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APPENDIX

Supporting Papers

CONFERENCE PRESENTATIONS

in

THE POLYMER PROCESSING SOCIETY (PPS)
ASIA / AUSTRALIA REGIONAL MEETING 1999

on

Innovation in Polymer Processing

held at

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THE POLYMER PROCESSING SOCIETY (PPS)
ASIA/AUSTRALIA REGIONAL MEETING 1999

PROCEEDINGS

INNOVATION IN POLYMER PROCESSING

In memory of Professor Morand Lambla
President of PPS 1995-97

Marriott Royal Garden Riverside Hotel
Bangkok, Thailand

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CONTROL OF POLYMER MORPHOLOGY DURING THE SMALL-SCALE MELT SPINNING OF MONOFILAMENT FIBRES

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INTRODUCTION

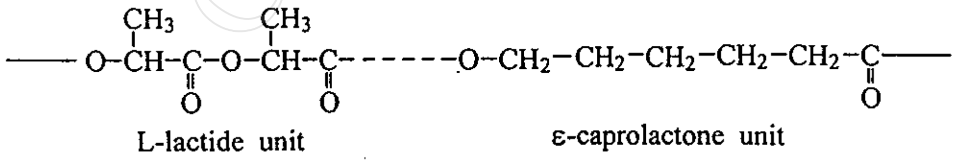
Nowadays, the production of synthetic polymer fibres for use in specialized applications has developed into an advanced technology all of its own. Because of their unique dimensions, fibres tend to be especially sensitive in their properties to subtle changes in their molecular structure. Therefore, it follows that, in order to be able to produce fibres with the required balance of properties for a particular application, it is necessary to be able to control the polymer's:

(a) ***chemical microstructure*** and ***molecular weight*** during the ***synthesis*** stage, and
(b) ***molecular orientation*** and ***semi-crystalline morphology*** during the ***processing*** stage

This paper describes some of the work currently in progress in Chiang Mai's **Biomedical Polymers Research Unit** on ***monofilament fibres*** for potential use as ***absorbable surgical sutures.*** In particular, the ways in which the polymer's morphology can be controlled during processing are discussed. By developing an understanding of how this can be done, it enables us to optimize the processing conditions in order to control the morphology and, hence, impart the required properties to the final product.

MATERIALS AND APPARATUS

An example of the type of polymer studied in this work is **poly(L-lactide-co-ε-caprolactone)**, a biodegradable copolyester consisting of a random sequence of L-lactide and ε-caprolactone units in an approximately 80:20 mole ratio. Number-average molecular weights were typically of the order of $\overline{M}_n = 30{,}000 - 50{,}000$.



$$-O-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\underset{\overset{\|}{O}}{C}-O-\overset{CH_3}{\overset{|}{CH}}-\underset{\overset{\|}{O}}{C}\text{------}O-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\overset{\|}{O}}{C}-$$

poly(L-lactide-co-ε-caprolactone), P(LL-co-CL)

The processing equipment used was a small-scale melt spinning apparatus which could handle batch sizes of as small as 4-5 g. A schematic diagram of the apparatus is shown in Fig. 1 overleaf.

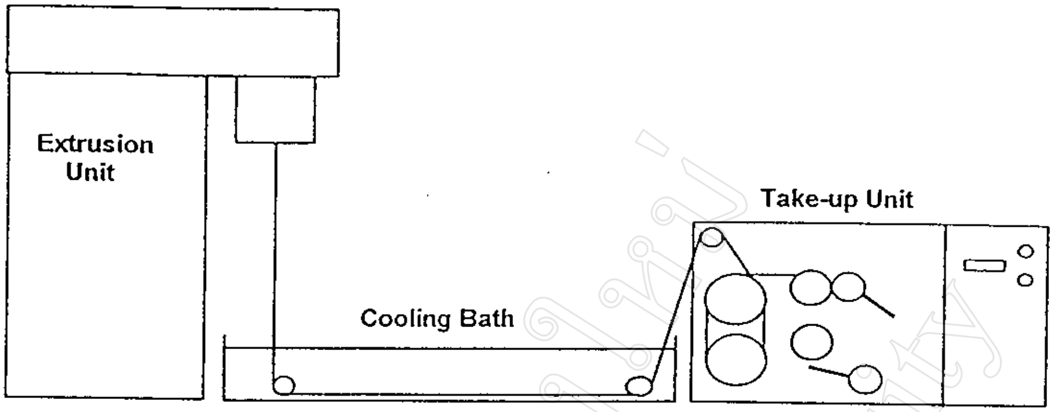


Fig. 1 Schematic diagram of the small-scale melt spinning apparatus.

PROCESSING CONDITIONS

The ***processing temperature*** used for melt spinning was carefully chosen with respect to the copolymer's melting range and thermal degradation temperature. The melting range was determined by differential scanning calorimetry (DSC) as being approximately 125-155°C, while the thermal degradation (initial weight loss) temperature was in the region of 230°C. Consequently, a processing temperature of 175°C was chosen, being sufficiently high to ensure complete melting of the copolymer, yet low enough to avoid or, at least, minimize the possibility of thermal degradation, in particular, transesterification. Residence times were therefore kept as short as possible.

Using the arrangement shown in Fig. 1 above, batch sizes of typically 5 g were extruded through single-hole spinnerettes to give monofilament fibres of the required diameter. The extruded fibre was cooled quickly, first by contact with the cool room air and then by passing through an ice-water bath. Finally, the fibre was wound up ***without drawing*** at a take-up speed matched with the extrusion rate. The purpose of this was to obtain ***undrawn*** and, therefore, ***unoriented*** fibres of controlled diameter. This then enabled the required ***molecular orientation*** and ***semi-crystalline morphology*** to be gradually built into the fibre in subsequent off-line ***annealing*** and ***hot-drawing*** steps. In this way, the ***spinning*** and ***conditioning*** steps were separated into a 2-stage process which allowed the development of the fibre's semi-crystalline morphology to be controlled more easily.

FIBRE MORPHOLOGY

As shown in Fig. 2 overleaf, the P(LL-co-CL) copolymer, following its synthesis and purification, i.e., **before** spinning, was a ***semi-crystalline*** material with a well-defined DSC melting peak. It is interesting to compare this with the DSC curve of the ***undrawn as-spun fibre***. After spinning, the DSC curve shows an additional exothermic ***crystallisation peak*** prior to and of similar size to the melting peak, a clear indication that the copolymer is in its so-called ***quenched amorphous state*** .

The obvious conclusion to be drawn from this is that, during the melt spinning process, the extruded fibre was cooled quickly at a rate which was too fast for crystallisation from the melt to occur. Thus, the as-spun fibre was amorphous. However, when re-heated slowly in the DSC, it could crystallise. This effect can be turned to good use in fibre processing since it allows the semi-crystalline morphology to be gradually built into the as-spun fibre in subsequent ***annealing*** and ***hot drawing*** steps at the appropriate temperatures.

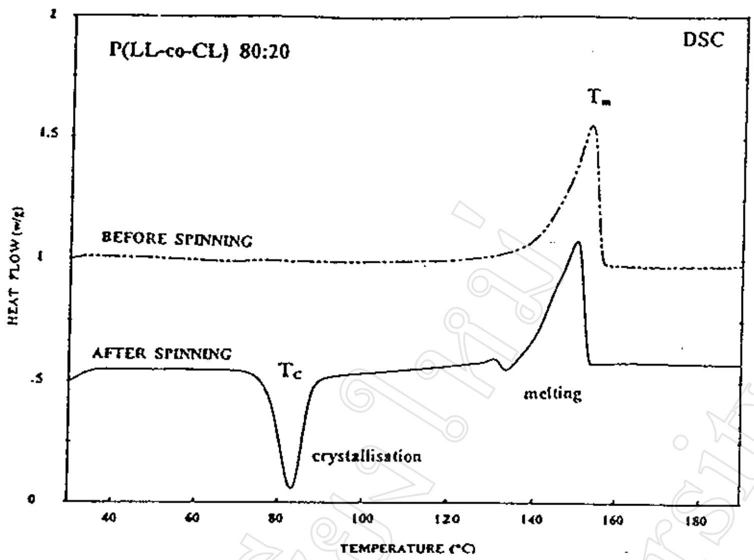


Fig. 2 DSC curves of the copolymer both before and after melt spinning.

CONCLUSIONS

1. Since a fibre's mechanical properties (tensile strength, modulus, elongation at break) are heavily dependent upon its morphology, it is logical to try to control this morphology as far as possible. In this way, the fibre's properties can be tailored to meet the demands of the intended application.

2. In the case of a speciality polymer where the correct balance of properties is of critical importance, it is often advantageous to be able to spin the initial fibre with as little molecular orientation and crystallinity as possible. The ability to do this depends mainly upon the rate of cooling of the extruded fibre being fast enough to prevent crystallisation from occurring.

3. Having produced an unoriented amorphous fibre, its normal semi-crystalline morphology can be built back into it in a more controlled way via off-line processes such as annealing and hot-drawing. Molecular orientation, crystallite size and distribution, and % crystallinity are all affected by how these processes are conducted and have an important bearing on fibre properties.

4. Throughout the fibre production process, the processing temperatures employed need to be carefully chosen with respect to the polymer's glass transition (T_g), crystallisation (T_c), melting (T_m), and thermal degradation (T_d) temperatures.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the National Metal and Materials Technology Center (MTEC) and the Department of Chemistry, Faculty of Science, Chiang Mai University.

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P-20

OPTIMIZATION OF THE DRAWING AND ANNEALING CONDITIONS FOR IMPROVING THE MECHANICAL PROPERTIES OF POLY (L-LACTIDE-CO-ε-CAPROLACTONE) MONOFILAMENT FIBRES FOR POTENTIAL USE AS ABSORBABLE SUTURES

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INTRODUCTION

Biodegradable polymers used as absorbable sutures include polyesters such as polyglycolic acid and poly(L-lactic acid)(1). Poly(L-lactide-co-ε-caprolactone), PLLC, is one of a series of copolymers chosen for study for the production of new absorbable monofilament surgical sutures with improved handling properties compared with current commercial materials. Suture properties are governed by various factors such as molecular weight, crystallinity, and morphology(2). Molecular weight and composition are initially controlled at the stage of polymer synthesis. In this work, a random PLLC copolymer with a mole composition ratio of 8:2 was used to spin fibres. The crystallinity and molecular orientation of the as-spun fibres were further developed by annealing and drawing under various conditions to give the required mechanical properties. A tensile testing machine was used to measure fibre's mechanical properties. Characterisation was carried out by means of differential scanning calorimetry, DSC.

EXPERIMENTAL PROCEDURES

Melt spinning PLLC, $\overline{M}_w$ =31600, was melted at 145-155°C and extruded through a 2 mm diameter single hole spinnerette. The monofilament fibre was passed through a water cooling bath (5-8°C) before being wound up on a spool with a take-up speed of 4 m.min^{-1}. The diameter of the as-spun fibre was in the range of 0.26-0.32 mm. After drying in a vacuum oven (60°C), the fibre was stored in a drying cabinet to prevent premature atmospheric hydrolysis.

Annealing The as-spun fibre was annealed in a vacuum oven at 80°C for 12 hrs.

Drawing The various conditions used for drawing the as-spun fibre were as follows:

(a) Drawing by an Instron machine at room temperature with different initial rates of 50, 100, 150, 200, 250% min^{-1} to a draw ratio (λ) of 4. The initial gauge length was 40 mm.

(b) Drawing at 60°C through a hot drawing unit 40 cm long. Drawing was performed at a constant rate of about 150% min^{-1} to a λ of 4.

(c) Alternate annealing and drawing was studied by first drawing the as-spun fibre under the same conditions as in (b) to a λ of 4 and then annealing at a constant strain at 60°C for 24 hrs. Finally, the fibre was drawn again under the same conditions to a further λ of 2, giving a final draw ratio of 4x2.

Fibre Testing The mechanical properties of the fibres were measured at room temperature using an Instron tensile testing machine at a cross-head speed of 20 mm.min^{-1}. The initial length of the specimens was 40 mm and the results taken as the average values of 3-5 tests. Thermal analysis of the fibres was carried out using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter at a scan speed of 10°C min^{-1}.

RESULTS AND DISCUSSION

The DSC thermogram of the as-spun fibre showed T_g, T_c and T_m values of about 32.0, 83.6 and 145.5°C respectively. After annealing the fibres at 80°C for 12 hrs. to build in crystallinity, heats of crystallisation (ΔH_c) and melting (ΔH_m), as obtained from DSC for the as-spun and annealed fibres were as shown in Table1. The annealed fibre showed no crystallisation peak (ΔH_c=0), indicating that maximum crystallisation had been included in the fibre during the annealing process. In contrast, the as-spun fibre was nearly completely amorphous ($\Delta H_c \approx \Delta H_m$ from the DSC curve). However, the annealed fibre was still brittle as indicated by its low stress at break from tensile testing. Table 1 also shows the stress and strain at break for these fibres. The extensibility (expressed as percentage strain) of the annealed fibre was much less than that of the as-spun fibre due to its crystallinity but with no molecular orientation to withstand high load.

Figure 1 shows the testing results for the fibres drawn with different initial rates as described in (a). As seen in this Figure, the fibre obtained from a drawing rate of 150% min^{-1} had the highest strength (97 MPa) which was much higher than that of the as-spun fibre (28 MPa).

Table 1. DSC ananlysis and tensile testing results for the fibres processed under various conditions.

Samples	ΔH_c (J/g)	ΔH_m (J/g)	Stress at Break (MPa)	Strain at Break (%)
As-spun fibre	25.08	27.02	28	1200
Fibre annealed at 80°C for 12 hrs.	-	31.75	25	300
Fibre drawn at 60°C	-	25.45	160	200
Fibre processed by alternate annealing and drawing	-	29.47	300	110

Drawing at the optimum rate at a higher temperature (60°C), as described in (b), was further studied. The fibre obtained was stronger, as indicated by its higher stress of 160 MPa, as shown in Table 1. However, the DSC thermogram showed no crystallisation peak and ΔH_m was not much less than that of the annealed fibre (see Table 1). This indicated that their crystallinities were similar. It was therefore concluded that drawing at a higher temperature not only induced crystallisation but also brought about molecular orientation in the direction of drawing. As a result, the fibre became stronger.

Attempts to increase fibre strength by alternate annealing and drawing were as described in (c). Further improvements were achieved, as shown in Table 1. The testing results for the strongest fibre and a commercial PDS II size 2-0 suture are plotted for comparison in Figure 2. The fibre strength is about 70% that of PDS II and indicates the degree of success. However, the fibre was still too stiff as seen from its higher initial slope (initial modulus= 1.11 GPa) than that of PDS II. Thus, stiffness needs to be controlled further at the stages of drawing and annealing in order to modify the fibre's morphology(3).

CONCLUSIONS

The as-spun fibre, spun through cooling water, was amorphous. Annealing the as-spun fibre induced crystallinity while drawing induced both crystallinity and molecular orientation. The optimum drawing rate at room temperature was found to be 150% min^{-1}. Increasing the drawing temperature to 60°C enhanced the fibre tensile strength. Alternate annealing and drawing led to further improvements with the fibre strength increasing to about 70% of that of PDS II. In conclusion, a combination of both drawing and annealing is clearly needed in order to develop the fibre morphology to achieve all of the required mechanical properties.

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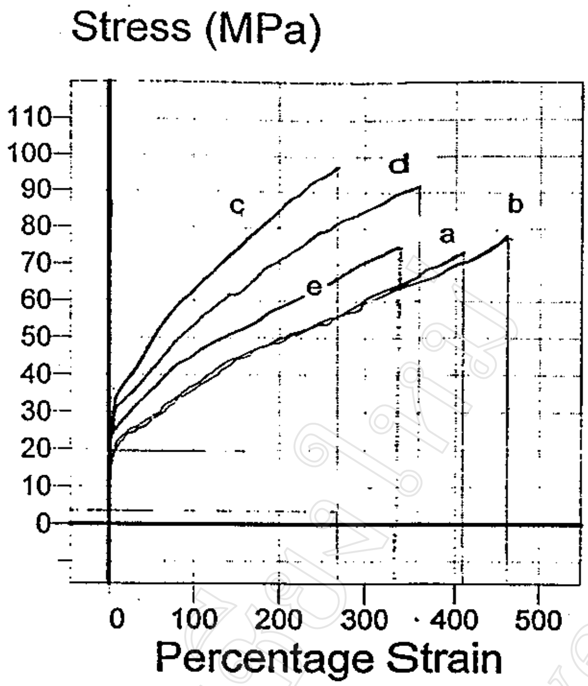

Figure 1. Stress-strain curves for fibres drawn at rates of

a. 50% min^{-1} b. 100% min^{-1}

c. 150% min^{-1} d. 200% min^{-1}

e. 250% min^{-1}

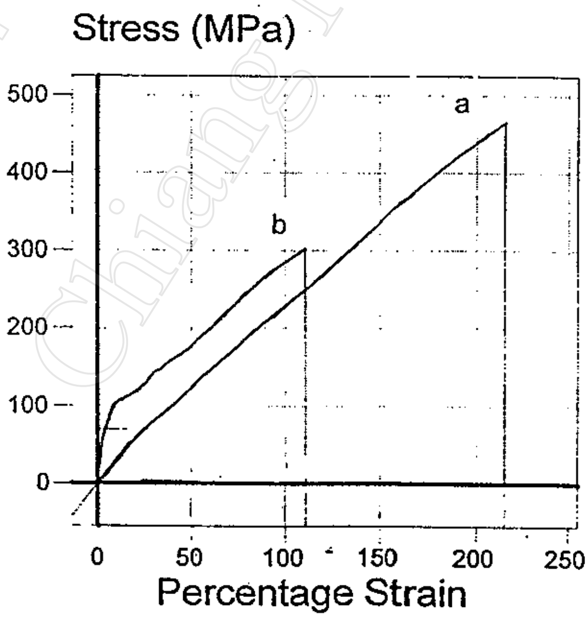

Figure 2. Comparison of stress-strain curves for fibres of

a. PDS II b. PLLC (annealed + drawn)

CONFERENCE PRESENTATION

in

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held at

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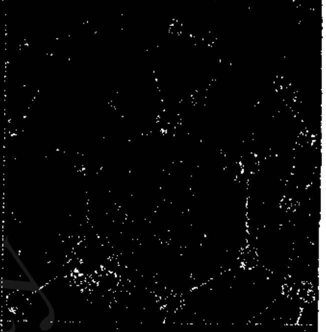
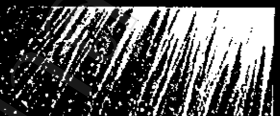
19 – 20 July 2000

oceedings การประชุมวิชาการทางด้านวิทยาศาสตร์และเทคโนโลยีวัสดุแห่งประเทศไทย ครั้งที่





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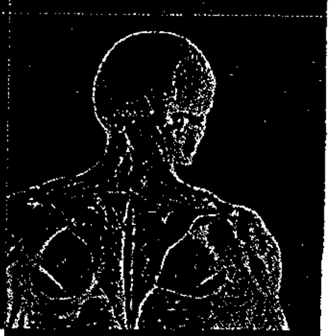

MTEC

ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ (MTEC)
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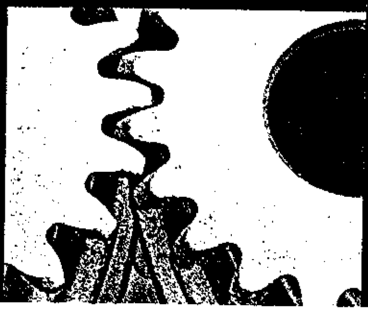

การหาเงื่อนไขในการดึงยืดและแอนนีลเพื่อปรับปรุงสมบัติเชิงกลของเส้นใยโมโนฟิลาเมนต์ พอลิ (แอล-แลคไทด์-โค-เอฟไซลอน-แคโพรแลคโทน) สำหรับใช้เป็นไหมละลาย

OPTIMIZATION OF THE DRAWING AND ANNEALING CONDITIONS FOR IMPROVING THE MECHANICAL PROPERTIES OF POLY (L-LACTIDE-CO-ε-CAPROLACTONE) MONOFILAMENT FIBRES FOR POTENTIAL USE AS ABSORBABLE SUTURES

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อรรถรงค์ วงศ์อาษา มณธิรา ศรีใย มังกร ศรีสะอาด อโนดาษ์ จารุจินดา และ คณารัฐ ณ ลำปาง
หน่วยวิจัยพอลิเมอร์ทางการแพทย์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

บทคัดย่อ

โครงสร้างสัณฐานของเส้นใยโมโนฟิลาเมนต์พอลิ (แอล-แลคไทด์-โค-เอฟไซลอน-แคโพรแลคโทน) ที่ได้จากการปั่นแบบหลอมสามารถถูกดัดแปรได้โดยการดึงยืดและแอนนีลหลายขั้นตอนร่วมกัน เงื่อนไขที่ใช้ในการดึงยืดและแอนนีลได้ถูกตรวจสอบเพื่อปรับปรุงสมบัติเชิงกลของเส้นใย เช่น โมดูลัส ความต้านทานการดึง และความสามารถในการยืด ให้เหมาะสมกับการทำศัลยกรรม ผลของอัตราการดึงยืด และ อุณหภูมิ หลังการแอนนีลที่ 80°ซ. ได้ถูกศึกษาโดยการใช้เครื่องทดสอบแบบดึง พบว่าอัตราที่เหมาะสมของการดึงยืดที่อุณหภูมิห้องคือ อัตราการดึงยืดเริ่มต้น 150 %ต่อนาที และพบว่าการดึงยืดเส้นใยที่อุณหภูมิสูงขึ้นที่ 60°ซ. เพิ่มความแข็งแรงให้กับเส้นใย ยิ่งไปกว่านั้นการดึงยืดสลับกับการแอนนีลยิ่งเพิ่มความแข็งแรงให้กับเส้นใยจนถึง 70% ของ PDS II ผลจากการศึกษาโดยเทคนิคดิฟเฟอเรนเชียลสแกนนิงคัลลอริเมตรี (DSC) พบว่าทุกเงื่อนไขของการดึงยืดและการแอนนีลมีผลทำให้เกิดผลึกด้วยปริมาณเท่าๆกัน แม้ว่าจะได้เส้นใยที่มีความแข็งแรงต่างกันก็ตาม ซึ่งสรุปได้ว่าผลึกที่เกิดขึ้นภายในเส้นใยมีการจัดเรียงตัวที่ต่างกัน จึงให้สมบัติเชิงกลต่างกัน

บทนำ

พอลิเมอร์ที่สลายตัวได้ทางชีวภาพที่ใช้ทำไหมละลาย มักเป็นพอลิเอสเทอร์ เช่น พอลิไกลคอลิคแอซิด พอลิ(แอล-แลคติคแอซิด)(1) เป็นต้น พอลิ(แอล-แลคไทด์-โค-เอฟไซลอน-แคโพรแลคโทน) เขียนย่อๆ ว่า P(LLA-co-CL) เป็นโคพอลิเมอร์ชนิดหนึ่งที่ได้เลือกมาศึกษาเพื่อใช้ผลิตไหมละลายแบบเส้นเดี่ยวชนิดใหม่ ที่คาดว่าจะมีสมบัติเชิงกลดีกว่าที่มีอยู่แล้วเชิงพานิชย์ สมบัติดังกล่าวถูกกำหนดโดยปัจจัยหลายอย่าง เช่น มวลโมเลกุล ความเป็นผลึก และโครงสร้างสัณฐาน(2) สำหรับมวลโมเลกุลและองค์ประกอบได้ถูกควบคุมแล้วที่ขั้นตอนของการสังเคราะห์พอลิเมอร์ ในงานที่นำเสนอนี้โคพอลิเมอร์ P(LLA-co-CL) แบบเดาสุ่มที่มีอัตราส่วนโมล 8:2 ถูกนำมาปั่นเป็นเส้นใย ความเป็นผลึกและการจัดเรียงตัวโมเลกุลภายในเส้นใยที่ปั่นได้ ถูกดัดแปรต่อไปโดยการแอนนีลและดึงยืดภายใต้เงื่อนไขต่างๆ เพื่อให้ได้สมบัติเชิงกลตามต้องการ เครื่องมือทดสอบแบบดึงถูกนำมาใช้วัดสมบัติเชิงกลของเส้นใย ลักษณะเฉพาะถูกศึกษาโดยการใช้เครื่องดิฟเฟอเรนเชียลสแกนนิงคัลลอริมิเตอร์ (DSC)

อุปกรณ์และวิธีการ

การปั่นแบบหลอม

P(LLA-co-CL), $\overline{M}_w$ = 31600, ถูกหลอมที่ 145-155°ซ. และให้ไหลผ่านรูสปินเนอเรตกลม เส้นผ่านศูนย์กลาง 2 มม. ได้เป็นเส้นใยแบบเส้นเดี่ยวผ่านลงสู่น้ำเย็น (5-8°ซ.) ก่อนม้วนเข้ากระสวยด้วยอัตราเร็ว 5 ม. ต่อนาที ได้เส้นใยปั่นหลอมเส้นผ่าศูนย์กลาง 0.26-0.32 มม. หลังจากทำให้แห้งในตู้อบสุญญากาศ (60°ซ.) แล้วเก็บ เส้นใยในตู้ปราศจากความชื้นเพื่อป้องกันการเกิดไฮโดรลิซิส

การแอนนีล

นำเส้นใยปั่นหลอมไปแอนนีลที่ 80°ซ. ในตู้อบเป็นเวลา 12 ชม.

การดึงยืด

เงื่อนไขที่ใช้ในการดึงยืดเส้นใยปั่นหลอมมีดังนี้

(ก) ดึงยืดเส้นใยด้วยเครื่องทดสอบแบบดึงที่อุณหภูมิห้อง ด้วยอัตราเริ่มต้น 50, 100, 150, 200 และ 250 %ต่อนาที จนได้อัตราส่วนการยืด (draw ratio, λ) เป็น 4 จากความยาวเริ่มต้น 40 มม.

(ข) ดึงยืดเส้นใยที่ 60°ซ. ผ่านแท่นความร้อนที่ยาว 40 ซม. ด้วยอัตราคงที่ที่ 300 %ต่อนาที จนได้ λ เป็น 4

(ค) ดึงยืดเส้นใยสลับกับการแอนนีล โดยดึงยืดเส้นใยภายใต้เงื่อนไขเดียวกับใน (ข) จนได้ λ เป็น 4 ก่อน แล้วแอนนีลโดยตรึงเส้นใยให้มีความยาวคงที่ ที่ 60°ซ. เป็นเวลา 24 ชม. สุดท้ายดึงยืดเส้นใยอีกครั้งภายใต้ เงื่อนไขเดิมจนยาวเป็น 2 เท่า ดังนั้น λ สุดท้ายจึงเป็น 4x2

ทดสอบเส้นใย

ทดสอบสมบัติเชิงกลของเส้นใยที่อุณหภูมิห้องโดยใช้เครื่องทดสอบแบบดึงด้วยอัตราการดึง 20 มม.ต่อนาที จากความยาวเริ่มต้น 40 มม. ผลการทดสอบได้จากการเฉลี่ยของการทดสอบ 3-5 เส้นใย การวิเคราะห์ทางความร้อนของเส้นใยทำโดยการใช้เครื่องดิฟเฟอเรนเชียลสแกนนิงคัลลอริมิเตอร์ Perkin-Elmer DSC-7 ด้วยอัตราการเพิ่มอุณหภูมิ 10°ซ. ต่อนาที

ผลการทดลองและวิจารณ์

เทอร์โมแกรม DSC ของเส้นใยปั่นหลอมแสดงค่า T_g, T_c และ T_m ประมาณ 32.0, 83.6 และ 145.5°ซ. ตามลำดับ หลังจากการแอนนีลที่ 80°ซ. เป็นเวลา 12 ชม. เกิดผลึกขึ้นภายในเส้นใย ความร้อนในการเกิดผลึก (ΔH_c) และความร้อนในการหลอม (ΔH_m) ที่ได้จากเทคนิค DSC สำหรับเส้นใยปั่นหลอมและเส้นใยหลังถูกแอนนีลแสดงค่าในตาราง 1 เส้นใยที่ถูกแอนนีลไม่แสดงพีคของการเกิดผลึกเลย (ΔH_c = 0) แสดงว่าผลึกได้เกิดในเส้นใยมาก่อนแล้วด้วยปริมาณที่มากที่สุดในขั้นตอนของการแอนนีล ในทางตรงกันข้าม เส้นใยปั่นหลอมเป็นอสัณฐานเกือบทั้งหมด ($\Delta H_c \approx \Delta H_m$ จากเส้นโค้ง DSC) แต่อย่างไรก็ตาม เส้นใยที่ถูกแอนนีลยังคงมีสมบัติเปราะซึ่งแสดงโดยค่าของความเค้นที่จุดขาดซึ่งมีค่าต่ำ ตาราง 1 แสดงค่าความเค้นและความเครียดที่จุดขาดของการทดสอบเส้นใยที่ผ่านกระบวนการต่างๆ ความสามารถในการยืด (แสดงเป็นเปอร์เซนต์ความเครียด) ของเส้นใยที่ถูกแอนนีลมี

ค่าต่ำกว่าของเส้นใยปั่นหลอมมาก ทั้งนี้เนื่องมาจากเส้นใยที่ถูกแอนนีลมีผลึกเกิดขึ้นมาก แต่ไม่มีการจัดเรียงตัวที่ดีที่จะสามารถรับแรงที่มากระทำได้

รูป 1 แสดงผลการทดสอบเส้นใยที่ถูกดึงยืดด้วยอัตราที่ต่างกันดังอธิบายใน (ก) จากรูปจะเห็นได้ว่าเส้นใยที่ถูกดึงยืด ด้วยอัตรา 150 %ต่อนาที มีความแข็งแรงที่สุด (97 MPa) ซึ่งแข็งแรงกว่าเส้นใยปั่นหลอมมาก (28 MPa)

ตาราง 1 ผลการวิเคราะห์ DSC และการทดสอบเส้นใยที่ผ่านกระบวนการภายใต้เงื่อนไขแตกต่างกัน

เงื่อนไขการเตรียมเส้นใย	ΔH_c (J/g)	ΔH_m (J/g)	ความเค้นที่จุดขาด (MPa)	ความเครียดที่จุดขาด (%)
ผ่านการปั่นหลอมเท่านั้น	25.08	27.02	28	1200
ผ่านการแอนนีลที่ 80°ซ.12 ชม.	-	31.75	25	300
ผ่านการดึงยืดที่ 60°ซ.	-	25.45	160	200
ผ่านการดึงยืดสลับกับแอนนีล	-	29.47	300	110

การดึงยืดเส้นใยด้วยอัตราการดึงยืด 300 %ต่อนาทีที่อุณหภูมิ 60°ซ. ดังอธิบายใน (ข) พบว่าได้เส้นใยที่แข็งแรงขึ้น (160 MPa) ดังแสดงในตาราง 1 แต่เทอร์โมแกรม DSC ไม่แสดงพีคของการเกิดผลึกและ ΔH_m มีค่าไม่ต่างจากของเส้นใยที่ถูก แอนนีลมากนัก (ดูตาราง 1) แสดงว่าเส้นใยใน 2 กรณีนี้มีผลึกปริมาณเท่าๆ กัน ดังนั้นจึงอาจสรุปได้ว่าการดึงยืดที่อุณหภูมิสูง ไม่เพียงแต่ทำให้เกิดผลึกขึ้นเท่านั้น แต่ยังเหนี่ยวนำให้เกิดการจัดเรียงตัวของสายโซ่โมเลกุลในทิศของการดึงยืด และด้วยเหตุนี้เองเส้นใยจึงแข็งแรงขึ้น

ความพยายามที่จะเพิ่มความแข็งแรงให้กับเส้นใยด้วยการดึงยืดสลับกับการแอนนีลดังอธิบายใน (ค) ได้ประสบความสำเร็จ ดังแสดงในตาราง 1 ผลการทดสอบของเส้นใยที่แข็งแรงที่สุดกับไหมละลาย PDS II ขนาด 2-0 แสดงใน รูป 2 เพื่อเปรียบเทียบ จากรูปนี้จะเห็นได้ว่าเส้นใยที่ปรับปรุงได้มีความแข็งแรงประมาณ 70% ของ PDS II ซึ่งกล่าวได้ว่ามีความสำเร็จในระดับหนึ่ง แต่อย่างไรก็ตาม เส้นใยยังคงกระด้าง ซึ่งดูได้จากค่าความชันเริ่มต้นที่ยังคงมีค่าสูง (โมดูลัส 1.11 GPa) มากกว่าของ PDS II ดังนั้นความกระด้างของเส้นใยจึงยังจำเป็นต้องถูกปรับปรุงต่อไป ซึ่งจะทำได้ในขั้นตอนของการดึงยืดและแอนนีล เพื่อให้ได้โครงสร้างสัณฐานที่เหมาะสมต่อไป(3)

สรุปผลการทดลอง

เส้นใยที่ได้จากการปั่นหลอมโดยผ่านน้ำเย็นมีโครงสร้างสัณฐาน แต่เมื่อแอนนีลแล้วจะเกิดผลึกขณะที่การดึงยืดทำให้ ทั้งเกิดผลึกและผลึกที่เกิดขึ้นถูกจัดเรียงตัวดีขึ้นด้วย อัตราการดึงยืดที่เหมาะสมที่อุณหภูมิห้องคือ 150 %ต่อนาที การเพิ่มอุณหภูมิขณะดึงยืดเป็น 60°ซ. ทำให้เส้นใยแข็งแรงขึ้น ยิ่งไปกว่านั้นการดึงยืดสลับกับการแอนนีลยิ่งเพิ่มความแข็งแรงให้กับเส้นใยจนแข็งแรงเป็น 70% ของ PDS II นั่นคือ การผสมผสานระหว่างการดึงยืดและการแอนนีล ควรต้องศึกษาเพิ่มเติมต่อไปในการพัฒนาโครงสร้างสัณฐานของเส้นใย เพื่อให้ได้สมบัติเชิงกลตามต้องการ

กิตติกรรมประกาศ

งานนี้ได้รับทุนสนับสนุนจาก ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ (MTEC) สำนักงานพัฒน วิทยาศาสตร์และเทคโนโลยีแห่งชาติ และคณะผู้วิจัยขอขอบคุณ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลั เชียงใหม่ ในการให้ความสนับสนุนมาโดยตลอด

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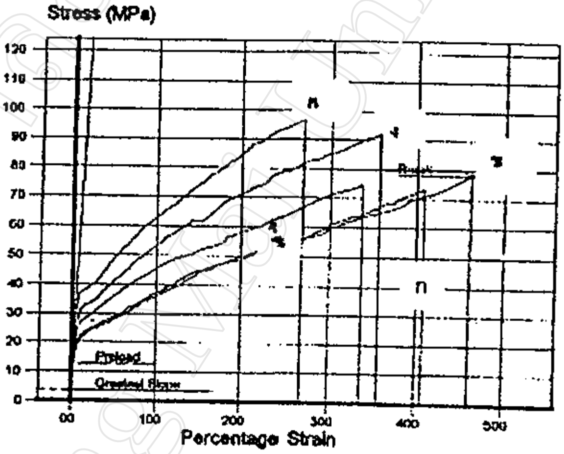
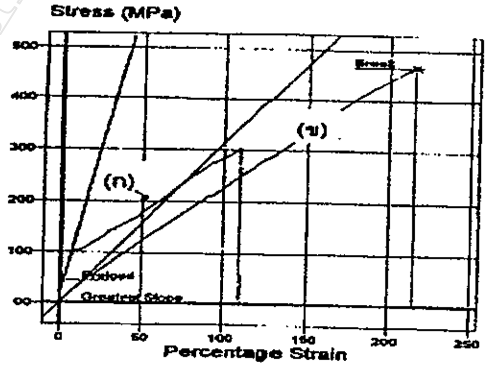


รูปที่ 1เส้นโค้งความเค้นความเครียดสำหรับเส้นใยที่ถูกดึงยืดด้วยอัตราการดึงยืดต่างๆกัน (ก) 50 %ต่อนาที ข) 100 %ต่อนาที (ค) 150 %ต่อนาที (ง) 200 %ต่อนาที (จ) 250 %ต่อนาที



รูปที่ 2การเปรียบเทียบเส้นโค้งความเค้นความเครียดสำหรับเส้นใย (ก) P(LLA-co-CL) ที่ถูกดึงยืดสลับกับแอนนีล (ข) PDS II

CONFERENCE PRESENTATION

in the

International Symposium

on

The Challenges of Polymer Science and Technology in the 21st Century

organised as part of the

26th Congress on Science and Technology
of Thailand

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18 – 20 October 2000

บทคัดย่อ
EXTENDED ABSTRACTS

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
FACULTY OF SCIENCE, CHULALONGKORN UNIVERSITY

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CONTROL OF POLYMER MORPHOLOGY DURING THE SMALL-SCALE MELT SPINNING OF MONOFILAMENT FIBRES

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บทคัดย่อ : ปัจจุบันเทคโนโลยีของการผลิตเส้นใยสังเคราะห์สำหรับใช้งานเฉพาะด้านได้มีการพัฒนาก้าวหน้าเป็นของตัวเอง ด้วยเหตุที่มีขนาดเฉพาะตัวสมบัติของเส้นใยจึงไวต่อการเปลี่ยนแปลงในระดับโครงสร้างโมเลกุล ดังนั้นในการที่จะผลิตเส้นใยที่มีสมดุลระหว่างสมบัติต่างๆ สำหรับการนำไปใช้เฉพาะทาง จึงจำเป็นที่จะต้องควบคุม (ก) โครงสร้างจุลภาคทางเคมีและน้ำหนักโมเลกุลในขณะสังเคราะห์ และ (ข) การเรียงตัวของโมเลกุลและสัณฐานกึ่งผลึกในขณะขึ้นรูป งานที่เสนอนี้มาจากบางส่วนของงานของหน่วยวิจัยพอลิเมอร์ทางการแพทย์ที่มหาวิทยาลัยเชียงใหม่เกี่ยวกับศักยภาพของเส้นใยโมโนฟิลาเมนต์สำหรับเป็นไหมละลายในงานศัลยกรรม โดยจะกล่าวถึงวิธีการในการควบคุมสัณฐานวิทยาของพอลิเมอร์ในขณะขึ้นรูป โดยการพัฒนาความเข้าใจในวิธีการ จะทำให้สามารถกำหนดสภาวะที่เหมาะสมของกระบวนการผลิตเพื่อที่จะควบคุมสัณฐานวิทยา และ ทำให้ได้ผลิตภัณฑ์ที่มีสมบัติตามต้องการ

Abstract: Nowadays, the production of synthetic polymer fibres for use in specialist applications has developed into an advanced technology all of its own. Because of their unique dimensions, fibres tend to be especially sensitive in their properties to subtle changes in their molecular structure. Therefore, it follows that, in order to be able to produce fibres with the required balance of properties for a particular application, it is necessary to be able to control the polymer's (a) chemical microstructure and molecular weight during the synthesis stage, and (b) molecular orientation and semi-crystalline morphology during the processing stage. This paper describes some of the work currently in progress in Chiang Mai's *Biomedical Polymers Research Unit* on monofilament fibres for potential use as *absorbable surgical sutures* . In particular, the ways in which the polymer's morphology can be controlled during processing is discussed. By developing an understanding of how this can be done, it enables us to optimize the processing conditions in order to control the morphology and, hence, impart the required properties to the final product.

Experimental Procedure: An example of the type of polymer studied is *poly(L-lactide-co-ε-caprolactone),* a biodegradable copolyester consisting of a random sequence of L-lactide and ε-caprolactone units in an approximately 80:20 mole ratio. The processing equipment used was a small-scale melt spinning apparatus which could handle batch sizes of as small as 4-5 g. The processing temperature of 175°C was carefully chosen with respect to the copolymer's melting range and thermal degradation temperature, being sufficiently high to ensure complete melting of the copolymer, yet low enough to avoid or, at least, minimize the possibility of thermal degradation. Batch sizes of typically 5 g were extruded through single-hole spinnerettes to give monofilament fibres of the required diameter. The extruded fibre was cooled quickly, first by contact with the cool room air and then by passing through an ice-water bath. Finally, the fibre was wound up *without drawing* at a take-up speed matched with the extrusion rate. The purpose of this was to obtain *undrawn* and, therefore, *unoriented* fibres of controlled diameter. This then enabled the required molecular orientation and semi-crystalline morphology to be gradually built into the fibre in subsequent off-line annealing and hot-drawing steps.

Results, Discussion and Conclusions: Before spinning, the copolymer was a *semi-crystalline* material with a well-defined DSC melting peak. However, after spinning, the DSC curve showed an additional exothermic crystallisation peak prior to and of similar size to the melting peak, a clear indication that the spun fibre was in its so-called *quenched amorphous state* . The obvious conclusion to be drawn from this is that, during the melt spinning process, the extruded fibre was cooled quickly at a rate which was too fast for crystallisation from the melt to occur. Thus, the as-spun fibre was amorphous. This can be advantageous since, having produced an unoriented amorphous fibre, its normal semi-crystalline morphology could be built back into it in a more controlled way via off-line processes such as annealing and hot-drawing. Molecular orientation, crystallite size and distribution, and % crystallinity are all affected by how these processes are conducted and have an important bearing on fibre properties. Throughout the fibre production process, the processing temperatures employed needed to be carefully chosen with respect to the polymer's glass transition (T_g), crystallisation (T_c), melting (T_m), and thermal degradation (T_d) temperatures.

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Keywords: poly(L-lactide-co-ε-caprolactone), absorbable sutures, monofilament fibres, melt spinning

CONFERENCE PRESENTATIONS

in the

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บทคัดย่อ
EXTENDED ABSTRACTS

การประชุมวิชาการ
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สมาคมวิทยาศาสตร์แห่งประเทศไทยในพระบรมราชูปถัมภ์
THE SCIENCE SOCIETY OF THAILAND UNDER THE PATRONAGE
OF HIS MAJESTY THE KING

คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์
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การสังเคราะห์และการหาลักษณะเฉพาะของพอลิเอสเทอร์ตัวใหม่บางชนิดที่สามารถสลายตัวทางชีวภาพสำหรับใช้เป็นไหมละลาย

SYNTHESIS AND CHARACTERISATION OF SOME NOVEL BIODEGRADABLE POLYESTERS FOR USE AS ABSORBABLE SURGICAL SUTURES

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บทคัดย่อ : ในการศึกษานี้ได้ทำการสังเคราะห์และหาลักษณะเฉพาะของพอลิ(แอล-แลคไทด์) โฮโมพอลิเมอร์ (พีแอลแอล) พอลิ(แอล-แลคไทด์-โค-เอปไซลอน-คาโพรแลคโทน) (พีแอลแอลซี)และ พอลิ(แอล-แลคไทด์-โค-เอปไซลอน-คาโพรแลคโทน-โค-ไกลคอไลด์) เทอร์พอลิเมอร์ (พีแอลแอลซีจี) การศึกษานี้เป็นส่วนหนึ่งของการศึกษาเพื่อพัฒนาวัสดุสำหรับไหมละลายโมโนฟิลาเมนต์ตัวใหม่เพื่อเป็นทางเลือกใหม่ของวัสดุเชิงพาณิชย์ที่ใช้อยู่ในปัจจุบัน การสังเคราะห์ทำโดยบัลค์พอลิเมอไรเซชันแบบเปิดวงที่อุณหภูมิ 140°C เป็นเวลา 72 ชั่วโมง โดยใช้สแตนนัสออกโทเอทเป็นตัวเริ่มปฏิกิริยาแบบโคออร์ดิเนชัน-อินเซิร์ตชัน การหาลักษณะเฉพาะของพอลิเมอร์ใช้เทคนิคการวิเคราะห์หลายวิธีร่วมกันคือ วิธีทางสเปกโทรสโกปี (โปรตอน-เอ็นเอ็มอาร์ และคาร์บอน13-เอ็นเอ็มอาร์) วิธีทางความร้อน (ดีเอสซี และทีจี) และ วิธีหาน้ำหนักโมเลกุล (การหาความหนืดของสารละลายเจือจาง)

Abstract: In this study, a range of poly(L-lactide) homopolymers (PLL), poly(L-lactide-*co*-ε-caprolactone) copolymers (PLLC) and poly(L-lactide-*co*-ε-caprolactone-*co*-glycolide) terpolymers (PLLCG) have been synthesized and characterised. This is part of a wider study to develop new absorbable monofilament surgical suture materials as posssible alternatives to the current commercial materials. The syntheses were carried out via ring-opening polymerisation in bulk at 140°C for 72 hours using stannous octoate ($SnOct_2$) as the coordination-insertion initiator. The polymerisation products were characterised by a combination of analytical techniques: spectroscopic methods (H1-NMR and C13-NMR), thermal analysis methods (DSC and TG) and a molecular weight method (dilute-solution viscometry).

Methodology: The ring-opening polymerisations of L-lactide alone, L-lactide and ε-caprolactone, and L-lactide, ε-caprolactone and glycolide were conducted in bulk using $SnOct_2$ as the initiator at a constant temperature of 140°C for 72 hours. At the end of the polymerisation period, the polymerisate was allowed to cool to room temperature before being purified by granulation followed by drying in a vacuum oven at 110°C for 48 hours.

Results, Discussion and Conclusions: The results of this study are shown in Table 1 below.

Table 1: Comparison of the homo-, co- and terpolymerisation products of L-lactide, ε-caprolactone and glycolide using $SnOct_2$ as initiator.

Polymer	Composition (mol %)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_d range (°C)	$[\eta]^*$ (dl/g)
Homopolymers						
PLL # 1	-	57	174	51	240-400	0.94
PLL # 2	-	49	156	68	280-410	0.78
Copolymers						
PLLC 80/20 # 1	79:21	29	144	30	210-470	1.44
PLLC 80/20 # 2	79:21	31	148	30	250-480	1.24
Terpolymers						
PLLCG 65/25/10	64:24:12	19	amorphous	-	210-440	1.26
PLLCG 70/15/15	70:14:16	34	amorphous	-	210-460	1.32
PLLCG 70/20/10	70:21:9	28	118	8	230-460	1.65

* measured in chloroform as solvent at 30°C

From the results obtained, it can be concluded that poly(L-lactide) homopolymer is unsuitable for use since its glass transition temperature, T_g, is too high (≈ 50-60°C) which gives rise to a monofilament fibre that is too stiff and springy. Also, its rate of biodegradation in the human body is considered to be slow for suture applications. Consequently, poly (L-lactide) needs to be modified in order to improve both its handling and healing characteristics as a potential suture material. In this work, the ε-caprolactone comonomer was used to decrease T_g and increase chain flexibility while glycolide increased hydrophilicity and rate of absorption. However, such co- or terpolymerisation has wide-ranging effects on all aspects of the polymer microstructure including the matrix morphology. This is vitally important for a fibre since it derives its tensile strength from its oriented semi-crystalline morphology. Introduction of ε-caprolactone and glycolide units into the PLL chain increased structural irregularity and therefore decreased crystallisability until, at some compositions, the terpolymer became amorphous. The results have served to emphasized that, when designing the molecular structure of these materials, all of these factors need to be taken into account in order to strike a balance between the required physical, chemical, mechanical and biological properties of the final fibre product.

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Keywords: L-lactide/ε-caprolactone/glycolide polymers, absorbable monofilament surgical sutures

16-24P-24

การสังเคราะห์และวิเคราะห์โครงสร้างย่อยของเทอร์พอลิเอสเทอร์แบบสุ่มของ แอลแลคไทด์ เอปไซลอน-แคโพแลคโทน และ ไกลคอไลด์ โดยมีสแตนนัสออกโทเอทเป็นตัวเร่งปฏิกิริยา และ ไดเอทธิลีนไกลคอลเป็นตัวเริ่มปฏิกิริยา

SYNTHESIS AND MICROSTRUCTURAL ANALYSIS OF RANDOM TERPOLYESTERS OF L-LACTIDE, ε-CAPROLACTONE AND GLYCOLIDE USING STANNOUS OCTOATE AS CATALYST AND DIETHYLENE GLYCOL AS INITIATOR

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บทคัดย่อ: การสังเคราะห์เทอร์พอลิเอสเทอร์แบบสุ่มของแอลแลคไทด์ เอปไซลอน-แคโพแลคโทน และ ไกลคอไลด์ ซึ่งเรียกชื่อเป็น พอลิ(แอลแลคไทด์-โค-แคโพแลคโทน-โค-ไกลคอไลด์) โดยวิธีบัลค์พอลิเมอไรเซชั่นแบบเปิดวงที่อุณหภูมิ 140 องศาเซลเซียส 72 ชั่วโมง โดยมีอัตราส่วนโดยโมลของมอนอเมอร์เริ่มต้นเท่ากับ 70:20:10 โมลเปอร์เซนต์ ได้ศึกษาผลของสแตนนัสออกโทเอทและไดเอทลีนไกลคอลที่ทำหน้าที่เป็นตัวเร่งปฏิกิริยาและตัวเริ่มปฏิกิริยา พบว่ากรณีใช้สแตนนัสออกโทเอทอย่างเดียวเข้าใจว่าสแตนนัสออกโทเอทจะทำหน้าที่เป็นตัวเริ่มปฏิกิริยาโดยผ่านกลไกแบบโคออดิเนชัน อินเสิรทชัน อย่างไรก็ตามเมื่อใช้ทั้งสองตัวร่วมกัน ไดเอทลีนไกลคอลจะทำหน้าที่เป็นตัวเริ่มปฏิกิริยาและสแตนนัสออกโทเอทจะทำหน้าที่เป็นตัวเร่งปฏิกิริยา ผลการจัดเรียงตัวของมอนอเมอร์ในเทอร์พอลิเมอร์จากคาร์บอน13-เอ็นเอ็มอาร์สเปคตรายืนยันโครงสร้างย่อยแบบสุ่ม ขณะที่จีพีซีและการหาความหนืดของสารละลายเจือจางแสดงว่าเมื่อใช้สแตนนัสออกโทเอทอย่างเดียวเป็นตัวเริ่มปฏิกิริยาจะได้เทอร์พอลิเมอร์ที่มีน้ำหนักโมเลกุลสูงขึ้น อย่างไรก็ตามน้ำหนักโมเลกุลไม่เป็นไปตามอัตราส่วนของสแตนนัสออกโทเอทและไดเอทลีนไกลคอล แสดงให้เห็นว่ากลไกของการเกิดพอลิเมอไรเซชั่นซับซ้อนซึ่งต้องศึกษาในรายละเอียดต่อไป

Abstract: Random terpolymers of L-lactide (LL), ε-caprolactone (CL) and glycolide (G), designated as poly(L-lactide-co-ε-caprolactone-co-glycolide), were synthesized by ring-opening polymerisation in bulk with a monomer feed composition of 70:20:10 mole % at 140°C for 72 hours. The effects of stannous octoate (SO) and diethylene glycol (DEG), in their respective of roles as catalyst and initiator, were studied. In the absence of DEG, SO by itself is understood to act as the initiator via a coordination-insertion mechanism. However, when SO is used in conjunction with DEG, the DEG becomes the preferred initiator with the SO acting as a catalyst. The monomer sequencing in the terpolymers, from their ^{13}C-NMR spectra, were consistent with a random microstructure, while GPC and dilute-solution viscometry showed that higher molecular weights could be obtained using SO alone as the initiator. However, the molecular weights did not exactly parallel the SO:DEG ratio, indicating a complex polymerisation mechanism which requires more detailed investigation.

Methodology: L-lactide (LL), ε-caprolactone (CL) and glycolide (G) were terpolymerised in bulk at a monomer feed composition of 70:20:10 mole % using SO as the initiator at a concentration of 0.02 % by mole. In subsequent experiments, DEG was added to give SO:DEG ratios of 1:1 and 1:2 by mole. The reagents were weighed into 25 ml, round-bottomed flasks under dry nitrogen in a controlled atmosphere glove box at room temperature. The flasks were then removed from the glove box and immersed in an oil bath with magnetic stirring at 140°C for 72 hours. At the end of the polymerisation period, the polymers were allowed to cool to room temperature. The crude polymer products were dried in a vacuum oven at 90°C for 48 hours prior to being characterised according to their chemical composition (^{1}H-NMR), chemical microstructure (^{13}C-NMR), thermal properties (DSC and TG) and molecular weight (GPC and dilute-solution viscometry in chloroform at 30°C).

Results, Discussion and Conclusions:

Terpolymer synthesized using	^{1}H-NMR	Viscometry	GPC			DSC			TG
	Terpolymer Composition (mole %)	[η] (dl/g)	M_n	M_w	M_w/M_n	T_g (°C)	T_m (°C)	ΔH (J/g)	T_d (°C)
SO	69:20:11	1.65	86,613	192,563	2.22	28	109.8	11.6	270-500
SO:DEG (1:1)	69:22:9	1.15	43,335	92,249	2.13	27	-	-	260-450
SO:DEG (1:2)	70:21:9	1.03	38,498	91,565	2.16	27	-	-	270-450

This study has demonstrated that poly(L-lactide-co-ε-caprolactone-co-glycolide), P(LL-co-CL-co-G), can be prepared by ring-opening polymerisation in bulk. The chemical compositions of the terpolymer products were determined from the peak area integrations in the ^{1}H-NMR spectra. The results in the above table clearly show that the initial termonomer feed ratios and final terpolymer compositions are very similar, as would be expected from near-quantitative conversion. Chain microstructure can be readily determined by ^{13}C-NMR. The appearance of multiple carbonyl (C=O) peaks indicated that various mixed triad sequences are present, consistent with a random terpolymer structure. The terpolymers were either completely amorphous or contained only a small amount of crystallinity, as deduced from either the absence of or only a small-sized melting peak. Since terpolymerisation introduced structural irregularity into the polymer chain, the terpolymers will be slower to crystallize than poly(L-lactide) homopolymer. High molecular weight terpolymers could be synthesized using SO alone. Addition of DEG as initiator decreased the molecular weight, as can be seen from the GPC and diluted-solution viscometry results.

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Keywords: poly(L-Lactide-co-ε-caprolactone-co-glycolide), biodegradable polyester, coordination-insertion polymerisation

การศึกษาการสลายตัวไฮโดรลิติกภายนอกร่างกายของไหมละลายผ่าตัดชนิดโมโนฟิลาเมนต์

IN VITRO HYDROLYTIC DEGRADATION STUDIES OF ABSORBABLE MONOFILAMENT SURGICAL SUTURES

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บทคัดย่อ : ได้สังเคราะห์แรนดอมเทอร์พอลิเมอร์ของแอล-แลคไทด์, เอปไซลอน-คาโพรแลคโทน และ ไกลโคไลด์ โดยบัลค์พอลิเมอไรเซชันแบบเปิดวงที่อุณหภูมิ 140 องศาเซลเซียส มีสแตนนัสออกโทเอทเป็นตัวเริ่มปฏิกิริยา สำหรับการขึ้นรูป เทอร์พอลิเมอร์จะถูกนำไปปั่นหลอมเป็นเส้นใยแบบโมโนฟิลาเมนต์โดยใช้เครื่องเอ็กซ์ทรูชันขนาดเล็ก เส้นใยที่ได้ถูกนำไปศึกษาและเปรียบเทียบการสลายตัวทางชีวภาพ "อิน วิโทร" กับไหมละลายสังเคราะห์ประเภทโมโนฟิลาเมนต์สามชนิดที่มีชื่อทางการค้าว่า โมโนคริล แมกซอน และพีดีเอช II ซึ่งเป็นไหมละลายที่มีการใช้งานทางด้านศัลยกรรมในปัจจุบัน ไหมละลายจะถูกแช่ในสารละลายฟอสเฟตบัฟเฟอร์เซไลน์ที่มีค่าพีเอชเริ่มต้น 7.40 ± 0.01 และมีการควบคุมอุณหภูมิให้คงที่ตลอดที่ 37.0 ± 1.0 องศาเซลเซียส ไหมละลายที่ผ่านการแช่แล้วจะถูกนำมาศึกษาสมบัติที่เปลี่ยนแปลงไป เช่น ค่าการทนต่อแรงดึง น้ำหนัก และพื้นผิว จากการทดลองพบว่า แรนดอมเทอร์พอลิเมอร์และโมโนคริลมีอัตราเร็วในการลดลงของค่าการทนต่อแรงดึงและน้ำหนักสูงกว่าแมกซอนและพีดีเอช II ตามลำดับ และเทอร์พอลิเมอร์มีอัตราเร็วในการลดลงของค่าการทนต่อแรงดึงและน้ำหนักใกล้เคียงกับโมโนคริลมากที่สุด ซึ่งความแตกต่างของลักษณะการสูญเสียสมบัติของเทอร์พอลิเมอร์ โมโนคริล แมกซอนและพีดีเอช II สามารถอธิบายได้ในรูปของความแตกต่างทางโครงสร้างเคมีและการจัดเรียงตัวทางกายภาพ

Abstract: A random terpolymer of L-lactide, ε-caprolactone and glycolide (PLCG) was synthesized by ring-opening polymerisation in bulk at 140°C using stannous octoate as the initiator. The terpolymer was melt spun into a monofilament fibre of approximate diameter 0.3 mm using a small-scale fibre extrusion apparatus. The *in vitro* hydrolytic degradation of this terpolymer fibre was studied and compared with 3 commercial synthetic absorbable monofilament surgical sutures. These 3 commercial sutures are marketed under the trade names of MONOCRYL, MAXON and PDS II. The samples were immersed in a phosphate buffer saline (PBS) solution at an initial physiological pH of 7.40 ± 0.01 and maintained at a temperature of 37.0 ± 1.0°C. Their hydrolytic degradations were followed via the changes in tensile properties, weight and surface appearance. From the results obtained, both the PLCG and MONOCRYL samples showed similar rates of tensile strength and weight reduction, faster than MAXON and PDS II. The differences between the property loss-time profiles of the PLCG, MONOCRYL, MAXON and PDS II could be interpreted in terms of their differences in chemical structure and matrix morphology [1].

Methodology: The *in vitro* hydrolysis experiments were performed at 37.0 ± 1.0°C by immersing the 4 different fibre samples in a phosphate buffer saline (PBS, pH 7.40) solution for various periods of time. At each sampling time, one set of samples was removed, filtered, washed with deionized water, dried to constant weight, and then analysed. Based on the initial and final weights, the % weight retentions of the samples were calculated after each degradation time interval. The mechanical (tensile) properties of the samples were measured at room temperature using a Lloyds LRX+ Universal Mechanical Testing Machine. All tests were carried out with the fibre sample wound once around two bollard grips. The gauge length was 40 mm and the crosshead speed was 20 mm min^{-1}. To follow the corresponding topology changes, a Jeol 5410 Scanning Electron Microscope was used. The various property changes were correlated as far as possible in the light of current theories.

Results, Discussion and Conclusions: As expected, it was found that the weight and tensile properties of the PLCG and the 3 commercial sutures decreased with hydrolysis time. Amongst the commercial sutures, PDS II showed the slowest rate of decrease in tensile strength while MONOCRYL showed the fastest. Whereas PDS II and MAXON still retained 50% of their original tensile strengths after 8 and 6 weeks respectively, MONOCRYL lost most of its strength after only 4 weeks. The tensile strength reduction rate of the PLCG fibre was comparable with MONOCRYL. Similarly, the PLCG and MONOCRYL samples showed faster weight losses than MAXON and PDS II. In all cases, the onset of weight loss occurred some time after the onset of tensile strength loss. Mechanistically, the results could be interpreted in terms of surface erosion leading to the formation of micro-defects which facilitated the diffusion of water into the bulk interior of the polymer matrix. Ester hydrolysis then took place inside the matrix, leading to a reduction in molecular weight and tensile properties, until the degradation products were small enough in size to diffuse out of the matrix resulting in mass loss. Surface analysis using SEM showed that at 4 weeks no surface changes had occurred in the MAXON and PDS II samples while MONOCRYL and PLCG both exhibited surface cracks. For MONOCRYL, the cracks were longitudinal and started after 3 weeks, while for PLCG the cracks were transverse to the fibre axis and started after 4 weeks. Weight losses in MONOCRYL and PLCG coincided with surface changes observed by SEM. The differences in the property loss-time profiles of the PLCG and commercial sutures could be ascribed to their differences in chemical microstructure and semi-crystalline morphology.

References: [1] Tomihata, K., Suzuki, M., Oka, T. and Ikada Y. (1998) *Polym. Deg. Stab.*, 59, 13-18.

Keywords: *in vitro* hydrolytic degradation, monofilament absorbable surgical sutures, biodegradable polyesters

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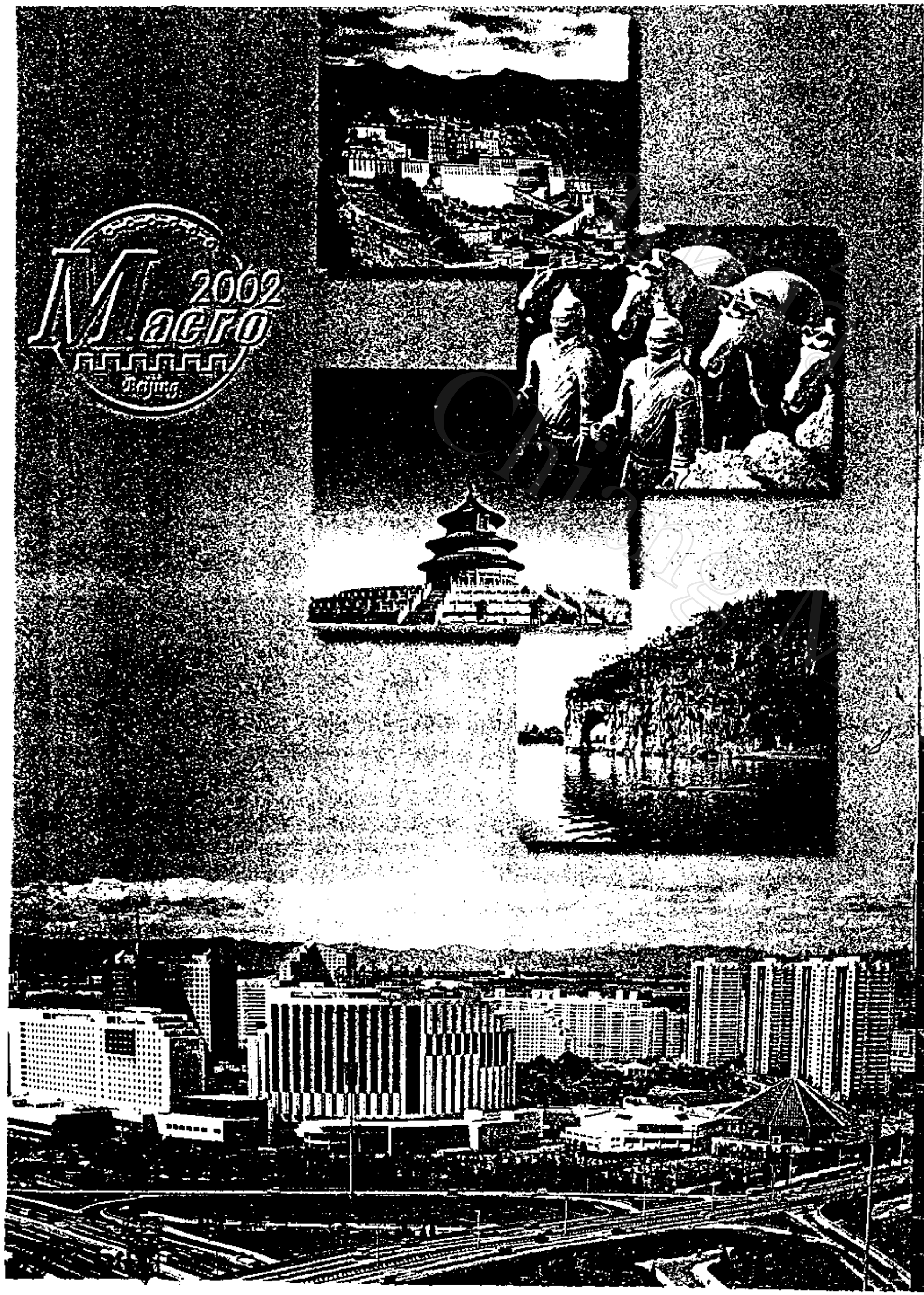

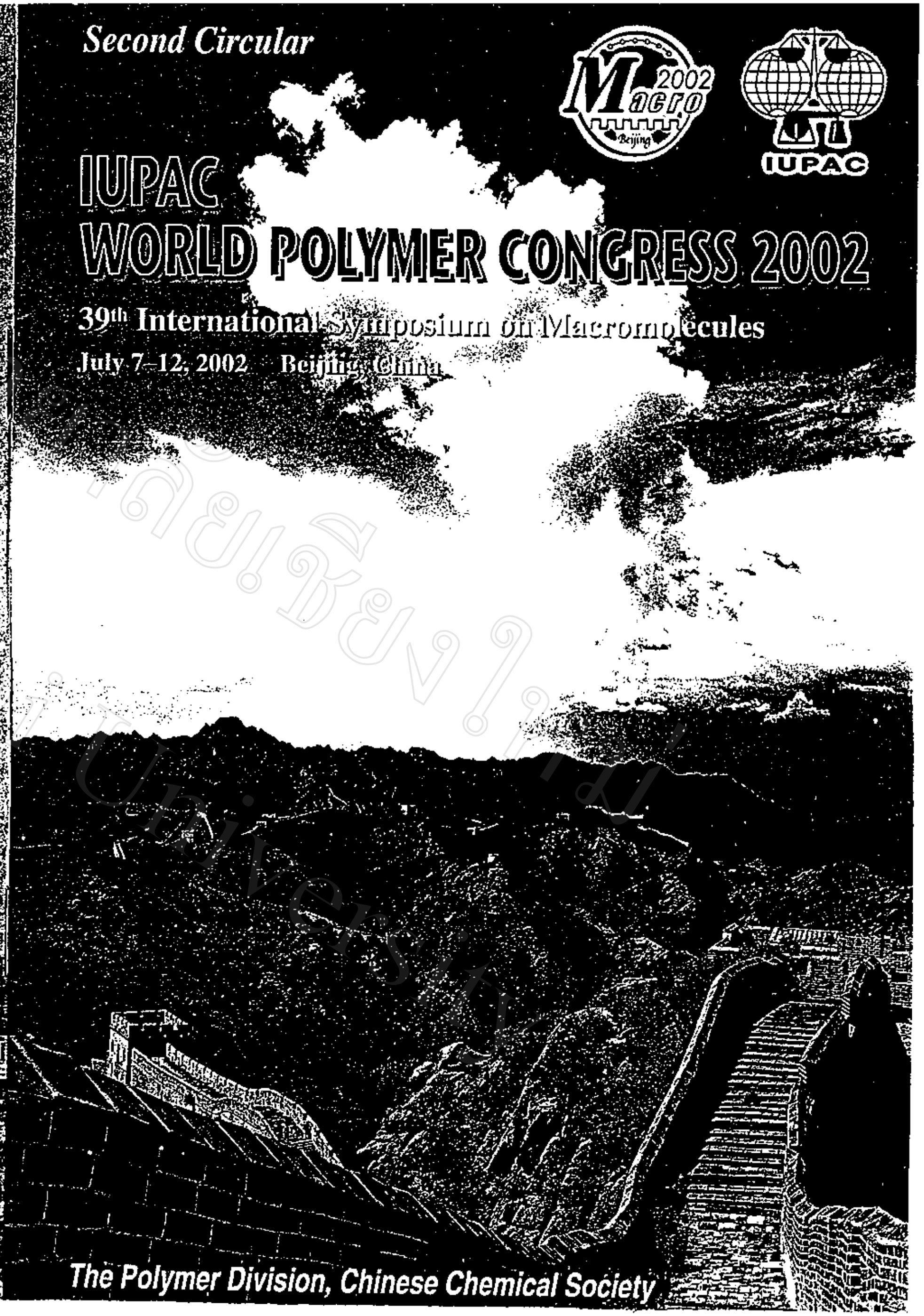

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DEVELOPMENT OF BIODEGRADABLE POLYESTERS FOR POTENTIAL USE AS ABSORBABLE SURGICAL SUTURES

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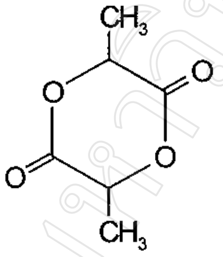
Introduction

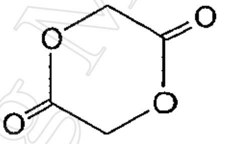
This paper describes some of the work which is currently being carried out in the Biomedical Polymers Research Unit in Chiang Mai on the development of biodegradable polyesters for potential use as absorbable surgical sutures. Particular attention is focussed on monofilament rather than multifilament sutures. This is an especially demanding area of application in which both the chemical microstructure of the polymer chain and its solid-state morphology need to be precisely controlled. Reaction control during synthesis and processing control during melt spinning are of critical importance. Some of the more important aspects of molecular design, synthesis, characterisation and processing will be briefly described.

Results and Discussion

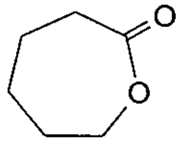
Both random and segmented block terpolymers of the 3 cyclic ester monomers: L-lactide, glycolide and ε-caprolactone (shown below) have been synthesized with L-lactide as the main component. The synthesis and characterisation of one of the random terpolymers was recently reported [1]. Polymerisations were carried out in bulk using tin(II) bis-2-ethyl hexanoate (stannous octoate) as a catalyst either alone or in conjunction with diethylene glycol as an initiator. The ring-opening polymerisation reaction proceeded via the so-called coordination-insertion type mechanism [2]. Microstructural characterisation was carried out via a combination of analytical techniques which included 1H- and 13C-NMR, DSC, TG, and GPC.



L-lactide



glycolide



ε-caprolactone

Monofilament fibres were produced using a small-scale melt spinning apparatus. In order to obtain fibres with the appropriate balance of properties, it is essential to be able to control not only the chemical microstructure during synthesis but also the molecular orientation and semi-crystalline morphology during processing. The extent to which this can be achieved to give fibres of the required morphology is an essential part of tailoring the fibre's properties to meet the specific demands of the absorbable suture application. This involves developing an understanding at the molecular level of how the polymer responds to the various conditions which are imposed upon it during the processing operations of extrusion, annealing and hot drawing. Some of the interdependencies of the underlying science and technology will be descibed in this paper.

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Factors influencing the small-scale melt spinning of poly(ε-caprolactone) monofilament fibres

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Abstract: Some of the main factors affecting the small-scale melt spinning of poly(ε-caprolactone), PCL, monofilament fibres have been studied. These factors included spinning temperature, extrusion rate, take-up rate, and draw ratio. The underlying influence of the polymer's own characteristic properties, in particular its chemical structure, transition temperatures (T_g, T_m) and crystallizability, were also interpreted within the context of the melt spinning process. Physically, the as-spun fibres obtained were uniform in diameter and smooth in surface appearance. They were also semi-crystalline (> 50%) in morphology. Mechanically, however, they were still very weak and highly extensible. Subsequent off-line cold-drawing at room temperature introduced the required degree of molecular orientation to reinforce the fibres, yielding tensile strengths of approaching 300 MPa. PCL fibres of precisely controlled physical dimensions and matrix morphology are attracting increasing interest for use in biomedical applications. This paper describes how this control can be achieved through the processing operation.

Keywords : poly(ε-caprolactone); small-scale fibre melt spinning; biodegradable polyester monofilament fibre

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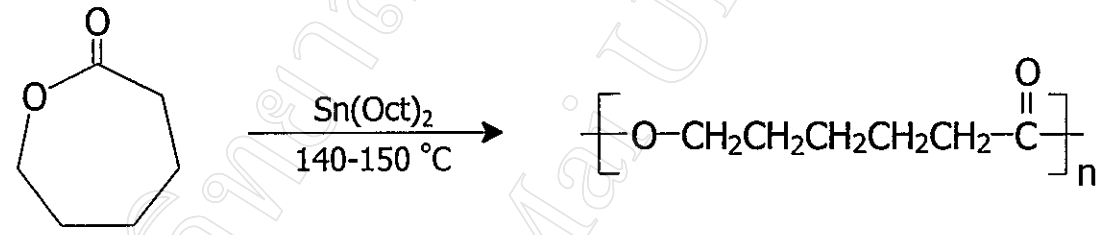
INTRODUCTION

Poly(ε-caprolactone), PCL, or simply polycaprolactone as it usually referred to, is a synthetic biodegradable aliphatic polyester which has attracted considerable research attention in recent years, notably in the specialist biomedical areas of controlled-release drug delivery systems, absorbable surgical sutures and nerve guides, and 3-dimensional (3-D) scaffolds for use in tissue engineering.[1-3] PCL is manufactured commercially via the ring-opening polymerization in bulk of ε-caprolactone, CL, using tin(II) bis(2-ethylhexanoate), commonly known as stannous octoate, $Sn(Oct)_2$, as a coordination-insertion catalyst at a temperature of, typically, 140-150 °C.



ε-caprolactone
CL

poly(ε-caprolactone)
PCL

As a commercial material, the main attractions of PCL are (1) its biodegradability, (2) its rather unique combination of polyolefin-like mechanical properties and polyester-like hydrolysability, (3) its compatibility with a wide range of other polymers, (4) its ease of melt processing due to its high thermal stability, and (5) its relatively low cost. On the other hand, its low melting point of around 60 °C and its very slow rate of biodegradation in the human body (2-3 years) have tended to restrict its usage as a homopolymer. Consequently, PCL has been used more as a component in polymer blends or in the form of a copolymer. For example, in its biomedical applications, PCL has been blended with polymers such as cellulose propionate, cellulose acetate-butyrate, poly(lactic acid) and poly(lactic acid - *co* - glycolic acid) for use in long-term drug delivery systems.[4-6] As a copolymer for suture applications, ε-caprolactone monomer has been copolymerized with L-lactide[7,8] and, most successfully, with glycolide[9,10] to yield a segmented triblock copolymer which is marketed under the trade name of MONOCRYL® (Ethicon, Inc.). Similarly, for use in absorbable nerve guides, ε-caprolactone has been copolymerized with DL-lactide[11] and trimethylene carbonate.[12]

However, it is on PCL as a homopolymer that this paper focusses its attention and, in particular, on its melt spinning as a monofilament fibre. As mentioned previously, PCL by itself is most suited biomedically to the design of long-term implantable systems, the most well-known commercial example of which is CAPRONOR® (Research Triangle Institute, USA), a biodegradable capsular delivery system for contraceptive control developed by Pitt and Schindler.[2,13] In fibre form, PCL has also been investigated for use in drug delivery systems,[14] as well as for "long-lasting" absorbable sutures,[15] and, most recently, 3-D scaffolds for tissue engineering applications.[16]

Yet, despite these applications, PCL fibres have received relatively scant attention in the literature, mainly because of their prohibitively low melting point. However, the exciting new developments which are taking place in tissue engineering may change this. Due to its ease of melt processing and its proven biocompatibility, PCL has been found to be well suited to rapid prototyping technologies such as fused deposition modeling (FDM) used in fabricating 3-D scaffolds for tissue growth.[16] Since the FDM method is essentially a melt spinning process, an increasing interest can be expected in the production of PCL monofilament fibres. Some of the factors which influence their melt spinning and the ways in which the polymer's chemical structure and molecular behaviour influence its processing characteristics are described in this paper.

EXPERIMENTAL

Polymer Material

The PCL used in this work was a commercial product (Aldrich Chemical Co., Product No. 44,074-4) with a stated number-average molecular weight, $\overline{M}_n$, of approximately 80,000 (GPC). It was supplied in the form of white beads which were dried in a vacuum oven at 40 °C for 24 hours before use in melt spinning. The polymer was not purified further by dissolution and reprecipitation since contact with organic solvents often leads to void formation in melt-spun fibres.

Polymer Characterization

The PCL beads, as supplied, were characterized according to those properties which were most relevant to their melt spinnability and solid-state morphology, namely: molecular weight, melting range, % crystallinity, crystallizability on cooling from the melt, thermal stability, and melt rheology.

Molecular weight determination was carried out by means of gel permeation chromatography (GPC) so that the $\overline{M}_n$ value could be compared directly with the supplier's own GPC $\overline{M}_n$ value of 80,000. The instrument used was a Waters 150-CV Gel Permeation Chromatograph employing both differential refractometer and viscometer detectors with universal calibration. Tetrahydrofuran (THF) was used as the solvent at a temperature of 30 °C and flow-rate of 1 ml min^{-1}.

However, when it was found that there was considerable variance between the experimental and supplier's GPC $\overline{M}_n$ values, two additional molecular weight methods were also used, namely: (1) light scattering and (2) dilute-solution viscometry. Light scattering, an absolute method for the determination of the weight-average molecular weight, $\overline{M}_w$, was performed using a Malvern Instruments 4700 Light Scattering Photometer equipped with an argon ion laser (wavelength = 488 nm). Again, THF was used as the solvent but, in this case, at 35 °C. Finally, dilute-solution viscometry was carried out using a Schott-Gerate

AVS300 Automatic Viscosity Measuring System with benzene as the solvent at either 25 °C or 30 °C.

The polymer's melting range, % crystallinity, and crystallizability on cooling from the melt were characterized using a Perkin-Elmer DSC7 Differential Scanning Calorimeter, while its thermal stability was determined using a Perkin-Elmer TGA7 Thermogravimetric Analyzer.

Melt rheology and, in particular, the dependence of melt flow index on temperature was measured using a Davenport Melt Flow Indexer, Model 10.

Melt Spinning Apparatus

The melt spinning apparatus used was a modular-design, small-scale fibre extruder manufactured by Ventures & Consultancy Bradford Ltd. (formerly Bradford University Research Ltd.), Bradford, UK. Its schematic arrangement is shown in Fig 1 with a more detailed diagram of the compression, melting and metering zones, comprising the cylinder, heating block, filter mesh and spinnerette, shown in Fig 2. The minimal dead volume within the system enabled sample sizes of as small as 10 g to be processed satisfactorily. The ice-water cooling bath was maintained at a temperature of 5-10 °C, while the vertical distance (air gap) between the spinnerette and the surface of the bath liquid was kept constant at 4 cm.

Fibre Testing

Following their melt spinning, the PCL monofilament fibres were characterized in terms of their uniformity of diameter and tested according to their solid-state morphology and mechanical properties. Mechanical (tensile) testing was performed using a Lloyds LRX+ Universal Testing Machine equipped with bollard-type grips and a 100 N load cell.

RESULTS AND DISCUSSION

Molecular Weight

The experimentally determined molecular weight averages, $\overline{M}_n$ and $\overline{M}_w$, are compared in Table 1 alongside the supplier's own $\overline{M}_n$ (GPC) value. In the case of dilute-solution viscometry, various Mark-Houwink Equations have appeared in the literature for PCL.[2] Of these, two of the most commonly reported are those shown in equations (1) and (2)

$$[\eta] = 1.25 \times 10^{-4}\ \overline{M}_n^{\ 0.82} \qquad \text{(in benzene at 25 °C)}^{17} \qquad (1)$$

$$[\eta] = 9.94 \times 10^{-5}\ \overline{M}_w^{\ 0.82} \qquad \text{(in benzene at 30 °C)}^{18} \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity in units of dl g^{-1}. These are the two equations that were used to calculate the viscometric $\overline{M}_n$ and $\overline{M}_w$ values in Table 1.

As the results in Table 1 show, the experimentally obtained values of $\overline{M}_n$ and $\overline{M}_w$ from the 3 different methods used are consistent with one another but the $\overline{M}_n$ values are significantly different from the supplier's $\overline{M}_n$ (GPC) value of 80,000. The reason for this is unclear but it may possibly be due to some hydrolytic degradation having occurred in the PCL beads since their manufacture. Whatever the reason may be, it illustrates the importance of not relying solely on the manufacturer's molecular weight data, especially where the polymer is moisture-sensitive and may unavoidably come into contact with air during storage.

Thermal Properties

The thermal properties of the PCL beads as supplied were characterized by a combination of differential scanning calorimetry (DSC) and thermogravimetry (TG). Their DSC heating and cooling curves are shown in Figs 3(a) and 4 respectively. As the heating curve shows in Fig 3(a), PCL is a semi-crystalline polymer of low melting range with a T_m (peak) of approximately 60 °C. The polymer's % crystallinity can be determined from its heat of melting, ΔH_m , via the equation:

$$\% \text{ crystallinity} \quad = \quad (\Delta H_m \times 100) \,/\, \Delta H_m^* \qquad (3)$$

where ΔH_m^* is the heat of melting of a 100% crystalline sample. For PCL, ΔH_m^* has been reported in the literature as having a value of 139.5 J g^{-1}.[19] Thus, the experimental value of ΔH_m = 90.0 J g^{-1} from Fig 3(a) yields a % crystallinity for the beads of 64%.

In addition to its crystallizability, the polymer's rate of crystallization on cooling from the melt is also an important consideration in melt spinning. As the DSC cooling curves in Fig 4 show, PCL is able to crystallize quite easily on cooling from above its melting range down to ambient temperature (70 → 20 °C) at cooling rates of up to 10 °C min^{-1}. This indicates that PCL is a relatively fast-crystallizing polymer, a property which can be ascribed to a high degree of chain flexibility and, because of its very low glass transition temperature (T_g = -60 °C), a high degree of chain segmental mobility at ambient temperature.

On comparing the curves in Fig 4, it appears that the crystallization exotherm ($\propto$ peak area) increases with increasing cooling rate, contrary to expectation. In fact, this is misleading since the peak areas cannot be compared visually because the curves are not normalized according to scanning rate. When the individual heats of crystallization, ΔH_c , are computed for each curve and then compared, it is found that each cooling rate gives a very similar value of ΔH_c in the range of 55-60 J g^{-1}. This demonstrates that, over the cooling rate range of 1-10 °C min^{-1}, the extent to which PCL can crystallize does not vary significantly. The only difference is in the temperature range over which crystallization occurs which, as would be expected, decreases with faster cooling.

It is also relevant to mention here that PCL is a polymer that can crystallize by itself on storage at room temperature. This is made possible by the fact that, at room temperature, PCL is almost 100 °C above its T_g and only 30-40 °C below its T_m. Thus, room temperature is, in effect, an 'annealing' temperature for PCL at which the polymer's chain mobility enables further crystallization to occur. Hence, it is not uncommon for the % crystallinity of PCL, after cooling from the melt, to increase during storage.

Other important considerations in melt spinning, indeed in melt processing in general, are the polymer's thermal stability in the melt state and the width of its processing range. This is particularly relevant in the case of aliphatic polyesters which are susceptible to transesterification reactions in the melt. These are degradative reactions which lead to a reduction in the average molecular weight (by intramolecular transesterification) and/or a broadening of the molecular weight distribution (by intermolecular transesterification). Both have an effect on the properties of the final product. The extent to which these reactions occur depends mainly on the chemical environment of the ester group, the reaction temperature, and time. Generally, transesterification precedes the onset of actual weight loss by volatilization and so the TG curve for the PCL beads in Fig 5 needs to be interpreted with caution. Whilst it may appear from the initial weight loss temperature of >250 °C that PCL has a very wide melt processing range (cf., T_m = 60 °C), in fact the processing range will be somewhat narrower than this suggests. Transesterification reactions may begin to occur at temperatures well below 200 °C and so the melt spinning temperature should be kept as low as the melt viscosity and filament line stability allow.

Melt Flow Index

The melt rheology and, more specifically, the melt viscosity of a fibre-forming polymer is of critical importance in its melt spinning since it has profound effects on filament line stability and dimensional control. The temperature-dependence of the melt viscosity of the PCL used in this work is shown in Fig 6 as a graph of melt flow index (MFI) against temperature at constant load (pressure). Measurements were made in accordance with ASTM Method D 1238 - 90b. It was found that the PCL could not be extruded smoothly at temperatures below 80 °C (i.e., at temperatures less than 20 °C above its melting range) due to too high a melt viscosity. Above 80 °C, the polymer's MFI increases (i.e., melt viscosity decreases) with temperature, as would be expected.

Indeed, this melt viscosity-temperature dependence can be described mathematically. It has been found that, for polymers of relatively low molecular weight, low melt viscosity, and at melt temperatures which are more than 100 °C above the polymer's T_g, as in the case of the PCL (T_g = -60 °C) used here, the melt viscosity-temperature (η_{melt} - T) dependence shows close adherence to the Arrhenius-type equation:

$$\eta_{melt} = A \exp(E/RT) \qquad (4)$$

where A is a constant (pre-exponential coefficient), E is the activation energy for viscous flow and R is the universal gas constant. Thus, a graph of ln η_{melt} against $1/T$ yields a reasonable straight line of slope E/R which, for most polymers that satisfy the above criteria, usually extends over about a 50-150 °C wide temperature range.[20]

Melt Spinning

One of the prime considerations in any melt spinning process is the melt spinning temperature. This is because the spinning temperature determines the melt viscosity which, together with the extrusion and take-up rates, determines the filament line stability. For the PCL used here, it was found that a spinning temperature of 85-90 °C yielded fibres of optimum quality in terms of their smooth surface appearance and uniformity of diameter. At higher spinning temperatures of up to 120 °C, the fibres obtained were still uniform in diameter but, as the melt viscosity decreased, the filament line started to show some initial signs of capillary instability.

As mentioned previously, PCL has a wide melt processing range due to its low melting point and high thermal stability. In such a case, it is preferable to choose a spinning temperature near the lower end of the range, usually around 20-40 °C above the melting range. The higher the temperature, the more heat that needs to be dissipated from the extruded fibre as it cools. Hence, increasing the spinning temperature above the required minimum should only be considered if it is really necessary to lower the melt viscosity. In addition to the spinning temperature, the other main processing variables are the extrusion rate (ram speed), take-up rate, spinnerette diameter, and the vertical distance from the spinnerette to the cooling bath. Together, these variables control the as-spun fibre diameter at the macroscopic level and the molecular orientation and semi-crystalline morphology at the microscopic level.

Prior to melt spinning, the PCL beads were first compressed into cylindrical rods. This was done by warming the beads (15-20 g) in the cylinder end-capped with a plain blanking plate under pressure from the ram. A temperature of 40-50 °C was found to be suitable for this purpose, just enough for the beads to soften and stick together without appreciable melting. Melt spinning from rods gave fibres of more consistent quality than from beads and also reduced the tendency for void formation.

A summary of the as-spun fibre diameters obtained under the various processing conditions used is given in Table 2. The effects of the individual processing variables are as would be expected, namely that the fibre diameter decreases with increasing spinning temperature (initially) and take-up rate but increases with increasing extrusion rate. By manipulation of these variables, together with the appropriate choice of spinnerette size, uniform PCL fibres of any required diameter could be reproducibly obtained.

The uniformity of the fibre diameters given in Table 2 is also notable in view of the fact that such slow spinning speeds were used. While slow speeds facilitate heat removal, they sometimes give rise to an oscillatory instability known as 'draw resonance', the cause of which can be traced back to the tensile stress to which the extruded fibre is subjected. However, draw resonance was not encountered in this work within the range of conditions studied, neither were cohesive or capillary fracture. The spinning dynamics were therefore deemed to be conducive to the establishment of a stable filament line.

Another important parameter in any fibre spinning process is the on-line 'draw ratio', also referred to as the 'spin stretch ratio'. Usually, in the case of a high melting point (T_m > 200 °C) fibre such as poly(ethylene terephthalate), which cools rapidly towards its glassy state, on-line drawing can impart substantial molecular orientation and, in doing so, can induce crystallization in the as-spun fibre.[21] However, in the case of PCL, on-line drawing merely stretches what is a highly extensible filament only just below its T_m range. The draw ratios reported in Table 2 therefore serve only to maintain filament line stability and control the fibre diameter. It is unlikely that they would have any significant effect on molecular orientation. In order to achieve this, separate off-line drawing at room temperature is required.

A final comment on the as-spun fibres, not apparent from Table 2, is that they were all semi-crystalline. The DSC curve shown in Fig 3(b) is typical. The combination of PCL's very low T_g and facile crystallization makes it extremely difficult, if not impossible, to produce amorphous fibres. Indeed, the as-spun fibres obtained here were all over 50% crystalline, even without the added inducement of chain orientation. Moreover, when chain orientation was introduced through off-line drawing, the % crystallinity of the fibre did increase slightly but not very much, as seen from the similar ΔH_m values in Figs 3(b) and 3(c). This evidence suggests that the kinetic and thermodynamic parameters associated with PCL's crystallizability from the melt are such that its % crystallization is determined more by the polymer's own characteristic properties, such as its temperature transitions and molecular weight, rather than the processing conditions. In support of this view, a marked (inverse) dependence of % crystallinity on molecular weight has already been established for PCL.[2]

Mechanical Testing

Finally, the mechanical properties of the as-spun fibres were examined by tensile testing. A typical stress-strain curve is shown in Fig 7(a). Even though the sample in Fig 7(a) was over 50% crystalline (from its DSC curve), it was still a very weak fibre which could be stretched easily to over 20 times its original length without breaking. This is indicative that the spinning process introduced very little if any molecular orientation along the fibre axis.

However, when the same as-spun fibre was drawn at room temperature to off-line draw ratios (OLDR) of 5, 10, 15, 20 and 25 and then re-tested, the stress-strain curves in Figs 7(b)-7(f) show quite clearly the reinforcing effects of orienting the fibre's semi-crystalline morphology. This demonstrates that the combination of on-line and off-line processing variables controls not only the fibre diameter but also the chain orientation and mechanical properties. More detailed studies of the effects of off-line drawing temperature and rate on fibre morphology and properties are continuing and will form the subject of a future paper.

CONCLUSIONS

The melt spinning process which has been described here is a simple batch-type discontinuous process for the production of monofilament fibres. It is suitable for small-scale experimental work, and even small-scale production, but not for the large-scale, high-speed production of commercial textile fibres. Since PCL is a speciality polymer which finds use in high-value but low-volume biomedical applications, this type of small-scale operation is well-suited to its melt spinning into fibres. In such highly specialized applications, the polymer's semi-crystalline morphology often needs to be precisely controlled in order to meet specific property requirements. This is especially true in the case of fibres which need to have the appropriate balance of physical, mechanical and biological properties, all of which depend on filament size and morphology. In order to achieve this balance, the various factors which affect the polymer's spinnability and crystallizability need to be clearly understood. This has been the main focus of this work.

Another advantage of the small-scale batch-type process is that it allows the process as a whole to be divided up into separate stages, thereby increasing the degree of control over structure formation. For example, in the first stage, the emphasis is placed on producing high-quality as-spun fibres of uniform diameter and smooth surface topography. Their % crystallinity and/or degree of molecular orientation are kept to a minimum during this initial stage. Then, in subsequent stages, the required matrix morphology can be gradually built into the fibres via a series of controlled off-line drawing and annealing steps.

For PCL, it has been shown here that the polymer's physico-chemical characteristics (chemical structure, transition temperatures) are such that they effectively pre-determine that the as-spun fibres will be semi-crystalline but largely unoriented. For certain fibre applications where tensile strength and modulus are not of critical importance, such as drug delivery systems and 3-D scaffolds for tissue growth, this type of morphology may be acceptable as it is. However, where strength and modulus are important, as in long-lasting absorbable sutures, an appropriate amount of chain orientation needs to be built in under controlled conditions.

The overriding conclusion from this work is that tailoring PCL fibres to meet the demands of a specific application requires precise processing control. This, in turn, requires an insight into what the molecules are doing at each stage of the operation. Melt spinning is a complex multi-variate process. Some of the most obvious variables have been discussed here, others have not. For example, sample parameters such as molecular weight and batch size may also have significant effects. Further studies of these factors and also of the various stages of structure formation through techniques such as X-ray diffraction and birefringence measurements are continuing.

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Table 1. Comparison of the various molecular weight values obtained for the PCL beads used in this work.

Mol. Wt. Method	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$
GPC			
Supplier's product data	80,000		
Experimentally found	26,500	52,800	1.99
Light scattering		45,100 [a]	
Dilute-solution viscometry	32,700 [b]	46,300 [c]	1.42

[a] as determined from a Zimm plot

[b] as calculated from equation (1)

[c] as calculated from equation (2)

Table 2. Summary of the effects of processing variables on the as-spun monofilament fibre diameter.

Spinning Temperature [a] *(°C)*	*Ram Speed* [b] *(mm / min)*	*Extrusion Rate* [c] *(m / min)*	*Take-Up Rate* [d] *(m / min)*	*On-Line Draw Ratio* [e]	*Fibre Diameter* [f] *(mm)*
85	2.0	0.12	0.60	5	0.91 ± 0.02
90	2.0	0.12	0.60	5	0.81 ± 0.02
100	2.0	0.12	0.60	5	0.80 ± 0.02
110	2.0	0.12	0.60	5	0.80 ± 0.02
120	2.0	0.12	0.60	5	0.79 ± 0.02
85	0.5	0.03	0.60	20	0.50 ± 0.02
85	1.0	0.06	0.60	10	0.66 ± 0.02
85	2.0	0.12	0.60	5	0.91 ± 0.02
85	2.0	0.12	0.60	5	0.91 ± 0.02
85	2.0	0.12	1.00	8.3	0.67 ± 0.02
85	2.0	0.12	2.00	16.7	0.49 ± 0.02

[a] as measured by the thermocouple, as shown in Fig 2

[b] constant rate of descent of the ram, as shown in Fig 2

[c] calculated from the ram speed via volume displacement

[d] wind-up speed on rollers of take-up unit, as shown in Fig 1

[e] on-line draw ratio = take-up rate ÷ extrusion rate

[f] average of 50 readings taken with a digital micrometer

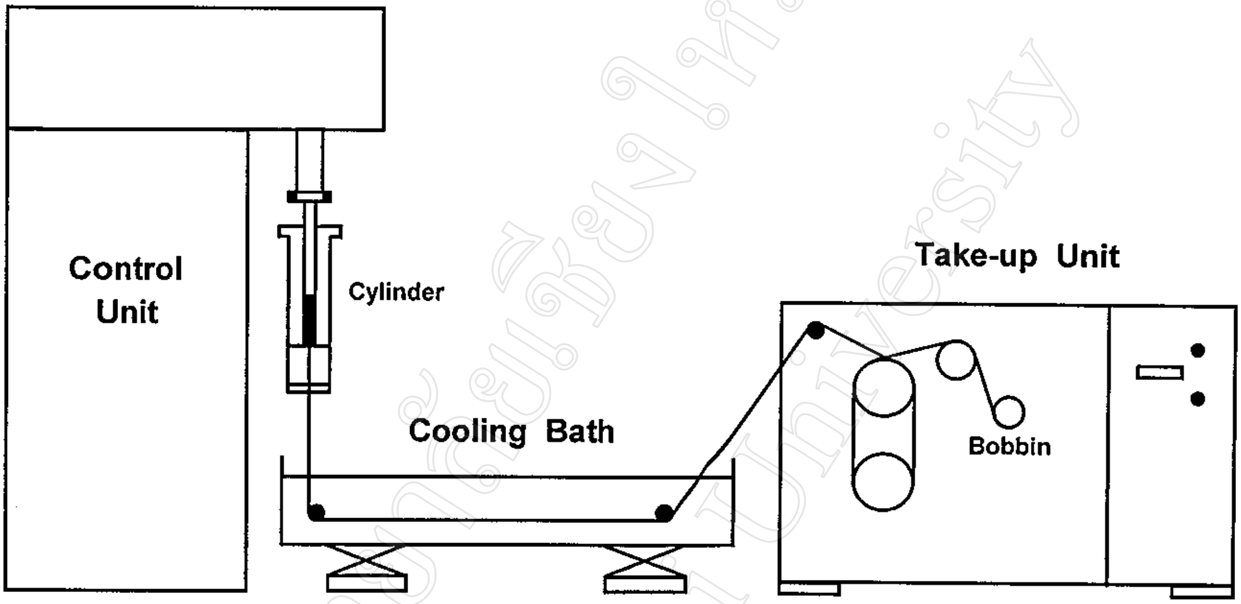

Figure 1. Schematic arrangement of the melt spinning apparatus.

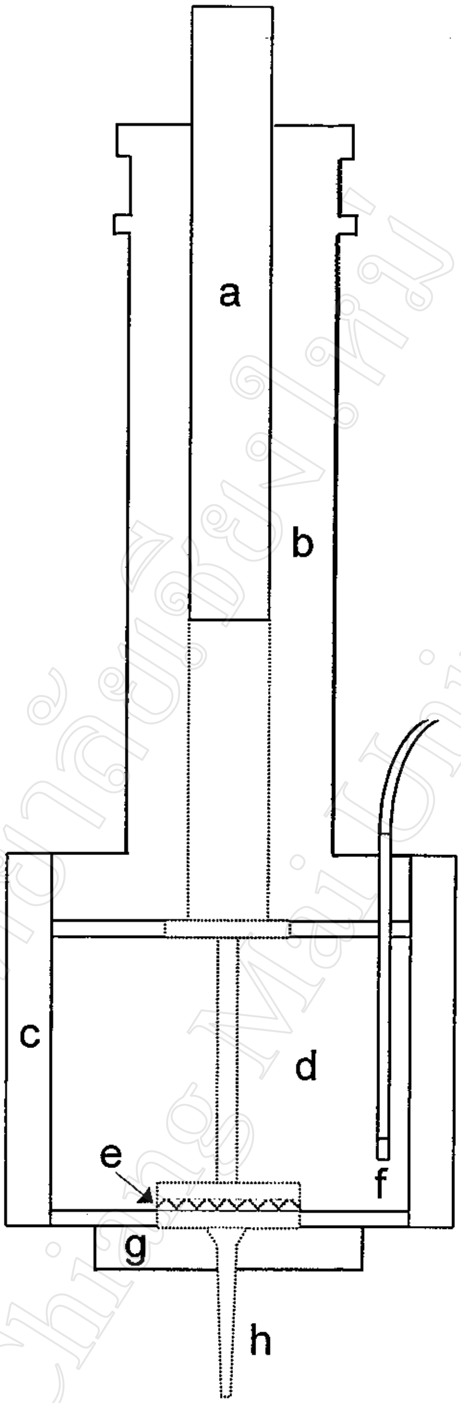

Figure 2. Schematic diagram of the compression, melting and metering zones showing the (a) ram, (b) cylinder, (c) band heater, (d) heating block, (e) stainless steel filter mesh, (f) thermocouple, (g) spinnerette, and (h) extruded monofilament fibre.

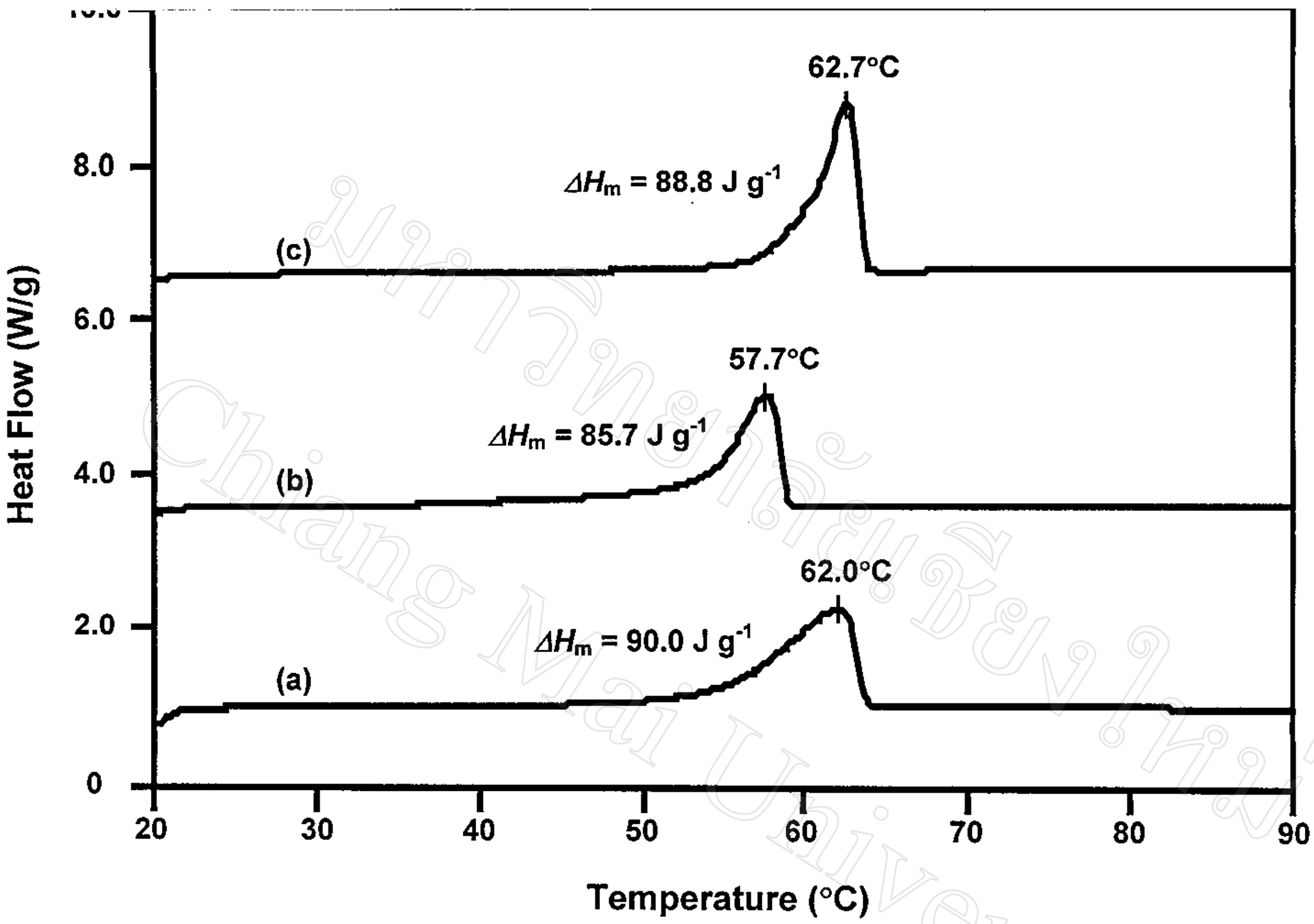

Figure 3. DSC heating curves showing the melting peaks of (a) the PCL beads, (b) an as-spun fibre and (c) an off-line drawn (x 25) fibre. (Heating rate = 5 °C/min)

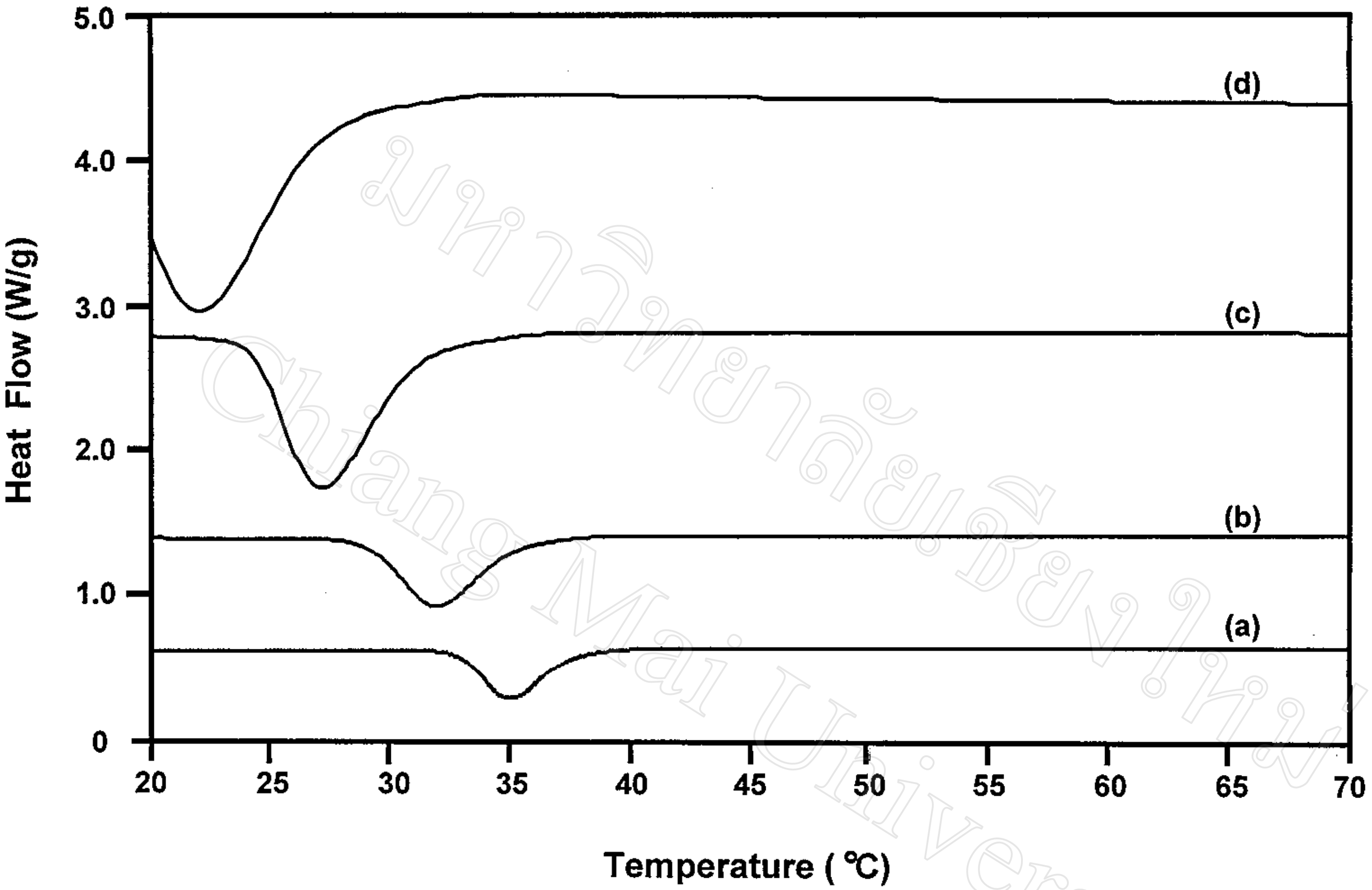

Figure 4. DSC cooling curves showing the PCL crystallization peaks at cooling rates of (a) 1 °C min^{-1} (b) 2 °C min^{-1} (c) 5 °C min^{-1} and (d) 10 °C min^{-1}.

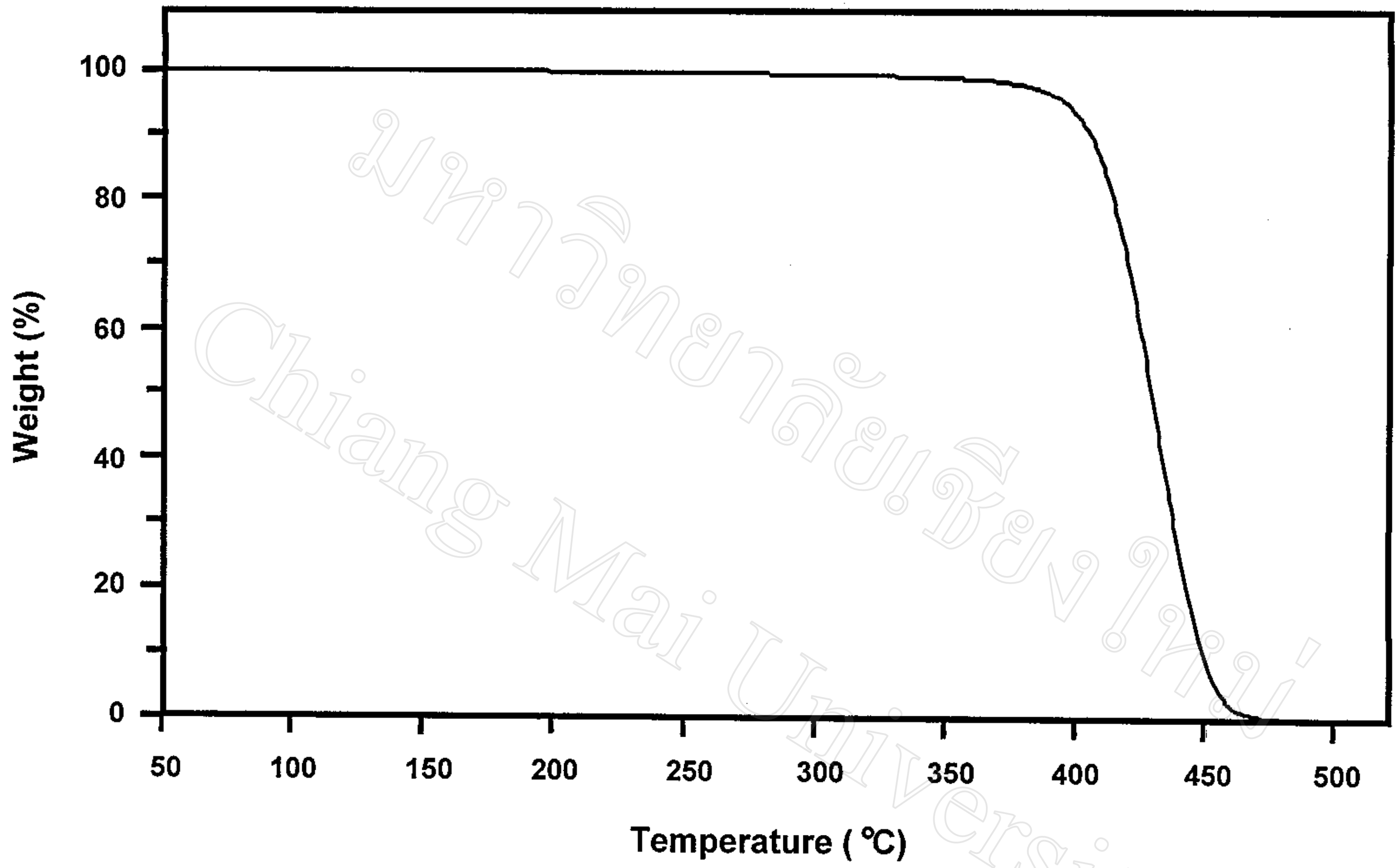

Figure 5. TG curve showing the thermal decomposition (weight loss) range of the PCL beads. (Heating rate = 20 °C min^{-1})

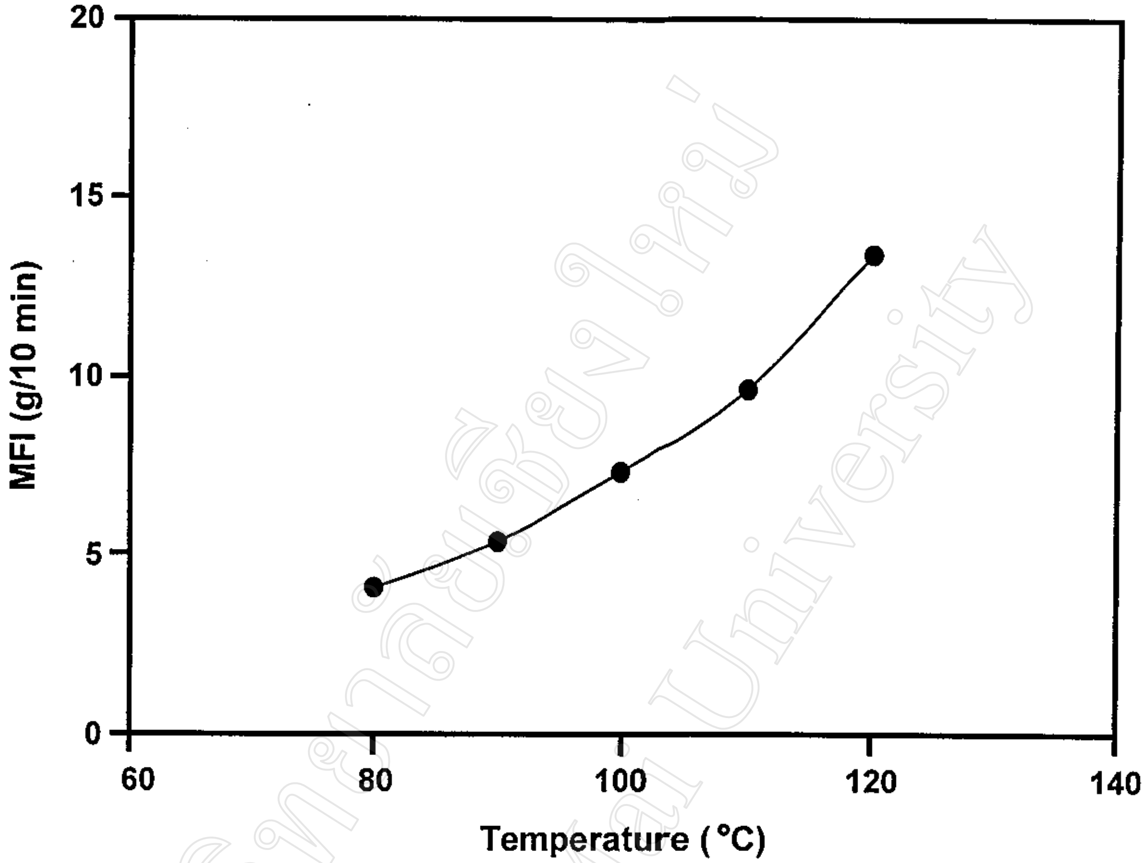

Figure 6. Graph showing the variation in melt flow index (MFI) with temperature under constant load for the PCL beads. (Load = 2.16 kg, pressure ≈ 300 kPa)

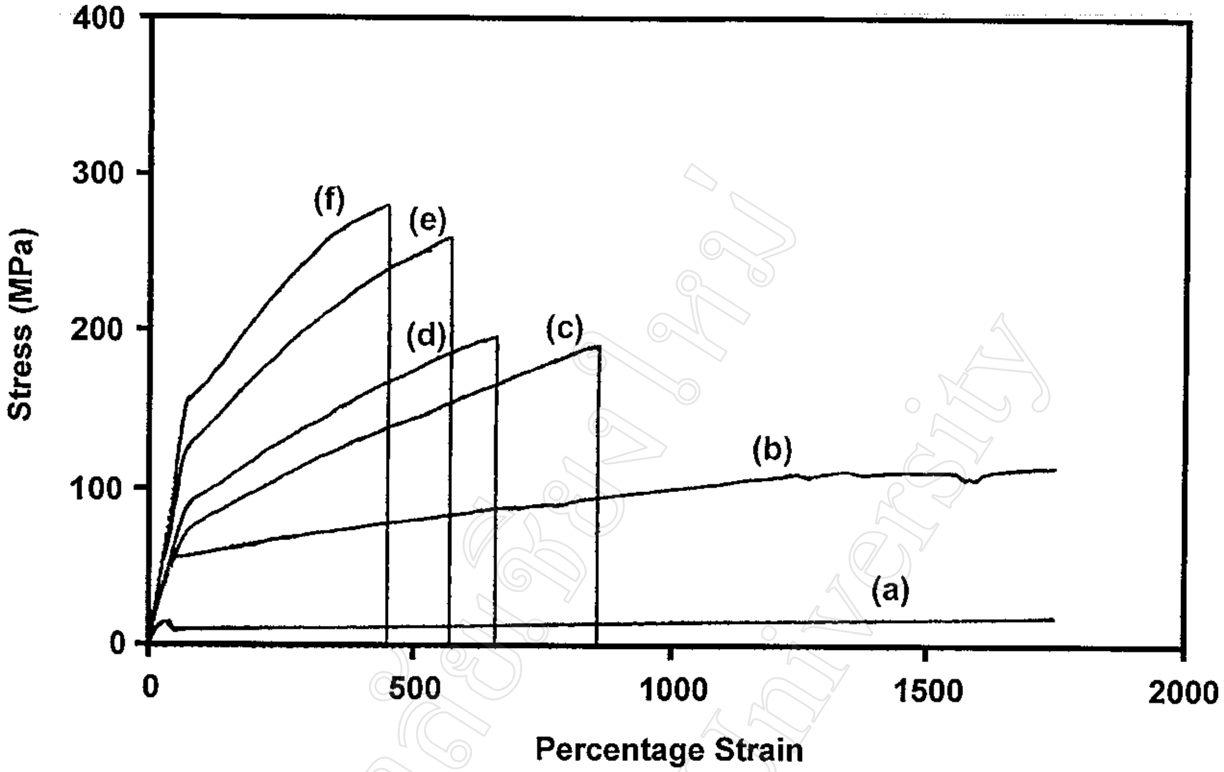

Figure 7. Stress-strain curves of the PCL fibres showing the effects of increasing the off-line draw ratio (OLDR) on tensile properties.
(a) as-spun fibre (b) OLDR = 5 (c) OLDR = 10 (d) OLDR = 15
(e) OLDR = 20 (f) OLDR = 25
(Initial gauge length = 40 mm, drawing rate = 20 mm min^{-1})