CHAPTER 6

IMPROVEMENT OF FIBRE PROPERTIES

6.1 Crosslinking

6.1.1 Previous Work

From the stress-strain diagram in Figure 5.6, it was found that the dry chitosan fibre had a stress and extension at break of 77.8 MPa and 39.2% respectively. These relatively weak, brittle properties can be improved through the application of either a chemical or a physical alteration to the fibre. Several authors have made claims concerning the production of fibres from chitosan. Hudson and co-workers [41] have published two reviews on chitosan fibres and most other applications of chitosan. With respect to the improvement of fibre properties through chemically crosslinking the as-spun dried fibre, the Fuji Spinning Company has claimed improvements in the mechanical properties of chitosan fibres by chemically reacting their product with epichlorohydrin and formaldehyde [42]. The strength of chitosan fibres, especially wet tenacity, is improved by crosslinking. Wei and co-workers also used epichlorohydrin and demonstrated a marked improvement in wet mechanical properties [43]. The post-spinning application of glyoxal, glutaraldehyde, phosphate ions and phthalate ions have also been reported [41].

In this project, epichlorohydrin was selected as a convenient base-catalysed crosslinking agent. An advantage of epichlorohydrin is that its

crosslinking does not eliminate the cationic amine function from the chitosan structure.

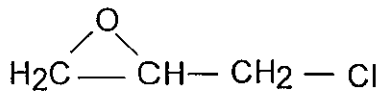
6.1.2 Experimental Procedure

The as-spun dried chitosan monofilaments were crosslinked by the method described by Wei et al [43]. In the procedure adapted for this work, 5 fibres, each of 30 cm length and produced at a ram speed of 12.9 mm/min and take-up speed of 4 m/min, were crosslinked by soaking in 200 ml of 2.00 x 10^{-2} M epichlorohydrin in 0.067 M NaOH in a 250 ml conical flask. The flask and its contents were purged with N_2, sealed and then placed in an oven at 40°C for 4 hrs. The crosslinked fibres were dried in a vacuum oven at 60°C for 4 hrs using the metal frame shown previously in Figures 4.6 and 4.7 (page 73). Finally, the dry fibres were tested mechanically using the Lloyds LRX+ Universal Testing Machine and the results compared with those of the uncrosslinked fibres.

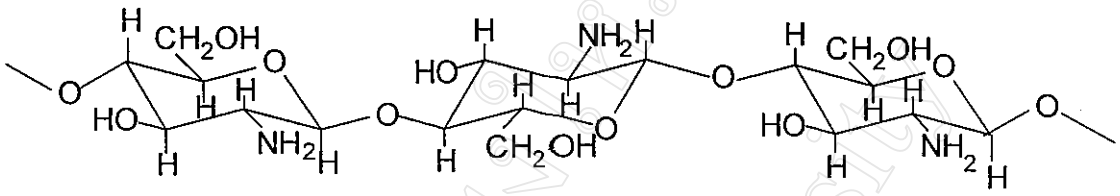
6.1.3 Mechanism of Crosslinking

The mechanism of crosslinking of chitosan by epichlorohydrin in shown in the following sequence of reactions. It is adapted from the crosslinking mechanism in epoxy resins [44]. The reaction is base-catalysed by the NaOH present in the solution.

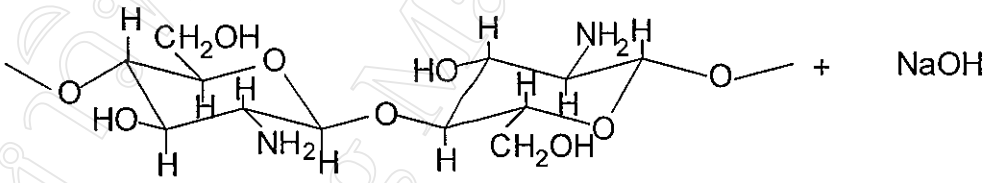
Epichlorohydrin

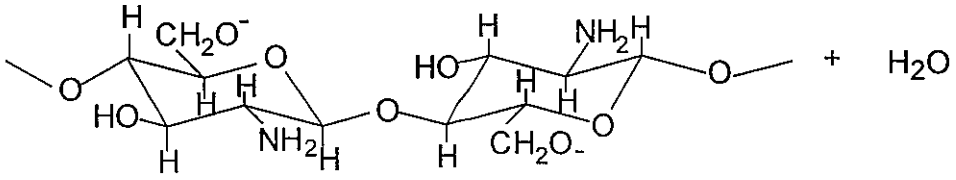


Chitosan

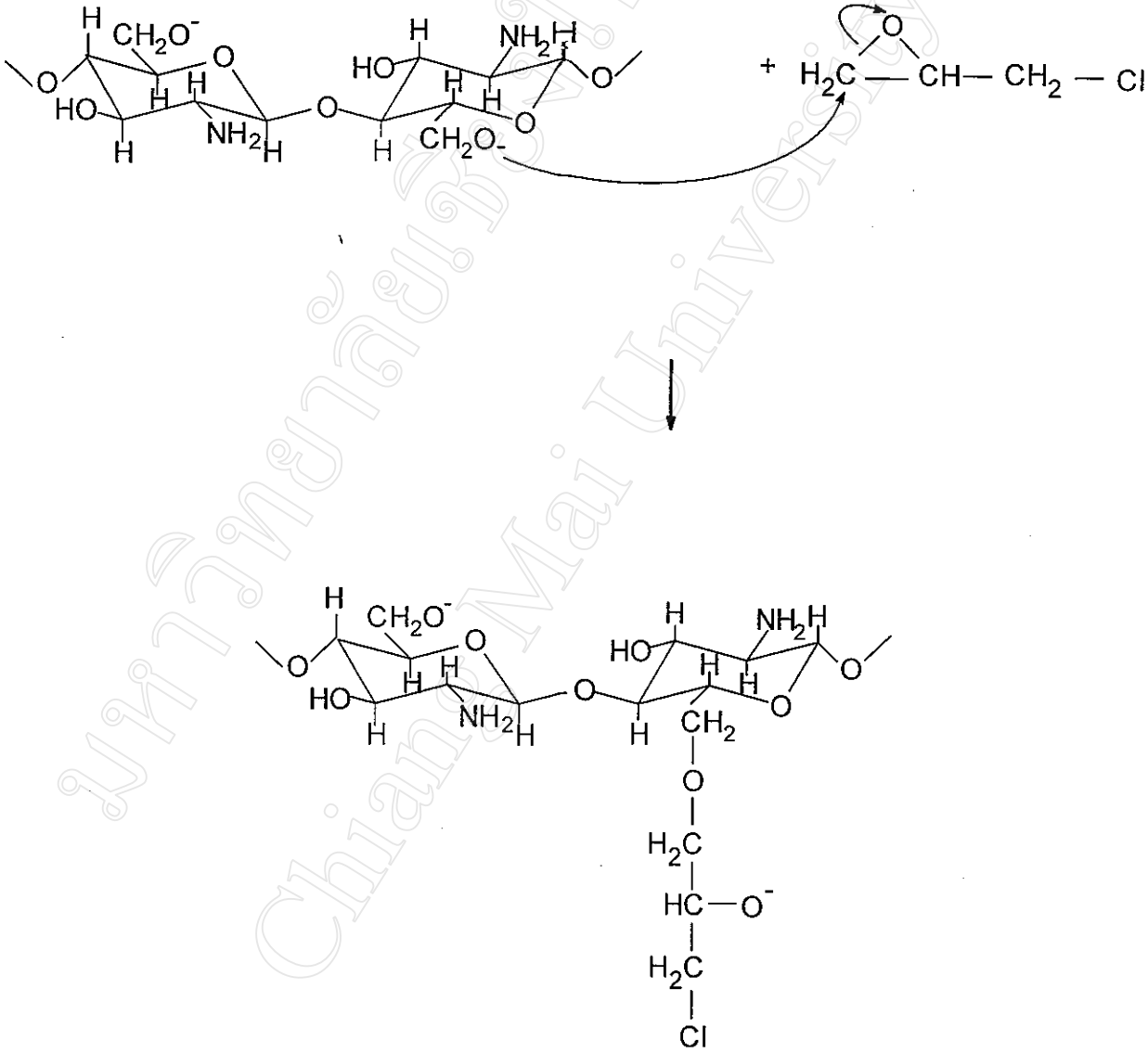


(i) Formation of phenoxy anion

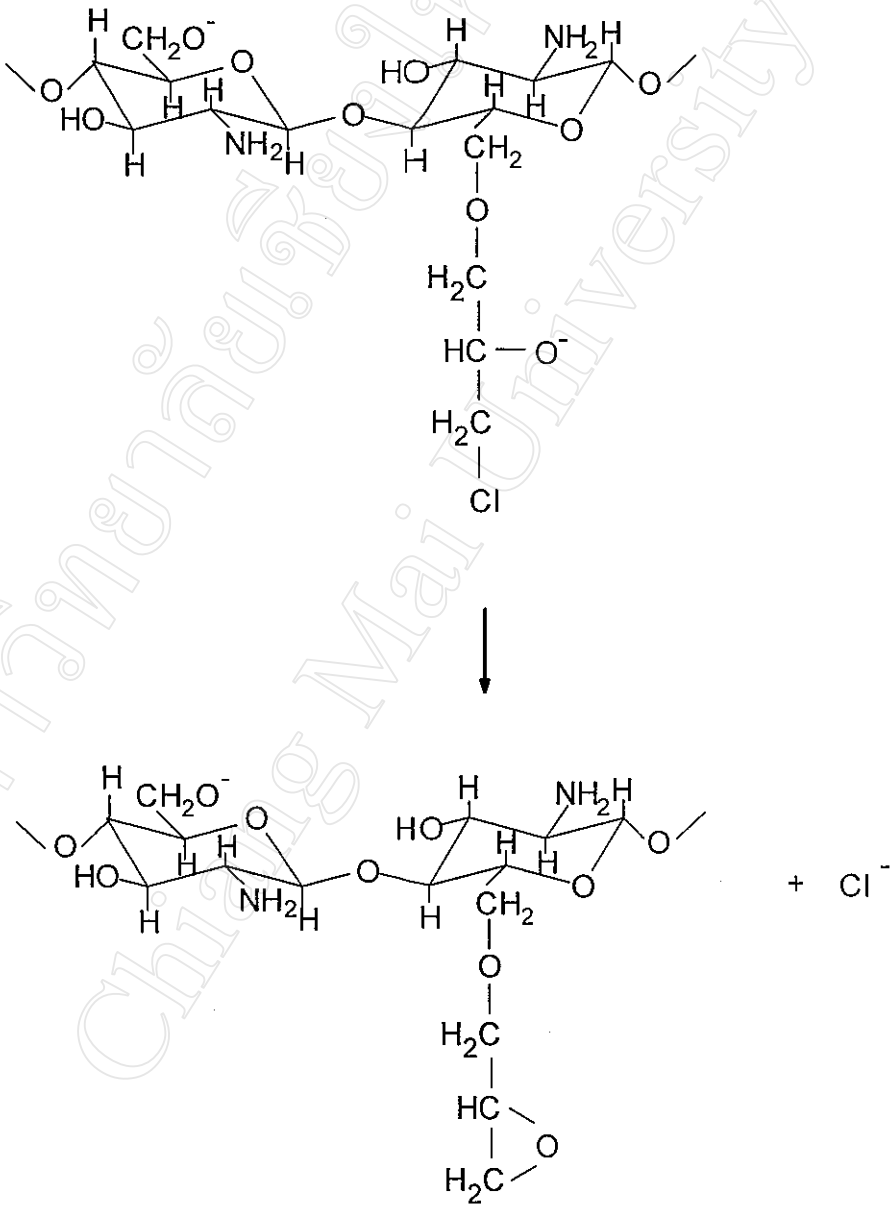




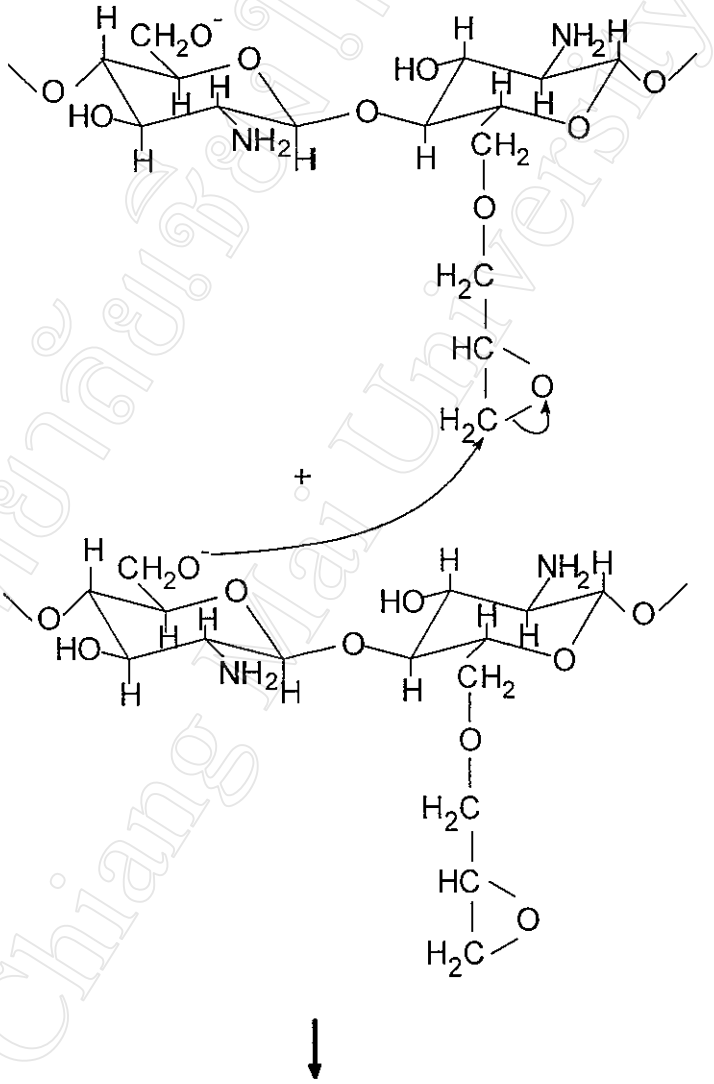
ii) Reaction of epoxy group of epichlorohydrin with phenoxy anion

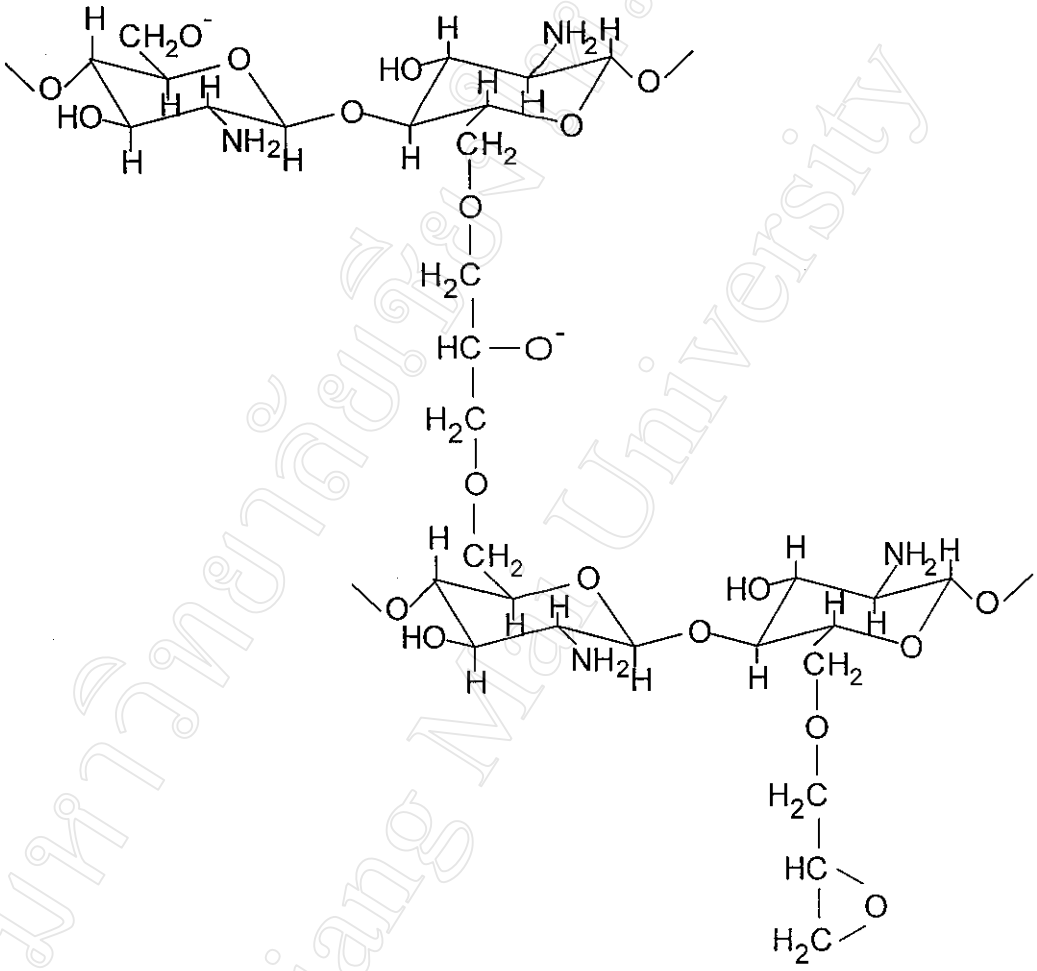


(ii) Elimination of chloride anion to form a glycidyl ether

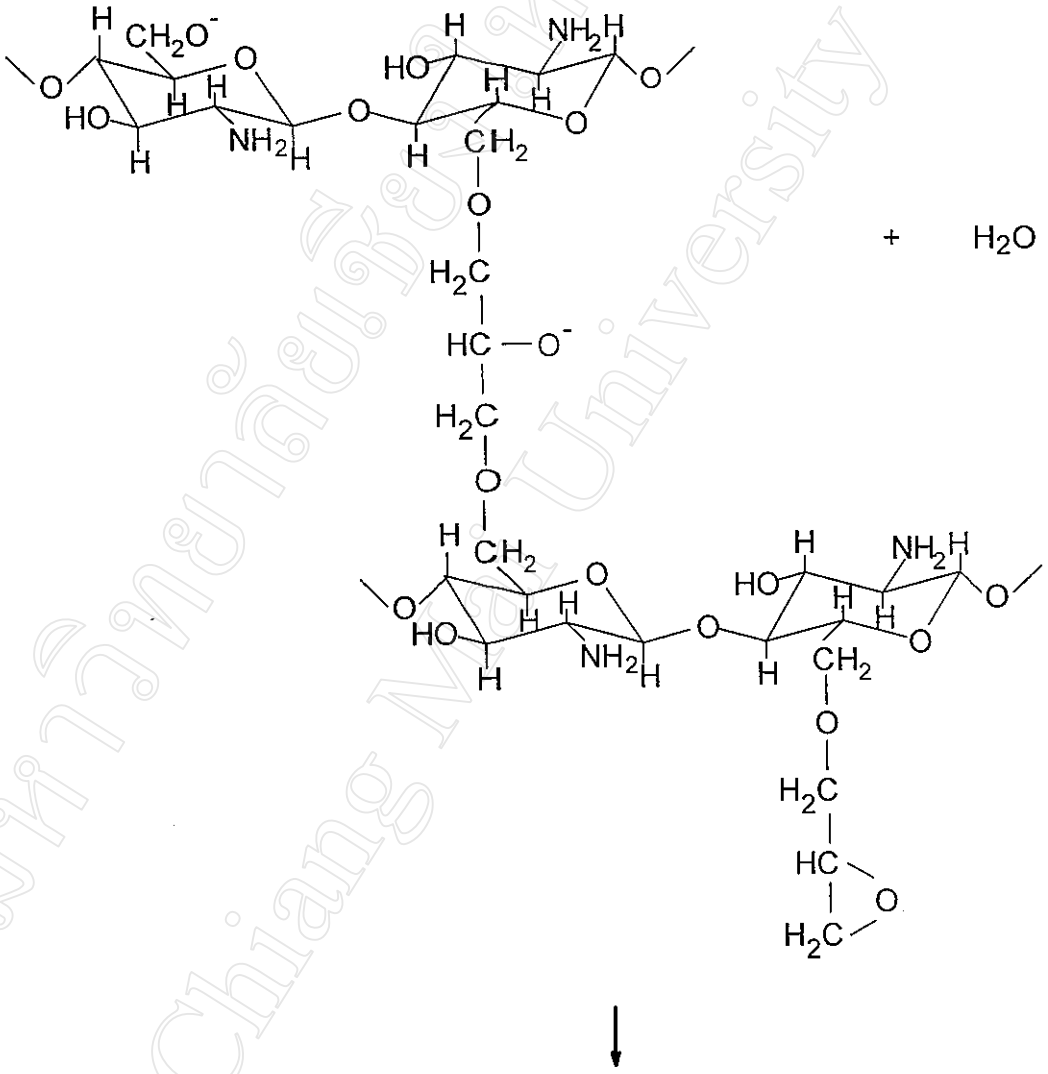


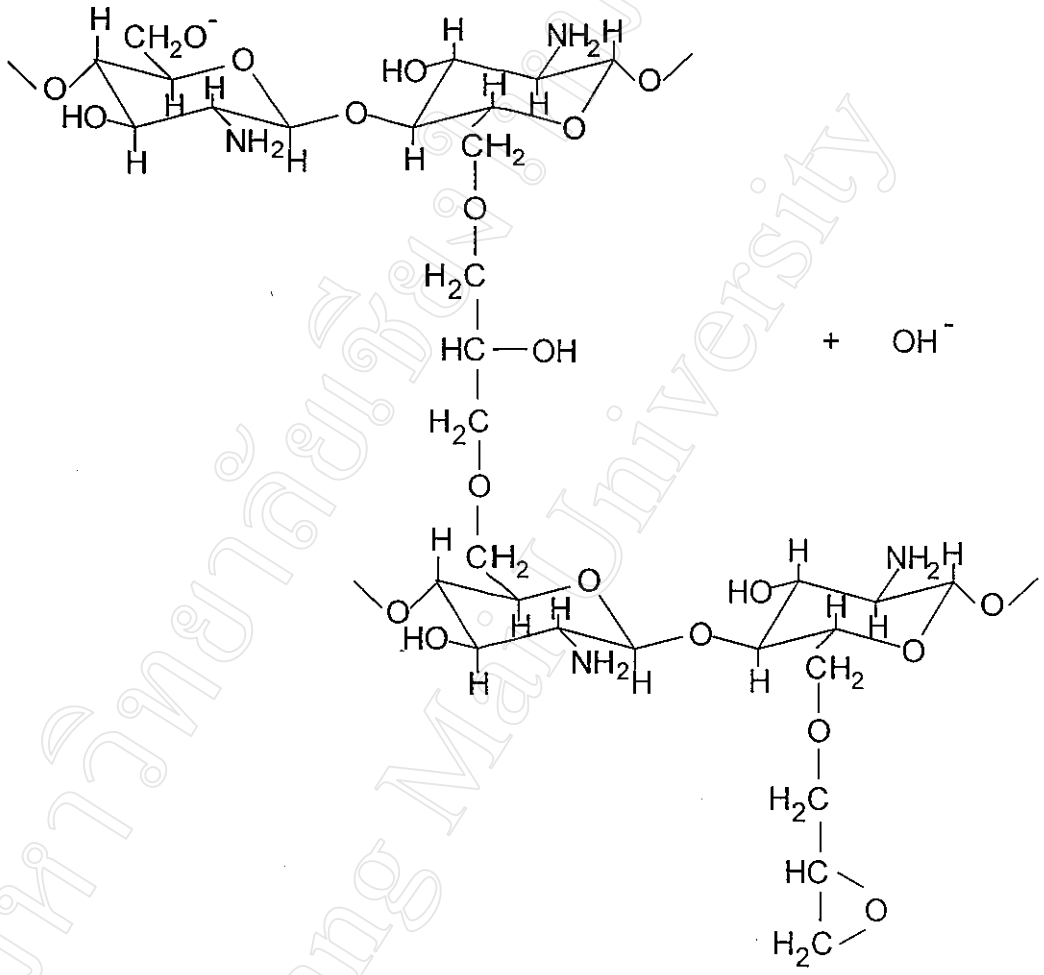
(iv) Reaction of epoxy group in glycidyl ether with another phenoxy anion





(v) Formation of hydroxyl group by protonation





6.1.4 Experimental Results

Normally, when crosslinked, polymers in general do not melt or dissolve. When the crosslinked chitosan fibres were tested according to their solubility in 1% aqueous acetic acid, it was found that they swelled but did not dissolve. This indicated that the chitosan chains had been successfully crosslinked by the epichlorohydrin producing 3-dimensional network structures, as represented in Figure 6.1. In contrast, the uncrosslinked chitosan fibres dissolved completely in 1% aqueous acetic acid.

As for melting, chitosan does not melt whether crosslinked or uncrosslinked; instead, it thermally degrades at low temperature. Consequently, melting cannot be used as an indicator of crosslinking in the case of chitosan.

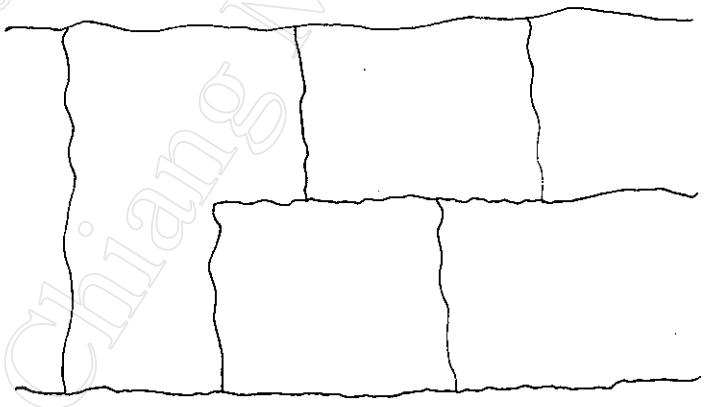


Figure 6.1: Simple representation of a 3-dimensional network polymer structure [21].

The tensile test results on the crosslinked chitosan fibre are shown in the stress-strain diagram in Figure 6.2. They were obtained under the same

test conditions as described previously on page 85. When compared with the uncrosslinked chitosan fibre's stress-strain diagram in Figure 6.3, it can be seen that:

(a) The stress at break of the crosslinked fibre (99.1 MPa) was significantly higher than that of the uncrosslinked fibre (77.8 MPa). This is consistent with crosslinking have taken place since the interchain bonds increase the energy required for tensile failure. However, even after crosslinking, the tensile strength (stress at break) is still below 100 MPa which is rather low for a monofilament fibre.

(b) The % strain at break of the crosslinked fibre (14.2%) was much less than of uncrosslinked chitosan fibre (39.2%). This is also consistent with crosslinking since the chains are not able to slip past each other under strain.

(c) The initial tangent modulus of the crosslinked fibre (2327.5 MPa) was higher than the uncrosslinked fibre (2221.9 MPa) leading to increase stiffness. This is a direct result of tieing the chains together and, thus, decreasing chain mobility. These structural changes at the microscopic level are reflected in the mechanical properties at the macroscopic level.

Therefore, the findings in (a), (b) and (c) combine to show that crosslinking produces a stronger fibre but also one which is stiffer and less extensible. This is as would be expected from a structural point of view. However, the overall mechanical properties, even after crosslinking, are still relatively poor for a fibre which is why chitosan fibres do not enjoy much commercial importance at the present time.

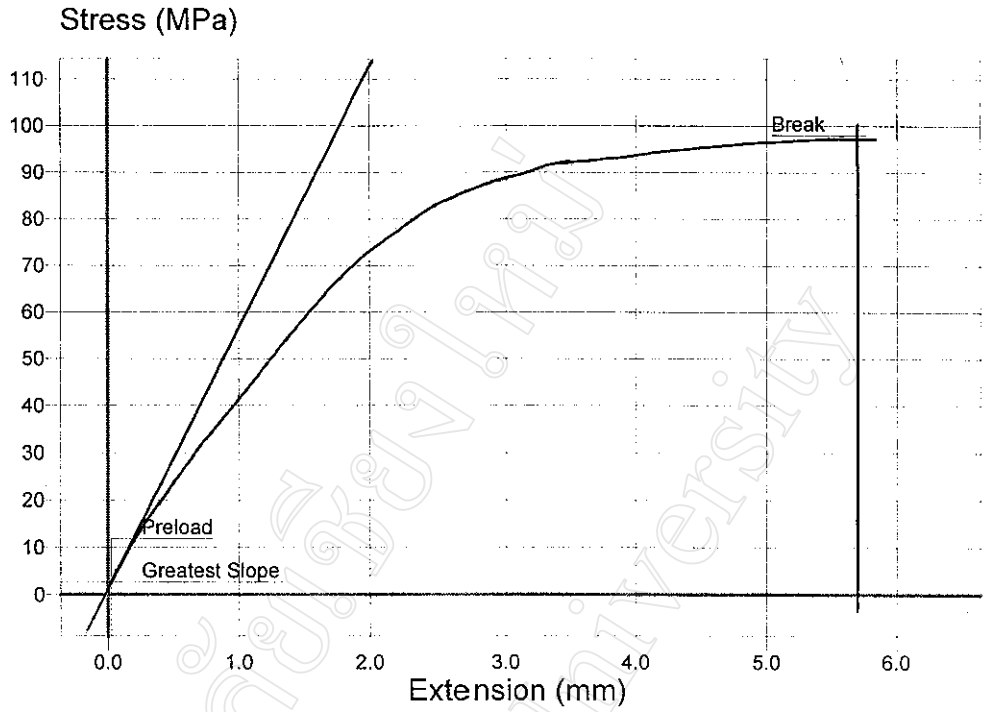


Figure 6.2: Stress-strain curve for crosslinked chitosan fibre produced at a ram speed of 12.9 mm/min and take-up speed of 4 m/min.

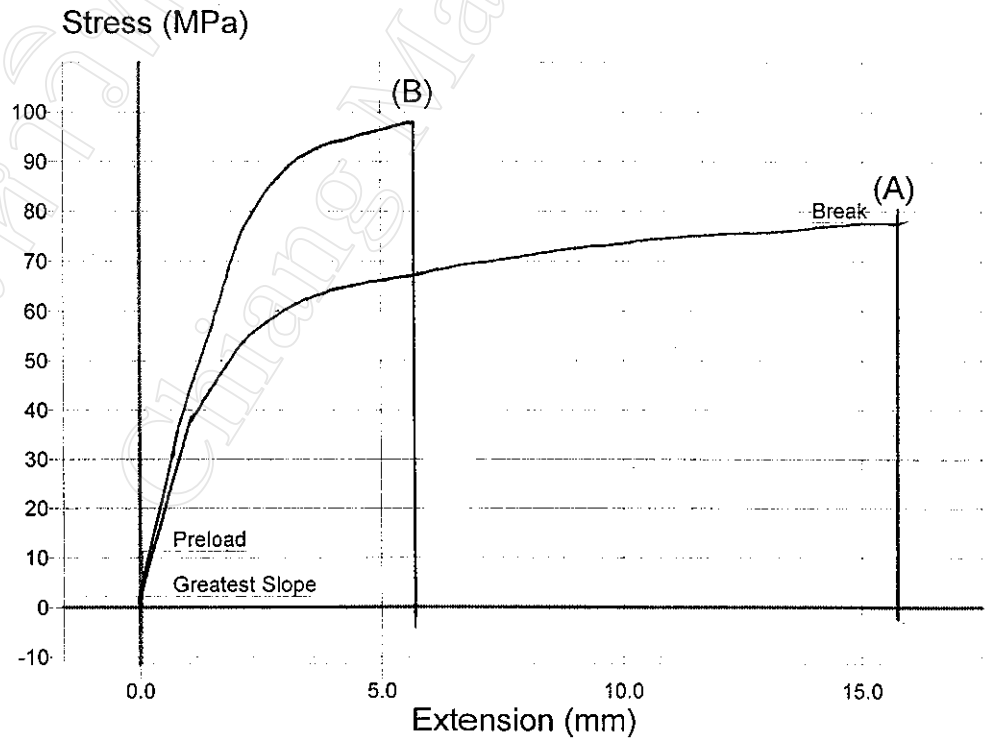


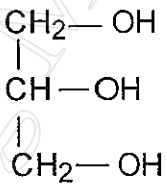
Figure 6.3: Comparison of the stress-strain curves for uncrosslinked (A) and crosslinked (B) chitosan fibres produced at a ram speed of 12.9 mm/min and take-up speed of 4 m/min.

6.2 Plasticisation

The addition of a plasticiser usually reduces stiffness, hardness and brittleness since interchain forces are effectively reduced. Plasticisation is usually restricted to amorphous polymers or polymers with a low degree of crystallinity because of the limited compatibility of the plasticiser with highly crystalline polymer [21].

In this work, glycerol was used as a plasticiser. It was used in aqueous solution to aid its diffusion in between the chitosan chains to increase the free volume. With more free volume and less interchain forces, the chitosan fibres could become softer and more pliable.

Glycerol



6.2.1 Experimental Procedure

The plasticising agent used was 5% v/v aqueous glycerol. The chitosan fibres (uncrosslinked) produced at a ram speed 12.9 mm/min and take-up speed 4 m/min were immersed in the glycerol solution overnight in a beaker. The fibres were then dried at 60°C for 4 hours under vacuum on a metal frame (see Figures 4.6 - 4.7 on page 73).

6.2.2 Experimental Results

After drying to remove water, the plasticised chitosan fibres were soft and pliable, in marked contrast to their hard, brittle nature before plasticisation. The effect of plasticisation is clearly seen in the stress-strain curves in Figure 6.4 and 6.5 which show that:

(a) The plasticised chitosan fibres were much more extensible (80.9% at break) then the unplasticised fibres (39.2%) as would be expected if there was more free volume and therefore less interchain forces between the molecules. The increased molecular mobility enables the molecules to slip past each other more easily under an applied stress.

(b) However, as the extensibility and pliability increases, plasticisation decreases the ultimate stress at break (tensile strength) and modulus. This is clearly shown in Figure 6.4 in which the stress at break of the plasticised fibre (27.9 MPa) is over 60% less than the original fibre (77.8 MPa). This serves to make what were originally quite weak fibres even weaker.

These results show that chitosan fibres can be plasticised by glycerol and their mechanical properties modified. However, what is still unknown is how long the plasticiser can remain in the fibre before it diffuses to the surface and volatilizes. Because fibres have such a high surface area to bulk ratio, plasticiser loss over time would be faster than in bulk plastics. This could be the subject of further work in extension of that described here.

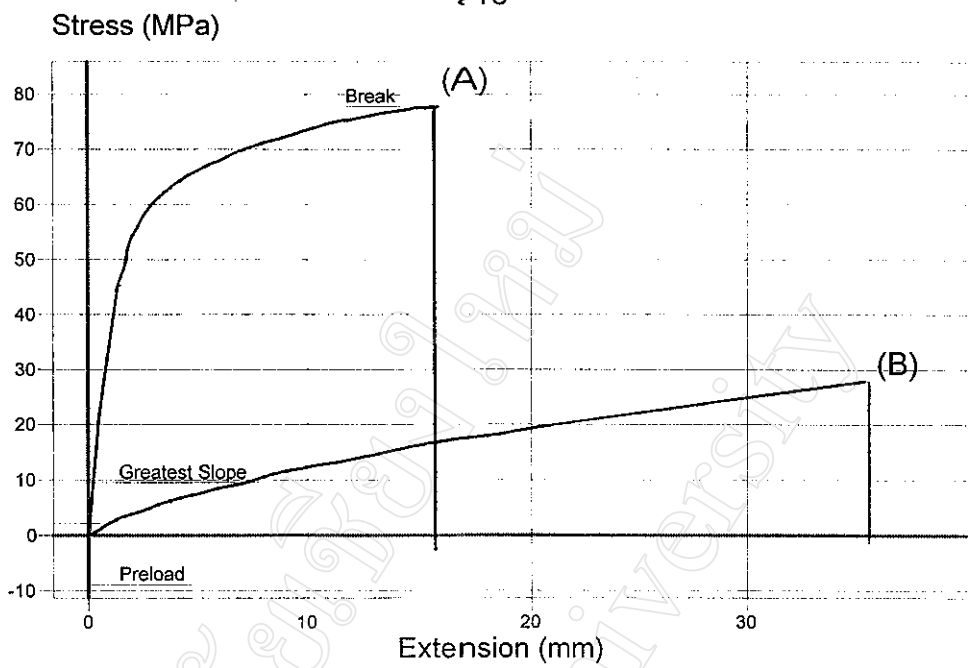


Figure 6.4: Comparison of the stress-strain curves for the unplasticised (A) and plasticised (B) chitosan fibres produced at a ram speed of 12.9 mm/min and take-up speed of 4 m/min.

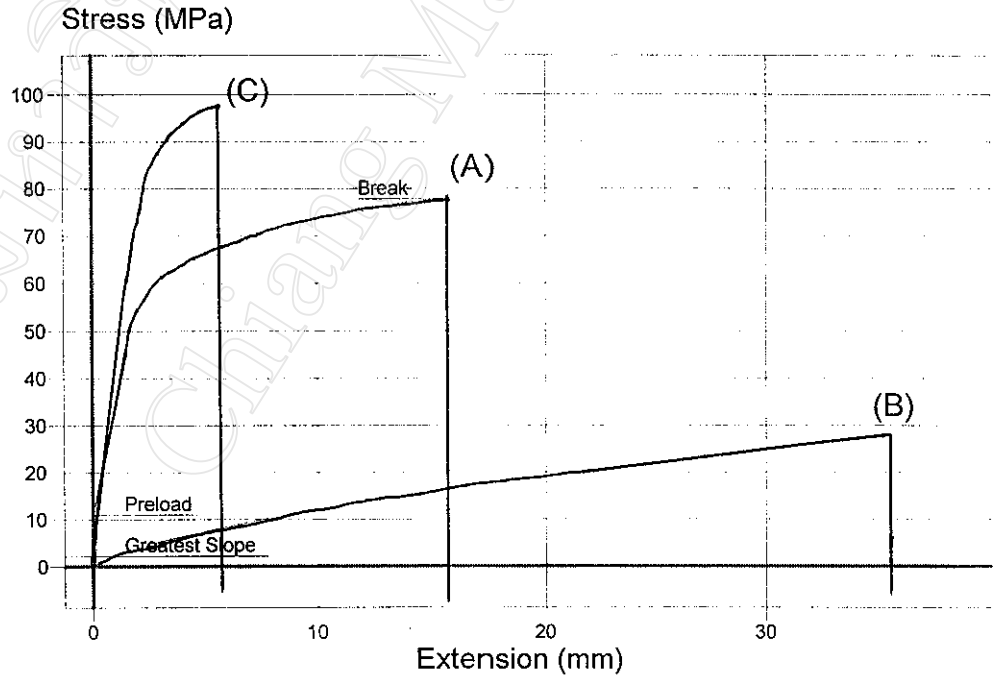


Figure 6.5: Comparison of the stress-strain curves for the original chitosan fibre (A), the plasticised fibre (B), and the crosslinked fibre (C) produced at a ram speed of 12.9 mm/min and take-up speed of 4 m/min.