Thickness and Gas Permeability Properties of PLA and PLA/EVOH/PLA before and after Thermoforming into Variable Tray Types.

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Introduction

Thermoformed trays are very popular in food packaging thanks to their ease of production, filling and sealing as well as to the relative low production costs. It is also known that thermoforming affects different properties of the sheet material, such as thickness, crystallinity and mechanical, optical and gas barrier properties.

Poly(lactic acid) (PLA) is a promising biodegradable thermoplastic polyester made from renewable resources. However, to broaden it's applicability in packaging the gas barrier properties of PLA should be improved.

Objective

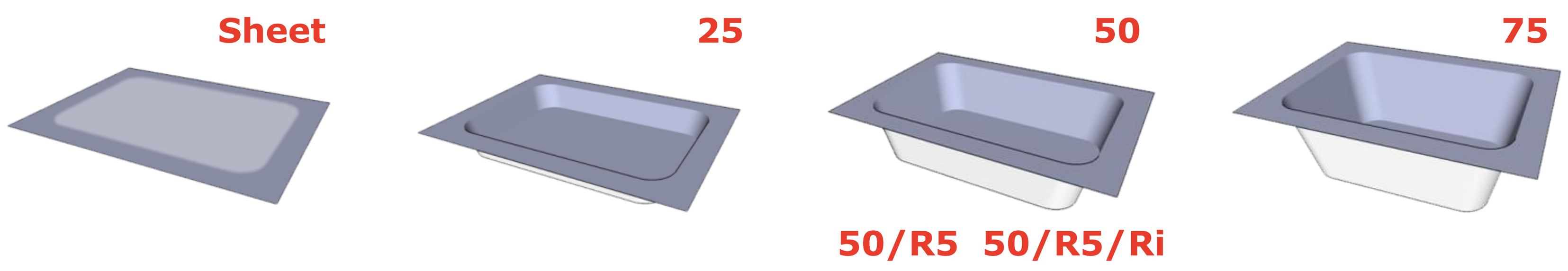
In collaboration with companies from the Belgian and Dutch food and packaging industry, the thickness, and O_2, CO_2 and water vapor permeability was studied before and after thermoforming 400-µm PLA monolayer and PLA/EVOH/PLA multilayer sheets into trays with variable drawing depths of 25, 50 and 75 mm and two extra 50-mm trays with variable radius of the corners; with and without ribs in the walls.

Materials & Methods

Thermoformable grades of PLA IngeoTM 2003D (NatureWorks LLC), EVOH resin J102B (32 mol% ethylene) and a modified PE adhesive (Kuraray, EVAL Europe) were (co-)extruded on a co-ex Collin cast line with 5 extruders at the QC lab of Kuraray, EVAL Europe (Zwijndrecht, Belgium) with target thickness of:

- 400 µm (PLA monolayer)
- 182/12/**12**/12/182 µm (PLA/adh/**EVOH**/adh/PLA multilayer)
- 182/24/**12**/24/182 µm (PLA/adh/**EVOH**/adh/PLA with doubled adhesive layers)

250x330 mm sheets were thermoformed into 5 tray types on a custom-made lab thermoformer, able to simulate industrial thermoforming processes at Cobelplast (Lokeren, Belgium). Using 4 different inserts in the mould, trays with variable depths of 25, 50 and 75 mm (radius corners ~1 mm), and a 50-mm tray with round corners (radius ~5 mm) were produced (design 25, 50, 75 and 50/R5). Tray type 50/R5/Ri was produced using an extra mould with the same characteristics as the 50/R5 mould but with inside oriented ribs (radius ~10 mm, depth 1 mm).



Results

Thickness

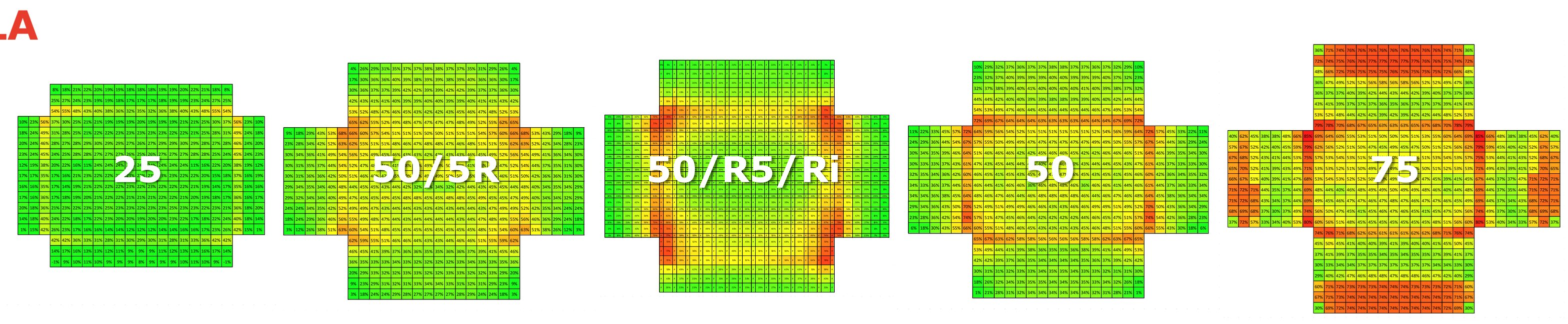
A grid of squares of ~1 cm² was drawn on the trays and the global thickness was measured as described by Buntinx *et al.* (Polymers, 2014). The percentage of thinning shown in colours was calculated in every square ('i') according to:

$$Thinning(\%) = \frac{d_0 - d_i}{d_0} \times 100\% \quad \text{[Eq. 1]}$$

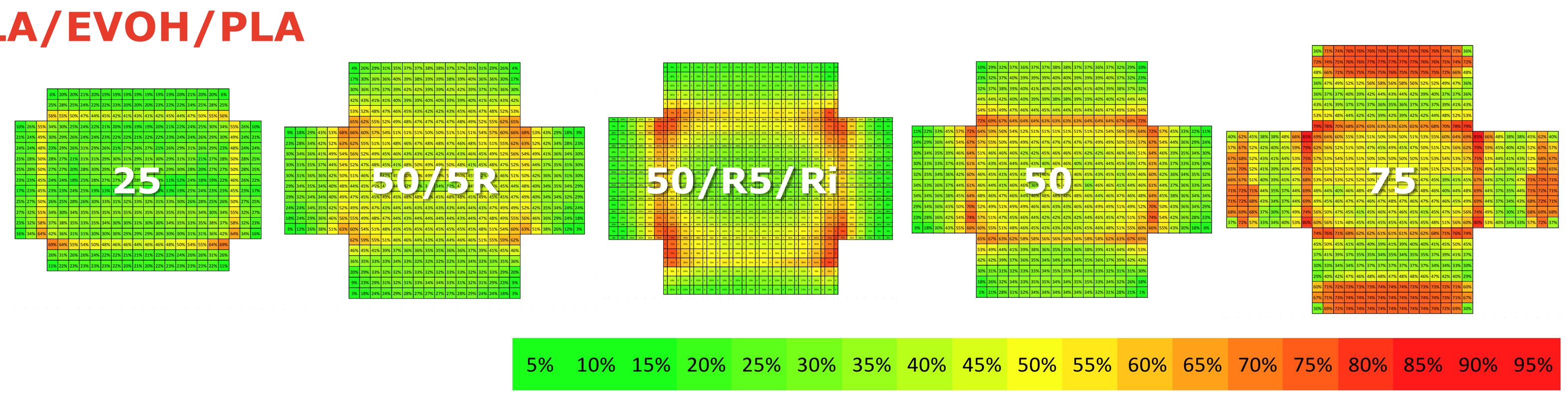
with d_0 and d_i the thickness of the sheet and square 'i', respectively.

Thinning increased with drawing depth, especially in the corners of the trays and in the side walls of the 75-mm trays of both test materials.

PLA



PLA/EVOH/PLA



The average measured thickness of the trays was calculated according to:

$$d_{average}(\mu m) = \frac{\sum_{i=1}^{n}(d_i \cdot A_i)}{\sum_{i=1}^{n} A_i} \quad \text{[Eq. 2]}$$

with A_i and d_i representing the area and thickness of square 'i' respectively.

Based on the assumption of a constant sheet volume during thermoforming, the theoretical thickness of the trays (d_{tray}) was calculated from:

$$A_0 \cdot d_0 = A_{tray} \cdot d_{tray} \quad \text{[Eq. 3]}$$

with A_0 and A_{tray} the area of the unconverted sheet and tray respectively.

	Sheet (d_0)	Tray 25	Tray 50/R5	Tray 50	Tray 75
Average measured thickness (µm)					
PLA	402 ± 11	311 ± 52	239 ± 74	229 ± 72	187 ± 81
PLA/EVOH/PLA	405 ± 15	285 ± 56	224 ± 69	217 ± 69	176 ± 75
Theoretical thickness, d_{tray} (µm)					
	400	276	217	217	180

PLA is a quite stiff material, these data suggest that some extra material might be pulled in the mould during thermoforming, causing somewhat higher average measured thickness than would be expected.

Oxygen permeability

The oxygen barrier properties of the PLA and PLA/EVOH/PLA sheets and trays were measured using MOCON instruments and recalculated in 3 different units.

The oxygen transmission rate (OTR, cc/[m².day.atm]) of the PLA/EVOH/PLA trays was 26-36x lower as compared to the respective PLA trays (rel. humidity 50% outside-90% inside).

The OTR increased with drawing depth as a consequence of thinning and surface increase, but no significant effect on PLA crystallinity was observed. Therefore the theoretical OTR (shown by the dotted line) is in good agreement with the measured OTR. The theoretical OTR (in cc/[package.day.atm]) is calculated from:

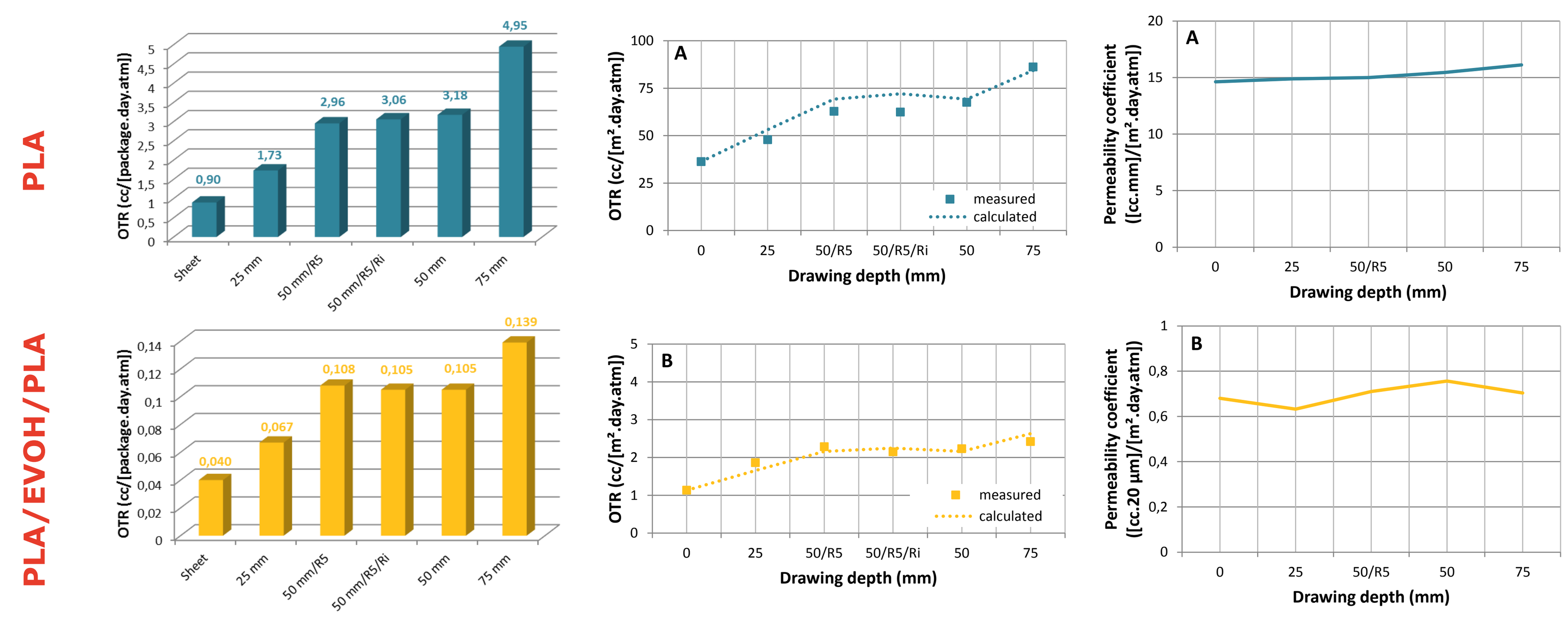
$$OTR_{tray} = \sum_{i=1}^{n} A_i \cdot \frac{d_0}{d_i} \cdot OTR_0 \quad \text{[Eq. 4]}$$

with A_i partial area with thickness d_i; d_0 and OTR_0 thickness and OTR in cc/[m².day.atm] of the sheet.

Assuming a constant sheet volume during thermoforming (Eq.3), the theoretical OTR of the tray (in cc/[m².day.atm]) can also be calculated using:

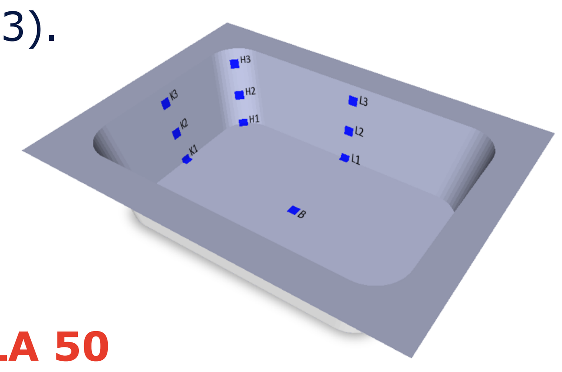
$$\frac{OTR_{tray}}{A_{tray}} = \frac{A_{tray}}{A_0} \cdot OTR_0 \quad \text{[Eq. 5]}$$

using Eq. 4 with n=1; A_i = surface of tray A_{tray}; and d_i = theoretical tray thickness d_{tray}.



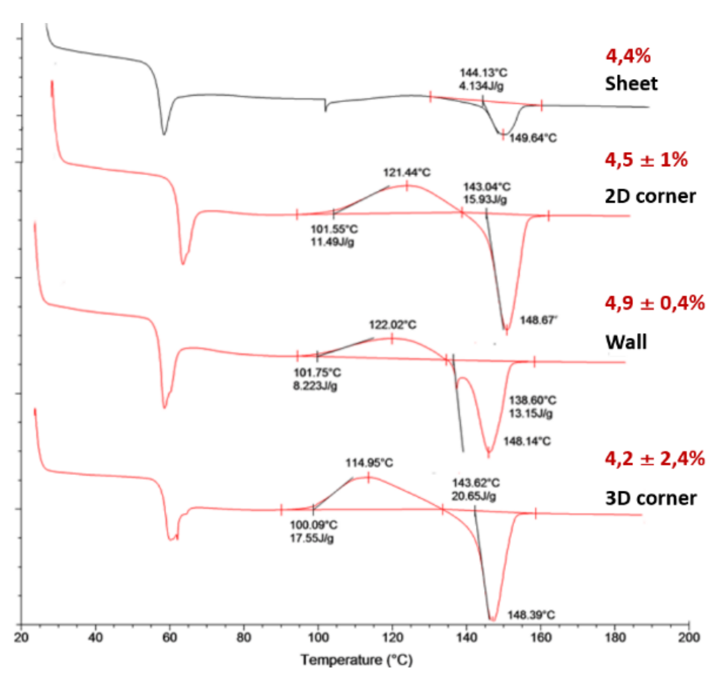
EVOH layer thickness

Microscopic individual layer thickness measurements in selected locations of the trays showed that the EVOH layer thinned fairly proportionally, representing ~3% of the total thickness in all different locations as shown for the 50-mm PLA/EVOH/PLA tray (n=3).



Location	EVOH µm	Total thickness	% EVOH
K1	4.4 ± 0.6	135.1 ± 1.1	3.3 ± 0.4
K2	7.3 ± 0.7	248.2 ± 2.5	3.0 ± 0.3
K3	7.4 ± 0.8	263.8 ± 7.9	2.8 ± 0.3
L1	5.1 ± 0.2	177.4 ± 0.8	2.9 ± 0.1
L2	7.8 ± 0.7	232.8 ± 5.4	3.3 ± 0.4
L3	8.0 ± 0.2	228.1 ± 1.4	3.5 ± 0.1
H1	3.3 ± 0.3	94.3 ± 5.7	3.5 ± 0.4
H2	6.6 ± 0.3	239.2 ± 1.0	2.8 ± 0.1
H3	9.8 ± 0.6	337.1 ± 2.1	2.9 ± 0.2
B	6.9 ± 0.1	211.3 ± 1.6	3.3 ± 0.0

DSC PLA 50



DSC analyses to test whether differences of theoretical and measured OTR values could be caused by altered crystallinity or potential reorientation of the polymer chains showed an extra peak of cold crystallization before the melting peak. This indicates reorientation of the PLA polymers caused by the thermoforming process. Moreover, the enthalpy of cold crystallization was higher in locations where more reorientation is possible: $\Delta Hcc_{3Dcorner} > \Delta Hcc_{2Dcorner} > \Delta Hcc_{wall}$.

Nevertheless, this did not influence the OTR as a result of the low crystallinity of the PLA polymer.

Permeability for O_2, CO_2 and water vapor

Sheet material	OTR[a]	OTR[b]	CO_2TR[a]	WVTR[c]
	cc/[m².day.atm]	cc/[m².day.atm]	cc/[m².day.atm]	g/[m².day]
PLA	38.2 ± 0.5	36.3 ± 0.04	139.4 ± 0.3	9.2 ± 0.001
PLA/EVOH/PLA	1.08 ± 0.03	1.76 ± 0.01	1.8 ± 0.08	2.8 ± 0.03
PLA/EVOH/PLA (2xadh)	-	1.70 ± 0.001	-	1.7 ± 0.05

[a]) 0% RH; [b]) 50-90% RV; [c]) 100%-0% RV

Co-extrusion of PLA and EVOH results in a multilayer sheet with an O_2 barrier that is ~35x better than monolayer PLA in dry conditions and ~22x better in humid conditions. The CO_2 barrier of PLA/EVOH/PLA sheets is ~77x better than PLA sheets. In addition, PE-based adhesive layers in PLA/EVOH/PLA can improve the water vapor barrier properties of PLA ~3 to 5x depending on the thickness of the adhesive layers.

Conclusion

This study confirms the applicability of PLA in food packaging, especially after co-extrusion with EVOH, thereby creating a high barrier packaging material.

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