CHAPTER 4

EXPERIMENTAL METHODS AND RESULTS FOR FIBRE SPINNING

4.1 Preparation of Chitosan Solution

Because chitosan contains primary amine (-NH_2) groups in its structural repeat unit, it can be readily protonated and dissolved by aqueous organic acids. Both formic acid and acetic acids have been widely used for this purpose. However, in this research project, ***aqueous acetic acid*** was preferred to aqueous formic acid as the solvent for dissolving chitosan because:

(a) it is cheaper in price and has a less noxious odour

(b) it is a weaker solvent which enables the chitosan to precipitate from solution more quickly and completely in the coagulation bath, as confirmed by experiment.

Therefore, the chitosan solution used in this work for fibre spinning was prepared as a 3% w/v solution of chitosan in 1% v/v aqueous acetic acid as solvent. The solution was prepared at room temperature in a 250 ml volumetric flask. After completely dissolving the chitosan in the solvent, the solution was stirred with a magnetic bar for a further 4 hours before being degassed under vacuum for 6 hours. This viscous chitosan solution, which was pale yellow in color, was the ***spin dope*** which was used in the subsequent wet spinning experiments.

4.2 Viscosity of Chitosan Solution

4.2.1 Falling Ball Viscometry [37]

A Haake Falling Ball Viscometer (Figure 4.1) was used to measure the viscosity of the chitosan solution. The viscosity is related to the time a ball takes to fall through a specific height of the solution. The rolling and sliding motion of the ball through the sample within a slightly inclined cylindrical measuring tube is described by means of the ***fall-time***.

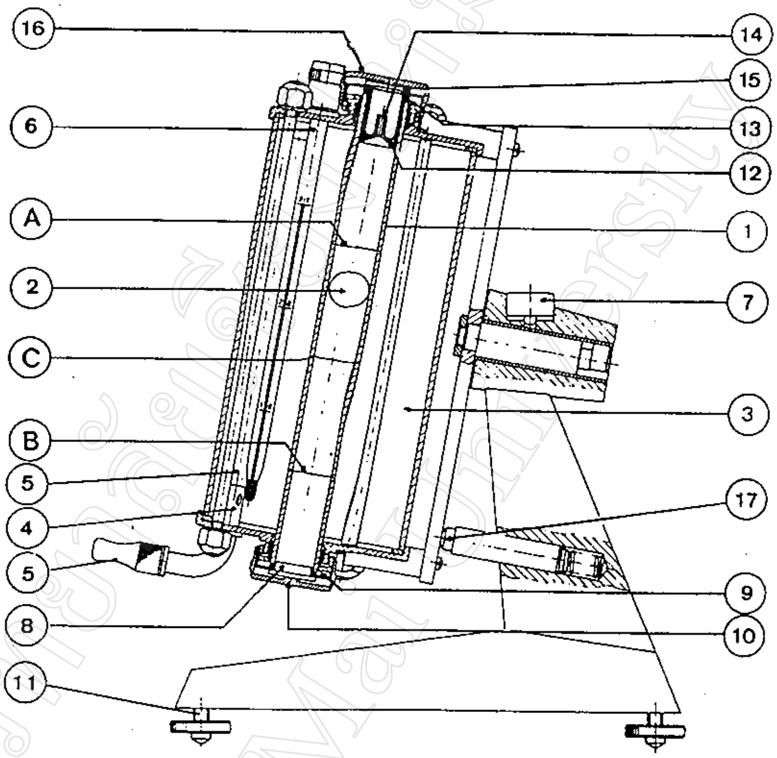
The viscometer's standard ball set contain 6 balls (Table 4.1) of which one is chosen which is appropriate to the viscosity of the solution to be measured (A → B fall-time > 100 sec).

The fall-time data is converted to ***dynamic viscosity***, η, in units of **millipascal seconds (mPa.s)** or **centipoise** (cP) through the equation:

$$\eta = K(\rho_1 - \rho_2)\,t \tag{4.1}$$

where

η = dynamic viscosity in mPa.s (= cP)
K = ball constant (see Table 4.1) in $\mathrm{mPa.cm^3.g^{-1}}$
ρ_1 = density of the ball (see Table 4.1) in $\mathrm{g.cm^{-3}}$
ρ_2 = density of the liquid sample at the test temperature in $\mathrm{g.cm^{-3}}$
t = fall-time of the ball in seconds (s)



1	Measuring tube with its ring marks A, B and C
2	Ball
3	Jacket room
4	Entrance nozzle for thermostated liquid: short piece of tube in 3
5	Exit nozzle: long piece of tube in 3
6	Precision thermometer
7	Water level
8	Stopper
9	Gasket
10	Screw cap
11	Levelling screw
12	Hollow stopper
13	Gasket
14	Capillary
15	Cover plate
16	Screw cap
17	Locking pin

Figure 4.1: Schematic diagram of the Haake Falling Ball Viscometer used for chitosan solution viscosity measurements [37].

Table 4.1: Haake Falling Ball Viscometer: ball calibration data / reproducibility tolerances [37].

HAAKE FALLING BALL VISCOMETER (Hoppler design)

Instrument No. : B/BH 78236
Measuring Tube No. : D 88484
Measuring Tube Diameter : 15.931 mm
Falling Distance (AB) : 100 mm (see Figure 4.1)

Ball No.	Composition	Diameter (mm)	Weight (g)	Density, ρ_1 (g cm^{-3})	Constant , K (mPa cm^3 g^{-1})	Measuring Range (mPa.s) (=cP)	Reproducibility (%)
1	borosilicate glass	15.83	4.610	2.222	0.00449	0.2-2.5	2
2	borosilicate glass	15.67	4.480	2.224	0.0455	2.0-20	1
3	nickel-iron alloy	15.63	16.265	8.144	0.0719	12-200	1
4	nickel-iron alloy	15.25	15.081	8.128	0.540	100-1200	1
5	stainless steel	14.28	11.723	7.709	4.54	800-10000	1.5
6	stainless steel	11.11	5.541	7.721	33.1	6000-75000	3

The test temperature of the sample must also be given in order to make the data complete. If the dynamic viscosity, η, is divided by the density of the sample, ρ_2, in g.cm^{-3}, the so-called ***kinematic viscosity***, ν, is obtained in units of ***centistokes*** (cSt) (= 10^{-2} cm^2.s^{-1}).

$$\nu = \frac{\eta}{\rho_2} \tag{4.2}$$

where

ν = kinematic viscosity in centistokes in cSt

η = dynamic viscosity in mPa.s

ρ_2 = density of the sample in g.cm^{-3}

4.2.2 Experimental Results

The chitosan solution for viscosity measurement was made up in 1% aqueous acetic acid to a 3% w/v concentration. The viscosity of the solution was determined using the viscometer assembly shown in Figure 4.2 and Ball No. 3 (Table 4.1). The measurements were made at a constant temperature of 25.0 ± 0.1°C and the results are shown in Tables 4.2 and 4.3.

Sample Solution	:	3% w/v chitosan in 1% aqueous acetic acid
Sample Volume	:	approx. 40 ml
Ball	:	No. 3 (nickel-iron alloy) – see Table 4.1
Temperature	:	25.0 ± 0.1°C

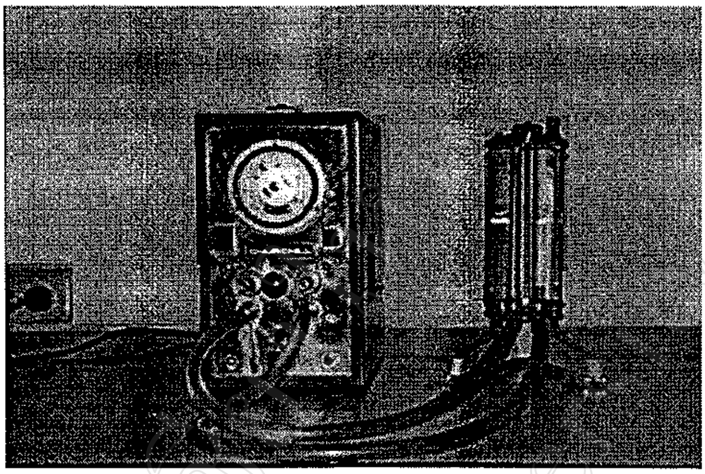


Figure 4.2: Photograph of the Haake Falling Ball Viscometer assembly used for viscosity measurements showing the viscometer (right) and the temperature controller (left).

Table 4.2 : Fall-time data for the chitosan solution.

Test No.	Fall-time (s)						Reproducibility* (± %)
	1	2	3	4	5	Average	
1	595.00	595.12	594.14	594.43	592.35	594.2	0.2
2	594.00	595.58	594.71	595.02	593.87	594.6	0.2
3	593.97	593.51	595.48	594.68	594.58	594.2	0.2

* these reproducibilities are all within the ±1% limits specified for Ball No.3 (Table 4.1)

Table 4.3: Calculated dynamic and kinematic viscosities of the chitosan solution.

Test No.	Average Fall-time t (s)	Dynamic Viscosity η (mPa.s)	Kinematic Viscosity ν (cSt)
1	594.2	304.4	298.4
2	594.6	304.6	298.6
3	594.2	304.4	298.4
Averages	594.3	304.5	298.5

SAMPLE CALCULATIONS (for Test No. 1)

From

$$\eta = K(\rho_1 - \rho_2)t$$

η = dynamic viscosity in mPa.s (= cP)

K = 0.0719 $\text{mPa.cm}^3.\text{g}^{-1}$

ρ_1 = 8.144 g.cm^{-3}

ρ_2 = 1.020 g.cm^{-3} (see note following)

t = 594.2 (s)

$$\eta = 0.0719\ \text{mPa.cm}^3\text{g}^{-1}\ (8.144 - 1.020)\ \text{g.cm}^{-3}\ .\ 594.2\ \text{s}$$

$$\boxed{\eta = 304.4\ \text{mPa.s}}$$

From

$$\nu = \frac{\eta}{\rho_2}$$

ν = kinematic viscosity in centistokes (cSt)

η = dynamic viscosity in mPa.s

ρ_2 = 1.020 g.cm^{-3}

$$\nu = \frac{304.4}{1.020} \text{ cSt}$$

$$\boxed{\nu = 298.4 \text{ cSt}}$$

NOTE: the density of the chitosan solution, ρ_2, was accurately determined at the test of temperature 25°C using a 25.00 ml density bottle previously calibrated with distilled water.

4.3 Wet Spinning Process

In the small-scale wet spinning equipment used in this work, all of the components which came into contact with the spin dope were made of either stainless steel or PTFE. There are several separate and independent units in the equipment so that modified procedures can readily be used if found to be necessary. Once filaments are being collected, either on the take-up unit or in the coagulation or wash bath, it is a simple matter to vary such parameters as ram speed and take-up speed so as to produce a range of samples for evaluation and determination of the optimum conditions of production.

4.3.1 Extrusion Unit

In the normal set-up used for wet spinning (see Figure 4.3), the spin dope is gently poured into the stainless steel cylinder and is forced at a constant rate (ram speed) through a spinneret by a piston which is driven into the cylinder by a motor-driven screw jack. The piston carries a PTFE seal and the solution is forced through a short length of fine stainless steel tubing to the spinneret which is below the surface of the liquid in the coagulation bath. To assist in shearing the solution, a small circle(s) of fine (e.g., 300-400 mesh) stainless steel gauze can be placed immediately behind the spinneret. The spinneret can either have a single hole or multiple holes depending upon whether monofilament or multifilament fibres are required.

However, in this work, it was found that the spinneret hole was so small (diam. 100 μm) and the spin dope so viscous that the spinneret tended to become clogged up by the precipitating polymer. Even when the spin dope could emerge from the spinneret, the extruded fibres were so fine that they tended to coil up and become entangled in the coagulation bath before they could be passed to the wash bath. Consequently, for ease of operation, the spinneret was removed and the stainless steel tube (diam. 1 mm) raised to just above (about 0.5 cm) the level of the liquid in the coagulation bath. This arrangement proved satisfactory for the production of monofilament fibres of diameter (when dry) of about 0.1-0.3 mm.

In the experiments carried out here, typically about 75 ml of spin dope was poured into a cylinder of internal diameter 2.5 cm. The spin dope was extruded at room temperature using ram speeds in the range of 5-12.9 mm/min and take-up speeds of 2-6 m/min.

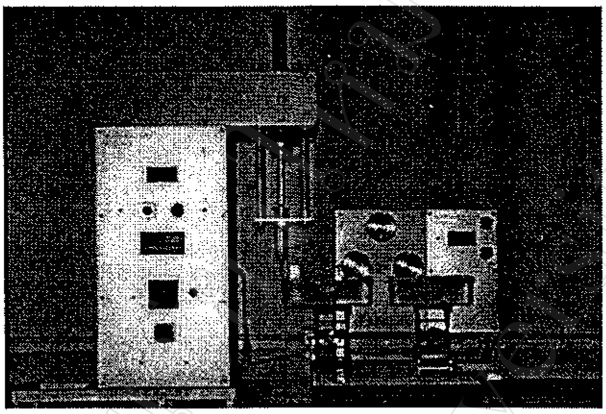


Figure 4.3: Photograph of the wet spinning apparatus.

4.3.2 Coagulation and Wash Baths

At first, two metal baths of dimensions 1 m x 10 cm x 10 cm were used as the coagulation and wash baths. However, it was found that they were too long for the coagulated fibres to be dragged along their full length without breaking. This was because the coagulated fibres were still too weak under tension to be drawn and taken up on-line.

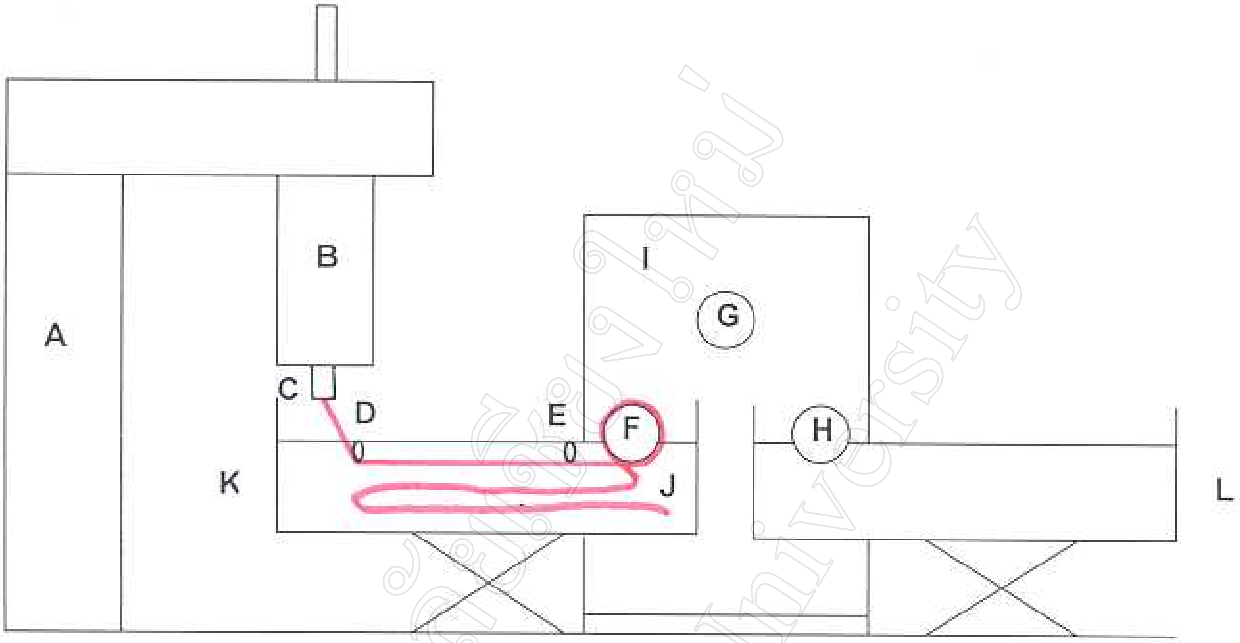
Consequently, the two metal baths were replaced by two smaller plastic baths 28.5 cm x 14 cm x 8 cm in dimension. Each was supported on an adjustable jack so that it could be lowered or raised as required. In this work, the coagulation bath contained 5% w/v sodium hydroxide (NaOH) in a distilled water : ethanol (90:10 v/v) mixture at room temperature. The NaOH was both a coagulating and a neutralizing agent while the ethanol was a dehydrating agent to help remove water from within the chitosan fibres. The coagulation bath was filled to within 1 cm of the top, as was the wash bath with distilled water. Filament guides were used to facilitate the passing of the fibre to the take-up roller F (see Figure 4.4). The first guide D was positioned 1 cm from the stainless steel tube C while the second guide E was 2 cm from the roller F. In the process itself, as the spin dope extruded from the tube C, the coagulating filament was gently led under guides D and E, then around roller F and back into the coagulation bath. With roller F rotating at the chosen take-up speed, the process then continued by itself until all of the spin dope had extruded. To ensure complete coagulation, the fibre was left to soak in the coagulation bath for 5 minutes before being transferred to the wash bath, as shown in Figure 4.5.

4.3.3 Take-up Unit

In this work, the coagulation, washing and drying processes had to be separated because of the very low tensile strength of the wet fibres. Using the same take-up speed as in the extrusion/coagulation step, the fibre was transferred from the coagulation bath to the wash bath via the three rollers F, G and H (see Figure 4.5). The fibres were then left to soak in the wash bath for 30 minutes before being carefully removed for drying.

4.3.4 Drying Process

Initially, the wet chitosan fibres from the wash bath were carefully wound up manually on PVC spools (diam. 6.1 cm) and then dried in a vacuum oven at 60°C for 4 hrs. However, because the wet fibres were so soft they tended to become flattened on wind-up, thereby producing fibres of



A : Extrusion unit

B : Cylinder

C : Stainless steel tube

D, E : Filament guides

F, G, H : Rollers

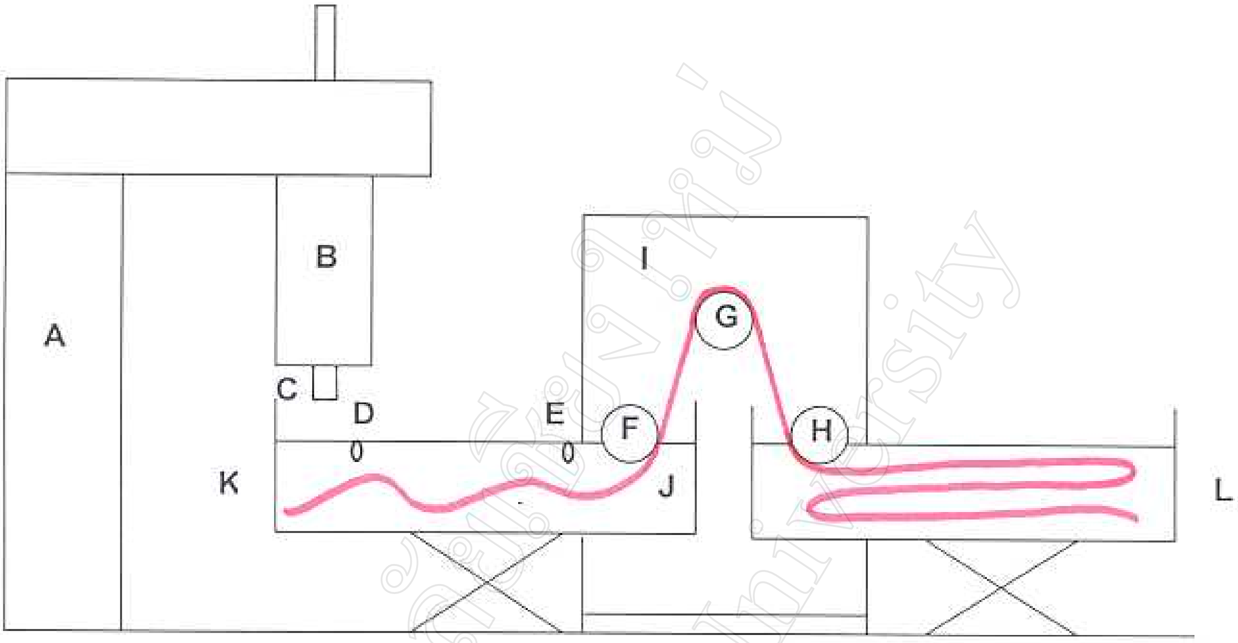
I : Take-up unit

J : Coagulated fibre (in red)

K : Coagulation bath

L : Wash bath

Figure 4.4: Schematic diagram of the wet spinning process: extrusion and coagulation steps.



A : Extrusion unit
B : Cylinder
C : Stainless steel tube
D, E : Filament guides
F, G, H : Rollers
I : Take-up unit
J : Coagulated fibre (in red)
K : Coagulation bath
L : Wash bath

Figure 4.5: Schematic diagram of the transfer of the coagulated fibre from the coagulation bath to the wash bath.

non-circular cross-section after drying. This problem was solved by using a purpose-designed metal frame, as shown in Figures 4.6 and 4.7, for hanging the fibres while they dried in the vacuum oven. The result was that the dried fibres obtained in this way were circular in cross-section and uniform in diameter.

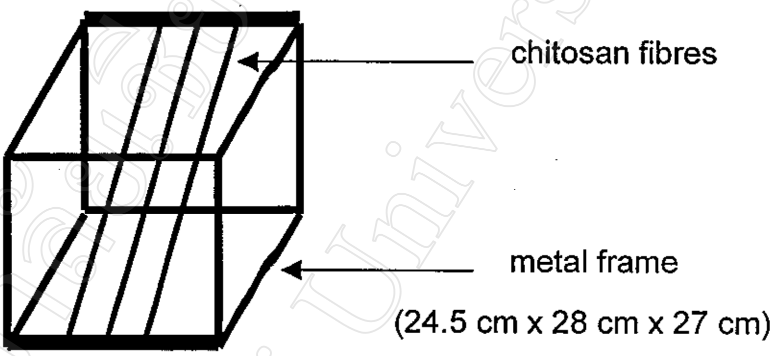


Figure 4.6: Diagram of the metal frame used for drying the chitosan fibres.

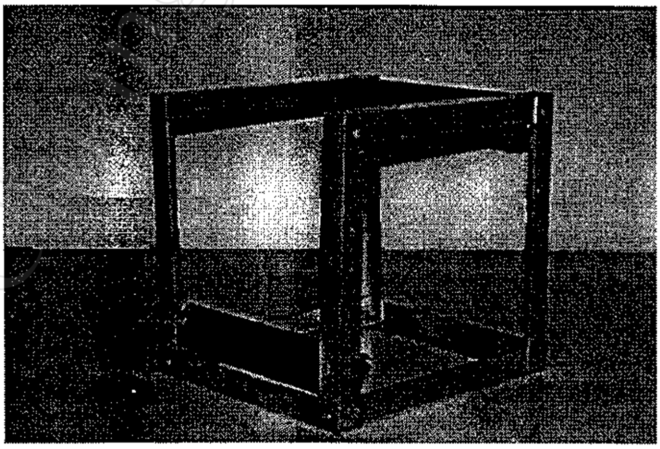


Figure 4.7: Photograph of the metal frame used for drying the chitosan fibres.

4.3.5 Processing Variables

4.3.5.1 Effect of Acetic Acid Concentration

In the case of the aqueous acetic acid solvent used in preparing the spin dope, two different concentrations of 1% v/v and 2% v/v were compared. Both gave chitosan solutions which were clear and light yellow in colour. However, the chitosan fibre coagulated faster from the 1% v/v solution in the NaOH coagulation bath. This was as expected since the 2% v/v acetic acid was a stronger solvent for the chitosan and therefore took longer to be extracted. Because the coagulation process needs to take place as quickly and as completely as possible in order to prevent the fibres from sticking together, the more dilute 1% v/v was the acetic acid concentration chosen for wet spinning.

4.3.5.2 Effect of Ram Speed

The ram speed was the downward velocity of the piston into the cylinder which, in turn, forced the spin dope out from the stainless steel tube and into the coagulation bath. Obviously, the higher the ram speed, the larger the volume of the spin dope which was ejected into the coagulation bath per unit time.

From the results in Table 4.4, when compared at a constant take-up speed of 2 m/min, it was found that the final fibre formed (i. e. after drying) increased in diameter as the ram speed increased from 5 to 12.9 mm/min. This is therefore a way of controlling the fibre diameter. However, another important consideration is that, as the fibre diameter increases, it takes a longer time for the coagulant to diffuse into the mass of the fibre which may necessitate a longer residence (soak) time in the coagulation bath. At each of the ram speeds used here, the final fibre diameter, when dry, was found to be consistent to within ±2% of the average value. This indicated that the processing conditions chosen were suitable for the wet spinning of good quality chitosan fibres of uniform diameter and circular cross-section.

4.3.5.3 Effect of Take-up Speed

The take-up speed was the speed at which the roller F (Figure 4.4) wound up the coagulated fibre after passing through the coagulation bath. Like the ram speed, the take-up speed could be adjusted to any value by the unit's controls.

From the results in Table 4.4, at a constant ram speed of 12.9 mm/min, it was found that the average fibre diameter decreased as the take-up speed increased from 2 to 6 m/min. This was because, when the take-up speed increased, the extruded fibre was stretched longitudinally as it coagulated, thereby decreasing the fibre's diameter. Another consequence of this stretching effect is that introduces a higher degree of molecular orientation along the fibre axis in the direction of draw. This, in turn, may influence the fibre's mechanical properties, as will now be described in the following Chapter 5.

Table 4.4: Combined effects of ram speed and take-up speed on the final diameter of the dried chitosan fibres.

Ram Speed (mm/min)	Take-up Speed (m/min)	Average Diameter* (mm)	Variation in Diameter	
			(mm)	(%)
5	1.5	0.238	± 0.022	± 2.2
	2	0.178	± 0.008	± 0.8
10	2	0.271	± 0.019	± 1.9
	3	0.224	± 0.014	± 1.4
12.9	2	0.309	± 0.010	± 1.0
	3	0.261	± 0.003	± 0.3
	4	0.230	± 0.002	± 0.2
	6	0.163	± 0.005	± 0.5

* average of 5 readings as measured with a micrometer (± 0.001 mm)

In Table 4.4, the results show the variation in diameter of the dried chitosan fibres with ram speed and take-up speed. The most suitable combination of ram speed and take-speed for wet spinning was taken as 12.9 mm/min and 4 m/min respectively since these conditions gave the lowest variation in diameter (± 0.2%) together with a smooth and uniform fibre surface. These conditions were therefore employed in all subsequent wet spinning experiments. However, this is not to say that these are the *optimum* conditions. In order to determine the optimum conditions for wet spinning, a much more detailed study than this would need to be carried out.