

Studies on Modified Chitosan Membranes. I. Preparation and Characterization

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SYNOPSIS

Chitin was isolated from prawn shells, and chitosan was prepared from it. The degree of *N*-deacetylation and the molecular weight were determined using IR spectroscopy and viscometry, respectively. A series of different modified chitosan membranes were prepared by blending with polyvinylpyrrolidone (PVP). These membranes were characterized by various techniques, including differential scanning calorimetry (DSC), wide-angle X-ray diffractometry (WAXD), and tensile testing. The physical, thermal, and mechanical properties were evaluated, and the change in these properties upon the addition of PVP into the blends has been discussed in terms of the amorphous and hydrophilic nature of PVP. Hydrophilicity of the blends increases due to the presence of PVP in the chitosan substrate. This helps in breaking the hydrogen bonds in between chitosan molecules and causes the blends to swell in three dimensions.

INTRODUCTION

Chitosan is an aminopolysaccharide and is derived from chitin: a principal structural component of animals and plants belonging to lower phyla. It is made up of D-glucosamine units, linked by β (1 \rightarrow 4) bonds. Generally, chitin is obtained from crustaceans or mollusks, and chitosan is prepared from its *N*-deacetylation. The amount of chitin compared with total dry weight of the animal is highest in crustaceans, mainly *Decapods* (60–70% chitin contents). The distribution and metabolism of chitin in animals and plants is not quantified, but it is considered that glycogen is the precursor of this biomaterial. Like chitin, chitosan is a white, nontoxic, odorless, and biodegradable substance. Because of its highly crystalline structure, chitosan is insoluble in common organic solvents, acids, and alkalies. However, it dissolves readily in weak inorganic acids in a wide range of concentrations, at ambient temperature; because of salt formation.^{1–3}

Owing to a high molecular weight (ca. 1×10^7 g/mol), chitosan forms viscous solutions in acetic and formic acids that can be used to cast membranes. Its membrane-forming properties have been investigated by several workers.^{4–6} When compared with synthetic polymers and some polysaccharides, chitosan can be blended with synthetic polymers to yield products whose physical and chemical properties have potential applications.^{7,8}

In the present study, chitosan was prepared from chitin and was blended with PVP. The cast membranes are characterized by their physical, thermal, and mechanical properties.

EXPERIMENTAL

Materials

Shells from the tail portions of the prawn (*Nephros norvegicus*) were obtained from a local seafood company in Northern Ireland and used as raw material. All the chemicals used were GPR grade, used as supplied, and obtained from BDH and Aldrich Chemical Cos. The thicknesses of all the membranes under investigation, unless mentioned, were kept

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between 22 and 25 μm (measured by digital micrometer RS Stock No. 601-906).

Preparation of Chitin Derived from Prawn Shells

Prior to the chemical treatments, prawn shells were washed, rinsed thoroughly, dried overnight at 60°C, and reduced in a hammer mill to a particle size of 970 μm .

For demineralization, the prawn flakes were treated with 1.25M HCl for 1 h, at a ratio of 4.25 kg/24 dm³ acid. The spent liquor was decanted and the prawn flakes were washed with water until neutral.

To deproteinize, approximately 1 kg of flakes was soaked in 3 wt % NaOH (3 dm³) in a 5 dm³ resin kettle. The mixture was heated to between 90 and 100°C with constant stirring for 0.5 h; the brown layer of NaOH was decanted and the flakes were washed with water. The above procedure was repeated twice with the same amount of caustic soda. The solid material left in the kettle was chitin.

Conversion of Chitin into Chitosan

Chitin flakes were deacetylated using 50 wt % NaOH at a ratio of 1 kg/10 dm³ in a resin kettle at 110°C for 1 h. The NaOH layer was decanted and the flakes were washed with water until neutral. This procedure was repeated twice with the same amount of caustic soda. The resulting chitosan flakes were washed with water and dried in an oven at 60°C for 1 week.

Characterization

A film of chitosan was cast for determining the degree of *N*-deacetylation. Chitosan (0.7 g) was dissolved in 1 wt % acetic acid (100 dm³). The solution was stirred overnight and later filtered through a sintered glass crucible before spreading onto a glass plate. The film was left for drying for 72 h at room temperature and later neutralized with NaOH (1 wt %) for 15 min. After neutralization, the film could easily be removed and rinsed with distilled water and dried in air at room temperature and stored over P₂O₅ in a desiccator. The IR spectrum was recorded with a double-beam Perkin-Elmer IR spectrophotometer, Model 398. The percent *N*-deacetylation of chitosan was determined by the base-line method as explained by Roberts and Domsey,⁹ using the relationship

$$\% N\text{-deacetylation} = (1 - A_{1655}/A_{3340} \times 1/1.33) \times 100 \quad (1)$$

where A is the logarithmic ratio of the absorbance and transmittance at the given wavenumber.

To determine viscosity average molecular weight (\bar{M}_v) of chitosan, a known concentration of the biopolymer was prepared using sodium chloride (0.2M) and acetic acid (0.1M) as the solvent system. The measurements were made at 25°C in a modified Ubbelohde viscometer tube fitted with a porosity 2 sintered glass filter. Flow times were recorded as an average of three runs. \bar{M}_v was calculated from the relationship

$$[\eta] = K_m \bar{M}_v^a \quad (2)$$

where $K_m = 1.8 \times 10^{-3} \text{ cm}^3/\text{g}$, $a = 0.93$, and $[\eta]$ = limiting viscosity number.¹⁰

Preparation of Membranes

Modified chitosan membranes were prepared from chitosan-PVP blends. An aqueous solution of PVP (concn 2.5 wt %, \bar{M}_w 700,000) was prepared and mixed with chitosan solutions (0.7 wt % in 1 wt % acetic acid) in appropriate volumes. The blended solutions were slowly stirred at room temperature for 24 h, filtered, and left overnight to release effervescence and spread onto a clean dry glass plate in a dust-free atmosphere at room temperature (19–22°C) and left to dry for a period of 72 h. The dried membranes were neutralized by immersing into a sodium hydroxide solution (1 wt %) for 15 min. After the alkaline treatment, the membranes were removed easily from the glass plate, rinsed, and left in distilled water (1 dm³) overnight. After drying in air, chitosan-PVP membranes were stored over P₂O₅ in a desiccator.

Chitosan membranes were prepared from 0.7 wt % solution in 1 wt % acetic acid, and a similar procedure was adopted as described above.

Density

Densities of the membranes were determined using a flotation method at 25°C. Carbon tetrachloride (density 1.623 g/cm³) and *n*-heptane (density 0.683 g/cm³) were used as solvents. Replicate measurements were made and the density of the membranes were reported as an average.

Water Contents

To determine the amount of water absorbed, the membranes were soaked in distilled water for 48 h at 37°C and later weighed by gently removing sur-

face water with a tissue paper. Weighing was continued until a constant weight achieved. Drying of the membranes was carried out at 60°C for 48 h in an oven under reduced pressure. Later, dried membranes were weighed and water contents were calculated using the formula

$$\text{Water contents (\%)} = (W_w - W_d/W_w) \times 100 \quad (3)$$

where W_d and W_w were the dry and wet weights of the membrane, respectively. To obtain reproducible results, three samples of a known area of the membrane were used for each measurement.

Mechanical Properties

Ultimate tensile strengths and percent elongations-at-break of chitosan and chitosan-PVP membranes were measured on an Instron Tensile Tester, Model 1102, at room temperature (17–19°C) and 40–46% relative humidity (measured by a digital hygrometer, Solomat LIS-355). A strain rate of 10 cm/min was selected. The tensile testing was continued until 10 similar samples gave reproducible stress-strain curves. The percent elongations-at-break (% EB) and ultimate tensile strengths (in MN/m²) were calculated using the following relationships

$$\% \text{ EB} = (L/L_0) \times 100 \quad (4)$$

where L_0 = original length of the sample and L = difference in the length at breaking point:

$$\text{Ultimate tensile strength} = \text{breaking load}/A \quad (5)$$

where A = cross-sectional area of the sample (i.e., thickness \times width).

Differential Scanning Calorimetry (DSC)

To study thermal properties, small pieces of the dried membranes (2–3 mm², 2–3 mg) were used. The samples were studied by a Perkin-Elmer DSC 7 linked with a thermal analysis controller/personal computer TAC 7/PC and a graphic plotter GSA 7. The DSC unit had been precalibrated with indium for the entire working range. The baseline was obtained using empty aluminum pans. A sample of the membrane was encapsulated in a pan and a lid was crimped onto it to maximize the contact between sample and the pan. A heating rate of 10°C/min and a temperature range of 40–450°C were selected for scanning in the N₂ gas atmosphere (flow rate: 40 cm³/min). The enthalpy change (ΔH), from 85

to 295°C, along with decomposition temperatures and maxima of thermograms were evaluated through the integrator in the DSC unit.

Wide-Angle X-Ray Diffractometry (WAXD)

The wide-angle X-ray diffractograms were recorded at room temperature using a Philips diffractometer, Model PW4620, with a goniometer PW4630 and recorder PM800. The X-ray source was Ni-filtered CuK α radiation (50 kV, 24 mA). The dried membranes of uniform thicknesses were mounted on the aluminum frames and scanned from 5 to 30° 2θ at a speed of 2° 2θ /min and a chart speed of 2 cm/min.

To measure percent relative crystallinity of chitosan and its modified membranes, an amorphous curve was constructed beneath the crystalline scatter,¹¹ and the areas of amorphous and crystalline peaks were measured using a “cut and weigh” method. The percent relative crystallinities were calculated from the following relationship:

$$\% \text{ Relative crystallinity} = (A_c/A_c + A_a) \times 100 \quad (6)$$

where A_c and A_a are the areas of crystalline and amorphous peaks, respectively. Triplicate runs were made on each sample to reduce the effects of air scattering, sample moisture, incoherent radiation, and sample absorption on the diffractograms.

RESULTS AND DISCUSSION

Preliminary Evaluation

All the membranes prepared in this work were transparent and colorless and showed no microbial or fungal growth upon storage in water or the dry state. During and after the preparation, chitosan-PVP membranes showed no sign of phase separation or precipitation. In the dry state, blended membranes were tough and flexible. But after soaking in water, they became softer; like chitosan membrane.

The degree of *N*-deacetylation of chitosan was 89.7%, and the molecular weight was 1.2×10^6 g/mol.

Crystallinity

The diffractogram of chitosan membrane consists of three major crystalline peaks at 10.2, 14.5, and 17.5° and a weak absorption band at 20° (Fig. 1). The blends of chitosan and PVP do not show much variation in the positions of the peaks, apart from

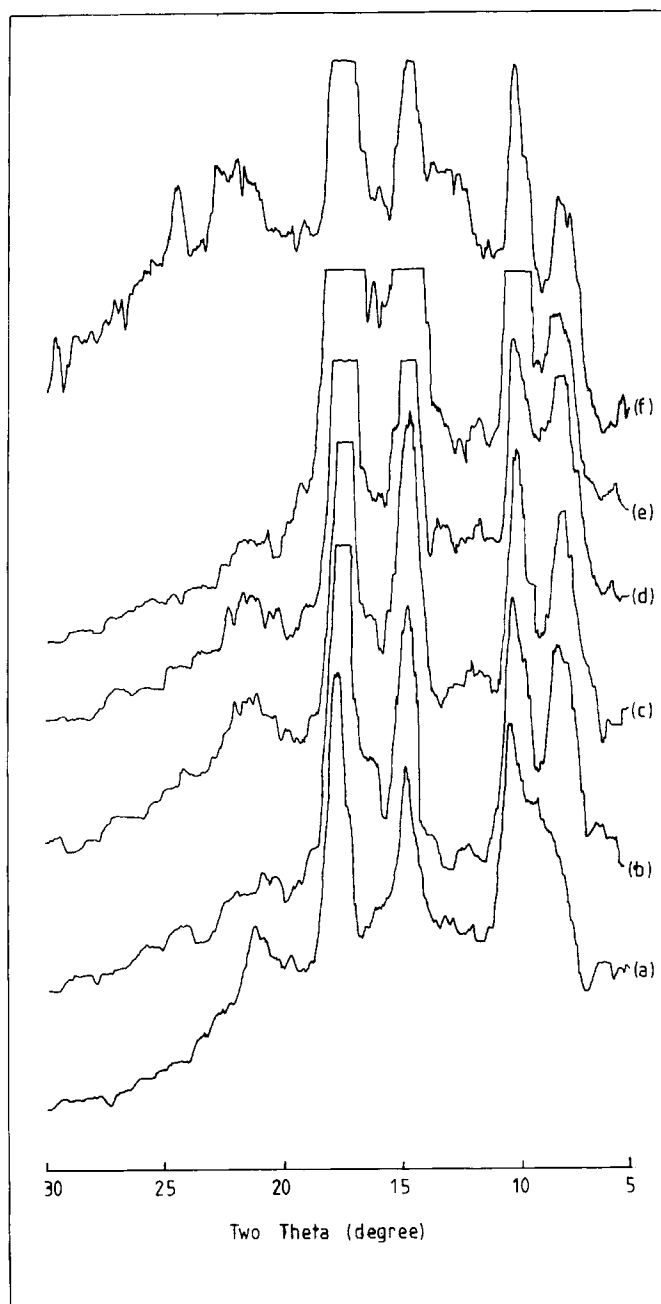


Figure 1 Wide-angle X-ray diffractograms of chitosan-PVP membranes (wt/wt): (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80; (f) 0/100.

the crystalline peak at 10.2° that splits into two absorption bands, viz. 7 and 10° . Generally, the intensities of crystalline peaks increase as the contents of PVP in the blends is increased. Diffractograms of PVP show a similar formation, but some additional peaks can be seen at higher 2θ values.

The percent relative crystallinities calculated from the ratio of crystalline and amorphous peaks are presented in Table I and compared with density

measurements. The crystallinities of chitosan-PVP blends decrease as the amount of PVP increases. PVP has the lowest crystallinity and density. The blend of 80/20 wt/wt[†] shows slightly higher crystallinity than chitosan but its corresponding density remains low. It could be due to the formation of the

[†] In this paper, the percentage of chitosan in the blends is always given first.

Table I Physical and Thermal Properties of Chitosan and Chitosan–PVP Membranes

Sample No.	Membrane Composition (wt/wt)	Density (g/cm ³) at 25°C ^a	Percent Relative Crystallinity ^b	Enthalpy Change (ΔH) ^c (cal/g)	Decomposition Temperature (°C)
1	Chitosan (100/0)	1.4245	52.87	164.61	142.47
2	Chitosan–PVP (80/20)	1.3157	55.25	169.46	239.60
3	(60/40)	1.3637	49.08	162.66	151.71
4	(40/60)	1.3401	52.80	229.59	142.73
5	(20/80)	1.2700	48.78	109.05	159.92
6	PVP (100/0)	0.9393	33.63	172.80	149.39

^a Standard error \pm 0.00020.

^b Standard error \pm 2.13.

^c Calculated from 85 to 295°C.

crystalline regions upon the addition of PVP, which are only detectable by X-rays. Furthermore, diffractograms indicate that it is the ratio of the crystalline and the amorphous areas that is important in determining crystallinity of the blends and not the height of the peaks.

Thermal Properties

The normalized DSC thermograms of chitosan and its blends are shown in Figure 2 and the values of enthalpy change and decomposition temperatures are summarized in Table I. The nature of thermograms of blends do not indicate separation of PVP at any temperature. The major thermal process takes place from 85 to 295°C with the loss of water between 60 and 70°C. All the samples decompose by giving out heat, showing exothermic decomposition with negative values of ΔH . No major change is observed in thermograms of chitosan–PVP above 300°C. The decomposition temperature of chitosan (142.47°C) is lower than the reported value, which could be due to a higher degree of *N*-deacetylation and a lower molecular weight.¹²

As the amount of PVP in the blends is raised, decomposition temperatures shift toward higher values. This suggests that the blends in the dry state are made up of stiff polymer chains and their stiffness increases as the amount of PVP in the blends is increased. The addition of PVP in chitosan membrane facilitates intermolecular hydrogen bonding and binds the two biopolymer chains together, therefore further restricting chain mobility in the dry state. The values of ΔH indicate variations in crystallinities and molecular arrangements of the two polymers. The blends of 80/20 and 40/60 wt/wt show higher values of enthalpy change than does

the chitosan membrane, whereas the 20/80 and 60/40 wt/wt blends show lower values of ΔH than do chitosan and PVP membranes. These variations are consistent with the percent relative crystallinities estimated from the X-ray diffraction measurements, but do not agree with the density values that show almost a continuous decline in the values as PVP contents in the blends are increased. Finally, the thermograms of PVP resemble an amorphous polymer, but the decomposition temperatures and the ΔH values are higher than expected. This could be due to the restricted chain mobility and extensively cross-linked structure formation in the PVP membrane during the desolvation process. Thermal properties of chitosan–PVP blends indicate that in the dry state different ratios of PVP help the blends to acquire different structural arrangements and chain conformations. This is also reflected in inconsistent enthalpy changes.

Mechanical Properties

The typical stress–strain curves of chitosan and chitosan–PVP membranes are shown in Figure 3. These curves resemble those of tough and brittle polymers. The effect of membrane composition on percent elongations-at-break and ultimate tensile strengths are shown in Figures 4 and 5. The tensile strengths and percent elongations-at-break decrease as the amount of PVP in the blends is increased. The highest value of tensile strength occurs with the chitosan membrane (10.58 MN/m²) and the lowest for 20/80 wt/wt blend (0.47 MN/m²). A 93% loss in the tensile strength is observed when the amount of PVP in the blend is increased from 20 to 80%. This loss is accompanied by a 37% decrease in the percent elongation-at-break. The de-

cline of tensile strengths in the blends is due to the presence of amorphous and hydrophilic PVP. Figure 6 indicates that the strength of the blends is inversely proportional to the water contents, due to similar reasons given above.

Water Contents

Figure 7 shows that the water contents of chitosan-PVP blends increase as the amount of PVP is raised. The blend of 80/20 wt/wt shows an overall improvement of 76% with respect to the chitosan membrane that has the lowest value. The improvement in water absorption capacity of the blends could be related to the amorphous and hydrophilic nature of PVP.

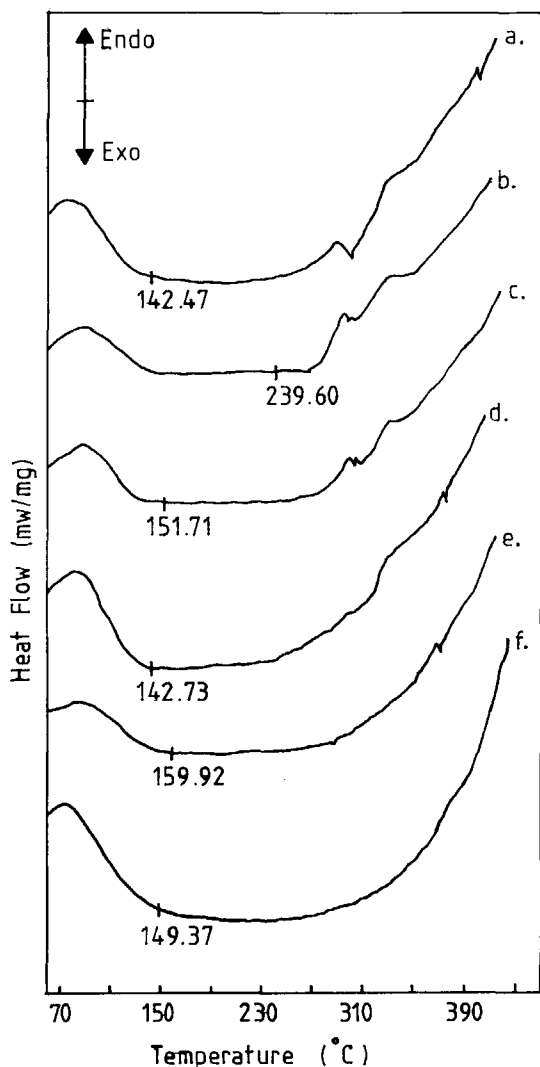


Figure 2 Normalized DSC thermograms of chitosan-PVP membranes (wt/wt): (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80; (f) 0/100.

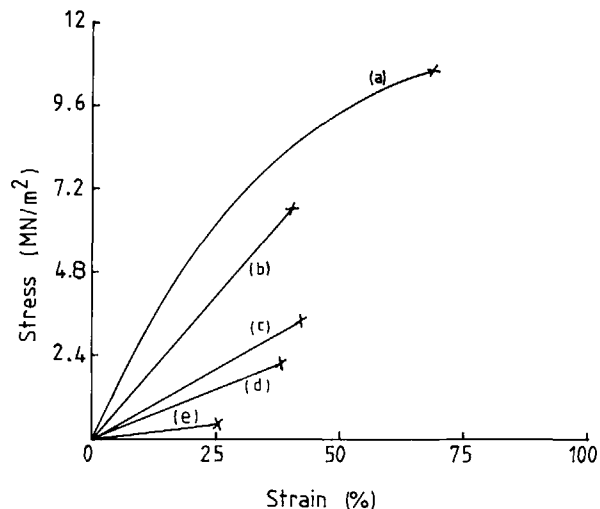


Figure 3 Typical stress-strain curves obtained for chitosan-PVP membranes (wt/wt): (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80.

CONCLUSIONS

The chitosan and blended membranes were transparent and colorless, and did not show any microbial or fungal growth upon storage. The blends appeared

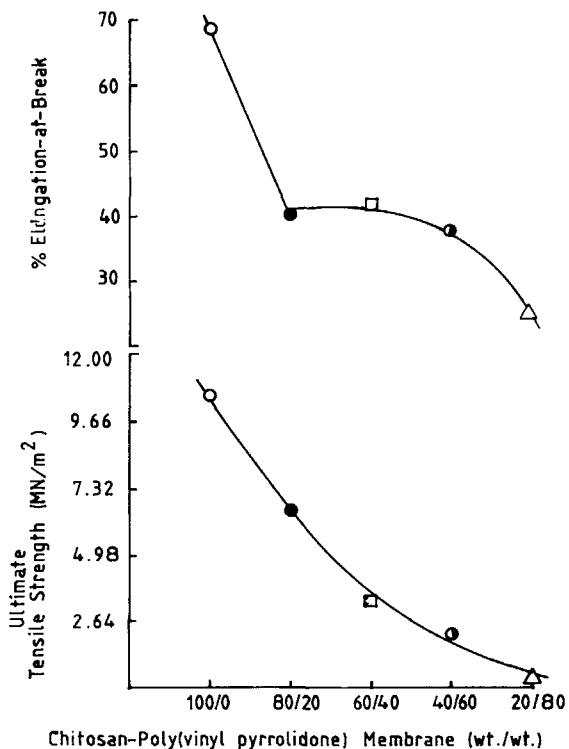


Figure 4 Effect of membrane composition on the mechanical properties.

tough and flexible in the dried state, but softened when soaked in water. Modified membranes have superior water absorption capacities to those of chitosan. The tensile strength of chitosan is higher than that of any other studied membrane, but has a lower percent elongation-at-break, exhibiting a brittle character due to a highly crystalline structure. The stress-strain curves of the blends resembled tough and brittle polymers. Their density, percent relative crystallinities, tensile strengths, and percent elongations-at-break were found to be decreased when the amount of PVP in the blends was raised, due to the amorphous nature of the added polymer. The decomposition temperature of chitosan was lower than the reported value because of a high degree of *N*-deacetylation and a lower molecular weight. The blended membranes appeared thermally stable and did not show phase separation upon heating. The decomposition temperatures and the enthalpy-change values indicated that in the dried state each membrane differs in its crystalline morphology. The 80/20 and 40/60 wt/wt blends appear more crystalline in nature, which could be due to the onset of crystallization, in the presence of PVP, during the desolvation process.

The improvement in water-absorption properties appears to be related to the presence of hydrophilic and amorphous PVP that breaks the weak intermolecular forces and hydrogen bondings by positioning itself in between chitosan molecules. This causes a three-dimensional change in the structure of the blends after coming in contact with an aqueous environment.

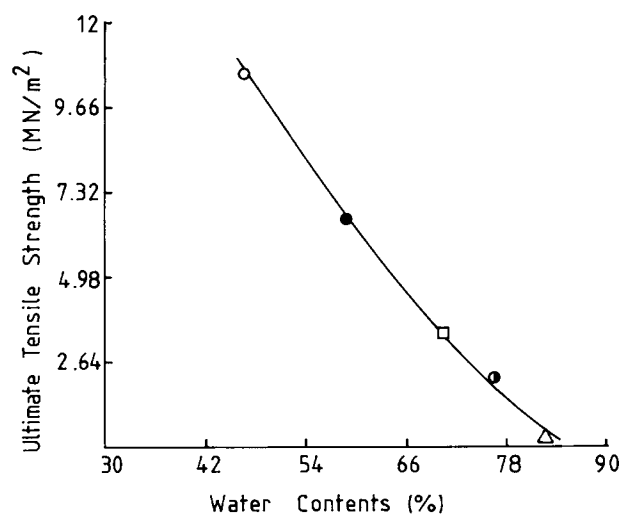


Figure 5 Dependence of tensile strength on the water contents of chitosan-PVP membranes (wt/wt): (○) 100/0; (●) 80/20; (□) 60/40; (●) 40/60; (△) 20/80.

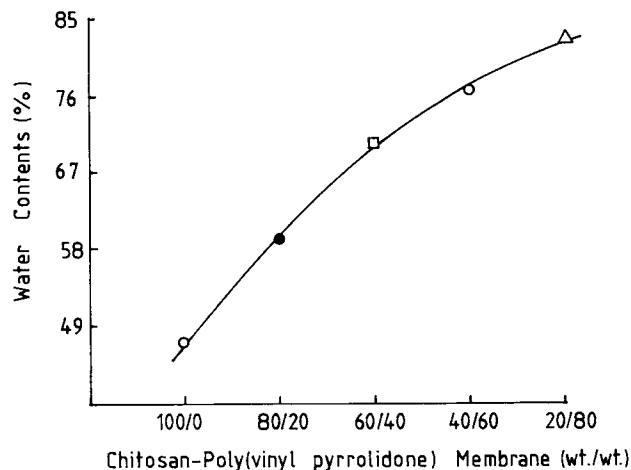


Figure 6 Water contents of modified chitosan membranes.

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