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

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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_2 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_2 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 smalll 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), β-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_2 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_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 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_gs 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 ΔH is the measured heat of fusion in $J\,g^{-1}$ and ΔH_c is the heat of fusion for the 100% crystaline 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° (2θ). The crystallinity was determined as previously reported (Marsh, 1986).

Dynamic electrical thermal analysis (DETA)

Measurements of dielectric constant, ε', and dielectric loss factor, ε'', 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 $1°C\,min^{-1}$. 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_2 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 μg sensitivity) properly enclosed in a glass chamber with connections through a vacuum line to a CO_2 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 μC PO210) was used. The entire system, comprising the electrobalance and the vacuum system, was enclosed in a thermostated chamber (25±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 $<10^{-3}$ 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_2 (completely free from water) to various pressures. The sorption process started when CO_2 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 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 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 α-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 α-transition of chitosan is so broad that it overlaps any other peak in that region (Fig. 5). The tanδ 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 (ΔH_f) and heat of crystallization (ΔH_c) of chitosan/PVA blends[a] measured by DTA

Chitosan	PVA	Sorbitol	Water	T_m (°C)	ΔH_f^b (J g^{-1})	T_g (°C)	T_m (°C)	ΔH_f^c (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
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

[a] For chitosan/PVA (2:1, w/w) there are no transitions (T_g, T_m, T_c) or peaks (ΔH_f, ΔH_c), [b] first run and [c] second run.

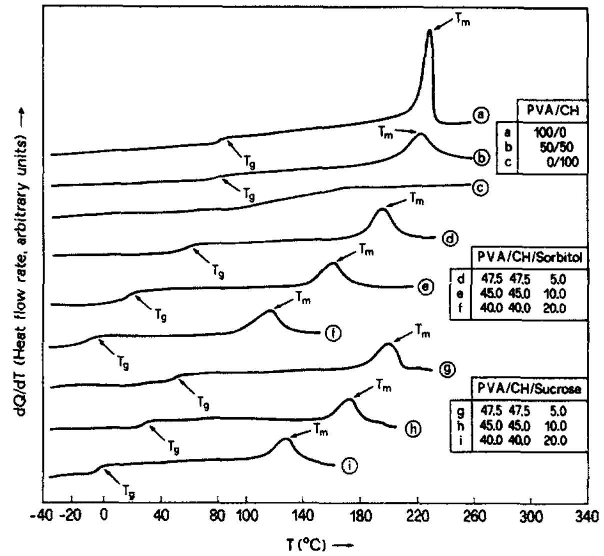

Fig. 1. DTA traces of chitosan/PVA blends obtained from second run.

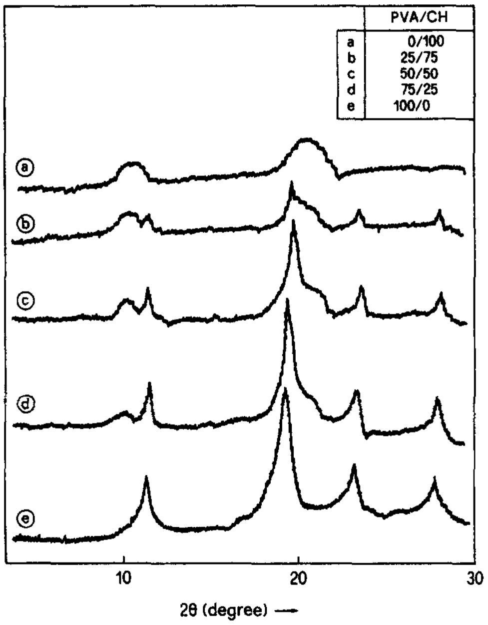

Fig. 2. Wide-angle X-ray diffraction patterns of chitosan/PVA blends.

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 γ peak (low temperature, ~−100°C) is usually assigned to local motions of the polysaccharide. Next to the γ peak there is the β peak, which resembles a shoulder peak. This peak was found to depress the γ peak (Lee *et al.*, 1996). It was shown that the higher

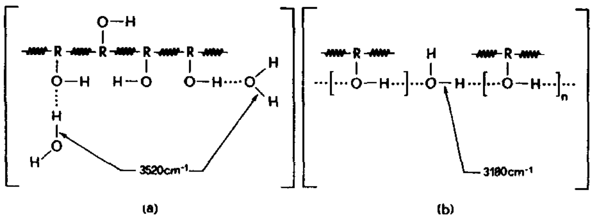

Fig. 3. (a) Amorphous PVA regions–water hydrogen bonds (weak interactions). (b) Intermediate PVA regions–water hydrogen bonds (strong interactions).

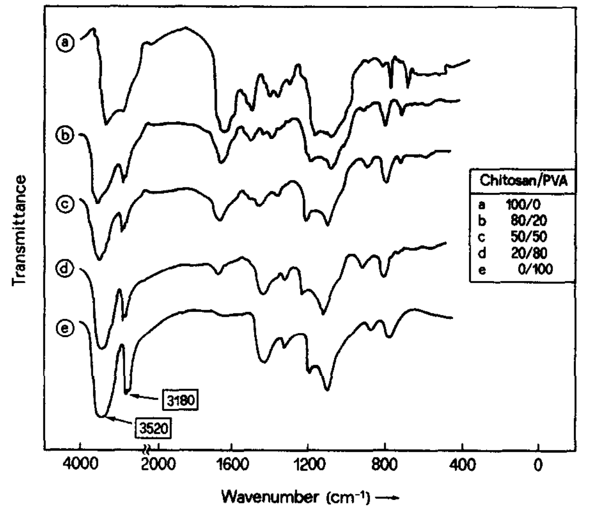

Fig. 4. FT-IR spectra of chitosan/PVA blends plasticized with 5% sorbitol.

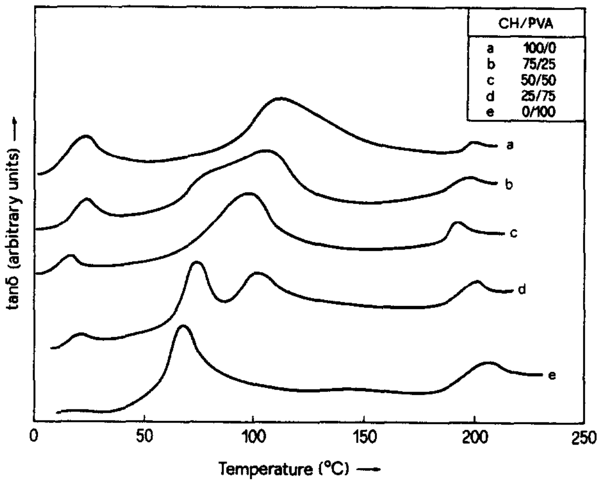

Fig. 5. DETA traces for plasticized chitosan/PVA blends.

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 β 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_gs 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_2O 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):

$$E_{\mathrm{blend}} = V_{\mathrm{PVA}}E_{\mathrm{PVA}} + (1 - V_{\mathrm{PVA}})E_{\mathrm{chitosan}} \tag{1}$$

$$E_{\mathrm{blend}} = \frac{1}{\frac{V_{\mathrm{PVA}}}{E_{\mathrm{PVA}}} + \frac{1-V_{\mathrm{PVA}}}{E_{\mathrm{chitosan}}}} \tag{2}$$

By using $E_{\mathrm{PVA}} = 0.2\,\mathrm{GPa}$ and $E_{\mathrm{chitosan}} = 1.2\,\mathrm{GPa}$ for non-plasticized homopolymers, we get 0.7 GPa and 0.34 GPa from Eq. (1) and (2), respectively. Our experimental values (~0.55 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):

$$E = w_1E_1 + w_2E_2 + \beta_{12}w_1w_2 \tag{3}$$

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. β_{12} is an empirical parameter usually calculated from Eq. (4):

$$\beta_{12} = 4E_{12} - 2E_1 - 2E_2 \tag{4}$$

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_2 equilibrium sorption

The gas permeability study was focused on CO_2 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_gs) determined from DTA, DETA and gas permeability measurements

PVA	Chitosan	Sorbitol	Water	DTA	DETA (tanδ)	O_2 permeability
45.0	45.0	5	5	59.3±2.2	66.7±1.9	63.5±2.4
42.5	42.5	10	5	31.5±1.9	36.8±1.5	34.2±1.9
40.0	40.0	15	5	−2.3±0.2	4.2±0.3	6.2±0.5
37.5	37.5	20	5	−18.9±0.3	−13.0±0.8	ND
32.5	32.5	30	5	−41.4±0.5	−36.5±1.6	ND
PVA	Chitosan	Sucrose	Water			
45.0	45.0	5	5	65.0±3.2	71.8±2.0	68.7±2.0
42.5	42.5	10	5	38.2±1.9	47.3±1.7	42.8±2.1
40.0	40.0	15	5	8.1±1.1	16.9±1.2	13.5±0.9
37.5	37.5	20	5	−10.2±0.7	−1.2±1.8	ND
32.5	32.5	30	5	−26.0±1.2	−9.3±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±5	305±20	26±4
42.5	42.5	10	5	47±3	270±18	37±5
40.0	40.0	15	5	35±5	214±15	45±6
37.5	37.5	20	5	19±2	135±17	61±7
32.5	32.5	30	5	10±1	60±8	75±9
PVA	Chitosan	Sucrose	Water			
45.0	45.0	5	5	64±7	346±30	25±2
42.5	42.5	10	5	55±6	295±180	30±2
40.0	40.0	15	5	40±5	250±24	33±3
37.5	37.5	20	5	28±2	173±13	37±4
32.5	32.5	30	5	17±3	97±7	40±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_2 in our case) occurs only in the amorphous areas, it is essential to calculate the volume fraction of the amorphous phase (α) 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:

$$\alpha = 1 - \rho X_c/\rho_c \tag{5}$$

where ρ is the density of the blend, ρ_c is the 100% crystalline taken as 1.34 g cm^{-3} and X_c, calculated from the determined value for 100% crystalline PVA, is 140.35 J g^{-1}.

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

$$\phi_1 = \frac{V_{1a}}{V_{1a} + V_2} \tag{6}$$

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:

$$\phi_2 = \frac{V_2}{V_2 + V_{1a}} \tag{7}$$

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^3 g^{-1} (Patel & Manley, 1995) and 0.689 cm^3 g^{-1} (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_2 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:

$$C = K_D p \tag{8}$$

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^3 (STP)/cm^3 (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 (ΔH_f = heat of fusion, x_C = percentage crystallinity) and volumetric (α = volume of amorphous area, ϕ_1 = amorphous phase fraction of PVA) properties of chitosan/PVA blends**

Wt % PVA	ΔH_f(J g^{-1})	x_c	p (g cm^{-3})	α	ϕ_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:

$$\ln k_D = \varphi_1 \ln k_{D1} + \varphi_2 \ln k_{D2} + (BV_3/RT)\varphi_1\varphi_2 \qquad (9)$$

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 $V_3 = 55\,\mathrm{cm^3\,mol^{-1}}$ for CO_2 (Patel & Manley, 1995), non-linear regression analysis of the data gives $B = -18.81\,\mathrm{J\,cm^{-3}}$, 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 cm^3 (STP)/(cm^3 Pa), respectively) to Eq. (9) the theoretically calculated values are derived (given in Table 5), which agree reasonably well with our experimental ones.

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 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)):

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

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:

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

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 presures 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:

$$\ln D = \varphi_1 \ln D_1 + \varphi_2 \ln D_2 + (aRT - 1)(\Delta E_{12}/RT)\varphi_1\varphi_2 \qquad (12)$$

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

$$\ln D = \varphi_1 \ln D_1 + \varphi_2 \ln D_2 - 0.5(\Delta E_{12}/RT)\varphi_1\varphi_2 \qquad (13)$$

The calculated ΔE values from Eq. (13) were within the range 0.84 to 1.67 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

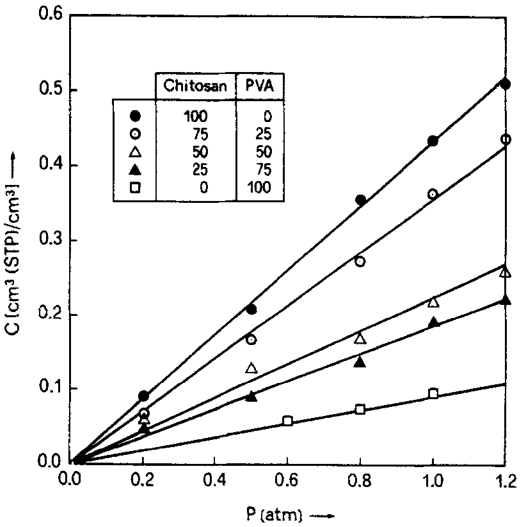

Fig. 6. Equilibrium sorption isotherms for CO_2 in chitosan/PVA blends.

Table 5. Experimentally determined and theoretically calculated (Eq. (9)) sorption parameters (k_D = Henry's law coefficient) for CO_2 in chitosan/PVA blends at 25°C

Chitosan	PVA	k_D (experimental)(cm^3(STP)/(m^3 atm))	k_D/α (experimental)(cm^3(STP)/(cm^3 atm))	k_D (theoretical)(cm^3(STP)/(cm^3 atm))	k_D/α (experimental)10^{-6} cm^3 (STP)/(cm^3 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

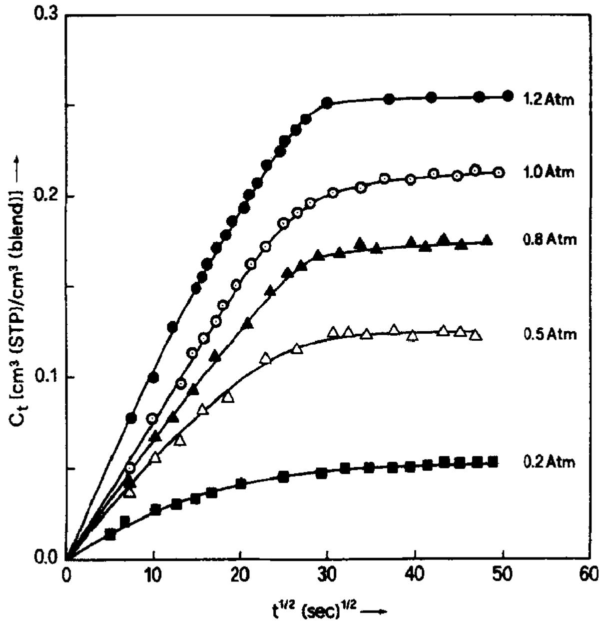

Fig. 7. Sorption rate curves for CO_2 in a 50/50 chitosan/PVA blend at various pressures. The various symbols indicate experimental values whereas the solid lines stand for semi-empirical values calculated from Eq. (12) using the average of D_l and D_e.

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):

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

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^2 s^{-1}), 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_2) 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_2 sorption experiments for chitosan/PVA systems at 25°C

Chitosan	PVA	Pressure (atm)	C_e (cm^3 of CO_2/cm^3 of blends)[a]	10^9 D_l(cm^2 s^{-1})[b]	10^9 D_e(cm^2/s^{-1})[c]	10^{15} P_l((cm^3 cm)/(cm^2 s Pa))[d]	10^{15} P_e((cm^3 cm)/(cm^2 s Pa))[d]
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

[a] C_e: calculated from figures C_t vs. $t_{1/2}$ (respective figures to Fig. 7).[b] D_l: diffusion coefficient calculated from Eq. (10).[c] D_e: diffusion coefficient calculated from Eq. (11).[d] P_l, P_e: permeability coefficients calculated from Eq. (15) using D_l and D_e, 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_l and D_e 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 $n \geq 7$.

Permeability coefficient

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

$$P = Dk_D \tag{15}$$

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_2 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_2 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).

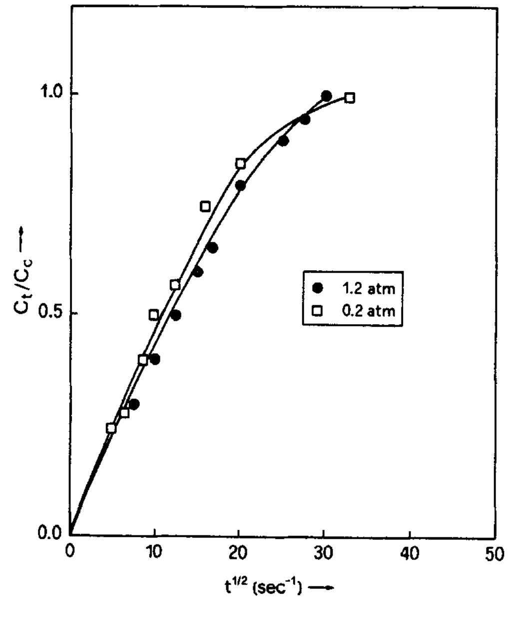

Fig. 8. Sorption curves (C_t/C_∞) for chitosan/PVA blends versus time. Solid line curves were drawn according to Eq. (14) for Fickian diffusion.

CONCLUSIONS

The T_gs 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_2 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_2 sorption and diffusivity, possibly because of strong intermolecular interactions. CO_2 diffusivity was studied because of its strong and effective bacteriostatic action toward preventing microbial growth. The CO_2 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_2/N_2 is used. The ratio of this mixture should not be altered, otherwise the package might collapse.

REFERENCES

Ahn, T.O., Kim, C.K., Kim, B.K., Jeong, H.M. and Huh, J.D. (1990) Binary blends of nylons with ethylene vinyl alcohol copolymers: morphological, thermal, rheological and mechanical behaviour. *Polym. Engng Sci.* **30**, 341–349.

Aiba, S., Izume, M., Minoura, N. and Fujiwara, Y. (1986) Chitosan based membranes for separation processes, In *Chitin in Nature and Technology*, ed. R.A.A. Muzzarelli, C. Jeuniaux & G.M. Gooday, pp. 396–398. Plenum Press, New York.

Arvanitoyannis, I., Kalichevsky, M.T., Blanshard, J.M.V. and Psomiadou, E. (1994) Study of diffusion and permeation of gases in undrawn and uniaxially drawn films made from potato and rice starch conditioned at different relative humidities. *Carbohydr. Polym.* **24**, 1–15.

Arvanitoyannis, I., Psomiadou, E. and Nakayama, A. (1996) Edible films made from sodium caseinate, starches, sugars or glycerol, Part 1. *Carbohydr. Polym.* **31**, 179–192.

Ashby, M.F. & Jones, D.R.H. (1985) *Engineering Materials*, pp. 59–61. Pergamon Press, New York.

ASTM (1989) *Annual Book of ASTM standards, D828-88, Mechanical Properties: Tensile Strength and Elongation.* American Society for Testing and Materials, Philadelphia.

Azuma, Y., Yoshie, N., Sakurai, M., Inoue, Y. and Chujo, R. (1992) Thermal behaviour and miscibility of poly(3-hydroxybutyrate)/poly(vinyl alcohol) blends. *Polymer* **33**, 4763–4767.

Blair, H.S., Guthrie, J., Law, T.-K. and Turkington, P. (1987) Chitosan and modified chitosan membranes. I. Preparation and characterization. *J. Appl. Polym. Sci.* **33**, 641–656.

Butler, B.L., Vergano, P.J., Testin, R.F., Bunn, J.M. and Wiles, J.L. (1996) Mechanical and barrier properties of edible chitosan films as affected by composition and storage. *J. Food Sci.* **61**, 953–961.

Daniliuc, L. and David, C. (1996) Intermolecular interactions in blends of poly(vinyl alcohol) with poly(acrylic acid): 2. Correlation between the states of sorbed water and the interactions in homopolymers and their blends. *Polymer* **37**, 5219–5227.

El Ghaouth, A., Arul, J., Ponnamplalan, R. and Boulet, M. (1991) Chitosan coating effect on storability and quality of fresh strawberries. *J. Food Sci.* **56**, 1618–1624.

Fukuda, M. (1996) Diffusion of moisture in poly(p-phenylene terephthalamide) film: analysis by the adsorption-controlled diffusion equation. *Polym. Engng Sci.* **36**, 558–567.

Furda, I. and Brine, C.J. (1990) *New Developments in Dietary Fiber*. Plenum, New York.

Hasegawa, M., Isogai, A., Onabe, F. and Usuda, M. (1992) Dissolving states of cellulose and chitosan in trifluoroacetic acid. *J. Appl. Polym. Sci.* **45**, 1857–1863.

Hasegawa, M., Isogai, A., Onabe, F., Usuda, M. and Atalla, R.J. (1992) Characterization of cellulose–chitosan blend films. *J. Appl. Polym. Sci.* **45**, 1873–1879.

Hasegawa, M., Isogai, A., Kuga, S. and Onabe, F. (1994) Preparation of cellulose–chitosan blend film using chloral/dimethylformamide. *Polymer* **35**, 983–987.

Hodge, R.M., Bastow, T.J., Edward, G.H., Simon, G.P. and Hill, A.J. (1996a) Free volume and the mechanism of plasticization in water swollen poly(vinyl alcohol). *Macromolecules* **29**, 8137–8143.

Hodge, R.M., Edward, G.H. and Simon, G.P. (1996b) Water absorption and states of semicrystalline poly(vinyl alcohol) films. *Polymer* **37**, 1371–1376.

Ishikura, S. (1993) Chitin and chitosan. *Gekkan Fudo Kemikaru* **9**, 62–64.

Kayim, I., Ozolinya, G. and Plisko, Y.. *(1980) Polym. Sci. USSR* **22**, 171–180.

Kim, J.H., Kim, J.Y., Lee, Y.M. and Kim, K.Y. (1992) Properties and swelling characteristics of cross-linked poly(vinyl alcohol)/chitosan blend membrane. *J. Appl. Polym. Sci.* **45**, 1711–1717.

Lee, Y.M., Kim, S.H. and Kim, S.J. (1996) Preparation and characteristics of β-chitin and poly (vinylalcohol) blend. *Polymer*, **37**, 5897–5905.

Marsh, R.D.L. (1986) A study of the wheat starch systems using X-ray diffraction. Ph.D. thesis, University of Nottingham.

Miya, M., Iwamoto, R. and Mima, S. (1983) Highly acetylated chitosan and its properties. *J. Appl. Polym. Sci.* **28**, 1909–1917.

Miya, M., Iwamoto, R. and Mima, S. (1984) FT-IR study of intermolecular interactions in polymer blends. *J. Polym. Sci.: Polym. Phys. Ed.* **22**, 1149–1151.

Muzzarelli, R.A.A. (1977) *Chitin*. Pergamon Press, Oxford.

Muzzarelli, R.A.A. (1996) Chitosan-based dietary foods. *Carbohydr. Polym.* **29**, 309–316.

Nakatsuka, S. and Andrady, A.L. (1992) Permeability of vitamin B-12 in chitosan membranes. Effect of crosslinking and blending with poly(vinyl alcohol) on permeability. *J. Appl. Polym. Sci.* **44**, 17–28.

Nielsen, L.E. (1978) *Predicting the Properties of Mixtures*, Chapter 2. Marcel Dekker, New York.

Ogura, K., Kanamoto, T., Itoh, M., Miyashiro, H. and Tanaka, K.. *(1980) Polym. Bull.* **2**, 303–310.

Okayama, T. and Ikari, K. (1992) Ethylene–vinyl alcohol copolymers. In *Poly(vinylalcohol) Developments*, ed. C.A. Finch. John Wiley & Sons, New York.

Okuda, H. (1995) Blood pressure control and role of chitosan. *Gekkan Fudo Kemikaru* **11**, 33–38.

Patel, K. and Manley, R.S.J. (1995) Carbon dioxide sorption and transport in miscible cellulose/poly(vinyl alcohol) blends. *Macromolecules* **28**, 5793–5798.

Perrin, L., Nguyen, Q.T., Clement, R. and Neel, J. (1996) Sorption and diffusion of solvent vapours in poly(vinyl alcohol) membranes of different crystallinity degrees. *Polym. Int.* **39,** 251–260.

Psomiadou, E., Arvanitoyannis, I. and Yamamoto, N. (1996) Edible films made from natural resources: microcrystalline cellulose (MCC), methylcellulose (MC) and corn starch and polyols—Part 2. *Carbohydr. Polym.* **31,** 193–204.

Quarashi, M.T., Blair, H.S. and Allen, S.J. (1992) Studies on modified chitosan membranes. II. Dialysis of low molecular weight metabolites. *J. Appl. Polym. Sci.* **46,** 263–269.

Rathke, T.D. and Hudson, S.M. (1994) Review of chitin and chitosan as fiber and film formers. *J.M.S.—Rev. Macromol. Chem. Phys.* **C34,** 375–437.

Ratto, J.A., Chen, C.C. and Blumstein, R.B. (1996) Phase behaviour of chitosan/polyamide blends. *J. Appl. Polym. Sci.* **59,** 1451–1461.

Smith, J.P. (1993) Bakery products. In *Principles and Applications of Modified Atmosphere Packaging of Food*, ed. R.T. Parry, pp. 134–169. Blackie Academic & Professional, London.

Tanigami, T., Shirai, Y., Yamaura, K. and Matsuzawa, S. (1994) Blends between two types of poly(vinyl alcohol)s with different syndiotacticities. *Polymer* **35,** 1970–1976.

Tanigami, T., Yano, K., Yamaura, K. and Matsuzawa, S. (1995) Anomalous swelling of poly(vinyl alcohol) film in mixed solvents of dimethylsulfoxide and water. *Polymer* **36,** 2941–2946.

Urbanczyk, G., Jeziorny, W., Urbaniak-Domagala, W., Wrzosek, H., Dorau, K. and Sztajnert, E. (1994) Macro- and microstructure of chitosan and butylchitin filaments and their basic properties. In *Chitin-World, Proceedings of the 6th International Conference On Chitin and Chitosan 1994*, ed. Z.S. Karnicki, A. Wojtasz-Pajak, M.M. Brzeski & P.J. Bykowski, pp. 175–182. Wirtschaftsverlag Neue Wissenschaft GmbH, Bremerhaven, Germany.

Wong, D.W.S., Gastineau, F.A., Gregorski, K.S., Tillin, S.J. and Pavlath, A.E. (1992) Chitosan lipid films: microstructure and surface energy. *J. Agric. Food Chem.* **40,** 540–544.

Yao, K.D., Liu, J., Cheng, G.X., Lu, X.D., Tu, H.L. and da Silva, J.A.L. (1996) Swelling behaviour of pectin/chitosan complex films. *J. Appl. Polym. Sci.* **60,** 279–283.

Zikakis, J.P. (ed.) (1984) *Chitin, Chitosan and Related Enzymes*. Academic Press, Orlando, Florida.