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Highlights

• Determination of O_2 and CO_2 transmission rate of whole perforated packages. • Determination of O_2 and CO_2 transmission rate for single perforations. • The ratio P_{CO2}/P_{O2} was different for non-perforated and perforated materials. • Temperature had limited effect on transmission rates for perforations.

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Determination of O_2 and CO_2 transmission rate of whole packages and single perforations in micro-perforated packages for fruit and vegetables

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ABSTRACT

Microperforated packages are in widespread use for whole and fresh-cut fruit and vegetables, and there is a need for a simple and cost efficient methodology to accurately determine gas transmission rates for different packages. This work demonstrates a static technique using a low cost gas analyser for determining the O₂ and CO₂-transmission rates and permselectivity for whole perforated and non-perforated packages stored at different temperatures. The work further demonstrated the possibility to calculate the transmission rates for single holes, and results for single perforations agreed well with results in other studies. The O_{2-} and CO_{2-} transmission rates in perforated packages were not significantly affected by temperature in the range 5-23 °C, whereas transmission rates increased with increasing temperature for non-perforated packages. Gas transmission measurements can be used within quality control, in the choice of appropriate packaging for different fruit and vegetables and as an important parameter in EMAP modelling.

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38 1. Introduction

39 Microperforated films are commonly used for modified atmosphere packaging (MAP) of fruits and vegetables with high respira-40 41 tion rates. Different headspace conditions can be achieved in the package depending on the interactions between respiratory activ-42 ity of the packaged produce and gas transfer through the polymeric 43 matrix and microperforations (Lucera et al., 2011). This technique 44 is often denoted equilibrium modified atmosphere packaging 45 46 (EMAP). The choice of product optimised film is crucial to obtain optimum modification of the atmosphere and avoid extremely 47 48 low levels of O₂ and/or high levels of CO₂, which could induce anaerobic metabolism with possible off-flavour generation and risk 49 of anaerobic microorganism proliferation (Beaudry, 2000; Watkins, 50 2000). 51

Knowledge of the gas transmission rate of the package is one of 52 the key factors in EMAP modelling, and the permselectivity ratio 53 P_{CO2}/P_{O2} , commonly denoted β , is an important parameter being 54 55 different for continuous and perforated materials (Beaudry, 2008). The gas exchange in a perforated package occurs almost en-56 tirely through the microperforations, and various mathematical 57 models have been proposed in order to describe the exchange of 58 gases through the perforations. The application of Fick's law is 59 60 widespread, and the modified model of Fishman et al. (1996) is 61 commonly used. Ghosh and Anantheswaran (2001) measured the 62 oxygen transmission rate (OTR) of microperforated films using a

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static method to compare the experimental data with the results predicted by published models. They found that the modified model based on Fick's law as proposed by Fishman et al. (1996) had very good agreement with the experimental data from the static method used in their study. However, all these mathematical models assume the uniform production of microperforations that are round, within the required size range, and unobstructed (Allan-Wojtas et al., 2008). Hence, if the perforations are irregular in size and thickness, methods for direct measurement of the gas transmission rate in perforated packages can be useful in many situations.

Dynamic or coulometric methods are commonly used for measuring OTR and carbon dioxide transmission rate (CO₂TR) of continuous film and packages. These methods are of doubtful application for perforated materials due to the gas convection taking place when the pressure on each side of the material is slightly unbalanced (Ozdemir et al., 2005). Another disadvantage of the coulometric method commonly used for films and packages, is that this equipment cannot measure gas transmission rate at temperatures lower than 10 °C (Abdellatief and Welt, 2012; Lucera et al., 2011), while the recommended storage temperature for fruit and vegetables is 5 °C or lower. Hence, most experimental systems for measuring the permeability of perforated or microperforated materials are static (Gonzalez et al., 2008). Ghosh and Anantheswaran (2001) used both a static and a flow-through technique to measure the OTR of microperforated films. They stated that the static method better simulates the actual package situation, and found that the repeatability of the static method was better than the flow through method resulting in lower standard deviation

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92 values. However, the disadvantage of the static method is that it 93 takes time to get the results. Generally, few published work are 94 found in literature on direct methods to measure the OTR and CO₂₋ 95 TR of microperforated films and packages. Ozdemir et al. (2005) 96 measured OTR and CO₂TR in non-perforated and perforated 97 35 µm polypropylene pouches using a static technique and a gas 98 chromatograph for gas concentration measurements. The measured gas transmission values were calculated for the flat film. 99 100 Gonzalez et al. (2008) used a static measuring system and a gas chromatograph to measure OTR and CO₂TR of single perforations 101 102 with different dimensions and thicknesses. Based on the experi-103 mental data, they proposed an equation describing the dependence of the transmission rates on the perforation area, where the only 104 input is the perforation size measured by an ocular microscope. 105 106 Their data predicted by the empirical equation was compared to 107 five other bibliographic models. The O₂ and CO₂ transmission rates 108 predicted by their empirical equation were very close to those ob-109 tained with the modified Fick's equation as described by Fishman 110 et al. (1996). However, using the empirical model proposed from 111 Gonzalez et al. (2008) still requires uniform holes in order to calcu-112 late the perforation area. Oxygen transmission rate for perforated 113 packages can also be measured using a dynamic accumulation method with inexpensive fluorescence oxygen sensing technology 114 (Abdellatief and Welt, 2012). However, this equipment does not 115 116 measure CO_2 , and hence, the CO_2TR cannot be measured for the 117 packages.

Another factor to be considered when working with perforated 118 119 packages is the perforation size in relation to the storage condi-120 tions (calm or convective). Allan-Wojtas et al. (2008) compared dif-121 ferent microscopy techniques to study the microstructure of 122 microperforations in plastic films and relate microperforation 123 microstructure to gas transmission characteristics under calm and convective conditions. They observed a linear increase of both 124 125 O₂ and CO₂ transmission rates with the area of the holes for micr-126 operforations in the range of $30-100 \mu m$, for diffusion under calm 127 conditions. Their study also indicated that microperforations larger 128 than 55 um can lose their diffusion constant if convection is pres-129 ent, and most consistent OTR results were achieved using numer-130 ous small holes rather than fewer large ones.

131 Although most of the gas exchange in a microperforated pack-132 age occurs through the perforations, in some packages with a 133 low number of perforations the gas flux will have a combination of transmission through the polymer material and transmission 134 135 through the perforations (Beaudry, 2008). Measuring on the whole package will take into account and simultaneously measure the 136 137 transmission rate through the polymer material and the perfora-138 tions at the conditions of intended storage. Larsen et al. (2000) 139 demonstrated a method for measuring OTR of whole packages de-140 noted the ambient oxygen ingress rate (AOIR) method. This meth-141 od has many advantages such as: (1) use of low cost equipment 142 compared to other commercial permeation equipment, but still with sufficient accuracy; (2) the method has high capacity and 143 many packages can be measured at the same time at different 144 conditions; (3) the OTR can be measured at most temperatures, 145 146 including freezing temperatures (Larsen, 2004), whereas many commercial available permeation instruments cannot measure at 147 148 temperatures lower than 5-10 °C; (4) the method measures on the whole package, including heat seals and other possible defects 149 created under the converting process, and after e.g. thermoforming 150 151 that stretches the materials giving gas transmission rates different from the flat film; (5) the method can be applied on most kinds of 152 153 whole packages consisting of different materials, including fibre 154 based materials.

155 The aim of this work was to further develop the AOIR-method 156 and verify the methodology on perforated packages including the 157 measurement of CO₂TR.

The results with this new alternative and simple low cost meth-158 od for measuring OTR and CO₂TR for whole packages with and 159 without perforations and the single perforations were compared 160 to other research works. Using the developed method, the influ-161 ence of storage temperature and the difference in β -values for 162 the continuous and perforated packages was also studied. The O₂ 163 and CO₂ transmission rates were studied using different films with different perforation sizes, perforation methods and amount of perforations.

2. Materials and methods

2.1. Packaging materials, preparation of samples, gas concentration measurements, equipment

2.1.1. Packaging materials and packaging procedure

Three series of high density polyethylene (HDPE) trays (Promens, Kristiansand, Norway) were flushed with the gas mixture 5% O₂, 10% CO₂ and 85% N₂ before sealing with three different top webs using a Polimoon 511VG tray sealing machine (Promens, Kristiansand, Norway).

One series of ten 1500 ml trays were sealed with a 12 µm polyester/40 µm polyethylene (PET/PE) (Amcor Flexibles, Ledbury, England) top web. The top web of all the packages was punctured once with an acupuncture needle before storage at 4 °C (named 'Mech-PET' in the following). The irregular hole made with the needle may simulate the shape of holes made by different mechanically puncturing equipment.

Another series of 1500 ml trays were sealed with an Amcor Pplus 12 µm PET/40 µm PE film (Amcor Flexibles, Ledbury, England) with four microperforations (named 'Micro-PET' in the following). The holes (1, 2, 3 or 4) were accordingly covered with septa just after sealing, creating packages with different transmission rates depending on the amount of perforations. The packages were stored at 5 °C, 10 °C and 23 °C during the sampling period. These series were run with 4 replicates.

A third series of 1100 ml trays were sealed with a 20 µm oriented polypropylene (OPP)/25 µm PE film from Sealed Air (Oslo, Norway) giving a non-perforated package with relatively high gas TR (named 'non-perforated package' in the following). These packages were stored at 5 °C and 23 °C during the sampling period, and were run with 4 replicates.

Pieces $(360 \times 267 \text{ mm})$ of 25 µm biaxially oriented polypropylene (BOPP) film (ScanStore Packaging AS, Middelfart, Denmark) without perforations and with different number of microperforations (denoted 3000, 4100 and 5000) were sealed on two sides giving pouches (named 'Micro-BOPP' in the following). The pouches were flushed with 5% O₂, 10% CO₂ and 85% N₂ using a tube and the volume of the packages was 1758 ± 99 ml. The pouches (five replicates of each) were stored at 4 °C during the sampling period.

All our samples were stored in Termaks environmental chambers (Termaks, Bergen, Norway) which are developed for accurate temperature control. A low circulation of air inside the chamber is obtained by conduct system which keeps most of the air stream outside the working chamber giving calm storage conditions. The air flow was measured in the range 0.2-0.4 m s⁻¹ using a Kimo thermo-anemometer VT100 (Emerainville, France).

2.1.2. Gas sampling and microscopy of perforations

Changes in headspace gas composition during time in the pack-213 ages were recorded using a CheckMateII O₂/CO₂ -analyser (PBI 214 Dansensor, Ringsted, Denmark). The headspace gas concentration 215 was measured several times during a storage period of 5–7 days. 216 The perforations on the different materials were cut from the 217

plastic film and mounted on microscope slides using tape. The film 218

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was covered with cover glass and examined under a Leica DM6000B Light Microscope (Leica Microsystems GmbH, Wetzlar, Germany) equipped with an Evolution MP <u>Colour</u> digital camera. We used a <u>10×</u> objective and grey scale images were captured. Images of <u>6</u>–8 perforations of each type were captured and the vertical and horizontal diameters (μ m) were noted.

225 2.2. Mathematical model, practical considerations and calculations

226 2.2.1. Mathematical model

OTR and CO_2TR were calculated from changes in volumetric fractions of the gases inside the package over time according to the theoretical framework outlined in several publications (Ghosh and Anantheswaran, 2001; Gonzalez et al., 2008; Larsen et al., 2000).

The O_2 and CO_2 transmission rates can be calculated by the following equation:

$$TR = -\frac{V}{t_f - t_i} \ln\left(\frac{C_{air} - C_f}{C_{air} - C_i}\right)$$
(1)

where *V* is the volume of the package, t_f the time of the final gas concentration measurement, t_i the time of the initial gas concentration measurement, C_{air} the volumetric concentration of gas in the air (0.21 O₂, and 0.03 CO₂), C_f the volumetric concentration of gas in the package at the final measurement, C_i the volumetric concentration of gas in the package at the initial measurement.

Solving Eq. (1) for the final volumetric gas concentration we ob tain the equation:

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$$C_f = C_{air} + (C_i - C_{air})e^{-\frac{TR}{V}(t_f - t_i)}$$
 (2)

enabling prediction of gas concentrations over time based on the
initial conditions similar to the prediction curves presented in Larsen et al. (2002).

The equations above can be used for both non-perforated (Lar-251 252 sen et al., 2000) and microperforated packages (Gonzalez et al., 2008) involving no metabolic activities. However, working with 253 non-perforated packages, one should be aware of the "volume in-254 255 crease effect" as described by Moyls (2004). For packages such as polyethylene with high OTR and flushed with N2, the volume of 256 the package will increase during time due to higher O₂ than N₂ 257 258 transmission rate. Hence, the total pressure inside the package will be higher than 1 atm, introducing an error into the theoretical 259 260 framework. This error can be minimised by performing the measurements early in the run, when oxygen pressure varies between 261 262 0 and 0.05 atm (Moyls, 2004).

263 2.2.2. Optimal initial conditions for OTR and CO₂TR estimation

To be able to measure changes in O₂ and CO₂ concentrations 264 265 due to transmission, one obviously has to have initial conditions 266 in the package differing from the outside air. However, which initial conditions that gives the best OTR estimation needs some con-267 268 sideration. If the initial atmosphere in the package has $C_{02} = 0\%$ and C_{CO2} = 21%, there will be a rapid change in concentrations the first 269 270 few hours. This means that timing of the measurements to obtain representative results has to be accurate. If, on the other hand, ini-271 272 tial concentrations of $C_{02} = 20\%$ and $C_{CO2} = 1\%$ are chosen, the change in concentration will be slow. This would require very 273 274 accurate concentration measurements. A compromise would be 275 much more robust by reducing the need for accurate timing and concentration measurements. Consequently the initial concentra-276 tions chosen in the presented work were around $C_{02} = 5\%$ and 277 278 $C_{CO2} = 10\%$.

The resolution and accuracy of the gas analysing instrument should also be taken into account. The CheckMate-instrument has different resolution and accuracy of the sensors in the various ranges. The zirconia sensor, measuring O_2 , the resolution is 0.1% absolute in the range above 10%, 0.01 in the range above 1% and 0.001 in ranges below 1%. The accuracy is ± 0.01 % absolute in range below 1% and ± 1 % relative in the range above 1%. The CO₂ infrared sensor resolution is 0.1% absolute with an accuracy of ± 0.5 % absolute and ± 1.5 % of reading. Hence, the highest accuracy of the O₂ readings will be in the range below 1% O₂, which is a range being difficult to obtain working with perforated packages where the transmission rate is high and the process is relatively unstable at the start of the measurement period. However, a very high accuracy of the gas transmission rate (gas TR) measurements is, in practical use, not necessary due to the large variation in all the other factors constituting a part of the modelling of optimal packages for fruit and vegetables.

2.2.3. Utilising more than two measurement time points

Calculating transmission rates from two time points alone can be vulnerable to measurement errors and dependent on several parallel tests to ensure stable results. To improve robustness of the calculations, more than two time points can be calculated. However, this does not fit into the existing formulae for transmission rates. A strategy for obtaining transmission rates indirectly in a spread sheet is the following (example using oxygen): (1) Make an initial guess of the OTR in one cell. (2) Make formulae for predicting the oxygen concentration at all included time points having the first time point as initial time and OTR from the given cell. (3) Make formulae for calculating the squared error between measured and predicted concentration and sum these up. (4) Use a solver to find the OTR value minimising the sum squared error.

The strategy described above can be used separately on one and one measurement series or on all series at the same time. The former can be used to find a mean transmission rate and its standard deviation across measurement series, while the latter will be an even more robust estimate of the true transmission rate. As a result, it is possible either to get more reliable results using the same number of parallels as usually done, or it can reduce the number of parallels without loss of accuracy.

Our calculations showed that the most stable and representative values for the gas TR values were obtained when the package was allowed to equilibrate for approximately 1 day before the first gas sampling, and the changes in O2 or CO2 concentration should be minimum 2% before the last gas sampling after 2-3 days depending on the type of package. The conditioning time of approximately 1 day before the first gas sampling was especially important for the packages flushed on the tray sealing machine, due to an unstable gas ingress process in the beginning of the test run probably caused by the initial vacuuming of the package in the tray sealer. In packages flushed with the gas mixture using a tube, the gas ingress process was more stable earlier in the test period. A longer storage period for the non-perforated packages was beneficial giving larges differences in CO₂-concentrations at the first and last sampling time reducing the errors in lower accuracy of readings.

3. Results and discussion

3.1. Gas transmission rates for non-perforated and perforated packages stored at different temperatures

Gas transmission for three different types of packages was mea-
sured and calculated according to the previous description. The re-
sults for both the whole packages and for single perforations are
presented in Table 1. The OTR and CO_2TR for the single perforations
were calculated by subtracting the transmission rate value for the
packaging material (0 perforations) from the transmission rate va-337
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Table 1

OTR, CO₂TR values and CO₂TR/OTR ratio for three types of packages with different number of perforations and single perforations measured at different temperatures.

Package	Perforations	Temperature	OTR/pkg (mL d ⁻¹)	CO_2TR/pkg (mL d ⁻¹)	Ratio CO ₂ TR/OTR	OTR/perf. $(mL d^{-1})$	$CO_2TR/perf.$ (mL d ⁻¹)	Ratio CO ₂ TR/OTR/perf
Mech-PET	1	4	284 ± 20	257 ± 34	0.9	279 ± 19	242 ± 33	0.9
Micro-PET	0	5	5 ± 1	15 ± 3	3.1			
	1	5	103 ± 5	108 ± 5	1.0	98 ± 5	92 ± 5	0.9
	2	5	185 ± 20	172 ± 13	0.9	90 ± 10	78 ± 7	0.9
	3	5	274 ± 17	241 ± 15	0.9	90 ± 6	75 ± 5	0.8
	4	5	366 ± 27	322 ± 26	0.9	90 ± 7	77 ± 7	0.8
Micro-PET	0	10	5 ± 1	19 ± 4	3.7			
	1	10	134 ± 18	124 ± 13	0.9	129 ± 18	105 ± 13	0.8
	2	10	193 ± 7	171 ± 3	0.9	94 ± 4	76 ± 2	0.8
	3	10	279 ± 8	251 ± 7	0.9	91 ± 3	77 ± 2	0.8
	4	10	368 ± 12	329 ± 8	0.9	91 ± 3	77 ± 2	0.9
Micro-PET	0	23	10 ± 1	41 ± 4	4.3			
	1	23	131 ± 22	137 ± 6	1.0	121 ± 22	96 ± 6	0.8
	2	23	224 ± 25	218 ± 28	1.0	107 ± 12	89 ± 14	0.8
	3	23	309 ± 14	295 ± 17	1.0	100 ± 5	85 ± 6	0.8
	4	23	374 ± 21	354 ± 18	0.9	91 ± 5	78 ± 5	0.9
Micro-BOPP	0	4	155 ± 39	267 ± 86	1.7			
	6 or 7	4	745 ± 51	693 ± 84	0.9	88 ±5	63 ± 13	0.7
	11	4	1083 ± 68	1013 ± 22	0.9	84±6	68 ± 2	0.8
	14 or 15	4	1434 ± 137	1229 ± 145	0.9	88 ±6	66 ± 8	0.8

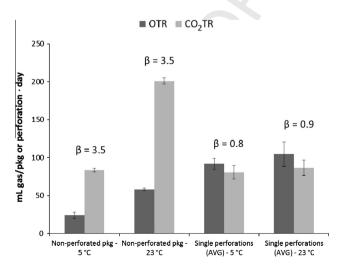
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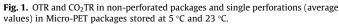
cro-perforated packages for fruit and vegetables. Journal of Food Engineering (2013), http://dx.doi.org/10.1016/j.jfoodeng.2013.05.035

lue of the whole package with perforation. The remaining gas TR
value for the perforations was then divided by the number of perforations, giving the gas TR per perforation.

346 Perforations made by the acupuncture needle had the highest 347 gas TR rate, almost threefold the values for the laser perforations in the PET/PE-film and BOPP-film (Table 1). The perforations in 348 349 the PET/PE-film had slightly higher gas transmission rates than the perforations in the BOPP-film. Gonzalez et al. (2008) measured 350 351 OTR and CO₂TR for Amcor P-plus film with different perforation sizes and thicknesses of the films. The calculated area (mean value) 352 for the laser perforations in the Amcor P-plus PET/PE-film in our 353 experiment was approximately 6500 µm². The results from Gonz-354 355 alez et al. (2008) showed that the OTR and CO₂TR for a perforation with an area of 6500 μ m² were approximately 135 and 356 357 115 mL gas d^{-1} , respectively. Our gas TR values for the perforations 358 in the Amcor P-plus film were lower but within the same range 359 (Table 1).

The permselectivity ratio P_{CO2}/P_{O2} , commonly denoted , is different for continuous and perforated materials (Table 1 and Fig. 1). The ratio in our experiment was in the range from 3.1 to 4.3 for Micro-PET, 1.7 for Micro-BOPP without perforations and





3.5 for the non-perforated package with OPP/PE as top web. The permselectivity ratio for different polymeric films can in general vary from 2 to 8 (Beaudry, 2008; Gonzalez et al., 2008; Ozdemir et al., 2005). However, since the packages in our experiment were a combination of HDPE trays with PET/PE and OPP/PE as top webs, and permselectivity values commonly are given for pure materials, it is difficult to find corresponding results to compare with in literature for this package. The ratio of oriented polypropylene is, according to Ozdemir et al. (2005), approximately three depending on its manufacturing conditions. They measured the ratio to 1.94 for 35 µm OPP film in their experiment, which is in the same range as our value of 1.7.

The permselectivity for the perforated materials in our study was in the range 0.9-1.0 for whole packages, and 0.8-0.9 for the single perforations (Table 1). Our values are in accordance with the findings of other authors (Fonseca et al., 2000; Gonzalez et al., 2008). Gonzalez et al. (2008) found the quotient CO₂TR/ OTR to be 0.89 ± 0.05 for the Amcor P-plus film used in their experiment, and Ozdemir et al. (2005) reported a permselectivity value of 0.87 for one single perforation in the 35 µm OPP film.

The influence of storage temperature on gas transmission rate is also different for continuous and perforated materials (Fig. 1). Storage at 5 °C compared to 23 °C showed no significant differences in gas TR for the average single perforations, whereas OTR and CO_2TR increased by a factor of 2.4 from 5 °C to 23 °C for the non-perforated package (HDPE-tray with OPP/PE top web). The finding for the single perforations is in accordance with the results in the work by Fonseca et al. (2000). They analysed the O₂ and CO₂ exchange rate through a single tube at 5 °C and 20 °C, and found that temper-392 ature had no significant effect on O_2 and CO_2 transfer coefficients in 393 this range of temperature. Other experiments on non-perforated 394 packages using the AOIR-method have demonstrated an increase 395 in OTR with higher temperatures (Larsen, 2004). The OTR increases 396 with about 9% per °C for many polymers above the glass tempera-397 ture (DeLassus, 1997). 398

3.2. Gas transmission rates for single holes – static, theoretical and exact data

In order to compare our results to other authors' work, the perforations were placed under a light microscope and the mean area for each type of perforation was calculated (using formulae for el-403

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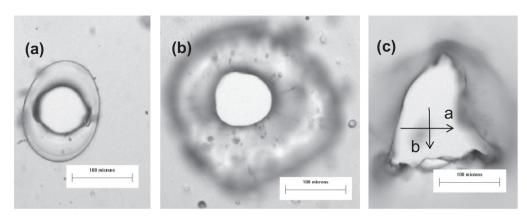


Fig. 2. Pictures of different perforations: (a) Micro-BOPP, (b) Micro-PET and (c) Mech-PET. a is the horizontal diameter, b is the vertical diameter.

Table 2 Horizontal and vertical diameters, mean area, theoretically calculated gas TR and measured gas TR rates by the static method through 3 types of perforations (mean values in mL O_2 and CO_2 d⁻¹).

Sample	а	b	Area	Fishman et al. (1996)		Gonzalez et al. (2008)		Measured – static method	
				OTR	CO ₂ TR	OTR	CO ₂ TR	OTR	CO ₂ TR
Micro-BOPP	76	77	4582 ± 472	127 ± 7	98 ± 6	114 ± 7	101 ± 6	87 ± 5	66 ± 8
Micro-PET	95	86	6425 ± 376	160 ± 5	123 ± 4	139 ± 5	122 ± 4	99 ± 16	84 ± 11
Mech-PET	175	92	12576 ± 4417	241 ± 39	185 ± 34	204 ± 39	179 ± 34	279 ± 19	242 ± 33

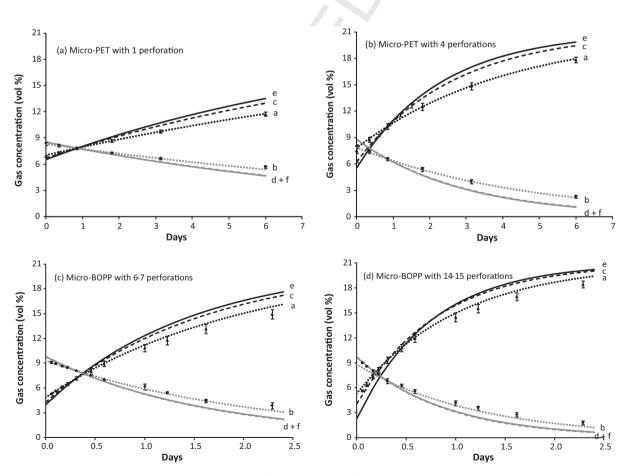


Fig. 3. Changes in gas concentrations during storage in packages with different number of perforations; exact, measured and theoretical. \blacktriangle exact O₂-values in packages; \blacklozenge exact CO₂-values in packages: (a) O₂ – our static method, (b) CO₂ – our static method), (c) O₂ – theoretical; Gonzalez et al. (2008), (d) CO₂ – theoretical; Gonzalez et al. (2008), (e) O₂ – theoretical; Fishman et al. (1996) and (f) CO₂ – theoretical; Fishman et al. (1996).

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lipse). Pictures of the three types of perforations are presented in Fig. 2. Accurate areas for the mechanical perforations were difficult to calculate, due to very irregular shapes of the perforations. Gas transmission rates were accordingly calculated theoretically using the equations described in Fishman et al. (1996) and Gonzalez et al. (2008). Theoretically calculated transmission rates and transmission rates calculated by our static method are presented in Table 2.

Our results using the static method is lower than the theoretically calculated values using equations from Fishman et al. (1996) and Gonzalez et al. (2008) for the micro-perforated materials, whereas the gas TR values for the mechanically perforated film was slightly higher using our static method (Table 2). However, the calculations for the mechanic perforations according to Fishman et al. (1996) and Gonzalez et al. (2008) might be uncertain due to difficulties in accurate calculation of the area for these irregular holes.

420 In order to study the best fit between the values given in Table 2 421 to exact O₂ and CO₂ concentrations in whole packages stored over 422 time, prediction curves (selected packages presented in Fig. 3) were made using Eq. (2). The predicted values for the whole pack-423 424 age according to the equations by Fishman et al. (1996) and Gonz-425 alez et al. (2008) were calculated by multiplying the OTR and CO₂TR for a single perforation (Table 2) with the number of perfo-426 rations and adding the permeability value of the whole container 427 without perforations. Measured values (Fig. 3) using the experi-428 429 mental values from the static method gave the best fit for all 4 430 samples compared to the exact values in the packages. The curves 431 based on the gas TR values measured by the static method were 432 very close to the exact gas concentrations for the two Micro-PET-433 packages, whereas slightly higher values were predicted using the static method for the Micro-BOPP packages. 434

435 The good results obtained using the static method as presented in this work make this method a versatile technique for determin-436 437 ing the O₂ and CO₂ transmission rate of whole packages, perforated 438 and non-perforated, and for single perforations for many types of 439 packages stored at realistic storage temperatures. The method uses 440 low cost equipment and is easy to use, and there will be no need 441 for the use of microscopy to study the perforations in order to cal-442 culate the perforation areas. A gas analyser is usually available in 443 most packaging facilities, including packaging houses for fruit 444 and vegetables, especially if they perform MAP. The measured 445 gas transmission values can be fit into programs for EMAP modelling for fruit and vegetables, giving accurate values for the gas 446 447 transmission in the packages. This method can also be useful in the quality control within the packaging facilities, screening the 448 449 variation in gas transmission in different film production batches.

450 4. Conclusion

451 Gas transmission rates were measured for three different types of perforated packages using a static method and a low cost gas 452 453 analyser. Gas TR in single perforations could also be calculated. 454 Perforations made by an acupuncture needle had the highest gas 455 TR rate, almost threefold the values for the laser perforations in 456 the PET/PE-film and BOPP-film. The permselectivity ratio P_{CO2}/P_{O2} is different for non-perforated and perforated materials. The ratio 457 458 in our experiment was in the range from 3.1 to 4.3 for Micro-PET, 1.7 for Micro-BOPP without perforations and 3.5 for the 459 non-perforated package with OPP/PE as top web. The permselec-460 461 tivity for the perforated materials in our study was in the range 0.9–1.0 for whole packages, and 0.8–0.9 for the single perforations, 462 which is in accordance with the findings of other authors. No sig-463

nificant difference was found between average values for OTR and CO₂TR for the single perforations in packages stored at 5° C, 10 °C and 23° C, whereas gas TR for the package with non-perforated OPP/PE film increased by a factor of 2.4 by storage at 23° C compared to 5° C. Comparing our experimental results to theoretical approximations used by other researchers showed that the measured values using the static method gave the best fit with exact values in the packages. The good results obtained using this static method makes it a versatile method for determining the transmission rate of whole packages, perforated and nonperforated, and for single perforations for many types of packages stored at realistic storage temperatures.

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