CHAPTER 7

MAIN CONCLUSIONS

The following main conclusions can be drawn from the experimental results described in Chapters 3-6. As the results have shown, the main aims of this research project, as started at the end of Chapter 1, have been achieved in this study of the wet spinning of chitosan fibres and their characterisation.

7.1 Characterisation

(a) From the moisture content determination, the chitosan raw material was found to have a moisture content in the range of 7.4-8.0% by weight. This is high for a polymer, showing that, when left in air, chitosan can absorb moisture easily due to its polar -OH and $-NH_2$ groups. Consequently, for accuracy in characterisation, chitosan should be kept under vacuum and dried before use.

(b) The molecular weight of the dried chitosan raw material was determined by dilute-solution viscometry using 0.2 M acetic acid / 0.1 M NaCl / 4 M urea. The urea in the solvent helped to prevent the reduction of solution viscosity due to acid-catalysed hydrolysis. From the results obtained, the viscosity-average molecular weight ($\overline{M}_v$) of the chitosan was found to be 2.46×10^5. Chitosan solutions are generally extremely viscous, even when dilute, due to a combination of high molecular weight, chains stiffness, and strong polymer-solvent interactions in solution.

(c) In this work, two different methods were used to determine the degree of deacetylation (DD) of chitosan: titration and solid-state ^{13}C-NMR.

In the titration method, the chitosan was first converted into chitosan hydrochloride which was then titrated with NaOH. From this method, the % DD obtained was 91.2%. From ^{13}C-NMR method, the % DD was 91.8%. Since ^{13}C-NMR is a more direct method which uses advanced analytical instrumentation to obtain the results, it should be more reliable. However, these results have shown that the titration method is also reliable too, provided that each step is carried out carefully.

(d) A study of the storage stability of chitosan in the 1% aqueous acetic acid solution used for wet spinning showed that the chitosan degraded quite quickly when stored at room temperature. The mechanism of degradation was acid-catalysed hydrolysis leading to random chain scission and could be followed by determining the change in $\overline{M}_v$ with time. However, this degradation could be largely prevented by storing the chitosan solution in the frozen state at <0°C.

7.2 Fibre Spinning

(a) The viscosity of the spin dope (3% chitosan in 1% aqueous acetic acid) is an important variable in the wet spinning process since it controls the rheology of the solution as it passes through the stainless steel tube and also the kinetics of coagulation.

(b) The coagulation bath contained 5% w/v sodium hydroxide (NaOH) in a distilled water : ethanol (90 : 10) mixture at room temperature. The NaOH acted as the coagulating and neutralizing agent while the ethanol was a dehydrating agent. The kinetics of the coagulation process was a complex balance of diffusion rate constants which governed the mass transfer of solvent out from the spin dope and into the coagulation bath.

(c) Both the ram speed and the take-up speed affect the physical and mechanical properties of the dried as-spun fibre. At constant take-up speed, increasing the ram speed increased the diameter of the fibre. However, when the take-up speed was increased at constant ram speed, the diameter of the fibre decreased because the fibre was drawn by the take-up roller. Thus, the diameter and degree of molecular orientation of the fibre can be controlled by balancing the ram and take-up speeds.

Figure 7.1 shows the effect of the ratio of the ram speed to the take-up speed on the fibre diameter at a constant ram speed of 12.9 mm/min and different take-up speeds of 2, 3, 4 and 6 m/min. As the ratio increases, the average fibre diameter also increases, as would be expected. However, the relationship is apparently non-linear, a finding which needs to be studied in more detail before any definitive explanation can be given.

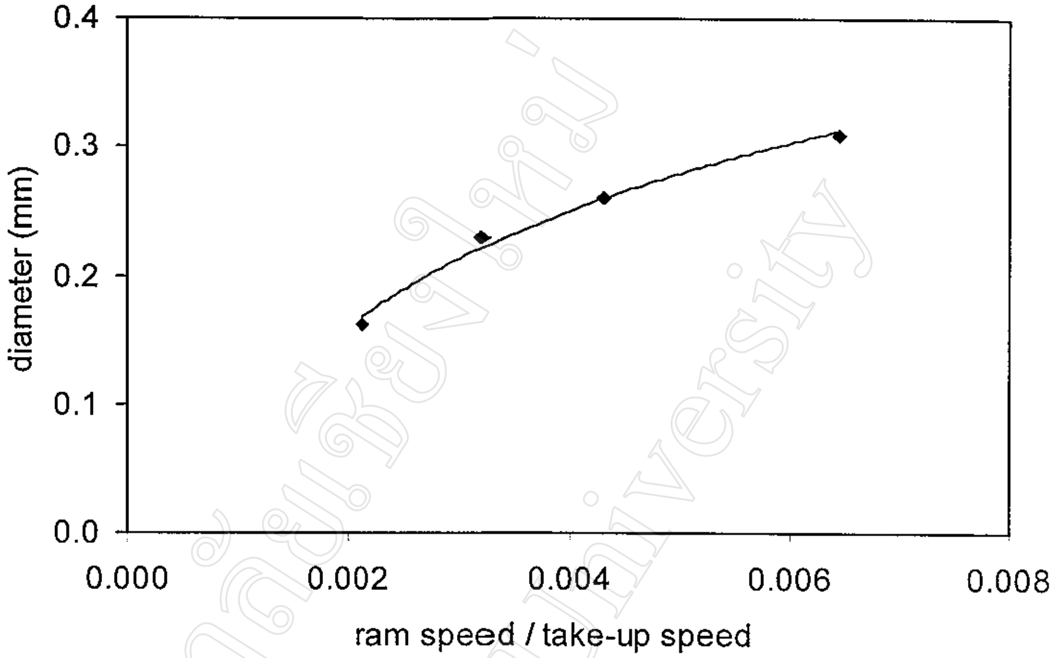

Figure 7.1: Effect of ram speed / take-up speed ratio on fibre diameter at a constant ram speed of 12.9 mm/min and different take-up speeds of 2, 3, 4 and 6 m/min.

7.3 Analysis of Fibre Properties

(a) Analysis of the stress-strain diagram from mechanical property testing showed that the dried as-spun fibres were hard, relatively weak and brittle materials. Their ultimate stress (< 100 MPa) at break were both relatively low compared with synthetic fibres of similar size. These rather poor mechanical properties have restricted the use of chitosan fibres in commercial applications.

(b) From scanning electron microscopy (SEM), the SEM image showed that the chitosan fibres were mainly smooth and uniform but with some localised irregularities dotted over the surface. There are many factors which can cause these irregularities such as shrinkage during the diffusion in coagulation process, friction between the coagulated fibres and the take-up roller, shrinkage in the drying process, and damage to the sample during sample preparation for SEM.

(c) Although X-ray diffraction (XRD) was able to indicate some degree of molecular orientation / semi-crystallinity, it appeared to be quite small and was difficult to quantify because the XRD peaks were broad and there was high background noise in the XRD pattern.

7.4 Improvement of Fibre Properties

The weak and brittle properties of the chitosan fibres could be modified by either crosslinking to make them stronger or plasticisation to make them softer.

7.4.1 Crosslinking

(a) The chitosan fibre's low tensile strength could be improved by crosslinking with epichlorohydrin. It was found that the stress at break of the crosslinked fibre (99.1 MPa) was higher than the uncrosslinked fibre (77.8 MPa) as a result of the 3-dimensional network structures generated by crosslinking. However, this increased tensile strength of the crosslinked fibre was still low for a monofilament fibre.

(b) The extension at break of the crosslinked fibre (14.2%) was reduced from that of the uncrosslinked fibre (39.2%) due to the chains being tied together by chemical bonds. Thus, crosslinking makes the fibre stronger but less extensible.

7.4.2 Plasticisation

(a) Plasticisation with glycerol succeeded in making the fibres softer which was reflected in their lower tensile strength, lower modulus, and higher elongation at break. However, this merely made what were already weak fibres even weaker and it is not clear what useful purpose this would serve unless it is combined with crosslinking. It should also be mentioned here that the absorption of water by chitosan is a type of self-plasticisation which can be turned to advantage in applications such as thin films for use as wound dressings. It should be possible to find a fibre application in which water absorption / plasticisation can also be an advantage.

(b) plasticiser retention with time was not studied in this work but is an important consideration in any extension of this study.

SUGGESTIONS FOR FURTHER WORK

In continuation of the research work carried out in the research work, the following suggestions for further work are now made:

1. In the coagulation process, the coagulation bath length is very important for processing. It may be useful to increase the length of the bath to increase the residence time for fibre precipitation so that spinning process can be a single-stage rather than a two-stage process.

2. The strength of chitosan fibres could be increased by the annealing and drawing. For this, the optimum temperature needs to be carefully determined so as to produce the appropriate amount of molecular motion without disrupting the existing crystalline regions.

3. The method of crosslinking, the chitosan fibre could be improved either by using a different crosslinking agent such as glutaraldehyde or a different method such as high-energy (electron beam, γ-ray) irradiation.

4. Similarly, the method of plasticisation could be improved. For example, the glycerol plasticiser could be added into the spin dope so that the as-spun fibre is already plasticised. Alternative, it could be added into the coagulation bath and/or wash bath instead [5]. In addition, once plasticised, the rate of loss of plasticiser from the fibre should be studied as a measure of its compatibility and volatility.

5. Chitosan is biodegradable polymer and chitosan fibres can be used in surgical applications such as wound coverings, burn therapy and tissue engineering. Other applications specific to chitosan fibres should be investigated, for example as a fibre reinforcement in the matrix of another biodegradable polymer. This may be useful in other biomedical applications such as absorbable bone fixation devices.