horizontal dashed line (0 hours) and the curve valid for a certain time. The migrated oxygen amounts to 0.07 mg/l after one hour and 0.25 mg/l after 12 hours. Subsequently permeation becomes more and more important.

Diffusivity and solubility depend on temperature according to an Arrhenius-type relation. Thus the time dependence of oxygen migration into the filled product depends on temperature as shown in Figure 6. The solubility used to calculate the data shown in Figure 6 was 0.073 ml (STP)/(ml · bar) for both temperatures. After about 4 (10) days a measurable steady state is attained at 23 °C (10 °C), i.e. the changes in the measured values are less than the measurement accuracy of the Mocon equipment. This fact emphasizes the importance of an adequate long period of conditioning if the oxygen permeation is to be measured under steady state conditions and not under transient state conditions. For oxygen permeation these calculations are confirmed by measurements which show that the conditioning period at 23 °C is 3 to 5 days depending on the wall thickness.

The real oxygen ingress results from permeation and migration as indicated by Figure 6. The dashed lines are the asymptotes to the permeation curves at 10 °C and 23 °C. Their gradients represent the permeation under steady state conditions. Once a steady state has been achieved the oxygen impact on the filled product can be calculated as the sum of the gradient of the dashed line plus the point of intersection with the y-axis.

Figure 7 shows the oxygen ingress through different plastic bottles used for oxygen sensitive foods. The pure PET bottle is not appropriate for oxygen sensitive products such as beer or juices. Already after 8 days the oxygen uptake by the beverage amounts to 1 mg/l. In Russia the pure PET bottles used for beer had a market share of about 45 % in 2006. However, the time between filling and the consumption of the beer is very short in Russia.

The composition of the bottle has a fundamental influence on the oxygen migration. The layer with the best barrier properties should be next to the filled product to reduce oxygen migration. Consequently – as seen in Figure 7 – the oxygen uptake through an externally coated bottle is very high in the first few days after filling. After three weeks the oxygen uptake of the beverage amounts to 1 mg/l.

In Germany the plastic bottle for beer had a market share of less than 10 % in 2006. In order to permit a longer shelf life either internally coated PET bottles or PET bottles with an oxygen scavenger are used in Germany. These measures to improve the barrier properties reduce the oxygen uptake to 1 mg/l in three or four months. Another way to obtain good barrier properties is to use PEN bottles. The examined scavenger bottle was a multilayer PET bottle with 2 % MXD6 (scavenger). In this case the scavenger was exhausted after three month. However, the literature shows that in other cases no scavenger was exhausted in scavenger bottles within an observation time of more than three month (53).

An important factor is however the cost of these bottles. The most expensive material is PEN (~ 0.3 € for a 32 g-bottle) but this can be used for returnable bottles in contrast to multilayer and coated bottles which are only used as one-way containers.

Closures

Figure 8 shows an overview of oxygen permeation through typical bottle closures used for oxygen sensitive beverages. The permeabilities were measured in accordance with DIN 53380 (56). Crown corks were measured with a metal adapter, the other closures were measured on original bottles.

One example is described here to highlight the magnitude of the values shown in Figure 8: A PVC-foamed crown cork has a permeability of 4.0 µg/(closure · d · 0.21 bar). Thus the oxygen permeation into a 0.33 liter glass bottle amounts to 2.16 mg/l over half a year (0.5 l glass bottle: 1.44 mg/l). The oxygen permeability can be reduced by one order of magnitude by using barrier liners. Thus oxygen permeation into a 0.33 l glass bottle can be reduced to 0.22 mg/l over half a year (0.5 l glass bottle: 0.14 mg/l). The best barrier properties, however, can be achieved by scavenger technology (58, 59).

Numerical simulation of permeation

Oxygen scavengers are used in plastic bottles and in bottle closures to reduce oxygen permeation. Up until now little is known about the extent to which scavengers are able to scavenge oxygen from the headspace and pre-existing oxygen from the beverage. Therefore, in a first step the oxygen reduction in a glass bottle filled with sterilized water and capped with an active plastic closure (with scavenger) was simulated. The results are shown in Figure 9. After 10 days the scavenger reduces the oxygen content from 0.2 to 0.1 mg/l in a 0.5 liter bottle. However, the activity of the scavenger must be related to the oxygen reaction with beer. In a second step the oxygen concentration in beer filled in a glass bottle and capped with the same closure was simulated. After 10 days the oxygen content in the beer bottle was reduced from 0.2 to 0.01 mg/l. Consequently, the oxygen reduction in beer is much faster than in sterilized water. Besides showing the oxygen concentration, Figure 9 shows the amount of oxygen which reacts with the beer and the scavenger, highlighting the scavenger effect. After 10 days, 0.17 mg/l of pre-existing oxygen reacts with the beer and only 0.02 mg/l with the scavenger. There is evidence that the simulated scavenger is barely able to reduce the dissolved oxygen. Only some oxygen in the headspace reacts with the scavenger.

The boundary conditions play an important role for the results of the simulation: The reaction kinetics of oxygen in beer was assumed to be of first order with a value of $2 \cdot 10^{-6}$ s^{-1}. The first order reaction kinetics of the scavenger was $5 \cdot 10^{-3}$ s^{-1}. Eventually the beer reacts faster than the scavenger since a) the mass of filled beer (which is itself a very good “oxygen scavenger”) is much higher than that of the scavenger and b) the permeation of oxygen in liquids is 3 to 4 magnitudes of order higher than in plastics. However, in combination with a good passive barrier the oxygen permeation through closures can be reduced to near zero.

5 Conclusions and summary

Beer is the most oxygen sensitive food. In the literature, limits of 1 mg/l are indicated. Even using a glass bottle with a standard crown cork the value of 1 mg/l is reached after six months. Problems arise when switching to plastic bottles. Using monolayer 0.5 liter PET bottles (32 g) the resulting oxygen uptake is about 10 mg/l after four months. The three main methods of barrier improvement are internal coating of PET bottles, the use of PEN bottles and the incorporation of oxygen scavengers into bottles (as blend or multilayer) and closures. With all three methods a reduction of the oxygen uptake to 1 mg/l after four months can be realized. When using plastic bottles the use of closures with an oxygen scavenger is a good option for limiting the oxygen uptake to an acceptable level. Although not focused on in this paper, the loss of carbon dioxide must also be kept in mind because this can give carbonated drinks a flat taste.

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Appendix

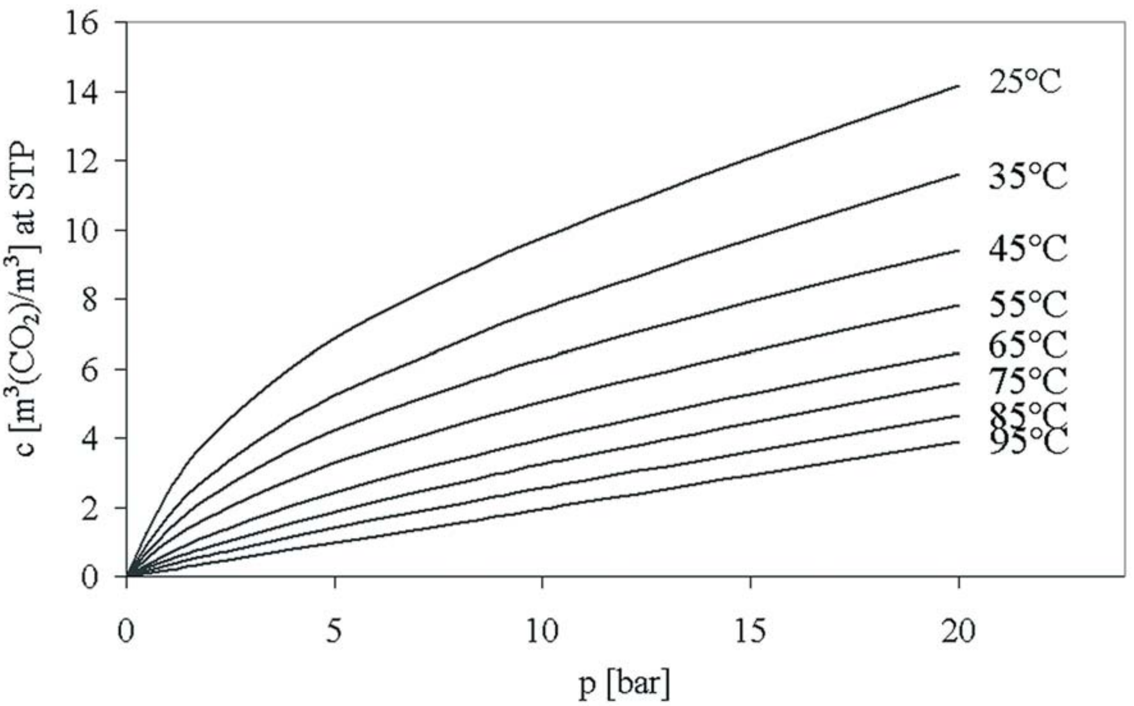

Fig. 1 CO$_2$ solubility in PET (amorphous volume fraction: 59 %) as a function of pressure calculated according to (43)

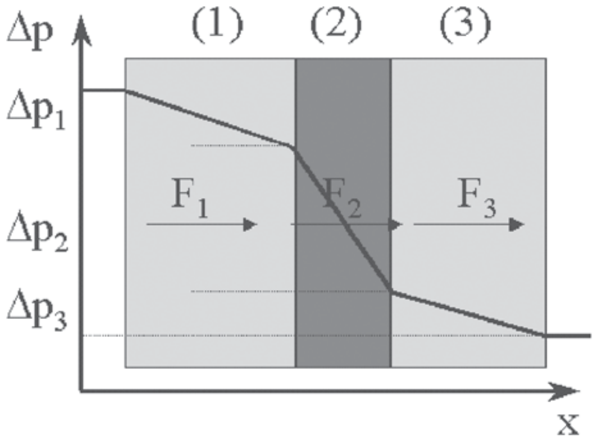

Fig. 2 Flux through a multilayer membrane

Fig. 3 Experimental set-up for testing bottles and closures

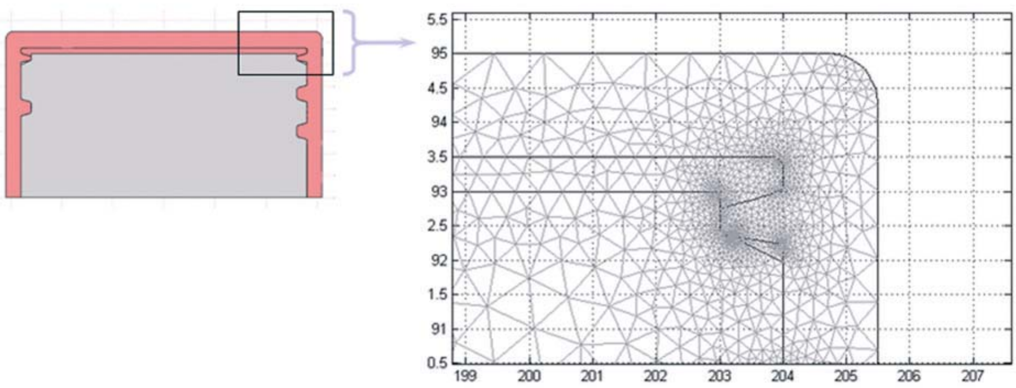

Fig. 4 Discretization of geometry using the Finite Element Method for simulating permeation

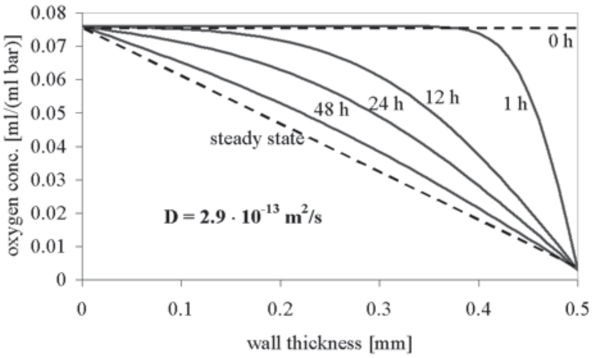

Fig. 5 Calculated oxygen gradients in a transient state in the wall of a partly crystalline 0.5 liter PET bottle (0.5 mm, 23 °C). The side with high oxygen values is exposed to the air.

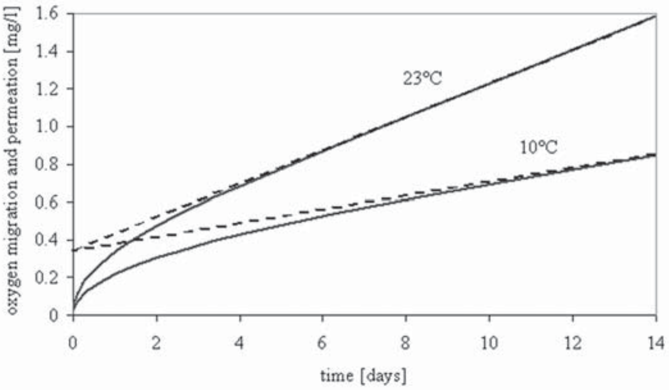

Fig. 6 Oxygen uptake through a 0.5 liter PET bottle into the filled product as a function of temperature and time

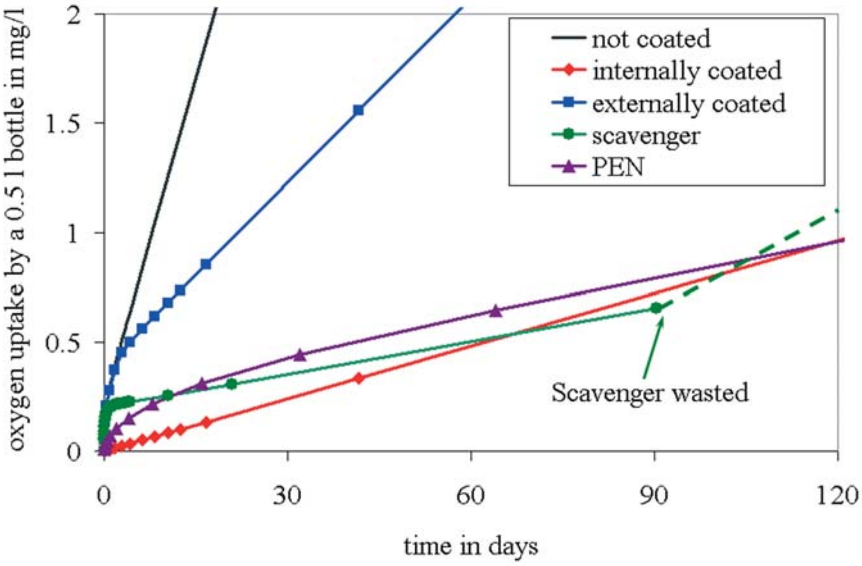

Fig. 7 Time dependent oxygen ingress through commercial plastic bottles (0.5 liter filling volume) used for oxygen sensitive foods. (The not coated and coated bottles are PET monolayer bottles, the scavenger bottle is a PET bottle with 2 % MXD6 as middle layer)

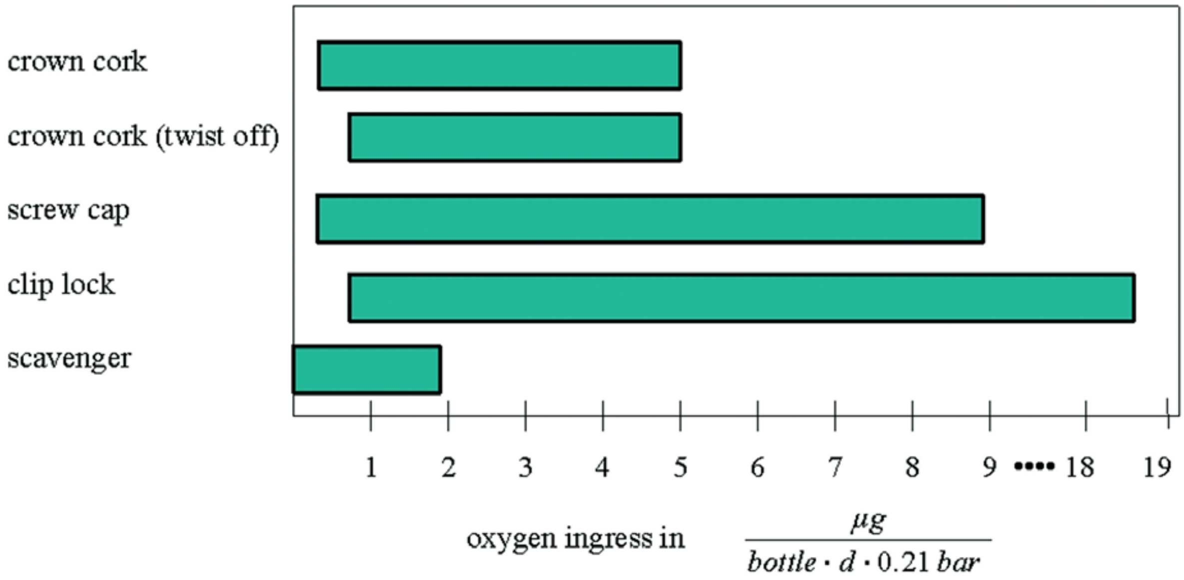

Fig. 8 Oxygen ingress through different bottle closures

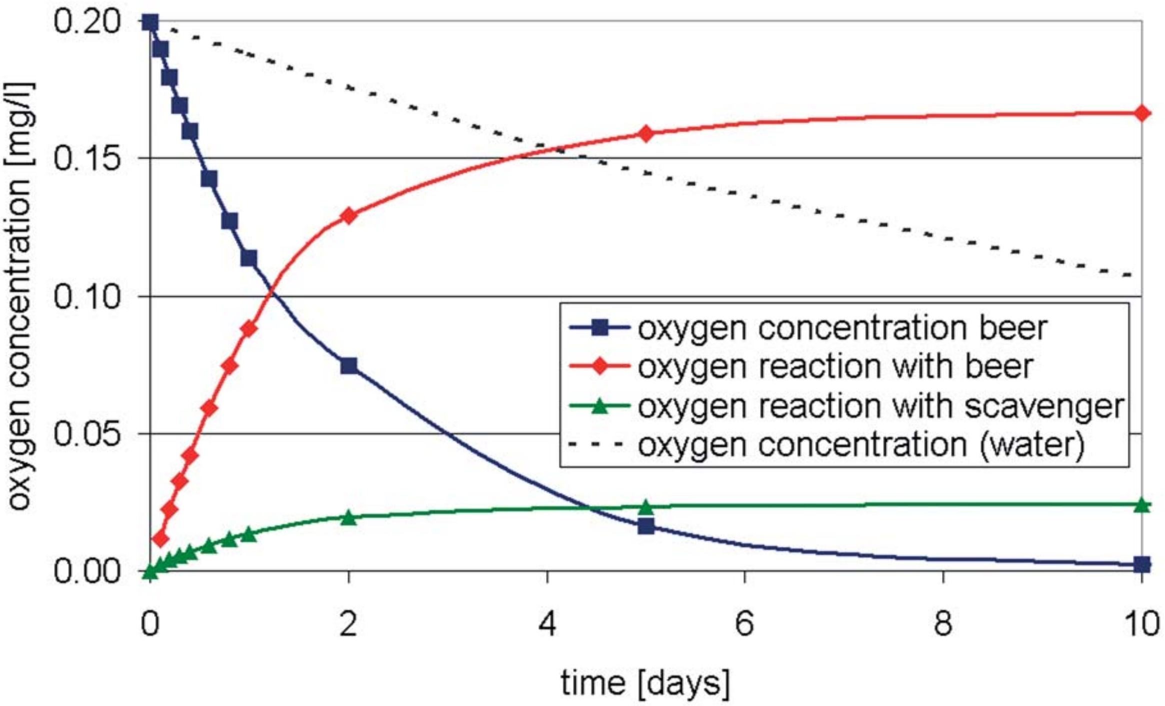

Fig. 9 Simulated oxygen concentration in water and beer filled in a glass bottle with an active plastic closure (with scavenger) as a function of time