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Physical properties of polyol-plasticized edible blends made of methyl cellulose and soluble starch

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Abstract

Aqueous blends of methyl cellulose and soluble starch, plasticized with glycerol or sugars, were prepared by casting, or by extrusion and hot pressing. The mechanical (tensile and flexural mode), thermal (differential scanning calorimetry) and gas and water permeation properties of these blends were investigated, after their conditioning at various relative humidities. The observed T_g depression for these polymer blends was proportional to the plasticizer content (water, glycerol and sugars). Although glycerol had a greater depressing effect on T_g than sorbitol, the latter had a greater impact than glycerol and xylose, as a plasticizer, on the mechanical properties (higher percentage elongation) of the soluble starch–methyl cellulose blends. The tensile strength and flexural moduli of these blends were shown to decrease drastically with an increase in the total plasticizer content. An indirect measurement of glass transitions, comparable to the ones determined with DSC, was obtained from the Arrhenius-type plots of the gas permeability–temperature relationships.

Keywords: Soluble starch; Methyl cellulose; Edible films; Biodegradable; Food packaging; Gas permeability; Plasticizers

1. Introduction

The increased consumer demand for high quality, long shelf-life ready to eat foods has initiated the development of mildly preserved products that keep their natural and fresh appearance as long as possible (Baldwin et al., 1995; Guilbert et al., 1996). Edible and biodegradable polymer films offer alternative packaging options, advantageous to the synthetic 'recalcitrant' packaging polymers because the former do not contribute to the environmental pollution (Arvanitoyannis et al., 1996; Krochta and De Mulder-Johnston, 1997). Although edible films are not meant to entirely replace synthetic packaging films, they do have the potential to substantially reduce the environmental burden due to food packaging, and to limit moisture, aroma and lipid migration between food components (Krochta et al., 1994; Krochta and De Mulder-Johnston, 1997). The potential of polysaccharides and proteins, as edible films, has long been recognized (Guilbert and Biquet, 1989; Gennadios and Weller, 1990; El Ghaouth et al., 1991, El Ghaouth et al., 1992; Wong et al., 1992; Gennadios et al., 1993a, Gennadios et al., 1993b, Gennadios et al., 1993c, Gennadios et al., 1993d, Gennadios et al., 1993e; Guilbert and Gontard, 1995; Lourdin et al., 1995; Guilbert et al., 1996), but apart from some very special applications (Kinsella, 1984; Krochta et al., 1994), polysaccharide- and/or protein-based edible films have not found extensive applications in the food industry yet (Kester and Fennema, 1986).

Unless genetically (high amylose content) or chemically (methylated, crosslinked) modified, starch can not form films with adequate mechanical properties (high percentage elongation, tensile and flexural strength). Paper and textile industries are two fields in which starch has found various applications in the formulation of adhesives and sizings (Wolff et al., 1951; Lloyd and Kirst, 1963; Young, 1984). The enhanced solubility of soluble starch (Arvanitoyannis et al., 1997) compared with the previously used gelatinized starches (Arvanitoyannis et al., 1996; Psomiadou et al., 1996) was the main reason for its usage in these blends.

Cellulose is the principal structural component of plants and the most abundant source of complex carbohydrate in the world (Engelhardt, 1995). Cellulose can be 'tailored' with appropriate chemical modification to produce cellulose ether–ester films (Psomiadou et al., 1996). The latter, being

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flexible and transparent, have moderate strength, resistance to oil and fat migration and act as moderate barriers to moisture and oxygen (Kester and Fennema, 1986, Kester and Fennema, 1989a, Kester and Fennema, 1989b; Hagenmaier and Shaw, 1990; Hanlon, 1992). Methyl cellulose (MC) was preferred to the previously used (Psomiadou et al., 1996) microcrystalline cellulose, MCC, because the latter does not mix well with starch, since it remains in the form of microparticulates. Instead, MC gives a far more homogeneous dispersion with starch and has lower hydrophilicity, and is thus a promising component for improving the poor moisture barrier performance of starch.

Although amylose and methyl cellulose (MC) were used alone in the past for coating applications (Bauer et al., 1969; Murray et al., 1971), soluble starch and MC have not been used together. In the fifth paper of this series (Arvanitoyannis et al., 1996, Arvanitoyannis et al., 1997; Psomiadou et al., 1996; Arvanitoyannis and Biliaderis, 1997), edible films were produced from soluble starch–MC blends and their physical–chemical properties were investigated and compared with films produced from other blends of similar composition.

2. Materials and methods

2.1. Materials

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

2.2. Preparation of samples

Soluble starch (starch–water 30% w/w) was rendered amorphous by gelatinizing and roller drying (one process) at 140°C; roller drier speed,10 rev min^{-1}; pressure, 32 psi (221 kPa); gap, 1 mm; diameter, 165 mm; and width; 150 mm.

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

2.3. Differential thermal analysis (DTA) measurements

DTA measurements were taken using a Shimadzu DTA equipped with a liquid N_2 cooling accessory and connected to an IBM/PC and a Hewlett Packard plotter. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The sample size for DTA was approximately 10 mg. Temperature calibration was made with cyclohexane, dodecane and octane. Heat flow calibration was made by reference to the known melting enthalpy of indium metal (purity 99.9%) from Goodfellows Metals. The purge gases used were dry helium and dry nitrogen. The apparent T_gs 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 and Taylor, 1952) was performed using the TableCurve™ software (Jandel Scientific), a non-linear least-squares-fitting package.

2.4. 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 on the film. Permeability (P) is the product of solubility (S) and diffusivity (D) and it is described by the following equation:

$$P = DS \tag{1}$$

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

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

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:

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

where d is the thickness of the film and θ is the time lag of the permeation. The time 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, Amerongen, 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:

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

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; Arvanitoyannis et al., 1992).

2.5. Water vapour transmission rate (WVTR)

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

2.6.2. Three point bending test

All samples (prepared by hot pressing at 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 at least for 3 weeks over saturated salt solutions at room temperature to obtain water contents which were measured on three replicates by drying at 105°C to constant weight.

3. Results and discussion

3.1. Thermal properties

In this study the plasticizer content was kept at low levels in order to minimize the chance of phase separation which would substantially complicate the study of these composite systems. This phenomenon, manifested by dual transitions in DSC and DMTA traces, has been previously reported for fructose–amylopectin and fructose–caseinate by Kalichevsky and Blanshard (1993) and Kalichevsky et al. (1993), respectively. However, this behavior was only noticed when the polyol content exceeded 20%; the tanδ profiles revealed one more relaxation at a lower temperature besides the α-relaxation of the polymer itself. At a constant moisture content this relaxation, attributed to the sugar, increased in magnitude with increasing fructose content. Colonna et al. (1997) have also shown dual transitions for potato starch films plasticized by 25%–30% glycerol based on thermomechanical measurements (DMTA); however, these authors attributed the low temperature transition (approx. − 40°C) to a combination of the plasticizer α-relaxation and starch β-relaxation. Such transitions are not discernible by DSC. In the present study, a single glass transition (Fig. 1) was observed by DSC for all polyol–water-plasticized soluble starch–methyl cellulose blends, reflecting the α-relaxation of the polymeric constituents. The presence of one glass transition (polymer) for the majority of binary, ternary or quartenary polymer blends examined may be attributed to a close proximity of the T_gs of the individual polymeric components (i.e. methyl cellulose and soluble starch), as well as to a similar plasticization behaviour in the presence of plasticizers as previously reported (Arvanitoyannis and Biliaderis, 1997). Indeed, for a series of polysaccharides (starch, pullulan, dextran, phytoglycogen, fructosylated amylose and amylopectin), widely differing in their molecular structure, branching, and conformation of glycosidic linkages, Bizot et al. (1997) have shown that the glass transition temperature of these polymers varies only by 5°C–20°C over a moisture content range of 5%–25% w/w. Moreover, these polymers exhibited parallel trends in the T_g-moisture

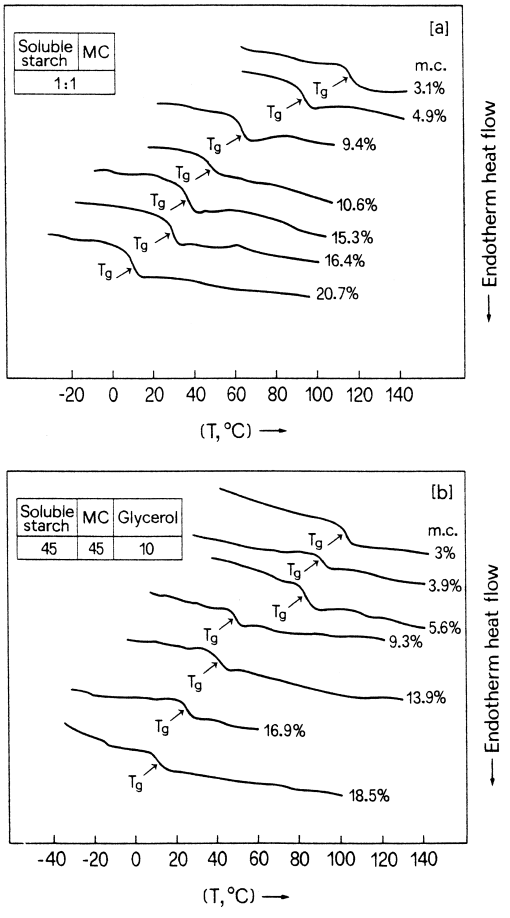

Fig. 1. Representative DSC traces (2nd run) of soluble starch–MC blends at different water contents showing the changes in C_p at T_g: (a) soluble starch–MC (50/50, w/w); and (b) soluble starch–MC–glycerol (45/45/10, w/w/w).

content plots, indicative of similar plasticization responses. It is unlikely, therefore, to distinguish by DSC individual α-relaxations of composite polysaccharide matrices because of their close proximity; according to Olabisi et al. (1979), it not possible to distinguish a phase separated system from a miscible one by DSC if the component T_gs are less than 20°C apart. Similarly, Kalichevsky and Blanshard (1992) reported only one glass transition for amylopectin–casein blends, whereas for gluten–amylopectin and gluten–casein mixtures two separate glass transitions of the two polymers were seen in the DSC traces; for the latter, substantial differences in chemical structure and hydrophobicity between gluten and amylopectin (or casein) may account for the observed difference in the T_gs (~20°C–50°C) of these materials, making them detectable by DSC in either pure form or in mixtures.

Modeling of T_g data for the various soluble starch–MC blends plasticized by water, glycerol or sugar (sorbitol and xylose), was carried out using an empirical equation, initially proposed for T_g modeling of synthetic polymer–plasticizer blends by Gordon and Taylor (1952):

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (5)$$

where w_1 and w_2 are the respective weight fractions of the polymer blend and water, T_{g1} is the T_g of the composite polymer matrix, T_{g2} is the T_g of the amorphous water, and k is a constant. It should be noted, however, that application of this equation as well as that of Couchman and Karasz (1978), assumes conditions of isotropic (molecularly mixed) systems, which certainly are not met in the case of the blends examined in the present study. Another weakness in using these approaches to model aqueous bipolymer systems is that with the existing methodology (cooling rates for sample preparation, and DSC and DMTA as probes of molecular relaxation processes) it is not possible to obtain data for water fractions between 0.40 and 1.0, thus making uncertain the interpolation of the results in this moisture content range. Nevertheless, the Gordon–Taylor (G-T) equation is a convenient empirical treatment to model the moisture content-dependence of T_g for composite matrices, allowing comparisons among samples. Attempts to model the T_g of water- and polyol-plasticized biopolymer mixtures by the Couchman–Karasz (C-K) thermodynamic approach (Kalichevsky et al., 1992, Kalichevsky et al., 1993; Kalichevsky and Blanshard, 1993) are also debatable, considering the component immiscibility and that obtaining calorimetric estimates of ΔC_p for the dry polymers is not experimentally feasible. Even for glassy water, there are two ΔC_p values reported in the literature; i.e. 1.93 J g^{-1} K^{-1} (Sugisaki et al., 1968) and 1.84 J g^{-1} K^{-1} (Hatley and Mant, 1993). To construct the state diagrams by the G-T equation, a T_{g2} of -135°C was used for water (Johari et al., 1987). The recorded T_g depressions of soluble starch–MC blends were proportional to the water content in the blend (Figs. 2 and 3). The constant k in Eq. (5) is equivalent to the ratio ΔC_{p2} ΔC_{p1}, where ΔC_{p1} and ΔC_{p2} represent the change in heat capacity for the pure polymer matrix and water, respectively, of the C-K equation. The ΔC_p values of polysaccharides, estimated by extrapolation, vary within a range from 0.3–0.5 J g^{-1} K^{-1} (Bizot et al., 1997). Therefore, a ratio 1.84/0.4 ≈ 4.5 may be considered as a reasonable value for k. It appears from Figs. 2–4 that the calculated R^2 values (~0.96–0.98) are rather close to the optimum value. In fact, a better fitting (reflected by higher R^2, ~0.99) can be obtained if no restriction is imposed upon the program regarding the k selection and the ensuing optimization of the T_g curve modeling. When such a protocol

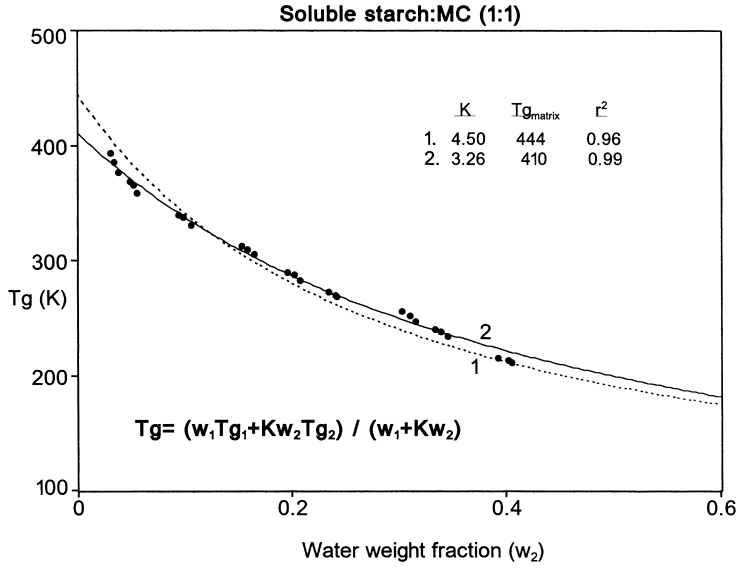

Fig. 2. Plots of T_g vs water content of soluble starch–MC (1:1) blend: (•, experimental data; lines give the corresponding Gordon–Taylor plots of the data for two k values).

was adopted, k varied within 3.24 and 4.85. In addition, the corresponding T_g values of the dry matrices, estimated by extrapolation, are in the range of ~394 to 410 K.

3.2. Gas permeability (GP)

The effect of altered barrier properties on the ability of an edible coating to control the gaseous environment of a food produce has been only partially investigated (Baldwin et al., 1995). Since only rather recently applications referring to edible coatings were published (El Ghaouth et al., 1991, El Ghaouth et al., 1992; Wong et al., 1992), the possibility of creating anaerobic conditions through the use of semipermeable edible coatings resulting in growth of *Clostridium botulinum* has not been thoroughly investigated yet (Baldwin et al., 1995). Gas permeation modeling based on the group contribution theory, as suggested by Salame (1986) for synthetic polymers has led to substantial discrepancies between predicted and experimental values. These were attributed to a variety of interactions of varying relative strength (i.e. water–polyol, polymer–water, polymer–polymer, accessibility or not of -OH groups). The GP measurements of the plasticized soluble starch–MC blends show proportional increases in GP to the plasticizer content as a result of weakening of the intermolecular forces between adjacent polymeric chains which facilitates chain mobility and redistribution of the originally existing voids. These results are in satisfactory agreement with GP measurements reported elsewhere on synthetic (Myers et al., 1960; Arvanitoyannis and Blanshard, 1993) and natural polymers (Arvanitoyannis et al., 1994, Arvanitoyannis et al., 1996; Psomiadou et al., 1996). The effect of various water contents on the gas permeability (O_2, N_2, CO_2) of soluble starch–MC films is shown in Figs. 4 and 5 and Table 1, Table 2.

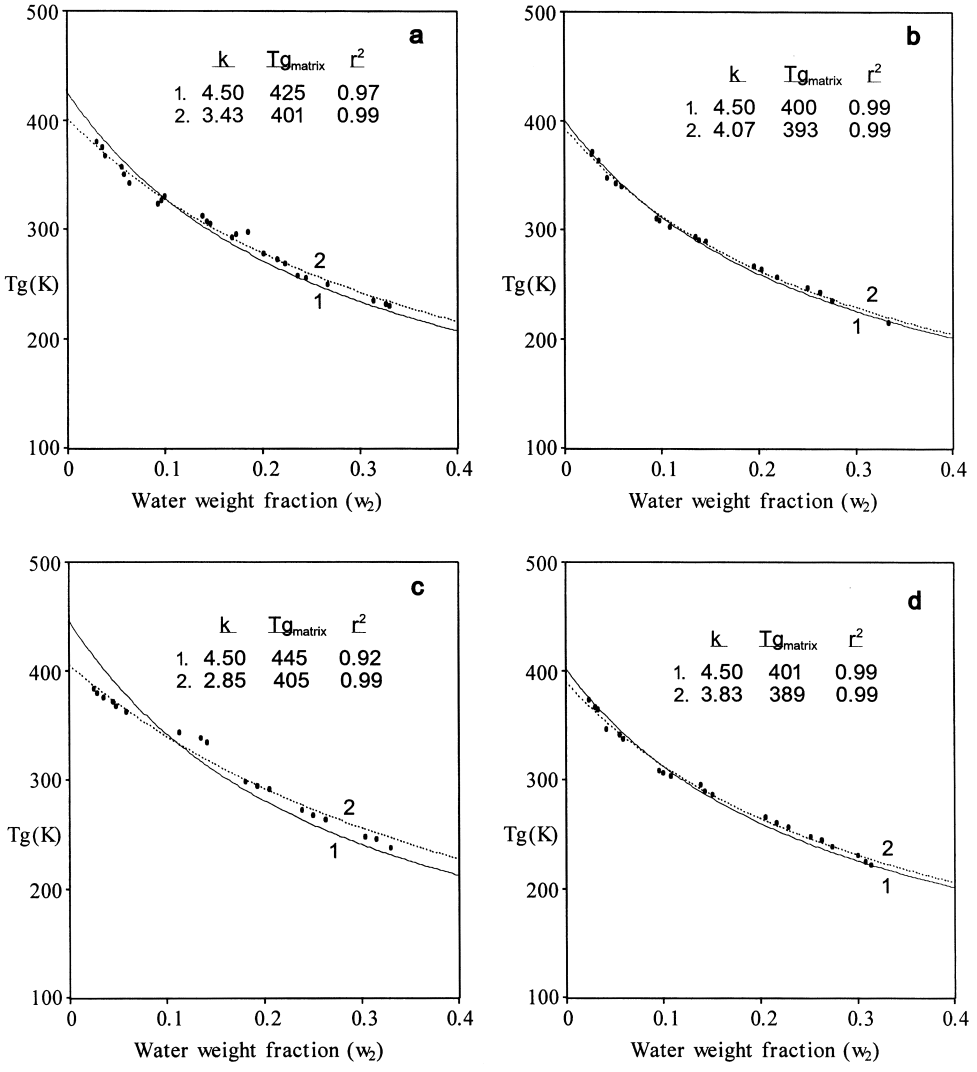

Fig. 3. Plots of T_g vs water content of soluble starch–MC–polyol blends: (●, experimental data; lines give the corresponding Gordon–Taylor plots of the data for two k values), (a) soluble starch–MC–glycerol (45/45/10, w/w/w); (b) soluble starch–MC–glycerol (40/40/20, w/w/w); (c) soluble starch–MC–sorbitol (45/45/10, w/w/w); and (d) soluble starch–MC–sorbitol (40/40/20, w/w/w).

Figs. 4 and 5 also show how an indirect determination of the glass transition temperature can be obtained from the inflection points of the GP-inverse temperature plots. Arrhenius plots are commonly employed to describe the temperature dependence of gas permeability coefficients for polymers (Doyon et al., 1991; Eichler and Miltz, 1993). Although it can be argued that gas permeabilities in the rubbery domain are best described by the Williams–Landel–Ferry (WLF) equation, it has been often observed that Arrhenius plots of gas permeability show a change in slope or an abrupt change as a result of increases in segmental mobility of the polymer chains at the glass transition zone (Brandt, 1959; Myers et al., 1960; Michaels et al., 1963; Hopfenberg and Stannett, 1973). This reflects differences in the activation energies in the rubbery vs the glassy state. The values obtained thereby were in reasonable agreement with those determined from DTA measurements, similar to those previously reported findings for natural polymer blends (Amerongen, 1947; Arvanitoyannis et al., 1996, Arvanitoyannis et al., 1997; Psomiadou et al., 1996). According to Di Benedetto (1963) quoted by Pace and Datyner (1979a), the microstructure of crystalline and semicrystalline polymers can be described in terms of local parallel chain bundles. The spherical gas molecule, embedded in a locally parallel chain bundle, may move either (a) along the axis of a 'tube' formed by adjacent parallel chains or (b) perpendicular to it. The (a) process is roughly considered as requiring no activation energy since the penetrant can make, in theory, 'jumps' of any length. It should be noted, however, that this is not entirely true since the process (a) stops, at least momentarily, whenever the penetrant encounters crystallites or chain entanglements at both ends of the 'tube'. Then, it is process (b), considered as the rate limiting process, that resumes. According to the latter, the required activation energy equals that necessary to produce minimum chain separation so that the penetrant can be accommodated (Pace and Datyner, 1979a, Pace and Datyner, 1979b, Pace and Datyner, 1979c). Since the average tube length was suggested to determine the average jump length in diffusion, the jump frequency is calculated by the

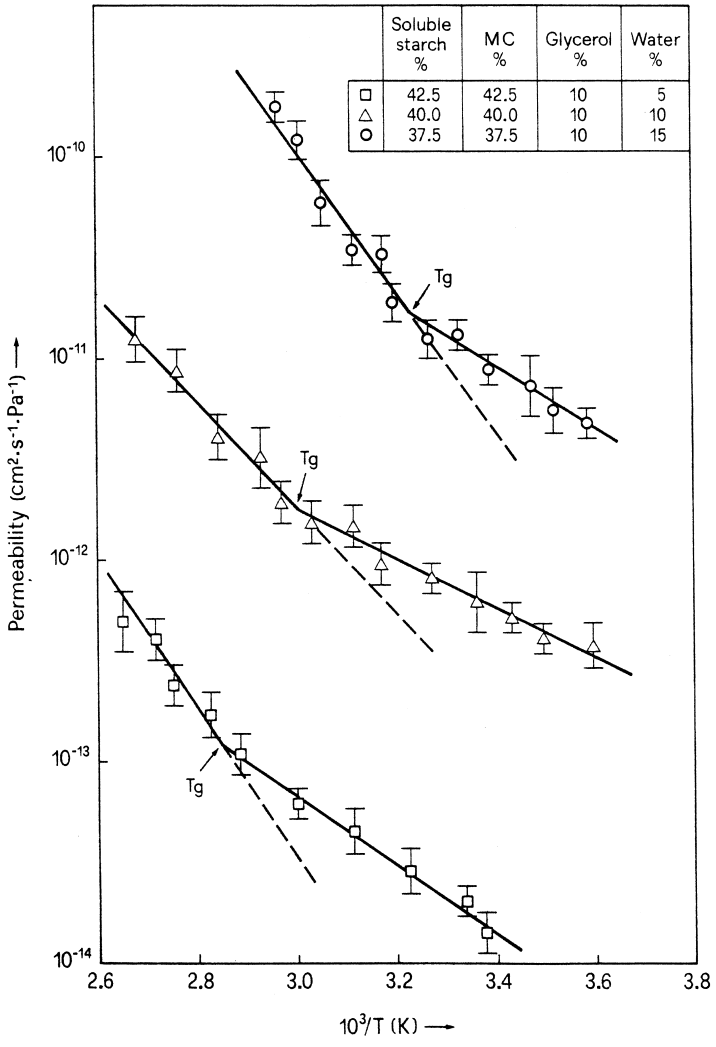

Fig. 4. Permeability of CO_2 in soluble starch–MC–glycerol blends plasticized with different amounts of water vs the inverse temperature [$(10^3/T)$, K]. The results give the average and the standard deviation of at least five measurements.

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

Soluble starch%	MC%	Glycerol%	Water%	O_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	N_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	CO_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	WVP ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$) $\times 10^{-11}$	T_g (°C)
47.5	47.5	0	5	$5.0(\pm 0.6)\times10^{-15}$	$4.7(\pm 0.5)\times10^{-16}$	$4.3(\pm 0.6)\times10^{-14}$	0.48 ± 0.03	93.5 ± 3.1
45.0	45.0	5	5	$9.8(\pm 1.5)\times10^{-15}$	$6.0(\pm 0.7)\times10^{-16}$	$8.5(\pm 0.7)\times10^{-14}$	3.2 ± 0.04	78.3 ± 2.7
40.0	40.0	15	5	$6.5(\pm 0.6)\times10^{-14}$	$5.3(\pm 0.4)\times10^{-15}$	$3.6(\pm 0.9)\times10^{-13}$	6.5 ± 0.05	37.4 ± 1.6
32.5	32.5	30	5	$4.7(\pm 0.3)\times10^{-11}$	$2.0(\pm 0.3)\times10^{-12}$	$4.2(\pm 0.3)\times10^{-10}$	20.7 ± 1.6	—
Soluble starch %	MC%	Sorbitol %	Water %					
45.0	45.0	5	5	$3.4(\pm 0.2)\times10^{-14}$	$6.9(\pm 0.8)\times10^{-15}$	$7.6(\pm 0.2)\times10^{-13}$	4.5 ± 0.5	67.8 ± 4.1
40.0	40.0	15	5	$8.8(\pm 1.8)\times10^{-14}$	$3.6(\pm 0.5)\times10^{-14}$	$5.4(\pm 0.4)\times10^{-12}$	7.9 ± 0.8	31.4 ± 3.0
32.5	32.5	30	5	$5.7(\pm 0.9)\times10^{-11}$	$4.3(\pm 0.6)\times10^{-12}$	$9.0(\pm 0.6)\times10^{-10}$	26.5 ± 2.9	—
Soluble starch %	MC%	xylose %	Water %					
45.0	45.0	5	5	$1.5(\pm 0.2)\times10^{-14}$	$5.7(\pm 0.6)\times10^{-15}$	$2.1(\pm 1.5)\times10^{-14}$	4.9 ± 0.03	72.0 ± 2.3
40.0	40.0	15	5	$9.9(\pm 0.5)\times10^{-14}$	$9.1(\pm 0.8)\times10^{-15}$	$8.5(\pm 0.3)\times10^{-13}$	8.6 ± 0.5	35.4 ± 1.9
32.5	32.5	30	5	$6.5(\pm 0.6)\times10^{-11}$	$4.9(\pm 0.6)\times10^{-12}$	$7.0(\pm 0.4)\times10^{-10}$	28.7 ± 1.7	—

frequency of those chain separations that allow penetrant passage between adjacent 'tubes'. The mean tube length is a function of the long range order–disorder and the presence and distribution within it of non-penetrable crystallites. This model was applied with reasonable success to well defined and determined vinyl and non-vinyl polymers (Pace and Datyner, 1979b, Pace and Datyner, 1979c). It may be suggested that a similar two-process (a) and (b) model is applicable in the starch-based natural polymer blends. In the case of our binary blends, plasticized by water or polyol, a considerable increase in mobility occurs as a result of higher polymer network flexibility. However, changes in polarity of the hydrated matrix as a result of water absorption may further complicate the solubility and diffusivity of gases and thereby affect the permeability values. Table 3 gives the activation energies required for permeation of gases through the composite polymer matrices. Tables 1 and 2 also show that at least a 3–4 orders of magnitude increase in gas diffusion rate occurs for the polyol-plasticized polymer blends compared with their respective free-plasticizer counterparts. This resembles the elsewhere reported observation that for synthetic polymers process (a) occurs at a rate of three orders of magnitude greater than the experimentally determined rate when both processes take place simultaneously (Pace and Datyner, 1979a). In other words, this means that whichever restrictions initially

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

Soluble starch%	MC%	Glycerol%	Water%	O_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	N_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	CO_2 ($cm^2\,s^{-1}\,Pa^{-1}$)	WVP ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$) $\times 10^{-11}$	T_g (°C)
45.0	45.0	0	10	$5.1(\pm 0.8)\times10^{-14}$	$3.9(\pm 0.8)\times10^{-15}$	$2.1(\pm 0.2)\times10^{-13}$	0.65 ± 0.05	84.9 ± 2.2
42.5	42.5	5	10	$8.0(\pm 0.9)\times10^{-14}$	$9.5(\pm 0.2)\times10^{-14}$	$8.4(\pm 0.7)\times10^{-13}$	7.2 ± 0.6	56.8 ± 2.6
37.5	37.5	15	10	$4.7(\pm 0.5)\times10^{-13}$	$2.5(\pm 0.8)\times10^{-13}$	$3.8(\pm 0.4)\times10^{-12}$	9.6 ± 0.9	22.9 ± 2.5
30.0	30.0	30	10	$3.0(\pm 0.7)\times10^{-10}$	$4.3(\pm 0.5)\times10^{-13}$	$3.2(\pm 0.2)\times10^{-9}$	25.9 ± 1.3	—
Soluble starch%	MC%	Sorbitol%	Water%					
42.5	42.5	5	10	$2.4(\pm 0.3)\times10^{-13}$	$8.6(\pm 0.9)\times10^{-14}$	$3.8(\pm 0.4)\times10^{-12}$	9.5 ± 0.8	43.9 ± 2.1
37.5	37.5	15	10	$8.7(\pm 0.8)\times10^{-13}$	$4.5(\pm 0.6)\times10^{-13}$	$2.5(\pm 0.2)\times10^{-11}$	14.9 ± 1.5	17.6 ± 1.9
30.0	30.0	30	10	$6.0(\pm 0.7)\times10^{-10}$	$6.3(\pm 0.5)\times10^{-11}$	$4.3(\pm 0.4)\times10^{-9}$	33.5 ± 2.9	—
Soluble starch%	MC%	Xylose%	Water%					
42.5	42.5	5	10	$3.8(\pm 0.5)\times10^{-13}$	$7.0(\pm 0.6)\times10^{-14}$	$8.5(\pm 0.7)\times10^{-13}$	8.3 ± 0.9	48.0 ± 2.8
37.5	37.5	15	10	$8.3(\pm 0.6)\times10^{-13}$	$4.9(\pm 0.5)\times10^{-13}$	$4.9(\pm 0.6)\times10^{-12}$	13.8 ± 1.5	21.3 ± 1.4
30.0	30.0	30	10	$7.5(\pm 0.3)\times10^{-10}$	$8.2(\pm 0.9)\times10^{-11}$	$4.0(\pm 0.3)\times10^{-10}$	29.6 ± 2.3	—

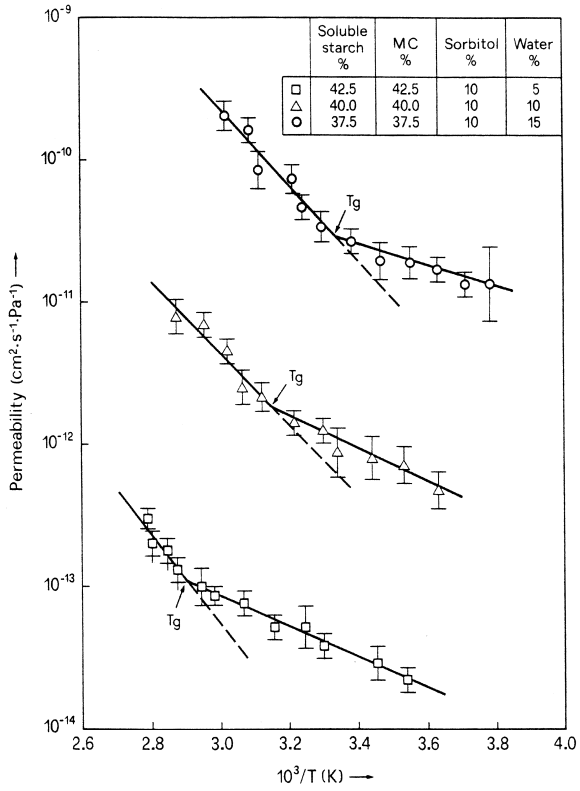

Fig. 5. Permeability of CO_2 in soluble starch–MC–sorbitol blends plasticized with different amounts of water vs the inverse temperature [(10^3/T), K]. The results give the average and the standard deviation of at least five measurements.

imposed upon the mobility of the penetrant through the rigid network of starch–MC blends, are levied in the presence of about 30% total plasticizer content. The Arrhenius relationship was used to follow the dependence of permeability on temperature

$$P = P_0 \exp(-E_P/RT) \quad (6)$$

where P is the permeability coefficient, E_P is the activation energy of permeation and R is the universal gas constant.

The corresponding logarithmic expression for Eq. (6) is:

$$\ln P = \ln P_0 - E_P/RT \quad (7)$$

The activation energies, summarized in Table 3, were derived by applying Eq. (7) both below and above the T_g regions (straight lines with different slopes).

3.3. Water vapour permeability (WVP)

WVP is usually determined by direct weighing because, despite its inherent problems, mainly related to water properties such as high solubility and cluster formation within the polymer and tendency to plasticize the polymer matrix (Schult and Paul, 1996), it is a simple and relatively reliable method. The major disadvantage of this method resides in its weakness to provide information for a kinetic profile, if such a response is required. In the latter case, the WVP is determined by using some state of the art methods such as dielectic properties or near infrared reflectance (NIR) (Bizet et al., 1995).

Natural polymers are characterized by extensive water clustering and plasticization of their matrix, properties regarded as important shortcomings in packaging

Table 3
Activation energies for permeation (E_p^a, 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)–MC blends. The results give the average and the standard deviation of five measurements

Soluble starch (%w/w)	Water (%w/w)	MC (%w/w)	N_2 ($T > T_g$)	N_2 ($T < T_g$)	O_2 ($T > T_g$)	O_2 ($T < T_g$)
85	15	0	46.2 ± 4.8	31.8 ± 2.9	45.2 ± 2.9	28.9 ± 3.9
75	15	10	50.1 ± 5.8	37.5 ± 3.9	57.8 ± 5.3	38.5 ± 3.1
65	15	20	61.6 ± 5.8	46.3 ± 5.8	68.3 ± 5.8	47.2 ± 4.8
55	15	30	66.4 ± 6.7	48.1 ± 4.8	78.9 ± 6.8	55.8 ± 5.9
47.5	5.0	47.5	88.6 ± 9.6	52.0 ± 5.8	86.6 ± 8.2	64.5 ± 5.0
42.5	15.0	42.5	60.6 ± 4.8	36.6 ± 4.8	60.6 ± 5.0	42.4 ± 3.8
Soluble starch–MC	Water	Glycerol				
37.5/37.5	5	20	38.5 ± 2.9	21.7 ± 1.9	44.3 ± 3.1	27.9 ± 2.0
Soluble starch–MC	Water	Sorbitol				
37.5/37.5	5	20	27.0 ± 2.9	18.2 ± 1.5	37.5 ± 3.9	23.1 ± 1.9
Soluble starch–MC	Water	Xylose				
37.5/37.5	5	20	34.7 ± 4.8	21.2 ± 1.9	47.2 ± 3.4	25.0 ± 1.8

[a]Calculated according to Eq. (7).

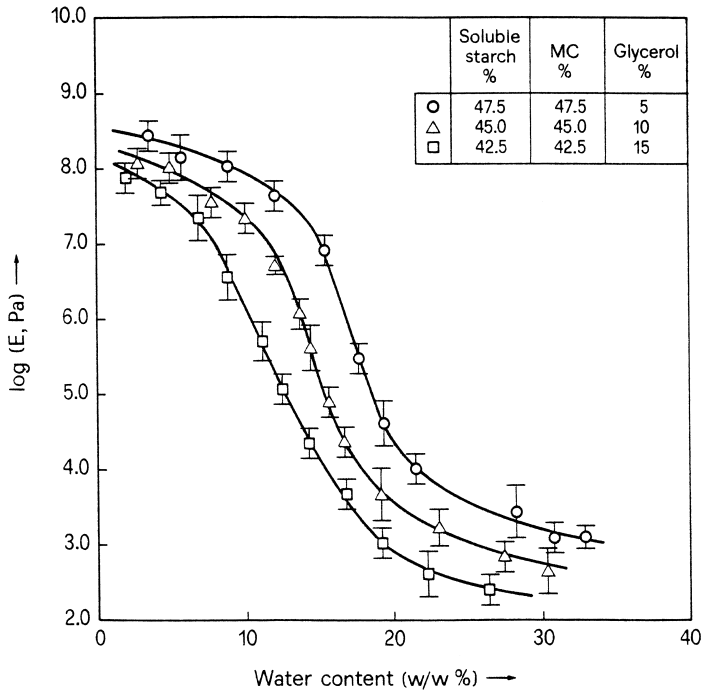

Fig. 6. Effect of water content on log flexural modulus determined from three point bend test of several soluble starch–MC–glycerol blends. The results give the average and the standard deviation of at least eight measurements.

applications. In fact, the soluble starch–MC blends tend to become increasingly hydrophilic with an increase in the total plasticizer content (water or water-sugar–glycerol) (Tables 1 and 2). Experimentation of polymer plasticization with computer simulation has shown that incorporation of a plasticizer in a polymer matrix leads to denser chain packing as a result of the enhanced flexibility of the polymeric chains (Takeuchi, 1990; Trommsdorff and Tomka, 1995).

3.4. Mechanical properties

3.4.1. Tensile strength — percentage elongation

Table 4 and Table 5 give the tensile strength and percentage elongation of composite polymer matrices made from soluble starch–MC at different water contents. The effect of conditioning these samples over various relative humidities on the mechanical properties is shown in Table 4. Increasing water or total plasticizer content resulted in a marked increase in percentage elongation of films due to extensive plasticization of these 'hygroscopic' polymers as previously observed both for synthetic and natural polymers (Okaya, 1992; Bader and Goritz, 1994; Hoseney, 1994; Lawton and Fanta, 1994; Lawton, 1996). In fact, though MC is the least hydrophilic of the cellulose ethers, MC film is still not a good moisture barrier (Baldwin et al., 1995).

Table 4
Tensile strength and percentage elongation of water plasticized soluble starch–MC blends

Soluble starch%	MC%	Water%	Tensile strength (MPa)	Elongation%
90	0	10	50.5 ± 5.4	4.2 ± 0.5
80	10	10	42.7 ± 4.0	6.5 ± 0.8
70	20	10	33.2 ± 2.9	8.0 ± 0.6
60	30	10	20.5 ± 2.0	9.5 ± 1.0
50	40	10	12.6 ± 1.1	10.6 ± 1.1
47.5	47.5	5	73.1 ± 5.9	4.0 ± 0.3
45.0	45.0	10	61.2 ± 6.5	8.9 ± 0.7
40.0	40.0	20	49.5 ± 4.0	16.7 ± 1.4
35.0	35.0	30	38.7 ± 3.5	24.5 ± 2.2

Both percentage elongation and tensile strength of films were shown to be strongly influenced by the plasticization level. Percentage elongation exhibited a considerable increase, up to three times the initial values (Tables 4 and 5), while the tensile strength dropped to lower than 50% of the original values.

3.4.2. Three point bend test

When water and another plasticizer (glycerol, sugar–polyol) coexist within a single or composite polymer matrix, it was previously shown that they have a synergistic action in terms of plasticization (Lloyd and Kirst, 1963; Kirby et al., 1993; Ollett et al., 1991; Arvanitoyannis et al., 1996; Lawton, 1996; Psomiadou et al., 1996). The three point bend test results (Figs. 6 and 7) show that the clear fall in modulus (~5–6 magnitude orders), most likely reflecting the glass transition region, becomes gradually less marked and less abrupt when the composite polymer matrix is plasticized by increasing amounts of water and polyol. This is in agreement with previous publications on plasticized wheat starch and soluble starch–sodium caseinate blends (Kirby et al., 1993; Arvanitoyannis et al., 1996). The presence of MC,

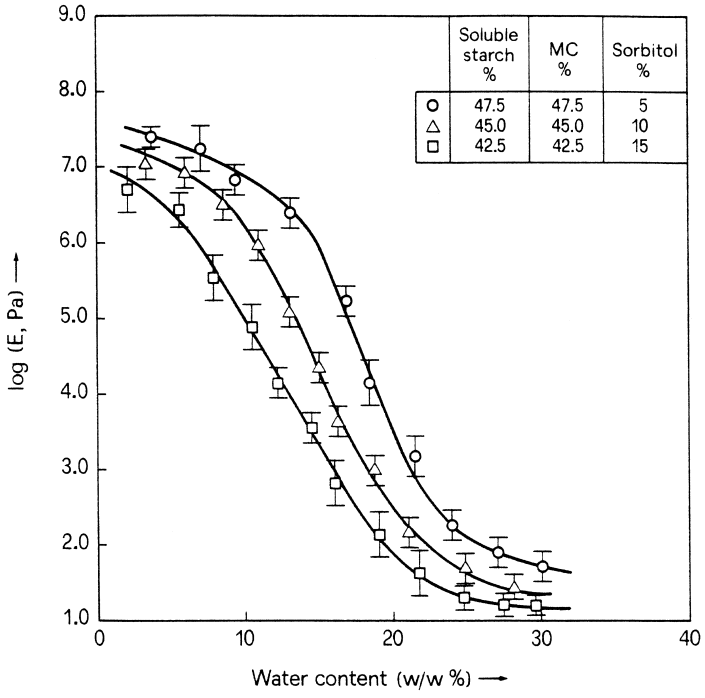

Fig. 7. Effect of water content on log flexural modulus determined from three point bend test of several soluble starch–MC–sorbitol blends. The results give the average and the standard deviation of at least eight measurements.

which has lower hydrophilicity than starch, is also believed to moderate the sharp drop in modulus observed for pure starch (Arvanitoyannis et al., 1996). Sodium caseinate was found to exhibit a similar action in starch–caseinate blends (Arvanitoyannis et al., 1996).

4. Conclusions

Edible blends based on soluble starch–MC blends, plasticized with water and/or other polyols, were studied with regard to their thermal, mechanical and gas and water permeability properties. It was shown that at a total plasticizer content higher than 15%, a substantial depression of the T_g and tensile strength occurred while the percentage elongation increased up to three times its original value. Further, the gas permeability of the soluble starch–MC blends increased proportionally to the total plasticizer content.

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Table 5
Tensile strength and percentage elongation of soluble starch–MC blends plasticized with water and glycerol, sorbitol or xylose

Soluble starch%	MC%	Glycerol%	Water%	Tensile strength (MPa)	Elongation%
45.0	45.0	5	5	59.4 ± 5.6	11.9 ± 1.6
40.0	40.0	15	5	43.3 ± 5.0	25.3 ± 1.9
32.5	32.5	30	5	33.5 ± 3.1	34.2 ± 3.5
Soluble starch%	MC%	Sorbitol %	Water%	Tensile strength (MPa)	Elongation %
45.0	45.0	5	5	54.6 ± 3.9	14.3 ± 1.3
40.0	40.0	15	5	35.2 ± 2.0	28.7 ± 2.4
32.5	32.5	30	5	28.4 ± 2.7	39.4 ± 3.3
Soluble starch%	MC%	Xylose%	Water%	Tensile strength (MPa)	Elongation %
45.0	45.0	5	5	48.4 ± 4.2	8.8 ± 0.9
40.0	40.0	15	5	32.5 ± 3.0	21.5 ± 2.3
32.5	32.5	30	5	25.6 ± 1.9	28.4 ± 2.9

CT96-1085, Enhancement of Quality of Food and Related Systems by Control of Molecular Mobility. It does not nesessarily reflect its views and in no way anticipates the Commission's future policy in this area.

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