Macromol. Symp. ***138****, 245–248 (1999)*

Effect of Polymer-Plasticizer Interactions on the Oxygen Permeability of Starch-Sorbitol-Water Films

S. Gaudin[1], D. Lourdin*[2], D. Le Botlan[3], P. Forssell[4], J.L. Ilari[1], P. Colonna[2]

[1] Ecole Nationale d'Ingénieurs des Techniques des Industries Agricoles et Alimentaires, 44322 Nantes, France

[2] Institut National de la Recherche Agronomique, 44316 Nantes, France

[3] Faculté des Sciences et des Techniques, UPRES A 6006, 44322 Nantes, France

[4] VTT Biotechnology and Food Research, P O Box 1500, 02044 VTT, Finland

SUMMARY: This study evaluated the oxygen permeability (O.P.) of starch-sorbitol-water films produced by casting. With a sorbitol content <20%, O.P. (0.15 10^{-16} $cm^2/s.Pa$ for 8.8% sorbitol) was lower than for other polymers classically used as oxygen barriers. With a sorbitol content >20%, O.P. (1.6 10^{-16} $cm^2/s.Pa$ for 24.9% sorbitol) was higher than for starch films without a plasticizer. These results were correlated with molecular mobility as determined by time-domain NMR. Low and high O.P. corresponded respectively to a decrease and an increase of molecular mobility relative to sorbitol content.

Introduction

The purpose of this study was to develop a starch-based formulation usable as a barrier (film or coating) to oxygen. The intended applications for food products (e.g. edible coatings) and non-food materials (biodegradable packaging) relate to global research on the improvement of agricultural products. Previous studies showed effects of additives such as glycerol or sorbitol on mechanical properties of starch-based materials[1-3)]. A relaxation map based on dynamic mechanical indicated the existence of two domains separated by a critical plasticizer concentration (dependent on plasticizer type)[3)]. With sorbitol, antiplasticization mechanical behaviour occurred at levels lower than ~20%, whereas plasticization was associated with phase separation for higher plasticizer contents. This paper considers the oxygen permeability (O.P.) of starch-sorbitol-water films with sorbitol content in relation to molecular mobility investigated by nuclear magnetic resonance (NMR).

CCC 1022-1360/99/$ 17.50+.50/0

Experimental

Samples: Wheat starch films were obtained from water solution by a previously described casting procedure [3]. Before testing, all films (mean thickness ~60 mm) were stored for 72 h at 25°C in an atmosphere with controlled relative humidity (RH) of 57%. After storage, the water content of the films (about 10%) was determined by the Karl-Fisher method, and the sorbitol content by ion-exchange chromatography. Samples for NMR experimentation were prepared in D_2O by an identical method and stored in a D_2O atmosphere to avoid -OD exchange with -OH. Films were then reduced to powder by a cryogrinder. Sorbitol and water content are expressed as a percentage of total weight.

Oxygen permeability measurements: Oxygen transmission rates through film samples were determined using a Mocon Ox-Tran 2/20 equipped with a Coulox sensor (Modern Control, Inc., Minneapolis, MN) operating according to the ASTM Standard Method [4]. The test cell was composed of two chambers separated by 5 cm^2 of film. Films were subjected on one side to 100% oxygen with a constant rate (20 cm^3/min) and on the other to nitrogen (10 cm^3/min). Nitrogen gas containing oxygen transferred through the film was conducted to the coulometric sensor, and measurements were obtained when steady state was reached. The RH of the two gases was controlled by a humidifier.

Nuclear magnetic resonance: The NMR study was performed on a low-field Minispec PC 120 Bruker (0.47 T) NMR spectrometer. Free induction decay signals were obtained using the following parameters: pulse width, 1.1 μs; detection mode, diode; relaxation delay, 2s; acquisition number, 128; attenuation, 28; and temperature, 20°C. Samples were placed in 10-mm diameter, 20-mm high tubes. NMR signals were sampled at 1 MHz, and time relaxation T2* was determined by the NLREG and CONTIN programmes[3].

Results and Discussion

Table 1 shows the O.P. of plasticized starch films with various sorbitol contents at 57, 70 and 90% RH. Oxygen permeability of other polymers are taken from reference [5].

The course of O.P., like that of antiplasticization[6], is discontinuous with increasing sorbitol content. Table 1 shows that O.P. with 57% RH decreased from 1.42 10^{-16} cm^2/s.Pa for films without sorbitol to 0.15 10^{-16} cm^2/s.Pa when 8.8% sorbitol was added. This value for starch films with reduced sorbitol level was lower than the 18.5 10^{-16} cm^2/s.Pa obtained with cellophane, a polymer generally used as an oxygen barrier. From 8.8% to 28.0% sorbitol content, values at 57% RH increased slowly, reaching 1.3 10^{-16} cm^2/s.Pa. When RH values were increased, O.P. for high sorbitol content (28.0%) showed a marked rise from 1.3 10^{-16} to 934.6 10^{-16} cm^2/s.Pa. As an increase in O.P. with RH was usually observed, the O.P. of 4.2 10^{-16} cm^2/s.Pa at 90% RH for low sorbitol content (8.8%) is relatively moderate. This remarkable reaction to oxygen of starch films containing a low level of plasticizer seems of potential interest for packaging or coating applications.

Table 1

Oxygen Permeability (10^{-16} cm^2/s.Pa)						
	Sorbitol content in starch based films					Other polymers
Relative Humidity	0%	8.8%	16.2%	19.9%	28.0%	-
57%	1.42	0.15	0.28	0.31	1.30	cellophane: 18.5
70%	-	0.65	-	-	19.40	PE hd: 494.0
90%	-	4.20	-	-	934.60	EVOH: 13.8 cellophane: 291.9

At the molecular level, NMR data indicated that 6% of the total signal of a starch sample without plasticizer and prepared in D_2O had 'liquid' and intermediate behaviour. Although the protons involved in this mobile part of the starch (i.e. those not belonging to hydroxyl functions) could not be clearly identified by this method, the average relaxation time $T_2{}^*$ of this phase was 105 μs. This parameter (Table 2), indicative of the mobility of the 'liquid' and intermediate phase of amorphous starch, was affected by the addition of sorbitol.

Table 2

Sorbitol content	Average $T_2{}^*$ (μs)
0.0%	105
14.2%	95
22.6%	68
28.2%	94

For a 14.2% to 28.2% sorbitol content in the starch-sorbitol-D_2O system, the relaxation time $T_2{}^*$ was lower than the value obtained for pure starch. These results indicate that sorbitol bound strongly to starch from the moment the first sorbitol molecules were added, inducing a decrease in the mobility of starch molecules in 'liquid' and intermediate phase. At the same time, a broadening of $T_2{}^*$ distribution peaks (Fig. 1) was observed when plasticizer content was increased. This effect was indicative of interactions other than those of starch and sorbitol, apparently corresponding to H-bond type sorbitol-sorbitol or starch-sorbitol-sorbitol interactions within sorbitol "clusters" associated with phase separation, as previously supposed[1-3]. The competition of these two types of interaction between the polymer and the plasticizer could account for the behavioural changes observed with low and high plasticizer content. The first effect, predominant with low sorbitol content, was a reduction of mobility for the most mobile parts of starch, leading to a decrease in the global mobility of the system. In this sorbitol concentration range, the O.P. related to molecular mobility was reduced. The second effect due to sorbitol clusters was predominant with high sorbitol content and enhanced the global mobility of the system. Simultaneously, O.P. increased, becoming more sensitive to RH.

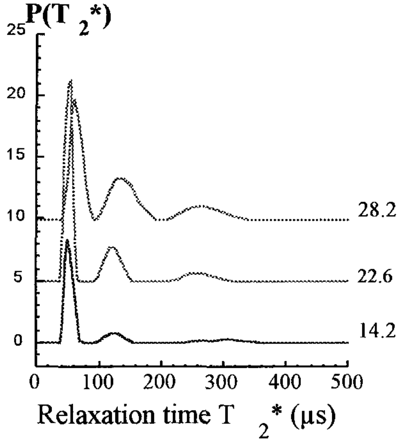

Fig. 1

Conclusion

Our results indicate the influence of molecular interactions on a behavioural property of the polymer-plasticizer system. In addition to oxygen permeability, many characteristics such as mechanical properties are controlled by molecular mobility. A good understanding of these mechanisms should allow precise adaptation of a polymer property by addition of a small quantity of agents.

References

1) D. Lourdin, L. Coignard, H. Bizot, P. Colonna, *Polymer*, **38**, 5401 (1997)

2) P.M. Forssell, J.M. Mikkila, G.K. Moates, R. Parker, *Carbohydrate Polymer*, 34, 275 (1997)

3) S. Gaudin, D. Lourdin, D. Le Botlan, J.L. Ilari, P. Colonna, Submitted to *J. of Cereal Science*

4) Reference ASTM. 1989 D 3985-81, *Annual Book of ASTM Standards*, American Society for Testing and Materials: Philadelphia, PA.

5) *The wiley encyclopedia of packaging technology*, M. Bakker ed., New York, John Wiley & Sons 1986.

6) D. Lourdin, H. Bizot, P. Colonna, *J. Appl. Polym. Sci.*., **63**, 1047 (1997)