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Edible films made from gelatin, soluble starch and polyols, Part 3

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The thermal and mechanical properties of edible films based on blends of gelatin with soluble starch plasticized with water, glycerol or sugars were investigated. Two different methods, known as 'the high temperature' and 'the low temperature' methods, consisting of casting aqueous solutions of blends at 60 and 20°C, respectively, were employed for the preparation of films. With increasing water, glycerol or sorbitol content, a drop of elasticity modulus and tensile strength (up to 50% of the original values for 30% plasticizer) was observed. The tensile strength and percentage elongation increased with high gelatin contents (>20% w/w). The development of a higher percentage renaturation of gelatin (reaching 70% for 5% water content) by the 'low temperature' method caused a reduction in gas and water permeabilities. The former decreased by one or two orders of magnitude for O_2 and CO_2, respectively. The semi-empirical model for calculation of gas permeability and the semi empirical equations for upper and lower limits of tensile moduli of composites were applied with limited success and the obtained values were compared to those experimentally determined. © 1997 Elsevier Science Ltd

INTRODUCTION

Proteins can be good film formers and may be used in coating formulations for fruits and vegetables. Protein films are effective as gas barriers (O_2 and CO_2) but their water vapour transmission rates through are high (Baldwin *et al.*, 1995). Collagen and its derivative, gelatin, among other proteins have been used for sausage casings and as gelling agents because of their abundant supply (Johnston-Banks, 1990). Collagen films extruded in the form of tubular sausage casing may be viewed as a convenient edible packaging material (Hood, 1987). Gelatin coatings, with or without polyols (i.e. glycerol), carrying antioxidants were effective in reducing rancidification when applied to cut-up turkey meat or to smoke-cured chicken by spraying or dipping (Klose *et al.*, 1952; Moorjani *et al.*, 1978). Edible wrappings based on blends of gelatin with farinaceous constituents have recently been marketed (Todd, 1982 quoted by Torres, 1994). Many of the major food-related and other industrial uses of gelatin are based on the structure/property relationships of gelatin for which water is an excellent plasticizer of the predominant amorphous regions (Slade & Levine, 1987). Comparatively greater is the number of publications reporting on film formation from starch or its components and their possible applications in the food industry (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; Griffin, 1994).

However, despite the above-mentioned applications, edible films have not been extensively used, in the past, in the food industry. The potential of protein edible films, rather as components of a blend or of a composite bi/multilayer system for regulating mass transfer in food systems, has been recognized by the food industry as offering numerous benefits (Keil *et al.*, 1960; Keil & Hills, 1961). Furthermore, it is anticipated that the potential functional and nutritional properties of such edible films, in conjunction with their enhanced biodegradability compared to other polymer systems, could almost certainly guarantee increased consideration in the immediate future.

Although the current work aims at producing a single polymeric phase containing soluble complexes, resulting after casting in homogeneous films, protein–polysaccharide interactions have been extensively used in other

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applications such as: protein recovery from dilute effluent streams; fractionation of purified proteins; inhibition of protein purification; inactivation of enzymes for food preservation; stabilization of foams and emulsions as fat replacers; and generation of textured products (Ledward, 1994; Morris, 1990). In the third paper of this series (Arvanitoyannis *et al.*, 1997; Psomiadou *et al.*, 1997), blends of gelatin and soluble starch were prepared in the presence of glycerol or sorbitol in order to study the thermal, mechanical and gas/water barrier properties of these blends and to compare them to other edible films.

MATERIALS AND METHODS

Materials

Soluble starch and gelatin (practical grade), glycerol, sorbitol and sucrose (analytically pure) were purchased from Wako Chemicals (Tokyo, Japan).

Preparation of samples in the glassy state

The preparation of samples of blends of soluble starch with gelatin, glycerol/sugars and water was carried out as elsewhere described (Arvanitoyannis *et al.*, 1994). Mixtures of gelatin and soluble starch were passed through the roller drier to obtain blends of appropriate composition 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.

High and low temperature preparation process (for permeability and tensile measurements)

Films of thickness range 0.8 mm ± 0.06 were prepared by casting 5% aqeous gelatin and 2% aqueous soluble potato starch solutions at 60 and 20°C on metal trays allowing further evaporation of water. The thickness of each sample was measured at eight different points with a micrometer and the average was taken. At 60°C the evaporation was completed within 6 h, whereas at 20°C it took one week. A template was used to cut testing strips from the films such as the testing section which measured 50×10 mm. In order to examine the physical properties of films as a function of moisture content, films were placed in relative humidity chambers over salt solutions or phosphorus pentoxide and the moisture content was determined by drying up to constant weight (Arvanitoyannis *et al.*, 1994, 1995).

Preparation of samples for dynamic mechanical thermal analysis (DMTA) and three-point bend measurements

Preparation of samples of gelatin/gelatinized potato starch (with 25% water) was carried out by pressing the samples (3.5 MPa) at temperatures 120–130°C for 15–20 min. Conditioning of samples at different relative

humidities was undertaken as previously described (Arvanitoyannis *et al.*, 1994).

Dynamic mechanical thermal analysis (DMTA) measurements

The dynamic mechanical thermal analyzer (DMTA, Mark II, Polymer Laboratories, Loughborough, UK) 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 taken at least to triplicate samples.

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 tan δ (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 (Tokyo, Japan) 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 carried out with cyclohexane, dodecane and octane. Heat flow calibration was achieved 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 Tg was determined from the second run after melting, quenching with liquid nitrogen and reheating at a heating rate of 2°C min⁻¹. The percentage crystallinity with DTA was calculated according to Gidley (1992).

Measurements of gas permeability and water vapour transmission rate (WVTR)

The measurements of gas permeability were carried out using a Davenport apparatus (London, UK) connected to an IBM/PC in accordance with ASTM D1434-66 (ASTM, 1966). Thickness was measured with a micrometer at 5 or 6 locations of the film.

Permeability (P) is the product of solubility (S) and diffusivity (D) according to the following equation:

$$P = D.S \qquad (1)$$

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

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

where J is the flux, $D_{i(ci)}$ signifies that the diffusion coefficient 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:

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

where d is the thickness of the film and θ is the time lag for 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. Overall, the relationship can be expressed by the following equation:

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

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 vapour 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 testing strips, 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 $\sim 30 \times 8 \times 2$ mm and stored for at least three 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. Three-point bend tests were carried out at room temperature using an Instron texturometer at a cross-head speed of 50 mm s^{-1} on samples previously equilibrated at various Rhs. The initial slope of the force/distance graph and the sample dimensions were used to calculate the Young's modulus. The peak force was recorded as well.

RESULTS AND DISCUSSION

Thermal and thermo-mechanical properties

The presence of water and sugars was found to have a significant plasticizing effect on starch and on gelatin (Tables 1 and 2). Depending on the extent of the induced plasticization (Tg lowering) the polyols and glycerol were found to have similar plasticizing ability. The effectiveness of a plasticizer in leading to phase separation of a protein–polysaccharide blend depends on the relative changes brought about on the polymers, the flexibility of the chains, the molecular size and the salt concentration. In general, with charged polysaccharides, incompatibility is enhanced with increasing salt concentration (Ledward, 1993). The DTA results (Fig. 1) did not support the existence of phase separation despite the well-accepted theory of thermodynamic incompatibility, favoured at high concentrations of different classes of polymers such as proteins and polysaccharides, which eventually leads to phase separation (Ledward, 1994). In all DTA traces it can be seen that the incorporation of polyols, in conjunction with the presence of water within the protein or the protein/starch matrix, resulted in broadening of the step transition in DTA (Figs 1a–f). Similarly, there was a gradual broadening of the tan δ peak (DMTA). The

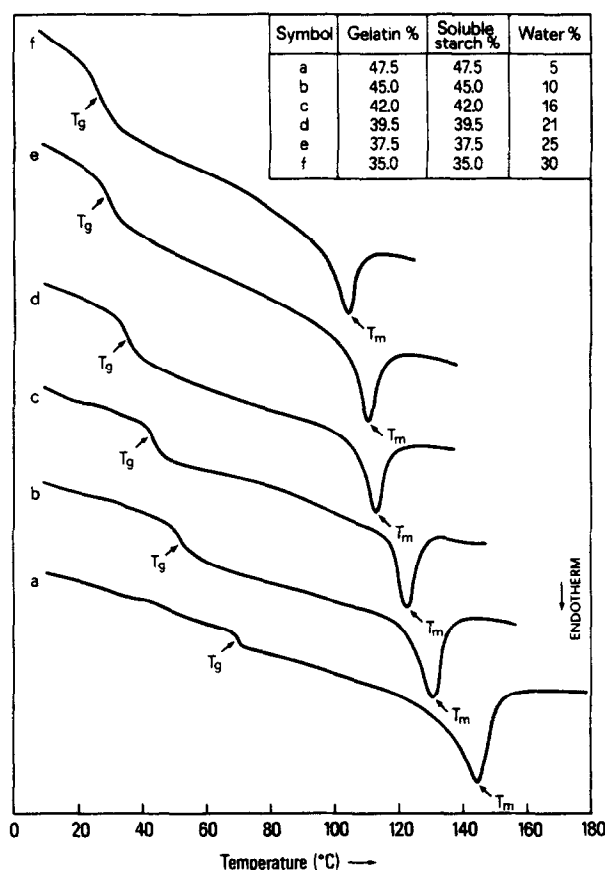| Symbol	Gelatin %	Soluble starch %	Water %
a	47.5	47.5	5
b	45.0	45.0	10
c	42.0	42.0	16
d	39.5	39.5	21
e	37.5	37.5	25
f	35.0	35.0	30

Fig. 1. Representative DTA traces for gelatin/soluble starch/ water blends.

Table 1. Thermal and thermomechanical properties of gelatin/soluble starch (1:1)/glycerol, gelatin/soluble starch (1:1)/sorbitol, gelatin/soluble starch 1:1)/sucrose blends, prepared with low- and high-temperature processes. The results are the average and the standard deviation of at least 3 or 5 measurements for thermal and permeability measurements, respectively

Low temperature process				DTA			Tg			
Gelatin	Soluble starch	Glycerol	Water	Tm	ΔH(J/g)	%Rn*	DTA	DMTA (E')	DMTA (tanδ)	Permeability (inflection)
47.5	47.5	0	5	144.2±2.1	21.4±1.3	68.9	69.2±2.2	70.5±2.4	73.6±2.4	67.0±1.5
45.0	45.0	5	5	140.3±1.6	19.8±0.9	67.3	61.6±1.9	63.0±2.0	66.9±1.9	59.4±1.7
40.0	40.0	15	5	128.5±1.5	15.5±0.7	59.3	52.4±1.3	53.6±1.8	58.0±1.8	50.3±1.6
34.5	34.5	26	5	115.6±2.0	12.1±1.1	53.7	38.0±1.4	39.4±1.4	45.0±1.7	35.2±1.5
Gelatin	Soluble starch	Sorbitol	Water							
45.5	45.5	4	5	139.5±1.4	20.2±1.8	68.0	56.8±2.0	57.6±1.8	62.5±2.1	54.7±1.0
40.5	40.5	14	5	127.8±2.0	14.9±1.2	56.3	47.9±1.7	49.3±1.6	55.0±1.9	45.6±1.6
35.0	35.0	25	5	114.5±2.1	11.1±0.8	48.6	34.4±1.5	35.7±1.2	41.8±1.5	31.8±1.5
Gelatin	Soluble starch	Sucrose	Water							
45.5	45.5	6	5	139.8±1.6	20.5±1.5	69.0	58.7±2.0	60.0±2.4	64.9±2.5	56.1±2.1
39.5	39.5	16	5	126.9±1.3	14.8±1.5	57.4	51.4±1.6	52.6±1.9	57.0±2.1	48.3±1.6
35.0	35.0	25	5	115.7±1.2	11.5±1.1	50.3	35.6±1.4	36.7±1.6	43.9±1.7	33.0±2.0
High temperature process										
Gelatin	Soluble starch	Glycerol	Water							
47.5	47.5	0	5	138.6±1.7	17.0±1.4	54.0	60.0±2.3	61.7±1.8	63.4±1.8	57.8±1.2
45.0	45.0	5	5	132.0±1.9	14.8±1.8	50.4	54.6±1.8	55.9±1.4	60.8±2.4	52.0±1.9
39.5	39.5	16	5	120.1±1.6	10.3±1.3	39.9	43.3±1.4	44.4±1.1	49.3±2.2	40.7±1.8
35.0	35.0	25	5	104.9±1.7	7.8±1.0	34.1	33.4±1.3	34.7±1.2	39.0±1.4	30.6±0.6
Gelatin	Soluble starch	Sorbitol	Water							
44.5	44.5	6	5	131.7±1.5	14.5±0.9	49.9	52.4±1.8	53.6±1.3	57.5±1.8	49.4±1.4
40.0	40.0	15	5	120.7±1.0	9.2±0.6	35.2	41.5±1.5	42.7±1.1	48.2±1.5	38.5±0.8
32.5	32.5	30	5	106.8±1.2	6.8±1.1	32.0	30.0±0.6	31.4±0.9	37.9±1.6	27.2±0.6
Gelatin	Soluble starch	Sucrose	Water							
45.5	45.5	4	5	131.4±1.4	14.3±1.3	48.1	53.1±1.8	54.5±1.9	59.6±2.1	50.6±1.9
40.0	40.0	15	5	119.8±1.8	8.7±0.6	33.3	42.7±0.9	44.0±1.5	49.7±1.5	39.6±1.6
34.5	34.5	26	5	108.6±0.8	6.7±0.7	29.7	31.6±1.4	32.5±0.8	38.3±1.7	23.8±1.7

*Percent renaturation calculated from $(\Delta H_{gelatin\ in\ blend} / \Delta H_{collagen}) \times 100$.

DTA thermograms of gelatin/soluble starch are strongly marked by the non-equilibrium nature of the melting process of gelatin (Fig. 1). At Tg, the amorphous fringes soften and take on the mobility and elasticity of a high viscosity rubbery liquid. Upon further heating the microcrystallites, initially surrounded by a viscoelastic fluid, are free to melt at Tm higher than Tg, thus rendering the gelatin/soluble starch blend to a melting fluid (Levine & Slade, 1988). The Tg recorded in the second run was always lower, by at least 4°C, compared to the first run. This Tg lowering should be attributed to increased plasticization by water or polyol because, after melting of the crystals, the released water or polyol, initially linked to the crystalline regions (Jolley, 1970), is redistributed throughout the amorphous matrix, thereby decreasing the Tg (Marshall & Petrie, 1980). The plasticizing effect of sugars such as glycerol and sorbitol on gelatin/starch/water blends was pronounced and is in agreement with previous publications (Kalichevsky et al., 1993a,b). Sucrose was similar to glycerol and sorbitol in its plasticizing effect on gelatin/starch/water blends provided that its content did not

exceed 20%. This is in contrast to the findings of Kalichevsky et al. (1993a,b) on the plasticization behaviour of sucrose on amylopectin and caseinate. The plasticization of a composite food matrix with polyols could be attributed to changes in the polymer network, mainly related to the creation of highly mobile regions, which allow an even more pronounced moisture uptake (Cherian et al., 1995).

No double peaks (tan δ) were recorded for the binary gelatin/starch blends, or even in the three component system, as long as polyol content remained below 15%, thus implying that the gelatin/starch blends did not phase-separate. However, when the polyol content exceeded 20%, double peaks were recorded. Similar observations on natural and synthetic polymers, indicating phase separation, have previously been made (Cherian et al., 1995; Bazuin & Eisenberg, 1986).

Interactions in the gelatin/water or gelatin/starch/water/polyol systems are between hydroxyl groups of starch chains, starch–water and starch–polyol molecules, as well as between polyol–polyol or water–polyol molecules (Tolstoguzov, 1994). The possibilities of

Table 2. Glass transition temperatures (Tg,°C) of blends of gelatin and soluble starch conditioned at different relative humidities

	Gelatin %	Water %	Soluble Starch %	Tg (°C)			
				DTA (2nd run)	DMTA (E')	DMTA (*tanδ*)	Permeability (inflection)
	85	15	—	57.1±1.8	58.3±1.4	61.9±2.1	55.3±1.4
	82	15	3	57.5±2.2	58.9±1.6	63.0±1.5	55.6±2.0
	75	15	10	58.2±1.6	59.7±1.5	64.7±1.8	56.0±1.8
	66	15	19	59.4±1.5	61.0±1.8	65.8±2.0	57.1±2.3
Low-temperature process	55	15	30	60.7±1.9	62.5±1.5	67.5±1.9	57.4±2.6
	33	15	52	62.5±1.8	64.2±2.5	69.5+2.2	59.3±2.7
	47	6	47	68.0±2.7	69.1±2.8	70.8±2.5	66.4±1.8
	45.5	9	45.5	61.7±1.9	63.2±1.9	64.9±1.9	60.7±2.4
	40	20	40	55.0±1.6	57.3±1.6	59.0±1.6	53.2±2.5
	34	32	34	39.3±2.0	42.4±1.3	46.3±1.7	37.8±1.6
	Gelatin %	Water %	Soluble Starch %				
	84	16	—	50.9±1.6	52.0±1.6	55.4±1.6	47.8±1.8
	81	16	3	51.8±1.7	52.7±1.4	56.0±1.8	49.2±1.6
	75	16	9	53.0±2.0	54.2±1.5	57.1±1.5	51.3±2.0
	64	16	20	54.1±1.8	55.4±1.7	57.5±1.9	52.5±1.7
High-temperature process	53	16	31	55.6±1.7	57.1±1.8	59.2±1.8	54.1±1.6
	45	16	39	56.3±1.5	57.8±1.6	60.1±2.0	55.0±1.8
	34	16	50	56.8±2.0	58.6±1.9	61.0±1.7	55.3±2.1
	47.5	5	47.5	66.1±1.6	66.5±2.1	67.2±2.2	64.8±2.3
	44.5	11	44.5	60.5±1.8	59.7±2.0	62.1±2.0	58.6±2.2
	40	20	40	50.2±1.2	52.1±1.3	54.0±1.7	47.8±1.4
	34.5	31	34.5	34.8±1.1	36.3±0.9	40.5±1.4	35.1±1.3

gelatin or starch hydrogen-bonding within the blends are greatly enhanced by the introduction of comparatively small size molecules such as water and polyols. Previous studies on protein–protein (casein–ovalbumin, casein–soybean globulin), protein–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 (Tolstoguzov *et al.*, 1985). Furthermore, it was found that the protein–polysaccharide systems are characterized by limited compatibility between their components, occasionally resulting in phase separation.

An increase in water content resulted in decrease of Tg (DTA, DMTA and permeability from Table 2) because of increasing starch–water hydrogen bonding interactions and decreasing intra- and intermolecular H-bonding between starch chains. This leads to lower interaction energy between starch chains which, in conjunction with the incorporation of water/polyols, could be considered as the main effect of the plasticizing molecules, manifested by a drop in flexural (Young's) modulus and by a decrease in Tg. For example, when the moisture content is higher than 60%, $Tg_{gel} = -22°C$ (Achet & He, 1995; Slade & Levine, 1987) whereas at moisture contents of approximately 10%, the Tg values range between 58 and 65°C (Table 2).

The glass transitions were more difficult to detect in the more complex systems, such as gelatin/soluble starch/polyol/water, in particular, at low moisture contents (< 7%). The synergistic effect of several components, resulting in broader transitions at Tg, made this phenomenon non-discernible from the baseline. How-

ever, when the moisture content exceeded the 'threshold' of 7%, the transitions were more clearly defined for most systems (Fig. 1), in agreement with previous publications (Bell & Touma, 1996; Zeleznak & Hoseney, 1987).

At a molecular level, the gelation of a gelatin solution involves the renaturation of random gelatin strands to the triple-helix structure that exists in native collagen. The renatured triple helices can be visualized as 'junctions' from which a three-dimensional network is formed (Achet & He, 1995). The thermal properties of gelatin were previously shown to depend greatly on the extent of renaturation. Tables 1 and 2 give the glass transitions (Tg), melting points (Tm), melting enthalpies (ΔHm) and percentage renaturation (%Rn) of gelatin and gelatin/soluble starch blends conditioned at various Rh. The percentage crystallinities were determined from the following equation:

$$\%Rn = \Delta Hm/\Delta H_{100\%renatured} = \Delta Hm/\Delta H_{collagen},$$
$$where \ \Delta H_{collagen} = 62.05 J g^{-1} \quad (5)$$

The latter value is the most widely accepted enthalpy for gelatin (Achet & He, 1995; Macsuga, 1972). Renaturation of gelatin chains is believed to occur via a three stage mechanism which is as follows:

$$(C) \xrightarrow{initiation} (NC) \xrightarrow{growth} (I) \xrightarrow{stabilization} 1/3(H) \quad (6)$$
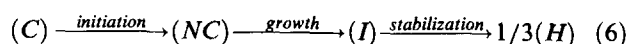
where (C) is the largely disordered random coil, (NC) is the chain conformation after initiation of the poly(L-proline) II type of helix, which also acts as the nucleus

of the growing helix, (I) is an intermediate ordered chain and 1/3 (H) stands for the chain in the collagen-like structure. The melting enthalpies determined by DTA reflect the conversion of all gelatin chains into the random coil state.

Mechanical properties — Tensile strength elongation

It is well-known that temperature preparation and relative humidity greatly affect the tensile strength and percentage elongation of films prepared from biopolymers (Bradbury & Martin, 1952). Therefore, two different methodologies for film preparation were adopted: a high and a low temperature process accompanied by conditioning of the samples over various relative humidities. The results from measurements of mechanical properties and, in particular, tensile strength, Young's modulus and percentage elongation of gelatin/soluble starch/water and gelatin/soluble starch/water/polyols films, are given in Table 3.

The percentage renaturation (Rn) (100% renatured equals 62.05J g^{-1} gelatin) (Achet & He, 1995) was shown to be considerably higher for the low, rather than the high temperature preparation process. In the low temperature process, the high %Rn could be possibly attributed to the partial extension of the molecular chains which, because of the unidirectional contraction of film on drying, have been oriented in the plane of the film. In contrast, for the high temperature process, due to delaying and reordering, the molecules are captured in a disordered and entangled condition characterized by low percentage renaturation (Table 1).

In all relative humidities, the low-temperature prepared films were considerably stronger (higher tensile strength and percentage elongation) than those of high temperature. Conditioning of films at high Rh resulted in their plasticization, thus substantially increasing their percentage elongation and exhibiting a drop in tensile strength ($\sim 20\%$ of the original value). Some representative stress–strain curves for gelatin/starch (1:1) films conditioned at various relative humidities are shown in Fig. 2. Although up to 60% Rh (Figs 2a,b), no obvious yield point is observed and the percentage elongation is quite low, at higher Rh a pronounced increase in percentage elongation was recorded. Furthermore, the samples conditioned at high Rh showed a clear yield point (Figs 2c–g). It is noteworthy that, even if the preparation temperature exceeds 60°C, no permanent degradation occurs during film preparation as shown in previous studies (Bradbury & Martin, 1952). In fact, crystallinity studies with X-rays confirmed this hypothesis because similar X-ray patterns were recorded for both high- and low-temperature prepared films (Bradbury & Martin, 1952). In order to get a better insight of the observed differences of tensile strength, the two film preparation methods were examined. In the low-temperature film preparation, a two-stage process has been

suggested: (a) formation of a gel and (b) its modification by contraction on drying. Conversely the high temperature method is known as the 'one stage method'. In this case, the molecules are considered to be in a closely packed condition at the time so that intermolecular bonding takes place. Consequently, any further growth in size of these bonded areas should be very limited because the molecules become entrapped in a randomly contracted state.

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 for tensile modulus can be deduced (Arvanitoyannis & Psomiadou, 1994; Arvanitoyannis *et al.*, 1995):

$$E_{blend} = V_{starch}E_{starch} + (1 - V_{starch})E_{gelatin} \qquad (7)$$

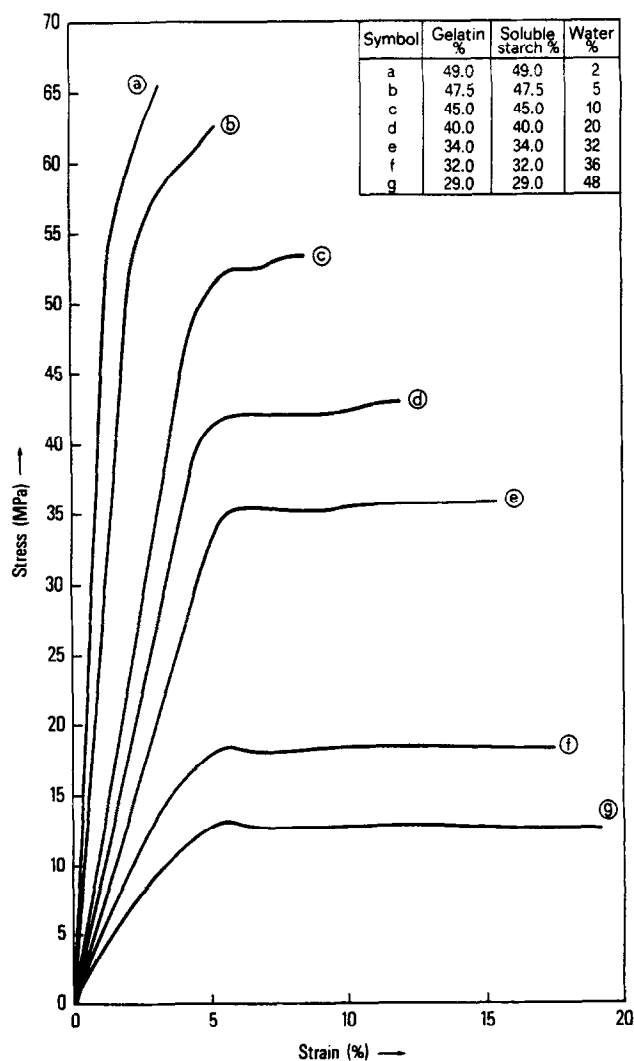$$E_{blend} = \frac{1}{\frac{V_{starch}}{E_{starch}} + \frac{1-V_{starch}}{E_{gelatin}}} \qquad (8)$$

Symbol	Gelatin %	Soluble starch %	Water %
a	49.0	49.0	2
b	47.5	47.5	5
c	45.0	45.0	10
d	40.0	40.0	20
e	34.0	34.0	32
f	32.0	32.0	36
g	29.0	29.0	48

Fig. 2. Effect of water content on tensile strength of gelatin/soluble starch/water blends.

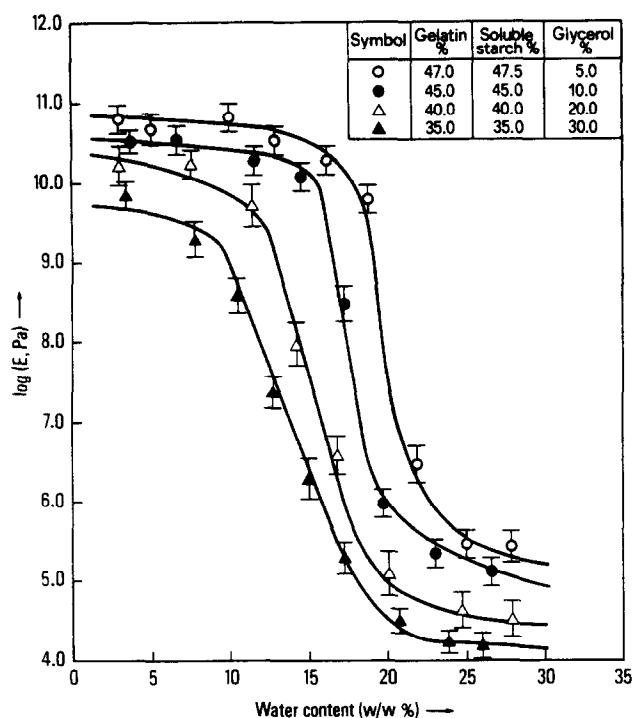| Symbol	Gelatin %	Soluble starch %	Glycerol %
O	47.0	47.5	5.0
●	45.0	45.0	10.0
△	40.0	40.0	20.0
▲	35.0	35.0	30.0

Fig. 3. Effect of water content on log flexural modulus, determined from three-point bending test, of gelatin/soluble starch/glycerol prepared by low-temperature process. The results give the average and the standard deviation of at least six measurements.

Although these two estimates are known as the upper (eqn 7) and lower (eqn 8) limits, when these equations were applied to starch/gelatin blends, no substantial differences were found. For example, if we apply the values $E_{starch} = 20$ MPa and $E_{gelatin} = 50.3$ MPa with 5% moisture (Arvanitoyannis *et al.*, 1997) to gelatin/soluble starch (47.5/47.5) the results obtained are 35.15 and 28.62 MPa from eqns 7 and 8, respectively. The theoretically calculated and the experimentally determined values (Table 3) are in quite satisfactory agreement.

In plasticized gelatin/soluble starch blends the efficiency of plasticization with the same amount of plasticizer is dependent on the gelatin/soluble starch ratio. Glycerol had a pronounced plasticizing effect on the mechanical properties of blends of gelatin/soluble starch/glycerol films (Table 3). Sorbitol was shown to act similarly to glycerol on the mechanical properties of gelatin/soluble starch blend. The increase in elongation due to sorbitol and sucrose was within the same range as that caused by glycerol.

Three-point bending test

The effect of water content on flexural modulus, determined by the three-point bend test, was slightly more pronounced on gelatin/soluble starch when sorbitol was used as plasticizer instead of glycerol (Figs 3 and 4). Similar effects on modulus of wheat starch or starch components (e.g. amylopectin) by the addition of water

and polyols (glycerol, glucose, xylose) have been reported (Kirby *et al.*, 1993; Ollett *et al.*, 1991, Kalichevsky *et al.*, 1992*a*,*b*, 1993*a*,*b*). It was further shown that with the addition of polyols, the fall in modulus, observed in the glass to rubber transition, becomes smoother and shifts toward lower water contents (Kirby *et al.*, 1993). This behaviour is also evident for the gelatin/soluble starch blends (Figs 3 and 4). However, for the gelatin/soluble starch blends there was a less dramatic fall since gelatin does not exhibit the abrupt drop in modulus shown for the soluble starch. Such behaviour may be attributable to the fact that gelatin exhibits a higher Tg than starch at water contents above 5% (Slade & Levine, 1987).

Water vapour transmission rate (WVTR)

One of the major problems envisaged in the extensive application of edible films was, and continues to be, their high WVTR. In general, it is much more difficult to make accurate sorption and transport measurements for water vapour than for most other penetrants because of the following characteristic properties of water: a tendency to adsorb on high energy surfaces such as glass or metal, relatively high vaporization heat; low saturation vapour pressure; high solubility in many polymer systems; a tendency to plasticize polymers and to cluster in the polymer matrix (Schult & Paul, 1996). In several publications (Gennadios *et al.*, 1993*b*–*d*) on

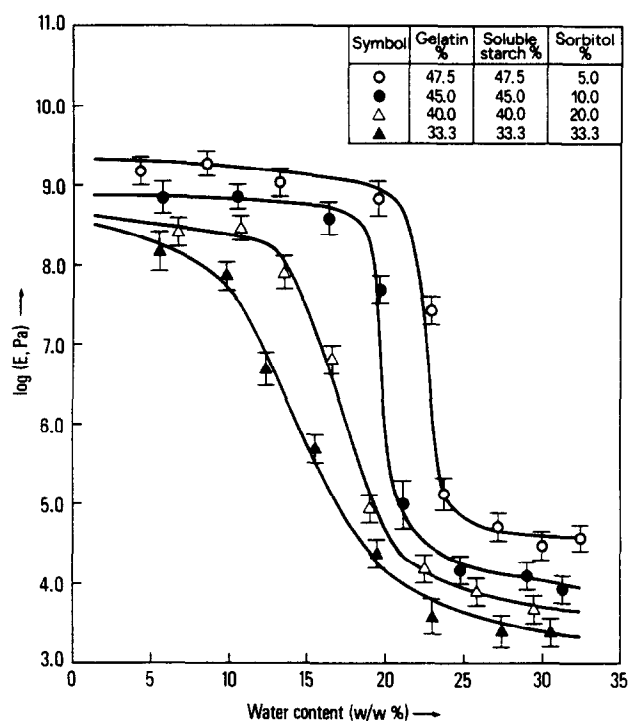| Symbol	Gelatin %	Soluble starch %	Sorbitol %
O	47.5	47.5	5.0
●	45.0	45.0	10.0
△	40.0	40.0	20.0
▲	33.3	33.3	33.3

Fig. 4. Effect of water content on log flexural modulus, determined from three-point bending test, of gelatin/soluble starch/sorbitol prepared by low-temperature process. The results give the average and the standard deviation of at least six measurements.

Table 3. Mechanical properties and water vapour transmission rate (WVTR) of gelatin/soluble starch (1:1)/glycerol, gelatin/soluble starch (1:1)/sorbitol, and gelatin/soluble starch (1:1)/sucrose blends, prepared by low- and high-temperature processes and conditioned at different relative humidities. The results give the average and the standard deviation of at least eight measurements

	Gelatin	Soluble starch	Glycerol	Water	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation %	WVTR (g m^{-1} sec^{-1} Pa^{-1})$\times 10^{-11}$
		47.5	47.5	0	5	60.5 ± 2.4	37.5 ± 0.9	1.8 ± 0.2	0.2 ± 0.01
		45.0	45.0	5	5	54.8 ± 1.9	30.9 ± 1.4	4.0 ± 0.1	1.8 ± 0.1
		40.0	40.0	15	5	47.0 ± 2.3	24.0 ± 1.2	9.5 ± 0.6	6.9 ± 0.4
Low-temperature process	34.5	34.5	26	5	40.6 ± 1.9	18.3 ± 0.7	25.1 ± 1.8	11.8 ± 1.1
	Gelatin	Soluble Starch	Sorbitol	Water				
	45.5	45.5	4	5	51.3 ± 2.1	28.0 ± 0.9	4.6 ± 0.4	2.0 ± 0.1
	40.5	40.5	14	5	44.9 ± 1.8	21.2 ± 0.8	11.5 ± 1.0	7.8 ± 0.5
	35.0	35.0	25	5	38.1 ± 1.5	14.4 ± 1.0	33.0 ± 1.8	12.6 ± 1.1
	Gelatin	Soluble starch	Sucrose	Water				
	44.5	44.5	6	5	52.5 ± 2.3	28.5 ± 0.8	3.8 ± 0.2	1.7 ± 0.2
	39.5	39.5	16	5	46.2 ± 2.1	22.3 ± 1.0	10.4 ± 0.8	7.2 ± 0.6
	35.0	35.0	25	5	39.0 ± 1.6	15.0 ± 0.9	28.6 ± 1.8	13.7 ± 1.2
	Gelatin	Soluble starch	Glycerol	Water				
	47.5	47.5	0	5	53.8 ± 0.8	29.6 ± 0.9	1.2 ± 0.1	0.3 ± 0.02
	45.0	45.0	5	5	50.1 ± 2.2	23.7 ± 1.2	2.8 ± 0.2	2.7 ± 0.3
	39.5	39.5	16	5	42.5 ± 2.4	17.6 ± 1.3	16.3 ± 1.2	8.9 ± 0.4
	35.0	35.0	25	5	35.8 ± 1.8	12.7 ± 0.8	38.0 ± 2.1	19.3 ± 1.3
	Gelatin	Soluble starch	Sorbitol	Water				
High-temperature process	44.5	44.5	6	5	47.4 ± 1.9	19.0 ± 1.1	2.6 ± 0.3	3.2 ± 0.2
	40.0	40.0	15	5	41.8 ± 2.2	14.2 ± 0.6	19.0 ± 0.9	11.4 ± 1.2
	36.0	36.0	23	5	38.3 ± 1.5	11.4 ± 0.8	26.4 ± 1.8	16.3 ± 1.4
	32.5	32.5	30	5	34.4 ± 1.7	8.7 ± 0.5	44.7 ± 2.2	27.4 ± 2.1
	Gelatin	Soluble starch	Sucrose	Water				
	45.5	45.5	4	5	48.3 ± 1.5	21.3 ± 1.4	2.5 ± 0.2	4.0 ± 0.3
	40.0	40.0	15	5	41.0 ± 1.7	15.5 ± 0.9	17.0 ± 1.2	13.2 ± 1.2
	34.5	34.5	26	5	35.1 ± 1.6	9.8 ± 0.6	41.3 ± 2.1	31.2 ± 2.4

WVTR of edible films and, in particular, films made from proteins or starch components such as gluten or amylose, the high WVTR values were attributed to 'clustering' of water molecules in their diffusion through microcavities. In the present paper, blends of gelatin with soluble starch were used in an attempt to study their interactions and their sensitivity to WVTR. An increase in the plasticizer content, either as water or as polyol (glycerol, sorbitol, sucrose), resulted in higher WVTR values (Table 3). These findings were elsewhere confirmed by theoretical calculations, using computer simulation, on starch and other, mainly amorphous, polymers (Takeuchi, 1990; Takeuchi & Okazaki, 1990; Takeuchi et al., 1990; Trommsdorff & Tomka, 1995).

Gas permeability (GP)

Although most edible films are not effective as WVTR barriers, they are quite efficient as gas barriers. A theoretical or empirical calculation of gas permeation in films has been the subject of several investigations because it directly relates to potential applications of the films (Salame, 1986; van Krevelen, 1990). A straightforward relationship between polar groups and solubility is not feasible because of the complexity of interactions and inherent difficulties in assessing factors such as accessibility of polar groups, the relative strength of water–water vs the water–polymer bonds and crystallite size, shape and degree of crystallinity of the food matrix, etc. The segmental mobility of the amorphous component (through which permeation occurs) in a semi-crystalline polymer generally differs considerably from that of a fully amorphous polymer, especially for rubbery polymers (Hedenqvist & Gedde, 1996). For some penetrant molecules, their size may be even too large to enter the available amorphous interlayer separating two crystallites. The generally accepted methodology, at least for amorphous synthetic polymers, for calculating gas permeability, was proposed by Salame (1986). In his simplified model, the so-called polymer permachor (π) is by definition proportional to the negative logarithm of a relative permeability. He further defined the product of $Nx\pi$ as a molar permachor (Π), an

additive molar function of permeability, according to the following equation:

$$Nx\pi = \Pi = \sum(N_i x\pi_i) \qquad (9)$$

where N = the number of characteristic groups per structural unit and π_i = the increment of the group i.

After the numerical value of π is calculated, the permeability at ambient temperature can be estimated as follows:

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

where P(298) is the permeability of a standard gas (i.e. N_2) in a standard polymer (i.e. rubber was arbitrarily chosen) and s is the scaling factor. By substituting log $P^*(298) = -12$ and $s = 0.122$ for nitrogen (van Krevelen, 1990), the following equation is obtained:

$$log P^*{}_{(298)} = -12 - 0.053\pi \qquad (11)$$

The applicability of this equation should be emphasized in that it is restricted only to amorphous polymers.

In order to apply the above-mentioned equations to semi-crystalline (*sc*) polymers, where the crystallites impose constraints on the amorphous chains and gathering of chain defects (i.e. chain ends and chain branches) imparts different properties to the amorphous phase of *sc* polymers, a further modification (Salame, 1986) is required, thus leading to

$$\pi_{sc} = \pi_a - 18 \ln a = \pi_a - 41.5 \log(1 - x_c) \qquad (12)$$

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

When the eqns 9–12 were applied to starch, the obtained values for dry amorphous samples were 6.99×10^{-20} and 2.4×10^{-19} cm^2 s^{-1} Pa^{-1}, for amylopectin and amylose, respectively. The values of nitrogen permeability for dry starch are significantly lower than the experimental ones (Table 4).The observed discrepancies, which are far more substantial in the case of films made from blends of natural polymers/biopolymers, might be attributed to several factors among which the most important are the following (Mueller-Plathe, 1991*a,b*, 1992; van Krevelen, 1990): (i) introduction of microcrystallites; (ii) accessibility of polar groups; (iii) the geometry of the voids — a 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) force fields; and (vi) relative strength of water–water vs the polymer–water bonds.

The water content greatly influences the films containing hydrogen bonding groups and the gas diffusivity

increases with water content, as can be seen from Fig. 5. This figure shows how Tg can be determined from permeability measurements, i.e. the inflection of the line from permeability vs the inverse temperature. A possible reason for such a change in the slope can be given. 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 polymer chains move further apart and the number of intra- and interchain hydrogen bonds decreases considerably (Trommsdorff & Tomka, 1995). The widening of the composite matrix structure due to incorporation of plasticizer molecules would enhance gas permeation (Table 4). Our results on gas permeability of gelatin films are in satisfactory agreement with those reported in a previous publication (Lieberman & Guilbert, 1973).

The thermal dependence of diffusivity on temperature was found to satisfactorily follow the Arrhenius equation:

$$D = D_0 \exp(-E_D/RT) \qquad (13)$$

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 eqn 13 describing diffusivity is:
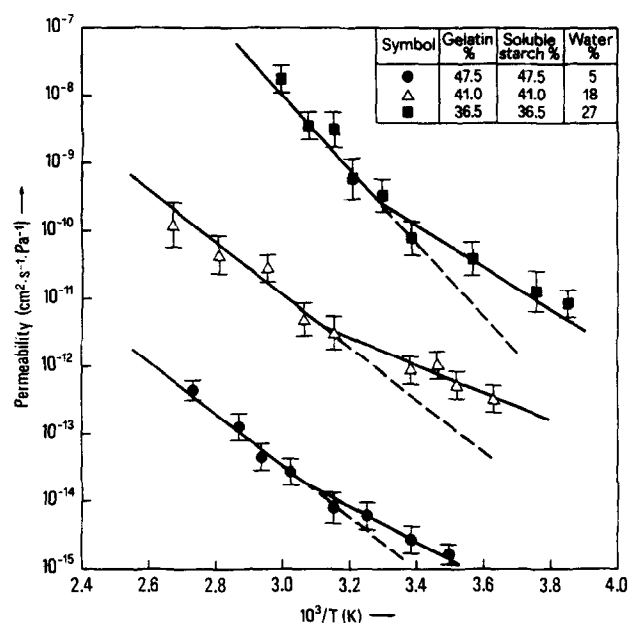
$$\ln D = \ln D_0 - E_D/RT \qquad (14)$$

Symbol	Gelatin %	Soluble starch %	Water %
●	47.5	47.5	5
△	41.0	41.0	18
■	36.5	36.5	27

Fig. 5. Permeability of CO_2 in gelatin/soluble starch/water blends (high-temperature process) derived from eqn 15 vs the inverse temperature (1/T). The results give the average and the standard deviation of at least six measurements.

Table 4. Gas permeability (O_2, N_2, CO_2 in cm^2 sec^{-1} Pa^{-1}) of gelatin/soluble starch (1:1)/glycerol, gelatin/soluble starch (1:1)/sorbitol and gelatin/soluble starch (1:1)/sucrose blends, prepared with low-and high-temperature processes conditioned over different relative humidities. The results give the average of at least five measurements at ambient temperature ($23 \pm 2°C$)

	Gelatin	Soluble starch	Glycerol	Water	O_2	N_2	CO_2
	47.5	47.5	0	5	$3.5(\pm0.2)\times10^{-16}$	$4.4(\pm0.3)\times10^{-17}$	$1.5(\pm0.1)\times10^{-15}$
	45.0	45.0	5	5	$9.3(\pm0.4)\times10^{-16}$	$1.2(\pm0.1)\times10^{-16}$	$4.2(\pm0.2)\times10^{-15}$
	42.5	42.5	10	5	$4.9(\pm0.4)\times10^{-15}$	$6.0(\pm0.4)\times10^{-16}$	$2.5(\pm0.1)\times10^{-14}$
	37.5	37.5	20	5	$6.4(\pm0.5)\times10^{-13}$	$8.4(\pm0.6)\times10^{-14}$	$3.8(\pm0.5)\times10^{-12}$
Low-temperature process	34.5	34.5	26	5	$4.3(\pm0.4)\times10^{-12}$	$5.8(\pm0.3)\times10^{-13}$	$2.6(\pm0.1)\times10^{-11}$
	Gelatin	Soluble starch	Sorbitol	Water			
	45.5	45.5	4	5	$1.8(\pm0.2)\times10^{-15}$	$2.8(\pm0.3)\times10^{-16}$	$9.0(\pm0.4)\times10^{-15}$
	42.5	42.5	10	5	$7.0(\pm0.4)\times10^{-15}$	$5.3(\pm0.4)\times10^{-16}$	$2.7(\pm0.2)\times10^{-14}$
	40.5	40.5	14	5	$8.4(\pm0.5)\times10^{-14}$	$4.6(\pm0.2)\times10^{-15}$	$2.3(\pm0.4)\times10^{-13}$
	35.0	35.0	25	5	$7.7(\pm0.6)\times10^{-12}$	$1.4(\pm0.2)\times10^{-13}$	$4.9(\pm0.2)\times10^{-12}$
	Gelatin	Soluble starch	Sucrose	Water			
	44.5	44.5	6	5	$1.2(\pm0.1)\times10^{-15}$	$0.4(\pm0.1)\times10^{-16}$	$2.1(\pm0.3)\times10^{-15}$
	42.0	42.0	11	5	$6.3(\pm0.4)\times10^{-15}$	$5.6(\pm0.4)\times10^{-16}$	$3.0(\pm0.2)\times10^{-14}$
	39.5	39.5	16	5	$7.0(\pm0.6)\times10^{-14}$	$4.8(\pm0.3)\times10^{-15}$	$1.4(\pm0.1)\times10^{-13}$
	35.0	35.0	25	5	$6.0(\pm0.4)\times10^{-12}$	$3.8(\pm0.3)\times10^{-13}$	$1.4(\pm0.1)\times10^{-11}$
	Gelatin	Soluble starch	Glycerol	Water			
	47.5	47.5	0	5	$4.7(\pm0.6)\times10^{-15}$	$3.3(\pm0.2)\times10^{-16}$	$1.8(\pm0.2)\times10^{-14}$
	45.0	45.0	5	5	$1.8(\pm0.2)\times10^{-14}$	$1.0(\pm0.1)\times10^{-15}$	$6.7(\pm0.4)\times10^{-14}$
	43.0	43.0	9	5	$7.0(\pm0.5)\times10^{-14}$	$5.2(\pm0.3)\times10^{-15}$	$1.2(\pm0.3)\times10^{-13}$
	37.5	37.5	20	5	$9.0(\pm0.4)\times10^{-12}$	$6.8(\pm0.4)\times10^{-13}$	$3.1(\pm0.4)\times10^{-11}$
High-temperature process	35.0	35.0	25	5	$6.9(\pm0.3)\times10^{-11}$	$4.3(\pm0.2)\times10^{-12}$	$1.7(\pm0.2)\times10^{-10}$
	Gelatin	Soluble starch	Sorbitol	Water			
	44.5	44.5	6	5	$3.0(\pm0.1)\times10^{-14}$	$1.8(\pm0.1)\times10^{-15}$	$6.0(\pm0.5)\times10^{-14}$
	42.5	42.5	10	5	$9.6(\pm0.5)\times10^{-14}$	$7.9(\pm0.6)\times10^{-15}$	$2.1(\pm0.2)\times10^{-13}$
	40.0	40.0	15	5	$2.1(\pm0.1)\times10^{-12}$	$1.5(\pm0.2)\times10^{-13}$	$4.9(\pm0.3)\times10^{-12}$
	32.5	32.5	30	5	$9.5(\pm0.6)\times10^{-11}$	$5.0(\pm0.3)\times10^{-12}$	$1.6(\pm0.1)\times10^{-10}$
	Gelatin	Soluble starch	Sucrose	Water			
	45.5	45.5	4	5	$2.0(\pm0.1)\times10^{-14}$	$2.5(\pm0.3)\times10^{-15}$	$8.3(\pm0.6)\times10^{-14}$
	40.0	40.0	15	5	$1.1(\pm0.1)\times10^{-13}$	$3.9(\pm0.2)\times10^{-14}$	$1.1(\pm0.2)\times10^{-12}$
	34.5	34.5	26	5	$9.4(\pm0.5)\times10^{-11}$	$5.7(\pm0.4)\times10^{-12}$	$1.6(\pm0.1)\times10^{-10}$

Similarly to eqn 13, the temperature dependence of permeability can be expressed as

$$P = P_0 exp(-E_P/RT) \qquad (15)$$

where E_P is the apparent activation energy of permeation, and

$$lnP = lnP_0 - E_P/RT \qquad (16)$$

The activation energies of diffusion and permeation were calculated according to eqns 14 and 16 for gelatin/soluble starch/polyols blends and are summarized in Table 5.

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'. 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 occurs, finally leading to annihilation of the original cavities.

CONCLUSIONS

The physical properties of edible films from gelatin and soluble starch plasticized by water or polyols (glycerol, sorbitol) were tested. Depending on the adopted method (low- or high-temperature process) considerable differences were recorded both in the mechanical and thermal properties. In general, the low-temperature preparation method was related to higher percentage molecular ordering, higher tensile strength and lower gas/water permeability. Addition of water or polyol to the gelatin/soluble starch blends resulted in plasticization of the polymer matrix as reflected by lower Tm, Tg and tensile strength but higher elongation values.

Table 5. Activation energies for diffusion (E_D*, kJ mol^{-1}) and permeation (E_P**, kJ mol^{-1}) both below (T < Tg) and above (T > Tg) the glass transition temperature (Tg) for gelatin/soluble starch/water/polyol blends prepared by the low-temperature process. The results give the average and the standard deviation of five measurements

Gelatin (%w/w)	Water (%w/w)	Soluble starch (%w/w)	N₂ E_P* (T < Tg)	N₂ E_P* (T > Tg)	N₂ E_P** (T < Tg)	N₂ E_P** (T > Tg)	O₂ E_P* (T < Tg)	O₂ E_P* (T > Tg)	O₂ E_P** (T < Tg)	O₂ E_P** (T > Tg)
85	15	0	6.2±0.7	5.0±0.4	8.1±0.7	6.3±0.7	5.6±0.4	4.5±0.5	7.5±0.8	5.7±0.6
80	15	5	7.1±0.8	5.8±0.6	9.7±0.8	7.8±0.5	6.7±0.8	5.4±1.0	9.0±1.0	7.0±0.8
70	15	15	8.2±0.5	7.0±0.3	12.0±1.1	9.4±0.8	7.7±0.6	6.4±0.9	10.8±0.9	8.3±0.7
55	15	30	9.0±1.1	8.1±0.7	13.4±1.2	10.5±1.1	8.5±0.5	7.8±0.8	11.7±0.8	9.8±0.8
47.5	5	47.5	12.5±1.3	11.2±1.1	15.3±0.9	12.0±1.3	11.9±1.2	10.7±1.4	13.4±1.4	11.2±1.0
40.0	20	40	7.2±0.7	6.0±0.5	10.8±0.8	7.6±0.6	6.5±0.6	5.4±0.8	10.0±0.8	6.9±0.8
35.0	30	35	3.1±0.2	2.1±0.1	4.2±0.5	2.7±0.3	2.7±0.2	1.8±0.4	3.5±0.4	2.4±0.3
Gelatin/ soluble starch	Water	Glycerol								
35.0/35.0	5	25	2.8±0.3	2.0±0.2	4.4±0.5	2.6±0.2	2.5±0.3	1.7±0.3	3.8±0.2	2.4±0.2
Gelatin/ soluble starch	Water	Sorbitol								
35.5/35.5	5	24	2.4±0.2	1.8±0.1	3.3±0.2	2.1±0.1	2.2±0.2	1.6±0.2	2.8±0.3	1.8±0.2
Gelatin/ soluble starch	Water	Sucrose								
34.5/34.5	5	26	2.5±0.3	1.6±0.2	2.9±0.3	2.0±0.2	2.2±0.3	1.3±0.1	2.5±0.3	1.7±0.3

*Calculated according to eqn 14. **Calculated according to eqn 16.

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