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Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water

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Abstract

Two methods, known as the low and the high temperature methods, which consist of casting aqueous solutions of hydroxypropyl starch and gelatin at 20 and 60°C, respectively, were employed for film preparation. The physical (thermal, mechanical and gas/water permeation) properties of these composite films, plasticized with water or polyols, were studied. An increase in the total plasticizer content resulted in a considerable decrease in elasticity modulus and tensile strength (up to 60% of the original values when 25% plasticizer was added), whereas the percentage elongation increased (up to 200% compared to the original values). The low temperature method led to the development of higher percentage renaturation (crystallinity) of gelatin which resulted in a decrease, by one or two magnitude orders, of CO_2 and O_2 permeability in the hydroxypropyl starch/gelatin blends. An increase in the total plasticizer content (water, polyols) of these blends was found to be proportional to an increase in their gas permeability. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Gas permeability; Edible films; Starch; Gelatin; Mechanical properties; Polyols; Glycerol

1. Introduction

Polysaccharides and proteins are well known for being good film formers. Although both of them can be reasonably effective as gas barriers (O_2 and CO_2) for coating applications, their water vapour transmission rates are elevated (Baldwin *et al.*, 1995; Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996). Gelatin is considered unique among hydrocolloids in forming thermo-reversible gels with a melting point close to body temperature (Achet & He, 1995, Johnston-Banks, 1990). Gelatin has already found many applications in the sausage industry as a casing component or gelling agent (Hood, 1987), and as a coating with antioxidants or farinaceous components for spraying or dipping food ingredients (Klose *et al.*, 1952; Moorjani *et al.*, 1978). Furthermore, gelatin has been used in the pharmaceutical industry as a binder for the production of hard capsules (Kellaway *et al.*, 1978) and in the textile industry because of its adhesive properties (Bradbury & Martin, 1952; Slade & Levine, 1987).

Starch, as the most important and abundant polysaccharide in nature, has been the subject of numerous research studies reporting, among others, on its film forming ability and its applications in the food industry (Arvanitoyannis *et al.*, 1994; Ollett *et al.*, 1991; Kirby *et al.*, 1993; Gennadios & Weller, 1990; Gennadios *et al.*, 1993a, 1993b, 1993c, 1993d, 1993e; Cherian *et al.*, 1995; Shogren, 1993; Lourdin *et al.*, 1995). However, since starch films exhibit moderately high tensile strength and become markedly brittle at very low moisture contents (below 6%), they have not found extensive applications as coatings or film formers (Healey *et al.*, 1974). The potential to use edible barriers for shelf life extension of foods has recently been recognized because of a variety of factors such as environmental legislation, consumer expectation for fresh foods and need for shelf life extension of foods (Krochta & De Mulder-Johnston, 1997).

This article aims to address the preparation of binary or ternary single phase blends, consisting of protein/modified polysaccharide/plasticizer and to compare the properties of these composite materials to those prepared from similar resources. In the sixth paper of this series (Arvanitoyannis *et al.*, 1996, 1997; Arvanitoyannis & Biliaderis, 1997a, 1997b; Psomiadou *et al.*, 1996), blends of gelatin/hydroxypropyl starch (HPS)/plasticizer (water and/or polyol) were prepared by the low or the high temperature method in order to study the physical properties and to suggest eventual applications.

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2. Experimental

2.1. Materials

HPS was a modified potato starch (hydroxypropyl group content/starch 15% w/w) gift from Nippon Starch (Osaka, Japan) and food grade gelatin (Merck), glycerol, sorbitol, sucrose (analytically pure) were purchased from Wako Chemicals (Japan).

2.2. High and low temperature preparation processes (for permeability and tensile measurements)

Films of thickness 0.8 ± 0.06 mm were prepared by casting and evaporating 5% aqueous gelatin and 2% aqueous HPS solutions at 60 and 20°C on metal trays. At 60°C the evaporation was completed within 6 h whereas that at 20°C required 1 week. The films were placed in relative humidity chambers over salt solutions or phosphorus pentoxide and the moisture content was determined by drying to constant weight.

2.3. 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^{-1} and a single cantilever bending mode at 1 Hz was calibrated each day and measurements were taken at least on triplicate samples. Thicker samples of gelatin/HPS were prepared by multiple casting at 60 and 20°C and then conditioned at different relative humidities (Arvanitoyannis *et al.*, 1994). The glass transition was defined as the mid-point between the onset of the fall in the elastic modulus $\Delta E'$.

2.4. Differential thermal analysis (DTA) measurements

DTA measurements were taken using a Shimadzu differential thermal analyzer equipped with a liquid N_2 cooling accessory. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The T_gs, defined as midpoint of the step transition, were determined from the second run after heating, quenching with liquid nitrogen and reheating at a heating rate of 10°C min^{-1}. Data analysis to fit experimental values of T_g to the empirical Gordon–Taylor equation (Gordon & 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, $\Delta Cp_1/\Delta Cp_2$. 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 $T_{g_{\mathrm{matrix}}}$, dotted line), and the other based on a k value of 4 (an approximate estimate of $\Delta Cp_1/\Delta Cp_2$, based on literature values of ΔCp for water and HPS/gelatin, solid line).

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

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).

Permeability (P) is well known to be the product of solubility (S) and diffusivity (D). Assuming that a unidirectional diffusion through a flat membrane occurs, permeability and diffusion can be expressed as follows:

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

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

where J is the flux and $D_{i(ci)}$ signifies that the diffusion coefficient is dependent on the concentration/composition of penetrant (c).

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 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 ($p_1 - p_2$), the area exposed (A), the permeation time (t) and a constant value (P), and is inversely proportional to thickness (x):

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

Water vapour transmission rate (WVTR) measurements were carried out as reported previously (Martin-Polo *et al.*, 1992).

2.6. Mechanical properties

2.6.1. 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 D828-88 (ASTM, 1989).

2.6.2. Three-point bending test

All samples were cut into bars ≈ 30 × 8 × 2 mm and stored for 3 weeks over saturated salt solutions. Their moisture content was measured on three replicates by drying at 105°C to constant weight. Three-point bend tests were carried out at 22 ± 1°C using an Instron texturometer at a cross-head speed of $50\ \text{mm s}^{-1}$ on samples previously equilibrated at various relative humidities. The peak force was recorded and the initial slope of the force/distance graph and the sample dimensions were used to calculate the Young's modulus.

3. Results and discussion

3.1. Thermal and thermal mechanical properties

Investigation of thermal properties of gelatin/hydroxypropyl starch (HPS)/plasticizer (water and/or polyol) blends showed that both water and/or polyols had a strong plasticizing action (regarding T_m and T_g depression), proportional to the total plasticizer content in the blend (Table 1). Although the effectiveness of a plasticizer in leading to phase separation has been long debated (Ledward, 1993, 1994), the DTA and DMTA results were not in favour of such a phase separation.

The observation of a pronounced broadening of the step transition in DTA traces (Fig. 1), in conjunction with the fact that no clear separation of the two peaks was recorded in the DMTA runs (tan δ), supports our assumption that no phase separation occurred, at least for total plasticizer content up to 25%. The T_g, determined from the second run, was always observed at temperatures of at least 6–7°C lower compared to the T_g determined from the first run. This marked difference in T_g between the first and second runs could be due to more homogeneous redistribution of the plasticizer (water and/or polyol) throughout the polymeric composite matrix which is now in an amorphous state after the melting of the microcrystalline regions (Jolley, 1970; Marshall & Petrie, 1980; Arvanitoyannis *et al.*, 1996).

Table 2 shows that the plasticization of this binary polymeric matrix (HPS/gelatin) caused by the polyols/water is rather strong, similar to reported findings (Kalichevsky *et al.*, 1993a, 1993b). The plasticization of the binary polymeric network with polyols results in high mobility regions characterized by their high moisture uptake (Arvanitoyannis *et al.*, 1996; Cherian *et al.*, 1995). Insofar as the total plasticizer content did not exceed 25%, no double peaks (tan δ, DMTA traces) were recorded. At higher than 25% total plasticizer content double peaks appeared, similar to the previously reported action of plasticizers (water, glycerol, sugars) both on polystyrene (Bazuin & Eisenberg, 1986) and on starch components (Cherian *et al.*, 1995; Kalichevsky *et al.*, 1993a, 1993b) or starch based polymer blends (Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996).

The state diagram of HPS/gelatin presenting experimental data from DTA is shown in Fig. 2a, whereas the respective diagrams of the ternary systems (HPS/gelatin/polyol, 45/45/10 and 40/40/20 w/w/w) are given in Fig. 2(b–e). In general, sucrose, 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 (G–T) plots (Fig. 2); i.e. the T_g of about 368 K for the dry HPS/gelatin blend is suppressed to 365 and 346 K for blends containing 10 and 20% glycerol and to 356 and 344 K for blends with 10 and 20% sucrose content, respectively. The G–T plots based on a k value of 4 were rather poor in describing the T_g depression ($r^2 = 0.86$–0.97), and gave higher estimates of T_g for the dry polymer matrix. However, it should be pointed out that it was possible to have this second dotted line (based on the theoretical approximation that $k \approx 4$) only in Fig. 2a,d whereas the program did not provide such a line for the rest of the figures.

Both the ternary (gelatin/starch/water) and the quaternary systems (gelatin/starch/water/sugars) are characterized by a variety of interactions occurring between them such as OH–OH (starch chains), HPS/gelatin–water, HPS/gelatin–polyol, polyol–polyol and water–polyol (Tolstoguzow *et al.*, 1985; Tolstoguzow, 1994). Since HPS has the same number of available –OH, compared to the non-modified starch, its interactions with the rest of the components appear to be considerable (T_g and T_m lowering). The plasticization of the composite matrix was shown, apart from the thermal properties (Tables 1 and 2, Fig. 1), by the considerable fall in flexural and tensile moduli as well. In Table 1, the percentage renaturation of gelatin in HPS/gelatin blends was calculated as follows:

$$\%\text{Rn} = \Delta H_m / \Delta H_{100\%\ \text{renatured}} = \Delta H_m / \Delta H_{\text{collagen}} \qquad (6)$$

where $\Delta H_{\text{collagen}} = 62.05\ \text{J g}^{-1}$ (Achet & He, 1995; Macsuga, 1972)

The percentage renaturation (crystallinity of gelatin) refers to transformation of the gelatin strands to triple-helix structure similar to the native collagen structure. It is thought that these triple helices act as 'initiators' for the development of a three-dimensional network. The renaturation (crystallization) of gelatin chains was suggested to take place by the following mechanism; a disordered coil is initially converted to a helix (II type) and an intermediate (I type) followed by a growth-determining stage finally resulting in a stable collagen-type structure (Arvanitoyannis *et al.*, 1997a & b; Achet & He, 1995).

The DTA determination of crystallinity is a destruc-

Table 1.
Thermal and thermo-mechanical properties of blends, based on HPS/gelatin (1:1) with glycerol, sorbitol and sucrose, prepared with low and high temperature process. The results give the average and the standard deviation of at least three or five measurements for thermal and permeability measurements, respectively

					DTA			T_g			
					T_m	ΔH (J g^{-1})	%Rn[a]	DTA	DMTA (E')	DMTA (tan δ)	Permeability inflection
Low temperature process	HPS	Gelatin	Glycerol	Water							
	47.5	47.5	0	5	145.0 ± 3.0	22.6 ± 1.3	72.8	73.0 ± 2.8	69.0 ± 2.0	76.0 ± 3.0	66.2 ± 3.0
	45.0	45.0	5	5	141.2 ± 2.5	20.5 ± 0.9	69.7	63.7 ± 1.9	65.0 ± 2.8	68.0 ± 3.0	62.0 ± 2.5
	40.0	40.0	15	5	130.1 ± 2.6	16.2 ± 1.2	62.0	54.0 ± 1.6	55.2 ± 2.0	60.1 ± 1.8	55.2 ± 2.0
	35.0	35.0	25	5	117.2 ± 1.9	13.4 ± 1.1	58.6	45.3 ± 1.8	47.1 ± 1.6	51.2 ± 2.2	44.0 ± 1.5
	HPS	Gelatin	Sorbitol	Water							
	46.0	46.0	3	5	142.8 ± 2.5	21.3 ± 1.8	70.9	66.0 ± 2.2	67.4 ± 1.8	71.7 ± 1.8	65.5 ± 2.5
	41.0	41.0	13	5	133.0 ± 1.9	17.2 ± 1.2	64.2	57.2 ± 1.8	59.0 ± 1.3	62.8 ± 2.2	57.0 ± 1.8
	35.5	35.5	24	5	116.4 ± 2.0	14.1 ± 0.9	60.8	46.1 ± 1.4	47.5 ± 2.0	52.3 ± 1.3	45.4 ± 2.2
	HPS	Gelatin	Sucrose	Water							
	45.5	45.5	4	5	141.7 ± 1.8	20.2 ± 1.7	68.0	66.8 ± 2.3	68.4 ± 1.7	72.8 ± 3.1	65.0 ± 3.0
	40.0	40.0	15	5	129.5 ± 1.9	16.0 ± 1.4	61.2	55.4 ± 1.9	57.0 ± 2.1	60.3 ± 2.5	56.5 ± 1.9
	35.0	35.0	25	5	116.6 ± 2.3	13.7 ± 0.9	59.9	43.9 ± 2.0	45.4 ± 1.5	49.0 ± 1.6	42.5 ± 2.4
High temperature process	HPS	Gelatin	Glycerol	Water							
	47.5	47.5	0	5	137.5 ± 2.4	17.3 ± 1.4	55.8	67.7 ± 2.3	69.0 ± 2.0	76.0 ± 3.0	66.2 ± 3.0
	45.0	45.0	5	5	132.0 ± 1.9	16.1 ± 1.2	54.8	57.5 ± 2.3	59.0 ± 2.4	62.6 ± 2.4	56.0 ± 3.1
	40.0	40.0	15	5	124.3 ± 1.6	11.2 ± 1.4	42.9	49.4 ± 1.8	50.9 ± 1.6	54.5 ± 1.6	51.4 ± 2.5
	35.0	35.0	25	5	113.4 ± 2.0	8.3 ± 0.6	36.3	40.6 ± 2.1	42.0 ± 2.1	46.0 ± 2.0	39.5 ± 2.0
	HPS	Gelatin	Sorbitol	Water							
	46.0	46.0	3	5	135.4 ± 1.9	17.2 ± 1.3	57.2	59.2 ± 1.9	60.8 ± 2.4	65.3 ± 1.7	58.0 ± 1.5
	41.0	41.0	13	5	124.2 ± 2.5	12.5 ± 0.9	46.7	52.0 ± 2.3	53.6 ± 1.8	57.5 ± 2.3	53.5 ± 2.8
	35.5	35.5	24	5	110.0 ± 1.8	9.0 ± 0.5	38.8	42.2 ± 1.5	43.9 ± 1.4	48.3 ± 2.1	41.0 ± 4.8
	HPS	Gelatin	Sucrose	Water							
	45.5	45.5	4	5	136.1 ± 2.1	16.4 ± 1.2	55.2	60.7 ± 1.8	62.1 ± 2.0	66.9 ± 2.5	62.5 ± 2.5
	40.0	40.0	15	5	128.0 ± 1.8	11.1 ± 0.8	42.5	50.0 ± 1.5	51.6 ± 2.5	56.7 ± 2.4	49.4 ± 1.7
	35.0	35.0	25	5	109.8 ± 2.4	7.9 ± 0.5	34.6	39.8 ± 1.9	42.0 ± 2.2	45.0 ± 2.2	41.2 ± 2.2

[a] Percentage renaturation calculated from ($\Delta H_{\text{gelatin in blend}}/\Delta H_{\text{collagen}}$) × 100.

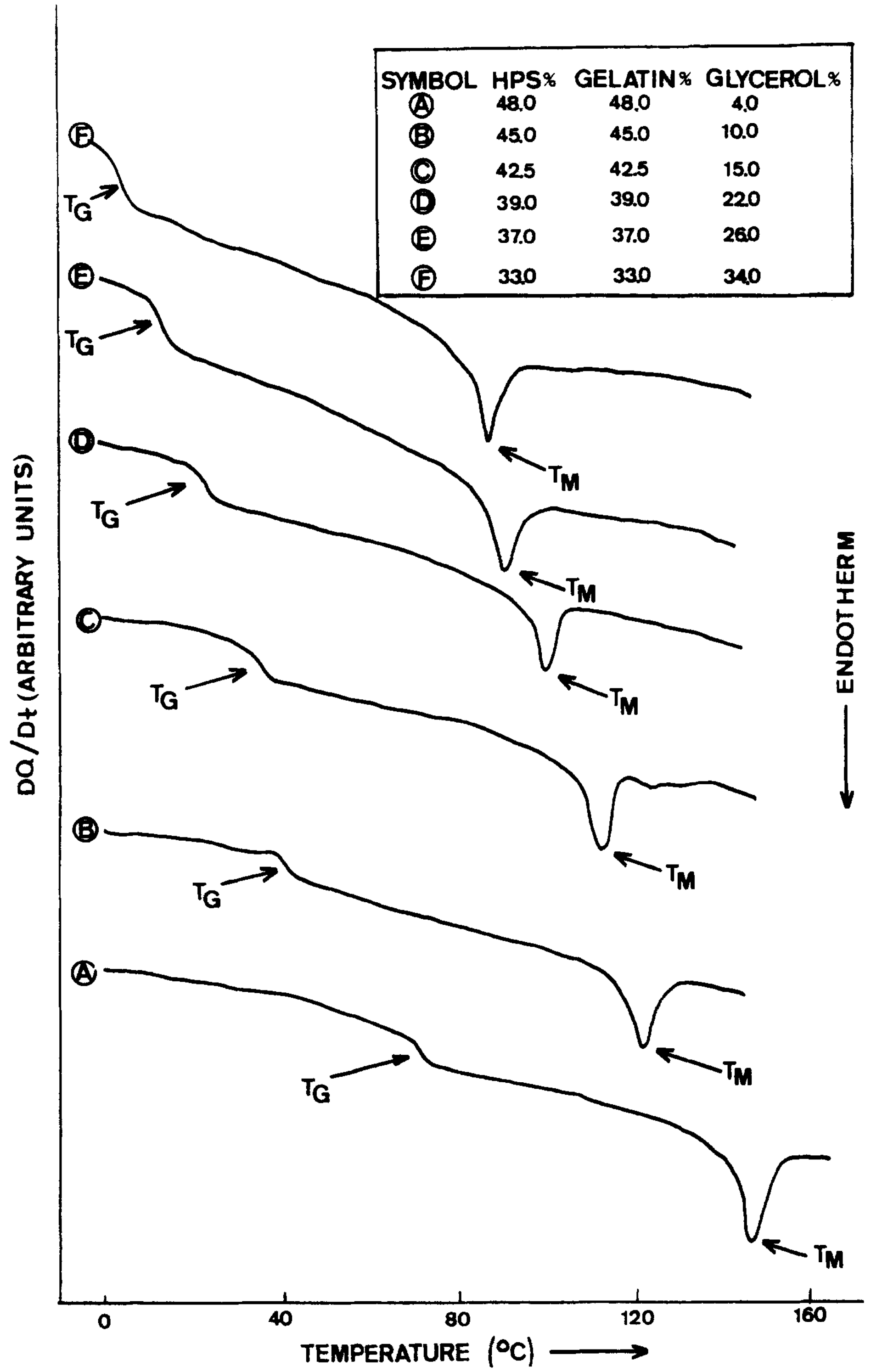


Fig. 1. Representative DTA traces of HPS/gelatin/glycerol blends (at 3% water content) prepared by the low temperature process.

tive method consisting of measuring the conversion of collagen-like gelatin chains into the random-coil state by increasing the temperature (Table 1). Since the enthalpy of the helix → coil transition is considered to arise solely from hydrogen-bond interactions, the effect of water content on gelatin crystallization was investigated as well. Table 1 shows that for dry blends the $\Delta H_{\mathrm{renatured}}$ remains low, whereas it increases proportionally with an increase in water content (up to 15%). This is attributed to the fact that the structural water, which is directly bound to the gelatin strands with hydrogen bonds, contributes to the stabilization/maturation of collagen-type structure. However, at water contents higher than 15% the HPS/gelatin system becomes very mobile thereby enhancing the

Table 2.
Glass transition temperatures (T_g, °C) of blends based on HPS and gelatin, conditioned at different relative humidities

HPS	Water	Gelatin	DTA (2nd run)	DMTA (E')	DMTA (tan δ)	Permeability (inflection point)
Low temperature process						
–	10	90	59.3 ± 2.5	61.2 ± 2.0	65.0 ± 2.6	57.0 ± 3.1
3	10	87	60.6 ± 3.0	63.0 ± 2.5	67.2 ± 1.8	59.5 ± 2.5
5	10	85	6.2 ± 1.8	63.8 ± 1.8	68.5 ± 1.9	61.3 ± 1.8
10	10	80	63.7 ± 2.5	65.4 ± 2.4	70.0 ± 2.3	62.0 ± 2.0
20	10	70	65.0 ± 3.2	66.2 ± 1.9	70.5 ± 3.0	63.5 ± 1.6
30	10	60	67.1 ± 2.6	68.0 ± 2.3	72.1 ± 2.8	66.0 ± 2.5
47.5	5	47.5	73.0 ± 2.8	73.6 ± 2.6	78.7 ± 2.5	70.7 ± 2.2
45.0	10	45.0	63.5 ± 1.5	65.1 ± 1.7	70.2 ± 1.7	64.0 ± 2.6
41.0	18	41.0	55.4 ± 2.0	56.8 ± 2.0	64.5 ± 2.1	57.2 ± 1.7
38.0	24	38.0	50.3 ± 2.3	51.7 ± 1.6	57.0 ± 2.4	49.5 ± 1.5
35.0	30	35.0	40.8 ± 3.2	42.0 ± 2.4	48.7 ± 2.5	41.8 ± 2.3
High temperature process						
–	10	90	53.5 ± 1.8	54.8 ± 3.0	59.4 ± 2.8	51.6 ± 1.8
3	10	87	55.0 ± 3.0	56.1 ± 2.1	62.0 ± 1.7	54.0 ± 2.7
5	10	85	58.2 ± 2.6	59.0 ± 1.5	64.5 ± 2.0	56.1 ± 2.5
10	10	80	59.4 ± 2.2	61.3 ± 1.9	67.0 ± 2.3	57.5 ± 1.7
20	10	70	60.5 ± 2.5	63.0 ± 2.5	69.3 ± 1.5	60.0 ± 2.3
30	10	60	62.3 ± 1.9	64.2 ± 1.6	70.5 ± 2.6	61.4 ± 1.9
47.5	5	47.5	67.7 ± 2.3	69.0 ± 2.0	75.7 ± 2.8	66.2 ± 3.0
45.0	10	45.0	59.5 ± 1.5	61.3 ± 1.8	67.5 ± 1.9	60.5 ± 2.4
41.0	18	41.0	50.0 ± 2.5	53.2 ± 2.7	59.0 ± 2.3	58.3 ± 1.8
38.0	24	38.0	45.6 ± 1.8	48.0 ± 2.3	54.3 ± 2.5	46.5 ± 2.5
35.0	30	35.0	37.0 ± 2.4	40.5 ± 2.5	46.6 ± 2.0	38.3 ± 1.9

number of interactions between the minor components (i.e. water–water, water–polyol) which disturb the renaturation process.

3.2. Mechanical properties

3.2.1. Tensile strength and percentage elongation

The results from mechanical measurements of HPS/gelatin/plasticizer films, prepared by the high and the low temperature methods, after their conditioning over saturated salt solutions are given in Table 3. Although according to the classical polymer theory crystallization at high temperatures is bound to result in better and more perfect crystal formation and chain alignment, in these experiments it was found that the percentage renaturation (%Rn) is greater for the low temperature process. These results are in agreement with previous findings (Arvanitoyannis *et al.*, 1994, 1995, 1996; Bradbury & Martin, 1952) where it was suggested that high %Rn is due to unidirectional contraction of films on drying thus allowing an extensive orientation of gelatin chains whereas, at high temperature, the chains are trapped in a disordered and entangled state described by low %Rn. Conditioning of films over various relative humidities resulted in higher percentage elongation (up to 62% of the original values for dry blends) and lower tensile strength (down to 30% of the original values) due to plasticization of the polymer composite matrix.

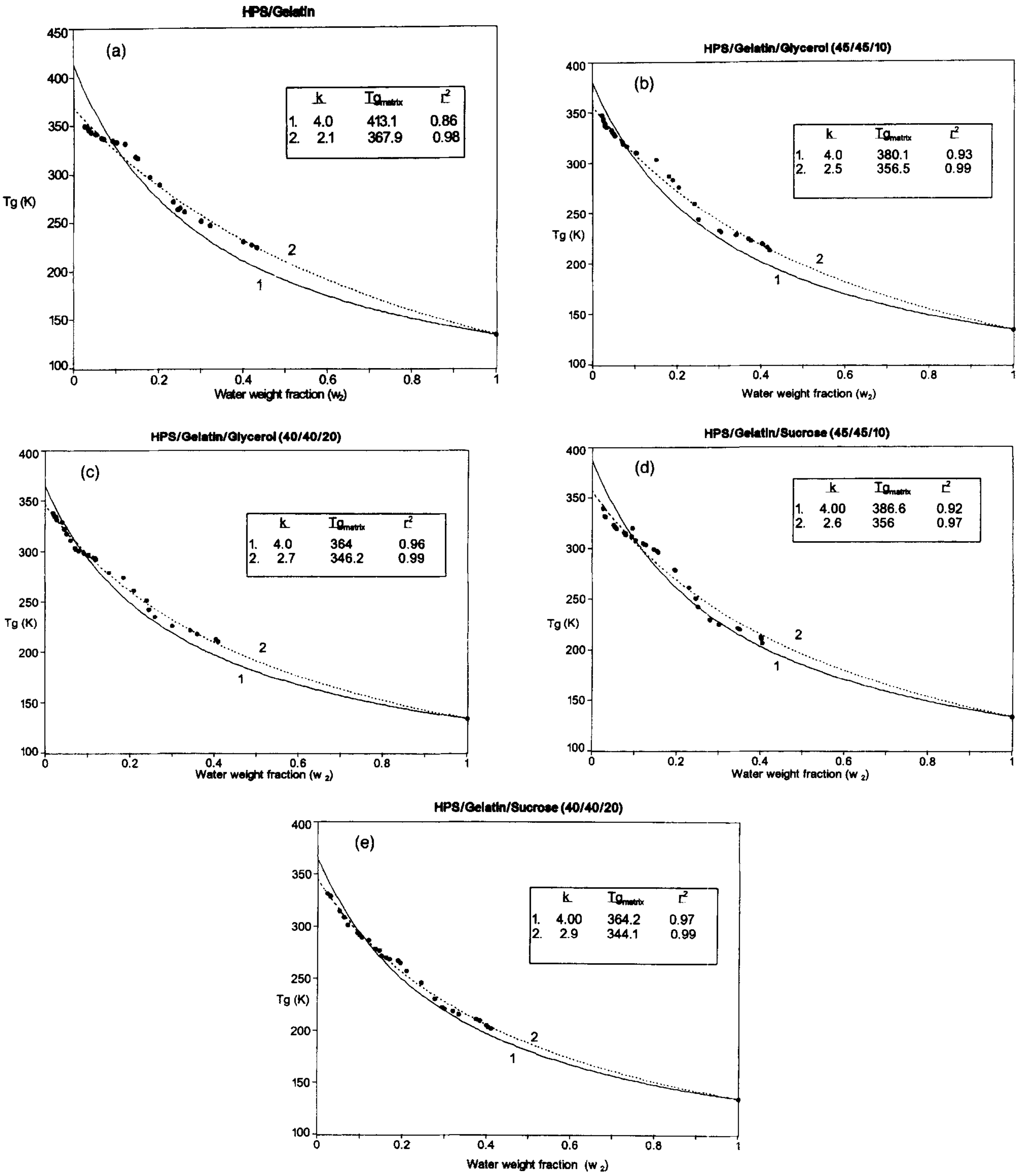
Fig. 3 shows some representative stress–strain curves for HPS/gelatin/glycerol samples. It is clear that Fig. 3a,b exhibits typical brittle fracture behaviour (van Krevelen, 1990) described by relatively high tensile strength, low percentage elongation and no yield point, whereas at high glycerol content a marked increase in percentage elongation was observed accompanied by a very clear yield point (Fig. 3c–g). Wide-angle X-ray diffraction patterns (WAXD) did not show any difference between the two film preparation methods (high and low temperature, Bradbury & Martin, 1952). Therefore, the different behaviour exhibited by the high temperature prepared films should be understood in terms of a closely packed state where extensive intermolecular bonding occurs. The latter inhibits further reorientation and better alignment of the gelatin and starch chains.

The two estimates for upper and lower limits of tensile modulus for composite materials or blends are given by the following equations (Ashby & Jones, 1985):

$$E_{\text{blend}} = V_{\text{HPS}}E_{\text{HPS}} + (1 - V_{\text{HPS}})E_{\text{Gelatin}} \tag{7}$$

$$E_{\text{blend}} = 1/\left(\frac{V_{\text{HPS}}}{E_{\text{HPS}}} + \frac{1 - V_{\text{HPS}}}{E_{\text{Gelatin}}}\right) \tag{8}$$

where E is the tensile or flexural modulus and V is the volume fraction of the respective component in the blend. If the values $E_{\text{HPS}} = 500$ MPa and $E_{\text{gelatin}} = 800$ MPa (Fakirov *et al.*, 1996) for 5% moisture are used to HPS/gelatin (1:1) the estimates obtained are 650 and 615 MPa, from Eqs. (7) and (8), respectively. The



(a)

	k	Tg_{matrix}	r^2
1.	4.0	413.1	0.86
2.	2.1	367.9	0.98

(b)

	k	Tg_{matrix}	r^2
1.	4.0	380.1	0.93
2.	2.5	356.5	0.99

(c)

	k	Tg_{matrix}	r^2
1.	4.0	364	0.96
2.	2.7	346.2	0.99

(d)

	k	Tg_{matrix}	r^2
1.	4.00	386.6	0.92
2.	2.6	356	0.97

(e)

	k	Tg_{matrix}	r^2
1.	4.00	364.2	0.97
2.	2.9	344.1	0.99

Fig. 2. State diagrams of HPS/gelatin(1:1)/polyol blends. T_g vs. water content (●, experimental data; solid and dotted lines give the corresponding Gordon–Taylor plots of the data for different *k* values). Numbers in parentheses refer to weight fraction ratios of blend components.

experimentally determined values (Table 3) are in satisfactory agreement with these two estimates.

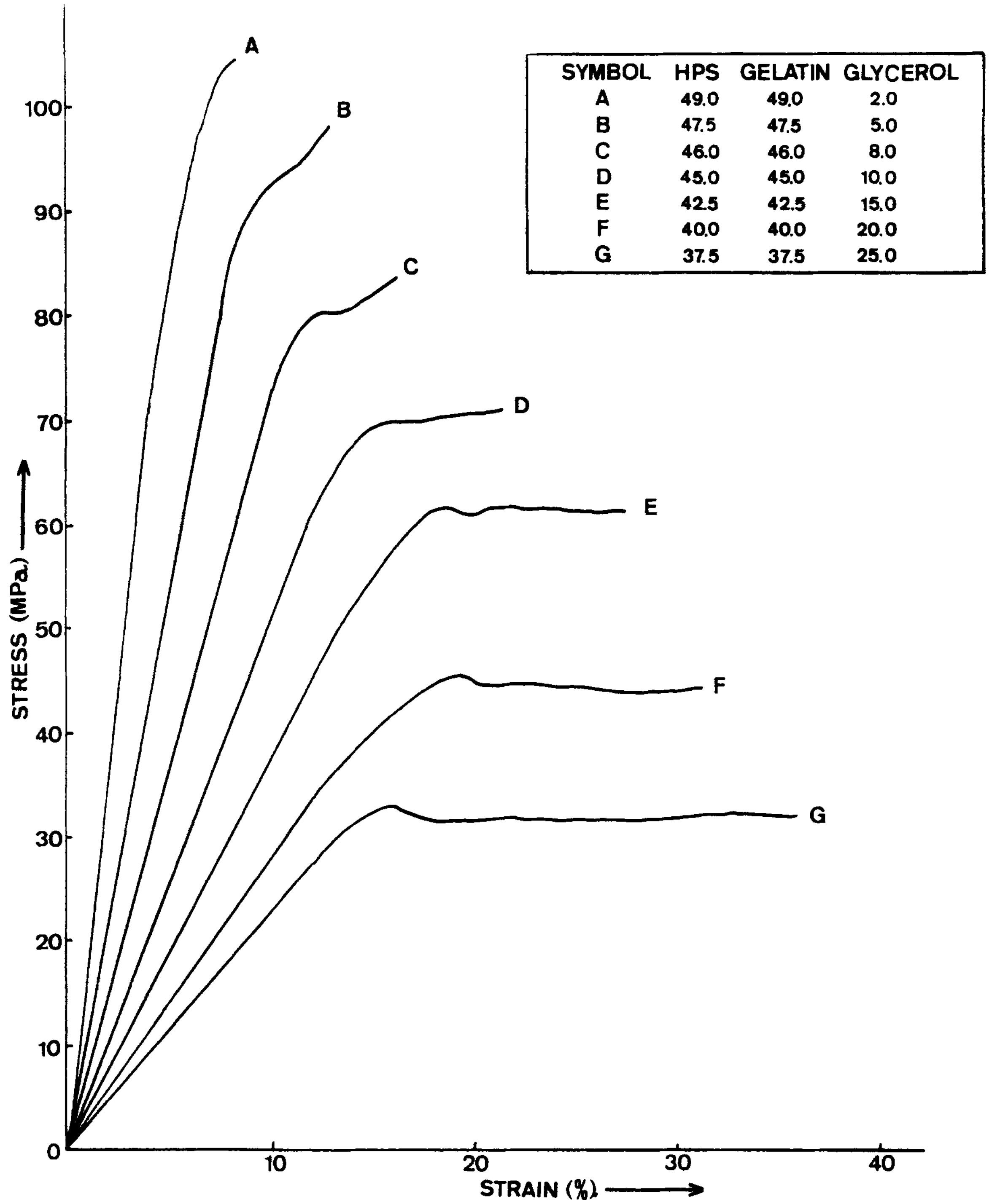
Depending on the nature of the plasticizer the extent of plasticization of the HPS/gelatin blend varies. Sucrose shows a slightly more pronounced plasticizing effect, lowering of tensile strength and modulus, than glycerol and sorbitol on the HPS/gelatin matrix. However, the increase in percentage elongation was greater for glycerol and sorbitol than for sucrose (Table 3) in agreement with findings reported elsewhere (Psomiadou *et al.*, 1996).

3.2.2. Three-point bend test

Figs. 4 and 5 show the effect of water content on the flexural modulus of HPS/gelatin/plasticizer blends. Sorbitol is

Table 3.
Mechanical properties and water vapour transmission rate (WVTR) of blends based on HPS/gelatin (1:1) with glycerol, sorbitol and sucrose, prepared by low and high temperature processes. The results give the average and the standard deviation of at least eight measurements

					Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	WVTR (g m^{-1} s^{-1} Pa^{-1}) × 10^{-11})
Low temperature process	HPS	Gelatin	Glycerol	Water				
	47.5	47.5	0	5	95.3 ± 8.0	770 ± 38	2.7 ± 0.4	0.1 ± 0.01
	45.0	45.0	5	5	84.2 ± 6.5	710 ± 29	6.9 ± 0.5	1.5 ± 0.1
	40.0	40.0	15	5	69.5 ± 5.6	550 ± 30	17.3 ± 1.4	5.2 ± 0.3
	35.0	35.0	25	5	55.0 ± 4.6	360 ± 19	38.5 ± 2.1	9.7 ± 0.4
	HPS	Gelatin	Sorbitol	Water				
	46.0	46.0	3	5	79.3 ± 7.0	634 ± 30	6.3 ± 0.5	1.6 ± 0.2
	41.0	41.0	13	5	71.2 ± 6.1	500 ± 25	19.5 ± 1.4	5.0 ± 0.5
	35.5	35.5	24	5	53.8 ± 5.2	310 ± 22	52.6 ± 3.3	10.2 ± 0.8
	HPS	Gelatin	Sucrose	Water				
	45.5	45.5	4	5	75.6 ± 7.2	640 ± 55	5.2 ± 0.6	1.4 ± 0.3
	40.0	40.0	15	5	67.2 ± 6.5	450 ± 35	17.8 ± 1.8	4.5 ± 0.5
	35.0	35.0	25	5	51.5 ± 4.6	290 ± 23	42.9 ± 2.8	11.0 ± 1.1
High temperature process	HPS	Gelatin	Glycerol	Water				
	47.5	47.5	0	5	86.7 ± 8.0	680 ± 45	2.4 ± 0.3	0.2 ± 0.02
	45.0	45.0	5	5	78.0 ± 6.3	590 ± 40	5.3 ± 0.6	2.1 ± 0.2
	40.0	40.0	15	5	61.2 ± 5.1	420 ± 21	30.8 ± 2.6	6.8 ± 0.5
	35.0	35.0	25	5	50.0 ± 4.2	280 ± 35	61.5 ± 5.2	13.9 ± 1.5
	HPS	Gelatin	Sorbitol	Water				
	46.0	46.0	3	5	80.4 ± 6.0	520 ± 40	4.8 ± 0.3	2.0 ± 0.3
	41.0	41.0	13	5	65.8 ± 4.5	330 ± 20	35.0 ± 0.9	7.8 ± 0.5
	35.5	35.5	24	5	54.3 ± 3.9	270 ± 19	52.5 ± 4.0	15.7 ± 1.4
	HPS	Gelatin	Sucrose	Water				
	45.5	45.5	4	5	78.9 ± 6.5	460 ± 35	4.5 ± 0.6	2.8 ± 0.2
	40.0	40.0	15	5	67.8 ± 5.2	300 ± 25	27.3 ± 1.9	10.5 ± 0.8
	35.0	35.0	25	5	49.0 ± 4.0	245 ± 18	58.2 ± 3.4	22.9 ± 1.7



SYMBOL	HPS	GELATIN	GLYCEROL
A	49.0	49.0	2.0
B	47.5	47.5	5.0
C	46.0	46.0	8.0
D	45.0	45.0	10.0
E	42.5	42.5	15.0
F	40.0	40.0	20.0
G	37.5	37.5	25.0

Fig. 3. Effect of glycerol content on the tensile strength of HPS/gelatin/glyoerol (at 3% water content) blends prepared by the low temperature process.

shown to have a more substantial effect than glycerol on the composite polymer matrix. In previous publications the plasticization of wheat starch, starch components and starch-based blends (cellulose/starch, caseinate/starch) with water and various polyols/sugars (glycerol, sorbitol, glucose, sucrose and xylose) was reported (Ollett *et al.*, 1991; Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996).

In general, a common observation in the composite polymer systems investigated was that the decrease in its modulus, within the glass–rubber transition area, became less abrupt and dramatic than that exhibited by HPS in the presence of a second component (caseinate, cellulosic, gelatin). The latter do not show such a dramatic fall because they are less hydrophilic than starch. Furthermore, gelatin has a higher T_g, of at least 7°C, than starch thus favouring the abrupt fall in the modulus of the latter.

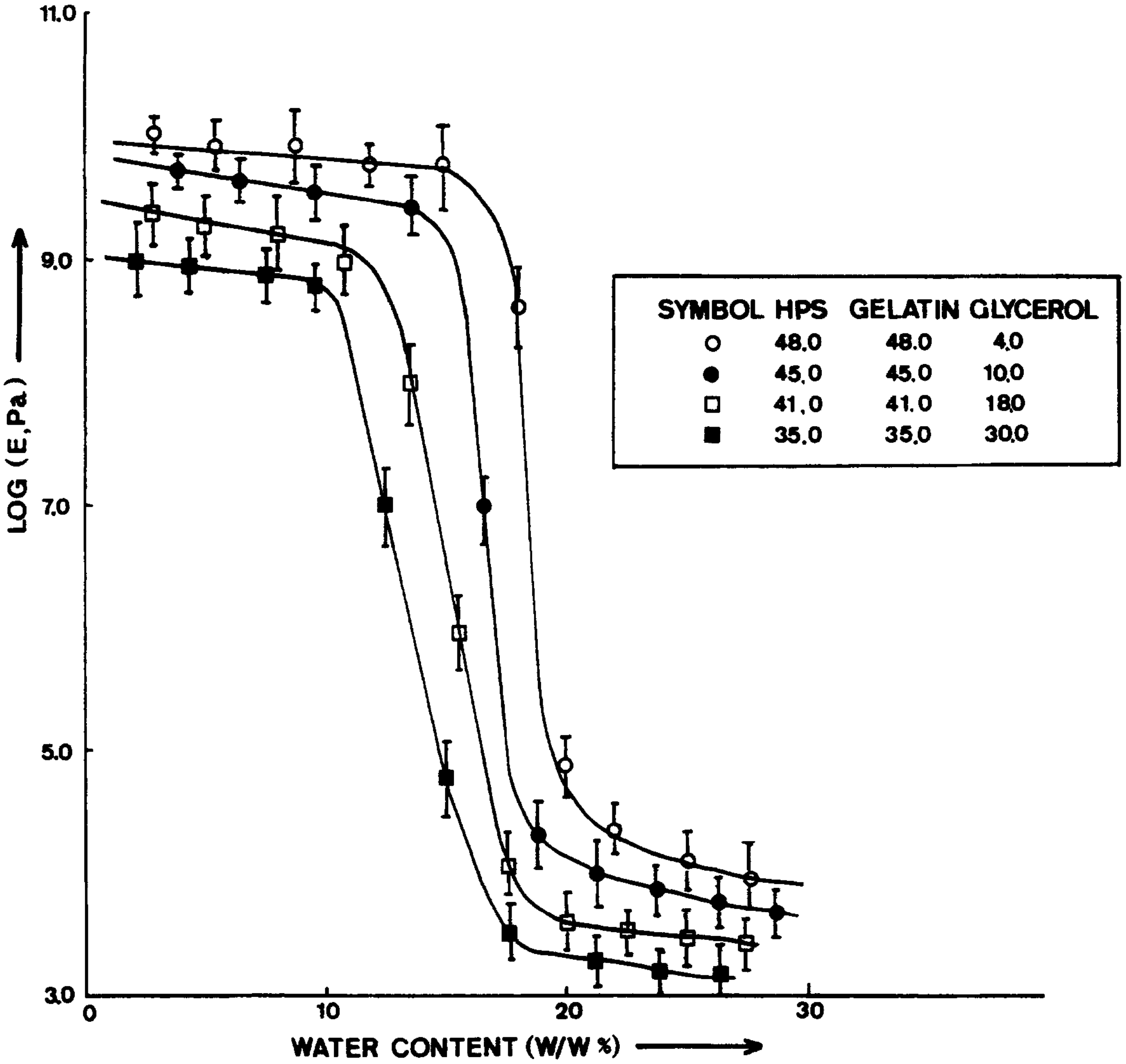


Fig. 4. Effect of water content on log flexural modulus, determined from the three-point bending test, of HPS/gelatin/glycerol blends prepared by the low temperature process. The results give the average and the standard deviation of at least six measurements.

3.3. Water vapour transmission rate (WVTR)

The high WVTRs of most edible films, apart from a limited number of exceptions such as waxes or modified natural polymers, impose many limitations upon their potential applications (Torres, 1994). WVTR determination is a crucial issue since the ability of water to plasticize polymeric surfaces and to cluster within the polymer matrix makes its determination more difficult (Schult & Paul, 1996). Similar complications in relation to the WVTR determination were reported previously for starch components (gluten, amylose) and for starch-based blends (starch–cellulosics, starch–caseinates) (Gennadios *et al.*, 1993a, 1993b, 1993c, 1993d, 1993e; Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996).

An increase in the total plasticizer content (water and polyol) in the polymer matrix was found to result in a proportional increase of the WVTR (Table 3). Although the mechanical properties do not show any considerable differences regarding the plasticizing effect of the two plasticizers on the HPS/gelatin blend, the WVTR measurements revealed that both sucrose and sorbitol had a stronger plasticizing action than glycerol, similar to the findings for soluble starch/gelatin blends (Arvanitoyannis *et al.*, 1997).

3.4. Gas permeability (GP)

Proteins are considered, in general, more effective gas barriers than polysaccharides. Therefore, the current combination aims at producing a blend with satisfactory gas permeability properties. A previous attempt to correlate the gas permeation to additive group contribution, following Salame's equation (Salame, 1986), initially suggested for the amorphous synthetic polymers, did not result in estimates approximating the experimental values for starch-based blends such as sodium caseinate/starch, cellulosics/starch and gelatin/starch (Arvanitoyannis *et al.*, 1996, 1997; Psomiadou *et al.*, 1996). Among the various reasons that

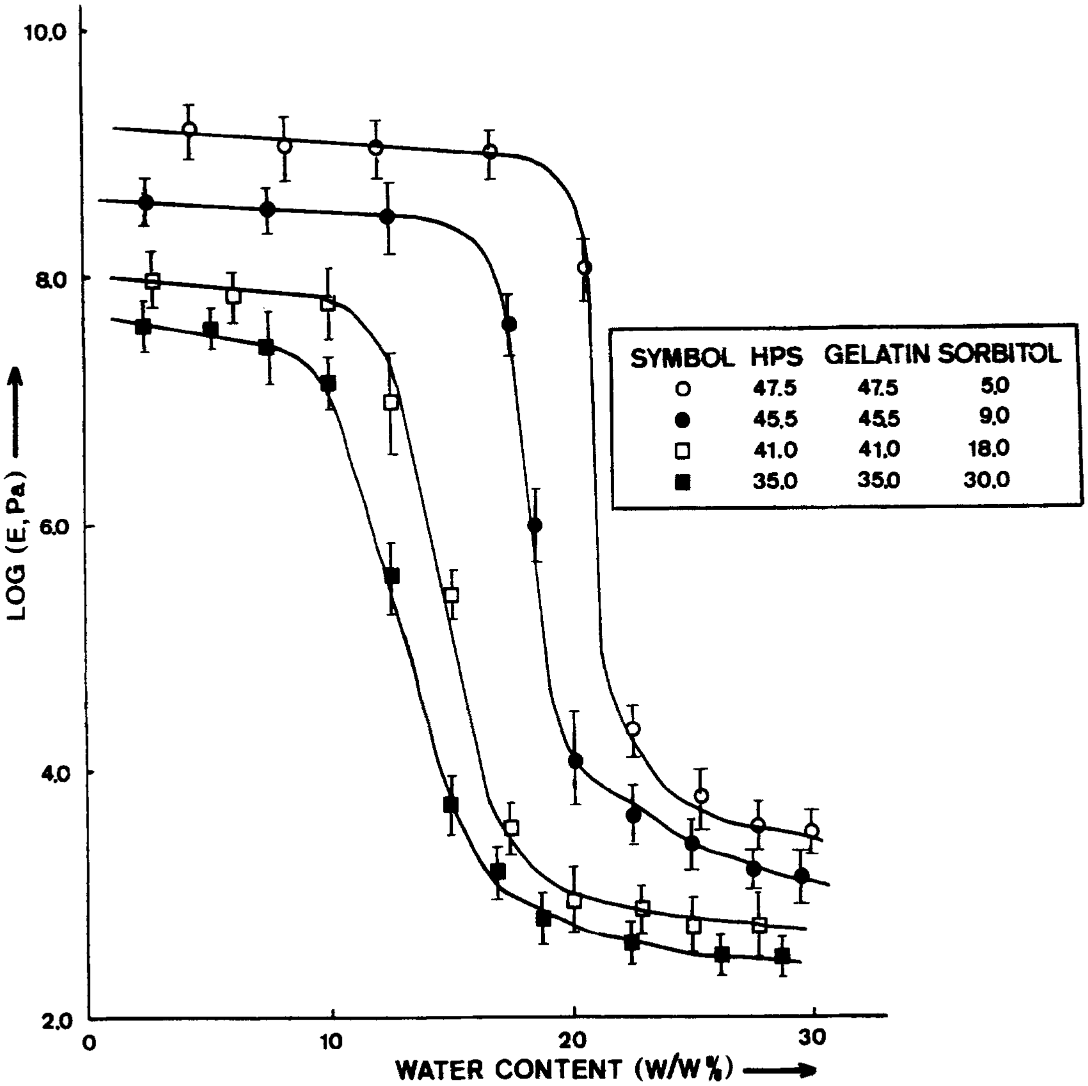


Fig. 5. Effect of water content on log flexural modulus, determined from the three-point bending test, of HPS/gelatin/sorbitol blend prepared by the low temperature process. The results give the average and the standard deviation of at least six measurements.

were suggested for explaining these discrepancies were the irregular formation of crystallites and voids, accessibility of polar groups and network geometry, and the relative strength of water–water, polyol–water and polyol–polyol versus the polymer–water and polymer–polyol bonds.

The water content has a marked effect upon the HPS/gelatin blends because it promotes the formation of even more hydrogen-bonded areas thus increasing the gas diffusivity and permeability. An increase in plasticizer content enhances the mobility of the polymer matrix thereby facilitating the gas diffusion and permeation (Table 4). Plots of gas permeability versus the inverse temperature are an indirect way (inflection of the line) of T_g determination (Fig. 6). This change in the slope could be explained as follows; the initially localized water over selected sites becomes more homogeneously widespread and of high mobility after swelling of the polymeric matrix at high water contents. Furthermore, the starch and the gelatin chains move apart because the number of intra- and interchain hydrogen bonds decreases proportionately to the water content increase (Trommsdorff & Tomka, 1995). Therefore, plasticization of the polymer composite matrix leads to widening of the latter, thus facilitating gas permeation, in agreement with previous findings for gelatin and starch-based blends (Arvanitoyannis *et al.*, 1997; Lieberman & Guilbert, 1973).

Many attempts have already been made to explain the temperature dependence of the diffusion coefficient and to establish a relationship between the penetrant size and the activation energy of diffusion. The theories are generally classified as free volume or molecular theories. The former are based on the 'fluctuation theory' (Pace & Datyner, 1979a, 1979b, 1979c) and are thermodynamic in nature since they do not take into account the detailed molecular structure of the polymer–penetrant system. In fact, they do predict a strong temperature dependence of E_D in the region above T_g. Molecular theories model the diffusion process in terms of specific postulated motions of the polymer chains

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

					O_2	N_2	CO_2
Low temperature process	HPS	Gelatin	Glycerol	Water			
	47.5	47.5	0	5	$1.3(\pm 0.2)\times 10^{-16}$	$1.2(\pm 0.1)\times 10^{-17}$	$0.6(\pm 0.1)\times 10^{-15}$
	45.0	45.0	5	5	$5.9(\pm 0.4)\times 10^{-16}$	$8.8(\pm 0.6)\times 10^{-17}$	$2.5(\pm 0.2)\times 10^{-15}$
	40.0	40.0	15	5	$2.0(\pm 0.2)\times 10^{-14}$	$7.4(\pm 0.3)\times 10^{-15}$	$1.1(\pm 0.2)\times 10^{-13}$
	35.0	35.0	25	5	$1.5(\pm 0.1)\times 10^{-12}$	$6.8(\pm 0.4)\times 10^{-13}$	$0.7(\pm 0.1)\times 10^{-11}$
	HPS	Gelatin	Sorbitol	Water			
	46.0	46.0	3	5	$4.5(\pm 0.5)\times 10^{-16}$	$8.7(\pm 0.7)\times 10^{-17}$	$2.0(\pm 0.1)\times 10^{-15}$
	41.0	41.0	13	5	$3.8(\pm 0.6)\times 10^{-14}$	$6.0(\pm 0.4)\times 10^{-15}$	$1.5(\pm 0.2)\times 10^{-13}$
	35.5	35.5	24	5	$4.0(\pm 0.5)\times 10^{-12}$	$5.8(\pm 0.4)\times 10^{-13}$	$2.2(\pm 0.3)\times 10^{-11}$
	HPS	Gelatin	Sucrose	Water			
	45.5	45.5	4	5	$3.6(\pm 0.4)\times 10^{-16}$	$8.0(\pm 0.6)\times 10^{-17}$	$1.7(\pm 0.2)\times 10^{-15}$
	40.0	40.0	15	5	$6.5(\pm 0.6)\times 10^{-14}$	$9.4(\pm 0.8)\times 10^{-15}$	$1.0(\pm 0.1)\times 10^{-13}$
	35.0	35.0	25	5	$1.4(\pm 0.1)\times 10^{-12}$	$6.7(\pm 0.5)\times 10^{-13}$	$0.5(\pm 0.1)\times 10^{-11}$
High temperature process	HPS	Gelatin	Glycerol	Water			
	47.5	47.5	0	5	$6.2(\pm 0.5)\times 10^{-15}$	$9.1(\pm 0.8)\times 10^{-16}$	$0.9(\pm 0.2)\times 10^{-14}$
	45.0	45.0	5	5	$9.5(\pm 0.7)\times 10^{-15}$	$1.7(\pm 0.2)\times 10^{-15}$	$4.6(\pm 0.3)\times 10^{-14}$
	40.0	40.0	15	5	$8.3(\pm 0.6)\times 10^{-14}$	$1.0(\pm 0.1)\times 10^{-14}$	$3.3(\pm 0.4)\times 10^{-13}$
	35.0	35.0	25	5	$7.0(\pm 0.4)\times 10^{-12}$	$1.4(\pm 0.2)\times 10^{-12}$	$2.9(\pm 0.3)\times 10^{-11}$
	HPS	Gelatin	Sorbitol	Water			
	46.0	46.0	3	5	$9.8(\pm 0.8)\times 10^{-16}$	$2.4(\pm 0.3)\times 10^{-16}$	$5.5(\pm 0.6)\times 10^{-15}$
	41.0	41.0	13	5	$8.5(\pm 0.6)\times 10^{-14}$	$1.1(\pm 0.2)\times 10^{-14}$	$4.0(\pm 0.3)\times 10^{-13}$
	35.5	35.5	24	5	$7.6(\pm 0.5)\times 10^{-12}$	$9.5(\pm 0.7)\times 10^{-13}$	$2.8(\pm 0.2)\times 10^{-11}$
	HPS	Gelatin	Sucrose	Water			
	45.5	45.5	4	5	$8.0(\pm 0.5)\times 10^{-16}$	$1.9(\pm 0.2)\times 10^{-16}$	$3.9(\pm 0.4)\times 10^{-15}$
	40.0	40.0	15	5	$1.4(\pm 0.1)\times 10^{-13}$	$8.0(\pm 0.7)\times 10^{-14}$	$0.8(\pm 0.1)\times 10^{-12}$
	35.0	35.0	25	5	$7.2(\pm 0.6)\times 10^{-12}$	$1.0(\pm 0.1)\times 10^{-12}$	$2.9(\pm 0.3)\times 10^{-11}$

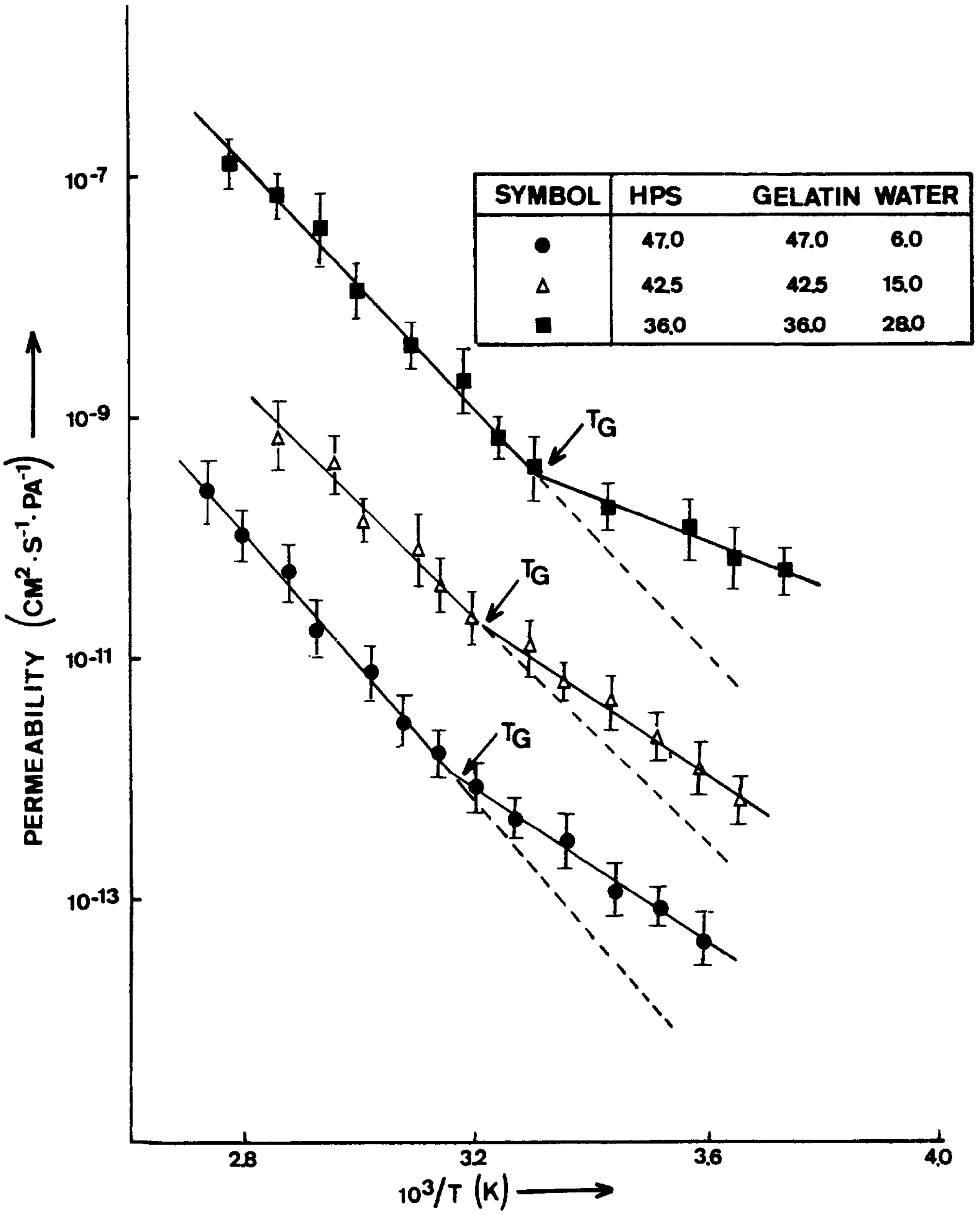


Fig. 6. Permeability of CO_2 in HPS/gelatin/water blends, prepared by the low temperature process, derived from Eq. (11) versus the inverse temperature (1/*T*). The results give the average and the standard deviation of at least six measurements.

(Pace & Datyner, 1979a). Determination of activation energies of diffusion (E_D) has previously shown that E_D remains practically constant above and below T_g while it undergoes a fast abrupt change in the T_g region (Amerongen, 1947, 1949; Arvanitoyannis & Blanshard, 1993; Arvanitoyannis *et al.*, 1994, 1996, 1997; Arvanitoyannis & Biliaderis, 1997a, 1997b). The Arrhenius equation satisfactorily describes the dependence of diffusivity on temperature:

$$D = D_0 \exp(-E_D/RT) \qquad (9)$$

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 Eq. (9) describing diffusivity is:

$$\ln D = \ln D_0 - E_D/RT \qquad (10)$$

Similarly to Eq. (9), the temperature dependence of permeability can be expressed as

$$P = P_0 \exp(-E_P/RT) \qquad (11)$$

where E_P is the apparent activation energy of permeation, and

$$\ln P = \ln P_0 - E_P/RT \qquad (12)$$

The activation energies of diffusion and permeation for HPS/gelatin blends were calculated according to Eqs. (10) and (12).

It has been previously suggested that, depending on the direction the penetrant moves within the polymer network, there are two distinct extreme models. According to the proposed polymer microstructure, the chain could be visualized as 'tubes' and the penetrant can either move parallel (process a) or perpendicular (process b) to them. Since process (a) does not require any E_D, the recorded E_D is an expression of process (b) and, in particular, it reflects the necessary energy for producing the required chain separation so that the penetrant can be accommodated. The two processes (a) and (b) occur effectively in series, so that whenever in process (a) the gas molecule encounters a crystallite or any entanglement is halted and obliged to circumvent it, process (b) is activated.

4. Conclusions

Edible films based on HPS/gelatin plasticized with water and/or polyols were prepared by the low and the high temperature methods. The low temperature method resulted in films with more densely packed polymer chains, increased molecular ordering, higher percentage crystallinity (determined from DTA and WAXD) and higher tensile strength and limited gas and water transmission rates. The presence of a plasticizer in the HPS/gelatin blends led to greater mobility of the polymer matrix as shown by their lower T_m, T_g and tensile strength but higher elongation and gas/water permeation values.

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