

1 Introduction: The structure of fibres

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1.1 Introduction

The specific chemistry of a given type of fibre is undeniably crucial in determining many features associated with its processing, performance and end-uses; but it may also be asserted that its physical structure—i.e. the organisation and geometrical arrangement of its component parts—is at least equal in importance. This accounts for the largely physical approach taken in the first chapter of a work devoted to the *Chemistry of the Textiles Industry*. The fact is that the two aspects cannot, and ought not to, be separated.

Hearle (1963) quotes the definition of a fibre according to The Textile Institute (1960) thus: “units of matter characterised by fineness, flexibility and a high ratio of length to thickness”. As he pointed out, this is an incomplete definition as far as textile fibres are concerned. It is deficient in several respects, but notably in that it omits any reference to what constitutes the actual make-up of a fibre, viz. its structure.

The reason for this undoubtedly lies in part in the huge diversity of features encountered in fibres of differing types and origins. It is possible to make some general statements, however, regarding the nature of textile fibres. Certain key features are now beyond dispute, and can be summarised simply. In the main, textile fibres are composed of:

Partially ordered, partially oriented assemblies of linear polymer molecules.

This definition serves well for the vast majority of textile fibres, but it prompts many questions. For example: “What exactly do ‘partially ordered’ and ‘partially oriented’ mean?”; “How are these concepts realised in practice?”; “Do the same features apply equally across a wide range of fibre types?”; and, importantly, “What bearing do such features have on the performance characteristics of fibres?”.

Since the inception of fibre structure research near the beginning of this century, such questions have challenged the minds of an impressive array of investigators, but the period between 1930 and the late 1960s, in particular, seems to have been characterised more by disagreement than by unanimity. At this point ideas regarding fibre structure were emerging almost as rapidly as the new fibres themselves were appearing on the market, and a great deal of confusion and controversy reigned. Many, often conflicting, models were produced, each representing an attempt to explain certain observed phenomena.

To a large degree, such graphical representations should be regarded as 'artists' impressions', since they were entirely qualitative, and not generally verified against any measurable parameters. Hearle (1991) warns against the dangers of "... confusing our aids to understanding improperly with reality". Although he made this comment in the specific context of nylon and polyester fibres, it does have more general applicability. This is not to detract from the value of pictorial representations, however: there is now a realisation that whereas no single view of fibre structure can of itself tell the whole story, a grain of truth almost certainly lies in all of them. Moreover, in recent years there has been a more concerted effort to find ways of quantifying the features described by the early models.

An area of increasing commercial importance is the exploitation of high-performance fibres. However, these materials differ almost in kind from the commodity fibres, and although brief consideration is given to them in section 1.2.3.2, no attempt is made to cover them in detail.

1.2 Classification of textile fibres

Textile fibres have been, and continue to be, derived from an enormous range of materials. Figure 1.1, showing just a few examples, can scarcely do justice to this diversity; nor is it possible here to do more than give an indication of the main chemical types and of their sources.

As was stated earlier, the overwhelming majority of fibres are polymeric in nature. In broad terms, they may be classified thus:

Natural

- Animal (protein) fibres
- Vegetable (cellulosic) fibres

Man-made

- Regenerated cellulose fibres
- Chemical derivatives of cellulose

Synthetic polymer

- 'First-generation' (up to 1970s): commodity domestic and industrial fibres
- 'Second-generation' (1970s on): high-performance and specialised fibres

Other

- Metal fibres
- Ceramic fibres

1.2.1 *Natural fibres*

1.2.1.1 *Animal fibres.* The most important textile fibres of animal origin are those based on the α -keratins, which are the proteins found in skin, horn,

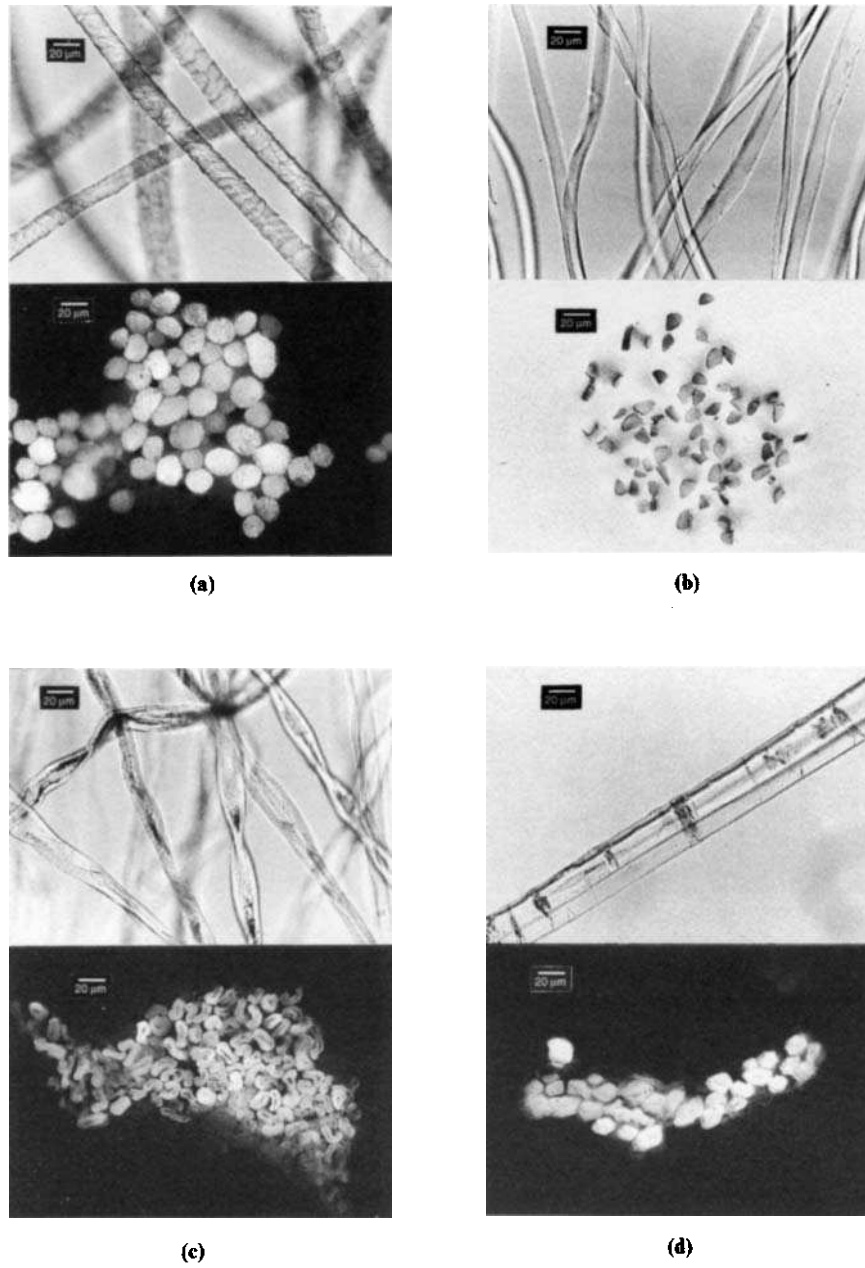


Figure 1.1 Optical micrographs of various fibres: (a) wool; (b) silk; (c) cotton; (d) flax.

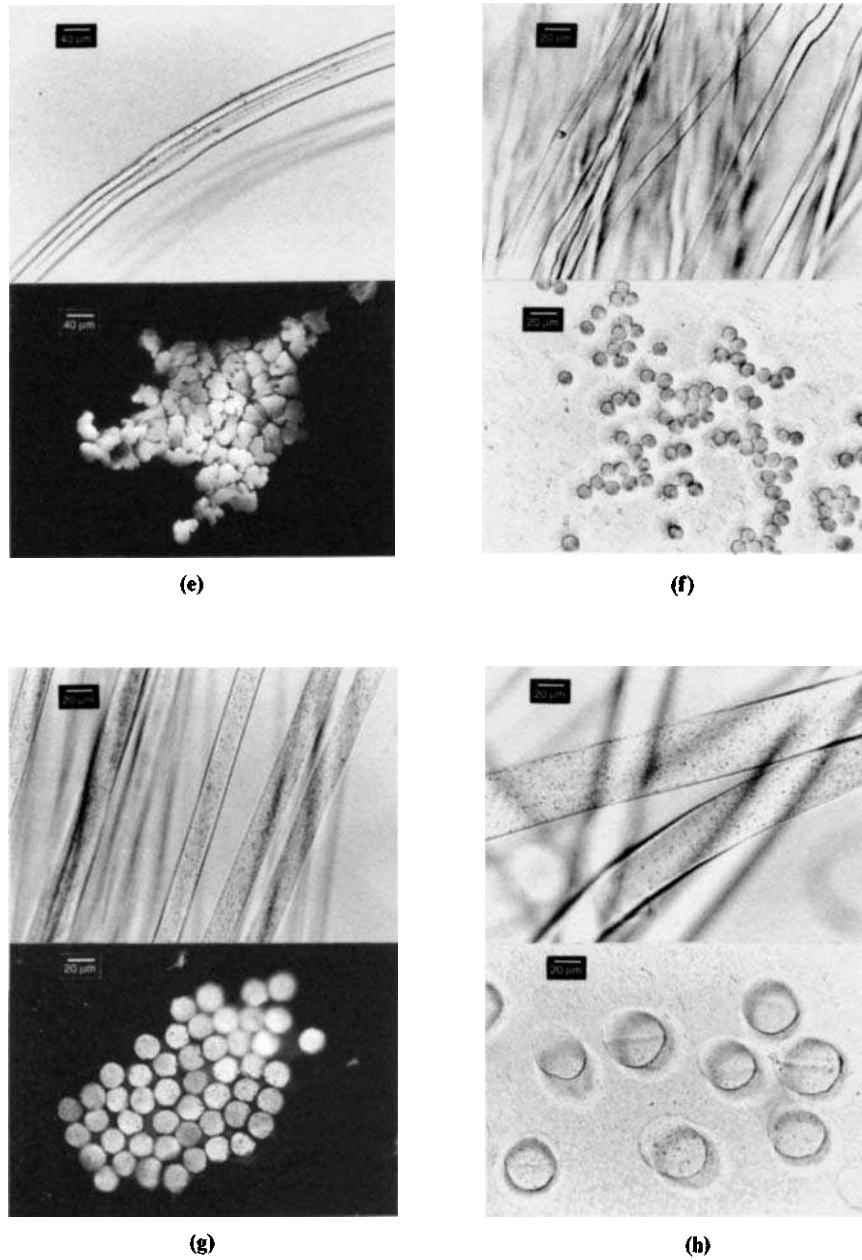


Figure 1.1 (Continued) (e) viscose carpet fibre; (f) Tencel solution-spun cellulosic; (g) nylon 6.6; (h) polyacrylonitrile ('acrylic').

nails, hair and other tissue, and which form the main chemical constituents of wool.

The wool keratin molecule consists of a highly complex sequence of amino acids. Typically the protein is mainly composed of eighteen amino acids with cystine, lysine, arginine, glutamic acid and aspartic acid important in the physicochemical nature of the fibre (Lewis, 1992). Moreover, this complexity is not confined to the individual molecules: the chemical composition varies over the length of the fibre itself. Near the root, for example, the cystine content is higher than it is near the tip.

The physical structure of wool is equally complex, being organised on several hierarchical levels, as shown in highly idealised form in Figure 1.2. The essential macroscopic components of the fibre are the cortex, which constitutes over 90% of the fibre mass, and the cuticle. In many varieties of wool the cortex has a bilateral structure in which approximately half of the cross-section is made up of *ortho*-cells, whilst the opposite side consists of *para*-cells. This unusual feature gives rise to several distinctive properties, including differential dye-affinity and differential swelling. The cortical cells are themselves composed of complex arrangements of smaller structural units including 'microfibrils' and 'macrofibrils'. The microfibrils are thought to contain bundles of left-handed 'coiled-coil ropes' which in turn are formed from the intertwining of the right-handed keratin helices.

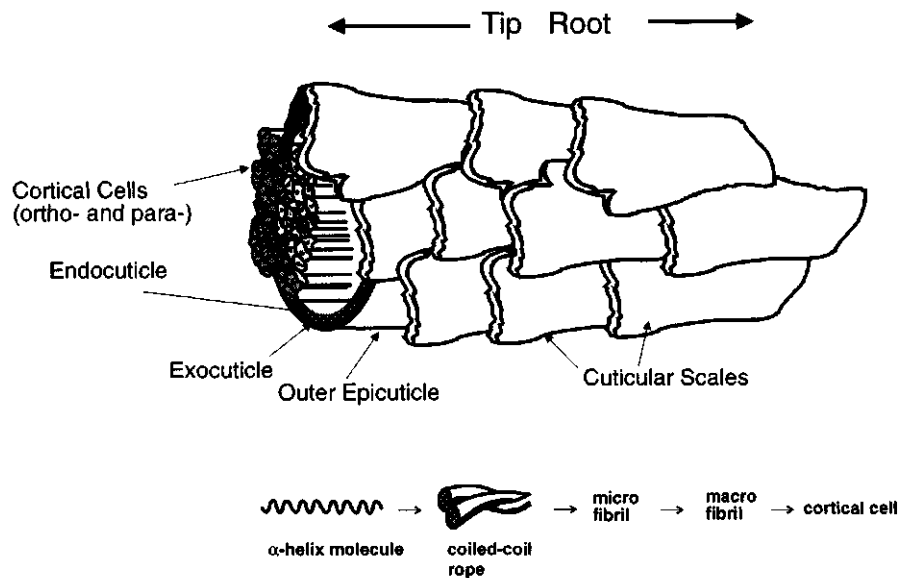


Figure 1.2 Highly simplified view of a wool fibre, showing cortical cells and cuticular scales.

The main feature of the cuticle is the overlapping scale cells, which point from root to tip. These impart the property of differential friction which, among other things, is responsible for the felting propensity of wool. The cuticle scales can easily be observed using light microscopy (see Figure 1.1a).

Keratin molecules are highly polar, rendering the fibre hygroscopic; wool has in fact a higher moisture regain than almost any other fibre. The same feature also accounts for the ease with which wool may be dyed.

The essentially helical configuration of the keratin chains and the microfibrils gives rise to very distinctive tensile properties. Since the helices may be extended with relative ease, the fibre is inherently compliant, extensible, and recoverable up to unusually large strains.

The other animal fibre of major commercial importance is silk, which is derived from the cocoon of the silk moth, *Bombyx mori*. Chemically, silk is a close relation of wool and hair, being a fibroin which shares many of the amino acids present in wool molecules. In contrast to wool and hair, however, the fibroin chains are believed to be nearly fully extended, highly crystalline, and almost perfectly aligned in the fibre direction, all of which contribute to the fibre's considerable stiffness and strength.

Bamford and Elliot (1963) give a detailed survey of the chemistry and structure of protein-based fibres, while Lewis (1992) presents an excellent collection of work relating to the chemistry of wool dyeing.

1.2.1.2 Vegetable fibres. The natural vegetable fibres are those based on cellulose, a substance found in the stems, leaves and seed-hairs of a wide range of plants, and formed in nature by photosynthesis under the assistance of a specific enzyme.

(a) *The cellulose molecule.* The cellulose molecule comprises a succession of glucose rings, as shown in highly idealised form in Figure 1.3. Several key features of this molecule give rise to important structural and mechanical characteristics in the fibre itself.

- (i) It is ribbon-like, with an approximately rectangular cross-section.
- (ii) It is relatively flexible, through rotation about the bridging oxygen links between the glucose rings.
- (iii) It features a high concentration of hydroxyl groups along its edges.
- (iv) It has directionality.

The flexibility of the cellulose molecule is much smaller than that of, say, polyethylene or rubber, but very much greater than those of high performance aromatic polyamides like Kevlar.

The ribbon-like form means that whereas bending out of plane (with respect to the glucose rings) is easy, in-plane bending is practically impossible except if accompanied by twisting.

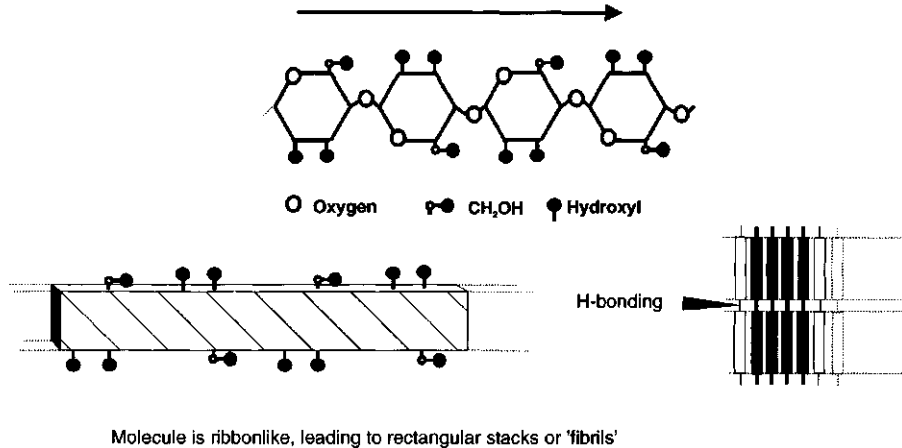


Figure 1.3 Key features of the cellulose molecule.

The adjacent edges of neighbouring chains can interact strongly through hydrogen bonding. This, together with the highly regular geometry of the molecule, provides a strong tendency towards the formation of crystals, and helps to stabilise the structure, once formed.

The molecules of cellulose in fact tend to group together to form microfibrils, which also have a ribbon-like form, and a more or less rectangular cross-section. These in turn can form even larger structural building blocks with, again, similar geometry.

Substances like cellulose, which contain hydrogen bonding, generally display effects at temperatures close to or above 100°C, as these bonds begin to dissociate. (The fact that water boils at this temperature is a manifestation of the same phenomenon.) Furthermore, any moisture present will have a dramatic plasticising effect, since water molecules can break down the hydrogen bonds. This has considerable implications, for example in laundering and other after-care treatments such as ironing.

The directionality of the molecules gives rise to the possibility of having at least two different crystal forms ('Form I' and 'Form II' respectively) in which they are arranged either parallel or antiparallel to one another.

(b) *The cotton fibre.* Of the many fibres of plant origin, cotton is without doubt that of greatest commercial importance, although flax, jute and hemp are also very significant.

Figure 1.1c shows the typical appearance of dry cotton fibres. The principal features are a 'kidney bean' cross-section, and the appearance of twists and kinks along the length (the so-called 'convolutions').

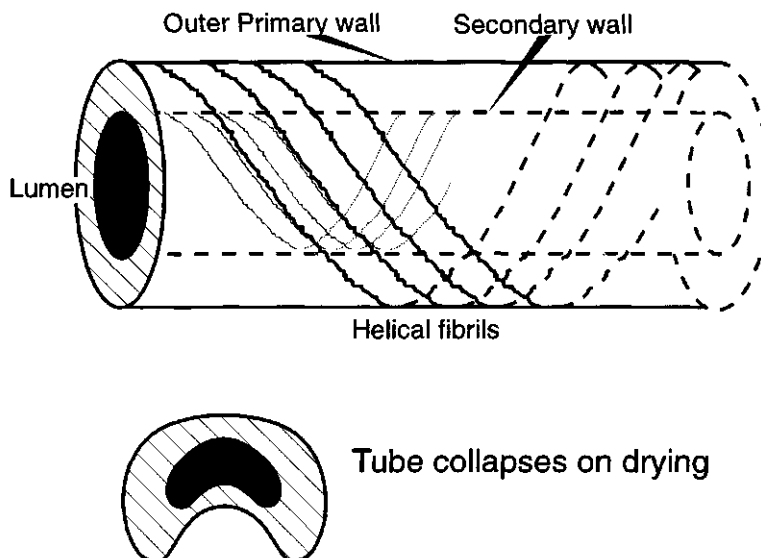


Figure 1.4 Highly simplified view of a cotton fibre, showing helical arrangement of the fibrils.

The structure of cotton and other vegetable fibres is described in detail by Bailey *et al.* (1963). During the first few days of growth, cotton fibres emerge as hollow cylinders 2–3 cm long, with a primary and secondary wall (shown greatly simplified in Figure 1.4). As the fibre matures, fibrils are laid down on the inner wall until the lumen — the hole down the centre — becomes quite small. When the boll opens, the fibres are cut off from the plant's transpiration system and dry out, whereupon the cylinder collapses. Hearle once likened this process to collapsing a roll of sticky tape.

Examination of the fibre whilst it is still growing, i.e. in moist conditions, reveals that the fibrils are actually laid down in a helical form — an interesting fact in the light of the comment made earlier regarding in-plane bending of the molecule.

The arrangement of the fibrils overall could be thought to resemble a twisted filament yarn with a hole down the centre, but it is further revealed that the helix angle remains constant throughout the thickness of the fibre. For an ideal twisted bundle of filaments the period would be constant, but the angle would vary from zero at the centre to a maximum at the surface. This means that the fibrils in cotton cannot be packed together perfectly; there must be occasional discontinuities of alignment. The value of the helix angle depends on the variety to some extent, but is normally about 21°.

It is also known that the sense of the helix reverses periodically along the length of the fibre. This is thought to provide torsional balance within the

structure. The macroscopic convolutions tend to occur at points along the fibre corresponding to where the reversals take place.

The development of the fibre structure is determined by the genetics of the plant. In particular, the polymerisation, or conversion from glucose to cellulose, actually takes place on the surface of an enzyme molecule which has a well-defined small number (*ca.* 30) of active sites. Thus a few polymer molecules grow together directly into the crystalline microfibril. Because they all grow in the same direction, they produce the parallel, rather than the anti-parallel, crystal form (Form I).

Brief consideration is given in section 1.4.2.1 to the influence of the cellulose and cotton structures on the mechanical properties of cotton fibres.

1.2.2 *Man-made fibres: regenerated cellulose and its derivatives*

To quote from Sharples (1963): "The amount of published scientific work on the chemistry of cellulose and its derivatives is so great that any attempt to cover the entire field in a short chapter would result in little more than a list". How much more pertinent this statement is some 30 years on. It is clearly impossible here to do more than present some fairly basic information.

The identifying feature of a regenerated fibre is that it constitutes, in effect, a physical rearrangement of the molecules originally present in some naturally occurring source, such as wood pulp. For this reason, the term 'man-made' is used to distinguish such fibres from the true synthetics, in which the polymer molecules are artificially produced.

By far the most important and well-known example of a regenerated fibre is viscose rayon. This material, originally produced in 1891, was in part a result of attempts to create artificial silk — an endeavour which, even today, is regarded by many as the 'holy grail' of fibre technology.

Viscose may be formed by dissolving raw cellulose in carbon disulphide and sodium hydroxide to produce a highly viscous liquid. Continuous cellulose filaments are then precipitated by extrusion of this fluid into sulphuric acid followed by zinc sulphate. The commercialisation of viscose rayon was due, in the main, to Courtaulds Ltd, and it is still one of their most successful products. Present-day commercial processes are broadly based on the original procedure, although they generally incorporate special features, providing a certain degree of control over the structure and physical properties of the resultant fibres.

The dissolution process brings about a physical disruption of the original structure, and imparts mobility to the molecules. This enables them subsequently to reorganise into a new configuration, and to adopt what is in fact the energetically-preferred Form II crystal unit cell (antiparallel chains). Curiously, the crystals of native cellulose represent a higher free-energy state; it is the physical constraints within the plant itself which dictate that this should be so.

The physical appearance of viscose fibres is typically as in Figure 1.1e. A distinguishing feature is the irregular, crenellated cross-section. The fibres also display a marked skin-core difference, which can be observed microscopically, and which gives rise to differential surface/bulk properties such as dye affinity. The crenellations have a profound influence on the optical properties, and in particular, on the lustre of fabrics made from viscose.

Nowadays many viscose-type products are available, ranging from fairly conventional low-modulus, medium-strength commodity fibres, to tough, high strength, high modulus fibres such as Tenasco, which is used extensively in the tyre industry.

Although there are now numerous other variants, probably the most commercially important chemical modifications of cellulose are:

Cuprammonium rayon

Hydrolysed cellulose acetate ('acetate')

Cellulose triacetate (Tricel)

Cellulose secondary acetate (marketed in the USA as Celanese).

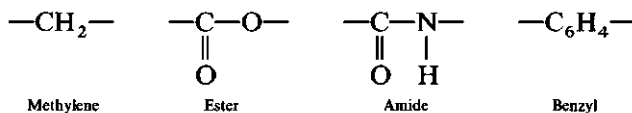
By and large, the appearance of these fibre types is similar to that of viscose, with the exception of cuprammonium rayon, which has a circular cross-section, and under the microscope appears homogeneous (classified as 'all-core').

An adverse side-effect of the conventional regeneration process is molecular degradation. This can be severe, resulting in average molecular weights as low as 10% of those in the source material, with an accompanying deterioration in strength and other properties. The recent development, again by Courtaulds, of the solution-spun cellulose Tencel has to a large extent eradicated this drawback. This, coupled with its superior dye-affinity and the fact that its manufacture uses non-toxic, fully-recyclable solvents, has given rise to substantial commercial interest in Tencel.

Wooding (1963) gives a very useful account of rayon and acetate fibres, as does Sharples (1963).

1.2.3 Synthetic polymer fibres

1.2.3.1 *First-generation fibres.* Many commodity synthetic fibres are based on polymers composed of chemical combinations of the same four groupings:



Each of these imparts certain characteristics to the polymer molecules, which render them particularly suitable for textiles use.

The methylene and ester linkages allow substantial freedom of rotation. There are usually only moderate van der Waals forces laterally, although a

certain amount of polarisation is associated with the carbonyl group, and this may provide somewhat stronger attraction.

The amide group is reasonably flexible, but because it forms strong hydrogen bonding, it also encourages crystallisation and cross-linking.

The aromatic ring is quite stiff, and this provides a rigid character. Some electronic interactions probably occur between neighbouring rings, which also favours crystallisation.

The history of the true synthetic polymer fibres arguably began with the research of Carothers in the late 1930s, which culminated in the development of the polyamides. Carothers had been studying the reactions of difunctional reagents such as glycols, $\text{HO}(\text{CH}_2)_m\text{OH}$, with aliphatic dicarboxylic acids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, amino acids, $\text{NH}_2(\text{CHR})_n\text{COOH}$, and others. Such reactions are known as condensation reactions, and polymers formed by this route are known as 'condensation polymers'. The early work prompted much further research, and another major group of condensation polymers—the polyesters—grew as an indirect result. In the formation of polyesters, the exact chemical steps may vary, dependent on the precise manufacturing process used, but in essence the condensation reaction takes place between a diglycol and terephthalic acid.

The polyamides and polyesters are the principal examples of condensation polymer fibres. Each in fact represents a large homologous group of materials, although the majority of their members are of only minor commercial significance. In the polyamide group the chief products are poly(caprolactam) (nylon 6) and poly(hexamethylene adipamide) (nylon 6.6), while poly(ethylene terephthalate) (also known as PET, 2GT, or simply polyester), is by far the most important polyester.

Nylon 6



6-Aminohexanoic acid

Nylon 6.6



Hexamethylene diamine

Adipic acid

PET



Terephthalic acid

Ethylene diglycol

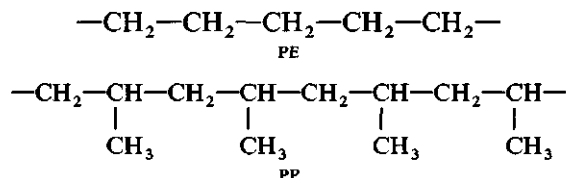
It may be noted that two distinct types of polyamide exist, typified by nylon 6 and nylon 6.6, respectively. In the former type, the monomer has a directionality, whereas the monomer of the latter is symmetrical. This difference leads to some specific differences between the crystalline structures and some physical properties of the two types.

The condensation polymers form a relatively small class of polymers (most others being so-called 'addition' polymers), yet they dominate the synthetic

textile fibres market. The polyamides and polyesters are also the most commercially important 'melt-spun' synthetics. This term arises from the fact that the filaments are produced by extrusion of molten polymer through a spinneret. The spun filaments are generally stretched and subjected to a variety of downstream processes. This gives rise to fibre products with a very wide range of physical characteristics. More will be said in section 1.4.2.2 concerning the structure-property relationships in melt-spun synthetics.

Notwithstanding their commercial dominance, it would clearly be wrong to imply that nylon and polyester are the only synthetic fibre types, and there are many others of commercial significance. As stated earlier, these are in the main addition polymers. Examples include the following.

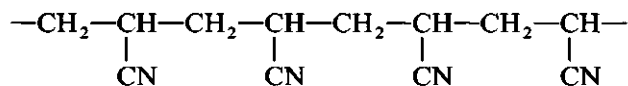
Polyolefins. The most important polyolefins are polyethylene (PE) and polypropylene (PP).



Both materials consist of flexible chain molecules and a short repeat unit, by virtue of which they are highly crystalline. However, their melting and softening temperatures are too low to enable them to withstand the rigours of laundering, etc. They also suffer quite markedly from adverse time effects, and thus find limited applications as commodity textile fibres. However, polypropylene, in particular, has high strength and fracture toughness. These attributes, coupled with its very low density (less than 0.9 g cm^{-3}), make it a valuable fibre for ropes and many industrial products.

By suitable techniques, the polyolefins may be manufactured with special properties—ultra-high stiffness and strength for example—which render them important as high performance fibres in certain industrial and military textile applications. In this context, they should really be regarded as second-generation fibres.

Polyacrylonitrile (PAN)

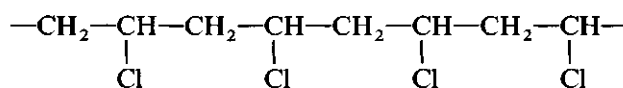


The 'acrylic' fibres, consisting of the homopolymer shown above together with a number of copolymers (modacrylics), and marketed under a variety of trade names—Courtelle, Orlon, Acrilan, Dynel and others, form a significant commercial group. As pointed out by Furness (1963), one of their chief assets is their ability to form bulked yarns.

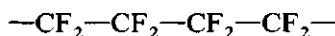
Acrylic fibre is an important wool substitute in many applications, such as carpets and upholstery. However, it tends to be rather harsh, and with a regain of virtually zero, it is not generally regarded as a 'comfortable' fibre. Consequently it is now generally blended with other fibre types for apparel end uses.

An important and growing application of PAN is in the production of high-performance carbon fibres.

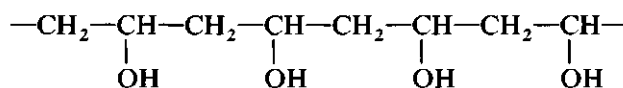
Vinyl fibres



Poly(vinyl chloride) (PVC)



Poly(tetrafluoroethylene) (PTFE)



Poly(vinyl alcohol) (PVA)

PVC, PTFE and PVA are probably the best-known examples of this group. PVC was one of the earliest of the addition polymer fibres, but suffers from low melting point and high plasticity. However, it is valuable for its fire-retarding properties.

PTFE, marketed by DuPont as TeflonTM, has remarkably high resistance to heat and chemical attack, coupled with an exceptionally low coefficient of friction. It is a valuable industrial fibre, but its high price generally prohibits its use where alternatives exist.

PVA is inherently water-soluble, but may be insolubilised by after-treatments, making it suitable for some textiles applications.

Furness (1963) gives a detailed account of the structure and properties of addition polymer fibres, while Goodman (1963) presents a valuable account of first-generation synthetic fibres in general.

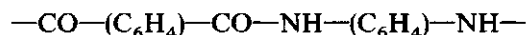
1.2.3.2 Second-generation fibres. The second-generation fibres are those, developed from the 1970s onwards, whose properties enable them to be used where there are special or highly demanding requirements. The term 'high performance' is often applied to fibres in this category, several of which have now replaced conventional engineering materials such as steel in a variety of applications, especially in fibre-reinforced composites, and where weight is an important consideration. High performance generally implies high stiffness and/or strength, but other features of importance include chemical and biological stability, fire retardancy (and/or resistance to high temperatures),

and high energy absorption. The latter is particularly crucial in situations requiring protection from impact, such as vehicle body panels.

Space does not permit a detailed examination of the high performance fibres here, but it is worth noting that the polymers of which they are composed fall broadly into three classes.

(a) *Liquid-crystalline ('rigid-rod') polymers.* These are typified by the aramid fibre Kevlar™. The term 'rigid-rod' arises from the fact that the monomer itself is inherently stiff. The macromolecular chains are, in consequence, rod-like. In solution they aggregate in much the same way that logs in a river tend to cluster together, to form 'liquid crystals'. Fibres produced from rigid-rod polymers are generally wet- or solution-spun.

Kevlar is DuPont's trade name for the fibre based on the aromatic polyamide:



Its properties include:

- Melting point in excess of 600°C
- Low combustibility
- Low relative density (*ca.* 1.44 compared with 2.55 for glass and 7.9 for steel)
- High specific strength (greater than 5 times that of mild steel)
- High specific modulus (greater than twice that of mild steel)
- Moderate ease of processing.

A good account of the performance characteristics of Kevlar is given by Wilfgong and Zimmerman (1977). Other fibres falling within the same class include the aromatic polyesters, and PEEK, poly(ether-ether ketone).

(b) *Flexible chain polymers.* This group of fibres is made up of the polyolefins (polyethylene and polypropylene), together with various copolymers. In these materials the molecular chains themselves are inherently flexible, which enables extremely high levels of chain extension and orientation to be achieved through stretching, solid-phase extrusion, and other methods. Polyolefin fibres can be produced with specific stiffness and strength close to or above that of the aramids, and with very low bulk density (less than 1 g cm⁻³ for polyethylene). They are almost chemically inert, making them very suitable for biomedical applications, and as reinforcement in concrete in some situations. However, they are limited by their low softening and melting temperatures, and by their susceptibility to creep and stress-relaxation.

(c) *Carbon fibre.* Carbon fibre warrants a class of its own, in that it is neither a liquid-crystalline polymer, nor a flexible chain polymer. It is in fact a modified fibre in the sense that it is generally produced from a precursor such as poly(acrylonitrile), pitch, or other source.

The essential process by which carbon fibre is formed is that of carbonisation

and 'graphitisation', although there are generally several other stages involved. Carbon fibre has a composition similar to that of graphite, and is extremely stiff and virtually incombustible. High performance carbon fibre is very brittle, which makes textile processing difficult. However, there are lower-modulus grades available, which are easier to process into staple yarns, and which retain many of carbon's other desirable properties.

The interested reader is referred, for a fuller account of high performance fibres, to Lewin and Preston (1985, 1989) and to Mukhopadhyay (1992). The latter, in particular, also gives a valuable presentation of current thinking on fibre structure–property relationships in a broader sense.

1.2.4 *Other types of fibre*

Recently, there has been a considerable level of interest in the development of fibres composed of non-polymeric materials, notably glasses, ceramics, and metals. However, a discussion of these types is beyond the scope of this chapter.

1.3 The problem of fibre structure

1.3.1 *Approaches to describing fibre fine structure*

1.3.1.1 *The nature of the problem.* As was stated initially, textile fibres consist, in the main, of partly crystalline, partly ordered linear polymers. This definition encompasses a vast range of fibre types. At one end of the spectrum are the 'general-purpose' materials, including cotton, wool, man-made fibres, and many of the melt-spun synthetic fibres with average performance characteristics, while at the other lie the high-performance fibres, such as the aramids and carbon fibre. The range of structural types is therefore equally vast. However, it is useful to focus on some common general features.

The concept of a linear polymer presents little difficulty. Most textile fibres comprise polymers with a backbone of carbon atoms. Covalent bonding along the chains gives potentially high strength and stiffness. There is generally no significant branching or cross-linking, but some form of interaction generally exists between molecular segments. Although these forces are very much weaker than those along the chains, they are nevertheless important in a number of respects. For example, they play a central role in crystallisation processes, and provide much of the stability of the ultimate structure. They may vary in strength from weak van der Waals forces, as in polyolefins, to relatively strong hydrogen bonds, as in cellulose.

What is meant by 'partially oriented' is rather less straightforward, but can be considered without too much difficulty. It refers to the extent to which

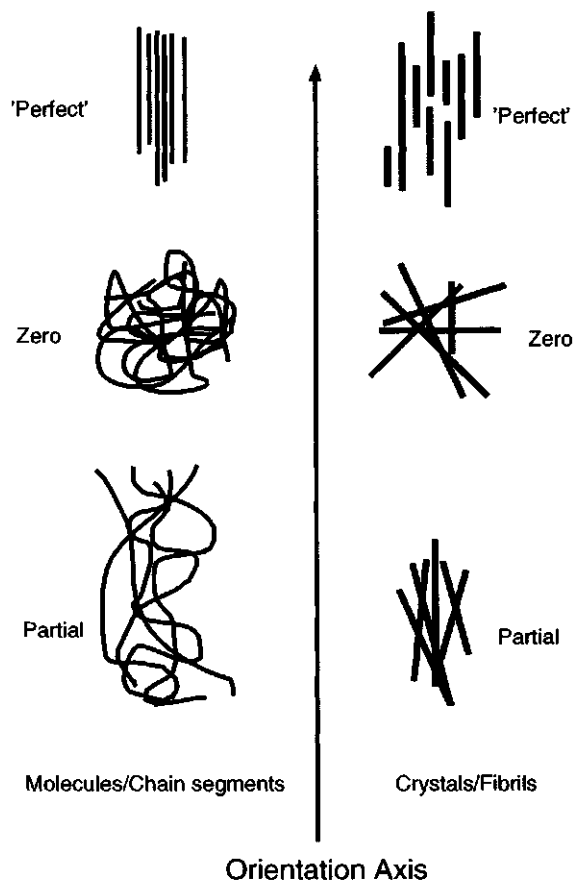


Figure 1.5 Various ways of visualising partial orientation.

molecular segments, whole molecules, or crystalline blocks are aligned with respect to the fibre axis. Perfect orientation implies that all molecular chain segments lie perfectly parallel to the fibre axis, providing considerable stiffness and strength in this direction. Figure 1.5 illustrates several ways of envisaging partial orientation.

The most challenging problem, however, is what is meant by 'partial crystallinity'. To begin with, the concept of a 'polymer crystal' warrants consideration. Crystals of low molecular weight materials are composed of a precisely regular three-dimensional lattice of points, each defining the position of a constituent particle (Figure 1.6). Except for its overall size, the crystal is completely specified by six unit cell parameters. It may be difficult to imagine how the enormously long chain molecules of a polymer could be

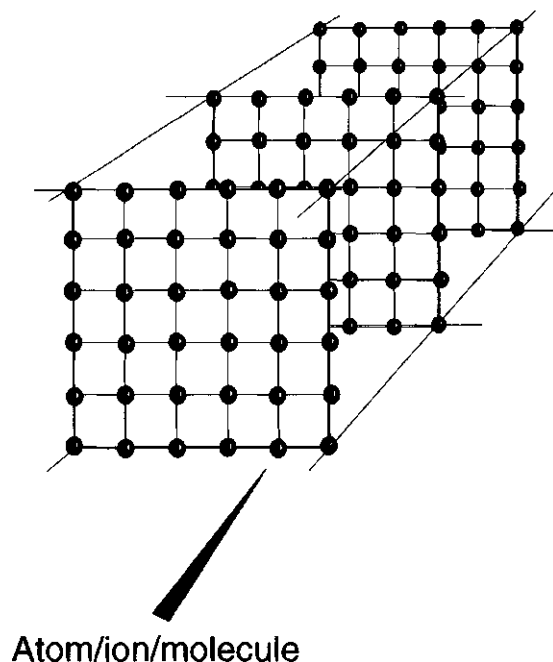


Figure 1.6 Representation of a simple crystal lattice.

organised into anything like such a lattice. For one thing, the molecules within any given sample vary in length one from another. However, if it is borne in mind that polymers (and certainly homopolymers, which account for the vast majority of textile fibres) comprise a repeating sequence of a relatively simple chemical unit — the monomer — then a way forward emerges. In most cases the molecular backbone provides some degree of rotational freedom at sufficiently high temperatures. Generally, the chain conformation of lowest free energy is also one of high geometrical regularity (e.g. the all-*trans* 'planar zigzag' form of polyethylene, based on the tetrahedral angle). This provides the regularity required for a crystal lattice. The geometrical repeat distance along a chain may not always coincide with the chemical repeat, but will generally be only a small integral multiple of it. It is this distance which usually defines one of the unit cell parameters. The remaining two lengths are easier to deal with, being simply related to the lateral packing of the molecules.

Figure 1.7 illustrates how the chains pack in a crystal of polyethylene. For clarity, the hydrogen atoms have been omitted. The unit cell is orthorhombic, with dimensions $a = 0.714$ nm; $b = 0.494$ nm; c (chain axis) = 0.255 nm. Interestingly, the dimension parallel to the molecular axis is actually the shortest.

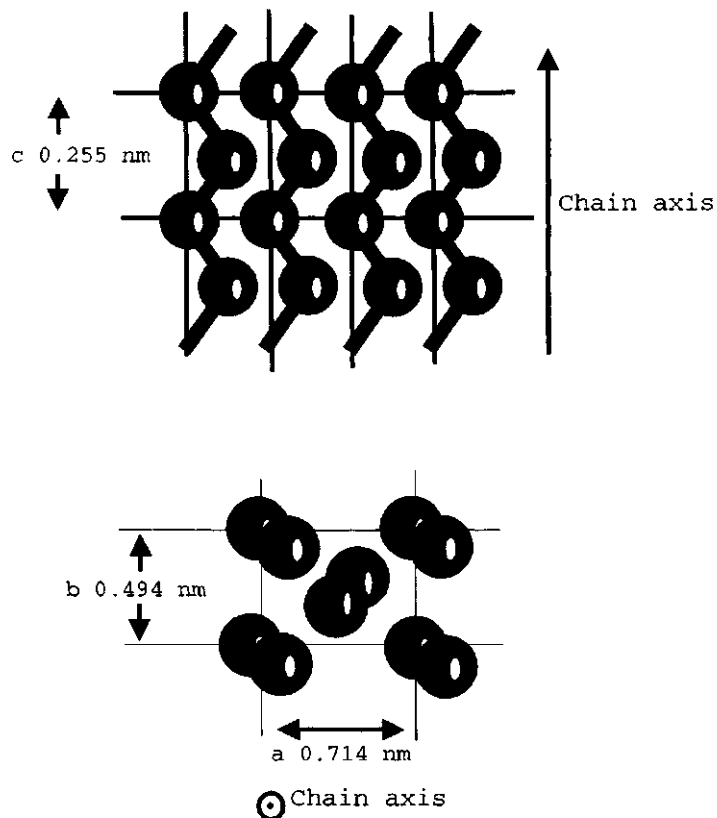


Figure 1.7 Packing of chain segments within the unit cell of a polyethylene crystal.

The unit cells of most textile fibres are now accurately characterised. As with conventional crystals, a variety of unit cell types exists, including monoclinic, triclinic and hexagonal.

However, it should be realised that polymer crystals represent a low state of order compared with those of conventional solids. They are almost always rather poorly developed, and certainly very much smaller—so much so that surface energy and surface irregularities generally produce a substantial depression of the melting point. This phenomenon can be exploited to assess the average size of polymer crystals.

Finally, and perhaps most significantly, the question of partial crystallinity presents a challenge simply because the number of ways in which the concept could be realised is virtually limitless.

1.3.1.2 *Model representations of fibre fine structure.* Attempts to describe fibre structure have traditionally focused on pictorial representations designed to account for one or more experimentally observed phenomena—the so-called ‘model’ approach. It is clear from the above discussion that no single view can hope to apply equally across such a diversity of materials, but this is not a criticism. There is no doubt that our current understanding of fibre structure would be considerably less advanced were it not for the vision of the early painters of these (with hindsight) over-simple pictures. The various models tended to divide into three broad types, which may be termed ‘two-phase’, ‘continuous structure’, and ‘intermediate’. The boundaries between these are largely artificial, however. Over the years opinion has differed widely as to the extent to which order is localised within fibre structure. A wealth of ideas developed, ranging more or less uniformly from structures containing no definite ordered phase at one extreme, to ones with no clear disordered phase at the other—and with just about everything in between.

(a) *Two-phase models.* In the 1920s and 1930s much attention centred on understanding the structure of the natural and man-made fibres. The melt-spun synthetics were yet to appear, but much of our present understanding of their microstructure is owed to these early studies.

The prevailing ideas at that time stemmed from a theory due to Nägeli (1928), who proposed that starch and certain vegetable materials comprised extremely small crystalline particles which he called ‘micelles’. These particles were bound together with other substances such as gums, giving an overall structure analogous to that of bricks in mortar.

X-ray diffraction techniques applied to textile fibres indicated significant structural regularity, but the presence of incoherent scattering implied this must co-exist with a substantial level of disorder. The initial conclusion was that textile fibres might also conform to a micellar structure. Measurements suggested the dimensions of the particles in various cellulosic fibres to be around $5 \text{ nm} \times 40\text{--}60 \text{ nm}$, which appeared to agree well with current estimates of the average length of a cellulose molecule.

It was generally assumed that fibres consisted of an amalgamation of hard, discrete and perfectly crystalline micelles embedded in a matrix of non-crystalline (amorphous) polymer, as illustrated in Figure 1.8.

A major characteristic of this structural view was the existence of two distinct phases, i.e. the crystals (or micelles) and the non-crystalline polymer. The term ‘two-phase’ applies to any structural model in which there is such a distinction.

(i) *The fringed micelle concept.* The arguments in favour of the micellar theory of fibre structure were persuasive, but there were a number of factors which did not accord well. One of the salient features of most commodity



Figure 1.8 Simplistic 'bricks-in-mortar' two-phase representation of fibre fine structure (similar to that due to Nägeli, 1928).

fibres is their ability to withstand quite large relative extensions (*ca.* 50%) without significant loss of physical form or elasticity. This range of deformation is quite unusual; the majority of non-polymeric solids fracture at a considerably lower strain — generally a few percent at most. It is difficult to envisage how a simple micellar structure could retain continuity at large deformations. It is likely that delamination would occur between the micelles and the matrix (to which they were assumed not to be intimately connected), leading to voids, cracks and other gross damage at comparatively small extensions.

A further, and more damning, criticism arose once better estimates of molecular length became available. It is now known, for example, that cellulose molecules are actually 400–1000 nm long, which is ten to twenty times longer than the early data suggested.

If the interpretation of the X-ray data is accepted as essentially correct, one is forced to the conclusion that the molecules must be ten or twenty times longer than the crystals themselves.

Abitz and co-workers (Abitz *et al.*, 1930; Gerngross *et al.*, 1930), who were studying gelatin and collagen at the time, suggested that individual molecules might pass alternately through several micelles, and through several intervening regions, to produce a structure similar to that illustrated in Figure 1.9. This view became known as the 'fringed micelle' concept, and was soon adopted by many other researchers as a plausible description of the structure of fibres in general.

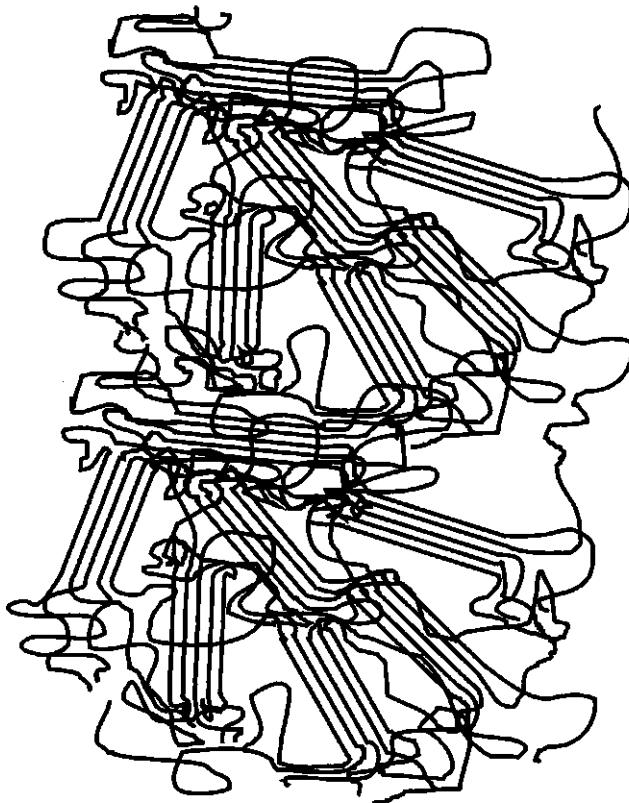


Figure 1.9 The fringed micelle model: an individual chain molecule may pass alternately through ordered and disordered regions.

A major advantage of this model was that it provided the structural continuity which was absent from those proposed earlier. Several alternative two-phase models later emerged, together with a good deal of controversy about which most closely described true fibre structure. The precise details of these vary, but most share the basic characteristic of two continuously linked, but geometrically separate, crystalline and non-crystalline regions. Among the most notable contributors to research in this area were Kratky and Mark (1937), Frey-Wyssling (1938), Hess and Kiessig (1944), and Hess *et al.* (1957).

(ii) *The fringed fibril concept.* Hearle (1958) proposed a two-phase structure which differed from previous models in an important respect: all previous fringed micelle variants showed chain molecules emerging exclusively from the ends of the crystallites, as depicted in Figure 1.10. Hearle (1958)

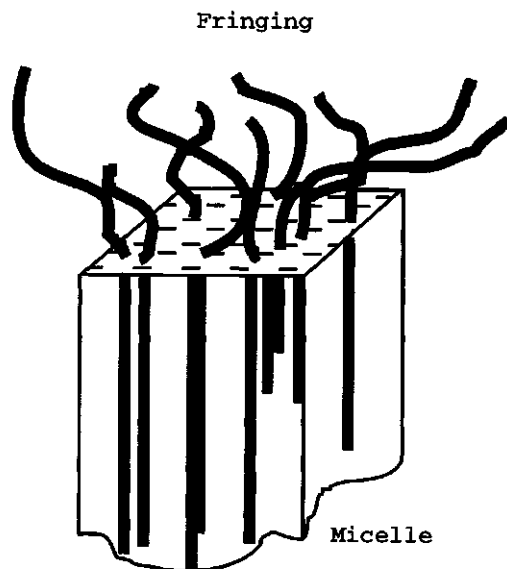


Figure 1.10 Commonly held view of the interface between ordered and disordered structural phases: chains emerge exclusively from the ends of crystallites.

pointed to the lack of rationale for this assumption, and proposed that chains could be expected to enter or leave a crystal at essentially any position along its length. His view of the structure of a fibre incorporated continuous 'fringed fibrils', giving rise to an arrangement similar to that shown in simplified form in Figure 1.11. This model had the advantage that it could be applied to fibres which various techniques revealed to possess long, needle-like features ('fibrils') as distinct from approximately cuboidal micelles.

(iii) *Chain folding.* More recent views of fibre structure included the notion of chain molecules folding back and forth on themselves. The work of Till (1957), Fischer (1958a,b), and others in the late 1950s, demonstrated that under suitable conditions single polymer crystals could be grown from dilute solution. It is now clear that the phenomenon applies quite generally over a wide range of crystallisable polymers. These single crystals appear as extremely thin, almost flat lozenges or 'lamellae'. Although they are sufficiently large to be observed easily using scanning electron microscopy, estimates suggest their thickness is confined to the range 10–20 nm. Electron diffraction experiments confirm, also, that their constituent molecules are invariably arranged with the main chain axes approximately parallel to the thickness. As there was no evidence for any substantial amorphous material associated with the single crystals, Keller (1957) proposed that the chains must fold, as illustrated in Figure 1.12. Chain folding is now in fact widely acknowledged

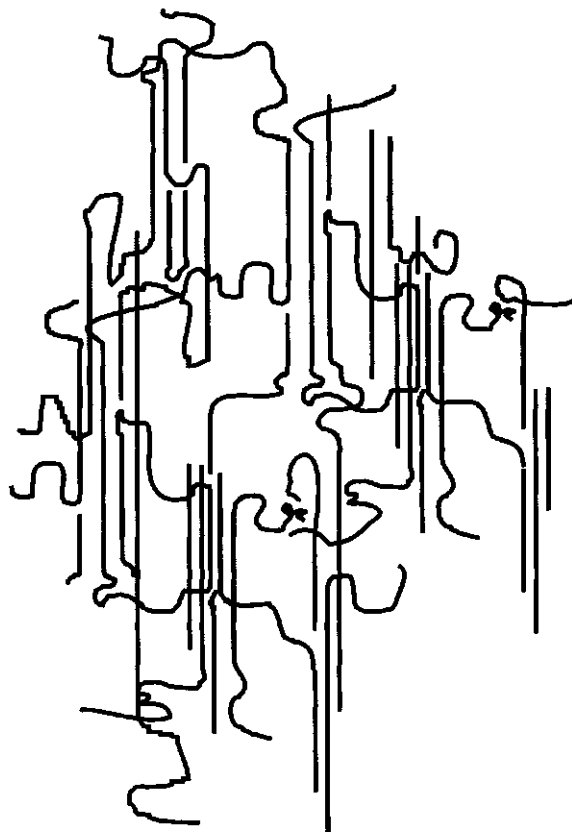


Figure 1.11 Fringed fibril representation (after Hearle, 1958), in which chains may enter or leave crystallites at any surface location.

to occur in many bulk polymers, such as thermoplastics. The inclusion of the phenomenon in fibre structure models was therefore a logical progression; there are, for example, modified fringed micelle and fringed fibril forms which incorporate chain folding.

Keller (1963) presents an excellent account of contemporary ideas regarding crystallinity in high polymers.

(b) *Continuous structure models.* Not all researchers accepted the notion of separate ordered and disordered phases. Staudinger (1932) believed that the molecules of high polymers would organise themselves into a single large, imperfect crystal as opposed to separate small, and essentially perfect, ones. His model of fibre structure was essentially as depicted in Figure 1.13. Other proponents of the continuous structure theory included Neale (1933), Carothers, and Hill (Carothers and Hill, 1932).

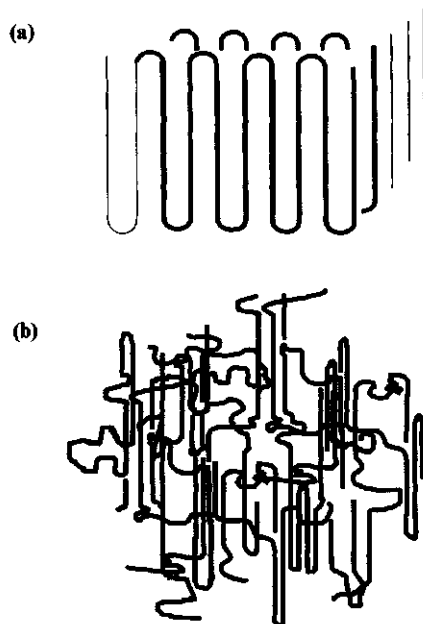


Figure 1.12 Schematic representations of chain folding: (a) folding in a polymer single crystal; (b) fringed fibril model incorporating some chain folding.

Although these models would not permit a separate disordered phase, it was acknowledged that some form of structural disorder nevertheless had to exist – the evidence from X-ray diffraction and other sources appeared to put this beyond any doubt. In Staudinger's representation, a key feature is the imperfection of the crystal itself. He maintained that such features as chain ends within the lattice could account for the experimental data.

(i) *Paracrystals*. Another continuous structure representation stems from the ideas of Hosemann (1950a,b, 1962), who put forward the existence of 'paracrystals'. These were essentially similar to the Staudinger crystal, but the disorder was supposed to arise from a somewhat different source. In a

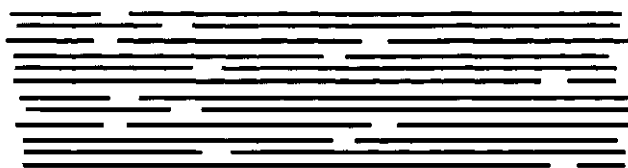


Figure 1.13 Arrangement of molecules in a large, but imperfect, fibre crystal as envisaged by Staudinger (1932).

Short-range order preserved

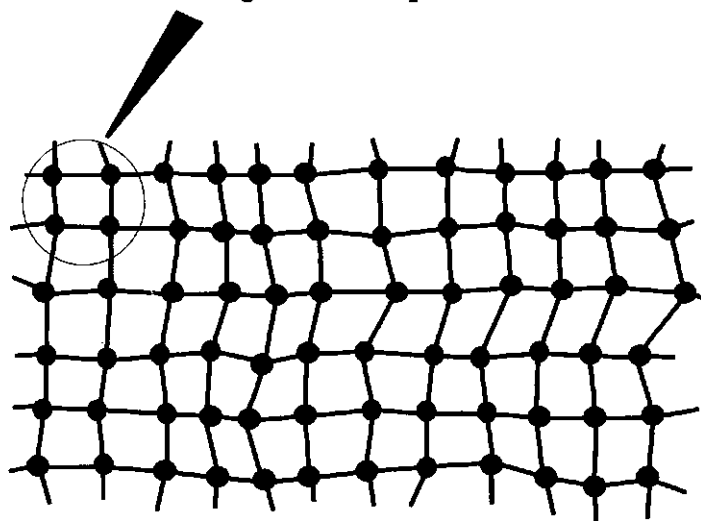


Figure 1.14 Representation of Hosemann's paracrystal in two dimensions: short-range order is preserved, but long-range order lost.

perfect crystal the lattice spacing is precise and exactly constant throughout the crystal. However, suppose there is a small, random variation in the lattice spacing, as illustrated in Figure 1.14 for the case of a hypothetical simple two-dimensional lattice. If the error is sufficiently small, the overall effect will be a loss of long-range coherence, but retention of the short-range regularity. The notion of order and disorder co-existing is preserved, but without the need to invoke two distinct phases.

(ii) *Amorphous-with-correlation.* An alternative point of view, expressed by Kargin (1958) and Mikhailov (1958), was that for the long (possibly entangled) molecules of a high polymer to crystallise in the conventional sense would require a degree of molecular freedom beyond what is likely to exist. This led to models, diametrically opposed to those of Staudinger, Hosemann, etc., in which the structure was thought of as essentially amorphous, the order arising from mutual aligning of molecular segments without their necessarily being in crystallographic register. While it is true to say that this view was not widely adopted by other researchers, there are sound arguments for incorporating the principle, at least in certain fibre types.

(c) *Intermediate views.* The two-phase and continuous models represent extreme views, but most current ideas tend to fall somewhere between the two, and to include more textural features than perhaps were previously recognised.

(i) *Defects.* Fibre crystals (whether of the fringed micelle type or not) are now thought to contain defects analogous to those observed in other materials such as metals — vacancies, impurities, dislocations, and so on. Indeed, given the physical form of polymer molecules, it would be surprising if such abnormalities were not present. Among other things, defects are thought to be responsible for plastic deformation processes in many crystalline fibres, since they impart mobility to the lattice.

(ii) *Assembly of crystalline fibrils.* Structural disorder need not arise from the presence of a true amorphous material, nor even from imperfections within crystals. A collection of otherwise perfect crystals would appear disordered if they themselves were imperfectly arranged. Figure 1.15 illustrates this point for a collection of rods of varying dimensions. Discontinuities, and possibly voids, at the crystal boundaries, distributed over the bulk of the material, can give rise to many of the features associated with disorder, such as the diffuse scattering and broadening observed in X-ray diffraction experiments on fibres.

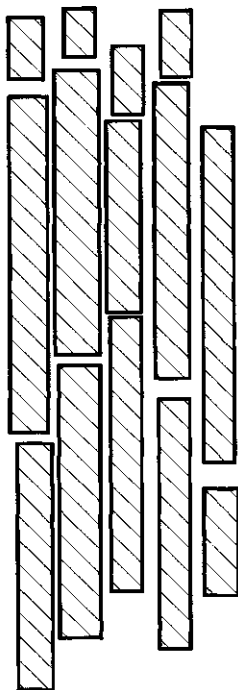


Figure 1.15 Structural disorder associated with the imperfect packing of various-sized rods.

1.3.1.3 *Structure parameters.* A major drawback to the model representation of fibre structure is its inherent subjectivity. Reference was made, in the introduction to this chapter, to 'artists' impressions', and it is certainly the case that such representations are generally capable of yielding at best qualitative information.

In applying a knowledge of structure to the elucidation of mechanical and other fibre properties a more concrete description is needed. For example, reliable prediction of the tensile behaviour of a fibre possessing a specific structural architecture requires hard numerical data rather than vague pictorial notions.

To deal with this criticism, Hearle and co-workers (Morton and Hearle, 1975; Hearle, 1977) devised a scheme whereby fibre structure would be described in terms, not of general geometrical arrangements, but of certain quantitative parameters.

In a simple crystalline solid the constituent particles are regularly arranged throughout the extent of the material, and only a very small number of unit cell parameters are required to specify its structure completely. Alternatively, if the material has a random configuration, such as in a simple liquid or a gas, it is possible to apply the statistics of large assemblies as was done, for example, in Maxwell's Kinetic Theory of Gases. Again, a small number of parameters is able to provide a complete description.

Conducting the equivalent exercise for a textile fibre is by no means a trivial matter. The problem is more difficult to address precisely because of their two-phase nature (partly ordered, partly disordered), coupled with the complexities associated with long-chain polymer molecules. At first sight it might appear necessary to locate all the various structural components, but to specify exactly the co-ordinates of the constituent atoms within the structure would require the determination of a vast number of parameters (of the order of three times Avogadro's Number), which would clearly be impossible.

However, Hearle (1977) asserted that as few as ten general parameters might suffice, of which six could be expected to exert the greatest control over a fibre's ultimate physical behaviour. The most important parameters having been identified, the task then becomes one of setting up suitable numerical scales upon which to measure them.

I. Degree of order. This is perhaps the most important parameter. Often referred to (inaccurately) as 'crystallinity', it expresses the fraction of material considered to exist in an ordered state within the fibre structure. In the case of a solid polymer, the perfect crystal represents the most efficient chain-packing arrangement possible, and the highest density. On the other hand, the imperfect packing of the amorphous chains leads to a lower density. Density is therefore a good indicator of the degree of order, and is typically used as a basis for the scale upon which degree of order is measured.

II. Degree of localisation of order. The two-phase and continuous structure models discussed earlier represent extreme views; in the former there is a clearly defined ordered phase, whereas in the latter there is no such concept, and the 'order' is deemed to permeate the entire structure in a rather diffuse way. One could regard these two extremes as defining two fixed points on a scale of 'localisation of order'. Experimentally, this parameter is more difficult to deal with than the degree of order, although it can be estimated from crystal size measurements using, say, X-ray diffraction techniques.

III. Length:width ratio of ordered units. The third important parameter is the average aspect ratio of the ordered units, specifically with respect to the fibre direction. For example, the units could be cuboidal micelles with similar width and length. Alternatively, they might be long fibrils, or thin, flat lamellae. The measurement scale for this parameter could run from zero for infinitely thin lamellae, to infinity for infinitely long fibrils. Micelles would have a value around unity. For the sake of symmetry, however, it is preferable to adopt a logarithmic scale, when the value for cubic crystals would be zero.

This third parameter may also be estimated from various diffraction techniques.

Hearle demonstrated the value of representing these first three parameters on a three-dimensional plot. The various fibre types are found to be located within fairly well-defined domains, as illustrated in Figure 1.16.

IV. Degree of orientation of ordered units. Any of the structures defined by the first three parameters can be envisaged with varying degrees of orientation of the ordered units. Orientation has a profound influence on most fibre properties, but notably on mechanical properties such as modulus, strength and extensibility.

Orientation can be estimated by using a variety of analytical techniques, including wide-angle X-ray diffraction (WAXD) and vibrational spectroscopy.

V. Size of ordered units. The size of the ordered units determines the overall scale of the structure, and is effectively a measure of its fineness or coarseness. It is thus analogous to the 'magnification' of the structure, and is quite distinct from the length:width ratio. Any of the structures discussed so far could be imagined to exist with a wide range of sizes.

VI. Molecular extent. The sixth parameter is analogous to fibre extent in slivers or yarns, and may apply to either ordered or disordered chains, or to some average over all the molecules within the structure (Figure 1.17).

The measurement scale for this parameter would range from near zero for a tightly coiled molecule, to unity for a fully-extended one.

The distinction between extent and orientation must be preserved. Figure 1.18 illustrates that it is possible to combine high orientation and low extent on the one hand, or low orientation and high extent on the other.

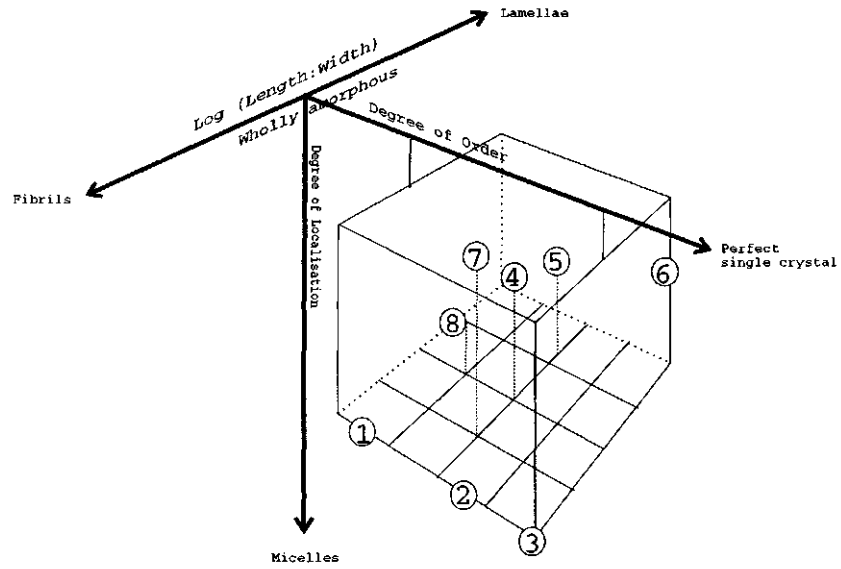


Figure 1.16 Representation of fibre structure parameters on a three-dimensional plot (after Morton and Hearle, 1975). Approximate location: 1, wool and hair; 2, silk; 3, cotton; 4, polyesters; 5, polyamides; 6, linear polyethylene; 7, acrylic; 8, viscose.

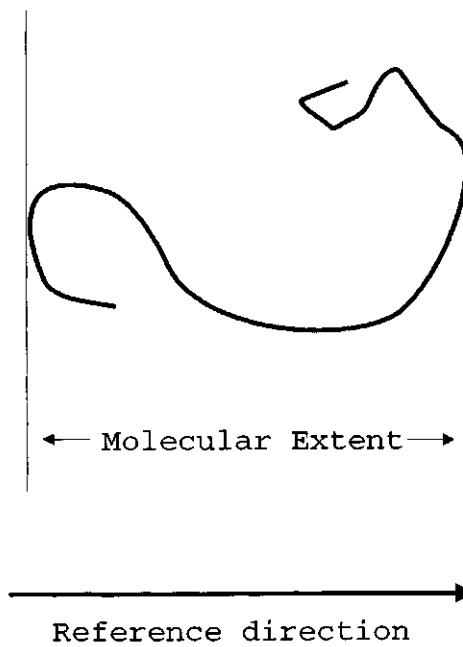


Figure 1.17 Definition of molecular extent.

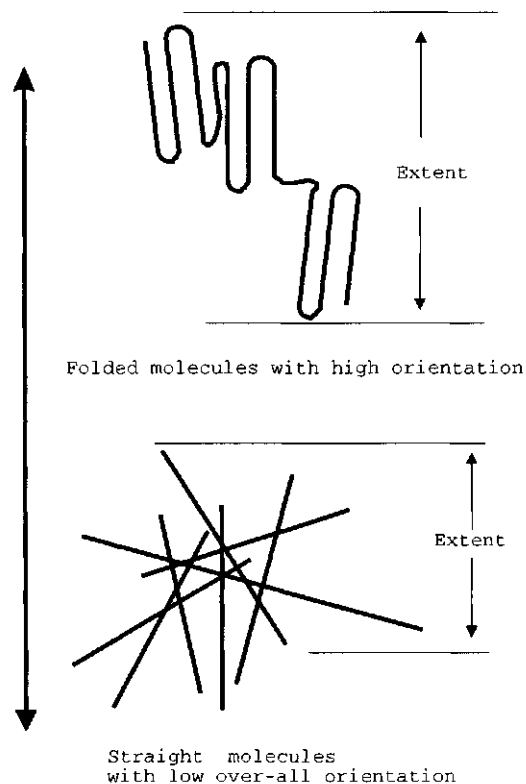
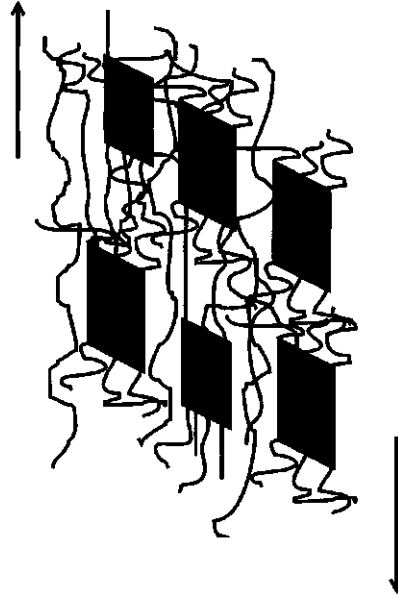


Figure 1.18 Two contrasting combinations of molecular orientation and molecular extent.

As with orientation, molecular extent will have a dramatic influence on properties such as strength and modulus.

VII. Shape of ordered units. Most simple models say little about the precise shape of the ordered units, either laterally, or when viewed in cross-section. The micelles (or other entities) tend to be assigned a vague cuboidal shape. However, certain aspects of fibre behaviour will no doubt be sensitive to whether the units have, for example, cylindrical, rectangular, or even lozenge-shaped profiles. The latter case in particular may be appropriate in melt-spun fibres, where there is evidence that the normal to the chain-fold surface may be regularly inclined to the fibre axis (see, for instance, Hearle and Greer, 1971). Such features may lead to the possibility of interlamellar shear within the structure of a fibre loaded in tension (Figure 1.19).



Structural inhomogeneities coupled with skewed crystals may increase shear effects

Figure 1.19 Two-phase structure model incorporating lozenge-shaped ordered units.

VIII. Relative orientation of disordered and ordered material. A well-developed fibre would feature equally high levels of amorphous and crystalline chain orientation. However, there will be cases where the ordered units are themselves well oriented, but the amorphous chain segments are essentially isotropic (Figure 1.20). Such a combination can arise when an initially highly-drawn melt-spun fibre, say, is heat treated at a temperature above its glass transition, enabling the amorphous regions to relax, and shrinkage to take place.

IX. Packing pattern of ordered units. The way in which the ordered units themselves aggregate will play a role in the overall fibre structure. As with shape, the packing both in cross-section and in profile needs to be taken into account. Whereas a random lateral arrangement such as that shown in Figure 1.21a might yield a uniformly distributed coarse-grain structure, more regular stacking could produce a 'pseudofibrillar' effect (Figure 1.21b). These two structures could be expected to have differing influences on, for example, the mechanics of fracture in tension. A further level of detail is the extent of staggering of the stacks (Figure 1.21c).

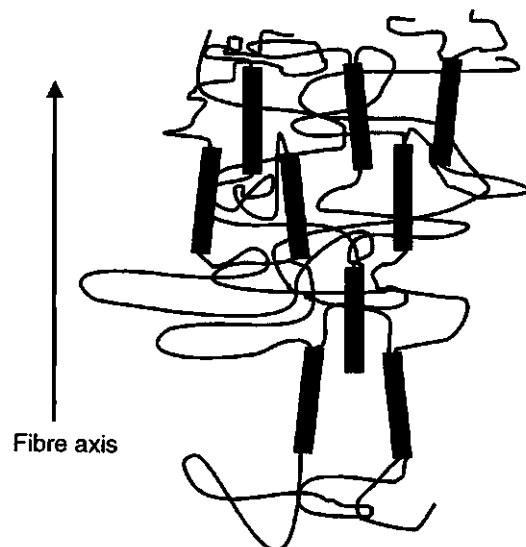


Figure 1.20 Combination of oriented ordered and unoriented disordered phases.

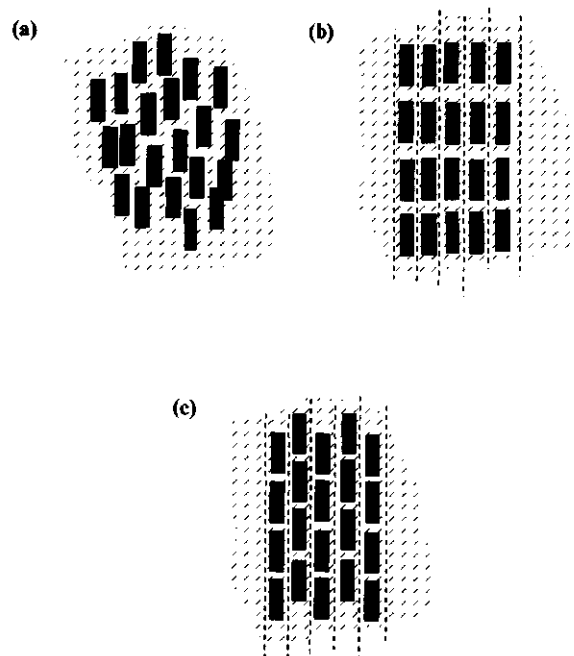


Figure 1.21 Various ways of visualising the lateral packing of ordered structural units: (a) random stacking; (b) regular stacking; (c) staggered stacking.

X. Degree of linking between ordered units. The fringed micelle and other two-phase views of fibre fine structure emphasise the continuity and cohesion provided by having individual molecules pass alternately through ordered and disordered regions. However, not every chain emerging from one crystalline surface will enter another; some will simply terminate in the intervening space between crystallites; others may re-enter the same crystal, forming loose loops; yet others may terminate within crystallites. These chain segments will contribute nothing towards the overall load-bearing capacity of the structure. Those chains that are effective are known as 'tie molecules'. Some of these may be stretched tightly between crystallites, and it is these that will bear the initial stress when the structure is loaded.

Figure 1.22 illustrates different types of chain segment which could emerge from the crystal surfaces. Hearle *et al.* (1988) attempted to develop quantitative structure models for melt-spun synthetic fibres which incorporate such features.

1.3.1.4 *Final comment on microstructure.* Views of fibre fine structure nowadays generally assume that for any given fibre type, and for any particular processing history, a combination of features will be present, which may include any or all of those discussed, and many for which space does

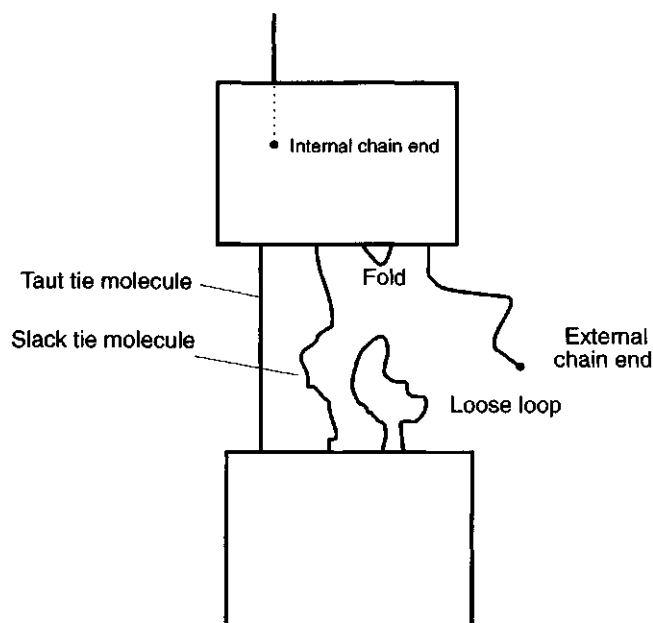


Figure 1.22 Illustration of different types of chain segments associated with the crystal–amorphous boundary.

not permit description. Hearle and Peters (1963) give an exhaustive and detailed account of the development of ideas relating to fibre fine structure.

1.3.2 *Comments on fibre macrostructure*

Over and above the submicroscopic fine structure detail of fibres lie larger-scale features which often form the distinguishing characteristics of a particular fibre type. These may be dictated by genetics in animal and vegetable fibres (for example the cuticular scales in wool, and the lumen in cotton), or they may arise from the crystallisation kinetics and other factors associated with the manufacturing process.

At a more macroscopic level still, there will often be physical features associated, for example, with the damage caused during processing and in end-use. It is inappropriate here to consider such aspects in detail. Rather, brief consideration will be given to two noteworthy phenomena. However, the interested reader is referred to Hearle and Peters (1963) for further discussion.

1.3.2.1 Spherulites. The 'spherulite' is perhaps the most frequently observed structural arrangement on a large scale in melt-crystallised polymers. However, although the existence of similar objects in metals and certain other substances had been recognised earlier, it was not until 1945 that their presence in high polymers was reported by Bunn and Alcock (1945).

Spherulites are, ideally (Figure 1.23a), spherical crystalline aggregates, whose diameter may range from the submicroscopic up to several millimetres. When viewed using polarised light they almost always display a 'Maltese cross' extinction pattern, indicating them to be birefringent entities in which the refractive index along a radius differs from that tangentially.

During crystallisation from the polymer melt, spherulites grow radially until either they impinge upon one another or they are stopped by other factors, such as quenching or the presence of non-crystallisable amorphous material. Under a polarising microscope they usually appear as either discrete circular features or as domains with line boundaries (Figures 1.23b and 1.23c).

Although spherulites are generally associated with isotropic bulk polymers, they are sometimes present in undrawn melt-spun fibres such as polyamides. When they do occur their dimensions can be comparable with the filament diameter. In this case they present a serious problem in downstream processing because they tend to act as regions of stress concentration, causing threadline breakage.

1.3.2.2 Kink bands. Many fibre types exhibit a phenomenon known as 'kink-banding', characterised by the appearance of linear criss-cross striations. These may be observed in either optical or scanning electron microscopy. Figure 1.24 shows an example of the effect in a polyester fibre.

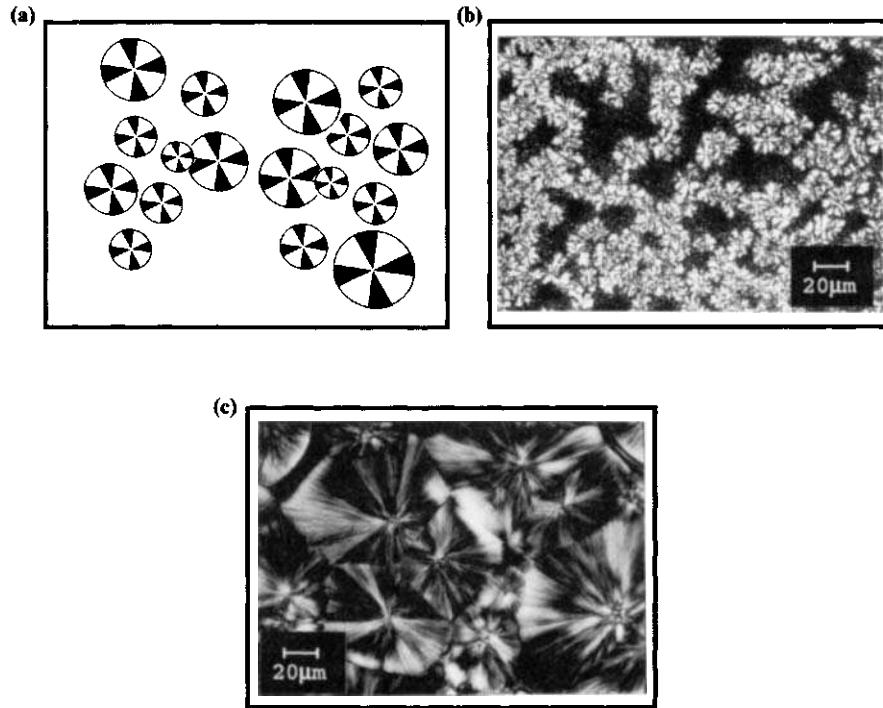


Figure 1.23 Spherulites in fibrous polymers: (a) idealised; (b) as observed in remelted, recrystallised polyester fibres; (c) as observed in remelted, recrystallised polypropylene film.

Kink bands are not inherent structural features in themselves, but arise from structural damage accompanying compressive loading. This is often encountered where bending occurs. In bending, the outer surface is subjected to extensional strain, but the inside surface is placed under compression. This compression causes buckling of the internal structure. Precisely what within the structure undergoes this buckling is not always clear, but is probably dependent on the fibre type. In the case of stiff fibres such as aramids it could be the straight-chain fibrils themselves which kink, whereas in melt-spun synthetics it is more likely to be shearing of intercrystalline amorphous material.

Contrary to what might be expected, textile fibres most commonly fail in use through compression rather than extension. This is because fibres generally yield more easily in compression than in tension. The fibres themselves are rarely stretched close to the point of tensile rupture, but repeated flexing within a fabric structure can induce compressional damage, leading eventually to failure.

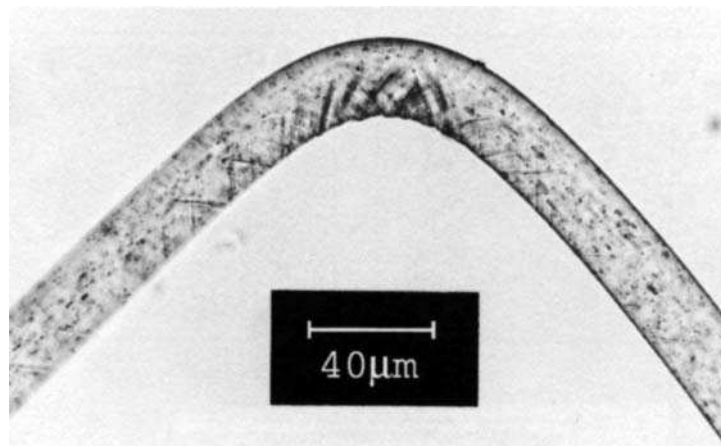


Figure 1.24 Optical micrograph showing kink-bands in a bent polyester fibre.

1.4 Relationship of structure to tensile properties

The salient technological feature of a fibre is its response to mechanical loading and/or deformation along its length, i.e. its tensile behaviour. Indeed, the tensile stress–strain curve is probably the single most important characteristic of a textile fibre.

Textile fibres display many phenomena which put them in a class apart from other materials. The stress–strain graph for a fibre is rarely a straight line as would be expected from a Hookean solid. Although it is often ascribed a ‘typical’ shape (Figure 1.25), in practice there are wide variations, both from one fibre type to another, and from one fibre to another within the same type. Except at quite small levels of extension, most fibres are inelastic, and so will fail to return completely to their original dimensions after stretching. The tensile behaviour is also highly temperature- and humidity-dependent in many cases.

It is appropriate to ask what influence the fine structure has on the ultimate physical behaviour of a fibre, and in particular, on its tensile properties. What structural features, for example, determine the characteristic shape of a fibre’s stress–strain curve? It should be realised that the influence of any particular feature will be highly complex, and it is not possible to do more than present a few general ideas here.

1.4.1 General influence of structural features

If the fine structure of a fibre may be described in terms of a two-phase assembly of ordered and disordered material, then both fractions must

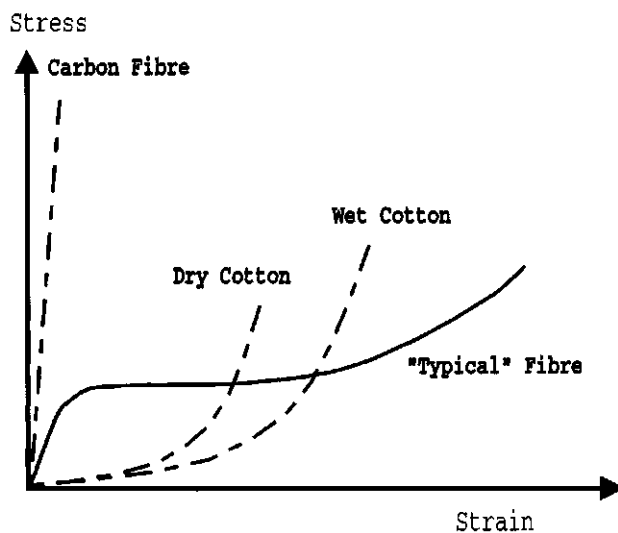


Figure 1.25 The 'idealised' fibre stress-strain curve, compared with those of cotton and carbon fibre (schematic).

contribute to some extent to the overall mechanical behaviour. At the very least, it ought to be possible to predict the initial modulus with some certainty.

Various researchers have attempted to develop suitable mechanical models to describe fibre tensile behaviour, and to relate these to actual structural features. Since the chain segments in a fibre crystal are more efficiently packed, and more fully extended, than they are in the amorphous regions, the crystalline modulus is generally significantly greater than the amorphous modulus. Bearing this in mind, one approach, due to Takayanagi (1964), is to devise mechanical models comprising crystalline volumes in combination with homogeneous amorphous blocks, as illustrated in Figure 1.26. The simplest model of this type assumes only two material properties—the crystalline and amorphous moduli. Depending on the relative abundance of the two phases, and how they are coupled mechanically, it is possible to predict a variety of results for the tensile modulus of the composite structure.

For fibres whose structure is continuous rather than two-phase, it may still be possible to arrive at a mechanical description. For example, if the structure is essentially crystalline, one might start by considering a single perfect crystal with its main chain axis lying exactly parallel to the fibre axis, and then make adjustments to allow for structural imperfections, misalignments and known macroscopic features (e.g. cell boundaries in animal and vegetable fibres).

1.4.1.1 *Time, temperature and anisotropy.* There are many complicating factors in relating fibre mechanics to structure, one of which is time

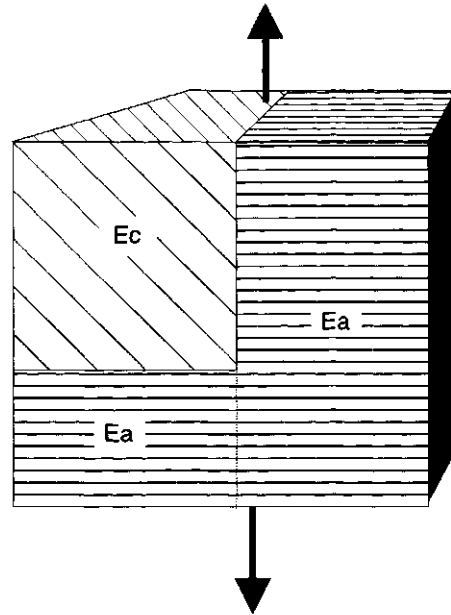


Figure 1.26 Simple Takayanagi model for the calculation of fibre modulus. E_a , amorphous modulus; E_c , crystalline modulus.

dependence. Most fibres are viscoelastic to a greater or lesser degree, which means their mechanical properties display a combination of elastic and plastic features. The phenomena of creep and stress-relaxation in fibres are manifestations of their viscoelastic nature.

Under normal conditions of use, time effects may be insignificant in many fibre types, but in others creep and stress-relaxation cause serious problems. It is important to find mechanical and structural models for such features, in order to understand the underlying causes better, and to offer ways of reducing such effects. An exhaustive study was made by Wilding and Ward (Wilding and Ward 1978, 1981, 1984; Ward and Wilding, 1984), who proposed a model for time-dependent phenomena in high-performance linear polyethylene, based on flow processes occurring in two parallel molecular phases (Figure 1.27). They showed that parameters such as molecular weight and the degree of cross-linking play an important role in suppressing creep and stress-relaxation.

Temperature has a profound effect on the tensile behaviour of most fibres. Where a two-phase structure is thought to exist, it is customary to regard the amorphous phase as a tangled network of disordered chains. At low temperatures this will display so-called 'energy-dependent' elasticity, and will be essentially glassy. However, at relatively high temperatures, where molecular mobility is sufficient, the amorphous phase may take on some of

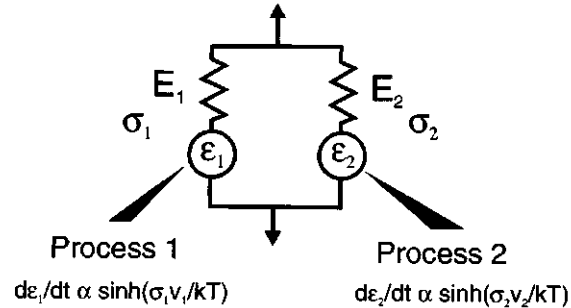


Figure 1.27 Mechanical model due to Wilding and Ward (1981, 1984) for time-dependence in high performance linear polyethylene fibres. Total strain $\varepsilon = \sigma_1/E_1 + \varepsilon_1 = \sigma_2/E_2 + \varepsilon_2$. E = spring stiffness, ε = strain, σ = stress, v = activation volume.

the characteristics of elastomers. At intermediate temperatures, it will display some features of both glasses and rubbers.

The ordered phase is likely to be much less sensitive to temperature. However, since plastic flow processes are generally highly temperature-dependent, the overall influence of temperature on the mechanical behaviour is far from obvious.

The influence of time and temperature on fibres having structures other than two-phase may be just as important, but the approach to analysing them may have to be quite different. For example, if there is no true amorphous phase, then rubber-like effects presumably cannot occur. However, such features as interfibrillar shear may take place, and these will be affected by the rate of deformation, temperature and, very often, whether or not moisture is present.

Additional factors such as the degree of anisotropy complicate the problem even further. The overriding principal, however, irrespective of the precise structural details, is that the higher the crystallinity and the more perfect the orientation, the higher will be the stiffness and strength.

Other parameters, such as yield stress and extensibility, tend to be influenced in the way one might intuitively imagine (e.g. yield strength increased, extensibility decreased).

1.4.2 Examples

This discussion of fibre structure has been of necessity brief, but it would be seriously incomplete if it did not pay some attention to structural features present in real fibres.

Since space is limited, attention will be restricted to two commodity fibres whose structural architectures are widely different, but which are commercially of equal importance, viz. cotton and melt-spun synthetics (typified by

polyamides and polyester). The reader is once again referred to the excellent work by Hearle and Peters (1963), and also to that by Woods (1955) for a wider discussion.

1.4.2.1 *Cotton*. The tensile curve of cotton (Figure 1.25) is very different from those of most other fibres in that it is smoothly concave to the point of rupture. Moreover, unlike the majority of other textile fibres, cotton is stronger when wet than when dry. These observations, if no other, require some explanation.

Since, in cotton, all the cellulose molecules produced grow directly into crystalline fibrils, true amorphous cellulose is virtually non-existent within the structure. For this reason, cotton fine structure is not generally regarded as two-phase. Nonetheless, X-ray and other data do show the existence of significant disorder. It is thought that this arises from factors such as the imperfect registration of neighbouring fibrils, and possibly also to crystal defects, together with the presence of small amounts of non-cellulosic substances.

In attempting to describe the tensile curve of cotton, since the fibre is essentially crystalline one could choose the tensile behaviour of a single cellulose crystal as a starting point. Using this assumption would imply a steep straight line, very different from the actual tensile curve. However, the inclination of the fibrils to the fibre axis will bring about a reduction in modulus. The simplest analysis yields:

$$E = E_f \times \cos^4(\alpha)$$

where E is the fibre modulus, E_f that of the fibril, and α is the helix angle.

The helix angle is therefore predicted to have a dramatic influence. Nevertheless, even allowing for this effect, the tensile graph would still be linear, and of a steeper slope than is encountered in practice.

A further factor is that because the helix angle reverses periodically, there is no real twist in the structure, only 'false' twist. This being the case, it is possible that when the structure is extended, the fibrils can rotate with comparative ease. This leads to a further reduction in the modulus. If there is moisture present, the process is made easier still, so that wet cotton would be expected to be less stiff than dry, as is indeed the case.

However, these effects alone cannot account for the characteristic concave shape of the true tensile curve. The explanation almost certainly lies in the convolutions. When the fibre is extended, one of the first processes to occur is the removal of the convolutions. This is similar to the removal of crimp in a fabric; it is easy initially, but becomes more difficult as the fibre is straightened.

The other curious property of cotton is its high wet strength. The explanation for this is thought to be that when the fibre is dry, extension generates high shear stresses between the helical layers of fibrils, promoting tearing of the structure, in which fibrils break in succession. In wet conditions, the reorganisation of the fibrils is assisted by the lubricating effect of the

water molecules. This favours more uniform load-sharing, and the strength tends towards that of a bundle of fibrils, rather than that of a single fibril.

1.4.2.2 Melt-spun synthetics. As was stated in section 1.2.3, the melt-spun synthetic fibres are dominated by the polyamides and polyesters. In broad terms, the properties of these two classes of material are similar, although there are some important differences. The typical tensile curves are similar to those shown in Figure 1.28.

(a) Likely fibre structure. The fibres are generally formed by melt extrusion followed by hot drawing. Because the molecules are relatively flexible, they reorganise under the influence of the applied shear stresses to produce a moderately high level of orientation. However, the considerable chain entanglements present in the melt will hinder crystallisation. As a result, melt-spun fibres are rarely more than about 50% crystalline. The remaining material is assumed to exist as an entangled amorphous network. This is close to the situation required for a two-phase system. The currently-accepted structural view is a combination of fringing and folding, as described by Hearle and Greer (1971). In their model the chain axes of the molecules within a lamella lie approximately parallel to the fibre axis, but owing to staggering of the folds, the normal to the lamellar surface is inclined to the fibre axis by approximately 42° . Similar models have been put forward by Peterlin (1971) and by Prevorsek *et al.* (1973).

Spherulite growth may be observed in undrawn melt-spun fibres, and has also been reported to exist in undrawn sections of drawn films and fibres (Keller, 1963).

There is at least one crucial distinction between the synthetic (including man-made) and natural fibres; in the former the constituent polymer molecules already existed prior to the fibre-formation process, which as a result becomes one of physical rearrangement; in the latter, the molecules develop simultaneously with the structure. The important consequence of this is that the fibre structure is effectively fixed by nature, whereas in the synthetics, it can be modified almost limitlessly in processing by control of such variables as temperature, draw ratio, and wind-up speed.

(b) Structure-tensile behaviour of melt-spun synthetics. Because a wide range of structural variations is possible for synthetic fibres, there is a correspondingly wide variation in tensile parameters. However, suffice it to say that, by and large, these materials can be considered as composites consisting of hard crystalline blocks embedded in an amorphous matrix.

The anticipated behaviour will depend upon the temperature range in which the fibres are operating. For example, at temperatures well below room temperature, the amorphous network might be expected to be glassy and brittle, so that the fibre itself will be brittle. At normal temperatures in, say,

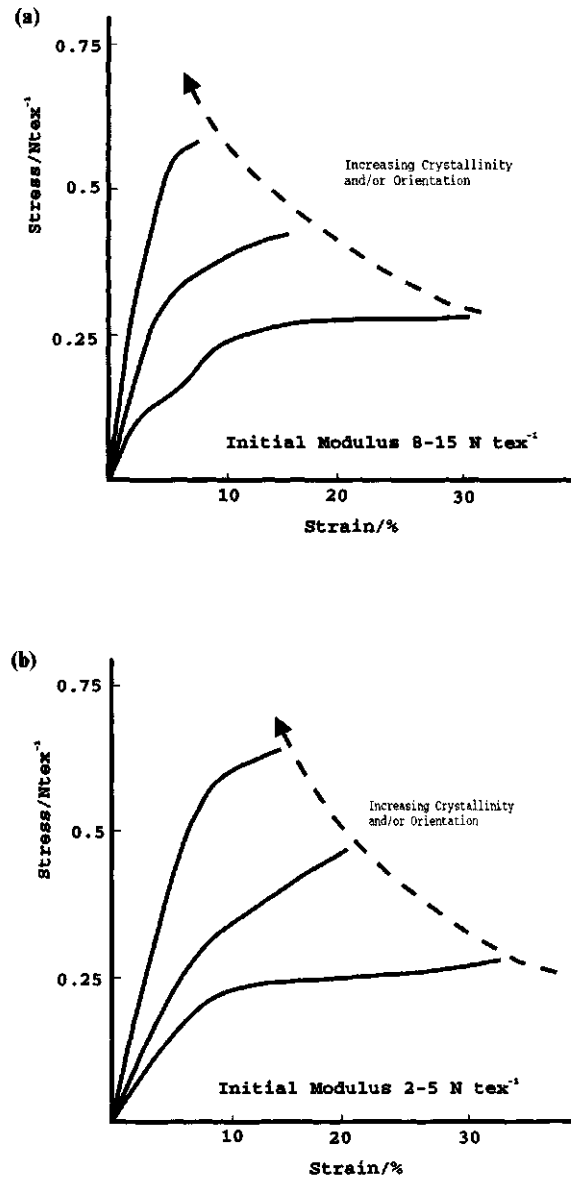


Figure 1.28 Typical stress-strain curves of polyester and nylon fibres, showing general effects of increasing crystallisation and orientation.

nylon, the amorphous molecules will have a degree of mobility, but there will still be hydrogen bonds. In this regime the matrix could be likened to a toughened rubber. The stress-strain curve would show some ductility. At temperatures above about 100°C, the hydrogen bonds will be dissociated, and the material will become significantly softened. (This effect is important, incidentally, in the heat-setting of nylon, and in ironing, since when the temperature is subsequently lowered, new hydrogen bonds can form, thus stabilising the deformed structure.)

Similar phenomena could be expected to occur in polyesters, with benzene ring interactions and steric hindrance replacing the hydrogen bonding. In addition, the inherent stiffness of the benzene rings ought to be reflected in a high tensile modulus as compared with the polyamides. This is in fact the case.

What has been discussed has been largely qualitative. Ideally, one would like to be able to make quantitative predictions for the tensile curves over their entire range. This is a daunting task and, not surprisingly, there have been few reported attempts, although Hearle *et al.* (1987) had a measure of success in describing the tensile curve for nylon 6.6 in terms of this composite model.

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References

- Abitz, W., Gerngross, O. and Herrmann, K. (1930) X-ray examination of gellatin micelles. *Naturwiss.* **18**, 754–755.
- Bailey, T.L.W. jun., Tripp, V.W., and Moore, A.T. (1963) Cotton and other vegetable fibres. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 422–454.
- Bamford, C.H. and Elliott, A. (1963) Synthetic polypeptides and fibrous proteins. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 46–110.
- Bunn, C.W. and Alcock, T.C. (1945) Texture of polythene. *Trans. Faraday Soc.*, **41**, 317–325.
- Carothers, W.H. and Hill, J.W. (1932) Polymerization and ring formation. XI. Use of molecular evaporation as a means for propagating chemical reactions. *J. Amer. Chem. Soc.*, **54**, 1557–1559.
- Fischer, E.W. (1958a) *Disc. Faraday Soc.*, **25**, 205.
- Fischer, E.W. (1958b) Oriented crystallization of polyethylene on sodium chloride. *Kolloid-Z.*, **159**, 108–118.
- Frey-Wyssling, A. (1938) *Submikroskopische Morphologie des Protoplasmas und seiner Derivate*, Gebrüder Borntraeger, Berlin; revised and translated as *Submicroscopic Morphology of Protoplasm* (1st English edn 1948, 2nd English edn 1953), Elsevier, Amsterdam.
- Furness, V.I. (1963) Fibres from addition polymers. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 524–533.
- Gerngross, O., Herrmann, K. and Abitz, W. (1930) Fine structure of gelatin micelles. *Biochem. Z.*, **228**, 409–425.
- Goodman, I. (1963) Synthetic fibre-forming polymers and co-polymers. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 111–130.

- Hearle, J.W.S. (1958) Fringed-fibril theory of structure in crystalline polymers. *J. Polymer Sci.*, **28**, 432–435.
- Hearle, J.W.S. (1963) Structure, properties, and uses. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, p. 621.
- Hearle, J.W.S. (1977) On structure and thermomechanical responses of fibres, and the concept of a dynamic crystalline gel as a separate thermodynamic state. *J. Appl. Polym. Sci.: Applied Polymer Symposia*, **31**, 137–161.
- Hearle, J.W.S. (1991) Understanding and control of textile fiber structure. *J. Appl. Polym. Sci.: Applied Polymer Symposia*, **47**, 1–31.
- Hearle, J.W.S. and Greer, R. (1971) Fibre structure. *Textile Progress*, **2**(4), 53.
- Hearle, J.W.S. and Peters, R.H. (eds) (1963) *Fibre Structure*, Butterworth & Co., London.
- Hearle, J.W.S., Prakash, R. and Wilding, M.A. (1987) Prediction of mechanical properties of nylon and polyester fibres as composites. *Polymer*, **28**, 441–448.
- Hearle, J.W.S., Prakash, R., Wilding, M.A. and Davis, H.A. (1988) The structural mechanics of nylon and polyester fibres: Approaches to theoretical understanding. In *Integration of Fundamental Polymer Science and Technology—2*, (Eds P.J. Lemstra and L.A. Kleintjens), Elsevier, London, pp. 540–544.
- Hess, K. and Keissig, H. (1944) Long-period interferences and micelle fiber—fine structure of synthetic polymers (polyamides and polyesters). *Z. physik. Chem.*, **A193**, 196–217.
- Hess, K., Mahl, H. and Gütter, E. (1957) Electron microscopic representation of long periodic intervals in cellulose fibers and comparison with the periods of other kinds of fibers. *Kolloid-Z.*, **155**, 1–19.
- Hosemann, R. (1950a) Röntgen interferences in materials with lattice perturbations obeying liquid statistics. *Z. Phys.*, **128**, 1–35.
- Hosemann, R. (1950b) Ideal paracrystal and the coherent Röntgen radiation scattered by it. *Z. Phys.*, **128**, 465–492.
- Hosemann, R. (1962) Crystallinity in high polymers, especially fibers. *Polymer*, **3**, 349–392.
- Kargin, V.A. (1958) Structure and phase state of polymers. *J. Polymer Sci.*, **30**, 247–258.
- Keller, A. (1957) Single crystals in polymers: Evidence of a folded chain configuration. *Phil. Mag.*, **2**, 1171–1175.
- Keller, A. (1963) The Crystallinity of High Polymers. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 332–390.
- Kratky, O. and Mark, H. (1937) Individual cellulose micelles. *Z. physik. Chem.*, **B36**, 129–139.
- Lewin, M. and Preston, J. (eds) (1985, 1989) *High Technology Fibres, Parts A and B*, International Fiber Science and Technology Series, (ISSN 0570-4898), Marcel Dekker Inc., New York.
- Lewis, D.M. (ed.) (1992) *Wool Dyeing*, The Society of Dyers and Colourists, Bradford.
- Mikhailov, N.V. (1958) On the phase structure of cellulose. *J. Polymer Sci.*, **30**, 259–269.
- Morton, W.E. and Hearle, J.W.S. (1975) *Physical Properties of Textile Fibres*, 2nd edn, Textile Institute and William Heinemann, London, pp. 32–38.
- Mukhopadhyay, S.K. (ed.) (1992) *Advances in Fibre Science*, The Textile Institute, Manchester, and Hobbs Ltd., Southampton.
- Nägeli, C. (1928) Micellartheorie. Original papers reprinted as *Ostwalds Klassiker*, No. 227 (Ed. A. Frey), Leipzig.
- Neale, S.M. (1933) The modification of natural cotton cellulose by swelling and by degradation. *Trans. Faraday Soc.*, **29**, 228–238.
- Peterlin, A. (1971) Molecular model of drawing polyethylene and polypropylene. *J. Mater. Sci.*, **6**, 490–508.
- Prevorsek, D.C., Harget, P.J., Sharma, R.K. and Reimschuessel, A.C. (1973) Nylon 6 fibers: changes in structure between moderate and high draw ratios. *J. Macromol. Sci.*, **B-8**, 127–156.
- Sharples, A. (1963) Cellulose and its derivatives. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 21–45.
- Staudinger, H. (1932) *Die hochmolekularen Organischen Verbindungen*, Springer-Verlag, Berlin.
- Takayanagi, M. (1964) Viscoelastic behaviour of crystalline polymers. *Kautschuk Gummi, Kunststoffstoffe, Plastomere, Elastomere, Duromere*, **17**, 164–173.
- The Textile Institute (1960) *Textile Terms and Definitions*, 4th edn, The Textile Institute, Manchester, p. 65.
- Till, P.H. (1957) Growth of single crystals of polyethylene. *J. Polymer Sci.*, **24**, 301–306.

- Ward, I.M. and Wilding, M.A. (1984) Creep behaviour of ultra-high modulus polyethylene: Influence of draw ratio and polymer composition. *J. Polymer Sci., Phys. Ed.*, **22**, 561–575.
- Wilding, M.A. and Ward, I.M. (1978) Tensile creep and recovery in ultra-high modulus linear polyethylenes. *Polymer*, **19**, 969–976.
- Wilding, M.A. and Ward, I.M. (1981) Creep and recovery of ultra-high modulus polyethylene. *Polymer*, **22**, 870–876.
- Wilding, M.A. and Ward, I.M. (1984) The creep and stress-relaxation in ultra-high modulus linear polyethylene. *J. Materials Sci.*, **19**(2), 629–636.
- Willgong, R.E. and Zimmerman, J. (1977) Strength and durability characteristics of Kevlar aramid fiber. In *Fiber Science* (Ed. M. Lewin), International Fiber Science and Technology Series (ISSN 0570-4898), Marcel Dekker Inc., New York, pp. 1–21.
- Wooding, N.S. (1963) Rayon and acetate fibres. In *Fibre Structure* (Eds J.W.S. Hearle and R.H. Peters), Butterworth & Co., London, pp. 455–479.
- Woods, H.J. (1955) *Physics of Fibres*, The Institute of Physics and John Wright & Sons, Bristol.