Development of Palladium-based Oxygen Scavenger: Optimisation of Substrate and Palladium Coating

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Complete List of Authors:	Yildirim, Selcuk; Institute of Food and Beverage Innovation, Röcker, Bettina; Zurich University of Applied Sciences, Institute of Food and Beverage Innovation Rüegg, Nadine; Zurich University of Applied Sciences, Institute of Food and Beverage Innovation Lohwasser, Wolfgang; Amcor Flexibles Kreuzlingen AG,

Keywords:	active packaging, oxygen scavengers, palladium

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Development of Palladium-based Oxygen Scavenger: Optimisation of Substrate and Palladium Coating

Selçuk Yildirim[*a], Bettina Röcker[a], Nadine Rüegg[a], Wolfgang Lohwasser[b]

[a] *Life Sciences and Facility Management, Zurich University of Applied Sciences, Campus Reidbach, 8820 Waedenswil, Switzerland*
[b] *Amcor Flexibles Kreuzlingen AG, Finkernstrasse 34, 8280 Kreuzlingen, Switzerland*

[*] *Corresponding author. Email: selcuk.yildirim@zhaw.ch*
Tel.: 0041 58 934 56 31

Abstract:
Oxygen scavenging films based on a palladium coating were developed to remove residual oxygen remaining in food packages after modified atmosphere packaging. Palladium (Pd) was coated on to a range of packaging films and in different thicknesses using magnetron sputtering technology. To improve the substrate surface, an additional silicon oxide (SiO_x) coating was also applied to the films before Pd-deposition. To determine the oxygen scavenging activity, the scavenger films were placed into an airtight cell, which was flushed with a gas mixture containing 2 % oxygen and 5 % hydrogen. The results showed that the oxygen scavenging activity was strongly dependent on the coating substrate as well as on the Pd-deposition thickness. Packaging films such as polyethylene terephthalate (PET), aluminium oxide coated PET, oriented polypropylene and polylactic acid were found to be the most suitable substrates for Pd-based oxygen scavengers. Moreover, it was demonstrated that the intermediate SiO_x layer between the substrate and the Pd-coating led to a substantial increase in the oxygen scavenging activity (up to 33 fold) for all applied packaging films. Additionally, it was shown that the optimal Pd-coating thickness for the investigated oxygen scavenging films lies between 1.1 and 3.4 nm. The resulting scavenger films have the potential to scavenge residual headspace oxygen of sensitive foods within a matter of minutes leading to shelf life extension and overall quality improvements.

Keywords: Active packaging, oxygen scavengers, palladium

Introduction

Packaging is an important process in food manufacturing [1]. It enables efficient storage, distribution, and sale of foodstuffs from production through to consumption. Moreover, packaging acts as a barrier which prevents deterioration of food and beverages due to environmental influences such as oxygen, water vapour, light and both chemical and microbiological contamination [2]. Over recent years, consumer demand for natural high-quality foods, which are non-processed or minimally processed, and which do not contain any preservatives but have an acceptable shelf life has increased significantly [3-5]. To respond to this need, the protective function of packaging has been further expanded through the development of innovative packaging solutions such as active packaging technologies. Several such technologies have been developed that interact with the food by adding compounds to the food or into the headspace surrounding the food, or by removing substances from the food or the headspace [6, 7]. These technologies aim to prolong the shelf life of food products [4, 7, 8] while ensuring their quality, safety and integrity.

The application of oxygen scavengers is one of the most important active packaging technologies which aims to remove any residual oxygen present in the food packaging [9, 10]. Although the food industry uses gas flushing or modified atmosphere packaging processes, the residual oxygen-concentration in the package remains between 0.5-5% [8, 10, 11] even at optimised conditions due to insufficient evacuation during the packaging process, the oxygen dissolved in the food itself being subsequently released into the headspace, oxygen permeation through the packaging material or poor sealing [8]. This residual oxygen negatively affects the quality and shelf life of several foods as it promotes the growth of aerobic microorganisms [10, 12] or leads to oxidation of the product [13]. As a result, it may affect the sensorial properties [14-16] of the product, may cause colour changes [11, 17-19] or nutritional losses [20-22]. With the application of oxygen scavengers the residual levels of oxygen inside the package can be reduced, in some cases to <0.01% oxygen, and actively controlled, which is not possible with other packaging systems [8].

Typically, the oxidative mode of action of scavengers is either chemical using, for example, iron or ferrous salts, ascorbic acid, photosensitive dyes, or unsaturated fatty acids, biochemical through the use of enzymes [5, 8, 10] or biological using immobilized yeast on a solid material [23]. The use of such oxygen scavenging technologies is generally limited due to the sensitivity of oxygen scavenging systems to environmental conditions such as pH and temperature, the water activity of the product [10], the presence of carbon dioxide in the headspace [7], and the requirement of humidity for the activation [10] and cost of such technologies [9]. Another hurdle for application is that typically oxygen scavenging capacities and, in particular, the oxygen scavenging rate are too low to improve the quality of those foods with a short shelf life [7, 11, 24].

Palladium (Pd) can catalyse the oxidation of hydrogen into water (**Figure 1**) [25], and can be used to remove the residual oxygen in the headspace of a packaging where the food is packaged with a modified atmosphere [26].

Insert here Figure 1

Figure 1: Catalytic oxidation of hydrogen with oxygen [25]

In this study, a palladium-based oxygen scavenging film was developed for food packaging applications. Palladium was coated on to packaging films using magnetron sputtering technology and hydrogen was introduced into the packaging as a part of the modified atmosphere. Assorted packaging films for Pd-coating and Pd-deposition thicknesses were evaluated to achieve high oxygen scavenging activities. Since previously preliminary results had shown that a coating of palladium on a silicon oxide (SiO_x) layer may improve oxygen scavenging rates [27, 28], all the packaging films were additionally coated with SiO_x before applying the Pd-coating.

Materials and Methods

Materials

A Pd coating was applied to varied substrates (Table 1). The substrates were either coated with Pd directly or after a coating of SiO_x (where x = 1.0 to 2.0 [27]) had been applied (Amcor standard process).

Table 1: List of substrates used for palladium coating

Insert here Table 1

Methods

Palladium Deposition

Magnetron sputtering was chosen as the deposition process because of the ease of deposition. A rectangular 750 mm wide and 125 mm long magnetron sputtering cathode (Leybold, PK 750) with sputtering target (Hereaus, Germany) was used as the deposition source. Argon was used as the plasma gas. The incoming gas rate of 250 ml/min resulted in a pressure level of $2*10^{-3}$ mbar. 3.8 kW electrical power was applied to the source. The web speed was adjusted depending on the desired layer thickness of palladium on the film. Pd-layer thicknesses were calculated according to the web speed: 20 m/min for 3.4 nm, 50 m/min for 1.1 nm, 100 m/min for 0.7 nm, 200 m/min for 0.4 nm and 500 m/min for 0.3 nm, and verified using X-ray fluorescence spectroscopy (XRF).

Measurement of Oxygen Scavenging Activity

An airtight steel cell with a total volume of 127 cm^3 was used for oxygen scavenging measurements. The cell contained two valves for gas flushing and a Plexiglas lid. An O_2-sensitive sensor spot (PSt6, 10 mm diameter, PreSens, Regensburg, Germany) was glued onto the inner side of the Plexiglas lid for the oxygen measurements. Palladium-coated films were cut (5 cm x 5 cm) and placed in the cell. The cell was subsequently flushed for 30 seconds at 1 bar with a gas mixture containing 2% oxygen, 5% hydrogen and 93% nitrogen. The oxygen concentration in the cell was measured by a non-destructive measurement method using fibre optic optodes Fibox 4 trace (PreSens, Regensburg, Germany). Oxygen concentrations were measured by linking a light-emitting (600 – 660 nm) optical fibre to the sensor spot. The sensor emitted more or less luminescence depending on the oxygen concentration in the cell. All measurements were carried out in a climate chamber (VP 600, Vötsch Industrietechnik, Balingen-Frommern, Germany) at 23 °C and 50 % relative humidity.

Statistical analysis

Each experiment was carried out using 3 independent replicates (n = 3). Statistical analysis was performed using the statistical software package R, version 3.0.1. The data were analysed by one-factorial analysis of variance. In order to detect differences between specific factor levels, a post-hoc analysis (pairwise t-testing) with error inflation correction following Tukey HSD was applied. All tests were done in a two-tailed (two-sided) setting and significance was assumed if $p<0.05$.

Results and Discussion

Effect of Coating Substrate on the Oxygen Scavenging Activity

To understand the effect of coating substrate on the oxygen scavenging activity, a range of different substrate materials (**Table 1**) were coated with 1.1 nm of Pd and the oxygen scavenging rates (OSR) were measured.
The reduction in oxygen concentration in the measurement cell is illustrated for those substrate materials with the highest OSR in **Figure 2**. Use of PET as substrate decreased the initial oxygen concentration from 2 % to 0 % within 18 minutes, which resulted in an OSR of 7992 $cm^3/(m^2*h)$ (**Figure 4**). When PET/AlOx or oPP was used as a substrate for the Pd-coating, the OSR decreased significantly to 3916 $cm^3/(m^2*h)$ and 3405 $cm^3/(m^2*h)$, respectively. This increased the time required for removal of all the initial oxygen to 37.5 and 31 minutes respectively. Coating of palladium on PET/Silicone and PLA resulted in moderate OSR (1587 $cm^3/(m^2*h)$ and 1161 $cm^3/(m^2*h)$). Nevertheless, PET/Silicone/Pd and PLA/Pd films completely removed the oxygen in the chamber within 61 and 110 minutes respectively. All other substrates resulted in lower OSR (**Figure 4**).

Insert here Figure 2

Figure 2: Reduction in oxygen concentration in the measurement cell with PET/Pd, PET/AlOx/Pd, oPP/Pd and PET/Silicone/Pd and PLA/Pd films using a palladium deposition thickness of 1.1 nm.
Mean values ± standard deviation (n=3).

Previously, it was demonstrated [27] that the addition of a SiO_x layer between the substrate film and the palladium coating led to an increase in the OSR of PET/SiO_x/Pd films. In the present study, this finding was confirmed not only for PET but also for all the tested substrates. **Figure 3** illustrates the reduction of oxygen concentration in the measurement cell, as an example, for those SiO_x/Pd coated substrate materials with the highest OSR. Coating of SiO_x significantly decreased the time necessary to remove all the initial oxygen from 2% to 0% from 18 to 6.5 min for PET, 37.5 to 10.5 min for PET/AlOx, and 31 to 18.5 min for oPP. PLA/SiO_x/Pd films removed the oxygen as quickly as PET/SiO_x/Pd films.

Insert here Figure 3

Figure 3: Reduction in oxygen concentration in the measurement cell with PET/SiO_x/Pd, PET/AlOx/SiO_x/Pd, PLA/SiO_x/Pd, LDPE/SiO_x/Pd and oPP/SiO_x/Pd films using a palladium deposition thickness of 1.1 nm and SiO_x pre-coating.
Mean values ± standard deviation (n=3).

The application of SiO_x led to a significant increase in the OSR, even for substrates which exhibited low OSR, such as paper, siliconised paper, non-woven 1 and 2, PP and LDPE, as well as those which exhibited very low OSR; Cellophane and Nature1A (**Figure 4**). This was particularly remarkable for PP, LDPE and non-woven1 where the OSR increased by 13.9

times, 16.6 times and even 21.7 times respectively. In addition, the initial high OSR of oPP and PET/AlOx could be further significantly increased from 3405 to 4888 $cm^3/(m^2*h)$ and 3916 to a remarkable 9815 $cm^3/(m^2*h)$ respectively. The maximum OSR was obtained with PLA/SiO_x/Pd (18,044 $cm^3/(m^2*h)$) and with PET/SiO_x/Pd (19,210 $cm^3/(m^2*h)$). Whereas with the application of SiO_x the OSR of the highly active PET film increased by 240 %, for PLA this increase was an extraordinary 1554 %. The differences in OSR between PLA/SiO_x/Pd and PET/SiO_x/Pd were, however, not statistically significant (**Figure 4**).

Insert here Figure 4

Figure 4: Comparison of oxygen scavenging rates of different materials, listed in Table 1, using a palladium deposition thickness of 1.1 nm.
Mean values ± standard deviation (n=3). OSR of substrates labelled with the same letter (capital = Pd, lower case = SiO_x/Pd) are not significantly different ($p < 0.05$).

According to the results obtained, it has been proven that the oxygen scavenging activity of Pd-coated films is strongly substrate dependent, in particular on the surface where the palladium is deposited. The exact mechanism of how the substrate affects the OSR is not yet fully understood. All substrates had an influence even when they were covered with SiO_x. Nyberg and Tengstal [25] found that in the presence of $H_2/H_2O/O_2$ gas, catalytic hydrogen oxidation can also occur via another reaction path (**Figure 5**) as water can be associatively adsorbed directly on the Pd-surface [29] and thereby interact with the adsorbed hydrogen and oxygen.

Insert here Figure 5

Figure 5: Reaction path of hydrogen oxidation in the presence of water [25].
Superscript letters *ad* and *g* stand for *adsorbed* and *gaseous* respectively.

In this study, since all the investigations were carried out at 50 % rel. humidity, it can be assumed that hydrophilic properties of the substrate materials led to an accelerated adsorption of H_2O on the surface which in turn might have promoted the catalytic reaction of palladium. However, further investigation of the surface characteristics is vital for a better understanding.

Effect of Palladium Deposition Thickness on the Oxygen Scavenging Activity

As well as the substrate on which the palladium is deposited, preliminary studies [28] have shown that the oxygen scavenging activity of Pd-coated films is also highly dependent on the palladium deposition thickness. Therefore, a range of different substrate materials, listed in **Table 1**, were coated with different Pd-deposition thicknesses (0.3, 0.4, 0.7, 1.1 and 3.4 nm) and the oxygen scavenging activity was evaluated.

Coating thickness of 0.3 nm resulted in negligibly low OSR for all substrates. For PET/Pd, PET/AlOx/Pd, oPP/Pd, PET/Silicone/Pd and PLA/Pd, an increase in OSR occurred with increasing Pd-coating thickness from 0.3 to 1.1 nm (**Figure 6**). A further increase from 1.1 to 3.4 nm led to a substantial rise in OSR for PLA/Pd (+46 %) and oPP/Pd (+90 %) whereas for PET/Silicone/Pd (-59 %), PET/AlOx/Pd (-10 %) and PET/Pd (-18%) a decrease in OSR was observed. However, the differences in OSR between 1.1 and 3.4 nm for PET/AlOx/Pd and PET/Pd were not significant. Oxygen scavenging activity of LDPE, PP, paper, paper/Silicone, Cellophane, Nature1A and the 2 non-woven materials was negligibly low at all Pd-deposition thicknesses (data not shown).

Insert here Figure 6

Figure 6: Comparison of oxygen scavenging rates of PET/Pd, PET/AlOx/Pd, oPP/Pd, PET/Silicone/Pd and PLA/Pd films with Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm.
Mean values ± standard deviation (n=3).
Bars labelled with the same letter within each substrate are not significantly different ($p < 0.05$).

Additionally, SiO_x coated materials (**Table 1**) were coated with different Pd-deposition thicknesses (0.3, 0.4, 0.7, 1.1 and 3.4 nm) and the oxygen scavenging activities were evaluated. Results revealed that a 0.3 nm Pd-coating on the SiO_x layer led to negligibly low OSR for all substrates (selected ones are shown in **Figure 7**). With PET/SiO_x, PET/AlOx/SiO_x, PLA/SiO_x, LDPE/SiO_x and oPP/SiO_x a continuous and substantial OSR increase was detected by increasing the Pd-coating thickness from 0.4 to 1.1 nm (**Figure 7**). Incerase of Pd coating thickness from 1.1 to 3.4 led to a significant increase in OSR for oPP/SiO_x, PET/AlOx/SiO_x and PLA/SiO_x. On the other hand it resulted a decrease in OSR for LDPE/SiO_x. With PET/SiO_x, the differences between 1.1 and 3.4 nm were not statistically different.

Insert here Figure 7

Figure 7: Comparison of oxygen scavenging rates of PET/SiO_x/Pd, PLA/SiO_x/Pd, PET/AlOx/SiO_x/Pd, LDPE/SiO_x/Pd and oPP/SiO_x/Pd films with Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm.
Mean values ± standard deviation (n=3).
Bars labelled with the same letter within each substrate are not significantly different ($p < 0.05$).

By far the greatest impact of Pd-coating thicknesses on the oxygen scavenging activity was found when applying PET or PLA films. **Figure 8** shows the reduction in oxygen concentration in the measurement cell as an example for PET/SiO_x/Pd films. Apart from 0.3 nm, with films of Pd-deposition thicknesses of 0.4, 0.7, 1.1 and 3.4 nm, the oxygen concentration could be reduced from 2 to 0 % within 28.5, 17.5, 6.5 and 6 minutes, respectively. Thus, this palladium enhancement from 0.4 to 3.4 nm meant that the OSR increased 5.3 times, achieving a maximum OSR of 23,533 $cm^3/(m^2*h)$ for PET/SiO_x/Pd (**Figure 8**). Similar results were obtained using PLA/SiO_x/Pd films where the initial oxygen concentration was reduced within 30, 11, 7 and 6.5 minutes, respectively (data not shown). OSR with 3.4 nm was 6.3 times higher than that of 0.4 nm (**Figure 7**).

Insert here Figure 8

Figure 8: Reduction in oxygen concentration in the measurement cell with PET/SiO_x/Pd films using Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm.
Mean values ± standard deviation (n=3).

Overall, it can be stated that, in the range of 0.3 to 1.1 nm, the higher the Pd-deposition thickness, the higher the oxygen scavenging activity of the applied packaging films with and without SiO_x layer. From 1.1 to 3.4 nm the OSR is considered to be substrate dependent. However, it seems that the optimal Pd-coating thickness for the developed oxygen scavenging films lies between 0.7 and 3.4 nm. A further increase in Pd-coating thickness is not expected to further improve the OSR when considering preliminary findings [28], where the obtained OSR continuously decreased when the coating thickness increased from 10 nm 100 nm with PET as a substrate. This behaviour might be due to the fact that the most favourable position for hydrogen is *on* the palladium surface, not in the bulk [30]. The interaction of atoms and molecules with surfaces is of great relevance and the rate of chemical reactions can be enormously increased by the presence of a catalytic surface [31]. Therefore, it is assumed that between 0.7 and 3.4 nm the maximal atomic surface of palladium is reached. Further surface studies should be conducted to build on these findings.

Conclusion

It has been demonstrated that the oxygen scavenging activity of palladium-based oxygen scavenging films is strongly dependent on the coating substrate as well as on the palladium deposition thickness. Optimisation of these parameters can result in scavenging films where the residual headspace oxygen of packaged foods can be scavenged very quickly. Thus, the resulting scavenger films have the potential to extend shelf life and improve the overall quality of oxygen-sensitive foods.

Acknowledgements

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Table 1: List of substrates used for palladium coating

Designation	Specification
Nature1A	Biodegradable film 80 µm (Nature 1A, FOLIEtec Kunststoffwerk AG, Rossleben, Germany)
Cellophane	Cellophane 25 µm (Transparent Cellulose Film, NatureFlex™ NP, Innovia Films Ltd, Wigton, UK)
Non-woven1	non-woven material 140 µm (1025B, DuPont, Luxembourg)
Non-woven2	non-woven material 180 µm (1073B. DuPont, Luxembourg)
oPP	Oriented polypropylene 20 µm (BSS, Taghleef Industries L.L.C., Dubai, United Arabic Emirates)
Paper	Kraft paper 60 µm (Unbleached MG Kraft Paper, Cartonal Italia, Castelfranco Veneto (VT), Italy)
Paper/Silicone	Silicone-coated paper 47 µm (paper thickness) (Backtrennpapier, paper 40g/m^2, Silicone ca. 0.6 g/m^2 each side, white, Walke AG, Herisau, Switzerland)
LDPE	Low-density polyethylene 50 µm (LDPE, Amcor Flexibles, Gent, Belgium)
PET	Polyethylene terephthalate 12 µm (Hostaphan® RNK, Mitsubishi Polyester Film GmbH, Wiesbaden, Germany)
PET/AlOx	Aluminium oxide coated polyethylene terephthalate 12 µm (CAMCLEAR® 48g, Celplast Metallized Products Limited, Toronto, Ontario, Canada)
PET/Silicone	Silicone coated polyester terephthalate 50 µm, (Silphan S 50M 1R13007 Clear, Siliconature S.P.A., Godega di Sant'Urbano, Italy)
PLA	Polylactic acid 20 µm (Taghleef Industries S.p.A., San Giorgio di Nogaro (UD), Italy)
PP	Polypropylene 50 µm (Amcor Flexibles, Gent, Belgium)

$$H_2 + \tfrac{1}{2}\, O_2 \xrightarrow{\text{Pd}} H_2O$$

Figure 1: Catalytic oxidation of hydrogen with oxygen [25]
86x22mm (300 x 300 DPI)

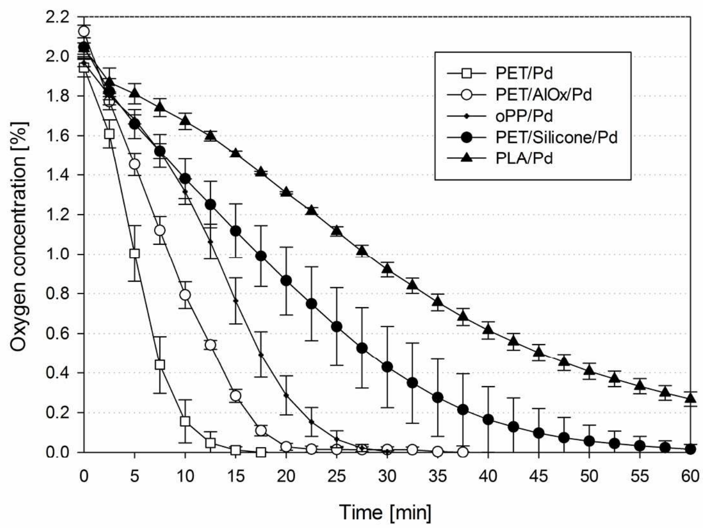


Figure 2: Reduction in oxygen concentration in the measurement cell with PET/Pd, PET/AlOx/Pd, oPP/Pd and PET/Silicone/Pd and PLA/Pd films using a palladium deposition thickness of 1.1 nm.
Mean values ± standard deviation (n=3).
199x159mm (300 x 300 DPI)

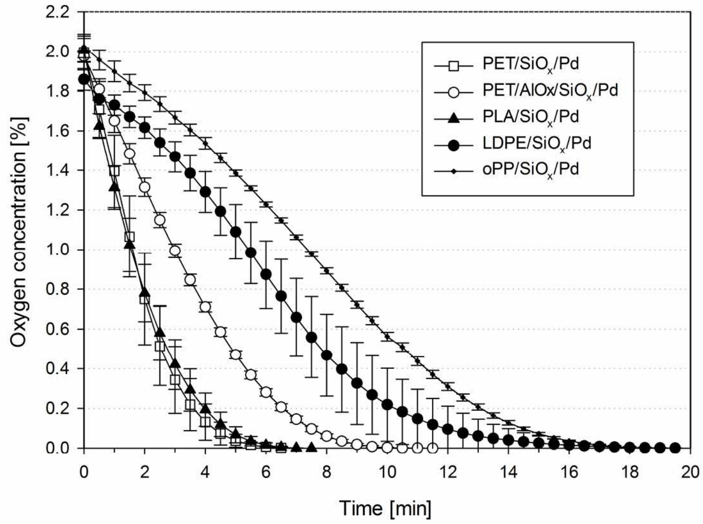


Figure 3: Reduction in oxygen concentration in the measurement cell with PET/SiOx/Pd, PET/AlOx/SiOx/Pd, PLA/SiOx/Pd, LDPE/SiOx/Pd and oPP/SiOx/Pd films using a palladium deposition thickness of 1.1 nm and SiOx pre-coating.
Mean values ± standard deviation (n=3).
199x159mm (300 x 300 DPI)

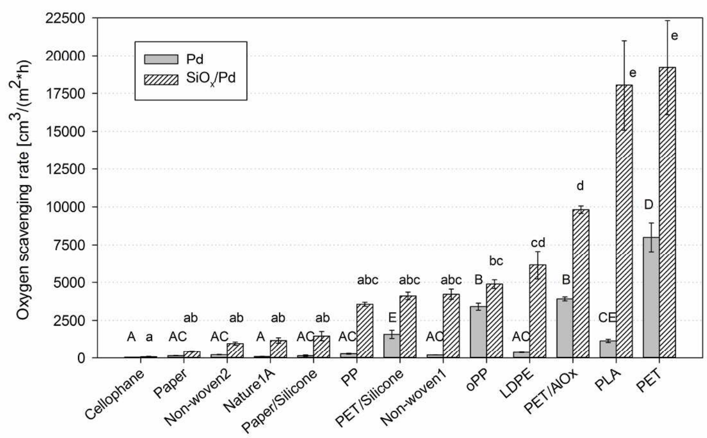


Figure 4: Comparison of oxygen scavenging rates of different materials, listed in Table 1, using a palladium deposition thickness of 1.1 nm.
Mean values ± standard deviation (n=3). OSR of substrates labelled with the same letter (capital = Pd, lower case = SiOx/Pd) are not significantly different ($p < 0.05$).
217x147mm (300 x 300 DPI)

$$O^{ad} + H^{ad} \rightarrow OH^{ad}$$

$$2\,OH^{ad} \rightarrow O^{ad} + H_2O^{ad} \rightarrow O^{ad} + H_2O^{g}$$

Figure 5: Reaction path of hydrogen oxidation in the presence of water [25]. Superscript letters ad and g stand for adsorbed and gaseous respectively.

66x12mm (300 x 300 DPI)

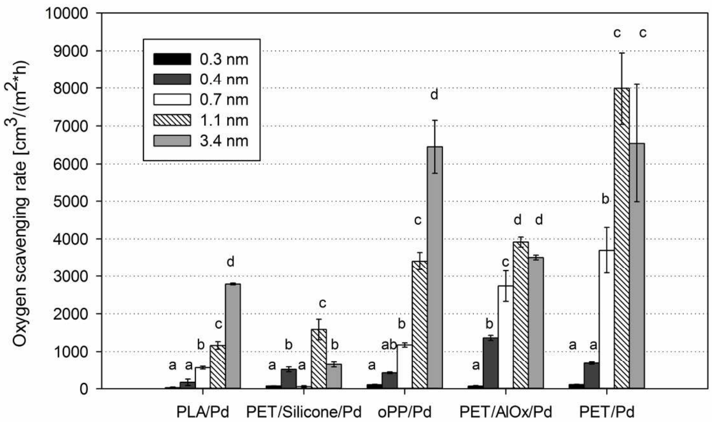


Figure 6: Comparison of oxygen scavenging rates of PET/Pd, PET/AlOx/Pd, oPP/Pd, PET/Silicone/Pd and PLA/Pd films with Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm.
Mean values ± standard deviation (n=3).
Bars labelled with the same letter within each substrate are not significantly different ($p < 0.05$).
192x125mm (300 x 300 DPI)

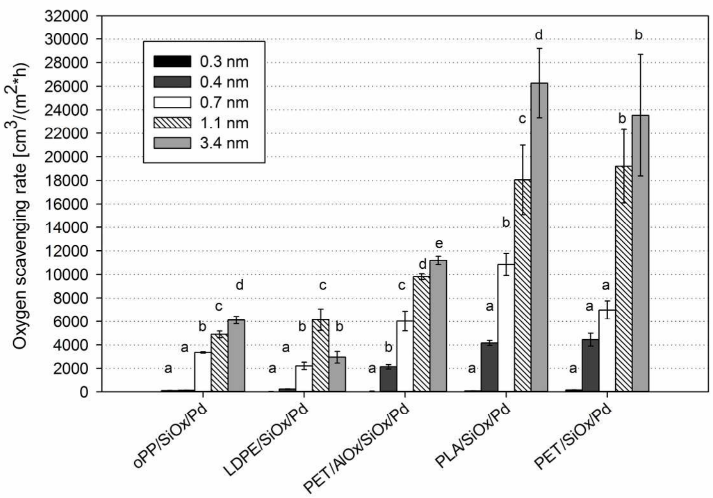


Figure 7: Comparison of oxygen scavenging rates of PET/SiOx/Pd, PLA/SiOx/Pd, PET/AlOx/SiOx/Pd, LDPE/SiOx/Pd and oPP/SiOx/Pd films with Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm. Mean values ± standard deviation (n=3).
Bars labelled with the same letter within each substrate are not significantly different ($p < 0.05$).

225x171mm (300 x 300 DPI)

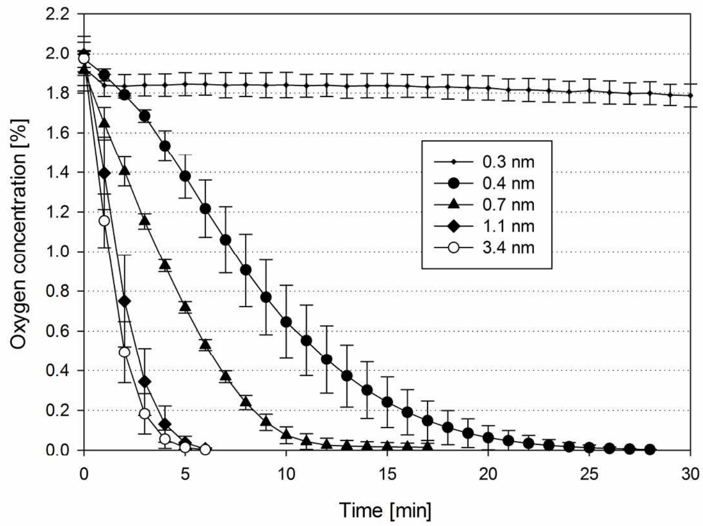
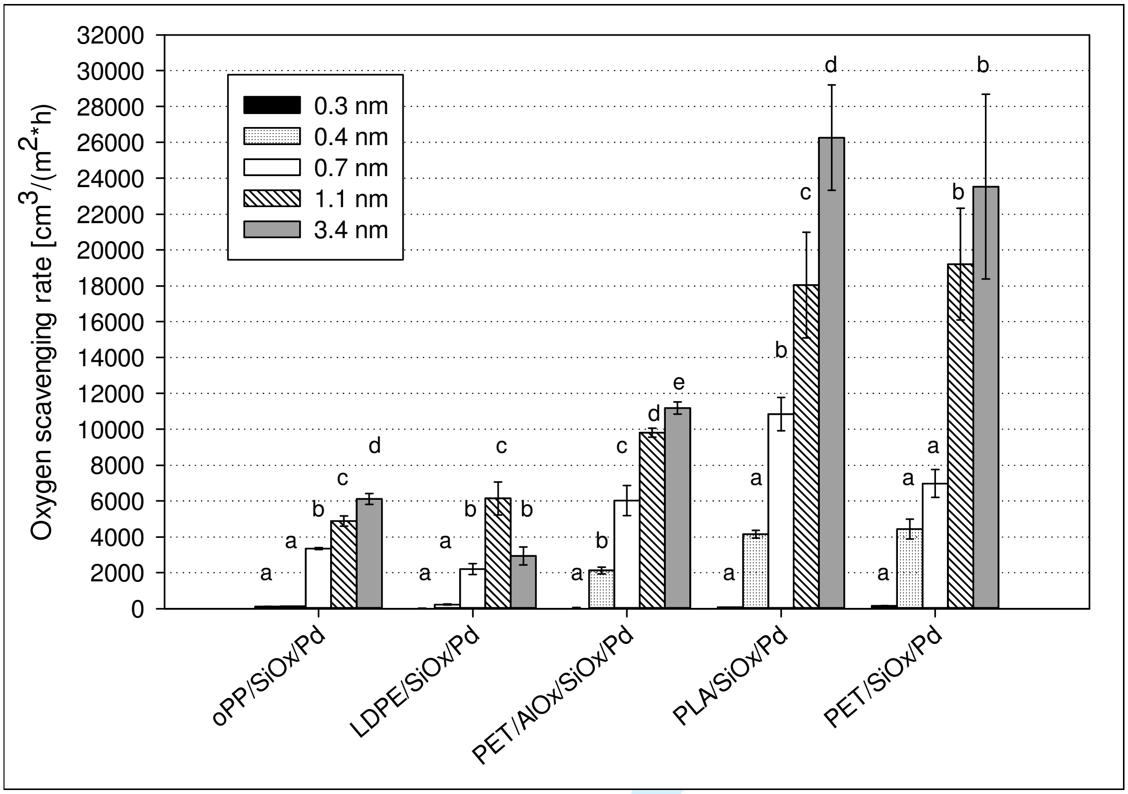


Figure 8: Reduction in oxygen concentration in the measurement cell with PET/SiOx/Pd films using Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm.
Mean values ± standard deviation (n=3).

199x159mm (300 x 300 DPI)

Development of Palladium-based Oxygen Scavenger: Optimisation of Substrate and Palladium Coating

Selçuk Yildirim*, Bettina Röcker, Nadine Rüegg, Wolfgang Lohwasser



Oxygen scavenging films based on a palladium coating were developed to remove residual oxygen remaining in food packages after modified atmosphere packaging. It was demonstrated that the oxygen scavenging activity of those films was strongly dependent on the coating substrate as well as the palladium deposition thickness. The resulting scavenger films have the potential to scavenge residual headspace oxygen of sensitive foods within a matter of minutes leading to shelf life extension and overall quality improvements.

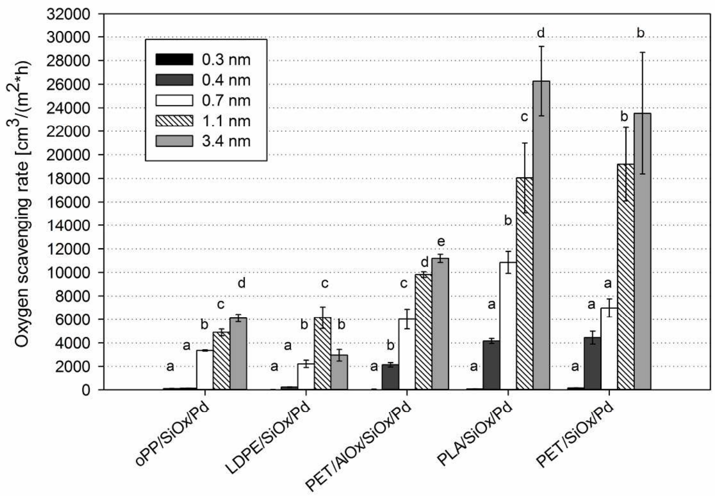


Figure GTOC
225x171mm (300 x 300 DPI)