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BIXIN AND ACETYL TRIBUTYL CITRATE IN POLYLACTIDE FILMS PRODUCED BY CASTING AND MELT PROCESSING: PERFORMANCE IN STABILITY AND PROTECTION OF FOOD PRODUCTS

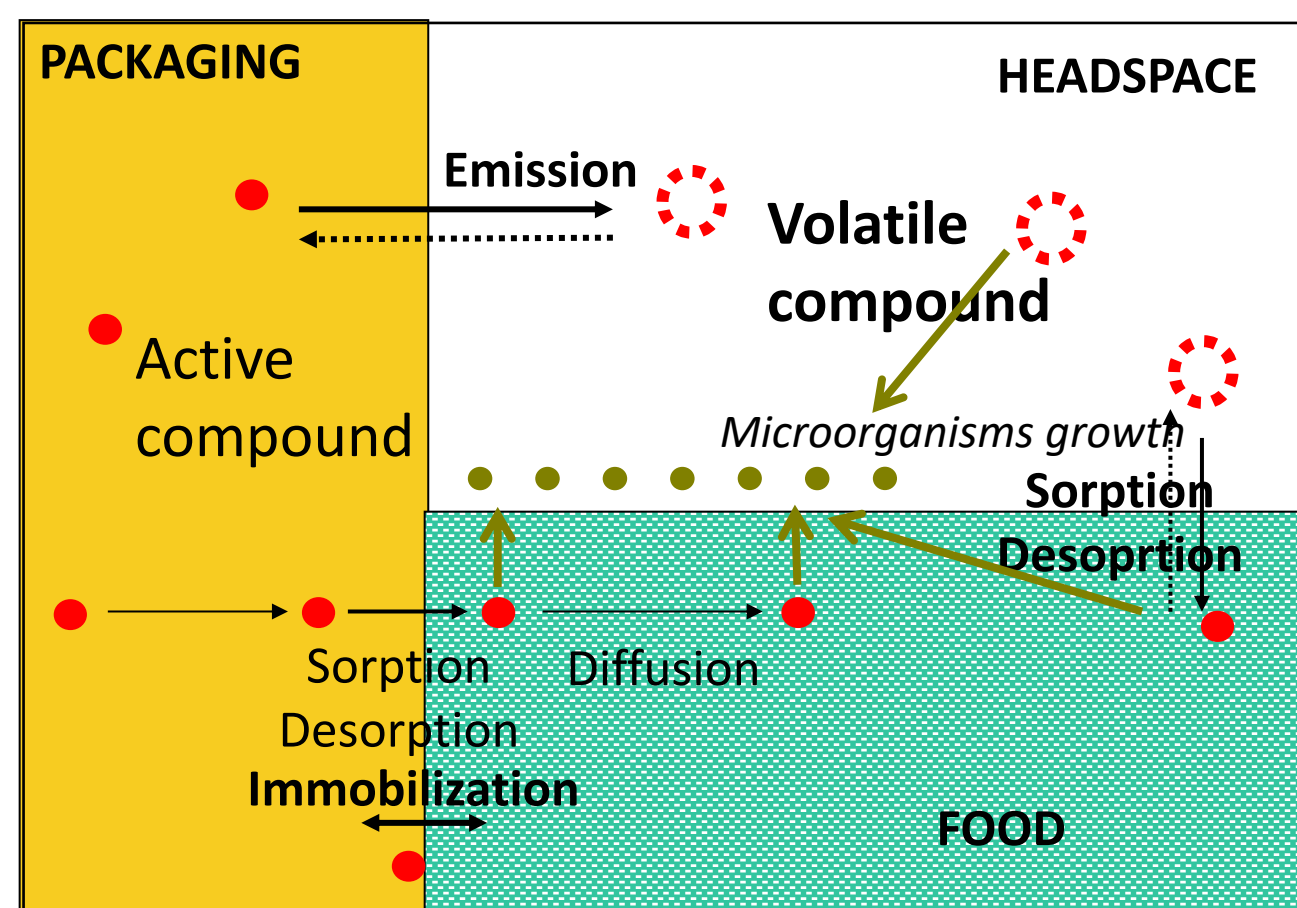
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Introduction

Active antioxidant biodegradable Food Packaging



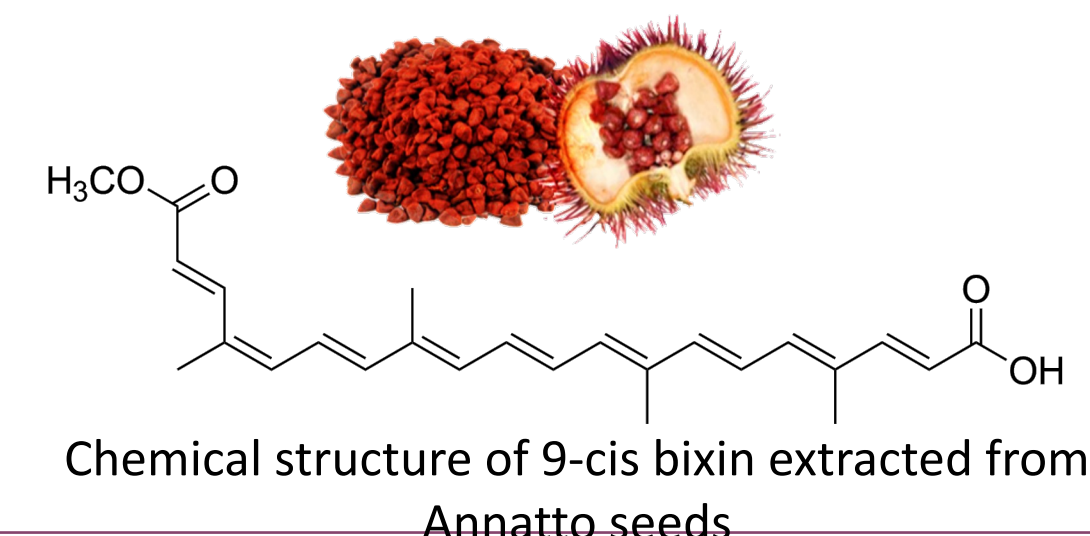
PLA is a bio-based and compostable commercial polymer already used widely in catering and processed-food packaging. Despite all the advantages of PLA, its barrier properties for food packaging applications need to be optimized.^{1,2}

Active biodegradable packaging materials are with this respect of particular interest for food manufacturers eager to improve the sustainability and environmental impact of their products, because they contribute maintaining food quality and safety. The incorporation of antioxidants into a polymeric structure to produce antioxidant active materials is an alternative way to extend the shelf-life of food products.

Bixin, a carotenoid with hydrophobic character, presents coloring and antioxidant properties and hence is a potential antioxidant additive for PLA. Here, we used bixin, a carotenoid with coloring and antioxidant properties and plasticized polylactide (PLA) as polymer matrix. Typical melt processes of PLA are carried out between 160 and 220 °C involving heat and shear, which can cause thermal degradation of the antioxidant. Considering bixin thermal low stability, PLA films were fabricated with bixin and the plasticizer acetyl tributyl citrate (ATBC) using different thermal processes.

Objectives

- Develop plasticized PLA films with bixin
- Analyse film properties and release kinetics of bixin
- Analyse thermal degradation of bixin and its impact on functionality
- Evaluate protection of food



Materials and Methods

Fabrication of PLA/ATBC/bixin films

PLA	PLA	Bixin (%)	ATBC (%)	Film Processing Method	
PLA	PLA	F1.cast	0.1	0	casting from CH ₂ Cl ₂ solution
PLA	PLA	F1A.cast	0.1	13	casting from CH ₂ Cl ₂ solution
PLA	PLA	F1_TP	0.1	0	casting + TP (160 °C, 6 min)
PLA	PLA	F1A_TP	0.1	13	casting + TP (160 °C, 6 min)
PLA	PLA	F1_IMTP	0.1	0	IM (160 °C, 2 min) + TP (160 °C, 4 min)
PLA	PLA	F1A_IMTP	0.1	13	IM (160 °C, 2 min) + TP (160 °C, 4 min)

TP: thermo-press (160°C/5 tons); IM: internal mixer (160 °C, 50 rpm)

The bixin degradation products were analyzed by UHPLC-PDA-MS (Waters Acquity, France): Mobile phases A (0.1% (v/v) formic acid in water), B (0.1 % (v/v) formic acid in acetonitrile). Isocratic elution with A/B 25/75 (v/v) at 0.6 mL.min⁻¹, using an Ethylene Bridged Hybrid (BEH) C18 column and a pre-column Vanguard BEH C18; settings of the mass spectrometer were: ESI+ ionisation, source parameters being a capillary 0.5 kV, sampling cone 40 V, source offset 80 V, 120 °C, desolvation 500 °C. The gas flow in the cone was 50 L.h⁻¹, the desolvation gas flow 1000 L.h⁻¹. The collision energy was 6 eV. The registered m/z ranged from 50 to 900 with a scan time of 0.5 s in centroid and an acquisition time of 10 min.

Evaluation of film properties

• **Optical barrier properties:** measured on films in quartz test cells from 200 to 800 nm in a UV-Vis spectrophotometer

• **Color stability:** Konica Minolta colorimeter measuring L*(luminosity), a* (red-green), and b* (yellow-blue) values. The total color differences (ΔE) caused by thermal processes when compared to casting films was calculated using the following equation

$$\Delta E = \sqrt{(L^* - L^*_{cast})^2 + (a^* - a^*_{cast})^2 + (b^* - b^*_{cast})^2}$$

• **Oxygen permeability:** GDP-C permeameter (25 °C, 0 % RH). Permeability (P) calculated by multiplying the measured oxygen transmission rate by the sample thickness. Diffusion (D) and sorption (S) coefficients were calculated with the help of the time-lag (t_{lag}) method.

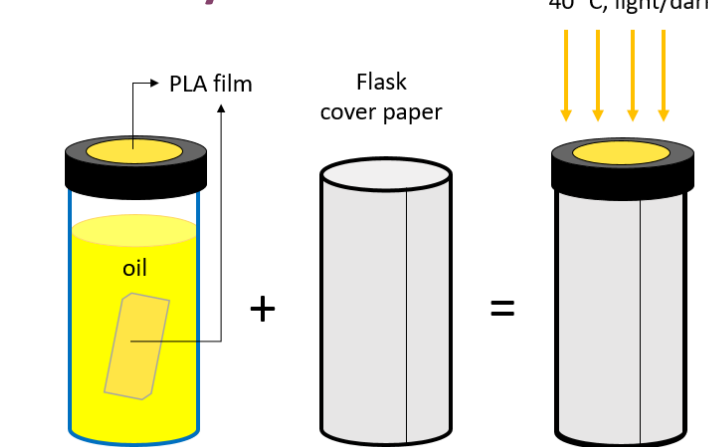
Release kinetics and food stability

Bixin migration kinetics in ethanol 95% v/v (used as a fat food simulant) was evaluated over 65 days at 40 °C. Quantification was made by spectroscopy and the overall mass transfer coefficient (K) of bixin was obtained using the following equation:

$$\frac{dC}{dt} = K \frac{A}{V} (C^* - C) - k_d C$$

C: bixin concentration in the food simulant (μg mL⁻¹);
C*: bixin concentration (μg mL⁻¹) in the inner part of the film;
K: overall mass transfer coefficient (m s⁻¹);
A: surface area of films;
V: volume of food simulant;
k_d: first-order kinetic degradation coefficient of bixin in ethanol 95% at 40 °C (2.155 s⁻¹ × 10⁻⁷)

Evaluation of the performance of MP films to protect the oxidative stability of sunflower oil.



Vials with Exchange surface of 3 cm² were placed under white lamps (4700 ± 200 lux) at RT. The peroxide value (PV) of the oil samples was periodically determined according to the IUPAC titration method for oils, fats and derivatives oils.

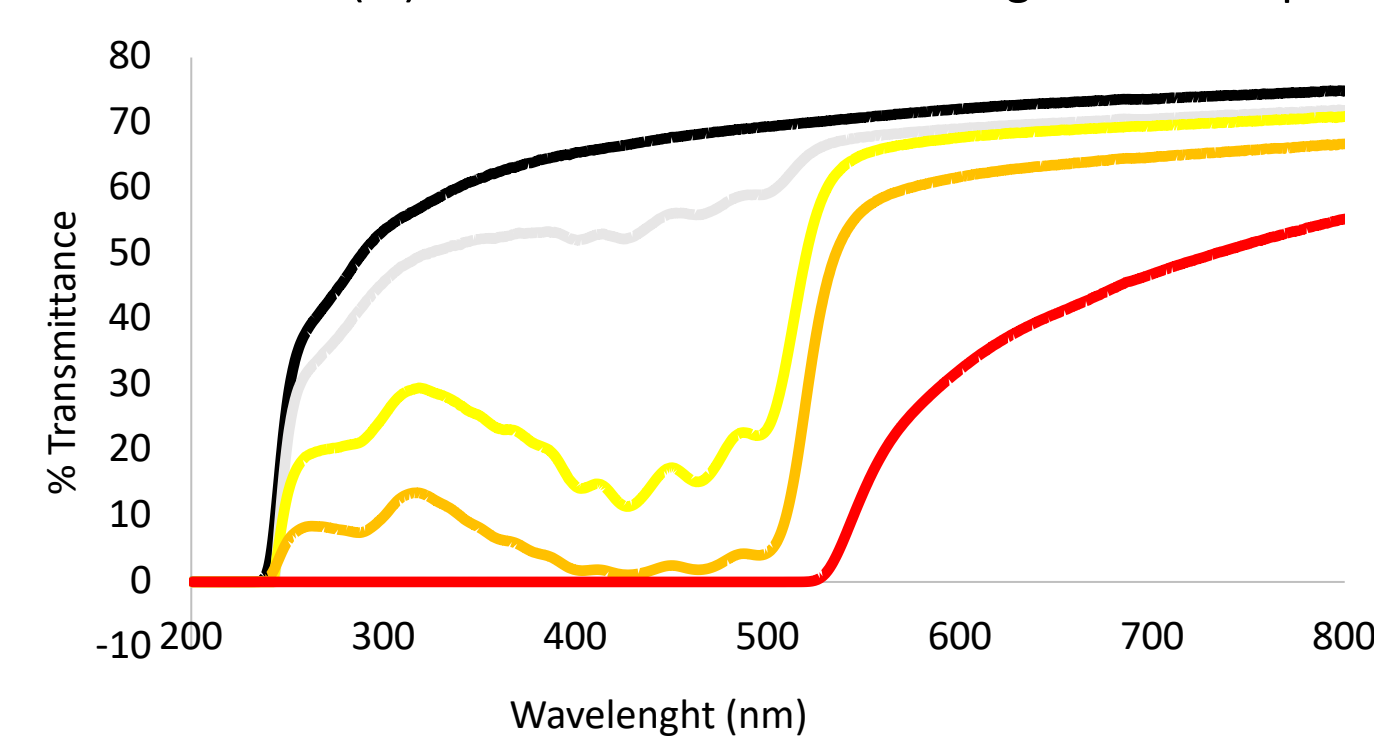
Results

Optical properties of PLA/ATBC/bixin films

PLA films produced by casting with different bixin concentrations (0 – 1%):



Light transmittance (%) from 200 to 800 nm through PLA films produced by casting:



Color changes caused by thermocompression for 6 min of cast films:

Casting	TP	TP films color parameters							Color changes caused by thermal treatment				
		L	a*	b*	Chroma	Δ a*	Δ b*	ΔE	ΔChroma				
FP		94.6	-0.4	2.4	2.6	0.1	0.0	0.2	0.4				
FPA		94.4	-0.5	2.7	2.7	0.0	0.3	0.3	0.3				
F1		93.0	-4.0	19.2	20.0	2.6	-43.8	43.8	-43.4				
F1A		91.5	-4.5	21.9	22.3	1.1	-44.7	44.9	-44.5				
F5		88.4	-7.7	84.7	85.1	-7.6	-24.1	25.5	-23.7				
F5A		88.2	-7.5	70.8	72.3	-9.3	-34.7	35.2	-33.3				
F10		83.7	2.9	105.5	105.5	-10.3	18.4	21.6	17.5				
F10A		84.9	-1.5	103.0	103.0	-11.0	13.7	18.2	13.2				

Visual color attributes, color parameters L, a*, b*, and Chroma of thermal treated pressed (TP: 160 °C for 6 min) and their color changes when compared to casting films

Properties after thermal treatment

Oxygen barrier properties of cast and thermo-compressed films for 6 min:

	P.10 ¹⁸	D.10 ¹²	S.10 ⁶
	[m ³ m m ⁻² Pa ⁻¹ s ⁻¹]	[m ² s ⁻¹]	[m ³ m ⁻³ Pa ⁻¹]
FP	3.31	3.3	1.0
FPA	5.06	4.9	1.0
F1	4.14	3.5	1.2
F1A	4.55	4.3	1.0
F5	3.04	2.8	1.1
F5A	5.08	5.2	1.1
F10	3.59	3.2	1.1
F10A	5.04	4.2	1.2

Bixin degradation in cast films after thermal treatment:

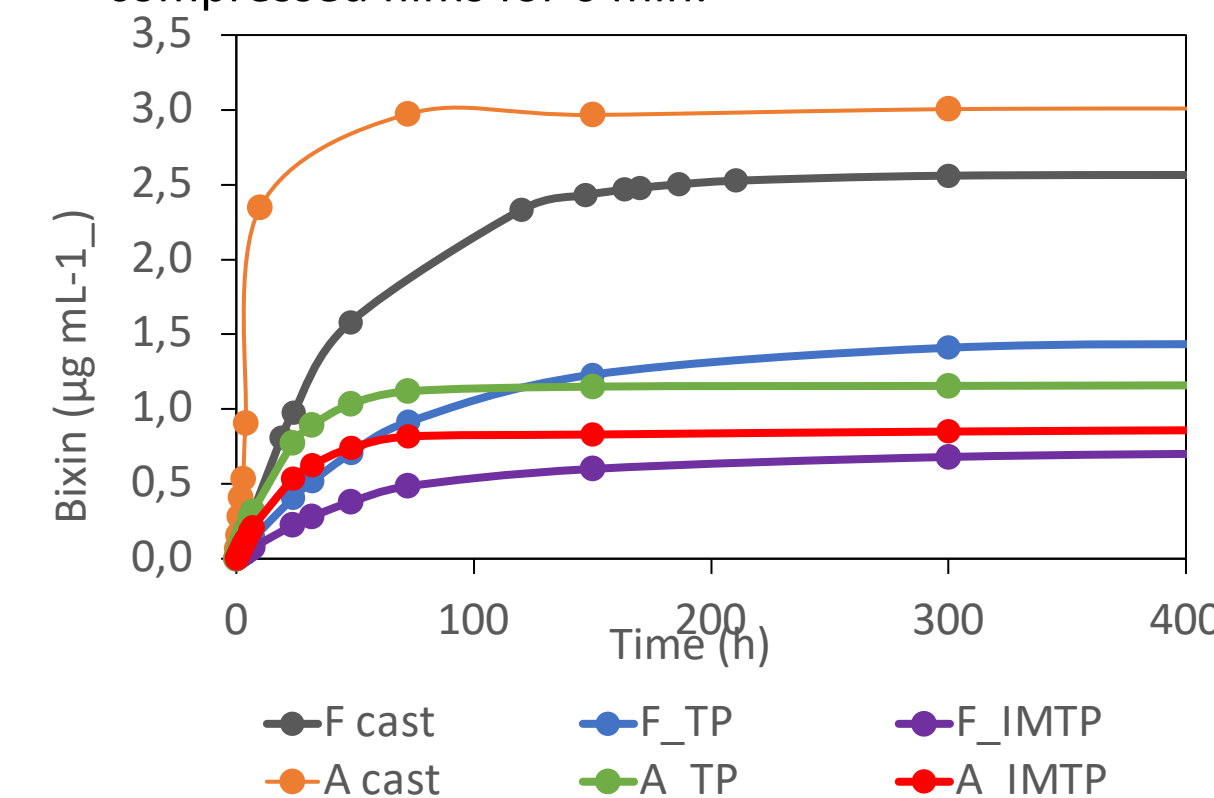
	Bixin (μg g ⁻¹)		Bixin degradation (%) at 160 °C	
	casting	TP - 4 min	TP - 6 min	
FP	-	-	-	-
F1	99.3 ± 0.3 ^c	62.9 ± 0.5 ^c	82.3 ± 2.1 ^{bc}	
F5	480.6 ± 16 ^b	62.7 ± 1.2 ^c	82.6 ± 0.5 ^{bc}	
F10	930.1 ± 22.2 ^a	60.5 ± 0.1 ^c	74.5 ± 1.9 ^c	
FPA	-	-	-	-
F1A	114.3 ± 14.0 ^c	83.2 ± 1.4 ^a	88.9 ± 3.3 ^a	
F5A	416.1 ± 5.0 ^b	74.6 ± 0.2 ^b	93.0 ± 0.1 ^a	
F10A	896.4 ± 16.7 ^a	75.3 ± 0.1 ^b	85.3 ± 0.3 ^{ab}	

Films without ATBC: FP (0% bixin); F1 (0.01% bixin); F5 (0.05% bixin); F10 (0.10% bixin). Films with ATBC: FPA (0% bixin); F1A (0.01% bixin); F5A (0.05% bixin); F10A (0.10% bixin). Values are given as mean ± SD (n=3). Different letters in the same column indicate significant differences (p < 0.05) among the films.

→ Heat treated films allow protection of sunflower oil in the light

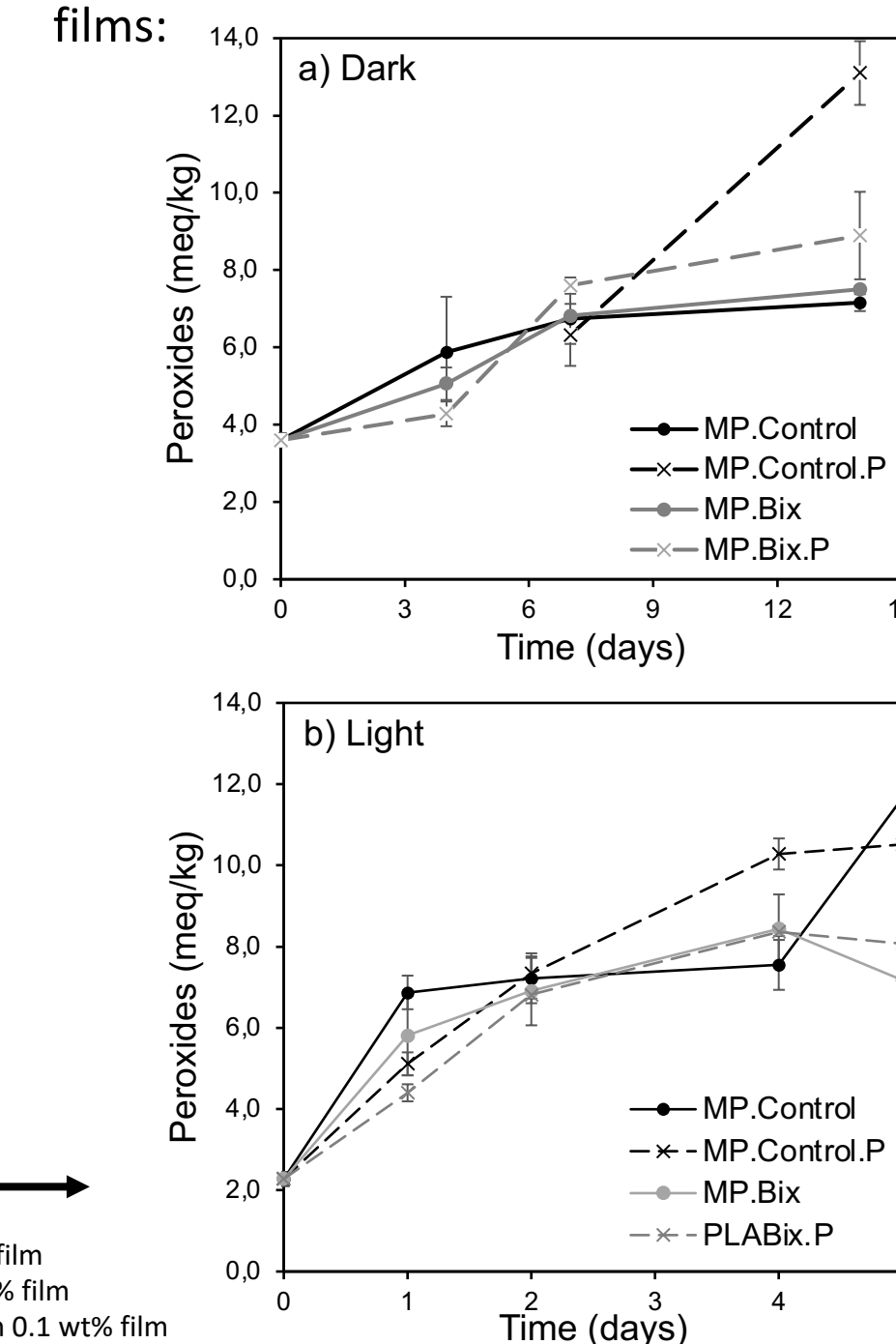
Release kinetics

Oxygen barrier properties of cast and thermo-compressed films for 6 min:



Antioxidant properties

Stabilization of sunflower oil with heat-treated films:



Conclusions

PLA films containing bixin were prepared after melt mixing or solution casting to obtain new packaging materials for light-sensitive food products. The melt mixing caused around 85% of bixin loss. The oxygen and light barrier properties of the PLA/bixin films remained however satisfying, although 9-cis-bixin was largely degraded. The analysis of the performance of the PLA/bixin films with an initial bixin content as low as 0.1 wt% to shield oxygen sensitive food from degradation showed their ability to the level of peroxides in sunflower oil. The light shielding property was more performing than protection delivered by mass transfer of antioxidants to oil. This shows that the degradation of this natural antioxidant during melt processing of polymers is not fatal for its performance. Bixin is therefore a very promising natural additive to improve the performance of commercial packaging materials for preserving the quality of various food products.

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