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Antiplasticisation and oxygen permeability of starch–sorbitol films

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Abstract

The thermomechanical properties and oxygen permeability of sorbitol–starch–water films were studied. Sorbitol had an antiplasticisation effect for contents below 21% (wt%), as indicated by a ten-fold drop in oxygen permeability 1.43×10^{-16} cm^3 cm/cm^2 s Pa for the sample not containing sorbitol and 0.15×10^{-16} cm^3 cm/cm^2 s Pa for the sample containing 8.8% of sorbitol. This behaviour was related to changes in secondary relaxations. The motions involved in these relaxations were reduced because of the connections established between starch and sorbitol, leading to decreased diffusion of oxygen molecules. For sorbitol contents above 21% (wt%), oxygen permeability increased slightly. Water produced a classic plasticising effect (an increase of oxygen permeability), but at low sorbitol content (8.8%) this was only moderate due to the effect of sorbitol itself (4.3×10^{-16} cm^3 cm/cm^2 s Pa for 23.8% of water). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Studies of the addition of plasticisers to starch were undertaken initially to decrease T_g below ambient temperature and obtain a supple and deformable rubbery material (Kalichevsky & Blanshard, 1993; Lourdin, Coignard, Bizot & Colonna, 1997a; Orford, Parker, Ring & Smith, 1989). However, these additives can produce an antiplasticiser effect by inducing rigidification of the glassy material through a lowering of the yield at break and an increase of the modulus. This type of behaviour has been observed in synthetic polymers such as PVC–dioctylphthalate (Horsley, 1957) and PC–dibutylethylenedibenzoate (Jackson & Caldwell, 1967a,b) and was recently suspected with starch containing low glycerol (Lourdin, Bizot & Colonna, 1997b) or sorbitol content (Gaudin, Lourdin, Le Botlan, Ilari & Colonna, 1999). The cause has not been clearly elucidated, but it would appear that local molecular mobilities play a preponderant role in the mechanisms involved. In the case of the sorbitol–water–starch system, the molecular relaxations studied by DMTA and NMR time domain (Gaudin et al., 1999) showed local mobilities (relaxation β) for starch that were strongly affected by addition of small amounts of sorbitol. This phenomenon could be due to the disappearance of local molecular mobilities and the appearance of the intrinsic mobility of sorbitol, or to a coupling between the β relaxation of starch and the α relaxation of sorbitol. In any event, a decrease of local mobilities in starch has been observed by NMR measurements. Above 21% (total wt%) of sorbitol and a water content corresponding to an equilibrium relative humidity of 0.57, the material behaves mechanically like rubber (i.e. a certain resistance to deformation), although this condition is not attributable to the lowering of T_g below ambient temperature. Though sorbitol has a depressing effect, the T_g value remains greater than 20°C even for the highest sorbitol contents. It has been considered that plastic behaviour is due to the appearance of clusters of sorbitol which allow some mechanical plasticity.

Reports concerning the antiplasticisation of the polycarbonate (Robeson, 1969), the polysulphones (Maeda & Paul, 1987a; Ruiz-Trevino & Paul, 1998), or the poly(phenylene-oxide) (Maeda & Paul, 1987b) indicate that a considerable modification in diffusional properties of gases such as O_2 or CO_2 occurs simultaneously with the increase of the mechanical modulus. For the starch–water system, Benczedi (1999) calculated free volume from experimental density measurements, observing a minimal free volume for a low water concentration (molar concentration between 0.288 and 0.640), which may be indicative of low permeability to gases.

The purpose of this study was to determine whether the antiplasticisation effect revealed by the mechanical properties of starch induced changes in oxygen permeability, as in the case of the synthetic polymers cited earlier.

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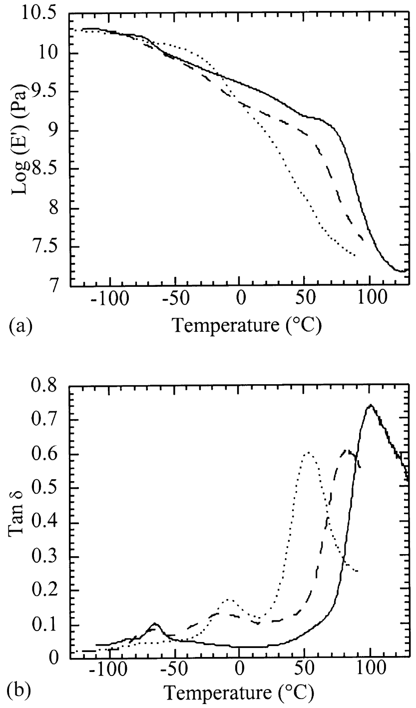

Fig. 1. Storage modulus (E') curves (1a) and tan δ curves (1b) obtained by DMTA at different sorbitol contents (0% —, 10% - - -, 25% …).

2. Materials and methods

2.1. Film preparation

The starch used for film preparation was an A-type wheat starch (27% amylose, 73% amylopectin) of commercial origin (F33, Olgivie Aquitaine). Sorbitol of technical quality was obtained from Prolabo (94126 Fontenay-sous-Bois Cedex, France).

For mechanical measurements, thick films (approximately 0.5 mm) were produced by thermomoulding to 140°C during a 10 min mix of native starch, sorbitol and water.

For permeability measurements, films were obtained by the casting method. Native wheat starch was solubilised in a high-pressure reactor at 138°C for 20 min using a 6% (w/w) suspension in ultrapure water (resistivity 18.2 MW cm) containing sorbitol from 0 to 28% (wt%). This procedure was performed under a nitrogen atmosphere to avoid any risk of degradation. The solution was then spread on a thermostated plate at 70°C. After evaporation of the solvent, a film was obtained.

After elaboration, the hydration of films containing various amounts of sorbitol was controlled by conditioning in different equilibrium relative humidities (ERH).

2.2. DMTA measurements

Thermomechanical measurements were performed on a DMTA MKIV apparatus (Rheometrics Scientific, USA) using the 3-point bending mode. Vibration frequency in bending mode was set at 1 Hz, and the heating rate at 3°C/min. Films were coated with a silicone-based hydrophobic grease to limit dehydration during experiments above room temperature. It was determined that a thin coating of grease had no effect on thermomechanical properties.

2.3. Oxygen permeability measurements

Oxygen permeability measurements were performed on a Mocon Ox-Tran 2/20 equipped with a Coulox sensor (Modern Control, Inc., Minneapolis, MN) operating to the ASTM Standard Method (ASTM, 1989) at atmospheric pressure. The test cell was composed of two chambers separated by the film (5 cm^2). Films were subjected to 100% oxygen on one side and nitrogen on the other. Nitrogen gas containing oxygen transferred through the film was conducted to the coulometric sensor. Measurements were made when oxygen flux was stabilised indicating that steady state was reached. The RH of the two gases was controlled by a humidifier. Temperature was 20°C.

2.4. Assays

Determination of the residual content of water after evaporation was performed by the Karl–Fisher method on a Mettler DL 18.

Sorbitol content was determined by ionic chromatography coupled to pulsed amperometric detection. Film samples (100 mg) were washed in ultrapure water (20 ml), with vigorous stirring to achieve complete leaching of the sorbitol in the solution. After centrifugation, the sorbitol in the supernatant was analysed using a DIONEX MA1 and an ESA Coulochem II amperometrical detector (room temperature; eluant: sodium hydroxide solution 480 mM; flow rate: 0.35 ml/min; detector sensitivity: 20 mA).

Water and sorbitol contents were determined in all final samples and expressed as total weight (wt%). The composition of the samples is indicated below as (sorbitol:water:-starch).

3. Results

3.1. Variations in thermomechanical properties

Fig. 1a and b shows variations of the E' modulus and tan δ as measured by DMTA on samples containing different sorbitol contents. The tan δ peak appearing at 100, 82 and 53°C was associated with loss of the storage modulus E' whose onset was situated at 78, 59 and 29°C, corresponding to the α relaxation for samples containing, respectively, 0% (0:13.5:86.5), 10% (10:9.9:80.1) and 25% (25:10.4:64.6) of sorbitol. The plasticising effect of sorbitol, (temperature decreasing of α relaxation associated with T_g), was clearly apparent.

To show the modifications in low relaxation temperature

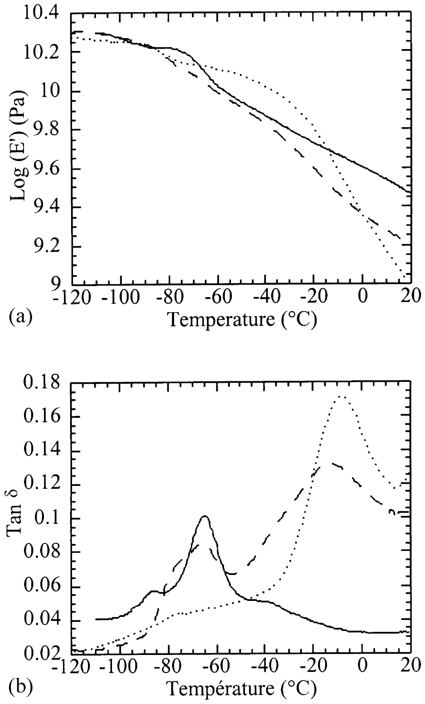

Fig. 2. Storage modulus (E') curves (2a) and tan δ curves (2b) obtained by DMTA at different sorbitol contents (0% —, 10% - - -, 25% …) between −120 and 20°C.

more precisely, a part of Fig. 1 (between −120 and + 20°C) is shown in greater detail in Fig. 2. The sample without sorbitol showed at least two peaks at −86 and −65°C attributed to local mobilities (Bradley & Carr, 1976; Nishinari & Fukada, 1980; Scandola, Ceccorulli & Pizzoli, 1991). For a sample containing 10% sorbitol, a large peak probably composed of two relaxations was observed between −80 and −60°C, and another intense peak appeared at −15°C. For a sample containing 25% sorbitol, local mobilities of the polymer between −60 and −90°C had almost totally disappeared, and a single very intense peak was observed, whose summit at −10°C corresponded to the principal sorbitol relaxation. Each peak of tan δ (Fig. 2b) was associated with a decrease of storage modulus E' with temperature, whose curves are shown in Fig. 2a. As there was no relaxation for the sample containing 25% sorbitol between −120 and −10°C, the storage modulus E' was greater than for samples containing 0 and 10% sorbitol in this temperature range. This behaviour was reversed above −10°C because of the large decrease of E' due to the principal sorbitol relaxation for the sample containing 25% sorbitol.

Table 1
Influence of sorbitol content on oxygen permeability and water sorption of starch films stored at 57% EHR

Sorbitol content (wt%)	Water content (wt%)	Oxygen permeability (10^{-16} cm^3 cm/cm cm^2 s Pa)
0.0	13.8	1.4 ± 0.3
8.8	10.4	0.14 ± 0.06
16.2	9.6	0.27 ± 0.03
20.0	9.2	0.32 ± 0.02
21.0	9.0	0.31 ± 0.02
24.3	10.4	1.45 ± 0.09
28.0	10.9	1.3 ± 0.2

3.2. Variation of oxygen permeability relative to sorbitol content

Films were conditioned at 57% relative humidity for 3 days before analysis (Table 1). Oxygen permeability dropped from 1.43×10^{-16} cm^3 cm/cm^2 s Pa for the sample without sorbitol (0:13.8:86.2) to 0.15×10^{-16} cm^3 cm/cm^2 s Pa for the sample containing less than 9% sorbitol (8.8:10.4:80.8). This value then increased slightly to 0.31×10^{-16} cm^3 cm/cm^2 s Pa for the film (21.0:9.0:70.0). Oxygen permeability increased, reaching 1.45×10^{-16} cm^3 cm/cm^2 s Pa for the film (24.3:10.3:65.3), i.e. a value close to that of the sample without sorbitol. The value obtained for the film (28.0:10.9:61.1) was slightly lower than the preceding one, but the standard deviation for this value was large. Nonetheless, this confirmed an increase as compared to the value obtained for the sample (21.0:9.0:70.0).

The permeability values measured in this study were quite different from those obtained by Arvanitoyannis, Psomiadou and Nakayama (1996), which showed 0.37×10^{-16} cm^3 cm/cm^2 s Pa for 0% of sorbitol and around 10^{-12} cm^3 cm/cm^2 s Pa for 28% of sorbitol. These discrepancies could be due to a different mode of sample preparation as well as to a difference in residual water content. However, the lowest value (0.15×10^{-16} cm^3 cm/cm^2 s Pa) obtained for 8.8% of sorbitol was comparable to that of the EVOH (i.e. 0.12×10^{-16} cm^3 cm/cm^2 s Pa at 0% ERH) (Salame, 1986) which is a material generally used as oxygen barrier. This property makes this type of starch based system of potential interest for limiting oxygen transfers.

3.3. Changes in oxygen permeability relative to equilibrium relative humidity (i.e. residual water content)

Changes in oxygen permeability relative to water content for samples containing 28.0 and 8.8% of sorbitol are indicated in Table 2 and Fig. 3. The water content of films at different ERH was determined from sorption curves obtained in a previous study. Due to rates and changes in oxygen permeability which depended strongly on the sorbitol content the curves in Fig. 3 are represented with two different scales. For the sample containing 28.0% sorbitol, an increase in permeability seems to be quasi-exponential with water content, reaching a value of 934.6×10^{-16} cm^3 cm/cm^2 s Pa for 29.0% of water. However, for the sample containing 8.8% sorbitol the increase in permeability relative to water content was fairly linear but moderate, reaching only 4.3×10^{-16} cm^3 cm/cm^2 s Pa for 23.8% of water. For an equivalent water content, a permeability 50 times greater (more than

Table 2
Oxygen permeability of starch films containing two different sorbitol contents and function of EHR and water content

EHR (%)	Sorbitol content (wt%)			
	8.8		28.0	
	Water content	Oxygen permeability (10^{-16} cm^3 cm/cm cm^2 s Pa)	Water content	Oxygen permeability (10^{-16} cm^3 cm/cm cm^2 s Pa)
57	10.7	0.15 ± 0.06	11.2	1.30 ± 0.40
60	11.0	0.24 ± 0.01	12.0	2.10 ± 0.30
70	13.0	0.60 ± 0.07	16.5	19.43 ± 2.20
80	16.5	2.70 ± 0.90	22.0	127.20 ± 35.40
90	23.8	4.30 ± 0.40	29.0	934.60 ± 48.20

200×10^{-16} cm^3 cm/cm^2 s Pa) was estimated for a sample containing 28.0% sorbitol. These values clearly show that the addition of a small quantity of sorbitol has a moderating effect on oxygen permeability despite large variations in equilibrium relative humidity.

4. Discussion

Although studies of the thermomechanical properties of thin starch-based films (around 100 μm) have already been conducted (Gaudin et al., 1999; Lourdin et al., 1997b), measurements concerning thick films in 3-point bending mode allow better observation of variations of storage modulus E' with temperature. The increase of E' through addition of sorbitol to starch is indicative of an antiplasticising effect attributable to the disappearance of local starch mobility(ies). This effect is masked by the large variations in thermomechanical properties resulting from the glass transition of sorbitol beginning at approximately −10°C. A high modulus can be expected with this type of material through the use of an additive whose glass transition temperature is higher than that of the material.

Permeability, defined as the product of the coefficients of solubility and diffusion, involves a thermodynamic factor (solubility) and a kinetic factor affected by molecular mobilities (diffusion). Glassy polymers are characterised by low mobility and long relaxation times, whereas rubbery polymers show the opposite qualities (Stern, 1994). Diffusion is therefore totally different in these two states. Permeability depends especially on the available free volume for diffusion of gas molecules within the polymer.

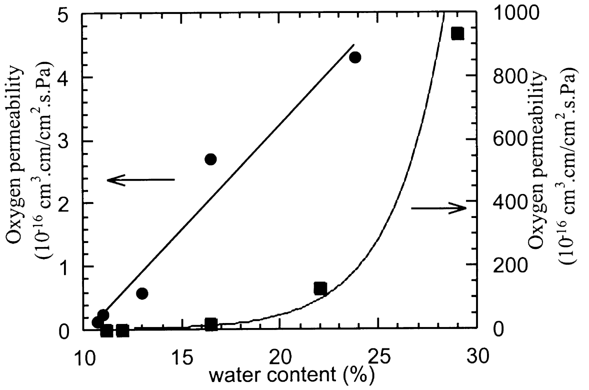

Fig. 3. Influence of water content (wt%) on oxygen permeability at ambient temperature for two sorbitol contents (wt%): 8.8% (●) (left scale) and 28.0% (■) (right scale).

4.1. Glassy state (ERH 0.57)

As demonstrated for mechanical properties (Gaudin et al., 1999), changes in oxygen permeability relative to sorbitol content showed a discontinuity at around 21% for an ERH to 0.57. Despite a decrease in glass transition from around 90–30°C (Lourdin et al., 1997a), film permeability decreased about ten-fold between 0 and 21% of sorbitol. Stern (1994) noted that in glassy state local motions are involved in the diffusion of small molecules. In starch without added sorbitol, local mobilities revealed by low relaxation temperatures favoured oxygen diffusion, whereas the loss of these mobilities, attributable to the creation of bonds between starch and sorbitol, decreased oxygen permeability in the polymer. This phenomenon is comparable to that observed in antiplasticised synthetic polymer such as polycarbonate (Robeson, 1969), polysulphones (Maeda & Paul, 1987a), poly(phenylene oxide) (Maeda & Paul, 1987b) and more recently the starch/water system (Benczedi, 1999). Another relaxation or relaxations resulting mainly from the addition of sorbitol do(es) not favour oxygen diffusion.

For sorbitol contents greater than 21%, Gaudin et al. (1999) showed that the mechanical plasticity of starch was not due to a rubbery state but the probable appearance of clusters of sorbitol, indicating that the matrix was still in the glassy state. Oxygen permeability, even though showing a reversal of tendency at 21% of sorbitol, did not increase abruptly, and the values obtained for high sorbitol contents were comparable to those for a sample without sorbitol. Therefore, the presence of clusters of sorbitol did not seem to favour permeability, probably because of the persistence of starch barrier properties highly interactive with a part of the sorbitol limiting oxygen diffusion.

4.2. Rubbery state (various ERH)

The minimum water contents required to obtain samples in rubbery state ($T_g < 20°C$) were evaluated on the basis of a previous study involving sorption measurements (Lourdin et al., 1997b). Water contents were approximately 19 and 15%, respectively, for 8.8 and 28.0% of sorbitol. For the sample containing 28.0% sorbitol, the marked increase in oxygen permeability with increasing water content was probably due to the transition from a glassy to a rubbery state. These results, corresponding to the behaviour generally observed in synthetic polymers, are attributable to high molecular mobility in the amorphous phase, which facilitates the diffusion of gas within the polymer. This state induces permeability linearly dependent on gas pressure (Rogers, 1985). However, this effect was not observed in the system containing 8.8% sorbitol. Contrary to expectations, the change between glassy and rubbery states did not seem very favourable to oxygen diffusion within the matrix. Strong interactions between starch and sorbitol persisted and were apparently dominant compared to the plasticising effect of water. This relative stability of permeability, despite variations in ambient humidity, is of potential interest in the context of applications requiring the persistence of good starch barrier properties.

5. Conclusion

Sorbitol allows the oxygen permeability of starch films to be modified. In glassy state, decreased permeability results from the creation of links between sorbitol and starch, reducing the motions needed for oxygen diffusion. Although the nature of the motions involved in secondary relaxations is not completely clear, it would appear that changes in these secondary relaxations are responsible for the antiplasticisation affecting mechanical properties as well as oxygen permeability.

The effect of water depends on the sorbitol content of the sample. It has often been observed that higher water content leads to increased permeability in hydrophilic biopolymer films. This effect, often explained by glass/rubber transition, was clearly present in films containing 28.0% sorbitol, but not in the sample containing 8.0% sorbitol. Although the nature of this effect is not entirely understood, it would seem of interest for potential applications of this type of material.

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