

Thermoplastic starch: improving their barrier properties

Almidón termoplástico: mejorando sus propiedades de barrera

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ABSTRACT

There are several strategies for improving functional properties of starch-based materials. Blending with more hydrophobic compounds and bilayer formation are the most common methods. Barrier properties of several formulations obtained by different processing methods were measured. The properties of some obtained materials were compared with those usually employed in food packaging. The most promising materials were those starch PCL blends, compatibilized with grafted poly(ϵ -caprolactone) with polar groups and PCL-starch bilayer films, showing a parallel resistance to mass transfer of two layers with respective good barrier to water vapor and oxygen. Their barrier properties met the food packaging requirements for a wide number of food products.

Key words: blends, bilayers, casting, thermo-mechanical processing.

RESUMEN

Existen diversas estrategias para incrementar las propiedades funcionales de materiales a base de almidón. Las mezclas con compuestos más hidrofóbicos y formación de bicapas son los métodos más comunes. Se determinaron las propiedades de barrera de diversas formulaciones obtenidas mediante diferentes métodos de procesamiento. Las propiedades de algunos materiales adquiridos fueron comparables a la de aquellos usados normalmente en empaques alimentarios. Los materiales más prometedores fueron aquellas mezclas almidón-PCL compatibilizadas con poli(ϵ -caprolactona) injertada con grupos polares y las materiales bicapas de almidón-PCL, que presentan dos capas paralelas con alta barrera al oxígeno y al vapor de agua, respectivamente. Las propiedades barreras de estos materiales se adecuaron a los requerimientos para empaqueo alimentario de un gran número de productos alimenticios.

Palabras clave: mezclas, bicapas, casting, procesamiento termo-mecánico.

Introduction

Of the biodegradable materials used to obtain packing films, starch is one of the most promising polymers, due to its low cost, thermo-processability, and abundance (García *et al.*, 2014; Alves *et al.*, 2015). Starch based-films exhibit some desirable properties, such as high barrier to oxygen, carbon dioxide and lipids, which represent an advantage in food packaging. However, these materials present several drawbacks such as their high water sensitivity and water vapour permeability (WVP), poor mechanical properties and retrogradation throughout storage (Ma *et al.*, 2009; Castillo *et al.*, 2014). The improvement of these characteristics is necessary for starch applications in the plastics industry.

The present work deals with the enhancement of starch-based materials by blending with other compounds and polymers more hydrophobic than the starch in order to adequate their barrier properties to the food packaging requirements. For this purpose, different strategies (polymer

blends, multilayer films by using different techniques of processing) were used.

Materials and methods

Materials

Corn starch was purchased from Roquette (Spain). Glycerol was obtained from Panreac Química, S.A. (Spain). Poly(ϵ -caprolactone) (Mn 80.000 Daltons) was provided by Fluka (Germany). Other reagents were provided by Fisher (Spain).

Methods

Starch-based films (blends and bilayers) were obtained by means of casting, melt blending-compression moulding and extrusion-compression moulding according previous investigations (Ortega-Toro *et al.*, 2014a,b; 2015; 2016a,b). The oxygen permeability (OP) was determined using an Oxtran 1/50 (Mocon, Minneapolis, MN) system considering the Standard Method D3985-05 (ASTM, 2010) at 25°C and 53% RH. The water vapour permeability (WVP)

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of films was determined according to a modification of E96-95 gravimetric method (ASTM, 1995), proposed by McHugh *et al.* (1993).

Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used to carry out statistical analyses of data through an analysis of variance (Anova). Fisher's least significant difference (LSD) was used at the 95% confidence level.

Results and discussion

Components and their ratio of the studied film formulations processed by different methods are reported in table 1.

One of the most important parameters in food packaging is the barrier properties of the materials. Figure 1 shows a map of barrier properties (WVTR vs. OTR) where the studied starch film formulations, obtained by different

methods, were located in order to compare them. The values are normalized at 100 μm of thickness. The values of barrier properties were affected by both the formulation and the processing method. The use of different formulations and techniques of processing resulted in enormous changes in water vapour barrier properties: from ~ 2500 g water vapour $\text{m}^{-2} \text{day}^{-1}$ in films prepared by casting to ~ 10 g water vapour $\text{m}^{-2} \text{day}^{-1}$ in bilayers and films compatibilized with PCL_g. In the same way, the OTR decreased from ~ 30 $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{bar}^{-1}$ (films by casting) until ~ 0.1 $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{bar}^{-1}$ (bilayers and films obtained by melt blending and compression moulding).

The starch-based films with the poorest barrier properties were those obtained by casting. In these films, weaker intermolecular interactions seem to occur in line with the film elaboration method. When the film forming dispersions were cast, water was evaporated slowly giving rise to a less compact matrix as compared with the starch matrices

TABLE 1. Components and ratio of components in the studied film formulations processed by different methods and conventional plastics⁽¹⁾ shown in figure 2.

Formulation	Components	Ratio
PCL	Poly(ϵ -caprolactone)	pure
S	Starch+Glycerol	1:0.3
S-HPMC20-CA	Starch+Glycerol+Hydroxypropyl cellulose+citric acid	1:0.3:0.2:0.01
S60	Starch+Glycerol+Poly(ϵ -caprolactone)	1:0.3:0.4
S60CA	Starch+Glycerol+Poly(ϵ -caprolactone)+citric acid	1:0.3:0.4:0.01
S80	Starch+Glycerol+Poly(ϵ -caprolactone)	1:0.3:0.2
S80-PCL _{g_5}	Starch+Glycerol+Poly(ϵ -caprolactone)+ Poly(ϵ -caprolactone) grafted with glycidyl methacrylate	1:0.3:0.2:0.05
S90-PEG	Starch+Glycerol+Poly (ϵ -caprolactone)+ Polyethylene glycol	1:0.3:0.1:0.02
S90CA	Starch+Glycerol+ Poly(ϵ -caprolactone)+citric acid	1:0.3:0.1:0.01
S95-H ₂ O	<i>Bilayer</i>	<i>Bilayer</i>
	1 st layer: Poly(ϵ -caprolactone)	1 st layer: pure
	2 nd layer: Starch+Glycerol+Poly(ϵ -caprolactone) Interface: water	2 nd layer: 1:0.3:0.05 Interface: pure
S95-SP	<i>Bilayer</i>	<i>Bilayer</i>
	1 st layer: Poly(ϵ -caprolactone)	1 st layer: pure
	2 nd layer: Starch+Glycerol+Poly(ϵ -caprolactone) Interface: water+potassium sorbate	2 nd layer: 1:0.3:0.05 Interface: 1:0.1
SAA	<i>Bilayer</i>	<i>Bilayer</i>
	1 st layer: Poly(ϵ -caprolactone)	1 st layer: pure
	2 nd layer: Starch+Glycerol Interface: water+ascorbic acid	2 nd layer: 1:0.3 Interface: 1:0.1
PS (1)	Polystyrene	-
PP (1)	Polypropylene	-
PET (1)	Polyethylene terephthalate	-
EVOH (1)	Polyvinyl alcohol	-
HDPE (1)	High-density polyethylene	-
LDPE (1)	Low-density polyethylene	-

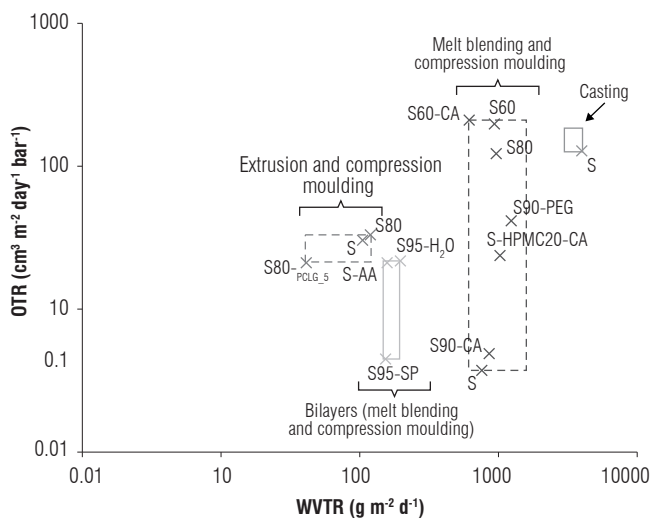


FIGURE 1. Map showing barrier properties of starch-based films with different formulation, obtained by different methods.

obtained by thermo-mechanical methods (melt blending, compression moulding and extrusion).

The starch blends with HPMC or PCL and the addition of CA and PEG promoted some changes in barrier properties, although, in most of the cases, an enhancement in WVP implied a worse OP. This effect was caused by the presence of more hydrophobic dispersed phases with higher oxygen permeability, which facilitated the transfer of gas molecules through the matrix.

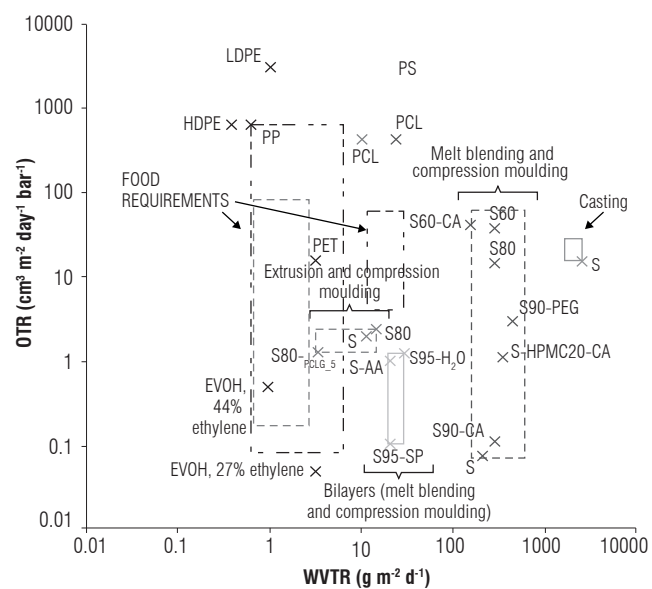


FIGURE 2. Map of barrier properties showing the developed films, some commonly used plastics in food packaging and barrier requirement ranges for some foods.

The most efficient methods for improving the barrier properties, especially WVP, were the formation of bilayer films with starch based and PCL layers and the use of PCL_g as compatibilizers between TPS and PCL phases in the blend films. In figure 1 the good barrier properties of bilayer films can be observed. They maintain the low OTR values of the starch films, but with highly improved WVP due to the parallel arrangement of PCL and starch layers, perpendicularly to mass transfer. Likewise, the starch-PCL blends compatibilized with PCL-grafted (PCL_{G_5}), obtained by extrusion and compression moulding, exhibited the greater water vapour barrier properties. These results were due to the compatibilizing role of PCL_{G_5} at interfacial level in starch and PCL phases, which promoted the interfacial adhesion of both polymers during extrusion of the blend. The reaction mechanisms involved in starch-PCL blends compatibilized were described in detail in a previous work (Ortega-Toro *et al.*, 2016b).

In figure 1 the differences in barrier properties of glycerol plasticized net starch films obtained by casting, melt blending and extrusion (30% glycerol) can be observed, despite the fact that these formulations had similar composition. Dry methods (melt blending, extrusion and compression moulding) gave rise to the formation of a more compact starch matrix in comparison to the casting method, which enhanced film barrier properties. This could be attributed to the compression process conditions which led to greater approximation of the starch chains and more densely packed matrices. When S and S80 (S-PCL blend) films obtained by melt blending in the roller mill or extrusion were compared, differences in barrier properties were also observed. Extrusion led to a notable reduction in WVP of both S and S80 films and lower oxygen permeability for S80, but higher for S films. Melt blending in the roller mill was less efficient than extrusion for defining a more closed polymer matrix probably due to the higher temperature, pressure and shear in the screw which induced differences in the chain packing of the melts, thus affecting mass transfer properties.

Figure 2 exhibits the map of barrier properties, showing the characteristic location of some plastics commonly used in food packaging in order to compare them. Likewise, the zones which define the requirements in barrier properties of different foods are plotted. The bilayer films and blends compatibilized with PCL-grafted showed values of barrier properties in the range of some commonly used plastics. As concerns WVTR, these films met the packaging requirements of some foods (Schmid *et al.*, 2012) such as meat and MAP products (10-50 g water-vapour m⁻² day⁻¹). Some

formulations even exhibited WVTR values of around 5 g m⁻² day⁻¹, meeting the requirements of nuts, snacks and coffee vacuum. Meanwhile, the OTR of these starch-based materials reached the highest requirements for food packaging (around 1 cm³ oxygen m⁻² day⁻¹ bar⁻¹). These materials exhibited comparable OTR values to Ethylene Vinyl Alcohol (EVOH) while their WVTR were close to those of Polystyrene (PS) and Polyethylene Terephthalate (PET).

Conclusion

According to studied barrier properties, the most promising materials were those blends compatibilized with grafted poly (ϵ -caprolactone) obtained by means of extrusion and compression moulding and those obtained as bilayer films incorporating antimicrobial/antioxidant agents at the interface processed by melt blending and double compression moulding. Obtained blends and bilayers showed barrier properties which met the food packaging requirements for a wide number of food products.

Acknowledgments

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Literature cited

- Alves, J.S., K.C. dos Reis, E.G.T. Menezes, F.V. Pereira, and J. Pereira. 2015. Effect of cellulose nanocrystals and gelatin in corn starch plasticized films. *Carbohydr. Polym.* 115, 215-222. Doi: 10.1016/j.carbpol.2014.08.057
- Garcia, P.S., M.V.E. Grossmann, M.A. Shirai, M.M. Lazaretti, F. Yamashita, C.M.O. Muller, and S. Mali. 2014. Improving action of citric acid as compatibiliser in starch/polyester blown films. *Ind. Crop. Prod.* 52, 305-312. Doi: 10.1016/j.indcrop.2013.11.001
- Ma, X., P. Chang, J. Yu, and M. Stumborg. 2009. Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. *Carbohydr. Polym.* 75, 1-8. Doi: 10.1016/j.carbpol.2008.05.020
- McHugh, T. H., R. Avena-Bustillos, and J. M. Krochta. 1993. Hydrophobic edible films: modified procedure for water vapour permeability and explanation of thickness effects. *J. Food Sci.* 58, 899-903. Doi: 10.1111/j.1365-2621.1993.tb09387
- Ortega-Toro, R., A. Jiménez, P. Talens, and A. Chiralt. 2014a. Effect of the incorporation of surfactants on the physical properties of corn starch films. *Food Hydrocoll.* 38, 66-75. Doi: 10.1016/j.foodhyd.2013.11.011
- Ortega-Toro, R., A. Jiménez, P. Talens, and A. Chiralt, 2014b. Properties of starch-hydroxypropyl methylcellulose based films obtained by compression molding. *Carbohydr. Polym.* 109, 155-165. Doi: 10.1016/j.carbpol.2014.03.059
- Ortega-Toro, R., I. Morey, P. Talens, and A. Chiralt. 2015. Active bilayer films of thermoplastic starch and polycaprolactone obtained by compression molding. *Carbohydr. Polym.* 127, 282-290. Doi: 10.1016/j.carbpol.2015.03.080
- Ortega-Toro, R., S. Collazo-Bigliardi, P. Talens, and A. Chiralt. 2016a. Influence of citric acid on the properties and stability of starch-polycaprolactone based films. *J. Appl. Polym. Sci.* 133, 1-10. Doi: 10.1002/app.42220
- Ortega-Toro, R., G. Santagata, G. Gomez d'Ayala, P. Cerruti, P. Talens, A. Chiralt, and M. Malinconico. 2016b. Enhancement of interfacial adhesion between starch and grafted poly(ϵ -caprolactone). *Carbohydr. Polym.* 147, 16-27. Doi: 10.1016/j.carbpol.2016.03.070
- Schmid, M., K. Dallmann, E. Bugnicourt, D. Cordoni, F. Wild, A. Lazzeri, and K. Noller. 2012. Properties of whey-protein-coated films and laminates as novel recyclable food packaging materials with excellent barrier properties. *Int. J. Polym. Sci.* 8, 1-7. Doi: dx.doi.org/10.1155/2012/562381