CHAPTER 1

MELT SPINNING

1.1 Introduction [1]

The viscose rayon method was developed towards the end of the last century and the melt spinning method for synthetic fibres was established in the early part of the 1930s. In the beginning of the history of spinning, progress in spinning techniques was mainly made by accumulating empirical facts; that is to say, by repeating a set of procedures such as setting a spinning condition and measuring the resultant properties and structures of the spun fibres. There were few studies on physico-chemical changes and on structural formation in the spinning fibres between the spinnerette and the take-up device. With the rapid advance of the synthetic fibre industry in the 1940s, a strong need arose to understand the basics of the spinning process in order to improve the productivity and quality control of the fibres. Consequently, towards the end of the 1950s, the melt spinning process started to be analyzed mathematically as an engineering problem and then later, in about the middle of the 1960s, a method for the quantitative description of the melt spinning process based on hydrodynamics, rheology and the theory of thermal conduction was established. Since then, studies on structural formation and crystallization during the spinning process have been extensively carried out such that the interrelationships between the various factors, as shown in Fig. 1.1, are now more clearly understood.

1.2 Spinning of Fibres [2]

The term ***spinning***, as used with natural fibres, refers to the twisting of short fibres into continuous lengths. In the modern synthetic fibre industry, the term is used for any process of producing continuous lengths by any means. A few other terms used in the fibre industry should also be defined. A ***fibre*** may be defined as a unit of matter having a length at

least100 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.*** If the filaments are assembled in a loose bundle, it is referred to as ***tow*** or ***roving***. These can be chopped into small lengths (an inch to several inches long) referred to as ***staple***. ***Spun yarn*** is made by twisting lengths of staple into a single continuous strand, while ***cord*** is formed by twisting together two or more yarns. Various yarn structures are shown in Fig.1.2.

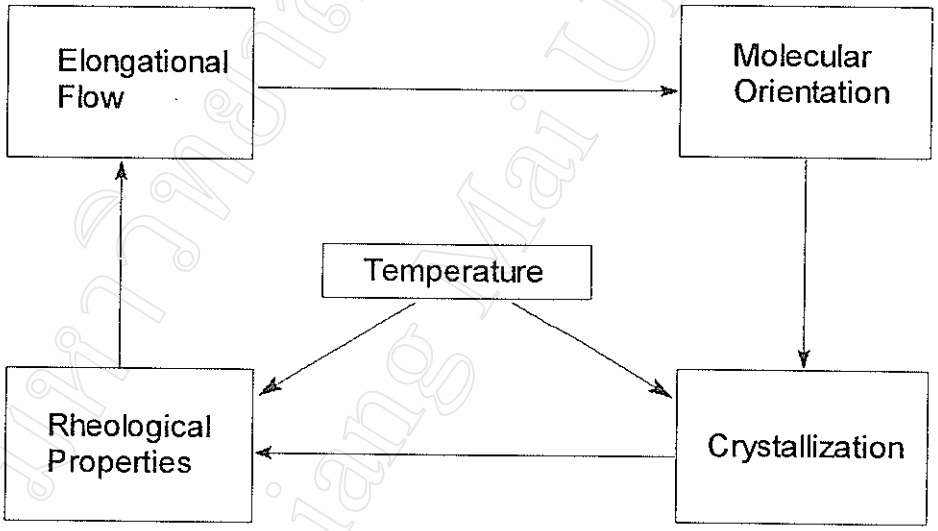


Fig. 1.1 Correlation between the main factors governing the melt spinning process [1].

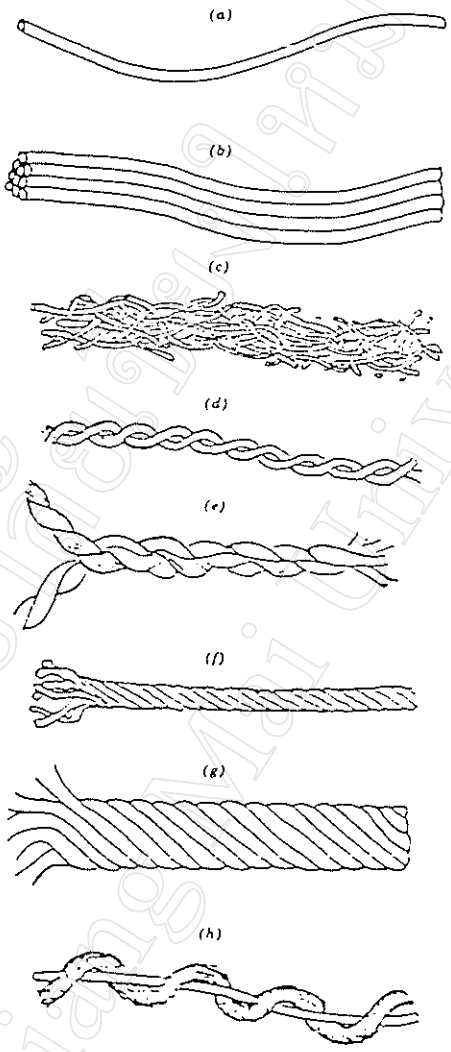


Fig. 1.2 Idealized diagrams of various yarn structures [3].

(a) Monofilament : solid, single strand of unlimited length
(b) Multifilament : many continuous filaments with some twist
(c) Staple : many short fibres twisted tightly
(d) Two-ply yarn : two single yarns twisted together
(e) Multiple yarn : plied yarns twisted together
(f) Thread : hard, fine-ply yarn
(g) Cord or cable : many plied yarns twisted into a coarse structures
(h) Combination : two dissimilar yarns plied together

The primary fabrication process in the production of synthetic fibres is the spinning (i.e. the formation) of the filament. In every case, the polymer is either melted or dissolved in a solvent and is converted into filament form by forcing through a die, called a ***spinnerette***, having one or more holes. The three major categories of spinning processes are ***melt***, ***dry*** and ***wet spinning***. All of these spinning processes proceed roughly according to a scheme of four stages. In the first stage, the liquid to be spun is extruded through the orifices of a spinnerette. The length of filament which can be obtained is governed by the spinnability. In the second stage, the actual filament begins to form. In this transition region, internal stresses equilibrate. In the first two stages, the filament retains its external shape. In the third stage, the still semi-liquid filament is drawn or stretched under its own weight causing a slight orientation of the chains to occur. In the fourth stage, the filament is drawn. The features of these three types of processes are shown in Fig. 1.3 and the typical cross-sections of the fibres produced by them are shown in Fig. 1.4.

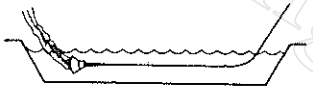
1.3 Melt Spinning [4]

The process of melt spinning is inherently simple. Molten polymer is pumped at a constant rate under high pressure through a plate called a spinnerette containing one or more small holes. The liquid polymer streams downward from the face of the spinnerette, usually into air. The filaments solidify and are brought together to form a thread before being wound up on bobbins. A subsequent drawing step is necessary to orient the fibres.

FIBRE SPINNING PROCESSES

Wet Spinning		*Dry or Solvent Spinning*		*Melt Spinning*	
Rayon	Acrilan acrylic	Acetate	Orlon acrylic	Nylon	Polyester
Creslan acrylic	Zefran acrylic	Vinyon	Modacrylic	Saran	Olefins

1. Raw material is dissolved by chemicals.
2. Fiber is spun into acid bath.

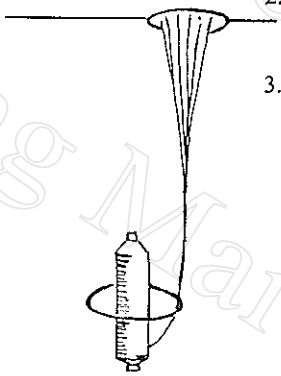


3. Fiber solidifies when coagulated by acid.

Oldest process
Most complex
Weak fibers until dry
Washing, bleaching, etc., required before use

(a)

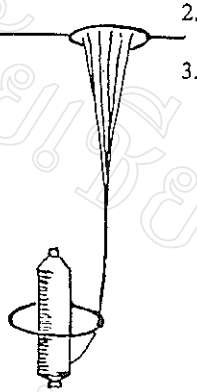
1. Resin solids are dissolved by solvent.
2. Fiber is spun out into warm air.
3. Fiber solidifies by evaporation of solvent.



Direct process
Solvent required
Solvent recovery required
No washing, etc., required

(b)

1. Resin solids are melted in autoclave.
2. Fiber is spun out into air.
3. Fiber solidifies on cooling.



Least expensive
Direct process
High spinning speeds
No solvent, washing, etc., required
Fibers shaped like spinneret hole

(c)

Fig. 1.3 Schematic diagrams of the three principal types of fibre spinning:[5]
(a) wet spinning (b) dry spinning (c) melt spinning

(a) (b) (c)

Fig. 1.4 Typical cross-sections of fibres produced by different spinning processes [2].
(a) melt-spun nylon from various shaped orifices
(b) dry-spun cellulose acetate from round orifices
(c) wet-spun viscose rayon from round orifices

The polymer is melted by contacting a hot grid in the form of steel tubing which is heated by an electric current or by hot vapours. It is usually necessary to protect the polymer melt from oxygen by blanketing it with a stream of an inert gas such as carbon dioxide or nitrogen. If the viscosity of the molten polymer is low, it may pass directly to the metering (constant) rate pump. For melt of high viscosity, however, a booster pump may be used. Other methods of melting have been proposed including the use of an extrusion-type screw, one section of which can serve as its own metering pump. Methods in which the metering pump is replaced, for example, by a source of gas pressure or other device, do not appear to offer sufficiently precise control to hold the denier of fine yarns constant.

The filaments emerge from the spinnerette face into the air and begin to cool. An air blast may be used to speed up the cooling process. After the filaments have travelled far enough to become solid (about 2 feet), they are brought together and wound up. Speeds of about 2500 ft./min. are usually employed.

To be suitable for melt spinning, a polymer must be stable at the melting and extrusion temperatures which are generally at least 20°C above its melting point. Four commercial melt-spun fibres are particularly

important: nylon 6.6, nylon 6, poly(ethylene terephthalate) and polypropylene.

1.3.1 Melting of the Polymer [6]

The lower limit of the spinning temperature is the temperature at which the polymer is completely molten. Usually the adequate melting temperature is the equilibrium melting point or 20°C to 40°C higher; the margin appears to be higher for higher molecular weight polymer.

The above criterion represents the lower limit of the temperature range which is acceptable for fibre extrusion. On the other hand, the determined temperature may be inconvenient from the point of view of polymer melt flow. For example, when high polymer molecular weights are used, it is better to increase the melt temperature to lower the melt viscosity. Nevertheless, it must be remembered that the total amount of heat will have to be removed later in the quench zone, so every attempt at elevating the spinning temperature beyond the absolutely necessary minimum should be given very serious consideration.

The upper limit of the melting temperature is usually governed by the polymer's thermal stability and does not require very extensive comment. In the case where the operable temperature range is wide, it may be preferable to gravitate towards the lower end of the scale. The upper limit is usually set by the temperature at which appreciable thermal degradation begins.

Before the molten polymer is formed into a continuous filament, it is usually passed through a so-called ***pack*** or ***filter***. In the very beginning of fibre manufacture, this element of equipment was only meant as a simple filter in order to separate minor impurites which may contaminate the polymer or cause discontinuities in the filaments or even plug the spinnerette hole. Removal of these accidental impurities is still important and this may be achieved by passing the polymer through one or more fine-mesh screens. In most contemporary spinning operations, packs are

being constructed of screen plug layers of sand, small metal balls, sintered metal plates or other materials to create a large number of fine channels. The polymer melt passing through such a filtering device experiences considerable shearing and this shearing proves to be highly beneficial to the spinning process.

1.3.2 The Spinnerette [6]

The spinnerette is the element of spinning hardware which serves to change the polymer shape into infinitely long cylinders. Spinnerettes are indeed serving the purpose and are serving it quite well but there is a number of side phenomena taking place during the extrusion of polymer through a capillary. These side phenomena, which result mainly from the shearing action on the extruding polymer, have a strong influence on both some engineering tasks and on the behavior of the polymer in the further processing stages up to the alteration of the final properties. In this respect, the spinnerette has, to a certain extent, a similar action to the filtering pack mentioned above. Some typical spinnerettes used in melt spinning are shown below in Fig. 1.5.

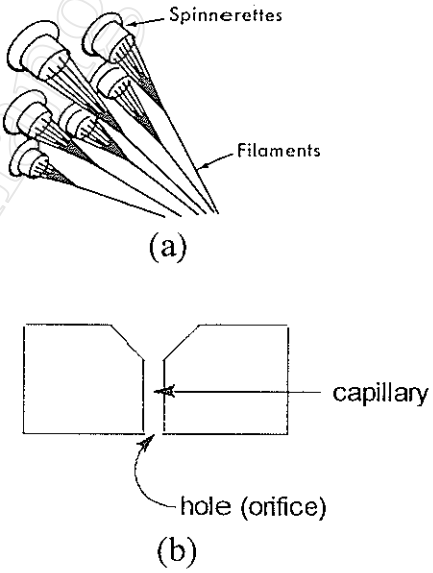


Fig. 1.5 Typical spinnerettes used in melt spinning.
(a) a series of multiple-hole spinnerettes [4]
(b) internal design structure of a single-hole spinnerette

1.3.3 Spinnability [7]

The maximum achievable filament length for a spinning process is known as the spinnability and depends on the viscosity, η, of the polymer melt and the rate, ν, of spinning. The filament length, L, passes through a maximum with increasing product, $\eta\nu$.

The occurrence of a maximum in the $L = f(\eta\nu)$ function means that the spinnability is governed by at least two processes: the cohesive fracture (or swell effect) and the capillary fracture (melt break or capillary break). A certain amount of elastic energy is, of course, stored in every viscoelastic fluid. This amount of energy also depends on the cohesive energy of the material. If a certain amount of stored energy is exceeded,. then the fibre undergoes what is known as cohesive fracture. On the other hand, the capillary fracture depends on the surface tension of the liquid as well as on its viscosity and the speed of the spinning process.

The first of these two mechanisms to occur causes a break in the filament. If the rate of spinning and/or the viscosity is too low, capillary fracture occurs and the liquid degenerates into single droplets because of the domainating effect of surface tension. Relaxation times which are too large because of viscosities being too high cause cohesive fracture, which is a brittle fracture. Viscosities can be too high because of, for example, high molar mass, high concentration, fast gel formation, or too low spinning temperature.

1.4 Drawing [5]

The filaments as spun are almost completely unoriented. Most of the stretching that occurs between the spinnerette and wind-up does so while the filament is still molten and so there is sufficient time for molecular orientation to relax before the polymer cools and crystallizes. Consequently, a separate drawing step is necessary to produce the orientation of the crystallites which is necessary for the required physical and mechanical properties. In the drawing step, somewhat lower speeds were traditionally required than can be achieved in spinning, so the two steps were usually carried out separately; now they are

often done in a continuous operation. A typical drawing (only) process is represented in Fig. 1.6 below.

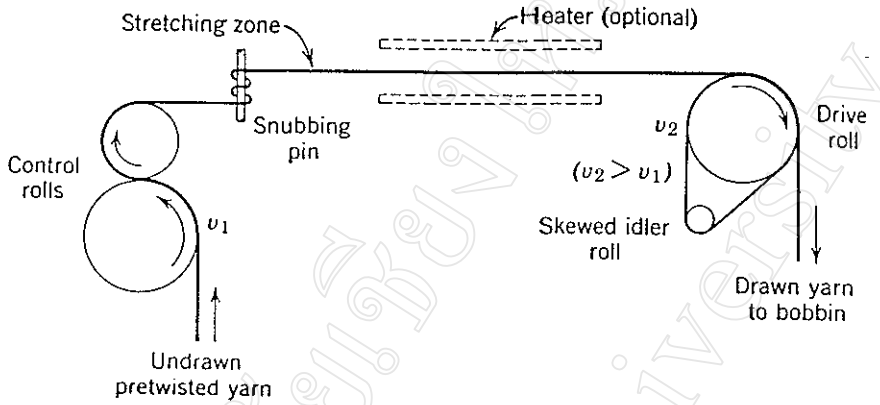


Fig. 1.6 Schematic diagram of a typical drawing process [5].

The drawing step utilizes two sets of rolls, as shown in Fig. 1.6, one to feed the undrawn yarn from a supply package at velocity v_1 and the other, moving about four times as fast, to collect the drawn yarn at velocity v_2. The filaments may pass over a metal pin between the two sets of rolls; drawing is localized in the neighbourhood of the pin. The yarn is then collected on a strong metal bobbin. Freshly draw yarn has a tendency to contract somewhat in length.

The combined spin-draw process was developed conventionally in the 1960s by coupling the spinning and drawing processes in series, as shown in Fig.1.7. As the demand for crimped yarn increased in the 1970s, the drawing and texturing processes were also combined into one process and a new spinning process was developed to produce partially oriented yarn (POY) with a spinning speed of 3,000-3,500 m/min. to produce the feed stock for integated draw texturing [1].

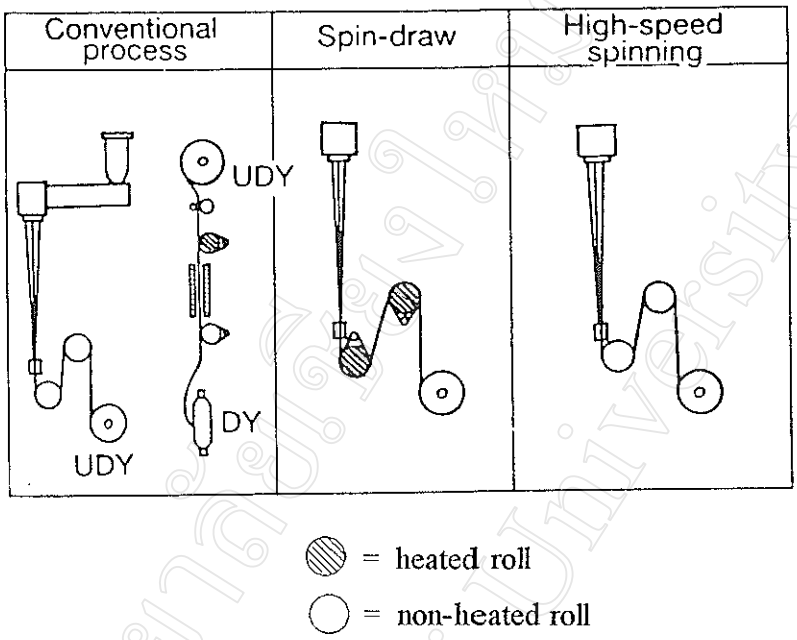


Fig. 1.7 Schematic production system for poly(ethylene terephthalate) (PET) yarn [1].

UDY = undrawn yarn
DY = drawn yarn

The changes that take place during the drawing (stretching) to which many artificial fibres are subjected are as follows [8]:

1. The molecules slide over each other; it would be quite impossible to draw any fibres in which the molecules were crosslinked (like rungs in a ladder) by more than about 100 per cent.
2. The molecules turn into the direction of draw, so that after being drawn they are oriented parallel to the fibre axis.
3. The crystallinity of the fibre is increased.
4. The properties of the fibre are modified by the increase in the degree of orientation.

1.5 Orientation and Crystallinity [8]

In the spinning process, the molecular chains are oriented by three processes: flow orientation outside or inside the spinnerette orifices and orientation by deformation. For the orientation of the molecular chains that occur in the spinnerette to be effective in orienting the filament, the rate of stabilization of the filament must be greater than the reciprocal relaxation time. This requirement applies only to the surface and not to the interior of the filament. The orientation of the molecule within the spinnerette thus has little influence on the orientation of the molecules in the finished filament.

Outside the spinnerette, the molecules also become oriented by flow. As the distance from the spinnerette mouth increases, the optical birefringence (the specific index of birefringence is the difference between the index of the axial refraction and the index of transverse refraction) increases first slowly and then rapidly up to a limiting value as determined by the rigidity of the filaments and then the resulting limited mobility of the molecules. This process produces the greatest observed proportion of orientation. Generally, fibres are expected to have positive birefringence because of the better alignment and orientation of the molecules along the fibre axis in both the crystalline and non-crystalline domains [9]. Finally, a smaller contribution comes from yet a third process, namely, an orientation of the chains through a deformation of the physical network which is formed.

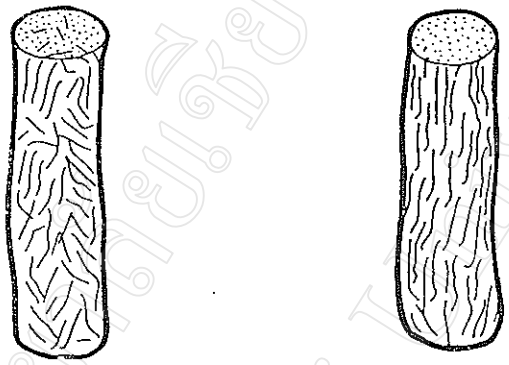
1.5.1 The Arrangement of the Molecules in a Fibre [8]

Evidence from several sources has shown that in natural fibres the long molecules are arranged more or less parallel to the longitudinal axis. There is a close and real analogy between the arrangement of the fibres in the yarn and the arrangement of the fibrous molecules in the fibres.

The main sources of evidence of this state of affairs are: (1) anisotropic swelling (2) birefringence, and (3) X-ray analytical data. It should be noted that the parallelisation of the molecules in natural fibres is not perfect and that it

varies considerably from one kind of fibre to another. This variation plays a notable part in determining the properties of natural fibres.

In flax, the molecules are highly oriented, very parallelised, and lie side by side along the length of the fibre; in cotton, some of the fibres also lie parallel but quite a large proportion of them lie at an appreciable angle to the fibre axis. This difference is illustrated in Fig.1.8.



cotton flax

Fig. 1.8 Orientation of the molecules in cotton and flax.

When tension is applied to the fibre, nearly all the molecules in the flax take their share of the load, since they are facing in the right direction, i.e., roughly parallel to the fibre axis. In contrast, those molecules lying approximately at right angles to the fibre axis take little or none of the load. Consequently, the tenacity of cotton is lower than that of flax.

short molecules long molecules

Fig. 1.9 To separate long molecules, greater cohesive forces must be overcome than with short molecules.
Long molecules are therefore essential for fibre strength.

Fig.1.9 illustrates how the area of attraction that has to be broken is greater in the case of long than short molecules. We are thus able to see why fibres which consist of very long molecules will be stronger than those consisting of shorter molecules.

In the case of man-made fibres, it is often possible to control the degree of orientation. The means by which the orientation is increased is invariably that of stretching. Consider a filament which has been extruded without any stretching being applied to it; the molecules will approximate to a random arrangment, as shown in Fig. 1.10, although there will probably be a slight degree of orientation of the molecules parallel to the fibre axis caused by the direction of flow through the spinnerette.

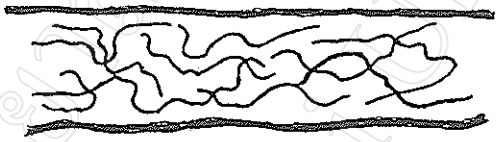


Fig. 1.10 Random arrangement of molecules in a fibre.

If, however, a material which consists of randomly arranged molecules is stretched in one direction, the molecules tend to orient themselves in that direction, as shown in Fig. 1.11.

Fig. 1.11 Orientation of molecules in a fibre after drawing.

1.5.2 Crystalline Regions

Evidence of birefringence, dichroism (an optical effect which it has been possible to link with fibre orientation) and X-ray analysis has been adduced to support the view that fibres are crystalline, but it is supposed that they are not

entirely crystalline. Today, the terms "micelles" and "crystallites" are used synonymously. Both refer to crystalline regions.

A fibre, as described previously, is made up of a large number of very long fibrous molecules. We can imagine that if care were taken to impose no stretching or flow during spinning, the molecules would be in random order as shown in Fig. 1.10, but that as soon as the fibre is stretched, the molecules turn into line with the fibre axis.

Whereas at first they lack any order, the time will come, as they are turned into line, when they will arrange themselves one with another in an orderly way. Arrangement in an orderly and regular way encourages crystallization to take place, crystals simply being ordered arrangements of molecules. If the molecules are long and flexible and have no cumbersome side chains, then they will fall readily into place with one another, as shown in Fig. 1.11 and the crystals will soon form and grow. Diagrams showing both ordered (crystalline) and random (amorphous) regions in fibres of different degrees of crystallinity are compared in Fig. 1.12.

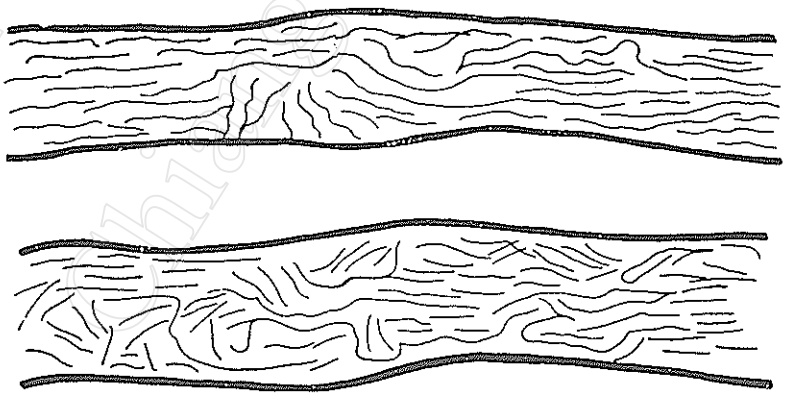


Fig. 1.12 Diagrams representing both ordered (crystalline) and random (amorphous) regions in the same fibre. (Lower diagram represents a lower degree of crystallinity than the upper. Note that in either case the longest molecules can pass from one crystalline region right through an amorphous region to another crystalline region.)

1.6 Theoretical Variables in Fibre Formation [6]

The number of process variables in fibre formation is usually seriously underestimated. Theoretical variables in fibre formation consider the most important properties of a polymer and the necessary changes the polymer must undergo to be transformed into a fibre. These theoretical variables may be enumerated as follows:

1.6.1 Number-Average Molecular Weight

In 1932, Mark [10] published his observations that, in the spinning process, with the essential variables equivalent, the maximum obtainable fibre tenacity increased with increasing the molecular weight of the polymer. The influence of molecular weight on fibre properties was considered very intriguing and therefore was the subject of numerous reexaminations. Sookne and Harris [11] found that molecular weight has a similar influence on the modulus of elasticity of the fibre.

1.6.2 Shear History of the Polymer

In the plastics industry, it was frequently noticed that a product made from the same polymeric raw material but on different machinery had different mechanical properties. Later, this phenomenon was recognized as a result of differences in thermal or shear histories, or both. Careful analyses of melt-flow properties showed that some of the flow properties that may be changed for the same polymer depend on whether or not the specimen was previously extruded.

1.6.3 Shear in the Capillary

The shear in the capillary is as important as the shear the polymer experiences prior to extrusion through the spinnerette. It may be noticed that an increase in shear during extrusion of the fibres from the spinnerrette,

other conditions being equivalent, gives fibres of increased tenacity. Shear in the capillary is treated here as a process parameter which can be varied relatively easily, while the previous shear history may be only partially diminished in the process.

1.6.4 Degree of Extension

During the filament extension, some kind of molecular displacement or rearrangement must take place. Such displacements certainly are not without influence on the intermolecular relations of the entanglements. Intuitively, its seems quite obvious that the morphology of crystalline structure, which is so strongly responsible for the final polymer properties, must depend to a large extent on the chain morphology which existed prior to the onset of crystallization.

1.6.5 Effective Time of Crystallization

The time span during which a polymer is able to crystallize presents rather a complex problem. It depends on several factors, such as distance between the spinnerette and the point of neck-drawing, the velocity of the filament, and the temperature range within which the rate of crystallization, at a given strain rate, assumes significance.

1.6.6 Rate of Crystallization

Basically, the rate of crystallization depends on temperature and strain. The preparation of the polymer for crystallization, in terms of previous shear experience and resulting chain morphology, seems to have an influence on the rate. Thus, the three parameters: chain morphology resulting from the sum of shear and thermal treatment and degree of extension, effective time of crystallization, and effective rate of crystallization are the main factors which determine the extent to which the polymer will crystallize in the quench zone.

1.6.7 Effective Temperature of Crystallization

Filament temperature normally decreases with increasing distance from the spinnerette, so at some point it becomes low enough for crystallization to begin. At the same time, the morphology and structure depend on the actual temperature of crystallization. All of these influences result in some kind of function relating crystalline fraction to the actual temperature of growth of these crystals.

1.6.8 Draw Ratio

Neck-drawing is the step which develops the final fibre structure. The outcome of neck-drawing is very strongly dependent on the structure which exists just prior to the drawing step. It may even be said with full justification that the structure of as-spun fibres dictates the draw ratio which should be applied to it. Thus, the spin draw ratio is the ratio of take-up velocity to the velocity of extrudate exiting from the capillary [12].

1.6.9 Rate of Drawing

The maximum draw ratio possible before the fibre ruptures, as well as the qualitative result of drawing, depends on the rate of drawing. It is rather difficult to ascertain whether the influence of the drawing rate is the same as its influence on all non-equilibrium processes, or whether it results from changes of actual temperature in the neck. The high heat of drawing dissipates less easily in cases when the process proceeds faster. It seems most probable that both effects are responsible for the observable influence of drawing rate on the outcome of the operation. The separation of these two effects represents an enormous task. As a rule, an increase in drawing rate results in a decrease of maximum draw ratio.

1.6.10 Actual Drawing Temperature

In most processes, heat is delivered to the fibre at the point of neck drawing, at least to initiate and localize the neck formation. At the same rate of drawing, the temperature range at which the necking is observable runs from somewhat below the actual melting point all the way down to the glass transition temperature of the polymer. The balance between the crystalline and non-crystalline fractions in the fibre structure before drawing strongly affects the temperature range within which the neck may occur. There seems to be qualitative evidence to suggest that the actual drawing temperature is higher than that indicated by the amount of heat delivered. However, the small size of the neck does not permit easy and accurate temperature measurements. Investigations of the fibre properties and analyses of fibre structure show that the same as-spun fibre drawn at the same rate but at different temperatures is converted into a product of different quality. All fibre properties, particularly mechanical and thermal, are affected.