CHAPTER 5

FIBRE PROCESSING AND TESTING OF THE P(LCG) TERPOLYMERS

In this part of the work, the knowledge and experience gained from the earlier polycaprolactone (PCL) melt spinning studies, as described in Chapter 3, was applied to the various polymers characterised in the previous Chapter 4. The same small-scale melt spinning apparatus was used, as described in Chapter 2, with batch sizes for pre-formed rod preparation being typically in the range of 15-20 g.

In this Chapter 5, attention is focussed especially on the P(LCG) 70 : 20 : 10 random and triblock terpolymers and on how their different chain microstructures affects their melt spinning and fibre properties. The P(LC) 80 : 20 random copolymer will be featured in the following Chapter 6 as the subject of a separate case study involving X-ray diffraction.

5.1 Processing Operation

5.1.1 Spinning Conditions

The most appropriate spinning temperature for each polymer sample was determined partly by reference to DSC and TG data and partly by trial and error. The processing conditions which were used for polymer rod preparation and fibre production were as given in Table 5.1. Of these conditions, the spinning temperature (T_{spin}) was the most critical variable since, for the given molecular weight of each sample, it was the sole determinant of the melt viscosity.

Table 5.1 Processing conditions used for melt spinning of the P(LCG) terpolymers.

Polymer	T_m (°C)	T_{rod} (°C)	T_{spin} (°C)	R.S. (mm min^{-1})	T.S. (m min^{-1})	OnLDR
P(LCG) random terpolymers (70 : 20 : 10)						
P(LCG) 1	109	60	150	2.0	0.6	5
P(LCG) 2	-	45	120	2.0	0.6	5
P(LCG) 3	-	45	130	2.0	0.6	5
P(LC) prepolymer (50 : 50)	-	50	130	2.0	0.6	5
P(LCG) triblock (70 : 20 : 10)	130	110	160	2.0	0.6	5

where

T_m = melting (peak) temperature (°C) from DSC curve
T_{rod} = temperature of polymer rod preparation (°C)
T_{spin} = temperature of melt spinning (°C)
R.S. = ram (piston) speed (mm min^{-1})
T.S. = take-up speed (m min^{-1})
OnLDR = on-line draw ratio

Fixed Conditions

spinnerette diameter = 2 mm (single hole)
air gap = 4 mm
cooling bath temperature = 5-10°C
stainless steel wire mesh = 2 x 300 mesh discs

As in the case of PCL previously, slow spinning speeds were again employed with the emphasis on producing fibres of uniform diameter with a minimum of molecular orientation and/or stress-induced crystallisation. This was so that the oriented semi-crystalline morphology could be built into the fibres in subsequent off-line drawing and annealing steps. Although slow spinning speeds facilitate heat remove, they can also give rise to an oscillatory instability known as ***draw resonance***. This effect was not observed with PCL previously but it was observed here to some extent in the case of the P(LCG) random terpolymers, seemingly as the molecular weight increased. Draw resonance manifests itself as small blobs of the polymer occurring in the filament line at regularly spaced intervals. As mentioned previously in Chapter 3, it's cause can be traced back to the tensile stress to which the extruded fibre subjected as it is pulled from the spinnerette. It is interesting to note here that while draw resonance occurred with the random terpolymers, it did not occur with the triblock terpolymer. This demonstrates how different chain microstructures, leading to different melt rheologies, give rise to different processing characteristics. Understanding these interdependencies at the molecular level represents a complex problem which is beyond the scope of this project. However, it must be considered a logical extension of it for future work.

The as-spun fibre diameters are compared in Table 5.2. Generally, the triblock terpolymer gave slightly larger diameter fibres of more uniform diameter than the random terpolymers. The random terpolymer fibre diameters are those of the uniform lengths of the fibre, not including any instances of draw resonance.

Table 5.2 Fibre diameters and on-line draw ratios of the as-spun terpolymer fibres.

As-spun Polymer Fibre	Fibre Diameter* (mm)	OnLDR**
P(LCG) random terpolymers (70 : 20 : 10)		
P(LCG) 1	0.76 ± 0.06	5
P(LCG) 2	0.64 ± 0.05	5
P(LCG) 3	0.75 ± 0.03	5
P(LC) prepolymer (50 : 50)	0.63 ± 0.06	5
P(LCG) triblock (70 : 20 : 10)	0.82 ± 0.02	5

* average of 10 readings taken with a digital micrometer

** OnLDR = on-line draw ratio = take up rate ÷ extrusion rate

5.1.2 Off-line Hot-Drawing

Off-line hot-drawing of the as-spun fibres was carried out as a means of increasing the degree of chain orientation within the polymer fibre, thereby strengthening the fibres in the direction of draw. The process utilized three main components: the initial feed unit, the intermediate hot-drawing unit, and the final take-up unit. Their arrangement is shown in Fig. 5.1. The off-line draw ratio (OffLDR) was controlled by the ratio of the final take-up speed to the initial feed speed.

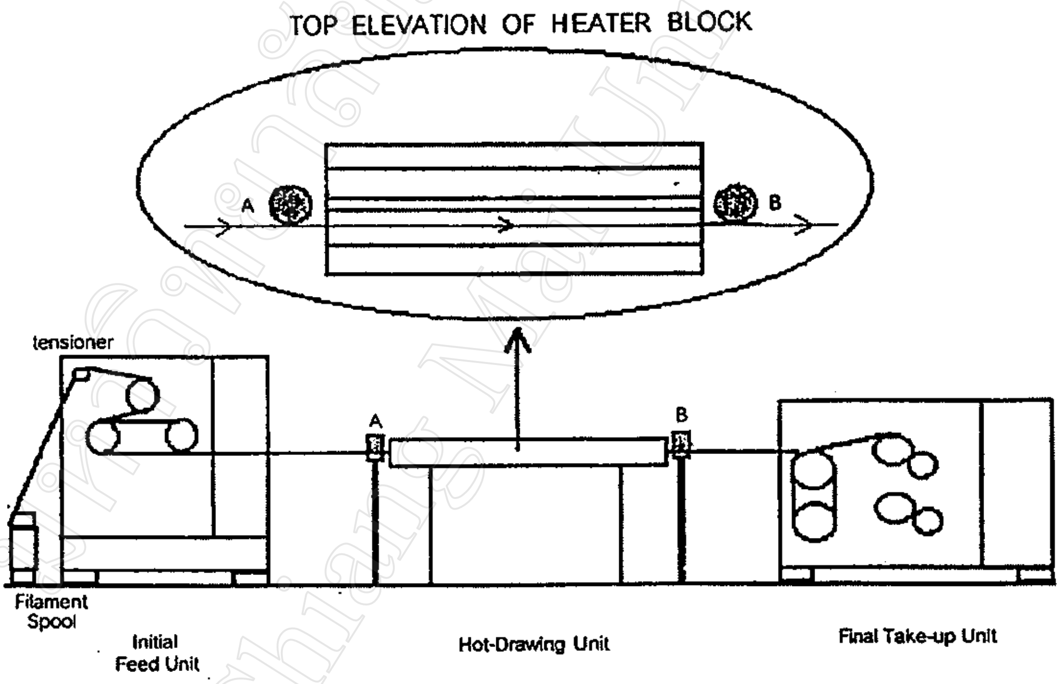


Fig. 5.1 Schematic arrangement used for off-line hot-drawing.
(A and B = filament guides)

The procedure used for off-line hot-drawing was as follows. While the temperature of the hot-drawing unit was stabilizing, the feed speed was set at 0.5 m min^{-1} and the take-up speed set to give a draw ratio of between 5-10. The filament was then led to the tensioner, passed over the top roll (clockwise) and wrapped 2 times around the lower 2 rolls of the initial feed unit in an anti-clockwise direction. Two stands, each with a ceramic grooved guide at the top, were placed at A and B (Fig. 5.1) to guide the filament through the hot-drawing unit. Finally, the filament from the hot-drawing unit was led to the final take-up unit by wrapping it 2 times around the thread-advancing roller in a clockwise direction and then onto the take-up spool.

The conditions used in this hot-drawing process (temperature, initial feed and final take-up speeds) were as shown in Table 5.3. The hot-drawing temperature (T_{draw}) was chosen as the temperature at which the fibre just started to soften without becoming too elastic. At the same time, the combination of the feed and take-up speeds was chosen to balance the two considerations of (1) a throughput speed slow enough to give a reasonable residence time inside the hot-drawing unit, and (2) a draw ratio which it was thought would be high enough to have a significant effect on the molecular orientation of the fibre without causing it to break.

Table 5.3 Conditions used in the off-line hot-drawing of the P(LCG) terpolymer fibres.

As-spun Fibres	T_{draw} (°C)	Feed Speed (m min^{-1})	Take-up Speed (m min^{-1})	Draw Ratio (OffLDR)
P(LCG) random terpolymers				
P(LCG) 1	50	0.5	2.5	5
P(LCG) 2	50	0.5	4.5	9
P(LCG) 3	50	0.5	4.0	8
P(LCG) triblock terpolymer	75	0.5	4.0	8

5.1.3 Annealing

Annealing is a post-spinning process designed to increase the polymer's % crystallinity by heating the fibre at a temperature intermediate between its T_g and T_m. In doing so, molecular motion is encouraged which can lead to segmental alignment and crystallisation.

The fibres which had previously been hot-drawn were wound up on bobbins and annealed in a vacuum oven at constant temperature for the periods of time shown in Tale 5.4. The ends of the fibre were fixed on the bobbin, thus preventing any shrinkage during annealing due to crystallisation. The rationale behind this annealing process is that it will build upon the molecular orientation introduced by the previous hot-drawing process by giving the aligned chains more time to arrange themselves into highly ordered crystalline regions. Crystallisation is often seen as the reverse of melting and is a time-dependent thermodynamic process which requires precise conditions in order to occur. It has profound effects on fibre properties, as will be seen in the following sections of this chapter.

Table 5.4 Annealing conditions used for the terpolymer fibres following hot-drawing.

Hot-drawn Fibres	Temperature (°C)	Time (hours)
P(LCG) random terpolymers		
P(LCG) 1	40	8
P(LCG) 2	50	24
P(LCG) 3	50	24
P(LCG) triblock terpolymer	75	6

5.2 Fibre Morphology

5.2.1 As-spun Morphology

As explained previously, the spinning conditions employed here (slow speeds, fast cooling, minimal on-line drawing) were specifically designed to produce as-spun fibres with as little molecular orientation and crystallinity as possible. This was so that the oriented semi-crystalline morphology, necessary to give the desired mechanical properties, could be developed in a more controlled way through subsequent off-line hot-drawing and annealing steps. Also, by separating the fibre production process into separate stages, it enabled the changes in fibre morphology to be followed more closely and the processing conditions adjusted accordingly.

This methodology was greatly facilitated by the fact that all of the P(LCG) terpolymers studied here were slow-crystallising materials which meant that their as-spun fibres could be easily produced in an amorphous state. Indeed, even poly(L-lactide), PL, homopolymer is slow-crystallising, unlike the PCL homopolymer previously in Chapter 3. This can be clearly seen from the DSC curve of the PL as-spun fibre in Fig. 5.2. The fact that the crystallisation exotherm from 90-100°C is almost as large as the melting endotherm from 160-180°C indicates that the as-spun fibre was in an almost completely amorphous state but which could be easily transformed into a semi-crystalline state by slow re-heating. The heat of melting, ΔH_m, of 55.6 J g^{-1} in Fig. 5.2 corresponds to a % crystallisation of the PL fibre of about 60%.

Consequently, on the basis of this PL evidence, it could be safely assumed that the P(LCG) terpolymers could also be easily spun as amorphous fibres since, because of their structural irregularity, they would be even slower to crystallise from the melt than PL. The validity of this assumption is confirmed by the DSC curves of the P(LCG) as-spun fibres in Figs. 5.3-5.6. None of the as-spun fibres show any signs of crystallisation or melting in their DSC curves, indicating that they are not only amorphous but are also unable to crystallise on slow re-heating, unlike PL. This is undoubtedly due to their high degree of structural irregularity making it more difficult for their chain segments to crystallise.

5.2.2 Effects of Hot-drawing and Annealing

After the as-spun fibres have been hot-drawn and annealed, their DSC curves do show melting peaks. The fact that the peaks are relatively small and broad tells us that the fibres % crystallinities are still low and that there is a wide distribution of crystal sizes. However, the fact that they can crystallise at all is vitally important as far as their properties are concerned. From the DSC curves in Figs. 5.3-5.6 and the results in Table 5.5, the following points are worth noting:

(1) There are significant differences between the T_m and ΔH_m values of the P(LCG) 1, 2 and 3 terpolymers even though their compositions are very similar (≈ 70:20:10). These differences may come from the terpolymers different monomer sequence distributions which result from their different conditions of synthesis. Since the monomer sequencing is transferred into the crystal, this may explain the different T_m and ΔH_m values.

(2) The P(LCG) triblock terpolymer exhibits the highest T_m and the most well-defined peak. This is to be expected since the terpolymer is structurally designed in such a way that its two P(LG) side blocks are the crystallisable components. Since these side blocks are relatively rich in L units (L:G = 92.6 : 7.4) and do not contain any flexibilizing C units at all, it is not surprising that they have a much higher T_m than the random terpolymers.

(3) In Fig. 5.5 (middle), it is worth noting that annealing alone can induce crystallisation. However, it is more effective when combined with molecular orientation from hot-drawing. Chain alignment along the fibre axis facilitates crystallisation by arranging

the chains in such a way that less energy is required to bring chain segments in close enough proximity to crystallise. Thus, sequential hot-drawing and annealing is an effective means of tailoring a fibre's semi-crystalline morphology to meet the specific requirements of a given application.

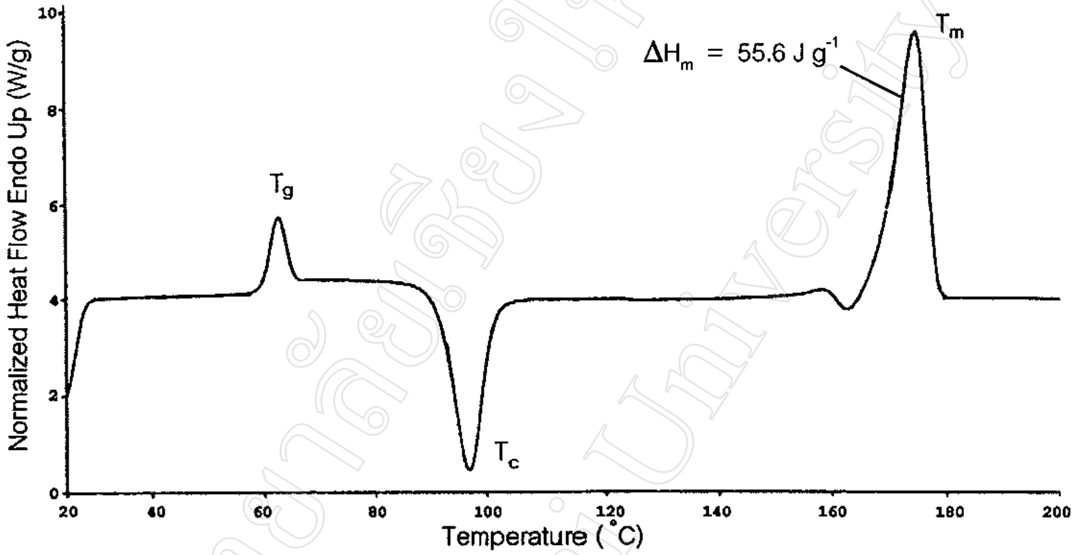


Fig. 5.2 DSC thermogram (heating) of the poly(L-lactide), PL, as-spun fibre.

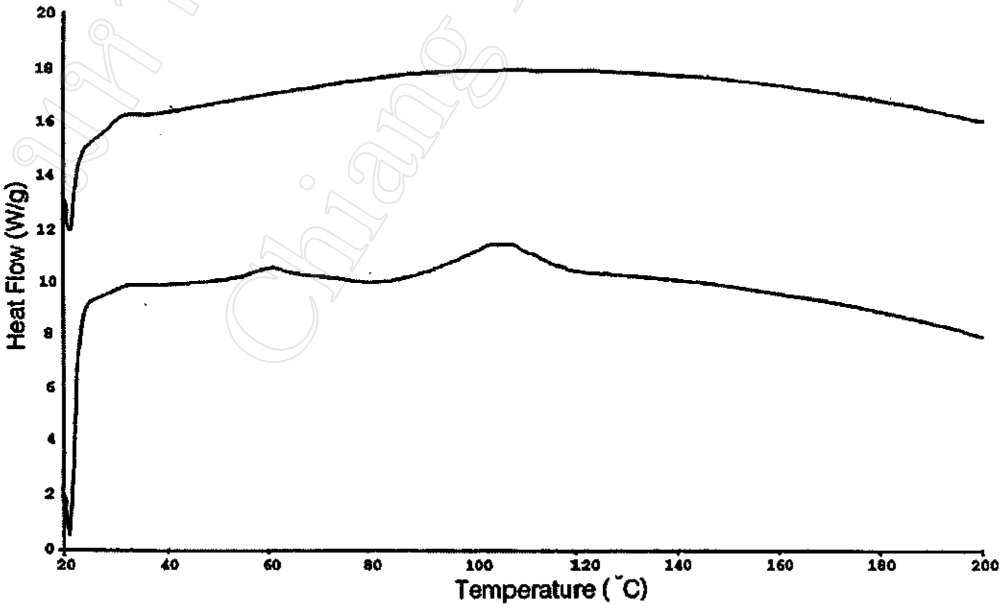


Fig. 5.3 DSC thermograms (heating) of the as-spun (above) and hot-drawn +annealed (below) P(LCG)1 random terpolymer fibres.

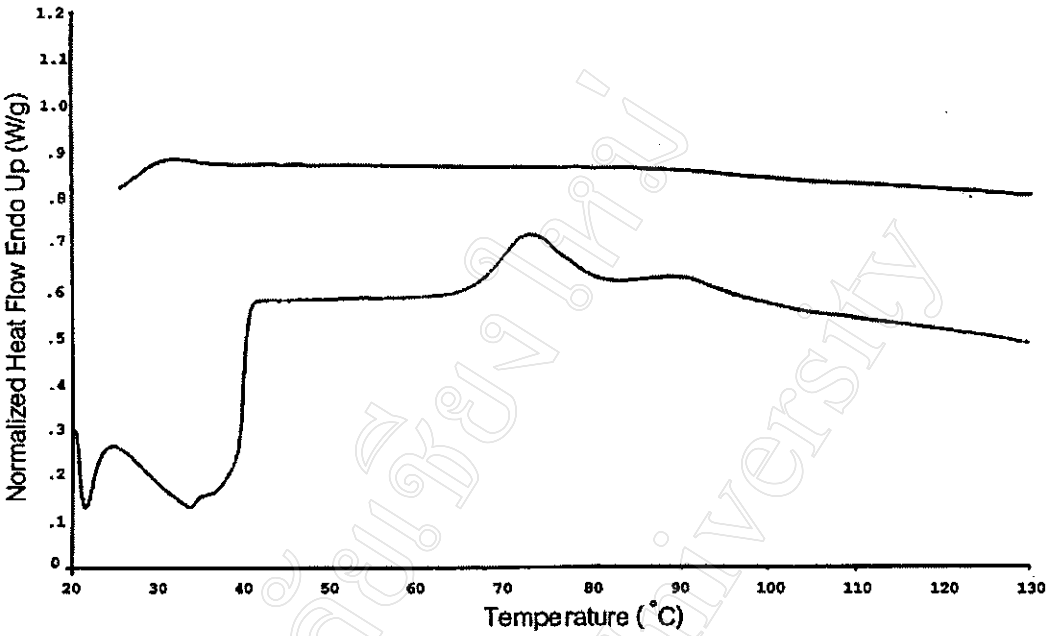


Fig. 5.4 DSC thermograms (heating) of the as-spun (above) and hot-drawn +annealed (below) P(LCG)2 random terpolymer fibres.

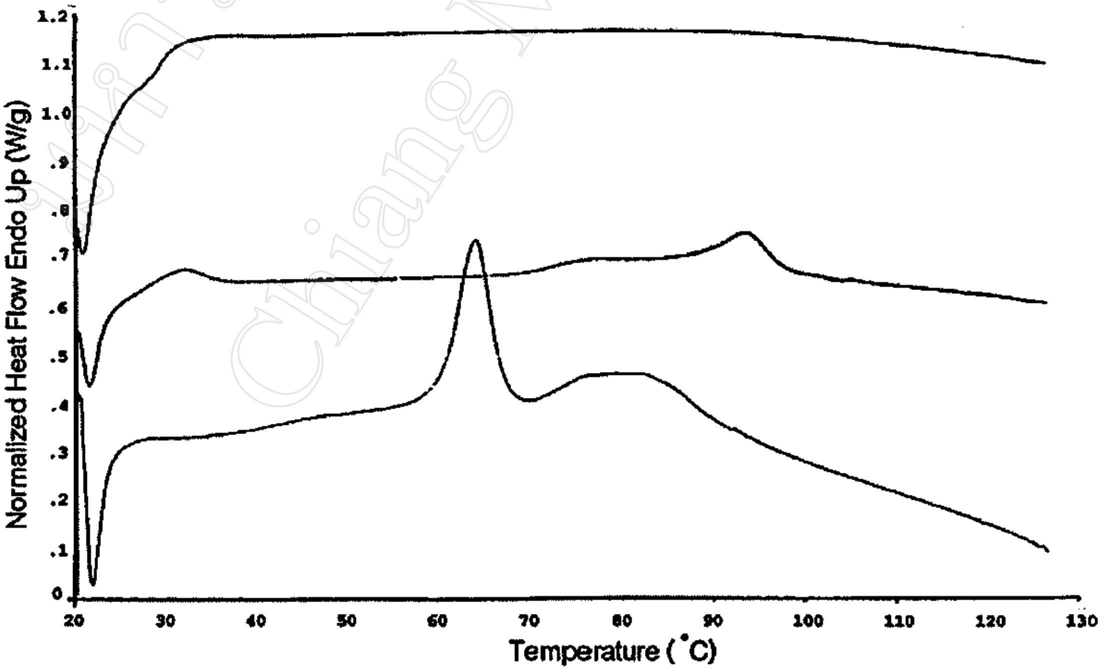


Fig. 5.5 DSC thermograms (heating) of the as-spun (above), annealed (middle) and hot-drawn +annealed (below) P(LCG)3 random terpolymer fibres.

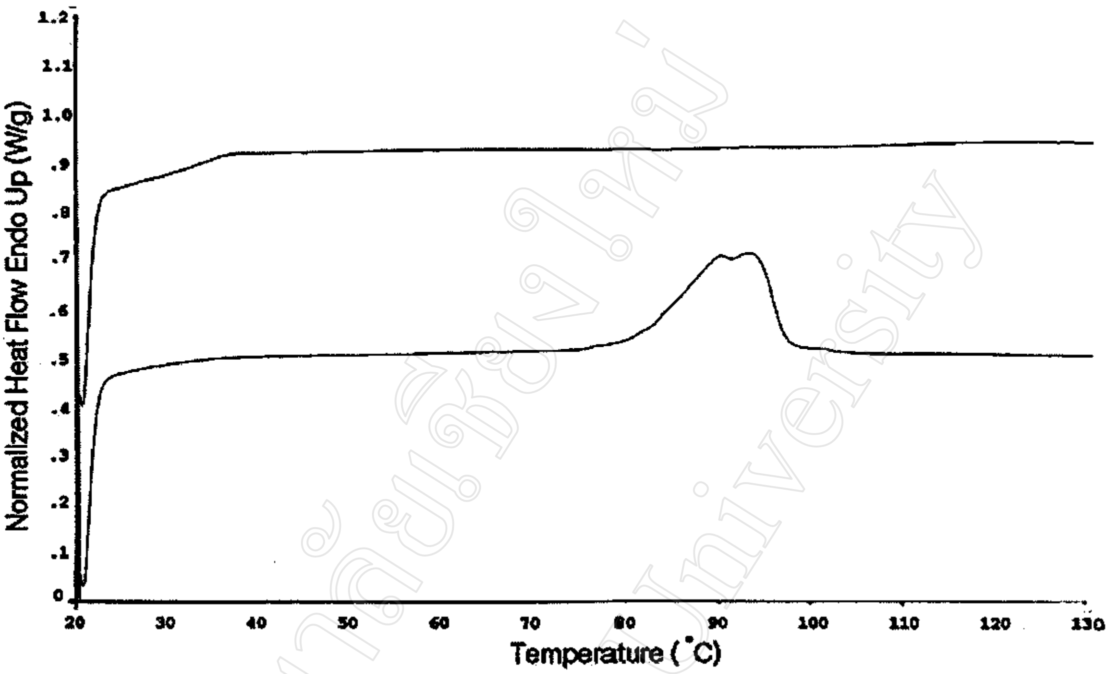


Fig. 5.6 DSC thermograms (heating) of the as-spun (above) and hot-drawn +annealed (below) P(LCG) triblock terpolymer fibres.

Table 5.5 DSC melting temperatures, T_m, and heats of melting, ΔH_m, for the polymer fibres at various stages of processing.

Fibre Processing Stage		T_m* (°C)	ΔH_m** (J g^{-1})
Poly(L-lactide) : as-spun		175	55.6
P(LCG) 1 random terpolymer : as-spun		-	-
	hot-drawn + annealed	107	18.9
P(LCG) 2 random terpolymer : as-spun		-	-
	hot-drawn + annealed	73	9.9
P(LCG) 3 random terpolymer : as-spun		-	-

Fibre Processing Stage	T_m* (°C)	ΔH_m** (J g^{-1})
annealed	96	13.6
hot-drawn + annealed	74	24.0
P(LCG) triblock terpolymer : as-spun	-	-
hot-drawn + annealed	139	16.6

* T_m = melting point, taken as the peak temperature of the main melting range

** ΔH_m = heat of melting $\propto$ % crystallinity

5.3 Fibre Testing - Mechanical Properties

5.3.1 Test Parameters and Conditions

The mechanical properties of a monofilament fibre are of fundamental interest because the fibre must possess sufficient strength to withstand processing by available machinery and provide the desired durability in its end-use. In this study, mechanical properties such as tensile strength, % elongation at break, and Young's (tensile) modulus were determined with the Lloyds LRX+ Universal Mechanical Testing Machine and the results correlated as far as possible with the fibre morphology, as described in the previous section.

Examples of the mechanical test results in the form of stress-extension curves are shown in Figs. 5.7-5.11 and the derived property values compared in Table 5.6. Each fibre sample was tested at least 5 times and the results averaged to give the values in Table 5.6. A minimum of 3 of the most similar curves were chosen for averaging. The test conditions employed were:

Initial gauge length = 40 mm
Cross-head speed = 20 mm/min
Load cell = 100 N
Grips = bollard-type
Temperature/humidity = ambient (25-30°C/50-70 % r.h.)
Data acquisition = stress-extension curves

5.3.2 Main Conclusions

From the results in Fig. 5.7-5.11 and the derived property values compared in Table 5.6, the main conclusions which can be drawn are as follows:

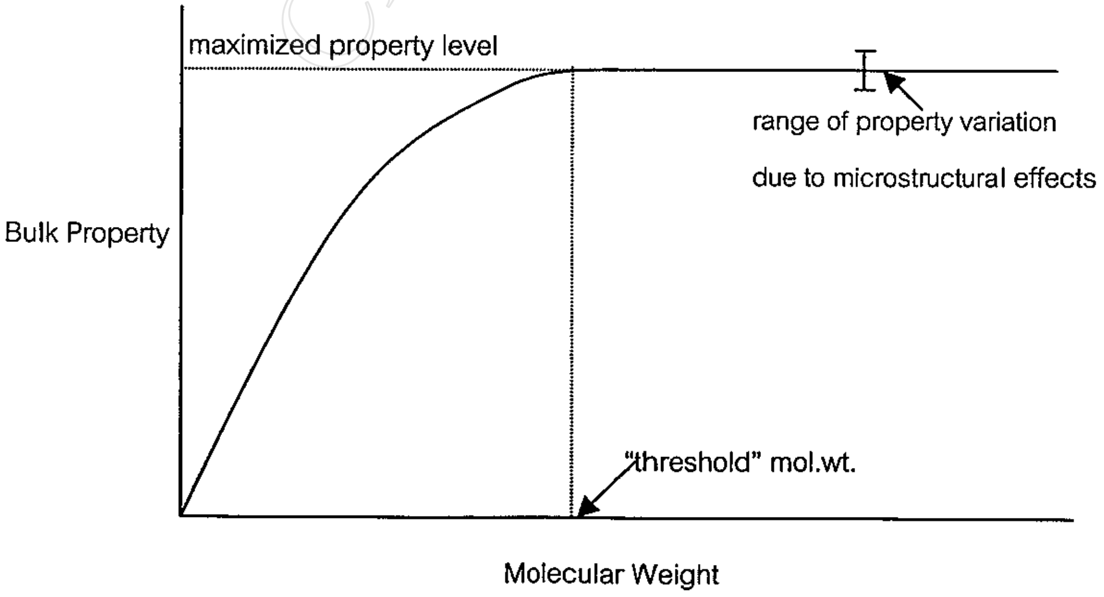
(1) Poly(L-lactide), PL, homopolymer is a hard and brittle fibre, as its stress-extension curves in Fig. 5.7 show. Its low elongation at break (6.2%, Table 5.6) is a consequence of the fact that PL is in its glassy state ($T_g \approx 65^{\circ}C$) at room temperature. This is the main reason why PL by itself is unsuitable for use as an absorbable surgical suture. PL fibres are too stiff and springy for this type of application which is why they need to be flexibilized with modifiying comonomers such as ε-caprolactone.

(2) All of the as-spun P(LCG) random and triblock terpolymer fibres are characterised by low tensile strength, high elongation at break, and low modulus. Basically, they are just weak elastic fibres with a minimum amount (if any) of molecular orientation and crystallinity. Indeed, they were so extensible that they did not reach breaking point within the limit of extension (700 mm, i.e., 1750% elongation) of the instrument. As explained previously, these as-spun fibres were merely intended to be precursors into which the semi-crystalline morphology would be built via subsequent off-line drawing and annealing steps. Comparison of the stress-extension curves of the as-spun and processed fibres

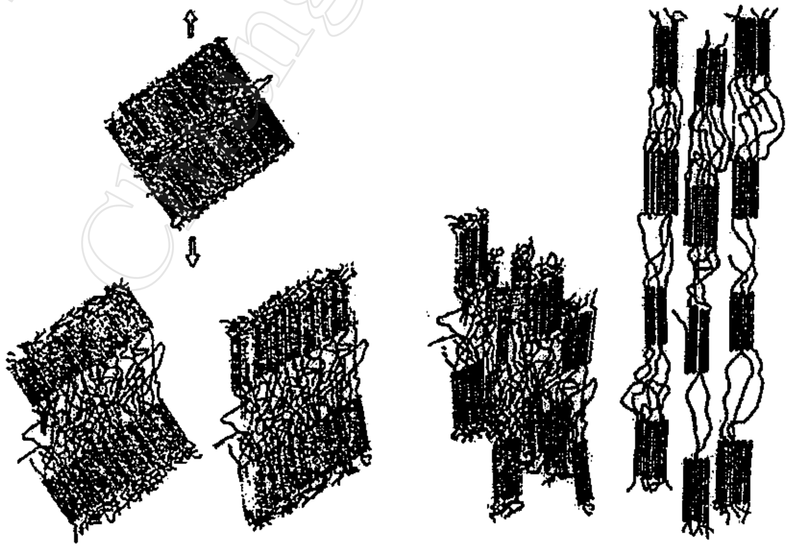
in Figs. 5.7-5.11 enables us to observe, albeit indirectly, to what extent this structure development had been achieved.

(3) The mechanical properties of the terpolymer fibres changed dramatically as a result of hot-drawing and annealing. In all cases, there were large increases in stress at break (tensile strength), decreases in elongation at break, and increases in initial modulus (Table 5.6). These changes were brought about by the development of an oriented semi-crystalline morphology in the fibres and are consistent with the previous DSC data. Again, as shown in Fig. 5.10, annealing alone has as effect but not as much as in combination with hot-drawing. Clearly, both molecular orientation and crystallinity are essential for a fibre's maximum level of mechanical properties to be attained. Thus, the results presented here confirm that the as-spun P(LCG) fibres can indeed be improved off-line as had been planned. To what extent they can be improved further requires more detailed studies of the drawing and annealing variables.

(4) When comparing the P(LCG) 1, 2 and 3 random terpolymer fibres, it appears that P(LCG) 1 is the weakest, presumably because it showed the greatest tendency for draw resonance. In addition, mechanical strength is strongly dependent on molecular weight up to a certain "threshold" level. It is quite possible that the P(LCG) random terpolymers synthesized here may have molecular weights which are still below this threshold level.



(5) When comparing the P(LCG) random and triblock terpolymer fibres, it is clear that the triblock fibres are both stiffer (higher modulus) and stronger (higher stress at break). This is undoubtedly due to their easily crystallisable side-blocks. Their melt rheology also seemed to be better, giving better spinnability with no apparent tendency for draw resonance. Their tensile strengths of around 150-200 MPa (see Fig. 5.11) are approaching those of commercial absorbable sutures such as "PDS" and "Maxon". It should also be noted in Fig. 5.11 (lower) that the stress-extension curves for the triblock fibres show 2 distinct ranges: (a) a short range of initial high slope (modulus) followed by (b) a much longer range of lower slope which extends up to the breaking point. The point at which the slope changes obviously corresponds to some significant event occurring in the polymer matrix during extension. It does not appear to be a "yield point" in the normal sense of the term but probably is associated with some form of molecular slippage. For example, it could be the point at which the microfibrillar structure from hot-drawing and annealing, having been initially deformed, is then forced to rearrange itself in order to be able to respond to the continuing applied stress. This suggestion is visualized in the diagram below.



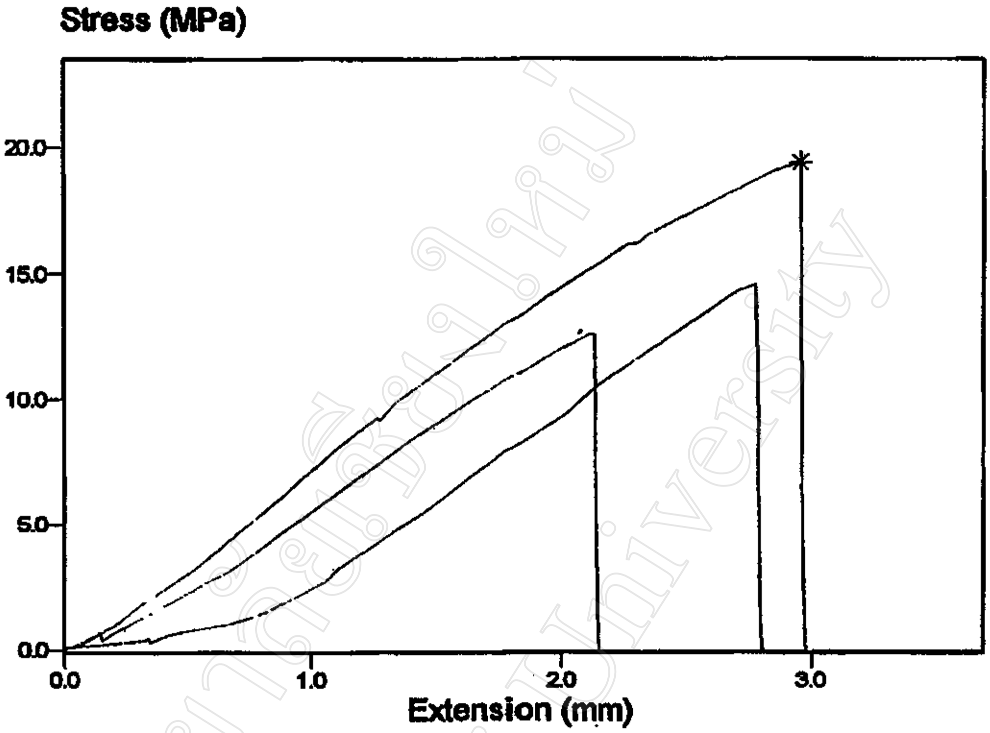


Fig. 5.7 Stress-extension curves of the poly(L-lactide) as-spun fibres.

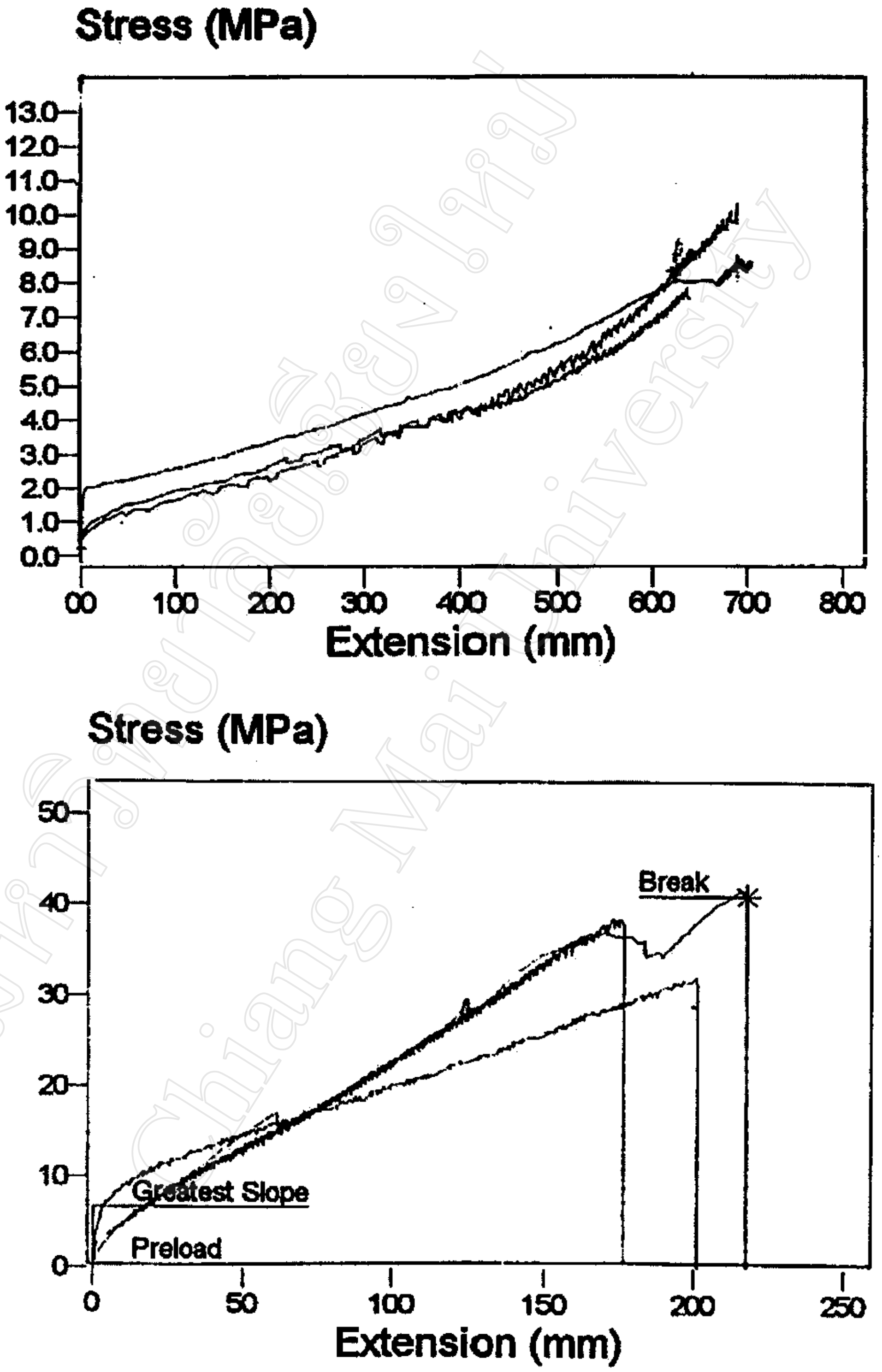


Fig. 5.8 Stress-extension curves of the P(LCG)1 random terpolymer as-spun (above) and hot-drawn + annealed (below) fibres.

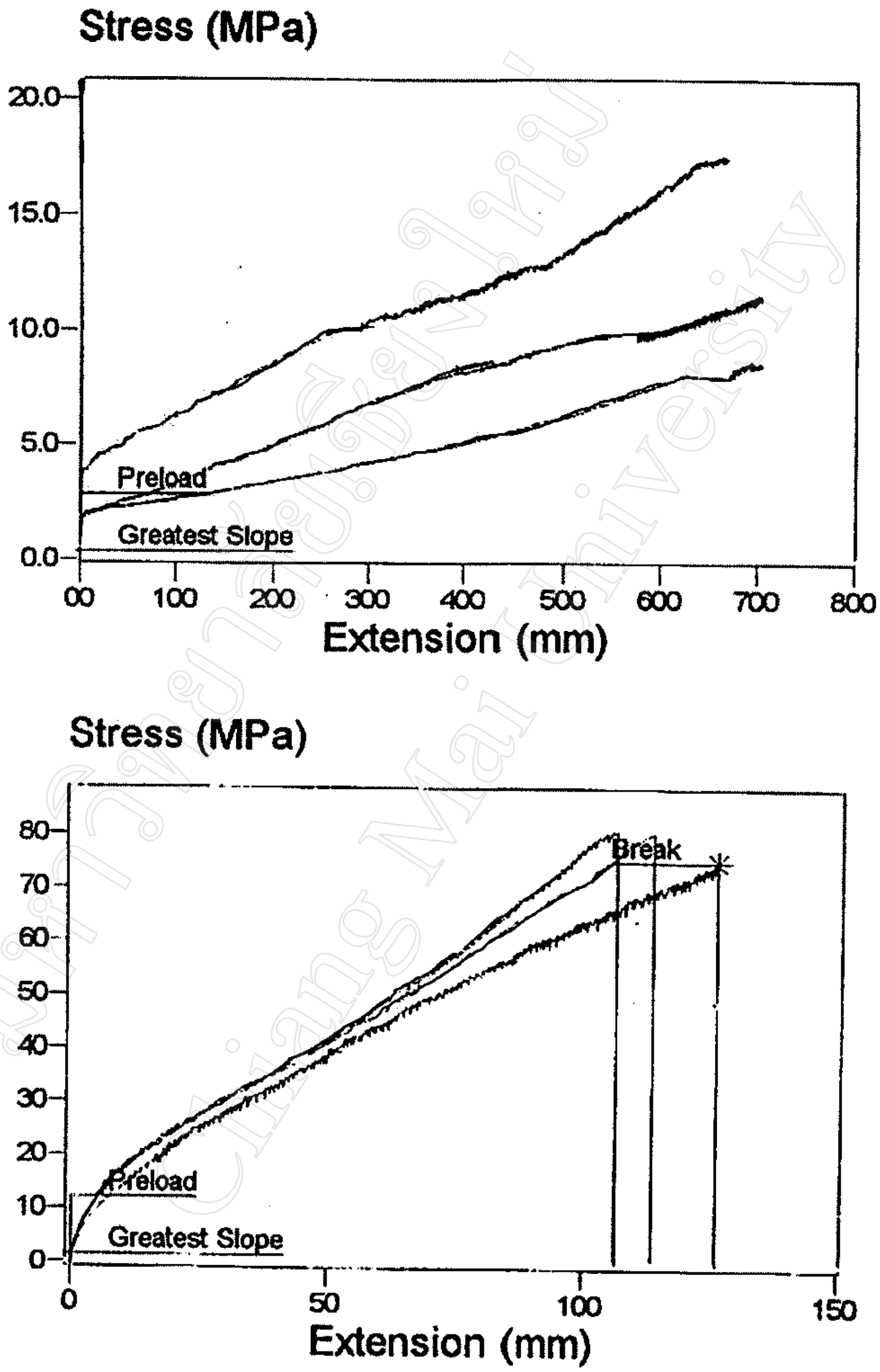


Fig. 5.9 Stress-extension curves of the P(LCG)2 random terpolymer as-spun (above) and hot-drawn + annealed (below) fibres.

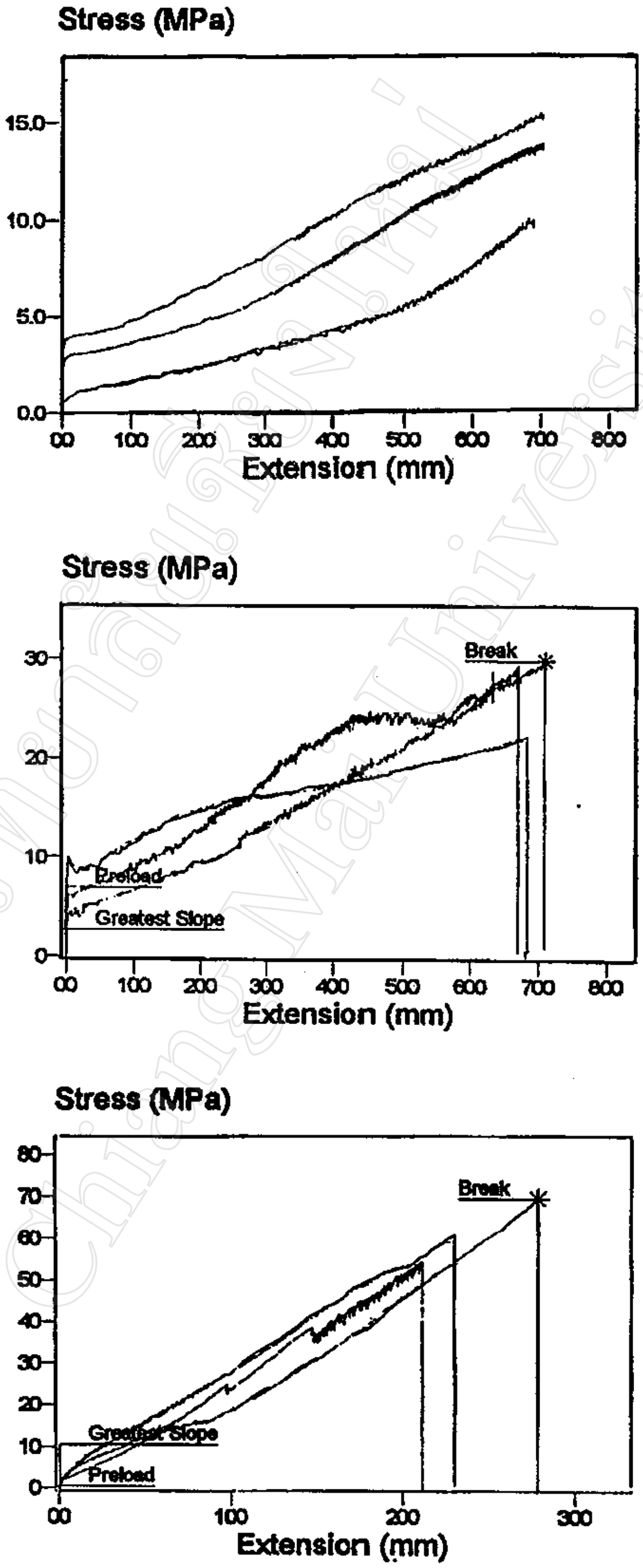
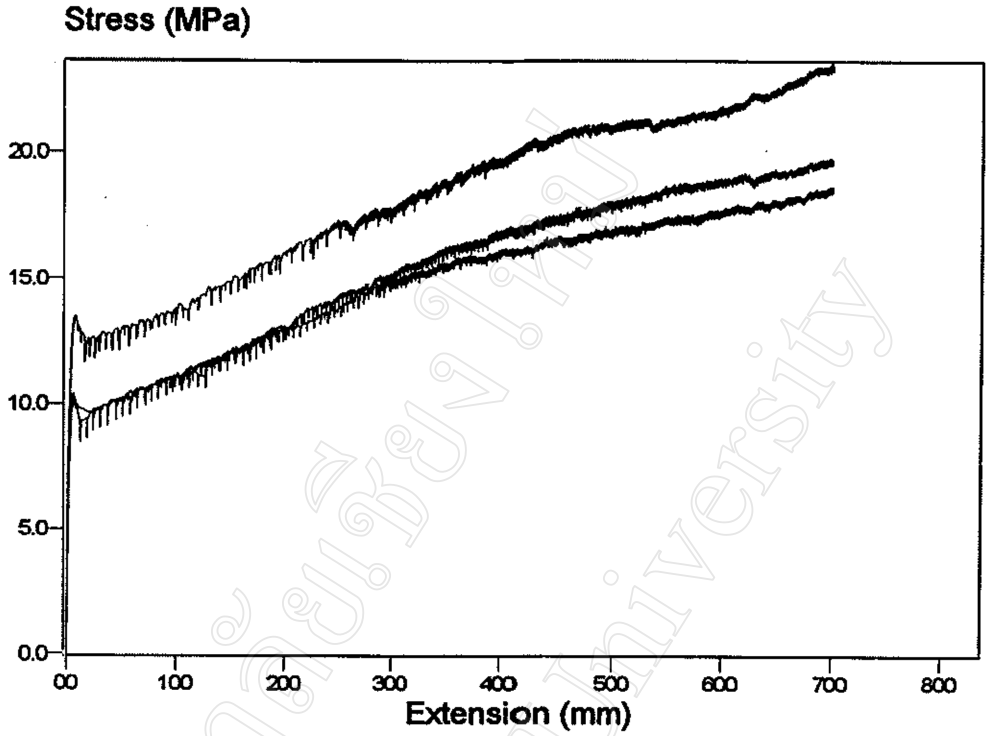


Fig. 5.10 Stress-extension curves of the P(LCG)3 random terpolymer as-spun (top) annealed (middle) and hot-drawn + annealed (bottom) fibres.



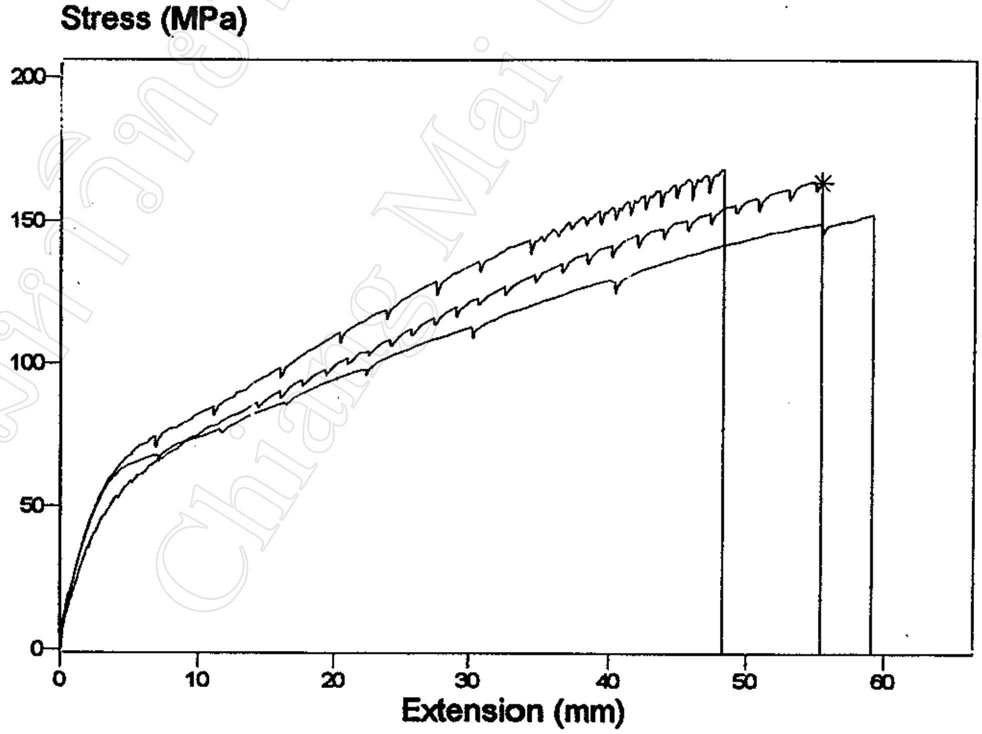


Fig. 5.11 Stress-extension curves of the P(LCG) triblock terpolymer as-spun (above) and hot-drawn + annealed (below) fibres.

Table 5.6 Comparison of the mechanical properties of the PL homopolymer and P (LCG) random and triblock terpolymer fibres.

Fibre Sample*	Average Diameter (mm)	Stress** at Break (MPa)	Elongation** at Break (%)	Young's Modulus** (Initial) (MPa)
Poly(L-lactide): as-spun	0.66	15.5	6.2	328.1
P(LCG) random terpolymers (70:20:10)				
P(LCG)1				
as-spun	0.76	ID	ID	116.8
hot-drawn + annealed	0.48	34.8	471.5	453.2
P(LCG)2				
as-spun	0.64	ID	ID	94.6
hot-drawn + annealed	0.40	83.5	237.2	668.5
P(LCG)3				
as-spun	0.75	ID	ID	35.6
annealed	0.72	27.1	1718.6	215.4
hot-drawn + annealed	0.60	66.7	536.2	465.8
P(LCG) triblock terpolymer (70 : 20 : 10)				
as-spun	0.82	ID	ID	284.1
hot-drawn + annealed	0.31	161.2	135.6	1461.5

* hot-drawing and annealing conditions as described in Tables 5.3 and 5.4

** average values of the most similar 3 readings from 5 tests

ID = indeterminate, sample did not break within the maximum limit of extension of the instrument.