

Study of diffusion and permeation of gases in undrawn and uniaxially drawn films made from potato and rice starch conditioned at different relative humidities

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The permeability coefficients of potato and rice starches were studied at different relative humidities and related to the diffusion and solubility rate over a range of temperatures (0–90°C). Inflections in the permeability and diffusivity plots versus $1/T(K)$ provide an indirect indication of the glass transition; these values are in satisfactory agreement with the results of differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) measurements. Both uniaxially drawn and undrawn films were evaluated and the permeability values were correlated with the % crystallinity (determined by wide angle X-ray scattering and DSC) that developed on storage. The incorporation of sugars (fructose, glucose and sucrose) in the starches and their subsequent storage at 20°C was related to the process of crystallization. Fructose and glucose, for example, induce an increase in the rate of crystallization but decrease the permeability, diffusivity and solubility, whereas sucrose, by retarding the crystallization, has precisely the contrary effects. The synergistic action of sugars and water in lowering the glass transition (T_g) by plasticizing the potato and rice starch films is explicable in terms of the Couchman–Karasz equation if not complicated by phase separation.

The values of the activation energies determined by experiment coincide with those calculated theoretically from given models where the % crystallinity is an important factor, which confirms the significance of crystallinity in the permeability of such films.

INTRODUCTION

Literature survey

The commercial importance of the selective permeability of natural and synthetic films to certain gases has led to several workers investigating the permeability–

diffusivity relationships for a wide range of film–gas combinations (Amerongen, 1947, 1949; Simril & Herschberger, 1950; Stannett & Szwarc, 1955; Waack *et al.*, 1955; Heilman *et al.*, 1956; Myers *et al.*, 1960; Braunish & Lenhart, 1961; Michaels & Bixler, 1961; Anrady & Sefcik, 1984; Wang & Porter, 1984; Arvanitoyannis *et al.*, 1992). A particularly strong interest has been shown recently in the effect of crosslinked polymeric films on the diffusivity and permeability of gases (Barrer & Skirrow, 1948; Pace & Datyner, 1979a,b,c; Andrady *et al.*, 1980; Andrady & Sefcik, 1983).

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Although the diffusion of gases in amylose acetate has been investigated (Patel *et al.*, 1977) and a study on the gas permeability of thermoplastic starch has been recently reported (Tomka, 1991), no similar study has been carried out on natural starches of different origins, e.g. rice and potato starch, and their blends with sugars (fructose, glucose and sucrose) and water.

Theoretical overview

It is generally accepted that Fick's first law (Zolanz & Fleming, 1992) of diffusion applies to the transmission of gases from one side of the film to the other:

$$J = -D \nabla C \quad (1)$$

where J is the flux, D is the diffusion coefficient and C refers to the local gas or penetrant concentration. Assuming that a unidirectional diffusion through a flat membrane occurs, then eqn (1) can be expressed as

$$J_i = -D_{i(c_i)} \frac{dc_i}{dx} \quad (2)$$

where $D_{i(c_i)}$ signifies that the diffusion coefficient is dependent on the composition of penetrant i . The formula for the determination of the diffusion constant is as follows:

$$D = \frac{d^2}{6\theta} \quad (3)$$

where d is the thickness of the film and θ is the time lag of the permeation. The lag is related to the time required by the gas to establish an equilibrium in an originally gas-free film. The extrapolation of the pressure increase-time curve to the zero-axis will produce the time lag (θ) (Amerongen, 1947, 1949). The quantity of gas (Q) that will then pass through the film is directly proportional to the difference in the pressure exerted by the gas on each face of the film ($p_1 - p_2$) and is inversely proportional to its thickness (x). It is also directly proportional to the area exposed (A) and the time (t) for which permeation occurs, and the relationship may be expressed with the following equation:

$$Q = \frac{PA t (p_1 - p_2)}{x} \quad (4)$$

where P has a constant value for a specific combination of gas and polymer at a given temperature and is variously known as the 'transmission factor', 'permeability factor (or P -factor)', 'permeability constant' or 'permeability coefficient' (van Krevelen, 1990). Assuming that the diffusion constant (D) is independent of concentration and Henry's law (the weight of the substance which dissolves in a constant mass of polymer is directly proportional to the partial pressure of the substance) applies, then the permeability and diffusion constant (P and D , respectively) are interrelated by eqn (5):

$$P = DS \quad (5)$$

where S is the solubility constant for a given permeant/polymer system.

The solubility of a gas in glassy synthetic polymers has been described by a series of models, including the dual-mode, matrix and free volume theory models. The dual-mode sorption model gives the local flux J as a total of two different sorption processes (Paul & Koros, 1976; Koros *et al.*, 1977; Chan *et al.*, 1978):

$$J = -D_D \frac{dC_D}{dx} - D_H \frac{dC_H}{dx} \quad (6)$$

where D_D and D_H refer to the mobility of dissolved and Langmuir sorbed components, respectively; and $C = C_D + C_H$, where C_D denotes gas 'dissolved' in accordance with Henry's law and C_H denotes gas 'absorbed into holes'.

The matrix model presupposes the existence of a single population (Raucher & Sefcik, 1983a,b). The diffusion coefficient is given by

$$\bar{D} = D_0 \exp(\beta c) \quad (7)$$

where β is a measure of the penetrant-induced depression of the polymer glass transition and c is the concentration of the sorbed penetrant.

The free volume theory of diffusion in synthetic polymers was first introduced by Fujita (Fujita *et al.*, 1960; Fujita, 1968) and, subsequently, various modifications have been suggested to improve its applicability (Frisch *et al.*, 1971; Vrentas & Duda, 1976, 1977, 1986). According to the free volume theory, the transport of molecules depends on the availability of free volume and energy to overcome the polymer-polymer attractive forces. The flux of penetrant can be described by

$$J = -D_T \frac{d\phi}{dx} \quad (8)$$

where D_T is the thermodynamic diffusion coefficient and ϕ is the fractional free volume. The fractional free volume V_f in a polymer is believed to be influenced by concentration, temperature and pressure (Stern *et al.*, 1983), such that

$$V_f = \phi_{fs}^0 + \Delta\alpha(T - T_s) - \Delta\beta(p - p_s) + \gamma\phi \quad (9)$$

where ϕ_{fs}^0 is the fractional free volume of the pure polymer at the reference temperature and pressure (T_s and p_s , respectively) — usually $T_s = T_g$ and $p_s = 1$ atm; $\Delta\alpha$ and $\Delta\beta$ are the differences in the thermal expansion coefficients and compressibilities above and below T_g , respectively; and γ is the parameter describing the ability of the penetrant to plasticize the polymer.

Finally, the effects of temperature on the transport (diffusion) and solubility rate are described in terms of an activated process following Arrhenius equations:

$$D = D_0 \exp(-E_d/RT) \quad (10)$$

$$S = S_0 \exp(-E_s/RT) \quad (11)$$

where E_d is the activation energy of diffusion and E_s is the heat of solution.

Of course the rate of gas permeation depends on the size, shape and polarity of molecules of the permeant as well as the ease with which the molecules may be condensed (van Krevelen, 1990). Indeed, it has been shown that the permeability coefficient can increase by at least three times when nylon-6, nylon-8, nylon-12 and their copolymers and cellulose films have been conditioned at 100% relative humidity (Hennessy *et al.*, 1967; Arvanitoyannis & Blanshard, 1993).

Starch — crystallization—gas permeation

Since starch is the principal food reserve polysaccharide in the plant kingdom and forms the major source of carbohydrates in the human diet it is not surprising that there have been many investigations of its semicrystalline character and of the process of re-crystallization after gelatinization (Moesi & Sterling, 1966; Kainuma & French, 1971, 1972; Sterling, 1978; Marsh & Blanshard, 1988) and the effect of sugars and water upon its crystallization (Erlander & Tobin, 1967, 1968; Gough & Pybus, 1973; Oosten, 1979, 1982, 1984; Evans & Haisman, 1982). However, no detailed investigation of the gas diffusivity and permeability of potato and rice starches and their blend with sugars and water has been reported.

Objectives

The aim of the work reported in this paper is:

- To study and compare the procedure of diffusion and permeation of a variety of gases (N_2 , O_2 and CO_2) in films made of potato and rice starch both above and below the glass transition temperature (T_g).
- To investigate the effect of introducing water (acting as a plasticizer) and sugars (promoting or retarding the crystallization process) upon the diffusion and permeation parameters of the starch films.
- To calculate the activation energies for diffusion and permeation and correlate them to the starch/sugar/water composition.

EXPERIMENTAL

Materials

Rice starch and potato starch were purchased from Fisons plc. D-Glucose, D-fructose and sucrose (analytical grade) were purchased from Sigma.

Experimental techniques

Preparation of samples in the glassy state

Rice and potato starch suspensions (starch/water 30%, w/w) were rendered amorphous by gelatinizing and roller drying (one process) at 140°C: roller drier speed, 10 rev min⁻¹; pressure, 32 psi (221 kPa); gap, 1 mm; diameter, 165 mm; and width, 150 mm.

Preparation of samples of blends of starches with sugars and water

Blends of rice and potato starches of various percentages (5–40%, w/w) of sugars (fructose, glucose and sucrose) and different water contents were prepared. The desired water/sugar solution was first pre-frozen and ground in a pestle and mortar under liquid N_2 and then mixed with the required amount of starch. After, the material had been allowed to rise to ambient temperature, it was then extruded by using a Brabender single-screw extruder at 80°C. The extrusion conditions were as follows: flow rate, $6.3\text{--}7.6 \times 10^{-3}$ kg s⁻¹; screw diameter, 1.25 cm, die diameter 0.25 mm; and, screw compression ratio, 1:1.

Preparation of films for permeability measurements

The starch/water or starch/sugar/water films were prepared according to the technique described by Arvanitoyannis and Blanshard (1993). However, the pressing temperatures and times were 90–95°C and 5–6 min, respectively.

Conditioning of starch samples at different relative humidities

Saturated solutions of various salts in water were used to obtain known relative humidities of air circulating in sealed enclosures, which were maintained at an ambient temperature of $23.0 \pm 1.0^\circ\text{C}$ with the aid of an incubator and a circulating fan (size 2, Gallenkamp).

The moisture content of the starch or starch/sugar samples was determined by drying the sample in a vacuum oven (60°C) to constant weight and then equilibrating over an appropriate saturated salt solution for 48 h.

Wide angle X-ray measurements

X-ray diffraction measurements were performed using a Philips PW10.20 diffractometer from 5–40° (2 θ). The crystallinity was determined according to the method described previously (Marsh & Blanshard, 1988).

Dynamic mechanical thermal analysis (DMTA) measurements of T_g

The dynamic mechanical thermal analyser (DMTA Mark 1, Polymer Laboratories, Loughborough), with a heating rate of 2°C min⁻¹, and a single cantilever bending mode at 1 Hz was calibrated each day and measurements were made on at least duplicate samples.

The glass transition may be defined as the midpoint between the onset of the drop in the elastic modulus $\Delta E'$ (obtained from the intercept of the 'glassy' baseline and the tangent to the point of the steepest drop in modulus) and the peak in $\tan \delta$ ($\tan \delta = E''/E'$, where E'' is the loss modulus). This procedure normally gave agreement within $\pm 3^\circ\text{C}$. The temperature difference between the $\tan \delta$ peak and the drop in elastic modulus ($\Delta E'$) gives a measure of the breadth of the glass transition region.

Differential scanning calorimetry (DSC) measurements

DSC measurements were made using a Perkin-Elmer DSC-2 equipped with a liquid N_2 cooling accessory and connected to an Amstrad PC and Epson printer. Hermetically sealed aluminium pans were used with an empty aluminium pan for reference. Temperature calibration was made with cyclohexane, dodecane and octane. Heat-flow calibration was made by reference to the known melting enthalpy of indium metal (purity 99.99%) from Goodfellows Metals. The purge gases used were dry helium and dry nitrogen.

The midpoint of the DSC step change in heat capacity (defined as T_g) generally occurs between the $\tan \delta$ peak and the temperature defined by the extrapolation of the two linear parts of the modulus E' (storage modulus).

Uniaxial drawing of films

Unidirectional stretching was carried out in the tangential gaps between rolls at different circumferential velocities. The starch films were transported by the feeding rolls at a rate V_1 and stretched by the drawing rolls at a rate $V_2 > V_1$. The stretching ratio λ equals V_2/V_1 . At the boundary of the film the starch is only subjected to a tension in the direction of the tangent to the boundary. The stress is here monoaxial so that the starch contracts freely both in the y -direction (transverse) and the z -direction (perpendicular to the film) and results in

monoaxial orientation. Figure 1 gives a schematic representation of the apparatus for the stretching of starch films (Ward, 1975).

Measurements of permeability

The measurements of permeability were carried out using a Davenport apparatus — which had been connected to a PC/2 IBM — for permeability coefficient measurements, according to ASTM D1434-66 (ASTM, 1966).

RESULTS AND DISCUSSION

Effect of water content on gas permeability (O_2 , N_2 and CO_2) in potato/rice starch and water films

Diffusion through a polymer film involves three steps: first, the migrating substance must dissolve in the polymeric material; secondly, it must diffuse through the material; and thirdly, it must leave the material by a reversal of the process that caused it to dissolve in the first step. All polymer films used in food packaging allow certain amounts of the atmospheric gases (O_2 and N_2) to dissolve in them; the same could be equally claimed for carbon dioxide (CO_2), which is an important gas in food and beverage packaging in spite of its being a minor component of the atmosphere (Brown, 1992).

The great solubility of carbon dioxide in most synthetic/natural polymers enhances its diffusion through the polymer mass, thus resulting in its plasticization. The introduction of low-molecular-weight substances, such as H_2O , monomers and oligomers, can plasticize natural (*trans*-polyisoprene) or synthetic (polyamides, polyesters) polymers usually by reducing the cohesive forces and thus facilitating the penetration (Arvanitoyannis *et al.*, 1992; Arvanitoyannis & Blanshard, 1993).

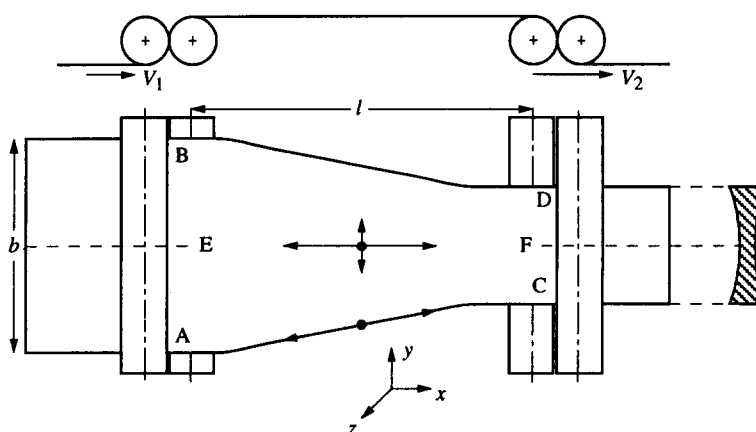


Fig. 1. Schematic representation of the apparatus for the stretching of films with a wide gap between feeding and stretching rolls and the cross-section of film with exaggerated concavity.

It is apparent that the gas molecule may move through the polymer substrate in two distinct ways: (a) along the axis of a 'tube' formed by adjacent parallel chains and (b) perpendicular to this axis by two polymer chains separating sufficiently to permit passage of the molecule. The first process may be regarded, to a first approximation, as requiring no activation energy and so occurring much more rapidly than the second. For the second process there is an activation energy equal to that necessary to produce a minimum chain separation that will accommodate the molecule. If processes (a) and (b) always occurred in parallel, process (a) would predominate and little or no activation energy would be observed. However, process (a) is halted whenever the molecule encounters a crystallite or sufficiently large chain entanglements at either 'end' of its confining 'tube'. Thereafter the gas molecule may progress only by moving through process (b) to an adjoining tube. Hence processes (a) and (b) occur effectively in series and the observed activation energy is that of the rate-limiting process (b) (Pace & Datyner, 1979a). Approximate calculations indicated that diffusion by process (a) occurs at least three orders of magnitude faster than macroscopically observed diffusion rates (Pace & Datyner, 1979b,c). Therefore, the absorption and incorporation of water molecules in potato and rice starch consist of plasticizing the polymer chains, thus leading to a reduction of the activation energy required for process (b) (Amerongen, 1947, 1949).

Previous publications have shown that high water contents in polymer films (i.e. cellulosic, poly(vinyl alcohol), protein and polyamide films) increase the permeability considerably (Myers *et al.*, 1960; Arvanitoyannis & Blanshard, 1993).

Figures 2–7 show the effect of different water contents (within the range 12–19%, w/w) upon the gas permeability and diffusivity (O_2 , N_2 and CO_2) in potato and rice starch films. Both permeability and diffusivity values are higher the higher the water contents in the starch films; that is,

for potato starch:

$$(P, D)_{19\%, w/w, H_2O} > (P, D)_{16\%, w/w, H_2O} > (P, D)_{13\%, w/w, H_2O}$$

and for rice starch:

$$(P, D)_{18\%, w/w, H_2O} > (P, D)_{15\%, w/w, H_2O} > (P, D)_{12\%, w/w, H_2O}$$

Rice starch films were found to be more permeable to gases (O_2 , N_2 and CO_2) than films derived from potato starch.

The inflection in the slope of permeability/diffusivity versus the inverse temperature ($10^3/T$, K) gives an indirect measurement of the glass transition temperature for Figs 2–13. The T_g values obtained from Figs 2–7 were compared to those determined with the aid of DSC and DMTA. From Table 1 it is apparent that there is an agreement between the T_g values obtained from DSC and the permeability measurements.

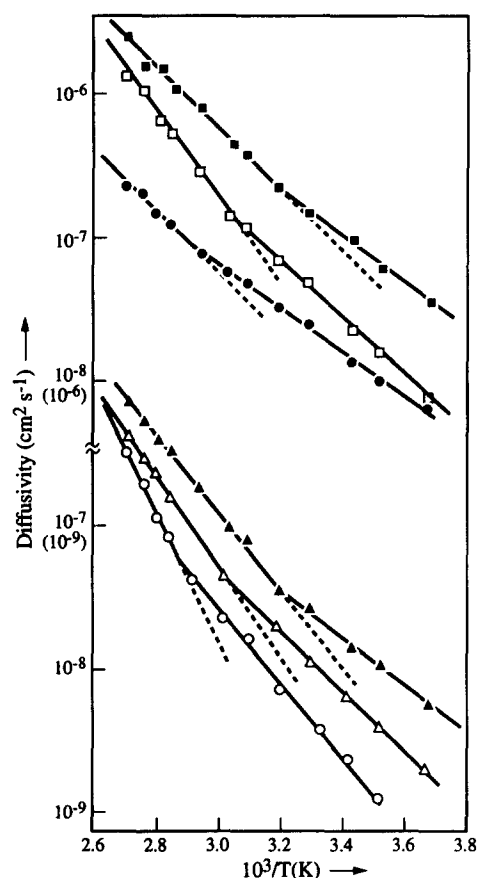


Fig. 2. Diffusivity of N_2 in potato and rice starch/water films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Potato starch/water (% w/w): ■, 81:19; □, 84:16; ●, 87:13. Rice starch/water (% w/w): ▲, 82:18; △, 85:15; ○, 88:12.

Table 1. Glass transition temperatures (T_g , K) of potato and rice starch (roller dried) conditioned at different relative humidities (RH)

Starch (%)	Water (%)	T_g (K)			
		DSC	E'	$\tan \delta$	Permeability ^a
<i>Potato starch</i>					
93.4	6.6	410.0	378.0	456.0	—
88.8	11.2	372.8	369.0	389.0	—
86.1	13.9	340.4	343.4	357.0	344.8 ± 2.1
84.4	15.6	324.5	326.0	351.0	327.9 ± 2.5
82.9	17.1	322.2	320.5	334.5	—
81.35	18.65	318.8	315.0	324.0	—
80.8	19.2	314.4	308.0	323.5	313.5 ± 1.4
<i>Rice starch</i>					
93.5	6.5	393.1	374.0	455.0	—
88.8	11.2	362.8	362.0	379.0	349.7 ± 3.4
86.3	13.7	340.1	336.0	351.0	—
84.8	15.2	327.4	332.0	345.0	329.5 ± 2.1
83.1	16.9	318.8	315.0	330.0	—
81.4	18.6	308.0	300.5	317.0	310.6 ± 2.2

^aMean value and standard deviation from five measurements ($x \pm SD$).

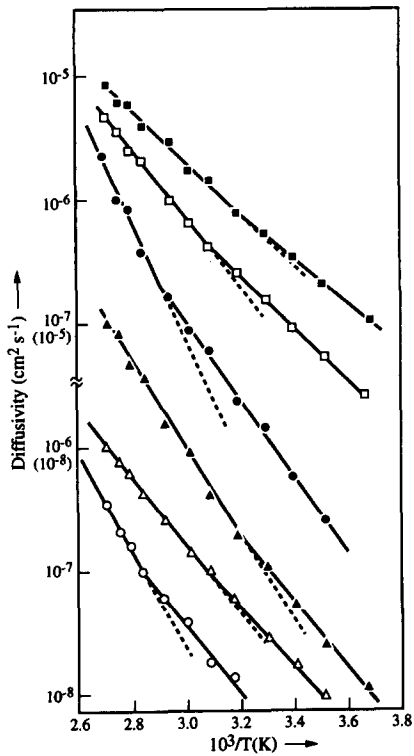


Fig. 3. Diffusivity of O_2 in potato and rice starch/water films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Annotation of curves according to starch/water composition, as in Fig. 2.

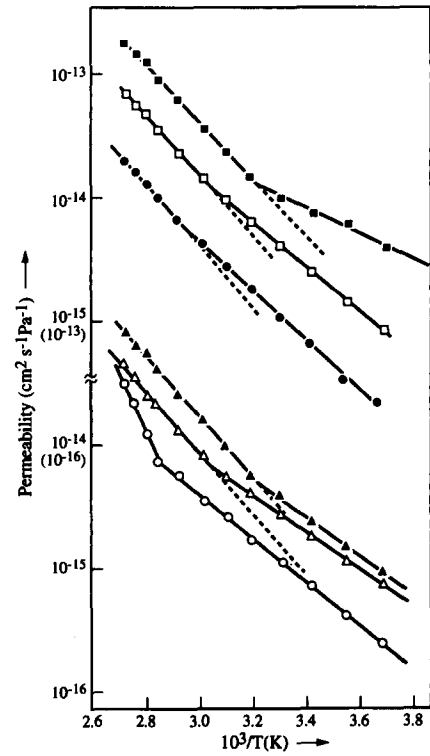


Fig. 5. Permeability of N_2 in potato and rice starch/water films (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water composition, as in Fig. 2.

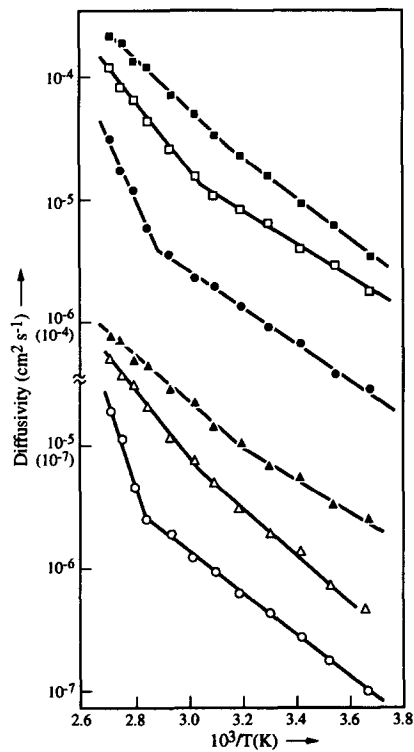


Fig. 4. Diffusivity of CO_2 in potato and rice starch/water films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water composition, as in Fig. 2.

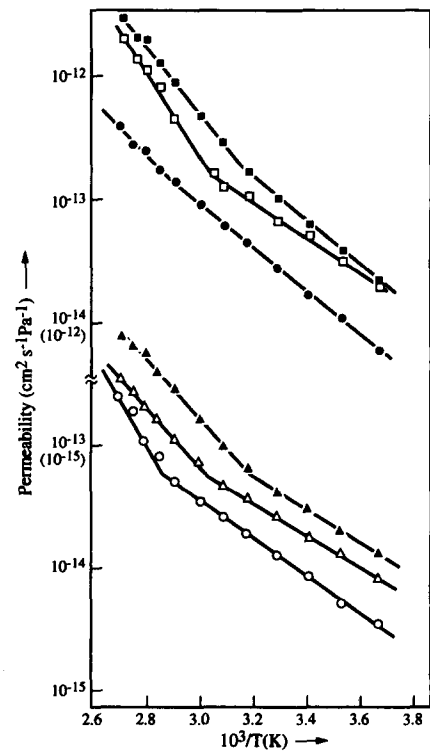


Fig. 6. Permeability of O_2 in potato and rice starch/water films (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water composition, as in Fig. 2.

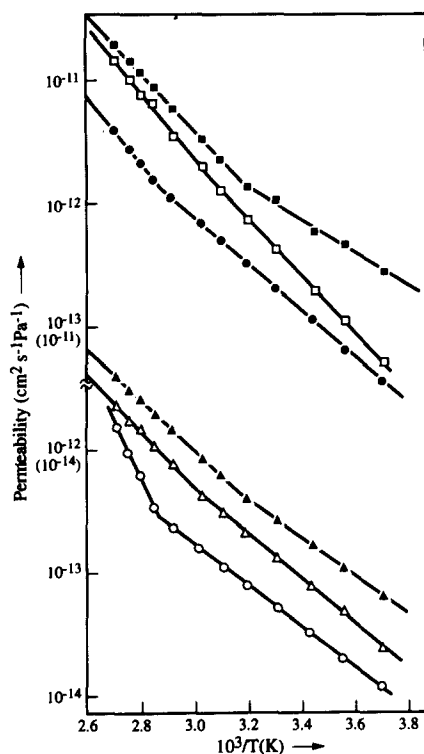


Fig. 7. Permeability of CO₂ in potato and rice starch/water films (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water composition, as in Fig. 2.

Effect of sugars on the gas permeability of potato/rice starch/water films

The effect of the incorporation of sugars into starch/water films can be understood in terms of the plasticizing effect of low-molecular-weight monomers/oligomers (Arvanitoyannis & Blanshard, 1993).

A number of sugars were studied in order to draw conclusions about the effect of each individual sugar upon the diffusivity/permeability of potato starch/water films (Figs 8–13, Table 2).

The plasticizing effects of glucose and fructose are higher than that of sucrose, which can probably be attributed to their greater mobility (lower molecular weight). Therefore, the diffusivity and permeability of potato starch/water films containing these two sugars is higher than those with sucrose (Figs 8–13). The combined effect of water and sugars upon the starch films, when no annealing or long-time storage takes place, is synergistic and results in extensive plasticization and enhanced diffusion rates which facilitate the penetration of gas molecules.

Effect of uniaxial drawing on the gas permeability coefficient in potato starch/water (81:19, w/w) and rice starch/water (82:18, w/w) films

Both annealing and uniaxial drawing induce crystallization, which is measured in terms of an increase in %

crystallinity due to a decrease in the amorphous imperfections, followed by an increase in the thickness of the lamellae and then orientational and conformational changes in polymeric chains (Michaels & Bixler, 1961). Previous investigations showed that the initial percentage crystallinity could increase up to four times both for synthetic and natural polymers (Michaels & Bixler, 1961; Arvanitoyannis *et al.*, 1992; Arvanitoyannis & Blanshard, 1993).

The draw ratios used in our experiments were limited to 1 and 2 but even these were only feasible at water contents greater than 10%, w/w. Higher ratios yielded a material which became intractably brittle on aging, presumably due to the amylopectin which, with a branched structure, cannot orient and pack as closely as the linear molecules of amylose (Young, 1984). It is clear that the action of water as a plasticizer in starch increased the tensile strength of starch films and made feasible the application of draw ratios 1 and 2.

Figures 14 and 15 show the influence of different draw ratios (0, 1 and 2) on the nitrogen and oxygen permeabilities of potato and rice starch films with 19 and 18% water contents, respectively.

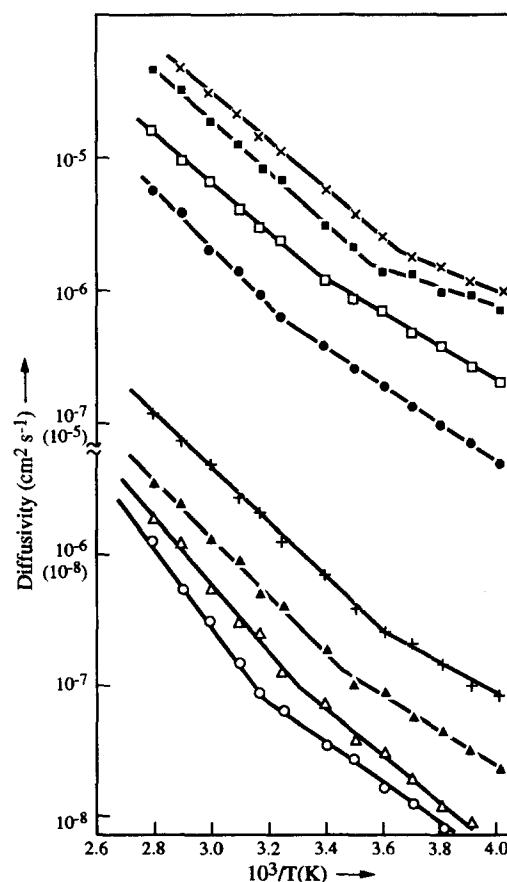


Fig. 8. Diffusivity of N₂ in potato starch/water/sugar films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Potato starch/water/glucose (% w/w): ●, 76:19:5; □, 71:19:10; ■, 61:19:20; ×, 51:19:30. Potato starch/water sucrose: ○, 76:19:5; △, 71:19:10; ▲, 61:19:20; +, 51:19:30.

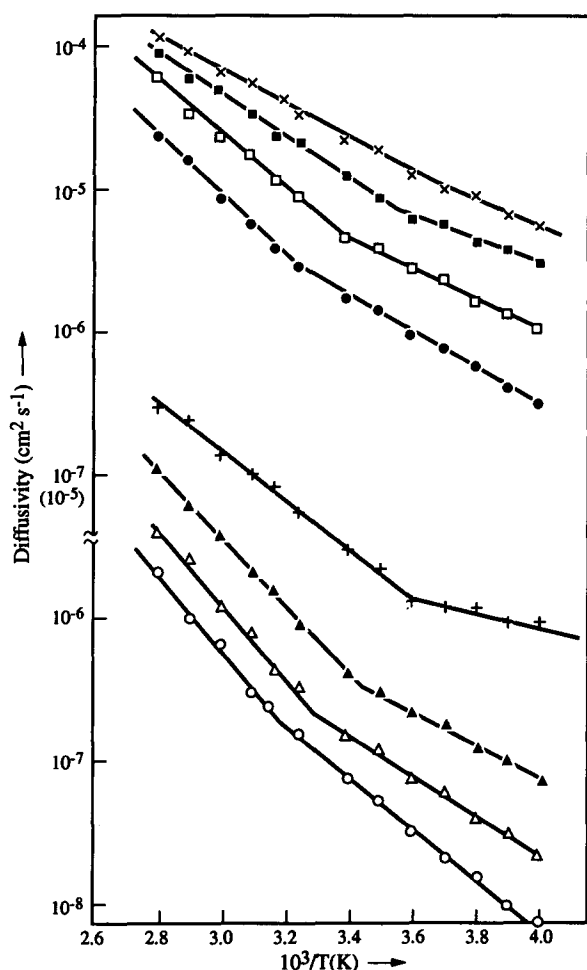


Fig. 9. Diffusivity of O₂ in potato starch/water/sugar films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water/sugar composition, as in Fig. 8.

Apart from the decrease in nitrogen permeability with the draw ratio, an increase in the glass transition temperature (T_g) of the starch/water films was also observed. In particular, the T_g both for potato and rice starch, as evidenced by the permeability measurements, increased by approximately 10°C on passage from a draw ratio of 0 to 2. These permeability results were also confirmed by DSC measurements (see Table 3).

Correlation of the percentage crystallinity in potato starch/water/sugar films with the composition and permeability of films

The potato starch/water/sugar blends were stored in incubators at temperatures of $T_g + 30^\circ\text{C}$ to promote the development of crystallinity. Measurements of % crystallinity were carried out by both DSC and wide angle X-ray diffraction, initially every 6 h and subsequently every 2–5 days, depending on the progress of crystallization.

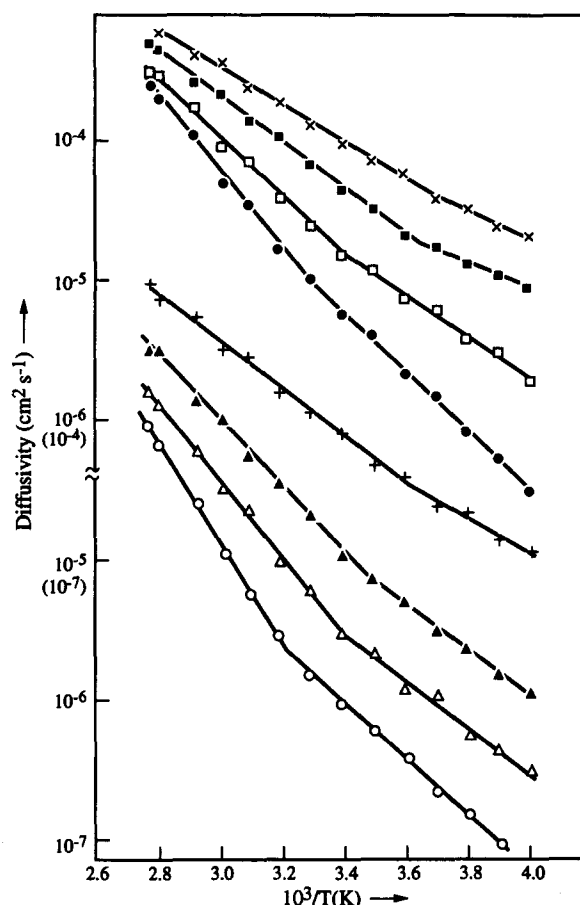


Fig. 10. Diffusivity of CO₂ in potato starch/water/sugar films (derived from eqn (3)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water/sugar composition, as in Fig. 8.

Figures 16 and 17 show that the percentage crystallinity of the potato starch/water/sugars (s/w/o) films influenced the permeability to N₂ in the following order:

$$(P, D)_{ps/w} < (P, D)_{ps/w/g} < (P, D)_{ps/w/f} < (P, D)_{ps/w/s}$$

where

ps/w: potato starch/water
ps/w/g: potato starch/water/glucose
ps/w/f: potato starch/water/fructose
ps/w/s: potato starch/water/sucrose.

The % crystallinity developed in the potato starch/water films was found to be higher the greater the water content. Although a significant amount of work has already been carried out on the crystallization of various starches in the presence of sugars at different relative humidities/moisture contents, the mechanism whereby the sugars moderate the crystallization process has not yet been clarified (Marsh, 1988; Levine & Slade, 1991).

The increase in the percentage crystallinity of potato

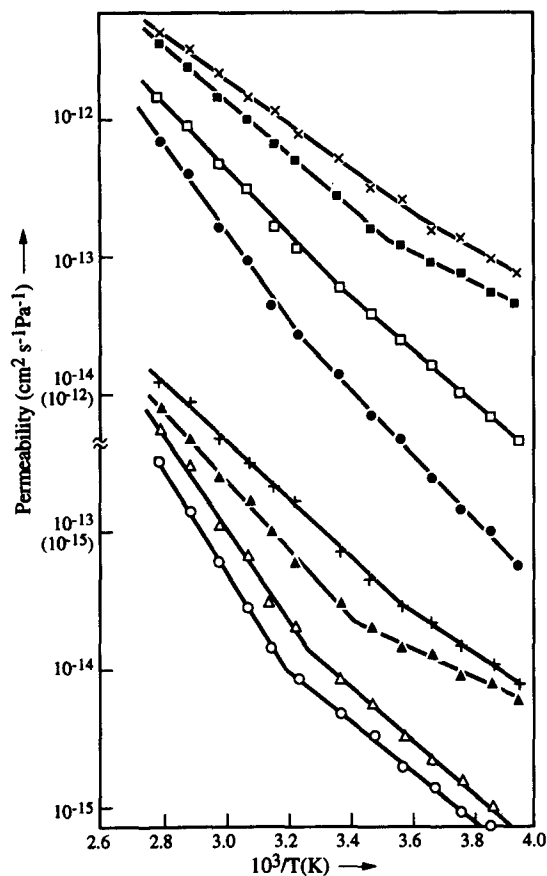


Fig. 11. Permeability of N_2 in potato starch/water/sugar film (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water/sugar composition, as in Fig. 8.

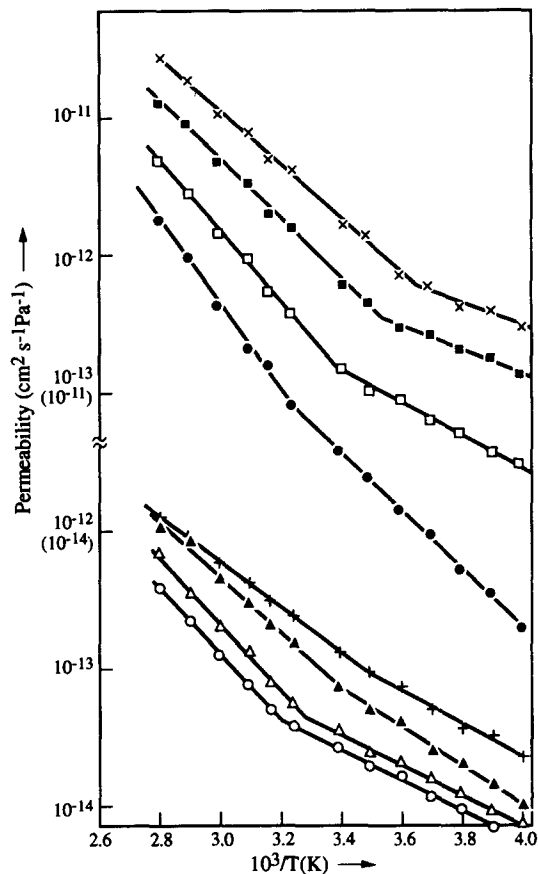


Fig. 12. Permeability of O_2 in potato starch/water/sugar film (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water/sugar composition as in Fig. 8.

starch in the presence of water could be attributed to the plasticization effect of water on the macromolecules, which promotes the reorganization of the molecules into a semicrystalline structure (Kainuma & French, 1972). The participation of water as an integral part of the hydrated B-type starch 'superstructure' was corroborated by the observation of a shift in X-ray powder pattern of B-type starch after its hydration. This shift in the diffraction maxima lattice plane spacings indicates an expansion of the crystal cell unit during water uptake (Colonna *et al.*, 1982). The intercrystalline amorphous regions also tend to expand during hydration, initiating in this way an alignment of the microcrystals (Duprat *et al.*, 1980).

Theoretical calculation of gas diffusivity and permeability in films made from starch/water/sugars. Calculation of activation energies for diffusivity and permeability

The logarithmic expressions for the Arrhenius equations (10) and (11) describing diffusivity and solubility, respectively, are as follows:

$$\ln D = \ln D_0 - E_D/RT \quad (12)$$

$$\ln S = \ln S_0 - E_s/RT. \quad (13)$$

In similar vein to eqns (11)–(13), the temperature dependence of permeability can be expressed as

$$P = P_0 \exp(-E_p/RT) \quad (14)$$

where E_p is the apparent activation energy of permeation, and

$$\ln P = \ln P_0 - E_p/RT. \quad (15)$$

The activation energies of diffusion and permeation were calculated according to eqns (12) and (15) for starch/water and starch/water/sugar films (Tables 4 and 5) using the experimental data of Figs 2–13. The activation energy of diffusion (E_d) is the dominant parameter in the diffusion process because it is the energy required for a dissolved molecule to jump from one 'hole' into another.

The calculation of permeability was based on the

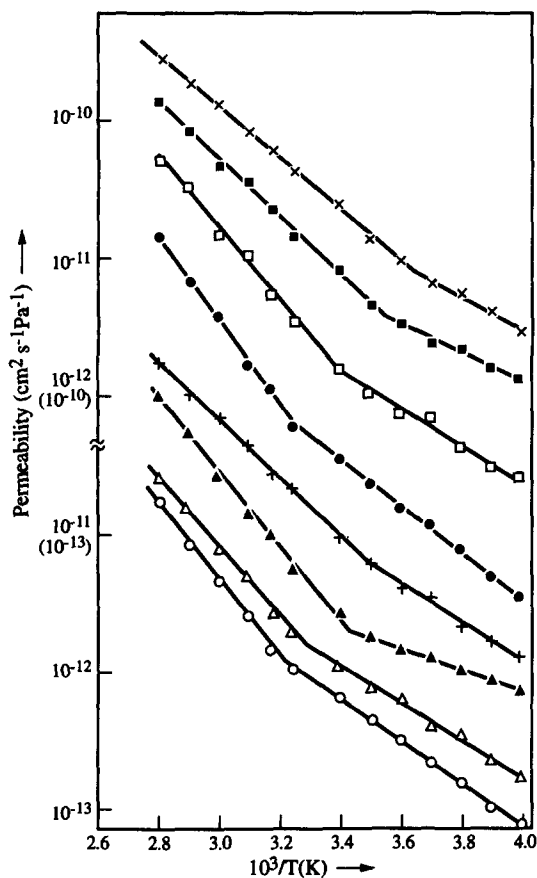


Fig. 13. Permeability of CO₂ in potato starch/water/sugar film (derived from eqn (4)) versus the inverse temperature ($1/T$ (K)). Annotations of curves are according to starch/water/sugar composition as in Fig. 8.

additive molar function, the so-called permachor (II) introduced by Salame (1986):

$$N \times \pi = \Pi = \sum_i (N_i \pi_i) \quad (16)$$

where π is an additive molar function of permeability, N are the number of characteristic groups per structural unit and i is the increment of the group i .

The numerical value of π being known, the permeability at ambient temperature can be estimated from

$$P(298) = P_{(298)}^* \exp(-S\pi) \quad (17)$$

where $P_{(298)}^*$ is the permeability of a standard gas (i.e. N₂) in a chosen standard polymer (i.e. rubber) and S is the scaling factor. By substituting $\ln P_{(298)}^* = -12$ and $S = 0.122$, the following equation is obtained, the applicability of which is unfortunately restricted to amorphous polymers:

$$\ln P_{(298)}^* = -12 - 0.053 \pi. \quad (18)$$

For semicrystalline (sc) polymers a further modification (Salame, 1986) is necessary, leading to

$$\pi_{sc} = \pi_a - 18 Lna = \pi_a - 41.5 \ln(1 - x_c) \quad (19)$$

where a is the amorphous volume fraction and x_c is the crystallinity.

The activation energies calculated according to the Arrhenius equations (12) and (15) both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g) are lower than the activation energies calculated for synthetic/natural polymers such as polyamides (15–48.0 kJ mol⁻¹) and *trans*-polyisoprene (12.3–45.2 kJ mol⁻¹) (Arvanitoyannis *et al.*, 1992; Arvanitoyannis & Blanshard, 1993). The higher the water content, the lower the activation energies for diffusion and permeation (Tables 4–6). In addition, the activation energies for gas diffusion and permeation of drawn films, where a development of crystallinity occurred, increased with an increase in the percentage crystallinity (% K).

However, when the eqns (16)–(19) were applied in starch (amylose and amylopectin) the obtained values for dry amorphous samples were 6.99×10^{-20} and 2.4×10^{-19} cm² s⁻¹ Pa⁻¹, respectively.

The values of nitrogen permeability for dry starch are significantly lower than the experimental ones (Figs 5–7). The observed discrepancy between the results of the Salame equations (eqns (16)–(19)) and experimental values could be possibly attributed to the fact that this model does not take into consideration the effect of moisture or relative humidity on the permeability of hydrophilic polymers (Eichler & Miltz, 1993) in conjunction with the existence of many more hydrogen-bonding groups in starch (and also in cellulose, or poly(vinyl alcohol) and proteins) compared with the polyamides (Arvanitoyannis & Blanshard, 1993).

In addition, the existence of water in starch complicates the issue because of its strong tendency towards hydrogen-bond formation. Although the existence of polar groups in the polymer matrix favours the sorptive affinity for water, other factors which have equally to be considered are

- the accessibility of the polar groups
- the relative strength of the water–water versus the polymer–water bonds
- the degree of crystallinity of the polymer matrix (van Krevelen, 1990).

Furthermore, depending on the water content, the water can be either strongly localized (low water contents) or mobile, which will be due to previous swelling of the polymer matrix (high water contents).

Trends in food packaging and correlation with the present investigation

As mentioned in a previous publication (Arvanitoyannis & Blanshard, 1993) there exists a strong tendency

Table 2. Glass transition temperatures^a (T_g , °C) of potato and rice starch/water/sugar mixtures from DSC and permeability measurements

Starch (%, w/w)	Water (%, w/w)	Sugar (%, w/w)	T_g (°C) (DSC)	T_g (°C)(permeability)
<i>Potato starch</i>	<i>Water</i>	<i>Sucrose</i>		
81	19	—	318.0 ± 1.5	317.0 ± 2.1
76	19	5	310.9 ± 2.0	310.0 ± 1.8
71	19	10	302.0 ± 2.8	303.4 ± 2.3
61	19	20	292.4 ± 2.5	290.5 ± 3.1
51	19	30	280.6 ± 1.4	278.7 ± 2.4
<i>Potato starch</i>	<i>Water</i>	<i>Fructose</i>		
76	19	5	309.9 ± 2.5	307.3 ± 1.5
71	19	10	293.1 ± 3.0	291.9 ± 2.2
61	19	20	280.2 ± 2.6	281.5 ± 2.0
51	19	30	273.4 ± 1.9	271.2 ± 1.7
<i>Potato starch</i>	<i>Water</i>	<i>Glucose</i>		
76	19	5	305.2 ± 2.7	306.4 ± 2.1
71	19	10	294.1 ± 3.4	292.5 ± 1.8
61	19	20	280.4 ± 2.5	281.2 ± 3.0
51	19	30	271.5 ± 2.9	272.8 ± 3.2
<i>Rice starch</i>	<i>Water</i>	<i>Sucrose</i>		
82	18	—	312.5 ± 3.0	311.8 ± 2.6
77	18	5	306.2 ± 2.4	304.2 ± 2.8
72	18	10	294.1 ± 3.0	293.5 ± 1.9
62	18	20	283.2 ± 2.5	281.4 ± 2.4
52	18	30	270.5 ± 2.9	272.6 ± 3.0
<i>Rice starch</i>	<i>Water</i>	<i>Fructose</i>		
77	18	5	301.2 ± 2.0	298.9 ± 2.5
72	18	10	289.0 ± 3.1	290.3 ± 2.8
62	18	20	278.4 ± 2.5	276.4 ± 1.6
52	18	30	271.5 ± 1.5	269.6 ± 3.1
<i>Rice starch</i>	<i>Water</i>	<i>Glucose</i>		
77	18	5	300.5 ± 2.0	298.6 ± 2.9
72	18	10	291.4 ± 2.3	288.8 ± 3.3
62	18	20	279.4 ± 2.5	276.0 ± 3.5
52	18	30	272.6 ± 3.0	270.9 ± 2.9

^aMean value and standard deviation from five measurements ($x \pm \text{SD}$).**Table 3. Effect of draw ratio on the glass transition temperature^a (T_g , K) (determined with DSC and from permeability measurements) and the percentage crystallinity (% K) determined with wide angle X-rays and (WAXRS) DSC measurements (according to Gidley, 1992)**

Starch (%, w/w)	Water (%, w/w)	Draw ratio	(T_g, K)		% K	
			DSC	Permeability measurements	DSC (100% helical amylopectin content)	WAXRS (100% crystalline)
Potato starch, 81	19	0	309.5 ± 0.9	310.1 ± 2.1	1.2	1.5
Potato starch, 81	19	1	314.2 ± 2.0	314.4 ± 1.7	5.9	7.2
Potato starch, 81	19	2	318.0 ± 1.6	319.2 ± 2.0	10.5	12.0
Rice starch, 82	18	0	305.5 ± 1.8	304.8 ± 1.5	1.9	2.3
Rice starch, 82	18	1	311.3 ± 1.1	312.1 ± 1.4	7.4	8.7
Rice starch, 82	18	2	317.0 ± 1.3	315.9 ± 1.7	12.0	13.4

^aMean value and standard deviation from five measurements ($x \pm \text{SD}$).

towards the synthesis of amorphous aromatic polyamides which are transparent and have very good barrier properties. However, the danger of an extensive pollution of the environment from non-biodegradable

materials has initiated research in the field of synthesis of novel biodegradable or modified natural polymers for packaging purposes. With this prospect in mind other workers have studied amylose films for gas

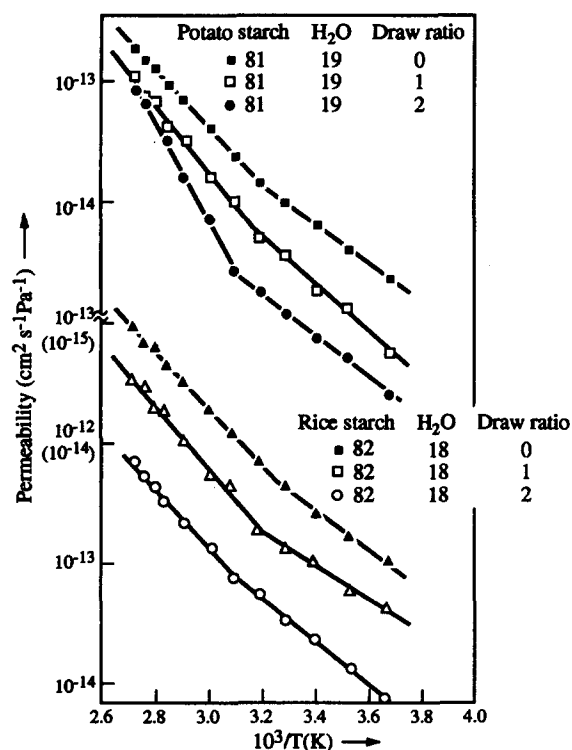


Fig. 14. Effect of draw ratio on permeability of N_2 in potato and rice starch/water films versus the inverse temperature ($1/T$ (K)).

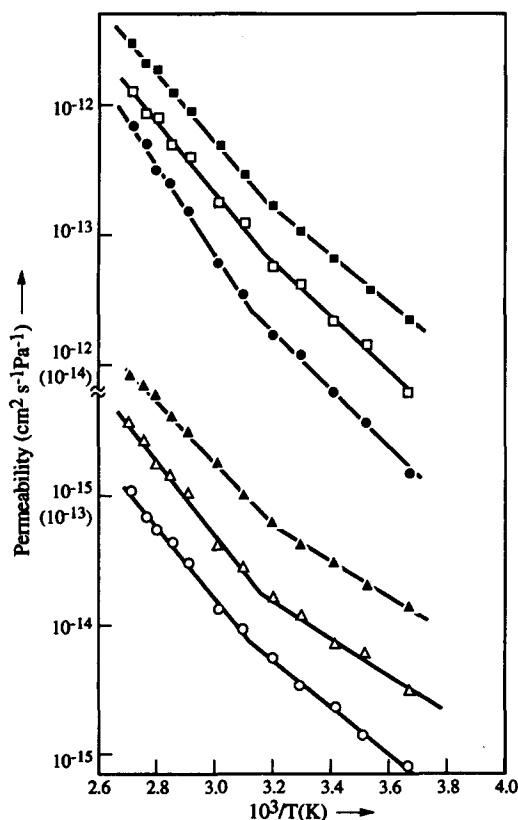


Fig. 15. Effect of draw ratio on permeability of O_2 in potato and rice starch/water films versus the inverse temperature ($1/T$ (K)). Annotation of curves as in Fig. 14.

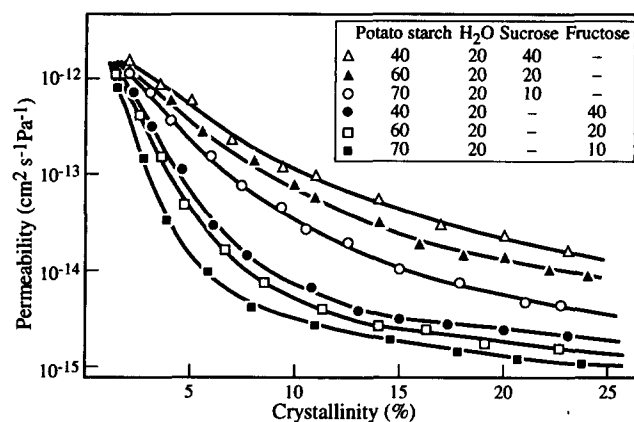


Fig. 16. Effect of sucrose and fructose composition on permeability of N_2 in potato starch/water/sugar films versus the developed percentage crystallinity (% K).

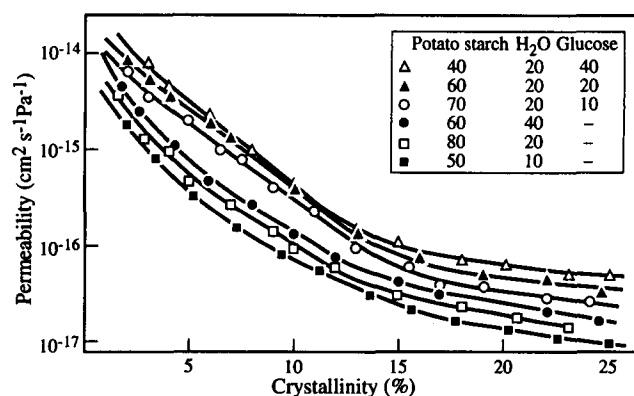


Fig. 17. Effect of glucose composition on permeability of N_2 in potato starch/water/sugar films versus the developed percentage crystallinity (% K).

permeability (Asanuma & Fujiwara, 1975a,b,c; Nakatsuka *et al.*, 1977) for food packaging, wrapping and coating purposes. Another avenue that has been partially explored is the preparation of films from blends of poly(vinyl alcohol), or any other compatible polymer, with starch (Young, 1984). The present investigation aimed to provide some additional information about the gas permeability of potato/rice starch films in the presence of water with or without oligosaccharides which could be of importance to research in novel food-packaging materials and to gain an understanding of the interactions between food-packaging polymers and the foods themselves.

CONCLUSIONS

The gas permeability of potato and rice starch/water films was found to depend greatly on the percentage crystallinity of starch and on the plasticizing action of water and sugars. Uniaxially drawn potato and rice

Table 4. Activation energies for diffusion (E_D^* , kJ mol⁻¹)^a and permeation (E_P^{**} , kJ mol⁻¹)^b both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g) for potato, rice starch/water mixtures

Starch (%, w/w)	Water (%, w/w)	N ₂				O ₂				CO ₂			
		E_D^*		E_P^{**}		E_D^*		E_P^{**}		E_D^*		E_P^{**}	
		$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$
<i>Potato starch</i>													
81	19	3.8 ± 0.10	2.6 ± 0.11	5.0 ± 0.32	3.3 ± 0.25	3.4 ± 0.30	2.3 ± 0.12	4.8 ± 0.31	3.2 ± 0.18	3.9 ± 0.22	2.8 ± 0.18	4.1 ± 0.39	2.8 ± 0.20
84	16	4.8 ± 0.31	3.3 ± 0.22	5.7 ± 0.41	4.2 ± 0.31	4.2 ± 0.35	3.1 ± 0.25	6.0 ± 0.48	4.0 ± 0.32	4.8 ± 0.35	3.7 ± 0.24	4.9 ± 0.38	3.6 ± 0.32
87	13	5.4 ± 0.45	4.0 ± 0.35	6.9 ± 0.56	5.1 ± 0.45	5.0 ± 0.42	3.9 ± 0.38	6.9 ± 0.53	5.7 ± 0.42	5.6 ± 0.51	4.3 ± 0.51	6.4 ± 0.50	4.6 ± 0.38
<i>Rice starch</i>													
82	18	3.2 ± 0.22	2.2 ± 0.20	4.7 ± 0.42	3.5 ± 0.21	3.1 ± 0.21	3.0 ± 0.30	4.5 ± 0.38	3.4 ± 0.30	3.1 ± 0.28	2.3 ± 0.19	4.2 ± 0.31	3.3 ± 0.28
85	15	4.6 ± 0.42	2.9 ± 0.24	5.6 ± 0.50	4.6 ± 0.38	4.4 ± 0.40	3.8 ± 0.33	6.8 ± 0.53	4.5 ± 0.38	4.5 ± 0.30	3.2 ± 0.21	5.4 ± 0.39	3.9 ± 0.32
88	12	6.2 ± 0.53	4.7 ± 0.42	7.2 ± 0.53	5.4 ± 0.53	5.3 ± 0.48	4.4 ± 0.41	7.5 ± 0.69	6.4 ± 0.39	5.2 ± 0.45	3.9 ± 0.28	6.7 ± 0.55	5.3 ± 0.47

^a E_D^* calculated according to eqn (12).^b E_P^{**} calculated according to eqn (15). $x \pm SD$ = average \pm standard deviation from five measurements.**Table 5.** Activation energies for diffusion (E_D^* , kJ mol⁻¹)^a and permeation (E_P^{**} , kJ mol⁻¹)^b for potato starch/water/sugar mixtures both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g)

Starch (%, w/w)	Water (%, w/w)	Sugar (%, w/w)	N ₂				O ₂				CO ₂			
			E_D^*		E_P^{**}		E_D^*		E_P^{**}		E_D^*		E_P^{**}	
			$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$
<i>Potato starch</i>	<i>Water</i>	<i>Glucose</i>												
76	19	5	3.6 ± 0.25	2.4 ± 0.18	4.7 ± 0.40	3.1 ± 0.19	3.2 ± 0.19	2.2 ± 0.21	4.5 ± 0.41	3.0 ± 0.28	3.6 ± 0.32	2.7 ± 0.32	3.8 ± 0.26	2.6 ± 0.19
71	19	10	2.8 ± 0.34	2.0 ± 0.15	4.3 ± 0.32	2.6 ± 0.23	2.5 ± 0.18	1.9 ± 0.18	3.9 ± 0.51	2.5 ± 0.21	3.2 ± 0.28	2.2 ± 0.21	3.2 ± 0.28	2.0 ± 0.14
61	19	20	2.3 ± 0.19	1.4 ± 0.12	3.4 ± 0.35	2.0 ± 0.18	2.0 ± 0.19	1.4 ± 0.12	3.3 ± 0.19	2.1 ± 0.20	2.6 ± 0.25	1.6 ± 0.11	2.7 ± 0.21	1.5 ± 0.11
51	19	30	2.4 ± 0.22	1.6 ± 0.18	3.7 ± 0.17	2.2 ± 0.22	1.5 ± 0.11	3.5 ± 0.24	2.0 ± 0.18	2.7 ± 0.19	1.6 ± 0.19	1.6 ± 0.10	2.6 ± 0.19	1.6 ± 0.12
<i>Potato starch</i>	<i>Water</i>	<i>Sucrose</i>												
76	19	5	2.9 ± 0.30	1.9 ± 0.15	4.4 ± 0.32	3.3 ± 0.19	2.9 ± 0.25	2.6 ± 0.23	4.2 ± 0.38	3.1 ± 0.29	2.8 ± 0.28	2.2 ± 0.20	4.0 ± 0.37	3.0 ± 0.28
71	19	10	2.5 ± 0.18	1.6 ± 0.18	3.9 ± 0.30	2.9 ± 0.21	2.5 ± 0.21	2.0 ± 0.18	3.5 ± 0.29	2.4 ± 0.09	2.3 ± 0.21	1.7 ± 0.13	3.4 ± 0.30	2.3 ± 0.28
61	19	20	1.7 ± 0.20	1.0 ± 0.10	3.2 ± 0.25	2.0 ± 0.12	1.9 ± 0.18	1.5 ± 0.14	2.9 ± 0.25	2.0 ± 0.11	2.6 ± 0.15	1.2 ± 0.09	3.0 ± 0.27	1.9 ± 0.16
51	19	30	1.9 ± 0.11	1.2 ± 0.07	3.6 ± 0.19	2.6 ± 0.14	2.0 ± 0.17	1.6 ± 0.15	3.0 ± 0.28	2.1 ± 0.12	1.8 ± 0.17	1.3 ± 0.10	3.1 ± 0.28	2.1 ± 0.20

^a Calculated according to eqn (12).^b Calculated according to eqn (15).^c $x \pm SD$ = average \pm standard deviation from five measurements.

starch/water films corroborated this assumption by showing lower permeability at higher percentage crystallinity. The glass transition temperatures (T_g) determined indirectly from the permeability measurements were in satisfactory agreement with those determined by thermal analysis.

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Table 6. Activation energies for diffusion (E_D , kJ mol⁻¹), and permeation (E_p , kJ mol⁻¹) for potato and rice starch/water mixtures at different draw ratios below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g)

Starch (%, w/w)	Water (%, w/w)	Draw ratio	N ₂				O ₂				
			E_d^*		E_p^{**}		E_d^*		E_p^{**}		
			$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	
<i>Potato starch</i>											
81	19	0	3.8 ± 0.10	2.6 ± 0.11	5.0 ± 0.32	3.3 ± 0.25	3.4 ± 0.30	2.3 ± 0.12	4.8 ± 0.31	3.2 ± 0.18	
81	19	1	6.5 ± 0.15	4.8 ± 0.20	7.4 ± 0.55	5.7 ± 0.35	5.8 ± 0.41	4.5 ± 0.25	7.1 ± 0.58	5.6 ± 0.29	
81	19	2	9.1 ± 0.32	6.4 ± 0.35	10.8 ± 0.78	7.5 ± 0.48	8.6 ± 0.62	6.0 ± 0.42	10.2 ± 0.79	7.9 ± 0.48	
<i>Rice starch</i>											
82	18	0	3.2 ± 0.22	2.2 ± 0.20	4.7 ± 0.42	3.5 ± 0.21	3.1 ± 0.21	3.0 ± 0.30	4.5 ± 0.38	3.4 ± 0.30	
82	18	1	6.0 ± 0.41	4.1 ± 0.23	7.8 ± 0.65	6.2 ± 0.35	5.5 ± 0.35	5.7 ± 0.42	7.3 ± 0.65	6.3 ± 0.44	
82	18	2	8.2 ± 0.66	5.5 ± 0.45	10.3 ± 0.82	7.0 ± 0.59	7.9 ± 0.60	8.2 ± 0.65	9.8 ± 0.88	7.3 ± 0.62	

^aCalculated according to eqn (12).^bCalculated according to eqn (15). $x \pm SD$ = average \pm standard deviation from five measurements.

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