CHAPTER 3

FIBRE PROCESSING AND MECHANICAL PROPERTIES OF POLYMERS

3.1 Introduction

A **fibre** may be defined as a unit of matter having a length at least 100 times its width or diameter. An individual strand of continuous length is called a **filament**. Twisting together filaments into a strand gives continuous filament **yarn** [59]. Fibres may be divided into two major groups, namely, natural fibres and man-made fibres. Natural fibres are classified into 3 groups: (a) animal fibres, for example, silk, wool and hair (b) mineral fibres, for example, asbestos and (c) vegetable fibres are subdivided into bast fibres, leaf fibre, seed fibres and fruit fibres.

Man-made fibres are classified into two broad categories, regenerated (natural polymer) and synthetic fibres. Regenerated fibres are obtained from biological materials that are converted into fibres by chemical processes and subsequent spinning. Synthetic fibres are produced from chemical reactions of simple polymer-forming materials [60].

One of the most important applications for fibres is a medical/hygiene application. Fibres used in relation to health care and surgery may be classified as biodegradable or non-degradable. All fibres used for this application must be non-toxic, non-allergenic, and non-carcinogenic and must also be able to be sterilized without imparting any changes in their physical or chemical characteristics. Traditionally, natural fibres such as cotton, silk and later viscose have been extensively used in all areas of medical and surgical care such as application area on the wound. Besides wound care, fibre-based structures in synthetic or natural form are used in extracorporeal devices that may be used to purify blood in kidneys, create artificial livers and function as mechanical lungs, as well as finding use in suture materials, artificial ligaments and cartilages, and cardiovascular implants [61].

In this research work, we pay attention on the use of synthetic fibres for the absorbable surgical suture application, as mentioned in Chapter 1.

3.2 Fibre processing

Primary fabrication process in production of fibres is spinning. The term **spinning**, as used with natural fibres, refers to the twisting of short fibres into continuous length. However, in the synthetic fibre industry for polymer materials, the term is used for any process of producing continuous lengths by melt, dry and wet spinning techniques [19, 62-63].

(i) In melt spinning, the polymer is heated and molten polymer is pumped through a plate containing one or a number of small holes, called a spinnerette, to produce mono or multifilament fibres. They are then cooled in order to solidify by blowing cold air or other gas on the filaments. Only polymers that can be melted without molecular degradation may be fabricated into fibres by this technique.

(ii) In dry spinning, a polymer dissolved in a solvent is fed to a spinnerette by pumping, and then the solvent is evaporated which is done by blowing air or inert gas. Dry spinning is suitable for thermally unstable polymers and the solvent used must be volatile.

(iii) Wet spinning is employed for thermally labile polymers for which no volatile solvent exists. In this technique, the liquid mixture of polymer in non volatile solvent is extruded directly into another solvent which either extracts the solvent from the filaments or enters into a chemical reaction causing the original polymer be recovered. The recovered polymer is insoluble in the solvent used, so it coagulates. The wet spinning bath is maintained at a constant temperature.

Other less common methods and variants on these basic processes have been studied such as **reaction spinning** of monomers or prepolymers is only suitable for very reactive starting materials. Insoluble and unmeltable polymers are subjected to **dispersion spinning** in which the fibre-forming polymer is dispersed in a solution of another polymer.

As mentioned above, the melt spinning process will be chosen to fabricate monofilament fibres in this research because obtained fibres have less impurity than any other spinning processes. The following section therefore describes in more details of the melt spinning technique. The fibre obtained is so-called as-spun fibre. Subsequently, crystallinity and molecular orientation of the as-spun fibre will be further developed by hot-drawing and annealing to give the required mechanical properties.

3.2.1 Melt-spinning

A basic form of the melt spinning process is illustrated in Fig. 3.1. Polymer, in the form of powder or chips, is fed from a hopper into an extruder where it is melted and transported to metering pump. The metering pump controls and ensures a steady flow of polymer to the spin pack where the polymer is filtered and forced through the capillaries of a mono or multifilament spinnerette. Before reaching the spinnerette, melted polymer passed through a so-called pack or filter. Filtration is needed in order to separate minor impurities which might otherwise accidentally contaminate the polymer and later on cause discontinuities in filaments or even plug the spinnerette holes. Removal of the accidental impurities is still important, and this may be achieved by passing the polymer through one or more fine-mesh screens. The polymer melts in passing through such a filtering device experiences considerable shearing, and this shearing proves to be highly beneficial. High shearing of the polymer in the pack helps to homogenize the polymer and purifies it from inhomogeneities in temperature distribution and consistency. The extruded filaments are drawn down to smaller diameters by the action of a godet roll, while they are simultaneously being cooled (quenched) by air blowing across the filament bundle. However, at quenching stage in melt spinning process, crystallization naturally will ensue and the crystallite orientation is very poorly developed. The necessary high orientation for fibre properties is achieved by stretching or drawing the crystalline threads. Finally, the resulting filaments are either wound onto a bobbin or they passed directly to another processing step such as drawing or texturing [63-65].

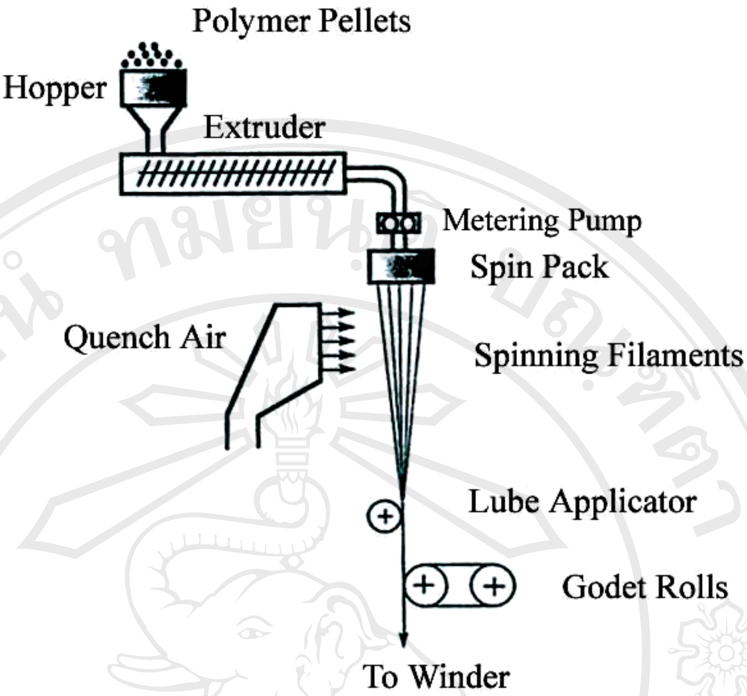

Fig. 3.1 Schematic representation of melt spinning system [66].

There are many variables for melt spinning process. One important variable is the spinning temperature. The lowest limit of temperature at which the polymer is completely molten is usually chosen. The adequate melting temperature is therefore at the equilibrium melting point or 20°C to 40°C higher, and margin appears to be higher for higher molecular weight polymers. The upper limit of melt temperatures is usually governed by polymer stability.

The spinnerette serves to change the polymer shape into infinitely long fibre controlled by spinnerette orifice shape and dimension. The spinnerette may consist of one or more holes depending upon whether monofilament or multifilament fibres are required. The larger individual hole diameters are for the more viscoelastic melts. Special spinnerettes having various unusual shapes (see in Fig. 3.2) have been used primarily with melt-spun types of fibres such as nylons and polyesters, though they may sometimes be used with other spinning systems too. The purpose of these designs is to increase surface area for improving some properties such as flexibility, dyeability, absorption, control of luster, transparency, or cover, to improve thermal properties, or to permit two different types of materials to be spun together to form a bicomponent fibre, for example, a higher gloss of triangular cross-sections, a greater stiffness if shapes are trilobal or cross-like, a better water-uptake of hollow fibres, etc. [19, 67].

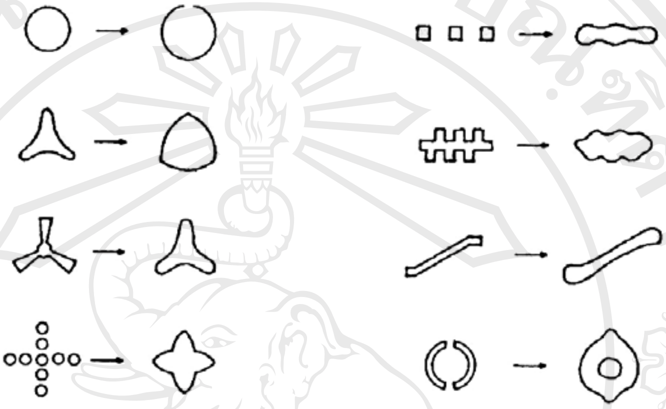

Fig. 3.2 Some cross-sections of holes in spinnerettes (left) and resulting cross-sections of fibres (right) [19].

Finally, take-up velocity of the wound-up or deposited filaments controls the productivity of the spinline. It also has a marked effect on the structure and properties of the melt spun filaments and how the spun filaments behave in subsequent processing steps such as drawing and texturing. For example, the as-spun filaments, which emerge from the spinnerette face into air and begin to cool, are almost completely unoriented that depend upon the rate of cooling in melt spinning and the conditions of take-up speed. Mezghani, K. and Spruiell, J.E. [68] reported the crystallinity and overall molecular orientation of poly(L-lactic acid) filaments which were produced by high speed melt spinning, were increased with increasing take - up velocity. It indicated that the take-up velocity was directly correlated to the mechanical properties of filaments. However, if the obtained fibres are completely occurred orientation and crystallization during spinning process with high take-up velocity, they may not be improved mechanical property further. Accordingly, the mechanical properties requirement can be controlled by preparation the as-spun fibres consisting of almost amorphous structure. The resulting fibres are then able to improve the mechanical properties in the off-line drawing process that the partial orientation of the polymer chains is achieved.

3.2.2 Hot-drawing

Drawing is a common commercial process for improving mechanical properties of fibres. The orientation is introduced by subsequent drawing after the polymer has first solidified in an unoriented state or a state of low orientation. One might envisage drawing as removing the **kinks** from the polymer chains and extending them along a common axis to promote closer packing at temperature above its glass transition temperature (see in Fig. 3.3(a)-(c)). Fig. 3.3(a) represents a schematic picture for an unoriented amorphous structure in as-spun fibre, then crystallization can occur randomly in solid amorphous fibre, which this process is called annealing (see Fig. 3.3(b) and the next section). Finally, crystallization and orientation can occur further during drawing in the draw direction as seen in Fig. 3.3(c). That is to say that drawing process not only induces orientation of crystallites which has already occurred but also induces orientation in amorphous region immersely and as a result, there appears higher crystallinity [9, 13].

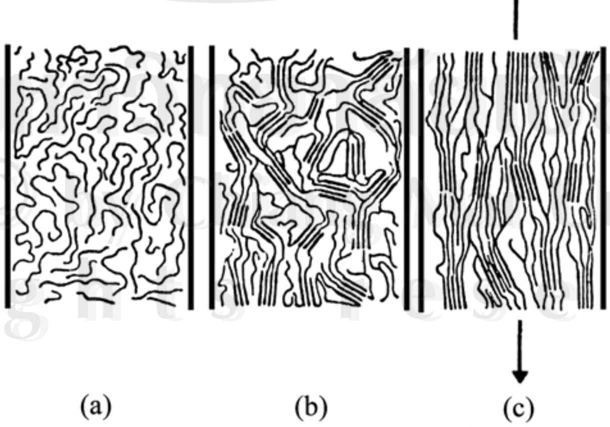

Fig. 3.3 Schematic representation of molecular and crystal orientation in (a) as-spun (b) annealed and (c) drawn fibre [69].

Normally, drawing process may be performed either by hand or using instrument. Fig. 3.4 showed a schematic of drawing process using instrument. There are two sets of rolls, one feeds an undrawn fibre from a supply package at velocity ν_1 while the other winds to collect the drawn fibre at velocity ν_2. The fibre passes over a snubbing pin between the two sets of rolls; drawing is localized in the neighborhood of the pin. The fibre is then collected on a metal or plastic bobbin [17]. The fibre may be drawn in a temperature range controlled by a tube furnace (optional) as shown in Fig. 3.4.

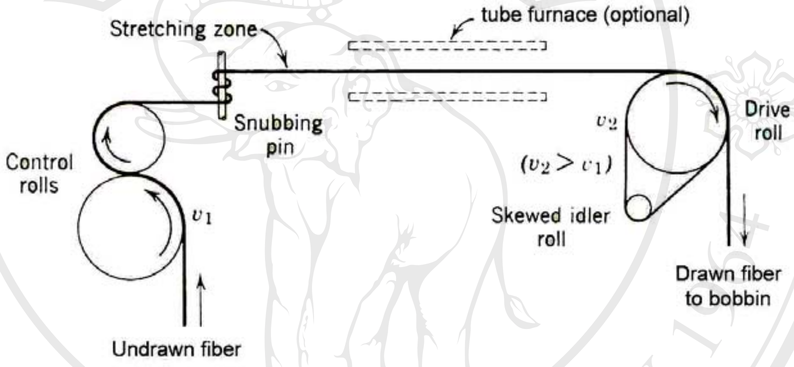

Fig. 3.4 Schematic diagram of a drawing process [17].

As a result of drawing, the fibre was extended to a final length determined by the difference between ν_1 and ν_2. The extension of the fibre may be represented by a term of draw ratio (λ) evaluated as follows.

$$\lambda = \frac{l}{l_0}$$

where l_0 and l are the initial and final lengths of the drawn fibre.
The draw ratio can also be determined by the ratio of the velocities (ν_1 and ν_2) of the two rolls, as below.

$$\lambda = \frac{v_2}{v_1}$$

Draw ratio is one of the factors which has effect upon the degree of molecular orientation. Okumura, W. et. al. [70] reported the fibre structure and mechanical properties of Poly(ethylene terephthalate), PET, fibres obtained by continuous drawing under heating with a CO_2 laser. It reveals that crystal orientation and crystallite size are dependent on the draw ratio. As draw ratio increases, orientation-induce crystallization and the tensile strength of the fibres also increase.

3.2.3 Annealing

Annealing is a process in which a polymer was heated under vacuum or in an inert atmosphere (to prevent oxidation) at a specified temperature to induce crystallization in polymer. Annealing temperature for a polymer is usually chosen in between its glass transition temperature T_g and melting temperature T_m. Annealing technique is often employed as a means of improving some fibre properties. Annealing fibre may be done in two ways for different particular purposes. One is in which a fibre is annealed under constant length, the so-called fixed annealing. The other is annealing a fibre under constant tension, so-called free annealing. Crystallization of polymer in free annealing process occurs randomly as shown in Fig. 3.3(b), resulting in brittle and low tensile strength. On the other hand, annealing under constant length or fixed annealing induces both crystallization and orientation of crystallites along the fibre axis, as seen in Fig. 3.5. This results in higher tensile properties in the fibre direction [32].

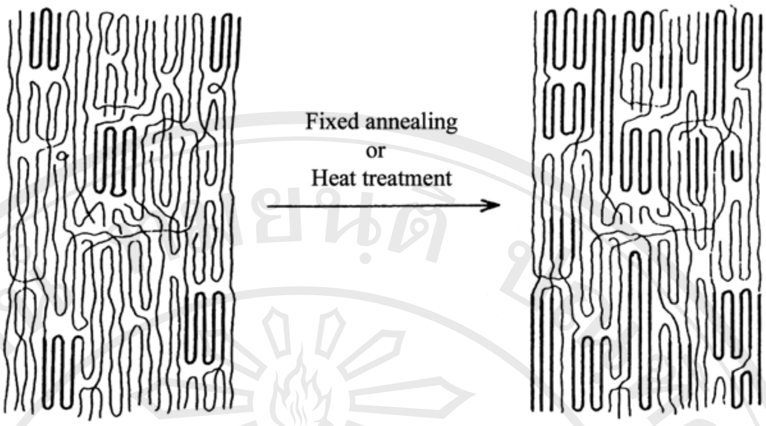

Fig. 3.5 Schematic representation of crystallization in fibre under annealing process [71].

3.3 Mechanical properties

Material selection for a variety of applications is quite often based on mechanical properties such as strength, toughness, flexibility, etc. Mechanical behavior of a material is determined by its response or deformation to an applied load or force**.** The ways in which the mechanical behavior can be determined have to be designed particularly to the specific properties of the materials, e.g. tension, compression, and shear, as illustrated in Fig. 3.6 [69, 72-74].

Tensile test is a measurement of the ability of a material such as fibre or filaments to withstand forces that tend to pull it apart and also to determine to what extent the material is able to stretch before breaking. This tension test is the most common type of stress-strain measurement. Fig. 3.6(a) shows the effect of applying tensile force or load (***F***) in a direction perpendicular to an uniform cross-sectional area (A_0) of a specimen of an initial length, l_0. As a result, the specimen extends to a final length, l, at the expense of reduction in its cross-sectional area.

Compression test is conducted in a manner similar to the tensile test, except that the force is compressive and the specimen contracts along the direction of the stress. Fig. 3.6(b) illustrates the effect of a compressive forces or load (F) pushing on specimen surfaces perpendicular to its uniform cross-sectional area (A_0).

Consequently, the specimen contracts from an initial length l_0 to l with increasing in its cross-sectional area.

Shear test is a measurement of the ability of a material to withstand maximum load required to shear the specimen so that the moving portion completely clears the stationary portion. Load or force (F) imposed parallel to the upper and lower faces, each of which has an area of A_0. The shear strain γ is defined as the tangent of the strain angle θ, as indicated in Fig. 3.6(c).

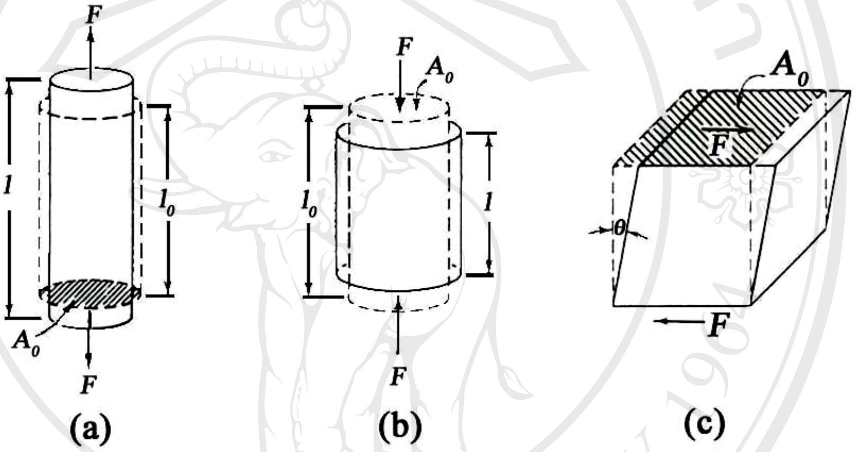

Fig. 3.6 (a) Schematic illustration of how a tensile load produces an elongation and positive linear strain. Dashed lines represent the shape before deformation; solid lines, after deformation. (b) Schematic illustration of how a compressive load produces contraction and a negative linear strain. (c) Schematic representation of shear strain γ, where γ = tanθ [72].

In this research project, we aim to produce monofilament fibres for suture application, so the tensile test is required. In the experiment, tensile strength is determined by stretching a fibre polymer of uniform dimensions. The specimen is deformed, usually extended to fracture, with a gradually increasing tensile load applied uniaxially along the fibre axis. Output of a tensile test is a record of load or force applied and the corresponding elongation occurs for a constant rate of loading.

Elongation is the increase in length of the specimen produced by the applied load. Results of tensile testing are usually illustrated in the form of a stress-strain curve as shown in Fig. 3.7. This figure is a typical stress-strain curve that obtained for a number of polymers. Specific terms such as stress, strain, ultimate strength, yield point, etc., are defined as below.

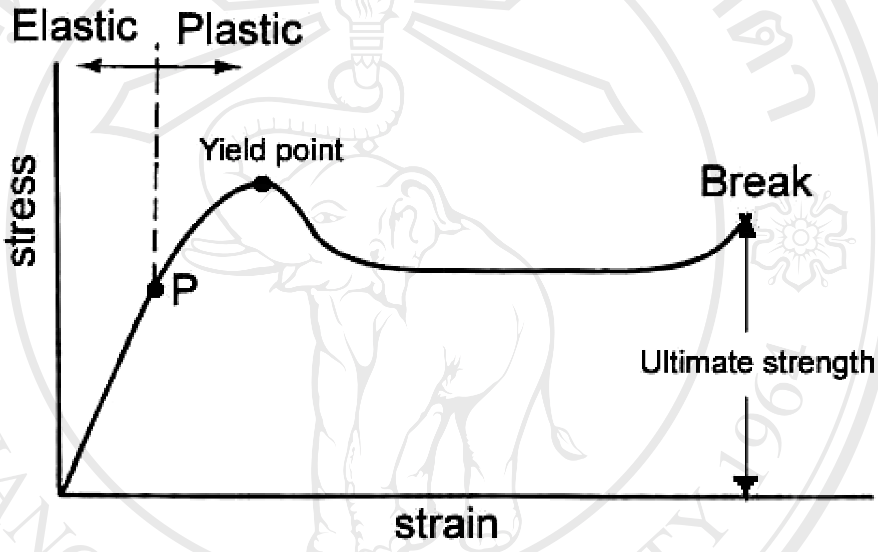

Fig. 3.7 A typical stress-strain curve for solid amorphous or semi-crystalline polymers.

Stress (σ) is defined as a force applied to produce deformation per unit area of the specimen perpendicular to the direction of force. Stress is therefore a ratio of an applied load to the corresponding perpendicular cross-sectional area. However, for simplicity, the cross-sectional area may be assumed constant, i.e. equivalent to the original cross-section at the beginning of testing. The stress is therefore evaluated as follows.

$$\sigma = \frac{F}{A_0}$$

where F is the instantaneous load applied to the specimen, in units of newtons (N) or pounds force (lb_f), and A_0 is the original cross-sectional area before any load is applied (in.^{2} or m^2). The unit of stress may be in megapascals, MPa (1MPa = 10^6 N/m^2), or pounds force per square inch, psi (145 psi = 1MPa).

Strain ($\in$) is defined as a ratio of elongation to the gauge length of the specimen, or simply stated as a change in length per unit of the original length, as written below.

$$\in = \frac{l_i - l_0}{l_0} = \frac{\Delta l}{l_0}$$

where l_0 is the original length before any load is applied, and l_i is the instantaneous length. Strain is unitless. Sometimes strain is also expressed as a percentage, in which the strain value is multiplied by 100.

Young's modulus (E) : In most traditional materials such as metals, their mechanical behavior obeys Hooke's law : stress is proportional to strain. That is they show linear-relationship between stress and strain. However, polymers behave differently. They may show much larger strains and the response to the stress is not linear. Young's modulus (E) which is defined as a ratio of stress and strain (see below) is therefore not constant. Figs. 3.8(a) and (b) show stress-strain diagrams for linear and non-linear response to the load applied. Linear relationship of stress and strain may be found in some polymers and their behavior is called **linear elastic deformation**.

$$E = \frac{\sigma}{\in}$$

Young's modulus is indicative of **stiffness**. The greater the modulus, the stiffer the material or the lower the modulus, the higher the flexibility. The Young's modulus is therefore a very useful parameter to indicate handling characteristics.

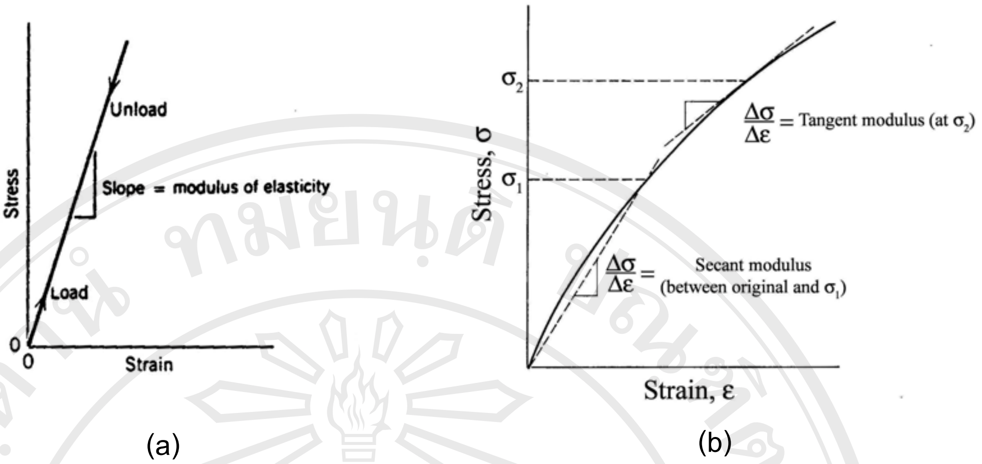

Fig. 3.8 Schematic stress-strain diagrams showing (a) linear elastic deformation for loading and unloading cycles and (b) non-linear elastic behavior and how secant and tangent moduli are determined [72].

Even though some polymers show non-linear behavior, initial portion of a stress-strain curve may appear approximately linear. In such case, initial modulus may be used. For some others, non-linear behavior might appear from the beginning, in these cases, either tangent or secant modulus as shown in Fig. 3.8(b) may be used. Tangent modulus is taken as the slope of the stress-strain curve at a specified stress, while secant modulus represents the slope of a secant drawn from the origin to a given point on the stress-strain curve.

Proportional limit (***P***) : When the applied load is continuously increased up to a point ***P*** (see Fig. 3.7), the actual curve deviates from the straight line and the point ***P*** is so called the **proportional limit**. Beyond this point, the sample's behavior is not elastic. The deformation below point ***P*** are relatively small and have been associated with bending and stretching of the interatomic bonds between atoms of the polymer molecules. Fig. 3.9(a) shows a simple drawing to illustrate straightening out of a molecular chain by bending and stretching in two-dimension. This type of deformation is instantaneous and recoverable. The deformation after point ***P*** but before the yield point occurs by uncoiling of molecular chains, as illustrated in Fig. 3.9(b). This deformation is recoverable but not instantaneously.

Yield point: The first point on the stress-strain curve at which an increase in strain occurs without the increase in stress. Beyond the yield point, extension occurs by displacement of molecules with respect to each other, intermolecular slippage (see Fig. 3.9(c)). The displaced molecules have no tendency to slip back to their original positions. These deformations are permanent and non recoverable and so called plastic deformation.

Yield strength: The stress at the yield point.

Ultimate strength: The maximum stress at which a material will be able to withstand when subjected to an applied load in tension.

Tensile strength: It is the stress at the maximum on the stress-strain curve. This corresponds to the maximum stress that can be sustained by a material in tension. If this stress is applied and maintained, fracture will result.

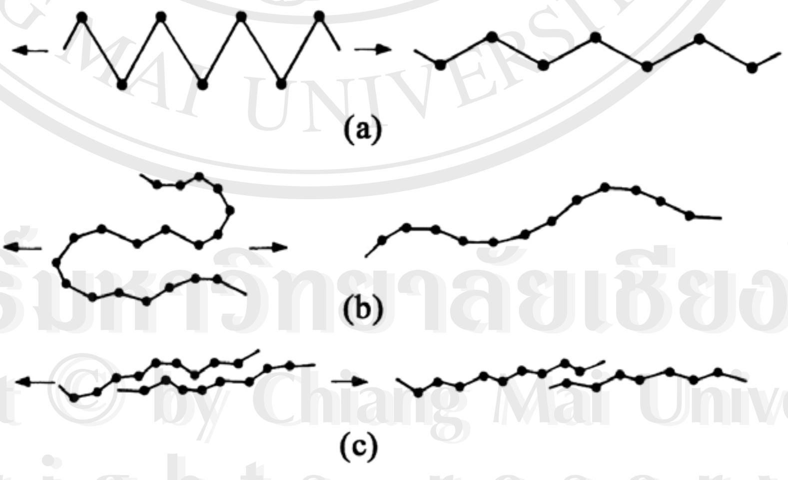

Fig. 3.9 Deformation occurred by (a) bending and stretching of interatomic bond (b) straightening out of a coiled portion in a molecular chain (c) intermolecular slippage [59].

Polymers can show various mechanical properties largely dependent upon their molecular structures and relative arrangements. A particular polymer can also show all the features of properties such as glassy, brittle, weak or rubbery depending on the conditions of testing, e.g. the rate of application of load, temperature, and time scale of measurement. It is therefore difficult to classify polymers as particular types of materials. However, it is helpful to specify their properties at a particular condition at testing from their stress-strain diagrams as described below.

Fig. 3.10 illustrates typical stress-strain curves obtained from polymers possessing different properties such as softness, brittleness, hardness and toughness. The area under the stress-strain curve is a measure of toughness of the polymeric material [12, 59]. Definitions of all other terms are as followed.

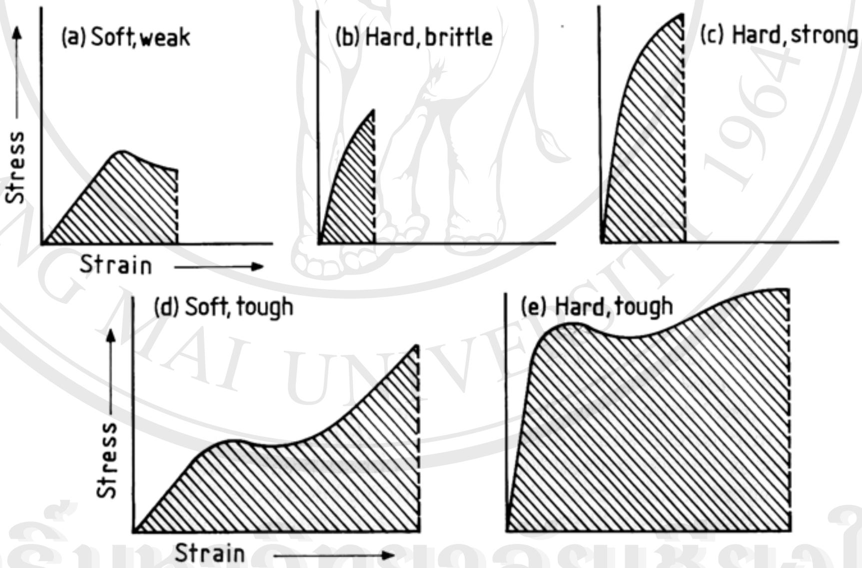

Fig. 3.10 Typical stress-strain curves [75].

A soft and weak material is characterized by low modulus, low (or no) yield point and moderate elongation at break.

A hard and brittle material is characterized by high modulus, no yield point and very low elongation at break.

A hard and strong material has high modulus, high yield stress, high ultimate strength and relatively low elongation at break.

A soft but tough material shows low modulus, low yield point but very high elongation and high stress at break.

A hard and tough material is characterized by high modulus, high yield stress relatively high elongation at break and high ultimate strength.

In addition, **ductility** is another important mechanical property. It is a measure of the degree of polymer deformation that has been sustained at fracture. On the other hand, a material which breaks readily is termed **brittle**. The tensile stress-strain behaviors for both ductile and brittle materials are schematically illustrated in Fig. 3.11.

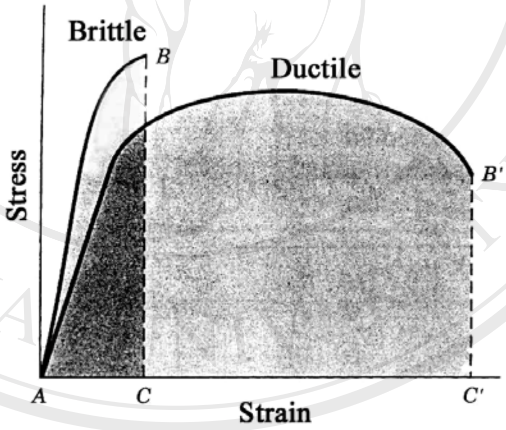

Fig. 3.11 Schematic representations of tensile stress-strain behavior for brittle and ductile materials loaded to fracture [72].

3.4. Effect of external factors on mechanical behavior

As described above, a stress-strain diagram is useful to identify polymer's mechanical properties at testing. However, mechanical behavior of polymer is affected by many factors; internal factors such as chemical structure, molecular architecture, copolymer composition and monomer sequence distribution, molecular weight and its distribution, morphology and crystallinity have already been discussed in chapter 1. Besides these internal factors, polymer's behavior responding to the applied load is also affected by external factors during testing. During tensile testing, there occurs development of the polymer's morphology induced by the load applied. The extent to which the development can go depend largely on the conditions used. For tensile testing of fibre, the conditions used are rate of extension or drawing, called strain rate, ambient humidity and temperature.

3.4.1 Influence of strain rate

Polymers tend to become less ductile and more brittle with increasing strain rate. As the rate of straining increases most polymers show a rise in modulus, a rise in yield stress and usually a drop in elongation to fracture. As an example of the influence of strain rate on mechanical behavior is demonstrated in Fig. 3.12. It shows that at a high strain rate unplasticized PVC is almost brittle with a relatively high modulus and strength. A low strain rate the same material exhibits a lower modulus and a high ductility, because at a low strain rate the polymer molecular chains have time to align themselves under the influence of the applied load. Thus the material is able to flow at the same rate as it is being strained [59].

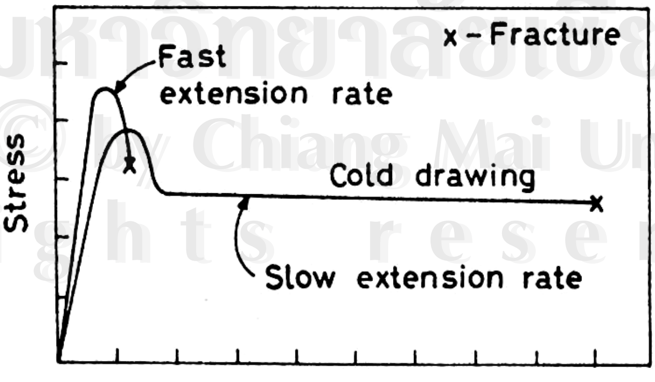

Fig. 3.12 Typical tensile behavior of unplaticized PVC [59].

3.4.2 Influence of temperature

The influence of temperature on the stress-strain behavior of polymers is in general opposite to the effects of strain rate. The load-elongation curves at a constant strain rate with increasing temperature are illustrated for a typical polymer sample in Fig. 3.13. At low temperatures, the load rises approximately linearly with increasing elongation up to the breaking-point, i.e. the polymer fractures in a brittle manner. At higher temperatures, a yield point is observed and the load falls before failure, sometimes with the appearance of a neck: i.e. ductile failure, but still a quit low strains (typically 10-20%). At still higher temperatures, under certain conditions, strain hardening occurs, the neck stabilizes and cold-drawing ensues. The extensions in this case are generally very large, up to 1000%. Finally, at even higher temperatures, homogeneous deformation is observed, with a very large extension at break. In an amorphous polymer this rubber-like behaviour occurs above the glass transition temperature so the stress levels are very low. However, ductile and brittle behaviour are most simply defined from the stress-strain curve as mentioned in section 3.3. Ductile behaviour shows a peak load followed by failure at a lower stress [76]. In conclusion, with increasing temperature, the modulus or stiffness of polymer tends to decrease, yield stress is reduced and yielding becomes more pronounced, and the polymer becomes more ductile. Since temperature greatly influences molecular motion.

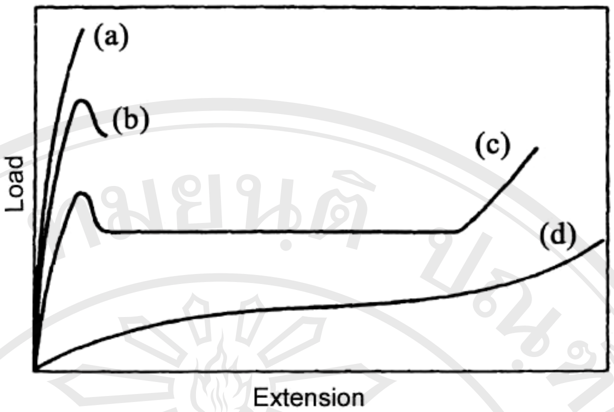

Fig.3.13 Load-extension curves for a typical polymer sample tested at four different temperatures, increasing from (a) to (d), showing different types of mechanical behaviour (a) brittle fracture (b) ductile failure (c) necking and cold-drawing and (d) homogeneous deformation(quasi-rubber-like behaviour) [76].

For examples of the effect of conditions on the behavior of polymers are demonstrated by stress-strain curves for samples of cellulose acetate when determined at different temperature in Fig. 3.14. This polymer exhibits ductile behavior at room temperature and at higher temperatures, a definite yield point and yield drop are present. However, as the temperature is lower to -85°F, yield is suppressed, strength is increased, and ductility is cut to about 12%. This behavior may be attributed to various molecular slippage effects [69].

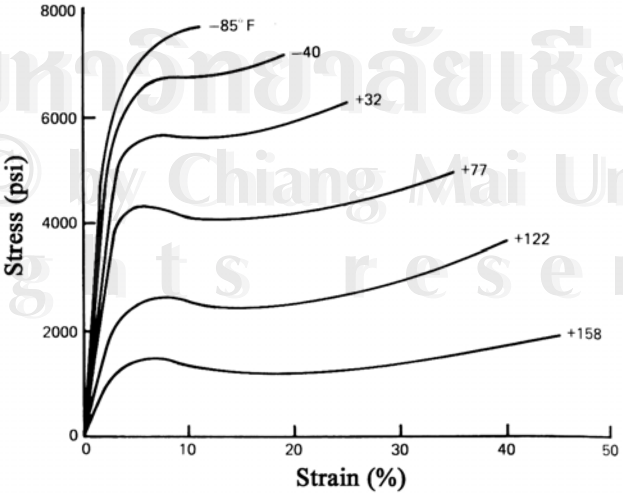

Fig. 3.14 Effect of temperature on tensile stress-strain curves of cellulose acetate [69].

In summary, mechanical properties of polymer revealed from its stress-strain curve depend not only on its molecular structures or morphology before testing but also depend upon the conditions used during testing, which have influence on morphology development until fracture.

One of polymer behaviors mentioned above is of most interest. It is cold-drawing. During cold drawing, the morphology changes immensely into a fibrillar structure in order to bare the load before its failure. When the fibrillar structure is obtained, its mechanical strength is ultimately high and useful for some particular applications. Therefore, cold drawing can be used to improve mechanical properties of polymer. Some amorphous and semi-crystalline polymers are normally capable of undergoing cold-drawing between T_g and T_m before ultimate failure. Polyethylene is a good example to illustrate how the morphology develop during cold-drawing until fracture as described below.

Fig. 3.15 shows a typical cold-drawing tensile stress-strain curve of a polyethylene specimen together with the shape of tensile specimen at several stages that has undergone large deformation from its original unoriented state. During the first rise in stress (***AB*** in Fig. 3.15), the cross-sectional area of specimen decrease uniformly with increasing length. The stress is proportional to the strain and Hooke's law is obeyed. The tensile modulus can be determined from this initial slope. As the strain and stress are increased until it reaches a maximum stress (at ***B*** in Fig. 3.15), a neck starts to form in the specimen. At the point ***B***, this is known as the yield point and permanent plastic deformation also takes place at this point. After yield point, the stress falls and settles at a constant and then starts increasing while the cross-sectional area at necked region extends along the specimen that is the process of **cold drawing** (see in Fig. 3.15). When the whole specimen is necked, strain hardening occurs and the stress rises until fractures at the point ***D*** [16, 77].

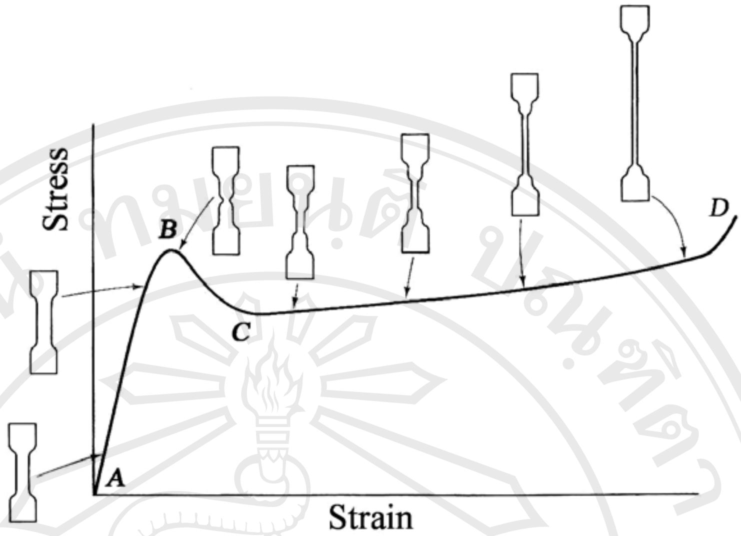

Fig. 3.15 Schematic represent of the stress-strain behavior of a semi-crystalline polymer. The shape of tensile specimens at several stages is indicated [78].

The morphology development during cold-drawing of polyethylene specimen above can be explained as the deformation of any semi-crystalline polymer fibre during applied drawing. Figs 3.16 and 3.17 demonstrate how the spherulitic and lamellar microstructure changes with deformation of a polymer fibre, corresponding to Fig. 3.15. The observation of these morphological changes with deformation provides the basis for understanding of the mechanisms of polymer changes. During the first stages of drawing (**AB** in Fig. 3.16), the spherulite tends to remain intact. The deformation is recoverable. The intermediate stage of deformation the crystals become distorted but remain essentially intact. The deformation is also recoverable but not instantaneously. Above some critical strain (at yield point, **B**) the deformation is irreversible. Spherulites slip past each other and amorphous regions along the spherulite boundaries lie to the draw direction. Towards the final stages (at **D** in Fig. 3.16), at high strain the spherulitic microstructure is lost, there appears to be a complete break-up of the original crystalline microstructure and a new fibre-like structure is formed. Steps in deformation at the level of lamellae can be pictured as shown in Fig. 3.17. Normally, the first deformation occurs in amorphous layer between lamellae or at the interspherulitic interface. Then, tie chain are extended and deformation occurs by slip-tilting of the crystalline lamellae until blocks of crystal are pulled out but are still attached to each other by tie chain. At sufficiently high strain the blocks become aligned along the draw direction and a fibrillar structure is obtained. In consequence of these processes, the number of chain folds decreases and the number of tie molecules increases. The latter and the partial interpenetration of lamellae increase the mechanical stability, tensile strength, and stiffness of the fibre [10, 13, 17, 78]. However, the morphology development and final structure obtained depend largely upon the rate of drawing and temperature, which are parameters to be controlled to achieve the final strength or mechanical properties desired for a particular application.

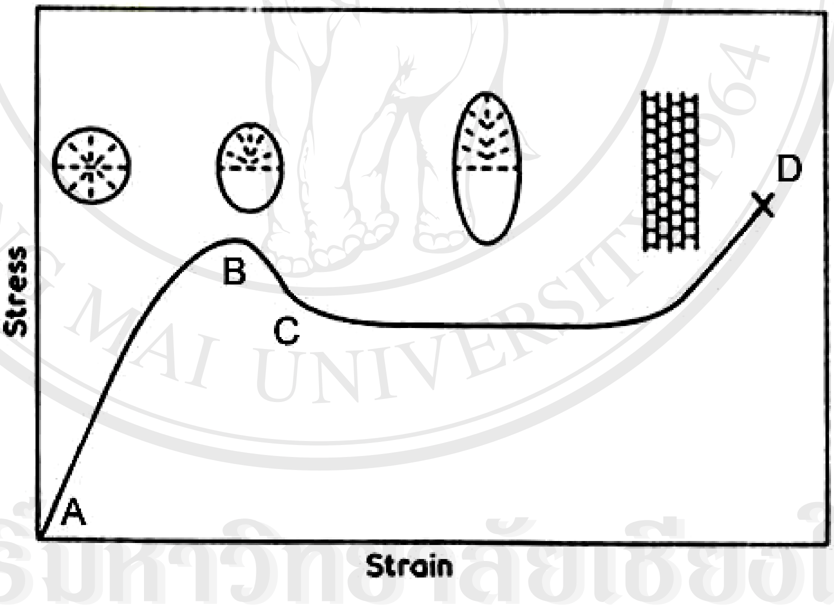

Fig. 3.16 Illustration of the change in spherulitic morphology during cold-drawing corresponding to Fig. 3.15 [16].

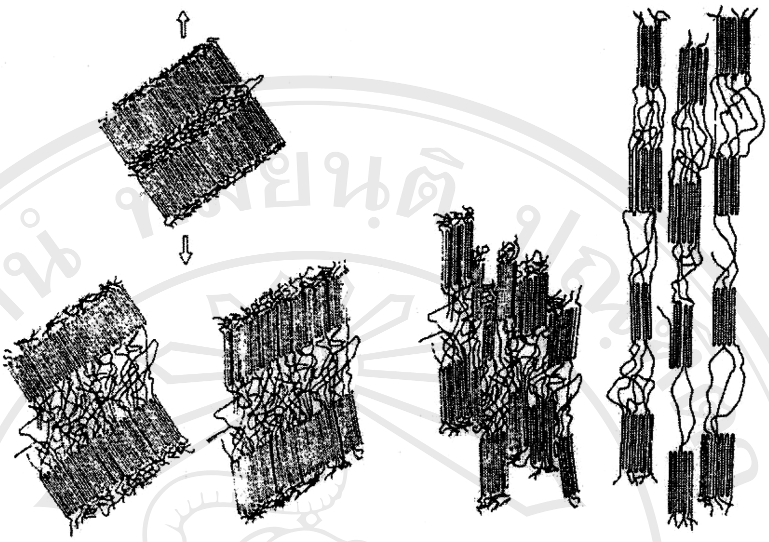

Fig. 3.17 Steps in deformation of semi-crystalline polymers [78].

3.5 Experiment of fibre production

In the production of fibre, we separated the procedure into two steps i.e. as-spun fibre preparation, and off-line hot-drawing and annealing. Firstly, as-spun fibre was produced by melt spinning process. The main purpose of this step was to obtain as-spun fibre of almost completely amorphous structure. This then enabled the required molecular orientation and semi-crystalline morphology to be gradually built in the fibre in the subsequent off-line hot-drawing and annealing step. Secondary, as-spun fibre obtained from the first step was then hot-drawn and annealed with various strain rates at suitable temperatures to modify its morphology until the desired mechanical properties were achieved.

3.5.1 As-spun fibre preparation

Fibres were first prepared using small-scale melt spinning apparatus which was manufactured by Ventures & Consultancy Bradford Ltd., Bradford, UK (see in Fig. 3.18) It could handle batch sizes of as small as 5-10 g of polymer.

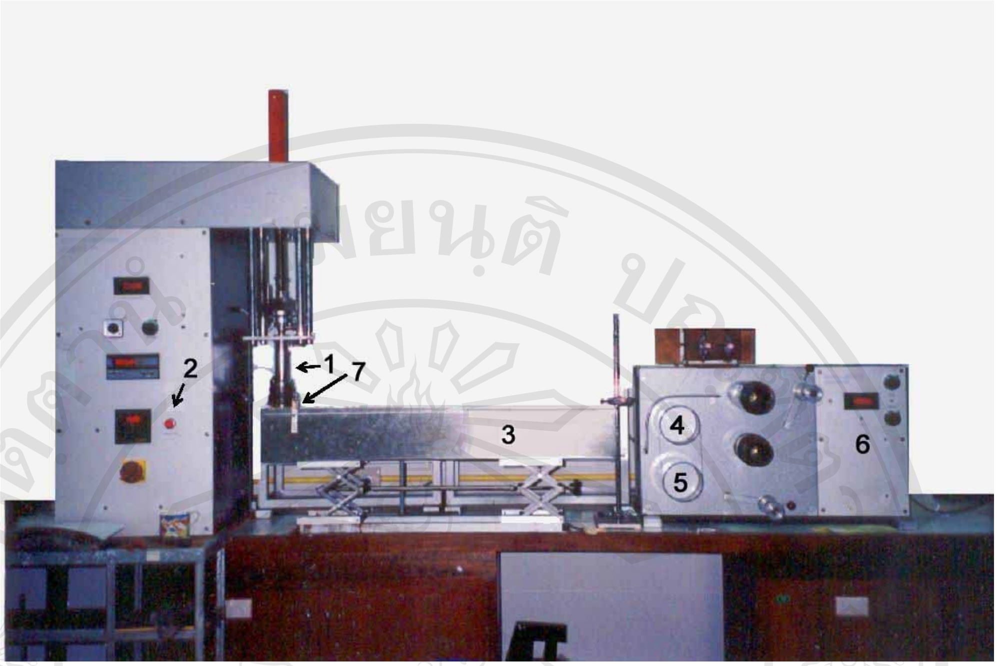

Fig.3.18 Illustration of the small-scale melt spinning apparatus.

1 = extrusion cylinder and heater block
2 = heater control switch
3 = cooling bath (ice-water)
4 = godet
5 = godet
6 = take up unit
7 = filament guide

A close view of some of the various accessories which were used for melt spinning are shown in Fig. 3.19 while complete assembled extrusion cylinder ready for melt spinning is illustrated in Fig. 3.20. A more detailed diagram of internal compression, melting and metering zones is shown in Fig.3.21.

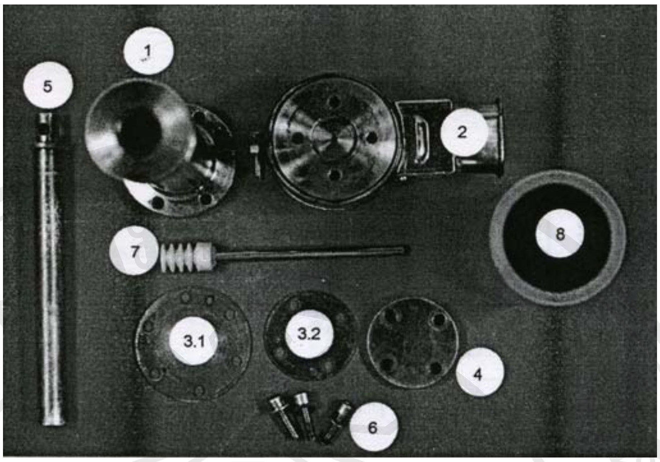

Fig. 3.19 Photograph of the various accessories used in the small-scale melt spinning apparatus

Key to figure:

1 = extrusion cylinder
2 = heating block fitted with band heater
3 = copper gaskets
    3.1 = gasket used between the extrusion cylinder and the heating block
    3.2 = gasket used between the heating block and the spinnerette
4 = single hole spinnerette (1 or 2 mm diameter)
5 = piston (ram)
6 = 20 mm cap screws
7 = filament guide
8 = PVC bobbin

Fig. 3.20 The assembled extrusion cylinder ready for melt spinning

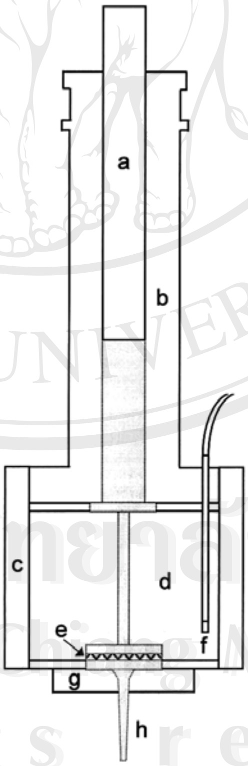

Fig. 3.21 Schematic diagram of the compression, melting and metering zones showing the (a) piston (b) cylinder (c) band heater (d) heating block (e) stainless steel filter mesh (f) thermocouple (g) spinnerette and (h) extruded monofilament fibre

Extrusion cylinder should have been prepared prior to use melt spinning procedure. The extrusion cylinder was attached to the heating block and a copper gasket by means of 20 mm cap screws that were lubricated with anti seizure compound. The spinnerette and another copper gasket were then bolted to the lower face of the heater block. It was necessary to insert a circular disc of fine stainless steel gauze in the center of the lower face of this heater block because it assisted the molten polymer to flow smoothly through the spinnerette that served a similar purpose to a screen pack in a conventional extruder as mentioned in section 3.2.1.

Polymer was inserted into the extrusion cylinder and the piston was placed in position. The extrusion cylinder was then arranged in the extrusion unit with the thermocouple and band heater in place. Switching on the heater and setting the temperature of 20-40°C below the melting temperature (T_{rod}) of polymer for 5 min, polymers were soften and stick together without actually melting. The polymer was compressed by piston in order to reduce the tendency for void formation until the piston could no longer move. The ram control switched off and heated up to the required spinning temperature. When the temperature approached the set value (T_{spin}), the ram control switched on again and the piston let down to compress the polymer with an appropriate ram speed. The molten polymer emerged from the spinnerette and cooled by contact with the room air before being passed through an ice-water quenching bath. The vertical distance from the spinnerette to the cooling bath was 4 cm, the fibre was wound 4 to 5 times in a clockwise direction around the two godets. Finally, wound on to the take-up spool through the traversing guide.

Processing conditions

The processing parameters used to prepare monofilaments of the poly(L-Lactide), random terpolymer, and block terpolymer monofilaments are shown in Table 3.1.

Table 3.1 The processing conditions used for melt spinning of poly(L-lactide), random and block terpolymers.

Polymer	**T_m[a] (°C)**	**T_{rod} (°C)**	**T_{spin} (°C)**	**R.S.[b] (mm/min)**	**Cooling bath (10-15°C) used**	**Extrusion rate[c] (m/min)**	**T.S.[d] (m/min)**	**OnLDR[e]**	**Spinnerette diameter (mm)**
Poly(L-lactide)	179	160	195	2.0	No	0.05	3.0	60	3
Random terpolymer	144	100-125	155	1.2	Yes	0.07	0.5	7	1
Block terpolymer	156	145-151	167	1.6	Yes	0.10	1.0	10	1

[a] T_m = melting point at the maximum of endothermic peak from DSC results

[b] R.S. = Ram (piston) speed (mm/min)

[c] Extrusion rate : for method of calculation, see the following page

[d] T.S. = Take-up speed (m/min)

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

Note; The internal diameter of the cylinder is 7.75 mm

Calculation of extrusion rate

The ram speed refers to the rate of vertical displacement (mm/min) of the piston as it descends into the extrusion cylinder. However, the rate of the fibre extruded from the spinnerette is more useful to determine extension (OnLDR) of the fibre collected on the spool. Therefore the ram speed is converted into an extrusion rate from the spinnerette as follows.

The extrusion rate can be calculated from the ram speed on the basis of assumption that volume of the molten polymer inside the cylinder displaced by the piston equals to the volume of the polymer exiting from the spinnerette.

Extrusion volume (inside the cylinder) = $\pi r_1^2 h_1 / \min$

Extruded volume exiting from the spinnerette = $\pi r_2^2 h_2 / \min$

where

r_1 = internal radius of the cylinder
r_2 = radius of the spinnerette hole
h_1 = distance that piston moves per min (ram speed)
h_2 = length of extruded fibre per min (extrusion rate)

by the assumption made:

$$\pi r_1^2 h_1 = \pi r_2^2 h_2$$

Therefore, calculated extrusion rate (h_2) is given by;

$$h_2 = \frac{r_1^2 h_1}{r_2^2}$$

The fibre obtained from the procedure explained above is referred to as the as-spun fibre. It is largely amorphous because of the extruded fibre is cooled quickly at a rate which is too fast for crystallization from the melt to occur and slow spinning speed was employed in order to obtain a minimum of molecular orientation. Using this approach and the conditions indicated in Table 3.1, monofilaments with a smooth surface were successfully produced with diameter of as-spun poly(L-lactide) fibre of

0.300-0.400 mm, 0.630-0.770 mm for random terpolymer fibre and 0.330-0.370 mm for block terpolymer fibre. These as-spun fibres were then vacuum dried and kept in a vacuum desiccator until required.

3.5.2 Off-line hot-drawing and annealing

As-spun fibres obtained as described in section 3.5.1 were largely amorphous with low crystallinity and molecular orientation (see section 5.2). Their mechanical properties were improved via off-line hot-drawing and annealing processes. Two sets of drawn fibres were prepared for different purposes.

First, as-spun fibres of the terpolymers were hot-drawn with draw rates as high as possible at various temperatures (30-80°C). From previous work [79, 80], it was found that drawing the fibre with a higher rate at a lower temperature induced more orientation in the amorphous regions. The reason is that at low temperature, molecular chain mobility is also low. As a consequence, molecular chains are forced by drawing to align along the fibre axis. However, if the draw rate is not high enough, the chains still have enough time for random movement resulting in lower overall orientation. In addition, crystallization induced during hot-drawing will occur less when drawing at a higher rate due to lack of time. As a result, the fibre will be more flexible, which is one of the most important properties in suture applications. In conclusion, the way in which a fibre should be drawn is by drawing at as high a rate as possible at a particular temperature to induce high molecular orientation along the fibre axis with moderate crystallinity. For this purpose, as-spun fibres of the terpolymers were then drawn by hand over a hot-drawing unit so as to control the rate as high as possible without tearing. Before drawing, each as-spun fibre was left for 30 sec in the hot-drawing unit to preheat at a chosen temperature in the range of 30-80°C. The fibre was then drawn by hand with the maximum rate. For each temperature, 3-5 as-spun fibres of each terpolymer were drawn. Their average draw ratio and draw rate obtained are shown in Table 3.2. These drawn fibres were then used for mechanical property and morphology studies, as described in chapter 5.

Second, as-spun fibres of the terpolymers were drawn to a high draw ratio followed by annealing at a high temperature to induce high crystallinity. The main purpose of this was to obtain fibres with high crystallinity with high orientation for crystal structure analysis by comparison with the crystal structure of poly(L-lactide), as described in chapter 4. Hot-drawn fibres of both terpolymers of low draw ratios, processed at low temperatures and without annealing were also studied for comparison using a new approach to their WAXD patterns. The drawing and annealing conditions for the post-spinning treatment of the poly(L-lactide), random and block terpolymer fibres used for structural analysis in chapter 4 are shown in Table 3.3. For this work, poly(L-lactide) [81] fibres were provided by the Biomedical Polymers Technology Unit.

Table 3.2 Average draw ratio and draw rate for off-line hot-drawing at various temperatures.

Polymer	$T_{drawing}$ (°C)	Draw rate (%/min)	Draw ratio
Random terpolymer	30	690	3.3
	40	1460	4.2
	50	2150	5.6
	60	3830	6.7
	70	6900	7.7
Block terpolymer	30	860	3.9
	40	1020	4.6
	50	1780	5.4
	60	3040	7.0
	70	5280	7.5
	80	4480	9.4

Table 3.3 Drawing and annealing conditions for post-spinning treatment of poly(L-lactide), random and block terpolymer fibres.

Polymer	**$T_{drawing}$ (°C)**	**Draw rate (%/min)**	**Draw ratio**	**$T_{annealing}$ (°C)**	**Annealing time (h)**
Random terpolymer	40	300 700	4.0 8.0	- 80	0 24
Block terpolymer	40	1000 1000	4.5 8.0	- 90	0 1
Poly(L-lactide)	70	2400	5	90	24