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Edible films made from natural resources; microcrystalline cellulose (MCC), methylcellulose (MC) and corn starch and polyols—Part 2

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Aqueous blends of microcrystalline cellulose (MCC) or methyl cellulose (MC) and corn starch with or without polyols were extruded, hot pressed and studied, after their conditioning at different relative humidities, in terms of their thermal, mechanical and water and gas permeability properties. An increase in water or polyol content showed a considerable increase in percentage elongation but also a decrease in the tensile strength of films. The presence of high cellulose contents increased the tensile strength and decreased the water vapour transmission of films. The development of crystallinity with time resulted in a decrease of both gas and water permeability. Several semiempirical models for calculation of gas permeability and tensile strength and tensile and flexural moduli were applied. The obtained values were compared to those experimentally determined and with the ones reported in the literature. On several occasions, quite significant discrepancies were found which were attributed to differences in molecular weight, percentage crystallinity and polymorphism.

INTRODUCTION

Although non-edible films have, in principle, better quality properties than edible films, which is reinforced by the small application number of the latter compared to the former, the inherent advantages of the edible films are also important and are as follows (Guilbert, 1986):

(1) lowering the cost and reduction of the environmental pollution;
(2) improvement of organoleptical characteristics and textural properties of foods;
(3) possibility of enrobing particular portions or layers of heterogeneous foods;
(4) preservation of flavour components and shelf life extension.

Cellulose, starch and their constituents are the two most important raw materials for the preparation of films. Cellulose, the principal structural component of plants, is the most abundant source of complex carbohydrate in the world (Engelhardt, 1995). The cellulose products in terms of chemistry could be classified to regenerated cellulose, precipitated cellulose and microcrystalline cellulose.

Microcrystalline cellulose (MCC) is a natural polymer whose chemical name is beta 1,4-glucan and should not be confused with α-1,4-glucan standing for starch. Although shorter cellulose fibers had attracted more interest in the past, recently there has been an upsurge in using lower levels of longer fibers for specialized uses and, mainly, for enhancing the functional properties of foods (Ang & Miller, 1991; Yamanaka & Watanabe, 1994).

Apart from native and microcrystalline cellulose, many derivatives of cellulose, such as esters or ethers, have been synthesized in an effort to 'tailor' cellulose to specific uses. It is precisely the enormous variety of structural options offered by cellulose ethers that features in the development work carried out on these products, in particular related to technologies directed at influencing and characterizing the distribution of substituents, obtaining special effects such as hydrophobic association by means of long chain aliphatic

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substituents and increasing or decreasing the biodegradability of these products (Walsrode, 1995). Most of the commercially produced cellulose ether production is accounted for by carboxy methyl cellulose (CMC) and methyl cellulose (MC) (approximately 83%). By derivatizing a series of hydroxyl groups with minor or polar substituents, it is possible to render the otherwise (on account of hydrogen bonding) strongly associated hydrophilic cellulose chains soluble in water and thus useful for applications in agriculture and in the food industry (Park *et al.*, 1994a, b, 1993; Krochta, 1992).

Starch is one of the most widespread polysaccharides in the vegetal kingdom and has found numerous applications either on its own (Krochta *et al.*, 1994; Jokay *et al.*, 1967; Herald *et al.*, 1995; Gennadios *et al.*, 1993a–e; Gennadios & Weller, 1990) or in blends with other synthetic polymers or monomers (Arvanitoyannis *et al.*, 1994; Sanderson, 1981; Sandford & Baird, 1983; Shogren, 1993; Garcia-Rodenas *et al.*, 1994; Peanansky *et al.*, 1991). The interest in starch has recently been reactivated because of its inherent biodegradability and its envisaged great potential for food packaging edible films (Arvanitoyannis *et al.*, 1994, 1996; Goheen & Wool, 1991; Griffin, 1994; Wool, 1989, 1995).

In the second paper of this series, blends of edible films (starches and MCC or MC) were used for the preparation of edible films with improved properties for food packaging applications. The behaviour of these films with regard to the thermal, mechanical and water and gas permeability was studied and compared to the values obtained from several semiempirical models.

EXPERIMENTAL

Materials

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

Preparation of samples in the glassy state

Potato and corn starch (starch/water 30%w/w) were rendered amorphous by gelatinizing and roller drying (one process) at 140°C; roller drier speed, 10 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 starches with MCC and MC with glycerol/sugars and water was carried out as elsewhere described (Arvanitoyannis *et al.*, 1994).

Preparation of films (thickness range; 0.05mm±0.001) for permeability measurements and conditioning of samples at different relative humidities were made as previously described (Arvanitoyannis & Blanshard, 1993; Arvanitoyannis *et al.*, 1994, 1992).

Wide angle X-ray diffraction pattern measurements (WAXDP)

X-Ray diffraction measurements were carried out using a Shimadzu (Japan) diffractometer from 5–40°C. The crystallinity was determined by dividing the crystalline area/crystalline + amorphous area) as previously reported (Marsh & Blanshard, 1988).

Dynamic mechanical thermal analysis (DMTA) measurements

The dynamic mechanical thermal analyser (DMTA, Mark II, Polymer Laboratories, UK) with a heating rate of 2°C/min and a single cantilever bending mode at 1 Hz was calibrated each day and measurements were taken 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 $\tan\delta$ ($\tan\delta = E''/E'$, where E'' is the loss modulus). This procedure normally gave values varying within a range of 2.5°C.

Differential thermal analysis (DTA) measurements

DTA measurements were taken using a Shimadzu DTA equipped with a liquid N_2 cooling accessory and connected to an IBM/PC and a Hewlett Packard plotter. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The sample size for DTA was approximately 10 mg. Temperature calibration was made with cyclohexane, dodecane and octane. Heat flow calibration was made by reference to the known melting enthalpy of indium metal (purity 99.9%) from Goodfellows Metals. The purge gases used were dry helium and dry nitrogen. The T_g were determined from the second run after melting, quenching with liquid nitrogen and reheating at a heating rate of 2°C/min. The percentage crystallinity with DTA was calculated according to Gidley (1992).

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

Measurements of permeability

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

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

Corn starch %	Water %	MCC %	DTA (2nd run)	DMTA (E'')	DMTA (tan δ)	Permeability (inflection)
85	15	0	61.2±1.3	62.8±1.7	66.1±1.5	60.5±0.8
80	15	5	63.6±1.2	65.9±1.2	69.0±2.1	64.2±1.1
75	15	10	65.0±1.4	67.7±1.4	71.4±1.4	66.4±1.2
70	15	15	66.8±1.3	69.5±1.5	75.6±1.7	68.0±1.5
60	15	25	69.2±1.5	71.3±1.8	77.5±1.6	70.5±1.3
55	15	30	70.6±1.8	72.4±1.1	79.6±1.5	71.4±1.4
45	15	40	72.1±1.6	74.0±1.5	82.0±1.0	73.5±1.5
47.5	5	47.5	124.8±1.9	127.1±1.8	136.9±2.2	—
45.0	10	45.0	97.3±2.0	99.5±0.9	109.2±1.6	—
42.5	15	42.5	74.2±1.6	76.4±1.2	88.3±1.5	75.6±1.2
40.0	20	40.0	57.0±1.7	59.3±1.4	69.5±1.3	55.8±1.5
37.5	25	37.5	43.2±2.1	45.6±1.3	56.3±1.4	44.6±0.8
35.0	30	35.0	22.1±1.2	21.0±1.7	38.4±0.9	20.5±1.1
78	17	2	58.3±1.5	59.5±1.9	62.8±1.9	55.6±2.0
71	17	12	59.5±1.7	61.8±2.1	66.9±2.1	58.7±1.5
65	17	18	61.0±1.3	60.4±1.5	70.5±1.5	60.5±1.6
58	17	25	65.2±1.1	67.1±1.8	76.0±1.8	66.7±1.4
51	17	32	68.1±1.4	69.2±2.0	80.5±1.5	69.8±1.2
43	17	40	71.2±1.3	70.6±1.7	84.8±2.0	72.5±1.6
28	17	55	77.0±1.6	76.1±1.9	89.3±1.6	78.0±1.5
47.0	6.0	47.0	110.9±1.5	109.4±2.3	123.6±1.8	—
45.0	10.0	45.0	92.2±1.6	91.5±1.2	110.2±1.3	—
42.0	16.0	42.0	67.3±1.5	68.4±0.9	79.6±1.8	66.2±1.6
39.0	22.0	39.0	49.8±1.0	48.5±1.3	63.5±2.1	53.4±1.5
37.0	26.0	37.0	34.5±1.3	36.7±1.4	45.6±1.5	36.0±1.1
35.0	30.0	35.0	17.1±1.2	18.5±1.5	23.0±0.9	16.2±1.7

detailed description of the method and the equations used were reported in previous publication (Arvanitoyannis *et al.*, 1996).

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

Three point bending test

All samples were cut with a scalpel, scissors or saw into bars ~30×8×2 mm and stored 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.

RESULTS AND DISCUSSION

Thermal and thermal mechanical properties

Similarly to the first publication of this series on starch-sodium caseinate blends (Arvanitoyannis *et al.*, 1996) the polyols were found to induce a quite extensive plasticization. If the polyols were to be classified with regard to their plasticization ability in the starch/MCC or starch/MC blends (Tables 1 and 2), the following order should be suggested:

Glycerol < Sorbitol < Glucose < Sucrose

The incorporation of polyols in the starch/cellulose blends did not result in phase separation even at high polyol contents. Both DMTA and DTA traces showed the presence of one unique peak contrary to our observation in the case of starch/sodium caseinate blends. The peaks [DTA, tan δ (DMTA)] however, became slightly broader than before thus evoking the previously mentioned preferential hydration of polyols which leads to lower water contents (Fig. 1, Arvanitoyannis *et al.*, 1996).

It can be said that the addition of MCC and MC have a beneficial effect upon the aqueous starch/polyol blend since it rather acts as a coplasticizer by improving the compatibility of polyol with starch contrary to sodium

Table 2. Thermal and thermomechanical properties of corn starch-MCC (1:1)/ glycerol, corn starch-MCC (1:1)/sorbitol, corn starch-MCC (1:1)/sucrose, corn starch-MCC (1:1)/ xylose blends. The results give the average and the standard deviation of at least three or five measurements for thermal and permeability measurements, respectively

Corn starch	MCC	Glycerol	Water	DTA	DMTA (tan δ)	DMTA (E')	Permeability (inflection)
47.5	47.5	0	5	118.5±2.5	130.0±4.1	113.4±2.0	—
45.0	45.0	5	5	93.2±1.9	98.5±3.0	87.5±1.7	—
42.5	42.5	10	5	59.4±1.4	70.3±2.3	52.3±1.8	56.4±1.9
40.0	40.0	15	5	37.3±1.7	42.5±1.8	34.0±1.5	38.5±1.6
38.0	38.0	19	5	−2.8±0.3	6.8±1.3	−5.1±1.2	—
34.0	34.0	27	5	−15.3±0.7	−5.7±0.7	−21.4±2.0	—
Sorbitol							
45.0	45.0	5	5	91.8±3.5	97.5±2.8	84.1±1.4	—
42.5	42.5	10	5	57.0±1.7	66.9±1.5	48.0±1.8	52.5±2.1
39.5	39.5	16	5	23.8±1.2	30.3±1.7	17.8±1.5	27.0±1.8
35.5	35.5	24	5	−14.1±0.6	1.7±1.2	−18.3±1.7	—
33.5	33.5	28	5	−28.1±0.9	−14.7±1.3	−32.5±1.0	—
Sucrose							
44.5	44.5	6	5	87.4±1.8	93.5±2.5	80.1±2.0	—
42.5	42.5	10	5	51.2±1.2	58.3±1.9	44.6±2.2	47.0±1.9
40.0	40.0	15	5	19.1±0.3	27.4±1.5	11.8±1.7	20.6±2.1
37.5	37.5	20	5	−10.0±0.4	−4.5±1.6	−22.5±1.5	—
34.5	34.5	26	5	−23.2±1.2	−13.9±1.0	NO[a]	—
Xylose							
45.0	45.0	5	5	84.2±1.9	88.0±2.2	77.1±1.8	81.2±2.3
43.0	43.0	9	5	49.6±1.4	53.4±1.7	40.3±1.2	44.3±1.8
39.5	39.5	16	5	11.3±0.3	17.3±1.8	7.4±1.4	15.2±2.0
37.5	37.5	20	5	−8.5±0.5	−1.2±1.2	−14.5±1.6	
35.0	35.0	25	5	−20.4±0.9	−12.2±0.9	NO[a]	

[a]NO: not observed because the run started from −50°C.

caseinate. Table 1 shows that the higher the water content the greater the depression of the T_g value (DTA, DMTA and permeability measurements). An indirect indication of the extent of plasticization is the drop of flexural modulus (see the three point bend test) with higher water or polyol contents.

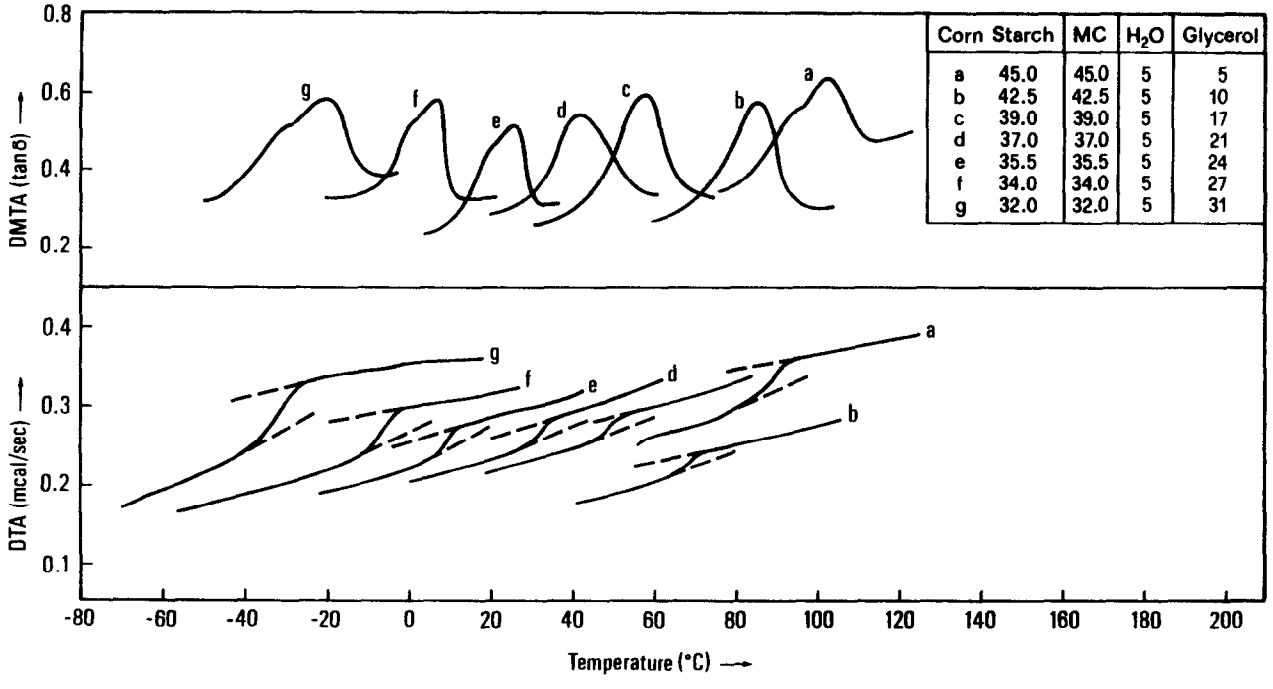

Fig. 1. Representative DMTA and DTA traces for corn starch/MC/water blends.

Table 3. Mechanical properties and WVTR of corn starch-MCC (1:1)/glycerol, corn starch-MCC (1:1)/sorbitol, corn starch-MCC (1:1)/sucrose and corn starch-MCC (1:1)/xylose blends at different relative humidities. The results give the average and the standard deviation of at least eight measurements

Corn starch	MCC	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	90.0±1.6	158.9±12.5	2.3±0.4	0.2±0.03
450	450	5	5	78.4±2.3	139.0±11.9	3.8±0.2	1.8±0.1
42.5	42.5	10	5	66.3±1.8	124.2±10.4	4.4±0.5	3.4±0.1
40.0	40.0	15	5	55.6±1.5	107.4±12.0	5.3±0.3	5.7±0.3
38.0	38.0	19	5	43.2±1.2	75.1±3.9	7.0±0.6	8.2±0.8
34.0	34.0	27	5	25.0±1.7	53.4±3.2	8.5±0.5	11.4±1.2
Sorbitol							
45.0	45.0	5	5	73.3±2.1	131.5±12.3	4.1±0.3	2.5±0.1
42.5	42.5	10	5	59.5±1.5	112.4±11.6	4.7±0.6	4.6±0.2
39.5	39.5	16	5	48.9±1.8	94.2±11.8	6.0±0.5	7.0±0.5
35.5	35.5	24	5	33.4±2.0	62.5±6.4	8.1±0.4	8.9±0.6
33.5	33.5	28	5	18.3±1.6	40.0±3.1	9.3±0.4	14.2±0.3
Sucrose							
44.5	44.5	6	5	65.0±1.4	120.5±12.1	2.9±0.2	3.8±0.4
42.5	42.5	10	5	51.8±1.8	103.0±11.9	3.4±0.3	6.2±0.3
40.0	40.0	15	5	43.4±1.3	82.7±7.5	3.5±0.5	8.4±0.6
37.5	37.5	20	5	31.2±1.6	52.9±5.2	3.3±0.3	10.5±0.9
34.5	34.5	26	5	21.0±2.0	33.5±3.3	3.1±0.2	16.3±1.4
Xylose							
45.0	45.0	5	5	63.9±1.8	119.6±11.5	3.6±0.2	2.8±0.2
43.0	43.0	9	5	52.4±2.2	104.3±10.8	4.5±0.4	4.5±0.3
39.5	39.5	16	5	41.7±1.7	81.2±7.5	5.6±0.5	7.4±0.6
37.5	37.5	20	5	32.6±1.5	50.8±4.6	7.4±0.6	9.7±0.5
35.0	35.0	25	5	20.5±1.2	34.7±2.9	8.8±0.8	13.6±1.2

Mechanical properties

Table 3 gives synoptically the tensile strength, tensile modulus and percentage elongation of corn starch/MCC/water with or without polyols. The corn starch/MC/water or polyol blends exhibited similar behaviour with regard to mechanical properties to the corn starch/MCC/water blends. These blends could be treated as composite materials from the viewpoint of the applied stress;

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

$$E_{\text{starch}} = \frac{1}{\frac{V_{\text{amylose}}}{E_{\text{amylose}}} + \frac{1 - V_{\text{amylose}}}{E_{\text{amylopectin}}}} \quad (2)$$

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

$$E_{\text{blend}} = V_{\text{starch}} E_{\text{starch}} + (1 - V_{\text{starch}}) E_{\text{sodium caseinate}} \quad (3)$$

$$E_{\text{blend}} = \frac{1}{\frac{V_{\text{starch}}}{E_{\text{starch}}} + \frac{1 - V_{\text{starch}}}{E_{\text{sodium caseinate}}}} \quad (4)$$

Although several, occasionally deviating, values for starch or for its constituents (amylose or amylopectin) were reported (Lourdin *et al.*, 1995; Warburton *et al.*, 1990; Young, 1984), and attributed to imperfections at macro- or microscopical level, the corn starch values (amylose/amylopectin: 28/72, Blanshard, 1987) derived from equations (1) and (2) for $E_{\text{amylose}} = 31.3$ MPa and $E_{\text{amylopectin}} = 16.5$ MPa with 5% moisture (Lourdin *et al.*, 1995) are 20.59 and 19.02 MPa, respectively. The modulus values for MC and MCC vary within a range of 71–137 MPa for cellulose I and cellulose II.

Study of the tensile strength at various storage times shows that the extent of embrittlement of corn starch/MCC/water blends is proportional to the duration of storage time (Fig. 2).

Regarding the mechanical properties, our results (Table 3) are in reasonable agreement with our theoretical calculations (same order of magnitude) and the occasionally observed variability of standard deviation should be primarily attributed to the following factors:

(1) differences in percentage crystallinity;
(2) possible non-uniform distribution of crystalline and amorphous regions in the films and;
(3) variations on the molecular conformation and crystal packing.

In addition to cellulose heterogeneity, the starch films are also chemically heterogeneous because they contain both amylose and amylopectin and, physically, they have both crystalline and amorphous phases. Therefore the interactions of starch with water cannot be expected to be homogeneously distributed within

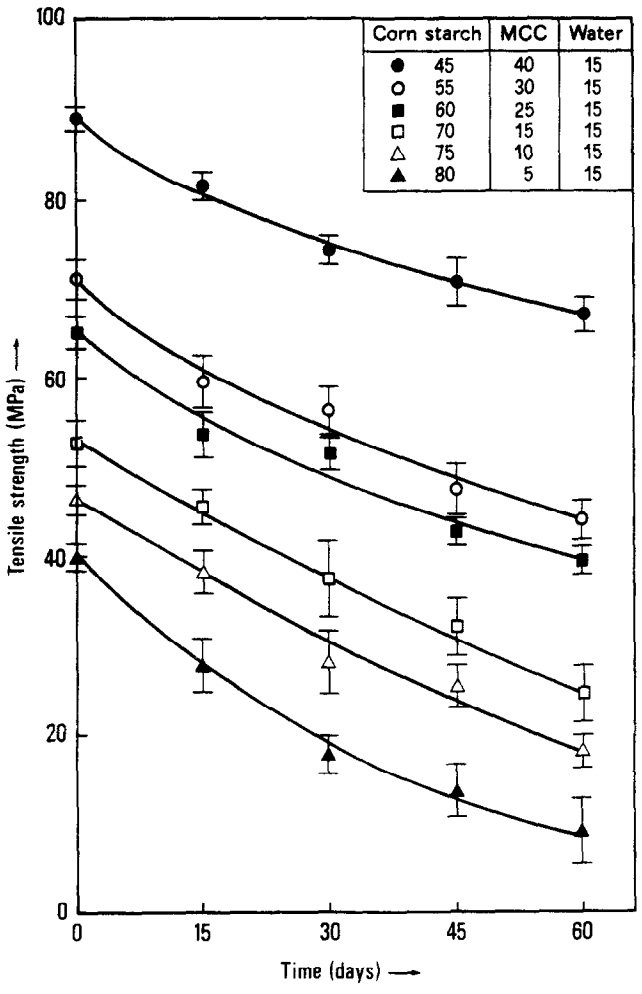

Fig. 2. Effect of storage time on tensile strength of various ratios of corn starch/MCC plasticized with 15% water. The results give the average and the standard deviation of at least eight measurements.

the entire structure. Probably, the binding of water depends more on the density and on the regularity of packing of the polysaccharide chains than whether the individual chains are linear or branched. Ethylene glycol and glycerol are considered the most effective plasticizers of starch (Young, 1984). Table 3 showed that polyols such as sorbitol and glucose displayed an even more pronounced antiplasticizing action, with regard to tensile strength and percentage elongation, upon starch.

The different behaviour of sucrose compared to glucose and sorbitol within the starch/MCC or MC matrix is obvious from Table 3. Sucrose exerts the same antiplasticizing action, as previously reported (Kalichevsky *et al.*, 1992a, 1993b; Cherian *et al.*, 1995; Arvanitoyannis *et al.*, 1996), resulting in considerably lower tensile strength and percentage elongation whereas both sorbitol and glucose impart lower tensile strength but higher percentage elongation (plasticizing action).

The incorporation of MC in starch matrix was found to have a rather beneficial effect resulting in a gradual increase of tensile strength and percentage elongation whereas when MCC was employed the tensile strength increased but the percentage elongation only slightly increased. Some further reasons that should be mentioned in an attempt to explain the occasionally recorded wide deviation range of mechanical properties (Table 3) are the following:

(1) The true rate is not constant but in fact was found to decrease with extension rate (Kausch, 1987).
(2) In our blends true strain softening may occur at the beginning of the large deformation process, as annealed or other structures are broken down, which could eventually promote a certain stress localization.
(3) In most polymer blends deformation is localized around the 'neck' and is later on propagated through the entire specimen occasionally accompanied by 'slipping' of the specimen (Haward, 1987).

Three point bending test

It becomes clear from Figs 3–5 that the effect of plasticizers (water or polyols) on the flexural modulus is directly proportional to their content in the blend. The

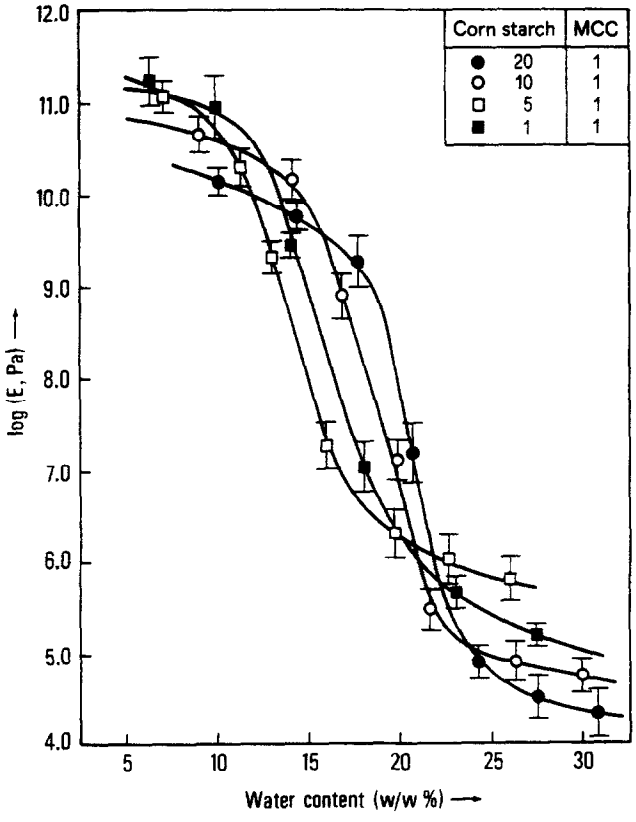

Fig. 3. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/MCC blends. The results give the average and the standard deviation of at least eight measurements.

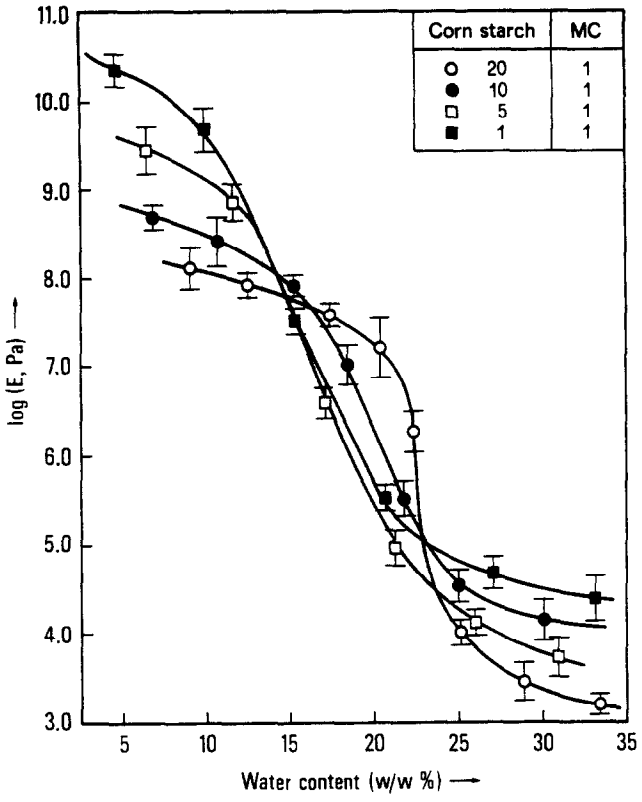

Fig. 4. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/MC blends. The results give the average and the standard deviation of at least eight measurements.

plasticization of the matrix, due to sucrose, was by far more marked than the one induced by the rest of polyols in agreement with previous publications (Kirby *et al.*, 1993; Ollett *et al.*, 1991). Comparison of the fall in modulus at higher plasticizer contents for starch/MCC or starch/MC blends shows that the latter's drop is smoother than the former's (Figs 3 and 4). A probable explanation might be that MC has a better film forming capability than MCC and it can also act as a compatibilizer between starch and polyols, in view of its higher flexibility, thus resulting in a more uniform system with regard to the mechanical properties.

Water vapour transmission rate

Table 3 shows that the higher the starch content the higher the WVTR. These results are in satisfactory agreement with the previous publication where it was stated and experimentally observed that starch sorbs more water than cellulose does (French, 1984). The difference curve between starch and cellulose indicates that about 0.8–1.0 mole of per D-glucopyranosyl unit is sorbed by starch in the relative humidity range of up to 40%. Although the so-called monolayer water could possibly be water of crystallization, in native cellulose (cellulose I), water is rather 'avidly' sorbed into the intercrystalline regions or onto the crystallite surfaces (Urquhart, 1959).

The native and MCC have a striking difference in behaviour which is at least partly related to the distribution of crystalline and amorphous regions in the film but also depends strongly on the molecular conformation and crystal packing (hydrogen bonding). One of the most apparent differences is that the water sorption and swelling capacity of treated cellulose (MCC or MC) is considerably greater than the native. Therefore our results (Table 3) agree with previously reported observation that under moisture conditions, one lattice dimension in cellulose II was shown to increase in order to accommodate a higher number of water molecules whereas this does not occur in the case of cellulose I (Hermans, 1946). Employment of MC resulted in a greater increase of WVTR because of the higher flexibility and swelling capability of MC compared to MCC (Table 3).

Gas permeability (GP)

The sorption of quite considerable amounts of water on natural and, in particular, on edible films complicates the issue of a straightforward assessment of GP. Furthermore the occasionally suggested theoretical or semiempirical approaches for calculating approximately the GP values proved to be succesful mainly for

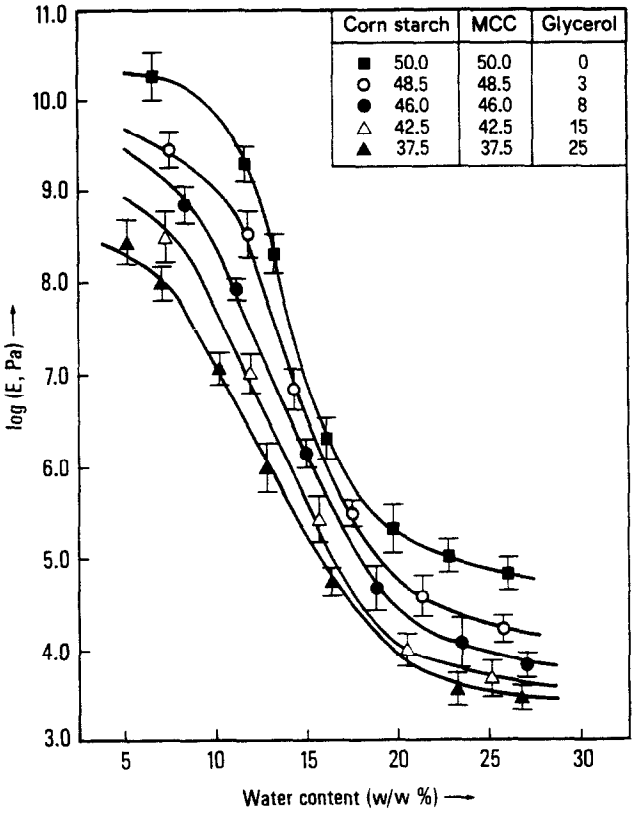

Fig. 5. Effect of water content on log flexural modulus, determined from three point bending test, of several corn starch/MCC/glycerol blends. The results give the average and the standard deviation of at least eight measurements.

Table 4. Gas permeability (O_2, N_2, CO_2 in $cm^2\ sec^{-1}\ Pa^{-1}$) of corn starch-MCC or MC (1:1)/glycerol, corn starch-MCC or MC (1:1)/sorbitol, corn starch-MCC or MC (1:1)/sucrose and corn starch-MCC(1:1)/xylose blends at different relative humidities. The results give the average of at least five measurements at ambient temperature (23±2 °C)

Corn starch	MCC	Glycerol	Water	O_2	N_2	CO_2
47.5	47.5	0	5	1.8×10^{-17}	3.2×10^{-18}	1.2×10^{-16}
45.0	45.0	5	5	2.4×10^{-16}	1.4×10^{-17}	2.0×10^{-15}
42.5	42.5	10	5	3.6×10^{-15}	6.5×10^{-16}	3.1×10^{-14}
40.0	40.0	15	5	1.0×10^{-15}	0.9×10^{-16}	1.1×10^{-14}
38.0	38.0	19	5	4.1×10^{-14}	2.1×10^{-15}	0.5×10^{-13}
34.0	34.0	27	5	3.0×10^{-13}	3.7×10^{-14}	0.7×10^{-12}
Sorbitol						
45.0	45.0	5	5	4.0×10^{-16}	4.3×10^{-17}	2.5×10^{-15}
42.5	42.5	10	5	5.1×10^{-15}	6.0×10^{-16}	3.6×10^{-14}
39.5	39.5	16	5	3.7×10^{-15}	2.8×10^{-16}	1.3×10^{-14}
35.5	35.5	24	5	2.3×10^{-14}	3.1×10^{-15}	2.5×10^{-13}
33.5	33.5	28	5	4.5×10^{-12}	0.7×10^{-13}	1.5×10^{-11}
Sucrose						
44.5	44.5	6	5	1.5×10^{-16}	0.9×10^{-17}	1.4×10^{-15}
42.5	42.5	10	5	2.6×10^{-15}	2.1×10^{-16}	2.5×10^{-14}
40.0	40.0	15	5	1.1×10^{-15}	0.8×10^{-16}	1.1×10^{-14}
37.5	37.5	20	5	2.4×10^{-14}	1.0×10^{-15}	3.0×10^{-13}
34.5	34.5	26	5	3.0×10^{-12}	0.7×10^{-13}	1.9×10^{-11}
Xylose						
45.0	45.0	5	5	1.6×10^{-16}	1.1×10^{-17}	1.0×10^{-15}
43.0	43.0	9	5	2.4×10^{-15}	3.5×10^{-16}	3.1×10^{-14}
39.5	39.5	16	5	1.5×10^{-15}	0.9×10^{-16}	1.2×10^{-14}
37.5	37.5	20	5	0.6×10^{-14}	1.3×10^{-15}	1.5×10^{-13}
35.0	35.0	25	5	3.0×10^{-13}	5.5×10^{-14}	2.9×10^{-12}
Glycerol						
47.5	47.5	0	5	2.2×10^{-17}	4.6×10^{-18}	2.0×10^{-16}
450	45.0	5	5	3.1×10^{-16}	2.3×10^{-17}	3.4×10^{-15}
42.5	42.5	10	5	4.5×10^{-15}	8.4×10^{-16}	4.7×10^{-14}
40.0	40.0	15	5	1.7×10^{-15}	2.9×10^{-16}	1.9×10^{-14}
37.0	37.0	21	5	5.3×10^{-14}	4.3×10^{-15}	1.2×10^{-13}
33.5	33.5	28	5	4.9×10^{-13}	4.6×10^{-14}	1.5×10^{-12}
Sorbitol						
45.0	45.0	5	5	6.1×10^{-16}	5.9×10^{-17}	3.8×10^{-15}
42.5	42.5	10	5	7.2×10^{-15}	8.3×10^{-16}	5.4×10^{-14}
40.0	40.0	15	5	6.5×10^{-15}	4.0×10^{-16}	2.6×10^{-14}
34.5	34.5	26	5	3.7×10^{-14}	5.3×10^{-15}	3.9×10^{-13}
32.5	32.5	30	5	6.4×10^{-12}	1.8×10^{-13}	2.8×10^{-11}
Sucrose						
45.0	45.0	5	5	2.8×10^{-16}	1.6×10^{-17}	1.7×10^{-15}
42.0	42.0	11	5	4.2×10^{-15}	3.4×10^{-16}	4.3×10^{-14}
40.0	40.0	15	5	2.0×10^{-15}	1.7×10^{-16}	2.2×10^{-14}
37.0	37.0	21	5	3.7×10^{-14}	3.9×10^{-15}	3.3×10^{-13}
34.0	34.0	27	5	5.1×10^{-13}	1.6×10^{-14}	4.5×10^{-12}

synthetic polymers (Salame, 1986; Arvanitoyannis & Blanshard, 1993) whereas the thereby obtained results for natural polymers deviated substantially (Arvanitoyannis *et al.*, 1994, 1996).

When Salame's equation was applied to cellulose the obtained value was 1.76×10^{-20} $cm^2.s^{-1}$. Pa^{-1} which is substantially lower than the experimentally found (Table 4) similarly to previously reported values for amylose and amylopectin (Arvanitoyannis *et al.*, 1994, 1996).

Table 4 and Figs 6 and 7 show that high MCC/starch or MC/starch contents in the blend decrease the GP of the blend whereas the incorporation of high water or polyol contents results in substantial enhancement of GP values. A possible explanation for that observed in GP might be that in dry starch the chains are packed rather insufficiently in comparison with cellulose and there are very small voids into which water could possibly penetrate with a relatively small volume increase. After uptake of about 10% water all voids are filled. Although it was previously claimed that amylose films are equivalent to cellulose films with regard to

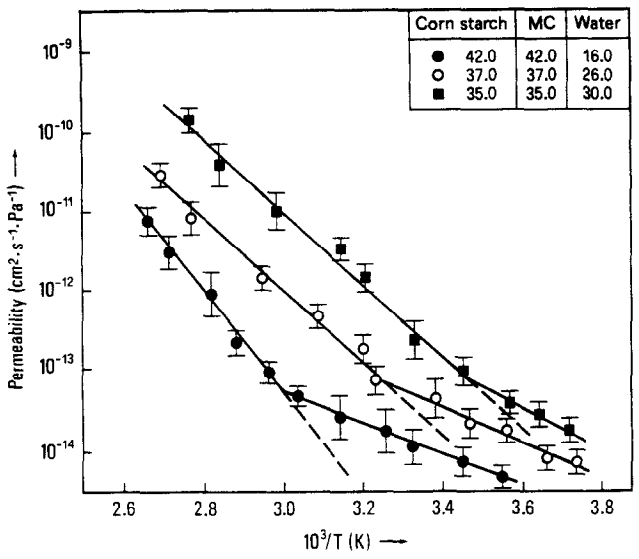

Fig. 6. Permeability of CO_2 in corn starch/MC/water films, derived from equation (6), vs the inverse temperature ($1/T$). The results give the average and the standard deviation of at least five measurements.

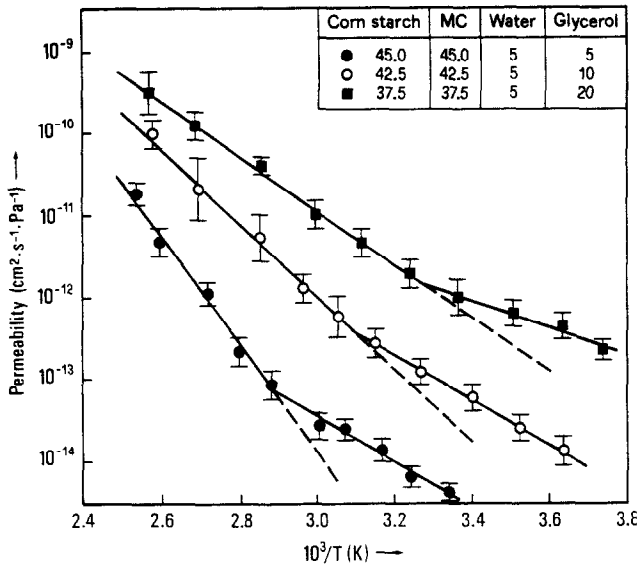

Fig. 7. Permeability of CO_2 in corn starch/MC/water/glycerol films, derived from equation (6), vs the inverse temperature ($1/T$). The results give the average and the standard deviation of at least five measurements.

water vapour permeability and to permeability to organic vapours (Rankin *et al.*, quoted by Young, 1984) we should bear in mind that we are currently dealing with starch, a far more complicated system, where many more interactions occur than in pure amylose/plasticizer systems. Therefore our results are only partly comparable to those reported for amylose.

The observed differences in GP behaviour (Figs 6 and 7, Table 4) between cellulose and starch could be possibly explained in terms of structural differences. All the cellulose structures consist of two independent polymer chains which are packed into layers of hydrogen bonded molecules without any interlayer hydrogen bonding.

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

The logarithmic expressions for the Arrhenius equations describing diffusivity and permeability are as follows:

$$\ln D = \ln D_0 - E_D/RT \quad (5)$$

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

where D_0 and P_0 are the diffusion and permeability coefficient, respectively, E_D and E_P are the activation energies of diffusion and permeability, respectively and R is the universal gas constant.

The equations (5) and (6) were used for the calculation of activation energies of diffusion and permeation for starch/water/polyol and starch/MCC or MC/water or polyols blends (Table 5).

The most important parameter in the diffusion process is admittedly the activation energy of diffusion (E_D) because it represents the energy required to enable the dissolved molecule to 'jump' into another 'hole'. Table 5 shows that larger molecules necessitate larger 'holes' and hence higher activation energies. At low temperatures, the rigid model prevails, where 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 channels connecting them to those already occupied by the gas/water vapour cavities occurs, finally leading to annihilation of the original cavities.

Correlation of GP with developed crystallinity with storage

Although it was initially attempted to determine the developed crystallinity by using DTA according to Gidley (1992), our first results showed rather considerable discrepancies when compared to those obtained with WAXDP. These discrepancies could be probably attributed to the interference of the dehydration energy of cellulose (energy required to desorb water from cellulose) with the endothermic peak of fusion of starch (Zang & Sapieha, 1991). In fact, the apparent enthalpy ΔH_{al} determined from the first run could be distinguished into two parts:

$$\Delta H_{al} = \Delta H_{ml}(a) + \Delta H_{dl}(b) \quad (7)$$

where ΔH_{ml} and ΔH_{dl} stand for the energy of fusion and energy of dehydration and (a), (b) stand for the degree of crystallinity and the water content of the composite, respectively.

Although at low cellullose contents (< 15%), the effect of starch crystallinity prevails over the water desorption process of cellulose, with increasing cellulose contents the latter gradually gains in importance.

Table 5. Activation energies for diffusion (E_D[a], kJ mol^{-1}) and permeation (E_P[b], kJ mol^{-1}) both below ($T < T_g$) and above ($T > T_g$) the glass transition temperature (T_g) for corn starch/water/MCC blends. The results give the average and the standard deviation of five measurements

Corn starch (%w/w)	Water (%w/w)	MCC (%w/w)	N_2				O_2			
			E_D[a]		E_P[b]		E_D[a]		E_P[b]	
			($T < T_g$)	($T > T_g$)	($T < T_g$)	($T > T_g$)	($T < T_g$)	($T > T_g$)	($T < T_g$)	($T > T_g$)
85	15	0	4.7±0.29	3.2±0.18	6.8±0.61	4.6±0.31	4.3±0.28	2.8±0.010	6.3±0.41	4.1±0.34
80	15	5	5.0±0.41	3.5±0.21	7.3±0.65	5.3±0.41	4.6±0.35	3.4±0.25	7.6±0.58	5.0±0.38
70	15	15	5.7±0.35	4.0±0.30	8.2±0.70	6.0±0.50	5.1±0.40	4.0±0.33	8.3±0.66	6.2±0.52
55	15	30	6.4±0.46	4.6±0.29	8.5±0.68	6.4±0.48	5.7±0.46	4.4±0.38	9.1±0.81	7.1±0.64
47.5	5.0	47.5	9.5±0.54	6.3±0.45	11.3±0.85	8.1±0.70	8.6±0.69	6.8±0.55	10.6±1.20	8.3±0.70
40.0	20.0	40.0	7.3±0.60	5.1±0.36	7.6±0.68	6.2±0.52	5.4±0.47	4.2±0.34	8.4±0.75	6.0±0.50
35.0	30.0	35.0	4.8±0.32	3.1±0.18	4.5±0.35	3.3±0.25	3.6±0.40	2.3±0.18	4.6±0.36	2.9±0.26
Glycerol 35.0/35.0	5	25	4.3±0.33	2.6±0.19	5.4±0.39	3.9±0.30	4.0±0.31	2.2±0.15	5.5±0.39	3.4±0.37
Sorbitol 35.5/35.5	5	24	3.5±0.38	1.9±0.08	4.3±0.31	3.0±0.21	2.5±0.19	1.4±0.09	4.3±0.28	3.0±0.33
Sucrose 34.5/34.5	5	26	6.7±0.48	4.8±0.30	8.6±0.72	6.2±0.42	5.3±0.43	3.6±0.23	8.1±0.65	6.2±0.44
Xylose 35.0/35.0	5	25	7.0±0.55	5.4±0.36	9.1±0.65	6.6±0.51	5.9±0.48	4.3±0.34	8.8±0.76	6.6±0.52

[a] Calculated according to equation (5).
[b] Calculated according to equation (6).

In previous experiments with polyethylene/cellulose blends there was need to resort to second runs in order to make sure that the recorded peak was exclusively due to polyethylene crystallinity (Zang & Sapieha, 1991). However, this was not feasible in our case, in view of the inherent sensitivity of starch to thermal treatment in the presence of water. Therefore, the percentage crystallinity of our blends was primarily determined with WAXDP and the results against permeability are shown in Fig. 8. The up to 20% recorded crystallinity after 60 days' storage resulted in lower permeability values by 3–4 magnitude orders. However, further experimentation over longer storage times (> 60 days) is required in order to assess the possible applicability of starch based blends for food packaging uses.

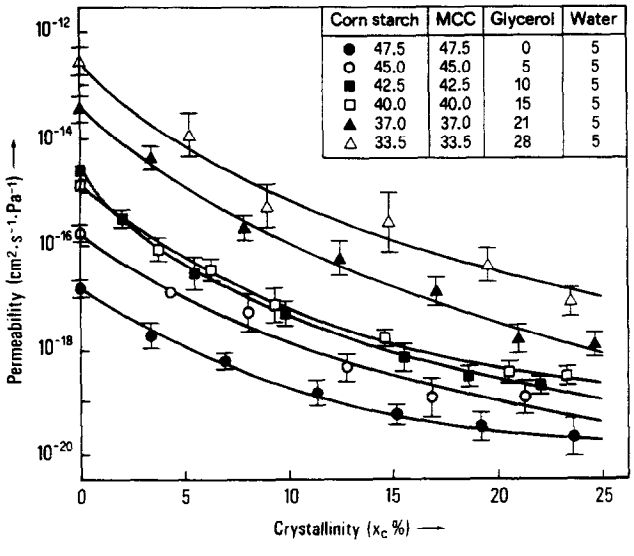

Fig. 8. Permeability of N_2 in corn starch/MC/H_2O blends vs storage time.

CONCLUSIONS

Edible films from corn starch with MCC or MC and water or polyols were prepared and the thermal mechanical and the mechanical properties, WVTR and GP were measured. High MCC or MC contents in aqueous starch/cellulose blends resulted in higher strength and elongation and lower WVTR and GP. When a plasticizer, either water or polyol, was incorporated in the blend, the percentage elongation, the WVTR and GP increased considerably whereas the thermal and mechanical properties showed a substantial decrease due to plasticization of the matrix.

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