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Temperature-dependent Oxygen Permeation through PET/MXD6-Barrier Blend Bottles with and without Oxygen Absorber

The oxygen permeability of PET bottles has a significant influence on the shelf-life of beverages that are sensitive to oxygen. To reduce the permeability, PET is blended with barrier materials like MXD6 (MXD6 is a mainly aliphatic polyamide resin which contains meta-xylylene groups). The aim of this study was to investigate the temperature dependence of oxygen permeation through PET/MXD6 blends. The oxygen content inside water-filled PET/MXD6-blend bottles with 2, 5 and 8 % wt. of MXD6 was determined at 5, 23, 38, and 55 °C. The MXD6 was applied both purely and with a catalyst that is enabling it to work as an oxygen absorber. The results were compared to PET bottles not containing MXD6. The oxygen partial pressure inside the bottles was measured as gaseous oxygen using an optical-chemical sensor. The activation energy of oxygen permeation was calculated to be in the range from 32.8 kJ/mol for PET bottles without MXD6 and up to 43.4 kJ/mol for PET bottles with 8 wt-% for the passive barrier of MXD6. In the barrier PET bottles with MXD6 in combination with a catalyst, the oxygen content in the water-filled PET bottles remained up to 0.2 mg O₂/L dissolved oxygen for a period of 6 months, depending mainly on the MXD6 concentration. This range was consistent for all applied temperatures. These data serve as a basis for the prediction/calculation of oxygen permeability of PET barrier materials at different temperatures and further for developing a standardization of oxygen absorber characterization concerning absorber kinetics and oxygen barrier.

Descriptors: PET bottle, Oxygen absorber, Oxygen permeation, Activation energy, MXD6

1 Introduction

Beverages, like beer or fruit juices are increasingly filled into PET bottles instead of glass bottles or metal cans [13]. However, these beverages are sensitive to oxidative deterioration. Beer, as one of the most oxygen sensitive food products, tolerates a maximum acceptable oxygen uptake of around 1 mg/L [8]. The oxygen barrier provided by plain Polyethyleneterephthalat (PET) is insufficient and has to be improved. Common practice to solve the problems is a) the plasma deposition of thin inorganic barrier layers on the inner surface (internal coating), b) the utilization of passive barrier polymers in monolayer and multilayer PET bottles or c) the application of oxygen absorbers in mono or multilayer PET bottles [5, 10, 14]. The internal coating is a promising technology, since it improves the barrier against oxygen, carbon dioxide and the barrier against migration [15, 18]. However coating-processes and the production of multilayer PET bottles cause more production complexity due to additional production steps and more complicated production devices needed, whereas the production of monolayer PET bottles from MXD6/PET-blend is less complex.

Monolayer bottles made from standard PET have proven to be unsuitable for the bottling of oxygen sensitive beverages. Assuming an often applied bottle weight for 0.5-L-bottles of 30 g, the oxygen permeability of a monolayer 0.5-L-PET bottle is in the order of approx. 0.2 to 0.3 mg/(bottle day bar). In this case the maximum tolerable oxygen uptake of beer of 1 mg O₂/L would be reached in 10 days. For passive as well as active barrier materials, the band width of achieved barrier values varies strongly even within a single category. When MXD6 as passive barrier is used as blend additive, the barrier improvement correlates to the MXD6-content in PET. An MXD6-content of 6 wt-% in PET reduces oxygen permeability by approx. 50 %, at 12 wt-% MXD6 by 70 to 75 % [4, 16].

The permeability of the above mentioned PET bottle can be reduced from 0.2–0.3 mg/(bottle day bar) to less than 0.005 mg/(bottle day bar) by using oxygen absorbers. However, when oxygen absorbers are applied additional influencing factors are relevant, besides the passive barrier, such as the activation, kinetics, capacity and duration of absorber activity. Thus the values even within the group of PET bottles with oxygen absorber vary by two orders of magnitude [12].

For high barrier PET bottles, the oxygen permeation through the closure becomes more important. Depending on the absorber formula, the oxygen permeability of plastics screw-on caps can be lowered to values of <0.001 to 0.01 mg/(closure day bar). Screw caps with exclusively passive barriers exhibit values of 0.01 to 0.05 mg/(closure day bar) [12]. The influence of closures was not in the scope of the current study.

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Tables and figures see Appendix

Several publications describe the correlation between the barrier performance of PET bottles and beer quality [5, 14, 15]. Orzinski showed that the lowest oxygen uptake of beer can be achieved by using oxygen absorbers (e.g. MXD6-based absorber working in combination with a catalyst) in PET bottles as blend material for mono- and multilayer bottles. The oxygen ingress was reported to be below 0.2 mg O₂/l for half a year applying PET blend bottles down to 2 wt-% MXD6 (with catalyst enabling it as oxygen scavenger) in PET. The oxygen barrier of this blend-bottle is sufficient for most oxygen sensitive beverages. However, when filling carbonated beverages like beer, the CO₂-barrier of a bottle with 2 % MXD6 is too low. Orzinski's study showed that 5 wt-% of activated MXD6 in PET should be the minimum for beer in order to realize a shelf life of 6 month or more [15].

The oxygen absorbing substance is either the polymer itself or an additive dispersed or solved in the polymer as in case of MXD6-blends. Substances used as additives in closures and compounds for closures are reported to be metal sulphites, ascorbic acid derivatives or ferrous compounds. These substances are not applied in blends for PET bottles.

The systems used so far are either PET copolyester or MXD6 with an additional catalyst to activate the reaction of the MXD6 with oxygen. In most cases the composition of the absorbing material is not published.

The absorber has to be stable at ambient conditions (21 volume-% oxygen in air). Thus the absorber must not react until bottling to ensure their shelf life. Oxygen scavenging reactions in currently commercial bottle closures are in some cases triggered by the humidity of the beverage. Activation before filling is not necessary in case of PET bottles with oxygen absorbers since the oxygen absorber in PET is thermally activated by the production process of the preforms which are subsequently blown to PET bottles. The oxygen permeability of PET preforms containing MXD6 blended into the PET is low. Therefore a delay between preform production and blowing/filling of the bottle is negligible in most cases.

Influence of temperature

Like the reaction kinetics, the change in permeability as a function of temperature can in most cases be described by the classical Arrhenius equation (11):

$$P = P_0 \cdot \exp\left(\frac{-E_p}{R \cdot T}\right) \quad (1)$$

where E_p is the activation energy for permeation. E_p is always positive so that the permeation rises with increasing temperature.

2 Intention of the study

This article places emphasis on the temperature dependence of permeation and on the activation energies of the oxygen permeation through PET bottles with passive and active MXD6 barrier grades for PET. The knowledge about the activation energy is of high interest for industrial applications: 1. According to the standards for permeation testing the oxygen permeation is measured at 23 °C

or 38 °C. However, the storage temperature will differ depending on the filled good and depending on the regional circumstances. 2. Based on knowledge about the activation energy of the oxygen permeation the permeation tests can be performed at higher temperatures resulting in shorter test periods. The oxygen permeability at lower temperatures can be calculated by applying Arrhenius's law. The current study is part of a standardization campaign for oxygen absorbers: The results will be utilized to establish a new test standard describing the testing of the kinetics of oxygen absorbers for PET bottles as well as for other package components like closures, sachets and labels with oxygen absorbers.

3 Material and Methods

3.1 PET bottles

The oxygen permeation measurements were performed with PET bottles made of MXD6/PET-blends with different MXD6-concentrations. The MXD6 acts as passive barrier and by adding a catalyst as oxygen absorber. The bottles were produced by INVISTA™ (Gersthofen, Germany). Table 1 summarizes the investigated materials with MXD6 acting either as passive barrier only or additionally as oxygen absorber.

3.2 Oxygen sensor bases on optical method

The principle of measurement is based on the effect of dynamic luminescence quenching by molecular oxygen that is described in detail in literature [6, 7]. The oxygen-meter uses a blue-green light source for exciting a sensor dye in the oxygen sensor. An optical polymer fiber acts as signal transducer between the optical sensor and a photodiode. The technique measures the luminescence lifetime of the activated state of the sensor dye. The luminescence lifetime negatively correlates to the oxygen partial pressure.

The used PSt6-sensor type is commercially available. This sensor membrane consists of an oxygen-sensitive indicator dye embedded in a silicone matrix. The technical data are shown in table 2.

3.3 Measurement of the oxygen ingress into the PET bottles

The PST6 oxygen sensor spots are located within the plastic bottles and the optoelectronic instrument is placed outside. Therefore, it is possible to measure the oxygen concentration content of the filled PET bottle versus time non-invasively. Optical chemical sensors measure both in aqueous and in gaseous (head space) phase. In this study, the trace oxygen sensor spot type PSt6 is placed onto the transparent closure which was adapted to the respective PET bottle. Three seals ensure the gas tightness of the closure (cf. Fig. 1), in order to avoid side diffusion between closure and bottle finish. The reading is achieved by screwing the polymer optic fibre integrated in a metal holder on the outside of the package directly above the trace oxygen sensor [6].

To obtain reliable results it is recommended to perform oxygen ingress measurements under realistic conditions. Measurements with the final product (beer, fruit juice) would give the best simulation of the 'real-life' situation, but beer will react with oxygen,

which makes it impossible to measure barrier properties of the packaging. Thus, a possibility to simulate the situation in a filled bottle is to use oxygen-free water.

The filling process of the bottles is performed in a nitrogen-flushed glove box. The oxygen content within the glove box is tested to be < 1 mbar oxygen. PET bottles are filled with nitrogen-saturated water (concentration of dissolved oxygen < 10 ppb) using a dosing pump adjusting the respective filling volume. In order to avoid bacteria growth, which will lead to oxygen consumption, silver nitrate is added in a concentration of 0.2 mmol/L by diluting a 0.1 N silver nitrate solution (Fluka, Germany). The bottles are sealed with oxygen tight closures coated with the trace oxygen-sensor spot type PSt6. The bottles contained around 0.52 L of water and around 5 cm³ headspace.

The safety screw was added to fix the cap. The oxygen partial pressure inside the bottle after the filling procedure was approximately 3 mbar. Since the oxygen permeation rate is strongly dependent on temperature and humidity, the bottles were stored in a controlled environment at different temperatures (5, 23, 38, 55 °C). The bottles were conditioned for 4 hours at 23 °C to adjust the temperature of the water inside the bottle before starting the measurement. The bottles were measured simultaneously using the OXY-10 trace device from PreSens, Regensburg. Values are mean value of five single measurements of different bottles. The oxygen partial pressure was calculated to the oxygen concentration with unit mg O₂/L. The error bars in the following diagrams are confidence intervals with a probability of error of 5 %.

In theory the measurement curves should follow an exponential equation that is based on the following differential equation [10, 11]:

$$\frac{dc}{dt} = \frac{Q_{O_2}}{V_F} - \frac{Q_{O_2}}{V_F \cdot S_F \cdot p_{air}} \cdot \left(1 + \frac{V_G}{V_F} \cdot \frac{1320 \frac{mg}{L \cdot bar}}{S_F} \right)^{-1} \cdot c \quad (2)$$

The equation describes the increase in concentration versus time dc/dt of dissolved oxygen in a bottle filled with water. The brackets include a formula that includes the distribution of oxygen between water and head space. The solution of this equation is:

$$c(t) = S_F \cdot p_{air} + \left\{ (c_0 - S_F \cdot p_{air}) \cdot e^{-\left[\left(\frac{Q_{O_2}}{V_F \cdot S_F \cdot p_{air}} \right) \cdot \left(1 + \frac{V_G}{V_F} \cdot \frac{1320 \frac{mg}{L \cdot bar}}{S_F} \right)^{-1} \cdot t \right]} \right\} \quad (3)$$

With:

Symbol	Illustration	Unit
Q _{O₂}	Oxygen flux into the bottle	mg · day ⁻¹
c(t)	Oxygen concentration in water, depending on time t	mg · L ⁻¹

S _F	Oxygen solubility in water (23 °C)	40mg·L ⁻¹ ·bar ⁻¹
p _{air}	Atmospheric pressure in air (average absolute pressure 965 mbar)	0.202 bar
c ₀	Oxygen concentration in water after filling (t = 0)	mg · L ⁻¹
V _G	Volume of headspace	= 0.005 L
V _F	Volume of water	= 0.52 L

4 Results and Discussions

4.1 Passive barrier PET bottles

The oxygen content of bottles without absorber filled with water was measured as reference. The result of this test series is shown exemplarily in figure 2. The permeation measurements were stopped after the oxygen content exceeds 1.6 mg/L since that is the measurement limit of the oxygen sensor PSt6. In the following, all measured values are indicated as dissolved oxygen in the unit mg/L.

Due to a reduced partial pressure difference between oxygen in the ambient air and the oxygen in the bottle the slope of oxygen ingress into the bottle decreases. The measured values (points in Fig. 2) can be fitted by equation 3 (lines in Fig. 2). Based on the data in figure 2 the oxygen permeation through the PET bottle for the different temperatures can be calculated with equation 3 as follows:

5 °C: 0.10 mg O₂/(day · bar)

23 °C: 0.19 mg O₂/(day · bar)

38 °C: 0.39 mg O₂/(day · bar)

55 °C: 0.84 mg O₂/(day · bar)

Application of Arrhenius' law results in the following equation describing the temperature dependence of the oxygen permeation through a PET monolayer bottle:

$$Q_{O_2, PET} = 7.6 \cdot 10^4 \frac{mg O_2}{day \cdot bar} \cdot \exp \left(- \frac{32.8 \frac{kJ}{mol}}{R \cdot T} \right)$$

To the authors knowledge there are no published data describing the activation energy for the oxygen permeation through PET bottles. However, in the literature activation energy values from 32.2 to 37.7 kJ/mol could be found for PET films [1]. Consequently the measured activation energy for oxygen permeation through PET bottles of 32.8 (±2.9) kJ/mol is comparable to these values for PET films.

Similar measurements were performed with PET bottles with additional passive barrier. The results of all measurements are summarized in table 3. For a better comparability the oxygen

permeation coefficients are calculated using the mean thickness of the PET bottle walls as indicated in table 3. The permeation area of the PET bottles was approximately 400 cm² and the mean thickness of the PET bottles (without screw thread) was 387 μm. The indication of the oxygen permeation coefficient related to 100 μm thickness and 1 m² permeation area instead of the oxygen transmission rate has the advantage that the values can be used to predict the oxygen permeability of PET bottles with other bottle weight and other permeation area.

The oxygen permeation is approximately halved when using 8 % (passive) MXD6 compared to the pure PET bottle. Comparable data can be found in literature for a temperature of 23 °C [3, 9, 17]. The exact reduction depends on the temperature since the activation energy of permeation is not the same for PET bottles and the PET bottles blended with MXD6. Overall, the oxygen permeability through PET bottles increases by a factor of 7.3 when increasing the temperature from 5 °C to 55 °C. Due to the higher activation energy the oxygen permeability of the MXD6-blended bottles increases by a factor of 11.7 when increasing the temperature from 5 °C to 55 °C. When the activation energy of permeation is known the measurement can be performed at higher temperatures and consequently the permeation measurement can be performed in a shorter time.

4.2 PET bottles with passive barrier and additional oxygen absorber

In the second step the oxygen concentration of water-filled PET bottles with MXD6 working as both a passive barrier and as oxygen absorber (due to use of a catalyst) was measured for a period of 180 days.

The results of the optical oxygen measurement of PET bottles with and without oxygen absorber in figure 3 show the oxygen content versus time. The oxygen content in the passive barrier bottles filled with water increases and consequently there is an oxygen uptake into the bottle. On the contrary, the oxygen content in the bottles with active barrier (due to catalyst) is more or less constant and therefore there is no oxygen uptake into the bottle, when the bottle is filled with water. However if the same bottle is filled with beer the oxygen content will be significantly lower compared to a bottle filled with water, due to the reaction of oxygen with beer. This difference of the oxygen content between beer and water filled bottle results in a residual permeation, if the bottle is filled with beer [10]. This residual oxygen permeability can be measured with the carrier gas method and is typically in the range of <0.005 to 0.1 mg/(bottle day bar) for a 0.5-l-PET bottle with MXD6 absorber [5, 12, 13].

According to figure 3, the oxygen content in the PET bottles with 2, 5 or 8 wt-% MXD6 with catalyst remains at a low level. Even after 180 days the oxygen partial pressure was below 0.2 mg/L for the absorber bottles with 2 % MXD6, below 0.04 mg/L for the absorber bottles with 5 % MXD6 and below 0.02 mg/L for that with 8 % MXD6. These low oxygen levels indicate that the absorber with 2, 5 and 8 wt-% is able to protect the filled beverage for at least 180 days the better the higher the MXD6-content is. The measured values and the confidence interval for 2 wt-%

MXD6 with catalyst are significantly higher compared to that of 5 and 8 wt-% MXD6. Since beer is especially sensitive to oxygen and has to be protected against loss of CO₂, 5 or 8 wt-% MXD6 with catalyst should be used for beer.

Whereas the oxygen uptake into passive barrier bottles depends on the temperature according to Arrhenius' law, the oxygen content in the bottles with catalyst is approximately the same for all temperatures. That indicates that not only the permeation but also the reaction of oxygen with the oxygen absorber follows Arrhenius' law and that the activation energy of oxygen reaction must be in the same order of magnitude than the activation energy of oxygen permeation.

To the authors knowledge there are no published data for activation energies for MXD6-based oxygen absorbers. However, the activation energy of the reaction kinetics of iron based absorber systems are in a range from 44 to 48 kJ/mol [2]. The knowledge about the activation energy of the reaction for MXD6-based oxygen absorbers would be of great interest in order to compare the temperature dependence of permeation versus reaction, but that was not the objective of this publication.

5 Conclusions

In this study the temperature dependent oxygen uptake in PET bottles with passive and activate barrier-MXD6-blends with 2, 5 and 8 wt-% MXD6 was investigated. The activation energies for the oxygen permeation through the passive barrier bottles were measured with an optical permeation method and are in the range of 32.8 kJ/mol (for PET bottles) to 43.4 kJ/mol (PET with 8 wt-% MXD6). The knowledge of the activation energies provides the possibility to calculate the oxygen permeability in the temperature range of 0 to 60 °C.

When using a MXD6 concentration of at least 5 wt-% in form of an oxygen scavenger, the oxygen concentration remains at a low level of <0.04 mg/L for at least 180 days. Not less than 5 wt-% MXD6 with an additional catalyst should be used for carbonated beverages like beer, since a MXD6 concentration of 5 wt-% has an additional barrier performance against CO₂ loss.

Another benefit of adding a catalyst is that the oxygen content in the PET bottles and consequently the residual oxygen permeation through the bottles are approximately independent of the temperature. This result is completely different to the behaviour of all known passive barrier materials, which show a strong temperature dependence of oxygen permeation. Additionally to the scientific aspect, these results will help the standardisation committee to prepare the standards for characterization of the oxygen absorber regarding absorber kinetics and oxygen barrier.

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Appendix

Table 1 Bottles tested in this study

Barrier PET bottles	
MXD6 (passive barrier)	MXD6 (with catalyst, oxygen absorber)
PET (reference)	–
PET with 2 wt-% MXD6	PET with 2 wt-% MXD6
PET with 5 wt-% MXD6	PET with 5 wt-% MXD6
PET with 8 wt-% MXD6	PET with 8 wt-% MXD6

Table 2 Technical Data of the PSt6-type sensor spot [6]

	Dissolved Oxygen	Gaseous & Dissolved Oxygen
Measurement range	0–1.8 mg/L (ppm) 0–56.9 µmol	0–20 % air-saturation 0–4.2 % oxygen-saturation 0–41.4 hPa
Limit of Detection (LOD)	1 ppb of dissolved oxygen	0.01 % air-saturation 0.002 % oxygen
Resolution at 20 °C and 1013 hPa	1 ± 0.30 µg/L (ppb) 10 ± 0.40 µg/L (ppb) 100 ± 0.50 µg/L (ppb) 1000 ± 4.0 µg/L (ppb)	0.002 ± 0.0007 % oxygen-saturation 0.02 ± 0.0009 % oxygen-saturation 0.2 ± 0.0015 % oxygen-saturation 2.0 ± 0.09 % oxygen-saturation
Accuracy (20 °C)	3% of the respective concentration	
Response time	<40 s; (<60 s with optical isolation)	<10 s; (<15 s with optical isolation)
Calibration	Conventional two-point calibration in oxygen-free environment (nitrogen) and a second calibration value, optimally between 1 and 2 % oxygen	
Temperature range	–10 to 50 °C	
Long-term stability	100,000 data points without drift	

Table 3 Activation energies and oxygen permeation coefficients of 0.5-L PET bottles with different concentrations of passive barrier measured at 5, 23, 38 and 55 °C

Flaschen	Oxygen Permeability in $\left[\frac{mg \cdot 100 \mu m}{d \cdot m^2 \cdot bar} \right]$				Activation energy of oxygen permeation in $\left[\frac{kJ}{mol} \right]$
	5 °C	23 °C	38 °C	55 °C	
PET bottle (reference)	9.4	18.3	38.0	80.9	32.8 ± 2.9
2 Gew.-% MXD6	8.7	15.9	35.6	72.7	32.7 ± 3.6
5 Gew.-% MXD6	4.2	9.5	29.6	54.4	40.4 ± 4.6
8 Gew.-% MXD6	3.5	6.7	26.0	53.4	43.4 ± 4.2

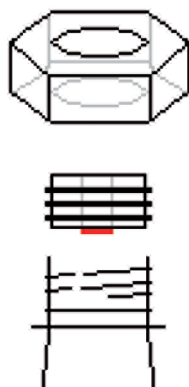


Fig. 1 Measurement set up

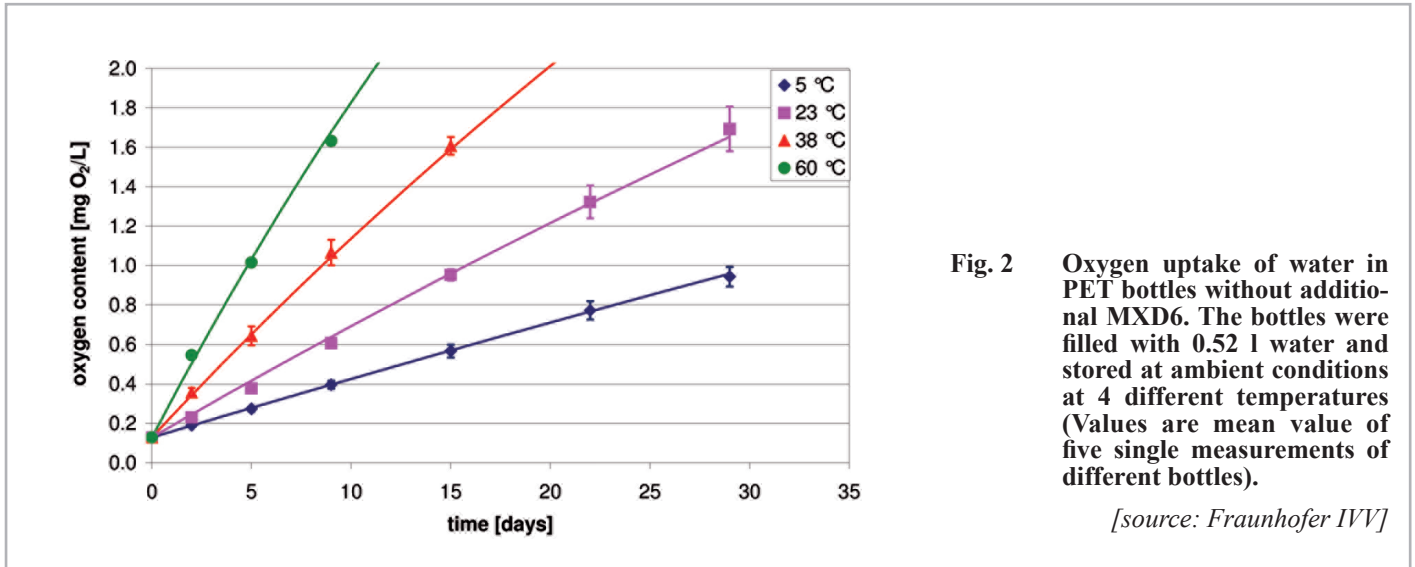


Fig. 2 Oxygen uptake of water in PET bottles without additional MXD6. The bottles were filled with 0.52 l water and stored at ambient conditions at 4 different temperatures (Values are mean value of five single measurements of different bottles).

[source: Fraunhofer IVV]

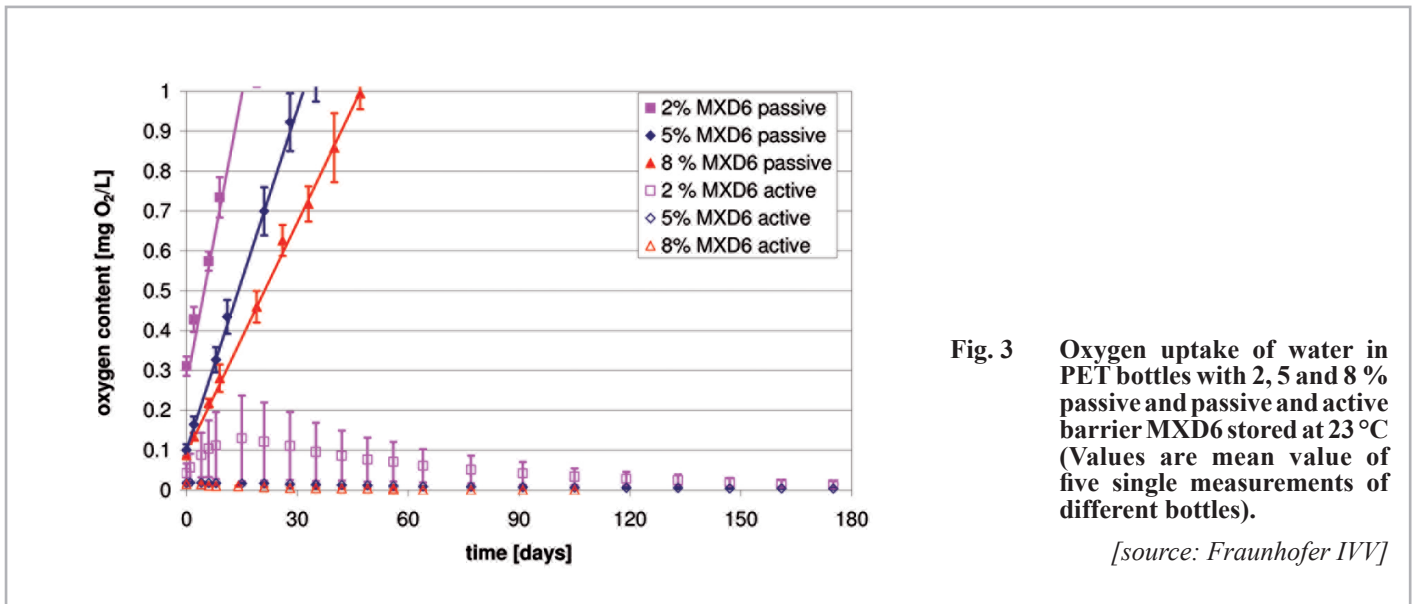


Fig. 3 Oxygen uptake of water in PET bottles with 2, 5 and 8 % passive and passive and active barrier MXD6 stored at 23 °C (Values are mean value of five single measurements of different bottles).

[source: Fraunhofer IVV]

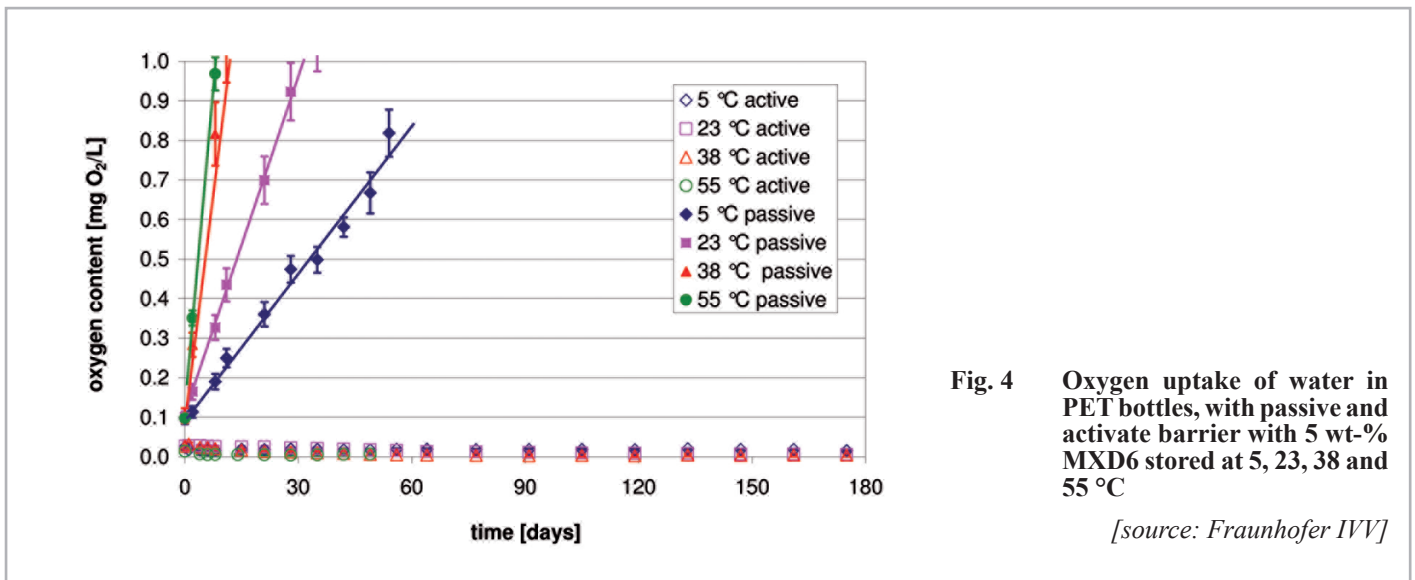


Fig. 4 Oxygen uptake of water in PET bottles, with passive and activate barrier with 5 wt-% MXD6 stored at 5, 23, 38 and 55 °C

[source: Fraunhofer IVV]