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Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends

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Aqueous blends of sodium caseinate and soluble starch, plasticized with polyols, were prepared by casting or by extrusion and hot pressing. The mechanical, thermal, gas and water permeation properties of these blends were studied after their conditioning at various relative humidities. With increasing plasticizer (water, polyols) content there was a progressive decrease of T_g of the blends. The plasticized blends also showed increased percentage elongation, whereas their flexural modulus and tensile strength exhibited a substantial drop. The gas permeability–temperature plots revealed Arrhenius-type relationships with an inflection in the glass transition temperature region. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Edible films or coatings have long been used empirically for food protection and shelf-life prolongation (Guilbert and Gontard, 1995). Wax coating, casein or lipoprotein—'skin forming'—coating and polysaccharide film formulation (such as starch and chitosan) are still the most representative examples of edible films (Guilbert and Biquet, 1989; Drake *et al*., 1991; Guilbert *et al*., 1996; Gennadios and Weller, 1990; Gennadios *et al*., 1993*a,b,c,d,e*; Wong *et al*., 1992; El Ghaouth *et al*., 1991; El Ghaouth *et al*., 1992; Lourdin *et al*., 1995). Edible films have to overcome several drawbacks, mainly related to their limitations in terms of their poor moisture barrier performance (apart from wax), colour and appearance, mechanical and rheological properties (Koelsch, 1994; Krochta *et al*., 1994, 1992).

Despite these shortcomings, edible films are also endowed with noteworthy properties such as being environmentally friendly, contribution to improvement of textural properties and preservation of volatile components and coherent structure (Kester and Fennema, 1986). However, edible films have not yet found extensive applications in the food industry (Kester and Fennema, 1986; Arvanitoyannis *et al*., 1996). The potential of polysaccharides and proteins as edible films has already been recognized by several research groups (Gennadios and Weller, 1990; Kester and Fennema, 1989*a,b*) and by the industry as well as being a very promising alternative, but only for special applications, to the omnipresent synthetic polymer packaging (Krochta *et al*., 1994).

Apart from some high amylose and modified starches (cross-linked, methylated), starch, in general, does not form tough, pliable and unsupported films. Nevertheless, it has found extensive use in the formulation of adhesives and sizings to improve the mechanical properties of items such as paper and textiles, in which the film-forming ability is of great importance (Lloyd and Kirst, 1963; Wolff *et al*., 1951; Young, 1984). Soluble starch was selected in this paper in view of the occasionally encountered solubility problems in the case of gelatinized corn starch-based films (Arvanitoyannis *et al*., 1996; Psomiadou *et al*., 1996).

Casein and casein derivatives have found many applications in the food and pharmaceutical industries (Southward, 1989; Kinsella, 1984). The unique characteristics of milk proteins make them excellent candidates for incorporation into edible films and coatings to control mass transfer in food systems. Sodium caseinate was used in our experiments because it is commercially available, has a satisfactory thermal stability and can easily form films from aqueous solutions due to its random coil nature and ability to form extensive intermolecular hydrogen, electrostatic and hydrophobic

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bonds (McHugh and Krochta, 1994*a,b*; Avena-Bustillos and Krochta, 1993; Krochta *et al.*, 1990).

In the present paper of this series (Arvanitoyannis *et al.*, 1996, 1997; Psomiadou *et al.*, 1996), edible films made from blends of soluble starch and sodium caseinate were prepared and studied with regard to their thermal, mechanical properties and their gas and water permeability. The obtained values were further compared to others already available in the literature for similar systems and some eventual possible uses were also suggested.

MATERIALS AND METHODS

Materials

Soluble starch and sodium caseinate (practical grade), glycerol, sorbitol, xylose (analytically pure) were purchased from Wako Chemicals (Japan).

Preparation of samples in the glassy state

Soluble 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.

The preparation of samples of blends of soluble starch with sodium caseinate with glycerol/sugars and water was carried out as described elsewhere (Arvanitoyannis *et al.*, 1994). Mixtures of sodium caseinate and soluble starch were passed through the roller-drier to obtain blends of appropriate composition. Preparation of films of sodium caseinate with soluble starch for permeability measurements (thickness range ~0.05 mm ±0.001) was carried out by casting their solutions at temperatures of 85–90°C for 15 min over Plexiglass plates. Thicker specimens for DTA tests were made by hot pressing (25 kN/600 cm^2, 110°C/15 min). Conditioning of samples at different relative humidities was made as previously described (Arvanitoyannis *et al.*, 1992, 1994; Arvanitoyannis and Blanshard, 1993;).

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 aluminium pans were used with an empty aluminium 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 heating above the T_g region, quenching with liquid nitrogen and reheating at a heating rate of 2°C/min. Data analysis to fit experimental values of T_g to the empirical Gordon–Taylor equation (Gordon and Taylor, 1952) was performed using the *TableCurve*® software (Jandel Scientific), a non-linear least-squares-fitting package:

$$T_g = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} \tag{1}$$

where w_1 and w_2 are the respective weight fractions of the polymer blend and water, T_{g_1} is the T_g of the composite polymer matrix, T_{g_2} is the T_g of the amorphous water, and k is a constant related to the strength of polymer–diluent interaction (the larger the k, the greater the plasticization effect). The k constant is equivalent to the ratio of the heat capacity changes at T_g of the pure diluent and the polymer matrix, $\Delta C_{p_2}/\Delta C_{p_1}$. A T_g of −135°C was used for water (Johari *et al.*, 1987). Two plots are presented: one based on the best data fitting (optimization for both parameters, k and Tg_{matrix}), and the other based on a k value of 4.5 (an approximate estimate of $\Delta C_{p_2}/\Delta C_{p_1}$, based on literature values of ΔC_p for water and starch/caseinate).

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

$$P = D.S \tag{2}$$

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

$$J_i = -D_{i(ci)} \frac{\mathrm{d}c_i}{\mathrm{d}x} \tag{3}$$

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

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

$$D = \frac{d^2}{6\theta} \tag{4}$$

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 pressure exerted by the gas on each side of the film (p_1-p_2) and is inversely proportional to its thickness (x). It is also directly proportional to the film area exposed (A) and the time (t) for which permeation occurs. This relationship can be expressed by the following equation:

$$Q = \frac{PAt(p_1 - p_2)}{x} \quad (5)$$

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; Arvanitoyannis *et al.*, 1992).

Water Vapour Transmission Rate (WVTR)

The WVTR measurements were carried out as previously reported (Martin-Polo *et al.*, 1992).

Tensile strength and percentage elongation

Tensile strength and percentage elongation were measured on dumbbells, after their exposure to various relative humidity environments to attain a desired level of moisture, using an Instron Universal Testing Instrument (model 1122) operated according to ASTM D828-881 (ASTM, 1989). Measurement conditions and calculations of tensile strength and percentage elongation were made as described previously (Arvanitoyannis and Psomiadou, 1994).

Three-point bending test

All samples (prepared by hot pressing 25 kN/600 cm^2, 110°C for 15 min) 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 a desired level of water content which was measured on three replicates by drying at 105°C to constant weight.

RESULTS AND DISCUSSION

Thermal properties

There has been a long debate regarding the homogeneous distribution of water in binary and ternary systems, particularly at a microstructural level. Although several new methods such as CP-MAS and NMR imaging have been employed toward this purpose, no concluding evidence has yet been published regarding this phenomenon. Therefore, in our study we assume that our binary or ternary blends are characterized by a homogeneous distribution of water. In all blends examined, a single glass transition was detected for the polymeric constituents (starch–caseinate blends), presumably due to the close proximity of the T_gs of the individual components and a similar plasticization response in the presence of water and other polyols. The T_g of our binary system based on soluble starch/sodium caseinate decreased as water content increased due to plasticization of the polymer blend. The state diagram of soluble starch/sodium caseinate presenting experimental data from DTA is shown in Fig. 1(a), whereas the respective diagrams of the ternary systems (starch/sodium caseinate/polyol, 45/45/10 & 42.5/42.5/15 w/w/w) are given in Fig. 1(b–e). In general, sorbitol, despite its greater molecular weight, exhibited a more pronounced plasticizing effect (greater T_g depression) than glycerol on the polymer matrix. This is in agreement with other findings on starch-based polymer blends (Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996). This is also reflected by the estimated T_gs of the dry polymer blends obtained from the Gordon–Taylor plots (Fig. 1); i.e. the T_g of about 503 K for the dry soluble starch/sodium caseinate blend is suppressed to 409 K and 397 K for blends containing 10% and 15% glycerol and to 398 K and 382 K for blends with 10% and 15% sorbitol content, respectively. The *G–T* plots based on a k value of 4.5 were not good fits in describing the T_g depression ($r^2 = 0.85$–0.95), and gave higher estimates of T_g for the dry polymer matrix than those obtained when the program was forced to optimize for both parameters.

Gas permeability

Although enrobing of perishable produce in an edible film or coating, to control respiratory gas exchange, suppress aerobic respiration and prolong storage life, has been known for a long time (Kester and Fennema, 1986; Lovings and Cutts, 1982), only very recently have coatings been used toward this purpose (Wong *et al.*, 1992; El Ghaouth *et al.*, 1992). Application of group contribution theory, initially coined for synthetic polymers by Salame (1986), in the case of natural polymers, did not result in particularly promising results (Arvanitoyannis *et al.*, 1994, 1996; Psomiadou *et al.*, 1996). Observed discrepancies between the empirical (group contribution theory) and experimental values might be explained by the following: accessibility of polar groups (–OH), the geometry of the voids in the polymer matrix, and the relative strengths of water–water, water–polyol versus the polymer–water and polymer–polyol composite blends (Mueller-Plathe, 1991*a*,*b*, 1992). Our results regarding the gas permeability measurements of our plasticized blends are in agreement with previously

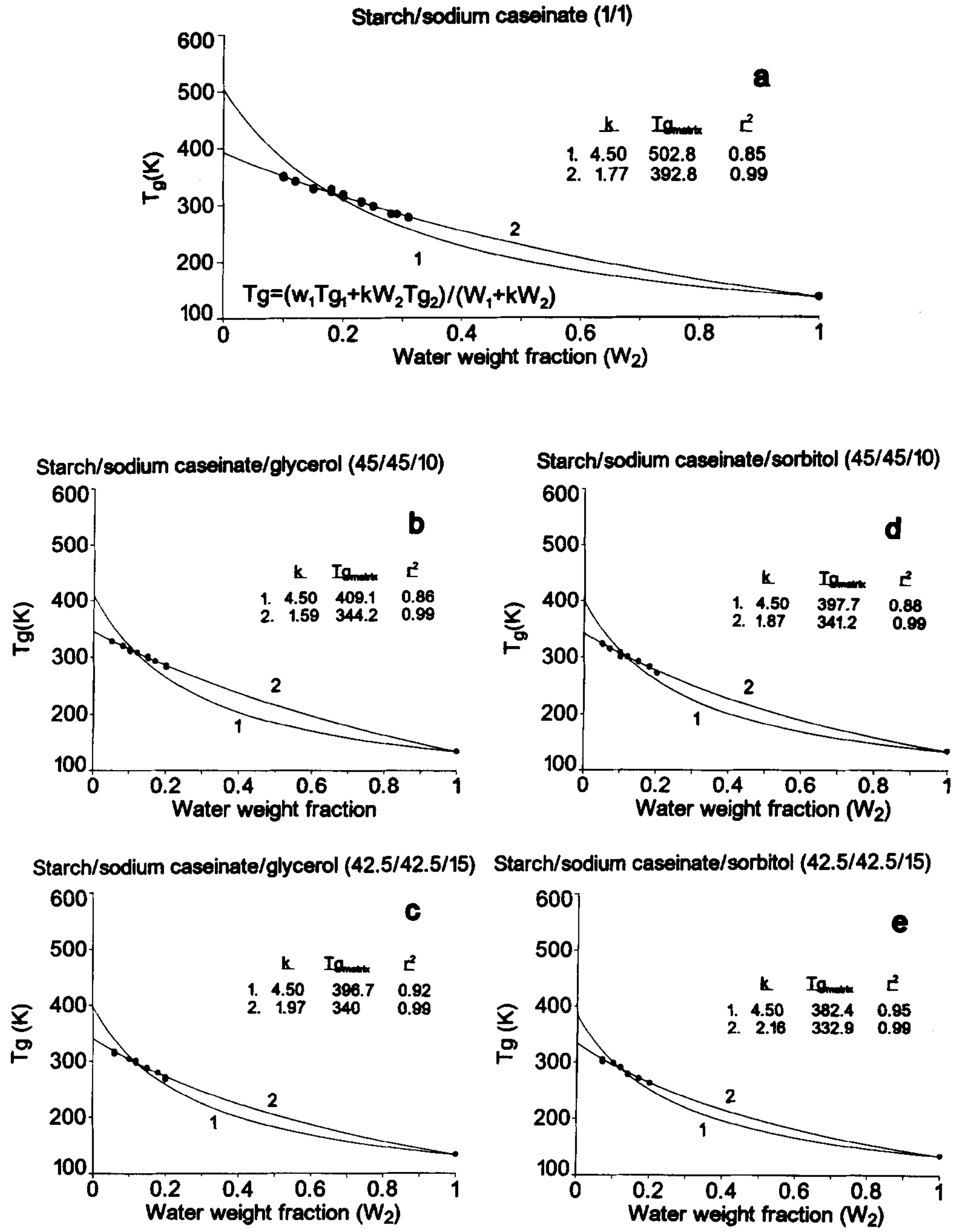

Fig. 1. State diagrams of soluble starch/sodium caseinate (1:1)/polyol blends. T_g versus water content (●), experimental data; solid lines give the corresponding Gordon–Taylor plots of the data). Numbers in parentheses refer to weight fraction ratios of blend components.

reported GP measurements for both synthetic and natural polymers (Arvanitoyannis *et al.*, 1994, 1996; Psomiadou *et al.*, 1996; Arvanitoyannis and Blanshard, 1993; Myers *et al.*, 1960). Figures 2, 3 and Tables 1 and 2 show the effect of different water contents on the gas permeability (O_2, N_2 and CO_2) of soluble starch/sodium caseinate films. The inflection in the slope of permeability vs the inverse temperature ($10^3/T$, K) plots gives an indirect estimate of the glass transition temperature (Figs 2 and 3). The T_g values obtained from permeability measurements were comparable to those obtained from the thermal properties (Fig. 1). This concurs with previously reported observations on other starch-based polymer blends (Arvanitoyannis *et al.*, 1994, 1996, 1997; Psomiadou *et al.*, 1996).

According to Pace and Datyner (1979*a*,*b*,*c*), the gas molecule can move through the polymer blend in two distinct ways: (a) along the axis of a 'tube' formed by adjacent parallel chains and (b) perpendicular to this axis. The latter process is the most predominant mechanism for gas transfer through polymer matrices. It is obvious that, though the first process requires no activation energy, the second requires activation energy for producing chain separation. In the case of our binary blends, which have already been plasticized either by water, or synergistically, by water and polyol, the mobility of the polymer network increases and the gas molecules require far less activation energy as shown in Table 3. The thermal dependence of diffusivity on temperature was found to satisfactorily follow an Arrhenius-type relationship.

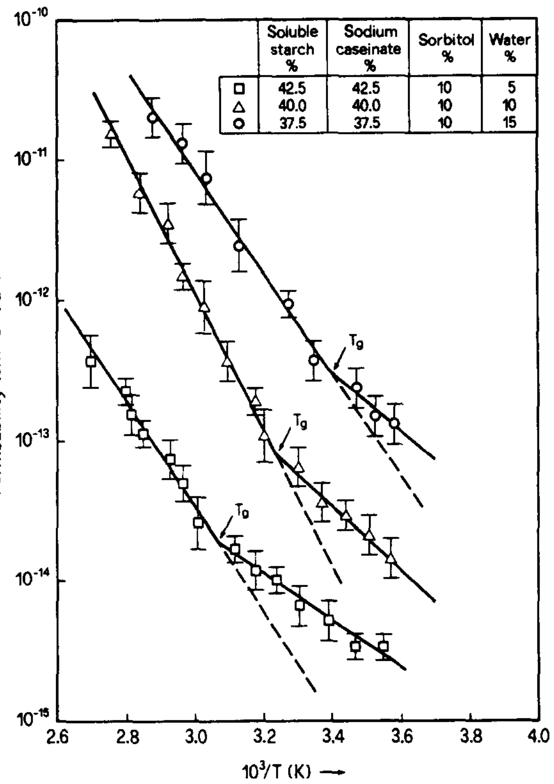

Fig. 2. Permeability of CO_2 in soluble starch/sodium caseinate/sorbitol blends plasticized with different amounts of water vs the inverse temperature [$(10^3/T)$, K]. The results give the average and the standard deviation of at least five measurements.

$$D = D_0 \exp(-E_D/RT) \tag{6}$$

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

The corresponding logarithmic expression for eqn (6) describing diffusivity is:

$$\ln D = \ln D_0 - E_D/RT \tag{7}$$

Similarly to eqn (6), the temperature-dependence of permeability can be expressed as

$$P = P_0 \exp(-E_P/RT) \tag{8}$$

where E_P is the apparent activation energy of permeation, and the corresponding logarithmic expression

$$\ln P = \ln P_0 - E_P/RT \tag{9}$$

Both gas diffusivity and permeability data followed Arrhenius-type relationships, from which the respective activation energies were calculated (Table 3).

Water Vapour Transmission Rate (WVTR)

Taking accurate and reproducible sorption and transport measurements for water vapour is a far more difficult and tedious task than for most other gas penetrants because of the high heat of vaporization, high solubility and cluster formation within the polymer, low saturation vapour pressure and tendency to plasticize the polymer matrix (Schult and Paul, 1996). In the case of natural polymers, it was shown that high heat of water

Table 1. Gas permeability (O_2, N_2, CO_2 in $cm^2 s^{-1} Pa^{-1}$, 22°C), WVTR (in $g m^{-1} s^{-1} Pa^{-1}$, 22°C) and glass transition temperature (T_g, K) (determined from the inflection of gas permeability vs inverse temperature) of soluble starch–sodium caseinate plasticized with glycerol, sorbitol, or xylose with 5% water content

Soluble starch %	Sodium caseinate %	Glycerol %	Water %	O_2 ($cm^2 s^{-1} Pa^{-1}$)	N_2 ($cm^2 s^{-1} Pa^{-1}$)	CO_2 ($cm^2 s^{-1} Pa^{-1}$)	WVPR ($g m^{-1} s^{-1} Pa^{-1}$)$\times 10^{-11}$	T_g (K)
47.5	47.5	0	5	$4.1(\pm 0.3)\times 10^{-16}$	$2.5(\pm 0.2)\times 10^{-17}$	$2.1(\pm 0.2)\times 10^{-15}$	0.25 ± 0.01	$365. \pm 2$
45.0	45.0	5	5	$9.3(\pm 1.0)\times 10^{-16}$	$7.5(\pm 0.6)\times 10^{-17}$	$6.4(\pm 0.5)\times 10^{-15}$	2.1 ± 0.03	$326. \pm 2$
40.0	40.0	15	5	$5.4(\pm 0.4)\times 10^{-15}$	$3.2(\pm 0.2)\times 10^{-16}$	$1.8(\pm 0.2)\times 10^{-14}$	5.2 ± 0.04	312 ± 1
32.5	32.5	30	5	$3.5(\pm 0.2)\times 10^{-12}$	$1.1(\pm 0.1)\times 10^{-13}$	$1.4(\pm 0.1)\times 10^{-11}$	15.1 ± 1.3	—
Soluble starch %	Sodium caseinate %	Sorbitol %	Water %					
45.0	45.0	5	5	$1.4(\pm 0.1)\times 10^{-15}$	$5.8(\pm 0.5)\times 10^{-16}$	$4.5(\pm 0.3)\times 10^{-14}$	3.3 ± 0.2	343 ± 2
40.0	40.0	15	5	$9.6(\pm 0.8)\times 10^{-15}$	$2.4(\pm 0.2)\times 10^{-15}$	$3.3(\pm 0.2)\times 10^{-13}$	6.4 ± 0.5	317 ± 3
32.5	32.5	30	5	$7.3(\pm 0.6)\times 10^{-12}$	$5.2(\pm 04)\times 10^{-13}$	$6.1(\pm 0.4)\times 10^{-11}$	21.3 ± 1.8	—
Soluble starch %	Sodium Caseinate %	Xylose %	Water %					
45.0	45.0	5	5	$0.5(\pm 0.1)\times 10^{-15}$	$3.5(\pm 0.4)\times 10^{-16}$	$9.7(\pm 1.2)\times 10^{-15}$	3.9 ± 0.02	344 ± 2
40.0	40.0	15	5	$7.8(\pm 0.6)\times 10^{-15}$	$8.0(\pm 0.7)\times 10^{-16}$	$6.6(\pm 0.5)\times 10^{-14}$	7.6 ± 0.3	315 ± 2
32.5	32.5	30	5	$5.3(\pm 0.4)\times 10^{-12}$	$3.7(\pm 0.4)\times 10^{-13}$	$4.0(\pm 0.3)\times 10^{-11}$	24.6 ± 1.5	—

vaporization and water clustering are primarily responsible for the recorded high WVTR, which continues to be one of the major drawbacks of natural polymers. An increase in the plasticizer content (water or water/polyol) resulted in the formation of a much more hydrophilic polymer matrix, which is considerably more susceptible to WVTR as can be seen from Tables 1 and 2. The pronounced increase in WVTR, due to plasticization of the starch/caseinate blends by water and polyols, is further corroborated by previous computer simulation experiments which confirmed that, in the presence of a plasticizer, there were greater inter-chain distances resulting in less efficient polymer chain packing (Takeuchi, 1990; Takeuchi and Okazaki, 1990; Takeuchi *et al.*, 1990; Trommsdorff and Tomka, 1995).

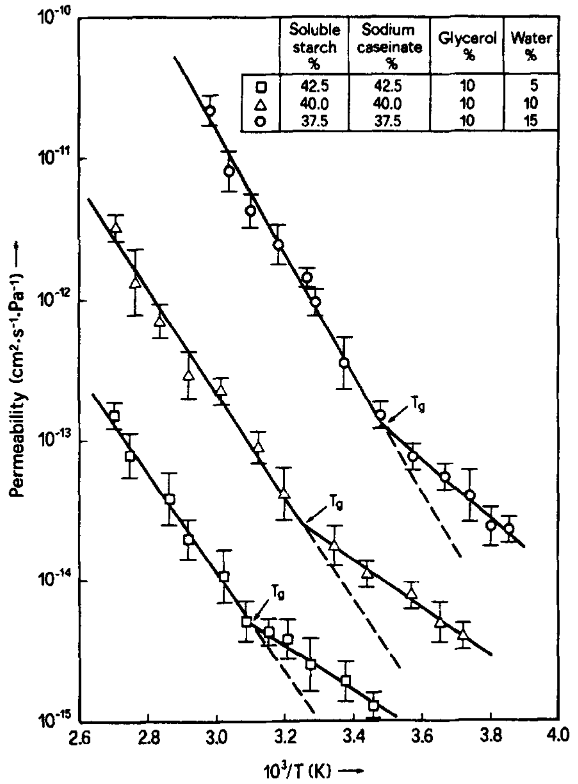

Fig. 3. Permeability of CO_2 in soluble starch/sodium caseinate/glycerol blends plasticized with different amounts of water vs the inverse temperature [($10^3/T$), K]. The results give the average and the standard deviation of at least five measurements.

Tensile strength—percentage elongation

The tensile strength and percentage elongation of films based on soluble starch/sodium caseinate at a standard water content are given in Tables 4 and 5. Table 4 shows the effect of varying moisture content on mechanical properties of soluble starch-based films. A clear increase in percentage elongation of films with increasing water and/or polyol contents was observed. These results should be attributed to the plasticization of the hygroscopic polymer matrix by water in agreement with previous publications (Lawton and Fanta, 1994; Lawton, 1996; Hoseney, 1994; Christensen *et al.*, 1982; Bader and Gortiz, 1994). In this respect, natural polymers behave similarly to synthetic polymers which are sensitive to moisture absoption (Okaya, 1992). Higher plasticization levels with polyols or polyol–water were shown to have a very pronounced effect both on percentage elongation and tensile strength of films. In fact, tensile strength decreased proportionally to the plasticizer content, whereas the percentage elongation showed a substantial increase in agreement with previous studies (Lawton, 1996; Arvanitoyannis *et al.*, 1996; Psomiadou

Table 2. Gas permeability (O_2, N_2, CO_2 in $cm^2 s^{-1} Pa^{-1}$, 22°C) and WVTR (in $g m^{-1} s^{-1} Pa^{-1}$, 22°C) and glass transition temperature (T_g, K) (determined from the inflection of gas permeability vs inverse temperature) of soluble starch–sodium caseinate plasticized with glycerol, sorbitol, or xylose with 10% water content

Soluble starch %	Sodium Caseinate %	Glycerol %	Water %	O_2 ($cm^2 s^{-1} Pa^{-1}$)	N_2 ($cm^2 s^{-1} Pa^{-1}$)	CO_2 ($cm^2 s^{-1} Pa^{-1}$)	WVTR ($g m^{-1} s^{-1} Pa^{-1} \times 10^{-11}$)	T_g (K)
45.0	45.0	0	10	$5.1(\pm0.6)\times10^{-15}$	$3.9(\pm0.3)\times10^{-16}$	$2.1(\pm0.2)\times10^{-14}$	0.42 ± 0.02	349 ± 2
42.5	42.5	5	10	$8.0(\pm0.7)\times10^{-15}$	$9.5(\pm1.1)\times10^{-16}$	$8.4(\pm0.7)\times10^{-14}$	4.1 ± 0.4	331 ± 2
37.5	37.5	15	10	$4.7(\pm0.4)\times10^{-14}$	$2.5(\pm0.2)\times10^{-15}$	$3.8(\pm0.4)\times10^{-13}$	7.4 ± 0.5	303 ± 2
30.0	30.0	30	10	$3.0(\pm0.4)\times10^{-11}$	$4.3(\pm0.4)\times10^{-12}$	$3.2(\pm0.2)\times10^{-10}$	19.5 ± 1.3	—
Soluble starch %	Sodium Caseinate %	Sorbitol %	Water %					
42.5	42.5	5	10	$2.4(\pm0.2)\times10^{-14}$	$6.5(\pm0.7)\times10^{-15}$	$3.8(\pm0.4)\times10^{-13}$	5.2 ± 0.4	326 ± 2
37.5	37.5	15	10	$8.7(\pm0.7)\times10^{-14}$	$3.9(\pm0.4)\times10^{-14}$	$2.5(\pm0.2)\times10^{-12}$	9.3 ± 0.8	298 ± 2
30.0	30.0	30	10	$6.0(\pm0.5)\times10^{-11}$	$5.2(\pm0.4)\times10^{-12}$	$4.3(\pm0.4)\times10^{-10}$	26.5 ± 1.5	—
Soluble starch %	Sodium caseinate %	Xylose %	Water %					
42.5	42.5	5	10	$2.5(\pm0.2)\times10^{-14}$	$5.5(\pm0.4)\times10^{-15}$	$8.5(\pm0.7)\times10^{-14}$	6.5 ± 0.5	327 ± 2
37.5	37.5	15	10	$7.0(\pm0.7)\times10^{-14}$	$3.8(\pm0.3)\times10^{-15}$	$4.9(\pm0.6)\times10^{-13}$	10.7 ± 1.1	300 ± 2
30.0	30.0	30	10	$3.6(\pm0.4)\times10^{-11}$	$6.7(\pm0.7)\times10^{-12}$	$4.0(\pm0.3)\times10^{-11}$	28.1 ± 2.0	—

Table 3. Activation energies for diffusion (E_D*, kJ mol^{-1}) and permeation (E_P, kJ mol^{-1}) of gases (N_2 and O_2) both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g) for soluble starch/water (and/or polyol)/sodium caseinate blends. The results give the average and the standard deviation of five measurements**

			N_2				O_2			
			E_D*		E_P**		E_D*		E_P**	
Soluble starch (%w/w)	Water (%w/w)	Sodium caseinate (%w/w)	(T>Tg)	(T<Tg)	(T>Tg)	(T<Tg)	(T>Tg)	(T<Tg)	(T>Tg)	(T<Tg)
85	15	0	33.7 ± 3.8	21.2 ± 2.7	53.9 ± 4.9	36.6 ± 2.9	32.7 ± 3.7	18.3 ± 2.1	50.1 ± 4.1	31.8 ± 3.5
75	15	10	38.5 ± 3.9	23.1 ± 2.0	59.7 ± 5.8	41.4 ± 4.4	36.6 ± 3.4	25.0 ± 2.8	64.5 ± 6.3	40.4 ± 4.4
65	15	20	44.3 ± 3.7	29.8 ± 2.4	68.3 ± 6.1	50.1 ± 5.7	41.4 ± 3.9	30.8 ± 3.4	71.2 ± 7.3	52.0 ± 5.1
55	15	30	52.0 ± 5.4	35.6 ± 3.8	74.1 ± 7.5	54.9 ± 5.6	54.9 ± 4.4	34.7 ± 3.6	77.0 ± 8.2	59.7 ± 6.5
47.5	5.0	47.5	78.9 ± 7.1	55.8 ± 5.3	98.2 ± 15.4	57.8 ± 5.2	82.8 ± 6.6	52.9 ± 5.6	91.5 ± 10.1	68.3 ± 7.3
42.5	15	42.5	61.6 ± 6.3	41.4 ± 4.3	65.5 ± 5.9	41.4 ± 5.0	52.0 ± 4.5	32.7 ± 3.6	63.5 ± 5.1	46.2 ± 5.8
Soluble starch /Sodium Caseinate	Water	Glycerol								
37.5/37.5	5	20	31.8 ± 2.2	18.3 ± 1.2	43.3 ± 3.1	18.3 ± 1.0	35.6 ± 3.4	21.6 ± 1.0	46.2 ± 4.3	25.0 ± 2.6
Soluble starch /Sodium Caseinate	Water	Sorbitol								
37.5/37.5	5	20	27.1 ± 2.8	19.6 ± 0.9	31.8 ± 3.5	20.6 ± 1.5	29.1 ± 2.1	19.7 ± 0.7	38.5 ± 3.0	21.2 ± 2.9
Soluble starch /Sodium Caseinate	Water	Xylose								
37.5/37.5	5	20	29.8 ± 3.4	21.6 ± 3.8	77.0 ± 5.0	37.1 ± 4.0	27.9 ± 3.7	20.6 ± 1.2	43.3 ± 5.6	22.1 ± 2.8

* calculated according to eqn. (7), ** calculated according to eqn. (9)

Table 4. Tensile strength and percentage elongation of water plasticized soluble starch/sodium caseinate blends

Soluble starch %	Sodium caseinate %	Water %	Tensile strength (MPa)	Elongation %
90	0	10	38.5±3.4	2.5±0.3
80	10	10	33.6±4.3	4.4±0.5
70	20	10	28.2±3.1	7.2±0.6
60	30	10	23.1±2.2	10.0±1.2
50	40	10	19.3±2.1	13.6±1.5
Soluble starch %	Sodium caseinate %	Water %	Tensile strength (MPa)	Elongation %
47.5	47.5	5	22.1±1.2	2.0±0.1
45.0	45.0	10	19.5±2.2	6.3±0.5
40.0	40.0	20	17.3±2.1	13.0±1.1
35.0	35.0	30	12.2±1.1	19.0±2.0

Table 5. Tensile strength and percentage elongation of soluble starch/sodium caseinate blends plasticized with water and glycerol, sorbitol or xylose

Soluble starch %	Sodium caseinate %	Glycerol %	Water %	Tensile strength (MPa)	Elongation %
45.0	45.0	5	5	38.2±3.6	8.2±1.1
40.0	40.0	15	5	32.0±2.2	18.5±1.6
32.5	32.5	30	5	22.5±2.3	26.8±2.5
Soluble starch %	Sodium caseinate %	Sorbitol %	Water %	Tensile strength (MPa)	Elongation %
45.0	45.0	5	5	36.3±3.4	9.5±0.6
40.0	40.0	15	5	29.4±2.3	20.9±1.8
32.5	32.5	30	5	20.2±2.1	29.7±2.7
Soluble starch %	Sodium caseinate %	Xylose %	Water %	Tensile strength (MPa)	Elongation %
45.0	45.0	5	5	33.1±3.4	2.4±0.2
40.0	40.0	15	5	27.2±3.3	15.2±1.3
32.5	32.5	30	5	19.0±1.2	18.0±1.5

et al., 1996). The decrease in tensile strength at high plasticizer levels could be attributed to the plasticizer absorption, due to which the blend is above the glass transition at the ambient testing temperature (22 ± 1°C).

Three-point bend test

The synergistic action of water and polyol on plasticization of starch and starch-based blends has been reported elsewhere (Kirby *et al.*, 1993; Ollett *et al.*, 1991; Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996; Lawton, 1996; Lloyd and Kirst, 1963). Our results, from three-point bend test, show that the fall in modulus (Figs 4 and 5) in the glass transition area vs water content becomes less abrupt with increasing amounts of polyol, as previously reported for wheat starch (Kirby *et al.*, 1993). The gradual fall in flexural modulus for soluble starch/sodium caseinate blends compared to starch alone could be attributed to the presence of sodium caseinate, which counterbalances the very sharp drop in modulus shown for pure starch (Arvanitoyannis *et al.*, 1996).

It has been shown elsewhere that the direction of applied stress is of primary importance regarding the response of a composite or a blend (Ashby and Jones, 1985; Arvanitoyannis and Blanshard, 1993) to mechanical deformation. Moreover, it is generally agreed that the modulus of polymer blends follows either eqn (10) or eqn (11), which describe the dependence of E on polymer blend composition:

$$E_{\text{blend}} = V_{\text{soluble starch}} E_{\text{soluble starch}} + (1 - V_{\text{soluble starch}}) E_{\text{sodium caseinate}} \tag{10}$$

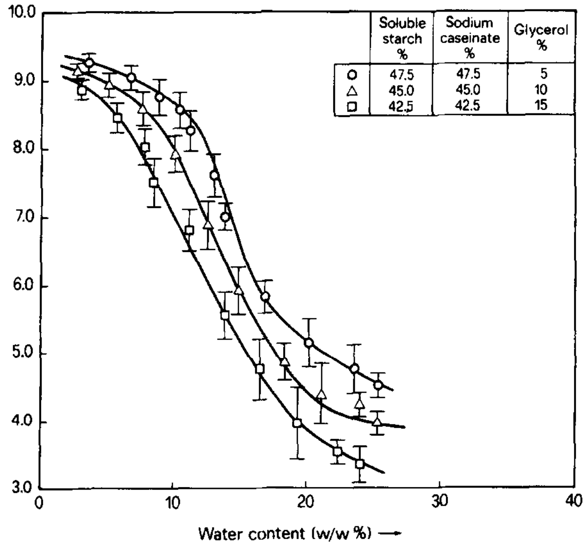

Fig. 4. Effect of water content on log flexural modulus determined from three-point bend test of several soluble starch/sodium caseinate/glycerol blends. The results give the average and the standard deviation of at least eight measurements.

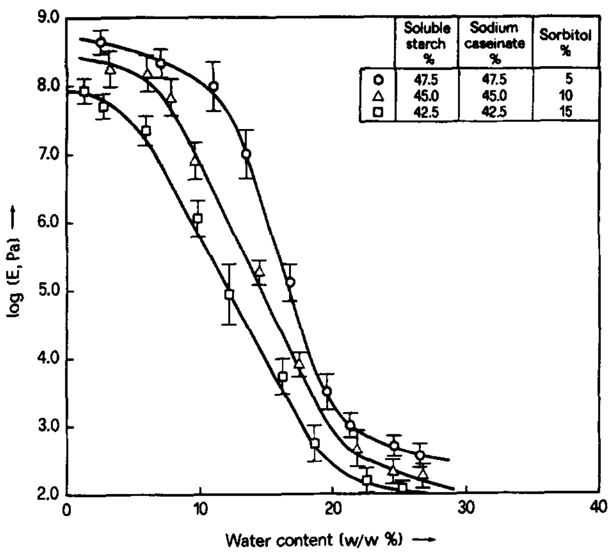

Fig. 5. Effect of water content on log flexural modulus determined from three-point bend test of several soluble starch/sodium caseinate/sorbitol blends. The results give the average and the standard deviation of at least eight measurements.

$$E_{\text{blend}} = 1/[(V_{\text{soluble starch}}/E_{\text{soluble starch}}) + (1 - V_{\text{soluble starch}})/E_{\text{sodium caseinate}}] \tag{11}$$

where E is the tensile or flexural modulus and V is the volume fraction of the respective component in the blend. Using these expressions, calculation of the upper (eqn (10)) and lower (eqn (11)) limit estimates for blends based on corn starch/cellulosics, showed discrepancies up to 50% from the experimental values, regarding the flexural modulus (Psomiadou *et al.*, 1996). In this work, application of eqns (10) and (11), by using $E_{\text{soluble starch}} = 7700\,\text{MPa}$ (our experiments) and $E_{\text{sodium caseinate}} = 6300\,\text{MPa}$ (Kalichevsky *et al.*, 1993), gave estimates of 7000 (eqn (10)) and 6930 MPa (eqn (11)), which are in reasonable agreement with the experimental values.

CONCLUSIONS

Edible films based on soluble starch/sodium caseinate blends, plasticized with water and/or other polyols, were studied with regard to their thermal, mechanical and gas and water vapour barrier properties. Macroscopically examined, the films appeared to be clear, suggesting a homogeneous distribution of the two or three components in the blend. At lower than 17% total plasticizer content, both thermal and mechanical properties of the blends remained within acceptable limits for packaging or coating applications. A marked change was observed in the mechanical properties at higher than 17% total plasticizer content possibly due to a disruption, at least in part, of the soluble starch/sodium caseinate amorphous matrix.

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