Chitosan and Modified Chitosan Membranes I. Preparation and Characterisation

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Synopsis

Chitosan has been prepared from prawn shell and crab shell chitin. The molecular weight of the material derived from prawn shells is higher than that obtained from crab shell. The molecular weight, tensile strength, elongation at the break, and hydrophilic properties of chitosan are extremely dependent on the degree of deacetylation achieved when chitin is hydrolyzed to chitosan. Graft copolymers have been prepared with chitosan and a series of vinyl monomers using both heterogeneous and homogeneous reaction conditions. The hydrophilic properties of chitosan can be modified by blending with poly(vinyl alcohol).

INTRODUCTION

The naturally occurring and very abundant polysaccharide chitin, consists mainly of β-(1-4)-2-acetamido-2-deoxy-D-glucose units, although during isolation some deacetylation may take place. It occurs widely in the exoskeletons of crustacea and insects and in the cell walls of some fungi and other microorganisms. The occurrence, isolation, and chemistry have been reviewed by Muzzarrelli.[1] The poly-(aminosaccharide) chitosan may be obtained from chitin by deacetylation using strong aqueous alkali, the degree of deacetylation depending on the severity of the treatment; some degradation generally occurs.[2] The degree of deacetylation is rarely greater than 30% unless special alkali fusion treatments are used.[3] Chitosan is soluble in dilute acids and strong films are readily prepared from these solutions. The present paper describes the preparation of chitosan membranes from the shells of prawns (nephrops norvegicus) and from crab shell chitin and an investigation of their properties.

EXPERIMENTAL

Chitosan was prepared from chitin derived from two sources, namely from prawn shells (PS) and crab shells obtained from Sigma Chemicals (SG). The crude prawn waste (10 g) was washed and dried as described previously,[4] and sieved to give a particle size range of 500–700 μm. The ground shells were treated with four successive portions of 3% sodium hydroxide solution at a liquor ratio of 6 : 1, and at a temperature of 70°C, with rinsing between each treatment. The first two treatments were for 15 min each, and the last two for

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30 min each. The treated mass was filtered, washed until neutral and dried at 80°C. The deproteinized shell was demineralized by two successive treatments with 1.25 *M* hydrochloric acid, each treatment for 30 minutes at room temperature at a liquor ratio of 10 : 1. The material was rinsed until free from acid and dried. The crab shell chitin was purchased from Sigma Chemical Company Ltd. and was used as supplied.

Preparation of Chitosan

Chitin flakes from both sources were treated with 50% w/w sodium hydroxide solution at 100°C, at a liquor ration of 10 : 1, for 30, 60, 120, 180, and 300 minutes, respectively; these were coded SG30, SG60, etc., PS30, PS60, etc., according to whether Sigma or prawn shell chitin was used, and to the time of treatment. A second series of samples was prepared by treatment of the chitin in a sealed container at 120°C, using the same alkali concentrations and times. After the alkali treatment the chitosan samples were washed until neutral, dried overnight at 80°, and extracted with acetone and then benzene to remove color. Chitosan films were made from a 2% chitosan solution in 1% acetic acid as previously described.[4]

Characterization of the Films

The acetyl content of the films was measured by the infrared spectroscopic technique described by Moore and Roberts.[5] The degree of deacetylation is given by,

$$\% \text{ Deacetylation} = \left(1 - \frac{A_{1655}}{A_{3450}} \times \frac{1}{1.33}\right) \times 100$$

where A_{1655} and A_{3450} are the absorbances at 1655 cm^{-1} and 3450 cm^{-1}, respectively. Since the internal infrared standard chosen is 3450 cm^{-1}, it is essential that the chitosan film is absolutely dry, and so the films were conditioned over phosphorus pentoxide. The results quoted are the average values for five samples. The thickness of the film sample is important and in all cases a film thickness giving a transmittance of 20–25% at 3450 cm^{-1} was used.

Molecular weight changes in the chitosan samples by various treatments were monitored by viscosity measurements in 2% acetic solution containing 0.8% sodium acetate. The measurements were made at 25°C in a modified Ubbelohde viscometer tube fitted with a porosity 2 sintered glass filter. Flow times were reproducible to within 0.2 seconds.

Molecular weights were calculated from the relationship

$$\log[\eta] = \log k + a \log M$$

where $k = 8.93 \times 10^{-4}$, and $a = 0.71$.[6]

Physical Properties of the Films

The mechanical properties of the membranes were evaluated by measuring their breaking stress and viscoelastic modulus. Breaking stress was determined using an Instron Universal Tensile Tester, Model 1102.

The gel swelling index (GSI) of the membranes was determined as follows: Samples of the membranes were placed in deionized water for 24 hours, removed, wiped with a dry tissue to remove surface water, and weighed. The sample was then reimmersed in water for a further 24 hours, removed, wiped, and weighed again. This was repeated at least five times or until a constant extrapolated time was achieved. (As there was a continuous loss of water by evaporation during weighing, an extrapolation method was used to correct the weight of the membrane). The wet sample was finally dried in a vacuum oven at 85°C and 60 mmHg, for 18 hours and before final weighing was conditioned over phosphorus pentoxide for 14 hours. The GSI is defined as,

$$\frac{\text{Wet weight of sample} - \text{dry weight of sample}}{\text{dry weight of sample}} \times 100\%$$

The water vapor permeability of the membranes was determined as follows: A polyvinylchloride cup (4 cm deep, 7.34 cm diameter) filled with water was covered with the membrane under investigation. The membrane was secured with a rubber band. After accurate weighing the assembly was placed in a constant humidity cabinet (Fig. 1). The atmosphere in the cabinet was maintained at 65% relative humidity using saturated aqueous magnesium acetate. The cup assembly was weighed quickly at various time intervals until a steady rate of transfer was obtained. All membranes were conditioned in the humidity cabinet.

This method assumes that the vapor pressure gradient within the film is the same as the vapor pressure difference between the air in the cup and the atmosphere in the cabinet. Under such conditions the permeability R of the membrane can be expressed as:

$$R = D \cdot S = JP/(P_1 - P_2)$$

where D is the diffusion coefficient S, the solubility of the water in the

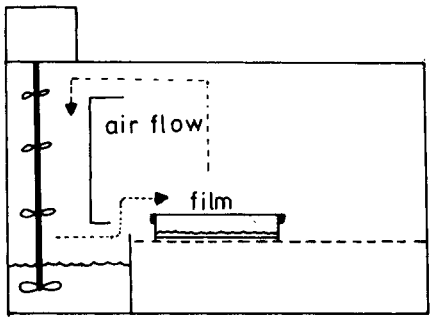

Fig. 1. Apparatus used for determination of water permeability.

membrane, the flux of water under steady-state conditions through the membrane, and R is the membrane thickness. P_1 and P_2 are the partial pressures of water vapor on each side of the membrane. J can be determined from the slope of a plot of weight loss of the cup versus time. The pressure difference (ΔP) was calculated as follows

$$\Delta p = (p_1 - p_2) = p_v(1 - 0.65)$$

where p_v is the vapor pressure of water at 19°C.

Preparation of Membranes from Chitosan / Poly(vinyl Alcohol) Blends

Poly(vinyl alchol) (12% acetylated) (PVA) was obtained from B.D.H. and was used as a 5% w/v aqueous solution. The solution was prepared by adding the required amount of PVA slowly with stirring to the requisite volume of distilled water at room temperature; stirring was continued overnight. For preparation of the membranes a suitable volume of the PVA solution was added with stirring to a solution of chitosan in 2% acetic acid, and stirring continued for one hour. The film was cast as previously described[4] and transferred to a 3% methanolic sodium hydroxide solution and left for three hours at 60°C, after which the film was rinsed, soxhlet extracted with methanol, and stored in distilled water until required.

Preparation of Graft Copolymers of Chitosan

Chitosan was used as a substrate for graft polymerization under heterogeneous conditions in the form of chitosan flakes and as an activated gel, and under homogeneous conditions as a solution in dilute acetic acid. These were prepared as follows:

Chitosan flakes (500–710) were soxhlet extracted for several hours with the solvent used for extraction of the homopolymer from the grafted sample. After removal of the solvent, the flakes were immersed overnight in distilled water and then dried.

Activated chitosan was prepared by dissolving chitosan flakes (3 g) in 2% acetic acid (100 cm^3) at room temperature and reprecipitating the chitosan by the dropwise addition of 10% sodium hydroxide solution while vigorously stirring. The precipitated gel was extracted with water to remove salt and excess alkali. The gel was made up to 100 cm^3 with distilled water and treated in the same way as the flakes. The activated chitosan was almost white compared with the pale yellow color of the flakes.

Graft Copolymerization Under Heterogeneous Conditions

Chitosan flakes (1 g) (or the precipitated gel) were placed in a 250-cm^3 round-bottomed three-necked flask and the suspension made up to 100 cm^3 with distilled water. After purging with nitrogen for 30 min, the suspension was stirred at a constant temperature on a water-bath and the required

amount of azobisisobutyronitrile in the minimum volume of acetone added followed by the dropwise addition of the monomer over 5 mins. When monomer addition was complete the nitrogen flow was continued for 15 min. When the appropriate reaction time had elapsed, the contents of the flask was stirred for a further 15 min at room temperature, the product removed, and extracted for 48 hours with a suitable solvent to remove any homopolymer. The copolymer was dried at 80°C under vacuum.

Graft Copolymerization Under Homogeneous Conditions

Chitosan (1 g) was dissolved in 2% acetic acid (100 cm^3), the solution stirred overnight and filtered through a sintered glass filter (porosity 1) before use. The solution in a 250-cm^3 round-bottomed three-necked flask was stirred and purged with nitrogen for 30 min. The initiator and monomer were then added and the polymerization continued as previously described. When the reaction time had elapsed, the contents of the flask were stirred for a further 15 min at room temperature, poured into a 500-cm^3 beaker and a 10% sodium hydroxide solution added with vigorous stirring until the polymer was completely precipitated. The gel obtained was extracted with a suitable subject to remove any homopolymer.

The extraction solvents used were dimethylformamide for poly(acrylonitrile) (PAN) and butanone for poly(methyl methacrylate) (PMMA) and poly(methylacrylate) (PMA). Methanol was used for poly(vinyl acetate).

Membrane Formation

The purified chitosan or graft copolymer gel (2 g) was dissolved in 2% acetic acid (100 cm^3) and stirred overnight. The solution was filtered through a sintered glass filter (porosity 1), spread on a clean glass plate, and left in a dark dust-free atmosphere at 10°C for 48–60 hours. The film was neutralized by two successive 10-min treatments with 2% aqueous sodium hydroxide solution, after which it could easily be removed from the plate. It was then thoroughly rinsed and stored in distilled water until use. The wet thickness could be controlled within the range 10–20 m. If thicker films were required a more concentrated solution was employed.

RESULTS AND DISCUSSION

The molecular weights and degree of deacetylation of the chitosan samples prepared by different treatments are shown in Table I. Auerbach[7] has suggested that viscosity measurements do not give a good indication of the molecular weights of chitosan samples, however, Lee[6] maintains that such measurements do give a reasonable guide to chain length. The molecular weights have been calculated using the constants obtained by Lee. Results obtained by Nud'ga et al.[2] give higher molecular weights than those reported in the present work. The authors, however, state that the viscosity measurements were made in 2% acetic acid, and no mention is made of added electrolyte. Figure 2 shows the extent of depolymerization occurring during the various deacetylation treatments.

TABLE I
The Effect of Preparation Conditions on the Degree of Acetylation and Molecular Weight of Chitosan

Sample	Deacetylation temperature (°C)	% Deacetylation (IR)	$\overline{MV} \times 10^{-5}$
PS 030	100	75.0	2.54
PS 060	100	77.2	1.86
PS 120	100	80.3	1.27
PS 180	100	83.8	0.78
PS 300	100	84.2	0.45
SG 030	100	74.5	0.92
SG 060	100	76.5	0.88
SG 120	100	77.9	0.78
SG 180	100	81.9	0.44
PS 30	120	76.5	1.72
PS 60	120	79.1	0.88
PS 120	120	81.70	0.50
PSO 300	120	87.8	0.27

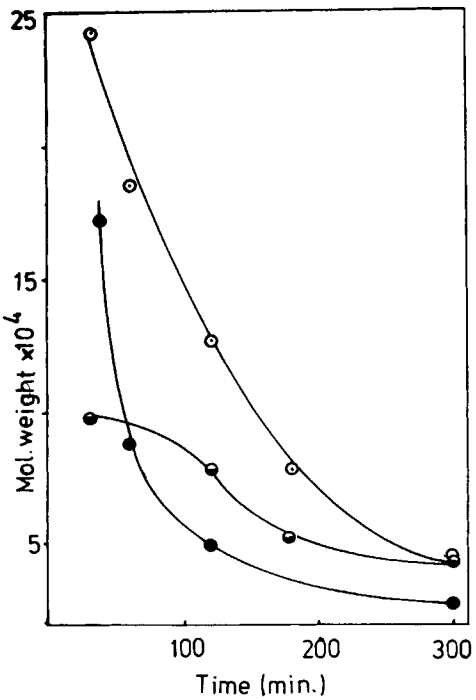

Fig. 2. The effect of time of deacetylation on the viscometric molecular weight of chitosan. ○ Prawn shell chitosan deacetylated at 100°C. ● Crab shell chitosan deacetylated at 100°C. ◒ Prawn shell chitosan deacetylated at 120°C.

Tensile Properties of the Membranes

The tensile properties of the films produced were measured at a constant rate of stress of 5 cm min. The tensile strength and elongation at the break of the films tested are shown in Table II. As expected, the tensile strength and elongation decrease with the severity of treatment and with increased deace-

TABLE II
The Tensile Properties of Chitosan and Chitosan Blends

Sample	Tensile strength (MNm^{-2})	% Elongation
PS 030	66.9	4.83
PS 060	65.2	4.61
PS 120	58.1	4.13
PS 180	36.0	2.39
SG 030	68.5	3.79
SG 060	66.7	3.49
SG 120	62.9	3.27
SG 180	61.6	3.07
SG 120/PVA 80/20	50.0	2.55
SG 120/PVA 60/40	51.3	3.45
SG 120/PVA 40/60	56.0	3.48
SG 120/PVA 20/80	46.3	13.78
PVA	60.0	105.00
PS/20/PVA 80/20	40.3	3.19
PA 120/PVA 60/40	41.6	4.78
PS 120/PVA 40/60	44.3	5.83
PS 120/PVA 20/80	42.9	16.53

tylation. The tensile strength and elongation of chitosan/polyvinylalcohol blended membranes made from crab shell chitin (SG 120) and prawn shell chitin (PS 120) can also be seen in Table II. The properties of the membranes from both sources of chitosan show similar trends. None of the blend membranes is as strong as the chitosan or the poly(vinyl alcohol) membranes and there is a gradual increase in strength ongoing from the 80/20 membrane to the 40/60 membrane but the 20/80 membrane shows a loss of strength. Small amounts of poly(vinyl alcohol) appear to considerably reduce the tensile properties of the chitosan, further amounts bringing about an increase in strength until the blend contains 80% poly(vinyl alcohol) and 20% chitosan. This is probably caused by a disruption in the order in the polymer structure and is borne out to some extent by wide-angle x-ray diffraction studies which indicated a lesser degree of crystallinity in 20/80 and 80/20 blends compared with the other blends and the constituent polymers. A plasticizing effect by the poly(vinyl alcohol) on the chitosan might have been expected but as shown by the change in extension this has not occurred, and the material has become less flexible and more brittle.

Hydrophilic Properties of the Membranes

The results of gel swelling index measurements are shown in Figure 3 for prawn shell chitosan/poly(vinyl alcohol) membranes. There is an improvement in the hydrophilic properties of the membranes on blending with poly(vinyl alcohol).

Adsorption-desorption of water vapor on chitosan membranes is shown for films of chitosan from both sources and for three different times of deacetylation treatment in Figure 4. The results show the expected hysteries effects. Chitosan samples from both sources show a similar trend in behavior in that with a decrease in acetyl content there is a decrease in moisture regain. These

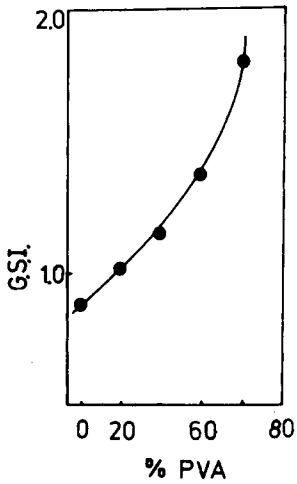

Fig. 3. Gel swelling index of chitosan/poly(vinyl alcohol) blends.

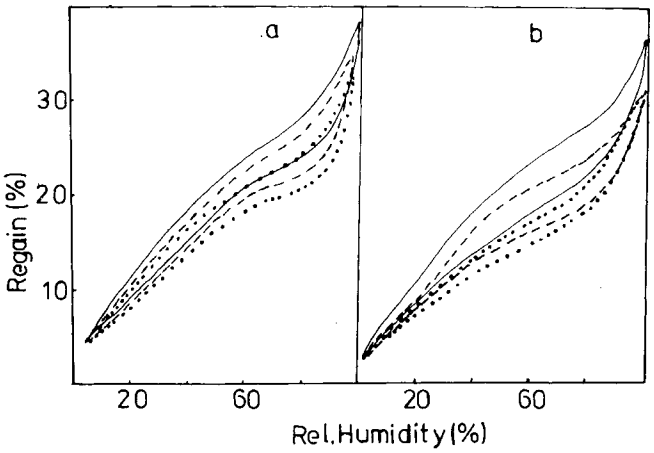

Fig. 4. The moisture regain of chitosan prepared from prawn and crab shells: (a) Prawn shell chitosan; (b) crab shell chitosan. —Deacetylated for 60 min; - - - - deacetylated for 120 min; · · · deacetylated for 180 min.

results appear to conflict with those of Filar and Wirick,[8] but do agree to some extent with the more recent work of Nakajima et al.[9] who reported that chitosan samples with a high amino group content and a long chain length showed a lower moisture regain than samples with a lower amino group content and a shorter chain length. These latter workers suggest that sample density is an important factor in determining moisture regain.

The results of the water vapor permeability measurements for chitosan films are shown in Table III. Within both the prawn shell and the Sigma series, the vapor permeabilities decrease with increasing duration of alkaliane hydrolysis. In other words, permeability falls as the degree of deacetylation increases. Cuprophane, which was included for purposes of comparison, appears to have a higher permeability to water vapor than any of the chitosan

TABLE III
Water Vapor Permeability of Chitosan Samples and Their Moisture Regain at 65% Relative Humidity

Sample	R (kg m^{-1} s^{-1})(Nm^{-2})$^{-1}$ × 10^4	Moisture regain (%)
Cuprophane	5.29	—
PS 30	4.69	19.1
PS 060	4.49	18.6
PS 120	4.30	18.3
PS 180	4.14	16.9
PS 300	3.99	16.0
SG 030	4.23	19.6
SG 060	4.08	18.5
SG 120	3.92	16.9
SG 180	3.82	16.8
SG 300	3.66	15.5

membranes. In addition, the prawn shell samples are more water permeable than the Sigma chitosan. Table III also shows the moisture regain of the films at 65% relative humidity. These values decrease with degree of deacetylation. It is possible that conversion of acetyl groups to amino groups results in a closer packing of the polymer chains and a decrease in hydrophilicity.

Reaction of Chitosan with Vinyl Monomers

The reaction of chitosan with acrylonitrile has been investigated by Nu'gda and co-workers[10] and the reaction conditions discussed. These workers showed that under alkaline conditions a high degree of cyanoethylation occurred and that at 20°C substitution took place mainly at the primary alcohol groups. At 70°C the amino groups were involved to the extent of about 30%. The conditions employed for homogeneous cyanoethylation are those described by Hamay and Yamada,[11] and the results are shown in Table IV. The extent of cyanoethylation is very dependent on the amount of alkali present. The infrared absorption spectra of the samples were found to be very similar. Figure 5 shows the spectra of samples 1, 2, and 3. The presence of the cyano group is indicated by the peak at 2250 cm^{-1}. In the case of reaction times of

TABLE IV
Extent of Cyanoethylation of Chitosan PS 120

1	1.75	4.50
2	3.50	26.40
3	7.00	34.76
4	14.00	44.30
5	28.00	138.30
6	1.76	0.74
7	3.50	6.17
8	7.00	9.98
9	14.00	22.07
10	28.00	62.35

Samples 1–5 treated at liquor ratio of 100 : 4 with 4% NaOH at 25°C.
Samples 6–10 treated at liquor ratio of 100 : 4 with 10% NaOH at 25°C.

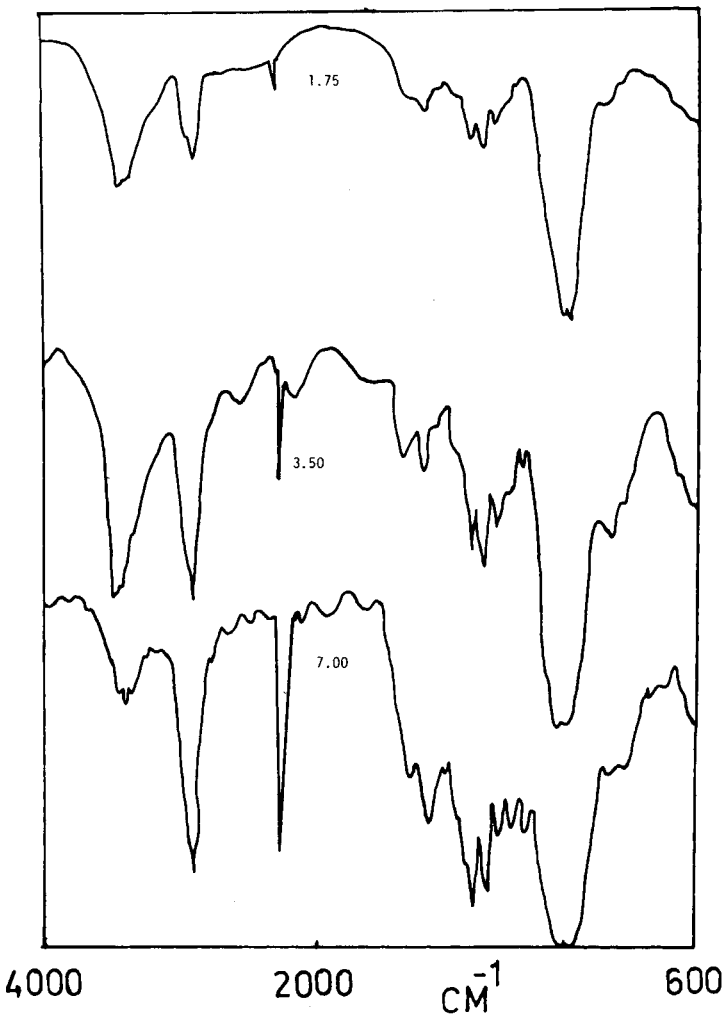

Fig. 5. Infrared spectra of prawn shell chitosan graft copolymerized in solution with acrylonitrile. Figures on the curves refer to the duration of the reaction.

14 hours or more with both concentrations of alkali, a white powdery product consisting of polyacrylonitrile homopolymer was formed. The infrared (IR) spectra along with the increase in sample weight would suggest that some poly(acrylonitrile) had been grafted on to the chitosan. As all the samples produced, however, were soluble in 2% acetic acid, the grafted "tail" of PAN must be relatively short and does not significantly modify the solubility of the chitosan. The membranes prepared from these samples in most cases retained their mechanical strength but were less hydrophilic than chitosan. The membranes were not examined further.

Heterogeneous graft copolymerization of acrylonitrile on to chitosan was carried out using chitosan flakes and activated chitosan. In the case of the flakes the grafted samples were either insoluble in 2% acetic acid or soluble only with difficulty. This was probably due to mainly surface grafting occur-

TABLE V
Heterogeneous Graft Copolymerization of Acrylonitrile onto Chitosan (SG 120) at 60°C for 240° min

Sample	AIBN conc (mol l^{-1})	Acrylonitrile (cm^3)	Grafting ratio (%)
1	0.001	5.0	4.16
2	0.002	5.0	5.45
3	0.004	5.0	5.06
4	0.006	5.0	4.18
5	0.008	5.0	3.21
6	0.010	5.0	2.51
7	0.004	2.5	3.10
8	0.004	7.5	8.60
9	0.004	10.0	9.26
PAN 1	0.01	10.0	—
PAN 2	0.01	20.0	—

ring. The effects of varying the monomer and initiator contents are shown in Table V.

Two samples of graft copolymers with different grafting ratios were prepared from activated chitosan. After extraction with DMF the products appeared to be similar to the gel-like starting material but paler in color. The infrared absorption spectra of the samples are shown in Figure 6. Comparison

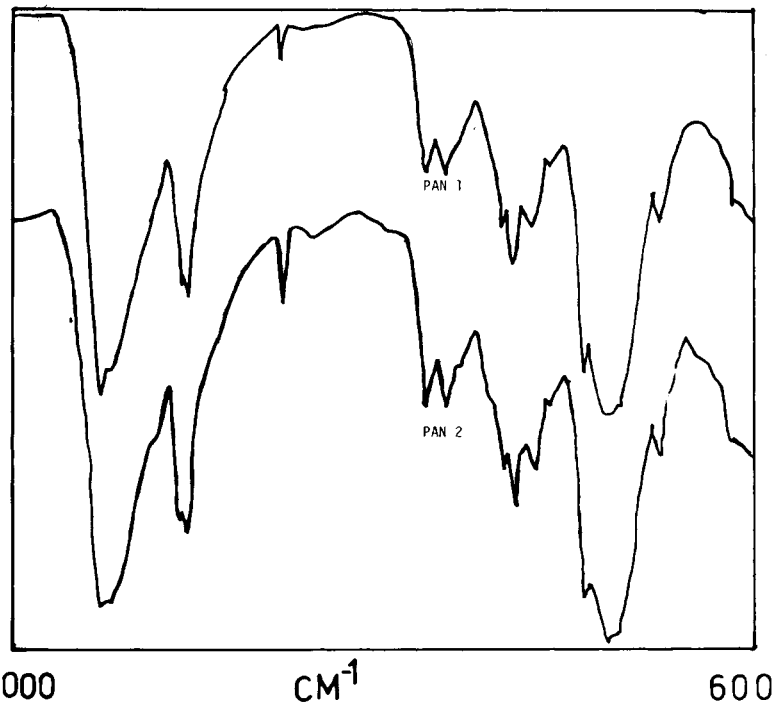

Fig. 6. Infrared spectra of heterogeneously grafted copolymers of acrylonitrile on prawn shell Chitosan. PAN 1 AIBN (0.01 mol l^{-1}), acrylonitrile (0.17 mol g^{-1} chitosan); PAN 2 AIBN (0.01 mol l^{-1}), acrylonitrile (0.34 mol g^{-1} chitosan).

TABLE VI
Graft Copolymerization of Methylmethacrylate (MMA) on to Chitosan (2.0 g)

Sample 1	MMA (cm^3)	AIBN (g)	Time (min)	Grafting ratio (%)
1	1.50	0.05	240	5.8
2	3.00	0.05	240	6.0
3	4.5	0.05	240	26.5
4	6.0	0.05	240	33.4
5	7.50	0.05	240	32.0
6	7.50	0.05	180	20.0
7	7.50	0.05	120	6.0
8	7.50	0.05	60	2.0
9	4.50	0.025	240	8.0
10	4.50	0.075	240	65.0
11	4.50	0.100	240	38.8

Reaction medium was distilled water (100 cm^3) for all samples.

of these spectra with those of the cyanoethylated material indicates that the PAN content could be little more than 10%. The films were transparent and pale yellow in color. The polymers had a solubility in 2% acetic acid of about half that of chitosan.

Table VI shows the results of graft polymerization of methyl methacrylate (MMA) on chitosan under various conditions. The infrared absorption spectra

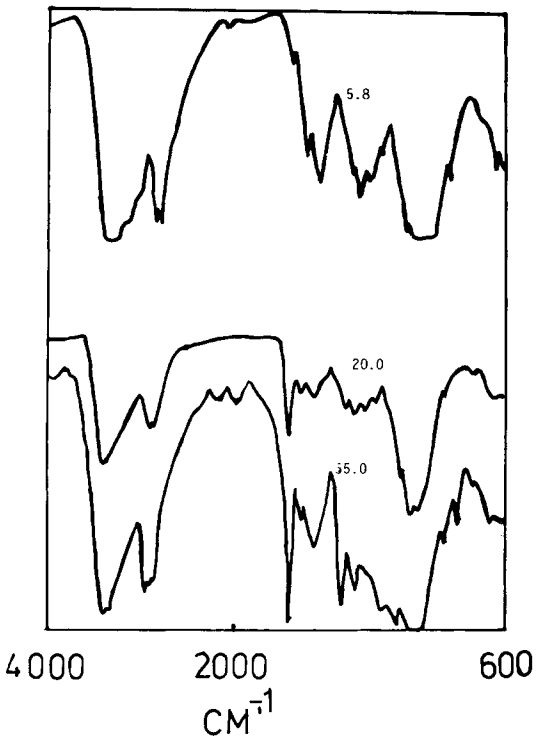

Fig. 7. Infrared spectra of graft copolymers of methylmethacrylate and chitosan. Figures on curves refer to graft ratio (%).

TABLE VII
Graft Copolymerization of Methylacrylate (MA) on to Chitosan Flakes (2.0 g) at 60°C for 240 min

Sample	MA (cm^3)	AIBN (g)	Grafting ratio (%)
1	1.50	0.05	16.7
2	3.00	0.05	18.2
3	4.50	0.05	19.6
4	3.00	0.075	20.0
5	3.00	0.100	22.6
6	4.50	0.025	22.3
7	4.50	0.075	18.9
8	6.0	0.05	21.1
9	7.50	0.05	19.8

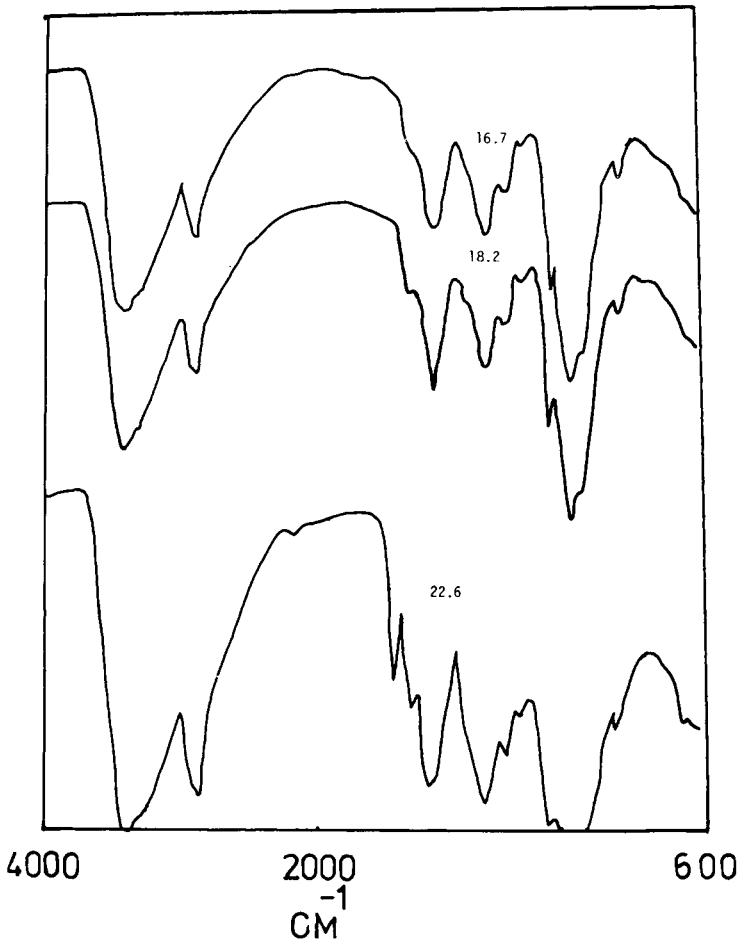

Fig. 8. Infrared spectra of graft copolymers of methylacrylate and chitosan. Figures on the curves refer to graft ratio (%).

of representative samples are shown in Figure 7. The amide group band at 1650 cm-1 appears to be stronger in the grafted samples than in the original chitosan, suggesting that the amino group participates in the grafting reaction. The chitosan flakes however when grafted with MMA could not be fully dissolved in 2% acetic acid or anhydrous formic acid and so membranes were not prepared.

Chitosan grafted with poly(methylacrylate) might be expected to be a better film-forming material than chitosan–PMMA, as the homopolymer in its partially hydrolyzed form is slightly soluble in water. Table VII shows the results of grafting methylacrylate (MA) on chitosan flakes. The grafting ratios shown are the averages for three experiments; the products were not reproducible. Figure 8 shows the infrared absorption spectra of three of these samples.

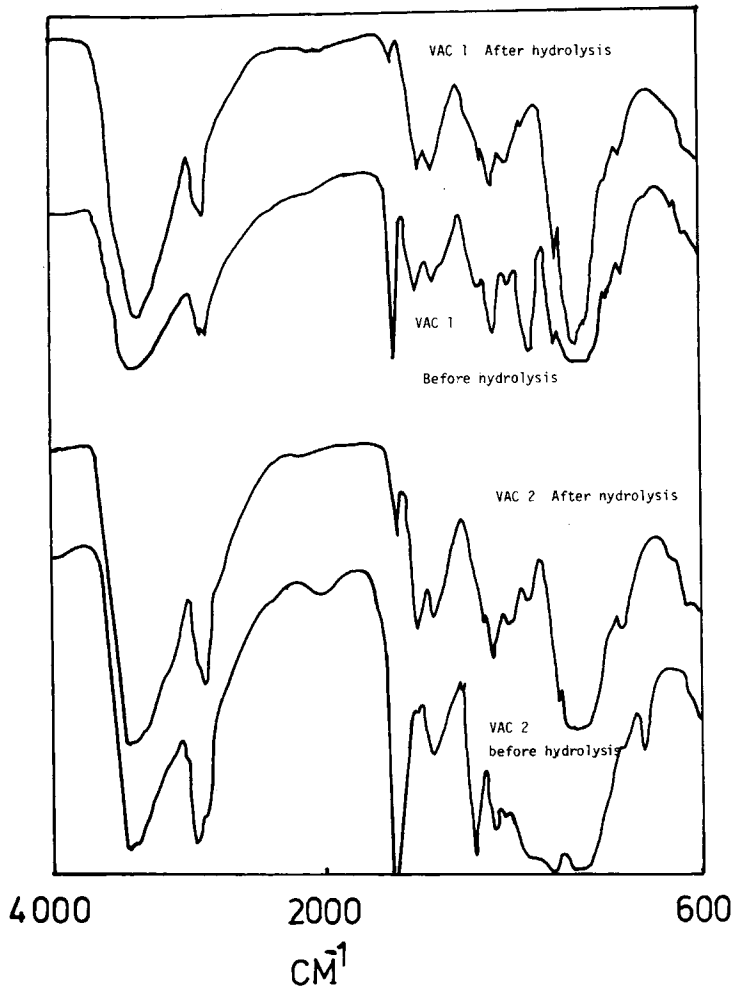

Fig. 9. Infrared spectra of vinylacetate graft copolymers of vinyl acetate and chitosan. VAC 1; acetic acid (90 cm^3), vinylacetate (10 cm^3), AIBN (0.1312 g); VAC 2; acetic acid (80 cm^3), vinylacetate (20 cm^3), AIBN (0.1312 g). Homogeneously grafted at 60°C for 240 min.

TABLE VIII
Graft Copolymerization of Vinylacetate on to Chitosan Flakes

Sample no.	Temperature (0°C)	Time (min)	Chitosan (g)	Vinyl acetate (cm^3)	Distilled water (cm^3)	AIBN (g)	% Grafting ratio
1	60	240	1.0	2.0	50.0	0.0328	5.12
2	60	240	1.0	2.0	50.0	0.0656	6.69
3	60	240	1.0	2.0	50.0	0.0984	8.29
4	60	240	1.0	2.0	50.0	0.1312	7.60
5	60	240	1.0	4.0	50.0	0.0984	5.74
6	60	240	1.0	1.0	50.0	0.0984	5.56
7	60	60	1.0	2.0	50.0	0.0984	8.89
8	60	120	1.0	2.0	50.0	0.0984	9.92
9	40	240	1.0	2.0	50.0	0.0984	10.48
10	20	240	1.0	2.0	50.0	0.0984	7.37
11	60	360	1.0	2.0	50.0	0.0984	7.94
12	60	240	1.0	3.0	50.0	0.0984	7.98
13	60	240	3.0	5.0	100.0	0.0328	6.23
14	60	360	3.0	6.0	100.0	0.0984	7.96
15	60	180	3.0	6.0	100.0	0.0984	9.10

The results are difficult to explain, for example, the infrared spectra of the samples with graft ratios of 16.7 and 18.2% show only a small shoulder at the carbonyl frequency, whereas the spectrum of the sample which has an apparent grafting ratio of 22.6% was a strong carbonyl absorption peak. Homogeneous grafting also gave variable products, some of which showed the typical carbonyl peak in their infrared spectra, while others did not.

Grafting vinylacetate on to chitosan under homogeneous conditions gave very poor reproducibility. After removal of the homopolymer by solvent extraction, the product was refluxed with 2% sodium hydroxide solution and washed overnight with water. Infrared spectra of the samples before and after alkali treatment are shown in Figure 9. From these it would appear that some vinylacetate had been grafted on to the chitosan, and also that alkaline treatment removed most of the acetyl groups. The infrared spectra of the samples after reflux indicate the presence of the amide I band at 1655 cm^{-1} and this together with the limited solubility in acetic acid indicates attachment of the graft through the free amino group. Table VIII shows the results of grafting vinyl acetate under heterogeneous conditions. The maximum degree of grafting obtained was 10.48% (sample no. 9). All the samples were found to be soluble in 2% acetic acid so few of the amino group appear to be involved in the grafting reaction.

CONCLUSION

Chitosan prepared from commercially available crab shell chitin has a lower molecular weight than chitosan prepared from prawn shells. The molecular weight of the final product depends on the severity of the deacetylation process and decreases as the time of deacetylation increases. Tensile strength and elongation at the break decrease with prolonged treatment in alkaline solutions. Membranes prepared by blending poly(vinyl alcohol) with chitosan

have lower tensile properties than pure chitosan. A small amount of poly(vinyl alcohol) in the blend produces a large reduction in strength and elasticity but this increases as the fraction of poly(vinyl alcohol) increases. At a ratio of 80/20 PVA/chitosan the tensile strength decreases again. The reason for this is not clear. Gel swelling studies show that the hydrophilicity of the blend increases as the level of poly(vinyl alcohol) in the mixture increases. Moisture adsorption decreases with increase in deacetylation. This is also reflected in the lowering of water permeability as the extent of deacetylation increases. This may be related to the relative chain-packing properties of the acetylated and deacetylated materials.

Poly(acrylonitrile)-g-chitosan polymers can be successfully prepared in the homogeneous reaction media but heterogeneous preparation yield materials insoluble in dilute acetic acid. The insolubility is probably due to surface grafting of chitosan particles. Attempts to produce poly(methyl methacrylate)-g-chitosan and poly(methylacrylate)-g-chitosan gave insoluble products. Membranes of poly(vinyl alcohol)-g-chitosan can be prepared by hydrolysis of poly(vinyl acetate)-g-chitosan. The extent of grafting in this latter case is low.

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