

# Physico-chemical studies of chitosan–poly(vinyl alcohol) blends plasticized with sorbitol and sucrose

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(Received 11 April 1997; revised version received 4 June 1997; accepted 9 June 1997)

The physical properties of chitosan/PVA/plasticizer blends, prepared by casting, were investigated. It was found that the thermal properties (melting point, heat of fusion) for PVA showed a decrease proportional to the plasticizers' content. The percentage elongation and CO<sub>2</sub> and water vapour permeability of chitosan/PVA blends were found to increase with an increase in plasticizer content. However, high plasticizer contents caused a substantial decrease in both tensile strength and modulus. The semi-empirical models, applied for calculating the mechanical properties and the CO<sub>2</sub> permeability, were in satisfactory agreement with the experimental values, apart from a certain variation, which should be probably attributed to differences in molecular weight, percentage crystallinity and percentage of hydrolyzed or deacetylated material (PVA and chitosan, respectively). © 1997 Published by Elsevier Science Ltd. All rights reserved

## INTRODUCTION

Poly(vinyl alcohol) (PVA) can be prepared by hydrolysis of a variety of poly(vinyl esters) and poly(vinyl ethers). Most commercially available PVA is produced from poly(vinyl acetate) (PVAc) (Tanigami *et al.*, 1994; Tanigami *et al.*, 1995). The structure of crystalline PVA was shown to be monoclinic (Hodge *et al.*, 1996a, b). The high crystallizability of PVA compared to PVAc should be attributed to the fact that the hydroxyl groups are of sufficiently small size to allow the chains to adopt a planar zig-zag conformation. PVA has found many applications in pharmaceuticals, cosmetics and in the paper and food industries, either alone or in blends with other polymers such as poly(3-hydroxy butyrate) (Azuma *et al.*, 1992), polyacrylic acid (Daniliuc &

David, 1996),  $\beta$ -chitin (Lee *et al.*, 1996) and cellulose (Hasegawa *et al.*, 1992a, b; Hasegawa *et al.*, 1994) among others.

Chitosan is the deacetylated product of chitin. After cellulose, chitin is the second most abundant polysaccharide in nature (Rathke & Hudson, 1994). Chitin is associated with other polysaccharides in the fungal cell walls, while in animal forms chitin is associated with proteins (Muzzarelli, 1977). The production of chitin is possible primarily as a secondary activity related to the marine food industry (Muzzarelli, 1977; Zikakis, 1984). Chitosan has been used in very wide range of applications such as prevention of water pollution by chelating heavy metals or radioactive isotopes (Muzzarelli, 1977), membrane separation (Aiba *et al.*, 1986), in medicine and biotechnology, and in the food areas either as food packaging material because of its antimicrobial action (Wong *et al.*, 1992; El Ghaouth *et al.*, 1991) or as

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dietary fiber and a potential medicine against hypertension thanks to its scavenging action for chloride ions (Furda & Brine, 1990; Ishikura, 1993; Okuda, 1995; Muzzarelli, 1996).

Numerous publications have reported on improving the selectivity of chitosan membranes by manipulating the chain flexibility of chitosan. Blending of chitosan with hydrophilic polymers like PVA, poly(vinyl pyrrolidone) or pectin appears to be a promising approach for producing polymers for specific uses (Blair *et al.*, 1987; Quarashi *et al.*, 1992; Yao *et al.*, 1996). Chemical crosslinking has also been occasionally suggested as a means to improve the properties of chitosan or chitosan-based blends (Nakatsuka & Andrady, 1992; Kim *et al.*, 1992).

Previous studies on chitosan/PVA blends were focused either on studying the plasticizing effect of water on these blends (Miya *et al.*, 1983) or on the crosslinking and swelling of them (Kim *et al.*, 1992). The aim of this investigation is to study the synergistic plasticizing action of low molecular weight compounds such as sorbitol and sucrose in conjunction with water on the structure and on the mechanical properties and CO<sub>2</sub> permeability of plasticized chitosan/PVA blends. Sorbitol and sucrose were selected to be used as plasticizers because both of them have imparted flexibility to the edible/biodegradable blends previously mixed (Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996) and they also constitute good nutritive substrates for promoting the degradation of these composite systems.

## EXPERIMENTAL

### Materials

Chitosan was purchased from Seigakaku Corporation (Tokyo, Japan). PVA (degree of polymerization and saponification; 3500 and 88%, respectively), sorbitol and sucrose (analytically pure) were purchased from Wako Chemicals Industries Ltd (Japan).

### Preparation of films

Two separate solutions of PVA (2% w/w) in water and chitosan (2% w/w) in 2% acetic acid were prepared. Chitosan was dissolved by stirring at 50°C for 3 h. The solutions were filtered to remove any undissolved impurities using a vacuum flask and an aspirator. The PVA solutions were then added, under vigorous stirring and heating, to the chitosan solution and then the plasticizer was added and mixed to the solution for 10–15 min until dispersed.

Plexiglass plates with an enclosed framing area (30 cm × 30 cm) were levelled and cleaned. The solution was cast in a circular area in the central part of the

plates and then spread uniformly. Films were dried for approximately 48 h at ambient conditions and then placed in chambers at various relative humidities (21, 53 and 74%).

### Differential thermal analysis (DTA) measurements

DTA measurements were taken using a Shimadzu DTA equipped with a liquid N<sub>2</sub> 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 carried out with cyclohexane, dodecane and octane. Heat flow calibration was carried out 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  $T_g$ s were determined from the second run after melting, quenching with liquid nitrogen and reheating at a heating rate of 10°C/min. The percentage crystallinity with DTA was calculated according to the formula  $\%X_c = \Delta H / \Delta H_c$  where  $\Delta H$  is the measured heat of fusion in J g<sup>-1</sup> and  $\Delta H_c$  is the heat of fusion for the 100% crystalline polymer.

### Wide-angle X-ray diffraction pattern (WAXDP) measurements

Wide-angle X-ray diffraction pattern measurements of chitosan/PVA/plasticizer blends at various moisture contents were carried out using a Shimadzu (Japan) diffractometer from 5 to 40° (2 $\theta$ ). The crystallinity was determined as previously reported (Marsh, 1986).

### Dynamic electrical thermal analysis (DETA)

Measurements of dielectric constant,  $\epsilon'$ , and dielectric loss factor,  $\epsilon''$ , were carried out using DETA (TA Instruments DEA). The dielectric spectra were recorded at a frequency of 10 Hz over the temperature range from 45 to 250°C and the heating rate was 1°C min<sup>-1</sup>. All the measurements were carried out on cast films with dimensions of 30 × 30 × 0.1 mm using a ceramic parallel plate sensor under nitrogen atmosphere.

### Mechanical properties

#### *Tensile strength and percentage elongation*

Tensile strength and percentage elongation were measured on testing strips, after their equilibration at various relative humidities, using an Instron Universal Testing Instrument (model 1122) operated according to ASTM, 1989 (D828-88). Measurement conditions and

calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis *et al.*, 1994).

### CO<sub>2</sub> sorption apparatus

Both equilibrium sorption and kinetic sorption experiments were carried out using the gravimetric method described elsewhere (Patel & Manley, 1995). The measurements were taken with a Sartorius (Germany) electrobalance (1  $\mu$ g sensitivity) properly enclosed in a glass chamber with connections through a vacuum line to a CO<sub>2</sub> cylinder, a mercury pressure gauge and a Pirani/Penning vacuum gauge. Constant pressure throughout the sorption experiments on polymers was maintained by adding a 12 L glass reservoir to the vacuum system. Polymer samples of known weight (700–950 mg) were suspended in a light aluminum pan by thin glass fibers close to the lower end of a 20 cm tube hanging down. In order to prevent any build-up of static charges in the tube, a radioactive material (500  $\mu$ C PO210) was used. The entire system, comprising the electrobalance and the vacuum system, was enclosed in a thermostated chamber (25 $\pm$ 0.5°C). In the early stages of the experiment the system was fully evacuated by using the liquid nitrogen trap and continuously pumping at a pressure < 10<sup>-3</sup> mm Hg in order to degas the sample and remove any volatile material. The evacuation continued until constant weight was maintained and then the system, apart from the electrobalance, was charged with CO<sub>2</sub> (completely free from water) to various pressures. The sorption process started when CO<sub>2</sub> entered the electrobalance chamber. The sample mass was continuously recorded with an IBM PC. The initially recorded linear increase of sample mass versus square time was finally levelled off to a plateau value that corresponded to the equilibrium sorption levels.

### Fourier transform infrared (FT-IR) analysis

The FT-IR spectra were recorded with a spectrometer (Nicolet, model 710 FT-IR) connected to a PC (Nicolet) and Colour Pro plotter (Fujitsu, model FPG 315-101). The samples were recorded as films since they were soluble in 2% acetic acid aqueous solution.

## RESULTS AND DISCUSSION

### Thermal (DTA) and dynamic electrical thermal (DETA) properties

The low molecular weight compounds added to chitosan/PVA blends are shown to lower the melting point and the glass transition ( $T_g$ ) of chitosan/PVA blends (Table 1, Fig. 1). Despite the presumed atactic

nature of PVA, especially when coming from PVAc as in this case, WAXDP showed that PVA has a high percentage crystallinity ( $x_c \sim 54\%$ , Fig. 2). The observed reduction in percentage crystallinity in chitosan/PVA blends could be due to crystallization disturbance of chitosan in the blend state (Miya *et al.*, 1984). In fact, it was previously shown (with FT-IR and WAXDP) that the crystalline character of PVA is not affected by the chitosan presence (Miya *et al.*, 1984). Therefore, the observed drop in crystallization should be attributed to the dilution of PVA in chitosan. No phase separation was observed in the plasticized blend for up to 20% of plasticizer. Phase separation is not promoted because of the tendency of PVA to develop hydrogen bonds with water and with our plasticizers (sucrose, sorbitol) which have hydroxyl groups (Fig. 1).

In the DTA traces (Fig. 1) there is a hardly discernible step transition ( $T_g$ ) in the trace of pure chitosan while no melting point appears. In contrast, PVA gives very sharp and well-defined peaks. The chitosan/PVA blends show a slightly smaller endothermic peak (due to dilution of PVA with chitosan) gradually moving to lower temperatures at higher plasticizer contents.

In fact, since PVA consists of amorphous and crystalline regions, there are two types of interactions of water/polyol with PVA: the weak interaction, according to which the water molecule is simply linked to either the oxygen or hydrogen of PVA (Fig. 3a), and the strongly bound interaction, in which the water molecule acts like a bridge by being intercalated in the polymeric hydrogen of the auto-associated PVA (Fig. 3b). The validity of this suggestion is also confirmed by FT-IR analysis, which showed two absorbances at 3520 and 3180  $\text{cm}^{-1}$  (Fig. 4). The latter values are in satisfactory agreement with previously reported values for the PVA/poly(acrylic acid) blend with water (3500 and 3186  $\text{cm}^{-1}$ , respectively, Daniliuc & David, 1996). Furthermore, it is important to note that the presence of self-associated molecules such as water, sugar and PVA improves the cohesion of the chitosan/PVA blend. As in the case of alcohols, the increase in the strength of interactions is in the following order: free (monomeric) OH < dimeric OH < polymeric OH.

The  $\alpha$ -transition ( $T_g$ ) observed by DETA falls approximately in the same region for the two homopolymers (75 and 65°C for PVA and chitosan, respectively). In fact, the  $\alpha$ -transition of chitosan is so broad that it overlaps any other peak in that region (Fig. 5). The  $\tan\delta$  values from DETA (Fig. 5) show an apparent broadening of glass transition regions, suggesting heterogeneity, possibly due to the coexistence of some chitosan-rich and PVA-rich region, similar to chitosan/polyamide (Ratto *et al.*, 1996).

There has been a long debate concerning the assignment of molecular motions and relaxation

Table 1. Melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), glass transition temperature ( $T_g$ ), heat of fusion ( $\Delta H_f$ ) and heat of crystallization ( $\Delta H_c$ ) of chitosan/PVA blends<sup>a</sup> measured by DTA

Chitosan	PVA	Sorbitol	Water	$T_m$ (°C)	$\Delta H_f^b$ (J g <sup>-1</sup> )	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_f^b$ (J g <sup>-1</sup> )	$T_c$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )
45.0	45.0	5	5	198.3±1.8	87.8±4.2	59.3±2.2	196.7±2.3	71.9±5.9	167.8±2.5	59.8±6.7
42.5	42.5	10	5	160.9±1.2	78.4±5.3	31.5±1.9	157.8±1.9	58.1±5.4	134.5±1.8	51.0±5.9
40.0	40.0	15	5	118.7±1.3	63.1±5.4	-2.3±1.8	117.0±1.8	46.8±3.8	92.6±1.4	41.8±5.4
37.5	37.5	20	5	85.6±1.9	49.7±3.2	-18.9±1.6	84.2±1.6	33.9±6.3	64.0±1.7	33.9±3.3
32.5	32.5	30	5	53.4±2.1	34.7±3.6	-41.4±2.0	52.7±2.0	25.1±2.9	35.8±1.6	25.9±2.9
60.0	30.0	5	5	206.5±2.7	184.8±6.3	65.8±3.1	205.1±2.4	155.9±8.8	174.7±2.1	109.1±3.8
56.7	28.3	10	5	180.4±2.1	133.8±3.3	37.5±2.8	179.3±1.9	104.9±7.5	139.4±1.7	71.1±5.9
53.3	26.7	15	5	135.7±1.8	102.8±4.1	6.3±0.4	134.2±1.5	80.3±7.9	97.9±0.9	59.8±7.5
50.0	25.0	20	5	104.8±1.9	72.7±4.3	-12.4±1.1	103.3±1.2	54.3±8.4	73.4±1.3	46.8±5.9
43.3	21.7	30	5	79.0±0.8	50.6±3.8	-31.0±0.8	77.8±1.5	35.5±2.9	48.5±0.8	38.0±3.3

<sup>a</sup>For chitosan/PVA (2:1, w/w) there are no transitions ( $T_g$ ,  $T_m$ ,  $T_c$ ) or peaks ( $\Delta H_f$ ,  $\Delta H_c$ ), <sup>b</sup>first run and <sup>c</sup>second run.

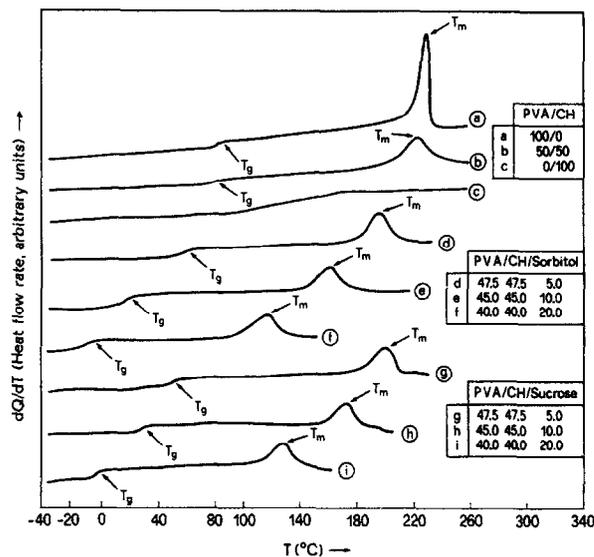


Fig. 1. DTA traces of chitosan/PVA blends obtained from second run.

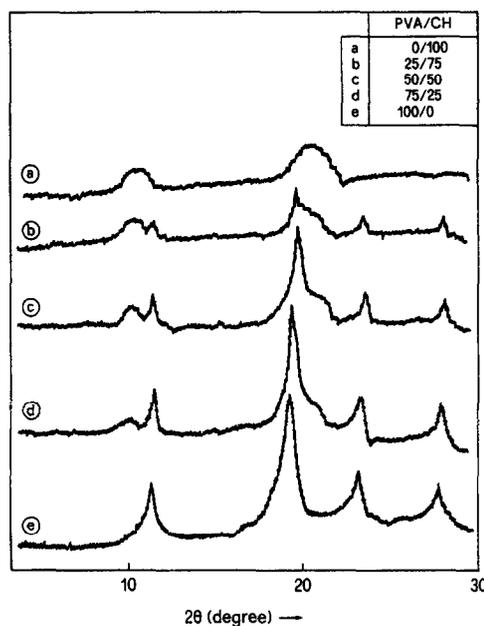


Fig. 2. Wide-angle X-ray diffraction patterns of chitosan/PVA blends.

behaviour understanding of chitosan in the solid state from neutralized solution (Kayim *et al.*, 1980; Ogura *et al.*, 1980; Ratto *et al.*, 1996). The transitions identified, using DMTA or DETA, vary within a wide range (90–140°C). It is generally accepted that there are three clear steps of thermal expansion that could be possibly attributed to breakdown of hydrogen bonds of varying stability. The  $\gamma$  peak (low temperature,  $\sim -100^\circ\text{C}$ ) is usually assigned to local motions of the polysaccharide. Next to the  $\gamma$  peak there is the  $\beta$  peak, which resembles a shoulder peak. This peak was found to depress the  $\gamma$  peak (Lee *et al.*, 1996). It was shown that the higher

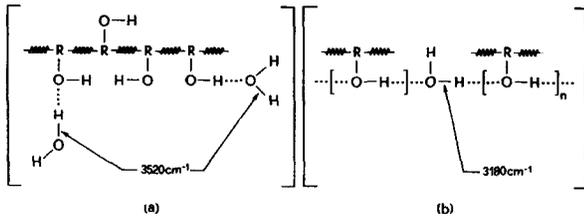


Fig. 3. (a) Amorphous PVA regions–water hydrogen bonds (weak interactions). (b) Intermediate PVA regions–water hydrogen bonds (strong interactions).

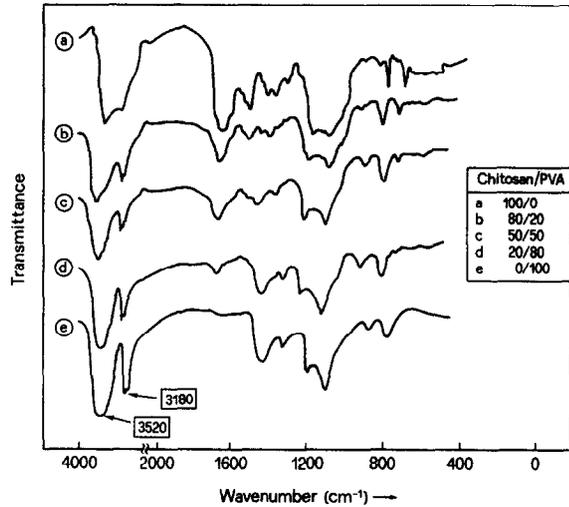


Fig. 4. FT-IR spectra of chitosan/PVA blends plasticized with 5% sorbitol.

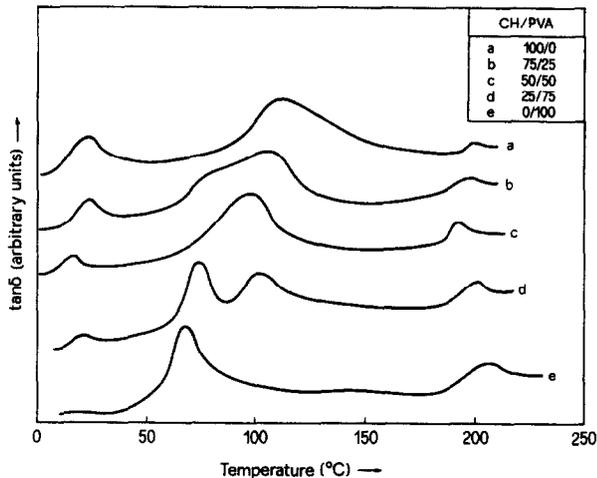


Fig. 5. DETA traces for plasticized chitosan/PVA blends.

the moisture or plasticizer content, the lower the transition temperature. Therefore, small amounts of water can have a favourable effect on the blend by strengthening the hydrogen bond network, thus hindering the gamma relaxation. On the other hand, above a certain amount of water (29% for PVA, Hodge, 1996), water–water bridges might initiate a certain loosening of the network and the  $\beta$  peak drops

to a lower temperature. In this study the DETA analysis was mainly focused on the two peaks, claimed to correspond to  $T_g$ , appearing at 85 and 110°C for PVA and chitosan, respectively. In fact, a comparison of  $T_g$ s determined from different techniques (DTA, DETA and gas permeability) was attempted. It can be seen from Table 2 that there is an apparent agreement among the  $T_g$  values determined using different techniques despite their inherent different principles.

### Mechanical properties

#### Tensile strength—percentage elongation

The data obtained from tensile strength, tensile modulus and percentage elongation for chitosan/PVA/H<sub>2</sub>O with or without polyols are summarized in Table 3. Since it is a two-component blend (chitosan/PVA), in order to calculate the tensile modulus it could be roughly treated as a composite material (Ashby & Jones, 1985):

$$E_{\text{blend}} = V_{\text{PVA}}E_{\text{PVA}} + (1 - V_{\text{PVA}})E_{\text{chitosan}} \quad (1)$$

$$E_{\text{blend}} = \frac{1}{\frac{V_{\text{PVA}}}{E_{\text{PVA}}} + \frac{1-V_{\text{PVA}}}{E_{\text{chitosan}}}} \quad (2)$$

By using  $E_{\text{PVA}} = 0.2 \text{ GPa}$  and  $E_{\text{chitosan}} = 1.2 \text{ GPa}$  for non-plasticized homopolymers, we get 0.7 GPa and 0.34 GPa from Eq. (1) and (2), respectively. Our experimental values ( $\sim 0.55 \text{ GPa}$ ) fall between these two extreme values. Property changes with composition are related to the degree of compatibility (Ahn *et al.*, 1990). In particular, the moduli of blends as a function of composition can also be expressed by the modified rule of mixtures (Nielsen, 1978):

$$E = w_1E_1 + w_2E_2 + \beta_{12}w_1w_2 \quad (3)$$

where  $E$  is the modulus of the blend,  $E_1$  and  $E_2$  are those of components, and  $w_1$  and  $w_2$  stand for the corresponding weight fractions.  $\beta_{12}$  is an empirical parameter usually calculated from Eq. (4):

$$\beta_{12} = 4E_{12} - 2E_1 - 2E_2 \quad (4)$$

By using 0.78 GPa and 0.1 GPa for plasticized (5% sorbitol) chitosan and PVA, respectively, we get  $\beta_{12} = -0.38$ . The calculated tensile modulus for PVA/chitosan (1:1) plasticized with 5% sucrose and 5% water is 345 MPa, which is in satisfactory agreement with the corresponding experimental value of 305 MPa (Table 3).

#### CO<sub>2</sub> equilibrium sorption

The gas permeability study was focused on CO<sub>2</sub> permeability because the latter has a very powerful inhibitory effect on bacterial and mould growth when present in concentrations higher than 20% (Smith, 1993).

Although several studies of gas sorption in

**Table 2. Glass transitions ( $T_g$ ) determined from DTA, DETA and gas permeability measurements**

PVA	Chitosan	Sorbitol	Water	DTA	DETA (tan $\delta$ )	O <sub>2</sub> permeability
45.0	45.0	5	5	59.3 $\pm$ 2.2	66.7 $\pm$ 1.9	63.5 $\pm$ 2.4
42.5	42.5	10	5	31.5 $\pm$ 1.9	36.8 $\pm$ 1.5	34.2 $\pm$ 1.9
40.0	40.0	15	5	-2.3 $\pm$ 0.2	4.2 $\pm$ 0.3	6.2 $\pm$ 0.5
37.5	37.5	20	5	-18.9 $\pm$ 0.3	-13.0 $\pm$ 0.8	ND
32.5	32.5	30	5	-41.4 $\pm$ 0.5	-36.5 $\pm$ 1.6	ND
PVA	Chitosan	Sucrose	Water			
45.0	45.0	5	5	65.0 $\pm$ 3.2	71.8 $\pm$ 2.0	68.7 $\pm$ 2.0
42.5	42.5	10	5	38.2 $\pm$ 1.9	47.3 $\pm$ 1.7	42.8 $\pm$ 2.1
40.0	40.0	15	5	8.1 $\pm$ 1.1	16.9 $\pm$ 1.2	13.5 $\pm$ 0.9
37.5	37.5	20	5	-10.2 $\pm$ 0.7	-1.2 $\pm$ 1.8	ND
32.5	32.5	30	5	-26.0 $\pm$ 1.2	-9.3 $\pm$ 2.1	ND

ND: not determined.

**Table 3. Tensile strength (TS, MPa), tensile modulus (TM, MPa) and percentage elongation (%E) of plasticized chitosan/PVA blends**

PVA	Chitosan	Sorbitol	Water	TS (MPa)	TM (MPa)	%E
45.0	45.0	5	5	58 $\pm$ 5	305 $\pm$ 20	26 $\pm$ 4
42.5	42.5	10	5	47 $\pm$ 3	270 $\pm$ 18	37 $\pm$ 5
40.0	40.0	15	5	35 $\pm$ 5	214 $\pm$ 15	45 $\pm$ 6
37.5	37.5	20	5	19 $\pm$ 2	135 $\pm$ 17	61 $\pm$ 7
32.5	32.5	30	5	10 $\pm$ 1	60 $\pm$ 8	75 $\pm$ 9
PVA	Chitosan	Sucrose	Water			
45.0	45.0	5	5	64 $\pm$ 7	346 $\pm$ 30	25 $\pm$ 2
42.5	42.5	10	5	55 $\pm$ 6	295 $\pm$ 180	30 $\pm$ 2
40.0	40.0	15	5	40 $\pm$ 5	250 $\pm$ 24	33 $\pm$ 3
37.5	37.5	20	5	28 $\pm$ 2	173 $\pm$ 13	37 $\pm$ 4
32.5	32.5	30	5	17 $\pm$ 3	97 $\pm$ 7	40 $\pm$ 3

polymers at temperatures below  $T_g$  showed that in many cases sorption isotherms rather deviate from Henry's law and their behaviour conforms satisfactorily to the dual mode sorption model (Patel & Manley, 1995), our experiments showed that Henry's law is applicable, at least at pressures up to 1.2 atm, where only the initial linear segment of the total isotherm is examined.

Since the gas sorption (CO<sub>2</sub> in our case) occurs only in the amorphous areas, it is essential to calculate the volume fraction of the amorphous phase ( $\alpha$ ) in the blends. The chitosan/PVA blend is semi-crystalline and very clearly defined melting peaks of PVA are detected at higher than 25% PVA content:

$$\alpha = 1 - \rho X_c / \rho_c \quad (5)$$

where  $\rho$  is the density of the blend,  $\rho_c$  is the 100% crystalline taken as 1.34 g cm<sup>-3</sup> and  $X_c$ , calculated from the determined value for 100% crystalline PVA, is 140.35 J g<sup>-1</sup>.

In a mixed amorphous phase system, volume additivity is assumed and the PVA amorphous phase volume fraction can be calculated as follows:

$$\phi_1 = \frac{V_{1a}}{V_{1a} + V_2} \quad (6)$$

where  $V_{1a}$  is the volume of the amorphous PVA and  $V_2$  is the volume of chitosan, both expressed per unit mass

of blend. Similarly, the chitosan amorphous phase volume fraction in the blend is calculated:

$$\phi_2 = \frac{V_2}{V_2 + V_{1a}} \quad (7)$$

Although chitosan is a semi-crystalline polymer according to the WAXDP, in terms of DSC/DTA chitosan is regarded as amorphous. Values of the specific volumes for amorphous PVA and chitosan were taken as 0.7874 cm<sup>3</sup> g<sup>-1</sup> (Patel & Manley, 1995) and 0.689 cm<sup>3</sup> g<sup>-1</sup> (Urbanczyk *et al.*, 1994; Rathke & Hudson, 1994). Table 4 summarizes the values of the parameters involved in the calculations from Eq. (5) and (6).

The equilibrium sorption isotherms for CO<sub>2</sub> in PVA, chitosan and PVA/chitosan (50/50) are linear and are shown in Fig. 6. The 50/50 (PVA/chitosan) blend isotherms lie between the two polymer components. This linear behaviour can be expressed in terms of Henry's law:

$$C = K_D p \quad (8)$$

where  $C$  is the equilibrium concentration of the penetrant,  $p$  stands for the penetrant pressure at equilibrium and  $k_D$  is the Henry's law constant in cm<sup>3</sup> (STP)/cm<sup>3</sup> (polymer). The Henry's law constants were obtained from the slope of the straight lines (sorption isotherms vs. pressure) shown in Fig. 6. The calculated

**Table 4. Thermal ( $\Delta H_f$  = heat of fusion,  $x_c$  = percentage crystallinity) and volumetric ( $\alpha$  = volume of amorphous area,  $\phi_1$  = amorphous phase fraction of PVA) properties of chitosan/PVA blends**

Wt % PVA	$\Delta H_f(\text{J g}^{-1})$	$x_c$	$\rho$ ( $\text{g cm}^{-3}$ )	$\alpha$	$\phi_1$
100	81.9	0.578	1.307	0.436	1
75	46.0	0.324	1.3096	0.683	0.662
50	28.0	0.198	1.3122	0.806	0.385
25	0	0	1.3147	1	0.257
0	0	0	1.3173	1	0

values for sorption parameters of chitosan/PVA blends are summarized in Table 5.

In the case of a miscible blend, by applying the ternary solution theory, the blend solubility coefficient can be analyzed in terms of its polymer components:

$$\ln k_D = \phi_1 \ln k_{D1} + \phi_2 \ln k_{D2} + (BV_3/RT)\phi_1\phi_2 \quad (9)$$

where  $R$  is the universal gas constant,  $B$  is the interaction energy density,  $V_3$  stands for the molar volume of the penetrant molecules and the subscripts 1 and 2 indicate the two components.

If  $B=0$  the relation between  $\ln k_D$  and blend composition is linear. By taking  $V_3=55 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{CO}_2$  (Patel & Manley, 1995), non-linear regression analysis of the data gives  $B=-18.81 \text{ J cm}^{-3}$ , which is in satisfactory agreement with previous published work (Patel & Manley, 1995). If we apply the experimental values of  $k_D$  for chitosan and PVA ( $0.1810$  and  $0.4250 \text{ cm}^3 \text{ (STP)/(cm}^3 \text{ Pa)}$ , respectively) to Eq. (9) the theoretically calculated values are derived (given in Table 5), which agree reasonably well with our experimental ones.

### $\text{CO}_2$ transport

Solubility curves ( $C_t$ ) against  $t^{1/2}$  for chitosan/PVA 50/50 blend at various pressures up to 1.2 atm are given in Fig. 7. From these curves  $\text{CO}_2$  diffusion coefficients were calculated according to the short- and long-term solution of the corresponding diffusion Eq. (10) and (11). The former is valid for conditions  $C_t/C_e < 0.5$  (Eq. (10)) while the latter is valid for  $C_t/C_e > 0.5$  (Eq. (11)):

$$C_t/C_e = \frac{4}{l} \left( \frac{D_1 t}{\pi} \right)^{1/2} \quad (10)$$

where  $D_1$  stands for the diffusion coefficient and  $l$  is the sample thickness. The value of  $D_1$  was calculated from the slope  $[(4/l(D_1/\pi)^{1/2})]$  of the initial linear region of plots of  $C_t/C_e$  against  $t^{1/2}$  by applying Eq. (6), as shown in Fig. 7. The diffusion coefficient  $D_e$  was also calculated from the long-term solution of the diffusion coefficient:

$$\ln(1 - C_t/C_e) = \frac{D_e t}{l^2} \pi^2 \quad (11)$$

The plot of  $\ln(1 - C_t/C_e)$  vs.  $t$  also gives a straight line with a slope of  $\ln \pi^2 D_e / l^2$ . If the two calculated

diffusion coefficients  $D_1$  and  $D_e$  from Eq. (10) and (11) almost coincide then the gas diffusion in the polymer can be described as Fickian. The values of  $D_1$  and  $D_e$  for various pressures are given synoptically in Table 6. It is obvious from Table 6 that pressure (within an acceptable range, i.e. 0.2–1.2 atm) does not affect the diffusion coefficients. The significance of diffusion coefficients can be understood by taking into account the activated state theory for blends, according to which the diffusion for penetrant molecules in a miscible blend can be calculated by the following equation:

$$\ln D = \phi_1 \ln D_1 + \phi_2 \ln D_2 + (aRT - 1)(\Delta E_{12}/RT)\phi_1\phi_2 \quad (12)$$

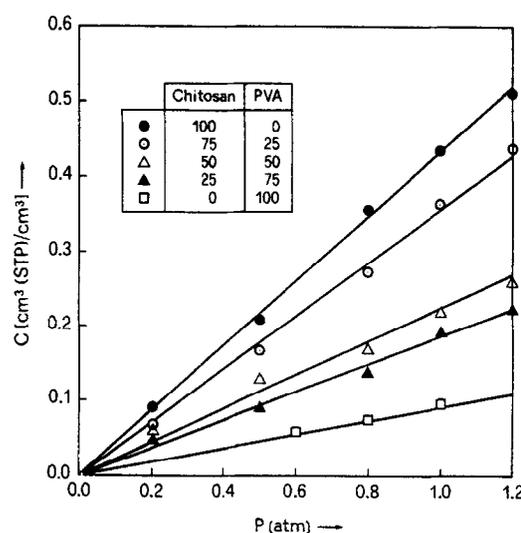
Equation (12) could result in a more simplified form by substituting  $aRT$  for  $-0.5$ :

$$\ln D = \phi_1 \ln D_1 + \phi_2 \ln D_2 - 0.5(\Delta E_{12}/RT)\phi_1\phi_2 \quad (13)$$

The calculated  $\Delta E$  values from Eq. (13) were within the range  $0.84$  to  $1.67 \text{ kJ mol}^{-1}$  depending on the pressure and blend composition.

### Semi-empirical calculation of diffusion coefficient

If a polymer specimen of known dimensions, already equilibrated at a relative humidity chamber, is exposed



**Fig. 6.** Equilibrium sorption isotherms for  $\text{CO}_2$  in chitosan/PVA blends.

Table 5. Experimentally determined and theoretically calculated (Eq. (9)) sorption parameters ( $k_D = \text{Henry's law coefficient}$ ) for CO<sub>2</sub> in chitosan/PVA blends at 25°C

Chitosan	PVA	$k_D$ (experimental)/(cm <sup>3</sup> (STP)/ (m <sup>3</sup> atm))	$k_D/\alpha$ (experimental)/(cm <sup>3</sup> (STP)/ (cm <sup>3</sup> atm))	$k_D$ (theoretical)/(cm <sup>3</sup> (STP)/ (cm <sup>3</sup> atm))	$k_D/\alpha$ (experimental)/(cm <sup>3</sup> (STP)/ (cm <sup>3</sup> Pa))
0	100	0.0789	0.1810	—	1.78
25	75	0.18180	0.2660	0.2131	2.61
50	50	0.2222	0.2757	0.2280	2.70
75	25	0.3500	0.3500	0.2871	3.43
100	0	0.2700	0.4250	—	4.17

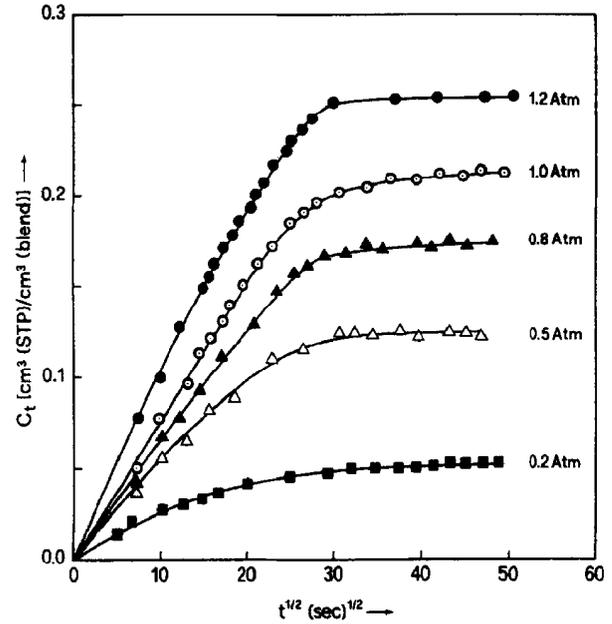


Fig. 7. Sorption rate curves for CO<sub>2</sub> in a 50/50 chitosan/PVA blend at various pressures. The various symbols indicate experimental values whereas the solid lines stand for semi-empirical values calculated from Eq. (12) using the average of  $D_1$  and  $D_e$ .

to standard gas pressure (penetrant), the sample weight increases with time and follows Fickian kinetics. The change in the reduced mass of the sample as a function of time is given by the following equation (Fukuda, 1996; Perrin *et al.*, 1996):

$$\frac{C_t}{C_e} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D\pi^2 t (2n+1)^2}{l^2}\right] \quad (14)$$

where  $C_t$  stands for the total amount of the diffusing substance entering a flat sheet at time  $t$ ,  $C_e$  is the corresponding quantity at equilibrium,  $D$  is the diffusion coefficient (cm<sup>2</sup>s<sup>-1</sup>),  $l$  is the film thickness (cm) and  $t$  is the time (s).

It must be pointed out that Eq. (14) is only valid when the gas or water vapour penetrates unidirectionally in the polymer with a constant diffusion coefficient from the plane surfaces. Since our samples are very thin films (30 μm, i.e. less than 1/100 of their width), penetrant sorption by the edges is considered negligible, in comparison to the plane surfaces, and should not be taken into account in our calculations.

On many occasions the diffusion can occur locally at various rates because of the plasticization effect due to increased mobility in polymer segments either with local penetrant (i.e. CO<sub>2</sub>) or with incorporated plasticizers.

The fitting of experimental sorption kinetics is carried out using the Fickian equation known as the concentration-dependent diffusion coefficient. The selection of the appropriate concentration-dependent

**Table 6. Results of CO<sub>2</sub> sorption experiments for chitosan/PVA systems at 25°C**

Chitosan	PVA	Pressure (atm)	C <sub>e</sub> (cm <sup>3</sup> of CO <sub>2</sub> /cm <sup>3</sup> of blends) <sup>a</sup>	10 <sup>9</sup> D <sub>1</sub> (cm <sup>2</sup> s <sup>-1</sup> ) <sup>b</sup>	10 <sup>9</sup> D <sub>e</sub> (cm <sup>2</sup> /s <sup>-1</sup> ) <sup>c</sup>	10 <sup>15</sup> P <sub>1</sub> ((cm <sup>3</sup> cm)/(cm <sup>2</sup> s Pa)) <sup>d</sup>	10 <sup>15</sup> P <sub>e</sub> ((cm <sup>3</sup> cm)/(cm <sup>2</sup> s Pa)) <sup>d</sup>
0	100	0.6	0.059	2.52	2.80	4.49	4.98
		0.8	0.072	2.57	2.74	4.58	4.88
		1.0	0.095	2.78	2.95	4.95	5.25
25	75	0.2	0.047	2.60	2.67	6.79	6.97
		0.5	0.090	2.70	2.93	7.05	7.65
		0.8	0.138	2.81	3.00	7.33	7.83
		1.0	0.190	2.75	2.95	7.18	7.70
		1.2	0.222	2.78	3.03	7.26	7.91
50	50	0.2	0.054	3.42	3.35	9.23	9.05
		0.5	0.125	3.10	3.14	8.37	8.48
		0.8	0.162	3.01	3.05	8.13	8.24
		1.0	0.216	2.85	3.23	7.70	8.72
		1.2	0.253	2.30	2.58	6.21	6.97
75	25	0.2	0.068	3.60	3.40	12.35	11.66
		0.5	0.170	3.72	3.90	12.76	13.38
		0.8	0.270	3.55	4.05	12.18	13.89
		1.0	0.360	3.80	4.34	13.03	14.89
		1.2	0.435	3.90	4.50	13.38	15.44
100	0	0.2	0.090	4.15	4.29	17.30	17.89
		0.5	0.210	4.30	4.61	17.93	19.22
		0.8	0.350	4.20	4.45	17.51	18.56
		1.0	0.430	4.25	4.54	17.72	18.93
		1.2	0.510	4.40	4.75	18.35	19.81

<sup>a</sup>C<sub>e</sub>: calculated from figures C<sub>t</sub> vs. t<sub>1/2</sub> (respective figures to Fig. 7). <sup>b</sup>D<sub>1</sub>: diffusion coefficient calculated from Eq. (10). <sup>c</sup>D<sub>e</sub>: diffusion coefficient calculated from Eq. (11). <sup>d</sup>P<sub>1</sub>, P<sub>e</sub>: permeability coefficients calculated from Eq. (15) using D<sub>1</sub> and D<sub>e</sub>, respectively.

diffusion law can only be made by a trial and error procedure and only a posteriori can the selection be judged as correct or not. The standard procedure is to test first the Fickian law with a constant value for the diffusion coefficient. Since the values of D<sub>1</sub> and D<sub>e</sub> obtained from Eq. (10) and (11) are very close (Table 6), their average is used in Eq. (14). The Gauss-Newton curve-fitting method (using values up to 30 for *n* in Eq. (14)) was used for the fitting of the entire curve. Satisfactory fitting quality (as shown in Figs 7 and 8 by comparing the calculated and the experimental curves) was obtained when *n* ≥ 7.

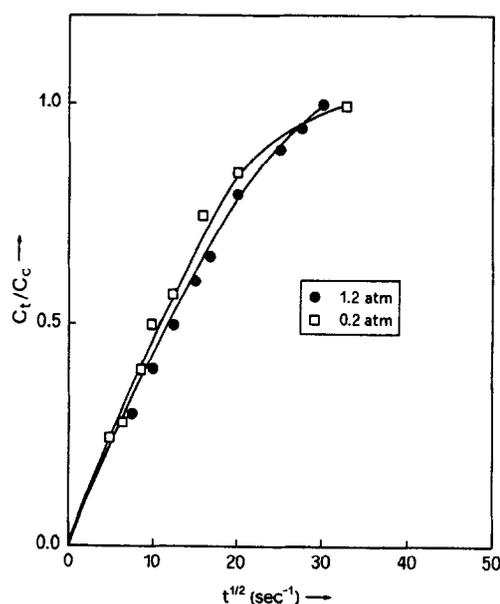
### Permeability coefficient

The permeability coefficient can be estimated using the solubility and diffusion as follows:

$$P = Dk_D \quad (15)$$

Although the permeability coefficients of glassy polymers usually decrease with pressure, in our experiments a similar trend was not observed for PVA/chitosan blends (Patel & Manley, 1995). The calculated CO<sub>2</sub> permeability coefficients for chitosan/PVA blends were in satisfactory agreement with the values reported elsewhere for PVA (Okayama & Ikari, 1992) whereas the values for chitosan were higher by two orders of magnitude than those reported for dry samples (Muzzarelli, 1977; Butler *et al.*, 1996). The observed

differences in O<sub>2</sub> permeability could be attributed to the plasticization of our chitosan films after their conditioning in the relative humidity (RH) chamber (53%) whereas the measurements reported in the literature refer to dry chitosan (0% RH).



**Fig. 8.** Sorption curves ( $C_t/C_\infty$ ) for chitosan/PVA blends versus time. Solid line curves were drawn according to Eq. (14) for Fickian diffusion.

## CONCLUSIONS

The  $T_g$ s of chitosan/PVA blends, plasticized with sugars and water, determined from DTA, DETA and permeability measurements were found to be in reasonable agreement. The tensile strength decreased proportionally to the plasticizer content whereas the percentage elongation increased considerably, particularly in the case of sorbitol. The carbon dioxide sorption curves were shown to obey the Fickian equation. The low levels of CO<sub>2</sub> should probably be attributed to the high level of hydrogen bonding in the plasticized and non-plasticized blends. From the semi-empirical equations lower values were obtained, compared to the actual values, for CO<sub>2</sub> sorption and diffusivity, possibly because of strong intermolecular interactions. CO<sub>2</sub> diffusivity was studied because of its strong and effective bacteriostatic action toward preventing microbial growth. The CO<sub>2</sub> transport results for PVA/chitosan blends are expected to be of interest to food packaging companies (e.g. the bakery industry) where a gas mixture of CO<sub>2</sub>/N<sub>2</sub> is used. The ratio of this mixture should not be altered, otherwise the package might collapse.

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