

THE PRODUCTION OF FIBRES FROM
CHITOSAN

Submitted in accordance with the requirements
for the degree of

DOCTOR OF PHILOSOPHY

by

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Being an account of work carried out in the
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April 1990



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ABSTRACT

A wet spinning procedure was developed for the production of chitosan fibres. The dope was prepared by dissolving 5% w/w medium grade chitosan in 2% aqueous acetic acid; after filtration and degassing, fibres were produced by extrusion of the dope into an aqueous NaOH bath and further drawing, washing, drying and winding. The effect of changes in the spinning conditions on the properties of chitosan fibres was studied; it was found that spinning variables such as jet stretch ratio, draw ratio and coagulation bath concentration had little effect on the fibre properties, though higher draw ratios would be obtained at lower jet stretch ratios and slightly improved tenacities were obtained using more dilute NaOH solutions as the coagulant. The drying methods, however, had a big effect on the fibre properties; the fibres obtained by air drying had a much higher extensibility than those dried by radiant heating. The addition of i-propanol to the dope gave much whiter fibres while the addition of Na_2SO_4 to the coagulation bath produced the strongest fibres.

Overall, the fibres produced in this work had tenacities between 0.61 and 2.48 g/dtex and extensibilities of 5.7 to 19.3%, with individual fibre decitex ranging from 2.5 to 7.5. The fibres had round cross-sections and a smooth surface when dried with heating or a rough surface when dried with acetone.

The chelating properties of the chitosan fibres were studied; it was found that upto 8% Cu(II) and 5% Zn(II) can be absorbed into the fibres within 40 minutes. The Cu(II) and Zn(II) ions had strong effects on the fibre tensile properties; both dry and wet strengths were remarkably increased with the absorption of metal ions. In addition, the fibres chelated with ZnSO_4 had a LOI estimated to be 52%.

The chitosan fibres were acetylated using acetic anhydride in methanol. It was found that 88% of the amine groups were acetylated within 30 minutes at 40 °C. The effects of temperature, time, ratio of anhydride to amine groups and the addition of water were studied; it was found that the addition of water to the methanol anhydride mixture greatly accelerated the reaction. Some O-acetylation was noticed in the reaction and this was removed by a treatment using 1 M aqueous NaOH.

The changes in fibre properties after acetylation were also studied. It was found that after the acetylation process, the fibre had a better thermal stability and improved dry and wet strength. However, the fibre lost its chelating ability when substantially acetylated.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. G C East for his kindness, guidance and encouragement. The author appreciates the supervision Dr. East has offered throughout this work. Appreciations are also due to Professor J E McIntyre for his interest in the work.

The author would like to thank the British Council and the Chinese government for providing the T.C. award and the living costs respectively. Thanks are due to all my friends in the Chinese community and lab. 203a for their friendship especially during my stay in the hospital.

The author wishes to thank the following members of the staff for their help during the work.

Mr. L Johnson for thermal analysis.

Mr. D F Storer and Mr. D E Baxter for their assistance in fibre production.

Mrs. S Hassell for providing the chemicals.

Mr. P Clegg for the help with the Instron machine.

Dr. M G Dobb and Miss H M Dyson for the SEM pictures.

Mr. J Harmer and Mr. J Lu for the X-ray diffraction patterns.

Mrs. V Whitehead for the help in the library.

To my parents and sisters

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Chapter one

INTRODUCTION

1.1 Introduction

Chitosan is a polyamino sugar composed essentially of 1→4 linked 2-amino-2-deoxy-β-D-glucan (see Fig 1.1). Though it exists naturally in some species of fungi, chitosan is mainly obtained as the deacetylated product of chitin which is a polysaccharide of 1→4-2-acetamido-2-deoxy-β-D-glucan. The discovery of chitin was made in 1811 by Braconnot (1) who, upon treatment of fungi with potassium hydroxide, obtained a nitrogen containing substance. In 1859, a modified chitin was obtained by Rouget (2) while boiling chitin in concentrated potassium hydroxide. This modified chitin, notable for its solubility in dilute acid solution, was studied again by Hoppe-Seiler (3), who named it chitosan.

Nowadays, with the advance in science and technology, it is well known that chitin and chitosan are synthesised by some unicellular organisms such as diatoms, chrysoflagellates and protozoa (4). Both polymers occur mainly in lower animals and plants whose foods are rich in nitrogen. Chitin and chitosan can be found in cell walls of fungi, moulds and yeasts, and in cuticular or exoskeleton of invertebrates such as crab, shrimp and insects (5).

The abundance of chitin and chitosan is obvious in many parts of the world. Such countries as Japan, USA, etc., where sea products are abundant, can provide chitin and chitosan on a scale of thousands of tonnes a year (6,7). However, the study of chitin and chitosan has until recently, developed quite slowly. The reason might be various, e.g., the scattered distribution of potential sources, the seasonal variations in supply of the raw material, the variability in

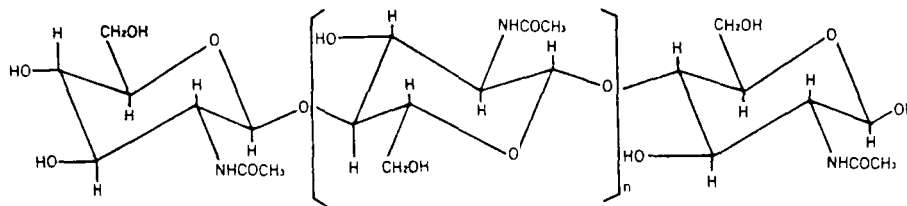


Fig 1.1A The chemical structure of chitin

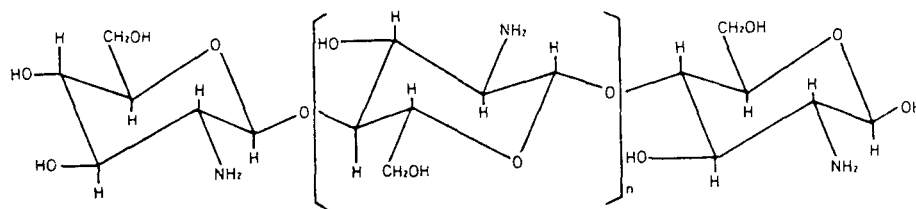


Fig 1.1B The chemical structure of chitosan

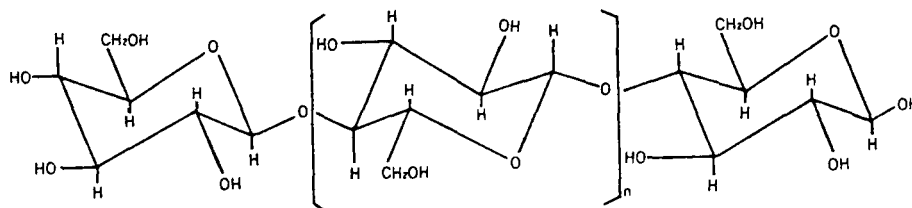


Fig 1.1C The chemical structure of cellulose

product quality, the difficulty of finding solvents for chitin, the lack of commercial interest, etc. However, since the 1950s, some unique properties of chitin and chitosan have been recognised by scientists in various fields. These properties such as biodegradability, biocompatibility, ease of chemical modification, and in the case of chitosan, the polycationic structure and excellent chelating ability, have stimulated research interests in chemistry, biochemistry, medicine, pharmacology, enzymology, microbiology, biotechnology, food science, agriculture, nutrition, plant pathology, marine science, macromolecular science, and many other related areas (8). Their applications range from slow release drugs, seed coating and cosmetics to wound dressings and surgical sutures (6,9).

The textile industry has had a connection with chitin and chitosan for over 50 years. The first chitin fibre was reported as early as 1926 (10,11). Over the years, there have been reports of other attempts to produce fibres (12,13). However, with the introduction of synthetic fibres in the 1940s, research interest in this area diminished. Recently, the appreciation of the properties of chitin and chitosan in respect of biodegradability, non-toxicity and wound healing has again aroused the interest of fibre scientists to produce chitin and chitosan fibres that might be used as surgical sutures and wound dressings. The present study is part of this effort.

1.2 Sources of chitosan

Occurrence of chitin

Chitin is the second most abundant natural polymer (5). Like cellulose

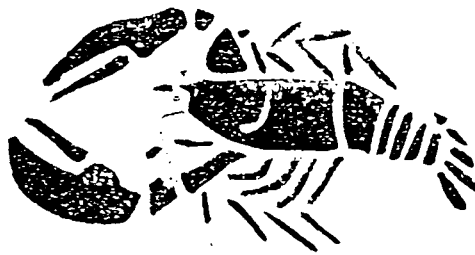
and collagen, it acts as a structural material (14). The distribution of chitin is indeed wide (see Fig 1.2), and it has been well reviewed by Muzzarelli in his book 'CHITIN' (5). However, it is mainly found in the cell walls of fungi, moulds and yeasts, in the cuticular or exoskeletal formations of most invertebrates. The species containing the most chitin are crustaceans such as crab, shrimp, prawn, lobster, etc. The chitin content in shells of those species is found to be between 14-35% of the dry mass (15). Insect cuticles are the other large source of chitin (16). Because of their obvious abundance, crab and shrimp waste from sea food processing factories are now the main source of commercial chitin. The capacity can be very large indeed, providing all sources are carefully used (6,7). It is reported that 700 tonnes of chitin were produced from crab shells in 1986, in Japan (6), and estimates of annual global production are given in table 1.1.

Table 1.1 Global estimates of annual chitinaceous material (17)

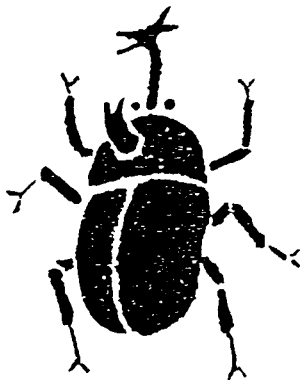
Chitin Resource	Quantity Harvested	Chitinaceous waste		Chitin
		wet weight	dry weight	
(kiloton)				
Shellfish	1,700	468	154	39
Krill	18,200	3,640	801	56
Clam/Oysters	1,390	521	482	22
Squid	660	99	21	1
Fungi	790	790	182	32
Insects		negligible		
Total	22,740	5,118	1,640	150



Crab



Shrimp



Insect



Fungi

Fig 1.2 The occurrence of chitin and chitosan

The production of chitin

Though pure chitin can sometimes be found in nature, chitin almost always exists together with some other substances (see Table 1.2). Thus, insect cuticles are composed of chitin and protein (18). Shells of crab and shrimp comprise chitin, protein and minerals (5). The production of chitin is therefore composed essentially of two steps, i.e., deproteinisation by alkali and demineralisation by acid. In some case, a decolorisation by organic solvent extraction or oxidation might be involved to remove pigments. The various ways which have been proposed in the past are summarised by Muzzarelli (5). A typical example is shown below.

Table 1.2 Characteristic compositions of chitinaceous wastes (17)

Origin of waste	Dry weight composition (%)		
	inorganic	protein/fats	chitin
Shellfish	25-50	25-50	14-35
Krill	24	61	7
Clam/Oysters	85-90	negligible	3-6
Squid	negligible	76-95	1-2
Fungi	negligible	25-50	10-25
Insects	negligible	60-80	0-8

Method of Hackman (19)

Shells are cleaned by washing and scraping under running water, and dried in an oven at 100 °C. 220 g of the shells are digested for 5 hr

with 2 l of 2 N hydrochloric acid at room temperature, washed, dried and ground to a fine powder. The finely ground material (91 g) is extracted for 2 days with 500 ml of 2 N hydrochloric acid at 0 °C, the content of the flask being vigorously agitated from time to time. The collected material is washed and extracted for 12 hr with 500 ml of 1 N sodium hydroxide at 100 °C with occasional stirring. The alkali treatment is repeated four more times. The yield is 37.4 g corresponding to 17%; there is no ash and the nitrogen content is 6.8%.

Occurrence of chitosan

Despite the fact that chitin is the second most abundant natural polymer, its deacetylated form, chitosan rarely occurs naturally. The polymer found in large quantities in crustaceans is without exception chitin. It was only in 1954 that natural chitosan was discovered for the first time by Kreger (20), in the mycelia and sporangiophores of *Hycomyces Blakesleeanus*. Since then, a few more species of fungi and also some crustaceans have been found to contain chitosan (21,22). Cell walls of *Mucor rouxii*, as reported by Bartnicki-Garcia & Nickerson (23), contain 32.7% chitosan.

The existence of chitosan in these species is reported to be due to the presence of an enzyme, deacetylase, which enables deacetylation to take place during the biosynthesis, though the mechanism is not clear (24). It was demonstrated by Bartnicki-Garcia (24) that deacetylation during biosynthesis may occur through three different pathways, i.e., by deacetylating the monomer unit followed by polymerisation, by polymerisation of the monomer unit first to chitin followed by deacetylation of the polymer to chitosan, or by a mixture of the above two procedures. None of these mechanisms, however, has

so far been established.

Despite the small quantity available naturally, the production of chitosan by fermentation of these special fungi could be a promising method provided that chitosan of satisfactory molecular weight and molecular weight distribution is obtained. And indeed, attention is being given to the controlled fermentation of *Mucor rouxii* in attempts to obtain chitosan of a similar quality to that produced by deacetylation of chitin (21,25,26).

The production of chitosan

Amide groups, especially those trans related, are quite stable in both acidic and alkaline conditions. Thus, acid and mild alkali have little effect on the C-2 amide group of chitin (5). To obtain chitosan from chitin, severe conditions, e.g., high temperature, high alkali concentration and long periods of treatment must be applied. However, even the most severe conditions, (such as fusing chitin with excess potassium hydroxide as reported by Horowitz, Roseman & Blumenthal (27)), cannot completely remove the acetyl groups. It is reported by Von Furth & Russo (28), in an early study, that three out of four acetyl groups can be readily removed from chitin. More recently, Wu & Bough (29) demonstrated that deacetylation levelled off after a certain period of alkali treatment, as shown in Fig 1.3.

Literature and patents concerning the above topic are indeed abundant. Again this information has been clearly arranged by Muzzarelli (5). One example of the many procedures is as follows:-

Method of Fujita (30)

Ten parts of chitin are mixed with ten parts of 50% sodium hydroxide,

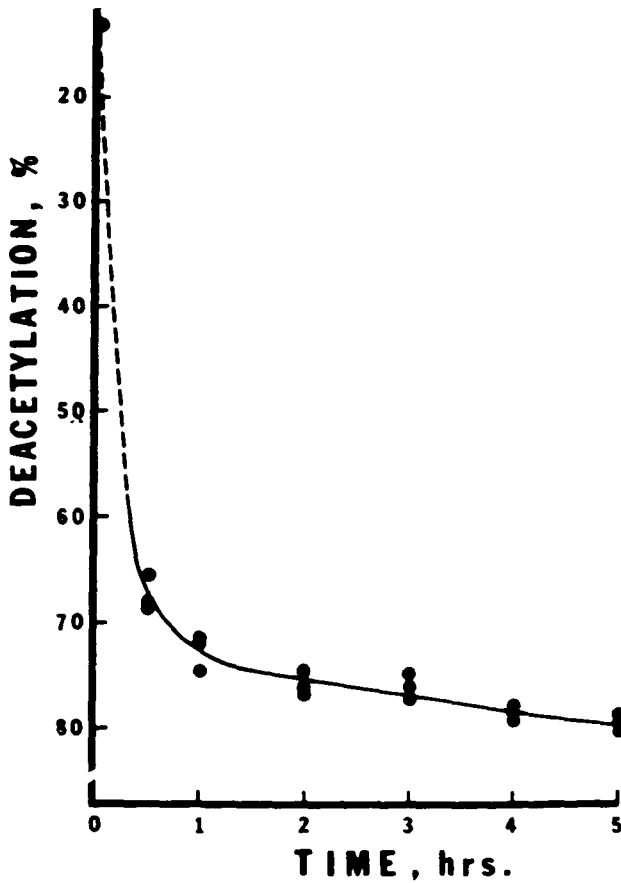


Fig 1.3 Degree of deacetylation versus time of alkali treatment (29)

kneaded, mixed with 100 parts of liquid paraffin, and stirred for two hr at 120 °C; then the mixture is poured into 80 parts of cold water, filtered and thoroughly washed with water; the yield is 8 parts of chitosan. The free amino group content is 0.92 per glucose residue.

Recently, extended research into possible applications of chitosan has stimulated demand for fully deacetylated chitosan. Thus, Mima et al (31) treated chitin in concentrated NaOH solution, followed by intermittent washing of the product with water and further deacetylation. This idea, though not new (32), seems to be effective. According to Mima et al, highly deacetylated chitosan, with upto 99% deacetylation could be obtained by the above method within 5 hr.

A similar procedure was used by Domard & Rinaudo (33), who obtained fully deacetylated chitosan by repeating the deacetylation process in aqueous NaOH solution. Thiophenol was added in order to trap oxygen and also to catalyse the reaction. The best conditions to obtain fully deacetylated chitosan are, according to them, (1) a molar ratio of NaOH four times that of the acetamide; (2) one hour treatment at 100 °C; (3) repetition of the process two or three times.

While all the above mentioned procedures were carried out under heterogeneous conditions, a homogeneous deacetylation process was reported by Sannan et al (34,35). This process, based on an old idea of alkali chitin (36), can give a partially deacetylated product with, it is claimed (34,35), the remaining acetyl groups much more evenly distributed along the polymeric chain. Thus, alkali chitin was prepared by steeping chitin with aqueous NaOH, the ratio of NaOH to chitin being 10:1. The mixture was then subjected to vacuum for 3 hr, followed by addition of ice with vigorous stirring. A final product of 45-55% acetylation was obtained after further purification. This 'hybrid' of chitin and chitosan was found to be water soluble.

A flow chart showing the commercial production of chitosan is given in Fig 1.4.

1.3 The characterisation of chitosan

The chemical structure of chitosan

The establishment of the structure of chitin and chitosan took quite a lot of effort and this has been reviewed by Agboh (37). Now, it is clear that chitin is a polymer of N-acetyl-2-amino-2-deoxy- β -D-

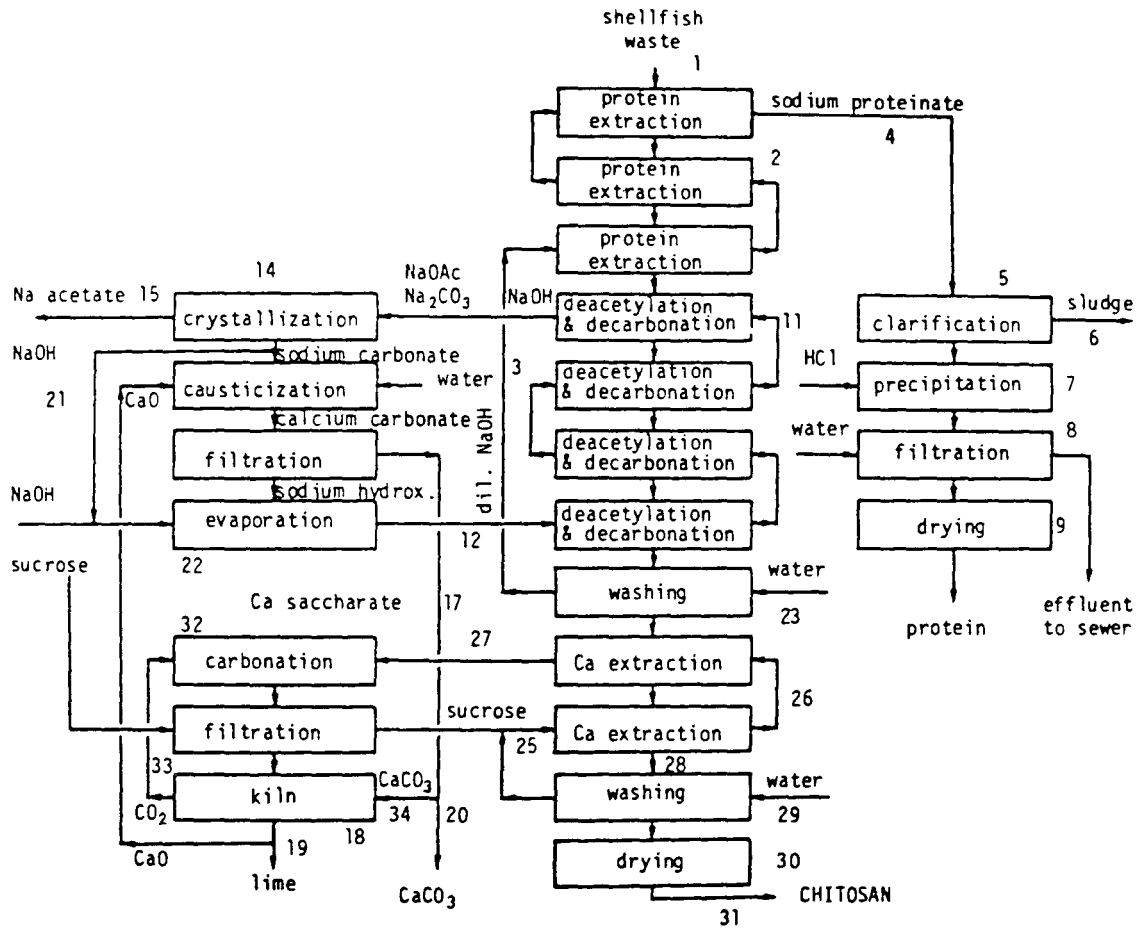


Fig 1.4 The production line of chitosan (5)

glucopyranose in which the repeating hexose units are linked by 1→4-glycosidic bonds (see Fig 1.5). Hence, as the deacetylated product of chitin, chitosan is actually poly-1→4-2-amino-2-deoxy-β-D-glucopyranose. Both chitin and chitosan can be regarded as derivatives of cellulose, since the chemical structures of chitin and chitosan are extremely similar to that of cellulose, except, at the C-2 position of the glucose residue where the -OH group in cellulose is replaced by the acetamido group in the case of chitin and the amino group in the case of chitosan. The chemical structures of chitin, chitosan and cellulose are schematically presented in Fig 1.1.

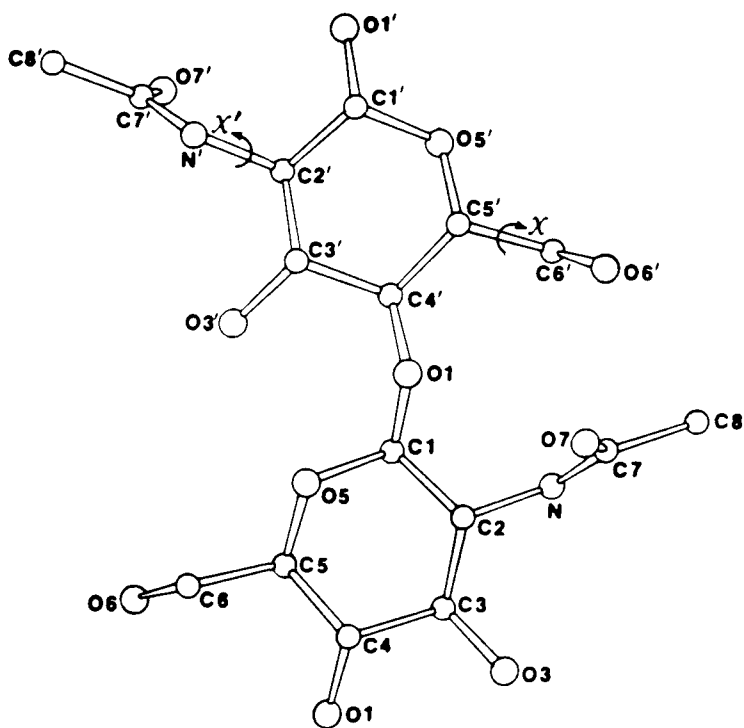


Fig 1.5 The repeating unit of chitin

The degree of acetylation

Theoretically, chitin and chitosan are the two extremes in chitinaceous material. The chemical structure of 'pure' chitin is characterised by

100% acetylation on the C-2 position of the glucosamine residue, while that of chitosan is 100% deacetylated. However, neither natural chitin nor chitosan exist in these two perfect states. Thus, chitin is the name given to the polymer where the majority of amine groups are acetylated while the majority of amine groups are free in chitosan (5). Properties such as solubility, crystallinity and chelating abilities are strongly affected by the degree of acetylation (5,34), defined as the percentage of amine groups acetylated. Therefore, the degree of acetylation (DA) merits special mention.

Over the past few years, a great deal of research work has been carried out to measure DA by various methods, both quantitatively and qualitatively. These methods, together with some property differences of chitin and chitosan are summarised below.

a. Measurement of DA based on elemental analysis

The theoretical background of this method is the different nitrogen contents in chitin as compared with chitosan. With the introduction of the acetyl group into the structure, chitin contains less nitrogen than does chitosan, as shown in table 1.3, below.

Table 1.3 Nitrogen content in relation to DA

DA(%)	0	25	50	75	100
Nitrogen content (%)	8.69	8.16	7.69	7.27	6.89
Carbon content (%)	44.72	45.48	46.15	46.75	47.29
Ratio of N/C	0.194	0.179	0.167	0.156	0.146

However, the nitrogen and carbon contents are sensitive to the moisture content of the sample which can be significant as chitin and chitosan both possess hydrophilic structures. Because of this, the absolute value of the nitrogen content may give misleading results if samples are not carefully dried or no calibration is given. Hence, in order to eliminate the effects of moisture, the degree of acetylation is normally based on the ratio of N/C (38).

Assuming the ratio of N/C=r, DA can be calculated as follow:-

$$r = \frac{\text{Nitrogen content}}{\text{Carbon content}}$$

$$= \frac{14.007}{72.066 + 24.022 \text{DA}} \quad \text{Hence}$$

$$\text{DA} = \frac{14.007/r - 72.066}{24.022}$$

b. Measurement of DA based on infrared absorption

The amide group gives characteristic IR absorption peaks at 1655, 1550 and 1313 cm^{-1} (39). These absorption by the amide group are essentially those of chitin as chitosan shows no such peaks. Therefore, by measuring the peak areas at these wavenumbers, it is possible to determine the degree of acetylation (40,41,42,43,44). Practically, however, the absorption peak at 1655 cm^{-1} is usually employed as it gives a higher sensitivity (43). Additionally, to calculate the DA requires the use of an internal standard. The C-H stretching peak at 2870 cm^{-1} and the -OH stretching at 3450 cm^{-1} were used by Miya (42) and Moore & Roberts (43) respectively. In the latter case,

$$\text{DA} = \frac{A_{1655}}{1.33A_{3450}} \times 100$$

where, A_{1655} is the absorption at 1655 cm^{-1} and A_{3450} at 3450 cm^{-1} .

c. Measurement of DA based on titration

When chitin is deacetylated, the amide groups are largely converted to free amine groups. Hence, it is possible to determine the extent of deacetylation by titration, as the amine groups are weak bases. A number of methods have been proposed; for example, Broussignac (45) titrated a solution of chitosan in excess acetic acid with alkali, following the titration potentiometrically. Moore (46) made use of the insolubility of chitosan in relatively concentrated mineral acids and determined the uptake of HCl by chitosan immersed in excess acid by back titration of aliquots of the supernatant liquor. Hayes & Davies (47) titrated solutions of chitosan hydrochloride salt against aqueous NaOH, using either an indicator, phenolphthalein, or potentiometry to determine the end point. A similar method was used by Wang (48), whose procedure is briefly quoted below:-

0.5 gram of sample is weighed into a 250 ml flask. This is followed by an addition of 30 ml 0.1 M HCl. The dissolution took 0.5-1 hour. After that, the solution was titrated with 0.1 M NaOH. Methyl orange was used as an indicator.

$$\%NH_2 = \frac{0.016(C_1V_1 - C_2V_2)}{G(100-W)} \times 100\%$$

where C1 concentration of HCl, mol/l

V1 amount of HCl added, ml

C2 concentration of NaOH, mol/l

V2 amount of NaOH used, ml

G weight of the sample, g

W moisture content, %

0.016 weight of NH₂ equivalent to 1 ml·mol/l HCl, g

$$DA = \frac{\%NH_2}{9.94} \times 100\%$$

However, all the above methods are useful only when the sample is sufficiently deacetylated to be soluble in dilute acid, i.e., this method is limited to chitosan. As for chitin, a similar titrimetric method involves the deacetylation of the amide group to release acetic acid. Thus, Rutherford & Austin (49) deacetylated chitin with concentrated NaOH, followed by addition of phosphoric acid to regenerate the acetic acid which was then distilled and collected. The number of acetyl groups present in the sample was thus obtained from the amount of acetic acid collected.

d. Measurement of DA based on circular dichroism (c.d.)

The principle of this method is the different c.d. response of glucosamine and N-acetyl-glucosamine over the range 200-250 nm. Thus, the $n-\pi^*$ transition of the N-acetyl-glucosamine gives a c.d. band located near 211 nm. According to Domard (50), the degree of acetylation can be obtained as $DA = \frac{161H_1}{161H_1 + 203(H_{100} - H_1)} \times 100\%$, where, H_1 is the height of the c.d. signal of the sample at 211 nm and H_{100} the signal height of the 100% acetylated sample (i.e., N-acetyl-glucosamine).

e. Measurement of DA based on UV spectroscopy

The u.v. molar absorption coefficients of the acetamide group of N-acetyl-D-glucosamine, N,N'-diacetyl-D-chitobiose and N,N',N'',N'''-tetraacetyl-D-chitotetraose at 220 nm are 177, 173 and 150 respectively, while that of glucosamine is below 1. Based on that, Aiba (51) proposed a new method for the determination of DA by

measuring the u.v. absorption of chitosan solutions at 220 nm. Thus, using the averaged coefficient between acetyl-glucosamine and chitobiose, i.e., 175, the DA value can be obtained quantitatively from the following equation:-

$$DA = \frac{16100A}{1750LC_2 - 42A}$$

where, A, absorbance at 220 nm, L, path length of u.v. cell (cm), C₂ concentration of chitosan solution (w/w %)

Muzzarelli & Rocchetti (52) in an earlier study reported that the molar absorptivity of N-acetyl-glucosamine is 130 times higher than that of glucosamine at 199 nm. Instead of using the absorbance at this wavelength to determine DA, as Aiba did at 220 nm, they obtained a first derivative curve in which they found a zero crossing point at 202 nm, irrespective of the solvent acid concentration. The height at 199 nm, H, was then used to calculate the concentration of N-acetyl-glucosamine, which is equal to 0.306H.

f. Measurement of DA based on pyrolysis-gas chromatography

This method, proposed by Lal & Hayes (53), is based on peak areas of products observed in the pyrolysis-gas chromatography of chitin and chitosan. By using various techniques such as the fragmentation patterns, comparison with known spectra and chromatography, Lal & Hayes were able to detect the pyrolysis products of chitin and chitosan and their retention times. In terms of peak areas, notable differences were recognised over certain bands, typically at 16.45 min., assumed to be acetic acid. Using these differences, relative values of the amine content were calculated.

g. Measurement of DA based on thermal analysis

It has been well known that chitin and chitosan have characteristic degradation temperatures, with that of chitin higher. Using this property difference, Alonson et al (54) measured DA from empirical correlations based on the weight losses associated with the main decomposition peaks. Thus, using the derivative curve of thermogravimetry, Alonson et al found that the weight loss at 280 °C becomes greater as DA decreases while the reverse effect happens at the peak near 320 °C. Based on this study, quantitative correlations were proposed between weight loss and the DA. To give one example, $Y=17.16-0.33X$, where Y is the percentage of acetyl groups, and X the percentage weight loss at 280 °C.

h. Measurement of DA based on n.m.r

N.m.r spectroscopy is one of the main techniques in structural determination. In the study of chitin and chitosan, it has also been used to determine the degree of acetylation of chitinaceous materials as differently acetylated samples give different signal intensities corresponding to the $-CH_3$ of the acetyl group. Thus, Hirano et al (22) measured the signal intensities of the acetyl methyl group and that of the methine and methylene groups, and hence DA could be calculated.

i. Solubility test

This is a qualitative test to distinguish chitin from chitosan. As chitin and chitosan have completely different solubilities, a dissolution test can indicate easily the degree of acetylation of a chitinaceous sample, using either an appropriate dilute acid, or

alternatively, a chitin solvent such as DMA-LiCl.

j. X-ray diffraction pattern

Chitin and chitosan give wide angle X-ray diffraction patterns that are significantly different (5,55). Based on that, a qualitative indication of the degree of acetylation can be made, at least, sufficient to distinguish chitin from chitosan.

The molecular weight of chitosan

The molecular weight of natural chitin is reported to be very high. It is estimated that the MW of chitin lies between 0.4-3.4 millions (56). From source to source, the MW of chitin may change considerably (see Table 1.4). This is natural because it is unlikely that an Japanese crab would synthesise chitin with exactly the same molecular weight as an American shrimp does. As a deacetylated product of chitin, chitosan is also a polymer of very high molecular weight, ranging from a few hundred thousand to millions (56). Yet, as can be expected, chitosan exhibits a wide MW dispersion, owing to the nature of the deacetylation process which is usually carried out using high alkali concentration and elevated temperatures (57). It is reported that considerable chain scission occurs when prolonged treatment is carried out, as required to produce fully deacetylated chitosan (31,33).

Several methods have been used to assess the molecular weight of chitosan; among them, Muzzarelli, Ferrero & Pizzoli (59) determined \bar{M}_w by light scattering in 8.5% formic acid + 0.5 M sodium formate. The refractive index increments were measured at four distinct concentrations of chitosan at the two wave-lengths 436 and 546 nm

Table 1.4 Some properties of chitin from different sources (58)

Sources	Percent soluble material	Molecular weight ($\times 10^{-6}$)	Average acetyl-content(%)	DA(%)
Limulus	82	1.8	17.2	79.8
Blue crab	58	1.6	15.0	67.8
Red crab	76	1.3	16.6	76.5
Dungeness crab	30	0.6	15.8	72.1
Shrimp	62	0.4	13.8	61.6

and from the results the value $dn/dc=0.174 \text{ ml}\cdot\text{g}^{-1}$ was obtained. Domard & Rinaudo (60) measured MW by osmometry and light scattering. For their fully deacetylated chitosan, they obtained $\bar{M}_n=0.24$ and $\bar{M}_w=0.44$ million respectively. Mima et al (61) used high performance liquid chromatography to characterise their highly deacetylated chitosan. Yet, the simplest and most rapid method seems to be the viscometric procedure. Three sets of Mark-Houwink constants are currently available. The first one was proposed by Lee (62), who measured three fractions of chitosan in a solvent composed of 0.2 M acetic acid, 0.1 M NaCl and 4 M urea. Using that system, Lee reported a K_m value of 8.93×10^{-2} , and an a of 0.71. In another report, Berkovich et al (63) obtained a K_m value of 111.5 and an a value of 0.147, using 0.167 M acetic acid and 0.47 M NaCl as solvent. Recently, a new set of constants were proposed by Roberts & Domszy (64), who determined K_m and a in 0.1 M acetic acid and 0.2 M NaCl, the values being $K_m=1.81 \times 10^{-3}$, $a=0.93$. This result was confirmed by

Maghami & Roberts (65), who also showed that K_m and a are not affected by the degree of acetylation over the range of 0-40%.

Like many other branches of the study of chitin and chitosan, great controversy exists regarding the three sets of constants, and a full criticism can be seen in the work of Maghami & Roberts (65). It seems that the values of $K_m=1.81 \times 10^{-3}$ and $a=0.93$ are the more acceptable as some other polyelectrolytes give similar values.

Reduction of molecular weight

While in some applications a high molecular weight is preferred, e.g., in waste water treatment, in many other fields, chitosan of a MW lower than naturally available is essential in order to obtain the required properties. A schematic representation (Fig 1.6) was given by Allan (66), showing briefly the relation between end use and molecular weight.

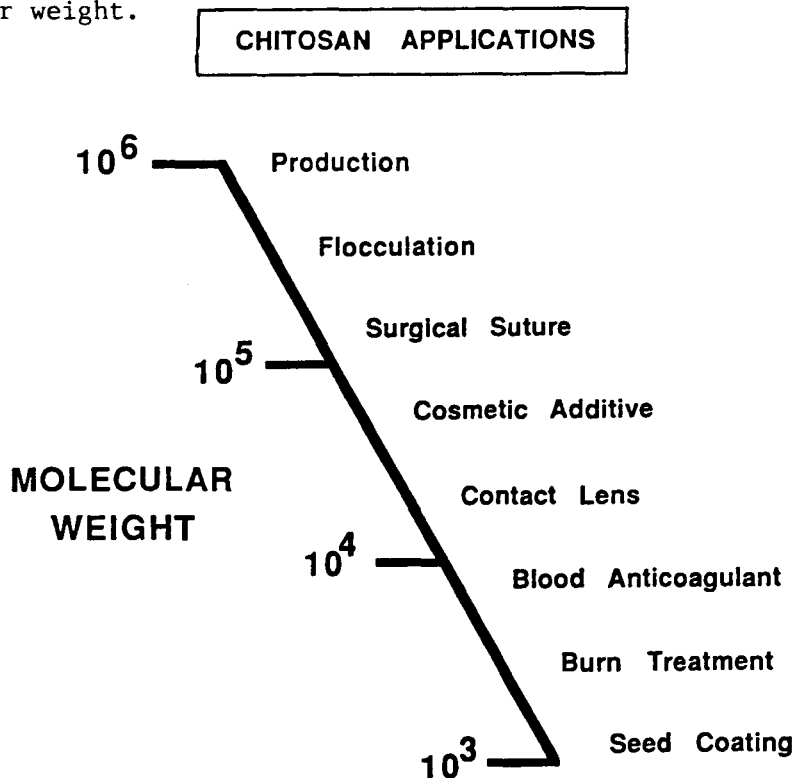


Fig 1.6 Relations between end use and molecular weight (66)

To obtain chitosan of various MW, some form of degradation must be applied. There are a few methods presently available. Firstly, MW can be reduced by means of acid hydrolysis, a common procedure in polysaccharide research. However, because of the stabilising effect by the C-2 nitrogen, hydrolysis of chitosan in acidic solutions such as aqueous HCl (67) is not as easy as in the case of cellulose.

Roberts & Domszy (64) in their work involving the determination of viscometric constants, reported a procedure in which chitosan was degraded by refluxing its solution in acetic acid. However, considering the time used, e.g., approximately 15 days to achieve 50% reduction, this method might not be very practical..

Secondly, breakdown of the molecular weight of chitosan can be achieved through shear degradation. As commonly used elsewhere, this method is especially useful when a narrow MW distribution is demanded. Thus, according to Lee (62), the MW of chitosan is reduced sharply in the initial stage of shearing, and it rapidly approaches a limiting value with repeated passes. The limit in molecular weight was affected by the solvent used; low MW can be obtained with a high solvent acid concentration.

Thirdly, reduction of molecular weight can also be achieved by mild oxidation. Using nitrous acid, Allan & Peyron (68) studied the kinetics of the depolymerisation process. Among the variables investigated, they found the degradation process is strongly affected by the concentration of chitosan and its degree of deacetylation, the concentration of nitrous acid, the pH and temperature of the reaction mixture, as well as the nature of the acid component of the reaction solvent (HCl or acetic acid).

Finally, chlorine was also found to be effective in reducing

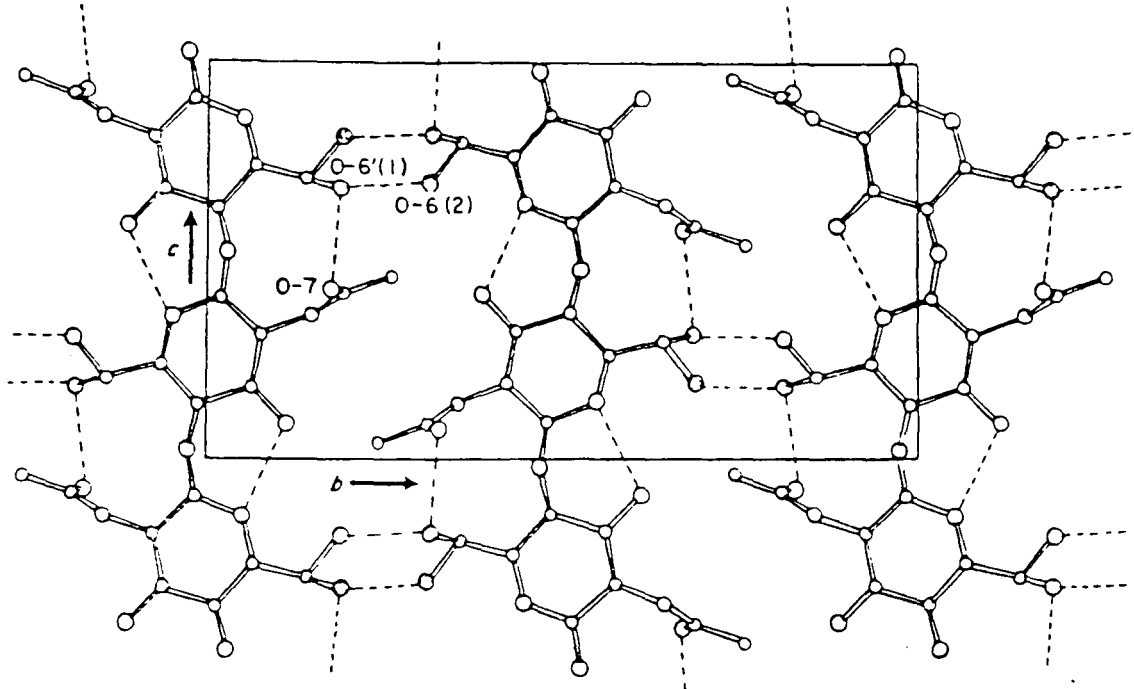
the molecular weight of chitosan. Thus, using Cl_2 in either basic, neutral or alkali conditions, Uragami et al (67) were able to obtain chitosan samples of molecular weight down to 2,000.

The crystal structure of chitosan

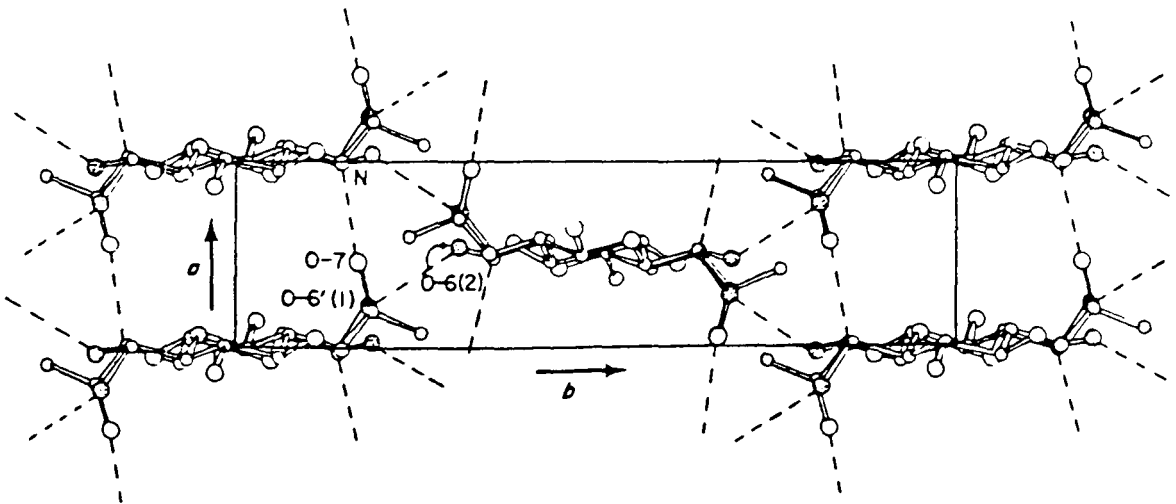
To start this section, it should be mentioned that the crystal structure of chitin has been thoroughly reviewed by Agboh (37). Therefore, only some of the essential features of the crystal structure of chitin will be discussed below.

Chitin exists in three different forms, the structural difference being the different chain arrangements (69) (see Fig 1.7 and Fig 1.8). Thus, α chitin comprises chains with an antiparallel arrangement. In this polymorphic form, the hydrogen bonding, either inter or intramolecular, is largely formed. Because of this, α chitin is the toughest and the more stable form compared to the others, β and γ chitin, which are composed of parallel chains and a mixture of parallel and antiparallel chains respectively. Table 1.5 shows the unit cell dimensions of α chitin proposed by various authors.

The first reported work on the crystal structure of chitosan was by Clark & Smith (72) in 1936. Using a tendon chitin fibre as a precursor, Clark & Smith obtained a chitosan fibre by deacetylation. From the X-ray diffraction pattern, they calculated the unit cell structure of chitosan as orthorhombic, with $a=8.9$, $b=17.0$ and $c=10.25$ Å. Further research work into the crystal structure of chitosan was lacking until 1981, when Samuels (76) characterised chitosan in the solid state. Using stretched chitosan films, Samuels obtained two distinct crystal patterns, namely form I and form II. Thus, the chitosan film prepared by casting a chitosan solution in formic acid



(a)



(b)

Fig 1.7 The crystal structure of β chitin (69)

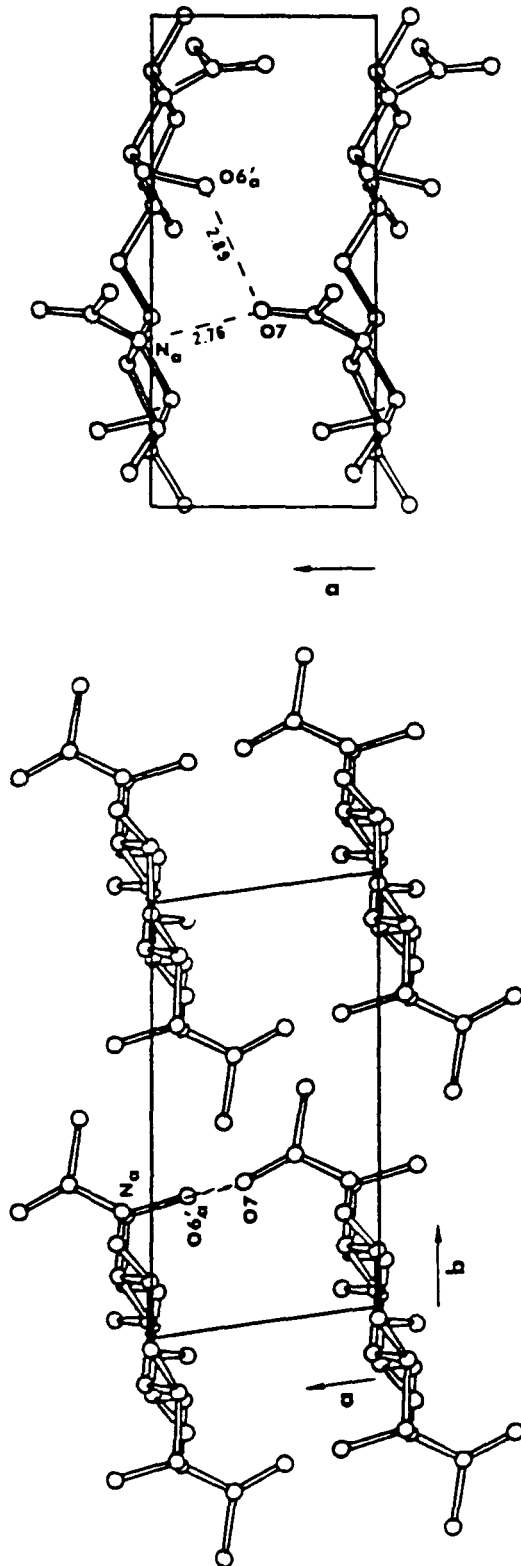


Fig 1.8 The crystal structure of β chitin (69)

Table 1.5 Unit cell dimensions of α chitin

Author	Year	Unit cell dimension (\AA)			NAG residues
		a	b	c	
Gonell (70)	1926	11.58	10.44	19.42	10
Meyer & Pankow (71)	1935	9.40	10.46	19.25	8
Clark & Smith (72)	1936	9.25	10.46	19.25	8
Lotmar & Picken (73)	1950	9.40	10.27	19.25	
Carlstrom (74)	1957	4.76	10.28	18.85	4
Dweltz (75)	1960	4.69	10.43	19.13	4
Blackwell et al (69)	1978	4.74	10.32	18.86	4

and subsequent drying in air at room temperature gives an orthorhombic pattern with lattice parameters $a=7.76$, $b=10.91$ and $c=10.30$. On the other hand, the form II chitosan, prepared by precipitating chitosan in NaOH gives $a=4.4$, $b=10.0$ and $c=10.3$. Similar results were obtained by Sakurai et al (77), who reported four sets of unit cell parameters (Table 1.6). Sample 1-1 and 1-3, prepared in formic acid by air drying and alkali precipitation, correspond well to the forms I and II, presumably due to the similar procedure involved in film preparation. Sample 3-1, however, gives c dimension substantially larger than those previously reported.

Though neither Samuels nor Sakurai mentioned reasons for the differences observed between the various parameters, there are quite a few possible explanations. Firstly, there could be variations due to differences in the degree of acetylation. The DA value may vary

Table 1.6 Unit cell parameters of chitosan
proposed by Sakurai et al (77)

Film	a(Å)	b	c
(1-1)	7.64	10.35	10.92
(1-2)	5.82	10.30	8.37
(1-3)	4.46	10.30	8.63
(3-1)	5.66	10.10	15.60

Procedures for preparation of chitosan films

1-1, cast at room temperature from the solution of chitosan-formic acid

1-2, film 1-1 subsequently treated with aqueous NaOH

1-3, neutralised and coagulated in aqueous NaOH from the solution of
chitosan-formic acid

3-1, cast at room temperature from the solution of chitosan-butyric
acid

from source to source. Besides, comparison of DA values may be misleading when different characterisation methods are used. It is clear, from the i.r spectra, that Sakurai's chitosan contains a high N-acetyl-glucosamine content. Therefore, some lattice parameters may be based on an imperfectly deacetylated chitosan and therefore more difficult to interpret. Secondly, the crystal structure of chitosan also depends on the method of preparing the sample. Both Samuels and Sakurai et al prepared chitosan film by drying chitosan solutions in air at room temperature without further treatment. As reported elsewhere, the above procedure was used to prepare a water soluble

chitosan salt, when the solvent acid combines with the solid chitosan. This 'impurity', strongly combined, will affect the crystal structure and may lead to larger lattice parameters. Indeed, in both cases, the sample prepared by air drying gives a c value substantially larger than that by alkali precipitation and further washing. Further, Sakurai et al were able to notice the effect of solvent acid size on the lattice parameter. The result, according to them, is that the unit cell parameters increase as acids of larger sizes are used. This phenomenon corresponds well with the suggested interpretation.

Ogawa et al (78) in a recent report, however, confirmed the early work by Clark & Smith (72). With a well purified chitosan sample, they obtained a film which was subsequently stretched by 100% in water at 100 °C. This film, assumed to be free of acid contamination, was annealed in a closed bomb of water at 190 °C with the film length constant. Using the above method, Ogawa et al were able to obtain a highly crystalline film. From the X-ray diffraction pattern (see Fig 1.9), the unit cell parameters were calculated as $a=8.24$, $b=16.48$ and $c=10.39$ Å, with the unit cell orthorhombic.



Fig 1.9 The new polymorph of chitosan proposed by Ogawa et al (78)

Darmon & Rudall (79) in their work involving the deacetylation of chitin, suggested that the chitosan lattice showed the same symmetry as the unit cell of α chitin. This is likely because the polymeric chain would possibly keep its original form and arrangement when the acetyl group is removed. Yet, despite the fact that α, β and γ chitin were found for chitin, no work has been reported concerning the parallel or antiparallel arrangement of chitosan chains.

1.4 Chemical modifications of chitosan

Chitosan can be regarded as a derivative of either chitin or cellulose, as pointed out earlier. Therefore, it can undergo virtually all the chemical reactions applied to chitin and cellulose. Moreover, because of the reactive nature of the free amine on the C-2 position, chitosan is probably the most easily modified polymer; it is not surprising, therefore, that a great deal of work has been carried out, modifying chitosan either through the C-6 and C-3 hydroxyl groups or through the C-2 amine. A brief summary is given in Fig 1.10.

Chitosan salts

Chitosan can form salts with a variety of inorganic and organic acids (see Table 1.7). Most of these salts are water soluble. Thus, chitosan can be dissolved in nitric and hydrochloric acids when the acid concentration is lower than 1%. Chitosan is soluble also in 0.5% phosphoric acid. Organic acids such as formic, acetic, propionic, oxalic, malonic, succinic, adipic, lactic, pyruvic, malic, tartaric and citric acids can dissolve chitosan when the acid concentration is in the range of 0.25-10% (80).

Organic solvents for chitosan have been divided into four

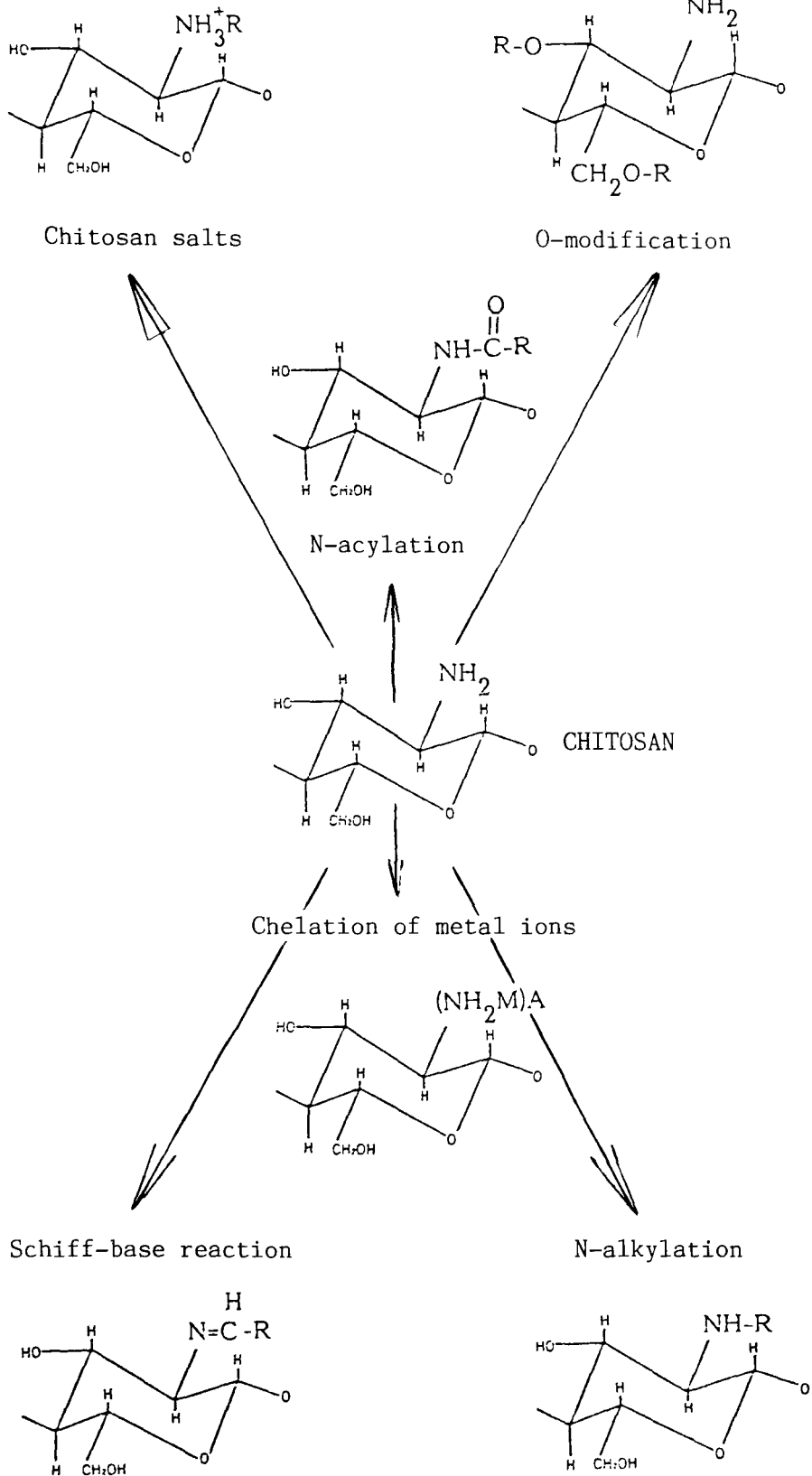


Fig 1.10 Chemical modifications of chitosan

Table 1.7 Chitosan salts (5)

(s, soluble ss, slightly soluble ins, insoluble)

Acetate	s	Lactate	s
monochloro-	s	laurate	ss
dichloro-	s	levulinate	s
monoiodo-	s	linoleate	ss
phenyl-	s	Malate	s
trimethyl-	s	maleate	s
acetacetate	s	malonate	s
acrylate	s	diethyl-	s
ethacrylate	s	mandelate	s
furacrylate	s	molybdate	ins
hydracrylate	s	phospho-	ins
adipate	s	Naphtenate, M_w 186	s
anthranilate	s	M_w 450	s
azelaate	s	Nitrate	ss
Benzensulfonate	s	Oxalate	ss
benzoate	s	Palmitate	ss
o-benzoyl-	ss	phosphate	ss
borate	s	phtalate	ss
iso-butyrate	s	picrate	ins
α -chloro-	s	propionate	s
hydroxy-	s	α -bromo-	s
n-butyrate	s	α -chloro-	s
α -bromo-	s	α -iodo-	s
Caproate	s	pyruvate	s
chromate	ins	Salicylate	ss
cinnamate	ss	sebacate	s
citrate	s	stearate	s
crotonate	s	succinate	ss
cyanate	ss	sulfanilate	s
Dilactate	s	sulfate	ins
dithiocarbonate	ss	sulfite	s
Formate	s	sodium bisulfite	ss
fumarate	ss	sulfosalicylate	s
Glycinate	ss	Tartrate	s
phenyl-	ss	terephthalate	ss
glycolate	s	tetrachloroaurate	s
di-	s	tetraiodomercurate	
thio-	s	thiocyanate	ss
Hydrobromide	s	tungstate	ins
hydrochloride	s	phospho-	ins
hydroiodide	s	meta-Vanadate	ss
hypochlorite	ss		

groups based on their solution viscosity behaviour (81). The first group where slightly non-Newtonian solutions with no clearly defined solubility limit are obtained includes 2 M aqueous solutions of acetic, citric, formic, glycollic, lactic, maleic, malic, malonic, pyruvic and tartaric acids. The second group contains 2 M dichloroacetic acid and 10% oxalic acid, and gives very non-Newtonian solutions. Chitosan solutions prepared in these two acids form gels when allowed to stand for long periods.

Chitosan samples are not well dissolved in the third and fourth groups of solvents. A slight degree of solubility is noticed in the third group of organic acids including 0.041 M benzoic acid, 0.036 M salicylic acid and 0.052 M sulphanic acid. In the fourth group, claimed to be non-solvents, are aqueous solutions of a series of compounds including DMF, DMSO, pyridine, etc.

Acetic acid is the common acid used to dissolve chitosan. In studying the tolerance of a 1% chitosan-acetic acid solution to common water miscible solvents, Filar & Wirick (80) found that organic solvents appear to exert very little effect on chitosan solution viscosity except in the case of polyols. Results are given in Table 1.8.

A few chitosan salts are insoluble in water. Because of that, chitosan solutions can be precipitated by several acids such as sulphuric, phosphotungstic, iodomecuric, iodobismuthic, molybdic, picric and tannic acids (5).

In attempts to produce a dry chitosan salt that is readily soluble in water, Austin & Sennett (82) reported a process where dry chitosan salts of carboxylic acids were prepared. In doing so, chitosan was dispersed in an organic solvent which is a solvent for

Table 1.8 Chitosan solution tolerance for common water
miscible solvents (80)

Solvent	Max. % solvent compatible	% acetic acid	Viscosity(cp)
Methanol	50	5	2480
Ethanol	50	5	2400
I-propanol	40	3	3440
Acetone	40	3	2020
Ethylene glycol	75	5	7600
Glycerol	80	3	60,000
Sorbitol	70	1	146,000
Water	/	1	2780

the organic acid but a non-solvent for chitosan. The chitosan picked up the organic acid rapidly. Several factors were found to have effects in salt formation and stability. Among them, particle size plays an important role, with the best results being obtained with the finest particles. The type of acid is also important in salt formation; formic and pyruvic acids were found to be the best acids.

N-acylation

N-acylation of chitosan can be readily carried out using acyl anhydride as the reactant. The early attempts to acetylate chitosan date back to a long time ago when chitosan was treated with acetic anhydride at 100-135 °C in a closed tube. The resulting product had properties similar to chitin (5). Acylation of chitosan using

carboxylic acids was also reported. The reaction was accelerated by dicyclohexylcarbodiimide. More recently, in their work involving gel preparation, Hirano et al (83-88) reported that novel N-acyl gels can be formed by addition of anhydride to a chitosan solution in aqueous acetic acid. Further work (89) by the same author indicated the importance of anhydride concentration and reaction medium. Thus, Hirano et al found that gels can be formed only when the molar ratio of anhydride to free amine exceeds 2.5, further increase of the ratio above 13 causing syneresis of the gel. The study of the effect of cosolvents (90) led to the conclusion that O-acylation can be introduced when water is used as the solvent, while selective N-acylation proceeds in a water-methanol mixture. In addition, the reaction was found to be much more rapid in the latter solvent system.

Moore & Roberts (91,92), in a later study, confirmed the results of Hirano et al. In their research into the formation of N-acyl gels, Moore & Roberts studied the effect of time, anhydride concentration, temperature and size of anhydride. Their results showed that gelation time decreases with increases in temperature and anhydride concentration. Further, they found gelation occurs much more rapidly in methanol, ethanol and formamide in comparison to other common solvents including water.

The mechanism of gelation was demonstrated by Moore & Roberts (92) to be the decreased solubility caused by a reduced degree of ionization due to the loss of free amine during acylation; the decreased solubility was reflected by the increase in solution viscosity, resulting finally in gelation. Thus, based on their viscosity measurement of the reaction medium and i.r spectra results,

Moore & Roberts concluded that the DA necessary to cause gelation was 73% irrespective of the reaction temperature.

The acetylation of chitosan leads to a regenerated chitin. It was found that acetylation was much faster than other acylations where larger acyl anhydrides were used. In a homogeneous system, gelation, i.e., DA larger than 73%, can be achieved within 1 min when elevated temperatures are used.

While all the acylations so far discussed were carried out under homogeneous conditions, Miya et al (93) reported a process in which chitosan films were acetylated. Thus, using methanol as the main solvent, they found the reaction was accelerated by the addition of water. No reaction was noticed without the presence of water. On the other hand, a complete 100% acetylation was achieved within 10 min when the solvent contained 50% water. In addition, considerable deformation of the film occurred when the water content exceeds 50%.

The effect of initial acetyl content was also studied. It was found that acetylation proceeds much more slowly when the sample had a lower initial degree of acetylation. Also, in studying the effect of the initial degree of crystallisation, Miya et al found the presence of water helps to destroy the crystal structure and thus accelerate the reaction. Slight O-acetylation was also noticed. This, as in other reports, was removed by dilute alkali treatment (86).

Schiff-bases and their reduced products

It is well known that Schiff-bases can be formed by the reaction between amines and aldehydes or ketones. Chitosan is one of the few natural polymers with free amine groups. Therefore, reaction of chitosan with aldehydes or ketones provides a convenient way for

structural modification.

Hirano et al (94) have reported that chitosan reacts readily with aldehydes in aqueous acetic acid solution. Using 10% aqueous acetic acid and 5% chitosan, gels formed when the mixture of chitosan and some aldehydes was stored overnight. In another report, Muzzarelli & Rocchetti (95) modified chitosan with aldehyde-acids and keto-acids, from which they obtained a series of polymers possessing such groups as carboxyl, primary and secondary amines and primary and secondary hydroxyl. The products showed excellent chelating properties. To prepare such an aminoacid glucan, 10 g of chitosan was suspended in 1.5 l water and excess (1.5 mol per mol glucosamine) of ketoacid was added. The resulting pH value was slowly adjusted to 4.5 with 0.2 M NaOH. The insoluble product was then reduced with sodium cyanoborohydride dissolved in water (5.85 g in 50 ml) and the pH value was finally adjusted to about 7 with 1 M NaOH. After 48 hours, the polysaccharide, in the aminoacid form, was washed, dialyzed against water and isolated.

More recently, Muzzarelli et al (96) obtained some amphoteric derivatives of chitosan, using similar procedures. These products such as N-carboxy-methyl and N-carboxy-ethyl chitosan are found to be excellent wound healing accelerators, in addition to being novel metal ion chelators.

The ability of chitosan to undergo Schiff-base reaction was used by Nud'ga, Plisko & Danilov (97) to protect the $-NH_2$ group in selective O-modification. They found that the reaction between amine groups and salicylic aldehyde was quantitative. The salicyclidene chitosan was stable under alkaline conditions while it could be decomposed in acidic media.

Reaction with halogen substituted compounds

Both -OH and -NH₂ groups are reactive with halogen substituted compounds. This offers an easy way for structural modification. Thus, halogen-substituted alkyl compounds react easily with chitosan, resulting in various alkylated chitosans with a variety of properties (98).

Typically, alkylation of chitosan with alkyl halides is carried out under basic conditions. However, in all circumstances, -NH₂ is more reactive than -OH. Therefore, in order to retain amine groups during the reaction, suitable precautions need to be taken. According to Nud'ga, Plisko & Danilov (97), O-substitution can be carried out after Schiff-base protection, as has already been mentioned above. The Schiff-base was then removed by the action of acetic acid.

Chelation of metal ions

The absorption of metal ions by chitosan was studied early by Sadov (99), Manskaya, Drozdova & Emel'yanora (100) and Andreev, Plisko & Rogozin (101). These early workers emphasised the ability of chitin and chitosan to absorb metal ions. However, the mechanism was not well defined until Muzzarelli (56) pointed out the chelating properties of chitin and chitosan. Three possible mechanisms might account for the uptake of metal ions; these are, ion-exchange, sorption and chelation, with chelation the most important. The above view was confirmed by the results of Yoshinari & Subramanian (102).

Though a number of reports are available on the chelation of metal ions by chitin and chitosan, the subject is still developing

in terms of the precise structure of the metal-chitin or chitosan complex. There are a few (103,104,105) proposed mechanisms in which one or two amine groups were involved in the complex. However, none of them has so far been widely accepted.

The interaction of the first row transition metal ions with chitin and chitosan is accompanied by the appearance of colour in almost all instances, namely red with titanium, orange with metavanadate, green with trivalent chromium and orange with hexavalent chromium, yellowish-brown with divalent iron, yellowish-green with trivalent iron, pink with cobalt, green with nickel and blue with copper (5).

In terms of the affinity of metal ions to chitin and chitosan, Muzzarelli et al (56) observed that chitosan absorbed metal ions in the order of $\text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Fe} > \text{Mn}$, in a 0.1 M KCl solution. Koshijima et al (106) found the order to be $\text{Hg} > \text{Cu} > \text{Fe} > \text{Ni} > \text{Cd} > \text{Mn} > \text{Co} > \text{Pb}$ for a 0.15 M Na_2SO_4 solution, while Yoshinari & Subramanian (102) recognised the order to be $\text{Ni} > \text{Zn} > \text{Co} > \text{Cu} > \text{Pb} > \text{Fe} = \text{Mn} > \text{Mg} > \text{Ca}$ for chitin. More recently, in a study on metal ion uptake onto chitosan using ion-selective electrodes, Kawano et al (107) found the order to be $\text{Hg} > \text{Ag} > \text{Cu} > \text{Cd} > \text{Pb}$. Further, the effects of anion was found in the order of $\text{CuSO}_4 > \text{Cu}(\text{Ac})_2 > \text{CuCl}_2 > \text{Cu}(\text{NO}_3)_2$.

1.5 The production of fibres from chitin and chitosan

To start this section, a summary of the research work into the production of fibres from chitin is given in Table 1.9 (A complete review of the work on chitin is given by Agboh (37)).

As can be seen from the table, a large number of systems have been proposed for producing chitin fibres. Each new study has

Table 1.9 The production of fibres from chitin

Authors	Year	Solvents used	Tenacity(g/dtex)
Kunike (10)	1926	conc. H_2SO_4	2.5
Knecht & Hibbert (11)	1926	conc. HCl	
Clark & Smith (72)	1936	aq. NaSCN	
Thor & Henderson (12)	1939	chitin xanthate 40% Cl_3CCOOH	
Austin & Brine (108)	1977	40% chloral hydrate 20% CH_2Cl_2	4.5
Balassa & Prudden (109)	1978	chitin xanthate	0.81-1.37
Tokura et al (110)	1979	HCOOH	0.61-1.43
Nakajima et al (111)	1984	DMAc-LiCl	3.57
Kifune et al (112)	1984	Cl_3CCOOH	1.48-3.92
Agboh (37)	1986	DMAc-LiCl	0.7-2.2

1 g/dtex= 0.0102 mN/tex

described either a new solvent or improved fibre properties. Yet, quite surprisingly, despite the advantage of being a much more easily soluble polymer, few reports were found in the literature dealing with the production of chitosan fibres. It was as recently as 1980 when the first report, by a Japanese company, claimed that chitosan fibres could be produced by dissolving the acetate in water. In their patented process (113), Mitsubishi Rayon used 0.5% aqueous acetic acid as solvent to prepare a dope containing 3% chitosan. The dope was then spun into 5% aqueous NaOH. The fibre possessed a tenacity of 2.44 g/denier, an elongation of 10.8% and a knot strength of 1.75 g/d.

In another patent just one month later (114), the same company reported another process in which 3% chitosan dopes in 1% aqueous acetic acid were extruded into an aqueous bath containing 2% Na lauryl sulfate. No fibre properties were given.

Later, in 1984, another Japanese company, Fuji spinning Co. Ltd. claimed a new process (115). From the limited source available, it appears that fibres were prepared by dissolving chitosan in di-chloroacetic acid, followed by precipitation in a basic bath containing $\text{CuCO}_3\text{-NH}_4\text{OH}$. The same company (116) reported another process in which a urea-acetic acid mixture was used as the solvent. The dope was extruded into a bath composed of 5% aqueous NaOH and alcohol, 90:10. For a 3.2 denier fibre, the strength was 12.2 grams, with an extensibility of 17.2%.

Recently, in preparing fibres from variously deacetylated chitosans, Tokura et al (117) reported that chitosan fibres can be prepared by extruding dopes in 2-4% acetic acid into a bath containing $\text{CuSO}_4\text{-NH}_4\text{OH}$ or $\text{CuSO}_4\text{-H}_2\text{SO}_4$. The fibres obtained were a complex of chitosan and copper, the latter being removed afterwards. In a private communication, the author claimed that the use of copper leads to a preferred arrangement of the chitosan chains such that the surface contained a high concentration of amine groups, a phenomenon which didnot normally occur. The properties of the chitosan fibres so produced are given in Table 1.10; some doubts must be expressed regarding the validity of some of these results, in particular, the knot strength values.

1.6 Properties and applications of chitosan

Chitosan is one of the few natural polymers that possesses free amine

Table 1.10 Properties of chitosan fibres reported by Tokura et al (117)

Samples	Denier	Tenacity (g/d)		Elongation (%)		Knot strength (g/d)		Relative tenacity
	(d)	Dry ^a	Wet ^b	Dry ^a	Wet ^b	Dry ^a	Wet ^b	Dry/Wet
Chitin fiber	8.5	1.28	0.23	8.4	15.6	0.45	—	0.18
	4.2	1.39	0.33	3.6	10.1	—	—	0.24
DAC fiber (DAC-45)	7.5	1.74	0.98	11.3	10.3	0.81	—	0.56
(Cu ads) - (DAC-51)	3.0	2.80	1.23	6.6	6.1	not measurable		0.44
(DAC-51)	3.5	2.26	1.09	9.6	7.6	—	—	0.48
(DAC-54)	4.7	2.41	1.32	9.3	7.1	—	—	0.55
(DAC-67)	4.4	1.95	0.67	14.2	11.3	1.36	—	0.34
(DAC-70)	7.0	1.55	1.28	8.8	7.7	—	—	0.83
(DAC-70)	6.4	1.28	0.68	18.9	14.2	1.17	—	0.53
(DAC-70)	6.3	1.71	1.57	8.9	7.4	—	—	0.92
(DAC-80) ^a	3.2	1.70	—	6.9	—	—	—	—
(DAC-80)	6.4	1.28	0.86	17.8	14.2	—	—	0.62
(DAC-84)	10.9	1.10	0.90	9.7	8.4	1.17	—	0.82
(DAC-84)	8.7	1.49	1.18	13.0	10.4	1.56	—	0.79
(DAC-90)	6.2	1.95	1.15	12.7	11.5	—	—	0.59
(DAC-90) ^c	7.1	2.56	1.13	37.3	21.0	2.06	3.33	0.44
(DAC-90) ^c	5.9	1.67	0.86	26.9	20.2	1.42	7.42	0.52
(DAC-90) ^c	10.0	0.77	0.64	41.4	58.13	0.77	5.84	0.83
(DAC-90) ^c	5.4	2.21	—	12.7	—	1.86	—	—

a: 20°C, 65% RH. b: 20°C, 100% RH. c: Concentration of spinning dope was 6.0% in 4% aqueous acetic acid. (Cu ads): copper adsorbed DAC-51 fiber before EDTA treatment. (DAC-80)^a: DAC fiber was coagulated in (b) coagulant system (without use of copper).

groups along its chains. Also, there are two hydroxyl groups in the repeating glucose residue. Because of this unique structure, chitosan possesses numerous special properties (5). According to Hirano (118), the main characteristics of chitosan are as follows:- (1) a renewable resource; (2) biodegradable; (3) biocompatible; (4) non-toxic; (5) biologically functional and (6) chemically modifiable.

In addition, owing to the nature of the nature of the free amine groups, chitosan is an excellent chelating polymer. In acidic solution, it is also a polycation.

The applications of chitosan are really wide. To give a brief summary, chitosan has been an additive to Japanese noodles (118), a clarifier for American swimming pools and a shampoo additive for German girls (119). A full review of its applications will require too large a section (5,120), however, some possible applications of fibres

made from chitosan are given below.

(1) Waste water treatment

This is actually the application where most chitosan (or even chitinaceous) material is being consumed. In this field, chitosan functions as a chelator for removal or recovery of hazardous metal ions (5), as a polycation for recovery of protein or clarification of polluted water or as a backbone for the absorption of waste dyestuff (121,122,123,124). Fibres or fabrics of chitosan are very useful here as it gives a form which is easily handled.

(2) Precursor for further modification

The free amine and hydroxyl groups make chitosan a very easily modifiable polymer. As stated earlier, there have been a number of derivatives of chitosan. These products such as carboxy -methyl chitosan, N-acyl chitosan, hydroxy -alkyl chitosan and metal ion modified chitosans may find better end uses in wound healing, metal ion chelation, water soluble fibres, non-inflammable fibres, etc. Further, chitosan fibres can be the basis for protein immobilisation and enzyme incubation (125). They can also act as a drug carrier for more sophisticated purposes.

(3) Wound healing accelerator

Crab shells have been used by the Korean people for the healing of wounds for a very long time. While the mechanism might appear to be shrouded in eastern mystery, in 1978, the wound healing properties of chitin were demonstrated in America. In the first international conference on chitin and chitosan, Balassa & Prudden (109) reported

that the healing of human wounds can be accelerated by as much as 75% simply because of the application of a dressing made of chitin. Many reports have been published (5,109,126,127), showing that chitin, chitosan and their derivatives can be used to accelerate wound healing in surgical and dental treatment.

During the fourth international conference on chitin and chitosan, Olsen (128) demonstrated that the wound healing properties of chitin and chitosan are due to: (1) controlled delivery of N-acetyl glucosamine or glucosamine from chitin and chitosan through enzymatic degradation; (2) mucopolysaccharide organisation of collagen; (3) inhibition of fibroplasia and selective tissue generation; (4) stimulation of the inflammatory components of wound healing.

(4) Suture materials

Chitin and chitosan are reported to be biodegradable and non-toxic (129). This makes them suitable candidates for suture materials. Though a few suture materials are currently available, however, none of them are perfect. Thus, Nakajima et al (111) has reported that chitin sutures can be produced with tensile strength about 50 Kg/mm^2 . The braided sutures were found to be maintained well in bile, urine and pancreatic juice, which are problem areas with other absorbable sutures. Toxicity tests also showed that the chitin sutures are negative in mutagenicity, acute toxicity, pyrogenicity, hemolysis and skin reaction.

(5) General textile uses

Chitosan has a very high moisture regain due to its many hydrophilic

groups; also, in view of the various functional groups present, its dyability should be excellent. Therefore, considering the potential comfort and outlook of chitosan fabrics, there should be a market if chitosan fabrics could be produced at relatively low costs. The basic problem is the supply of the raw material. Thus, if the production of large quantities of chitosan becomes economical by various means, e.g., insect farming or fermentation of fungi, the potential uses of chitosan should be extensive.

1.7 Aims of the present work

The main objective was to establish a procedure so that chitosan fibres can be produced with properties applicable as wound dressing or hopefully suture material. Though a few patents concerning the production of chitosan fibres were available at the beginning, much remained unknown of chitosan and its fibres such as the effects of spinning conditions on fibre properties and the basic properties of chitosan in fibre form. Therefore, it is the aim of the present work to carry out such investigations.

The conversion of chitin to chitosan and reversely, chitosan to chitin have already been extensively studied. However, no report was found dealing with the conversion of chitosan to chitin in fibre form. In view of the anticipated ease of the processing of chitosan fibres and the better thermal and chemical stability as well as the wound-healing properties of chitin fibres, the conversion of chitosan fibres to chitin fibres was thought to be worthy of study. Therefore, it was also the aim of the present work to carry out such investigations to see if chitin fibres could be made

indirectly from chitosan fibres. Also, if this could be, it was intended to study the property differences between the two fibres. Naturally, with the previous experience of producing chitin fibres in this laboratory, it would be possible to compare the chitin fibres made indirectly from chitosan with the fibres made directly from chitin.

Chapter two
EXPERIMENTAL

2.1 Materials

Chemicals

Acetic acid: 99% glacial, Aldrich.

NaOH: pellet, general purpose reagent, Wharfedale Laboratories.

Acetic anhydride: analytical grade, Koch-light Laboratories Ltd.

Methanol: analytical grade, BDH.

I-propanol: analytical grade, BDH.

Glucosamine: analytical grade, BDH.

Na_2SO_4 : general purpose reagent, BDH.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$: analytical grade, BDH.

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: analytical grade, BDH.

Chitosan was supplied by Protan laboratory in three viscosity grades, namely, high, medium and low with respect to the viscosity of a 1% solution in 1% aqueous acetic acid. The material was used as supplied.

Most of the fibre spinning was done with the medium grade. Some basic properties of the three grades of chitosan were indicated by the supplier, as shown in table 2.1.

2.2 Characterisation of chitosan samples

Viscosity measurements of chitosan dope

The viscosity of concentrated chitosan solutions was obtained on a Haake Rotovisko cylinder type rotational viscometer. A detailed

Table 2.1 Properties of the original chitosan samples (130)

Grade	Viscosity (cp)	DD value (%)	Impurity content (%)
Low	50	81.0	0.70
Medium	750	84.0	1.23
High	2790	80.4	0.89

description of the instrument can be seen in Agboh's thesis (37).

The cup used in this work was the SV1 type with measuring head type M1500. Most of the time the sensitivity was adjusted to $E=0.3$ and speed reduction to $R=1$. The shear rate, shear stress and viscosity can be calculated from the following equations:-

$$D=0.89n$$

$$t=12.4S$$

$$V=13920S/n$$

where

D: shear rate, S^{-1}

n: actual test speed, min^{-1}

t: shear stress, Pa

S: scale grade

V: viscosity, $\text{mPa.S}(\text{cp})$

Spinnability test

A simple spinnability test was carried out by injecting a small amount of dope, usually 5 ml, into the precipitant. The method used a plastic syringe, a needle and a beaker. The spinnability was judged by (1),

solution viscosity, (2), ease of filament formation and (3), strength of the resulting filament.

Elemental analysis

Elemental analysis was carried out on a Carlo Erba Instrumenziome elemental analyser, model 1106 in the Chemistry Department. In measuring C, H and N contents, 1 mg of the sample was weighed; the sample was then burned in oxygen at 1000 °C. After that, the resulting mixture was carried by helium into a gas chromatographic column. The C, H and N contents were calculated from the peak areas of CO₂, H₂O and NO₂.

In measuring Cu(II) and Zn(II) contents, the sample was firstly digested in sulphuric acid to remove the organic material. The Cu(II) and Zn(II) contents were then measured by atomic absorption. This analysis was also performed in the Chemistry Department.

Infrared spectroscopy

I.r spectra were recorded on an Unicam SP 1025 infrared spectrophotometer. Chitosan films were prepared by casting a 0.5% solution on a glass slide, with subsequent immersion in a dilute solution of ammonia. The film was then stripped off the slide in water, washed and carefully fixed on a window made on a piece of plastic. The film was then partially dried in air, before it was fully dried under an infrared lamp.

On some other occasions, chitosan films were made by casting a 0.5% chitosan solution onto a glass slide and air drying at room temperature. To allow study of the acetylation reaction, the dry film was stripped off the slide and acetylated in 5% acetic anhydride in methanol for 1 hour at 40 °C. The film was washed well with methanol

and dried at 60 °C. An i.r spectrum was then recorded. The film was then treated with 1 M aqueous NaOH overnight, washed with water and dried. A further i.r spectrum was recorded after the film was dried with an infrared lamp.

p-Toluene sulphonic acid treatment

The purification process was carried out under similar conditions as mentioned by Agboh (37). 22.5 grams of toluene-4-sulphonic acid was measured into a 500 ml flask; the mixture was stirred until the solid was fully dissolved in i-propanol. Then 10 grams of chitin or chitosan was measured into the flask. The treatment was carried out at 75 °C in a water bath for 2 hours. After that, the mixture was filtered using a sintered glass crucible.

2.3 Wet-spinning of chitosan fibres

Dope preparation

In this work, acetic acid was used as the solvent acid. To prepare chitosan dopes, aqueous acetic acid was first prepared by mixing X ml of glacial acetic acid with Y ml of distilled water. Z grams of chitosan was then measured into a plastic jar, followed by addition of W ml of the acid solution. The mixture was stirred overnight to produce a clear, viscous solution. Solvent acid concentration and dope concentration can be obtained from the following equations:-

$$c\% = \frac{Xq'}{Xq' + Yq''} \times 100$$

where

c%: w/w percentage concentration of the solvent

q' : density of glacial acetic acid, 1.049 g/ml

q'' : density of distilled water, taken as 1 g/ml

X : amount of acetic acid, ml

Y : amount of distilled water, ml

$$C\% = \frac{Z}{Z+Wq} \times 100$$

where

C%: w/w percentage dope concentration

q : density of the solvent, taken as 1 g/ml

Z : amount of chitosan, g

On occasion, dopes were made up using a co-solvent such as methanol or iso-propanol; where those were used will be indicated in the results section.

As chitosan is a highly hydrophilic polymer, under normal conditions it absorbs moisture. Moreover, the chitosan sample used in this work contained quite a high insoluble fraction. Therefore, the weight of chitosan sample, even if completely dried, will give a misleading result in calculating the concentration. To give a more accurate measurement of the dope concentration, a known amount of clean filtered dope was taken and weighed. It was then dried at 60 °C under vacuum for 24 hours. The dry weight of the chitosan left divided by the initial weight of the dope was taken as the exact dope concentration.

Filtration of the dope

In this work, filtration of the dope was carried out in a special filtration unit separate from the spinning unit. A brief description is given as follows:-

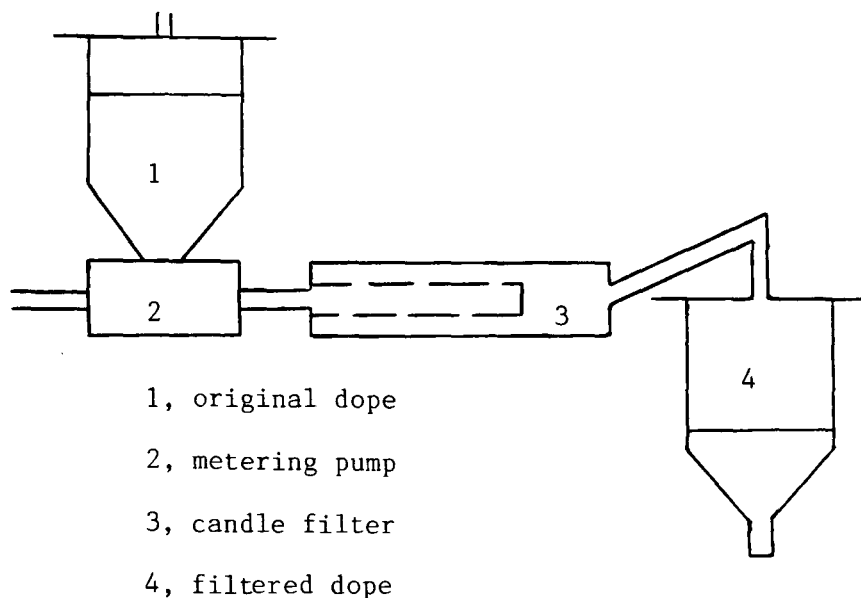


Fig 2.1 The filtration system

As can be seen from Fig 2.1 and Fig 2.2, the filtration unit comprises three main parts, i.e., a pot, a gear pump and a candle filter. When in operation, nitrogen pressure is exerted on the top of the pot and the dope is forced to flow into the gear pump which sends it steadily into the candle filter at a controlled rate. The candle filter, a standard cellulose acetate filter, was wrapped with cotton wool and tightly bound by a piece of polyester cloth to give efficient filtration.

In this work, because the original chitosan contains about 1% impurities, a prior filtration was also carried out by using a steel mesh fixed on the bottom of the pot. The mesh made the filtration much easier and ensured a longer use of the candle filter.

Starting with a clean unit and a well dissolved dope, the filtration was carried out in the following way:-

- a. The steel mesh was fixed properly at the bottom of the pot

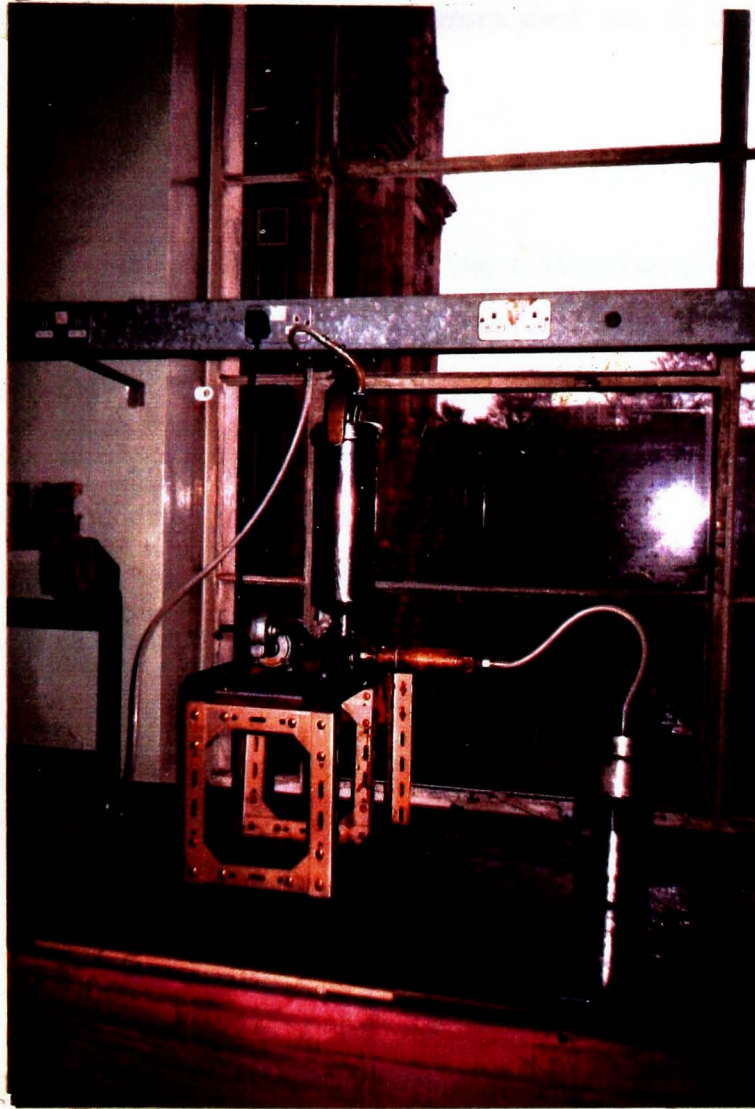


Fig 2.2 The filtration unit

so that the space between the edge of the mesh and the internal surface of the pot was the minimum.

- b. The dope was poured into the pot.
- c. The pot was properly sealed and N_2 pressure was applied. In the filtration process, the pressure used was 10 lb/in^2 .
- e. The pump was switched on.

Deaeration of the dope

The dope usually contains bubbles after the filtration process; the bubbles are brought in mainly from the dissolution stage. It is necessary to remove the bubbles before spinning. In this work, two ways were used to deaerate the dope. One was to store the dope in the pot after filtration and let the dope degas naturally. This usually took a few days for the dope to be free of bubbles. The other way was to apply a vacuum to the dope and degas the dope under reduced pressure. In this method, the removal of bubbles took about 3-5 hours, far less than the first one. However, despite the greater speed of this procedure, some problems occurred when this method was used; the evaporation of solvent tended to thicken the dope and caused skin-formation on the surface. To avoid this, some 10 ml of solvent was put into the pot (on the top of the dope) before the vacuum was applied.

Extrusion

The extrusion of dope was brought about by the use of a gear pump; the pump used was in most cases of a capacity of 0.4375 cc/rev. and with a variable speed of 3-27 revolutions per minute. Nitrogen pressure was applied to ensure a steady supply of dope to the pump,

the pressure being 30 lb/in² in all the spinning experiments. The dope passed through the gear pump to an extrusion unit before precipitation started. The extrusion unit comprised three parts, i.e., a jet, a spinneret and a jet nut together with some filtering material to ensure a clean flow of the dope. The spinneret used in this work was of 20 holes, 80 um in diameter.

While most of the work used this equipment (fully described by Agboh (37)), in some of the later work, a small extrusion unit was used, together with the existing bath and take-up rollers. The new extrusion unit comprised an acid resistant pump with a capacity of 1 ml/min, the existing jet, jet nut and the spinneret (see Fig 2.3).

The jet extrusion rate was adjusted by adjusting the speed of the gear pump. With a fixed extrusion rate, the jet stretch ratio was adjusted by adjusting the take-up speed of roller 1 (see Fig 2.4).

The extrusion rate v and the jet stretch ratio can be calculated from the following equations.

$$\begin{aligned} v &= \frac{C}{S} \\ &= \frac{cN}{3.14nd^2/4} \times 10^6 \\ &= \frac{4cN}{3.14nd^2} \times 10^6 \\ r &= \frac{v'}{v} \end{aligned}$$

where

C: flow rate, ml/min.

S: cross-sectional area of the spinneret holes.

c: gear pump capacity, ml/rev.

N: pump speed, rev/min.

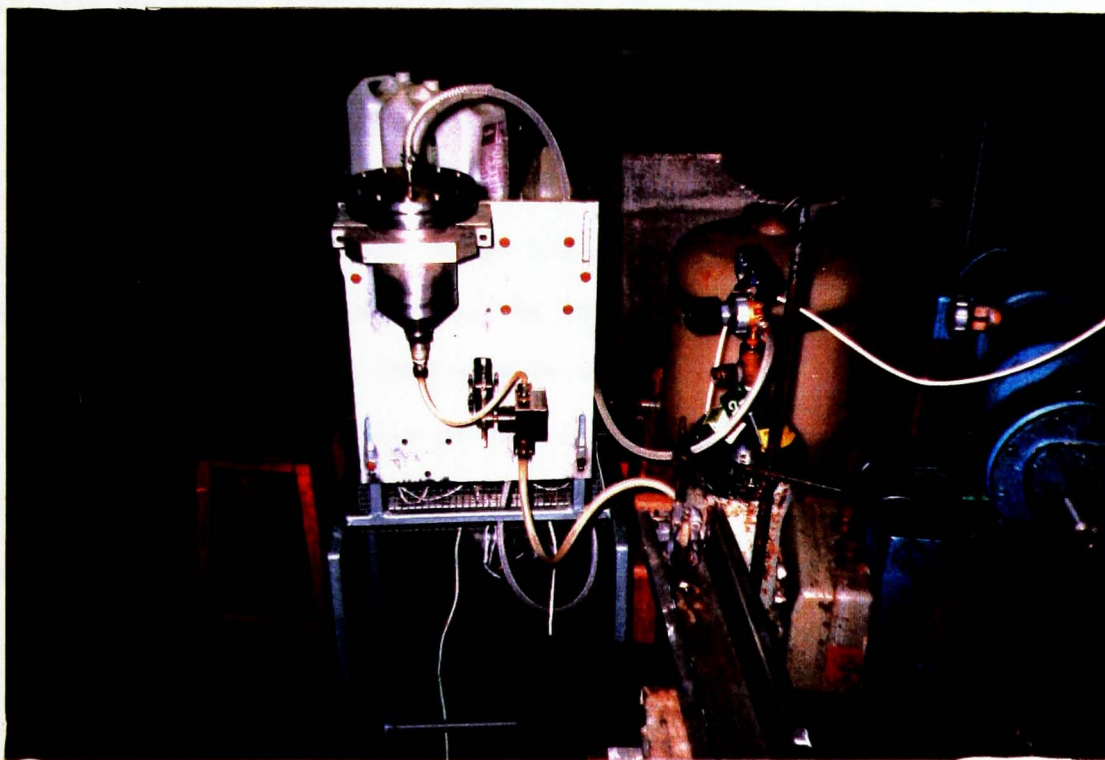


Fig 2.3 The extrusion unit

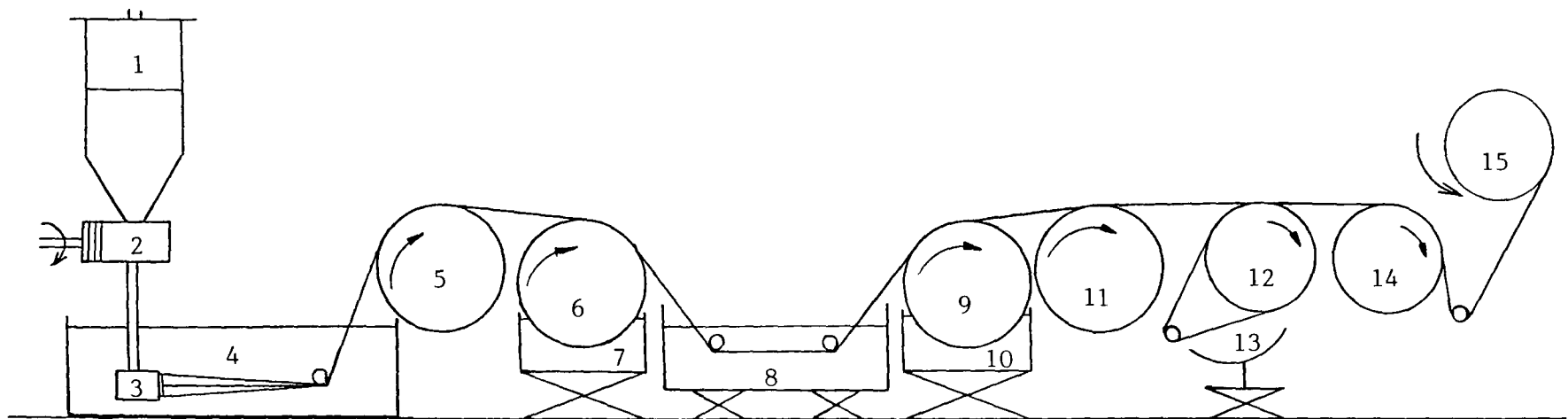
- d: spinneret hole diameter, μm .
- n: hole number
- r: jet stretch ratio
- v: extrusion rate, m/min.
- v': take-up speed, m/min.

Coagulation

In this work, the coagulation bath used was usually a 5% aqueous NaOH solution. To prepare this solution, 200 grams of sodium hydroxide pellets were firstly weighed into a plastic jar. Then, 500 ml distilled water was added. The mixture was stirred well till the solid was fully dissolved. After that, the jar was allowed to stand for cooling. In the next step, the concentrated solution was diluted to 5% by mixing it with 3300 ml more water.

In studying the effect of NaOH concentration on the fibre properties, 150 grams of NaOH pellets were dissolved in 2850 ml of distilled water to prepare a 5% aqueous NaOH bath. Chitosan fibres were prepared using this bath at a jet stretch ratio 0.4, with the draw ratio at the highest possible. Then, 900 ml of distilled water was added to the bath; fibres were again produced with the same jet stretch ratio and at the maximum draw ratio. The bath was further diluted to 3% and 2% by additions of 1250 and 2500 ml distilled water respectively, yarn samples being collected at each concentration.

In studying the effect of the addition of salts to the coagulation bath, 600 grams of sodium sulphate was dissolved in 3600 ml of hot water. Spinning was carried out with this solution as the coagulation bath. After the initial failure to obtain sample fibres (because of the low coagulating power), 42 grams of NaOH (dissolved



1. pot, 2. gear pump, 3. jet, 4. the coagulation bath, 5. advancing roller one, 6. roller two, 7. washing bath, 8. hot water draw bath, 9. roller three, 10. washing bath, 11. roller four, 12. roller five, 13. radiant heater, 14. roller six, 15. the winder.

Fig 2.4 The wet-spinning line for the production of chitosan fibres

in 58 ml of distilled water) was added into the bath, and fibres were prepared as usual.

In further studies of the coagulation behavior of the sodium sulphate bath, the effect of zinc and copper ions was examined by the addition of their concentrated aqueous solutions. The zinc sulphate solution was prepared by dissolving 120 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 200 ml water while that of copper sulphate was prepared by dissolving 60 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 200 ml water.

In studying the effect of coagulation bath temperature, the salt bath (containing 600 grams of sodium sulphate, 3600 ml water and 1% w/w NaOH) was held at 40 °C overnight. Wet-spinning was carried out as usual.

A long bath 120 cm in length was used for the spinning. The effective length was adjusted to around 100 cm, allowing space for the jet and the proper angle for taking-up of the wet filaments (see Fig 2.5).

Drawing

The drawing process was carried out between rollers 2 and 3 (see Fig 2.6) on the spinning system. A hot water bath was used as the drawing medium; in general, its temperature was set at the highest possible, i.e., 80-85 °C. The draw ratio was adjusted by adjusting the surface speed of roller 3. The draw ratio can be calculated from the following equation.

$$R\% = \frac{v'' - v'}{v'} \times 100$$

where

R%: percentage draw ratio

v' : surface speed of roller 2, m/min.

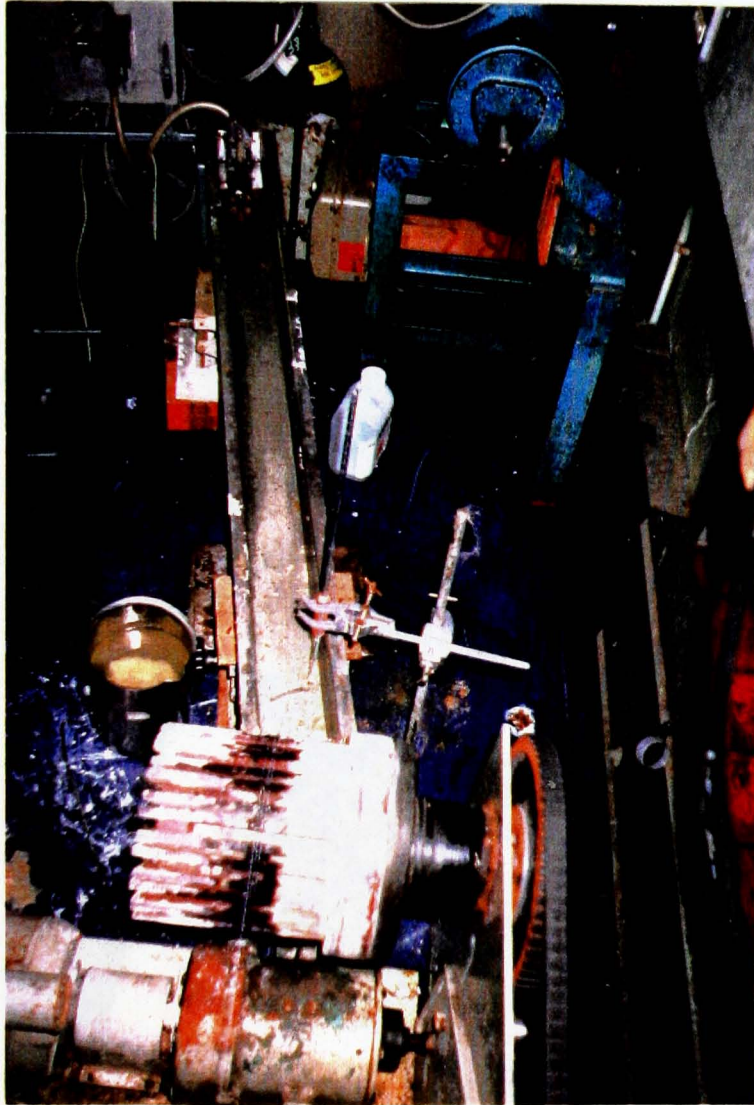


Fig 2.5 The coagulation bath

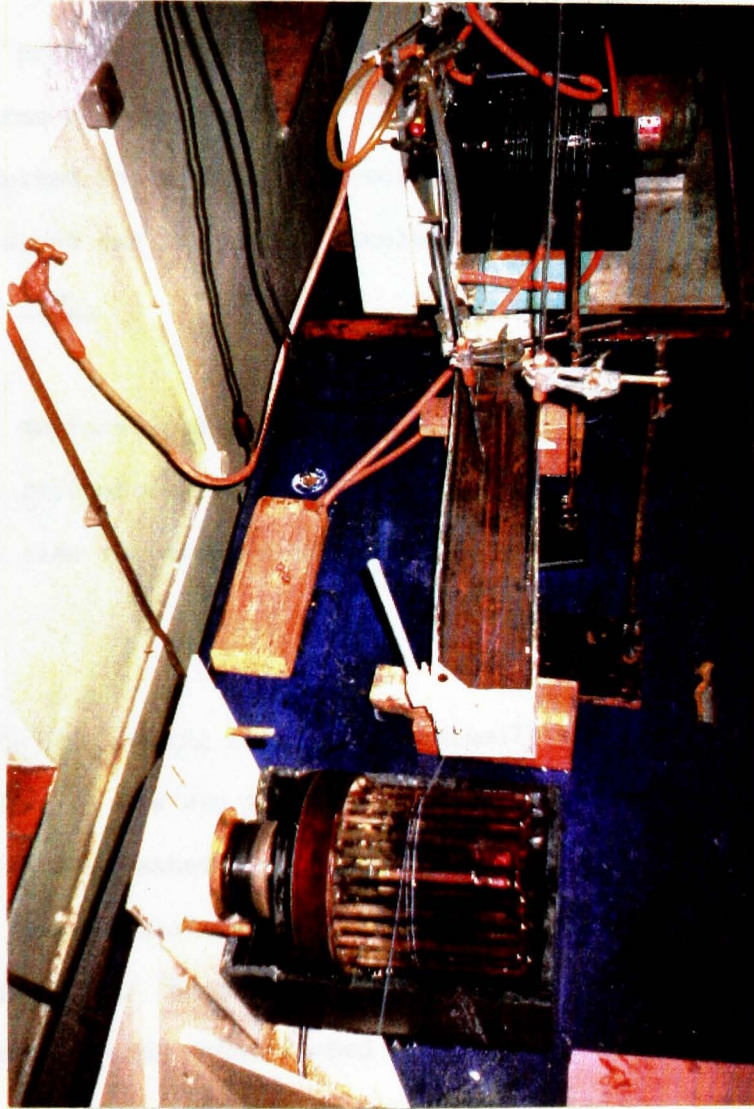


Fig 2.6 The hot water draw bath

v'' : surface speed of roller 3, m/min.

Two ways were used to measure the surface speed of the advancing rollers. At the beginning of the present study, a tachometer was used to indicate the speed. This method is simple and direct, yet the speed measured may not be accurate as often the reading was not steady. In view of this problem, an alternative method was used, in which the speed (in terms of revolutions per minute) was measured by measuring the time required to complete 10 revolutions. Using the circumference, the surface speed can be easily calculated as

$$V = \frac{60L}{t}$$

where

V: surface speed, m/min.

L: circumference, m.

t: time required to rotate one revolution, s.

Washing

In this work, the washing process was actually composed of four stages. The first one was the washing bath situated under roller 2; the filaments were washed in a stationary bath to remove the surface liquid from the coagulation bath. They were then washed in hot water in the drawing bath. Finally, the filaments were passed through roller 3 where running water washed them thoroughly before entering into the fourth bath under roller 4 (see Fig 2.7).

Drying

Two ways were used in this work to dry the wet filaments. The first comprised passing them through an acetone bath situated under roller 3 and allowing them to dry naturally or in a slight air stream (when

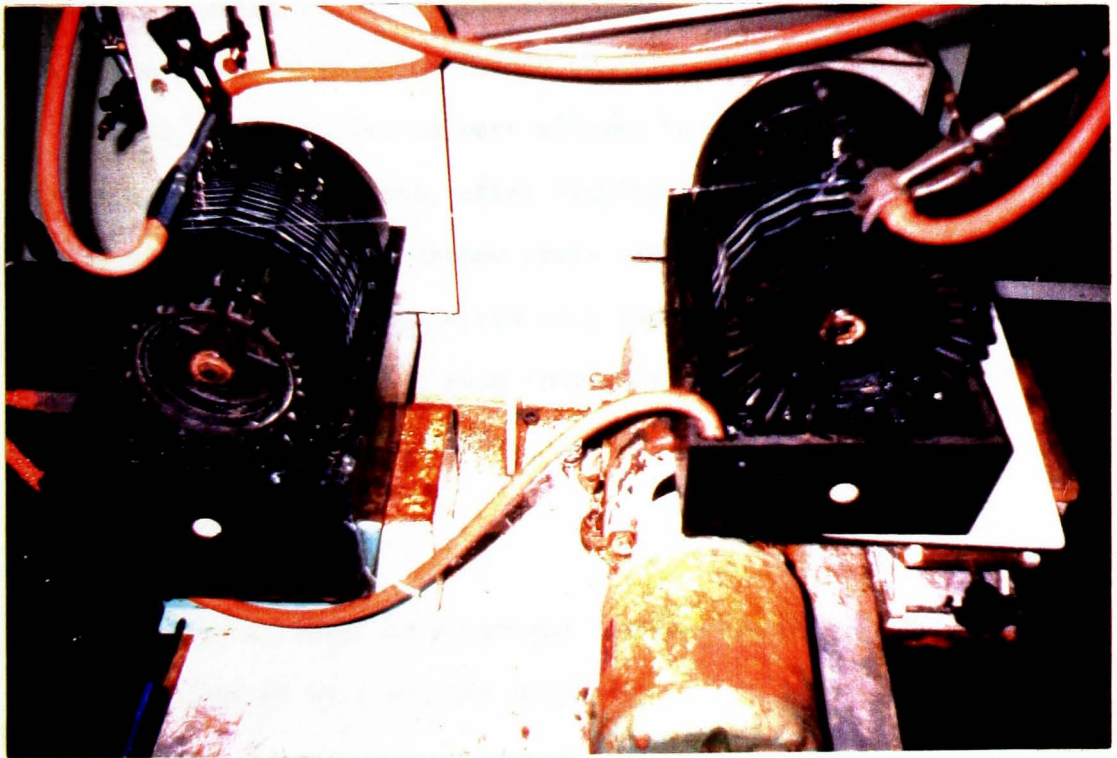


Fig 2.7 The washing unit

this method was used, the running water bath was moved to roller 2). In this method, the wet filaments passed over roller 3 with 6-10 turns. It then proceeded to the chrome reels onto which air blows through a funnel. The second was carried out by passing the wet filaments over the chrome reels which were heated from beneath by a radiant heater. The temperature could be adjusted by the power supplied. To improve the efficiency and also to prevent the fibre from being overheated, a jet of compressed air was applied from the top, again using an inverted filter funnel (see Fig 2.8).

On one occasion, fibres were allowed to dry in air. In doing so, the wet filaments, after drawing in the hot water bath, were advanced through the chrome reels without radiant heating. The filaments were then collected in a paper box where they were allowed to dry naturally at room temperature. Next, the filaments were wound up onto paper bobbins.

Winding-up

Winding-up was achieved on a Leesona S precision cone winder. The speed was adjusted by the power supplied.

Summary of the spinning process

A brief description of the whole wet spinning process for the production of chitosan fibres is summarised as follows:-

- a. Solvent was prepared.
- b. Chitosan was dissolved in the solvent at the desired concentration.
- c. Dope was filtered and degassed.
- d. Coagulation bath was prepared.

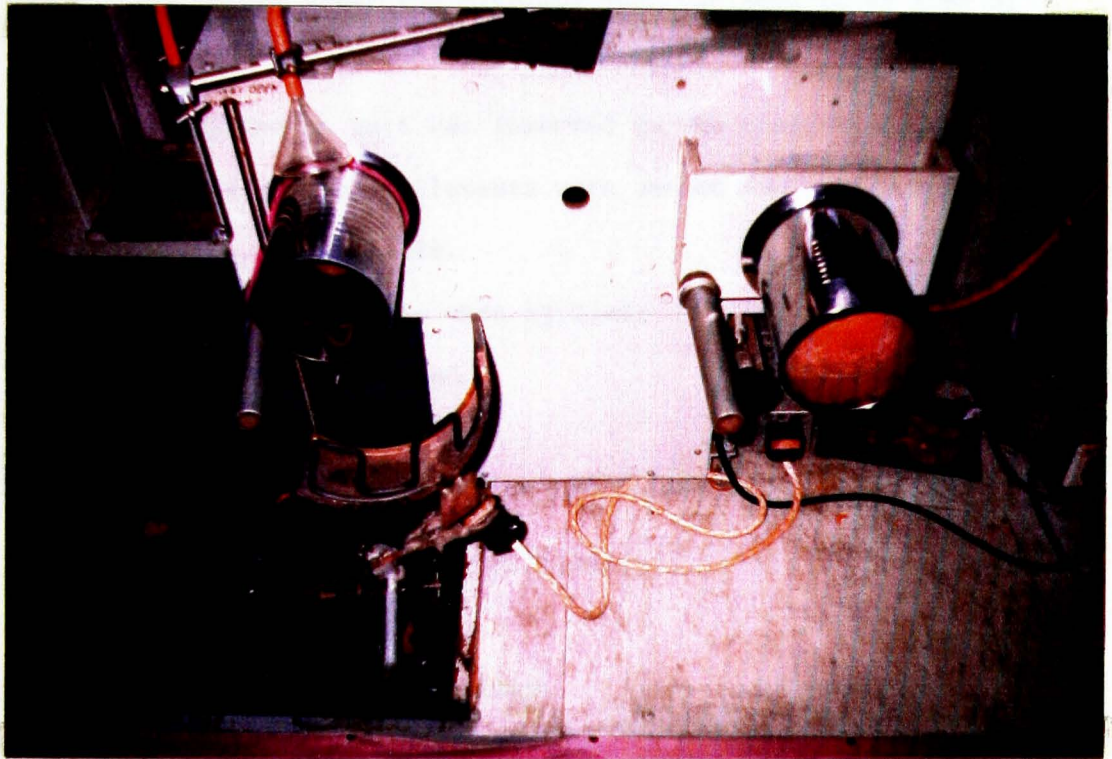


Fig 2.8 The drying unit

- e. Drawing bath was heated to 80-85 °C.
- f. Nitrogen pressure was applied to the spinning dope.
- g. Gear pump was switched on and it was adjusted to the required speed.
- h. Rollers 1, 2, 3, 4 were adjusted to the desired speeds.
- i. Spinneret was attached to the jet nut.
- j. The jet nut together with the spinneret was fixed onto the jet holder after the extruded dope was seen to be free of bubbles.
- k. The spinneret unit was immersed in the coagulation bath.
- l. The newly formed filaments were passed over rollers 1, 2, 3, 4 and the chrome reels.
- m. Heater and air flow were applied.
- n. Fibres were collected.

2.4 Characterisation of chitosan fibres

Measurement of yarn linear density

The linear density is usually expressed in two ways, i.e., denier and decitex. The former refers to the weight of a 9,000 metre length of yarn while the latter refers to that of 10,000 metres. In this work, the product obtained was a yarn composed of 20 individual filaments. Therefore, the decitex of the individual fibres is obtained as an averaged value from the yarn decitex, which was measured as follows:-

- a. L metres of yarn were measured. Depending on the amount of the material available, L varied from 10 to 100 metres.
- b. The fibre was conditioned for 24 hours at 20 °C, 65% RH.



c. It was carefully weighed.

Linear density in decitex can be calculated as follow:-

$$Dtex = \frac{W \cdot 10^4}{L}$$

where

W: weight of the yarn, grams.

L: length of the yarn, metres.

Measurement of fibre tensile properties

In this work, tensile properties were measured on an Instron tensile tester, model 1122, with load cell type 1105. Details of the measurements are as follows:-

- a. Preparation of samples. This was done by sticking sample fibres on a paper square with side 20 mm. Usually ten samples were tested.
- b. Conditioning of the sample at 20 °C, 65% RH for 24 hours.
- c. Calibration of the machine. The cross-head speed in this work was set at 10 mm/min. The chart speed was either 100 or 200 mm/min depending on the fibre extensibility.
- d. Test.

The strength can be directly read out on the resulting chart.

Extension equals the length on the chart divided by the ratio of chart speed to cross-head speed. From the two sets of data, the fibre tenacity and elongation can be calculated from the following equations.

$$T = \frac{S}{Dtex}$$

$$E = \frac{L}{20} \times 100\%$$

where

T: fibre tenacity, gram/decitex

S: fibre strength, grams

E: fibre elongation, %

L: fibre extension at break, mm

The tensile factor of the fibre can be obtained from the above two values of T and E, i.e., tensile factor equals to $T \cdot E^{0.5}$.

From the load-extension diagram, the initial Young's modulus can also be obtained. It is equal to the slope of the initial straight part of the diagram corresponding to the elastic deformation.

Fibre density test

The fibre density was obtained using mixtures of tetrachloroethylene and toluene. The test began by immersing a small bundle of fibres in 10 ml of toluene, followed by the addition, drop by drop of the second solvent. The fibre density was taken as equal to the density of the liquid mixture when the fibre showed no sign of floating or sinking. The volume of tetrachloroethylene added, X, was used to calculate the fibre density.

$$q = \frac{q' \cdot 10 + q'' \cdot X}{10 + X}$$

where

q: fibre density, g/cm³

q': density of toluene

q'': density of tetrachloroethylene

X: amount of tetrachloroethylene added, ml

Measurement of moisture regain

In this work, the following two procedures were used to determine the moisture regain.

a. Chitosan fibres (0.6 gram) in a weighing bottle were dried

at 60 °C under vacuum for 48 hours. After that, the bottle was weighed together with the fibres. The dry mass of the fibres was thus obtained. Next, the fibres were conditioned at 20 °C for one week in desiccators, each with a different humidity. The values chosen were 20%, 65%, 90% and 100%; these were obtained by using a saturated solution of aqueous $ZnSO_4 \cdot 7H_2O$, the standard conditioning room, a saturated solution of potassium acetate and distilled water respectively. The weights of the fibres were recorded each time after one week. The fibres were then acetylated for 24 hours, using 100 ml 5% acetic anhydride in methanol, and further treated with 1 M aqueous NaOH overnight. After washing and drying, the same procedure was used to determine the moisture regain of the acetylated chitosan fibres.

The moisture regain can be calculated from the following equation.

$$R\% = \frac{W'' - W'}{W'} \times 100\%$$

where

R%: moisture regain, %

W': dry mass of the fibre, gram

W'': weight of the conditioned fibres, gram

The moisture content can be worked out as follows:-

$$C\% = \frac{W'' - W'}{W''} \times 100\%$$

- b. In this method, the moisture content was obtained from the TGA curve, using conditioned samples.

Thermal gravimetry

TGA was carried out on a Dupont 951 Thermal Gravimetric Analyser with

a monitoring unit model 2000. Samples were conditioned at 20 °C, 65% R.H. for two days before tests were made. Most of the time, the amount of fibre used was around 10 mg, prepared by cutting the yarn into very short lengths. A heating rate of 10 °C/min was used. All experiments were carried out in nitrogen, flow rate 50 ml/min.

Differential scanning calorimetry

DSC was carried out on an Dupont 910 Differential Scanning Calorimeter, with an monitoring unit model 2000. Typical experimental conditions were: sample weight, 3 mg, heating rate, 10 °C/min and N₂ 50 ml/min.

X-ray diffraction

Wide-angle X-ray diffraction studies were carried out in the textile physics laboratory in this Department. A Hilger and Watts Y 90 generator with a sealed off type X-ray tube was used. The exposure time was set at 4 hours.

Scanning electron microscope

SEM picture was taken in the textile physics section of this Department, using a 'Stereoscan' scanning electron microscope.

Ultra-violet and visual spectroscopy

U.V spectra were recorded on a Perkin-Elmer ultra-violet spectrophotometer, model 402. A 1% w/w solution was prepared by dissolving 0.25 g chitosan fibres in 25 ml 2% aqueous acetic acid solution which was also used as the reference. Visual spectroscopy was fulfilled on a SP8-150 spectrophotometer in the Colour Chemistry Department.

2.5 Acetylation of chitosan fibres

Several procedures were used to acetylate chitosan fibres. In general, acetylation was achieved using acetic anhydride in methanol as solvent. Occasionally, water was added to the methanol-anhydride mixture. Details are given in the following examples, the methods being evolved during the study, using some basic information from studies on chitosan films (93).

Example 1

A 5% v/v acetic anhydride solution was prepared by diluting it with methanol. 10 ml of this solution was measured into a stoppered test tube equipped with a condenser which was then placed in a water bath. When the liquid reached the required temperature, 2 metres of chitosan yarn was added to the solution with stirring, so that the yarn was fully immersed in the solution. The reaction was carried on for the required time. After that, the solution was poured off, some 10 ml of 1 M aqueous NaOH was added to remove O-acetylation. The mixture was stored at room temperature overnight. After that, the yarn was washed with distilled water until free of alkali.

The above procedure was used to study the effect of temperature and time on the acetylation of chitosan fibres, which had a decitex of 177 (a yarn with 20 individual filaments), prepared by the normal spinning procedure using acetone as the drying agent.

Example 2

50 metres of chitosan yarn was measured into a 150 ml conical flask. To the flask was added 50 ml of methanol. A varying amount (0.04 to

10 ml) of acetic anhydride were added to the mixture with stirring. The reaction was carried on at room temperature for two days with occasional stirring. After that, the solution was poured off. 50 ml of 1 M NaOH was added. De-O-acetylation was carried out overnight. After that, the fibre was washed until free of alkali.

The above method was used to assess the effect of molar ratio of acetic anhydride to free amine on the acetylation of chitosan fibres. The molar ratio was changed from 0.1 to 50. At low ratios, accurate measurement of the acetic anhydride was ensured by using dilute solutions of acetic anhydride in methanol.

Example 3

One gram of chitosan fibres was weighed and placed in a 150 ml conical flask which was then dried under vacuum at 80 °C to constant weight. After that, 10 ml of distilled water and 50 ml of methanol were added. The mixture was left for 20 minutes before 5 ml acetic anhydride was added. Acetylation was carried out at room temperature for 24 hours with occasional stirring. Next, the solution was poured off and the fibre was dried under vacuum for 24 hours at room temperature before the oven was heated to 80 °C (this was to prevent the reaction of chitosan fibres with the remaining anhydride). The fibre was then dried to constant weight. After that, 50 ml of 1 M NaOH was added. De-O-acetylation was carried out at room temperature overnight. The fibre was then washed until free of alkali before it was again dried to constant weight.

The above procedure was used to measure the weight increase during the acetylation of chitosan fibres.

Example 4

5% acetic anhydride in methanol was prepared as before. Prior to acetylation, 2 metres of chitosan yarn was dried at 80 °C under vacuum for 24 hours. Then, to the dried fibre was added 10 ml of the 5% acetic anhydride. Varying amounts of water (0 to 3 ml) were immediately added, followed by stirring. Acetylation was carried out at room temperature for half an hour with vigorous stirring. After that, the solution was poured off, the yarn was dried under vacuum before it was washed with water and dried again.

This method was used to assess the effect of addition of water on the acetylation of chitosan fibres.

Example 5

A piece of knitted chitosan fabric was added to 20 ml of 5% acetic anhydride in methanol. The mixture was held at 40 °C for one hour. After that, the solution was poured off and 20 ml of 1 M NaOH was added. De-O-acetylation was carried out at room temperature overnight. The acetylated fabric was then washed with distilled water until free of alkali.

Example 6

10 metres of chitosan yarn was cut into pieces of 40 mm length. These short lengths were boiled with 5% acetic anhydride in methanol for periods of time between 5 and 40 min; then, the solution was poured off. The fibres were dried under vacuum for 24 hours. De-O-acetylation was not carried out since it normally led to fibre swelling and filament adhesion after drying.

The above method was used to test the effect of acetylation on

the tensile properties of chitosan fibres.

2.6 Chelation of metal ions by chitosan

CuSO_4 and ZnSO_4 were the two main salts used in the chelation studies. In preparing chitosan complexed with different amounts of metal ions, 4 metres of chitosan fibres (0.0242 gram) was treated with 20 ml copper sulphate solution containing different amount of copper ions; the solution were prepared as shown in Table 2.2.

Table 2.2 Preparation of the CuSO_4 solution

Sample	1	2	3	4	5	6
0.015 M CuSO_4 , ml	0.1	0.5	2	5	8	10
Water, ml	19.9	19.5	18	15	12	10
Molar ratio of Cu(II) to chitosan	0.01	0.05	0.2	0.5	0.8	1.0

In studying the effect of copper and zinc ions on the mechanical properties of chitosan fibres, 0.01 M solutions of CuSO_4 and ZnSO_4 were prepared. 20 ml of the solutions was brought into contact with 4 metres of chitosan fibres, cut into lengths of 4 cm. The chelation was carried out at room temperature for 5, 10, 20, 40 min and one day, with mechanical shaking. After that, the salt solution was poured off and the fibres were washed thoroughly with distilled water before they were dried in vacuum at room temperature. Mechanical properties of the fibres were tested as described in section 2.4.

Chitosan fabrics were dyed with 0.01 M salt solutions for 30 minutes at room temperature with shaking. The fabrics were then washed with distilled water and allowed to dry naturally.

Chapter three

RESULTS AND DISCUSSION

Part I. The production of chitosan fibres

3.1.1 Introduction

The conversion of polymeric materials to fibres makes use of the three conventional procedures, i.e., melt, dry or wet spinning. All three methods require a homogeneous phase for spinning; the first method requires a polymer melt, which is impossible in the case of chitosan as it has a melting point higher than its decomposition temperature. In the second and third methods, a polymer solution must be prepared, with the added restriction in dry spinning that the solvent be sufficiently volatile to be removed during spinning. As all solvents for chitosan are aqueous acid solutions, dry-spinning seems likely to be difficult. The only method left is therefore the wet spinning procedure, which typically involves the dissolution of the polymer, filtration and degassing of the dope followed by extrusion of the purified dope into a coagulating bath with subsequent washing, drawing and drying.

Before spinning the chitosan, it was considered useful to characterise the raw material being used. The following describes the results of some characterisations of the chitosan samples used although limitations in time prevented molecular weight determination via solution viscosity measurement. Then, the wet spinning process developed for the production of chitosan fibres will be described, with emphasis on the effects of spinning conditions on the fibre properties. Some essential features of chitosan fibre especially its

chelating behaviour will also be described.

3.1.2 Characterisation of the chitosan samples

a. Degree of acetylation

The degree of acetylation was calculated from the elemental analysis of the samples using the N/C ratio. For the medium grade chitosan, carbon and nitrogen contents were found to be 40.35% and 7.4%. The carbon content is lower than the calculated value of both pure chitin and pure chitosan (47.29% for pure chitin and 44.72% for pure chitosan). This can be attributed to the moisture and impurities in the polymer.

Based on the N/C ratio, the degree of acetylation for the medium grade chitosan was 17.9%, which corresponded well to the value indicated by the supplier, i.e., 16.0%. The residual acetyl content was confirmed by i.r spectra (Fig 3.1) where the 1655 cm^{-1} band indicated the presence of amide groups. (Analyses were not performed for the high and low viscosity grade, the values stated by the supplier being accepted (see table 2.1)).

b. Purity of the raw material

The chitosan supplied by Protan Laboratory contained about 1% insoluble material. This insoluble part was readily removed from chitosan solutions by the use of a candle filter. However, the filtered solution still appeared brownish, indicating the existence of some soluble impurities, possibly in part chemically bonded to the chitosan as chitosan itself is by no means coloured. Fig 3.2

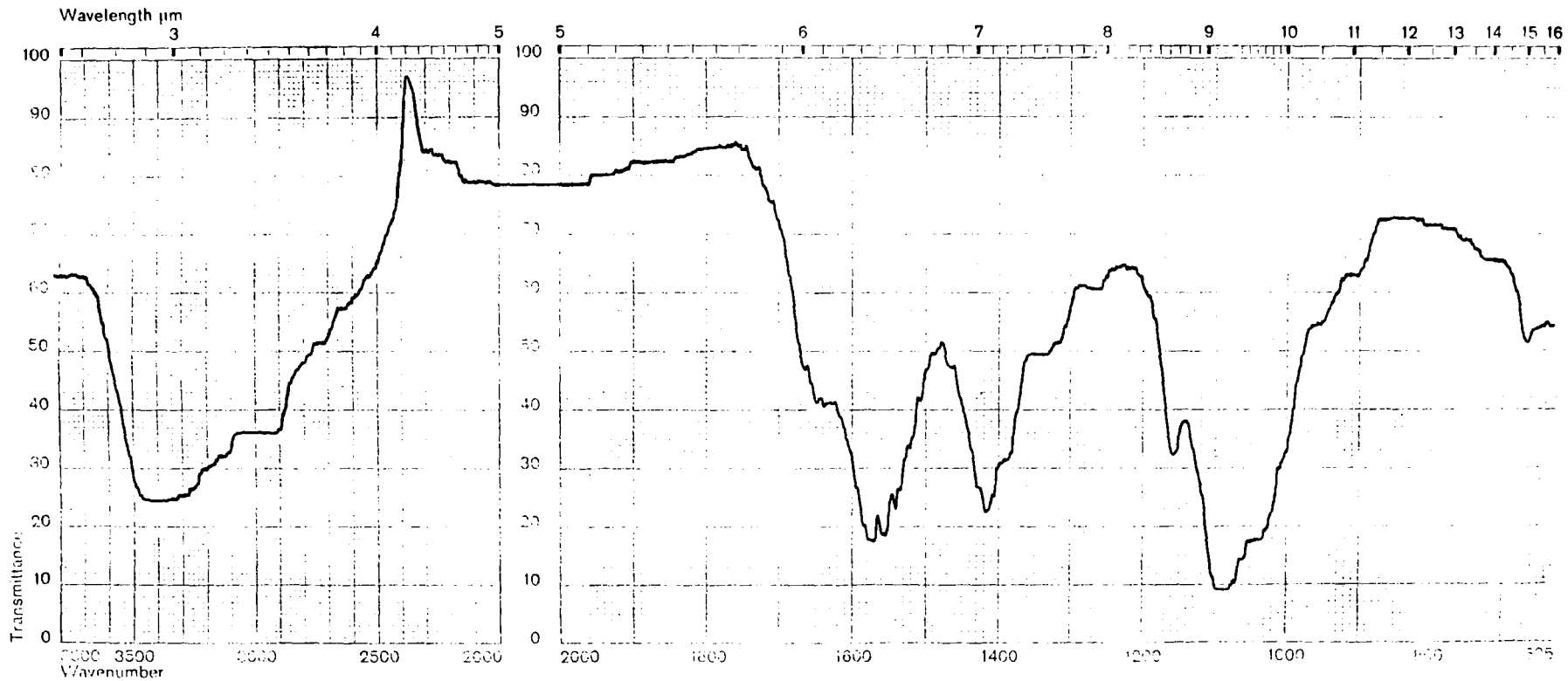


Fig 3.1 I.r spectrum of chitosan film (medium grade)

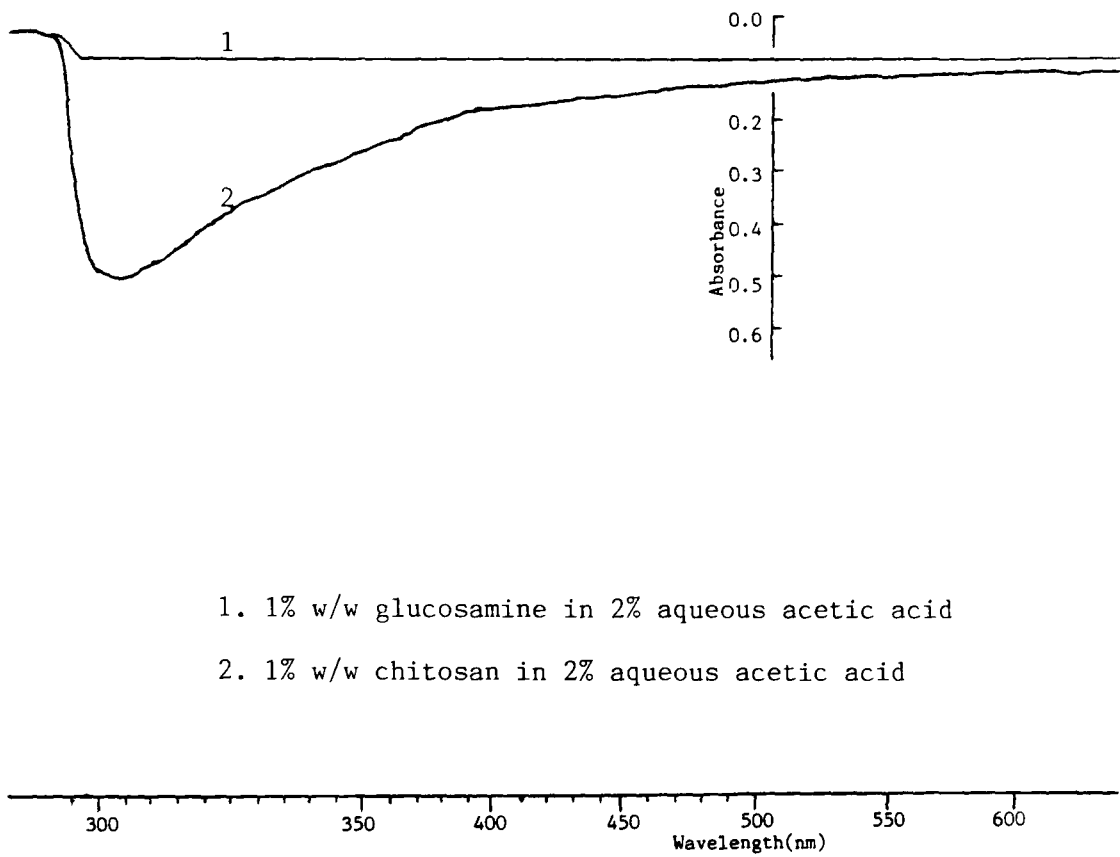
shows the U.V spectra of a 1% solution of glucosamine in 2% aqueous acetic acid and that of a 1% solution of the medium grade chitosan; the medium grade chitosan showed a broad absorption between 290 and 500 nm. This confirms the existence of some coloured material possibly organic pigments or heavy metal ions.

Earlier work in this Department (37) showed that some coloured material can be removed from chitin using a treatment with p-toluene sulphonic acid in i-propanol. The same treatment was applied to chitosan; it was found that after the treatment, some coloured substance was removed from chitosan, as can be seen from the U.V spectrum of the filtered solution (Fig 3.3); the spectrum showed a broad absorption between 280 to 460 nm, indicating the removal of some coloured material. However, the treated chitosan was still not white.

No purification process was applied to the chitosan before spinning, apart from the filtration process with a candle filter. With 2% aqueous acetic acid as solvent and 5% NaOH as coagulant, the fibres obtained were pale yellow in appearance.

3.1.3 Solvent for wet-spinning

As was pointed out in section 1.4, chitosan can be dissolved in a variety of organic and inorganic acids. Because of their potential attack on both the polymer and the equipment, inorganic acids were not considered as spinning solvents. Although the list of possible organic acids was long, aqueous acetic acid was chosen as the preferred solvent. Later on, various advantages of using acetic acid were realised. First, the reaction between primary amine and carboxylic acid may occur during dope preparation, extrusion,



- 1. 1% w/w glucosamine in 2% aqueous acetic acid
- 2. 1% w/w chitosan in 2% aqueous acetic acid

Fig 3.2 U.V spectra of chitosan and glucosamine solutions (1%)

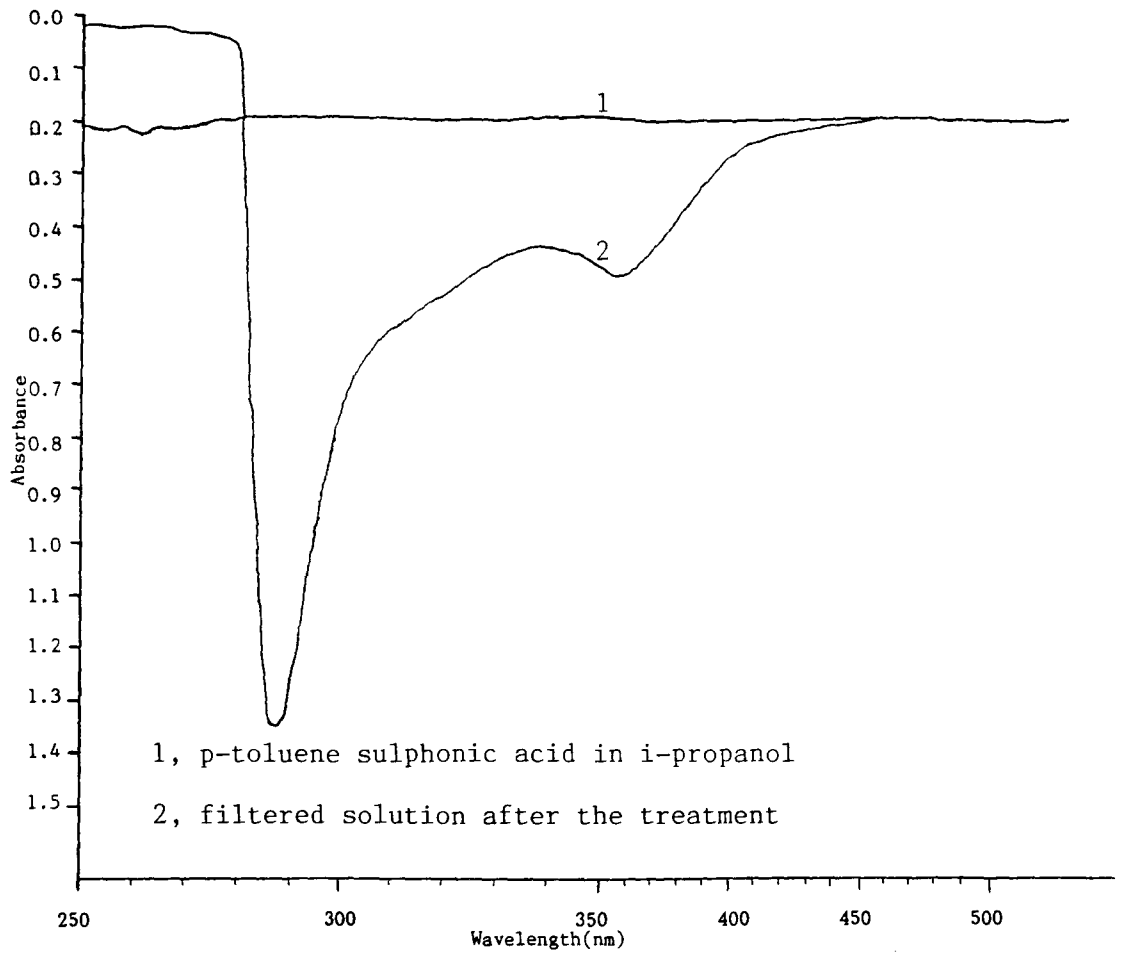


Fig 3.3 U.V spectrum of p-toluene sulphonic acid solution in i-propanol after treatment of chitosan

coagulation and other processes. When acids other than acetic acid are used, this minor reaction would cause structural irregularity. Second, acetic acid is one of the most water soluble organic acids. Whilst its smell is not pleasant, it is not as bad as the longer chain acids. Finally, acetic acid is probably the cheapest organic acid. This would be especially important in the event of commercial production.

From the few reports available on the production of chitosan fibres, Mitsubishi Rayon (113) used 0.5% aqueous acetic acid to prepare a 3% chitosan dope. Tokura et al (117) used 2-4% aqueous acetic acid. All other reports (50) concerning the dissolution of chitosan usually employ 2% aqueous acetic acid. As far as fibre spinning is concerned, the lowest possible acid concentration is beneficial in many respects; for example, a lower acid concentration means a lower degree of hydrolysis of the polymer during dope preparation and additionally, a lower degree of corrosion to the equipment. On testing, however, it was found that 0.5% acetic acid couldnot dissolve the low viscosity grade chitosan to a concentration above 7%. On the other hand, 2% aqueous acetic acid solution easily dissolved the same chitosan. Thus, 2% aqueous acetic acid was used as the solvent to start with.

3.1.4 Dope characterisation by viscosity measurement

Of the properties affecting the spinnability of a polymer, viscosity of the dope is one of the most important. Too high a dope viscosity causes difficulty in dope preparation, filtration and degassing. On the other hand, too low a viscosity can cause difficulty in thread formation and low spinning efficiency. Therefore, a good spinning

process requires a dope of appropriate viscosity.

Chitosan is a polymer of very high molecular weight. In dilute solution, it behaves as a polycation with rigid chains. In concentrated solutions, e.g., a spinning dope, it exhibits typical non-Newtonian properties. Tables 3.1-5 show the effects of shear rate, molecular weight, concentration and temperature on the viscosity of chitosan dope.

Table 3.1 Effect of shear rate on dope viscosity at 25 °C
(4.65% w/w medium grade chitosan in 2% aqueous acetic acid)

Shear rate S^{-1}	0.89	1.78	3.56	7.12	14.24	28.48	56.96
Viscosity (poise)	104	104	94.0	78.3	61.3	46.3	33.0

From table 3.1 and Fig 3.4, it can be seen that the 4.65% chitosan dope showed a typical shear-thinning effect, indicating that the concentrated chitosan solution is a non-Newtonian pseudoplastic fluid. This can be attributed to the existence of interchain forces such as hydrogen bonds involving -OH and -NH₂ groups and physical chain entanglement. Fig 3.5 shows the curve of logV versus logD; it can be seen that when D is less than 2 S^{-1} , the curve becomes a horizontal line, indicating the Newtonian properties of the solution at low shear rates. When D is larger than 2, logV decreases sharply with increase in logD; the slope was obtained as -0.3. Using the empirical power law equation, i.e., $V=V_1D^{(n-1)}$, the value of the flow index for the 4.65% medium grade chitosan in 2% aqueous acetic acid

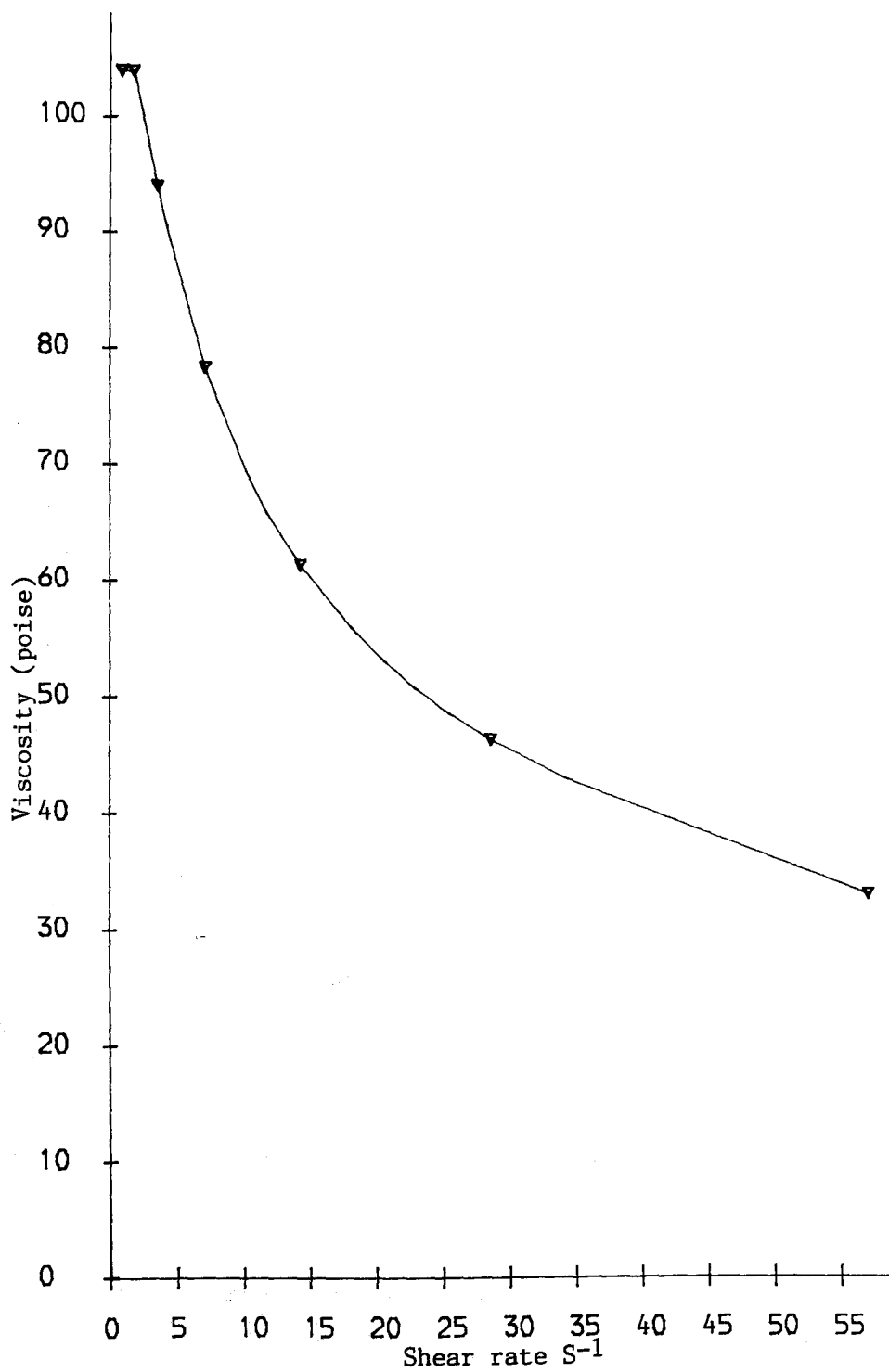


Fig 3.4 Effect of shear rate on dope viscosity

(5% medium grade chitosan in 2% aqueous acetic acid)

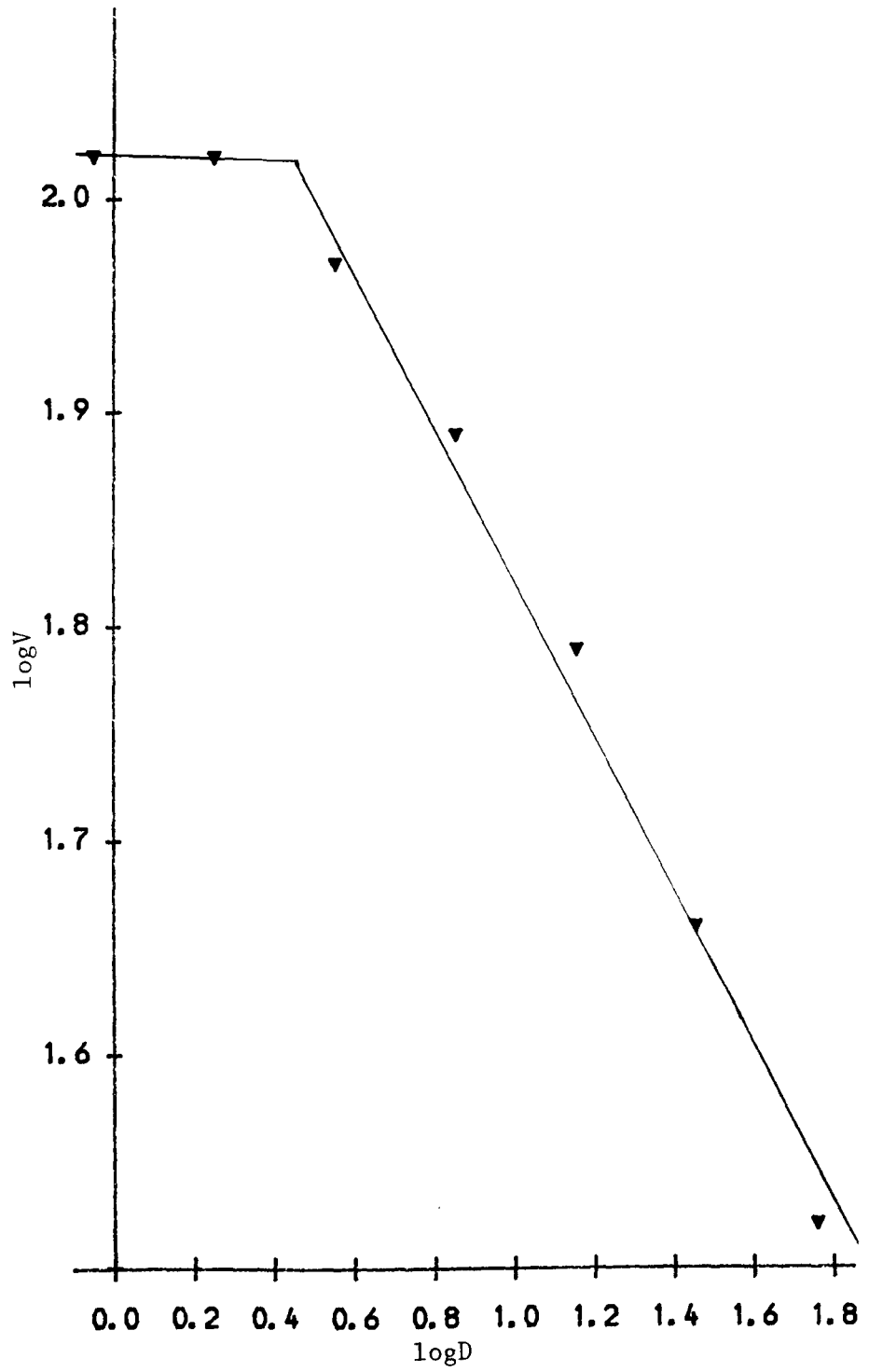


Fig 3.5 The logV versus logD curve of a 5% chitosan solution

was obtained as 0.7.

Table 3.2 Effect of co-solvent (5% w/w chitosan, medium grade, 25 °C)

Shear rate S^{-1}	0.89	1.78	3.56	7.12	14.24	28.48	56.96
Viscosity, normal*	104	104	94.0	78.3	61.3	46.3	33.0
(poise) 30% MeOH**	334	271	198	146	99.2	67.9	43.1

* Solvent, 2% aqueous acetic acid

** Solvent, methanol:water:acetic acid=30:70:2 (by volume)

Table 3.2 and Fig 3.6 show the results of the addition of co-solvent on the dope viscosity. It is clear that the dope viscosity is increased substantially with the use of methanol as co-solvent; the dope now behaves as a non-Newtonian fluid even at very low shear rates. The curve of $\log V$ vs $\log D$ gives a slope of -0.5. The flow index of the medium grade chitosan in the methanol aqueous acetic acid is therefore 0.5. Compared to the value of 0.7 obtained for the same chitosan in 2% aqueous acetic acid, it can be concluded that the use of methanol as co-solvent leads to a much more non-Newtonian chitosan dope.

Table 3.3 and Fig 3.7 show the results of viscosity measurement on samples of high, medium and low grade chitosan in a solvent composed of water, methanol and acetic acid, 70:30:2. It is obvious that the values for the high grade are substantially larger than those of the medium grade which is again substantially larger than that of the low grade, at the same dope concentration. Additionally,

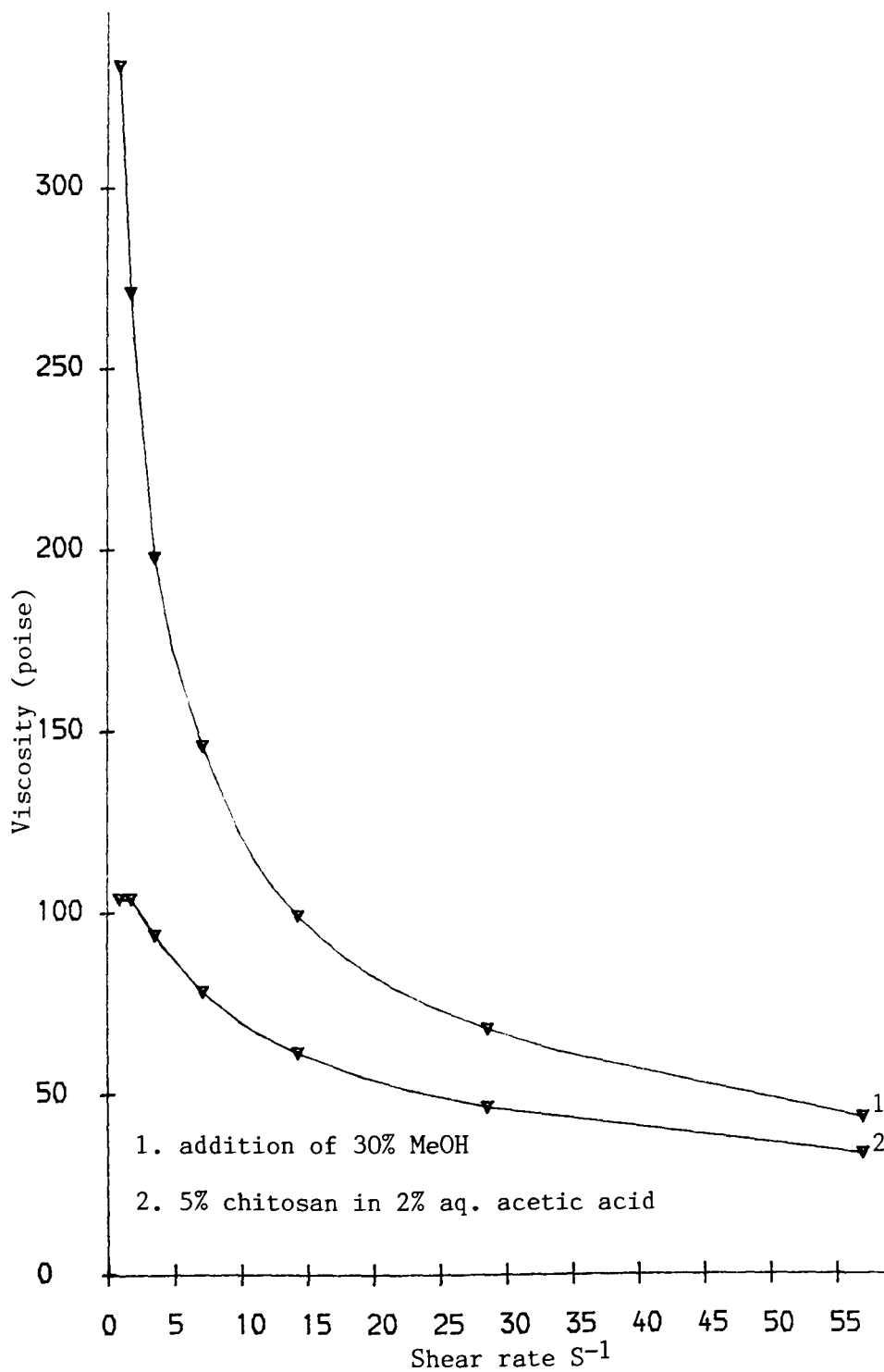


Fig 3.6 Effect of addition of MeOH on the viscosity of chitosan solution

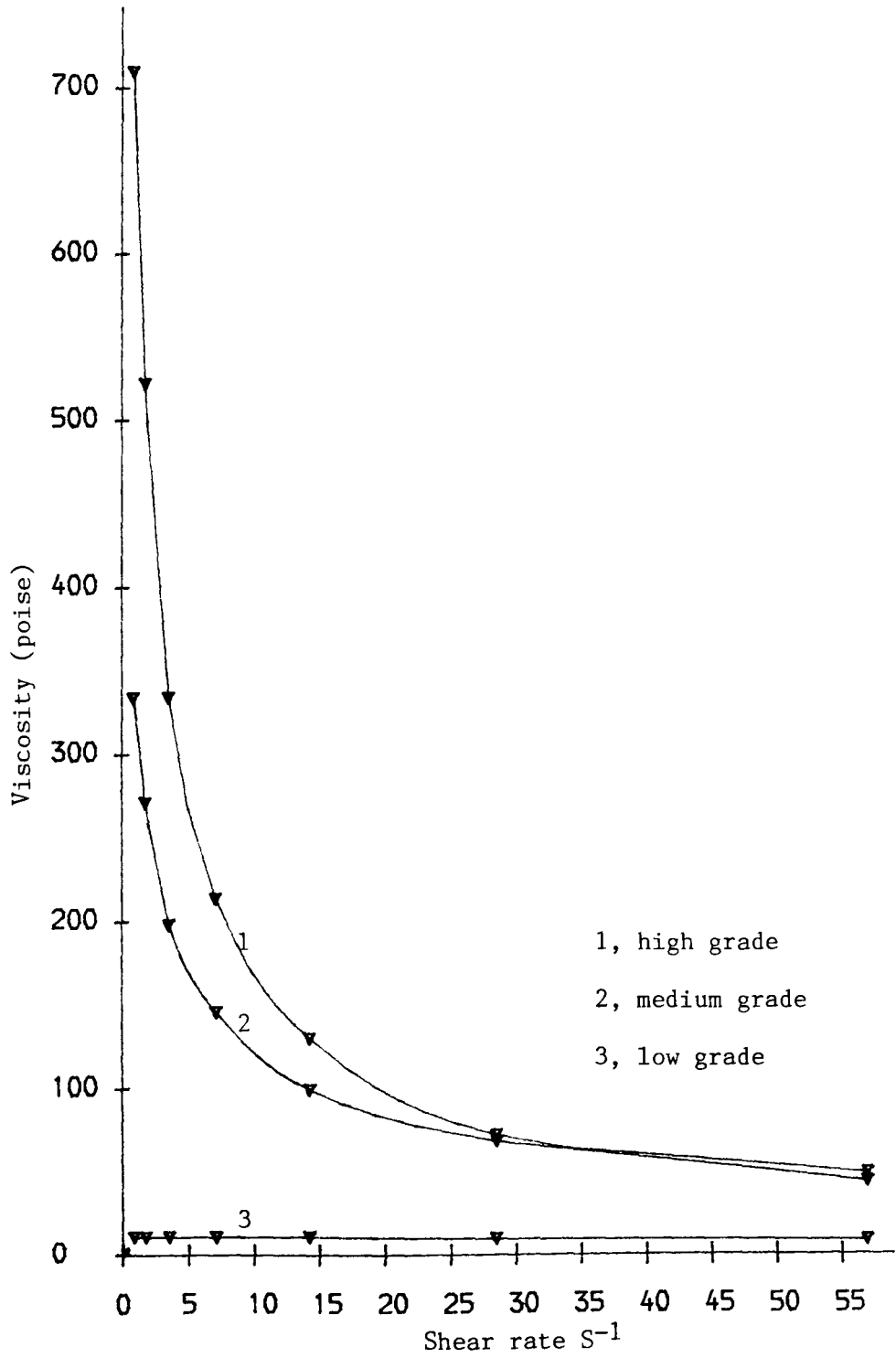


Fig 3.7 Effect of molecular weight on the viscosity of chitosan solution

Table 3.3 Effect of molecular weight (polymer concentration, 5%)

Shear rate S^{-1}	0.89	1.78	3.56	7.12	14.24	28.48	56.96
Viscosity, high	710	522	334	214	130	71.8	48.3
(poise) medium	334	271	198	146	99.2	67.9	43.1
low	10.4	10.4	10.4	10.4	10.4	9.14	7.83

solvent composition: AcOH, MeOH, H₂O=70, 30, 2 (by volume)

it can be seen that the viscosity of the high and medium grade are very sensitive to the shear rate while that of the low grade is unchanged until the shear rate exceeds $14 S^{-1}$. The logV vs logD curves give flow index values of 0.3 for the high grade, 0.5 for the medium grade and 0.9 for the low grade when the shear rate exceeds $14 S^{-1}$.

Table 3.4 Effect of temperature on dope viscosity

Temperature °C	25	30	40	50	60	70	80	90	100
Viscosity (poise)	33.3	29.7	22.5	17.0	13.7	9.14	5.87	3.92	1.96

shear rate, $14.24 S^{-1}$, polymer concentration, 5%, medium grade chitosan in 2% aqueous acetic acid

The effect of temperature on dope viscosity is shown in table 3.4 and Fig 3.8. It is clear that the dope viscosity drops sharply with the increase in temperature. This is natural as when the

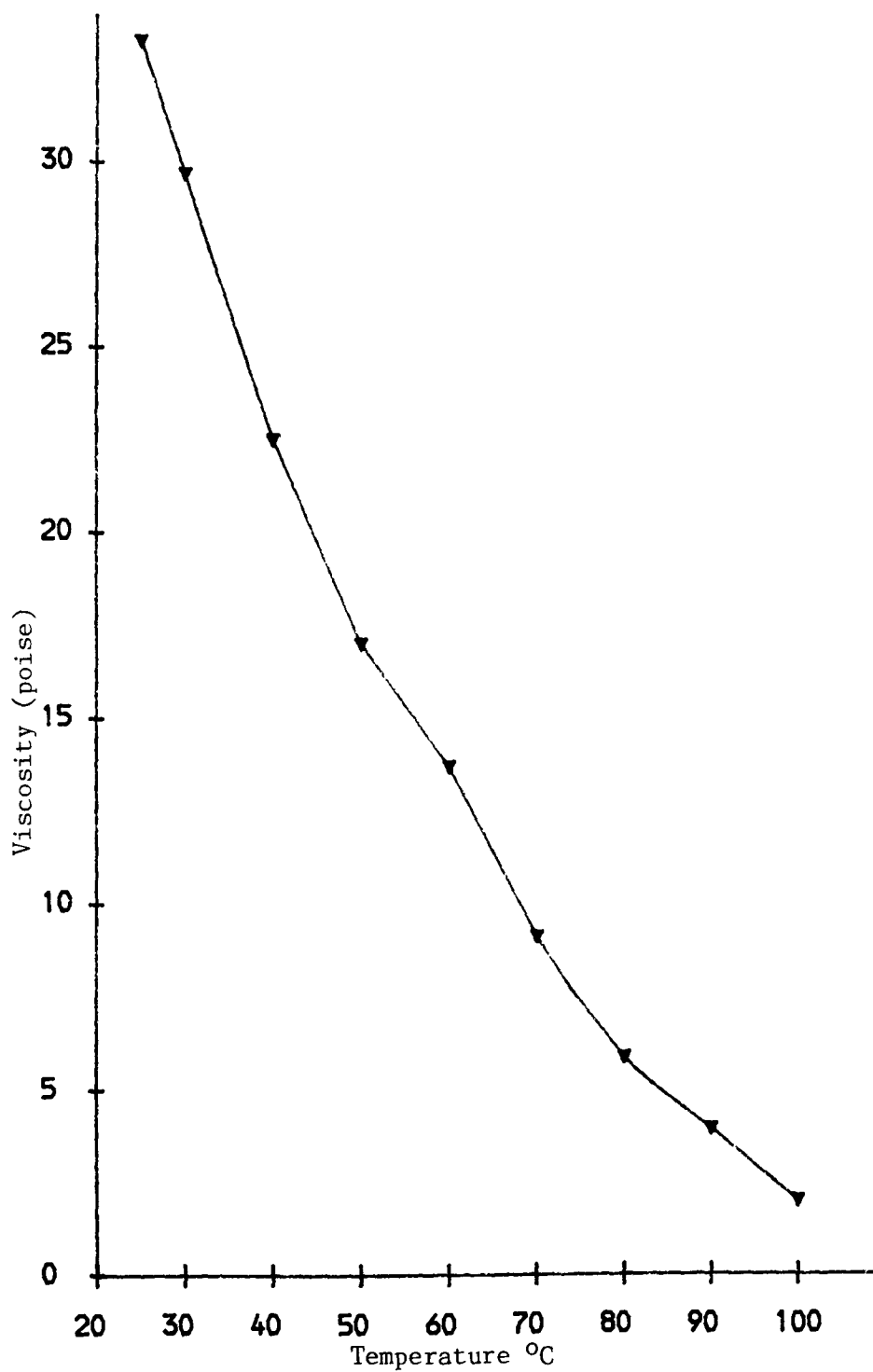


Fig 3.8 Effect of temperature on the viscosity of chitosan solution
(5% medium grade chitosan in 2% aqueous acetic acid)

temperature is raised, the chain movement becomes more intense and as a result, inter chain forces such as hydrogen bonding and chain entanglement are bound to be reduced. The dope viscosity follows an empirical equation of $V=K\exp(\frac{E}{RT})$, where an increased temperature leads to a decreased dope viscosity (V, viscosity, K,R, constants, E, activation energy and T, temperature). (A full analysis of the data is given in appendix I).

Table 3.5 Effect of concentration on dope viscosity

Shear rate S^{-1}	0.89	1.78	3.56	7.12	14.24	28.48	56.96
Viscosity, C=2.76%	10.4	10.4	10.4	10.4	10.4	10.4	8.48
(poise) 3.37%	41.8	41.8	41.8	36.5	30.0	24.8	18.9
4.65%	104	104	94.0	78.3	61.3	46.3	33.0
5.86%	543	438	339	243	168	115	74.4

medium grade chitosan in 2% aqueous acetic acid

Table 3.5 shows the dope viscosity of chitosan of four different concentrations at different shear rates. It can be seen that the medium grade chitosan behaved as a Newtonian fluid at dope concentration 2.76%, when the viscosity showed no change until the shear rate exceeds $28.48 S^{-1}$. With the increase in dope concentration, a sharp increase in dope viscosity was noticed, with the fluid becoming more and more non-Newtonian. This can be easily explained by an empirical equation, $V=KC^n$, where V is the dope viscosity. K and n are constants and C is the dope concentration. (Appendix I contains the detailed analysis).

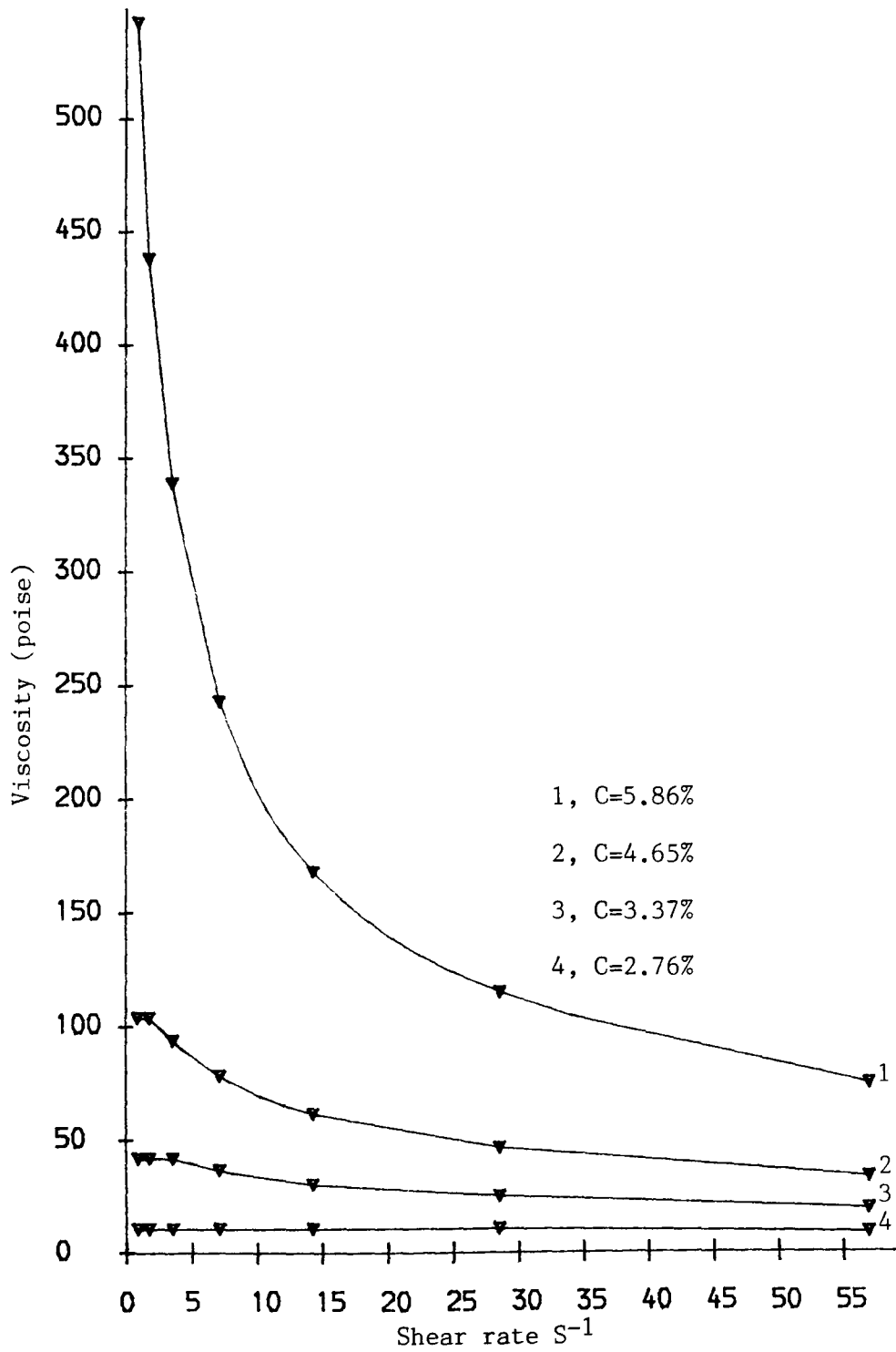


Fig 3.9 Effect of concentration on the viscosity of chitosan solution

3.1.5 Dope concentration for wet spinning

Table 3.5 clearly indicates that the viscosity of chitosan dopes increases rapidly with increase of concentration. For the medium grade chitosan, the viscosity reached 100 poises when the dope concentration was about 5%. Beyond that, the dope became far too viscous for normal wet spinning. Most of the previous studies (37,131) on wet spinning indicate the fact that below a certain limit, a high dope concentration is favorable as far as fibre properties are concerned; the work by Agboh(37) indicated that dope concentration had little effect on the properties of chitin fibres. As a high dope concentration means a high spinning efficiency (this is especially important in industrial applications), preliminary work on the production of fibres from chitosan used 5% medium grade chitosan in 2% acetic acid as the spinning dope; this is the highest concentration which still allowed proper dissolution, filtration and deaeration.

3.1.6 Coagulant

A few coagulation systems were available in the literature. These were, 5% aqueous NaOH (113), 2% Na lauryl sulphate (114), $\text{CuCO}_3\text{-NH}_4\text{OH}$ (115), aqueous 5% NaOH mixed with alcohol (90:10) (116), $\text{CuSO}_4\text{-H}_2\text{SO}_4$ and $\text{CuSO}_4\text{-NH}_4\text{OH}$ (117). It is obvious that, to precipitate chitosan from its acidic solution, the simplest way is to destroy the solvent acid. Indeed, most of the systems quoted above were basic solutions. Because chitosan is a chelating polymer, the presence of Cu(II) in the coagulation bath would produce chitosan fibres with absorbed metal ions. This was obviously not attractive in the early stages of the work as pure chitosan fibres were the

required product. In addition, it was hoped to use these fibres as precursors for chitin fibres; the presence of metal ions might cause problems in studies of the acetylation process. Other systems were also considered. However, initially, it was recognised that the simplest way to obtain fibres was actually to precipitate chitosan solutions with an alkali solution. Therefore, sodium hydroxide solution was chosen as the coagulating bath.

Before wet-spinning on the laboratory plant, the coagulation behaviour of aqueous NaOH solutions of concentrations ranging from 1 to 10% were prepared. It was found that 5% chitosan solution didnot solidify rapidly when NaOH concentrations lower than 5% were used. In view of the fact that a low alkali concentration means a low coagulating power (usually resulting in fibres with better mechanical properties (37)) and the fact that a low alkali concentration is not only economically beneficial but also safe to operate with, the NaOH concentration in the preliminary work was chosen as the lowest which still allowed continuous filament formation (in the syringe and needle test). Thus, the concentration used was 5%, which is the same as used by Mitsubishi Rayon (113).

3.1.7 Arrangement of the wet-spinning line

The wet spinning plant used in this work was the same as described by Agboh (37) in the production of chitin fibres. It comprised six essential parts, i.e., the extrusion unit, the coagulation bath, the washing unit, the drawing unit, the drying unit and the winder. The extrusion unit used by Agboh was used in the initial stage of the present work. It was later replaced by another unit (mobile) for two reasons. Firstly, there was the problem of degassing the dope. With

the old extrusion unit, it was very difficult to degas the dope properly, no matter how heating and vacuum were applied. It was noticed that bubbles were generated in a well deaerated dope when it passed through the metering system. The reason was not clear; it was assumed to be due to the design of the block to which the pump and pot were attached; the block comprised some horizontal and vertical channels where, it was thought, bubbles could be trapped. Therefore, in the initial stages of this work, spinning frequently failed because of the remaining bubbles. Secondly, the pump fitted to the system was of standard material. The acidity of the spinning solution proved harmful to the gears. Thus, the pump was found to be corroded after use. This would further contribute to the formation of bubbles and more seriously, the contamination of the dope. (As a replacement pump in acid resistant material would have been too expensive, this plant was not used further).

A mobile unit with an acid resistant pump was then used for the main spinning experiments. This unit overcame the shortcomings described above.

In normal spinning trials, the jet extrusion rate was adjusted to around 13 metres/min. This low extrusion rate (compared to 26 m/min normally used by Agboh (37)) had three obvious advantages, i.e., potentially a slower coagulation because of longer residence times of the newly formed filaments in the bath, a longer period of time available for spinning a given volume of dope and a greater ease of processing.

Spray washing of the fibres was used in the present work. In addition to this, two extra washing baths (situated under rollers 2 and 4) were used. The first one was designed to take off the

surface liquid from the coagulation bath so as to protect the spray washing bath from contamination and also to improve its washing efficiency. The washing bath under roller 4 ensured the cleanliness of the fibres before drying.

Three ways of drying the wet filaments continuously were used. The acetone washing method proved to be very efficient. Comparing the acetone extraction with the usual radiant heat drying, it was found that the former gave fibres with a rougher surface, as will be shown later. It was found that the yarn produced by acetone washing contained well separated individual filaments while those obtained by radiant heat drying did not. However, the yarn dried by radiant heat had better tensile properties, under otherwise similar conditions as shown later.

Drying by the radiant heater method was the main drying procedure used (Acetone drying is bound to be too costly and not without hazard). The heating was achieved by a radiant heater situated under the 5th roller. Its temperature was controlled by the power supplied which was adjusted to the lowest which still allowed proper drying of the wet filaments.

Winding-up was achieved with a Leelsona 995 S precision cone winder. Though the earlier work by Agboh indicated difficulty (37), in the present work, winding-up of the yarn with this machine proved easy. There are two key factors. Firstly, the yarn must be dried before collection on the winder. This is because the strength of the wet yarn is substantially lower than that of the dried one. In addition, the friction is higher for the wet yarn. Whereas an imperfectly dried yarn proved difficult to wind, it was easy to wind the dried one. Secondly, the winding-up speed was also very important

in a continuous winding operation. Too low a speed resulted in the accumulation of unwound yarn while too fast a speed caused yarn breakage.

Thus, the proper arrangement of the spinning line for the production of chitosan fibres was decided as follows. Firstly, the extrusion unit was the mobile one with an acid resistant pump. Secondly, the newly formed filaments were washed with water continuously in three baths. Third, the filament was drawn in a hot water bath. Finally, the yarn was dried with radiant heating and wound up continuously on a cone winder.

3.1.8 Studies of the spinning variables

Wet spinning may be considered the most complicated process for fibre production. As fibres are formed by the extrusion of the polymer dope and subsequent coagulation, drawing, washing and drying processes, there are many spinning variables. Though it is difficult, with limited time, to investigate all possible variables, it is necessary to make some effort to try to understand the fibre forming process. The following tables summarise the study of several of the spinning variables.

Table 3.6 shows the effect of jet-stretch ratio on the maximum draw ratio and the properties of the fibres thus obtained. It can be seen that the extent to which the newly formed filaments can be drawn is largely dependent on the extent of jet stretching applied. This phenomenon has already been studied in other wet-spinning systems; it was (132) reported that in the acrylic system, high jet-stretch ratios resulted in filaments with a high 'spin orientation', developed from the stretching of the viscoelastic fluid by the take-up reel and

Table 3.6 Effect of jet stretch ratio on maximum draw ratio
and their effects on fibre properties

JS ratio	0.20	0.32	0.41	0.46	0.67
Maximum draw ratio, %	60.0	39.6	37.1	23.2	12.7
Linear density, dtex	147.2	105.9	85.0	85.0	63.7
Dry strength, gram	254.4	191.2	164.0	154.1	108.6
Dry tenacity, g/dtex	1.73	1.80	1.93	1.81	1.70
Extensibility, %	4.9	5.6	5.4	5.6	8.7
Wet strength, gram	74.7	50.9		39.7	25.6
Wet tenacity, g/dtex	0.40	0.51		0.48	0.47
<i>Wet</i> Extensibility, %	12.7	16.2		13.7	16.4

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 um

Extrusion rate: 15.0 m/min.

Coagulant: 5% aqueous NaOH at room temperature

Jet-stretch ratio: 0.20, 0.32, 0.41, 0.46, 0.67

Draw ratio: maximum workable

Drying method: heat drying

fixed upon coagulation. The dope used in this work was 5% chitosan (medium grade) dissolved in 2% aqueous acetic acid. This solution was earlier found to be non-Newtonian. Thus, though no experiment was carried out to investigate the effect of jet-stretch ratio on the 'spin orientation' of the newly formed filaments, it is reasonable to

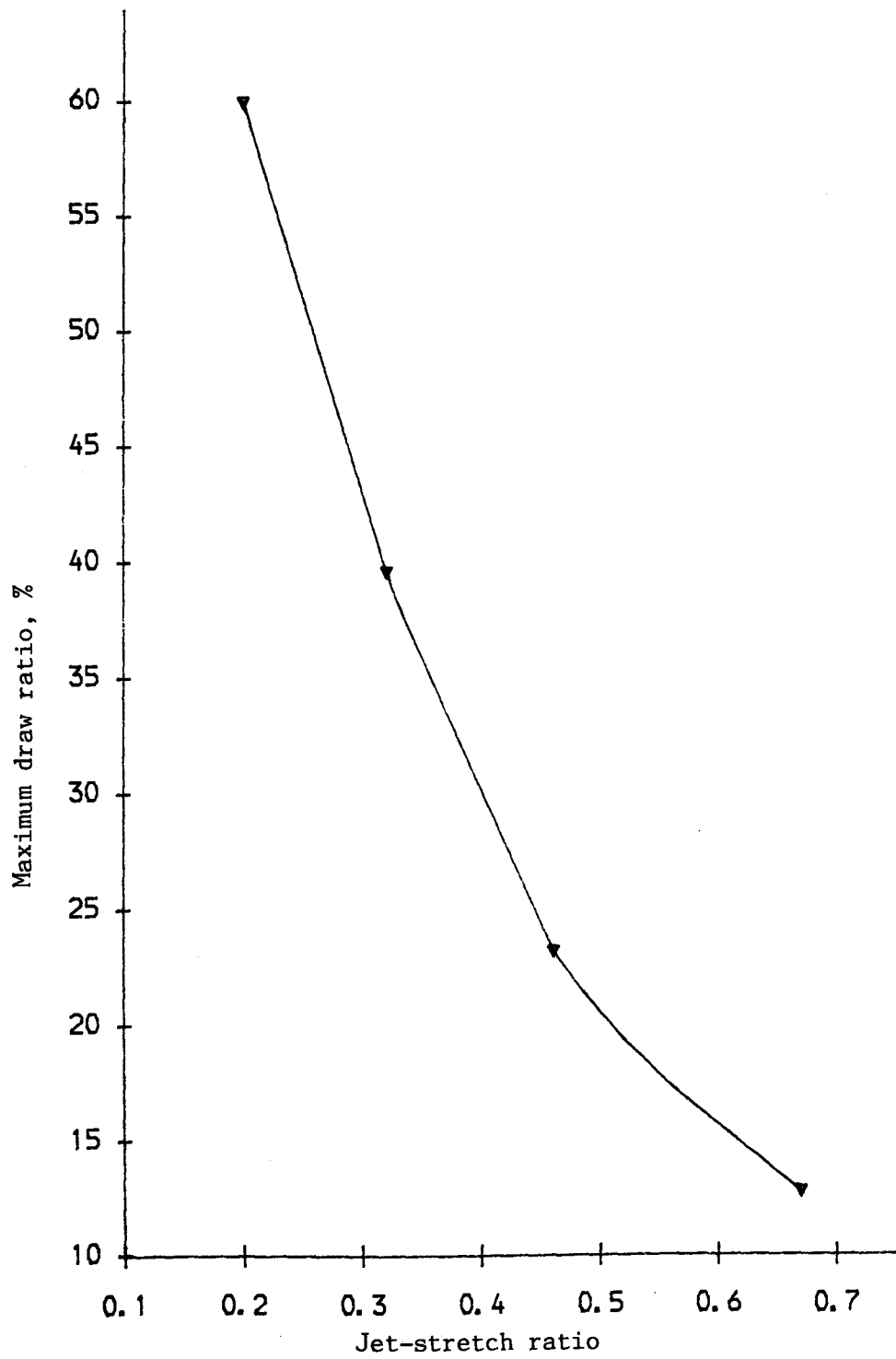


Fig 3.10 Effect of jet-stretch ratio on the maximum draw ratio

suggest that a certain degree of molecular orientation was developed during coagulation; the extent of orientation is proportional to the take-up speed which is equivalent to the jet-stretch ratio.

Therefore, the maximum draw ratio, determined by the history of stretching applied to the material (if other conditions are the same), is inversely related to the jet-stretch ratio.

Interestingly, however, though the variation in draw ratios was quite large, i.e., from 60% to 12.7% when the jet-stretch ratio was 0.20 and 0.67 respectively, the differences between the mechanical properties of chitosan fibres thus obtained were very small. In fact, the tenacities fell within the range of 1.70 to 1.93 g/dtex; the strongest sample was obtained at a jet-stretch ratio of 0.41.

Thus, though a slight advantage of spinning at a jet-stretch ratio of 0.41 was noticed, overall, the jet-stretch ratio has little effect on the mechanical properties of these fibres. A similar conclusion was drawn by Agboh (37) in the wet-spinning of chitin.

Table 3.7 Effect of JS ratio on fibre properties at draw ratio=10%

JS ratio	0.44	0.53	0.62	0.71	0.80	0.89
Linear density, dtex	87.5	68.3	55.6	51.1	50.3	45.3
Strength, gram	116.2	103.9	98.9	88.2	76.7	66.4
Tenacity, g/dtex	1.33	1.52	1.78	1.73	1.53	1.47
Extensibility, %	12.4	11.4	8.0	8.3	12.6	10.1

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 μm (foot notes continued)

Extrusion rate: 13.0 m/min.

Coagulant: 5% aqueous NaOH at room temperature

Jet-stretch ratio: 0.44, 0.53, 0.62, 0.71, 0.80, 0.89

Draw ratio: 10%

Drying method: heat drying

Table 3.7 shows the effect of jet-stretch ratio on the fibre properties at a fixed draw ratio, 10%. The results showed that while the fibre linear densities decreased with the increase in jet-stretch ratio, fibre tenacities at first increased with the increase in jet-stretch ratio and then decreased. A maximum value of fibre tenacity was obtained at a jet-stretch ratio of 0.62. The initial increase (JS ratio 0.44 to 0.62) in fibre tenacities might be due to the 'spin orientation' developed by jet-stretching, as discussed earlier; the fibre extensibilities in this region decreased with increase in jet-stretch ratios. However, a further increase in jet-stretch ratio resulted in decreased fibre tenacity. The reason is not clear; it might be suggested that under a higher take-up speed, the dope is insufficiently coagulated. Therefore, the orientation developed by jet-stretching was not preserved. Indeed, the fibres showed increases in extensibilities in this region of jet-stretch ratios.

Table 3.8 shows the effect of draw ratio on the mechanical properties of chitosan fibres at a jet-stretch ratio of 0.53. The maximum draw ratio at that spinning condition was around 30% which is quite low compared to other wet-spinning systems such as the wet spinning of acrylic fibres where the newly-formed filaments are

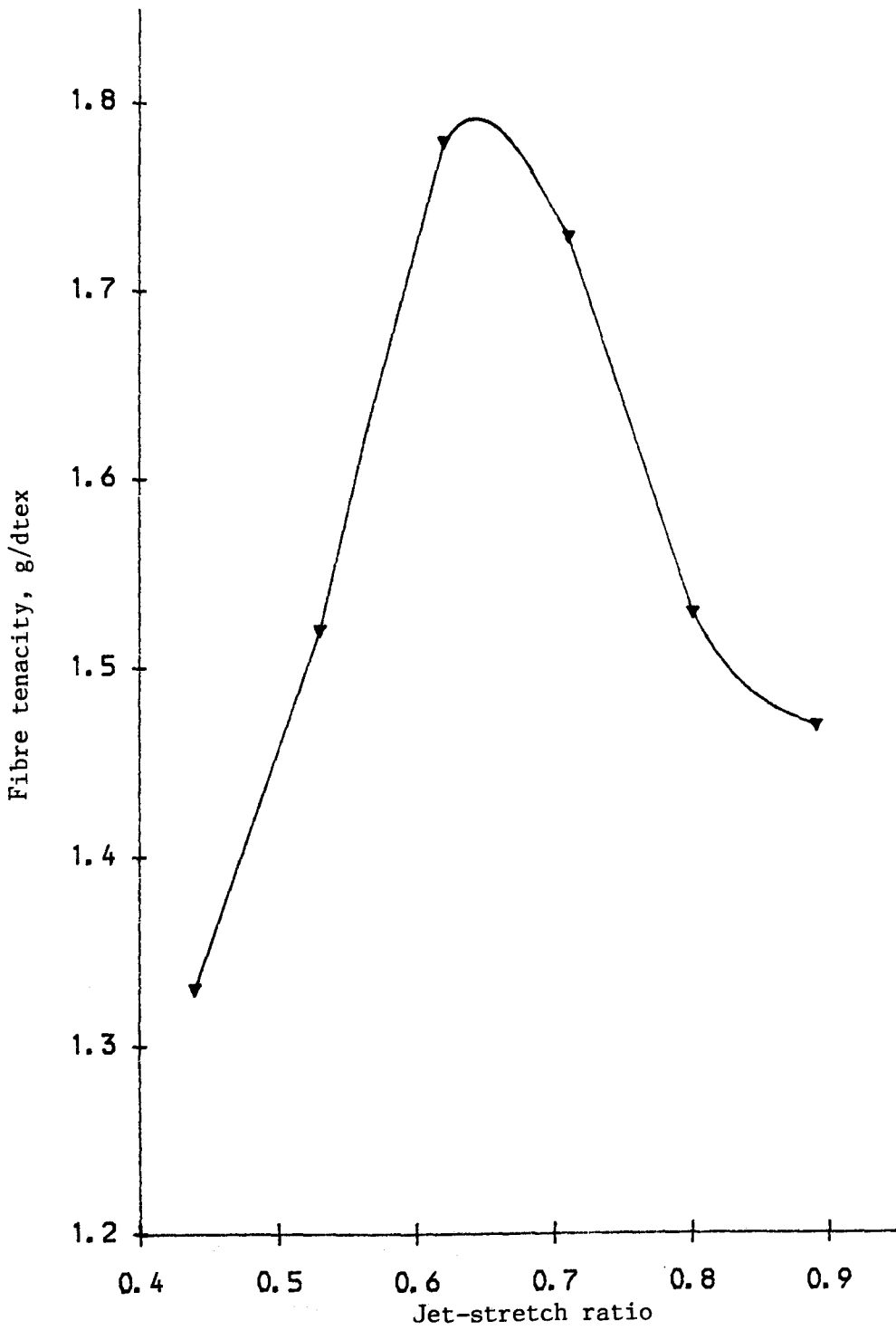


Fig 3.11 Effect of jet-stretch ratio on fibre tenacities at DR=10%

Table 3.8 Effect of draw ratio on fibre properties

Draw ratio, %	0	12.8	17.8	24.4	28.2
Linear density, dtex	69.7	66.7	68.6	63.3	62.5
Strength, gram	103.0	101.5	104.4	109.1	110.6
Tenacity, g/dtex	1.48	1.52	1.52	1.72	1.75
Extensibility, %	16.4	11.6	11.8	12.1	9.2

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 um

Coagulant: 5% aqueous NaOH at room temperature

Extrusion rate: 13.0 m/min.

Jet-stretch ratio: 0.53

Draw ratio: 0, 12.8, 17.8, 24.4, 28.2%

Drying method: heat drying

usually drawn with a ratio of a few hundred percent. However, this low draw ratio is quite similar to that obtained by Agboh (37) for chitin; the reasons will be discussed later.

From the table, it is clear that increases in draw ratios resulted in decreased fibre linear densities, increased fibre tenacities and decreased fibre extensibilities, as commonly seen elsewhere. One exception was noticed in the case of the fibre drawn for 17.8% which had a higher fibre linear density than that drawn for 12.8%. This could be explained by possible errors arising from the spinning system, such as errors in setting roller speeds.

Table 3.9 Effect of dope temperature on fibre properties

Temperature, °C	20	30	40	50
Fibre tenacity, g/dtex	1.14	0.78	0.61	0.71
Extensibility, %	6.0	16.0	8.5	9.0

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 5 holes, 150 um

Extrusion rate: 14.8 m/min.

Coagulant: 5% aqueous NaOH at room temperature in a short bath

Jet-stretch ratio: 0.53

Draw ratio: 10%

Drying method: heat drying

In studying the effect of dope temperature on the mechanical properties of chitosan fibres, the spinneret used was a 5 hole, 150 um in comparison to the normal 20 hole, 80 um one; this replacement was due to the experimental requirement for a more accurate temperature control of the extruding dope. As already mentioned in section 3.1.3, increases in dope temperature reduced dope viscosity. As a result, spinning was not possible above 50 °C when the dope tended to stick on the spinneret orifice, apparently due to low dope viscosity. In addition, it was observed that bubbles were formed in the extruded dope when the dope was heated. From the mechanical properties shown in table 3.9, it can be seen that under the same spinning conditions, the yarn spun at room temperature had the highest tenacity though an

increase in fibre extensibility was obtained when higher dope temperatures were used. In view of the above points, it appeared that room temperature is the appropriate temperature to spin chitosan fibres from these dopes.

Table 3.10 Effect of molecular weight on fibre properties

	low grade	medium grade	high grade
Maximum draw ratio, %	35.0	30.0	15.0
Tenacity, g/dtex	1.62	1.96	1.84
Extensibility, %	7.8	7.2	7.1

Dope: 5% chitosan of low, medium and high grade in 2% aqueous AcOH

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 μ m

Extrusion rate: 13.0 m/min.

Coagulant: 5% aqueous NaOH at room temperature

Jet-stretch ratio: 0.53

Draw ratio: maximum workable

Drying method: heat drying

From table 3.10, it can be seen that with an increase in polymer molecular weight, the maximum draw ratio decreased. This is natural as when the molecular weight is increased, the inter-chain forces are likely to increase, when the polymer solution would show resistance to the drawing operation. As far as the fibre properties are concerned, the medium grade chitosan gave the highest tenacity which is 1.96 g/dtex.

Compared to the value of 1.62 and 1.84 obtained for the low and high grade chitosan, it can be concluded that the molecular weight in this region had little effect on fibre mechanical properties.

Table 3.11 Effect of concentration of the coagulation bath

Concentration, %	5	4	3	2
Maximum draw ratio, %	57.4	77.8	70.4	74.1
Linear density, dtex	78.0	71.9	76.6	77.4
Yarn strength, gram	141.2	142.7	147.7	156.3
Yarn tenacity, g/dtex	1.81	1.98	1.93	2.02
Extensibility, %	10.4	7.5	7.0	7.8

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 um

Extrusion rate: 13.6 m/min.

Coagulant: 5% aqueous NaOH, dilution to 4, 3, 2%

Jet-stretch ratio: 0.4

Draw ratio: maximum workable

Drying method: heat drying

It is generally agreed that in the wet-spinning system, a slow coagulation leads to fibres with superior mechanical properties; in the acrylic system, the coagulation is usually slowed down by adding solvent (e.g., DMAc) into the water bath, so as to obtain fibres with a more homogeneous and less porous structure. In the case of the

production of chitosan fibres using aqueous NaOH as a coagulant, the obvious way to reduce the coagulation power is to reduce the NaOH concentration. Though early work with a syringe and needle type test proved that 5% aqueous NaOH is the lowest alkali concentration which still allows continuous filament formation, it was thought that under practical spinning conditions, when finer extrusion holes are used, it might be possible to obtain fibres with still lower alkali concentrations. Results showed that the normal 5% aqueous NaOH solution could be diluted to 2% and still allow steady fibre formation. Though no work was done on the effect of NaOH concentration on the gel swelling factor of the newly formed filaments, it was observed that with the decrease in alkali concentration, the filaments formed in the coagulation bath became much more swollen. Slight increases in the maximum draw ratio were also obtained. With regard to the mechanical properties of the resulting fibres, the fibre tenacity seemed not to be so much affected by changes in the NaOH concentration though a slight increase in fibre tenacity was obtained in the case of the 2% NaOH bath. These results therefore indicate that the coagulation bath concentration (in the region of 2-5%) is a relatively minor parameter in the wet-spinning of chitosan fibres. This in a way points out that when a stationary alkali bath is used for fibre production, the properties of the resulting fibres will be relatively stable while the NaOH in the bath is continuously destroyed by the solvent acetic acid.

Effect of addition of salt to the bath

So far production of chitosan fibres with aqueous NaOH bath proved successful; the normal 5% bath can be diluted to 2%, giving better

mechanical properties. By comparing the chitosan process so far developed with that for viscose rayon, it was thought useful to examine the effect of adding some salt to the coagulating bath.

Sodium sulphate is the salt normally used in viscose rayon spinning. In wet spinning of polyvinyl alcohol fibres, both sodium sulphate and ammonium sulphate have been frequently used (133). Other possible salts that might be used included sodium acetate, as it is the product of the reaction between the solvent acid and the coagulant, i.e., acetic acid and sodium hydroxide. However, as ammonium sulphate and sodium hydroxide would give rise to ammonia, ammonium sulphate was not examined as an additive to the coagulating bath. In addition, sodium acetate has a low dehydrating power (134). Therefore, sodium sulphate was chosen as the salt in the coagulating bath.

Table 3.12 Wet spinning of chitosan fibres with salt bath

Bath composition	600 g Na ₂ SO ₄ , 3600 ml H ₂ O, 42 g NaOH
Dope	5% medium grade chitosan in 2% aqueous AcOH
Extrusion rate	13.6 m/min.
Jet-stretch ratio	0.4
Draw bath	water, 80-85 °C
Maximum draw ratio	75.9%
Drying	radiant heating
Yarn linear density	74.3 dtex
Yarn tenacity	2.48 g/dtex
Extensibility	5.7%

From table 3.12, it can be seen that quite strong fibres were produced when coagulation bath containing Na_2SO_4 was used. The fibre tenacity was 2.48 g/dtex, the highest so far obtained. Compared to the previous spinning trials, it was found that the draw ratio obtained in this experiment was quite high. This may contribute to the high strength obtained. In addition, because of the use of concentrated Na_2SO_4 , it was possible to reduce the NaOH concentration to 1%. This low alkali concentration further reduced the coagulation power of the bath. It is then reasonable to suggest that under a lower alkali concentration, the neutralisation of acetic acid by NaOH was slowed down, resulting in a more homogeneous fibre structure before drawing. Further, Na_2SO_4 is a strong dehydrating agent. When the newly extruded dope is in contact with the salt bath, severe dehydration takes place. This might result in a quick gelation which may contribute to the high strength obtained.

In addition, it was noticed that when the salt bath was used, a reddish brown material was formed in the coagulation bath which was not seen in the previous experiments. It was assumed that this material might either be impurities in the chitosan which were removed and precipitated out upon the use of Na_2SO_4 in the coagulation bath, or a reaction product between chemicals in the dope with those in the bath. To prove the second assumption, a concentrated Na_2SO_4 solution was prepared. Aqueous acetic acid was then added drop by drop to the Na_2SO_4 solution. Interestingly, it was found that a similar reddish brown material was soon produced. This lends support to the possibilities that acetic acid may react with some impurity metal ions such as Fe(II), Fe(III), Cu(II), etc.

when coloured precipitates can be produced.

Effect of coagulation bath temperature

So far in all the spinning processes, the coagulation bath temperature was normally at room temperature. It was recognised that not to control the coagulating temperature was not satisfactory. Yet no effort was made to make or buy a thermostatically controlled bath. However, the following trial was carried out to examine briefly any advantage from using a higher coagulating temperature.

The bath in this experiment was composed of 600 grams of Na_2SO_4 and 3600 ml of water, plus 1% w/w NaOH. It was conditioned in a water bath at 40 °C overnight. Then, wet-spinning was carried out with this solution using the normal procedure. However, it was not possible to pull out fibres continuously as spinning broke down, apparently due to dope sticking to the spinneret surface. Efforts were made to cool the bath down using dry ice but spinning was still not possible.

Effect of draw bath temperature

The draw bath temperature was normally set as high as possible, i.e., 80-85 °C. In studying the effect of draw bath temperature, a steady spinning line was set-up to give yarns continuously drawn, dried and wound. Then, the draw bath was cooled down by addition of dry ice and ice. With the normal bath temperature, the yarn obtained had a strength of 152.1 gram and an extensibility of 7.9%. When the bath was cooled to around 50 °C, the yarn had a strength of 147.6 grams and an extensibility of 8.6%. At about room temperature (20-30 °C), continuous spinning was not possible as frequent filament breakage was encountered on the drying roller, apparently due to the filaments

being too swollen.

Effect of drying and winding-up procedures on fibre properties

As was briefly pointed out earlier, three ways were used to dry the chitosan fibres during production. These were the acetone bath method, the radiant heater method and the air drying method. Acetone drying gave a chitosan yarn with the individual filaments well separated, in comparison to the samples dried by radiant heating where the individual filaments were frequently stuck together (see section 3.1.9A). Interestingly, the acetone drying method gave a yarn with inferior mechanical properties which was attributed to the rapid loss of water which possibly made the fibre more porous.

The radiant heater drying was very efficient. However, it might be possible that the sudden loss of water on heating leads to high internal stresses in the fibres and therefore to a more brittle structure. In view of this, an air drying method was used to dry a sample of chitosan yarn, to allow comparison. The yarn was dried in this method by passing it over the 5th roller with the normal number of turns. Then it was collected underneath in a relaxed form. The yarn was then left to dry in air overnight, after which it was wound on to a paper bobbin for testing.

Some property differences noted are tabulated in table 3.13.

In studying the effect of winding-up on fibre properties, two ways were developed for collecting the resultant chitosan yarn. The first was to collect the chitosan yarn as normal onto paper bobbins while the second was simply to leave the dried yarn unwound. Some property differences observed are tabulated in table 3.14.

Table 3.13 Properties of fibres with different drying methods

Drying method	radiant heating	air drying
Yarn decitex	77.2	85.6
Yarn strength, gram	152.1	157.5
Yarn tenacity, g/dtex	1.97	1.84
Extensibility, %	7.9	19.3

Dope: 5% medium grade chitosan in 2% aqueous acetic acid

Nitrogen pressure: 30 lb/in²

Spinneret: 20 holes, 80 μ m

Extrusion rate: 13.6 m/min.

Coagulant: 600 g Na₂SO₄, 3600 ml H₂O, 42 g NaOH

Jet-stretch ratio: 0.4

Draw ratio: 60.0%

Drying method: radiant heating and air drying

Table 3.14 Properties of fibres with different winding-up method

Collecting method	collected on winder	unwound
Yarn decitex	77.2	80.2
Yarn strength, gram	152.1	155.3
Yarn tenacity, g/dtex	1.97	1.94
Extensibility, %	7.9	9.0

Spinning conditions as in table 3.13

From the above two tables, it can be seen that the properties of chitosan fibres were strongly affected by the drying methods. The air dried yarn had a higher yarn decitex and a slightly higher yarn strength than the one dried by radiant heating. However, the overall yarn tenacity showed a preference for the one dried by radiant heating. This is because under radiant heating, the yarn is dried under tension and a certain degree of molecular orientation is thus developed. The difference in molecular orientation can be seen in the X-ray diffraction patterns as will be shown later in section 3.1.9. Interestingly, however, the air dried yarn had a much higher extensibility than the one dried by heating. This, as with the yarn tenacity, may be due to the difference in chain orientation in the yarn.

Winding-up procedures had only a small effect on the fibre properties, though a slightly lower yarn tenacity and a slightly higher yarn extensibility were obtained for the unwound yarn. This may be due to the slight tension applied to the yarn when it was continuously wound onto the paper bobbin which resulted in a small extension of the yarn.

Effect of adding iso-propanol to the dope

Table 3.15 shows the results of the production of chitosan fibres using i-propanol as co-solvent. As can be seen from the table, the chitosan fibres obtained with i-propanol as co-solvent had similar mechanical properties as the fibres with 2% aqueous acetic acid as the solvent. However, the fibres obtained in this way had a much whiter appearance than the normal one. This could possibly be due to the removal of coloured material by the use of i-propanol. The

Table 3.15 Production of chitosan fibres using i-propanol as co-solvent

Chitosan	medium grade, 30 grams
Solvent	11.4 g AcOH, 171 g i-propanol, 387.6 g water
Extrusion rate	13.1 m/min.
First roller speed	8.26 m/min.
Jet-stretch ratio	0.63
Third roller speed	9.38 m/min.
Draw ratio	13.6%
Fifth roller speed	9.45 m/min.
Yarn linear density	64.5 dtex
Yarn strength	117.7 grams
Yarn tenacity	1.82 g/dtex
Yarn extensibility	6.3%

results of a visual reflectance test on the normal chitosan fibres and the ones using i-propanol as the co-solvent are shown in table 3.16.

Table 3.16 Visual reflectance test of two samples of chitosan fibres

Wave length(nm)	reflectance (%)		Wave length(nm)	reflectance (%)	
	Normal	I-propanol		Normal	I-propanol
400	24.96	37.70	560	55.27	63.71
420	30.36	42.77	580	56.64	65.11
440	35.52	47.30	600	57.67	66.18
460	40.26	51.12	620	58.44	66.87
480	44.66	54.33	640	59.13	67.61
500	47.83	56.94	660	59.86	68.40
520	51.09	59.65	680	60.58	69.17
540	53.30	61.83	700	61.22	69.84

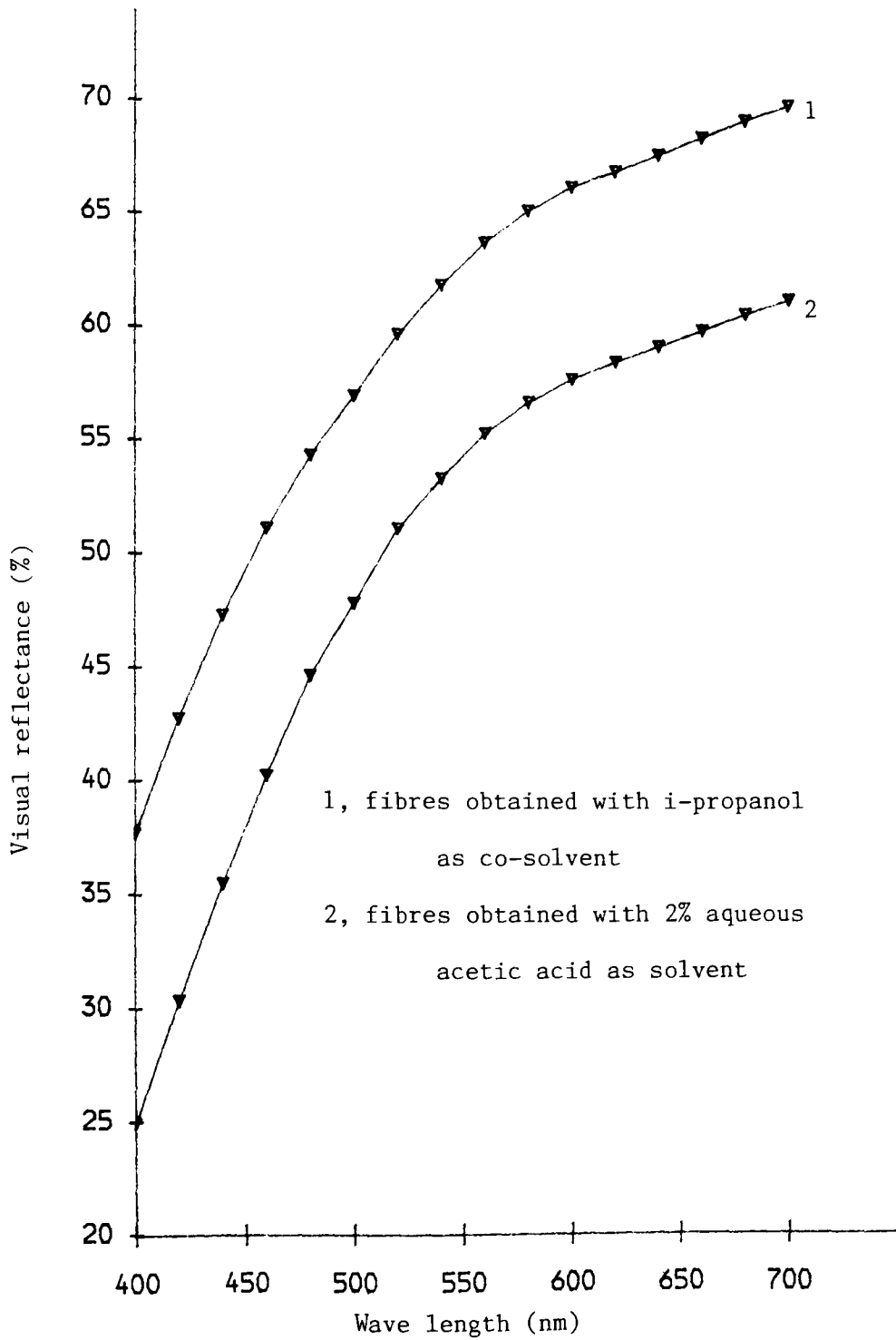


Fig 3.12 Visual reflectance test of two samples of chitosan fibres

3.1.9 Properties of chitosan fibres

A. Morphological properties

The morphological properties of man-made fibres are dependent on the spinning process. The following comments therefore are characteristic of the specific spinning conditions used.

Overall, chitosan fibres obtained in this work were of round cross-section (Fig 3.13 and Fig 3.14). This is quite abnormal as ordinary viscose rayon and alginate fibres have obviously non-circular cross-sections. In the case of viscose rayon, a round cross-section is indicative of slow coagulation and regeneration and correlates with excellent mechanical properties. As mentioned before, the chitosan fibres obtained in this work have tenacities of around 2 g/dtex. As for the coagulation process, the neutralisation of acetic acid by 5% NaOH is a straightforward reaction. There may be two reasons why chitosan fibres have round cross-sections. Firstly, unlike viscose rayon and alginate systems where a fibre skin is formed by a rapid regeneration of the outer sheath upon contact with coagulants, skin formation may be difficult because the diffusion of acetic acid outwards would tend to swell the newly formed skin. Therefore, as the counter-diffusion of acetic acid and NaOH proceeds, coagulation may occur relatively homogeneously. Secondly, the NaOH solution is a strong dehydrating agent. Therefore, a rapid loss of water may occur when the newly formed filament is in contact with the coagulant before extensive neutralisation has taken place. These two factors combined may offer a possible explanation for the formation of the round cross-section.

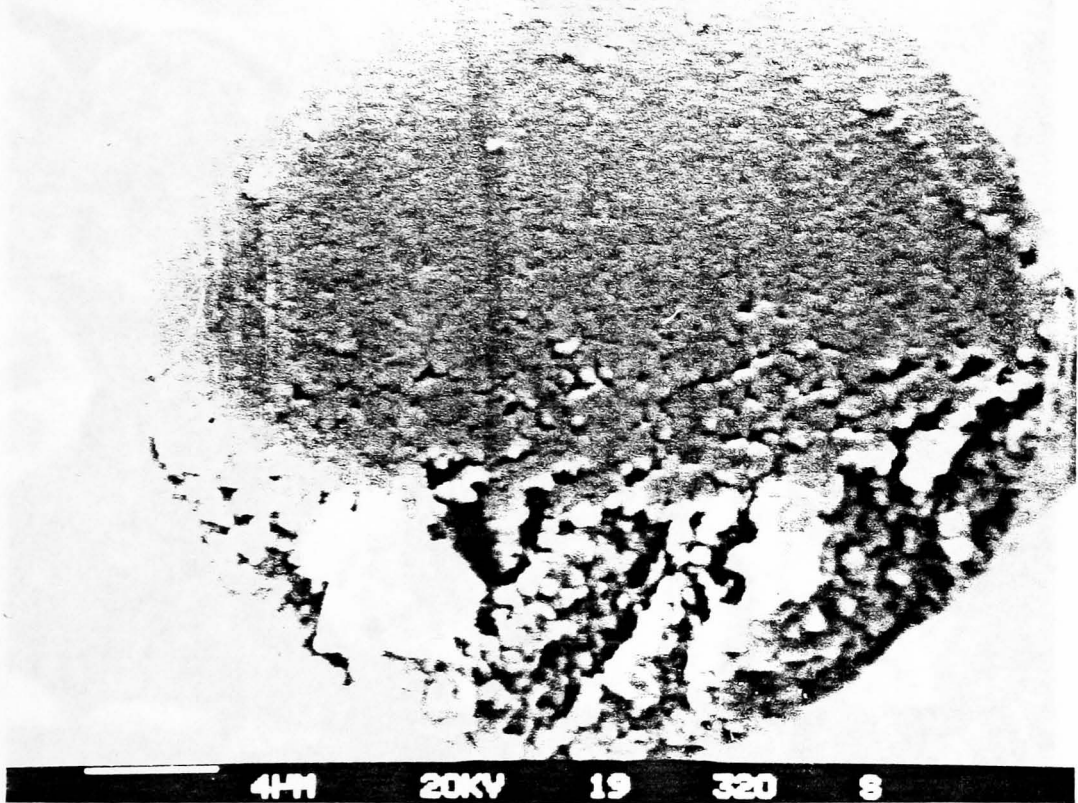


Fig 3.13 Cross-section of chitosan fibre (acetone drying)



Fig 3.14 Cross-sections of chitosan fibres (radiant heating)

3. Moisture regain

Like all other natural polymers, chitosan possesses some hydrophilic groups such as -OH, -NH₂ and -COOH. The moisture regain at different relative humidity is high. It is reported that at 95% R.H. the moisture regain is roughly 14.2%. This is equal to that of cotton of equal weight. In the present work, results showed that chitosan fibres gained an 16.2% moisture when conditioned at 95% R.H. at 27°C for 2 weeks. It

As can be seen in Fig 3.15, the fibres prepared by radiant heating had a much smoother surface as compared with the fibres prepared by acetone drying method (Fig 3.16). The reason might be because radiant heat drying is a relatively slow drying procedure while in acetone drying, rapid loss of water occurs when the wet yarn is in contact with acetone. However, the yarn dried with radiant heating had individual filaments strongly adhered together (Fig 3.17) while in acetone drying the individual filaments were well separated (Fig 3.18). This phenomenon was noticed earlier by Tokura et al (117). The reason might be due to the fact that in heat drying the wet filaments were dried under tension and thus led to fibre adhesion.

B. X-ray diffraction pattern

Fig 3.19 shows the X-ray diffraction patterns of the air dried, heat dried fibres and the fibres prepared by using i-propanol as co-solvent. It can be seen that the air dried fibre had a lower degree of orientation than the heat dried fibres as the diffraction is more diffuse in the case of the air dried fibres than the heat dried one. All three samples seem to have very low degrees of crystallisation although no quantitative calculations were performed.

C. Moisture regain

Like all other natural polymers, chitosan possesses many hydrophilic groups such as $-OH$, $-NH_2$ and $-NH-COCH_3$. The moisture regain of chitosan is high. It is reported (80) that at 51% R.H, the moisture content is roughly 14.2%. This is equal to 16.6% in terms of regain. In the present work, results showed that chitosan fibres picked up 16.2% moisture when conditioned at 65% R.H, 20 °C for a week. In

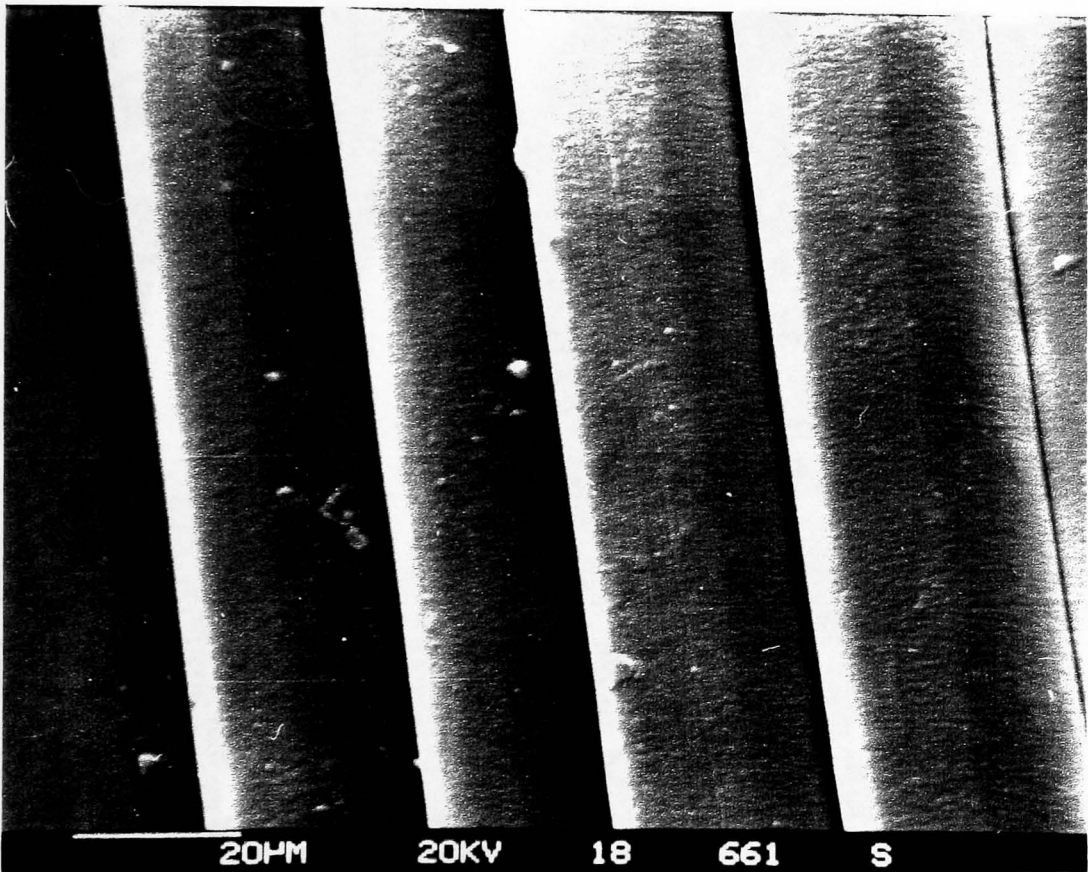


Fig 3.15 SEM picture of chitosan fibres (radiant heating)

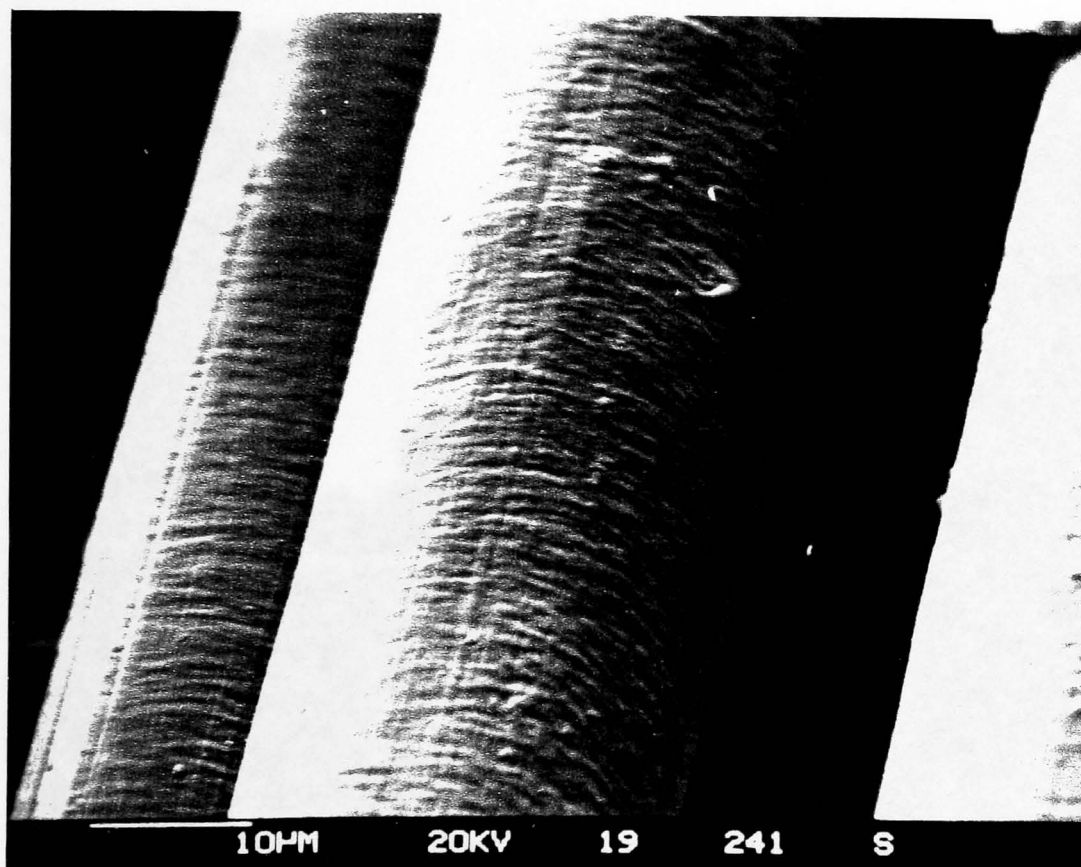


Fig 3.16 SEM picture of chitosan fibres (acetone drying)

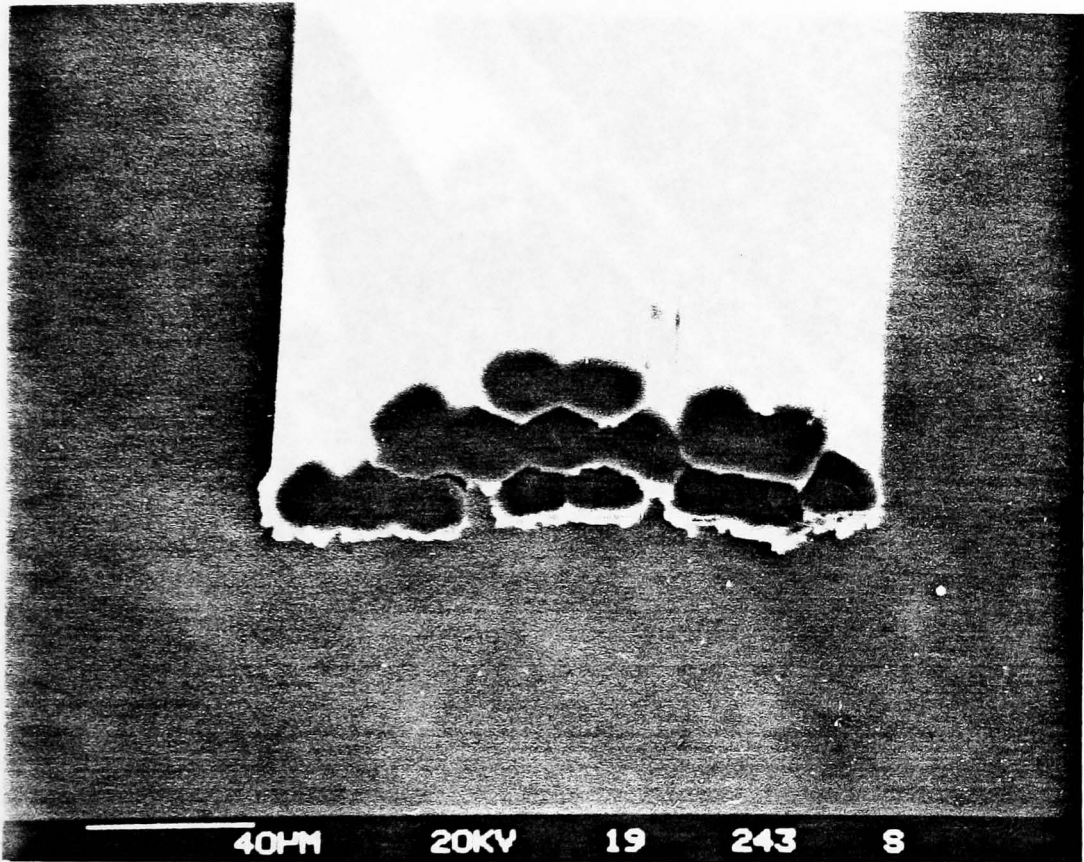


Fig 3.17 SEM picture of chitosan fibres (radiant heating)

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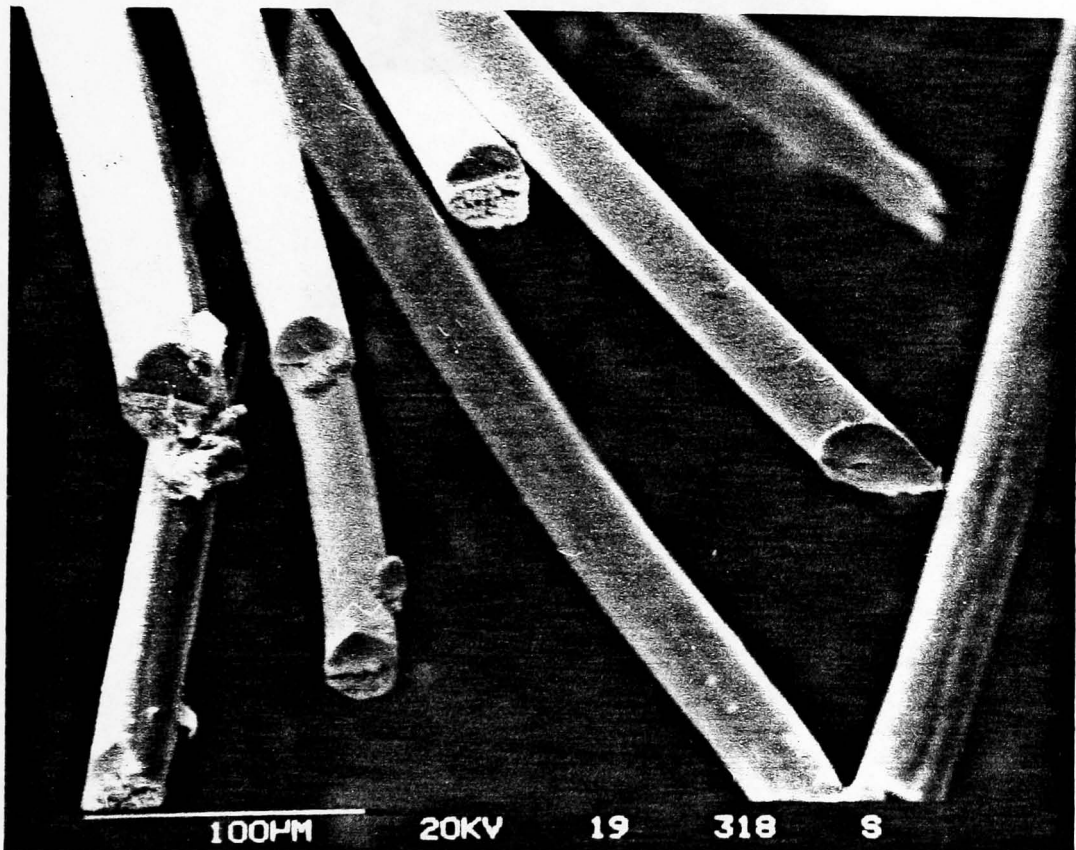
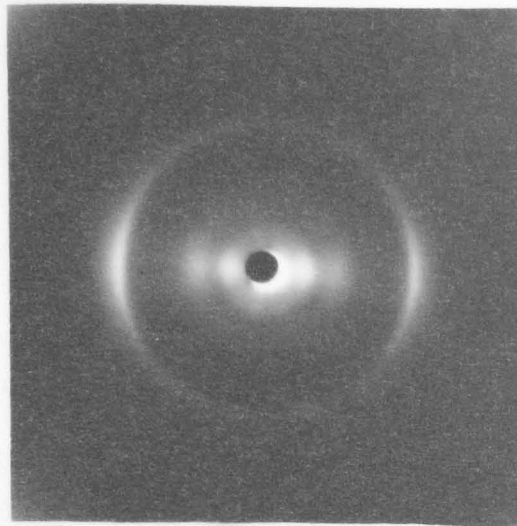
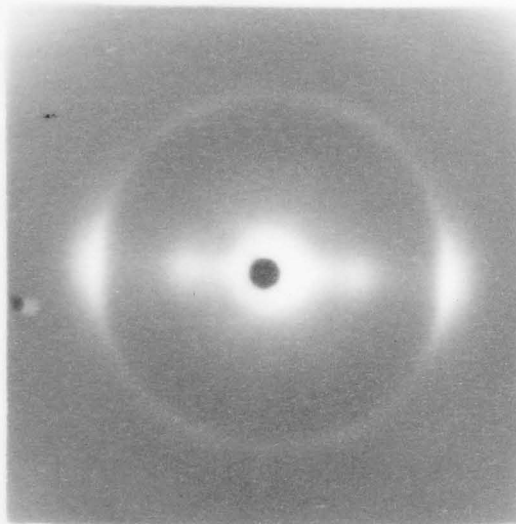


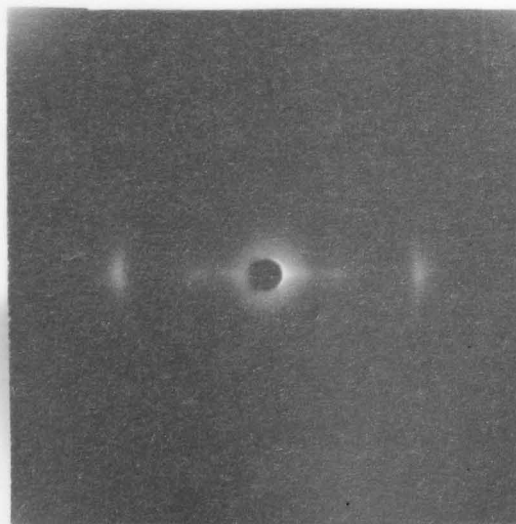
Fig 3.18 SEM picture of chitosan fibres (acetone drying)



Air dried
sample

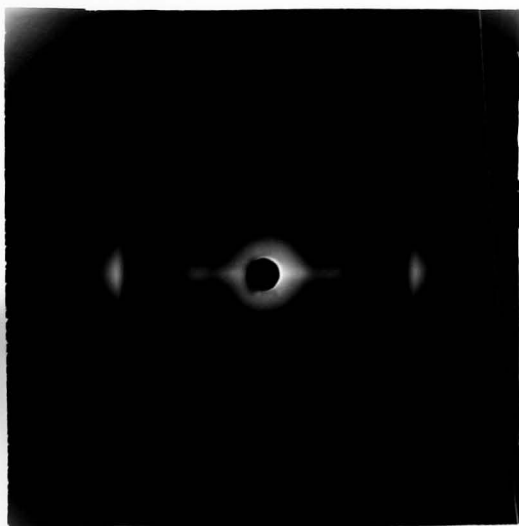
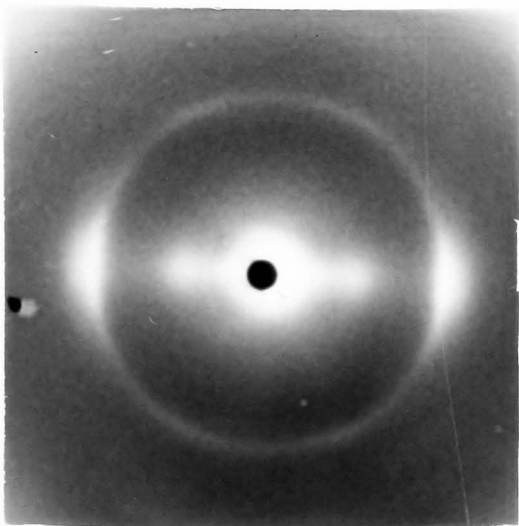
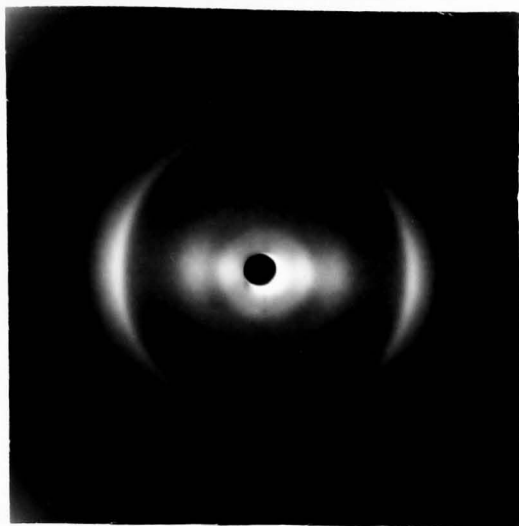


Radiant heat
dried sample



Sample spun
with i-propanol
co-solvent

Fig 3.19



addition, the relative humidity has a great effect on regain as shown in table 3.17 and Fig 3.20.

Table 3.17 Moisture regain of chitosan fibres

Relative humidity (%)	20	65	90	100
Moisture regain (%)	8.8	16.2	29.2	48.9

The moisture regain of chitosan fibres was also obtained by TGA (see Fig 3.21). The curve showed that preconditioned fibres lost water gradually when the temperature is raised, reaching a maximum rate at $T=69^{\circ}\text{C}$. The result from TGA is 15.1%, a slight difference from the standard weighing procedure.

D. Tensile properties

From the early yarn samples prepared, it became clear that the chitosan fibres produced were of rather low extensibility, though with a tenacity around 2 g/dtex. Compared to synthetic fibres, the tensile properties of chitosan fibres are relatively poor. The problem was how to achieve better strength and extensibility. It was recognised that the low extent to which the fibres could be drawn might be the main obstacle; when 5% NaOH was used as the coagulant, the maximum draw ratio was only 60% using a jet-stretch ratio of 0.2. This low draw ratio was thought to be due to the high inter-chain molecular forces which cause filament breakage if higher draw ratios were attempted.

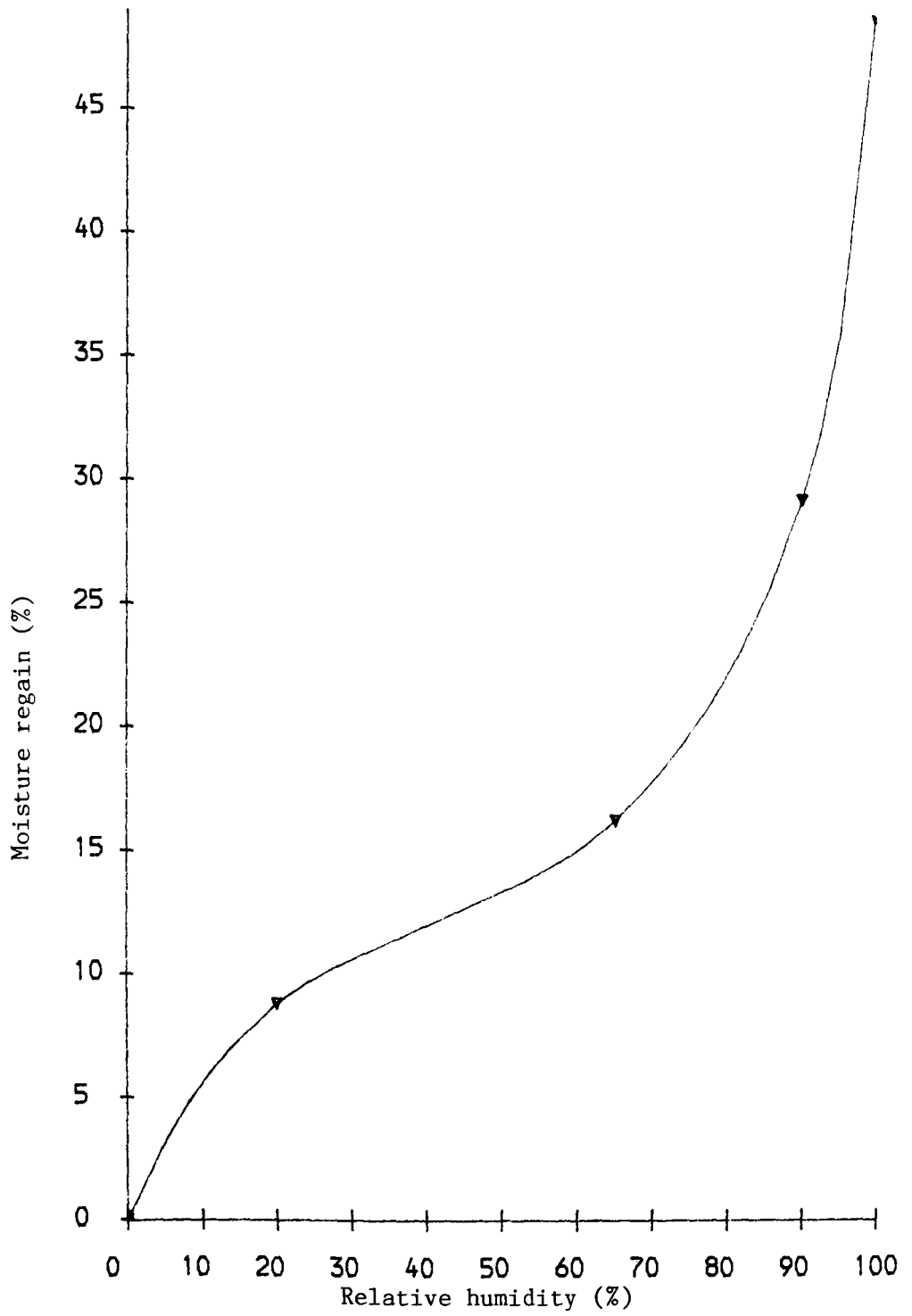


Fig 3.20 Moisture regain of chitosan versus relative humidity

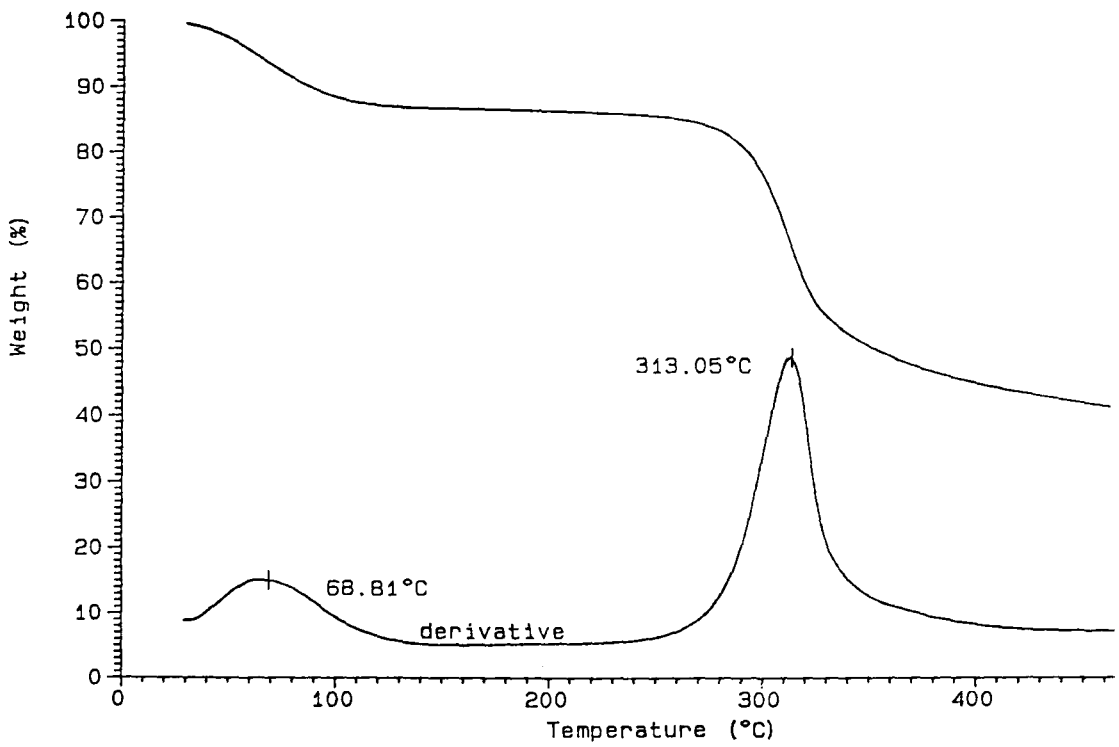


Fig 3.21 TGA curve of chitosan fibres (10 °C/min.)

On the other hand, the fibres obtained in this work would be strong enough to be used as wound-dressing material, especially, for example if compared with alginate (135). Indeed, the yarn obtained in this work could be knitted easily into fabrics.

The spinning process had some effect on the tensile properties of chitosan fibres. As expected, drawing of the newly formed filaments increased fibre tenacity, at the expense of extensibility. Drying the fibre under tension gives strong but inextensible fibres. On the other hand, if the filaments are allowed to dry naturally in air, the extensibility can be very high, 19.3% as compared to 7.9%. However, the naturally dried fibres were found to be strongly adhered to each other.

A typical load-extension diagram of chitosan fibres is shown in Fig 3.22. From the figure, it can be seen that the fibres are of rather high initial modulus, indicating the existence of strong inter-chain forces.

The effect of relative humidity on tensile properties was studied. It was found that fibre strength is very sensitive to R.H. Under the same testing conditions, the fibre strength (conditioned at 90% R.H) is only half of the same fibre conditioned at 20% R.H. The absorption of water reduces the inter-chain forces and therefore reduces the tensile strength. This can be further seen from the initial modulus which decreases with increase in R.H. These phenomena were similar to those noticed in viscose rayon fibres.

E. Thermal stability

From the TGA curve (see Fig 3.21) obtained from the spun yarn, it

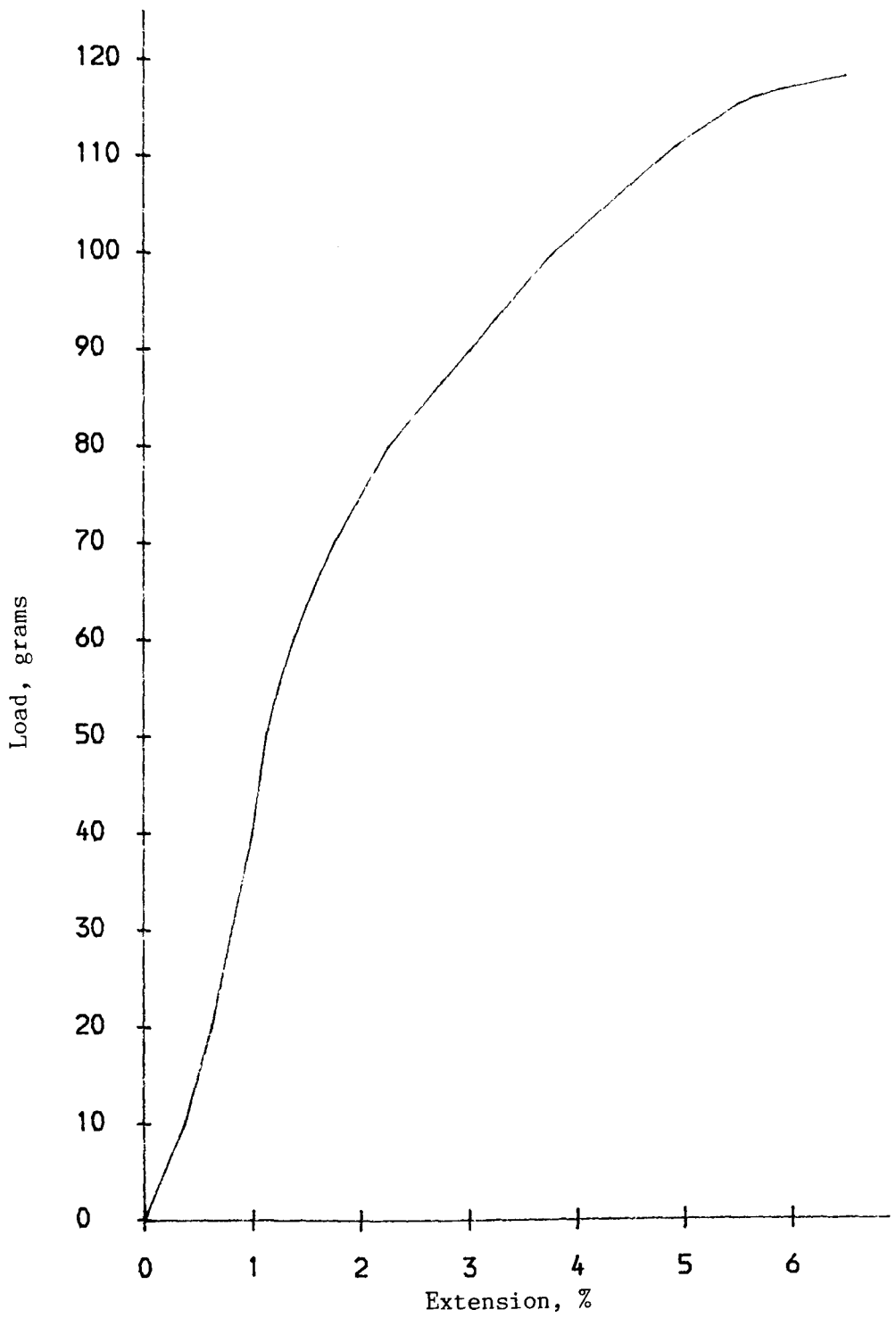


Fig 3.22 Typical load-extension diagram of chitosan fibres

Table 3.18 Effect of R.H on tensile properties

Relative humidity (%)	20	65	90	100
Strength, gram	162.8	128.2	89.4	29.0
Extensibility, %	5.8	6.1	5.6	11.5

Sample fibres were prepared with the i-propanol method

can be seen that under a nitrogen atmosphere, the weight loss starts at $T=220^{\circ}\text{C}$, reaching a maximum decomposition rate at $T=313^{\circ}\text{C}$. The weight loss at 313°C is associated with a release of heat as shown in the equivalent DSC curve (Fig 3.23).

The effect of temperature on chitosan is reflected by the tensile properties obtained after heat treatment of chitosan fibres at different temperatures for different periods of time. The results are shown in table 3.19.

Table 3.19 Effect of heat treatment (in air) on tensile properties

Temperature, $^{\circ}\text{C}$	normal		100		175		250	
Time, min.			5	10	5	10	5	10
Strength, gram	117.7	114.9	117.5	118.2	114.7	96.0	95.5	
Extensibility, %	6.3	7.4	7.2	7.5	7.4	4.4	4.7	

From table 3.19, it can be seen that short heat treatments had

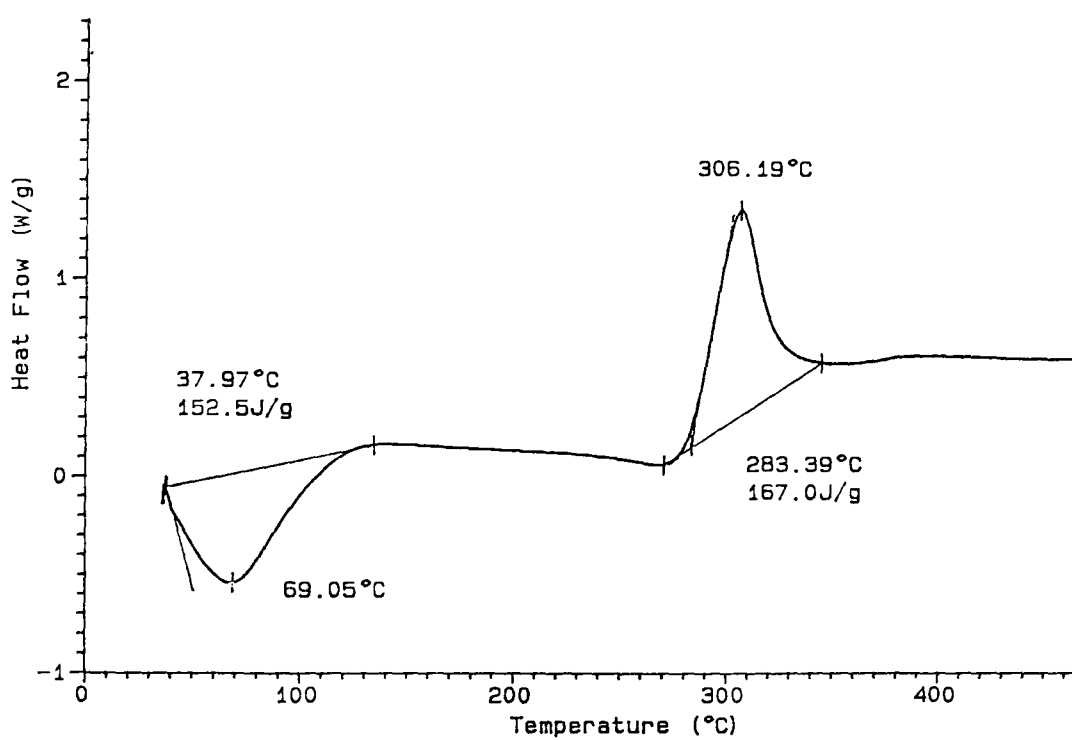


Fig 3.23 DSC curve of chitosan fibres (10 °C/min.)

little effect on the tensile properties of chitosan fibres at temperatures below 175 °C. However, at a temperature of 250 °C, chitosan fibres rapidly lost both strength and extensibility. The reason is presumed to be due to thermal degradation in which molecular scission occurs. It is worth mentioning that the chitosan gradually lost solubility in 2% aqueous acetic acid upon heat treatment (table 3.20). Moreover, the fibre became brownish after the 5 minute treatment at T=250 °C.

Table 3.20 Solubility change during heat treatment

Temperature, °C	normal	100		175		250	
Time, min.		5	10	5	10	5	10
Breakage time, s	6.5	32.3	29.9	33.2	40.2	over 30 min	

Solubility was expressed as the time required to break the treated yarn, when it is immersed in a 2% aqueous acetic acid solution, with one end linked to a weight of 0.3298 gram.

The results clearly indicated that the solubility of chitosan fibres decreases as the severity of the heat treatment is increased, with the fibres treated at 250 °C becoming actually insoluble. The mechanism is not clear at present, but possibilities could include the loss of $-NH_2$ as well as some cross linking reactions.

F. Chelating properties of chitosan fibres

It is already well known that chitosan can chelate transition metal

ions. The subject has been extensively studied (5,56). Literature information indicated that chitosan can chelate such metal ions as Cu(II), Zn(II), Cr(II), Co(II), Ni(II), etc. According to Muzzarelli et al (56), the chelating power is in the order of Cu, Ni, Zn, Co, Fe and Mn, in a 0.1 M KCl solution. In addition, the anion has a significant effect on the chelation; under similar conditions, the sulphate salts have the strongest affinity for chitosan (107).

The chelation properties of chitosan fibres havenot so far been studied; this is not surprising as little work exists in the literature dealing with the production of chitosan fibres. However, chitosan in fibre form may offer some unique applications of its chelating ability. For example, chitosan fabrics might be easily handled in removing heavy metal ions from waste water. It was thought worthwhile to study the chelating properties of chitosan fibres.

In view of its distinct colour and popularity, Cu(II) was chosen as an example to study the chelation behaviour of chitosan fibres. Zn(II) was also used because it has a reputation for producing flame retardancy and also has a special effect in wound-healing (136).

Two ways were used to apply different amounts of metal ions to chitosan fibres. The first method used variations in the ratio between the amount of metal ion and the fibre. The second used time to control the uptake. The results are shown in table 3.21 and 3.22.

From the two tables, it can be seen that it is possible to obtain different levels of copper ions in chitosan fibres with each of the two methods. In the first method, the

Table 3.21 Effect of molar ratio of Cu(II) and chitosan on the uptake of Cu(II) to chitosan fibres

Amount of Cu(II), ml	0.1	0.5	2	5	8	10
Amount of water, ml	19.9	19.5	18	15	12	10
Molar ratio, Cu/NH ₂ , %	1	5	20	50	80	100
Carbon content, %	39.6	38.0	32.4	29.6	30.05	29.9
Cu content, %	0.3	1.3	4.25	8.0	8.35	8.35
Glucosamine/Cu, molar ratio	117.3	26.0	6.8	3.3	3.2	3.2

0.015 M aqueous CuSO₄ solution was used. 4 metres of chitosan fibres (0.0242 gram) were treated in the above CuSO₄ solution diluted to various concentrations. The treatment was continued for 24 hours.

Table 3.22 Effect of time on the chelation of Cu(II)

Time, min.	5	10	20	40	one day
Carbon content, %	35.5	32.8	31.85	30.05	27.8
Cu content, %	2.75	4.4	6.0	7.65	9.0

20 ml of 0.01 M aqueous CuSO₄ solution was brought in contact with 4 metres of chitosan fibres (0.0242 gram)

amount of copper ions absorbed increased proportionally with the increase in the ratio of copper ions used. An equilibrium figure of 8.35% was obtained when the molar ratio between Cu(II) and chitosan was 80%. In the second method, the amount of copper ions absorbed

by chitosan increased steadily with time (Fig 3.24). Comparing the amount of copper absorbed at 5, 10, 20 and 40 minute treatment to that obtained after one day's treatment, it can be seen that the absorption of copper ions by chitosan is a relatively rapid process.

Table 3.23 Effect of time on the chelation of Zn(II) to chitosan

Time, min.	5	10	20	40	one day
Carbon content, %	38.35	36.35	34.75	33.1	30.55
Zn content, %	0.55	1.95	3.4	5.15	6.25

20 ml of 0.01 M ZnSO₄ was brought in contact with 4 metres of chitosan fibres (0.0242 gram).

The uptake of the metal ions has a great effect on the tensile properties of chitosan fibres. The results are given in tables 3.24 and 3.25.

Table 3.24 Effect of Cu(II) on the strength of chitosan fibres

Amount of Cu(II), %	0	2.75	4.4	6.0	7.65	9.0
strength, gram	117.7	117.6	123.5	133.0	136.4	148.0
Dry extensibility, %	6.3	12.8	14.0	15.0	14.6	14.8
strength, gram	29.0	42.6	53.4	66.4	73.9	78.4
Wet extensibility, %	11.5	16.6	19.4	20.8	22.1	19.8

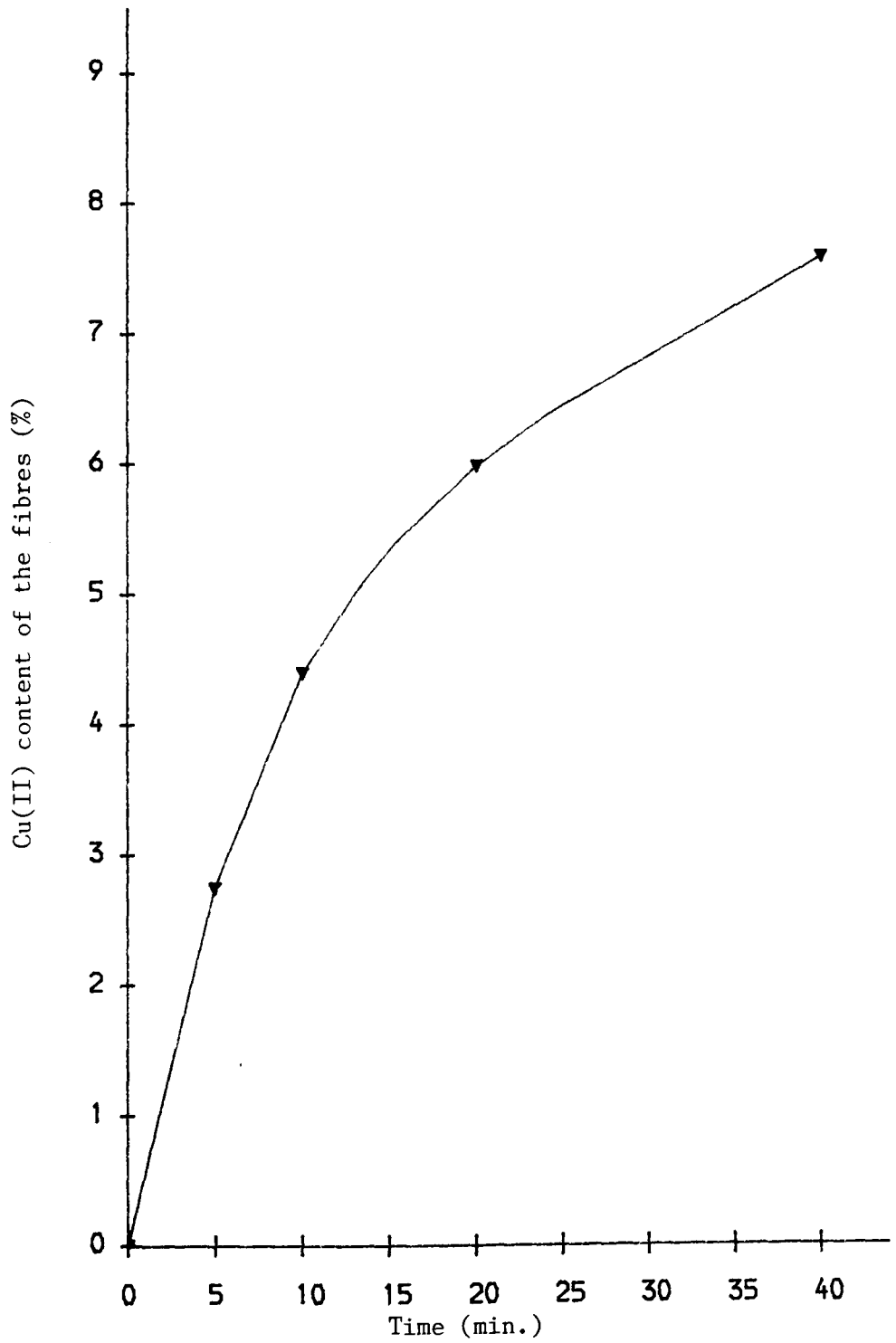


Fig 3.24 Effect of time on the chelation of Cu(II) to chitosan fibres

Table 3.25 Effect of Zn(II) on the strength of chitosan fibres

Amount of Zn(II), %	0	0.55	1.95	3.4	5.15	6.25
Dry strength, gram	117.7	125.0	134.4	137.8	142.5	148.1
Dry extensibility, %	6.3	11.7	12.4	11.1	11.6	11.5
Wet strength, gram	29.0	30.1	31.3	34.4	38.7	46.8
Wet extensibility, %	11.5	12.8	14.4	17.8	18.6	16.0

The effect of the uptake of Cu(II) and Zn(II) on the mechanical properties of chitosan fibres is shown in tables 3.24, 3.25 and Fig 3.25, 3.26. It is obvious that in both systems, both dry and wet strength were enhanced by the uptake of metal ions, with substantial increases in fibre extensibilities. The increase in fibre strength can be explained by the enhanced inter-chain molecular forces, which result from the cross-linking effect from three-dimensional chelation. However, it is interesting to notice that although over the same periods of time, chitosan fibres absorbed more copper ions than zinc ions, the zinc-chitosan fibres had the higher dry strength. However, the copper-chitosan fibres had far better wet-strength than the zinc-chitosan fibres; the wet strength is more than double that of the original one when the chitosan absorbed 9% copper ions.

The absorption of Cu(II) produced distinctly blue chitosan fibres. This is most easily visualised by the knitted chitosan fabric, with a blue colour obtained after one hour treatment in 0.01 M aqueous CuSO_4 at room temperature. Interestingly, the Cu(II)

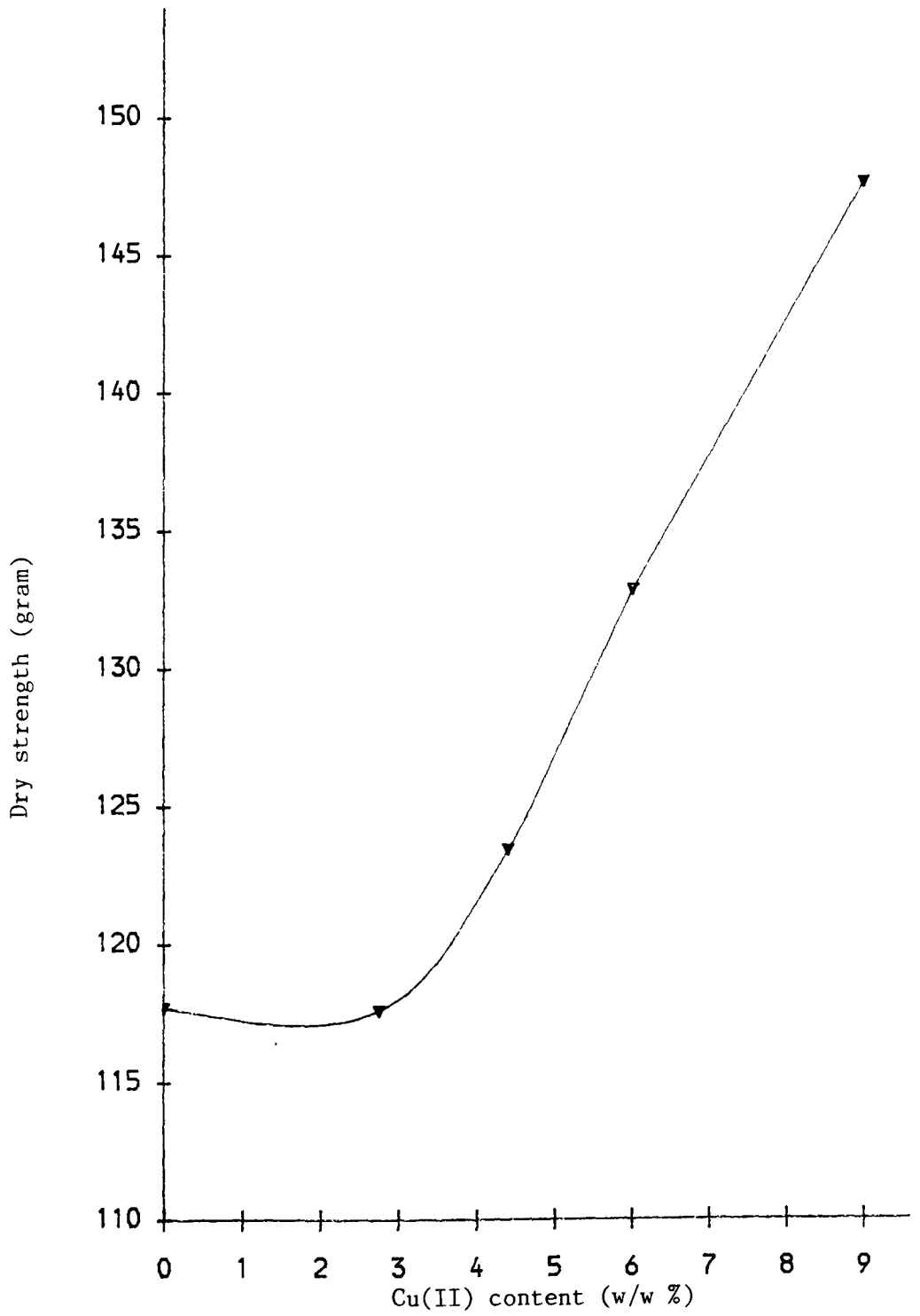


Fig 3.25 Effect of Cu(II) on the dry strength of chitosan fibres

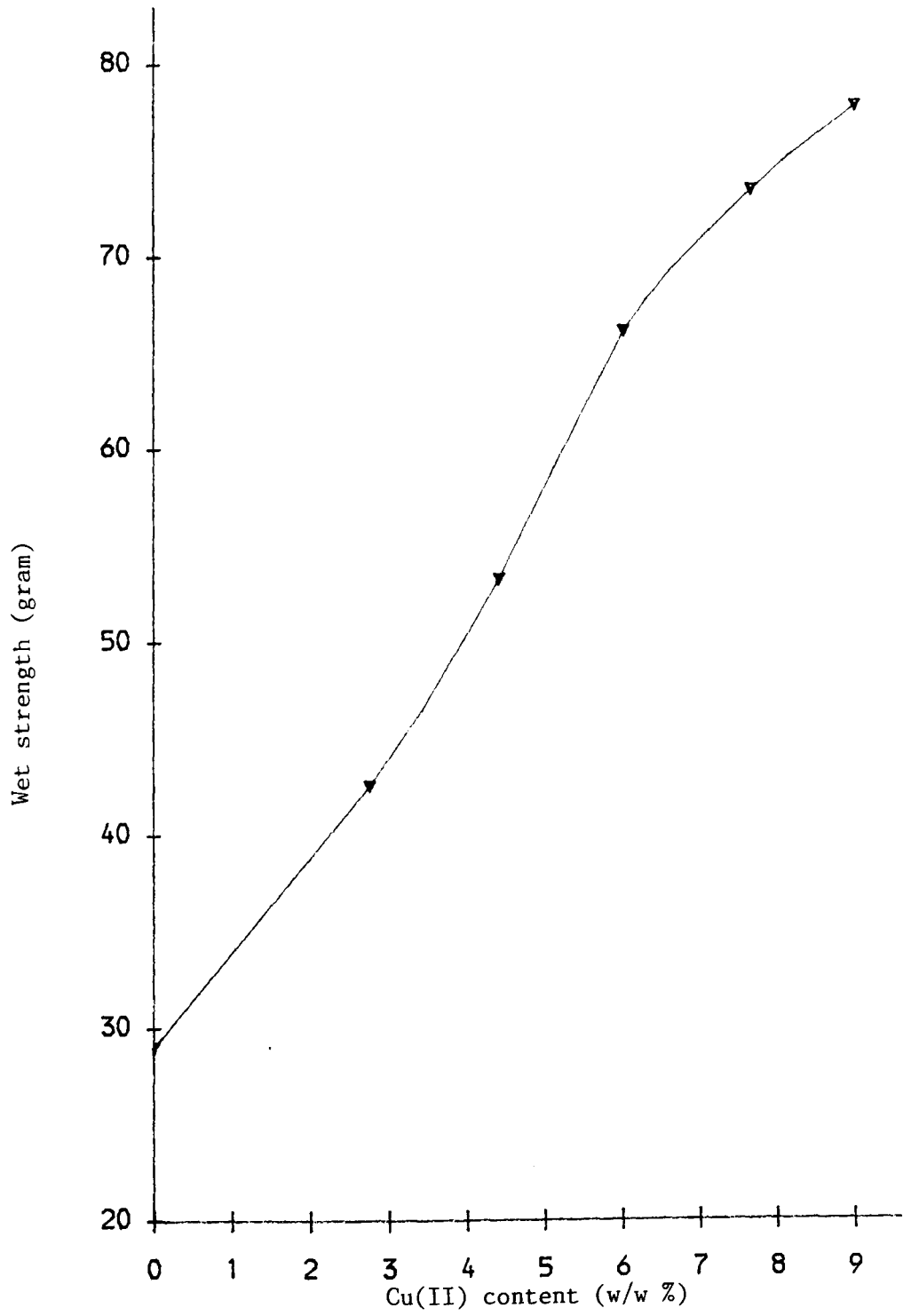


Fig 3.26 Effect of Cu(II) on the wet strength of chitosan fibres

can be readily desorbed by treatment in EDTA. As chitosan is soluble in acidic media, some sodium carbonate was added to the solution. Thus, a mixture of 0.1 M EDTA disalt and 0.4 M Na₂CO₃ removed Cu(II) within 5 minutes. The result is shown in table 3.26.

Table 3.26 Desorption of Cu(II) by EDTA

Time, min.	0	1	2	5	10
Carbon content, %	28.05	35.05	36.45	38.2	37.65
Cu content, %	7.3	3.7	1.9	nil	nil

Table 3.27 Strength changes after EDTA treatment

Time, min.	0	1	2	5	10
Cu content, %	7.3	3.7	1.9	nil	nil
Strength, gram	150.5	138.2	129.6	126.8	125.0
Extensibility, %	14.6	17.1	16.5	18.4	19.2

From table 3.26 and Fig 3.27, it can be seen that half of the copper ions absorbed by the fibres were removed within the first minute, indicating that the removal of copper ions from chitosan fibres with EDTA is a very rapid process; the fibre was found to contain no copper ions after 5 minutes treatment. The removal of copper ions

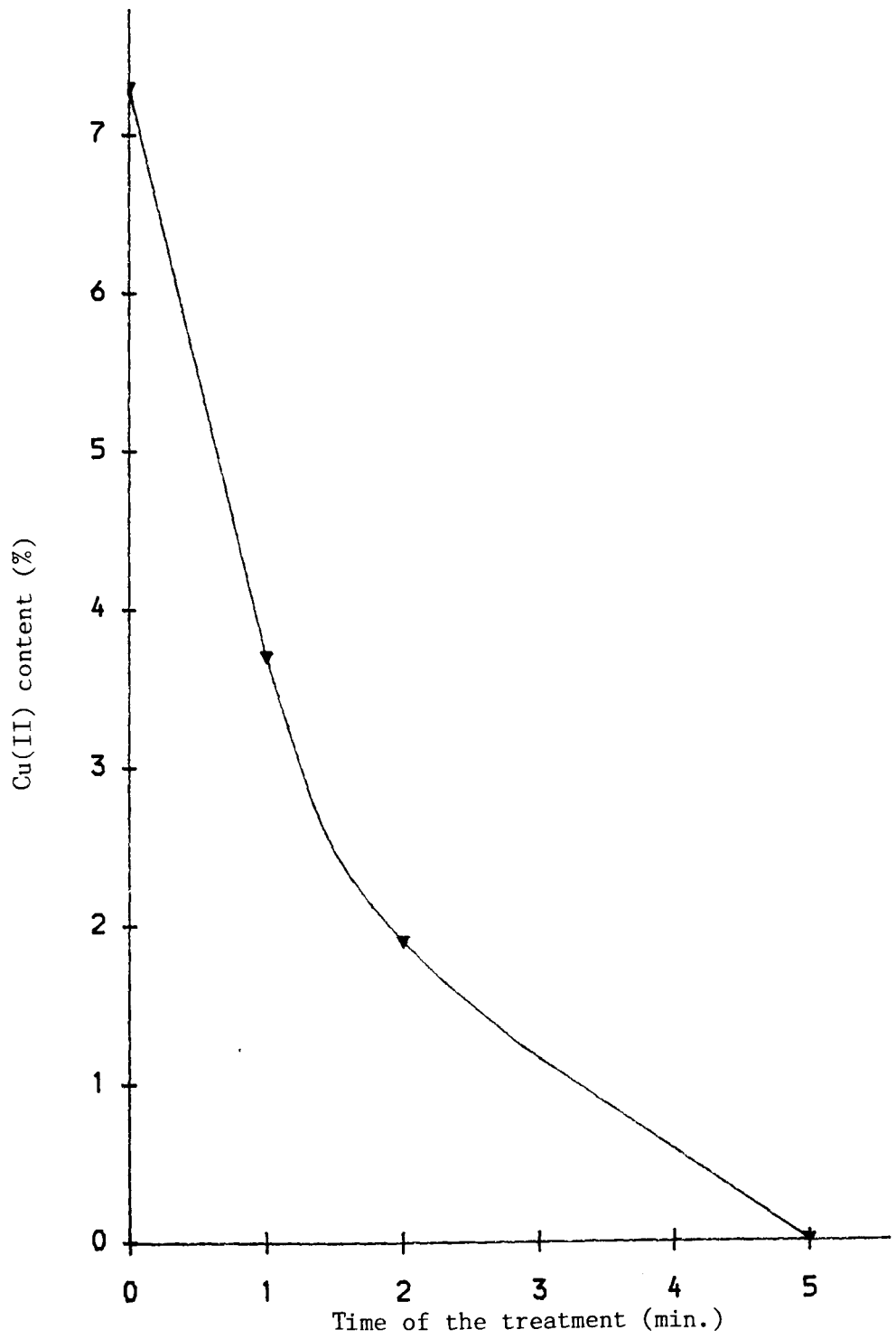


Fig 3.27 Desorption of Cu(II) from chitosan fibres with EDTA

from the fibre leads to decreased fibre strength, as shown in table 3.27. This decrease in fibre strength with removal of copper ions is the reversal of the phenomenon observed earlier where increased fibre strength was obtained when copper ions were applied to chitosan.

The increase in fibre extensibility after the copper ion removal is quite high. This might be attributed to the disorientation effect caused by swelling. It was noticed that the fibre shrank greatly in the aqueous CuSO_4 solution. Starting with a piece of yarn 100 cm long, the length contracted to 88.9 cm in 0.01 M aqueous CuSO_4 within 1 hour. After treatment of the chelated fibre in 0.1 M EDTA disalt and 0.4 M Na_2CO_3 , the length was 90.6 cm. This might well explain the increased extensibility after chelation.

While the mechanical properties were improved by the uptake of metal ions, the flammability of chitosan fibres were also improved dramatically. Whereas the untreated chitosan fibres burned very easily upon ignition, both copper and zinc treated fibres were not easily burned. A newly formed chitosan yarn was contacted with 0.1 M ZnSO_4 solution for 30 seconds. The fibres were found to contain 12.15% zinc. The carbon content was as low as 20.4%. When tested, it was found that the fibres started burning at 52% oxygen content. The ash was tar-free. Elemental analysis showed that the ash contained 0.75% carbon, 0.35% nitrogen, 0.5% hydrogen, 5.7% sulfur, with a zinc content as high as 73%.

Part II. Acetylation of chitosan fibres

3.2.1 Introduction

The conversion of a polymer to fibre form may take two paths, a direct one or an indirect one. Direct spinning of the polymer is the more obvious procedure; however, in some cases, where the conversion of the polymer to a liquid phase is difficult or economically unfavourable, an indirect method might be employed. A typical example is the viscose rayon process where fibres are obtained by conversion of cellulose to its xanthate derivative which is decomposed after or during the spinning.

Chitin may be considered still as a polymer with a limited range of solvents and a limited extent of solubility. Even though recent discoveries indicate that it can be dissolved in DMAc-LiCl, dissolution is still difficult (as the chitin requires a pretreatment (37)) and the solvent is relatively expensive. On the other hand, the deacetylated product, chitosan is readily soluble in dilute aqueous acids, offering a convenient and relatively cheap spinning process. By acetylation of the resultant chitosan fibres, it might be possible to obtain chitin fibres indirectly (the two ways of obtaining chitin fibres are schematically illustrated in Fig 3.28).

In addition to this indirect way of obtaining chitin fibres, acetylation of chitosan fibres could have future importance. As more and more attention is now paid to the possibility of producing chitosan from fungi, the raw chitinaceous material in the future may be chitosan instead of chitin from crab and shrimp waste.

And therefore, in order to obtain chitin products, it would then become necessary to develop acetylation procedures.

In the present study, chitosan fibres were prepared as described in section 3.1. No further treatment was applied before they were acetylated.

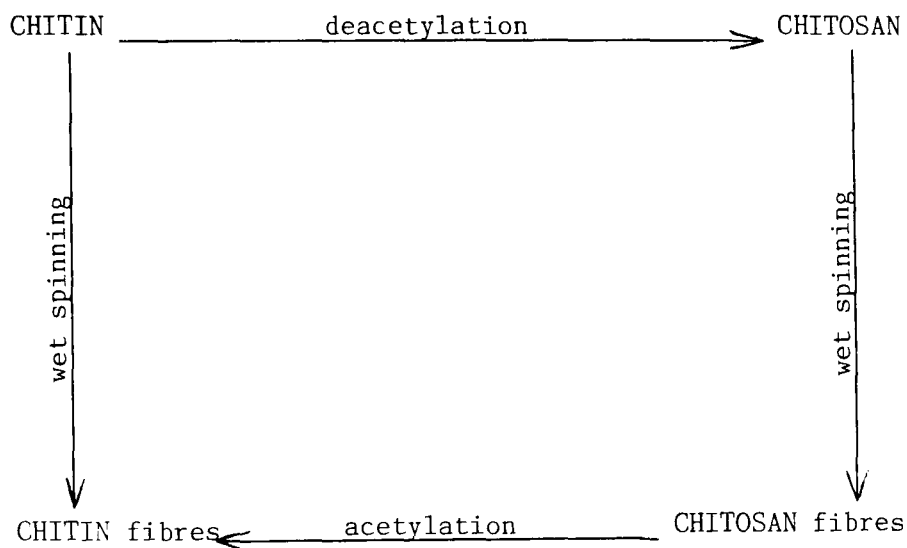


Fig 3.28 The two routes of producing chitin fibres

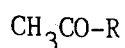
3.2.2 General

Reagent

The nature of this reaction is to introduce an acetyl group onto an primary amine group. Chemically, it is an easy reaction and there are many acetylating reagent available for amine groups. The problem is then the speed, efficiency, selectivity and convenience of the reaction. Virtually all the carbonyl compounds listed in table 3.28 acetylate the primary amines. However, some reactions such as the ester-amine reactions are likely to be too slow. Furthermore, acetyl

chloride is probably far too reactive. The choice was then made to begin the study of the acetylation via the anhydride. In fact, all work (91,92,93) on the acetylation of chitosan in the literature uses acetic anhydride as the reagent, except on one occasion, where acetic acid and a carbo-di-imide catalyst were used (5).

Table 3.28 Possible carbonyl compounds for the acetylation of chitosan



where R=

halide, Cl, Br, etc.

anhydride, CH_3COO

ester, CH_3O , CH_3CO , PhO , etc.

Solvent

Most reported work (91,92,93) on the acetylation of chitosan either homogeneously or heterogeneously, has used methanol as solvent. This may have two advantages. Firstly, reaction of chitosan with acetic anhydride has N-selectivity in methanol, as reported by Hirano (90). The mechanism was not given; it seems that in the presence of an excess of primary -OH, the reaction of hydroxyl groups on chitosan with anhydride is limited. Secondly, Moore & Roberts examined a variety of organic solvents, including pure acetic anhydride. Their results showed that solvents with a solubility parameter around 13.1 gave the fastest reactions. They further concluded that methanol was the best solvent for the acylation of chitosan.

The major disadvantage of methanol is that it is not an inert solvent. It is likely that acetic anhydride would react with

methanol, giving methyl acetate. Despite that, it was used as the solvent in the present work because of the high reaction speed and selectivity just described.

Analytical method

The degree of reaction, i.e., degree of acetylation of the treated chitosan fibres, may be measured in a number of ways, as reviewed in section 1.3. These methods include elemental analysis, i.r. spectra, titration, U.V spectra, thermal analysis, N.M.R, etc. However, two criteria are obvious in the study of acetylation of chitosan fibres. Firstly, the method must cover the full range of acetylation from 0 to 100%. Titration needs chitosan or acetylated chitosan to be in solution form. It is not suitable here because on acetylation, chitosan readily loses its solubility in dilute acid. Though a similar titrimetric method for chitin, proposed by Rutherford & Austin (49), may be used, its disadvantage is the large amount of sample needed and the long period of time required. For similar reasons, i.r spectra are also not suitable because of the difficulty in preparing a film from the acetylated sample. In fact all the methods that require chitosan or acetylated chitosan to be dissolved are not suitable here because chitosan and acetylated chitosan have completely different solvent systems. Thus, U.V and n.m.r procedures were also excluded.

Of the few methods left, the second criteria makes the choice even more limited. In a study involving the preparation of a number of samples, the testing method must be efficient. Thermal analysis and pyrolysis methods are time consuming, and in addition, the method of calculation was not well developed.

In view of the above points, elemental analysis was used as the main analytical method. This method is simple and gives quantitative results with quite good accuracy. Solubility of the treated fibre in 2% aqueous acetic acid was also used as a qualitative method to follow the reaction.

The nitrogen content gives a direct indication of the degree of acetylation, as pure chitin contains 6.89% N while pure chitosan contains 8.69%. Practically, however, as both chitin and chitosan have moisture regains as high as 16%, and it is not convenient to dry the sample completely before analysis, the ratio of nitrogen to carbon content was used to calculate the degree of acetylation as discussed in section 1.3.

Preliminary experiments

In their study of the acetylation of chitosan dissolved in aqueous acetic acid solution, Hirano et al (89) noticed that the amount of acetic anhydride must be in excess if gelation is to occur. The minimum molar ratio between anhydride and primary amine was reported as 3. In another report, Miya et al (93) found that the degree of acetylation of the resulting product, other conditions being equal, was dependent on the molar ratio between anhydride and primary amine. This use of an excess amount of reagent was also noticed by Moore & Roberts (91). The excess anhydride may be consumed in side reactions, mainly, hydrolysis of anhydride by water, reaction of anhydride with -OH either in the solvent or on chitosan.

In the present work, it was the intention to acetylate the chitosan in fibre form not in solution or film form. The fibre samples were prepared by spinning a 5% medium grade chitosan, with

5% aqueous NaOH as coagulant, washed, drawn and dried with acetone (section 3.1).

Using the chitosan in fibre form made it easy to measure the sample weight as it can be readily expressed in terms of the fibre length. In view of the amount necessary for an elemental analysis and the ease of carrying out the experiment, 2 metres (0.034 gram) of the yarn were generally used.

A 5% solution of acetic anhydride in methanol was used as the main acetylating reagent. This gave a large excess amount of anhydride to primary amine when 10 ml of reagent was used.

The preliminary experiment on the acetylation of chitosan fibres was carried out by mixing 2 metres of chitosan fibres with 10 ml of 5% acetic anhydride in methanol, allowing reaction to occur for one day; de-O-acetylation with 1 M aqueous NaOH was carried out overnight. The results showed that the chitosan fibres were readily acetylated, with apparently a slight degree of O-acetylation. The 1 M dilute NaOH treatment overnight certainly removed some acetyl groups, as the degree of acetylation (DA) drops after the treatment. Results are shown in table 3.29.

3.2.3 Studies of the reaction conditions

From table 3.29, it appeared that the acetylation of chitosan fibres was readily achieved simply by mixing chitosan fibres and acetic anhydride. This is not surprising as information in the literature claims that chitosan in solution or chitosan films can be readily acetylated using acetic anhydride in methanol (91,92,93). With regard to the acetylation of chitosan in solution and film form, several acetylating conditions have been studied. It has been found (93)

Table 3.29 Preliminary results of acetylation of chitosan fibres

Sample	Original fibre	Acetylated fibre	Acetylated fibre+NaOH
Nitrogen content, %	7.4	6.2	6.3
Carbon content, %	40.35	42.85	42.75
Ratio of N/C	0.183	0.145	0.147
DA, %	17.9	103.0	95.6

Two metres of chitosan fibres were treated with 5% acetic anhydride in methanol for one day following 1 M aqueous NaOH treatment for 24 hours.

that increases in temperature and molar ratio of anhydride to chitosan give a rapid acetylation. In addition, Miya et al (93) found that the water content in the acetylating medium is crucial if a high degree of acetylation is to be obtained. In the present work, the effects of temperature, time, molar ratio of acetic anhydride to the amine groups on chitosan and the water content in the acetylating medium were investigated in order to understand better the acetylation of chitosan fibres. Results are given in tables 3.30-3.33.

Table 3.30 shows the effect of temperature on the acetylation of chitosan fibres. It can be seen that a relatively low degree of acetylation was obtained at 20 °C within half an hour. However, as the temperature was increased, a large increase in the degree of acetylation was obtained, with the highest value being obtained at 40 °C. Further increase in temperature showed little effect on the degree

Table 3.30 Effect of temperature on the acetylation of chitosan fibres

Temperature, °C	20	30	40	50	60
Carbon content, %	42.40	41.30	42.30	42.75	41.90
Nitrogen content, %	7.40	6.40	6.35	6.45	6.40
Ratio of N/C	0.174	0.155	0.150	0.151	0.153
Degree of acetylation	34.1%	76.4	88.5	86.7	81.8

2 metres of chitosan fibres were reacted with 10 ml of a 5% v/v acetic anhydride in methanol for 30 minutes, followed by treatment with a 1 M aqueous NaOH at room temperature overnight.

of acetylation obtained, with the values obtained at 50 and 60 °C being slightly lower than that obtained at 40 °C. The increased reaction speed with increase in temperature may be the result of many effects such as an increased rate of diffusion within the fibre, increased reactivity and increased fibre swelling. The slight decrease in the degree of acetylation beyond 40 °C may be explained by the increased rate of side reactions, which results in a more extensive consumption of acetic anhydride. However, as the reaction on a fibre involves many variables such as the fibre fineness and the homogeneity of the fibres etc., further studies on this reaction would be very valuable.

Table 3.31 shows the results of the effect of time on the acetylation of chitosan fibres. It can be seen that the acetylation of chitosan fibres is a reasonably rapid process; 84% of the amine groups were acetylated within half an hour. Further treatment gave

Table 3.31 Effect of time on the acetylation of chitosan fibres

Time, min.	15	20	30	120	240
Carbon content, %	42.05	39.8	43.8	43.8	43.75
Nitrogen content, %	7.35	6.4	6.65	6.35	6.35
Ratio of N/C	0.175	0.161	0.152	0.145	0.145
Degree of acetylation, %	33.6	62.5	84.1	102.1	101.8

2 metres of chitosan fibres were reacted with 10 ml of a 5% v/v acetic anhydride in methanol at 40 °C. The fibres were treated with 10 ml of 1 M NaOH overnight.

more acetylation of the sample. As can be seen, O-acetylation has occurred during prolonged treatment. This is natural because reaction between the hydroxyl groups and the active anhydride molecules are bound to occur during the treatment. However, as will be shown later, this side effect can be removed by a treatment with dilute NaOH solution.

Fig 3.29 shows that the process of acetylation follows a sigmoidal curve. The reaction accelerates readily, reaching a maximum rate at around 50% acetylation or, 17-18 minutes reaction. Thereafter, the reaction slows down as it approaches completion.

Table 3.32 shows the effect of molar ratio between acetic anhydride and $-NH_2$ on the acetylation of chitosan fibres. It can be seen that only a very low degree of acetylation was achieved when the ratio is lower than 1.6. The DA reached only 75% when the ratio is 1.6; this degree of acetylation is about the same as usually reported

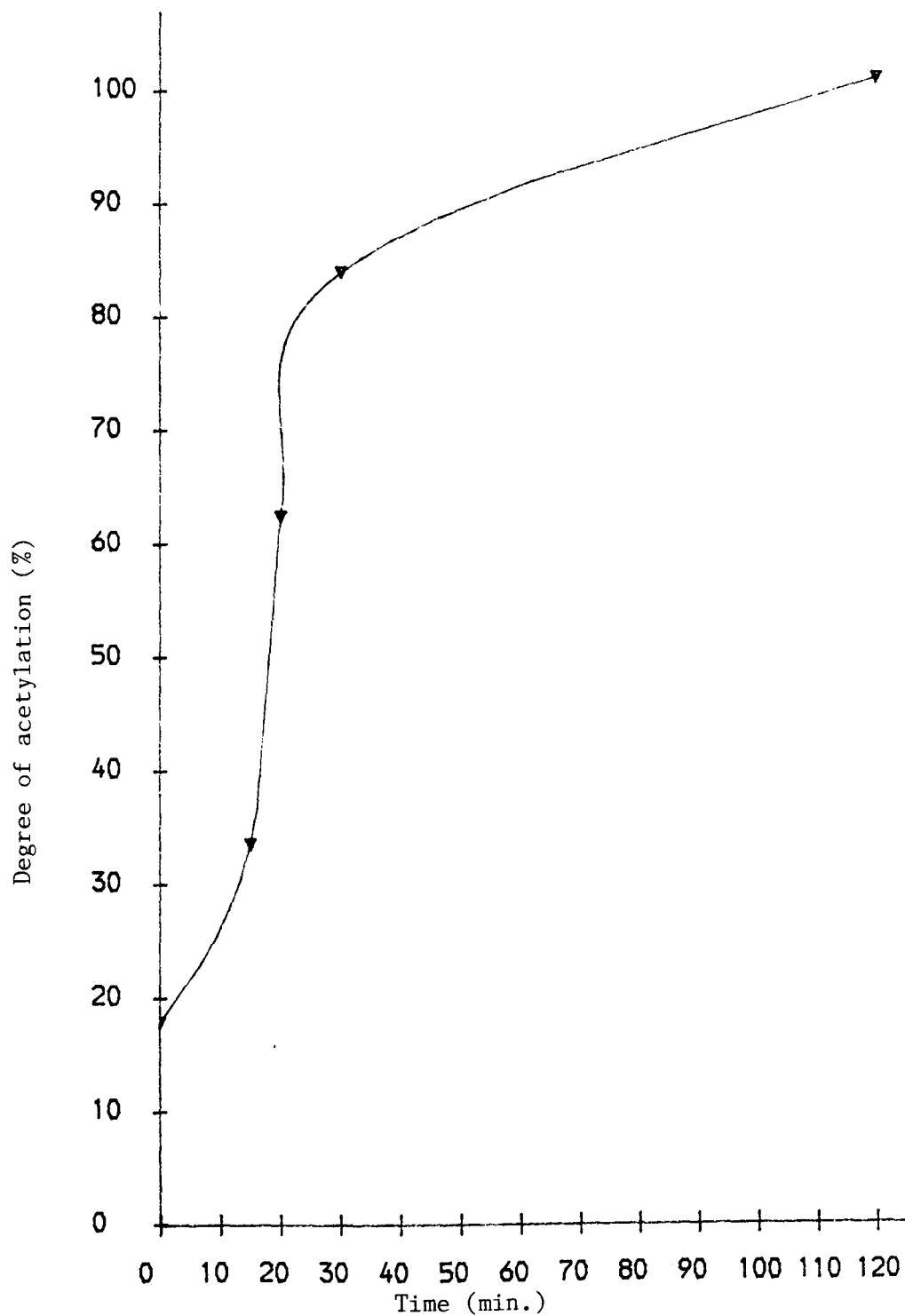


Fig 3.29 Effect of time on the acetylation of chitosan fibres

Table 3.32 Effect of molar ratio of anhydride to -NH_2 on acetylation

Molar ratio	0.2	0.4	0.8	1.6
Carbon content, %	40.5	40.35	39.45	39.95
Nitrogen content, %	7.4	7.05	6.35	6.2
Ratio of N/C	0.183	0.175	0.161	0.155
Degree of acetylation, %	19.2	33.8	62.2	75.7

Table 3.32 continued

Molar ratio	3.2	6.4	12.8	50
Carbon content, %	42.9	43.1	42.6	42.3
Nitrogen content, %	6.06	6.1	5.9	6.0
Ratio of N/C	0.141	0.142	0.138	0.142
Degree of acetylation, %	113.5	112.1	121.0	111.2

For reaction conditions see section 2.5

for chitin. Over acetylation was noticed when the ratio exceeded 3.2; this was presumed to be due to accompanying O-acetylation, a conclusion confirmed later by i.r. spectroscopy.

Table 3.33 clearly shows the effect of water on the acetylation of chitosan fibres. It can be seen that the degree of acetylation was almost unchanged when no water was added. Comparing the first two

Table 3.33 Effect of water content on the acetylation of chitosan

Water content (ml added)	Dried fibres	Normal fibres	1	2	3
Carbon content, %	40.75	40.7	42.8	42.6	42.75
Nitrogen content, %	7.3	7.2	6.0	6.0	5.9
Ratio of N/C	0.179	0.177	0.140	0.141	0.138
Degree of acetylation, %	25.6	29.6	115.9	114.1	122.5

2 metres of chitosan fibres were treated with 10 ml of 5% acetic anhydride in methanol with addition of different amounts of water. Reaction was carried out for 30 minutes at room temperature.

results, it can be seen that even the moisture normally present in the fibre can accelerate the reaction. When relatively large amounts of water are present, acetylation proceeds very rapidly as more than 100% acetylation was achieved within half an hour.

3.2.4 The properties of the acetylated fibres

General

Properties are closely related to the chemical structure of the substance. Any changes in the chemical structure would mean changes in its properties of various kinds. When chitosan fibres are acetylated, the change in chemical structure is the conversion of an active primary amine to a relatively inert amide group. It would be

expected that the reduction in the basicity of the polymer would be reflected in its solubility. Further, the introduction of acetamido groups into the structure should make the polymer soluble in chitin solvents such as DMAc-LiCl. Apart from the obvious changes in solubility, such properties as fibre strength, extensibility and thermal stability should also be affected. In some cases, there may be significant improvements. These changes have been studied in the present work, as the following results show.

Solubility

It is obvious that chitin and chitosan have completely different solvent systems. Chitosan is known to be soluble in most dilute acidic media while chitin has few convenient solvents. It is only recently that an inert solvent, DMAc-LiCl, has been found for chitin. Even though chitin and chitosan are not well defined, i.e., there is no clear boundary between the two, it will be expected that there will be a clear distinction in their solubility behaviour.

During the acetylation process, the primary amine is converted to an acetamido group. When highly acetylated, chitosan fibres lost solubility in 2% aqueous acetic acid solution. More interestingly, the acetylated fibre was found to be soluble in DMAc containing 7% LiCl. At room temperature, dissolution of acetylated chitosan took a few days. On warming, dissolution was very rapid. In addition, the fibre disintegrated into pieces during the process. SEM pictures of the partly dissolved fibre shows the dissolution in progress, Fig 3.30.

Weight gain during the acetylation process

In the solid state acetylation of chitin fibres, the microfibrillar structure remains unchanged. The conversion of chitin to chitosan is actually the conversion of $-NH_2$ to $-NHCOCH_3$. The conversion is 100% as it is evident from the analysis. In the case of the acetylation of chitin, the residue is 101, and that of $-NH_2$ is 12. A very small amount of pure chitosan to pure chitin with a weight gain of 20% is obtained by weighing the sample fibres before and after the reaction.

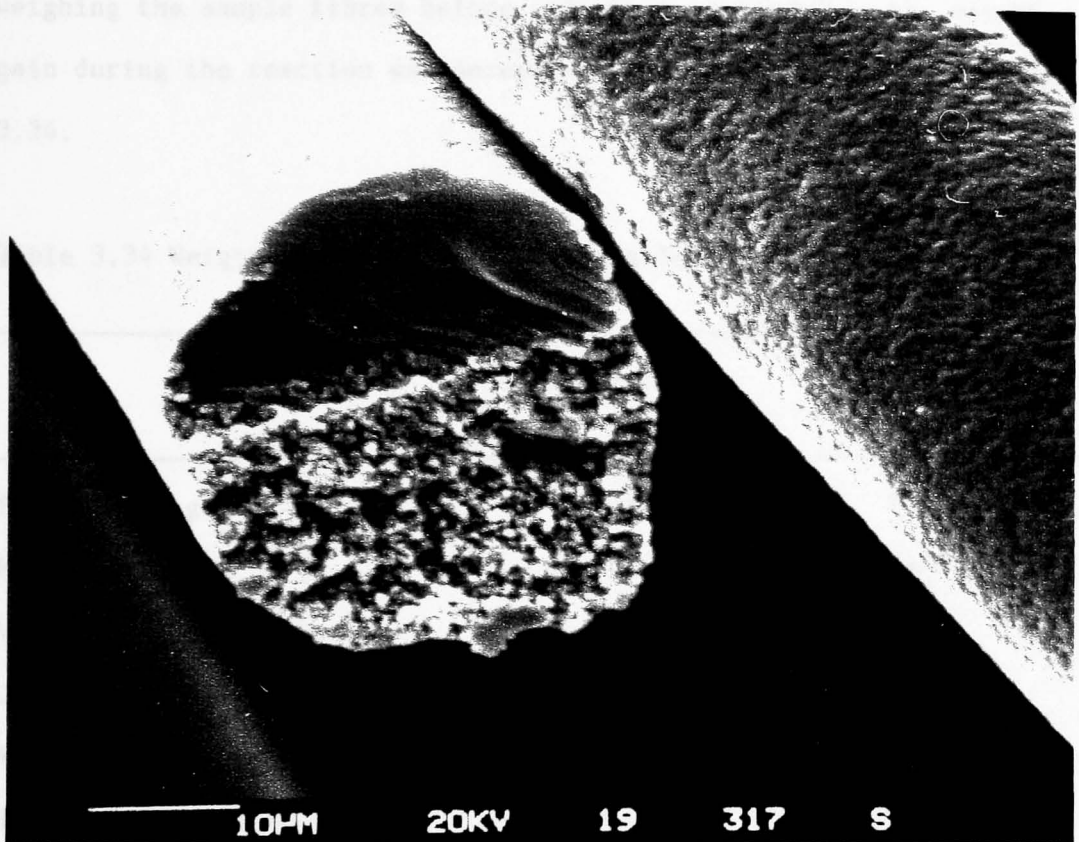


Fig 3.30 SEM picture of the acetylated chitosan fibres partly dissolved in DMAc-LiCl

Weight gain, g
Overall weight gain, g
Percentage, %

Assuming the degree of acetylation of the chitin molecule sample is 2, with a dry mass of 2, and a small gain after acetylation

In the solid state acetylation of chitosan fibres, the backbone structure remains unchanged. The conversion of chitosan to chitin is actually the conversion of $-NH_2$ to $-NHCOCH_3$. The fibre gains a $-COCH_2$ unit from the reaction. As the molar mass of the repeating glucosidic residue is 161, and that of $-COCH_2$ is 42, a complete conversion of pure chitosan to pure chitin means a weight increase of 26%. By weighing the sample fibres before and after acetylation, the weight gain during the reaction was determined. Results are shown in table 3.34.

Table 3.34 Weight gain during the acetylation of chitosan fibres

	Reference	Sample
Dry weight, g	0.8995	0.9277
Methanol, ml	100	100
Water, ml	20	20
Anhydride, ml	0	5
Weight gain, g	-0.0036	0.2571
Percentage, %	-0.40	27.71
1 M NaOH, ml	75	75
Weight gain, g	-0.0240	-0.0837
Overall weight gain, g	-0.0276	0.1734
Percentage, %	-3.1	18.7

Assuming the degree of acetylation of the starting chitosan sample is D, with a dry mass of M, and a weight gain during acetylation

of W, the increase in degree of acetylation D_i can be worked out as follows:-

$$\text{Residue weight } W_r = 201D + 161(1-D)$$

$$\text{Molar number of residues} = \frac{M}{201D + 161(1-D)}$$

$$\text{Increased acetyl content } A_i = \frac{W}{42}$$

$$D_i = \frac{A_i}{N_r}$$

$$= \frac{W(201D + 161(1-D))}{42M} \times 100\%$$

where,

W_r : residue weight

D : degree of acetylation of the original sample

N_r : molar number of the residues

M : original weight, g

A_i : increased acetyl content, mole

W : weight gain, g

D_i : increased degree of acetylation, %

Four samples were acetylated, using different amounts of acetic anhydride. The weight of each sample was carefully measured. Weight gains were recorded in table 3.35. The above method was used to calculate the increase in the degree of acetylation. Compared to results obtained from the N/C ratio by elemental analysis, it was found that the two groups of results corresponded well, with that from the weight gain being slightly lower than that from elemental analysis. This deviation may be attributed to the possible weight loss in the acetylation process associated with the loss of small

dust particles, loss of chitosan of low molecular weight, etc.

Table 3.35 Effect of acetylation on weight gain of chitosan fibres

Sample	1	2	3	4
Weight, g	0.9455	0.9557	0.9584	0.9500
Anhydride, ml	0.0	0.3	0.6	1.2
Weight gain, g	-0.0082	0.0495	0.1086	0.1833
Percentage, %	-0.87	5.18	11.33	19.29
DA increased, %	-3.4	20.3	44.5	75.7
Sample DA, %	5.6	29.3	53.5	84.7

Original chitosan had a degree of acetylation of 9%

Table 3.36 Comparison of DA from different procedures

Weight gain method, %	5.6	29.3	53.5	84.7
Elemental analysis, %	0.86	36.6	60.8	97.2

The variation of chelating ability with the degree of acetylation

Compared to the amido groups in chitin, the primary amine groups in chitosan are better electron donors and therefore possess higher chelating ability. This difference in the chelating ability of chitin and chitosan has been well documented. Earlier workers found that

acetylated chitosan films showed little chelating ability as they remained white in copper sulphate solution (5). In the present work, it was found that the chelating ability of chitosan fibres were greatly affected by the degree of acetylation. Moreover, results were brought to a quantitative level, as shown in table 3.37.

Table 3.37 Effect of DA on the chelating ability of chitosan fibres

Sample	1	2	3	4
Carbon content, %	27.6	32.05	34.65	41.55
Nitrogen content, %	5.35	5.55	5.6	6.1
Degree of acetylation, %	0.86	36.6	60.8	97.2
Cu content, %	8.25	5.45	3.55	0.65
Molar ratio of NH ₂ to Cu	2.9	2.9	2.8	1.2

The variation in i.r spectra with the degree of acetylation

As chitosan fibres and the acetylated fibres have different solvent systems, chitosan films were used to study the changes in chemical structure. It was found that after the acetylation three changes had obviously occurred in the i.r spectrum of the acetylated film; these were the enhanced absorption peaks at 1313, 1655 and 1740 cm⁻¹ (Fig 3.31). It is assumed that the 1313 cm⁻¹ peak is due to the methyl group of the acetyl group; the 1655 cm⁻¹ peak is from the amido absorption. The 1740 cm⁻¹ peak is possibly from absorption of ester groups as O-acetylation is likely to occur during the treatment. In

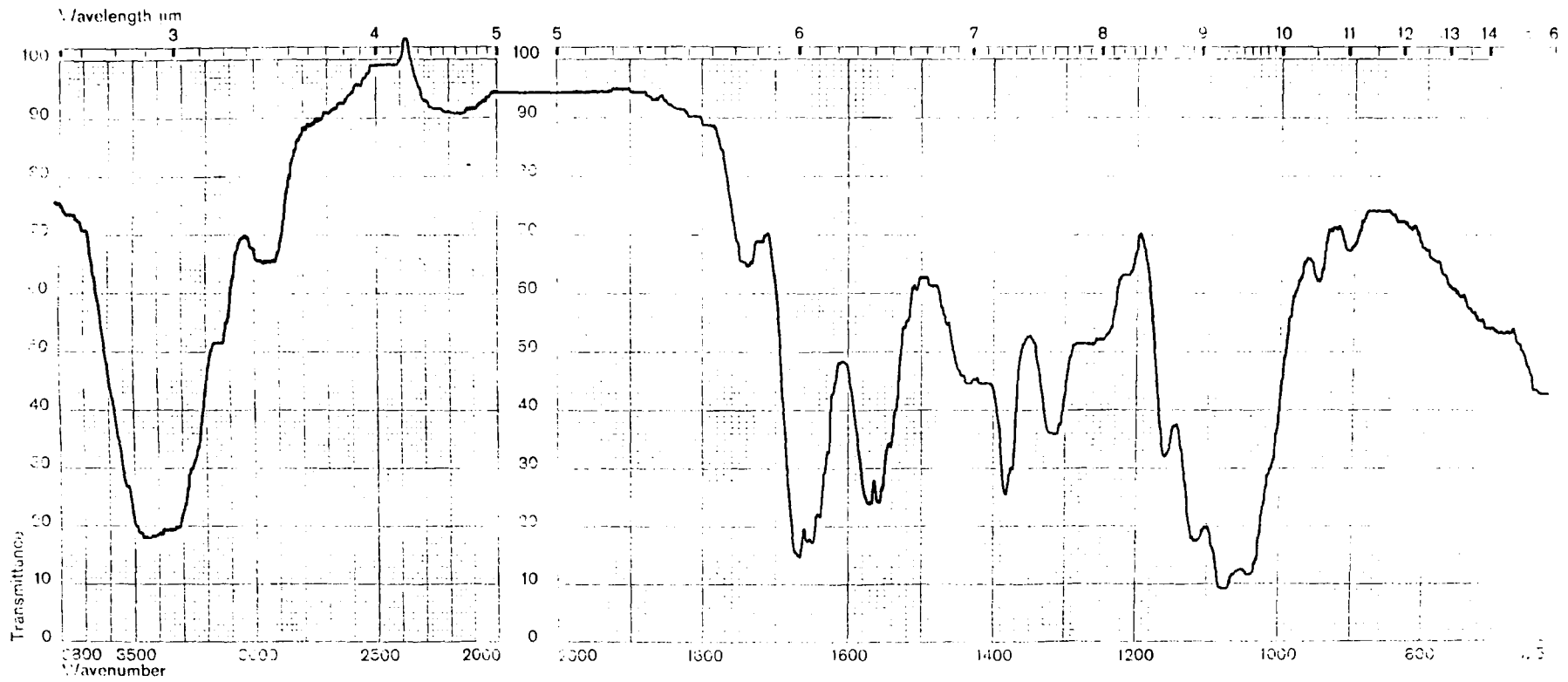


Fig 3.31 I.r spectrum of the acetylated chitosan film

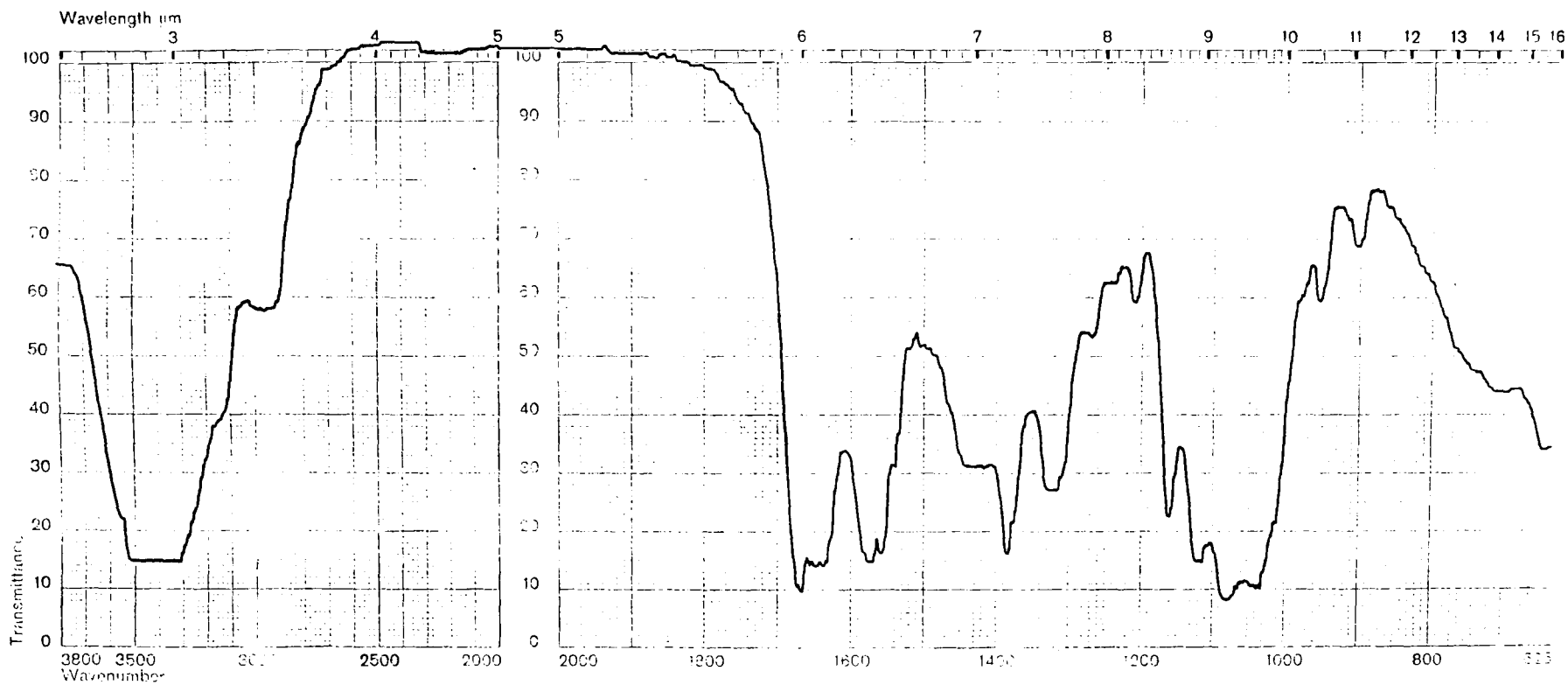


Fig 3.32 I.r spectrum of the acetylated chitosan film, after dilute NaOH treatment

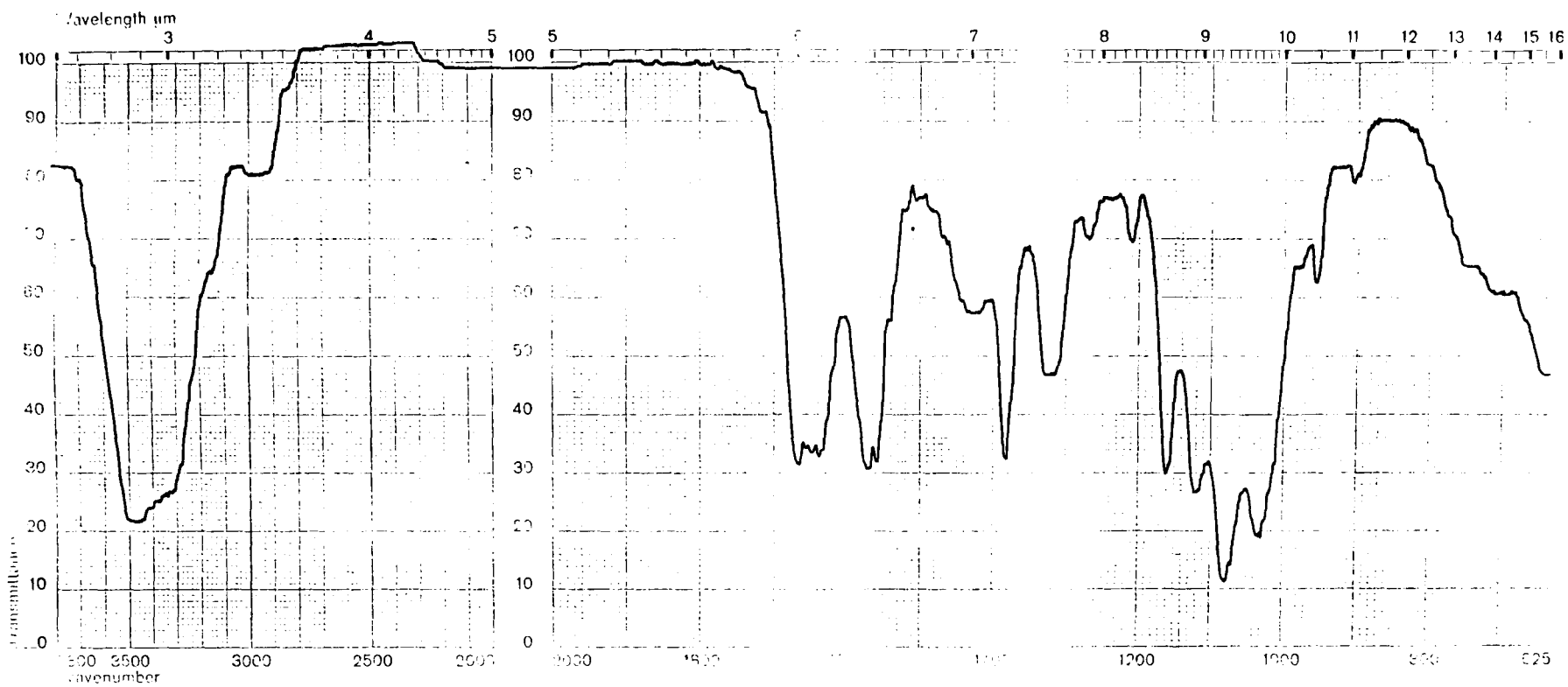


Fig 3.33 I.r spectrum of natural chitin film (cast from DMAc-LiCl solution)

support of this, comparing Fig 3.31 to Fig 3.32, it can be seen that the 1740 cm^{-1} peak can be removed by a dilute NaOH solution treatment, as would be expected from the removal of the O-acetyl groups. Fig 3.33 shows the i.r spectrum of chitin (cast from DMA-LiCl) for comparison.

X-ray diffraction pattern after acetylation

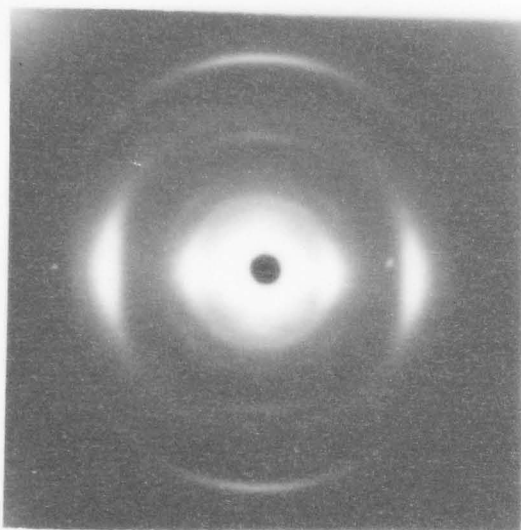
The X-ray diffraction patterns of the chitosan fibres (samples spun using i-propanol as co-solvent) and the acetylated chitosan fibres (DA=75.7%) are shown in Fig 3.34. It can be seen that significant changes have occurred during acetylation, with the fibre becoming more crystalline. Comparing the acetylated sample with that obtained by Agboh for chitin (37), it was found that the two were very similar.

DSC studies before and after acetylation

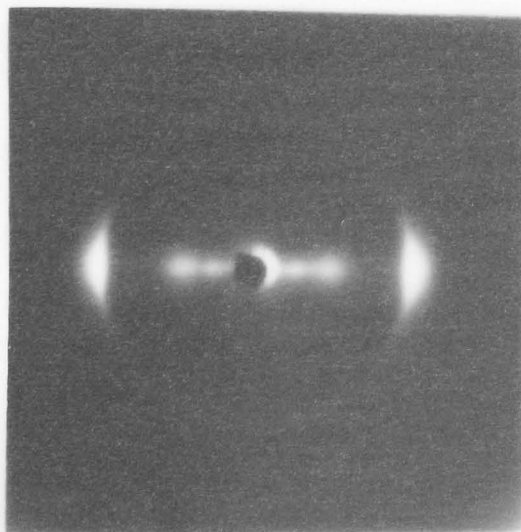
The DSC curves of chitosan and acetylated chitosan are shown in Fig 3.35. The obvious change is that after acetylation, the decomposition peak changes from the exotherm of chitosan to an endotherm for the acetylated product, in addition to the higher decomposition temperature. The change reflects the increased chemical stability of the acetylated form.

TGA changes during the acetylation

Similar to the changes observed in DSC studies, the acetylated chitosan fibres showed TGA traces characteristic of greater thermal stability, as shown in Fig 3.36-3.39. The increased degree of thermal stability can be seen more obviously on the derivative curves,

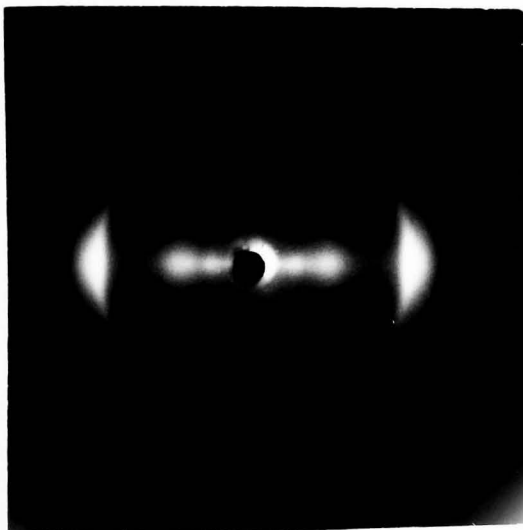
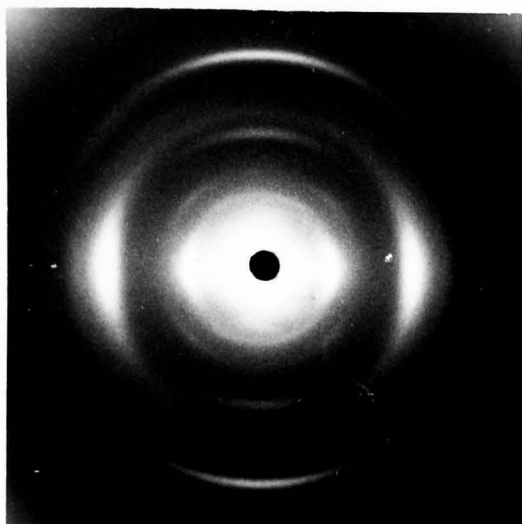


Acetylated sample, DA=75.7%



Original fibre, DA=17.9%

Fig 3.34 X-ray diffraction patterns before and after acetylation



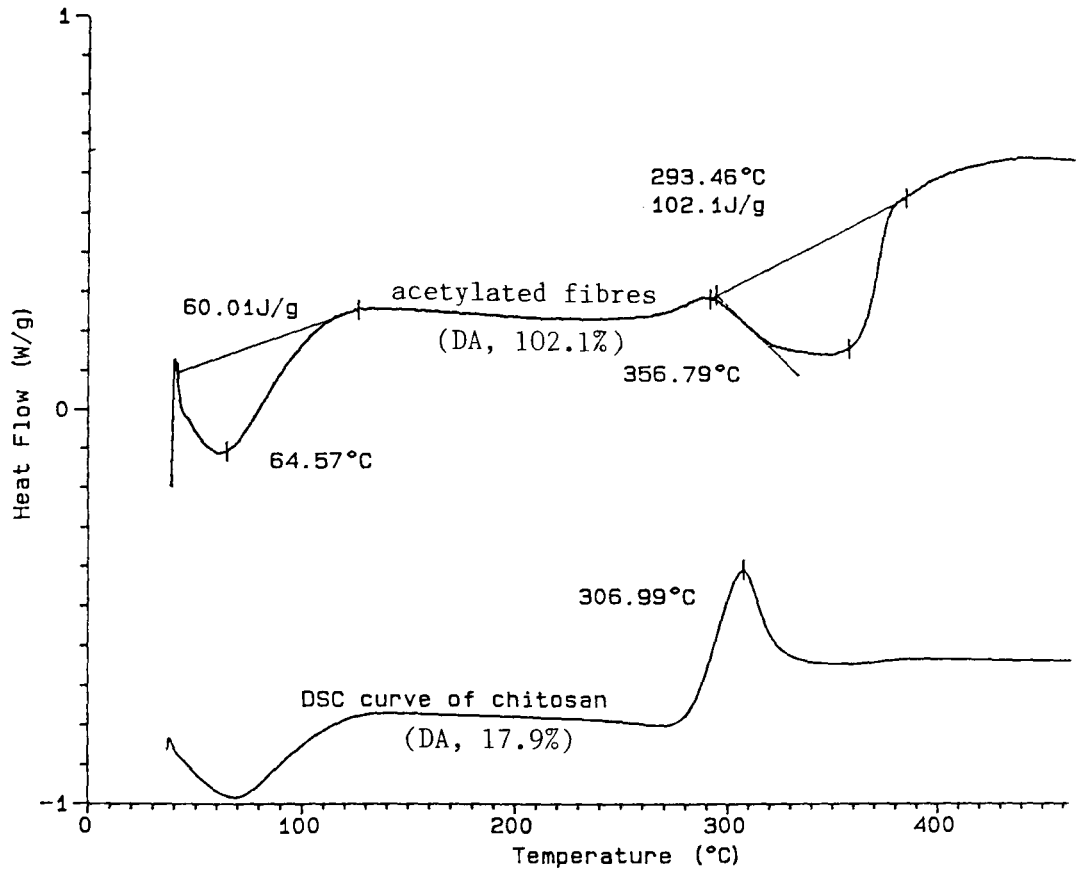


Fig 3.35 DSC curves of chitosan and acetylated chitosan fibres

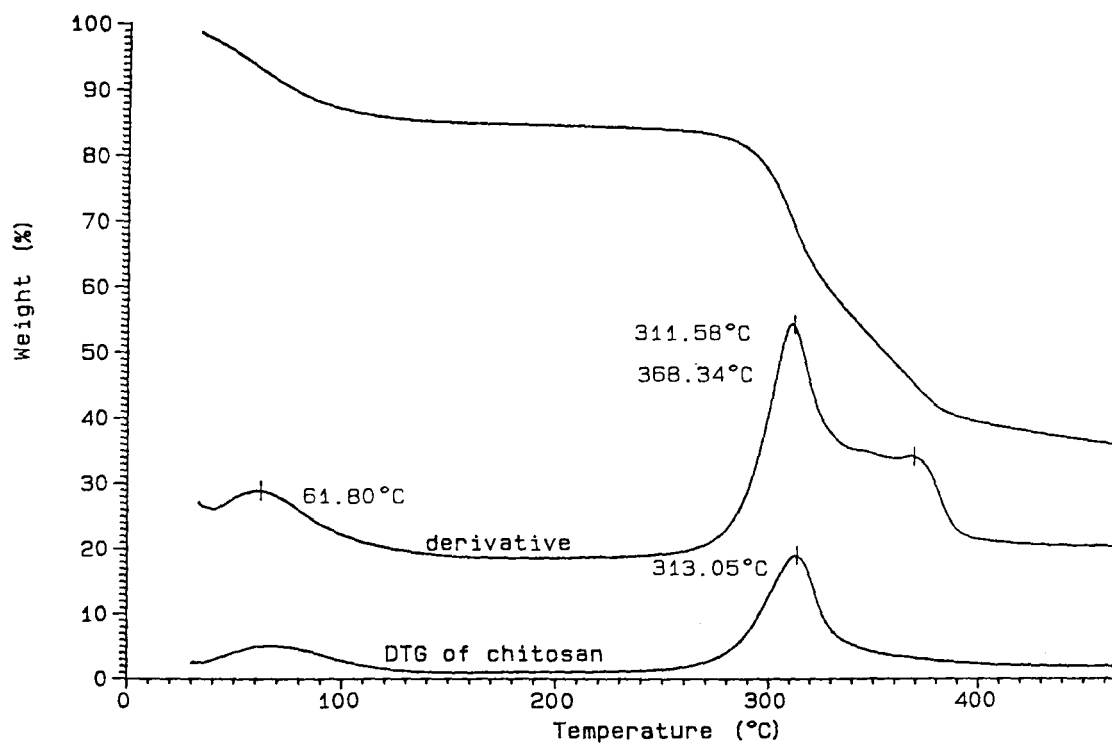


Fig 3.36 TGA curve of acetylated chitosan fibres, DA=33.8%

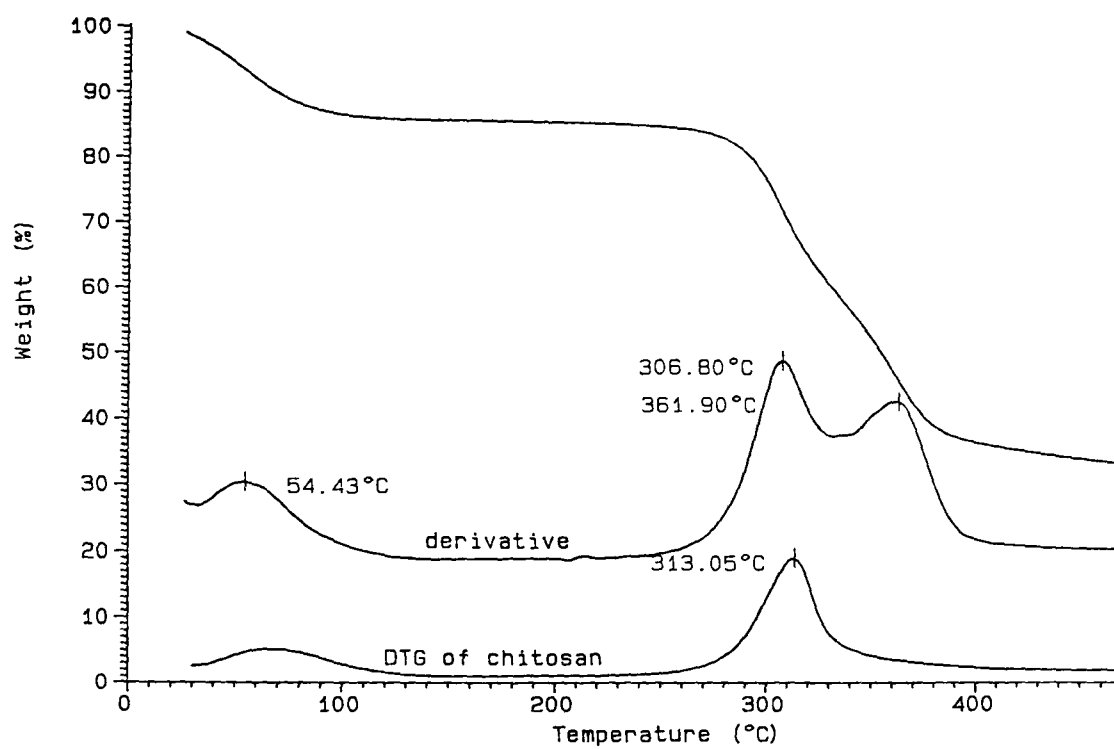


Fig 3.37 TGA curve of acetylated chitosan fibres, DA=62.2%

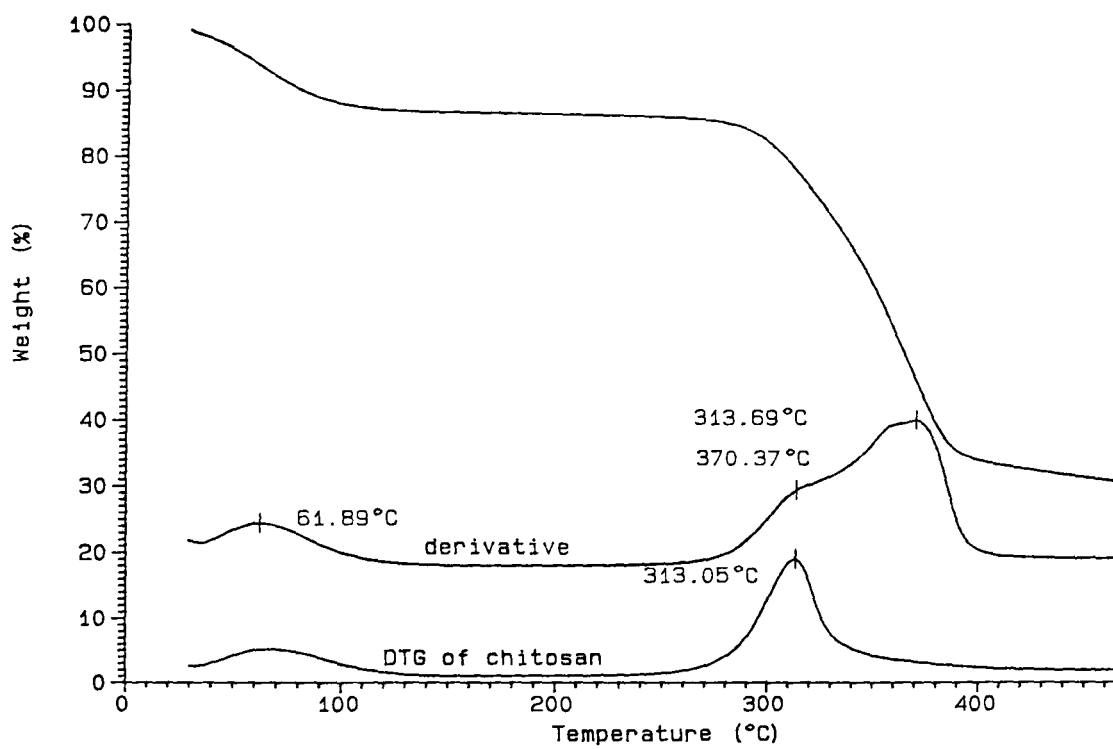


Fig 3.38 TGA curve of acetylated chitosan fibres, DA=84.1%

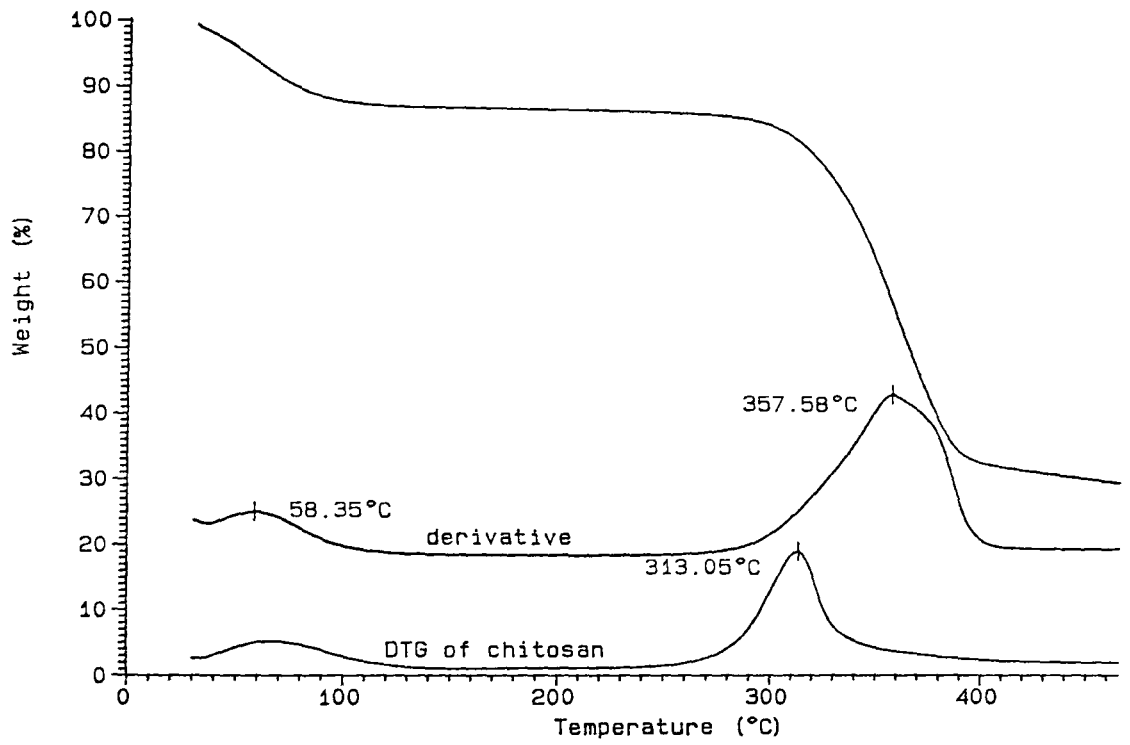


Fig 3.39 TGA curve of acetylated chitosan fibres, DA=102.1%

where two peaks were noticed on samples with partial acetylation. This is possibly due to a two stage decomposition of the sample when the unstable glucosamine residues decompose first and the acetylated residues decompose later.

Tensile properties of the acetylated samples

Table 3.38 Effect of acetylation on fibre strength and extensibility

Boiled for (min.)	0	5	10	20	40
Dry strength, grams	122.7	112.1	115.3	123.2	132.9
Extensibility, %	6.2	7.8	8.4	8.7	8.8
Wet strength, grams	12.2	3.4	5.7	34.0	39.5
Ratio of wet/dry strength	0.1	0.03	0.05	0.28	0.30

For conditions, see section 2.5

From the table, it can be seen that during the acetylation of the chitosan fibres, the fibre strength showed an initial decrease and then an increase in both dry and wet strengths. This can be due perhaps to an initial decrease in fibre orientation because of the swelling and an initial decrease in structural regularity when the fibre is partially acetylated. Further acetylation of the fibre gave the fibre a more regular chitin structure. This would allow the fibre an increased degree of crystallisation as already noticed earlier. As a result, the fibre regained strength; moreover, the wet strength showed a substantial increase when the fibre was sufficiently acetylated.

Chapter four

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions and recommendations for future work

Once experience had been gained, the wet spinning of chitosan could be carried out over a wide range of experimental conditions. All three grades of chitosan samples available, differing mainly in molecular weight, could be converted into fibre form. The medium grade sample gave the strongest fibres and was used for the majority of the spinning trials. However, the other two samples were not much weaker and indicated that there might be some advantage in exploring other molecular weight samples. Presumably, as the molecular weight is lowered further, it might be possible to use higher solid contents though whether this will necessarily lead to better fibre properties needs further investigation.

There was no time available in the present study to study the effect of varying the DA of the chitosan. There may be far better fibre properties when the DA became closer to zero as the structure will become more regular. On the other hand, it might be interesting to use a chitosan of much higher DA, the highest DA still allowing solubility in acetic acid, as if it is necessary to convert this to chitin fibres, the further extent of acetylation will be only a small amount.

The solvent used in this work was 2% aqueous acetic acid solution. Though there was no effort to investigate the effect of varying the acetic acid concentration on fibre properties, a 2% solution was used because it is the lowest which still allows proper dissolution of the chitosan dope. It is interesting to suggest here that of the various organic and inorganic acids available for

chitosan, there might be some acids, other than acetic acid, which would produce chitosan fibres with better properties. Further work is required to prove this.

The study of the effect of spinning variables on the fibre properties showed that chitosan fibres can be produced over a wide range of experimental conditions without significant changes in fibre properties. Higher draw ratios can be obtained at lower jet-stretch ratios. However, the improvement in fibre properties was very small. Drawing of the fibres increased fibre tenacity at the expense of fibre extensibility. The dilution of the 5% NaOH bath made it possible to draw the fibres to a larger extent and hence stronger fibres were produced; the lowest possible NaOH concentration was 2%. Drying the fibres in air produced much more extensible fibres when compared to the fibres dried with radiant heating. The addition of Na_2SO_4 into the coagulation bath had a large effect on the strength of the fibres produced; the yarn had a tenacity of 2.48 g/dtex, the strongest obtained in the present work.

The chitosan fibres produced in this work had properties quite similar to viscose rayon, normal type. The fibres had a range of tenacities between 0.61 and 2.48 g/dtex, with extensibilities of 5.7 to 19.3%. The tensile properties are comparable to those reported in the literature (2.44 g/denier with 10.8% extensibility as reported by Mitsubishi Rayon (113)). The tensile properties of the chitosan fibres produced in this work and those of the common textile fibres are shown in table 4.1.

Of the properties unique for chitosan, the chelating characteristics were studied. It was found that the chitosan fibres can chelate upto 8% Cu(II) and 5% Zn(II) within 40 minutes. The

Table 4.1 Properties of chitin, chitosan and some typical commercial fibres

Fibre	Fibre count, dtex	Specific gravity	Moisture regain*, %	Tenacity (g/dtex)	Extensibility (%)	Initial modulus (g/dtex)	Work of rupture (g.cm/dtex.cm)
Cotton	1-2	1.54	7-8.5	2.3-4.5	3-10	36-75	0.18
Wool	4-10	1.32	14-16	0.9-1.8	30-45	22-36	
Viscose rayon	1-9	1.52	12-16	1.5-4.5	9-36	45-70	0.27
Cellulose acetate	5	1.30	6-6.5	1.0-1.26	23-45	23-37	0.20
Cellulose triacetate	4	1.30	2.5-3	1.1-1.26	25-40	32-41	
Acrylic	2-6	1.17	1.5	1.8-4.5	16-50	36-50	0.45
Polyester	2-5	1.38	0.4	2.5-5.5	10-45	90-135	0.90
Nylon 6.6		1.14	4-4.5	3.6-8	16-45	23-45	1.53
Alginate (calcium)		1.78	17-23	0.9-1.8	2-14		
Chitin (37)	4-7	1.39	10-12.5	1.2-2.3	7-33	26-54	0.1-0.3
Chitosan**	2.5-7.5	1.39	16.2***	0.61-2.48	5.7-19.3	43***	0.2***

*, 65% R.H., 20 °C, **, present work, ***, for fibres prepared using i-propanol as co-solvent

chelation of the metal ions into the fibres had significant effects on the fibre tensile properties; both the strength and extensibility increased with the absorption of the metal ions. The most important change was noted on the wet strength of the fibres for when 8% copper ion was chelated, the wet strength was more than double the original value. The uptake of metal ion made the fibre non-inflammable; the LOI was around 50% when 12% zinc was applied to the fibres.

The acetylation of chitosan fibres, producing chitin fibres, was readily achieved with the use of acetic anhydride in methanol. The results were similar to those reported for the acetylation of chitosan in solution or chitosan film. The acetylation was affected by the reaction temperature, time, molar ratio between anhydride and the amine groups on chitosan and the water content in the reaction medium. Below 40 °C, the reaction was largely accelerated by increasing the temperature. The degree of acetylation follows a sigmoidal curve with the reaction time, with 100% acetylation achieved within 120 minutes. The molar ratio of acetic anhydride to the free amine groups on chitosan needs to exceed 3 in order to obtain full acetylation of the chitosan fibres. In addition, the water present in the reaction medium significantly accelerated the acetylation reaction.

The acetylated chitosan fibres had a range of properties different from the original chitosan fibres. Highly acetylated product no longer dissolved in 2% aqueous acetic acid but was found to be soluble in a chitin solvent, DMAc-LiCl. The acetylated fibres had better thermal stability as the result of the conversion of the active amine group to the relatively inert amido group. The degree of acetylation had an effect on the chelating properties of chitosan

fibres; the molar ratio between Cu(II) and the free amine groups in chitosan was around 3, as can be calculated from table 3.37.

It is interesting to speculate on the acetylation of the fibre since it could occur either homogeneously throughout the fibre or, perhaps more likely, from outside inwards. Further studies of the fibre at intermediate degrees of acetylation would help to decide this.

APPENDICES

Appendix I Calculations of the constants for viscosity measurement

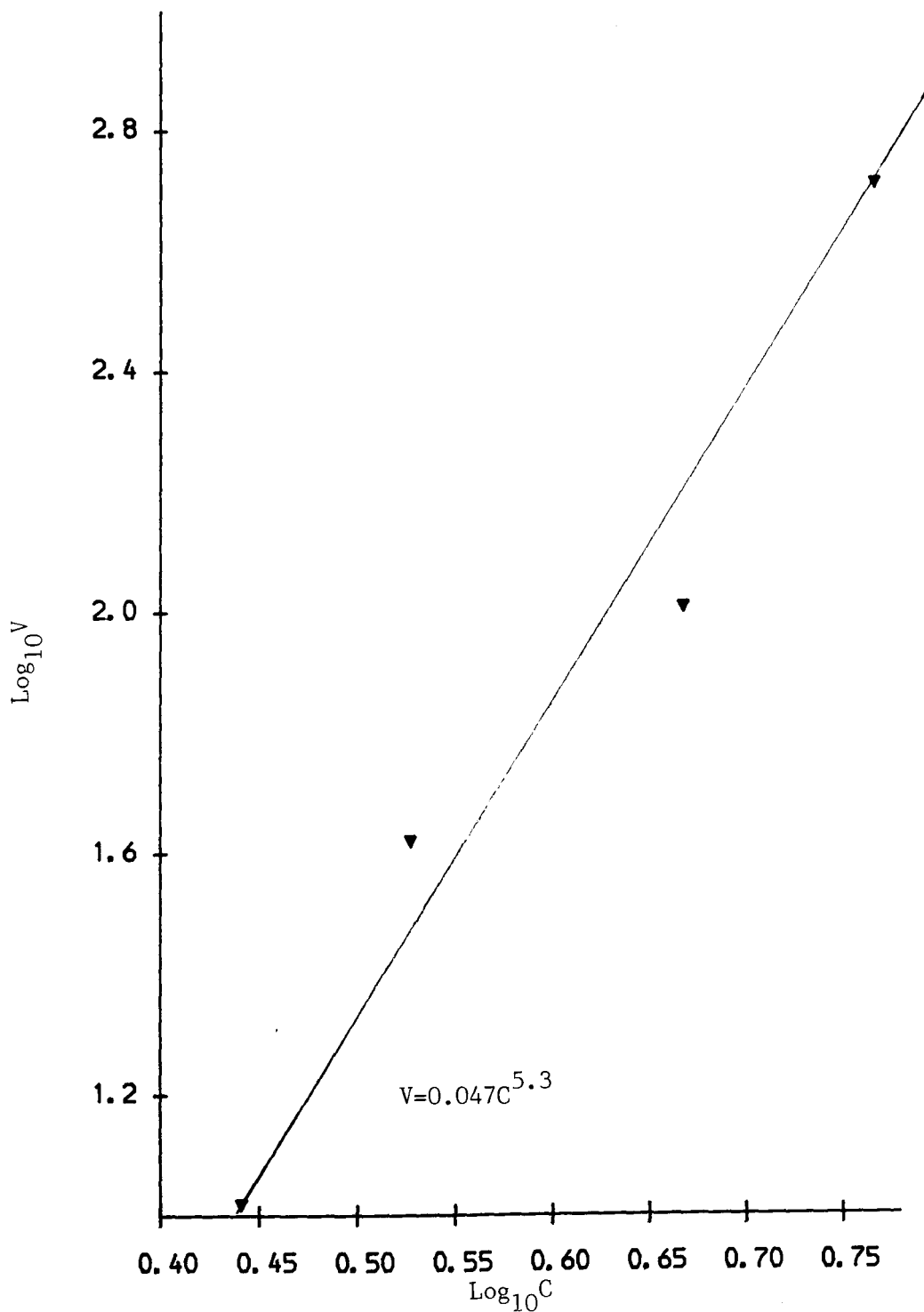


Fig A.1 The $\text{Log}_{10}V$ versus $\text{Log}_{10}C$ curve of chitosan at 25 °C
(Viscosity versus dope concentration)

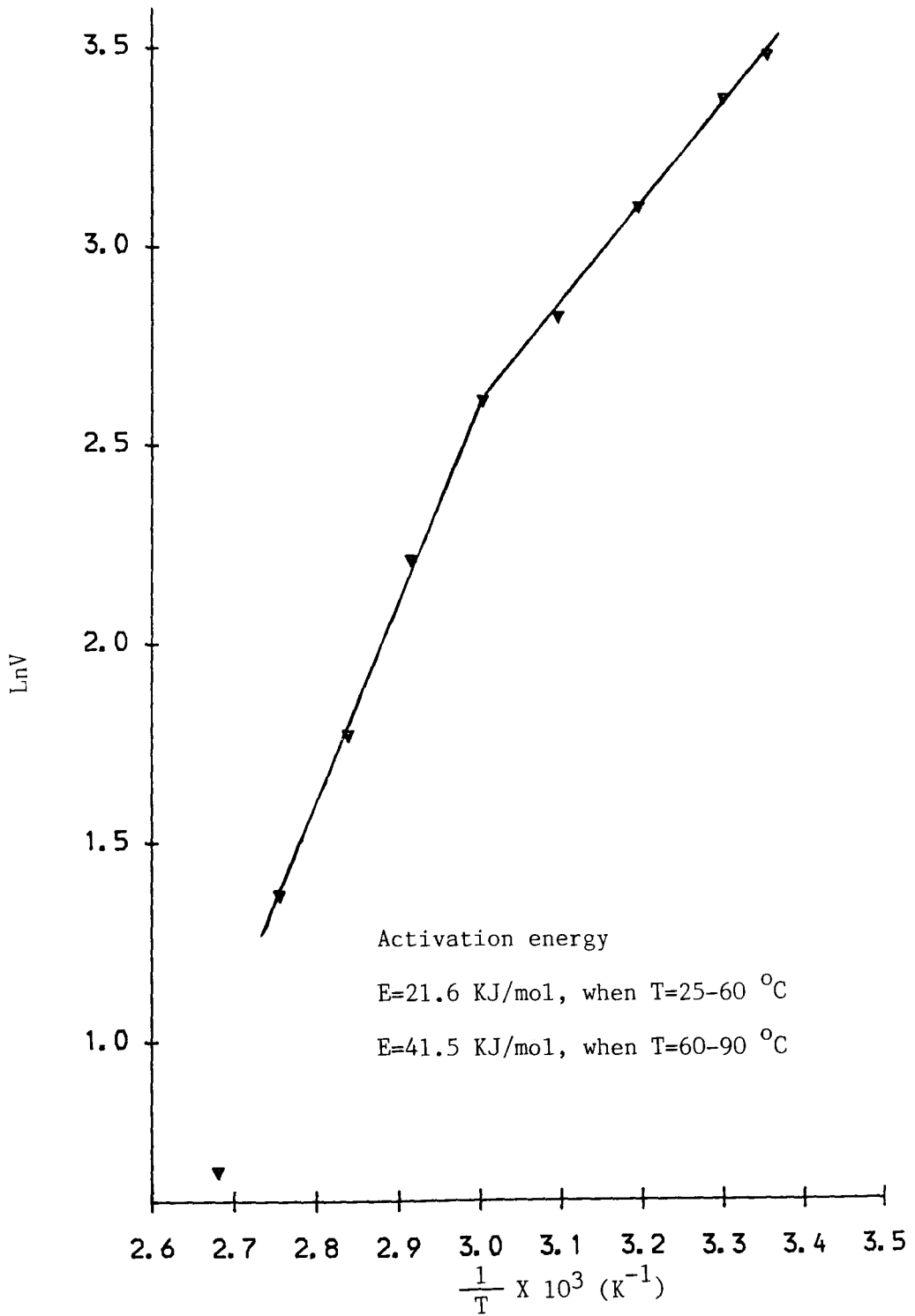


Fig A.2 The LnV versus T^{-1} curve of a 5% medium grade chitosan dope
(Viscosity versus temperature)

Appendix II Typical load-extension curves

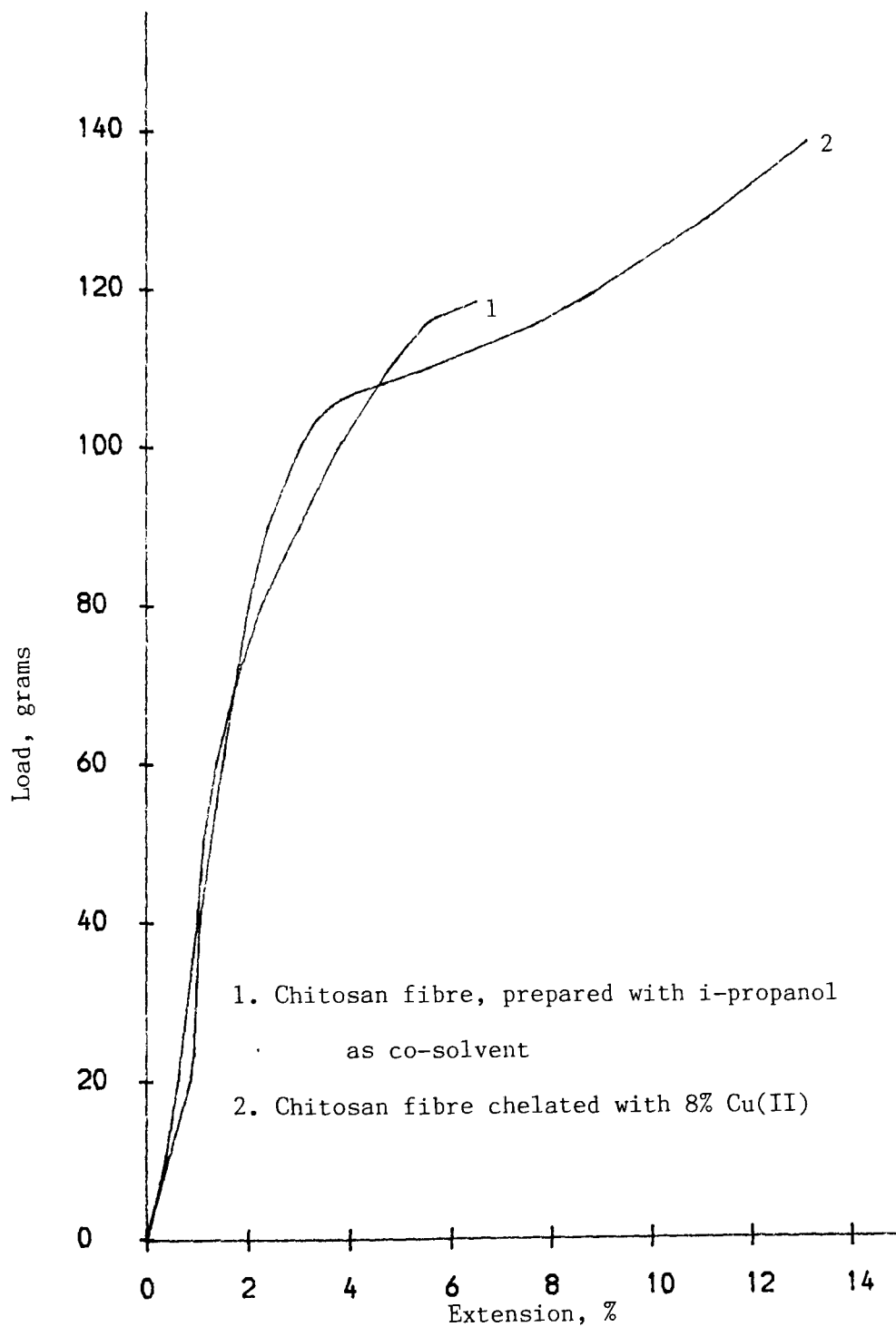


Fig A.3 Load-extension curves of chitosan fibre and chitosan fibre chelated with 8% Cu(II)

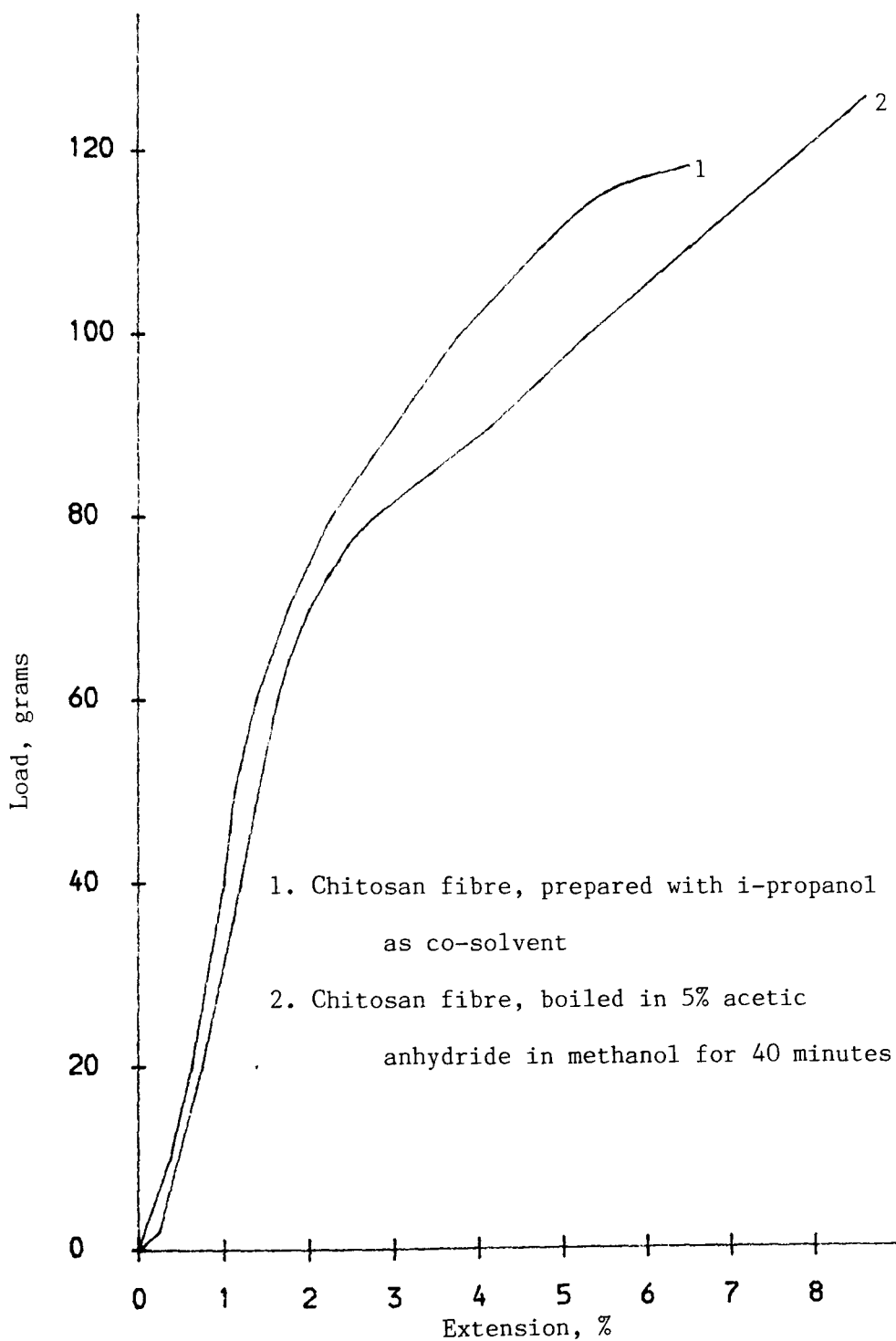


Fig A.4 Load-extension curves of chitosan fibre and the acetylated chitosan fibre

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