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Gas transport properties of starch based films

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Abstract

This paper deals with gas transport properties of starch based films. Oxygen permeability of plasticised starch, octanoated starch, starch–EVOH blend, and PE–starch multilayer was first studied. The best gas barrier properties of starch based films are generally obtained for low water and plasticiser contents.

It was then shown that the interesting low permeability of these systems is due to the low *solubility* of gases. These results broaden the scope of starch gas transport properties, which are generally discussed in terms of mobility (i.e. gas *diffusivity*).

Keywords: Thermoplastic starch; Water; Glycerol; Gas permeability; Gas solubility; Gas sorption

1. Introduction

Starch gas permeability has been studied for several years in order to replace synthetic polymers in packaging applications. Gas permeability of starch, modified starch and plasticised starch membranes have been studied as a function of water hydration (Gaudin, Lourdin, Forssell, & Colonna, 2000; Sala & Tomka, 1993). In general, starch films present rather good barrier properties at low hydration levels and plasticiser content compared to conventional membranes such as EVOH (copolymer of ethylene and vinylic alcohol) or polyamide often cited as references for oxygen barrier properties.

The problem with starch based membranes is to find the proper balance between good barrier properties and mechanical performances. Generally, high plasticiser content is preferred in order to obtain a soft material, but in this case the barrier properties are evidently lower. The second problem is that mechanical and barrier properties are highly dependant on water activity.

In the first part of this paper, we present permeability behaviour of four systems designed to achieve a good balance between barrier properties and conditions of use: 'highly' plasticised starch (glycerol > 12%), octanoated starch, starch–EVOH blend, and PE–starch multilayer. Of course, all the proposed systems leading to 'real' materials can also lead to limited barrier properties compared to more academic starch systems containing low amounts of water and plasticisers.

The second aim of this paper is to discuss/explain the particularities of 'non-real systems' (more academic ones), i.e. containing low amounts of water and plasticisers.

Arvanitoyannis, Kalichevsky, Blanshard, and Psomiadou (1994) have produced a great deal of data on permeability and diffusion behaviour of starch based materials as a function of temperature, water, glucose and fructose contents. In a first approximation, Arrhenius plots of diffusion coefficients and permeability show classical behaviour:

- Theoretically, the permeability coefficient (Pe) is the simple product of diffusivity (D) and solubility (S), which roughly follow an Arrhenius relation as a function of temperature. Thus, the resulting permeability almost follows the same type of relation. As Arrhenius plots of

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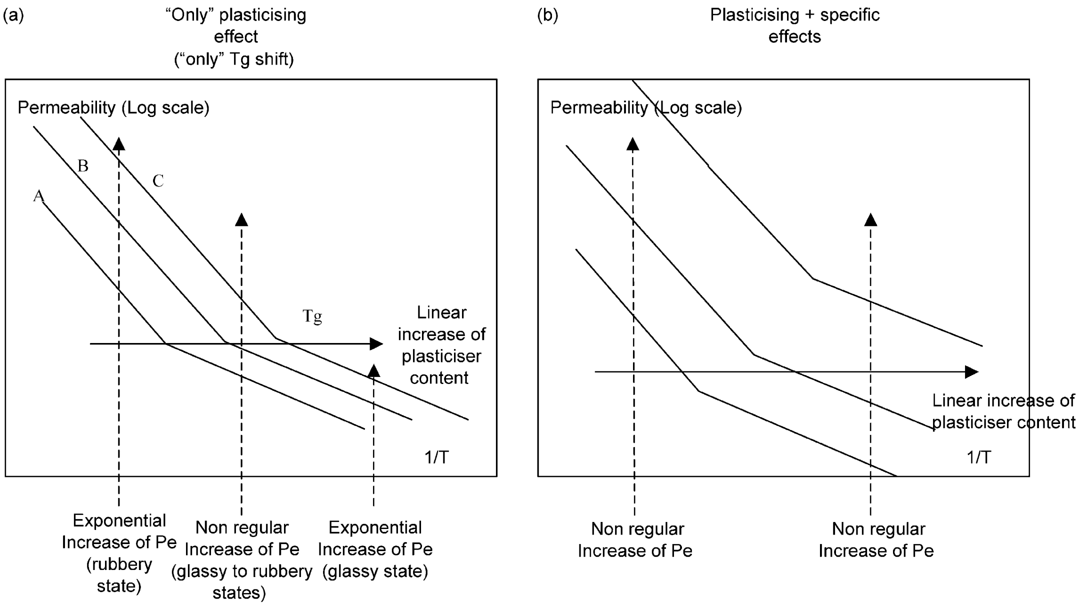

Fig. 1. Illustration of the plasticizing effect on permeability with schematic curves (A)–(C) drawn for three plasticiser contents increasing from (A) to (C).

both permeability and diffusivity have an inflexion point near the glass transition, this same inflexion point is observed for *calculated* solubility (from $PE = DS$).

- It is known that the glass transition is regularly shifted as a function of plasticiser content. In a limited range of plasticiser content, the T_g decrease can almost be considered as linear. This is an approximation, as the Couchman relation also takes into account the water content which varies as a function of plasticiser content (Gaudin et al., 2000). As a consequence, permeability or diffusivity vary exponentially as a function of a linear plasticiser content increase at constant temperature as shown in Fig. 1. Finally, as permeability activation energy is higher above T_g, transport properties are more sensitive to plasticiser content above T_g.

Looking more cautiously at Avranitoyiannis et al. (1994) data, Arrhenius permeability plots show not only horizontal shifts, but also vertical ones (Fig. 1b), suggesting that polyols act as more than model plasticisers (Fig. 1a). Polyols are also able to develop specific interactions or morphologies leading to more complex behaviour.

Indeed, non-classical behaviour has been reported by Gaudin et al. (2000) who have studied oxygen permeability of sorbitol plasticised TPS at *low* plasticiser and water contents. They reported a decrease in oxygen flux (10-fold drop) from 0 to 8.8% plasticiser and attributed that effect to an antiplasticisation phenomenon related to the increase of the starch secondary relaxation for starch/sorbitol systems. Sorbitol can develop strong interactions with starch, which could in turn affect its macromolecular motion and limit oxygen permeability. As a result, permeability decrease is explained by *diffusivity decrease*.

To the best of our knowledge, the majority of the studies devoted to starch or other hydrophilic polymer barrier properties have been discussed using a permeability approach. Nevertheless, it can be seen in the data presented by Avranitoyiannis et al. data (1994), that the diffusion coefficient increases by 3 orders of magnitude in a temperature range of 100 °C, while permeability varies by only with 2. The decrease of the associated *calculated* solubility (negative activation energy) with temperature limits the barrier properties loss as a function of temperature or plasticiser content due to diffusion effect. This intrinsic effect of gas solubility in transport properties is generally not studied. However, complex variations of solubility as a function of temperature (negative and positive) have been observed on other systems (Crank & Park 1968).

It is for this reason that the second part of the paper will focus on the effect of low amounts of water and plasticiser on gas solubility: the aim is to determine the effect of solubility on non-classical permeability behaviour obtained when an antiplasticisation mechanism is suspected. The gas solubility will be determined by a direct microgravimetric method (gas weight uptake). An additional advantage is to obtain data on brittle samples, which are not easy to characterize by permeability measurements.

2. Materials and methods

2.1. Materials

2.1.1. Reference materials

- The starch used for film preparation was an A-type potato starch (25% amylose, 75% amylopectin) provided by the Roquette company (Lestrem, France).
- Plasticised starch granules were obtained by extrusion: a dry blend of starch plasticised with glycerol was prepared

according to the following steps. Native starch was weighed and introduced in a turbo-mixer. Glycerol was then slowly added, while the starch was gently mixed (300 rpm). After completion of glycerol addition, the mixture was stirred at high speed (3000 rpm) to obtain a homogeneous dispersion. The mixture was then placed in a vented oven at 170 °C for 45 min and occasionally stirred, allowing vaporisation of water and diffusion of glycerol into the starch granules. After cooling, water was added to the mixture (20 wt%, dried starch basis) that was once more dispersed at high speed in the mixer (3000 rpm).

- Starch octanoate was obtained from potato starch by reaction with octanoyl chloride (Aburto et al., 1997) at ENSIACET (Toulouse, France). The degree of substitution (*DS*) was determined by ^{1}H NMR: *DS*: 2.8 as already described (Aburto et al., 1997).
- Low density polyethylene (LDPE) was provided by ATOFINA
- Maleic anhydride grafted polyethylene was provided by ATOFINA (LACQTENE 1003 FE 23) and extruded to form a thin film (25 μm) (orevac OE 330).
- EVOH/starch blends granules were obtained by extrusion at 150 °C from mixing of EVOH granules (ethylene vinylic alcohol was supplied by ATOFINA- SOARNOL AT 4403) and plasticised starch granules (made with the protocol previously described).

2.1.2. Film elaboration

Films were obtained by the casting method in water or chloroform depending on their nature, or by thermomoulding as following:

- *Unmodified starch films* (35 μm) were obtained by the aqueous casting method previously described by Gaudin, Lourdin, Forssell, and Colonna (2000) with or without plasticiser. They have been noted as casted starch.
- *Starch octanoates films* were obtained by the casting method in trichloromethane. A solution of modified starch is obtained in the solvent (5% wt/vol) and then spread on an anti-adhesive plate. Natural evaporation is obtained within 1 h. Residual solvent is then removed by annealing 2 h at 60 °C in a ventilated oven. The films thicknesses were equal to135 μm.
- Thin films (54 μm) of *EVOH/plasticised starch* were obtained by compression of granules at 150 °C between heated plates.
- *Multilayer films* (five layers: LDPE/PEg/casted starch/-PEg/LDPE) were obtained by thermomoulding at 120 °C under pressure with a laboratory press equipped with heated plates (Graseby, Specac, UK) and a constant thickness film maker (Graseby, Specac, UK). The diameter is approximately 3 cm and edges are cut to the useful dimensions for permeation properties and water sorption. The inner starch layer is weighed before moulding and hydrated under 11% RH (LiCl saturated solution) for convenient adherence. The constant final thickness (64 μm) corresponds to two external layers of LDPE+PEg (24 μm) and an internal layer of plasticised starch (16 μm). The given typical thicknesses were directly obtained on tested samples after delamination of the complex film.

2.2. Methods

2.2.1. Conditioning

After preparation, films were stored under controlled relative humidity (RH) over conveniently saturated salt solutions at 20 °C. The saturated salt solutions used were: $NaHSO_4$ (50% RH), and KCl (88% RH). All samples were stored until sorption equilibrium, except multilayers which were stored 2 weeks under 88% RH.

2.2.2. Permeation measurements

Three apparatus (noted *m*1 to *m*3) were used to perform oxygen and carbon dioxide transfers during permeation measurements. Depending on the apparatus, two methods were used to determine permeability. The experiments were made either at constant pressure (flux recording) or using a constant volume (pressure recording). The choice of the apparatus depended on membrane geometry and brittleness. For example, the academic apparatus (see *m*2 below) systematically lead to the sample breaking when plasticisers were removed (water and part of glycerol) during desorption under vacuum. The method employed is indicated in Table 1 (*m*1, *m*2 or *m*3).

- *m*1 corresponds to oxygen permeability measurements at constant pressure (1 atm) using a Mocon Ox-Tran 200 H equipped with a coulometric sensor operating according to the ASTM Standard Method (ASTM, 1989). The test cells were composed of two chambers separated by the film which surface was reduced to 5 cm^2 with metallic masks sealed with epoxy glue. The upstream chamber was filled with 100% oxygen and the downstream one with nitrogen. Films were previously equilibrated before testing at the chosen hygrometry. Then, the relative humidity of the gases was controlled in the two chambers by a humidifier and equal to the previous one used for storage. Measurements were made in the steady state, e.g. at constant flux. The temperature was 20 °C.
- *m*2 corresponds to measurements at constant volume and variable pressure. The permeability apparatus consists of a two compartment permeation cell. The permeability was obtained by measuring the pressure increase in the downstream compartment using a datametrix pressure transducer (MKS baratron 121 A). The membrane was outgazed in situ during 48 h at high vacuum using an oil diffusion pump.
- *m*3: gas permeability was measured at 25 °C according to a dynamic isobaric method. The film (5 cm^2) was glued

Table 1
Oxygen and carbon dioxide permeability coefficients for different starch based samples and relative humidities

	Samples	Relative humidity (%)	Measurement method	O_2 permeability (mol/Pa m s)	CO_2 permeability (mol/Pa m s)
Starch based mono-layer films	Starch octanoate *DS* 2.8	0, 57	*m*2	19,300, 20,000	118,280, 129,460
	LDPE (used below for multilayer)		*m*2	597	2100
	Starch blend (28% sorbitol TPS+EVOH) 50/50 wt/wt		*m*2	7590	
	EVOH (used above)		*m*1	0.6	
	Starch 12% glycerol	50	*m*1	0.53	
	Starch 18% glycerol	50	*m*1	1.19, 1.89	
	Starch 25% glycerol	50	*m*1	4.66	
	Starch films:	50			
	Amylose (0–30% glycerol)		See footnotes	3.6–8[a]	
	Amylopectin(0–30% glycerol)		(next column)	2–11[a]	
	Pure amylose	0		±0[b]	19–30[b]
Starch based multi-layer films	PE/PEg/A12%G[c]/PEg/PE	88	*m*3	Not detected	
	PE/PEg/A18%G[c]/PEg/PE	88	*m*3	3.6	
	PE/PEg/A25%G[c]/PEg/PE	88	*m*3	Not detected	

[a] From Crank and Park (1968).

[b] Rankin J. C., Wolf, I. A., Davis, H. A., & Rist, C. E. (1958). *Industrial Engineering Chemistry*, *3*, 120–123.

[c] G, glycerol.

(epoxy glue) on a metallic sheet separating the two chambers of the permeation cell. Each compartment was continuously purged by controlled fluxes: helium in the upstream compartment, O_2 or CO_2 in the second one. The fluxes were identical to prevent any pressure difference between the two chambers. The amount of transferred gas was analysed by gas chromatography (Varian 3800).

2.2.3. Sorption measurements

Sorption measurements were performed on two kinds of starch films (15 μm), containing 0 or 12% glycerol. The apparatus consists of a microgravimetric balance (Setaram TGDTA 92) allowing weight uptake determination by a constant electromagnetic compensation between sample and a reference cells (Joly, Goizet, Schrotter, Sanchez, & Escoubes, 1997). In order to get good accuracy on weight uptakes, two precautions were taken: (i) a volume of carbon fibres equivalent to that of the films contained in the sample pan was introduced into the reference cell to compensate buoyancy. Previous experiments have clearly demonstrated that the use of carbon fibres does not present any water or gas sorption. (ii) The two cells kept at a constant temperature (20 °C) and filled with starch film and carbon fibres, respectively, were strongly degassed under vacuum until constant weight. Two types of experiments were performed. The first one consisted of gas solubility determination on degassed samples. Thus, after high desorption, a CO_2 or O_2 pressure equal to 1 atm was applied to the apparatus and the gas uptake evolution was followed as a function of time until equilibrium. The second type of experiments were performed in two steps in order to determine gas sorption on hydrated starch films: (i) 60–70 mg of starch film was set in the sample cell and degassed. Then, a water evaporator (also degassed after immersion in liquid nitrogen) was allowed to deliver discrete relative humidity regulated by a specific thermostated bath. This temperature was precisely defined as a function of the sample temperature to deliver a chosen hygrometry (50% RH in our study). When the evaporator was opened, the relative humidity increased almost instantaneously to 50% and the water uptake was recorded as shown in Fig. 4. (ii) After equilibrium (constant weight), the gas valve (oxygen or carbon dioxide) was opened until the pressure transducer (MKS Baratron 122B) reached atmospheric pressure.

3. Results and discussion

3.1. Gas barrier properties

Plasticised starch, octanoated starch, starch–EVOH blend, and PE–starch multilayer oxygen permeabilities are reported in Table 1 and compared with the literature. The results can be separated in two simple groups: good, and low or bad barriers. Bad barrier properties were obtained with grafted starch and EVOH/starch blends and good barrier properties with systems involving classical plasticised starch.

3.1.1. Low barrier materials

- The *octanoated starch* samples showed barrier properties lower than LDPE which is often taken as a reference for its low barrier properties. Several explanations can be proposed: (i) compared to unmodified starch, all hydrogen bonding interactions are destroyed and octanoated starch is totally amorphous, (ii) compared to highly plasticised starch, the internal plasticisation due to grafting acts differently: Gaudin et al. (2000) supposed that plasticisers in starch create a strong network of hydrogen bonds, which decreases gas mobility, even when high plasticiser or water contents are introduced, (iii) the grafted chains act as macromolecule separators. This case was observed for crosslinked starch which presented a permeability *increase* for a low increase of crosslinking density (Rioux, Ispas-Szabo, Aït-Kadi, Mateescu, & Juhasz, 2002). The above comments would suggest that good barrier properties should be obtained with samples having a lower *DS*, and grafted with a shorter alkyl chain. Therefore, the problem would then achieve a good compromise between barrier and mechanical properties with such a modified starch: if the internal plasticisation is sufficient to avoid the addition of external plasticiser, the associated barrier properties are very low, as observed here. If an additional external plasticisation is necessary, the problem would then be to find an adequate plasticisation system: polyols do not seem to be very well adapted (Fringant, Rinaudo, Foray, & Bardet, 1998), and the other tested structures are only really adapted to nearly completely modified starch (*DS* ∼3), e.g. glycerol triacetate for starch triacetate. The system tested in this work has interesting performances since it shows good breathable properties for non-barrier applications (high permeability). Its low hydrophilicity leads to identical permeability values at 0 and 57% RH associated with a rather good selectivity: the ratio of CO_2 and O_2 permeability coefficient is around 6, instead of 3 for most of synthetic polymers (Germain, 2000).

- EVOH is the reference material in packaging applications due to its high barrier property towards oxygen and its interesting mechanical properties. Blended with starch, the system is heterogeneous and leads to good mechanical properties (Savary, 1992), which are supposed to be due to a good compatibility between the two components. Nevertheless, we have observed low barrier properties on the studied starch/*EVOH* blends (Table 1). This result can be explained in two ways: (i) the weak adherence between phases is sufficient for mechanical properties, but leads to microporosity; (ii) the starch/EVOH ratio was not very well selected. Indeed, the 50/50 weight/weight proportion corresponds to a 43–57% starch–EVOH volume ratio. This ratio could lead to a complex morphology involving an important contribution of interfaces.

3.1.2. Good barrier materials

As barrier properties are dependant on film composition, the influence of the amounts of plasticiser and water will be discussed in the following.

- The permeability of starch samples, containing several plasticiser contents (0, 12, 18 and 25%) is given in Table 1 and compared with values reported from the literature. The obtained values are in a good agreement with Gaudin et al. (2000): the barrier performances are generally excellent whatever the plasticiser contents, when the moisture content does not exceed 15–20 wt% (dry starch basis), which indeed corresponds to the inflexion point always on the starch water sorption isotherms (Fringant et al., 1996). The value generally given for a high barrier membrane corresponds to a permeability coefficient less than 16×10^{-18} mol/Pa m s (Germain, 2000). The influence of antiplasticisation phenomenon on permeability leading to a Pe decrease when plasticiser content increased is not observed in our case, probably because it has been reported for amounts lower than 12% (Gaudin et al., 2000).

  As shown in Fig. 2, the permeability coefficient varies exponentially with the glycerol content in the range 12–40 wt%. A continuous evolution is noticed even if the glass transition is lowered below the temperature of the permeability test (20 °C) for the highest plasticised systems. A change of slope should be theoretically expected in this domain as explained in Fig. 1 and showed by a ‘non-regular’ (that is to say not exponential) permeability increase. The large increase in permeability is generally interpreted by a diffusivity increase, but the solubility contribution to this permeation evolution increase has still not been clarified.

  Forssell, Lahtinen, Lahelin, and Myllärinen (2002) have obtained a lower plasticisation effect on gas transport phenomenon working with the same materials and roughly under the same conditions. The permeabilities reported by Forssell et al. (2002) are approximately constant below 10% plasticiser and increase only 3 times from 10 to 30 wt% glycerol. Elsewhere, Gaudin et al. (2000) also noticed large discrepancies between their results on sorbitol plasticised starch and those from Arvanitoyiannis, Psomiadou, and Nakayamma (1996). Generally, it can be remarked that gas permeability values

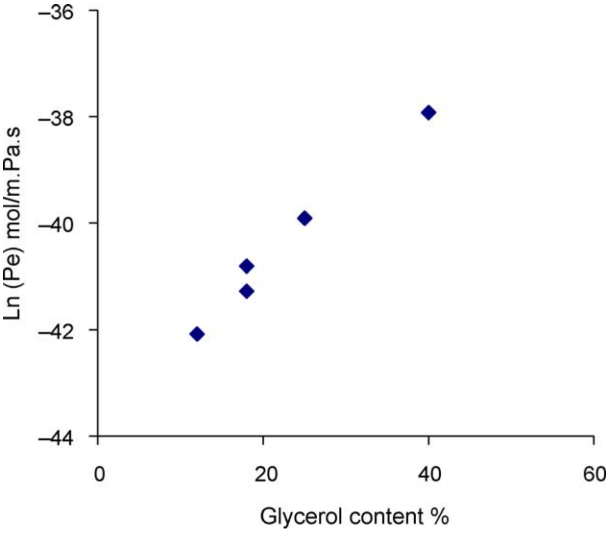

Fig. 2. Effect of glycerol content in thermoplastic starch on oxygen permeability.

reported from literature seemed to be roughly the same for low water and plasticiser contents. In contrast, these properties can be very different for higher contents, suggesting that the conditions of film processing and stabilisation (before and during measurements) have a very significant influence on the material structure and its properties. For example, the processing conditions can have an influence on the sample crystallinity. Arvanitoyiannis et al. (1994) showed that a three order of magnitude decrease of permeability can be obtained from totally amorphous to semicrystalline starch; this is a maximum of amplitude, but low crystallinity rates can lead to non-negligible decrease of permeability (Arvanitoyannis et al., 1996). As retrogradation leads to an increase of barrier properties, the straight line in Fig. 2 should show (in absence of recrystallisation)a 'more exponentially' shape. This should better correspond to the theoretical plasticisation effect presented in Fig. 1a ('glassy to rubbery').

- Gas barrier properties of starch are generally high when water activity is maintained below 65% RH. One way to limit the water sorption in starch is to use multilayer films and in this case hydrophobic polymer is used as the external layer. Table 1 shows gas barrier properties of polyethylene/starch (PE/starch) multilayers processed under 15% RH, and conditioned 15 days at 88% RH before characterization. The experimental system used for this series of samples was not very sensitive, but the results clearly illustrate the high barrier properties of starch systems, when they are protected from water sorption by the presence of PE.

  In fact, the originality of PE/starch multilayers is the especially long time of multilayers equilibration, 15 days, compared to the equivalent geometries of EVOH–PE systems which are water-equilibrated in less than one day. These special properties will be discussed elsewhere on starch multilayers (Dole, Averous, Joly, Della Valle, & Bliard, 2004).

Lastly, it is obvious that this part is not an exhaustive panorama of barrier properties of starch based materials. We can also not conclude that blends of starch or grafted starch generally behave as bad barriers. It remains, however, that the best barrier properties are generally obtained for starch containing low contents of plasticiser and water, which render the film unadapted for packaging (low mechanical properties).

3.2. Gas sorption

The CO_2 and O_2 solubility coefficients were determined at 1 atm using a laboratory designed gravimetric method. The experimental data also allowed the evaluation of the sorption kinetics.

Two materials were studied: unplasticised starch and plasticised starch with 12 wt% glycerol. Two different conditions were applied to each film before gas sorption measurements:

(i) the samples were initially desorbed and dried;
(ii) after desorption, the samples were hydrated at a relative humidity equal to 0.5 leading to water content in the polymer of about 12% (the exact content is given below). The results allow to discuss the influence of plasticisation on gas sorption properties at dry state and at 50% RH to compare the effect of glycerol and water, both introduced in the same proportion.

3.2.1. Gas sorption on unplasticised starch and plasticised starch at dried state

Fig. 3 presents the evolution of CO_2 and O_2 weight uptakes as a function of time for the different materials previously desorbed under vacuum. Low sorption levels (less than 0.1%) were observed for all of the film types. In order to check the experimental reproducibility on such low values, two experiments were made for both gases on unplasticised starch (Fig. 3). A precision of 10% can be estimated on the equilibrium uptake from the obtained results.

The gas solubilities of unplasticised starch expressed in weight percentages are equal to 0.08 and 0.04% for CO_2 and O_2, respectively. These values correspond to a gas uptake of, respectively, 53 and 30 μg for a dried membrane of 67 mg. Plasticised dried starch leads to lower solubility values for CO_2 (0.03%) and no values are reported concerning O_2 solubility since in this case the measurements are largely under experimental sensitivity.

Concerning gas sorption kinetics, diffusion coefficients cannot be obtained with good precision. The sample thickness is low (about 15 μm) and the equilibrium is rapidly obtained, in a few minutes. Due to the non-instantaneous establishment of gas pressure which leads to physical perturbations, the points relative to the beginning of gas uptake cannot be determined (Fig. 3). Thus, it seems to be difficult to represent the evolution

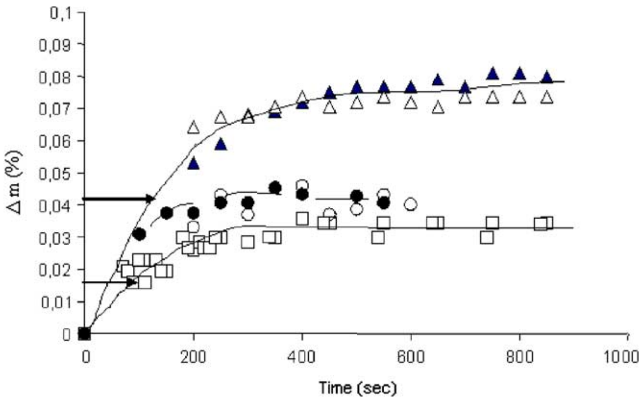

Fig. 3. CO_2 and O_2 uptakes (wt% dried basis) as a function of time (t). CO_2 contents for two unplasticised samples (▲ and △) (to see reproducibility) and for plasticised starch (□). O_2 uptakes for two similar samples (○ and ●) for unplasticised starch films.

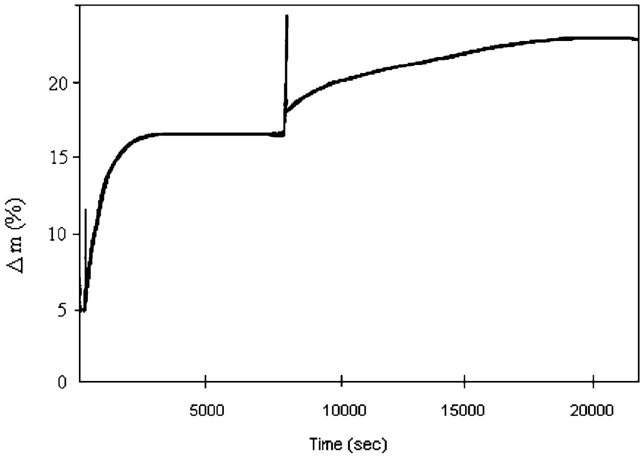

Fig. 4. An example of CO_2 uptake realised on a previously hydrated membrane. The first step is related to moisture regain followed (after equilibration at 50% RH) by a kinetic curve of CO_2 sorption (initial vertical bars are due to physical perturbations of the microbalance beam when water or CO_2 partial pressures were made).

of the uptake as a function of the square root of time and to calculate the diffusion coefficient using Fick's second law. Nevertheless, the time at half sorption has been pointed out on Fig. 3 for CO_2 (see arrows). No great variation is observed between the unplasticised and the plasticised samples. As permeability is related in the case of a Fickian mechanism to the product of gas solubility and diffusion coefficient, it can be suggested that the observed permeability decrease (as a function of the plasticiser content) seems to be related more to a *solubility effect* than to a diffusivity one. Arvanitoyannis et al. (1994) have pointed out the reverse effect, i.e. a diffusivity one. However, as permeability measurements remain very difficult to perform in the absence of water due to film brightness, no more literature can be discussed.

3.2.2. Gas sorption on unplasticised and plasticised starch equilibrated at 50% RH

These experiments consisted of two steps. Firstly, the samples were hydrated until an equilibrium water uptake was obtained. Gas pressure (1 atm) was then applied to the hydrated sample and the evolution of the sample weight was followed as a function of time. An example of the curve obtained for CO_2 sorption on hydrated plasticised starch is reported in Fig. 4.

In the first step of the experiment, the water uptake is slightly lower for the glycerol containing sample than for the unplasticised starch (12 and 14%, respectively) as already reported (Myllärinen, Partanen, Seppala, & Forssell, 2002).

Concerning the second step of the experiment, e.g. the gas sorption on hydrated samples, it should be emphasized that the gas uptake is much higher than the values measured for the same samples at dried state (Table 2). The gas uptake ratio (dried polymer weight basis) is equal to about 5–6% and corresponds to a weight increase of about 3–4 mg for a polymer sample of about 67 mg. Surprisingly, these values are about 100-fold higher than the values determined at dried state. Elsewhere, no great differences are observed as a function of the glycerol plasticisation of the membrane. In fact, the CO_2 uptake on hydrated samples is equal to 5.5 and 5.9% for unplasticised and plasticised starch, respectively. The O_2 uptake obtained on hydrated unplasticised starch is also about the same order of magnitude (5%), and has not been determined for plasticised starch. This particularly high gas solubility does not seem to be linked to that of the gas solubility into the water previously sorbed by starch because (i) at 50% RH the majority of the water is known to be linked to the polymer matrix; water clusters (or free water) are present at higher RH (Fringant et al., 1996); (ii) nevertheless, if this last case is considered for our working pressure, the potential quantity of dissolved gas (CO_2 or O_2) in the amount of water present in hydrated starch leads to a much lower value than our experimental results (Weast & Astle, 1979); (iii) no sorption selectivity is observed between CO_2 and O_2 (Table 2), while the ratio of their respective concentration in water is equal to 28 (near that of our working conditions) (Weast & Astle, 1979).

When considering the sorption kinetics (Fig. 4, second step), it should be noticed that the time to reach gas sorption equilibrium on the pre-hydrated materials is very important compared to gas sorption experiments at dry state and even for the previous simple water sorption experiments (Fig. 4, first step). The sorption half-time is more than one order of magnitude greater (Table 2) for these samples. This unexpectedly behaviour could be explained by a much lower gas mobility into the hydrated

Table 2
Oxygen and carbon dioxide solubilities (wt% dried membrane basis at 1 atm) for starch and plasticised starch

	Unplasticised starch				Plasticised starch (12 wt% glycerol)	
	0% RH		50% RH		0% RH CO_2	50% RH CO_2
	CO_2	O_2	CO_2	O_2		
Gas solubility, wt% (dry basis)	0.08	0.04	5.5	5	0.03	5.9
Sorption half-time $t_{\frac{1}{2}}$ (s)	133	–	1800	–	90	2600

Sorption half-time ($t_{\frac{1}{2}}$) is given to illustrate the variations of the associated gas mobility.

membrane or possibly by a complex sorption mechanism in our study conditions (gas/H_2O special interactions may occurred).

Thus the presence of water in the sample *considerably* modifies the gas *sorption* mechanisms.

3.2.3. Discussion on glycerol and water effects

First of all, if the water and plasticiser contents were higher, the impact of potential morphology changes (crystallisation or retrogradation) has to be taken into account. However, the observed gas solubility increase (as a function of water content) suggests the absence of reorganisation during testing, or an insignificant influence of retrogradation: retrogradation reduces both free volume and available sorption sites.

It is then important to underline that quite similar contents of water and glycerol (about 12% by weight) act completely differently:

- the addition of glycerol in dried starch leads essentially to a decrease of the gas solubility and to a lower water uptake at the lowest water activities ($aw < 0.6$);
- the addition of water to unplasticised starch leads to increased gas solubility as well as a decreased gas mobility which is observed by the longer amount of time necessary to reach the sorption equilibrium.

The only possible conclusion is a modification of site availability: water could open a large number of sites which are not opened by glycerol. These new sites are more difficult to access and the mobility of molecules is lower for the hydrated samples. In contrast, glycerol seems to be placed in sites, which already exist in the dried starch structure, acting as competitors for sorption: the solubility is then lower. Recently, Smits, Kruiskamp, Van Soest, and Vliegenthart (2003) demonstrated the existence of specific interactions between dry starch and glycerol.

The hydrated plasticised samples have nearly the same gas sorption properties as hydrated unplasticised samples, thus showing the strong influence of the presence of water in such a polar polymer on gas sorption.

Finally, compared to dried starch, the theoretical increase of permeability after hydration and plasticisation should be due more to *a solubility increase* than a diffusivity increase as often described in the literature.

4. Conclusion

The first part of this study was devoted to systems scapable of offering mechanical properties good enough to be developed, e.g. starch or grafted blends. The conclusions remain classical: the best barrier properties are obtained for low plasticisers contents (water included), rendering the systems too brittle. No good compromise was found between mechanical and barrier properties.

Concerning gas solubility measurements devoted to simple systems, starch/plasticisers (water and glycerol), the discussion underlined:

- the particularity of dry systems: their high barrier properties as compared to hydrated systems are due to lower gas solubility. This relatively ‘low’ solubility at dried state has rarely been measured. As far as we know, values produced by the literature for usual polymers are most often calculated from the permeation equation ($P = DS$) and thus could not be directly used for comparison (Pauly, 1989).
- the particularity of low hydrated starch (under 50% RH): water specific sorption creates an ‘inert’ free volume available further for a surprisingly high gas solubility.
- only water can open this free volume; glycerol has a very different behaviour on gas transport properties.

The development of starch based gas barrier films must be done taking into account solubility and diffusion behaviours separately. This paper only opens the discussion, showing the limited interest of an experimental approach which stops at the determination of permeability.

Important data is still missing to understand thermoplastic starch systems, i.e. solubility and diffusivity at higher water and plasticiser contents, and their variation with temperature, in order to separate:

- thermodynamic and kinetic effects
- glass transition shifts and specific effects

Work is currently being undertaken to study gas transport phenomenon.

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