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Edible films made from sodium caseinate, starches, sugars or glycerol. Part 1

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The physical properties of edible films, based on blends of sodium caseinate with starches of different origin (corn and wheat) plasticized with water, glycerol or sugars, were studied. An increase in water or sugar/glycerol content resulted in a considerable decrease in the modulus of elasticity and in the tensile strength of films. The tensile strength and the water vapor permeability decreased with an increase in sodium caseinate contents (> 10% w/w). The development of crystallinity caused a reduction in gas and water permeabilities. Semi-empirical models for calculation of gas permeability and tensile strength and tensile moduli were applied with limited success and the obtained values were compared to those experimentally determined. © 1997 Published by Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The continuously increasing interest of consumers in quality, convenience and food safety have encouraged further research into edible films and coatings (Krochta *et al.*, 1990, 1994; Martin-Polo *et al.*, 1992; Park *et al.*, 1993, 1994a, b; Stuchell & Krochta, 1994; McHugh *et al.*, 1993, 1994; McHugh & Krochta, 1994a, b; Magoshi *et al.*, 1992; Herald *et al.*, 1995; Kester & Fennema, 1989a, b). The reinvention of 'edible films' was due mainly to their numerous applications, such as coatings for sausages, chocolate coatings for nuts, fruits and vegetables and occasionally wax coatings (Park *et al.*, 1994a, b; Santerre *et al.*, 1989; Meheriuk & Lau, 1988; Drake *et al.*, 1991; Motlagh & Quantick, 1988; Drake & Nelson, 1990; Camirand *et al.*, 1992), which were reported in several, recently published reviews (Krochta, 1992; Koelsch, 1994; Kester & Fennema, 1986; Brake & Fennema, 1993) and a book (Krochta *et al.*, 1994).

Although the use of edible films has a multipurpose objective, the following targets could be considered among the most important ones: restriction of moisture loss, control of gas permeability, control of microbial activity (i.e. chitin has antimicrobial action), preservation of structural integrity of the product and gradual release of enrobed flavours and antioxidants in food (El Ghaouth *et al.*, 1991; Wong *et al.*, 1992; Vojdani & Torres, 1990; Rico-Pena & Torres, 1990, 1991; Biquet & Labuza, 1988; Torres *et al.*, 1985).

Several publications have already reported on the film formation from casein/sodium caseinate (Kalichevsky *et al.*, 1993b; Garcia-Rodenas *et al.*, 1994; Krochta, 1992; Krochta *et al.*, 1994; Avena-Bustillos & Krochta, 1993) and starches (Arvanitoyannis *et al.*, 1994; Ollett *et al.*, 1991; Kirby *et al.*, 1993; Gennadios & Weller, 1990; Gennadios *et al.*, 1993a–e; Cherian *et al.*, 1995; Shogren, 1993; Lourdin *et al.*, 1995).

However, to the best of our knowledge, blends of these two components have not been used for preparation of films. Casein and casein derivatives vary in molecular weight (19 000–23 900) and have been extensively used in the food industry (dairy, meat and confectionery) and in medical and pharmaceutical applications as well (Southward, 1989; Kalichevsky *et al.*, 1993b; Kinsella, 1984).

In the first paper of this series, blends of sodium caseinate and starches were prepared in order to study the behavior of these materials with regard to their thermal and mechanical properties, and their gas and water permeability. A comparison of these properties, with those of films studied previously from similar resources, and suggested potential uses were further made.

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EXPERIMENTAL

Materials

Wheat and corn starch and sodium caseinate (practical grade), glycerol, D-glucose, sucrose, xylose (analytically pure) were purchased from Wako Chemicals (Japan).

Preparation of samples in the glassy state

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

The preparation of samples of blends of starches with sodium caseinate and glycerol/sugars and water was carried out as described elsewhere (Arvanitoyannis *et al.*, 1994). Corn starch (starch/water 30% w/w) was rendered amorphous by gelatinizing and roller drying (one process) at 140°C; roller drier speed, 10 rpm; pressure, 32 psi (221 kPa); gap, 1 mm; diameter, 165 mm; and width, 150 mm. Mixtures of sodium caseinate and gelatinized wheat or corn starch were passed through the roller drier to obtain blends of appropriate composition. The preparation of films of caseinate, with wheat or corn starch for permeability measurements, was carried out by pressing the samples at temperatures 85–90°C for 15 min.

The preparation of films (thickness range: 0·1 mm±0·001) for permeability measurements and conditioning of samples at different relative humidities were made as previously described (Arvanitoyannis & Blanshard, 1993; Arvanitoyannis *et al.*, 1994, 1992).

Wide angle X-ray diffraction pattern measurements (WAXDP)

X-Ray diffraction measurements were carried out using a Shimadzu (Japan) diffractometer from 5 to 40°C. The crystallinity was determined by dividing the crystalline area/(crystalline + amorphous area) as previously reported (Marsh, 1986).

Dynamic mechanical thermal analysis (DMTA) measurements

The dynamic mechanical thermal analyzer (DMTA, Mark II, Polymer Laboratories, UK) with a heating rate of 2°C/min and a single cantilever bending mode at 1 Hz was calibrated each day and measurements were taken in at least triplicate.

The glass transition was 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 tanδ (tan$\delta = E''/E'$, where E'' is the loss modulus). This procedure normally gave values varying within a range of 2·5°C.

Differential thermal analysis (DTA) measurements

DTA measurements were taken using a Shimadzu DTA equipped with a liquid N_2 cooling accessory and connected to an IBM/PC and a Hewlett-Packard plotter. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The sample size for DTA was approximately 10 mg. 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 99·9%) from Goodfellows Metals. The purge gases used were dry helium and dry nitrogen. The T_gs were determined from the second run after melting, quenching with liquid nitrogen and reheating at a heating rate of 2°C/min. The percentage crystallinity with DTA was calculated according to Gidley (Gidley, 1992).

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

Measurements of permeability

The measurements of gas permeability were carried out using a Davenport apparatus connected to an IBM/PC in accordance with ASTM D1434-66 (ASTM, 1966). Thickness was measured with a micrometer at five or six locations of the film.

Permeability (P) consists of solubility (S) and diffusivity (D) and it is described by the following equation:

$$P = D.S \tag{1}$$

Assuming that a unidirectional diffusion through a flat membrane occurs, then diffusion can be expressed as follows:

$$J_i = -D_{i(ci)} \frac{dc_i}{dx} \tag{2}$$

where J is the flux, $D_{i(ci)}$ signifies that the diffusion coefficient is dependent on the composition of the penetrant and c refers to the local gas or penetrant concentration.

The formula for the determination of the diffusion constant is as follows:

$$D = \frac{d^2}{6\theta} \tag{3}$$

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 thickness (x). It is also directly proportional to the area exposed (A) and the time (t) for which permeation occurs, and the relationship can be expressed with the following equation:

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

where P has a constant value for a specific combination of gas and polymer at a given temperature and it is variously known as the 'transmission factor' or 'permeability factor/constant/coefficient' (van Krevelen, 1990). Water vapor transmission rate (WVTR) measurements were carried out as previously reported (Martin-Polo *et al.*, 1992).

Mechanical properties

Tensile strength and percentage elongation

Tensile strength and percentage elongation were measured on dumbbells, after their equilibration at various relative humidities, using an Instron Universal Testing Instrument (model 1122) operated according to ASTM, 1989 (D828-88). Measurement conditions and calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis & Psomiadou, 1994).

Three-point bending test

All samples were cut with a scalpel, scissors or saw, into bars ~30×8×2 mm and stored for at least 3 weeks over saturated salt solutions at room temperature to obtain water contents which were measured on three replicates by drying at 105°C to constant weight.

RESULTS AND DISCUSSION

Thermal and thermal–mechanical properties

Although binary systems, e.g. starch/water and starch/sugars, have been quite extensively studied (Kalichevsky *et al.*, 1992a, b, 1993a, b; Trommsdorff & Tomka, 1995), a three component system tends to become even more complicated with regard to the interactions between the different components. It was previously shown that the gelatinized starch/water interactions are strong and particularly localized at the early stages of sorption whereas, at high water contents (>20%), a certain portion of water was exhibiting liquid-like properties. Sodium caseinate was preferred over casein for use in the preparation of blends with starch, because it has a higher water uptake than casein (3–7% higher when conditioned at the same RH). Therefore, water will be more homogeneously distributed throughout the entire blend mass which may favourably influence the mechanical properties of the blend.

The presence of water and sugars had a significant plasticizing effect on starch and on sodium caseinate (Tables 1–4). Depending on the extent of the induced plasticization (T_g lowering) the sugars could be classified as follows (Table 3): glycerol < sorbitol < xylose < sucrose.

A general observation for all DMTA and DTA traces is that the incorporation of sugars, in conjunction with the presence of water within the starch and/or the protein matrix, resulted in substantial broadening of the tanδ peak or of the step transition (Fig. 1d–f both for DMTA and DTA). The limited plasticizing effect of

Table 1. Glass transition temperatures (T_g, °C) of blends of corn starch and sodium caseinate conditioned at different relative humidities. The results give the average and standard deviation of at least three or five measurements for thermal and gas permeability (N_2) measurements, respectively

Corn starch %	Water %	Sodium caseinate %	T_g (°C)			
			DTA (2nd run)	DMTA (E')	DMTA (tanδ)	Permeability (inflection)
85	15	0	61·2±1·3	62·0±1·4	64·9±1·4	60·8±1·0
80	15	5	62·9±0·9	63·5±0·8	67·2±1·6	63·3±1·2
75	15	10	64·5±1·2	65·2±1·6	70·0±1·3	64·6±1·5
70	15	15	66·0±1·4	67·0±1·3	73·8±1·2	67·3±1·1
60	15	25	68·0±0·9	68·6±0·7	75·2±1·4	68·5±0·8
55	15	30	69·1±1·1	70·0±1·2	78·3±1·5	69·7±1·2
45	15	40	70·9±1·5	71·5±1·4	81·2±1·6	71·3±1·3
47·5	5	47·5	122·0±2·1	122·8±2·2	134·5±1·0	—
45·0	10	45·0	93·5±1·8	94·7±1·5	106·2±1·7	—
42·5	15	42·5	71·3±1·9	70·6±1·0	86·4±1·6	73·4±0·9
40·0	20	40·0	54·5±1·5	55·2±1·4	67·8±1·5	53·0±0·8
37·5	25	37·5	40·4±2·0	39·6±1·6	54·5±1·8	41·8±1·2
35·0	30	35·0	19·5±1·5	20·4±1·2	35·0±1·7	18·9±0·7

Table 2. Glass transition temperatures (T_g,°C) of blends of wheat starch and sodium caseinate conditioned at different relative humidities. The results give the average and standard deviation of at least three or five measurements for thermal and gas permeability (N_2) measurements, respectively

			T_g (°C)			
Wheat starch %	Water %	Sodium caseinate %	DTA	DMTA (E')	MTA (tanδ)	Permeability
78	17	2	56·4±0·8	54·9±1·5	60·3±1·7	49·5±1·2
71	17	12	57·6±0·6	58·2±0·9	63·5±1·8	58·3±0·9
65	17	18	59·2±1·1	59·9±1·3	66·7±1·3	60·3±1·3
58	17	25	63·1±1·3	62·0±1·2	71·0±1·5	62·7±1·2
51	17	32	65·9±0·9	67·2±1·4	74·2±1·6	66·5±1·1
43	17	40	69·3±1·2	70·4±1·1	77·5±0·9	70·7±0·9
28	17	55	74·6±1·1	76·2±0·8	81·9±1·4	74·2±1·5
48·0	4	48·0	114·3±2·1	112·5±1·8	119·5±1·8	—
46·0	8	46·0	95·6±1·8	98·0±1·5	107·5±1·2	—
42·5	15	42·5	66·8±1·7	64·3±0·9	75·2±1·4	61·5±1·8
40·0	20	40·0	49·7±1·8	51·2±1·7	59·4±1·5	51·7±1·0
37·0	26	37·0	33·2±1·5	31·5±1·3	41·6±1·8	34·7±1·2
35·0	30	35·0	14·4±0·7	12·9±1·1	21·7±1·4	12·1±0·8

Table 3. Thermal and thermomechanical properties of corn starch/glycerol, corn starch/sorbitol, corn starch/sucrose and corn starch/xylose blends. The results give the average and the standard deviation of at least three or five measurements for thermal and gas permeability (N_2) measurements, respectively

Corn starch %	Glycerol %	Water %	T_g (°C)			
			DSC	DMTA (tanδ)	DMTA (E')	Permeability
95	0	5	116·4±2·3	125·5±6·2	106·8±4·1	—
90	5	5	88·8±3·4	93·4±3·3	85·4±2·3	83·2±1·0
85	10	5	55·4±2·5	66·5±2·1	44·5±1·8	52·6±1·3
80	15	5	33·0±1·2	38·2±1·0	31·1±0·5	32·5±1·6
76	19	5	−4·2±2·0	3·3±1·1	−6·7±2·1	—
68	27	5	−19·1±3·1	−11·0±2·0	−2·2±1·6	—
Corn starch	Sorbitol	Water				
90	5	5	85·0±6·4	91·2±3·2	77·5±3·4	81·4±2·4
85	10	5	50·0±3·2	61·1±2·0	40·2±2·0	45·3±1·3
79	16	5	11·5±0·4	14·6±1·2	9·6±1·8	—
71	24	5	−10·0±2·2	−4·4±0·5	−13·2±2·1	—
67	28	5	−23·6±2·5	−18·9±2·1	−29·0±2·2	—
Corn starch	Sucrose	Water				
89	6	5	82·0±4·1	88·7±4·1	76·5±4·3	84·2±3·1
85	10	5	47·1±2·3	52·8±2·0	41·4±2·4	49·0±2·0
80	15	5	3·1±1·2	12·3±0·5	0·6±2·0	—
75	20	5	−14·3±2·5 −53·1±2·1	−9·0±2·2 −50·5±2·0	−18·9±1·3 −60·2±1·9	—
69	26	5	−28·5±3·0 NO*	−21·3±3·1 −65·3±2·1	−35·0±1 NO*	—
Corn starch	Xylose	Water				
90	5	5	80·6±6·1	83·9±5·1	71·0±6·1	78·8±4·2
86	9	5	46·2±5·0	49·0±4·0	36·4±3·2	39·7±3·3
79	16	5	−4·1±2·4	3·3±1·2	−9·8±2·0	
75	20	5	−11·2±1·2 −60±2·5	−4·4±0·9 −55·6±2·6	−16·1±3·1 −61·5±2·9	
70	25	5	−25±2·0 NO*	−17·0±3·1 NO*	−33·2±4·0 NO*	

*NO: not observed because the run started from −50°C.

sugars such as sucrose and xylose on starch/water blends, reported elsewhere (Kalichevsky *et al.*, 1993a) and attributed to the preferential hydration of sugar molecules, was not confirmed in our case (Table 3). On the contrary, sucrose and xylose had an even more pronounced plasticizing effect than glycerol and sorbitol on starch/water blends provided that their content did not exceed 15%. The plasticization of the composite food matrix with polyols or glycerol could possibly be due to changes in the polymer network, mainly related to the creation of highly mobile regions, which allow even more pronounced moisture uptake (Cherian *et al.*, 1995).

Below 15% sugar content no double peaks were recorded, implying that the starch/sodium caseinate blends do not phase separate which is in agreement

Table 4. Mechanical properties and water vapour transmission rate (WVTR) of corn starch/sodium caseinate/water blends at different relative humidities. The results give the average and the standard deviation of at least eight measurements

Corn starch %	Water %	Sodium caseinate %	Tensile strength (MPa)	Young's modulus (MPa)	Elongation %	WVTR (g/m s Pa)$\times 10^{-11}$
85	15	0	38·3±2·1	23·8±2·4	6·2±0·4	7·3±0·2
80	15	5	33·4±2·2	24·7±2·1	6·9±0·5	7·2±0·3
75	15	10	30·7±1·9	25·6±1·8	9·0±0·7	7·0±0·4
70	15	15	26·9±1·6	26·4±1·9	11·8±1·1	6·8±0·2
60	15	25	20·0±2·2	28·0±·2·3	14·9±1·2	6·5±0·1
55	15	30	17·1±1·3	28·8±2·5	19·2±1·7	6·1±0·2
45	15	40	13·3±1·2	29·5±2·2	28·0±2·5	5·4±0·1
47·5	5	47·5	22.0±0·4	30·1±2·7	30·2±2·6	5·9±0·2
45·0	10	45·0	21.4±0.2	29·0±2·5	32·6±2·5	6·8±0·3
42·5	15	42·5	20.7±0·5	27·7±1·9	34·0±1·8	8·0±0·2
40·0	20	40·0	17.8±0·3	25·9±2·3	38·0±3·2	9·1±0·4
37·5	25	37·5	13·0±0·3	24·0±2·2	37·1±1·9	11·4±0·5
35·0	30	35·0	11.1±1·0	21·7±2·4	39·5±0·6	14·5±0·6

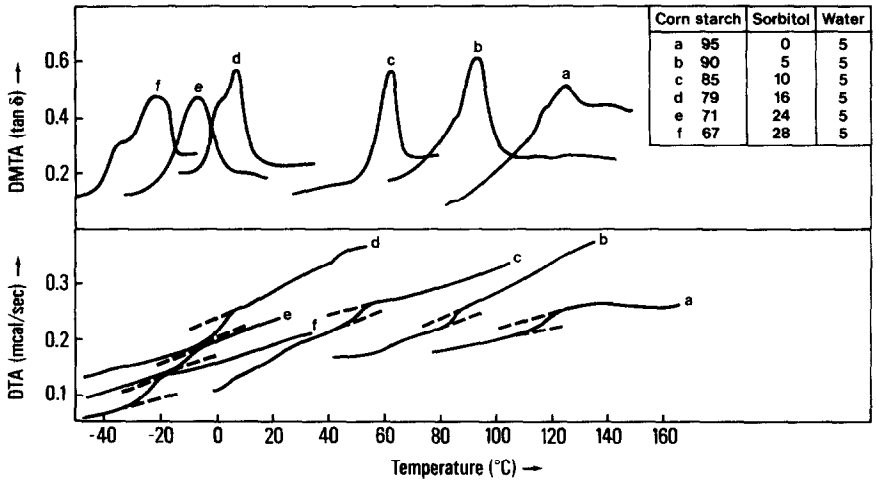

Fig. 1. Representative DMTA and DTA traces for corn starch/sorbitol/water blends.

with results reported by other researchers (Kalichevsky *et al.*, 1993b). When the polyol content exceeded the threshold of 15%, double peaks were recorded (Table 3), as previously found for natural and synthetic polymers (Cherian *et al.*, 1995; Bazuin & Eisenberg, 1986). This behavior is indicative of component incompatibility in the blend (i.e. between starch and polyol). The previously observed high and low temperature peaks (recorded by DMA) in the case of binary (gluten–glycerol or gluten–sucrose) or ternary (gluten–glycerol–sucrose/sorbitol) systems (Cherian *et al.*, 1995) was not confirmed by our experiments (DTA and DMTA) involving starch–sodium caseinate–plasticizer systems.

The interactions of molecules in the wheat starch–water or corn starch–water–sugar systems may be attributed to the interactions between hydroxyl groups of starch chains, starch–water and starch–sugar molecules, but also to sugar–sugar or water–sugar interactions (Tolstoguzow, 1994). The possibility of hydrogen bonding of starch within the blends increases considerably with the introduction of comparatively small size molecules, i.e. water and sugars. Previous studies on protein–protein (casein–ovalbumin, casein–soybean globulin), water and protein–polysaccharide systems have shown that the compatibility of the blend components is greatly affected by thermal treatment or their previous thermal history (Tolstoguzow *et al.*, 1985). It was also found that the protein–polysaccharide systems are characterized by limited compatibility between their components, occasionally resulting in phase separation.

The increase in water content resulted in a decrease of T_g (DTA, DMTA and permeability from Tables 1–4) due to increased starch–water hydrogen bonding and to decreasing number of intra- and intermolecular H-bonds between starch chains. This leads to lower interaction energy between starch chains, which in conjunction with the increased interchain distances, because of incorporation of water/sugars, could be considered as the main effects of the plasticizing molecules. This is manifested by the drop of flexural (Young's) modulus

and by the decrease in T_g (DTA, DMTA, permeability measurements).

Mechanical properties

Tensile strength–elongation

The tensile strength, Young's modulus and percentage elongation of corn starch/water/sugars or sodium caseinate films are given in Tables 5 and 6. It was previously shown that tensile strength and elongation of films prepared from different corn starches decrease with decreasing amylose content, because the branched molecules (amylopectin) cannot orientate and pack as closely as linear amylose molecules (Lourdin et al., 1995).

In the case of polymer composites and blends, depending on the direction of the applied stress with regard to the polymer chain orientation in the blend, two estimates (Equations 5 and 6) for tensile modulus can be deduced (Arvanitoyannis & Psomiadou, 1994; Arvanitoyannis *et al.*, 1995):

$$E_{\text{starch}} = V_{\text{amylose}}E_{\text{amylose}} + (1 - V_{\text{amylose}})E_{\text{amylopectin}} \quad (5)$$

$$E_{\text{starch}} = \frac{1}{\frac{V_{\text{amylose}}}{E_{\text{amylose}}} + \frac{1-V_{\text{amylose}}}{E_{\text{amylopectin}}}} \quad (6)$$

When a third component participates in the blend then the above equations could be modified accordingly:

$$E_{\text{blend}} = V_{\text{starch}}E_{\text{starch}} + (1 - V_{\text{starch}})E_{\text{sodium caseinate}} \quad (7)$$

$$E_{\text{blend}} = \frac{1}{\frac{V_{\text{starch}}}{E_{\text{starch}}} + \frac{1-V_{\text{starch}}}{E_{\text{sodium caseinate}}}} \quad (8)$$

However, estimates obtained for the upper (Equations 5 and 7) and lower (Equations 6 and 8) limits, when these equations were applied to starch (amylose/amylopectin blends) and to starch/sodium caseinate blends, showed no substantial differences. For example, if we apply the values $E_{\text{amylose}} = 31{\cdot}3$ MPa and $E_{\text{amylopectin}} = 16{\cdot}5$ MPa with 5% moisture (Lourdin *et al.*, 1995) to corn starch (amylose/amylopectin: 28/72, Blanshard, 1987) the obtained results are 20·59 and 19·02 MPa from Equations 5 and 6, respectively. It is obvious that there is a discrepancy, of approximately 40%, between the theoretically calculated and the experimentally determined values (Tables 5 and 6). Even greater differences between the theoretical and the experimental values were previously reported and were attributed to the higher molecular weight of components in native starches compared to pure amylose and amylopectin (Lourdin *et al.*, 1995). However, it is noteworthy that similar tensile strengths were obtained for films cast from corn starch and from a solution containing 75%, by weight, amylopectin and 25%, by weight, amylose (Young, 1984).

It should be mentioned that the mechanical prop-

Table 5. Mechanical properties and water vapour transmission rate (WVTR) of corn starch/glycerol, corn starch/sorbitol, corn starch/sucrose and corn starch/xylose blends. The results give the average and the standard deviation of at least eight measurements

Corn starch %	Glycerol %	Water %	Tensile strength (MPa)	Young's modulus (MPa)	Elongation %	WVTR (g/m s Pa)×10^{-11}
95	0	5	44·7±2·1	28·5±1·9	3·9±0·3	0·3±0·01
90	5	5	40·0±2·2	23·9±2·1	5·2±0·4	2·5±0·1
85	10	5	37·6±3·0	20·0±1·8	6·4±0·5	4·8±0·2
80	15	5	30·4±2·6	17·4±1·7	8·0±0·6	8·6±0·3
76	19	5	25·9±2·4	14·2±1·6	8·9±0·8	11·4±0·5
68	27	5	17·2±1·3	8·9±0·7	10·8±1·3	15·0±0·6
Corn starch	Sorbitol					
90	5	5	41·9±3·6	30·5±2·3	5·8±0·4	1·7±0·1
85	10	5	38·3±4·8	26·9±2·0	6·9±0·5	3·1±0·2
79	16	5	32·1±3·9	20·8±1·8	8·5±0·5	5·9±0·3
71	24	5	27·6±2·2	13·9±1·1	9·7±0·7	8·4±0·2
67	28	5	19·3±1·8	10·1±0·9	11·6±1·5	10·8±0·8
Corn starch	Sucrose					
89	6	5	37·5±2·5	24·2±1·9	3·7±0·5	3·3±0·2
85	10	5	33·3±2·9	19·5±2·2	3·5±0·4	6·7±0·4
80	15	5	26·0±1·8	15·0±1·7	3·2±0·3	9·8±0·9
75	20	5	20·8±1·5	11·7±1·0	3·0±0·2	14·0±1·6
69	26	5	16·5±1·3	8·4±0·9	2·9±0·3	18·2±1·5
Corn starch	Xylose					
90	5	5	39·3±3·6	26·7±2·1	4·3±0·4	1·8±0·3
86	9	5	34·5±2·9	21·6±1·9	5·7±0·5	3·4±0·4
79	16	5	28·0±2·6	17·0±1·6	7·0±0·6	5·7±0·4
75	20	5	23·8±1·9	12·5±1·4	8·1±0·6	7·6±1·1
70	25	5	17·5±1·5	9·3±0·8	9·0±0·8	9·3±1·2

Table 6. Percentage crystallinity (%Xc) of corn starch/glycerol, corn starch/sorbitol, corn starch/sucrose and corn starch/xylose blends determined from DTA (according to Gidley, 1992) and WAXDP after storage of films for 45 days

Corn starch %	Glycerol %	Water %	DTA	WAXDP (100% crystalline)
95	0	5	8·0	9·2
90	5	5	11·2	13·0
85	10	5	15·3	16·2
80	15	5	16·0	17·0
76	19	5	13·4	15·0
68	27	5	11·5	12·9
Corn starch	Sorbitol			
90	5	5	7·5	8·8
85	10	5	10·7	12·3
79	16	5	14·9	16·4
71	24	5	12·5	13·9
67	28	5	11·6	13·0
Corn starch	Sucrose			
89	6	5	5·2	6·3
85	10	5	7·4	8·5
80	15	5	8·6	10·0
75	20	5	6·9	8·0
69	26	5	5·4	6·5
Corn starch	Xylose			
90	5	5	1·3	1·8
86	9	5	2·5	3·6
79	16	5	3·9	5·0
75	20	5	2·8	4·3
70	25	5	1·5	2·4

erties measured by other researchers (Warburton *et al.*, 1993) for maize grit extrudates were considerably higher (10–20 times). Such variations were explained by differences in density as well as the size and number of cavities present (Lourdin *et al.*, 1995). Further work has to be conducted with microscopy or image analysis in order to clarify the nature of these differences.

In plasticized starches the efficiency of plasticization with the same amount of plasticizer is dependent on the amylose/amylopectin ratio (Lourdin *et al.*, 1995). The mechanical properties of blends of glycerol/corn starch showed a quite pronounced plasticizing effect (Tables 5 and 6).

Sorbitol has almost the same effect as glycerol on the mechanical properties of corn starch. It should be noted, however, that the increase in elongation was slightly greater compared to the one caused by incorporation of glycerol. A possible explanation might be the higher hydroxyl number of sorbitol. At this point the behavior of sucrose containing seven free -OH has to be noted, because it caused a decrease of both the tensile strength and the elongation (Tables 5 and 6). In the case of xylose, the starch/xylose blends showed a behavior (from the mechanical properties viewpoint) similar to that of sorbitol. However, another factor that we should bear in mind, is the effect of developed crystallinity during storage of the films. It is well known from synthetic polymers that high crystallinity, in conjunction with chain orientation, have a positive influence upon the tensile strength whereas the gas diffusion and permeation are substantially reduced (Arvanitoyannis *et al.*, 1994; Arvanitoyannis & Blanshard, 1993). The starch-based films appeared to be adequately strong, especially when the amylopectin content is low since the branched molecules show very limited orientation and packing ability compared to amylose (Young, 1984).

Novamont tried to modify starch (within the frame of an innovatory R and D program) into a mechanically superior form devoid of crystallinity (not detectable with X-rays and DTA) and marketed several products possessing good mechanical properties (Bastioli, 1995). Older reports (Wolff *et al.*, 1951) claim that amylose films produced by casting from water solutions, and not by high pressure molding, can reach adequate tensile strength (3–7 MPa depending on the amylose content) and be comparable to polyethylene (Griffin, 1994). However, in other publications the tensile strength of dry corn films was reported as high as 89·5 MPa (Young, 1984). Our values are in reasonable agreement (same order of magnitude or even closer) with recently published data on starch films reporting values in the range 40–60 MPa (Lourdin *et al.*, 1995; Lawton & Fanta, 1994).

As shown in Table 6 at higher plasticizer levels (> 10%) there is increased crystallinity rate (WAXDP, DTA), possibly due to enhanced diffusion of molecular chains segments following two months storage, especially for the glycerol/sorbitol plasticized films (Table 6). Corn starch/sodium caseinate films plasticized with water and aged over 2 months at room temperature were found to embrittle more and develop lower tensile strength with time (2 months), despite the development of crystallinity (Fig. 2). This rather surprising mechanical behavior of the blends could be probably attributed to the formation of localized crystalline regions involving starch (WAXDP 2θ angle).

Three point bending test

From Figs 3 and 4 is obvious that the effect of water content on flexural modulus, determined by the three point bend test, was more pronounced on corn starch when sucrose was used as plasticizer instead of glycerol. Previous publications are in agreement with our observations that the addition of water and polyols (glycerol, glucose, xylose) plasticize the wheat starch (Kirby *et al.*, 1993; Ollett *et al.*, 1991). It has been shown that with the addition of polyols, the fall in modulus with increasing water contents at the glass transition becomes somewhat smoother (Kirby *et al.*, 1993), which is in agreement with our findings (Figs 3 and 4). The corn starch/sodium caseinate blends showed a less dramatic fall (Fig. 5) because the modulus of sodium caseinate did not follow the sharp drop exhibited by starch and this could be, probably,

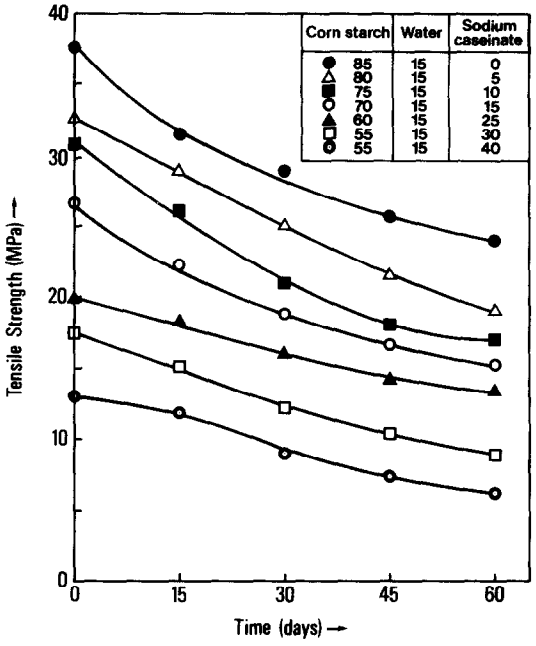

Fig. 2. Effect of storage time on tensile strength of various ratios of corn starch/sodium caseinate plasticized with 15% water.

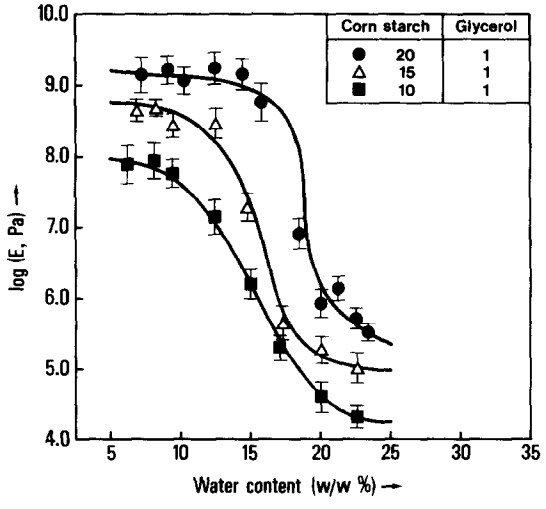

Fig. 3. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/glycerol blends. The results give the average and the standard deviation of at least eight measurements.

attributed to the fact that sodium caseinate has a higher T_g than starch at water contents above 5% (Kalichevsky *et al.*, 1993b). If we apply Equations (7) and (8) to starch/sodium caseinate blends [$E_{starch} = 8200$ MPa (Lourdin *et al.*, 1995) and $E_{sodium\ caseinate} = 6300$ MPa (Kalichevsky *et al.*, 1993b) we get $E_{blend} = 7250$ and 7120 MPa, respectively. These theoretical calculations are in good agreement with our experimental results (7500–8000 MPa, Fig. 5) and with those previously reported by other researchers (7500–8500 MPa, Lourdin *et al.*, 1995; Lawton & Fanta, 1994).

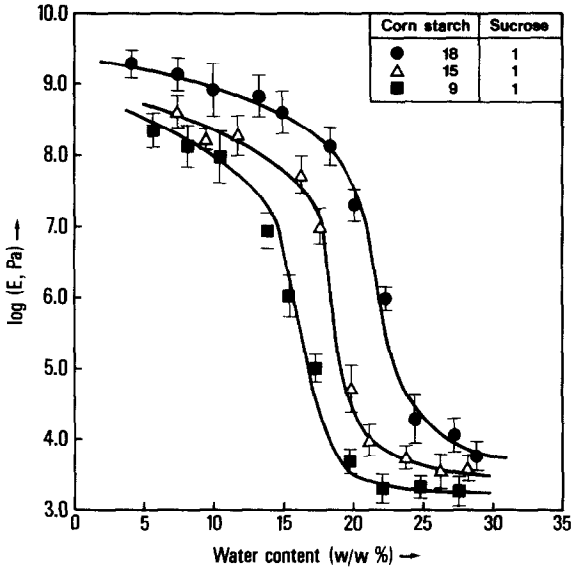

Fig. 4. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/sucrose blends. The results give the average and the standard deviation of at least eight measurements.

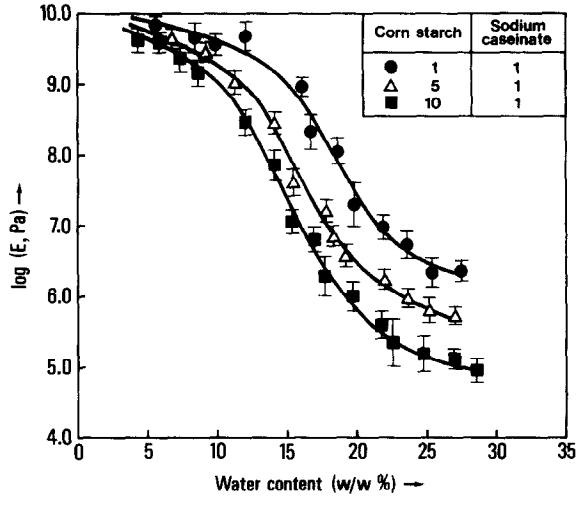

Fig. 5. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/sodium caseinate blends. The results give the average and the standard deviation of at least eight measurements.

Water vapor transmission rate (WVTR)

As has been already pointed out in several publications (Gennadios *et al.*, 1993b–d) films made from gluten or amylose have high *WVTR* due to 'clustering' of water molecules in their diffusion through microcavities, and this constitutes one of the major drawbacks for their use in commercial applications. In the present paper we used blends of corn starch with sodium caseinate in an effort to restrict the WVTR. Table 4 shows that an increase of sodium caseinate in the blend is accompanied by a proportional decrease in WVTR (from 7·3 down to $5{\cdot}4\times10^{-11}$) which is due to the less hydrophilic

nature of sodium caseinate compared to corn starch (Kalichevsky *et al.*, 1993a, b). When the plasticizer content, either as water or as sugar (glycerol, sorbitol, sucrose and xylose), increased in the blend, the WVTR augmented (Table 5). The increase in WVTR could be either attributed to greater interchain distances in the presence of plasticizer, shown elsewhere with computer simulation (Takeuchi, 1990; Takeuchi & Okazaki, 1990; Takeuchi *et al.*, 1990; Trommsdorff & Tomka, 1995) or to a denser packing of polymer chains.

Gas permeability (GP)

Although in synthetic polymers only rather negligible amounts of water are absorbed (Arvanitoyannis & Blanshard, 1993), in the case of edible films and, in particular, in starch or starch/sodium caseinate blends it is assumed that every polar group can interact with at least one water molecule. It should be also noted that difficulties in establishing a straightforward relationship between polar groups and solubility arise from the complexity of the interactions and the inherent difficulties in assessing factors such as accessibility of polar groups, the relative strength of water–water vs the water–polymer bonds and the degree of crystallinty of the food matrix.

Although several researchers working mainly in the field of polymer science have tried to put together the contributions of each group so that an empirical approach for synthetic polymers (summarized by van Krevelen, 1990) becomes feasible, whenever this approach was adopted for food systems its predictability was not that effective (Arvanitoyannis *et al.*, 1994). In this respect the additive molar function, the so called permachor (Π), was first introduced by Salame (1986):

$$Nx\pi = \Pi = (N_i x \pi_i) \tag{9}$$

where π is an additive molar function of permeability, N is 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:

$$P_{(298)} = P^*_{(298)}\exp(-S\pi) \tag{10}$$

where $P_{(298)}$ is the permeability of a standard gas (i.e. N_2) in a chosen standard polymer (i.e. rubber) and S is the scaling factor. By substituting ln $P^*_{298} = -12$ and $S = 0{\cdot}122$ (van Krevelen, 1990), the following equation is obtained, the applicability of which is, unfortunately, restricted to amorphous polymers:

$$InP^*_{(298)} = -12 - 0 \cdot 053\pi \tag{11}$$

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

$$\pi_{sc} = \pi_a - In\alpha = \pi_a - 41 \cdot 5In(1 - x_c) \tag{12}$$

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

When Equations 9–11 were applied to starch (amylose and amylopectin) the obtained values for dry amorphous samples were $6{\cdot}99\times10^{-20}$ and $2{\cdot}4\times10^{-19}$ cm^2/s Pa, respectively. The values of nitrogen permeability for dry starch are significantly lower than the experimental ones (Table 7).

The observed discrepancies could be attributed to various reasons among which the most important are the following (Mueller-Plathe, 1991a, b; Mueller-Plathe, 1992; van Krevelen, 1990): (i) introduction of microcrystallites; (ii) accessibility of polar groups; (iii) the geometry of the voids, the larger number of small spheres in the all-atom model leaves a larger number of smaller interstitial voids, and the diffusion rate decreases; (iv) size of the model polymer network; (v) details of microstructure; (vi) force fields and (vii) relative strength of water–water vs the polymer–water bonds.

The water content influences greatly the films containing hydrogen bonding groups and the gas diffusivity increases with water content as can be seen from Figs 6 and 7. In these figures it is demonstrated how T_g determination can be made from permeability measurements; i.e. the inflection of the line from permeability vs the inverse temperature. A possible explanation for such a change in the slope is that, in the first instance, a strong localization of the initially sorbed water occurs over a limited number of sites, whereas at higher water contents, the film matrix may swell, thus resulting in an even higher mobility of the sorbed water molecules. At high water contents it is believed that the starch chains move further apart and the number of intra- and interchain hydrogen bonds decrease considerably (Trommsdorff & Tomka, 1995). The widening of the matrix structure due to incorporation of plasticizer molecules would enhance gas permeation (Table 7).

The thermal dependence of diffusivity on temperature was experimentally found that it fits satisfactorily the Arrhenius equation:

$$D = D_0\exp(-E_D/RT) \tag{13}$$

where D_0 is the diffusion coefficient, E_D is the activation energy of diffusion and R is the universal gas constant.

The corresponding logarithmic expression for Equation (13) describing diffusivity is:

$$InD = InD_0 - E_D/RT \tag{14}$$

Similarly to Equation (13), the temperature dependence of permeability can be expressed as:

$$P = P_0\exp(-E_P/RT) \tag{15}$$

where E_P is the apparent activation energy of permeation, and:

$$\ln P = \ln P_0 - E_P/RT \tag{16}$$

Table 7. Gas permeability (O_2, N_2, CO_2 in $cm^{-2}s^{-1}Pa^{-1}$) of corn starch/glycerol, corn starch/sorbitol, corn starch/sucrose and corn starch/xylose blends. The results give the average and the standard deviation of at least five measurements

Corn starch %	Glycerol %	Water %	O_2	N_2	CO_2
95	0	5	3.7×10^{-17}	5.2×10^{-18}	2.5×10^{-16}
90	5	5	5.4×10^{-16}	3.1×10^{-17}	3.9×10^{-15}
85	10	5	6.5×10^{-15}	8.2×10^{-16}	5.3×10^{-14}
80	15	5	2.3×10^{-15}	1.8×10^{-16}	1.8×10^{-14}
76	19	5	1.7×10^{-14}	4.5×10^{-15}	0.9×10^{-13}
68	27	5	7.4×10^{-13}	8.4×10^{-14}	1.6×10^{-12}
Corn starch	Sorbitol				
90	5	5	7.6×10^{-16}	8.5×10^{-17}	3.9×10^{-15}
85	10	5	8.2×10^{-15}	9.8×10^{-16}	6.2×10^{-14}
79	16	5	6.4×10^{-15}	7.3×10^{-16}	2.4×10^{-14}
71	24	5	5.9×10^{-14}	6.4×10^{-15}	4.4×10^{-13}
67	28	5	7.8×10^{-12}	1.1×10^{-13}	6.2×10^{-11}
Corn starch	Sucrose				
89	6	5	2.3×10^{-16}	1.6×10^{-17}	3.6×10^{-15}
85	10	5	6.0×10^{-15}	4.5×10^{-16}	5.3×10^{-14}
80	15	5	1.9×10^{-15}	1.0×10^{-16}	2.4×10^{-14}
75	20	5	5.5×10^{-14}	2.4×10^{-15}	7.3×10^{-13}
69	26	5	6.8×10^{-12}	1.5×10^{-13}	4.6×10^{-11}
Corn starch	Xylose				
90	5	5	3.4×10^{-16}	1.9×10^{-17}	2.2×10^{-15}
86	9	5	5.3×10^{-15}	6.7×10^{-16}	6.4×10^{-14}
79	16	5	3.2×10^{-14}	1.5×10^{-16}	2.7×10^{-14}
75	20	5	1.5×10^{-14}	2.1×10^{-15}	3.3×10^{-13}
70	25	5	6.7×10^{-13}	9.2×10^{-14}	5.4×10^{-12}

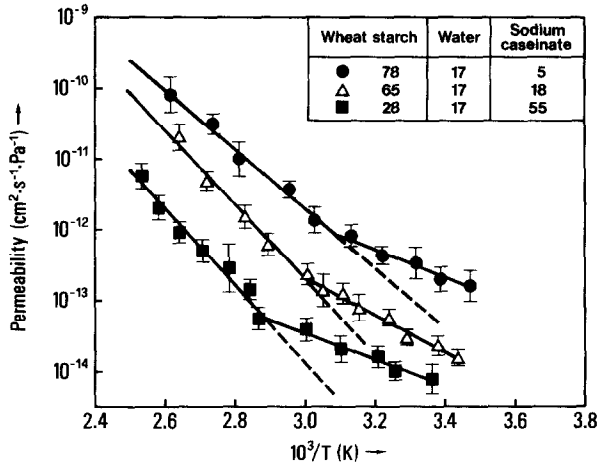

Fig. 6. Permeability of O_2 in wheat starch/sodium caseinate films, plasticized with 17% H_2O, (derived from Equation 16) vs the inverse temperature ($1/T$(K)). The results give the average and the standard deviation of at least five measure-

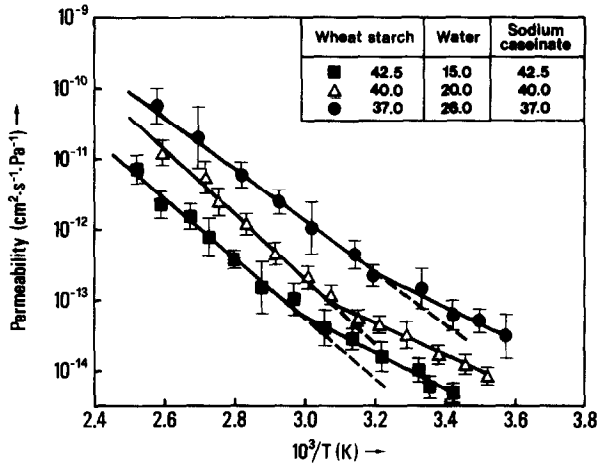

Fig. 7. Permeability of O_2 in wheat starch/water/sodium caseinate films, plasticized with 17% H_2O, (derived from Equation 16) vs the inverse temperature ($1/T$(K)). The results give the average and the standard deviation of at least five measurements.

The activation energies of diffusion and permeation were calculated according to Equations (14) and (16) for starch/water/sugar and starch/sodium caseinate/water or sugars (Table 8).

The activation energy of diffusion (E_D) is considered to be the most important parameter in the diffusion process because it is the energy needed to enable the dissolved molecule to 'jump' into another 'hole'. Obviously, larger molecules necessitate larger 'holes' and, hence, higher activation energies as can be seen from Table 8. The gas diffusion through the film matrix could be visualized as following two different modes depending on temperature. At low temperatures, one may assume that diffusion is effected by small oscillations of gas molecules which are trapped in small local voids (Gelin, 1994). At higher temperatures, formation of new cavities and creation of interconnecting channels

Table 8. Activation energies for diffusion (E_D[a], kJ/mol) and permeation (E_P, kJ/mol) both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g) for corn starch/water/sodium caseinate) blends. The results give the average and the standard deviation of five measurements**

Corn starch (% w/w)	Water (% w/w)	Sodium caseinate (% w/w)	N_2				O_2			
			E_D[a]		E_P[b]		E_D[a]		E_P[b]	
			$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$
85	15	0	4.7±0.29	3.2±0.18	6.8±0.61	4.6±0.31	4.3±0.28	2.8±0.10	6.3±0.41	4.1±0.34
80	15	5	4.9±0.34	3.3±0.21	7.6±0.55	5.0±0.28	4.0±0.25	3.0±0.17	7.0±0.38	4.5±0.40
70	15	15	5.3±0.19	3.8±0.25	8.0±0.72	5.7±0.40	4.8±0.30	3.4±0.16	7.5±0.46	5.3±0.28
55	15	30	5.8±0.23	4.1±0.33	8.6±0.65	6.4±0.35	5.3±0.32	3.6±0.26	8.2±0.42	5.9±0.40
47.5	5	47.5	8.9±0.72	5.7±0.29	10.5±1.16	7.5±0.18	8.0±0.51	5.2±0.32	9.8±0.53	7.0±0.55
40	20	40	5.5±0.60	3.6±0.18	7.1±0.81	5.4±0.33	4.8±0.39	3.1±0.20	6.6±0.60	5.1±0.42
35	30	35	2.7±0.15	1.5±0.07	4.0±0.35	2.9±0.15	2.4±0.06	1.2±0.07	3.4±0.28	2.6±0.09
Corn starch	Water	Glycerol								
69	5	26	3.8±0.12	2.5±0.08	4.9±0.10	3.6±0.09	3.5±0.08	2.1±0.09	4.5±0.32	3.2±0.11
Corn starch	Water	Sorbitol								
71	5	24	2.1±0.09	1.2±0.06	3.4±0.06	2.2±0.05	1.6±0.02	0.9±0.04	3.0±0.19	1.8±0.05
Corn starch	Water	Sucrose								
69	5	26	5.0±0.45	4.1±0.35	7.4±0.60	5.3±0.50	4.5±0.31	3.5±0.16	6.9±0.42	4.8±0.19
Corn starch	Water	Xylose								
70	5	25	5.2±0.43	4.0±0.35	7.7±0.58	5.4±0.30	4.8±0.28	3.3±0.20	7.1±0.50	5.0±0.28

[a]Calculated according to equation (14).
[b]Calculated according to equation (16).

occurs, finally leading to annihilation of the original cavities (Gelin & Karplus, 1977).

The relationships between crystallinity of the various starch/sodium caseinate/water blends, as a result of storage and permeability, are shown in Figs 8 and 9. It is obvious that the higher the plasticizer content and the lower the percentage crystallinity (its development necessitates longer times), the higher the oxygen permeability. The exact opposite effect is observed when the sodium caseinate content increases, i.e. lower gas permeabilities were shown, since the sodium caseinate is less plasticizable than corn or wheat starch.

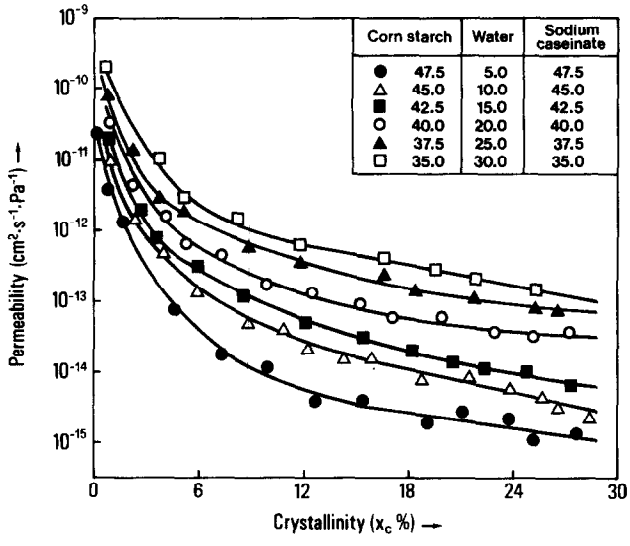

Fig. 8. Effect of various water contents on permeability of O_2 in corn starch/sodium caseinate. (1:1) films vs the developed crystallinity (% X_c).

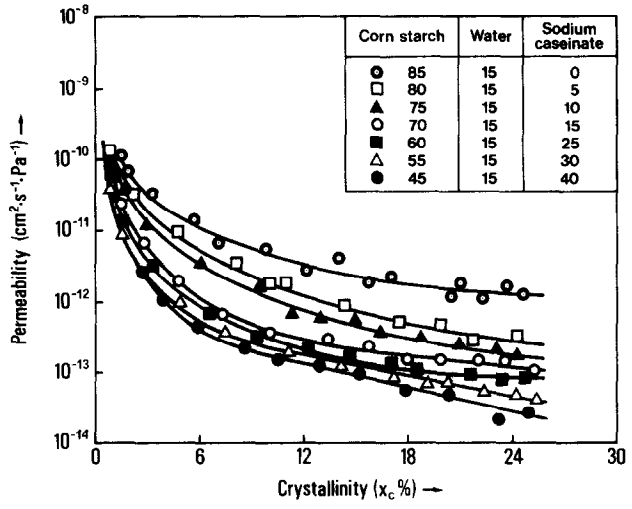

Fig. 9. Effect of various sodium caseinate contents on permeability of O_2 in corn starch films plasticized with water (15% w/w) vs the developed percentage crystallinity.

CONCLUSIONS

Edible films, from wheat and corn starch with sodium caseinate plasticized by water or several sugars/glycerol, were tested with regard to their compatibility, mechanical strength, and gas and water vapor permeabilities. Most films, with water contents < 15% w/w, had suffi-

cient strength, acceptable gas barrier properties and showed no phase separation. When the water/sugar content exceeded the threshold of 15% total plasticizer content, both thermal and mechanical properties showed a pronounced change because of the disruption of the starch/sodium caseinate matrix.

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