Acta Agrophysica, 2006, 7(1), 151-159

WATER VAPOUR TRANSMISSION PROPERTIES OF WHEAT STARCH-SORBITOL FILM

Danuta M. Napierała, Alina Nowotarska

Department of Physics, University of Agriculture
ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@au.poznan.pl

Abstract. The barrier properties of wheat starch-sorbitol cast film with respect to water vapour at three water activity gradients: 0.33, 0.54, 0.94 and temperature range 297- 309 K have been determined. The water vapour permeability was found to be influenced by the water behaviour obeying the Fickian law. Temperature dependence of the permeability coefficient, obtained from the steady-state permeation flux and revealing Arrhenius-type relationships, permitted a calculation of the mean activation energy of water vapour transport through the film. High value of the activation energy for the permeation process at the water activity gradient of 0.54, in comparison to other water activities gradients studied, suggests that in these conditions hydrophilic starch-sorbitol film can be an effective barrier for water vapour.

Keywords: starch film, water vapour transmission, permeation coefficient, diffusion, sorbitol

INTRODUCTION

Biodegradable films based on natural polymers can act as barriers to moisture, which makes them good alternatives to packaging materials for food products. However, compared with synthetic films, the major limitations of these films in food packaging are their relatively low water resistance and poor vapour barrier properties that result from their hydrophilic nature [17]. Starch has been singled out as one of the most promising candidates for future plastic materials because of its attractive combination of price and performance [13]. Numerous studies have been made on starch-based films cast from a solution or gel [1,2,4,7,9,10,14,15]. Reports do show that conditions during the film formation as well as storage conditions and plasticizer presence affect the crystallinity, microstructure of films, mechanical and permeability properties. Water vapour permeability is one of the most important and widely studied properties of edible films. The factors affecting water vapour transport are: the composition, temperature and relative humidity [11]. Understanding the mode of transport of water vapour through the film is important for improving the moisture barrier properties of polymer film.

It was shown previously by dynamic thermal mechanical analysis that wheat starch film plasticized by sorbitol [12] reveals the glass-rubber transition in the range of 270-300 K related with the presence of polymer complexes with sorbitol.

The aim of this work was to determine water vapour transport properties of the same polymer film at variable water vapour activity and temperature range below glass-rubber transition.

MATERIALS AND METHODS

Materials

Unmodified wheat starch and D-Sorbitol from Sigma Chemical Co. were used throughout. Silica gel blue (Chemika, Fluka) and silica gel E, micro porous (Macherey Nagel, Dorem, Germany) were used as desiccants. In order to prepare saturated solutions which provide a constant relative humidity (RH) environment [16], analytically pure $MgCl_2 \cdot 6H_2O$ (RH = 33%), $Mg(NO_3)_2 \cdot 6H_2O$ (RH = 54%) and KNO_3 (RH = 94%) from POCh, Gliwice, were used.

Film preparation

Wheat starch films were prepared by the casting/solvent evaporation method on glass Petri dishes, described previously [12]. To produce the films, 2.5% starch solution was cooked under cover at the boiling point for 1 hour, stirring vigorously on magnetic stirrer. Sorbitol was added to the starch solution at the ratio of 4:10 by weight. The final film solutions were dried in an incubator at 309 K for 48 hours. Starch-sorbitol films were conditioned in polyethylene bags for 7 days before testing.

Films thickness and moisture content

Film thickness was measured using a micrometer (Sylvac S229, Swiss) of 0.001 mm accuracy. Measurements were made at different 8-10 points along two arbitrary diameters of the film sample and the average value was calculated. Film specimens had a mean thickness ranging from 0.06 to 0.11 mm.

The moisture content of starch-sorbitol films was determined by drying the films at 383 K to constant weight (for 12 hours). The initial moisture content of all the films was 5-6% and did not change when the films were stored at water activity of 0.33 and 0.54 while it increased up to 15% ± 2 at water activity of 0.94.

Measurement of water vapour transmission

Water vapour permeability was measured with the gravimetric method [10], using special 125 cm^3 polypropylene cups. They had covers with 3.2 cm diameter holes. The films were cut circularly with a diameter slightly larger than the diameter of the hole. After placing well dried 20 g of silica gel blue and 40 g of silica gel E in each cup, which occupied above half of the cup volume, they were covered with the film. The exposed film area was 8.04 cm^2. Silica packing washer and parafilm were used to seal the system. The cups were placed in desiccators containing saturated salt solution at the bottom, which provided appropriate water activity. Cups were weighed with an accuracy of 0.1 mg, on the Gibertini E50S balance, every 24 h until a steady-state increase in weight was achieved.

The water vapour pressure on the silica-gel inside of the film was assumed to be zero. On the outside the water vapour pressure was calculated by multiplying water activity a_w in the desiccators by the pressure of saturated vapour at given temperature. The samples were tested at a_w gradients of 0.33, 0.53 and 0.94 using the relevant saturated solutions at three control temperatures: 297 ±1, 303 ±1 and 309 ±1 K, in an incubator. For the possible contribution of starch film and polypropylene cup to the vapour transfer, cups with no films were used as the control sample and the rates were first corrected by subtracting the polypropylene values.

The water vapour transmission rate (WVTR) was calculated by applying least-squares analysis to linear variation in weight vs. time. WVTR was obtained by dividing the slope of the linear function by total area of the film.

Permeability coefficient P was a product of the WVTR and the thickness of film dividing to the water vapour pressure difference on each side of the film [3].

RESULTS AND DISCUSSION

Water vapour pressure and temperature are the most significant physical factors determining the water vapour transport through a film. High water permeability, observed in natural polymer films, considerably restricts their use as potential packaging material. Like other biopolymers with hydrophilic groups, the starch-sorbitol film exhibits water activity and temperature dependent permeability. The kinetics of the water vapour transmission through the starch-sorbitol film in the temperature range of 297-309 K and under three different water activities – 0.33, 0.54 and 0.94 exhibited a linear character, as shown Figure 1 and Figure 2.

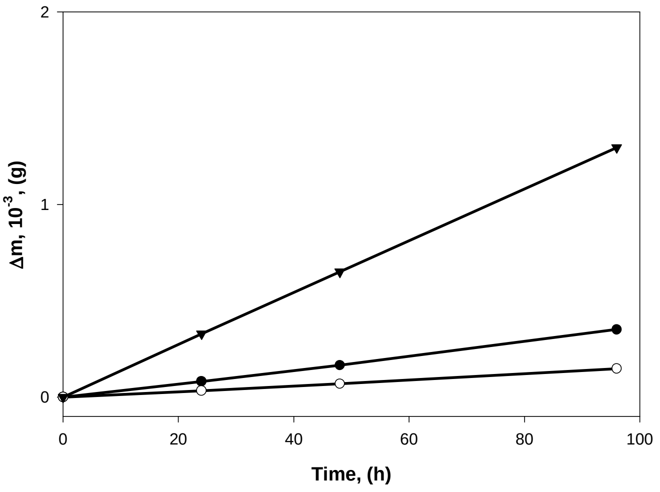

Fig 1. Kinetic curves of water vapour transmission by the starch-sorbitol film at 303 K and under the water activity a_w = 0.33 (●), 0.54(○), 0.94(▼), respectively

The linear character of the curves indicates steady-state water vapour transport and permits determination of the values of WVTR, presented in Table 1 for all the water activities and the temperature range studied.

The lowest WVTR values in the starch-sorbitol film were obtained at 297 K and under the water activity of 0.54. Generally, WVTR increases with increasing temperature in a starch film with sorbitol and it is several times higher when the water vapour activity approaches 1. It is worth noting the very high correlation coefficients for all the least square linearizations, $R^2 > 0.99$.

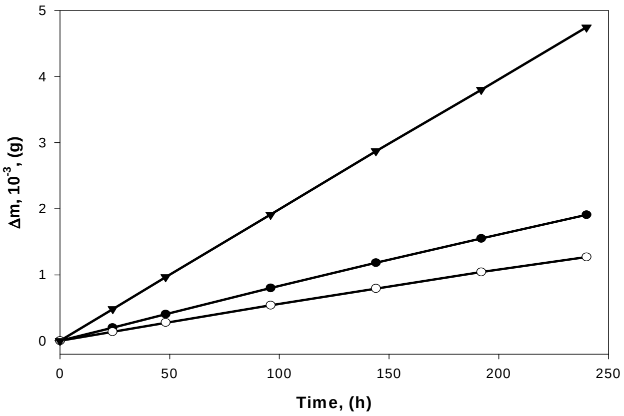

Fig 2. Kinetic curves of water vapour transmission by the starch–sorbitol films at 309 K and under the water activity a_w = 0.33 (●), 0.54 (○), 0.94 (▼), respectively

Table 1. Steady-state water vapour transmission rate (WVTR) through the starch-sorbitol film at different water activity a_w and temperature T

a_w	T (K)	dm/dt (g h^{-1}) 10^{-3}	Correlation coefficient, R^2	WVTR (g m^{-2} h^{-1})
0.33	297	1.43 ± 0.05	0.999	1.78
	303	3.67 ± 0.09	0.999	4.56
	309	5.32 ± 0.06	0.999	6.62
0.54	297	0.85 ± 0.03	0.998	1.06
	303	1.55 ± 0.04	0.999	1.93
	309	7.97 ± 0.07	0.999	9.91
0.94	297	8.25 ± 0.02	0.999	10.26
	303	13.49 ± 0.03	0.999	16.78
	309	19.75 ± 0.04	0.999	24.56

The main processes considered in the transport of water vapour through the polymer film stimulated by the water activity gradient are: water vapour absorption on the polymer surface, solubility of vapour in the polymer lattice, diffusion of water vapour through the polymer matrix and water vapour desorption on the back boundary surface [16]. Water solubility is not affected by thermal treatment [5], therefore the temperature effect of water permeability corresponds to water diffusion changes.

The steady-state water vapour diffusion can be described by the Fick law. It is based on the assumption that the rate of transmission of diffusing substance through the surface *S* (diffusion stream density) is proportional to the concentration gradient perpendicular to the surface [1,4]:

$$J = \frac{dm}{dt}\frac{1}{S} = -D\frac{dc}{dx} \tag{1}$$

where *D* is the diffusion coefficient.

Taking into account that the one-dimensional water vapour concentration gradient through the film is equal to the gradient of its density on the sides of the films, which is ensured by the experimental conditions, the diffusion coefficients have been calculated from the Fick law. The values of water vapour permeability and diffusion coefficients at the set conditions of temperature and water vapour activity are given in Table 2.

Table 2. The values of permeation coefficient *P*, diffusion coefficient *D* and activation energy E_P of water vapour transport through the starch-sorbitol film at different water activity and temperature. The sixth column contains the values of water binding energy E_B calculated from equation (3)

a_w	*T* (K)	*P*, 10^{-11} (g m^{-1} s^{-1} Pa^{-1})	*D* 10^{-9} (m^2 s^{-1})	E_P (kJ mol^{-1})	E_B (kJ mol^{-1})
0.33	297 303 309	3.37 3.89 4.14	4.63 5.45 5.88	13.1 ($R^2 = 0.958$)	2.84 ± 0.08
0.54	297 303 309	0.39 0.71 4.70	0.54 0.99 6.68	160.0 ($R^2 = 0.911$)	1.68 ± 0.12
0.94	297 303 309	6.30 7.40 7.74	8.65 10.36 11.00	13.1 ($R^2 = 0.912$)	0.16 ± 0.02

The temperature-dependence of permeability in a polymer film can be expressed as [1]:

$$P = P_0 \exp(-E_P / RT) \tag{2}$$

where E_P is the apparent activation energy of permeation, *R* – gas constant, *T* – temperature.

The inflection in the slope of permeability vs the inverse temperature plots gives an indirect estimate of the activation energy. The activation energy of the water vapour permeation at low (0.33) and high (0.94) water vapour activities was about 13 kJmol^{-1}, whereas for 0.54 activity the activation energy was over 10 times higher (Tab. 2). The water vapour activity is temperature dependent [8] and it defines the binding energy of water molecules by the relation:

$$E_B = -RT\, ln\, a_W \tag{3}$$

On the basis of this relation the water binding energy E_B was determined in the temperature range studied (Tab. 2), which enabled their comparison with the activation energy of the water vapour permeability through the film. The differences between the activation energy of water vapour transport and the water binding energy for the three water activity values considered indicate that the water transportation process through a starch film with an addition of sorbitol at higher water vapour pressure is much more complex than that at lower activity of 0.33 at which the activation energy of water vapour transport is not much higher than the water binding energy.

Table 3. Water vapour permeability of starch-sorbitol film and some edible and common packaging materials

Polymer	Water vapour permeability (g m^{-1} s^{-1} Pa^{-1}) 10^{-11}	References
Wheat starch-sorbitol,	0.39-7.74	Present study,
Potato starch-sodium caseinate-sorbitol	5.2-26.5	[1] Arvanitoyannis, Biliaderis (1998)
Potato starch-glycerol, thermoplastic compression molded	7.3	[2] Arvanitoyannis *et al* (1996)
Maize starch	0.3-15	[7] Krogars *et al*. (2003)
Yam starch	9.6-18.1	[10] Mali *et al*., 2002
Amylose-glycerol	119	[14] Rindlav-Westling (1998)
Amylopectin-glycerol	143,5	[14] Rindlav-Westling (1998)
Wheat gluten	3.8 - 240	[16] Roy et al. (2000)
Gellan-glycerol	19.4	[17] Yang, Paulson (2000)
Chitosan	0.44-1.14	[6] Kittur *et al*. (1998)
LDPE[1]	0.09	[14] Rindlav-Westling (1998)
EVOH[2]	0.29	[14] Rindlav-Westling (1998)
HDPE[3]	0.03	[11] McHugh *et al*. (1993)
Polyester	0.25	[11] McHugh *et al*. (1993)

[1] Low density polyethylene, [2] Ethyl vinyl alcohol, [3] High density polyethylene.

Table 3 gives the water vapour permeability values *P* for a few known biopolymers and synthetic polymers. As follows from the data, despite significant differences in the conditions of measurements the values of *P* are comparable for natural polymers. Synthetic materials are characterized by the lowest permeability. The permeability *P* of starch film with sorbitol determined at the water activity of 0.54 at 297 K is close to the value obtained for polyester, which means that in certain conditions natural polymers can act as effective barriers for water vapour transportation.

CONCLUSIONS

1. The starch film plasticized by sorbitol, due to their hydrophilic characters, exhibits temperature and water activity gradient–dependent water vapour permeation. The permeation coefficient is higher than for synthetic polymer films but, on the other hand, is much lower than that for starch polymer components – linear amylose and branched amylopectin.
2. The most protective barrier to the water transport is the starch-sorbitol film under the intermediate water activity gradient of 0.54.

REFERENCES

1. **Arvanitoyannis I., Biliaderis C.G.:** Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends. Food Chemistry, 62(3), 333-342, 1998.
2. **Arvanitoyannis I., Psomiadou E., Nakayama A.:** Edible films made from sodium caseinate, starches, sugars or glycerol. Part I. Carbohydr. Polym., 31, 179-192, 1996.
3. **Ayranci E., Būyūktaş B.S., Çetin E.E.:** The effect of molecular weight of constituents on properties of cellulose-based edible films. Lebensmittel-Wissenschaft und-Technologie, 30, 101-104, 1997.
4. **Garcia M.A., Martino M.N., Zaritzky N.E.:** Lipid addition to improve barrier properties of edible starch-based films and coating. J.Food Sci.,65(6), 941-947, 2000.
5. **Hernández-Muñoz P., Villalobos R., Chiralt A.:** Effect of thermal treatments on functional properties of edible films made from wheat gluten fractions. Food Hydrocolloids, 18, 647-654, 2004.
6. **Kittur F.S., Kumar K.R., Tharanathan R.N.:** Functional packaging properties of chitosan films. Z. Lebensm. Unters Forsch A, 206, 44-47, 1998.
7. **Krogars K., Heinämäki J., Karjalainen M., Niskanen A., Leskelä M., Yliruusi J.:** Enhanced stability of rubbery amylose-rich maize starch films plasticized with a combination of sorbitol and glycerol. Int. J. Pharmac., 251, 205-208, 2003.
8. **Labuza T.P.:** Moisture Sorption: practical aspects of isotherm measurements and use. Minneapolis, MN; American Association of Cereal Chemists, 1984.

9. **Lawton J.W.:** Effect of starch type on the properties of starch containing films. Carbohydr. Polym., 29, 203-208, 1996.
10. **Mali S., Grossmann M. V. E., Garcia M.A., Martino M.N., Zaritzky.:** Microstructural characteri-zation of yam starch films. Carbohydr. Polym., 50, 379-386, 2002 .
11. **McHugh T.H., Avena-Bustillos R., Krochta J.M.:** Hydrophilic edible films: modified procedure for water vapor permeability and explanation of thickness effects. J.Food Sci., 58(4), 889-903, 1993.
12. **Napierała D.M., Biskupski P., Nowotarska A., Poliszko S.:** Glass-transition in starch-sorbitol film. Acta Agrophysica, 4(1), 105-113, 2004.
13. **Petersson M., Stading M.:** Water vapour permeability and mechanical properties of mixed starch-monoglyceride films and effect of film forming conditions. Food Hydrocolloids 19, 123-132, 2005
14. **Rindlav-Westling A., Stading M., Hermansson A-M., Gatenholm P.:** Structure, mechanical and barrier properties of amylose and amylopectin films. Carbohydr. Res., 36, 217-224, 1998.
15. **Rioux B., Ispas-Szabo P., Aït-Kadi A., Matescu M.A., Juhász J.:** Structure-properties relationship in cross-linked high amylose starch cast films. Carbohydr. Polym., 50, 371-378, 2002.
16. **Roy S., Gennadios A., Weller C.L., Testin R.F.:** Water vapor transport parameters of a cast wheat gluten film. Industrial Crops and Products, 11, 43-50, 2000.
17. **Yang L., Paulson A.T.:** Mechanical and water vapour barrier properties of edible gellan films. Food Research International, 563-570 33, 2000.

PRZEPUSZCZALNOŚĆ PARY WODNEJ W FILMACH SKROBI Z SORBITOLEM

Danuta M. Napierała, Alina Nowotarska

Katedra Fizyki, Akademia Rolnicza
ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@au.poznan.pl

Streszczenie. Filmy skrobi pszenicy z sorbitolem, otrzymywane metodą kastingową, poddane zostały badaniom zdolności transmisji pary wodnej, przy trzech gradientach aktywności pary wodnej: 0.33, 0.54 i 0.94 oraz w zakresie temperatur od 297 do 309 K. Z pomiarów ustalonego strumienia masy pary wodnej wyznaczono szybkość przepływu pary wodnej, współczynnik przepuszczalności oraz współczynnik dyfuzji. Na podstawie temperaturowej zależności współczynnika przepuszczalności, analizowanej we współrzędnych równania Arrheniusa, określona została energia aktywacji w procesie transportu pary wodnej przez filmy skrobiowe. Wysoka wartość energii aktywacji przy gradiencie aktywności wody 0.54, sugeruje, iż w tych warunkach hydrofilowy film skrobi uplastycznionej sorbitolem może stanowić skuteczną barierę dla przepływu pary wodnej.

Słowa kluczowe: film skrobiowy, transmisja pary wodnej, współczynnik przepuszczalności, dyfuzja, sorbitol