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Emma Pignères, Sébastien Gaucel, Fanny Coffigniez, Nathalie Gontard, Elaura Baghe, et al.. Deciphering the respective roles of coating weight and number of layers on the mass transfer properties of polyvinyl alcohol coated cardboards. Progress in Organic Coatings, 2024, 195, pp.108627. 10.1016/j.porgcoat.2024.108627 . hal-04678049

HAL Id: hal-04678049
https://hal.inrae.fr/hal-04678049v1

Submitted on 26 Aug 2024

Progress in Organic Coatings 195 (2024) 108627

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Deciphering the respective roles of coating weight and number of layers on the mass transfer properties of polyvinyl alcohol coated cardboards

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ARTICLE INFO

Keywords:
Coated cardboards
Polyvinyl alcohol
Oxygen transmission rate
Water vapor transmission rate
Number of layers

ABSTRACT

Coated cardboards are emerging as alternatives to plastics in the field of food packaging. Cardboard is a cellulose-based porous material, with very poor barriers to gases and water vapor, which are often required for primary packaging materials and food protection. One method to improve its performance is to coat one or more layers of barrier polymer. The choice of the nature of the polymer is key to achieve specific barrier properties, but other parameters are also at stake, such as the properties of the cardboard supports, the polymer coating weight or the number of coating layers. In this study, the respective roles of cardboard support, coating weight and number of layers on the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of fatty acid grafted poly(vinyl alcohol) (PVOH) coated cardboards were investigated. Then, a correlation between these parameters and the obtained transmission rates was attempted. Finally, the experimental values were compared to predicted values, using the series resistance model, which conventionally links the OTR and WVTR of a multilayer material to the OTR and WVTR of each layer. The limitations of using such model with coated cardboards were highlighted, and hypotheses regarding the structure/properties relationship of such materials were formulated based on scanning electron microscope images, allowing the examination of the surface of the coated materials.

1. Introduction

In response to the persistent plastic pollution the planet is facing [1], papers and cardboards appear as emerging eco-friendly alternatives to plastic in the field of food packaging. Cellulose is the most abundant renewable polymer on Earth. Cellulose-based materials are bio-based, 100 % non-competing with food, and biodegradable in the most common environmental conditions prevailing on Earth, thus appearing to be a key solution for solving the resource burden and the long-term fate issues of plastic packaging. However, cellulose based materials do not own all the required functional properties to fully answer the specifications needed for food packaging application. Indeed, cellulose based materials, e.g. in the packaging sector, principally papers, cardboards, and moulded cellulose, are porous materials with poor barriers to oxygen, grease, water vapor and liquid water, properties that are often required to protect food products. Replacing plastic packaging by new alternatives should not compromise the food preservation, as it is the main role of packaging. Switching a current packaging by a less performant alternative could, in some cases, increase the food loss and wastes and thus, the global environmental impact [2–5]. Other cellulosic materials, such as microfibrillated cellulose and nanocellulose can be produced from cellulose and present better barrier properties to grease and oxygen. Another alternative to improve the barrier properties of cellulose-based materials is to apply a thin layer of high barrier polymer on the cellulosic substrate. Solvent based coating technologies, such as blade coating used in the present study, are used in the paper industry due to the possibility to apply low amounts of polymer. This strategy has made possible to give cellulose-based materials barrier properties comparable to those of conventional plastics [6].

Each food category has different needs [7]. For products that are very

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https://doi.org/10.1016/j.porgcoat.2024.108627
Received 2 May 2024; Received in revised form 11 June 2024; Accepted 17 June 2024

sensitive to oxidation or moisture ingress, very high barrier packaging is required, whereas more permeable materials are needed for fresh respiring products. It is therefore crucial for the food packaging sector to be able to predict the appropriate polymer coating layer in terms of composition and thickness in order to achieve a target property value for a specific application. Gas and water vapor permeability of multilayered materials can conventionally be calculated using the series resistance model. In the case of polymer-coated cardboards, the coating weight determines the thickness of the coating layer and thus the mass transfer properties of the entire material. Most authors have observed this expected increase of the material performance with increasing coating weight [8–18]. Other empirical models have even been proposed based on experimental results to predict water vapor transmission rate as a function of coating thickness or weight [15,19,20], confirming a relation between both variables. Although there is a correlation between the transfer rate and the coating thickness or weight, this relationship does not seem to fit the series resistance model when considering a two-layer (cardboard and coating layer) structure, as shown for prediction of water vapor transmission rates of beeswax and paraffin coated on micro fibrillated cellulose, where the experimental values differ from the predicted ones [21]. Indeed, gas and water vapor transmission rates are influenced not only by the coating weight but also by the cardboard support properties, such as roughness, porosity or surface energy [11,22–26]. Some authors proposed modified series resistance models, considering the porosity of the substrate and the penetration of the coating layer into the pores or defects of the dense substrate layer [27] evidencing the more complex case of porous materials. Both degree of penetration and thickness of the coating layer showed an impact on gas transmission rate and separation factor between two gases, highlighting the relevance of including these parameters in the series resistance model. Furthermore, some authors highlighted a minimum coating weight to cover the fibers with a homogeneous layer and therefore reach gas barrier improvement [9,11,17], or a minimum number of layers [28,29]. A recent study showed the huge benefit of applying several coating layers instead of one, highlighting better results with 6 layers of 1 $g.m^{-2}$ of poly(vinyl alcohol) than 2 layers of 3 $g.m^{-2}$ on oxygen transmission rate (OTR) [30]. This was the first study showing the impact of the number of layers on OTR, independently of the coating weight. This effect had also been shown on water vapor transmission rate (WVTR) with dispersion coatings [31,32]. Many other studies which showed the impact of the number of layers on mass transfer properties also increased the total coating weight when going from one to several layers [9,10,12,33]. It was therefore difficult to distinguish the effect of the number of layers from the effect of the coating weight. To the best of our knowledge, very few studies were conducted considering coating weight and number of layers independently, on both OTR and WVTR, nor tried to find a relationship between these parameters and the final mass transfer properties achieved. However, this knowledge and understanting are essential to develop a packaging with the just necessary quantity of polymer, allowing to correctly protect food from its sensitivities and keeping a biodegradable and eco-friendly packaging.

In this paper, poly(vinyl alcohol) (PVOH) coated cardboard structures (twelve structures with different coating weights and numbers of layers) were produced and studied to put in evidence the role of the coating thickness but also of the number of layers and the final structure on the OTR (Oxygen Transmission Rate) and WVTR (Water Vapor Transmision Rate) of the resulting multilayer materials. PVOH is a synthetic polymer obtained by the hydrolysis of polyvinyl acetate and is widely produced worldwide [34]. It was chosen for its good barrier properties to oxygen [35], its ability to be coated in aqueous solution and in very low coating weights on cardboard by using a pilot-scale blade coating technology. Since PVOH is a highly hydrophilic polymer [36,37], fatty acids were grafted by chromatogeny grafting to increase PVOH hydrophobicity [38] and bring liquid water and water vapor barrier performance [19,39] to the coated cardboards. The impacts of the number of layers and coating weight of PVOH on the OTR and WVTR were then discussed and assessed for two different cardboard supports and at laboratory and pilot scales. They were put in relation with the microscopic structure achieved. Then, the OTR and WVTR of these structures were tentatively predicted using the series resistance model and compared with the experimental values.

2. Materials & methods

2.1. Materials

Two cardboard supports were used in this study: the bleached Cupforma Natura and the unbleached CKB Nude grades from Stora Enso (Sweden) with basis weights of 260 and 230 $g.m^{-2}$ and thicknesses of 370 and 445 μm, respectively. Both cardboards are three-layer fiber structures with chemi-thermomechanical pulp in the middle layer. Their porosity was calculated according to these two parameters and the following equation:

$$\varphi = 1 - \frac{bw}{l \times d_{cellulose}} \tag{1}$$

where φ is the cardboard apparent porosity (dimensionless), l is the thickness of the cardboard (cm), bw is the cardboard's basis weight ($g.cm^{-2}$) and $d_{cellulose}$ is the cellulose density (considered equal to 1.5 $g.cm^{-3}$). Based on this equation, Cupforma Natura had a lower porosity (0.53) than CKB Nude (0.66). Cupforma Natura support had also lower surface roughness, as described by their Bendtsen values: 300 $mL.min^{-1}$ for Cupforma Natura vs 400 $mL.min^{-1}$ and 700 $mL.min^{-1}$ for CKB Nude, top and reverse surfaces respectively. The Bendtsen value was measured according to ISO 5636-3 standard, using a pressure of 1.47 kPa. Finally, Cobb values were measured on both supports, at 23 °C and 50 % RH and during 60 s and 600 s. Cobb 60s were 18 $g.m^{-2}$ and 22 $g.m^{-2}$ for Cupforma and CKB Nude respectively. The same value was found on both sides of the cardboard supports. Cobb 600 s were 71 $g.m^{-2}$ (recto) and 73 $g.m^{-2}$ (verso) for Cupforma support and 83 $g.m^{-2}$ (recto) and 82 $g.m^{-2}$ (verso) for CKB Nude.

PVOH used was a commercial brand, Poval 15–99 (Kuraray, Japan), with a 99–99.8 % hydrolysis rate, a molecular weight of 95,000 and 95 % of dry content. On one hand, a fully hydrolyzed (99–99.8 %) grade was selected to better react with chromatogeny grafting. On the other hand, the high molecular weight was chosen for food contact approval and best runnability on the pilot coater.

2.2. Preparation of materials

2.2.1. PVOH solution manufacturing before coating

PVOH is obtained by the hydrolysis of polyvinyl acetate, contrary to most vinyl polymers, which result from the polymerization of the corresponding monomers. Before coating, a PVOH solution was prepared according to the following protocol. PVOH was dissolved in cold water. The temperature was then increased to 90–95 °C, and the solution was heated for 45 min at 90–95 °C. Subsequently, the temperature of the solution was regulated to approximately 50 °C so that various controls could be carried out before the coating step, both at laboratory and pilot scales. The coating process used on the pilot coater requires a PVOH solution with a lower concentration (11%w/w vs. 16%w/w at lab scale), which induces a decrease in the Brookfield viscosity (170 mPa.s vs 290 mPa.s at lab scale, measured at 100 rpm) to obtain good coverage of the fibers.

2.2.2. Pilot scale coated cardboards

The coating trials were performed by the Centre Technique du Papier (Grenoble, France). Each cardboard was coated with an 11 % w/w PVOH aqueous solution at pilot scale using a soft-tip blade coating technique, with a speed of 50 $m.min^{-1}$. Regarding CKB Nude, coating was applied on the smoother surface (Bendsten value of 400 mL.min^{-1}). Soft-tip blade coating technique generates a "level coating", meaning that the surface of the coated substrate is smooth and even, but the coating weight might not be the same everywhere, depending on the roughness of the uncoated substrate. After coating, the coated cardboard reel was dried using electrical infra-red dryer (power around 20KWh) (Solaronics, France), 1 single air dryer (130 °C) and 1 double air dryer (150 °C) (BMB Packaging, Italy). Several coating weights and numbers of layers were applied as summarized in Table 1. The codification used presents the type of cardboard, the total coating weight and the number of layers: CN_8_2L is for CKB Nude, coated with 8 g.m^{-2} of PVOH, applied in 2 layers. Our objective was to reach less than 5 % of non-cellulosic component, corresponding to 14 g.m^{-2} of PVOH for Cupforma support and 12 g.m^{-2} for CKB Nude support. This limit was chosen by the authors to be as close as possible to a 100 % cellulosic packaging. A maximum of 11 g.m^{-2} was coated. All the coated cardboards were approved for home-compost and industrial compost according to EN ISO 14855-1-2013 and EN 13432 standards respectively.

2.2.3. *Lab scale coated cardboards*

Two references were also produced at laboratory scale by volumetric rod coating, using an Elcometer 4340 Automatic Film applicator coater (Elcometer, UK) and a speed of 7 m.min^{-1}. These trials were performed at the CTP. CKB Nude cardboard support and a 16 % *w*/w PVOH solution were used. After coating, samples were dried during 15 min in a drying oven (80 °C) and 5 min on a half-moon dryer (60 °C) to obtain a coated cardboard with a plan surface.

2.2.4. *Gas-phase esterification of cardboards*

Laboratory and pilot scale coated cardboards were submitted to gas-phase esterification on both sides, using palmitoyl chloride (C16) as reagent. This treatement, commonly called chromatogeny, is patented by the Centre Technique du Papier to bring hydrophobicity [19,38]. First, the cardboard reel was preaheated with infra-red at 60 °C. Then, between 0.3 and 0.5 g.m^{-2} of palmitoyl chloride reagent was applied via an anilox roll on the surface of the cardboard. Both the reagent feeding tank and anilox roll were at 60 °C, as the cardboard. The machine speed was 70 m.min^{-1}. The reagent and the cardboard were then exposed on a heated cylinder to a controlled temperature of 190 °C for 2 to 3 s. Finally, the by-products (HCl and free fatty acids) or unreacted fatty acid chlorides were washed by flushing with air at 310 °C at a speed of 50 m.min^{-1}.

Only two references (CF_8_2L_WG and CN_8_2L_WG, Table 1) were also produced without grafting in order to assess the role of the chemical grafting on the water vapor barrier properties of the samples.

2.2.5. *Self-supported PVOH films*

PVOH (16.5 g) was dissolved in 150 mL cold distilled water. The solution was stirred continuously using a magnetic stirrer and heated at 90–95 °C for 45 min. After 45 min, stirring was stopped, and the aqueous solution was maintained at 45–50 °C on a heating plate until it was used. Then, the PVOH solution was poured into Petri dishes to get 1.5 L.m^{-2} films and evaporated first at 80 °C for 15 min and then at 60 °C for 5 min in an oven (same drying conditions as for the cardboard coated at the lab scale). The films were let for 24 h under ambient conditions in the Petri dishes, removed from the dishes and stored at 50 % RH and ambient temperature for at least two weeks before characterization.

2.3. *Characterization of materials*

2.3.1. *Thickness*

The thickness of uncoated and coated cardboards was measured at five points equally distributed on the sample using a hand-held micrometre with a resolution of 1 μm (Digimatic micrometre 0–25 mm, Mitutoyo Corporation, Kawasaki, Japan). For self-supported PVOH films, the thickness was measured at ten points. In the case of Oxygen Transmission Rate (OTR) measurements, the thickness was measured after the analysis. In the case of Water Vapor Transmission Rate (WVTR) measurements, the thickness was measured both before and after the measurement. Before the WVTR measurement, the thicknesses were measured outside the testing surface to avoid damaging the samples.

2.3.2. *Oxygen transmission rate*

As recommended by Pignères, Vercasson et al., (2024), coated cardboards samples were sandwiched between two adhesive aluminium foils (item number 105–259, Ametek SAS, France), defining a disk-shaped surface with a diameter of 4 cm and an area of 1.26 × 10^{-3} m^2 [40]. Besides, epoxy resin (Devcon® 5 Minute®, reference 14270, ITW Performance Polymer) was added to the edges of the samples, between the two aluminium foils, to further decrease the risk of O_2 leakage. For uncoated cardboard samples, which were much more permeable than the coated samples, the surface was reduced to 4.5 × 10^{-4} m^2, with a sample diameter of 2.4 cm, in order to limit the O_2 flow rate and have enough measurement points for the analysis. No aluminium foil was used for PVOH films, as it is not a porous asymmetric material and therefore no edge effects can occur. OTR was then measured using a commercial equipment, comprising a measuring cell divided into two chambers (PreSens GmbH, Germany), a temperature probe (Pt100, PreSens GmbH, Germany), an integrated O_2 sensor (PSt6, PreSens GmbH, Germany), a Polymer optical Fiber for Use with Minisnesors (PreSens GmbH, Germany) and a Fibox Trace 4 (PreSens GmbH, PreSens), as described elsewhere [40]. The sample was placed in between the two chambers of the measurement cell: for coated and uncoated cardboards, a perfluoropolyether oil-based grease, which can safely be used in oxygen-rich environments (Krytox™ GPL 205, The Chemours Company), was used between the sample and the metal part, on the side opposite the seal, to increase tightness. Before starting the measurement, a 50 % RH N_2 flush was done for 10 min in both upper and bottom chambers, to remove all O_2. Then, the upper chamber was closed, and a 50 % RH O_2 flux was passed into the bottom chamber, with a flow rate of 35 nmL.min^{-1}. The measurement was performed at 23 °C and 50 % RH. It was stopped when the O_2 concentration reached 2 % in the upper chamber, except for the most barrier materials which were stopped before, to shorten the measurement time. All samples were prepared in triplicates and conditioned at 50 % RH for 48 h prior to OTR characterization. For the most barrier coated cardboard samples, which were more variable, up to five replicates were done. Three replicates were done for self-supported PVOH films. For all the measurements, the coated side faced the O_2 sensor. The O_2 permeability, noted P (in mol.m.m^{-2}.s^{-1}.Pa^{-1}), was determined by fitting the Fick's first law (Eq. (2)) to experimental data:

$$\frac{dn}{dt} = P \times \frac{A}{l} \times \left(p_{low} - p_{up}\right) \tag{2}$$

where n is the O_2 quantity in the upper cell (mol), A the surface area of the sample (m^2), l the thickness of the sample, including the cardboard and coating thicknesses (m), p_{low} and p_{up} the O_2 partial pressures in the lower and upper cells respectively (Pa).

For coated cardboards, OTR (cm^3.m^{-2}.day^{-1}) parameter is more convenient to use and was calculated, considering an O_2 partial pressure gradient ΔP of 101,325 Pa (= 1 atm) via the following equation (Eq. (3)):

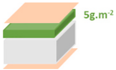
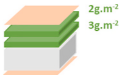
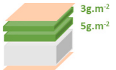
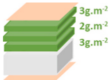
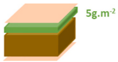
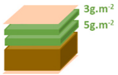
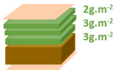
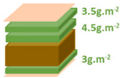
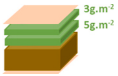
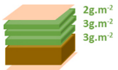
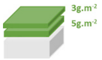
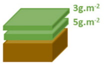
$$OTR = \frac{P \times 3600 \times 24 \times \Delta P \times V_m}{l} \tag{3}$$

where V_m is the molar volume of O_2 (cm^3.mol^{-1}) at 23 °C.

The first values of the measurements were removed, to ensure that steady-state regime was reached and that the O_2 in the lower cell had reached 100 %, and thus, an O_2 partial pressure of 1 atm between both chambers.

Table 1

Summary of tested samples, with the type of support, PVOH weight, theoretical thickness and number of layers, coating process scale, and their OTR and WVTR results.

Reference	Scheme	Coating process scale	Total PVOH weight (g.m^{-2})	PVOH coating thickness[a] (µm) 🟩	Fatty acid chloride grafting 🟧	OTR[b] (cm^3.m^{-2}.day^{-1})	WVTR[c] (g.m^{-2}.day^{-1})
Cupforma (CF)		No coating	0	0	No	1.5 × 10^7 ± *0.06 × 10^7*	387.4 ± *18.1*
CF_5_1L		Pilot	5 ± 0.39	3.8 ± *0.3*	Yes	2.0 × 10^6 ± *0.2 × 10^6*	106.3 ± *15.7*
CF_5_2L		Pilot	5 ± 0.57	3.8 ± *0.5*	Yes	5.1 × 10^4 ± *0.9 × 10^4*	7.8 ± *0.7*
CF_8_2L		Pilot	8 ± 0.68	6.1 ± *0.6*	Yes	8.1 × 10^3 ± *1.2 × 10^3*	4.4 ± *0.7*
CF_8_3L		Pilot	8 ± 0.61	6.1 ± *0.5*	Yes	7.2 × 10^3 ± *4.6 × 10^3*	3.5 ± *0.7*
CKB Nude (CN)		No coating	0	0	No	1.2 × 10^7 ± *0.03 × 10^7*	344.4 ± 7.5
CN_5_1L		Pilot	5 ± 0.34	3.8 ± *0.3*	Yes	7.6 × 10^5 ± *0.4 × 10^5*	31.7 ± *4.3*
CN_8_2L		Pilot	8 ± 0.53	6.1 ± *0.5*	Yes	2.9 × 10^4 ± *0.4 × 10^4*	5.4 ± *1.0*
CN_8_3L		Pilot	8 ± 0.59	6.1 ± *0.5*	Yes	7.5 × 10^1 ± *6.4 × 10^1*	4.0 ± *0.9*
CN_11_2 + 1 L		Pilot	11 ± 0.62	8.4 ± *0.5*	Yes	3.1 × 10^4 ± *1.2 × 10^4*	10.7 ± *4.5*
CN_8_2L_lab		Laboratory	8 ± 0.27	6.1 ± *0.3*	Yes	2.9 × 10^3 ± *5.6 × 10^3*	6.1 ± *1.0*
CN_8_3L_lab		Laboratory	8 ± 0.35	6.1 ± *0.3*	Yes	8.2 × 10^1 ± *14.3 × 10^1*	5.6 ± *2.5*
PVOH		No coating	NA	105 ± 26 (OTR) 88 ± 9 (WVTR)	No	3.4× 10^0 ± *1.8× 10^0*	5.2 ± 0.7
*PVOH_5		No coating	NA	3.8	No	1.0 × 10^2 ± *0.7 × 10^2*[d]	118.8 ± 15.9[d]
*PVOH_8		No coating	NA	6.1	No	6.2× 10^1 ± *3.9 × 10^1*[d]	74.2 ± 10.0[d]
CF_8_2L_WG		Pilot	8 ± 0.46	6.1 ± *0.4*	No	Not measured	3.1 ± *1.1*
CN_8_2L_WG		Pilot	8 ± 0.50	6.1 ± *0.4*	No	Not measured	4.5 ± *1.2*

*OTR and WVTR of theoretical 5 g.m^{-2} and 8 g.m^{-2} PVOH films were calculated from O_2 and water vapor permeability respectively measured on respectively 105 ± 26 µm and 88 ± 9 µm thick PVOH films. These values were calculated for easier comparison with the OTR and WVTR values measured on coated cardboards with equivalent PVOH coating weights.

[a] A density of 1.31 ± 0.01 g.m^{-2}, experimentally measured in this study, was taken for calculating the theoretical PVOH coating layer thickness.

[b] 23 °C – 50 % RH.

[c] 23 °C – 0–50%RH.

[d] Standard deviations were calculated based on the standard deviation of the O_2 and water vapor permeability of PVOH films, as well as standard deviation of the PVOH density.

2.3.3. Water vapor transmission rate

Water vapor transmission rate (WVTR) of each material was determined gravimetrically. As for Oxygen Transmission Rate measurements, all samples except PVOH films were sandwiched between two adhesive aluminium foils (reference 427.140, 3 M, USA). Samples were hermetically sealed in glass permeation cells (with Teflon seals), defining an exposed disk-shaped surface with a diameter of 3.4 cm and an area of 9.08×10^{-4} m^2.

Cells were filled with silica gel (RH = 0 %, assuming that RH on the silica gel side was negligible). Permeability cells were placed in a humidity and temperature-controlled incubator (HPP260, Memmert, Germany) regulated at 23 °C and 50 % RH. For coated cardboards, PVOH faced the 50 % RH side. Cells were weighted 2 times per day for 5 days using a 4-digit balance (QUINTIX224-1S, Satorius Lab Instruments GmbH & Co) to measure the mass uptake as a function of time.

WVTR ($g.m^{-2}.day^{-1}$) was calculated using the following equation (Eq. (4)):

$$WVTR = \frac{w}{A} \tag{4}$$

where w is the slope of the mass uptake vs. time ($g.day^{-1}$) and A is the exposed sample area (m^2).

Water vapor permeability for the self-supported films, noted WVP (in $mol.m.m^{-2}.s^{-1}.Pa^{-1}$), was calculated as follows (Eq. (5)):

$$WVP = \frac{WVTR \times l}{3600 \times 24 \times M_{H_2O} \times \frac{\Delta HR}{100} \times P_{vap,sat}} \tag{5}$$

where l is the thickness of the sample, M_{H_2O} is the water molar mass ($g.mol^{-1}$), ΔHR is the relative humidity difference on either side of the sample (%) and $P_{vap,sat}$ is the saturating vapor pressure at the measurement temperature (Pa).

WVTR measurements were done in 5 replicates for each material. A blank cell, without any silica gel was also performed, to ensure that the samples reached the steady-state regime.

2.3.4. Scanning electron microscopy and image analysis

Samples were observed using a Scanning Electron Microscope (SEM), equipped with backscattered electron dectector. Before observation, all the samples were metallized using a Mini Sputter Coater (SC7620, Quorum, UK), at 6×10^{-2} mbar and 20 mA for 45 s. Samples were observed using a 10 kV electrons beam (Phenom ProX, ThermoFischer, Denmark). SEM images (TIFF format) were then uploaded on Fiji software ImageJ-win64 [41]. Images were converted into 8-bit, to get greyscale images. Then, they were adjusted using threshold function to get black and white images: only black pixels (value of 0 on the 0–255 scale) were selected. Finally, the analysis function of the software was used to determine the surface of the black pixels, assimilated as defects of the materials, compared to the sample's surface. Only the surfaces greater than 10 μm^2 were considered for counting, to remove the isolated pixels which would not be representative of the defects.

2.3.5. Bulk density of PVOH

The PVOH film density ρ (in $g.m^{-3}$) was measured using a gas pycnometer (AccuPyc II 1345, Micromeritics) using nitrogen. PVOH films were cut into small pieces and placed in a 1 cm^3 cell. The mass of the PVOH sample was measured beforehand with a 4-digit balance (QUINTIX224-1S, Satorius Lab Instruments GmbH & Co). The measurement was performed in triplicates. Ten cycles were repeated on each replicate.

2.3.6. Theoretical coating thicknesses

The theoretical thickness of the PVOH coated layer applied on cardboard supports, l_{th} (in m), is the thickness of an equivalent self-supported PVOH layer. It was calculated using the coating weight w (in $g.m^{-2}$) and the bulk density of PVOH ρ (in $g.m^{-3}$) measured previously, via the following equation (Eq. (6)):

$$l_{th} = \frac{w}{\rho} \tag{6}$$

The theoretical coating thicknesses calculated for the total coating weights are reported for each reference in Table 1. Their standard deviation was also calculated, using the standard deviations of the coating weights and bulk density.

3. Results & discussion

3.1. Experimental mass transfer properties of PVOH coated cardboards

All OTR replicates were represented on Fig. 1, to show the heterogeneity of the results. Despite the reduced test surface area, oxygen permeation kinetics for uncoated cardboards were very fast: values reported for uncoated cardboards in Fig. 1 a) and b) were calculated based on four to six measurement points over less than 1 min of test. Considering the short duration of the experiment, the O_2 concentration in the bottom chamber may not have had time to reach 100 %, and thus, the O_2 partial pressure difference between the upper and the bottom chambers was probably below 1 atm, suggesting that the OTR values calculated for the uncoated cardboards were underestimated. They were thus considered as minimal values only.

Less variability was observed for WVTR and therefore only means with standard deviations were represented. Regarding some of the most barrier samples (CN_8_2L, CN_8_3L, CN_8_2L_lab, CN_8_3L_lab, CF_8_2L_WG and CN_8_2L_WG), the blank samples had mass variations close to the mass variations of the samples themselves, underlying the limits of the method used for high barrier materials.

3.1.1. Impact of the PVOH coating

All the coated samples had significantly lower OTR and WVTR than the uncoated cardboards. This was expected due to the good barrier properties of PVOH compared to the raw cardboards: minimum values for OTR were $1.5 \times 10^7 \pm 0.06 \times 10^7$ $cm^3.m^{-2}.day^{-1}$ and $1.2 \times 10^7 \pm 0.03 \times 10^7$ $cm^3.m^{-2}.day^{-1}$ for Cupforma and CKB Nude respectively, and WVTR values were 387.4 ± 18.1 and 344.4 ± 7.5 $g.m^{-2}.day^{-1}$ respectively, as similarly presented in the literature [17,22,29,42]. Regarding PVOH films, an O_2 permeability of $1.8 \times 10^{-18} \pm 1.1 \times 10^{-18}$ $mol.m.m^{-2}.s^{-1}.Pa^{-1}$ and a water vapor permeability of $1.9 \times 10^{-13} \pm 0.3 \times 10^{-13}$ $mol.m.m^{-2}.s^{-1}.Pa^{-1}$ were measured. For PVOH with similar degree of hydrolysis, the literature provided the following values: 8×10^{-19} $mol.m.m^{-2}.s^{-1}.Pa^{-1}$ for O_2 permeability (50% RH and 35°C) [37], and 6.9×10^{-15} $mol.m.m^{-2}.s^{-1}.Pa^{-1}$ [43] and 4.5×10^{-11} $mol.m.m^{-2}.s^{-1}.Pa^{-1}$ [44] for water vapor permeability. Though similar values were found for O_2 permeability, more differences were observed with water vapor permeability: this can be attributed to differences in PVOH properties, such as molecular weight or crystallinity, which is affected by drying conditions for instance, and differences in the relative humidity gradients that were used (50–100 % RH vs 0–50 % RH).

Based on the measured PVOH density, which was 1.31 ± 0.01 $g.cm^{-3}$, and on the PVOH coating weight applied to the cardboard supports, the theoretical thicknesses of the equivalent self-supported PVOH layers were calculated. Knowing the PVOH permeability and theoretical thicknesses of the PVOH layers, OTR and WVTR values for theoretical, i.e. assimilated as self-supported ones, PVOH layers of 5 $g.m^{-2}$ and 8 $g.m^{-2}$, corresponding to thicknesses of 3.8 and 6.1 μm, were calculated from (Eq. (3)) and (Eq. (5)) respectively (Table 1 and Fig. 1) and compared to those of the uncoated cardboards. OTR values of 99.9 ±

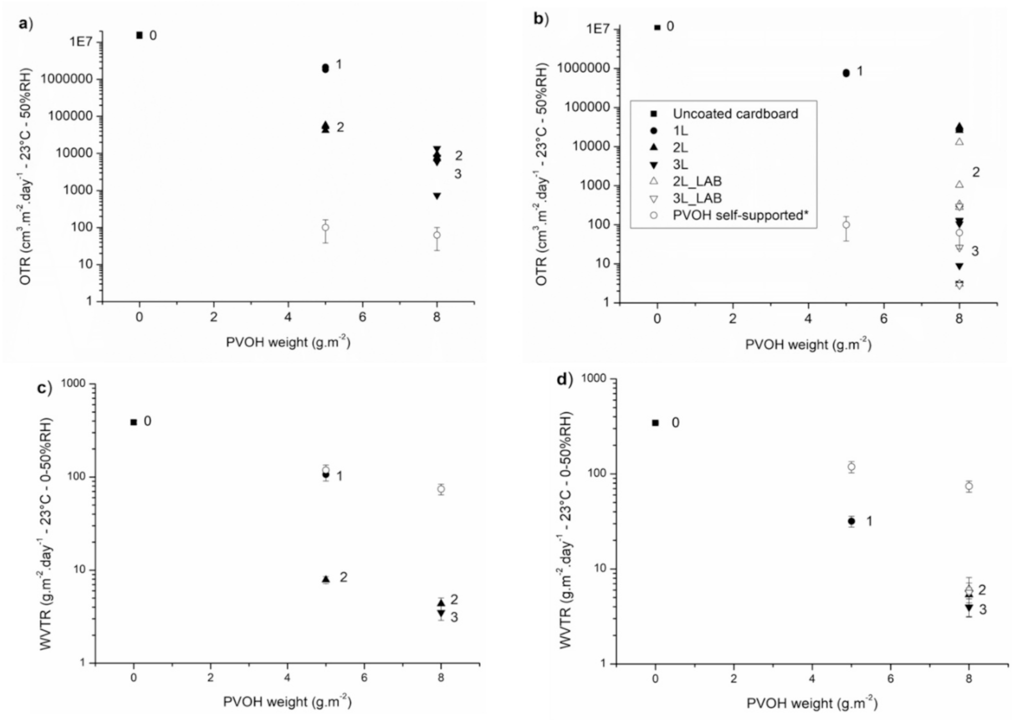


Fig. 1. Oxygen transmission rates and Water Vapor transmission rates obtained on uncoated and grafted PVOH coated (a) and (c) Cupforma and (b) and (d) CKB Nude cardboards, produced at pilot and laboratory scales, and (*) theoretical values calculated for PVOH self-supported films with equivalent weights (doi: 10.57745/MQXHG9).

61.4 cm^3.m^{-2}.day^{-1} and 62.4 ± 38.4 cm^3.m^{-2}.day^{-1} were found for 5 g.m^{-2} and 8 g.m^{-2} PVOH layers respectively, which were more than 10^5 times lower than the minimal OTR values measured for uncoated cardboards (Table 1). Regarding WVTR, 118.8 ± 15.9 g.m^{-2}.day^{-1} and 74.2 ± 10.0 g.m^{-2}.day^{-1} values were found for 5 g.m^{-2} and 8 g.m^{-2} PVOH layers, between 3 and 5 times lower than for uncoated cardboards (Table 1). As expected, increasing PVOH coating weight led to increased PVOH theoretical thickness and thus lowered calculated OTR and WVTR for the corresponding PVOH self-supported layers.

These values could be considered as a good approximation of the minimal expected OTR and WVTR for coated cardboards with similar coating weights, apart from a potential effect of the grafting. Regarding OTR, experimental values were higher than these approximations for low coating weight. For higher coating weights, they became closer, even lower for some replicates. Concerning WVTR, experimental values were lower than their PVOH self-supported counterparts.

3.1.2. *Impact of the coating weight*

As for the theoretical values calculated for PVOH self-supported layers, an increase of the coating weight applied to cardboards always led to a decrease of the transmission rate values, for both oxygen and water vapor, and whatever the cardboard (Fig. 1). It is worth remembering that the current work focused on low coating weights, in order to minimize the amount of synthetic materials.

OTR values of materials produced at pilot scale with a total coating weight of 8 g.m^{-2}, deposited in two or three layers (CF_8_2L, CN_8_2L, CF_8_3L and CN_8_3L) were compared to the value previously obtained by Guezennec (2012) for 8.7 g.m^{-2} of PVOH coated on a 219 g.m^{-2} kraftboard, in two layers. The OTR value in the literature was 2500 cm^3.m^{-2}.day^{-1} at 23 °C and 0 % RH, which was between CN_8_2L and CF_8_2L, CN_3L and CF_8_3L values (Fig. 1), underlying the coherence of our results. On the other hand, OTR values below 1 cm^3.m^{-2}.day^{-1}.atm^{-1} were found for grafted PVOH coated cellulose films with a coating layer of around 5 μm [19], i.e. between 3 and 30,000 times lower than the OTR found in the present work for pilot scale materials with a coating weight of 8 g.m^{-2}, i.e. 6.1 μm theoretical coating thickness (Table 1). This gap could be due to differences in substrate's roughness, porosity and surface energy, as well as process conditions such as drying of the coating, coating speed or pressure applied, highlighting the importance of all these parameters on the final barrier properties, even when comparing the same polymer and same coating weight or thickness.

WVTR values for both Cupforma and CKB Nude samples with 8 g.m^{-2} of PVOH applied in two layers could also be compared to literature values. 8 g.m^{-2} coated samples reached 4.4 ± 0.7 g.m^{-2}.day^{-1} for Cupforma support and 5.4 ± 1.0 g.m^{-2}.day^{-1} for CKB Nude, which were slightly higher than what was found in the literature for PVOH coated cardboard with 7.7 g.m^{-2} of PVOH coated in two layers on paper, for which a WVTR of 2.5 g.m^{-2}.day^{-1} was obtained [45]. A WVTR of 2.5 g.m^{-2}.day^{-1} was also found for the 8.7 g.m^{-2} PVOH coated cardboard previously mentioned and studied by Guezennec (2012) [43]. However, this remains the same order of magnitude as our results, showing their consistency.

3.1.3. *Impact of the number of layers*

More than the coating weight, the number of layers has a paramount impact. Two layers of 3 g.m^{-2} and 2 g.m^{-2} successively applied on Cupforma cardboard, allowing a same total coating weight of 5 g.m^{-2} than previous one-layer-coated samples, divided by more than 300 times the OTR of the overall material compared to the uncoated cardboard vs 7.6 times for one-layer coating, and by 49.3 times its WVTR vs 3.6 times for its one-layer counterpart (Fig. 1): preserving the total coating weight, two thinner layers give better results than one thicker one. The impact of the number of layers was also recently observed by Christophliemk et al. (2023) on OTR: samples with two thick layers of 3.7 and 3.0 g.m^{-2} of PVOH had much higher oxygen transmission rates than samples with six layers of 1 g.m^{-2}, showing the greater efficiency of applying multiple thin PVOH layers instead of few thick ones [30]. Applying six thin layers of dispersion coating, containing a binder, clay, talc and colourant on a cardboard, using flexographic printing process, also showed better

WVTR performance than applying the same coating in one layer using classic rod coaters: the first samples were free of cracks, as contrary to the last ones, due to better flexibility of thin layers [32]. The better performance of a 3-layer and 2-layer coating instead of a 1-layer coating was also shown in the literature for WVTR, even though increasing the number of layers resulted in increased coating weight [10,33], making number of layers and coating weight interdependent parameters. The results in the present study clearly confirmed the positive impact of increasing the number of layers on both OTR and WVTR, without increasing the total coating weight, which is interesting from environmental and economical points of view.

At 8 g.m^2, the effect of the number of layers was not as important as at 5 g.m^{-2}. Increasing the number of layers from two to three enabled to reach lower OTR values for CKB Nude samples and for some of Cupforma replicates, however, there was more heterogeneity in the obtained values and no significant impact was shown on the resulting WVTR, staying close to 4 g.m^{-2}.day^{-1}. This plateau was also observed by Shen et al. (2019): increasing the total weight and number of layers of PVOH/alkyl ketene dimer coating did not allow to go lower than 2 g.m^{-2}.day^{-1} [45]. This plateau was not observed on OTR but might appear at higher grammages.

3.1.4. *Impact of the position of the layers*

The impact of the number of layers and coating weight was evidenced both on OTR and WVTR. So far, all the layers were on the same cardboard's side. Therefore, the coating of an additional layer on the opposite side to the already coated side was assessed. CN_8_2L and CN_11_2 + 1 L had both 8 g.m^{-2} on one side, and CN_11_2 + 1 L had an extra 3 g.m^{-2} layer on the other side. As shown in Table 1 no improvement was observed regarding oxygen and water vapor barrier properties. Moreover, it is worth noting that it resulted in more variability.

One hypothesis could be that 3 g.m^{-2} is below the sufficient minimum coating weight, i.e. coating weight allowing to cover all the cellulosic fibers, required to get barrier properties, as already observed in the literature: Schmid et al., (2014) indicated that PVOH thickness must be sufficient to "exceed" the cardboard roughness [19], and Stinga (2008) found a minimal coating weight varying according to the PVOH reference also, from 3 or 6 g.m^{-2} for Mowiol 28–99 to 10 g.m^{-2} for Mowiol 4–88 and Mowiol 4–98: the less hydrolyzed the PVOH, the higher the minimal coating weight [46]. When using "level" coating technologies, as used in the present study, the higher the roughness, the higher the heterogeneity in coating weight across the cardboard surface. Therefore, it can be assumed that the minimal coating weight required to cover the fibers may increase with the cardboard support roughness.

Thus, adding a thin layer of PVOH on the other side can be interesting from a packaging application perspective, to get a packaging that seals itself with polymer on both sides, without changing the barrier properties: a layer of PVOH can be heat-sealed to another layer of PVOH, which is not the case between a layer of PVOH and a layer of cardboard alone.

3.1.5. *Impact of the cardboard support*

The impact of the cardboard support was also studied and highlighted using the Barrier Improvement Factor (BIF) [28,47], as shown in Fig. 2. BIF is a dimensionless value, calculated as follows (Eq. (7)):

$$BIF = \frac{WVTR\ (uncoated\ cardboard)}{WVTR\ (coated\ cardboard)} \tag{7}$$

where *WVTR* (*uncoated cardboard*) is the water vapor transmission rate of the uncoated cardboard (in g.m^{-2}.day^{-1}) and *WVTR* (*coated cardboard*) is the water vapor transmission rate of the coated cardboard (in g.m^{-2}.day^{-1}).

The BIF values were only calculated for WVTR. Since no exact OTR values could be measured for uncoated cardboards, the comparison between both cardboards would have not been relevant.

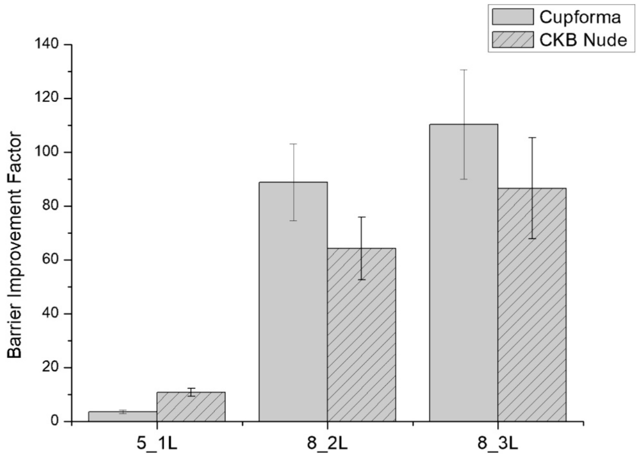


Fig. 2. Barrier Improvement Factor for WVTR, comparing two cardboard supports: Cupforma and CKB Nude.

When applying one layer of 5 g.m^{-2}, the reference with CKB Nude cardboard achieved much better performance than the reference with Cupforma: 31.7 ± 4.3 g.m^{-2}.day^{-1} versus 106.3 ± 15.7 g.m^{-2}.day^{-1}. When applying higher PVOH weight in more than one layer, the difference between the two cardboard supports tended to be reversed but was not significant anymore. This last observation suggested that from two layers and more upwards, the cardboard support does not play a role anymore, which seems logical since the second layer is applied on a PVOH layer, erasing the differences between the cardboards. However, the cardboard support does have an impact for the first coated layer.

According to the suppliers' technical sheets, CKB Nude cardboard has a higher surface Bendtsen value than Cupforma, i.e. a higher surface roughness. Higher roughness implies higher coating penetration [22] and higher volume needed to reach a full coverage of the cardboard support [48]. Thus, in the present work, it seems that higher coating penetration led to better barrier properties.

3.2. *SEM observations of the coated surface to explain the effect of the coating weight and of the number of layers*

To explain the results obtained in the previous section, samples were analysed using SEM technique. The images showed that the deposition of 5 g.m^{-2} of PVOH in one layer was not sufficient to cover all the fibers: CF_5_1L and CN_5_1L did not have a full and homogeneous PVOH coating and fibers were still visible (Fig. 3). This explains the relatively low decrease in OTR of these samples as compared to the ones with two or three layers, and the absence of improvement observed when adding one layer of 3 g.m^{-2}. On the contrary, applying 5 g.m^{-2} in two successive layers (CF_5_2L) led to full coverage of the cardboard's fibers, which explains the better barrier properties of this sample compared to the one with only one layer. It confirms the concept already presumed: the minimum coating weight to cover the cardboard support can be decreased by applying it in several layers.

These observations are coherent with what Gällstedt et al. (2005) observed on chitosan and wheat gluten coated paperboards: low coating weight did not yield a fully continuous coating and therefore did not enhance the barrier properties of the material [49]. Shen et al. (2021) observed single and double polyvinyl alcohol/alkyl ketene dimer/nanoclays coatings of 6.5 and 12 g.m^{-2} respectively at SEM and concluded that two layers were necessary to reach a complete coverage of fibers, suggesting a minimum number of layers as well [29]. What remains unclear in that study is if 6.5 g.m^{-2} applied in two layers would have been sufficient, since coating weight increased with the number of layers. Finally, three layers were found to be necessary to obtain a full

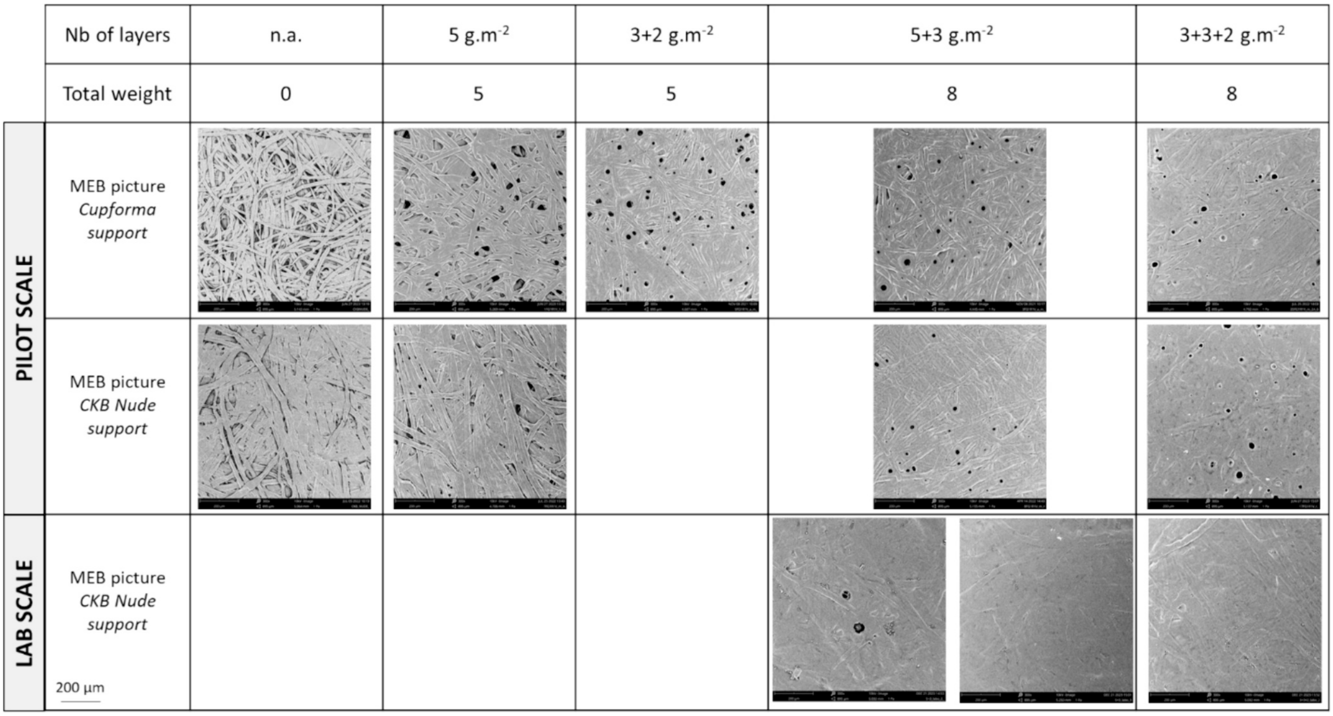


Fig. 3. Coated cardboard's surface observed with scanning electron microscope – 10 kV (doi: 10.57745/MQXHG9).

coverage of fibers in another study [32], showing the variability of the minimum number of layers and coating weight, depending on the cardboard support and coating properties. Closure of the pores of the cardboard support is necessary to decrease the OTR and is a priority over the barrier properties of the polymer coating itself: despite its low barrier to O_2, shellac coating enabled to decrease the OTR just by closing the pores [26].

For all samples with a good coverage of the fibers, i.e. with at least two successive coating depositions, circular shapes were observed at the surface. The SEM images obtained in our study are two-dimension images, and thus, only enable to see the surface shape, not the depth. It was not possible with such images to know whether they were actual holes in

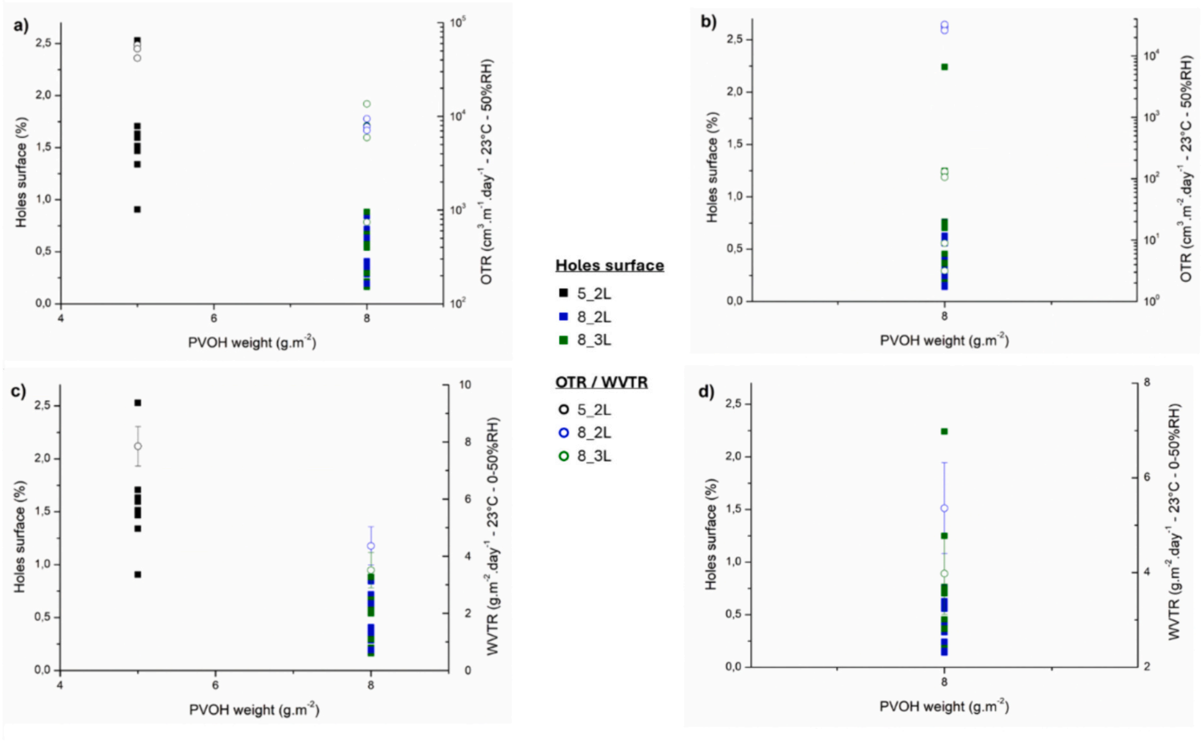


Fig. 4. Comparison between OTR and WVTR (o) and holes surface ratio (■) in Cupforma (a et c) and CKB Nude (b and d) coated samples with minimum two layers of PVOH.

the coating, i.e. reaching the cardboard surface, or if these holes only affect the upper coated layer, leading to fluctuations of the overall coating thickness. However, the term "holes" was used for the rest of the article for easier reading and understanding.

A hypothesis was that these holes could be blisters or bubbles, which were often observed at the interface between coating polymer and coated film [50]. Circular holes in multilayer PVOH coated cardboards were also observed in other studies and assimilated to craters or holes, due to blistering effect [30,43]. Their depth could be measured and was sometimes bigger than the PVOH theoretical thickness [30]. Our hypothesis was that these bubbles or blisters could be responsible for an increase in oxygen and water vapor transmission rates, and for the heterogeneity of the results.

A correlation between the OTR and WVTR values and the total surface of the holes measured on ten pictures per reference was attempted for samples with two or three coating layers and coating weights of 5 and 8 g.m^{-2} (Fig. 4) (Table S1 in Supplementary material). As for Fig. 1, all replicates were represented for OTR whereas means and standard deviations were shown for WVTR. Regarding hole surface, all measurements were shown as well.

As shown in Fig. 4, the hole surface was quite different from a sample to another, supporting the hypothesis that these holes would be responsible for the variability in OTR results. Generally, the bigger the holes surface, the higher the OTR and WVTR, supporting the second hypothesis that the holes would decrease the barrier performance of the final coated material. The same holes surface was observed between CF_8_2L and CF_8_3L and between CN_8_2L and CN_8_3L, which is coherent with WVTR values, which are also not significantly different between two and three layers. However, OTR was lower for samples with three layers. Even though the total hole surface in the upper layer remains the same, increasing the number of layers may help cover the holes present in the previous layers and slow down the O_2 transport through the holes (Fig. 5). Moreover, this could also explain the great variation in OTR results observed for CN_8_3L and CF_8_3L: the holes may be randomly distributed on the samples of a same reference, resulting in more holes in some samples than in others or in holes that are closer to the holes from the bottom or upper layer, leading to bigger fluxes and thus, higher oxygen permeability (Fig. 5).

These bubbles or blisters could be due to the PVOH solution foaming properties and coating process. Indeed, in pilot process used in the present work, PVOH was applied on the cardboard reel by a roller soaking in the PVOH solution, and no deaerator was used in the PVOH solution. The perpetual movement of this roller may have been responsible for bubbles formation, which remained in the PVOH coating. Thus, to confirm or infirm the importance of holes and the role of pilot scale process in holes formation, OTR and WVTR were also measured on laboratory coated samples, where movements within the PVOH solution were limited.

3.2.1. Impact of the coating scale

No or very few holes were observed on these samples (Fig. 3). Thus, the absence of holes in the laboratory coated samples confirmed that the holes observed in the pilot-coated samples were due to the coating process used. Laboratory process did not involve a roller soaking in the PVOH solution, limiting the foaming of the solution: foamability of the PVOH solution was thus suggested as a first explanation for the holes observed in the pilot scale samples. However, other differences between pilot and laboratory scale coating processes are worth to be highlighted as they may have an impact on the final structure of the coated samples as well. First, different strategies were used for coating deposition: the contact time between the coating slurry and the cardboard before metering was longer at pilot scale than at laboratory scale. Metering process itself was also different: while coating weight is controlled by the blade angle and application pressure at pilot scale, the coating weight is monitored by the type of grooved wire bars which are used at laboratory scale. In the latter case, a pressure is also applied, but is different from the one at pilot scale. Finally, dyring was done at higher temperature at pilot scale than at laboratory scale. A combination of these factors together with the limitation of foaming properties of the PVOH solution may explain the differences observed between the laboratory and pilot coated samples properties.

Moreover, although heterogenous, OTR values for two-layers coated samples were much lower than their pilot-coated counterparts (Fig. 1) and reduced by 10 when considering the mean values (Table 1), which confirms the role of the holes in the higher OTR obtained for pilot-coated samples. The heterogeneity of the results obtained for laboratory-coated samples could be attributed to the occasional presence of holes (Fig. 3), although they were rare. Nevertheless, no significant difference in OTR was observed for samples with three layers, showing the efficiency of increasing the number of layers in limiting the impact of the holes.

No significant difference was observed between both scales for WVTR, which were already low for pilot-coated cardboards. This suggests that OTR measurement are more sensitive to pinholes and cracks than WVTR, which would also explain the more repeatable results observed on WVTR than OTR. WVTR was already shown to be less sensitive to coating layer defects such as holes and cracks than OTR [12]. Indeed, Bakker et al. (2022) showed that 3 layers of alkali-soluble resin-stabilized waterborne barrier coating was needed to achieve good gas barrier properties, whereas only 2 layers were needed to significantly decrease the water vapor transmission rate of the paperboard [33].

3.3. Prediction of mass transfer properties based on the series resistance theory

Since laboratory-scale coated samples were almost defect-free, they were compared to theoretical values, calculated based on the series resistance model, to assess the validity of such model for coated cardboards. This model relies on the properties of each layer, i.e. uncoated cardboard and PVOH layers, which were thus measured. The presence of holes in the pilot coated samples hamper the use of such a prediction model based on the hypothesis of a homogeneous dense coating layer.

Based on OTR and WVTR of PVOH layers and uncoated cardboards (Table 1), the series resistance model (Eq. (8)) was used to calculate the theoretical OTR and WVTR of all coated cardboards (Fig. 6):

$$\frac{1}{TR_{coated\ cardboard}} = \frac{1}{TR_{uncoated\ cardboard}} + \frac{1}{TR_{PVOH\ layer(s)}} \tag{8}$$

where $TR_{coated\ cardboard}$, $TR_{uncoated\ cardboard}$ and $TR_{PVOH\ layer(s)}$ (in cm^3.m^{-2}.day^{-1} or in g.m^{-2}.day^{-1}) are the transmission rates of the multilayer

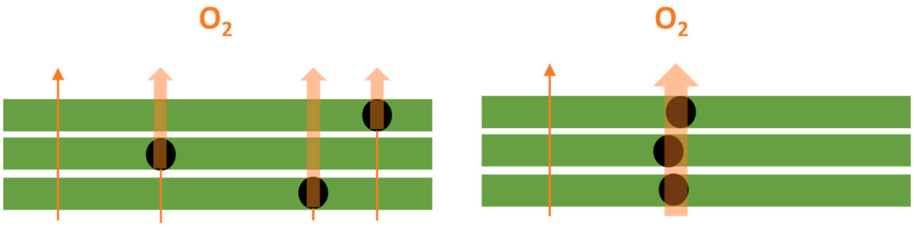


Fig. 5. O_2 fluxes through the layers, depending on the position of the holes in the layers.

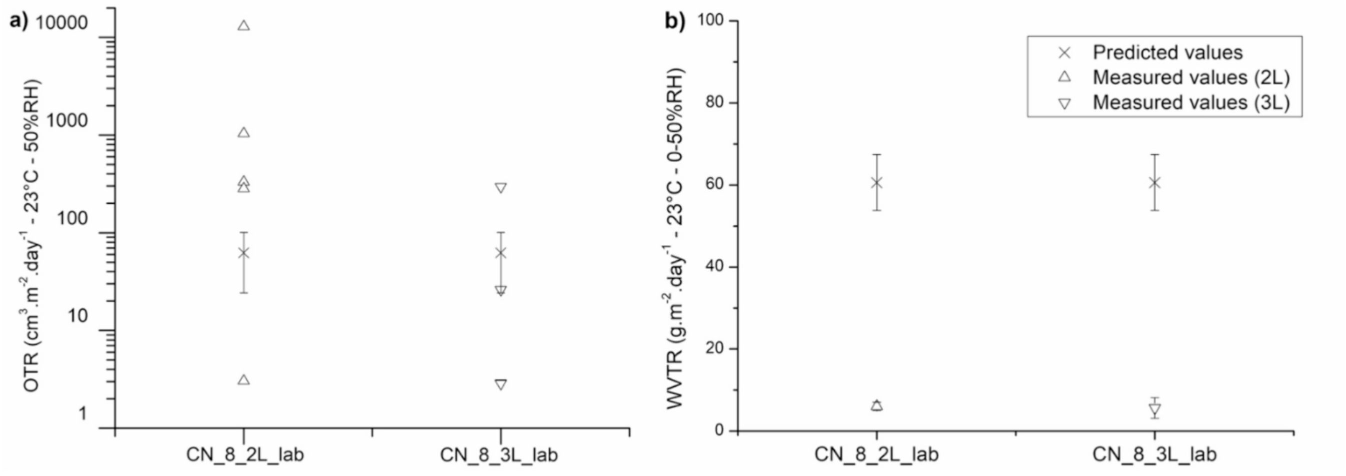


Fig. 6. Comparison between predicted and measured (a) OTR and (b) WVTR values for laboratory scale coated samples (CN_8_2L_lab and CN_8_3L_lab) (doi: 10.57745/MQXHG9).

material, the uncoated cardboard and the PVOH layer(s) respectively.

It was hypothesized that the PVOH-coated layer would have the same barrier properties as the self-supporting structure. Since only the total PVOH coating weight was considered influencing the coating thickness, one value was found per coating weight, whatever the number of layers. The coating weight standard deviation was not taken into consideration in this calculation: an 8 g.m^{-2} PVOH layer was considered.

For 8 g.m^{-2} coating, experimental results obtained for WVTR were around 10 times lower than predicted values (Fig. 6). A first explanation for the lower experimental values for both samples was that coated cardboards were grafted with fatty acids, which according to some studies increase the hydrophobicity and decrease the WVTR of PVOH coated cardboards [19,39]. However, its role in the water vapor transmission rate of grafted materials was not observed in all conditions: indeed, Stinga (2008) showed that grafting improved the water vapor barrier of PVOH coated cardboards at 38 °C and 90%RH, whereas no improvement was observed at 23 °C and 50%RH: the water vapor barrier was essentially brought by the PVOH in these last conditions. To confirm or infirm this last hypothesis, complementary tests were performed in our study on ungrafted materials coated with the same amount of PVOH than the grafted samples, CF_8_2L_WG and CN_8_2L_WG, using pilot process (see Supplementary material – Fig. S1). No significant difference in WVTR compared to the grafted materials at 0–50%RH and 23 °C was noted, supporting the conclusion that PVOH was the major contributor of the water vapor barrier under these conditions. The absence of effect of the grafting observed on these materials and conditions might be explained by the low relative humidity on each side of the material: water vapor sorption isotherms of grafted and ungrafted cellulose showed bigger differences in the water vapor uptake when relative humidity increased [51,52]. Thus, an effect could be expected at higher relative humidity (50–100 % RH for instance).

Regarding OTR, experimental results were slightly higher in average, but some replicates reached lower values than the predicted ones. These lowest results obtained were assumed to be representative of hole-free samples and were 20 times lower than the theoretical values. Thus, the series resistance model seems unable to predict OTR and WVTR of coated cardboards. Three hypotheses explaining the lower experimental values for both OTR and WVTR could be proposed.

a. The actual PVOH total coating weight would be higher than the target one, due to process variability.

A higher coating weight would result in a higher thickness than the theoretical one, calculated based on the target coating weight. This hypothesis alone cannot explain the difference observed: indeed, a factor of at least 10 was found between the predicted and experimental values, which mean that the coating thickness would be at least 10 times higher than predicted, i.e. 60 μm. Such high increase of thicknesses would have been detected when measuring the thickness of the coated samples during OTR and WVTR measurements. Yet, no significant difference was observed between uncoated and coated samples thicknesses, suggesting very thin coating layers. Moreover, the coating weight was monitored on the samples after coating process, and low standard deviations were measured (Table 1).

b. The PVOH coated layers would not have the same barrier properties as the self-supported PVOH films, due to different structures.

Guezennec (2012) already showed differences in OTR between PVOH casted film and coating layer, due do different drying conditions resulting in differences in the surface quality. In our study, the set drying temperature and time were similar for self-supported films and laboratory coated cardboards; however, they were not done in the same oven which might induce different real conditions. Moreover, a half-moon drier was used for the laboratory coated cardboards, implying pressure, which was not the case when drying the self-supported films. Temperature conditions during manufacturing process can impact the final structure of PVOH films and thus, its barrier properties: a recent study showed that increasing the annealing temperature from 60 °C to 160 °C increased the degree of crystallinity of the films, which in turn decreased the oxygen permeability from 8.0 × 10^{-19} mol.m.m^{-2}.s^{-1}.Pa^{-1} to 2.0 × 10^{-19} mol.m.m^{-2}.s^{-1}.Pa^{-1} [34]. Moreover, the film forming was different and the series resistance model considered one uniform layer of PVOH, whereas PVOH coating was applied in several layers, which also might give a different structure than one thick layer and could explain the better barrier properties of the coated structure.

Using (Eq. (3)), (Eq. (5)) and (Eq. (8)), a reverse approach was conducted to calculate the hypothetical O_2 and water vapor permeability of the PVOH layers, considering that the series resistance model was correct, but that the O_2 and water vapor permeability of the PVOH layer initially considered were not the true ones. For OTR, the lowest experimental values for each reference were considered.

Corrected calculated values for O_2 permeability of PVOH were between 8.2 and 8.8 × 10^{-20} mol.m.m^{-2}.s^{-1}.Pa^{-1} and water vapor permeability was between 1.5 and 1.6 × 10^{-14} mol.m.m^{-2}.s^{-1}.Pa^{-1}, respectively 20 and 10 times lower than the ones measured on self-supported PVOH films. Such low O_2 permeability values were obtained in the literature for PVOH films with a slightly lower hydrolysis degree (9.4 × 10^{-20} mol.m.m^{-2}.s^{-1}.Pa^{-1}) [43]. The corrected water vapor permeability is also closed to values found by Guezennec (2012) (6.9×10^{-15} mol.m.m^{-2}.s^{-1}.Pa^{-1}). Thus, they could possibly be the permeability values of the PVOH coated layer, as assumed by the second hypothesis. More in-depth study of the internal structure of the material, such as the crystallinity of the PVOH layer compared to the self-supported film would be necessary to confirm or infirm this hypothesis.

c. The coated samples would present a three-layer structure, including an impregnation layer.

The presence of an impregnation layer has been reported in previous studies [6,53]. It seems in the present study that such impregnation layer would even enhance the overall barrier property of the multilayer much more than the simple additivity of individual barriers would let expect. The presence of an impregnated layer would necessitate to adapt the series model resistance (Eq. (8)) by considering this third layer which is tricky in practice since thickness and permeability of the impregnated layer are not known a priori and really difficult to experimentally assess. Even by upgrading Eq. (8) to a three-layer structure, it is not obvious that it will be sufficient to predict the permeability of the multilayer. Indeed, additional interfacial effects between layers could interfere and are not considered in the calculation, making this three-layer model unreliable. Other studies suggested that the model to consider was more complex than a three-layer model [54].

This hypothesis could be assessed by observing the edge of the sample. It would give indication regarding the presence or not of an impregnation layer. However, cutting of the samples is a critical step that need to be solved in order to be able to make such observations. And measuring the transmission rate of the impregnated layer would be challenging as well.

4. Conclusion

PVOH coated samples with different barrier performances were obtained, highlighting the relationship between oxygen and water vapor transmission rates and coating weight, but also with the number of layers, position of layers, cardboard support and the final coating layer quality. It was shown that a good coverage could be reached by applying several coating layers: 5 g.m^{-2} in one layer was not enough to ensure a good coverage whereas 5 g.m^{-2} in two layers gave good coverage and significantly lower barrier properties. This result is promising to achieve good barrier properties while decreasing the total amount of polymer needed, which is interesting from environmental and economical points of view.

Moreover, pilot coating process was responsible for the formation of bubbles or blisters in the PVOH layer, being responsible for preferential pathways for O_2 molecules. Water vapor transport seemed less sensitive to these bubbles or blisters. This would explain a high variability in OTR results for the most barrier samples, as well as higher values than samples produced in laboratory, and without any defects. Better controlling the defects in the coating would be valuable to decrease variability in the material performance. One solution could be to add a deaerator in the PVOH solution to decrease its foaming properties. A relationship was attempted between the number of holes and the transmission rate to try to find a new and more reliable model: however, although a correlation between both parameters seemed to be evident, the huge heterogeneity of these holes makes it difficult to make exact predictions.

Finally, laboratory scale samples without any visible defects showed lower experimental values than theoretical ones for both OTR and WVTR, making the series resistance model unable to predict the barrier properties of such defect-free structures either. This limit might be due to the difference between properties of the polymer as a self-supported film and as a coating or by a different material structure than an expected two-layer one. This last hypothesis could be due to the presence of an impregnation layer, due to the porosity of the cellulosic substrate.

Most probably, a combination of these parameters could be the reason for the differences of results observed: observations of the edge of the samples and analysis of the PVOH layer properties would help determine what is the contribution of each of the above hypotheses.

Overall, different barrier properties were obtained according to the coating weight and number of layers and can thus be applied to different applications. This study is part of a wider project aiming at developing packaging materials with precise specifications, defined according to different food categories requirements.

Funding acknowledgment

This work was granted by the French National Research Agency (EcoFreshChain project, ANR-20-CE21-007-01).

CRediT authorship contribution statement

Emma Pignères: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sébastien Gaucel:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Fanny Coffigniez:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Nathalie Gontard:** Funding acquisition, Conceptualization. **Elaura Baghe:** Resources, Methodology. **Laurent Lyannaz:** Writing – review & editing, Validation, Resources, Methodology, Funding acquisition, Conceptualization. **Philippe Martinez:** Writing – review & editing, Validation, Funding acquisition, Conceptualization. **Valérie Guillard:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization. **Hélène Angellier-Coussy:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

doi:10.57745/MQXHG9.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2024.108627.

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