CHAPTER 6

DISCUSSION AND CONCLUSIONS

6.1 Polypropylene

In the melt spinning of polypropylene, it was found that the monofilaments obtained were partially crystalline, as shown by their DSC thermograms (Fig. 5.10 on page 92). Their % crystallinities at various spin-draw ratios are shown in Fig. 6.1.

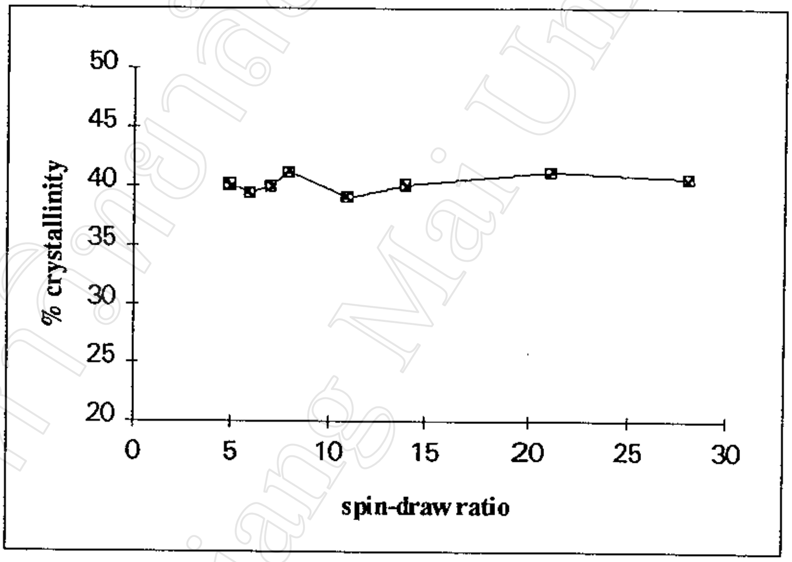


Fig. 6.1 Effect of spin-draw ratio on the % crystallinity of the spin-drawn polypropylene monofilaments.

Spinning temperature = 205°C
Cooling/drawing temperature = ambient (≈ 25.0°C)

From the results in Fig. 6.1, it appears that the spin-draw ratio has little or no effect on the % crystallinity of the spin-drawn monofilament. This is despite the undoubted molecular orientaton effect of the spin-drawing process in the direction of the fibre axis which, in theory at least, should induce further crystallisation to take place. The most logical explanation for this somewhat unexpected result is related to the polymer's rate of cooling after it has emerged from the spinnerette. If the emerging thread is spin-drawn before it has had sufficient time to completely solidify from the melt, then, in effect, all that will happen is that the molecules in the amorphous melt (or semi-solid polymer) will merely undergo viscoelastic deformation without any increasing inducement to crystallisation. Molten polypropylene filaments are known to have a high heat content and therefore take longer to cool [16]. Consequently, "on-line" spin drawing, under the conditions used in this work, has not had any significant effect on the % crystallinity of the polypropylene monofilaments produced.

On the other hand, the average filament diameter and denier do decrease significantly with increasing spin-draw ratio, as Figs. 6.2 and 6.3 show. This is as would be expected from the drawing process which naturally results in a decrease of the filament's cross-sectional area. Decreasing denier affects both the breaking tenacity and the initial modulus of the monofilament. The effects of the spin-draw ratio on these mechanical properties were illustrated previously in Figs. 5.24 and 5.25 (page 122) in which the strength and modulus were seen to increase with increasing spin-draw ratio. This is probably due to the greater ease of orientation of the molecules in the melt state at high spin-draw ratio. In other words, the molecular orientation in the as-spun monofilament increases with spin-draw ratio, both in the amorphous and crystalline phases, leading to greater strength.

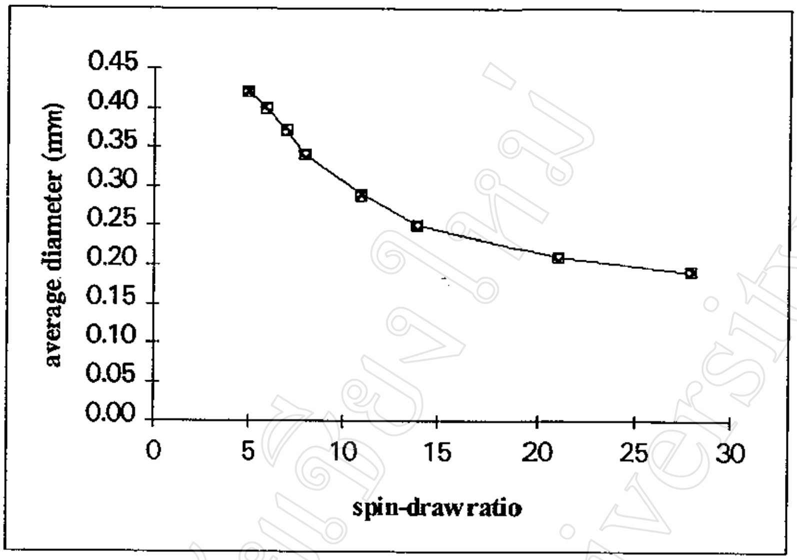


Fig. 6.2 Average diameters of the spin-drawn polypropylene monofilaments as a function of spin-draw ratio.

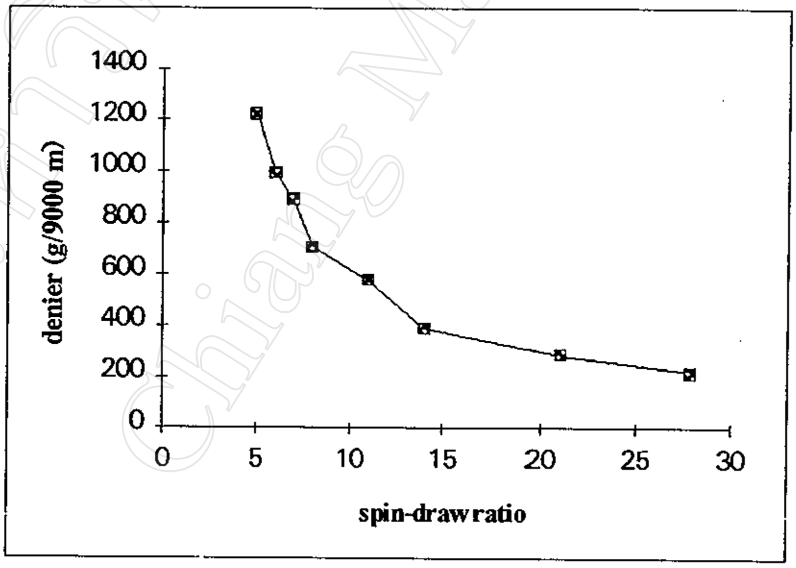


Fig. 6.3 Deniers of the spin-drawn polypropylene monofilaments as a function of spin-draw ratio.

The increases in breaking tenacity and modulus explain why the % elongation at break decreases with increasing spin-draw ratio, as shown in Fig. 6.4. Because greater molecular orientation will be obtained at higher spin-draw ratios, as more polymer chains are stretched and aligned nearly parallel to the fibre axis, the monofilaments become harder but more brittle. Consequently, the % elongation at break will be reduced since there is less scope for longitudinal deformation. The following Fig. 6.5 compares the % elongations at break of the spin-drawn and spin-drawn/off-line hot drawn polypropylene monofilaments.

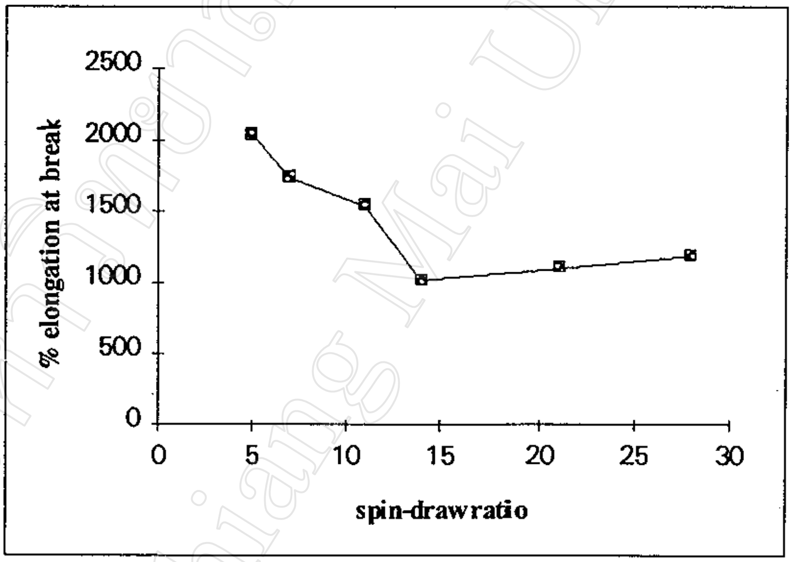


Fig. 6.4 % Elongations at break of the spin-drawn polypropylene monofilaments as a function of spin-draw ratio.

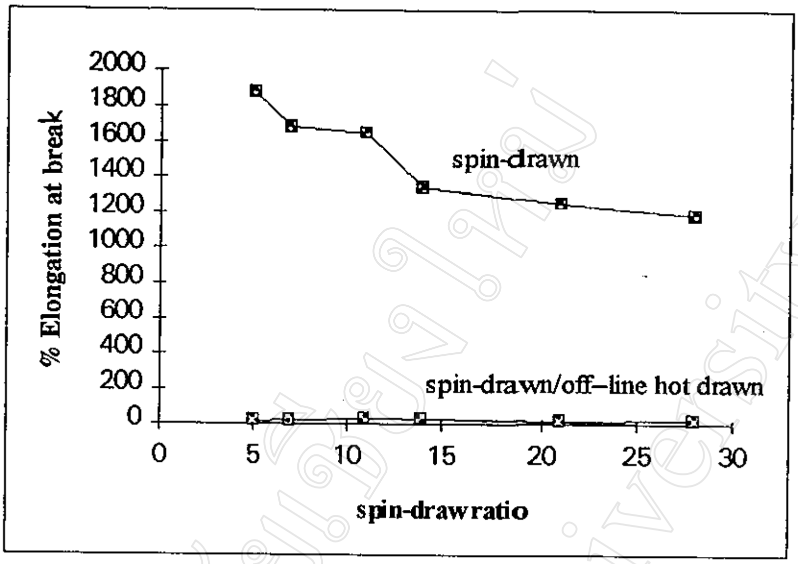


Fig. 6.5 Comparison of the % Elongations at break of the spin-drawn and spin-drawn/off-line hot drawn (OLDR 8 and T_{OLHD} = 120°C) polypropylene monofilaments as a function of spin-draw ratio.

It can therefore be concluded that the spin-drawn polypropylene monofilaments produced in this work are still not as strong as they should be. Their mechanical properties are inferior to those of commercial products. In addition, photomicrographs of the as-spun monofilaments showed that they contain defects, such as necking, which limit their strength. It was for these reasons that refinements to the fibre production process were considered, such as thermal conditioning and off-line hot drawing.

It was speculated that a "thermal conditioning zone" (TCZ) may help to increase the molecular orientation in the filament. In this study, the TCZ used was an electrically-heated column placed directly under the spinnerette. The emerging filament from the spinnerette was passed down through the TCZ to delay the cooling rate in the upper region of the threadline before being cooled by exposure to the cool room air. It was found that filaments which had been passed through the TCZ had slightly higher breaking tenacities than those which had not, as shown in Table 6.1. Possibly the TCZ may have helped in some way to increase the molecular orientation in the filament or perhaps increased the crystallite size (rather than the % crystallinity - see Table 6.1) through its effect the rate of cooling. However, no discernable trend was observed between in moderating tenacity and the actual TCZ temperature used. This is an aspect of the work which needs to be studied further.

It has been suggested that a TCZ may be suitable for use with a high-speed spinning process, as shown in Fig. 1.7 on page 11. The drawing can often be omitted in high-speed spinning in which drawn yarn may be produced economically in one step. However, the full development of such a one-step technology requires the development of a high-speed winder. This high-speed spinning process has already been extensively investigated and, today, high-speed spinning at 6000-8000 m/min. is in commercial operation for the production of synthetic yarns such as nylon and polyester [1]. Polyester (PET) fibres, for example, spun at 5000-6000 m/min, have exhibited high degrees of crystallinity, comparable to those of drawn fibres.

Table 6.1 Breaking tenacities of polypropylene monofilaments SDR 7 both with and without the use of a temperature conditioning zone (TCZ).

Condition	Average TCZ Temp.* (°C)	Breaking Tenacity x 10^2 (N/tex)	Crystallinity (%)
TCZ1	103	6.74	40.4
TCZ2	87	6.99	39.8
TCZ3	74	6.86	39.5
without TCZ	-	5.92	40.0

* for actual TCZ column temperature ranges, see Table 5.2 - 5.4 on pages 83 and 84

The off-line hot drawing process, as shown in Fig. 1.6 on page 10, has also been studied in this work as a means of improving the mechanical properties of the polypropylene monofilaments. Here, the drawing process is carried out as a separate step from the spinning operation. The following Fig. 6.6 compares the % crystallinities of the spin-drawn and spin-drawn/off-line hot drawn polypropylene monofilaments. The results show that the % crystallinities of the spin-drawn/off-line hot drawn monofilaments are significantly higher than those which were spin-drawn (on-line) only. The additional off-line hot drawing process also had the effect of increasing the Young's modulus, as shown in Fig. 6.7.

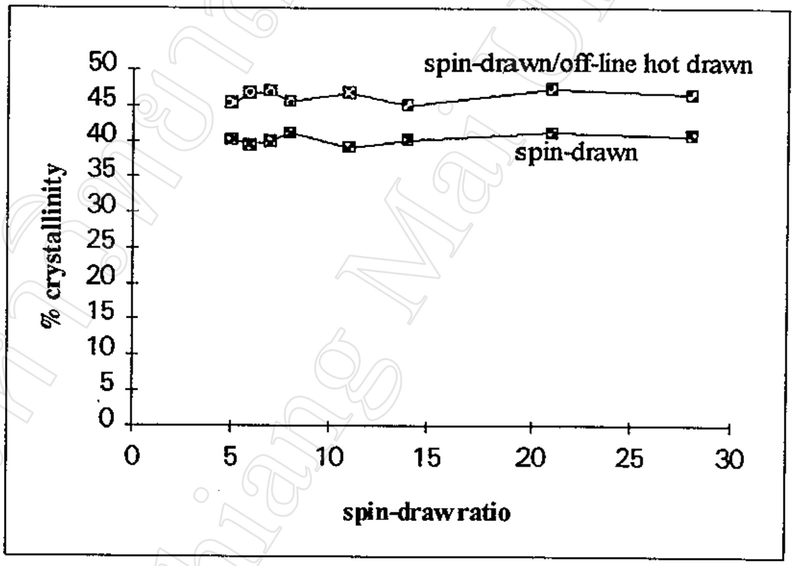


Fig. 6.6 Comparison of the % crystallinities of the spin-drawn and spin-drawn/off-line hot drawn (OLDR 8 and T_{OLHD} = 120°C) polypropylene monofilaments as a function of spin-draw ratio.

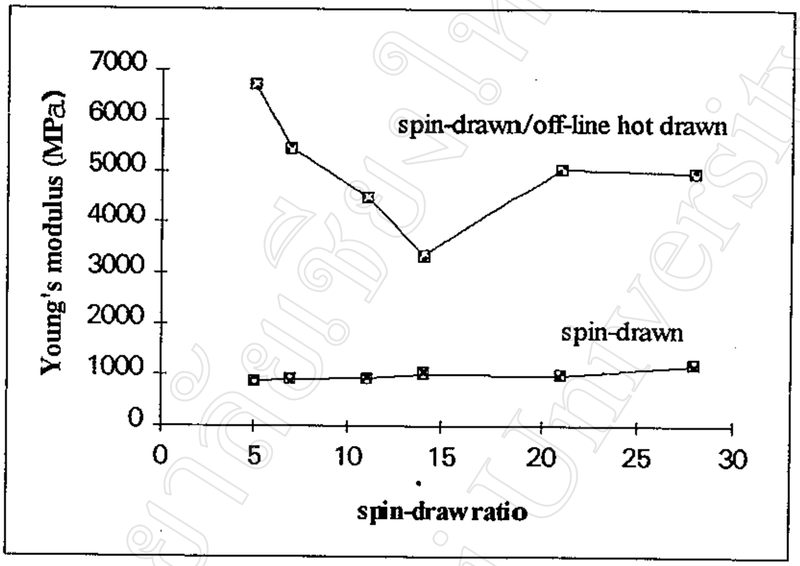


Fig. 6.7 Comparison of the Young's moduli of the spin-drawn and spin-drawn/off-line hot drawn (OLDR 8 and T_{OLHD} = 120°C) polypropylene monofilaments as a function of spin-draw ratio.

These results can perhaps best be explained in terms of the mechanism of deformation that takes place under mechanical stress. In general, many semi-crystalline polymers in bulk form have a spherulitic structure. Each spherulite consists of numerous chain-folded ribbons or lamellae that radiate outwards from the center. Separating these lamella are areas of amorphous material, as shown in Fig. 6.8. Adjacent lamellae are connected by tie-chains that pass through these amorphous regions.

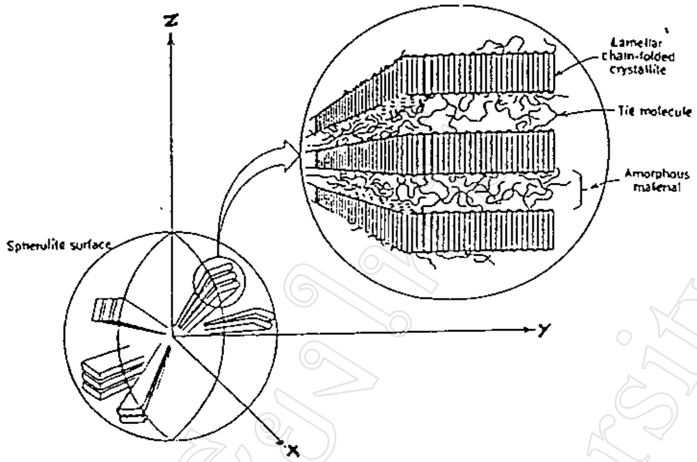


Fig. 6.8 Schematic representation of the detailed structure of a spherulite [41].

The mechanism of mechanical deformation is best described by the interaction between the lamellae and the intervening amorphous regions in response to an applied tensile load. The lamellae and the interlamellae amorphous material, prior to deformation, are shown in Fig. 6.9(a). During the intial stage of deformation (Fig. 6.9(b)), the lamellae ribbons simply slide past one another as the chains within the amorphous regions become extended. Continued deformation in the second stage occurs by the tilting of the lamellae so that the chain folds become aligned with the tensile axis (Fig. 6.9(c)). Next, crystalline block segments separate from the lamellae, although the segments remain attached to one another by overlapping chains (Fig.6.9(d)). In the final stage (Fig. 6.9(e)), the block segments and tie-chains become oriented in the direction of the tensile axis.

As the degree of stretching is increased, the amorphous regions are implicated as the source of the increased stiffness in the drawn state. Going from a low to a high draw ratio increases the volume fraction of such extended-chain molecules, these being sheared off the surfaces of the ordered regions in the crystalline block segments which are displaced relative to each other, as shown in Fig. 6.10. These changes in morphology and molecular orientation are the reasons behind the observed increases in % crystallinity and Young's modulus.

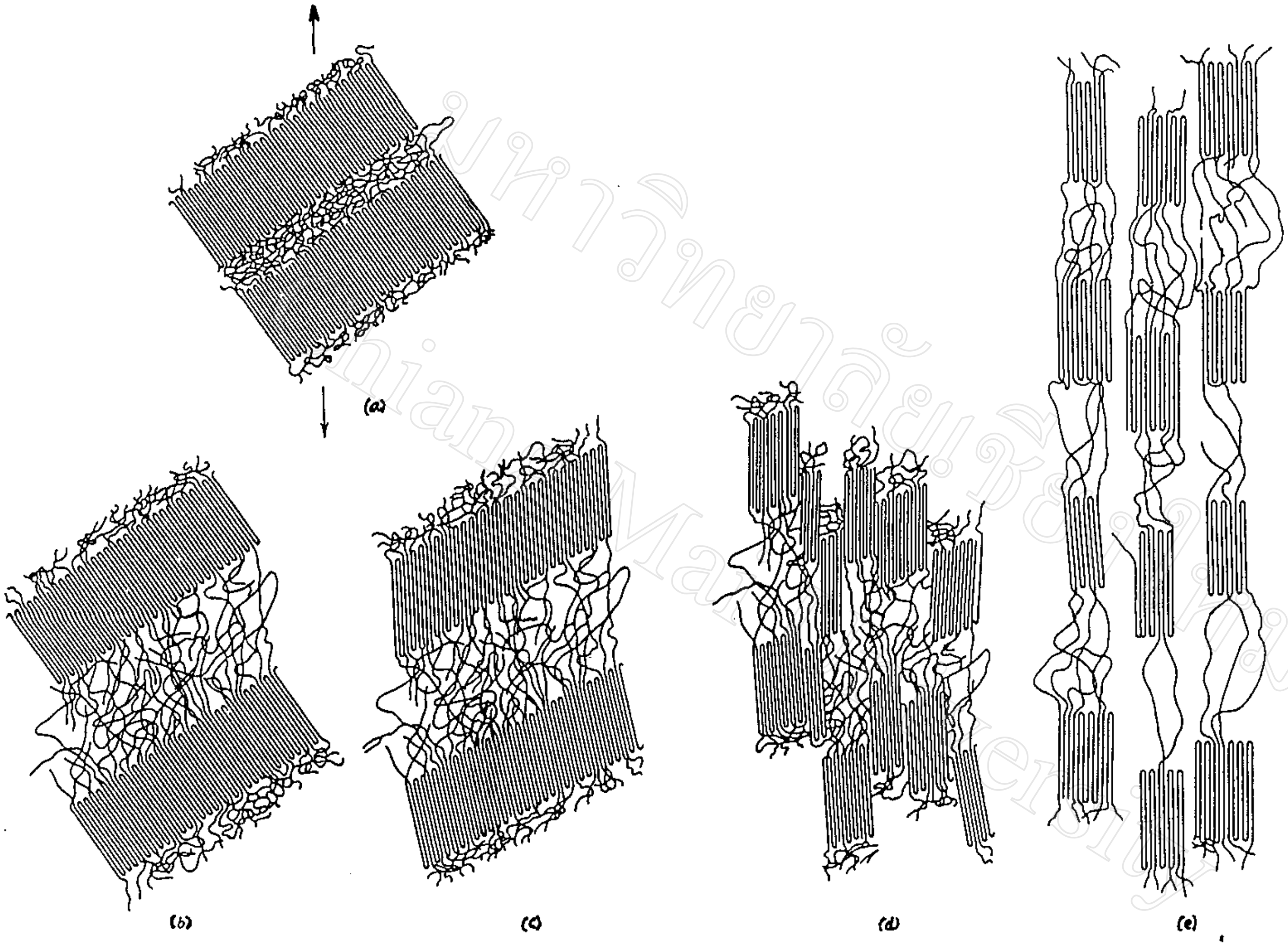


Fig. 6.9 The various stages in the tensile deformation of a semi-crystalline polymer [41].

Low off-line hot draw ratio High off-line draw ratio

Fig. 6.10 Longitunidal views of low and high off-line hot draw ratio fibre structures [49].

Another interesting feature of polypropylene morphology was highlighted by the DSC thermograms in Figs. 5.11 and 5.12 (page 96) which revealed multiple melting peaks. This phenomenon has also been observed in previous studies on samples annealed at high temperature [50], crystallized at an appropriate temperature [51], or oriented in some way [52]. In the most similar of these studies to this present one, Samuels [52] suggested that the multiple melting peaks in spin-drawn isotactic polypropylene fibres indicated the presence of crystals of different shapes and sizes and/or disordered crystals. For example, the presence of two distinct crystalline morphologies - lamellae and fibrillar forms - in the same sample, each requiring slightly different amounts of energy in order to melt, could explain the appearance of multiple DSC melting peaks.

A further refinement to fibre processing was annealing of the spin-drawn/off-line hot drawn monofilaments at a temperature just below their melting range. This annealing is designed to increase the % crystallinity by increasing chain mobility in the amorphous regions, thereby further improving the mechanical strength. From the results obtained in this work, both the temperature and time of annealing need to be carefully chosen in order to obtain a significant improvement. The highest temperature used (155°C) for the longest time (5 hrs.) was the only combination to show a significant increase in % crystallinity (see Table 5.10 on page 97).

Finally, from the photomicrographs of the polypropylene monofilaments, as shown in Fig 5.18 (page 104-105), the monofilaments were, for the most part, uniform but still contained some bulk and surface defects. It has been argued that the distribution of the polymer melt into several partial melt streams after it leaves the extruder requires uniform temperature distribution at the extruder outlet in order to achieve uniform filament quality at the individual spinning positions [16]. Some typical defects in the monofilament, as shown in Fig. 5.20 (page 107), were undoubtedly weak points in mechanical testing. Adams [53] has suggested that the most essential morphological requirements for high-modulus fibres are: (a) high molecular orientation (b) ordered lateral packing of molecules, and (c) low concentration of axial defects. Further work needs to be done here, particularly on the avoidance of voids and necking, if high quality fibres with consistent properties are to be produced.

6.2 Poly(L-lactic acid-co-ε-caprolactone), P(LLA-co-CL)

Polymers which are useful as raw materials for fibres generally have number-average molecular weights ($\overline{M}_n$) of not lower than 10,000 to 15,000. The higher range of molecular weight reaches approximately 300,000 [9], while Mark [10] quotes 6,000 as the lowest limit of molecular weight for any of the popular fibre-forming polymers.

In this work, the poly(L-lactic acid-co-ε-caprolactone) 8:2 and 7:3 samples synthesized for use in melt spinning had $\overline{M}_n$ values of the order of 30,000 [33]. Both samples could be melt spun but the extruded monofilaments were not strong enough to be wound up by the take-up unit. Furthermore, the monofilaments were non-uniform in diameter and tended to neck under their own weight as the threadline increased in length. The main reasons for the poor quality of the P(LLA-co-CL) monofilaments are considered to be:

(1) the polymer molecular weights were still too low, resulting in low melt viscosities for melt spinning and poorly developed mechanical properties of the spun fibre

(2) the melt spinning temperature was also slighty too low, resulting in incomplete melting of the polymer as it emerged from the spinnerette; however, if the molecule weight is too low, as suspected in (1), then increasing the spinning temperature will exacerbate further the low melt viscosity problem; thus, the polymer's characteristics (∝ molecular weight) and the processing conditions need to be balanced against each other and optimized.

Following melt spinning, it was found that the P(LLA-co-CL) 8:2 monofilament exhibited a very distinct crystallization peak in its DSC thermogram, as shown in Fig. 5.13 (page 98). This is a clear indication that the monofilament was, to a certain extent at least, quenched cooled in the air when it emerged from the spinnerette. This gives rise to a special morphological state called the "quenched amorphous state" in which the polymer, which would normally be semi-crystalline, is completely amorphous or, at least, much less crystalline then it would be if it had been allowed to cool from the melt more slowly. These changes in morphology which occur during the polymer's cooling from the melt and re-heating during DSC analysis are represented schematically in Fig. 6.11.

Heat treament (isothermal annealing) of the P(LLA-co-CL) monofilaments was studied as a means of improving mechanical properties. These improvements may result from an increase in polymer molecular weight and/or crystallinity. It was found that annealing of the P(LLA-co-CL) 8:2 and 7:3 monofilaments, at temperatures just below their respective melting ranges, gave higher heats of fusion, as shown in Table 5.11 (page 101). This was due to increases in % crystallinity, as confirmed by the disappearance of the crystallisation exotherm in the thermogram of P(LLA-co-CL) 8:2 monofilament (Fig. 5.14 on page 99). Thus, isothermal annealing does have a significant part to play in post- spinning processing.

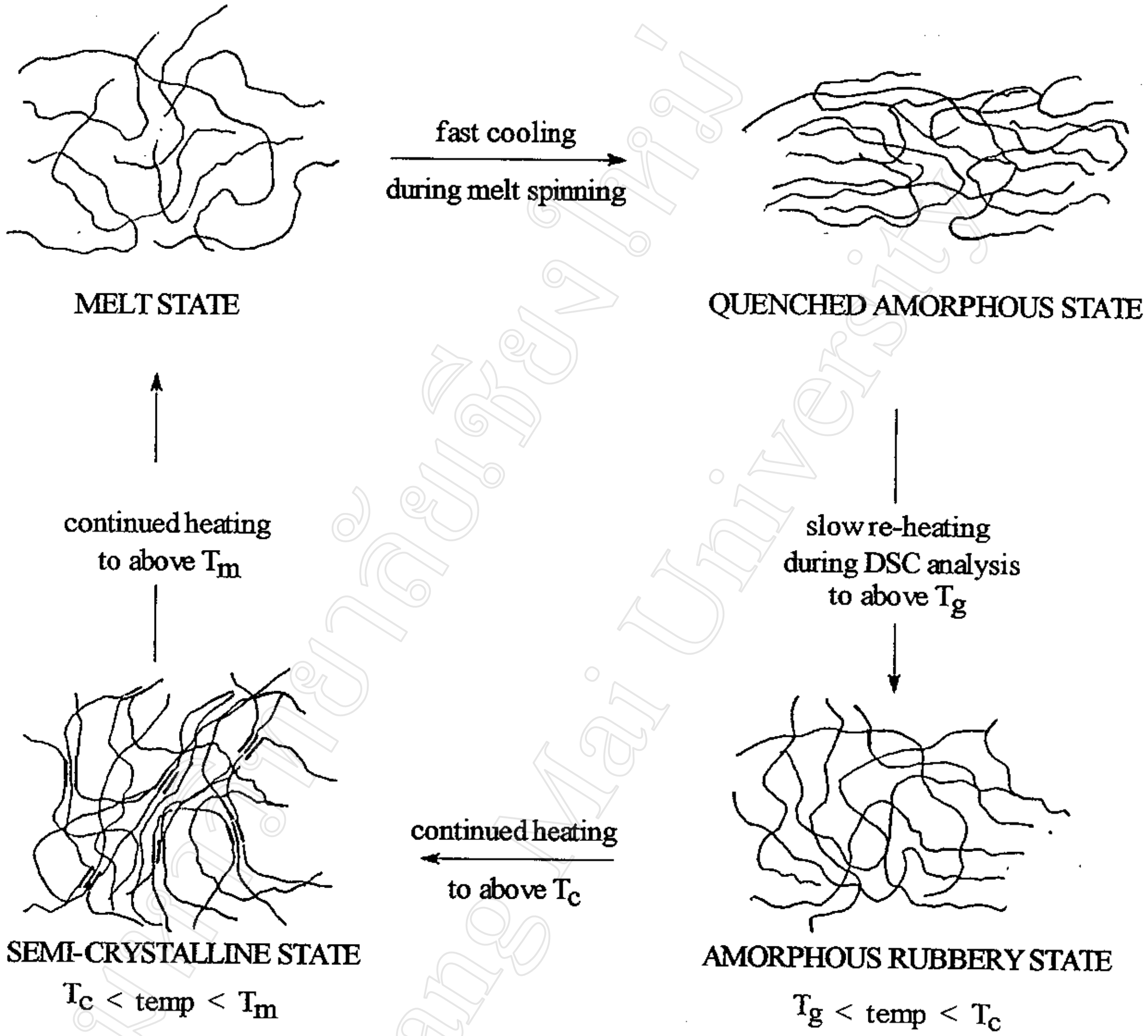


Fig. 6.11 Schematic representation of the changes in P(LLA-co-CL) 8:2 monofilament morphology which take place during fast cooling from the melt followed by slow re-heating.

Table 6.2 compares the mechanical properties of commercially available monofilament surgical sutures and the P(LLA-co-CL) monofilaments.

Table 6.2 Comparison of the mechanical properties of commercially available monfilament surgical sutures and the P(LLA-co-CL) monofilaments.

Polymer	Stress at break (MPa)	Young's Modulus (MPa)	% Elongation at break
P(LLA-co-ε- CL) 8:2	25	773	46
P(LLA-co-ε- CL) 7:3	30	606	166
Monocryl (4-0)	839	878	37
Monocryl (2-0)	928	741	54
Maxon (2-0)	790	2600	50
PDS II (4-0)	674	1163	54
PDS II (2-0)	800	1117	71

From the results in Table 6.2, the very low values of stress at break of the P(LLA-co-CL) monofilaments, compared with the commercial sutures, emphasize their relatively poor quality. Improvements obviously need to be made in terms of both higher molecular weight and optimized processing conditions. Another interesting feature of the results is the much higher % elongation at break of the P(LLA-co-CL) 7:3 monofilament, a clear reflection of its elastic nature. In marked constrast, the 8:2 copolymer was quite brittle. This illustrates the flexibilizing effect of the CL units and also the importance of the proximity of the copolymer's glass transition temperature, T_g, to room temperature. It was found that the T_g of the P(LLA-co-CL) 8:2 monofilament was about 32°C (slightly above room temperature), as shown in its DSC curve in Fig. 5.13. Therefore, being in its glassy state at room temperature, the

P(LLA-co-CL) 8:2 monofilament was quite brittle. In constrast, the P(LLA-co-CL) 7:3 monofilament had its T_g below room temperature and was therefore in its rubbery state. This accounts for its very much higher % elongation at break in the direction of the tensile stress. The 7:3 monofilament was, to all intents and purposes, an "elastic fibre".

In the final part of this study, the *in vitro* biodegradation of the P(LLA-co-CL) 7:3 monofilaments in a pH 7.40 phosphate buffer at 37.0°C was investigated for a period of 11 weeks. The weight loss profile, compared with that of commercial MAXON sutures, was shown previously in Fig. 5.30 (page 159). The results showed that the P(LLA-co-CL) 7:3 monofilaments were indeed hydrolysable, at a comparable rate to MAXON, and therefore potentially biodegradable. Weight loss represents the diffusion out of the polymer matrix of low molecular weight hydrolysis products. A mechanistic view of the absorption process which takes place in a suture material is shown in Fig. 6.12.

The first step in any polymer biodegradation process in which hydrolysis is the dominant mechanism is the adsorption of water and wetting at the polymer surface. This is then followed by ester hydrolysis at the surface leading to the formation of micro-defects which facilitate the diffusion of water into the bulk interior of the polymer matrix. As water diffuses into the polymer's semi-crystalline matrix, as shown in Fig. 6.12, ester hydrolysis occurs preferentially in the amorphous regions where the chains are more loosely packed than in the highly-ordered crystalline regions. This can help to explain why the net remaining % crystallinity of the polymer usually increases slightly during the initial weight loss period. Fig. 6.13, shows how the heat of fusion, which is directly propotional to the % crystallinity, increases over the period of the biodegradation experiment.

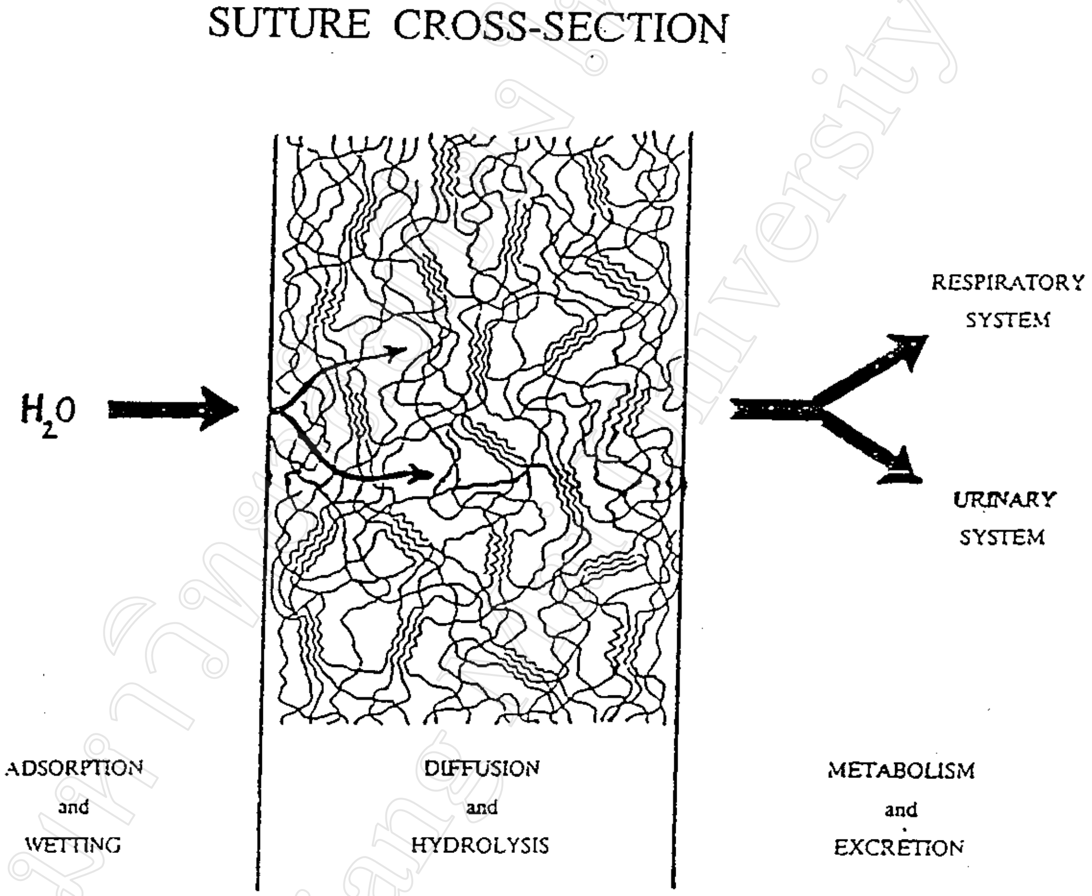


Fig. 6.12 The various physical, chemical and biological processes involved in suture absorption.

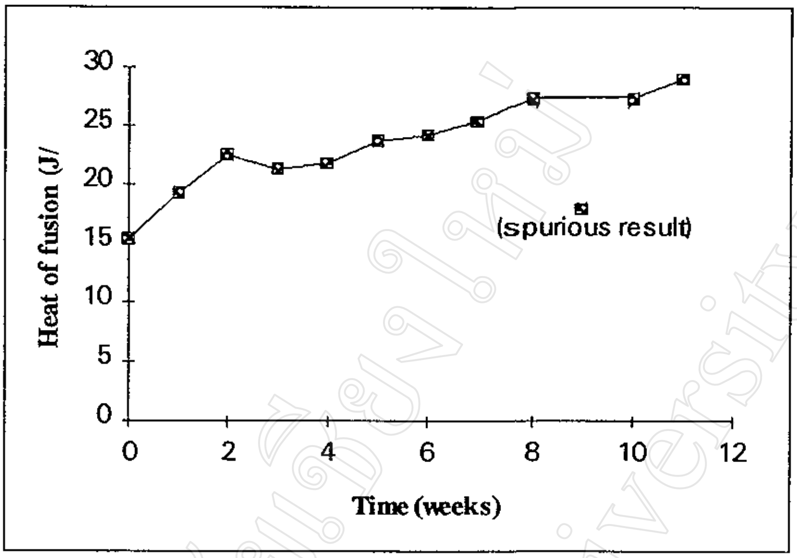


Fig. 6.13 Variation in the heats of fusion of the P(LLA-co-CL) 7:3 monofilaments during the period of the *in vitro* biodegradation experiment.

Finally, the pH of the phosphate buffer immersion medium was monitored throughout the period of the experiment. It was found that the initially adjusted pH 7.40 decreased with time. It is thought that this decrease in the pH was caused by the release into solution of water-solution acidic compounds formed as the products of the samples' hydrolysis breakdown.

In overall conclusion, monofilament production requires a large number of process steps as the monofilament properties are determined by many factors including: the type of polymer, how it melts in the extruder, the actual melt temperature, the design of the spinnerette, the spin-draw ratio, and the nature of the heated draw zone [5]. This project has looked at the effects of some of these factors and, by and large, they are now well understood. However, melt spinning is a complicated process, the key to which is to be able to know and control what the molecules in the polymer are doing at all stages of operation. The knowledge and experience gained from this project, although far from complete, have at least provided some useful guidelines for further improvements to be made to the overall process in future projects.

SUGGESTIONS FOR FURTHER WORK

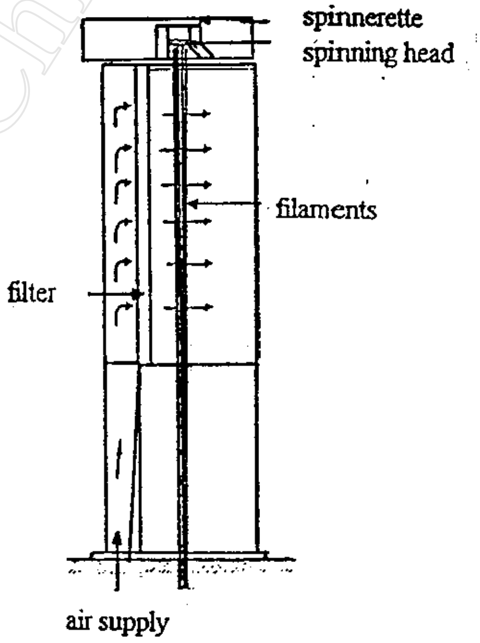
In continuation of the work described in this thesis, the following suggestions for further work are made:

1. For both polypropylene and poly(L-lactic acid-co-ε-caprolactone), P(LLA-co-CL), it is considered that higher quality monofilaments would be produced if the process were to be divided into two distinct stages:

STAGE 1: MELT SPINNING in which the main objective would be to produce low-orientation filaments of uniform diameter. No attempt would be made at spin-drawing. The extruded monofilament would simply be wound up at the same speed as the extrusion (ram) speed.

STAGE 2: OFF-LINE PROCESSING in which the semi-crystalline morphology would be gradually built into the monofilament through off-line processes such as annealing and hot drawing. The separation of this processing step from the melt spinning step would enable the polymer's morphology to be developed in a more controlled way in order to obtain the required balance of mechanical properties.

2. The use of a "thermal conditioning zone" (TCZ) just below the spinnerette is an aspect of the work which warrants further attention. Furthermore, rather than it being a heating zone, a possible refinement to the above melt spinning (STAGE 1) process, which would be especially useful for the slow cooling polypropylene, would be a quenching zone to accelerate the cooling of the threadline. An example of such a system is shown below [16]:



The quench air is fed into a box and then flows through a filter pack into the quenching chamber. For polypropylene, the quench air is frequently cooled to about 13 to 18°C because polypropylene filaments have a large heat content. The filaments are directed downward from the spinnerette and cooled. In order to achieve completely uniform quenching of the individual filaments, the quench air must not be turbulent.

3. In the case of the P(LLA-co-CL), the polymer should be pre-formed into a rod before melt spinning if possible. This would help to improve the polymer's melt rheology, in particular the homogeneity of the melt stream as it flows through the spinnerette. It would also help to decrease the amount of voids in the spun fibre. Its melt spinning temperature also seems to be quite critical, due to its relatively low melt viscosity, and therefore needs to be optimized very carefully.

4. A more complete physical and microstructural characterization of the polymers could be achieved by the utilization of other advanced analytical techniques such as X-ray diffraction. This would enable the % crystallinities to be determined directly and compared with the DSC heats of fusion.

5. In this project, the 11-week duration of the *in vitro* biodegradability study proved to be too short. The P(LLA-co-CL) copolymer exhibited an incomplete weight loss with about 80% still remaining. This timescale should be increased to 24 weeks to enable a more complete mass loss profile to be obtained.