ANTIMICROBIAL BILAYER FILMS OF STARCH AND POLYESTER-BLEND WITH CARVACROL.

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INTRODUCTION

- Starch has been widely studied for developing biodegradable films, since it is renewable, sustainable, biodegradable, available and affordable. However, starch-based materials are associated with poor mechanical and water vapor barrier properties, which limited their application. In this sense, the development of multilayer structures that combine starch layers with hydrophobic polymers such as biodegradable polyesters is a promising approach to overcome starch drawbacks. Thus, the multilayer strategy allows for taking advantage of complementary properties of different materials, where one layer impart moisture resistance and mechanical stability and the other one acts as a gas barrier.

- In addition, active compounds such as essentials oils or their compounds can be incorporated into bilayer structures by different methods in order to provide added value to these materials, since they are able to maintain and enhance the quality and safety of packaged foods.

✓ To develop active bilayer films based on cassava TPS and polyesters with carvacrol (CA), which was incorporated either, **dissolved in the casting solution** or **sprayed between the two layers** of films before the thermocompression step.

✓ To study the **effect** of the **bilayer processing method** on the **functional and antimicrobial properties** of the films

MATERIALS & METHODS

✓ Mechanical properties
✓ Water vapour permeability
✓ Antimicrobial activity
✓ Release kinetics of CA in food simulants

RESULTS

Table 1. Tensile properties and water vapour permeability (WVP) of monolayers and polyester-starch bilayer films with and without carvacrol (CA). Mean values ± standard deviation. C subscript indicates the application of casting method for polyester layer.

Formulation	EM (MPa)	TS (MPa)	E (%)	Thickness (μm)	WVP ($x10^{12}$ g/msPa)
PLA-PHBV$_c$	1272 ± 18^g	21.8 ± 0.8^c	2.1 ± 0.2^a	116 ± 5^a	11.9 ± 0.6^c
PLA-PHBV-CA$_c$	520 ± 77^e	21 ± 2^c	130 ± 2^e	141 ± 11^b	9.6 ± 1.2^b
PLA-PHBV$_c$/TPS	756 ± 30^f	9.2 ± 1.3^b	1.4 ± 0.4^a	251 ± 7^d	32 ± 13^d
PLA-PHBV-CA$_c$/TPS	480 ± 52de	5 ± 2^a	1.2 ± 0.6^a	216 ± 16^c	38 ± 5^d
PLA-PHBV	460 ± 41^d	8.6 ± 0,9^b	7 ± 4^b	116 ± 9^a	4.2 ± 0.3^a
PLA-PHBV/TPS	293 ± 43^c	5 ± 0.7^a	3 ± 2^a	174 ± 10^b	14 ± 2^c
PLA-PHBV/CA/TPS	182 ± 36^b	5.2 ± 0.7^a	25 ± 4^c	161 ± 12^b	57 ± 17^e
TPS	51 ± 13^a	4.1 ± 0.3^a	75 ± 7^d	155 ± 8^b	283 ± 6^f

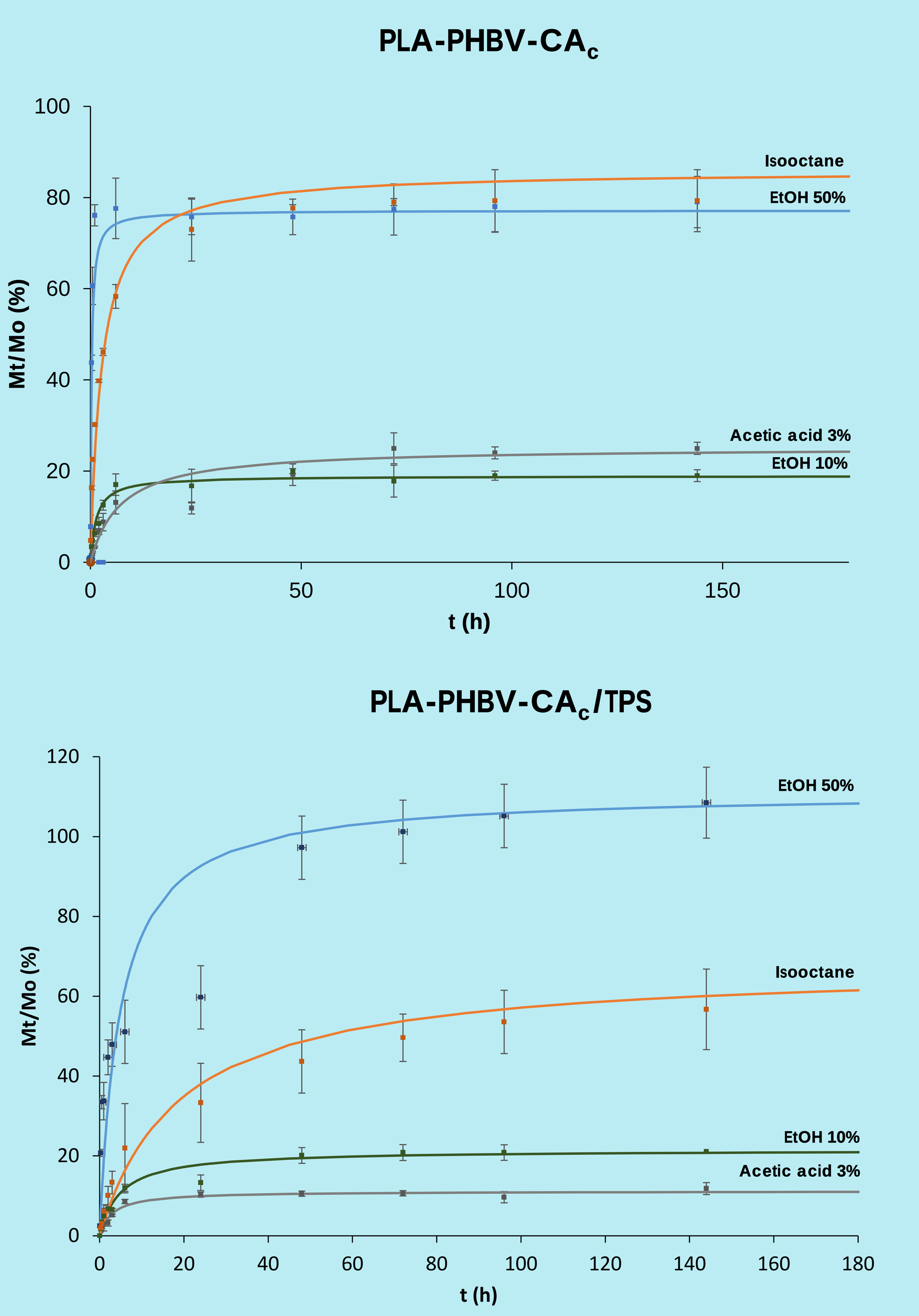

Figure 1. Ratio of carvacrol delivered from the cast polyester monolayer and the corresponding bilayer with starch in each simulant, with respect to the theoretical initial amount, as a function of the contact time (points) and Peleg's fitted model (lines).

- Polyester casted monolayers were stiffer, more resistant to break and less stretchable and CA incorporation greatly plasticized them. This monolayers were also more permeable to water vapor, but CA significantly reduced their WVP.

- Starch-polyester bilayer films also exhibited better tensile properties when polyester layer was obtained by casting, whereas the better water vapor barrier capacity was shown in those bilayers prepared from monolayers obtained by compression molding.

- The CA release was almost total in the non polar simulants, whereas in polar simulants only the 20% de the initial amount was release from both structures, PLA-PHBV-CA$_c$ and PLA-PHBV-CA$_c$/TPS

- No notable antimicrobial effect was observed for the CA thermoprocessed bilayers, while CA-polyester cast bilayer films showed high antimicrobial capacity (Figure 1), coherently with the higher retention of CA in the film during the processing method. These polyester-starch bilayer films inhibited the microbial growth of both bacteria through the contact with both polyester and starch sides.

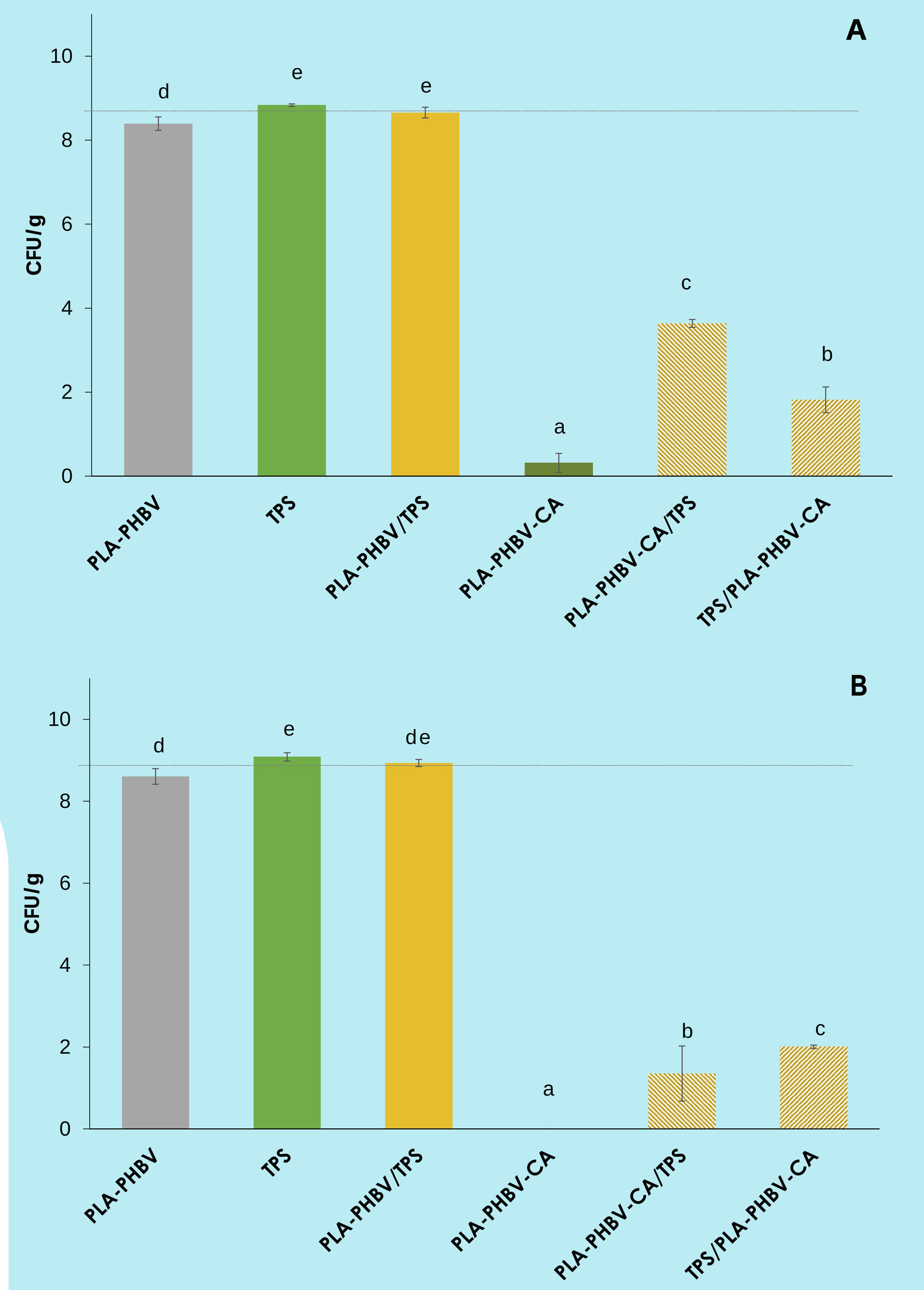

Figure 2. Effect of PLA-PHBV monolayer and polyester-starch bilayer films with carvacrol (CA) on the growth and survival of (A) *L. innocua* and (B) *E. coli* after 6 days of storage at 10ºC. Values obtained for the contact of culture medium with TPS (TPS/PLA-PHBV-CA) or polyester film side (PLA-PHBV-CA/TPS) are given for bilayer films.

CONCLUSION

The combination of starch and biodegradable polyesters with CA in bilayer structures allowed for obtaining films with adequate mechanical properties and a reduction of 85% in the WVP with respect to that of TPS films. The most appropriate method to incorporate the active compound in the bilayer structures was to dissolve the CA in the polyester casting solution, since this approach gave rise to the higher CA retention and therefore significantly higher antimicrobial activity.