1

An introduction to fibre structure

1.1 General introduction

1.1.1 The nature of matter

Fibre physics is the study of the structure and physical properties of fibres. These two aspects are not, however, independent: the properties must be explained by the structure, which they also help to elucidate. Because of this connection, it is appropriate to start this book on the physical properties of fibres with a review of what is known about their structure. There is much detail, only partly superseded by more recent work, in the book edited by Hearle and Peters [1] and the review by Hearle and Greer [2]. Other information is in the general references given at the end of the chapter.

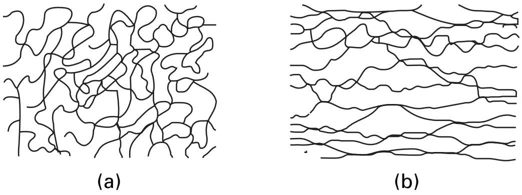
Matter is composed of atoms linked together by bonds of varying strength. It is the arrangement of these atoms and the strength of the bonds between them that determine the physical properties of materials. Thus with light atoms, such as those of helium, attracted to one another by very weak forces, the energy of the atoms is sufficient (except at very low temperatures) to cause them to move about independently, and the material is a gas. The material will also be a gas (though with a higher liquefaction point) if it is made up of heavier atoms, or of molecules composed of two or three atoms held together by strong forces (valency bonds), provided that the forces between the individual molecules are weak. These weak forces are often called van der Waals forces, since they are the cause of one of the deviations of a real gas from an ideal gas, which were considered by van der Waals in his modification of the gas laws. If the molecules are heavy enough, and the attractive forces strong enough, then the atoms will not have sufficient energy at room temperature to move freely away from one another, and the substance will be a liquid or a solid.

Some materials are made up of giant molecules. For example, in a crystal of diamond, all the atoms are linked to one another by valency bonds in a regular three-dimensional network. This gives a very hard, non-fusible material. In graphite, which is also pure carbon, the atoms are linked only in single planes by valency bonds; the forces between the planes are weak, so the material is one that easily splits up into sheets, and these will slide over one another, giving a lubricating action. In linear polymers, the linking is in only one dimension. If there is flexibility in the main-chain covalent bonds and only weak bonding between the long-chain molecules, there is nothing to prevent thermal energy from causing the chains to take up a disordered, random, tangled arrangement, as suggested in Fig. 1.1(a). When the material is tensioned, the molecules straighten out, giving a large extension, Fig. 1.1(b). This extension is reversible, since on releasing the tension the molecules return to the random tangle. This is the rubbery state, though some crosslinks are introduced in vulcanisation to give cohesion to the material. At lower temperatures or with stronger bonding, such an amorphous polymer material is a glassy plastic. Other linear polymers can crystallise into regular lattices to give plastics such as polyethylene of intermediate stiffness. From these examples, we see that the characteristics of matter are determined by its molecular arrangement.

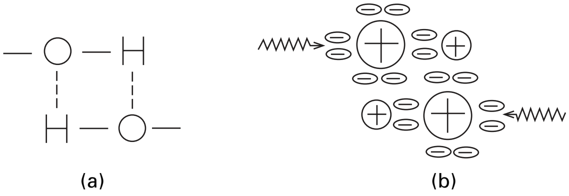
1.1.2 Intermediate bonds: hydrogen bonding

In addition to the ordinary covalent bonds that link atoms in a molecule and the usual weak van der Waals interactions between molecules, there is another class of bonds of intermediate strength, which are very important in influencing fibre properties. The best-known example is the hydrogen bond, which forms between hydroxyl (—OH) groups. Figure 1.2(a) gives a schematic representation of this bond, and Fig. 1.2(b) illustrates, in a very inexact manner, the way in which it might arise by a sharing of electrons from the outer rings of the hydrogen and oxygen atoms.

Water illustrates the importance of hydrogen bonding, both in its own properties and in its occurrence as the commonest 'fibre plasticiser'. Below 0 °C, the hydrogen bonds are strong enough to hold the water molecules together as a crystalline solid, although the mass of the molecules is less than that of many substances (propane, butane, hydrogen sulphide, chlorine, nitrogen, oxygen, to name but a few) that are gases at this temperature. At atmospheric pressure, between 0 and 100 °C, water is a liquid of limited volume in equilibrium with water vapour. The water molecules are


(a) (b)

1.1 (a) Disordered arrangement of long-chain molecules in rubber. (b) Oriented arrangement of molecules in stretched rubber.



(a) (b)

1.2 Two schematic representations of a hydrogen bond: (a) bonding; (b) electron arrangement in outer rings.

in a mobile dynamic equilibrium, with hydrogen bonds continually breaking and re-forming. Above 100 °C (at atmospheric pressure), all the molecules disperse into a gas. At ordinary temperatures, therefore, hydrogen bonds are in a very sensitive state: they are on the verge of breaking and thus are easily affected by changes of temperature, by applied stresses and by chemical and structural changes. Deliberately or inevitably, this results in considerable effects in some fibre materials, such as cellulose and nylon. This affects fibre behaviour, processing and usage; the fibre molecules under various conditions may be held rigidly together, be free to move in a dynamic equilibrium or be completely free of one another, except for chain entanglements.

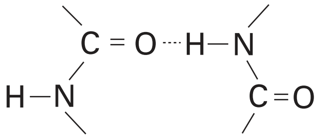
Hydrogen bonds can also form, as illustrated in Fig. 1.3, between —CO·NH— groups, which are found in polyamide and protein fibres.

In some fibres, there may be other bonds of intermediate strength. Thus, in the acrylic fibres, the asymmetry of electron arrangement in the —C≡N group, illustrated in Fig. 1.4, results in a moderately strong electrical interaction. In polyester fibres, and others based on aromatic polymers, there is an interaction between benzene rings.

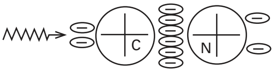
1.1.3 The nature of fibres

Fibres have been defined by the Textile Institute [3] as units of matter characterised by flexibility, fineness and a high ratio of length to thickness. To these characteristics might be added, if the fibre is to be of any use for general textile purposes, a sufficiently high temperature stability and a certain minimum strength and moderate extensibility.

The characteristic dimensions of fibres are the basis of their use and need to be stressed: individual fibres (or elements of a continuous filament) weigh only a few micrograms, and their length/width ratio is at least 1000:1, so that a single cotton fibre scaled up to be as thick as a thumb would be 100 m long. In addition to the need to be made of materials that can be produced in this special form with adequate stability for use, ordinary textile fibres must be, at least partly, elastic up to breaking extensions between 5 and 50%. This is an unusual intermediate range of extensibility, since glasses and crystalline solids are less extensible, whereas rubbers are much more extensible. The materials that meet these needs are almost all partially oriented,



1.3 Schematic indication of hydrogen bonds between —CO · NH— groups.



1.4 Electric dipoles in the acrylonitrile side group.

partially crystalline, linear polymers. A remarkable fact is that almost all the general textile fibre market is met by six polymer types: the natural polymers, *cellulose* and *proteins*, and the synthetic (manufactured) polymers, *polyamide*, *polyester*, *polyolefin* and *vinyl* (including acrylic).

The above comments relate to fibres for the traditional textile uses. More recently, a second generation of high-performance fibres has been introduced for functional applications. They have high strength and low extensibility. Some of these are linear polymer fibres. Others are inorganic networks, which, provided that they are fine enough, have the necessary flexibility. Glass and asbestos (which is no longer used because it is a health hazard) are the two older fibres in this group. At the other extreme, elastomeric fibres are used where a high stretch is specially needed.

There are other sorts of fibres, which fall outside the main theme of the book. There are fibres in living organisms, of interest to biologists: these include wood fibres, used in paper but too short for textiles, and a variety of connective tissues. Of commercial interest, there are fibres with special properties for particular uses. Metal fibres may be used for decorative purposes or for special purposes, such as reducing static electricity. Other fibres are used medically, for example to assist wound-healing. Finally, there are ‘smart fibres’, which can be used as transducers or change with the environment.

1.2 Methods of investigation of structure

1.2.1 Sources of evidence

The elucidation of fibre structure has been based on many sources of information, which include:

- the chemistry of the fibre material – its preparation, composition, molecular formula and reactions;
- the absorption of infrared radiation;
- Raman scattering of light;
- optical and X-ray diffraction studies;
- optical microscopy;
- electron microscopy and electron diffraction;
- nuclear magnetic resonance;
- optical properties;
- thermal analysis;
- density;
- general physical properties.

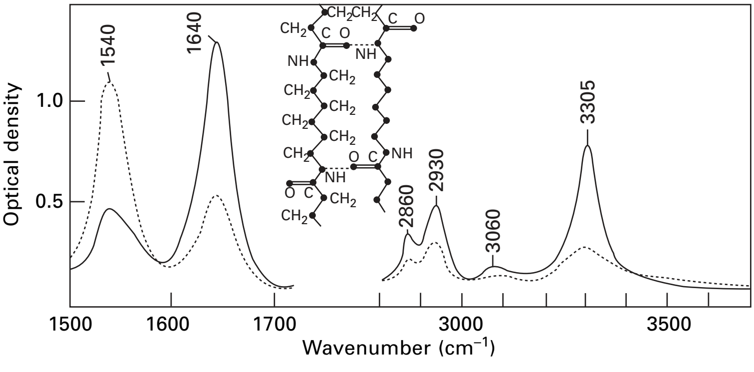
Of these, the chemistry is a subject of its own, of which the results will be assumed here; the optical, thermal, density and general physical properties are the subject of the remaining chapters of this book; and optical microscopy is a subject of which the general principles are well known and the techniques are covered in specialised textbooks. The remaining sources are specialised techniques, which it may be useful to describe briefly here.

A general comment should first be made. All the techniques are subject to errors and artefacts, and a direct unambiguous interpretation of experimental results is rarely possible. Indeed, there is a danger of a vicious circle: detailed calculations based on a particular model of structure may unjustifiably be taken as evidence in support of the model. Views on fibre structure have therefore to be built up from a collection of largely circumstantial, possibly unreliable, evidence. Unfortunately, no individual is an expert in evaluating all the techniques; and it is easy to place most reliance on the stated results of techniques with which one is less familiar and so less aware of the difficulties of interpretation. However, despite these difficulties, there is a general consensus on many aspects of fibre structure.

1.2.2 Absorption of infrared radiation and Raman scattering

When electromagnetic waves interact with matter, they are scattered and absorbed. In infrared spectroscopy, radiation with wavelengths between 1 and 15 μm is absorbed at certain characteristic frequencies, which yield structural information. Elastic scattering does not give molecular information, though light scattering does give larger-scale information. Raman spectroscopy results from the few photons that are inelastically scattered.

By using an infrared spectrometer, the variation in absorption can be found and plotted against wavelength, or, more commonly, its reciprocal, the wavenumber. This is illustrated in Fig. 1.5, which is the absorption spectrum of nylon. The peaks occur where the frequency of the electromagnetic waves corresponds with the natural frequency of vibration between two atoms in the material. If these are associated with



The peaks are due to:
3305 cm^{-1} stretching of N—H
2930 and 2860 cm^{-1} stretching of $\mathrm{C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix}$
1640 cm^{-1} stretching of C=O
1540 c^{-1} uncertain, involves —NH and neighbouring bonds

1.5 Infrared absorption spectrum of nylon: Full-line: electric vector perpendicular to fibre axis. Broken line: electric vector parallel to fibre axis. Inset: Crystal structure of nylon 6.6 (Bunn and Garner [5]). (After Bamford, *et al.* [4]).

an electric dipole, then the variations in the electric field set up the vibration, and energy is absorbed from the radiation. The fundamental oscillations occur at wavenumbers less than 4000 $\mathrm{cm^{-1}}$. These give strong absorptions and so can be studied only in very thin films or fibres. At higher wavenumbers, nearer optical frequencies, absorptions will occur that are due to harmonics of the fundamental frequencies. The absorption spectrum in this range is more complex and less used, but, since the absorptions are weaker, thicker specimens, such as fibre bundles, can be studied.

The wavenumber at which absorption takes place depends primarily on the nature of the two atoms and of the bond between them. Thus there will be absorption frequencies characteristic of such groupings as $>\mathrm{C{-}H}$, $>\mathrm{C{=}O}$, $>\mathrm{C{-}O{-}}$, $\mathrm{{-}O{-}H}$, $>\mathrm{N{-}H}$, $>\mathrm{C{-}C}<$, $>\mathrm{C{=}C}<$ and so on. To a smaller extent, the absorption frequency is influenced by the other groups in the neighbourhood: for example, the absorption frequency for a carbon–hydrogen bond in a terminal group, $\mathrm{{-}CH_3}$, is different from that for the same bond in a chain, $\mathrm{{-}CH_2{-}}$.

The first use of infrared absorption is therefore as an aid to the identification of the presence of certain groups in the molecule, leading to the determination of its chemical formula. The method can also be used in routine analysis to identify and estimate quantitatively the presence of given substances, even in small quantities in a mixture, by observation of their characteristic spectrum. For instance, it can be used to determine the amount of water in fibres.

Other structural information can also be obtained. If the infrared radiation is polarised, then the oscillation of the atoms will vary from a maximum for one orientation to a minimum for an orientation at right angles. The variation in the absorption spectrum with the direction of polarisation can therefore be used to investigate the degree of orientation of the molecules in a fibre. For example, in nylon, the $>\mathrm{N{-}H}$, $>\mathrm{CH_2}$ and $>\mathrm{C{=}O}$ absorption bands all show weak absorption when the vibration direction of the electric vector is along the molecular chain and strong absorption when it is vibrating perpendicular to the chain axis. The curves in Fig. 1.5 demonstrate the high molecular orientation of drawn nylon.

In addition to determining the degree of orientation of the molecules as a whole, polarised infrared may also be used to find the direction in which a particular group points in a molecule of unknown form. For example, two different forms, α and β, of the synthetic polypeptide poly-L-alanine show a difference. It is deduced that the $>\mathrm{C{=}O}$ and $>\mathrm{N{-}H}$ bonds move from a transverse direction between molecules in β towards a direction parallel to the chain axis between coils within α molecules. This is useful in determining the molecular configuration in polypeptides and proteins (see Section 1.6.3).

An advantage of the infrared absorption method is that it is influenced by all the molecules in the fibre, in both the crystalline and non-crystalline regions, whereas the X-ray diffraction method gives detailed information only about the crystalline regions of the fibre. For example, the infrared spectrum gives evidence of the presence of α- and β-forms of protein molecules in the non-crystalline regions of protein fibres.

In some materials, owing to the influence of the surroundings, an absorption will occur in the crystalline regions but not in the non-crystalline regions. Polyethylene, for example, shows a strong double peak at 725 cm^{-1}. In shorter-chain paraffin hydrocarbons, this double peak is found in the solid (crystalline) state, but only one component is present in the liquid (non-crystalline) state. The presence of a doublet is thus evidence of crystalline material. From an examination of the relative magnitudes of the two peaks, the proportion of crystalline material can be estimated. Furthermore, by using polarised infrared, the orientation in the two regions could be separately determined.

In a similar way, Sandeman and Keller [6] have found absorption bands in the infrared spectrum of nylon that are characteristic of crystalline order, and these may be used to determine the degree of crystallinity. Other bands are characteristic of chain folds [7].

One special technique that may be useful is the exposure of a material to the vapour of heavy water, D_2O. This may lead to the replacement of hydrogen atoms in the material by deuterium atoms, which can be detected by the change in the infrared absorption, consequent on the greater weight of the deuterium atom. This technique has been applied to viscose rayon and other forms of cellulose [8], in which the —OH groups in the cellulose molecule are replaced by —OD groups. Only the non-crystalline regions are accessible to the heavy water, and consequently the infrared absorption spectra of the hydroxyl groups in the crystalline and non-crystalline regions are separated and can be studied independently.

In Raman spectroscopy, the incidence of the photons shifts electrons from one state to another. The energy of the change comes from the photon. Consequently the scattered photon has a different energy and hence a different frequency. The effects are manifested in the visible region. Broadly speaking, Raman spectra are influenced by material structure in a way similar to that described for infrared absorption spectra, but the greater complication of the interaction yields more directional information. Raman spectroscopy has become a powerful tool for investigating fibre structure as a result of the development of Raman microscopes. With a spot size less than a fibre diameter, spectra can be obtained from single fibres. If the fibre is mounted on an extension stage in the microscope, it is possible to observe the shift in the spectral lines with fibre extension [9]. In this way it is possible to show which parts of the structure are changing. An account of the use of Raman spectroscopy in various ways in the study of aramid, polyester and carbon fibres is given by Young [10].

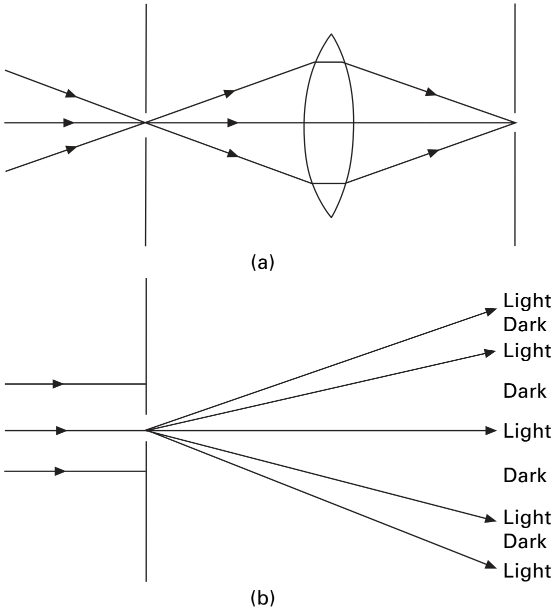
1.2.3 Optical and X-ray diffraction studies

Diffraction may be viewed as a problem in information theory. For example, when a beam of light is passed through a photographic slide, the light is scattered in many directions. By using a lens in the right place, we can recombine this scattered information about the picture into an image on a screen. But the information is there before it is recombined, and diffraction is the science of understanding and using this information in all sorts of ways. Image formation is thus merely one branch of diffraction in its most general sense, and there are many circumstances in which images cannot be formed or are not the most useful means of obtaining the required information about the object.

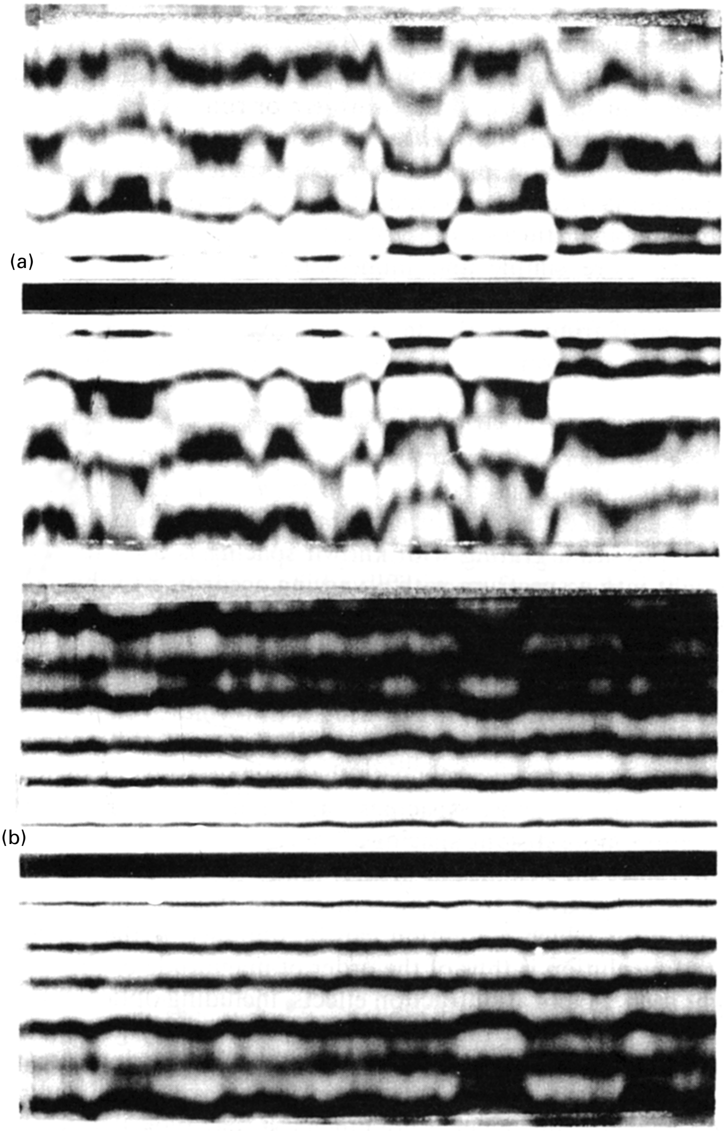
In a narrower sense, diffraction is the study of the particular patterns that may be found when waves pass through or round objects (or holes) of particular shape. For example, there is a characteristic diffraction pattern from a single slit. The difference between the image that must be focused at a particular place and the angular diffraction pattern that can be intercepted anywhere is shown in Fig. 1.6.

An example of the use of optical diffraction in fibre physics is shown in Fig. 1.7 taken from work by Lynch and Thomas [11]. A single fibre will diffract a parallel beam of light into a pattern of fringes that gives a means of measuring its diameter accurately or of showing up changes in diameter. If the fibre is gold-coated, as in Fig. 1.7(a), the pattern is relatively simple, since all the scattering is from the edge of the fibre; but if light also passes through the fibre and is scattered internally, a much more complicated pattern (Fig. 1.7(b)), is found. In this pattern, there must be a great deal of useful information on internal fibre structure The problem is how to understand the phenomenon in sufficient detail to extract this information.

The scattering of a fine beam of light is another diffraction phenomenon that can be used to obtain information about the internal structure of polymer films [12], which may be related to fibre structure. This is analogous to the formation of a halo round the moon when it is seen through a cloud. The radius and breadth of the halo give some information about the distribution of spacings between the particles that scatter the light, for example, the crystallites within a fibre. More complicated patterns can also be made to yield information about the shape of the scattering particles and differences in spacing in different directions.



1.6 (a) Formation of image of a slit. (b) Diffraction pattern of slit.



1.7 Diffraction pattern of a nylon fibre: (a) as received; (b) coated with gold to minimise effects of internal structure. From Lynch and Thomas [11].

The use of polarised light in either of the above two techniques changes the pattern and thus, in principle, increases the available information about structure if it can be interpreted.

The diffraction patterns from objects with some regular repetitive structure are more simple and immediately useful. Thus a diffraction grating of regularly spaced lines, illuminated normally by parallel light, will give a set of fringes, with the maxima of the bright bands at angles ϕ defined by the relation:

$$n\lambda = a \sin \phi \tag{1.1}$$

where n is an integer, λ the wavelength of light and a the spacing of the lines in the grating.

Measurements of ϕ enable values of a to be found (though, more usually, in ordinary physics a grating with known spacing is used to find λ or to disperse light into a spectrum with ϕ varying according to the value of λ). Any distortion in the grating will cause a disturbance in the diffraction pattern. In the extreme, an irregular grating would give a very complicated pattern: but the structural information would still be there if it could be extracted.

Equation (1.1) illustrates two general features of diffraction effects. Firstly, the angle varies inversely with the spacing, so wide-angle patterns give information on close spacings, and narrow-angle patterns give information on more distant spacings. Secondly, since sin ϕ cannot be greater than 1 and n cannot be less than 1 (for the first fringe away from the centre), the smallest possible value of the spacing a for which a solution can be obtained is the wavelength λ. The limit of resolution is thus of the order of magnitude of the wavelength of the light used[1]. Optical-diffraction effects, including optical microscopy, even by using ultraviolet radiation, will therefore give information only on relatively coarse features of fibre structure with spacings greater than about 0.1 μm. Indeed, optical microscopy becomes very difficult as soon as one approaches 1 μm, which is not much less than typical fibre diameters.

Atomic and molecular spacings are more than a thousand times smaller than this: typical values lie between 0.1 and 0.5 nm. Consequently, in order to obtain information about the fine structure of fibres, we need to use much shorter electromagnetic waves, namely X-rays. X-ray diffraction is a most important tool for the study of fibre structure, firstly because it gives information at the most important level of fine structure, and secondly because focusing of X-rays is not possible, so that diffraction methods have to be used.

As before, wide-angle diffraction will give information on the finest inter-atomic spacings, and narrow-angle diffraction will give information on longer spacings, of the order of 10–100 nm. As before, an irregular structure will give a complicated pattern, which is difficult to interpret from the image on a photographic plate. However, three advances have made the technique more powerful than was available to the pioneers of X-ray diffraction: arrays of detectors give enhanced quantitative information on the diffraction pattern; computer software then enables the data to be analysed and interpreted; and the increased power of synchrotron radiation reduces exposure times and allows small spot sizes to be used. Dynamic X-ray diffraction is possible, for example on a moving threadline.

As with optical diffraction, the simplest diffraction patterns arise when the X-rays are scattered from a regular, repetitive lattice. This is the subject of X-ray diffraction by crystals, which has proved an immensely powerful tool since the first patterns were observed by von Laue in 1912.

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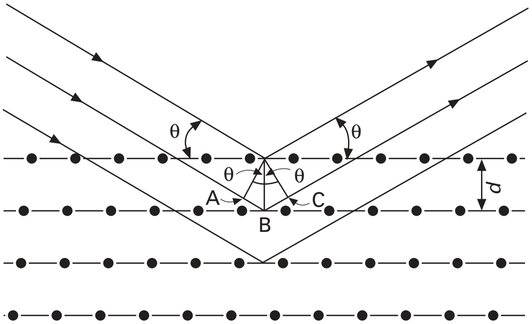
[1] A detailed plot of intensity variation over the central fringe will bring the limit down a little below λ. The limit of resolution of an optical microscope at its best is usually taken to be 0.6λ.

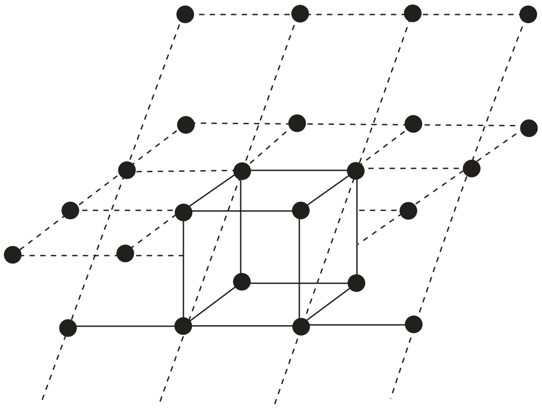
A crystal can be regarded as made up of layers of atoms, themselves regular in their two-dimensional plan, stacked regularly on top of one another[2]. Although analysis of the diffraction from such a three-dimensional lattice is more complicated than for a simple grating, it does result in a very similar equation; for it can be shown that, if a beam of X-rays is directed at a crystal, it is strongly reflected whenever it strikes layers of atoms at an angle θ, shown in Fig. 1.8, such that:

$$n\lambda = 2d \sin \theta \qquad (1.2)$$

where n is an integer, λ the wavelength of the X-rays and d the distance between the atomic layers. Under these conditions, the reflections from the individual layers reinforce one another: at other angles, they interfere with one another. Since, as is illustrated in Fig. 1.9, one can find many layers of atoms of varying density in



1.8 Reflection of X-rays from a crystal lattice. Retardation of rays reflected from successive layers = AB + BC = 2d sin θ.



1.9 Planes of atoms in a cubic crystal.

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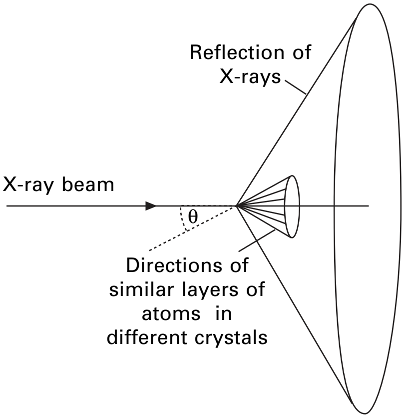
[2] The concept of atomic layers must not be interpreted too literally. Except in special cases, it does not mean that there are sheets of matter separated by spaces: it is merely a means of describing a repetitive structure, in which the atoms will be fairly uniformly distributed in three-dimensional space.

different directions, there will be a series of characteristic angles of incidence (relative to the crystal axes) at which strong reflections will be obtained. From these angles and from the variation in intensity of the reflections, the general crystal structure can be worked out, and particular atoms can be identified in position. The details of the diffraction pattern will be influenced by the whole form of the atomic arrangement in three dimensions; and there are a variety of methods available to help in the difficult problem of deducing the crystal lattice structure from the diffraction pattern.

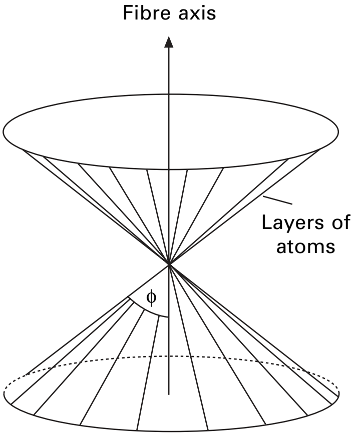
In fibres, however, we are not dealing with single crystals: we have a mass of small crystallites. These will usually be oriented parallel to the fibre axis, but it is simpler to consider first the diffraction pattern that is found when there is no preferred orientation. This is what we get if we pass an X-ray beam through powdered crystals and is called a powder photograph.

The condition that a particular reflection should occur is that the layer of atoms should make the required angle with the X-ray beam. This will happen for a series of orientations of the crystals distributed around a cone. The X-rays will be reflected around a cone of twice this angle, as shown in Fig. 1.10. Furthermore, since all orientations of the crystals are present, all the other reflections will occur, with the appropriate layers of atoms distributed round cones giving the characteristic angles of incidence. The powder photograph is given by the intersection of a photographic plate with these cones and will be a series of circles, subtending angles determined by the distances between layers of atoms in the structure. An example is the X-ray diffraction photograph of *Ardil*, a regenerated protein fibre of a type no longer produced (shown later in Figure 1.13(a)).

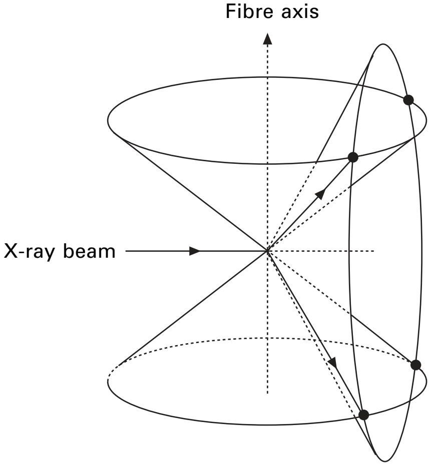
If there is a preferred orientation of the crystals, then the pattern is different. We may suppose that all the crystals are lined up with one of the crystal axes parallel to the fibre axis. Now, layers of atoms giving rise to a particular reflection will make a constant angle, ϕ, with this crystal axis, but, if there is no preferred orientation perpendicular to the fibre axis, the layers can occur at a series of positions distributed around the fibre axis on a cone, as shown in Fig. 1.11. If an X-ray beam is directed



1.10 Reflection of X-rays from powdered crystals. Atomic layers giving a characteristic reflection angle are distributed around a cone.



1.11 Distribution of a particular layer of atoms at angles on a cone round the fibre axis.



1.12 Intersection of the two cones, giving fibre diagram of four spots.

at right angles to the fibre axis, the reflections will now occur, not round a whole cone, but only at those four angles at which the cone of Fig. 1.10 (defining the characteristic angles of reflection) intersects with the cone of Fig. 1.11 (defining the angles at which the particular layers of atoms occur). This is illustrated in Fig. 1.12. The restriction on the angles at which the crystals lie has reduced the X-ray diffraction pattern from the full circles of the powder photograph to the sets of four spots occurring symmetrically in each of the four quadrants of the fibre photograph. Each of the layers of atoms will contribute different sets of four spots, and these will be repeated at different spacings for different values of n in equation (1.2). There are two special cases: if $\phi = \pi/2$, then the cone of Fig. 1.11 becomes a plane cutting the other cone in only two places, and the reflections occur as two spots on the equator of the photograph; and, if $\phi = (\pi/2 - \theta)$, the two cones just touch, and the four spots coalesce into two, this time at the poles. If $\phi < (\pi/2 - \theta)$, no reflections occur.

Although they were made around 50 years ago, the various X-ray diffraction patterns found in fibres are well illustrated in Fig. 1.13 by a set of comparative pictures. Figure 1.13 (n) is an example of a pattern of a completely crystalline, completely oriented fibre, namely, asbestos. The symmetrical pattern of sharp spots is clearly apparent. The other patterns in Fig. 1.13 are much less sharp, but the way in which they deviate from the idealised pattern yields extremely valuable information about fibre structure. For example, if the orientation is not completely perfect, one can get reflections over a range of angles, and the spots broaden out into arcs. The transition from a fibre with no preferred orientation of the crystals, through a moderately oriented fibre, to a highly oriented one is shown in Figs 1.13(a), (b) and (c) for a regenerated-protein fibre, wool and silk, respectively.

The X-ray diffraction photographs of fibres may be used for various purposes. Since the patterns for each type of fibre are different, as illustrated in Fig. 1.13, they may be used for identification, but their main use is to give information about fibre structure. If the position of a large enough number of spots is known with sufficient accuracy, then the exact crystal structure in which the molecules are packed can be worked out, and this has been done for several fibres. Even when there is not sufficient information to do this, one can deduce much that is useful. If the patterns are different, then the crystal structure must be different. For example, there is a slight difference in the spacing of the spots in Figs 1.13(d) and (e) for hemp and Fortisan[3], respectively. This shows up the difference in the crystal structures of native and regenerated celluloses.

The broadening of the spots into arcs shows a decrease in the degree of orientation. This is illustrated in Figs 1.13(e), (f), and (g) for Fortisan, high-tenacity viscose rayon and ordinary viscose rayon. The arcs in these photographs gradually diminish in intensity as the distance from the middle of the arc increases. But, in the photograph for cotton (Fig. 1.13(h)), the arcs end sharply: this is due to the fact that the crystals are arranged on spirals round the fibre axis, so the range of orientations relative to the fibre axis is sharply defined. From the angles subtended by the arcs, one can calculate the spiral angle in the fibre.

Mercerised cotton (Fig. 1.13(i)) is interesting because it shows a double pattern with the spacings characteristic of both natural and regenerated cellulose. Similarly, in delustred viscose rayon (Fig. 1.13(j)), there is a faint ring outside the main pattern, which is due to reflection from the titanium dioxide present. Another circumstance in which a double pattern is obtained occurs with almost all fibres; this is the superposition on the characteristic crystal-diffraction pattern of a diffuse background due to scattering from non-crystalline regions of the fibre. From a study of the relative intensities of the two effects, estimates of the degree of crystallinity can be made.

Broadening of the spots into arcs is characteristic of poor orientation, but a broadening along a radius of the pattern is characteristic of crystallites that are either very small or very imperfect, so that the characteristic angle of reflection from a layer of atoms

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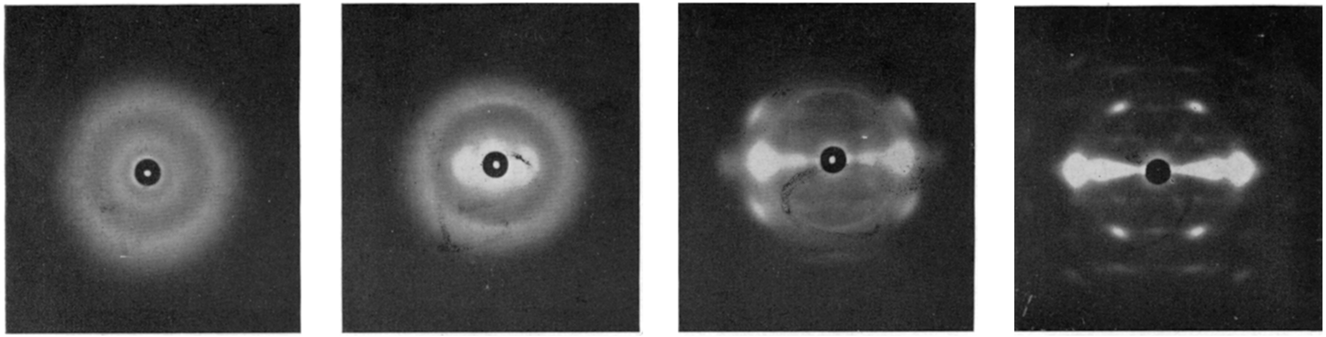
[3] Fortisan, which is no longer produced, was a highly oriented cellulose fibre, produced by regeneration from cellulose acetate.

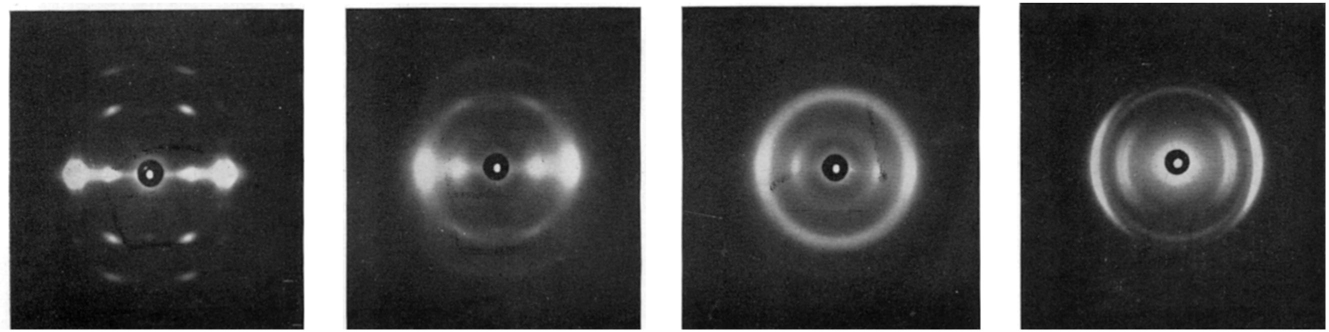


(a) Regenerated protein fibre (*Ardil*)

(b) Wool

(c) Silk

(d) Hemp



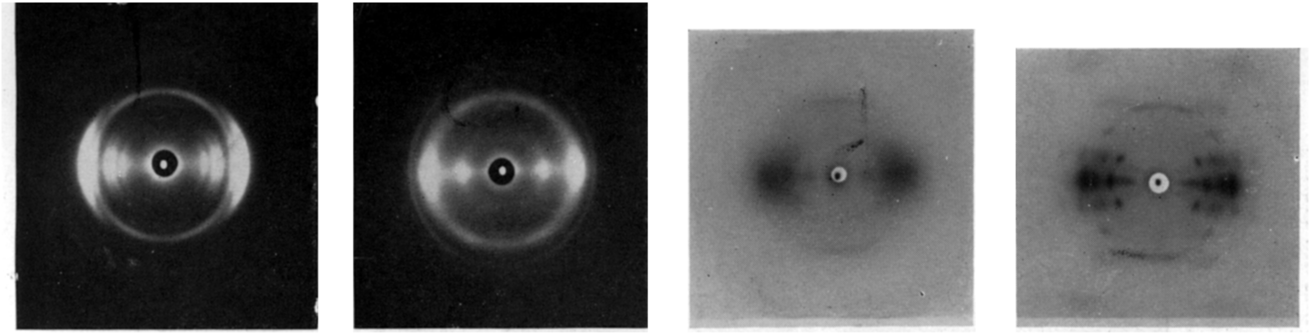
(e) *Fortisan* (regenerated cellulose)

(f) High-tenacity viscose rayon

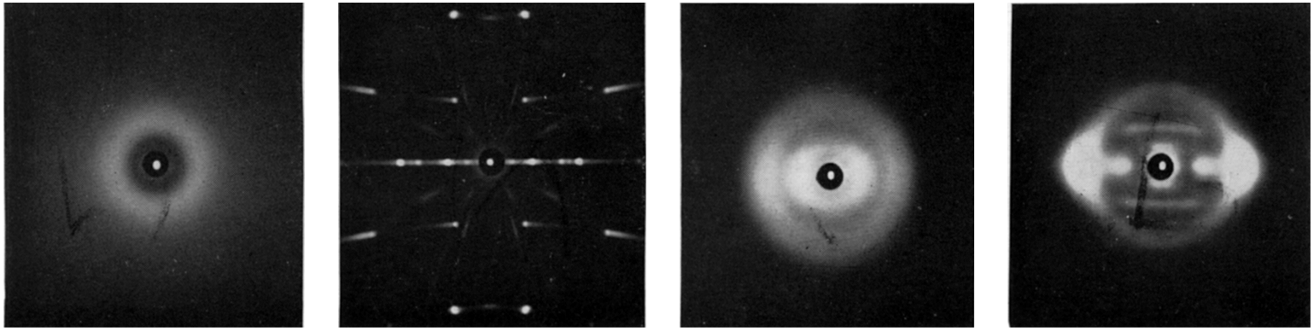
(g) Standard viscose rayon

(h) Cotton

1.13 X-ray-diffraction photographs of fibres (photographs by J. A. Howsmon, American Viscose Corporation).

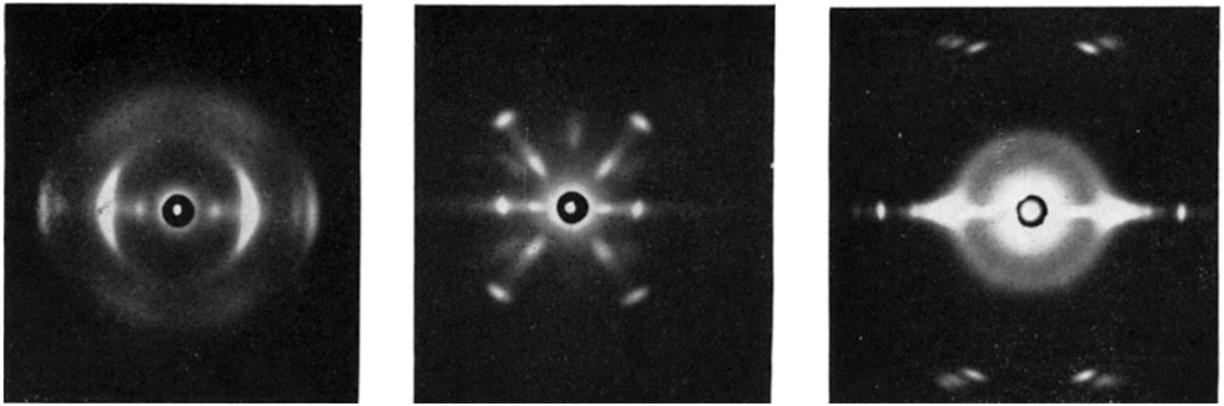


(i) Mercerised cotton (j) Dull viscose rayon (k) Unannealed Dacron polyester fibre (l) Annealed Dacron polyester fibre



(m) Glass fibre (n) Asbestos (o) Acetate (p) Nylon

1.13 (Continued)



(q) *Orlon* acrylic fibre (r) *Saran* copolymer fibre (s) Polyethylene

1.13 (Continued)

is less sharply defined. An example is the X-ray diffraction pattern of unannealed polyester fibre (Fig. 1.13(k)): after annealing, the spots are sharper (Fig. 1.13(l)). We may similarly compare the photographs for two mineral fibres, glass and asbestos (Figs 1.13(m) and (n)); the first is a single halo, characteristic of a completely amorphous material, and the second contains a large number of sharp spots, characteristic of a highly crystalline material.

The reflections giving the patterns discussed above occur at angles up to about 10°, but one can obtain other useful information from the reflections that occur at very small angles, close to the X-ray beam. It follows from equation (1.2) that, since $\sin\theta$ will be nearly zero, these must be due to the occurrence of much larger values of d. Studies have been made with θ as small as 10 seconds, corresponding to $d = 2000$ nm. In a few special materials, such as porcupine quills, sharp reflections have been obtained, indicating the presence of some repeat in the structure at a large spacing, but usually a diffuse halo is found. This is due to the scattering of X-rays by small crystallites in the fibre. A detailed study of these narrow-angle photographs can therefore lead to information about the size, shape and arrangement of the crystallites.

1.2.4 Electron microscopy and related techniques

Electrons, although usually regarded as particles, can act as if they were waves with a wavelength of the order of 0.005 nm. They can be focused by bending their paths in electric and magnetic fields in the same way that light rays are bent by lenses. Electron microscopes can form an image with a limit of resolution that is far smaller than is possible with an optical microscope. A limitation is that the specimens must be in a vacuum.

Obtaining sufficient contrast is one of the many technical difficulties in electron microscopy, and fibres are not the easiest specimens to deal with. The specimens used in ordinary transmission electron microscopy must be very thin (less than 0.1 μm thick), both to allow the passage of electrons and to avoid confusion arising from the great depth of focus. With some difficulty, it is possible to cut fibre sections of this thickness in order to make direct observations of the internal fine structure. Staining with heavy-metal compounds may be used to enhance contrast. A danger in this work is that some of the features that are observed may be caused by the section-cutting itself.

A great deal of useful information has come from the study of replicas, either of a cut face of the fibre or of the fibre surface, made in some suitable material. The contrast is often emphasised by a technique that consists of depositing heavy-metal atoms on the specimen from a given angle to give the appearance of shadows. Internal detail may also be shown by peeling a layer off the fibre to expose a new internal surface for replication. Another technique that may be used is to examine the fragments that are left behind after mechanical or chemical degradation of fibres. The polymers of which fibres are composed may also be examined as thin films.

As well as focusing an image, the electron-diffraction pattern of crystal lattices can be obtained. In general, this gives much the same sort of information about orientation and crystallinity as comes from X-ray diffraction, but with the advantage that it can be obtained from a particular area of an electron microscope picture, rather than from the whole of a bulky specimen. In dark-field electron microscopy, an image is formed from a particular selected band of diffracted electrons. This technique can therefore be used to show up the presence of crystalline regions, which will diffract in the selected direction and appear light against a dark background (or the reverse in negative contrast).

As an alternative to the method of viewing thin specimens in transmission, it is possible to form an image from electrons reflected from a surface. However, this cannot be done very effectively in a conventional, direct electron microscope, although some interesting studies of surface damage were made in the 1950s. A much better method for examining surface detail is *scanning electron microscopy* (SEM). The principle of this method is that a fine spot of electrons is traversed across the specimen and some response is used to form an image on what is, essentially, a television screen scanned synchronously with the spot. In the usual mode of operation, where the scattered electrons picked up by a collector are used to generate the image, the picture looks like an ordinary enlarged image of the specimen as viewed along the column followed by the electrons forming the spot. There are other modes of use that give further information. The main use of scanning electron microscopy in fibre science has been in the range of medium to high magnification, which is near or beyond the limit of the optical microscope. The scanning electron microscope has the great advantage of a much larger depth of focus.

The early applications of electron microscopy to fibres are discussed by Chapman [13], Hearle and Greer [2], Hearle and Simmens [14] and Hearle *et al.* [15]. Since then there have been important advances in techniques. Some of these come from the general developments in electronics, digital processing and information technology. Spot sizes have been reduced in scanning electron microscopy and scanning has been applied to the transmission mode. Resolution has been improved, so that, in appropriate samples, individual atoms in a crystal can be seen. Increased sensitivity reduces exposure times and limits radiation damage.

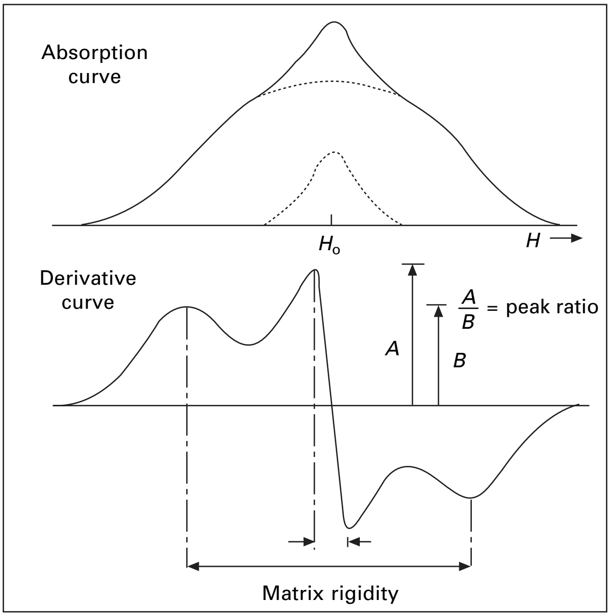
An order of magnitude increase in voltage has enabled high-voltage electron microscopes to be used with thicker specimens. Bryson *et al.* [16] have used tomography to make a quantitative determination of the twist angles in the helical assembly of the intermediate filaments (microfibrils) in the macrofibrils of the ortho-cortex of wool, as shown later in Figs 1.45 and 1.46. If a specimen is observed at a series of tilt positions, a three-dimensional tomograhic reconstruction can be produced. Computer graphics then enables this to be viewed at any angle and measurements to be made.

Scanning allows images to be formed from other signals. Atomic force microscopy is a useful way of examining fibres. In its simplest form, a probe with a minute tip mounted on a cantilever arm rests on the surface of the specimen. As it moves across the surface, the tip rises and falls and the deflection of the cantilever is a measure of force. This can be viewed as a line showing the surface profile or scanning over an area and conversion of the response to a grey scale gives an image of the surface topography. Atomic force microscopy can be used in other modes. For example the tapping mode gives a measure of the stiffness of the material. This can be used to show differences in elastic modulus in different parts of a fibre cross-section [17]. An example of the use of the atomic force microscope is a study of the morphology, nano-mechanical properties and effects of moisture absorption in cotton by Maxwell *et al.* [18].

1.2.5 Nuclear magnetic resonance (NMR)

The nuclei of many atoms possess a magnetic moment. As a result, the nucleus can be caused to resonate if it is put into an appropriate alternating magnetic field. Typical values would be a field of 1.5 tesla oscillating at 60 MHz. Structural information comes from the influence of the fields of neighbouring atoms on the resonance. When the atoms can resonate independently, as in a liquid, they all do so at the same frequency, though high resolution shows that there is really a set of separate finely spaced frequencies, which give information on the structure of the molecules themselves. In a solid, however, the rigidity of the system causes a strong interaction between neighbouring molecules, and this results in a broadening of the frequency response. This effect will be greatest in a crystalline region and less in a non-crystalline region.

As usual in resonance phenomena, the energy absorbed can be caused to vary in two ways: in this system, either by scanning through a range of frequencies, with a maximum at the resonant frequency, or by running through a change of magnetic field at constant frequency. The latter procedure is usually adopted, and a typical response for a solid polymer is shown in Fig. 1.14. Differentiation of the curve aids interpretation. The ratio of the intensity of the broad band to the intensity of the narrow band gives a measure of the crystalline/non-crystalline ratio in the material.



1.14 Nuclear magnetic resonance curve for a solid polymer. From Statton [19].

What is even more interesting is the fact that the width of the broad band gives a measure of the rigidity of the more highly ordered material. Statton [19] has shown that this decreases with temperature owing to the increasing thermal oscillation in the crystal lattice, but it is also interesting that it increases on drawing nylon and increases still more on hot stretching.

Statton, as indicated in Fig. 1.14, terms the parameter derived from the broadband width the *matrix rigidity*, since the width depends on how firmly the resonating atom is held within the surrounding matrix of highly ordered material. In a perfect crystal, the width would be great; in a small or defective crystal, it would be less. In a similar way, the width of the narrow band could indicate how firmly individual atoms are held within their matrix of less ordered regions.

1.3 Approaches to polymer fibre structure

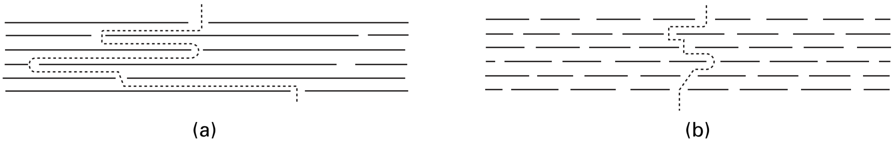
1.3.1 Requirements for fibre formation from linear polymers

An essential requirement in fibre structure is some means of ensuring continuity, and strength, along the length of the fibre. Because of the fineness of fibres, transverse strength is of much less importance. In the linear polymer fibres, it is the long-chain molecules that provide this continuity. In considering what type of molecular arrangement of linear macromolecules will be necessary in a fibre-forming structure, we can be helped by considering the larger-scale problem of how a textile yarn is made up.

A mass of raw cotton consists of a large number of long, fine fibres, arranged irregularly and tangled up, just like the molecules in rubber (Fig. 1.1(a)). In order to make this into a yarn, we must cause the fibres to line up more or less parallel to one another and then insert twist, which leads to lateral compression in the yarn and so causes frictional forces to hold the parallel fibres together. However, the twist must not bind the fibres together into a solid rod, which would destroy the flexibility and porosity required in the textile yarn.

From this, we can see by analogy that the basic requirements for fibre formation would be:

- long-chain molecules, corresponding to the long fibres that make up yarns: if the molecules or fibres are too short, there will be a loss of strength as illustrated in Fig. 1.15;
- a more or less parallel arrangement of the molecules;
- lateral forces to hold the molecules together and give cohesion to the structure;



1.15 Effect of length of fibres (or molecules) on strength: (a) long fibres showing a cohesion; (b) short fibres, showing possibility of easy breakage.

- some measure of freedom of molecular movement in order to give the necessary extensibility to the fibre and some openness to give room for moisture absorption and uptake of dyes.

It will be noted that twist is not included, since it is not a fundamental requirement but only a means of bringing lateral frictional forces into play in yarns.

In fibres, the lateral forces serve a second purpose, that of maintaining the oriented arrangements of the molecules. Without them, there would be a return to the disordered arrangement characteristic of rubbers.

1.3.2 Order and disorder in fibre structure

Fibres, as well as sheets or blocks of the same polymers, do not have the macroscopic form of crystals, but the X-ray diffraction patterns of most fibres show sharp spots in a four-point diagram, which is characteristic of an oriented crystal lattice, accompanied by an amorphous halo. This indicates that the fibres consist of *partially oriented*, *partially crystalline*, *linear polymers*. There is no problem in understanding partial orientation as a structure in which the chain molecules approach but do not fully achieve an alignment parallel to the fibre axis. However, there are many different ways in which crystallinity can be incomplete. The literature contains a great diversity of pictures. To some extent, these are interpretations that differ for different fibres. However, they are all two-dimensional or quasi-two-dimensional views of three-dimensional structures; few have a quantitative basis; and all reflect the ideas and graphical skills of the authors.

The diffraction evidence that the structure was a mixture of order and disorder was supported by values of density and moisture uptake and by other analytical techniques. However estimates of the relative amounts of order and disorder differ according to method used, as shown in Table 1.1. What is fairly consistent is that there is twice as much disorder in regenerated cellulose as in cotton. Another measure is accessibility

Table 1.1 Percentage of disordered material in various celluloses (approximate average values from published literature†)

Technique	Cotton	Wood pulp	Mercerised cotton	Regenerated cellulose
X-ray diffracton	27	40	49	65
Density	36	50	64	65
Deuteration	42	55	59	72
Moisture regain (sorption ratio)	42	49	62	77
Hailwood Horrobin	33	45	50	65
Non-freezing water	16	–	23	48
Acid hydrolysis	10	14	20	28
Alcoholysis	10	15	25	–
Periodate oxidation	8	8	10	20
Dinitrogen tetroxide oxidation	23–43	–	–	40–57
Formylation	21	31	35	63
Iodine sorption	13	27	32	52

†Values summarised by Jeffries *et al.* [20].

(Table 1.2), which indicates the availability of internal surfaces, volumes or —OH groups in cellulose. Again there is uncertainty because values differ according to the agent used (Table 1.3).

The dimensions of the crystalline regions, deduced from the diffraction data, are of the order of 10 nm, which is around 1000 times less than the length of the molecules. This suggested a *fringed-micelle* model of fibre structure. Figure 1.16(a) shows an early view of the structure after crystallisation from a melt . One can see how this sort of structure would arise if one considers a large pile of beads on strings arranged in a tangled mass. If the beads have hooks on them and several people start fastening them together, each person will build up a compact region of strings of beads fastened together in regular order. But, after a time, the actions of one person will begin to interfere with those of another: it will not be possible for some chains to be fastened

Table 1.2 Percentage accessibilities of celluloses measured by exchange of hydroxyl hydrogens for deuterium†

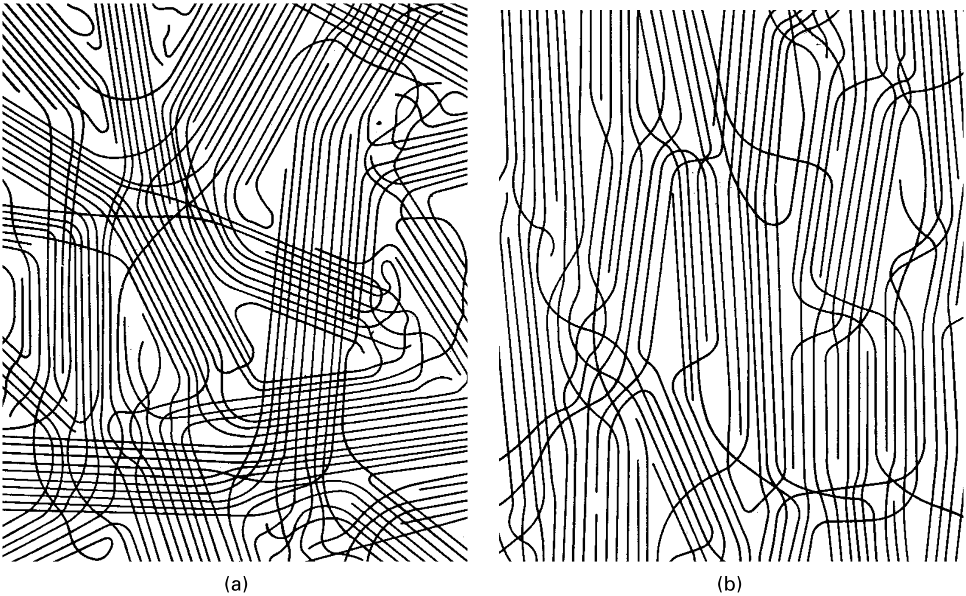
Celulose	Accessibility	Cellulose	Accessibility
Bleached cotton	44	Kenaf	49
Mercerised cotton	66	Flax	50
Finely ground cotton	87	Cotton linters	50
Sulphite pulp	57	Ramie	53
Mercerised sulphite pulp	70	Rayon	78
Jute	48	Potato starch‡	97
		Birch xylan‡	99

†From results of Skachkov and Sharkov [21] by a modified method of Sepal and Mason [22].
‡Soaked to the point of no more swelling in the H_2O–D_2O mixture. These highly accessible non-cellulosic polysaccharides are included for comparison.

Table 1.3 Accessibility and molecular weight

Measurement	Purified cotton (%)	Mercerised cotton (%)
Periodate oxidation: potential accessibility without crystal disruption†	40	–
Water ($D_2^{18}O$): some crystal penetration‡	48.8	63.9
Water (D_2O): readily accessible§	36.0–37.2	48.1
N,N-Diethylaziridinium chloride: readily accessible¶	19–21	32–33
Diphenyl Fast Red 5BL: readily accessible‖	2.5 (5.4 m^2/g††)	4.5 (9.9 m^2/g††)

† Rowland and Cousins [23].
‡ Guthrie and Heinzelman [24].
§ Rousselle and Nelson [25].
¶ Bose *et al.* [26].
‖ Johnson *et al.* [27].
†† Percentages calculated from an estimated 220 m^2/g of surface for completely accessible cellulose chains.

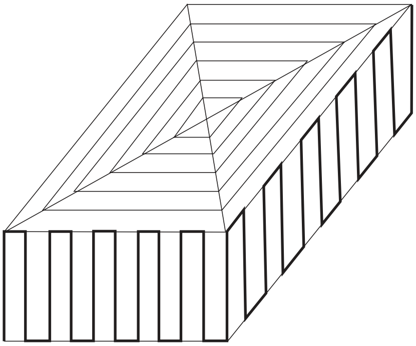


1.16 Fringed micelle structures: (a) in unoriented (undrawn) fibre; (b) in oriented (drawn) fibre. From Bunn [28].

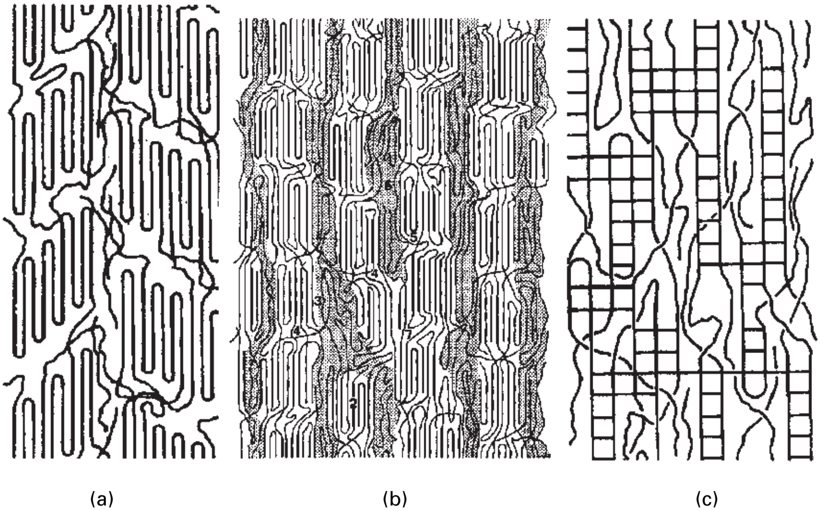
up any further because they are already fixed elsewhere. The hooking-together of the strings continues until finally there are several regions of beads fastened together, whereas between them the strings go off in various directions and can be fastened together only where two beads happen to pass close to one another. This is an exactly analogous arrangement to that shown in Fig. 1.16(a). There are the crystalline regions of regular order and the non-crystalline region, where the molecules can only be linked together in a few places. The process of formation is also analogous for, if an irregular mass of chain molecules is crystallising, crystallites will form at various places and continue to grow until they interfere with one another. The drawing process for melt-spun fibres would leads to orientation, as indicated in Fig. 1.16(b).

Figure 1.16 was proposed in the context of nylon and polyester fibres, but is now directly relevant only to stiffer molecules such as cellulose. Note that all the molecules fringe off at the edge of the crystallites to continue as tie-molecules to other crystallites. Chain folding occurs only in the amorphous regions between the crystallites. Academic studies of slow crystallisation in laboratory conditions showed other forms.

It was found that polymers, including those used in fibres, could be crystallised from dilute solution so as to give single crystals. In these lamellar crystals, the chain molecules are folded back and forth as illustrated schematically in Fig. 1.17. Similar folding may occur in fibres, and this has led to the suggestion of a modified fringed-micelle structure, in which there is a mixture of fringing and folding at the end of each micelle. Figure 1.18(a) illustrates this form of structure, but was drawn with angled ends to the crystallites in order to explain a feature of the crystal lattice of nylon 6.6 (see Fig. 1.47). Typically, Fig. 1.18(a) is too uniform a structure. There



1.17 Schematic illustration of chain-folding in a single crystal.



1.18 Views of fine structure of nylon fibres. (a) A common working model proposed by Hearle and Greer [29]. Angled ends are based on small angle X-ray diffraction pattern of nylon 66. (b) From Murthy *et al.* [30], based on X-ray diffraction studies of nylon 6. (c) An alternative form, from Hearle [31].

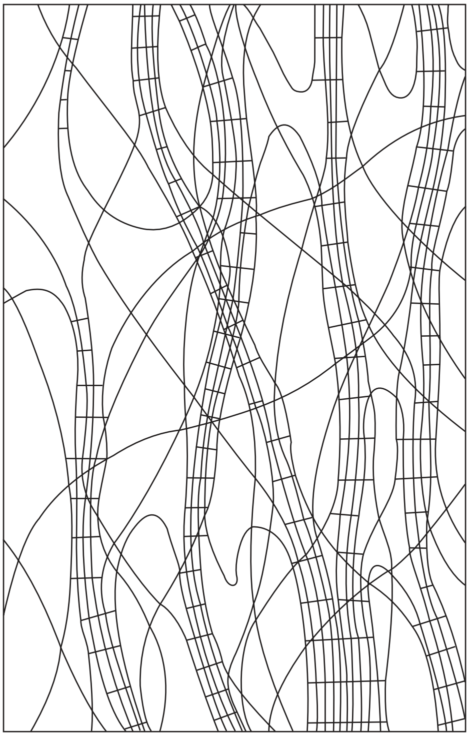
would be some variation in crystal size and packing as indicated in Fig. 1.18(b), which is based on X-ray diffraction studies of nylon 6 [30].

Two general points should be made. Firstly, because the structure consists of blocks within a matrix, a typical crystallinity of 50% requires that the spacing between crystallites averages one-third of the crystallite dimensions. Such tight packing is not compatible with a random placing of crystallites and leads to the quasi-fibrillar form shown in Fig. 1.18(a,b). The driving force to crystallisation will lead to the tie-molecules being somewhat extended and not random coils. Secondly, as discussed in Chapter 18, rapid quenching may lead to a more uniform structure as illustrated in Fig. 1.18(c) [31]. Large crystals have a lower internal energy than small crystals, so that annealing tends to give a growth in crystal size. For polymers, in contrast to metals, where defects can move and eliminate boundaries between crystals, this requires the small crystals to melt and reform as new larger crystals. This major change is not possible when the crystals have grown to a certain size. Consequently. the crystal size, which depends on processing conditions, is limited to a maximum of about 10 nm.

Bulk crystallisation of polymers from the melt or from more concentrated solution leads to a spherulitic structure. Such a structure starts from crystallisation as folded-chain lamellae on separate nuclei; the crystals then grow with successive branching, until the spherical region is established. Ultimately, the separately growing spherulites meet. Fringed-micelle structures are the limiting form of spherulitic crystallisation when the number of nuclei becomes so large that they are very close together and there is no room for the spherulitic branching to develop. This is typical in fibre production, with rapid solidification, but there are circumstances in which occluded spherulites occur in nylon fibres. After drawing, they become ellipsoids.

With stiffer molecules, fibrillar textures are observed in electron microscopy. For low crystallinity fibres, as in cellulose, Hearle [32, 33] proposed a fringed-fibril structure, as-illustrated in Fig. 1.19. This combines (a) a fibrillar form and (b) the ideas inherent in the fringed-micelle structure of distinct crystalline and non-crystalline regions with chain molecules running continuously through each type of region. The highly crystalline high-performance fibres have a more tightly packed fibrillar structure.

Polymers such as polyethylene have been found to crystallise in lamellar forms linked by tie-molecules.



1.19 Fringed-fibril structure.

In natural fibres, genetic control leads to the lay-down of specific fibrillar forms. As discussed later, cotton may be completely crystalline, with disorder coming from imperfect register between fibrils, and wool contains fibrils separated by a chemically different matrix.

A more radical difference in views of fibre structure results from a questioning of the concept of well-defined crystalline and non-crystalline regions. Even in 1930, there had been those who regarded the structure as uniformly partly ordered. This view was revived by Kargin [34], who suggested an amorphous structure with some correlation between the positions of neighbouring chains. Hosemann [35, 36], on the other hand, suggested a paracrystalline structure in which the lattice parameters are subject to a more-or-less random disturbance. This leaves the crystal lattice locally somewhat distorted, and certainly without any long-range order.

Others have taken over ideas from metal physics and suggested that the disorder is due to crystal defects (vacancies, folds, chain ends, extra units, crossing of and twisting chains, and so on) at particular points within the crystal. These last two models substitute internal imperfections in the crystallites as a source of disorder instead of separate non-crystalline regions. Reneker and Mazur [37] have proposed explicit models for defects in polyethylene. An additional —CH_2— group or a switch between neighbouring chains would be local disturbances within a continuous distorted crystal lattice. However the molecules in most textile fibres have much longer repeats (38 atoms in 14 goups in nylon 66), so that an additional repeat unit could not be incorporated without destroying the crystal.

The above comments briefly describe the diverse forms of polymer crystallisation. The experimental evidence on disorder could also be explained by the size of crystalline regions. Small crystals imperfectly packed together would give a poor X-ray diffraction pattern, a lower density and accessibility to the surfaces of the crystallites or crystalline fibrils. It is now recognised that because different fibres are made of different polymers and are produced in different ways, there may be major structural differences, and one should not look for a single form of structure. In particular, there will be differences between natural fibres, which grow very slowly as living cells or are slowly extruded as silks, and manufactured fibres, formed by high-speed extrusion and drawing.

1.3.3 A general view

A more general approach to the problem can be made by considering what parameters are needed to give a reasonable specification of fibre structure. Because the structure is intermediate between one that can be specified by a unit cell and one that can be specified by statistical parameters, a complete description would need the position of almost all the atoms to be individually stated, namely, around 10^{16} parameters per fibre. This is obviously impossible. Fortunately, we can select a limited number of parameters, which characterise the most important features. The list proposed by Hearle and coworkers [2, 38–40] is:

- degree of order;
- degree of localisation of order;
- length/width ratio of localised units;

- degree of orientation;
- size of localised units;
- molecular extent.

The first three can be taken together in a triaxial plot, as shown in Fig. 1.20(a), and the other three then regarded as applying to any structure defined by the first three. The various forms of structure already discussed are indicated by their positions on the plot. In Fig. 1.20(b), the likely positions of various fibres are marked.

Degree of order would be theoretically defined as the mean value of some correlation function relating the position of neighbouring chains. Practically, it could be defined in terms of density by the expression:

$$\text{degree of order} = \frac{\rho - \rho_{\text{am}}}{\rho_{\text{cr}} - \rho_{\text{am}}} \tag{1.3}$$

where ρ is the fibre density, ρ_{am} the density of amorphous (non-crystalline) material and ρ_{cr} the density of crystalline material.

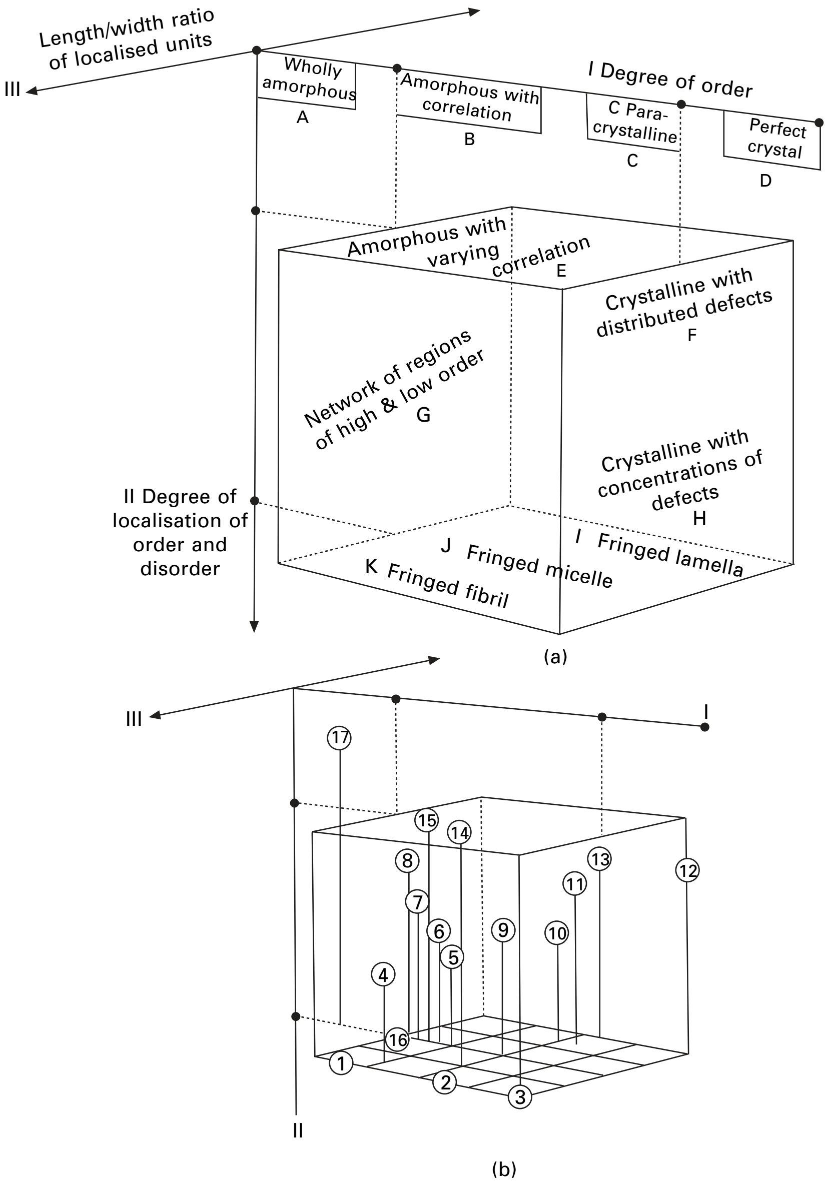
The values of degree of order would range from zero for a completely amorphous fibre to unity for a perfectly crystalline fibre. The experimental methods of density determination will be discussed in Chapter 5. Alternatively, estimates of degree of order could be obtained by other methods, such as X-ray diffraction, accessibility, infrared absorption or NMR studies.

Figure 1.21 illustrates a range of degrees of order. In a continuous structure, the whole material would be of the same degree. However, a given average value, say 50%, could correspond to many other different combinations, as indicated by the three distributions of local degree of order shown in Fig. 1.22.

Degree of localisation of order would be theoretically defined by some measure of the spread of values of degree of order taken over zones a few molecules wide. The uniform distribution A in Fig. 1.22, would have a low value, B would be larger, and C would have the largest value, since it represents a split into separate ordered and disordered regions. Experimentally, values of the degree of localisation of order must be estimated from indirect evidence, such as electron microscope views of the fine structure.

The *length/width ratio* of the units is a more straightforward parameter, ranging from infinity for very long fibrils down to unity for cubic micelles and to zero (or minus infinity on a logarithmic scale) for extensive flat sheets. It is tacitly assumed here that the 'length' refers to the direction of the chain axis. In lamellar crystals, the ratio would be more commonly regarded as thickness/width.

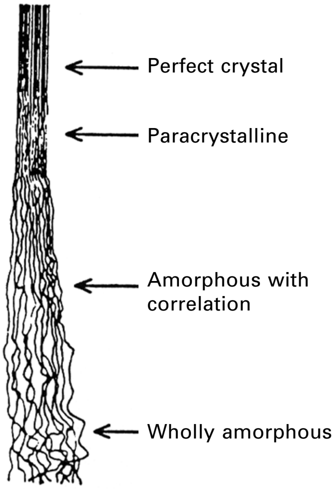
An important point to stress is that all the parameters can vary continuously and there are no sharp boundaries between the various forms of structure indicated in Fig. 1.20(a). One form merges into another. At some point, the disorder in a paracrystalline structure becomes too great to pick out the regular lattice and the structure is better regarded as amorphous with correlation. As correlation varies from place to place, it may become distinct enough to discern separate regions of high and low order, which will eventually be so distinct that they are to be regarded as crystalline and amorphous. The uniform disorder of the paracrystal can be replaced by distributed point defects; and then, if these defects come together, they may eventually be so large that they are



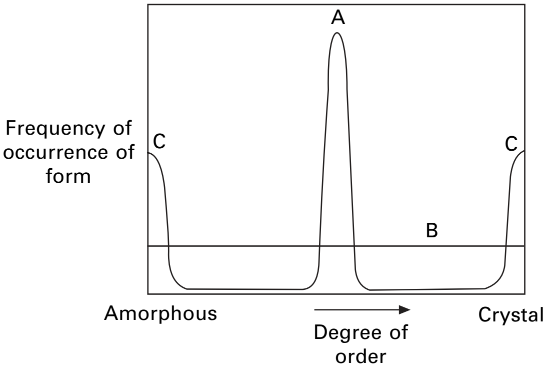
(a)

(b)

1.20 (a) Schematic representation of fibre structure in terms of three major variables. (b) Possible location of various materials on the plot: (1) wool and other hair fibres; (2) silk; (3) cotton and other plant fibres; (4) model rayon and lyocell; (5) ordinary rayon; (6) triacetate; (7) secondary acetate; (8) regenerated-protein fibres; (9) polyester fibre; (10) polyamide fibre; (11) polypropylene fibre; (12) linear polyethylene fibre; (13) branched polyethylene fibre; (14) acrylic fibre; (15) polyvinyl chloride fibre; (16) spandex fibre; (17) rubber, atactic polystyrene. From Hearle [38]. The newer high-modulus fibres would be further out along the line ①-②-③.



1.21 Range of degrees of order of packing of chain molecules, as drawn by Howsmon and Sisson [41], with identification of forms by Hearle [38].



1.22 Three of many possible distributions of degree of order in a 50% crystalline fibre: A, uniform intermediate order; B, all degrees of order equally represented in different regions; C, mixture of highly ordered and highly disordered regions. From Hearle and Greer [2].

better regarded as amorphous regions. As fibrils become shorter, they are eventually better regarded as elongated micelles; and then flattened micelles merge into small lamellae.

The two parameters, *degree of orientation*, defined theoretically by a mean angle between the chain molecules and the fibre axis, and *size of localised units*, indicating the difference between a coarse and a fine texture, do not give rise to any basic conceptual difficulties of definition and experimental estimates can be made.

Molecular extent is more difficult. Direct measurement is not possible and it is not included in drawings of structure, except for simple examples such as Fig. 1.15. As shown by an analogous example at a larger scale, it has a major effect on strength. The strength of a textile yarn depends not only on fibre length but also on the extent to which the fibre is folded back on itself. Drafting is used to remove folds. In highly folded forms, as shown in Fig. 1.23, molecular extent approximates to fold length. With few folds, fibre length is more important.

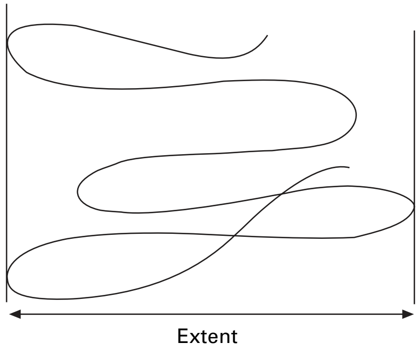
In addition to the six listed, there are other aspects of fine structure that could be specified and that may be important in some circumstances. There are other features of the shape of localised units. Fibrils may be cylindrical or ribbon-like. There are fine details of packing, such as the relative extent of fringing and folding. There are the details of interconnection between crystalline regions. There may be distributions of values of the length/width ratio, degree of orientation and size of localised units parameters; and so on. However, with adequate means of theoretical analysis, it becomes possible to predict many fibre properties from a knowledge of the chemistry of the chain molecule, of the six parameters of fine structure, and of any special larger-scale structural features.

1.3.4 Order, orientation and extent

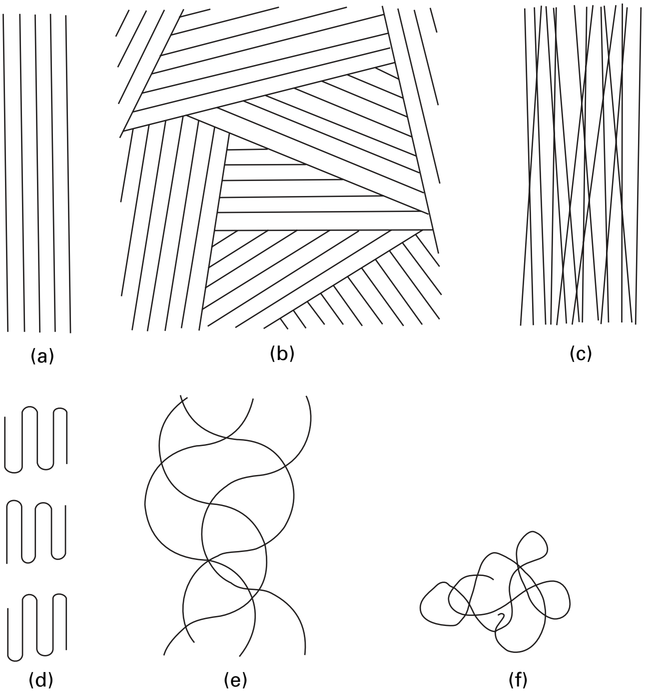
Degree of order, degree of orientation and molecular extent are often confused. This is because, at the extremes, they do come together as high or low values (Fig. 1.24(a), (f)). A perfectly ordered structure must be perfectly oriented with fully extended chains, and a completely disordered structure must be completely disoriented with short fold lengths. But these are not practical cases. In intermediate situations the three parameters are unrelated. Figure 1.24(b–e) illustrates this. A very highly ordered structure may be completely disoriented because it is composed of separate crystals pointing in all directions. A very low degree of order can occur owing to chain entanglement and lack of register with very little angular deviation from perfect orientation. A highly oriented structure may have short chain folds. A sequence of semicircular folds can give high extent and zero orientation. Other conflicting combinations can be found.

1.3.5 Limiting values of parameters

In ordinary substances composed of small molecules, it is possible to work disorder out of the system. If faults come to the edge of the crystal, they disappear. A large



1.23 Extent of a long chain in a structure.



1.24 (a) Maximum order, orientation and extent. (b) Higher order, zero orientation. (c) Low order, high orientation. (d) High orientation, low extent. (e) Zero orientation, high extent. (f) Minimum order, orientation and extent.

crystal grain can grow by rearrangement of atoms near its boundary until it eliminates a smaller grain. This is not possible in polymer systems, since, if one crystallite is caused to grow, then the connections along the polymer chains cause a disturbance elsewhere. It is easy to imagine this if one thinks of packing a tangle of string into aligned regions corresponding to crystals. Once the initial stage of ordering is over, an improvement in one place can only come with an upset somewhere else.

As a result, once fibres have crystallised with a given degree of order, it is very difficult to make more than marginal improvements (say, from 50 to 60%) in the degree of order by any treatment. On thermodynamic grounds, it is clear that there will be (below the melting point) a driving force towards increased order, which brings the structure closer to the ideal of a single crystal, and that this will continue until further progress is blocked by the complexity of molecular entanglement. Nevertheless, significant rearrangements, such as an increase in size of crystalline regions and of the space between them, or the pushing out of defects from inside a crystal into non-crystalline regions, or major mechanical deformation of the structure, can be made without much change in the overall degree of order.

With the polymers that are used for most fibres (although not necessarily with polyethylene), it also seems likely that there will be a driving force towards localisation of order. The reasons for this were discussed by Hearle and Greer [2]. The argument is that a uniform intermediate degree of order is not very favourable in either entropy

S or internal energy U. Given the above restriction that the average degree of order cannot increase, there would probably be a lowering of free energy ($U - TS$) by part of the material becoming more highly ordered, with much lower internal energy and not too large a decrease in entropy, and the other half becoming more disordered, with a large increase in entropy and with very little change in internal energy. Mechanistically, we can imagine crystalline regions growing and pushing the disorder out ahead to pile up in larger amorphous regions.

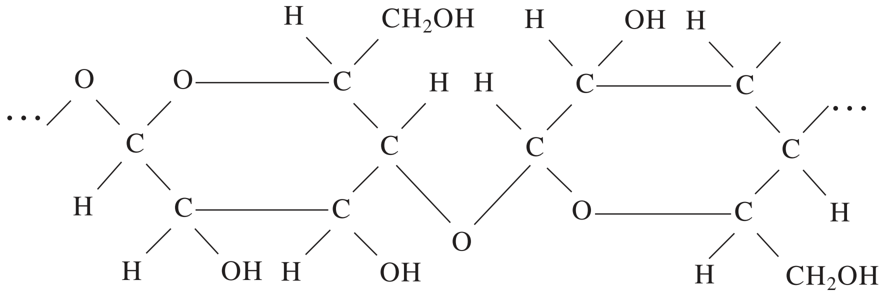
The requirements listed are satisfied in the common textile fibres. But, in specialised fibres, there are differences: for example, in the high-modulus inorganic fibres, continuity is achieved in other ways, and, in elastomeric fibres, orientation is not required.

1.4 Cellulose fibres

1.4.1 Cellulose

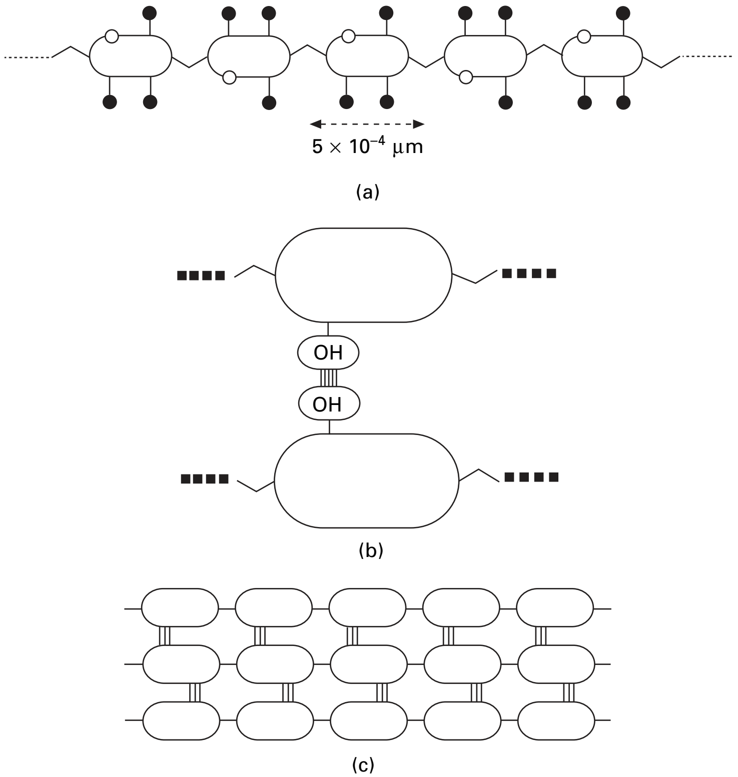
We now turn to individual fibre types and discuss their chemical constitution, fine structure and larger-scale morphology. Cellulose fibres, particularly cotton since it continues to account for a major share of the world's fibre usage, will be covered first.

The cellulose molecule consists of a series of glucose rings joined together, with the formula:



It is instructive to consider a simple schematic representation of its essential features. It is a long-chain molecule (Fig. 1.25(a)), made up of groups that are linked together by valency bonds. The strength of these bonds is such that, if the whole strength of the chain could be utilised, it would have a strength more than ten times as great as that of the strongest commercial cellulose fibre. The chain can be extended in length indefinitely. A minor feature that is worth noting is that the chain has direction, owing to the asymmetry of the atoms in the glucose rings. Protruding from the chain are —OH (hydroxyl) groups, which can link up with other hydroxyl groups by means of hydrogen bonds (see Section1.1.2). This results in the linking together of neighbouring chains as shown in Fig. 1.25(b). Water molecules can also be attached by the same sort of bond. The chains have a strong preference to assemble into crystals (Fig. 1.25(c)). In non-crystalline regions, hydrogen bonds will form within the disordered assembly of chain segments.

The cellulose molecule is ribbon-like in form. Although stiff in comparison with

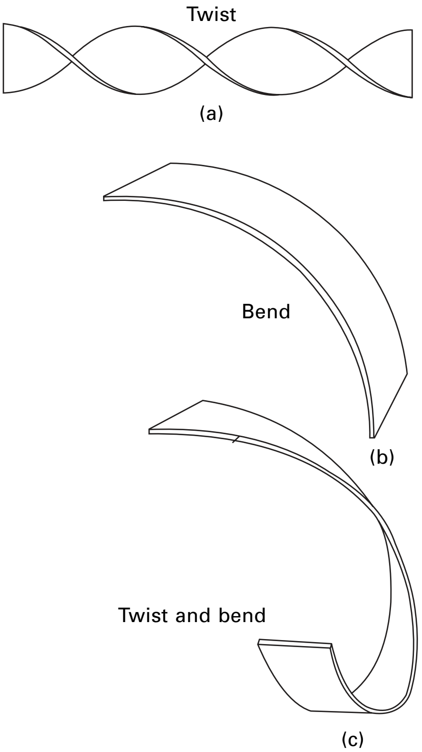


1.25 Essential features of the cellulose molecule: (a) the chain; (b) crosslinking by hydrogen bonds; (c) schematic representation of a crystal.

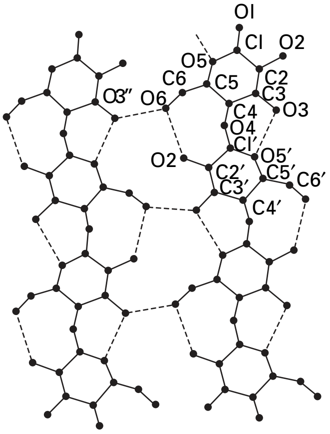
a molecule such as polyethylene, the ribbon does have considerable freedom to bend and twist in the way indicated in Fig. 1.26. As shown in Fig. 1.27, the hydrogen bonding is partly intramolecular and partly intermolecular. An important feature is that the bonding is only in one plane, which gives sheets of molecules only weakly linked between the sheets by van der Waals forces.

Because of the problems of dissolving cellulose, exact determination of the distribution of molecular weights is difficult [43]. In native cellulose fibres, the chains are estimated to contain about 10^4 glucose rings. The complete chain is, therefore, about 5 µm long by 8×10^{-4} µm wide. This ratio of length to width is about the same as that in a cotton fibre (3×10^4 µm long by 15 µm wide). In making a viscose solution for spinning into rayon, the chain length is considerably reduced. This demonstrates a general dilemma in manufactured fibre production. Increased chain length in the fibre would give better properties, but if the molecules are too long, extrusion into fibres is not possible.

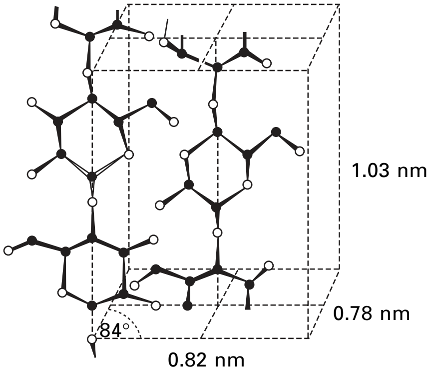
The crystal structure of native cellulose is known as cellulose I, but there is still some uncertainty about its exact form. A slightly modified version of the structure proposed by Meyer and Misch [44] is shown in Fig. 1.28 and gives the features needed to understand structure–property relations. Different studies give the following



1.26 Ways in which a ribbon-like molecule can be deformed by twisting and bending.



1.27 Hydrogen bonding between cellulose molecules. C1, O1, etc., are positions of carbon and oxygen atoms; hydrogen atoms complete the valencies; hydrogen bonds are shown by dotted lines. From French (42).



1.28 A schematic view of the crystal lattice of cellulose I, adapted from the drawing by Meyer and Misch [44], which has anti-parallel chains. Hydrogen bonded sheets are in the plane of the paper. The sheets in the middle of the cell are staggered with respect to those on the front and back faces.

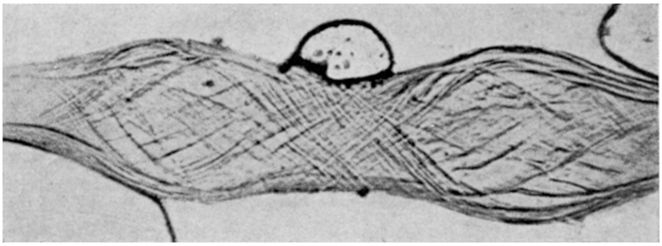
ranges for the cell dimensions [42]: *a*, 0.814–0.825; *b*, 0.778–0.786; *c*, 1.033–1.038 nm. When these fibres are mercerised, by treatment with strong caustic soda, a second X-ray diffraction pattern appears superimposed on the original one, replacing it as mercerisation becomes complete. This corresponds to a structure known as cellulose II. The *a* and *b* dimensions are close to those for cellulose I, but the *c* value is 0.914 nm and the angle between *b* and *c* is 62° compared with 84° for cellulose I. Regenerated-cellulose fibres also contain cellulose II. It is generally thought that cellulose I is a parallel structure with chains pointing in the same direction but cellulose II is anti-parallel. Other crystal forms are found after some treatments [42].

Mercerisation also results in a reduction in the proportion of crystalline material present in the fibres. In addition to mercerisation, which is a fairly old process, there are other forms of modification of cellulose fibres, particularly cotton, that are of commercial importance. Various chemical treatments replace the hydroxyl groups in the non-crystalline regions by other groups in order to modify such properties as electrical resistance, moisture absorption and rot resistance. However, the most important treatments are those that cause a resin to polymerise and react with the hydroxyl groups inside the cotton. This results in chemical crosslinks (sequences of covalent bonds) between the cellulose molecules. This stabilises the structure, gives it a set and, in fabric form, reduces the likelihood of creasing and wrinkling. Resin-treated crosslinked cottons of this type are now of great importance.

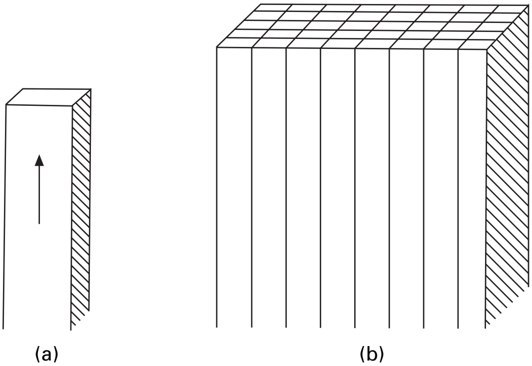
1.4.2 An integrated view of the fine structure of cotton

The evidence from many sources that cotton and other natural cellulose fibres are 'two-thirds crystalline, one-third non-crystalline' is somewhat misleading. One should really say that the X-ray-diffraction pattern (density, accessibility, etc.) is such that it is equivalent to that of a mixture of large crystalline regions and large amorphous regions in the ratio 2:1. Other interpretations are possible. Hearle [38] has pointed out that the X-ray diffraction results could be explained by the small size of the crystalline fibrils, the density by imperfect packing and the accessibility by the fibril surfaces. The current consensus is that natural cellulose fibres are essentially 100% crystalline and that the disorder is mainly due to the fact that very small crystalline units are imperfectly packed together. The amount of actual material in any region that is not part of a crystal lattice is probably small.

An important feature of natural cellulose is that it is aggregated into fine microfibrils. A coarse fibrillar structure was observed many years ago under the optical microscope, as shown in Fig. 1.29, and is rather clearly shown in SEM pictures, such as the fibre fracture shown in Fig. 19.14 on page 517. The examination of surface replicas or disintegrated material showed up the presence of the ultimate microfibrillar texture. The biological evidence is that, in growing cells, enzyme complexes join glucose molecules into long-chain cellulose molecules. These naturally form microfibrils with thicknesses of about 4 nm. All the molecules will point in the same direction in the parallel crystal lattice of cellulose I without chain folding. The fine structure is an assembly of fine microfibrils without amorphous regions as proposed by Manley [45]. The crystallisation is driven by minimisation of the free energy. Since the strongest attractions are at the edges of the molecules, as indicated in Fig. 1.30(a), the minimum energy form is likely to be a ribbon-like crystal of the type shown in Fig. 1.30(b). At this scale, the proposed units can be identified with the observed microfibrils.



1.29 Fibrillar structure of cotton, as shown by an optical microscope. Photograph by W. L. Balls.



1.30 (a) Schematic representation of single cellulose molecule. (b) Assembly in microfibril.

The fibrils themselves have many of the characteristics of molecules. They are relatively small in cross-section (less than an order of magnitude greater than a single molecule), they are relatively flexible, and they are attracted to one another strongly by the possibility of hydrogen bonding at the edges and more weakly by van der Waals forces between the faces. The fibrils can thus be expected to 'crystallise' into flat sheets or lamellae, which will then stack in parallel layers. There is evidence of long standing of coarse concentric lamellae observed in the optical microscope, and a lamellar association of fibrils on a finer scale is also found in electron microscope studies.

The model described above is one that commands confidence because it can be derived either from a theoretical consideration of how the system would be expected to behave or by deduction from experimental observations of real cellulose fibres. But the model is too simple and tidy. It omits the disorder that is known to be present.

As it stands, the whole assembly of molecules would be regarded as coalescing into one single crystal, in which the identity of the original fibrils was lost. Remembering that the crystal lattice has not been settled, one is tempted to speculate whether, as in some other systems, such as asbestos, there is some special feature of the cellulose crystal lattice that gives an identity to the fibrils. The problem has an analogy in the behaviour of yarns. If two zero-twist continuous filament yarns are brought together, they merge, and it becomes impossible to say to which yarn a given fibre belongs. However, if the individual yarns have some twist, they retain their separate identities.

Detailed experimental evidence on disorder comes from the electron diffraction studies of Ingram [46], which show that, whereas there is often crystallographic register between adjacent fibrils, this does break down in places, and also that, at intervals along the fibres, there are positions in which the crystal lattice is defective. It remains a matter of speculation whether these discontinuities are due to chance fluctuations in the system, to some structural feature such as is hinted at in the last paragraph, or to an occasional chemical discontinuity in the cellulose molecules.

There is one source of disturbance of the simple model that is clearer. The fibrils are laid down on the inner surface of cell walls in a helical orientation. Even in a single layer, this must give rise to some strain and possible splitting between fibrils. In some plant cells, the successive layers run in different directions, so that the register between layers would be lost. Even when a similar helical orientation persists through the thickness, as in the secondary wall of cotton, complete crystallographic register is impossible between successive layers, since each layer must contain fewer chains and fibrils as the circumference is reduced. Splitting between lamellae will be relatively easy.

Finally, but perhaps most important of all, the influence of water in leading to disorder must be considered. In the presence of water, the minimisation of free energy by crystallisation is always in competition with minimisation by forming hydrogen bonds by association with water, in other words by swelling, by the attempt to go into solution.

The formation of the fibre occurs in the wet state, and it is thus highly swollen. When drying does occur, the fibrils will associate, as already suggested, but, like any crystallisation of long-chain units, appreciable disorder might be introduced owing to some entanglement or mismatching of fibrils. Subject to these limitations, the material would be expected to collapse down to a somewhat disordered modification of the model already discussed, which, in its idealised form without any disorder, would be the presumed minimum energy state for dry natural cellulose.

What happens on re-exposure to water? Experimentally, it is known that there is a progressive increase in absorption as humidity increases and that in liquid water there is limited swelling but not solution of the material. One can suggest three reasons why the fibrillar network does not dissociate completely in water:

1. Once strain is relieved by some opening up of the structure, regions where fibrils are in crystallographic register with one another may remain as stable entities.
2. There may be that a dynamic equilibrium, in which there are always some fibrils associated together, although the actual groups are continually changing.
3. There may be some tie-molecules linking separate fibrils together.

At any ordinary relative humidity, the network would be partly opened up, whereas in water, where much chemical processing is done, the fibre would be much more highly swollen. Crosslinking reactions will serve to stabilise the structure by linking the fibrils together permanently: this gives rise to increased resistance to plastic deformation.

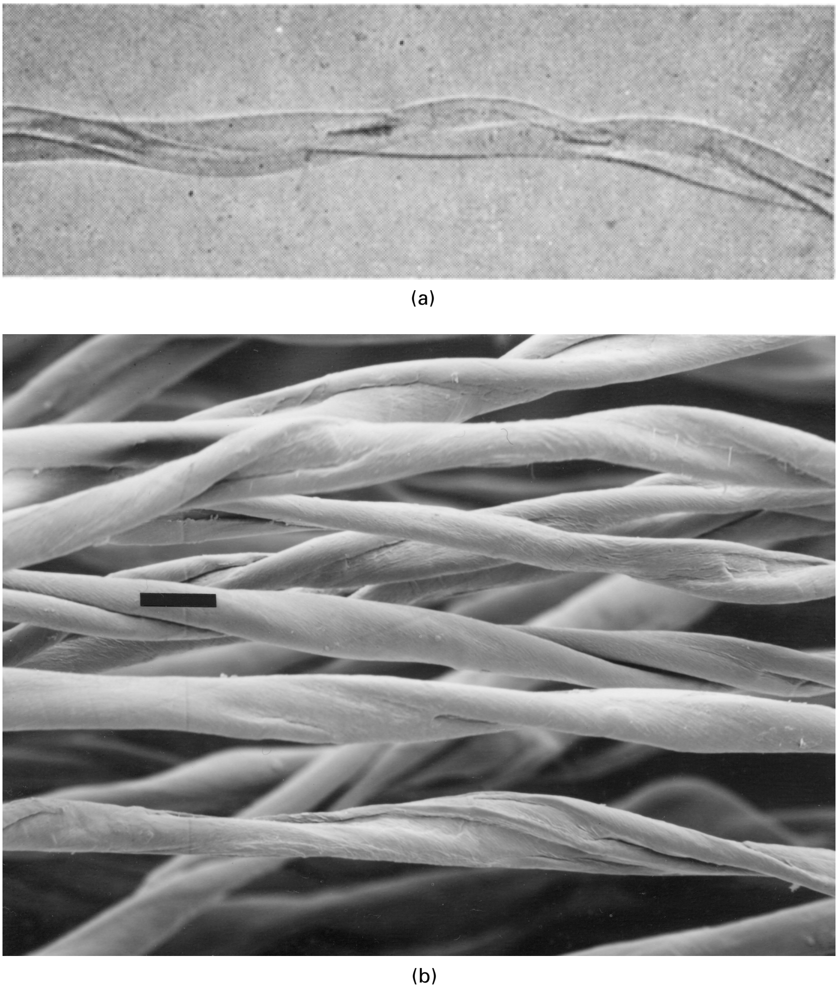
1.4.3 The gross morphology of cotton

The cotton fibre appears as a long, irregular, twisted, and flattened tube, tapering somewhat at its tip. Figure 1.31(a) is a typical illustration of the middle portion of a cotton fibre, showing the presence of convolutions. These are more strikingly shown in an SEM picture (Fig. 1.31(b)). Hearle and Sparrow [47] showed, by comparison with observations of a rubber tube, that the formation of convolutions was a natural consequence of the collapse of a helical structure. For American Upland cottons, measurements with an opto-electronic sensor show 11 to 13 crimps/cm [48].

In cross-section, mature fibres have the form shown in Fig. 1.32. On the outside there are a thin cuticle and primary cell wall and in the centre there is a narrow collapsed lumen, but the bulk of the fibre is made up of the secondary cell wall. During growth, this is deposited on the inside of the primary cell wall, in a series of daily growth-rings as shown in Fig. 1.33. Figure 1.34 shows a schematic representation of the various layers of which the fibre is composed. The layers themselves will be made up of stacks of the lamellae described in the last section.

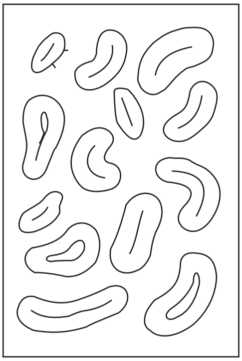
Hebert [50] reports that the primary wall has a 'basket-weave orientation or alignment of the fibrils'. Studies of fibres at two weeks post-anthesis (after flowering) indicate that the primary wall has a crystallinity index of 30% and a fibril diameter of 2.98 nm, compared with 70% and 4.22 nm for mature fibres at seven weeks post-anthesis [51].

In the thick secondary wall (S_2 layer), there is a helical orientation of molecules and fibrils. It may be noted that the helical orientation can be shown up in various ways: optical birefringence, for direction of the chain molecules; X-ray diffraction, for the axis of the crystal lattice; electron microscopy, for the microfibrils; optical microscopy, for the coarse fibrils. There has been some uncertainty as to whether the

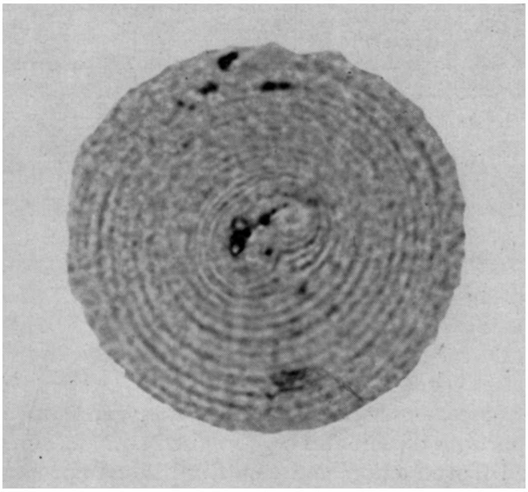


1.31 Cotton fibre: (a) portion of cotton fibre (photograph by E. Slattery); (b) scanning electron micrograph of convolutions is mature cotton fibre, bar = 18.9 μm.

pitch or the angle of the helix remains constant: the evidence now indicates that the angle is almost constant through the fibre. At intervals along the fibre, the sense of the helix reverses, as shown in Fig. 1.35. It was once thought that the helix angle varied with fibre variety, but Hebert *et al.* [52] and Morosoff and Ingram [53] indicated that, if a correction is made for the effect of convolutions, the helix angle is always the same, independent of genetic variety, and through most of the thickness a value in the range 20–23°, though it may be up to 35° in the outer layers. On drying, the fibre collapses to give the typical cross-sectional shape shown in Fig. 1.36. Kassenbeck [54] has pointed out that, after collapse, the different regions of the cotton fibre, indicated in Fig. 1.37, have important differences in structure. As can be expected from the collapse of a cylinder composed of concentric lamellae, and is easily



1.32 Typical cross-sections of mature cotton fibres.

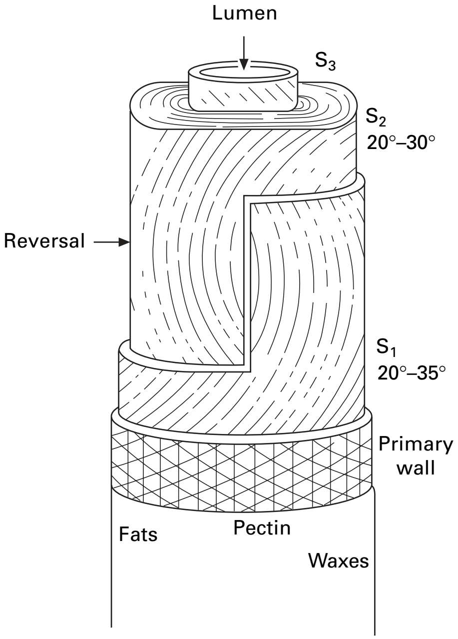


1.33 Cross-section of swollen cotton fibre showing daily growth rings. Photograph by US Department of Agriculture, after Kerr [49].

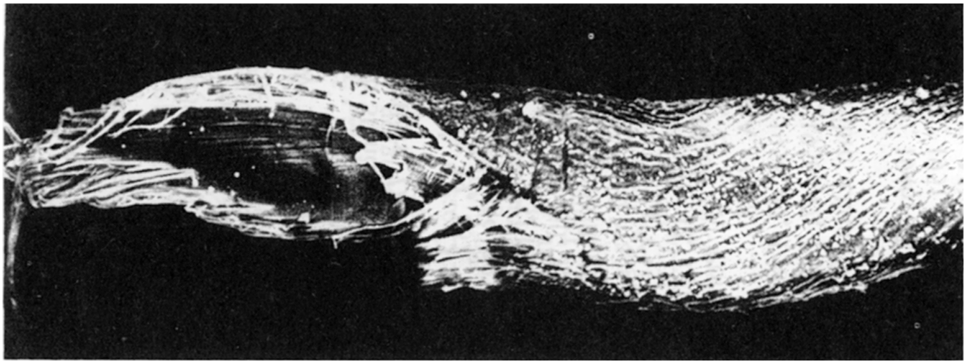
demonstrated by collapsing a roll of adhesive tape, there will be: (a) an appreciable opening up of structure in the regions C and N, where there is reversal of curvature, and thus an excess circumferential length; (b) a tightening in region A, where there is an intensification of curvature; and (c) little change in tightness in region B. Kassenbeck has shown that regions C and N are the most susceptible to chemical reaction and that A is the least susceptible.

1.4.4 Other natural cellulose fibres

Other cellulose fibres, such as flax, hemp, jute and sisal, differ from cotton in several ways. They often contain a larger proportion of non-cellulosic impurities. They are all multicellular fibres, with very small individual cells bonded together into long strands in the plant stem or leaf. During the preparation of the material for processing,

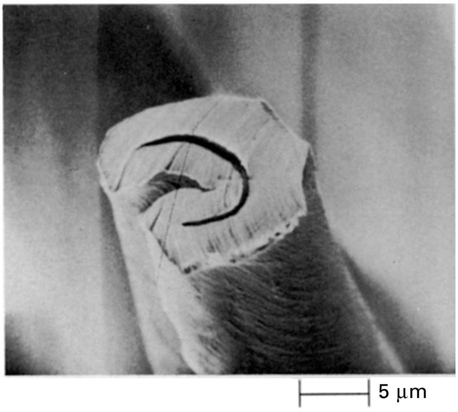


1.34 Morphological structure of the cotton fibre. From Jeffries *et al.* [20].

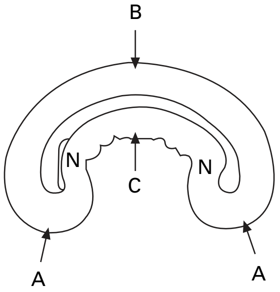


1.35 Scanning electron micrograph showing reversal adjacent to back of a cotton fibre.

the strands are broken down into shorter fibres. The fibre dimensions are, however, somewhat indeterminate, since the extent of breakdown may vary. In all natural cellulose fibres, the molecules are highly oriented parallel to one another in fibrils, but they spiral round the fibre, thus reducing the degree of orientation parallel to the fibre axis. In flax, ramie, hemp and other bast fibres, the spiral angle is small, less than 6°, so that these fibres are highly oriented and give high strength and low extensibility.



1.36 Scanning electron micrograph of cotton fibre cross-section. Picture by J. T. Sparrow.



1.37 Zones A, B, C and N in a mature cotton fibre. From Kassenbeck [54].

Table 1.4 Different forms of regenerated cellulose and modified cellulose fibres

Type	Process and structure-determining factors
Nitrocellulose[a]	Regeneration of cellulose nitrate
Cuprammonium	Solution in cuprammonium hydroxide; coagulation in water
First viscose rayon	Sodium cellulose xanthate in caustic soda into acid bath
Viscose, regular[b]	Zinc salt added to acid bath, giving skin–core structure
Lilienfeld[a]	Viscose into 65% sulphuric acid with concurrent stretch
Fortisan[a]	Regenerated from highly stretched acetate fibres
High-tenacity (HT) viscose[b]	High zinc and modifiers in solution; 'all skin'
Modal staple[c]	Modifications to viscose and weak acid bath
Polynosic[c]	High-viscosity viscose allowing gel formation
Crimped staple	Viscose modifications cause skin bursting
Cordenka HT yarn	Addition of formaldehyde to viscose process
Lyocell, e.g. Tencel	Regeneration from solution in an amine oxide
Liquid-crystal routes[d]	Cellulose derivatives in organic solvents or inorganic acids
Fibre B[e]	Liquid crystal solution in phosphoric acid into acetone
Acetate	Secondary cellulose acetate dry spun from acetone solution
Triacetate	Cellulose triacetate dry spun form $CH_2{\cdot}CCl_2$ solution

[a] Not now commercial.
[b] Coagulation + regeneration → stretch.
[c] Coagulation + stretch → regeneration
[d] Various patented processes, not commercialised.
[e] Laboratory process by Boerstel [55].

1.5 Regenerated and modified celluloses

1.5.1 Manufactured cellulosic fibres

Since the first production of regenerated cellulose fibres at the end of the 19th century, many different forms have been produced, as shown in Table 1.4. The degree of polymerisation in ordinary rayon is of the order of 500, which is less than one-tenth of the length of the molecules in native cellulose, but may be higher in improved forms. The crystal structure of regenerated-celluloses is cellulose II. The proportion of crystalline material present is low, being about one-third of the total, except for the experimental liquid-crystal fibres. The degree of orientation of regenerated-cellulose fibres depends on the extent to which they have been stretched during spinning. Values of the optical orientation factor (that is, the ratio of the birefringence of the fibre to the birefringence of a fibre with perfect axial orientation of the molecules) are given in Table 1.5, together with those of some natural fibres for comparison. With fibres of such a low degree of order, there must be substantial non-crystalline regions, and the most likely view of the fine structure of ordinary viscose rayon is the fringed-micelle structure, as discussed in Section 1.3.2 and shown in Fig. 1.16. The stiffness of the cellulose molecule would inhibit chain folding at the ends of crystallites. The disorder in the solution will result in chains folding back on themselves in non-crystalline regions. There are other forms of viscose rayon, and we must consider the diversity.

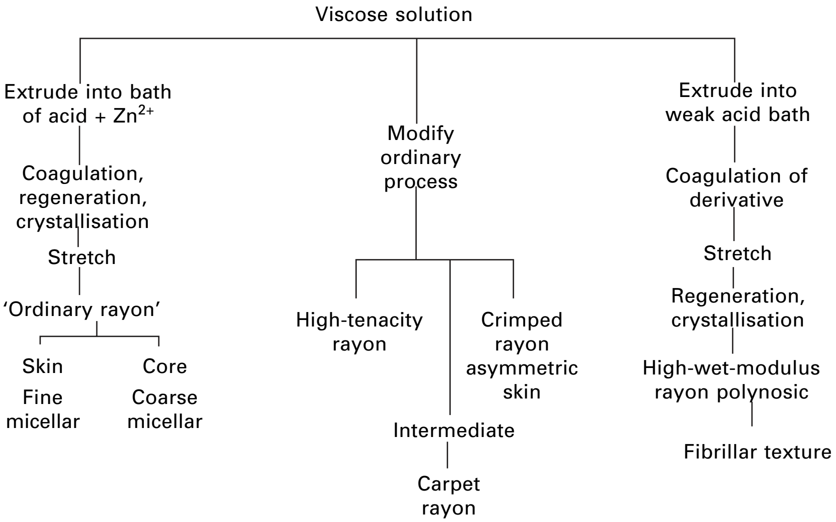
1.5.2 The diverse forms of viscose rayon

Figure 1.38 shows various routes of regeneration of fibres from a viscose solution. In the ordinary process, the resulting fibre has an irregular cross-section with a marked difference between skin and core, as shown in Fig. 1.39. The skin forms immediately after extrusion and then collapses as solvent is removed. The lateral pressures push the ribbon-like molecules into what starts as radial orientation in the plane of the cross-section, though this swings round to a perpendicular direction in the cusps of the serrations. The orientation effects are shown up by examination in polarised light, as in Fig. 1.39.

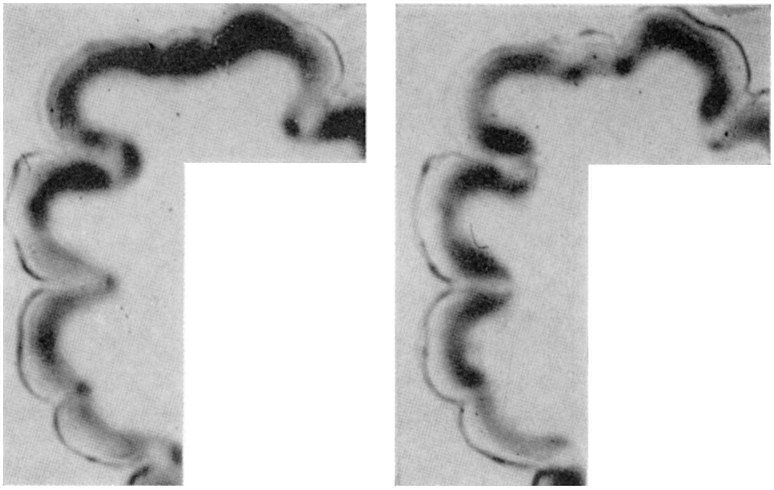
The skin is believed to have a finer texture than the core and to be stronger. It is formed by regeneration through the intermediate zinc cellulose xanthate. The rates of the alternative reactions are such as to favour this route over direct regeneration of the sodium salt by the acid, but it is prevented in the core because the low mobility of the zinc ions prevents them from getting in fast enough. The finer texture of the material regenerated indirectly is probably due to the fact that the bivalent zinc ions will attract the molecules into a network before regeneration.

Table 1.5 Optical orientation factors of cellulose fibres, (after Hermans [56]

Fibre	Orientation factor
Viscose rayon, low stretch	0.54
Viscose rayon, high stretch	0.88
Cuprammonium rayon	0.74
Ramie	0.97
Sea Island cotton	0.72
American cotton	0.62

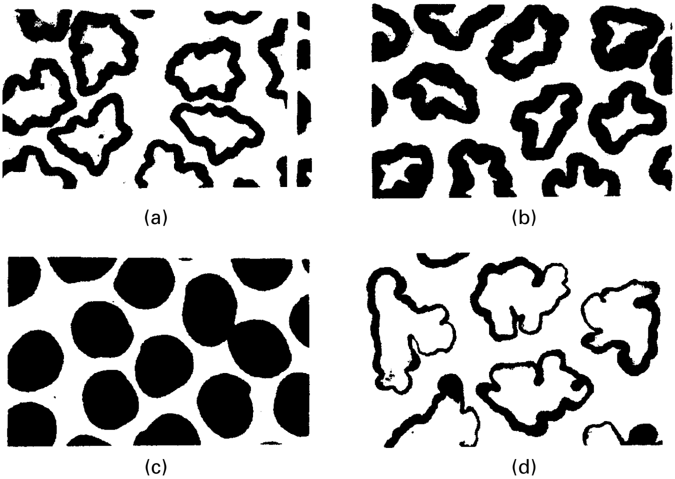


1.38 Schematic representation of fibres produced by the viscose process.


(a) (b)

1.39 Section of viscose rayon fibre, dyed with Sky-Blue FF, showing optical dichroism when viewed in polarised light. The dark patches in the skin correspond to orientation of the crystallites parallel to the direction of polarisation: (a) plane of polarisation is N–S; (b) plane of polarisation is E–W. After Joshi and Preston [57].

As shown in Fig. 1.40, various modifications of the process have led to an increase in skin thickness and, ultimately, to all-skin fibres with a round cross-section. These are the high-tenacity rayons, introduced first for tyre cords but now also used for other textile purposes. There is also attention to other details, such as the distribution of chain lengths, in the later high-tenacity rayons. In another modification, an



1.40 Cross-sectional shapes of viscose fibres with differential dyeing of skin: (a) regular viscose rayon; (b) *Tenasco*, early high-tenacity rayon with thicker skin; (c) *Tenasco* Super 108, an 'all-skin' fibre; (d) crimped staple viscose rayon with asymmetric skin. From Woodings [58].

asymmetrical skin, caused by the first skin bursting open, is produced; these are the crimped rayons.

A greater difference occurs in the production of high-wet-modulus (modal or polynosic) rayons. A solid fibre of a cellulose derivative is first formed and oriented by stretching. Regeneration of cellulose and crystallisation then occur in what is already a solid, oriented fibre. The resulting structure is fibrillar in texture, and the fringed-fibril structure (Fig. 1.19), is probably the best model. Lyocell fibres such as *Tencel* [59], which are directly regenerated from an organic solvent of cellulose, are fibrillar in texture. The bonding between fibrils is weak, so that fibrillation occurs easily. This can be a defect, but can also be exploited to make a soft fabric.

In all these forms of rayon, the degree of orientation can be varied by altering the amount of stretch, though there are limits to the extent to which this is possible. A higher orientation can be produced in the more weakly bonded acetate fibres, and regeneration of cellulose was then used to make *Fortisan*, which was a highly oriented, high-modulus fibre that is no longer made. High crystallinity and high orientation can be achieved by liquid crystal routes, similar to those used for aramid fibres, but the side groups on the cellulose molecule mean that the achievable mechanical properties are less good.

Cellulose fibres may also be modified by additives, e.g. delustring by titanium dioxide, or by chemical reactions used to crosslink the cellulose molecules.

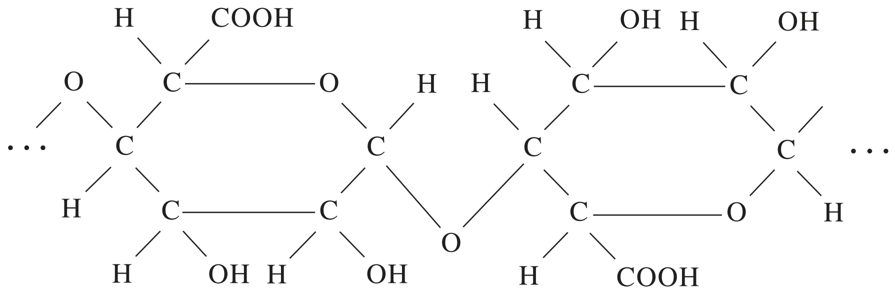
1.5.3 Cellulose acetate

In acetate fibres, the most important of the chemically modified cellulose fibres, the cellulose is chemically treated in solution so that the hydroxyl groups are replaced by acetyl ($CH_3 \cdot CO \cdot O$—) groups. In ordinary commercial acetate (more exactly known as secondary cellulose acetate), about five out of six of the hydroxyl groups are replaced in this way. Fibres made of this material contain a smaller proportion of crystalline material than do regenerated celluloses. There are three reasons for this reduction in crystallinity: (a) the acetyl groups are comparatively inert, hydrogen bonding is not possible, and thus the attractive forces between the molecules are weaker; (b) the acetyl groups are bulky, preventing the close approach of the chain molecules; and (c) the structure is irregular, with some acetyl and some hydroxyl groups protruding from the chain, so preventing the formation of a regular crystalline order. As a consequence of these effects, acetate fibres are weaker, more extensible, and less dense and absorb less water than cellulose fibres. They also have a low softening point, whereas unmodified cellulose fibres cannot be melted and decompose first.

The large-scale production of secondary cellulose acetate was largely a historical accident arising from difficulties in the early processing of a fully acetylated cellulose. These difficulties have been overcome, and triacetate fibres, in which all the hydroxyl groups are replaced by acetyl groups, have been produced. Because of the greater regularity of structure, these fibres are more highly crystalline than ordinary acetate fibres. They also absorb less water because of the removal of all the hydrophilic hydroxyl groups. Their practical advantages are a higher softening point, greater dimensional stability, and the fact that materials made from them are crease-resistant and can be heat-set.

1.5.4 Alginate and other fibres

Alginic acid, which can be obtained from seaweed, has the formula:



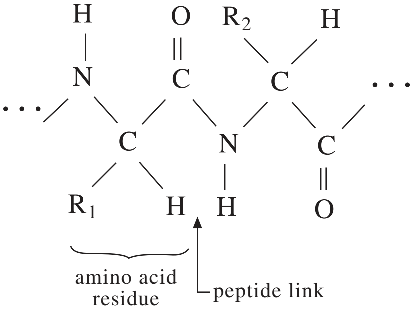
Highly oriented and highly crystalline alginic acid fibres can be obtained, but they are subject to degradation because of their acidity. The acid may be neutralised to give metallic salts, which will also form fibres. Calcium alginate is soluble in soap and water and can be exploited as removable scaffolding threads in fabrics. Crosslinking is needed to give stability for ordinary use.

Various other polysaccharides, such as chitin and its derivative chitosan, are made into fibres for medical uses.

1.6 Protein fibres

1.6.1 Protein chemistry

Proteins are formed by the polymerisation of amino acids (with the general formula $NH_2 \cdot CHR \cdot COOH$) by means of peptide links (—CO·NH—) to give long-chain molecules with the general formula:



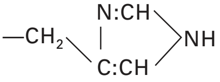
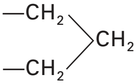
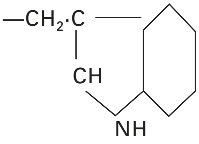
Twenty amino acids are named and represented by three or one letter designations. They contain different side groups (R_1, R_2, etc.). It is the variation in the order and amount of these groups that determines the properties of the material and gives rise to the large number of natural proteins that play a vital part in animal and plant life. In effect, there is an 'alphabet' of side groups. Advances in proteomics and the link to DNA have enabled the amino acid sequences in proteins to be accurately determined. An old estimate in Table 1.6, which is adequate for our purposes, gives comparative proportions occurring in the raw materials of various protein fibres. This is a list of 18 amino acids because the amides asparagine and glutamine are included with aspartic and glutamic acids. It should be noted that these figures are approximate, since the chemical constitution of the protein may vary from fibre to fibre, or even from one part of a fibre to another. More recent figures for wool are given by Höcker [61].

Two forms differ from the simple formula. Proline has a ring of three —CH_2— groups, which join on to replace —H in the neighbouring —NH group and distort the form that the molecule can take. Cystine, which links neighbouring chains, is derived from cysteine, R = —$CH_2 \cdot SH$, which is the amino acid, by a subsequent reaction.

There are various sorts of crosslinks that can form between neighbouring protein molecules.

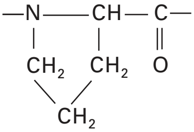
- Hydrogen bonds can form between the —NH— and —CO— groups, linking neighbouring main chains together:

Table 1.6 Side groups in protein fibres (after Harris [60])

Type	Side group	Amino acid	Proportion (g amino acid per 100 g protein) in:		
			Silk fibroin	Wool keratin	Casein
Inert	—H	Glycine	43.8	6.5	1.9
	$—CH_3$	Alanine	26.4	4.1	3.5
	$—CH(CH_3)_2$	Valine	3.2	5.5	6.02
	$—CH_2{\cdot}CH(CH_3)_2$	Leucine	0.8	9.7	10.55
	$—CH(CH_3){\cdot}CH_2{\cdot}CH_3$	Isoleucine	1.37	—	5.27
	$—CH_2{\cdot}C_6H_5$	Phenylalanine	1.5	1.6	6.46
Acidic†	$—CH_2{\cdot}COOH$	Aspartic acid	3.0	7.27	6.70
	$—CH_2{\cdot}CH_2{\cdot}COOH$	Glutamic acid	2.03	16.0	22.03
Basic†	$—CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	Lysine	0.88	2.5	8.25
	$—(CH_2)_3{\cdot}NH{\cdot}C(NH)NH_2$	Arginine	1.05	8.6	3.94
		Histidine	0.47	0.7	3.24
Hydroxyl	$—CH_2OH$	Serine	12.6	9.5	5.87
	$—CH(OH){\cdot}CH_3$	Threonine	1.5	6.6	4.53
	$—CH_2{\cdot}C_6H_4OH$	Tyrosine	10.6	6.1	6.28
Ring‡		Proline	1.5	7.2	10.54
Double§	$—CH_2{\cdot}S.S{\cdot}CH_2—$	Cystine	—	11.8	0.40
Miscellaneous	$—CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_3$	Methionine	—	0.35	3.50
		Tryptophane	—	0.7	1.37

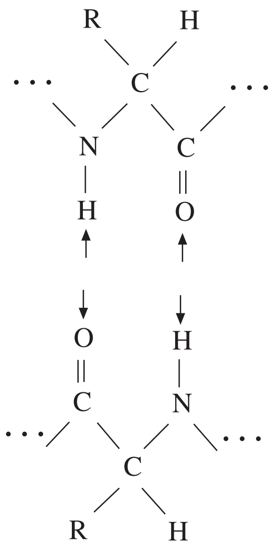
[†] May be present in ionised forms, e.g. $—CH_2{\cdot}COO$ and $—(CH_2)_4{\cdot}NH_3^+$. The acids may also be present as acid amides, e.g. $—Ch_2{\cdot}CONH_2$.

[‡] Fits into the chain molecule as:

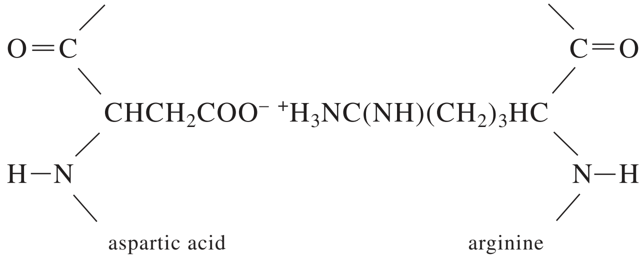


This results in some distortion and loss of flexibility in the chain.

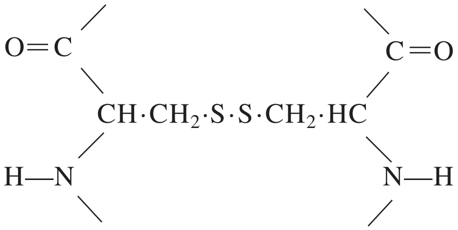
[§] Joins on between two protein chain molecules or between two positions in the chain. There may also be small amounts of the related cysteine, cysteinic acid, lanthionine and thiocysteine groups.



- Hydrogen bonds may form between hydroxyl groups present in the side chains.
- Since there are both acidic and basic side chains, salts may form between them, holding the side chains together by electrovalent forces. A typical example would be:



- The cystine linkage is a covalent crosslink between adjacent chains, which turns the many chain molecules into a single network molecule. The linkage is:



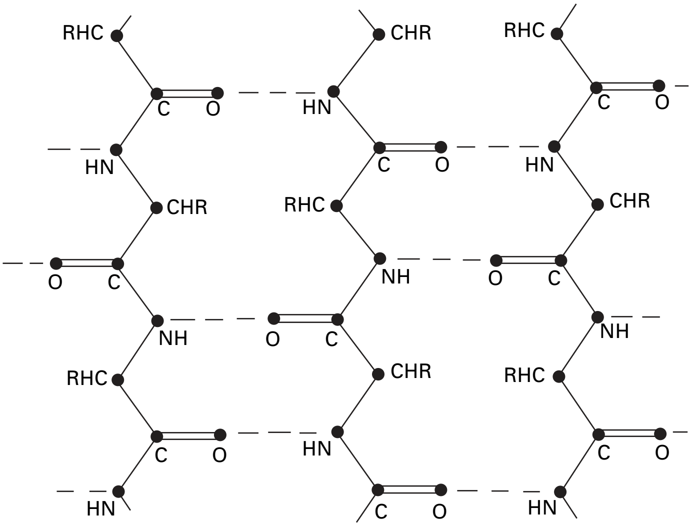
All these crosslinks play an important part in determining the form of the protein. For example, single long-chain molecules may fold up into a compact ball held together by internal crosslinks; these are known as *globular proteins*, and their large molecules will crystallise in the same way as inorganic molecules. Alternatively, the molecules may be more or less extended and linked to their neighbours; these are the *fibrous proteins*. Globular proteins may be unfolded, or denatured, by heat or other chemical treatments and can then be drawn into fibres.

1.6.2 Silk

The two most important protein fibres for textile uses are silk and wool. The main constituent of silk is one of the simpler proteins, *fibroin*. The figures in Table 1.6 show that almost all the side groups are of four simple types: $—H$, $—CH_3$, $—CH_2OH$ and $—CH_2C_6H_5OH$. The sulphur-containing side groups are almost completely absent, and the others are present only in small quantities. The links between molecules will therefore be mostly main-chain hydrogen bonds, with a few hydrogen bonds and salt linkages between side chains.

Examination of the X-ray diffraction pattern of silk shows that molecules in the crystalline regions must be present as fully extended chains of the sort shown in Fig. 1.41. This is a zigzag form because of the limitation on the angles between adjacent valency bonds. There is an axial repeat of 0.7 nm, corresponding to two amino acid residues. The molecules in silk are fairly highly oriented parallel to the fibre axis, and the material is moderately highly crystalline. The general structure is believed to be composed of crystalline and non-crystalline regions in the same way as cellulose, though the mode of formation may mean that there is little or no folding of chains back on themselves.

It has been suggested [62] that in the fibroin molecule, which is about 140 nm long, there are two segments, about 17 nm long, in which all the tyrosine and other bulky side groups are concentrated, the rest of the molecule being entirely of glycine, alanine and serine side groups. The segments with bulky side groups would not



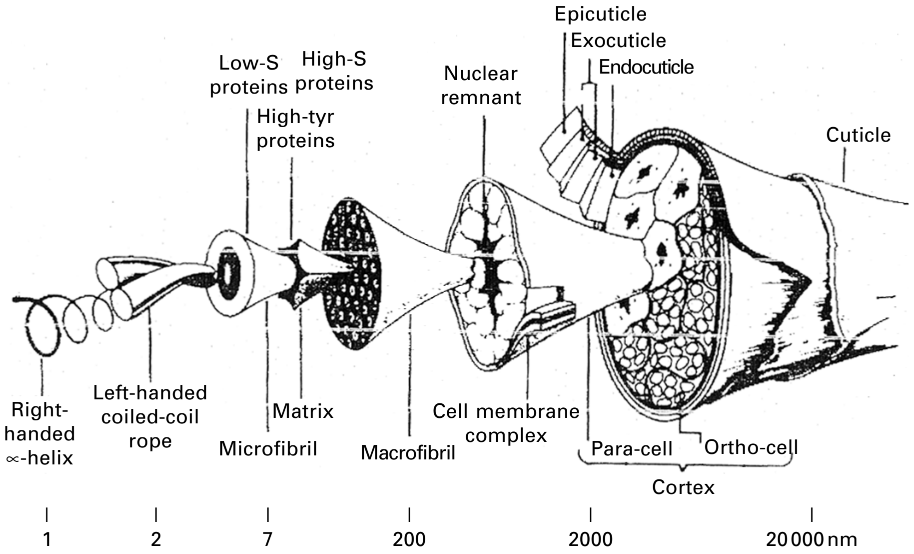
1.41 Extended-chain molecules of silk fibroin and β-keratin, packed in sheets in crystal.

crystallise so easily and would therefore form the major part of the non-crystalline regions, while the crystalline regions would be made up from the parts of the molecules with simple, easily and regularly packed side groups. This would make silk a natural block copolymer (see Section 1.7.1), composed partly of crystallisable and partly of non-crystallisable segments. Thus, in considering effects occurring mainly in the non-crystalline regions (for example, moisture absorption), the presence of certain side groups in much higher proportions than in the silk as a whole must be taken into account.

The silk fibre, as it is spun by the silkworm, consists of two triangular filaments of fibroin, stuck together with a gum called sericin.

1.6.3 Molecular form and assembly in wool (levels 2 to 6)

Wool and hair have the most complicated structures of any textile fibres (Fig. 1.42), with ten levels of structure from fundamental particles to the whole fibre (Fig. 1.43) [63]. The specific features start at level 2, the molecular constitution. Table 1.6 shows that almost all possible side groups are present in appreciable proportions. Many of these contain active groups so that side-chain linkages are important. The values in Table 1.6 for wool keratin are for whole fibres, which actually consist of many proteins in different parts of the fibres. In particular, there are differences of composition between the crystalline microfibrils (intermediate filaments, IFs)[4], which make up about 40% of the fibre, and the amorphous matrix [61].



1.42 Structure of wool fibre, as drawn by Robert C. Marshall, CSIRO, Melbourne.

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[4] Microfibril, often abbreviated to fibril, is the term used in describing fibre structures and is most appropriate when discussing the relation to properties. Intermediate filaments is a term used in biology to describe a category of protein structures with many functions in living organisms. Hard keratins, such as hair, and soft keratins, as in skin, constitute one group of intermediate filaments.

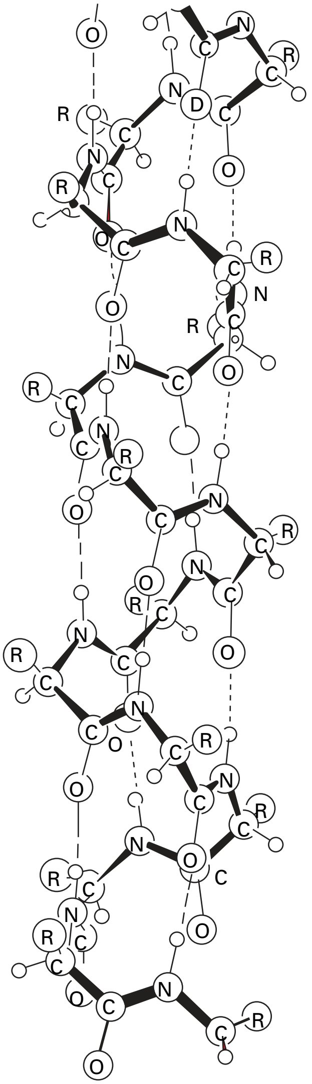
<table>
<tr><th colspan="2">Level</th><th colspan="7">Fibre structure</th></tr>
<tr><td colspan="2">9 20 cm × 20 µm</td><td colspan="7">Whole fibre: length, area, shape, scales, crimp, variability</td></tr>
<tr><td rowspan="2">8</td><td rowspan="8">Med-ulla</td><td colspan="4">Cortex</td><td colspan="3" rowspan="2">Cuticle</td></tr>
<tr><td>Ortho</td><td>Para</td><td>Meso</td><td></td></tr>
<tr><td>7 2 µm</td><td colspan="3">Cells: major part + nuclear remnants</td><td>CMC</td><td rowspan="3">Endo</td><td rowspan="3">Exo</td><td rowspan="3">Epi</td></tr>
<tr><td>6 0.2 µm</td><td colspan="3">Macrofibrils + matrix</td><td rowspan="5">Lipids, proteins etc.</td></tr>
<tr><td>5</td><td>Whorls</td><td colspan="2">Parallel array</td></tr>
<tr><td>4</td><td colspan="3">Composite of:
Microfibril + Matrix</td><td rowspan="3">Protein etc.</td><td rowspan="3">Protein etc.</td><td>Lipid etc.</td></tr>
<tr><td>3 7 nm</td><td>Intermediate filaments</td><td colspan="2">Matrix detail</td><td rowspan="2">Surface chemistry</td></tr>
<tr><td>2 1 nm</td><td>Keratin proteins</td><td colspan="2">Keratin-associated proteins</td></tr>
<tr><td>1 0.5 nm</td><td colspan="8">Atoms</td></tr>
<tr><td>0</td><td colspan="8">Fundamental particles: quantum theory</td></tr>
</table>

1.43 Levels of structure in wool and hair (CMC = cell membrance complex).

The protein families in wool are (a) two low-sulphur IF keratins, which contain relatively simple, crystallisable sections, joined to terminal domains with a more complex chemistry, containing cystine and making up part of the non-crystalline material; (b) high-sulphur and high-glycine/tyrosine keratin-associated proteins, which contribute the remainder of the non-crystalline regions. Because of the high concentration of crosslinking cystine, the non-crystalline material acts as a rather highly crosslinked amorphous polymer.

Two different crystal structures, with different X-ray diffraction diagrams, can occur in keratin (and in many other similar proteins). In wool as grown and used, there is a structure known as α-keratin, but, if the fibre is stretched (and it can be extended up to 50% in water, or a maximum of 100% in steam), there is a gradual and reversible transformation to another form known as β-keratin, which has an X-ray diffraction pattern similar to that of silk fibroin (Fig. 1.41). This is, therefore, an extended chain, but the axial repeat in β-keratin is only 0.68 nm, indicating that there is some slight distortion.

The crystal structure of α-keratin is a slightly distorted form of the helical structure proved for simple synthetic polypeptides by Pauling and coworkers [64, 65]. In earlier models, such as that proposed by Astbury and Bell [66], it had been taken for granted that chemical and fold repeats must coincide, but, in fact, this is unnecessary. In Pauling's α-helix, there are 3.6 amino acid residues per turn, with the length of one turn giving the axial repeat of 0.55 nm. An impression of the model is given in Fig. 1.44. In keratin, the axial repeat is only 0.51 nm. There may be some crumpling of the helix in order to fit in bulky side groups. However, the shortening can mostly be

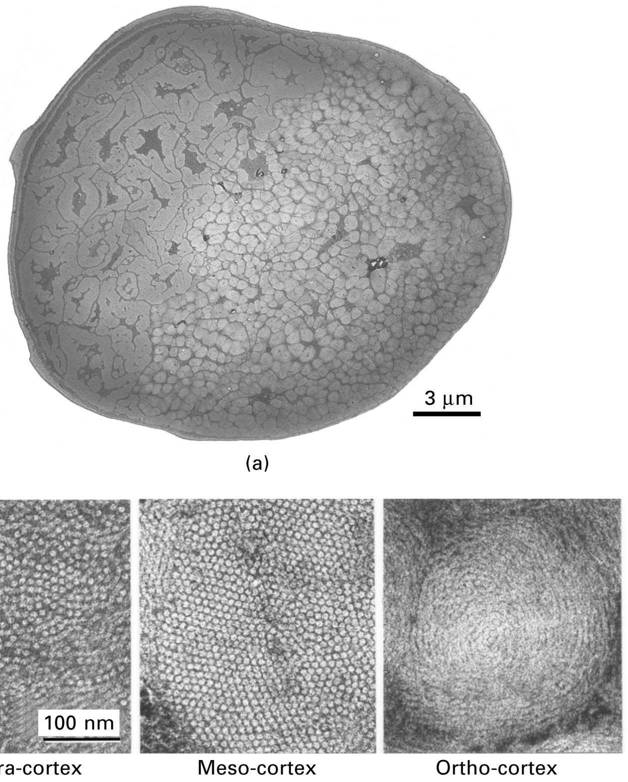


1.44 α-Helix structure for polypeptides and proteins suggested by Pauling.

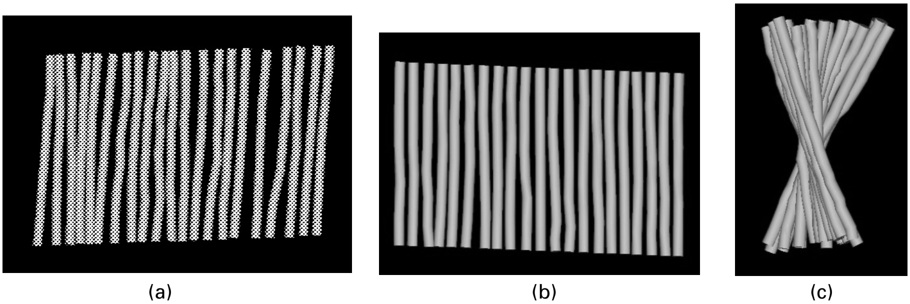
attributed to the multiple twisting of the molecules: two chains form a dimer, two dimers a protofilament, two protofilaments a protofibril, two protofibrils a half-filament, and two half-filaments giving an intermediate filament with 32 molecules in the cross-section [61].

In considering the physical properties, however, the exact details of the molecular folding are of less importance than the fact that the helical form of α-keratin molecules allows them to be opened out to extended chain β-keratin, giving a high extensibility. It is also possible, by appropriate relaxation treatments in steam, to contract the fibres to a length about 30% less than the original unstretched length. In these *supercontracted* fibres, the molecules must be still more highly folded, or randomly coiled, or recrystallised without axial orientation.

The microfibrils in wool are about 7 nm in diameter, packed at spacings of about 10 nm and separated by a matrix. However, there is a difference in structure in cells in different parts of the fibre, as shown by the transverse section in Fig. 1.45. In the meso-cortex, which is not always easily differentiated from the para-cortex, long microfibrils are packed in a hexagonal array, which is perpendicular to the section, so that the fibrils run parallel to the fibre axis. In the para-cortex, the fibrils are also parallel to the fibre axis, but are not as tightly and regularly packed as in the meso-cortex. A poorly defined macrofibrilllar structure with more matrix between macrofibrils can be seen in the meso- and para-cortex. In the ortho-cortex, the macrofibrils appear as whorls. At the centre the fibrils appear circular, indicating that they are perpendicular to the section, but there is increasing ellipticity at increasing distance from the centre. This indicates that the fibrils are twisting round at increasing angles. As in a twisted continuous filament yarn, the length of one turn of twist is constant across the macrofibril. Electron microscope tomography by Bryson *et al.* [16] enables the structures to be seen more clearly and quantitative estimates of the fibril angles to be made (Fig. 1.46). In the para-cortex, the fibrils are slightly wavy but generally parallel to the



1.45 Electron microscope picture of transverse section of a high-crimp wool: (a) whole fibre; (b) macrofibrils. From Bryson *et al.* [16].


(a) (b) (c)

1.46 Reconstructed tomograms of macrofibrils in wool showing orientation of microfibrils: (a) in para-cortex; (b) in meso-cortex; (c) in ortho-cortex. From Bryson *et al.* [16].

fibre axis; in the meso-cortex, the fibrils are straighter; in the ortho-cortex, there is the changing angular orientations of a helical assembly.

1.6.4 The gross structure of wool

The wool fibre consists of a roughly circular cylinder, tapering from the root to the tip, and with the complex structure illustrated in Fig. 1.42. It is a multicellular and multicomponent fibre. The major component is the cortex, which leads to a simple view that wool is a bicomponent fibre divided into ortho- and para-cortex. As described in Section 20.6.2, this leads to the helical crimp of wool with the para-cortex on the inside, unless the fibre is swollen in alkali when the curvature is reversed. Crimp formation depends on the distribution of ortho- and para-cortex in wool and hair. An asymmetric distribution gives crimp; a symmetric distribution does not. In addition to the difference in fibril orientation described above, the para-cortex is reported to contain more cystine groups, crosslinking the chain molecules (see Section 1.6.1) and is more stable and less accessible to dyes than the ortho-cortex, which contains more glycine/tyrosine proteins. In some wools, a meso-cortex can be observed as distinct from the para-cortex. In coarse wools, there may be a medulla at the centre made up of a different type of cell, but in fine wools this is absent.

Between the cells, there is a cell membrane complex containing a mixture of lipids, proteins and small amounts of other compounds [67].

At the surface of the fibre, there are cuticle cells or scales. These scales face towards the tip of the fibres and cause a directional effect, which is important in the frictional behaviour of wool (see Section 25.5). On the surface of the scales, or possibly as a continuous sheath around them, there is a membrane called the *epicuticle*, which may influence the surface properties of the fibre and act as a barrier to diffusion. Between the cuticle and the cortex is another thin layer, called the sub-cuticle membrane.

1.6.5 Regenerated-protein fibres

The regenerated-protein fibres such as those made from casein, which are no longer commercial, have X-ray diffraction patterns which show that most of the material in the fibres is non-crystalline. Such crystallites as are present are more or less imperfect and are made up of protein chains in an extended form, that is, a structure similar to β-keratin. The constitution of casein is given in Table 1.6. It contains a wide variety of side groups.

Proteins have been produced from bioengineered goat's milk in an attempt to mimic the high strength of spider silk. However, when these are spun from solution, they give low-strength fibres with a poorly ordered structure. The means of forming the fibre is more important than the protein composition.

1.7 Synthetic fibres for general use

1.7.1 Chemical constitution

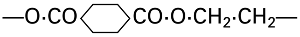
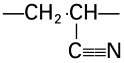
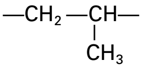
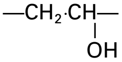
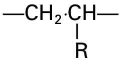
The synthetic fibres in major use for general textiles since the 1950s are the polyamides, nylon-6 and 6,6, the polyester, polyethylene terephthalate (PET), acrylic polyacrylontrile (PAN) and polypropylene (PP). They are all linear polymers. In addition to the basic repeat unit, there may be small proportions of other groups inserted, within chains, at chain ends, or as chain branches, in order to modify such fibre properties as dyeability. This is particularly true of acrylic fibres, in which up to 15% of a minor component, which is usually another vinyl monomer with some other side group, –R, is present. Some other polyamides and polyesters are used as fibres. There are also modacrylic fibres with less acrylonitrile, usually about 50%, in the chain. Other vinyl and vinylidene copolymers are or have been used for some fibres of limited use. Polyethylene has limited use as a general texture fibre. Most recently, polylactic acid (PLA) has been introduced as a textile fibre. The chemical formulae of the polymers are given in Table 1.7.

It is worth noting the features that make synthetic polymers suitable for fibres by causing them to be partly crystalline. First, the chains must be regular, so that a favourable packing at one point is repeated all along the chains. Secondly, the chains must have a shape that enables them to pack closely together and so cause the attractive forces between chains to be effective. Thirdly, the attractive forces should, inherently, be relatively strong. Fourthly, there must be some flexibility. These features work together, so that some deficiency in one can be compensated by another, but generally they are all satisfied in the best fibre-forming polymers.

Copolymerisation, as a means of mixing components, may occur in several ways. Because of the need for regularity of repeat, random copolymers, –ABBAAABAABABBBAABA–, are unlikely to be suitable. Block copolymers, –AAAAAAAAABBBBBBBBB–, on the other hand, will contain separate sequences that are long enough to crystallise. Alternatively, the second component may be grafted on as a branch of the main chain.

Another general point should be noted. Natural fibres, which are laid down slowly under genetic control, have a well-defined structure that is not easily changed. To a slightly less extent, fibres formed from solution, especially if chemically regenerated as in viscose rayon, are locked in structures that are distinctly separated from the liquid state. In contrast to this in the melt-spun synthetic fibres, polyamides, polyesters and polypropylene, the solid and liquid states are only weakly separated by

Table 1.7 Synthetic fibre constitution

Fibre type	Chemical formula of principal repeat unit
Polyamide:	
nylon 6,6	$\mathrm{—NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO—}$
nylon-6	$\mathrm{—NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO—}$
Polyester:	
polyethylene terephthalate	
Acrylic:	
polyacrylonitrile	 $\mathrm{—CH_2{\cdot}\underset{\displaystyle C{\equiv}N}{\underset{\vert}{CH}}—}$
Polyolefin:	
polyethytlene	$\mathrm{—CH_2—}$
polypropylene	 $\mathrm{—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—}$
Polylactic acid	$\mathrm{—CO{\cdot}CH(CH_3){\cdot}O—}$
Other addition-polymer fibres:	
polyvinyl cholride	$\mathrm{—CH_2{\cdot}CHCl—}$
polyvinyl alcohol	 $\mathrm{—CH_2{\cdot}\underset{\displaystyle OH}{\underset{\vert}{CH}}—}$
other vinyl monomers	 $\mathrm{—CH_2{\cdot}\underset{\displaystyle R}{\underset{\vert}{CH}}—}$
vinylidene monomers	$\mathrm{—CH_2{\cdot}CR_2—}$

comparatively small temperature differences, with some structural mobility occurring well below the melting point. The nature of the cooling process and subsequent heat treatments leads to differences in structure. Whereas, we can describe *the structure* of a cotton fibre, we can give only broad indications of the sorts of structure that occur in melt-spun fibres. The evidence in the literature from analytical studies is strictly applicable only to the particular sample being studied and often the provenance is not well specified.

1.7.2 The structure of polyamide fibres

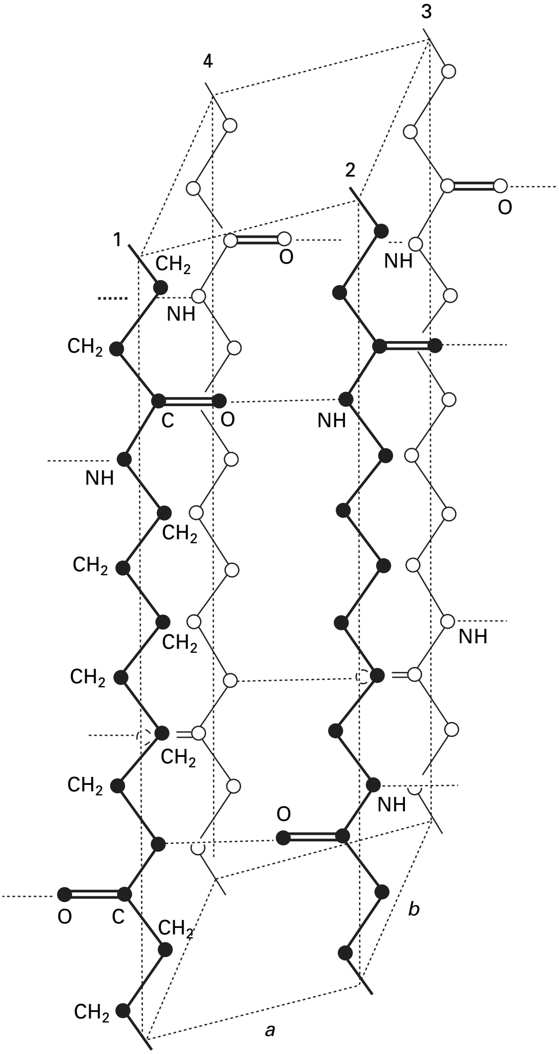
The two most important polyamide fibres, nylon 6 and nylon 6.6, contain the same groups in the same proportions along the chain. The only difference is a reversal in the order of alternate $\mathrm{—CO{\cdot}NH{\cdot}CH_2—}$ sequences. As a result, there will be small differences in shape and packing. In addition, the nylon 6 repeat is half the length of the nylon 6.6 repeat; and the nylon 6 molecule, but not that of nylon 6.6, has a directional character:

$$\mathrm{.....CO{\rightarrow}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\rightarrow}NH}\ldots$$

These differences cause some not very well understood differences in structure, and some consequent slight differences in properties.

From a physical point of view, the important features of these molecules are the length of the repeat and the occurrence of alternate sequences of —CH_2— and —CO·NH— groups. The long repeat unit, 1.7 nm, in nylon 6·6 with 38 atoms means that any mismatch in crystal packing will result in a substantial region of disorder and not a localised defect. Individual crystals can occur only in a limited range of sizes: 1.7, 3.4, 5.1, 6.8, 8.5, 10.2 … nm.

The —CH_2— sequences will be flexible at room temperature, with only a weak attraction for their neighbours. On the other hand, the —CO·NH— groups will attract one another strongly by hydrogen bonding. Under the action of these forces, the polyamides crystallise, and the usual crystal lattice of nylon 6.6 is shown in Fig. 1.47. However, owing to the difficulties of sorting out chains, crystallisation will not be

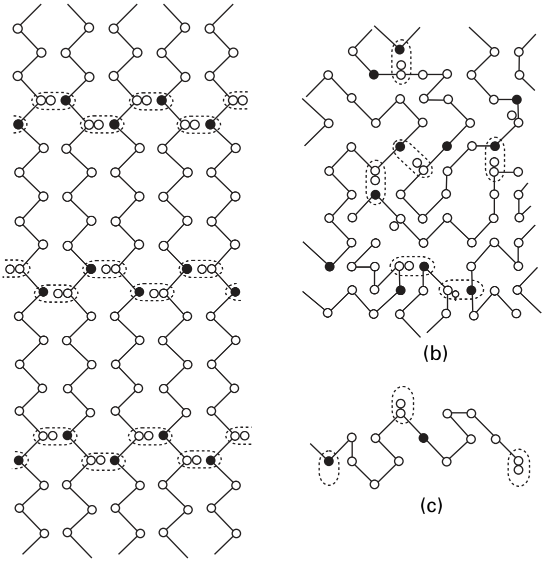


1.47 Crystal structure of α-nylon 6.6 [5].

complete, and we can also expect to find disordered regions within the fibre. Fig. 1.48 illustrates schematically the nature of the packing of nylon 6 in a crystalline region and in an amorphous structure that would occur if molten nylon was so rapidly quenched that crystallisation was prevented. The disordered region would be a rather highly crosslinked rubber with sequences of five —CH_2— groups between the linked —CO·NH— groups. Many important properties derive from this structure and from the fact that the hydrogen bonds between the —CO·NH— groups are rather easily ruptured. Absorption of water plasticises disordered regions, since some direct hydrogen bonding is lost.

Both nylon 6 and nylon 6.6 do have more than one crystal lattice form, and transitions between these can occur. The structural effects of these changes are not clear.

The experimental evidence indicates that nylon fibres have a *degree of order* equivalent to about 50% crystalline, but this covers a variety of forms and dimensional parameters. The *degree of localisation of order* will depend on the fibre history. A common working model, drawn in slightly different ways by different authors, is a modified fringed-micelle structure with chain folding at the ends of the crystallites and tie-molecules linking the crystallites. One interesting feature of the nylon 6.6 crystal unit cell is that the cross-face (1234 in Fig. 1.47) makes an angle of 48° with the chain axis. This led Hearle and Greer [29] to propose the type of modified fringed-micelle structure shown in Fig. 1.18(a). This fits in with various experimental observations on fibre structure and is probably a reasonable representation of the structure of annealed nylon fibres, though the real structure is likely to be less neat



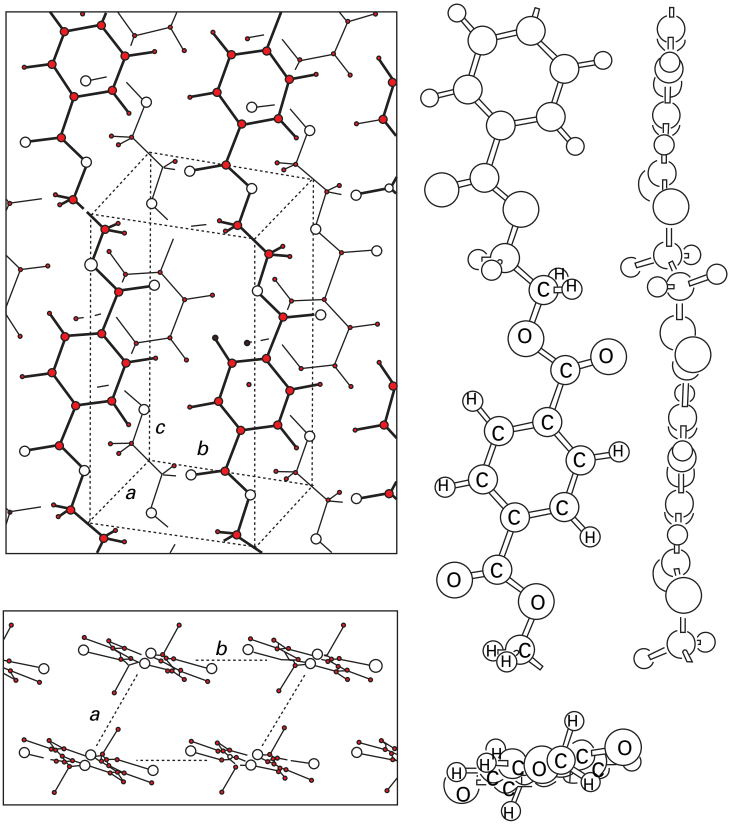
1.48 (a) Schematic representation of nylon crystal lattice. (b) Disordered region. (c) Sections of chains between crosslinks. (For convenience, the repeat is that of nylon 6).

than the diagram and must be transformed by the viewer into a three-dimensional assembly. Figure 1.18(b) is an attempt by Murthy *et al.* [30] to show a structure of nylon 6 related to X-ray diffraction observations.

The characteristic *size of localised units* is about 15 nm, with a *length/width ratio of localised units* not much greater than one. As noted in Section 1.3.2 the pseudo-fibrillar form results from the fairly close packing of the crystallites and the tie-molecules will be somewhat extended. The separation into distinct regions is probably not as complete in rapidly quenched material. In these circumstances, the possible structure shown in Fig. 1.18(c) has a lower degree of localisation of order with an intimate mixture of crystallographically registered chain segments and disorganised chain segments. Thermomechanical influences on structure will be followed up in Chapters 18 and 20.

As with all synthetic fibres, the *degree of orientation* can vary over a wide range, depending on the conditions of drawing and relaxation during fibre manufacture. The tightness of structure, shown in Fig. 1.18, means that the crystallites must be locally well oriented in zones. There is electron diffraction evidence that the orientation is close to the fibre axis direction, but differs slightly in different zones [68]. Most of the disorientation will be in the disordered regions. Owing to the high flexibility of an aliphatic chain, with about two bonds per random link, the molecules will be fairly tightly coiled and entangled in the melt, so that the *molecular extent* will be small, though it may be elongated somewhat by intermolecular attractions. Drawing will lead to an increase in molecular extent, but will still leave appreciable chain folding either at the ends of crystals or among tie-molecules. The entanglements of the chains eventually lock the structure, which leads to rupture. There is a maximum draw ratio, which limits the degree of orientation and molecular extent. Further thermal processing under appropriate tensions will give more highly oriented, high-tenacity yarns, used in tyre cords and other industrial products.

The original process for making nylon fibres started with a polymerisation operation, which produced polymer chips. The chips were melted and extruded at 1000 m/min or less into a cooling zone and wind-up of a solid undrawn fibre. Some structure may persist in the melt or be imposed by the viscous forces in the thread-line. Once the thread cools sufficiently below its melting point, crystallisation starts from a few nuclei. The crystal growth rate would be relatively rapid, though slow in comparison with extrusion rates. If crystallisation were to continue at this temperature, a coarse spherulitic structure would result. But, in reality, rapid cooling inhibits the growth of spherulites and greatly increases the number of nuclei. The subsequent crystallisation on these nuclei, either in the threadline or on the package, will give rise to unoriented variants of the micellar or more uniform structures shown in Fig. 1.18. It is not uncommon for steam to be inserted at this stage to speed up the crystallisation on the nuclei. In the next operation, the structure is transformed by drawing, which causes a length increase of about four times, with a corresponding reduction in diameter. Drawing is a plastic (irrecoverable) process, which makes the oriented fibres suitable for use as textiles. The details of the structural changes in drawing are obscure, but must involve disruption of crystallites and re-formation in the oriented structures of the type shown in Fig. 1.18 and discussed above. At various stages during or subsequent



1.49 Crystal structure of polyester fibre (Terylene), viewed from side and above, and (right) configuration of molecules in the crystal [70].

to the formation operations, heat and mechanical treatments may cause further changes in structure. In some circumstances, occluded spherulites, which after drawing are ellipsoids, remain and have been used as a way of delustring nylon.

Since nylon was first manufactured, there has been an increasing continuity of processing. Direct polymerisation feeds molten polymer to extrusion and the unoriented solid fibre can be fed directly to the rollers that impose drawing. Usable fibre is produced in a single operation. The structural changes are not very different from what happens in a discontinuous process. High-speed spinning gives bigger differences. When fibre is wound up directly, without the drawing stage, there is an increase in orientation as wind-up speeds increase to 2000 m/min, and then a transition in structure formation between 2000 and 3000 m/min. Changes in crystal form, size and orientation in nylon 6 are described by Heuvel and Huisman [69].

1.7.3 Polyester (PET) fibres

Polyester fibres are very similar to polyamide fibres: both are made in the same way, by melt-spinning and drawing, from linear condensation polymers. The PET molecule contains two sorts of group. There is an aliphatic sequence, —$CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot CO$—, containing about the same number of chain links as the —CH_2— sequences in nylon; this aliphatic sequence would be flexible at room temperature and would give rise only to weak van der Waals interactions with neighbouring chains. The differences from polyamides are mostly due to the benzene ring. This will give some stiffness to the chain and, in particular, will impede deformation of disordered regions. Furthermore, there is an appreciable electronic interaction between neighbouring benzene rings, which gives intermolecular bonding with a function similar to the hydrogen bonding in polyamides. The crystal lattice of PET is shown in Fig. 1.49.

Two interesting comments on polymer constitution can be made in connection with polyesters. Firstly, aliphatic polyesters, which were originally studied by Carothers along with polyamides, are unsuitable for use as textile fibres. The influence of the benzene ring is needed to give firmness to the structure. Secondly, it is only when the benzene ring lies on the chain axis, because it is joined at opposite ends, that the molecular shape leads to close enough packing for easy crystallisation. If the ring is off axis, as in the chemically similar phthalate and isophthalate forms, with the ring joined at adjacent or next-but-one positions, then the shape impedes crystallisation.

PET does not crystallise as readily as nylon. The rapidly quenched, undrawn fibre from slow-speed spinning is amorphous. However, as the chains are pulled into alignment during drawing of the fibre, they lock into crystalline register. This can be demonstrated by the fact that, during drawing, the optical orientation factor, giving the overall orientation, increases continuously; but the X-ray diffraction orientation factor indicates axial orientation of the crystals as soon as the crystallisation is sufficient to give the diffraction pattern. The crystallinity of drawn fibre is about 50%. The crystallites are more elongated than in nylon, with a probable length/width ratio of 2 or more. Subject to the above comments, the structure of polyester fibres is micellar with chain folding or more uniform order/disorder, which is similar to that described for polyamide fibres and shown in Fig. 1.18.

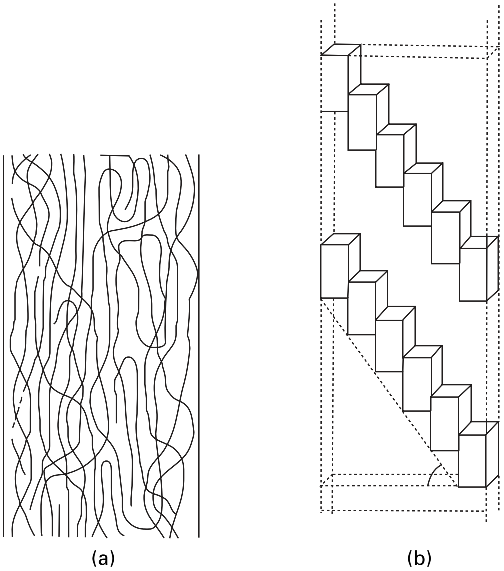
The engineering development of high-speed spinning had important consequences for polyester fibre production. The amorphous undrawn fibre is not very stable. Its structure changes with time, especially if ambient temperatures are high. Consequently, drawing must take place at a controlled time after wind-up of the undrawn fibre. As wind-up speeds increase, there is competition between the rate of orientation as the filament is elongated and the rate of relaxation of the molecules within the attenuated filament. Above about 3000 m/min, thread-line orientation is high enough to cause crystallisation on cooling. This enables the wind-up of a partially oriented yarn (POY), which is stable and suitable for supply to yarn texturing companies. The development of orientation is then completed by drawing due to the difference of input and output speeds on a draw-texturing machine. There is an economic advantage related to production rates in dividing the orientation process in this way. For untextured yarns, drawing of POY can be combined with other processes, such as warping.

As wind-up speeds are further increased, crystallinity increases. Above about 5000 m/min, it is possible to produce polyester yarns that can be used in textiles without further processing, though they are more extensible than conventional polyester yarns. Information on the effect of spinning speed on polyester fibre formation, structure and properties is given in a number of research studies by several authors in the book edited by Ziabicki and Kawai [71] The uncertainty about the structure of the melt-spun polyester fibres is illustrated by Fig. 1.50, which shows two views of a polyester fibre spun at 5000 m/min by different authors in this book. Admittedly, these were drawn to refer to particular ideas, but nevertheless they give very different impressions of the nature of the structure.

As with nylon, additional thermal processing gives more highly oriented, high-tenacity polyester yarns.

1.7.4 Other polyesters

Fibres can be made from polyesters with different numbers of —CH_2— groups. One now in commercial production is polytrimethylene terephthalate (PMT)[5] with three —CH_2— groups. The added flexibility of the molecule leads to properties more like those of nylon. A stiffer chain, which gives higher modulus fibres, occurs in polyethylene naphthalate (PEN), in which the benzene ring is replaced by the double naphthalate ring. These other polyester fibres are melt-spun and can be expected to have structures similar to those described for nylon and PET.



1.50 Two views of the structure of PET filaments spun at 5000 m/min, both from the same book: drawn by (a) Heuvel and Huisman [69] and (b) Shimizu *et al.* [71].

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[5] An alternative terminology refers to the number of —CH_2— groups: 2GT for PET, 3GT for PTT, etc.

1.7.5 Polyolefin fibres

Polyethylene is not a particularly good material for textile fibres[6]. For reasons that will be made clearer in Section 18.3.3, it is too soft and extensible. It does, however, have some usage. Polypropylene is more widely used.

Both these polymers have a fairly simple repeat, and there are not the alternating sequences of the polyamide and polyester fibres. Linear polyethylene (made by the low-pressure route, with Ziegler catalysts) readily takes up a very highly ordered form, of high density, equivalent to about 80% crystalline. This is probably best regarded as an assembly of lamellar crystals, separated by narrow crystal-defect zones. The older, branched polyethylene (made at high pressure) is somewhat less ordered.

Polypropylene, because of the side groups, cannot achieve as high a crystallinity as linear polyethylene. The bulky $—CH_3$ side group also causes polypropylene molecules to take up a helical form in the crystal lattice, with three repeats in one turn of the helix. The helical crystal lattice is rather easier to stretch than the extended-chain lattice of polyethylene.

Polypropylene demonstrates an interesting example of the need for regularity of structure to secure crystallisation in a polymer. During polymerisation, the successive $—CH_2{\cdot}CH(CH_3)—$ sequences can be added in either a right-handed or a left-handed screw direction, owing to the stereochemistry of the chain. If these forms occur at random, the chain will have an irregular shape, impossible to remove by subsequent manipulation, and will not crystallise. This is atactic polypropylene, which is unsuitable for making fibres. But, if units are added on in the same sense, to give the isotactic form, the molecule is regular and will crystallise. It was the discovery of a means of controlling the polymerisation that led to the production of isotactic polypropylene fibres. By causing some atactic sequences to be present, the degree of order can be reduced if necessary.

Another regular form, syndiotactic, has a regular alternation of right- and left-handed groups.

1.7.6 Polylactic acid (PLA) fibres

Polylactic acid, which is made from corn starch and not from oil, is a condensation polymer that is melt-spun into fibres. The structure can be expected to be similar to other melt-spun fibres.

1.7.7 Acrylic and related fibres

The acrylic fibres are very different from the melt-spun synthetic polymer fibres; they also differ more among themselves. The variations in the nature and means of incorporation of the minor component cause some differences; the nature of the method of production from solution, by either dry or wet spinning, causes others. But even pure polyacrylonitrile is rather unlike most other polymers.

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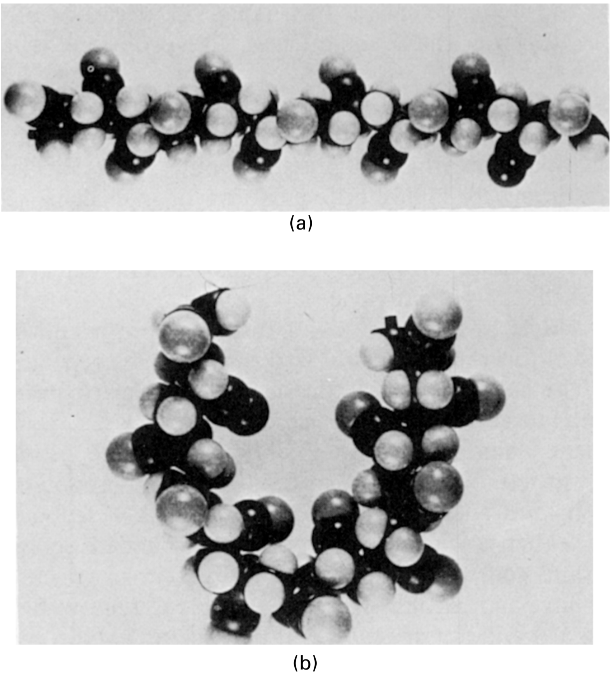
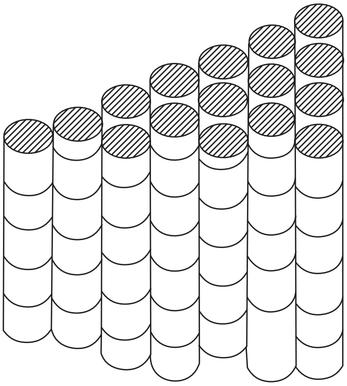
[6] High-modulus polyethylene (HMPE) is covered in the next section on high-performance fibres.

Figure 1.51(a) shows a model of the polyacrylonitrile molecule. Because of the influence of the —C≡N side group, it normally coils into a three-fold helix, to take up a cylindrical form, which, as indicated in Fig. 1.51(b), is only moderately flexible. The interactions between the —C≡N groups, while strong because of the electric dipoles, are not very specifically directed. As a result, the cylinders tend to pack together in a regular hexagonal array, like sticks of chalk in a box, but without being in register along their length. This is a pseudocrystalline order, illustrated in Fig. 1.52.



1.51 (a) Model of polyacrylonitrile molecule. (b) Bending of model.



1.52 Pseudo-crystalline packing of cylinders, typical of polyacrylonitrile.

Owing to the usual problem of sorting out long polymer chains, the highly ordered, pseudocrystalline material will make up only about half of the total material. In the other regions, there will be a more disordered structure, with the cylindrical chains crossing one another, though still held rather firmly together by the electrostatic forces. Internally, acrylic fibres have a coarse fibrillar form. This is due to the occurrence, early in the process of fibre formation, of voids containing solvent; the voids later collapse and are then drawn out during stretching of the fibre. The spongy solid incorporating the voids becomes the fibrillar network.

There are also modacrylic fibres with less acrylonitrile, usually about 50%, in the chain. Other vinyl and vinylidene copolymers are used for some fibres of limited use.

1.7.8 Elastomeric fibres

Coarse elastomeric fibres can be made from natural rubber. The structure is a network of flexible chains, which are cross-linked by covalent bonds in vulcanisation.

Spandex fibres, of which *Lycra* is a notable example, are more important. They are defined as having at least 85% of a segmented polyurethane. The molecules are alternating block copolymers of soft and hard segments. The soft segments, which make up 60–90% of the polymer, are randomly coiled aliphatic polyethers or co-polyesters; the hard segments are crystallisable aromatic di-isocyanates. The result is a fringed micelle structure. The low crystallinity means that the crystalline blocks can be randomly oriented and linked together by highly coiled, flexible tie-molecules. Alternatively, the association of hard segments can be regarded as providing domains that crosslink the elastomeric network.

1.7.9 Some gross features of synthetic-fibre structure

In general, synthetic fibres are lacking in large-scale structural features. There is evidence for the presence of a skin, or of a radial variation in structure, in some fibres.

Melt-spun synthetic fibres extruded through circular spinnerets have a circular cross-section. However, shaped spinnerets lead to shaped fibres, with the sharp forms of the spinneret somewhat rounded as the molten polymer in the thread-line reduces in surface area under the forces of surface tension, tending towards the circular form. Trilobal and multilobal fibres are typical examples.

In solution-spun fibres, loss of solvent after the formation of a skin can give other shapes. Acrylic fibres often have a dumb-bell shape.

A more striking form of gross structure occurs in bicomponent fibres. A variety of forms is possible. Two streams of polymer may be extruded together from the same spinneret: a side-by-side arrangement gives an asymmetric structure with built-in crimp; a radial arrangement gives a core–sheath form for surface character or bonding. Alternatively, small zones of a second polymer may be dispersed within the main polymer fibre.

Other inclusions, delustrant, pigments, anti-static conductors, and so on, may be added to synthetic fibres to give required properties.

1.8 High-performance fibres

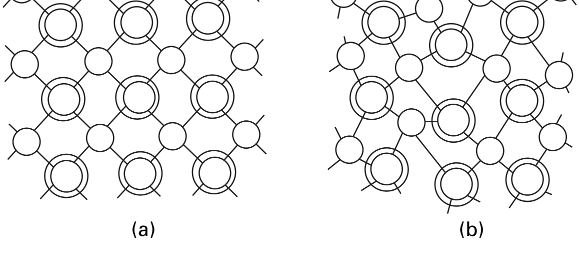
1.8.1 Fibres for engineering uses

In the final quarter of the 20th century, a new generation of manufactured fibres with high-performance properties were produced for engineering end uses. Their precursors were glass and asbestos fibres, though asbestos is no longer used for health and safety reasons. Unlike textile materials for clothing and household uses, which require a high fibre extensibility (in the range of 5–50% or, more often, 10–30%) and where strength is less important, so that moduli are relatively low, most of the textiles for engineering uses require maximum stiffness, usually accompanied by high strength. In addition to glass, which is on the borderline of general textile acceptability, the high-modulus, high-tenacity (HM–HT) fibres include: ceramics, such as alumina and silicon carbide; carbon or graphite fibres; and highly oriented polymeric fibres, such as the para-aramids, *Kevlar*, *Technora* and *Twaron*, other liquid-crystal polymer fibres, such as *Vectran*, PBO and M5, and the high-modulus polyethylenes *Spectra* and *Dyneema*.

There are also some HM–HT materials that are often referred to as fibres, but do not have the dimensions characteristic of textile fibres. Boron fibres and others made by vacuum deposition on a substrate are too thick; and single crystal whiskers are usually too thin and short. Both of these types may also be regarded as excluded from the textile category because of their extremely high cost.

1.8.2 Inorganic fibres

High mechanical and thermal resistance requires strong chemical bonding. In the ceramic fibres, this results from an array of covalent bonds in three dimensions, which holds the atoms together in the material. In the perfect crystal, the geometry will be a regular lattice, as represented schematically for a material such as silicon carbide, SiC, in Fig. 1.53(a). In fibre form, as single crystal whiskers, a particular direction will be aligned along the fibre axis. Commercial fibres, produced by heat treatment of a precursor, will not have such a regular structure. The most likely form



1.53 Schematic two-dimensional representation of the structure of a material such as silicon carbide: (a) crystalline; (b) amorphous. In the actual material, the atoms are distributed over three dimensions, to give a more complicated network.

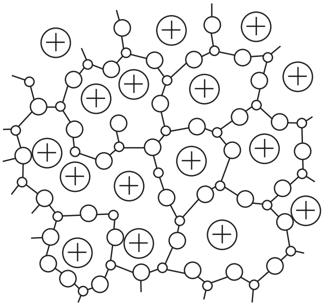
is a polycrystalline collection of variously oriented microcrystals. An alternative possibility is an amorphous structure, with distorted bonding between atoms, as illustrated in Fig. 1.53(b). It must be remembered that the real structures, whether crystalline or amorphous, are three dimensional, and the viewer must use imagination to transform the picture from the two-dimensional form, which is easier to represent. In silicon carbide, the geometry of the linkage is relatively simple, because both carbon and silicon have valencies of four, and so fit into a tetrahedral lattice with the C and Si atoms in equivalent positions. Oxide fibres, such as X_2O_3, are more complicated because of the valency differences.

The alumina fibre FP is reported to be almost pure polycrystalline α-Al_2O_3 with a grain size of about 0.5 µm [72]. *Nicalon* silicon carbide fibre is reported to contain ultra-fine β-SiC crystals [73].

Ceramic fibres may contain a mixture of components. For example, *Nicalon* may contain up to 30% of silica, SiO_2, and carbon; and *Nextel* is a 70/28/2 mixture of $Al_2O_3/SiO_2/B_2O_3$. *Tyranno* is a ceramic fibre composed of silicon, titanium, carbon and oxygen (Si-Ti-C-O), which is reported to have a non-crystalline microstructure [24]. A development from FP fibre, called PRD-166, consists of α-alumina with 20% of zirconia.

In glass, the amorphous bonded network of silica, SiO_2, is opened up by the presence of electrovalently bonded metal ions, which come from the metal oxides in the formulation. A schematic representation is shown in Fig. 1.54. The mechanical, chemical, thermal and electrical performance depends on the composition used in glass manufacture. For low-grade staple fibre, used, for example, as thermal insulation in buildings, this will be determined mainly by price, and the glass would be about 75% silica, the other main constituents being the oxides of sodium, Na_2O, and calcium, CaO. Continuous filaments for more demanding applications may be made of E-glass, containing only small amounts of alkali, Na_2O and K_2O, more CaO, and also oxides of boron, B_2O_3, aluminium, Al_2O_3, iron, Fe_2O_3, and magnesium, MgO. The high-strength S-2 glass is also a magnesium oxide, aluminosilicate type, low in alkali and high in magnesium [74].

Asbestos, although no longer used, is interesting in the way in which it forms fibres [75]. The crystal lattice is naturally curved and so bends round to form a



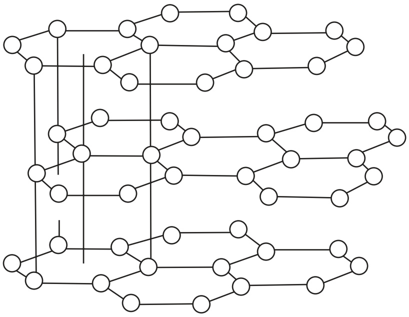
1.54 Schematic representation of the structure of glass, composed of silica, SiO_2 and metal oxides.

cylinder with a diameter in the chrysotile form of asbertos of 17.5 nm. Crystallisation can continue to a limited extent on inner and outer layers before the distortion becomes too great. Hollow cylindrical crystallites have peak diameters of 10 nm inside and 25 nm outside. When the rock is broken down, the resulting fibres are bundles of these cylindrical crystallites.

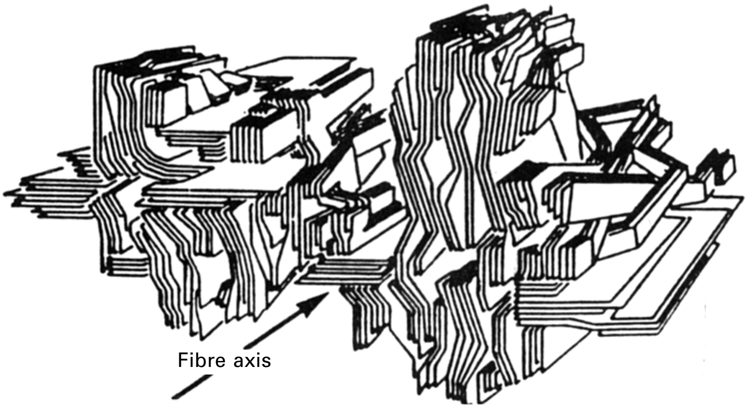
1.8.3 Carbon fibres

High-strength carbon fibres have a structure based on the graphite crystal lattice, shown in Fig. 1.55. This consists of two-dimensional sheets (planar polymer molecules) of carbon atoms, which are held together strongly by covalent bonds and are arranged in parallel layers, 0.335 nm apart, with much weaker van der Waals forces between the layers. In turbostratic graphite, the individual layers are not aligned but are irregularly rotated relative to one another, and the spacing between layers is increased to 0.344 nm. The perfect crystalline form of graphite very easily splits into microscopically thin sheets, which slide over one another in graphite lubricants.

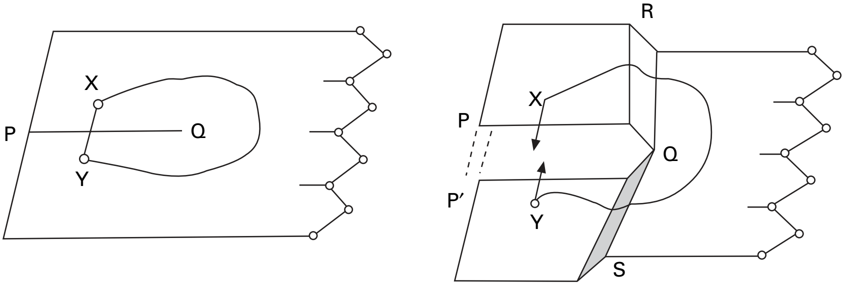
In carbon fibres, this degree of perfection is not achieved. Electron microscope examination of thin sections shows clear lattice fringe images, but also appreciable disorder [76]. The exact forms of structural disorder are not well understood, and carbon fibres from different precursors, or with different processing histories, will have different types and degrees of disorder. It is known that the orientation of the graphite sheets in high-strength and high-modulus carbon fibres is predominantly in planes parallel to the fibre axis, but with varying orientation in the direction perpendicular to the fibre axis. A schematic representation of the sort of complication that may be present is shown in Fig. 1.56, but many other variant sketches have been drawn. At a first level of comprehension, it is possible to imagine a structure composed of microcrystals of graphite, each perfect or turbostratic and oriented in a particular direction, but with the microcrystals differing in orientation in separate zones, which make up the total solid. The shapes and interconnections of the zones would be important structural parameters. At the next level, one can imagine distortion and curvature of the sheets as they pass through the structure. Different authors have drawn a variety of arrangements of whorls and interweaving of sheets and ribbons



1.55 Crystal lattice of graphite. Note staggering of layers indicated by vertical lines.



1.56 Schematic representation of the structure of a carbon fibre. Courtesy of D. J. Johnson [77].



(a) (b)

1.57 Possible interconnection defect in graphitic structure: (a) single sheet with two connecting routes between X and Y; (b) split of sheet along PQ, giving a connecting route outside Q but with the direct route on separate planes.

within the fibre, and the real forms will vary with the precursor and the process used to make the carbon fibre. The one common feature is that the planes are predominantly aligned with one direction parallel to the fibre axis.

The most important type of disorder may be at the level of molecular perfection. The carbon atoms in the intermediate low-strength carbon fibres, which are used as thermally resistant fibres, are much more irregularly bonded together, and the subsequent transformation to planar graphite molecules may not be complete. It is possible to imagine defects that connect graphite layers together. For example, instead of the perfect sheet of Fig. 1.57(a), there might be a cut along the line PQ, and lines of dislocations upwards along RQ and downwards along QS, as suggested in Fig. 1.57(b). Although molecular continuity remains between X and Y along a route outside Q, the direct connexion is to separate neighbouring layers containing P and P′. Such a defect would form part of a network of dislocations, with the total structure being an assembly of interconnected planar molecules, arranged with the planes parallel to the fibre axis.

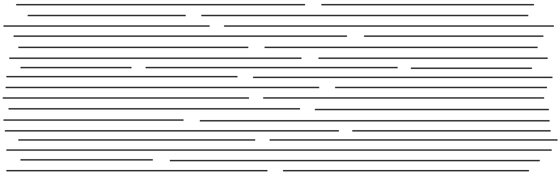
An ironical feature of the production of carbon fibres is that, although the ultimate goal of the heat treatment under tension appears to be the formation of a perfectly oriented structure of perfect sheets in order to maximise tensile strength and stiffness, such a perfect fibre would have serious faults in other ways. Some disorder is needed to hold the sheets together and optimise performance.

1.8.4 HM–HT polymer fibres

In order to achieve high stiffness and high strength in linear polymer fibres, it is necessary that the chains should be highly oriented and highly chain extended, as shown ideally in Fig. 1.58. This type of structure can be produced from polymers at the opposite ends of the spectrum. Very stiff chains with strong interactions easily self-assemble. Very flexible chains with weak interactions can be highly drawn. With polymers such as polyamides and polyesters, there is no self-assembly into the required form, and entanglements and interactions cause the fibre to break at lower draw-ratios.

The para-aramid fibres *Kevlar* and *Twaron* are manufactured by dry-jet wet spinning in which the extruded solution passes through an air-gap before entering a coagulation bath. They are composed of the aromatic polyamide, poly(p-phenylene terephthalamide) or PPTA:

This is a stiff molecule with strong interactions to neighbouring molecules, both at the benzene rings and by hydrogen bonding at the —CO·NH— groups. In solution, the self-attracting rod-like molecules form elongated liquid crystals, like logs in a stream. High shear at the point of fibre formation then lines up the crystals parallel to the fibre axis. The resulting fibre structure consists of fully extended chains, packed together with a very high degree of crystallinity and a very high orientation. There is some disorder, originating from boundaries between liquid crystals and imperfections of packing within crystals, and some departure from perfect orientation. Heat treatment under tension improves the structural perfection, and there are both less well-ordered, lower-modulus forms, such as *Kevlar* 29, and better-ordered, higher-modulus forms, such as *Kevlar* 49 and 149, on the market.

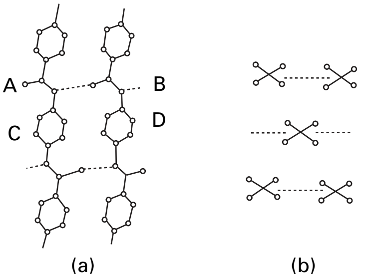


1.58 A diagram drawn by Staudinger [78] in 1932, which shows the ideal form for a linear polymer fibre with high strength and stiffness.

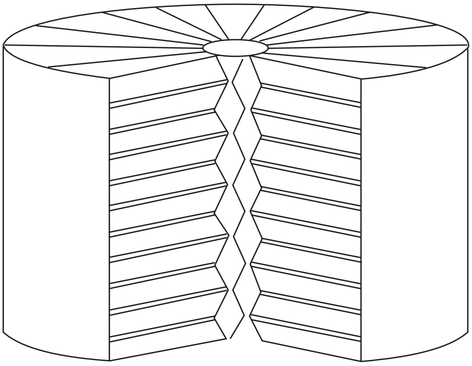
The crystal lattice of PPTA is illustrated in Fig. 1.59. Several features are noteworthy. Firstly, because of the alternation of ring and linear forms, it follows that the transverse planes, AB, containing the —CO—NH— groups have a lower density of covalent bonds than those containing rings, CD. Secondly, there are planes, shown in Fig. 1.59(a), in which neighbouring molecules are hydrogen bonded and thus more firmly held together than between the layers in the perpendicular direction, above and below the paper. This gives rise to anisotropy in the directions normal to the fibre axis, with the possibility of preferred orientation. The geometrical effects, as distinct from the intermolecular bonding, are less marked than they might be because the benzene rings in the acid and amine components are angled as shown in Fig. 1.59(b). At the level of fine structure, though the fibres are highly crystalline and highly oriented, there is an axial pleating of the crystalline sheets, which are radially oriented, as illustrated in Fig. 1.60.

There are a number of other HM-HT polymer fibres produced by dry-jet wet spinning with structures generally similar to that described above, but without the special feature of pleating.

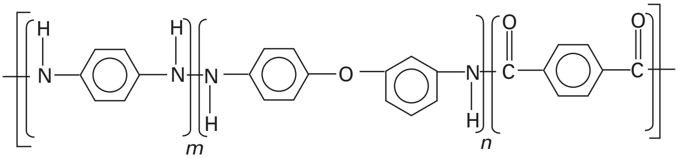
Technora [79] is an aromatic copolyamide with the chemical structure:



1.59 Molecular packing in PPTA crystal: (a) set of hydrogen bonds in a sheet; (b) view along the chains showing separate sheets and different directions of benzene rings.

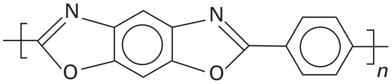


1.60 Radial pleated structure of a para-aramid fibre (Kevlar).

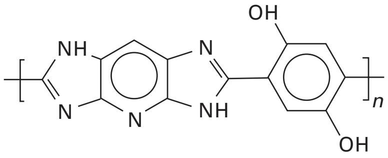


Unusually, *Technora* is spun from an isotropic, not a liquid-crystal, solution.

Poly(*p*-phenylene benzobisoxazole), usually referred to as polybenzoxazole or PBO, in *Zylon* fibres, is a stiffer molecule with triple rings in the chain:



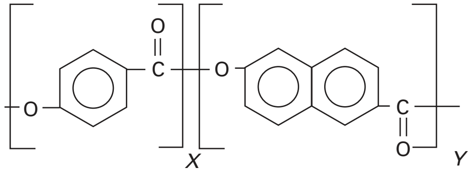
As mentioned above, PPTA has weak connections between planes and PBO similarly lacks strong interactions in all transverse directions. This led Sikkema [80] to synthesise poly {2,6-diimidazo[4,5-b:**4′**, **5′** –e]-pyridinylene-1,4(2,5-dihydroxy)phenyloene} (PIPD):



The hydroxyl groups lead to hydrogen bonding in all transverse directions, which improves shear and axial compression resistance in the 'M5' fibre.

Other variants of the stiff chain scenario were investigated by Perepelkin [81] in Russia. As mentioned above, cellulose fibres can also be produced by a similar liquid-crystal route [55].

All the above fibres are made from solutions in strong acids by dry-jet wet spinning. Fully aromatic polyesters are another type of stiff chain. With limited co-polymerisation, they form thermotropic liquid crystals, which can be melt-spun to produce highly oriented, chain-extended fibres. However, the molecular weight cannot be too high in melt-spinning, so that subsequent solid-state polymerisation is needed to give the chain length required for high performance, This offsets the economic benefit of melt-spinning. The commercial fibre of this type is *Vectran* [82], with the formula:



The alternative route towards the idealised structure shown in Fig. 1.58 is to use flexible molecules with weak interactions, which can be 'combed out' to give chains that are highly extended and highly oriented, and packed with a high crystalline order. Examples are the gel-spun, HMPE fibres *Dyneema* and *Spectra*, made from very high molecular weight polyethylene. The crystal lattice consists of extended chains of carbon atoms, with attached hydrogen atoms. This gives very efficient bonding along the polymer molecules, with a high density of covalent bonds across all planes, but very weak van der Waals bonding between chains.

Highly oriented fibres can also be made by super-drawing of melt-spun polyethylene fibres with lower molecular weight or by solid-state extrusion of high molecular weight polyethylene, but the strength is less than gel-spun fibres.

HM–HT fibres, which are perfect single crystals of linear polymer molecules, can be made by solid-state polymerisation of diacetylenes [83]. These are interesting academically in terms of their mechanical properties, because of their structural perfection and, more practically, for their electrical properties.

1.8.5 Gross features

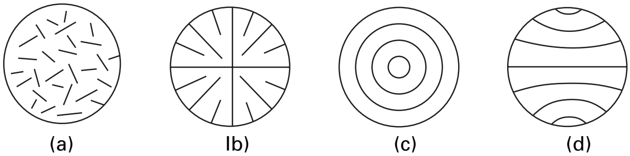
Larger-scale structural features, such as voids or packing differences, can result from the structure of precursor fibres or from effects in fibre manufacture. This is certainly true for carbon fibres, where there are differences among fibres made from acrylic, rayon and pitch precursors.

Where, as in carbon and para-aramid fibres, the crystal lattice contains sheets, there are varying possibilities of orientation in the plane perpendicular to the fibre axis, This may be random, radial, circumferential or across the fibre, as indicated in Fig. 1.61. Random arrangements are likely when there is no stress field generated by thermal or other shrinkage effects, but it is easy to envisage that stress can bias the structure into radial or circumferential arrangements. The form may not be the same over the whole cross-section; for example, there may be different orientations in core and sheath. The transverse arrangement of Fig. 1.61(d) develops in pitch-based carbon fibres.

1.9 Specialist fibres

1.9.1 Diverse functions

In addition to the common textile fibres and the high-performance fibres, there is now a great variety of fibres with special properties that match a wide range of specialist applications. These fibres are largely beyond the scope of this book, but they will be mentioned here with some comments on structure.



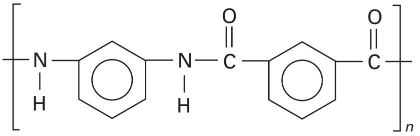
1.61 Orientation in the fibre cross-section: (a) random; (b) radial; (c) circumferential; (d) across the fibre.

1.9.2 Thermal and chemical resistance

Another engineering requirement is for high-temperature applications, which may be combined with good mechanical performance. The HM–HT ceramic and carbon fibres considered above have high thermal resistance. Glass and the polymer fibres, except HMPE, can be used for moderately high temperatures.

For other uses, moderate or poor mechanical performance is adequate. Some are weak and brittle fibres. For insulation, rock and slag wools, which are low-grade materials with a glassy structure, are used. Somewhat better textile properties are given by partially carbonised fibres, which can be made from acrylic or rayon precursors. The current commercial processes involve heat treatments of acrylic fibres, which are similar to the initial stages of carbon fibre production. The polyacrylonitrile molecule is first cyclised into a ladder-like chain, which is then oxidised. Further heat treatment displaces oxygen and nitrogen and develops three-dimensional bonding in the final black fibres. There are also three-dimensional networks in the thermoset resin fibres, *Basofil* from melamine–formaldehyde and *Kynol* from phenol–formaldehyde.

There are other applications, such as aircraft interiors and protective clothing, where good textile qualities are required as well as thermal resistance. The meta-aramid fibre *Nomex* is made of poly(*m*-phenylene terephthalamide):



The shape of the molecule prevents liquid-crystal formation, and the fibres have a partially oriented, partially crystalline structure, which is generally similar to that of other synthetic textile fibres, such as nylon and polyester. PBO, which is described above, has very high thermal stability and flame resistance. Fibres from other polymers, which include five-membered and benzene rings, but with shapes that give partially crystalline structures, are the aramid and poly(aramide-imide) fibres, such as *P84* and *Kermel* [84], and polybenzimidazole (PBI) [85].

Many of the fibres described above have good resistance to particular chemicals, but there are some fibres introduced particularly for chemical resistance [86]. They include polytetrafluoroethylene, *Teflon*, $(\text{—CF}_2\cdot\text{CF}_2\text{—})_n$, which also has good thermal resistance and low friction, and a number of chlorinated and fluorinated hydrocarbons. Other chemically resistant polymers are polyetheretherketone (PEEK), polyphenylenesulphide (PPS), and polyetherimide (PEI).

1.9.3 Fibres with other properties

Other types of fibre have the particular physical properties needed for special applications, but their details are outside the scope of this book. Non-woven fabrics of lead fibres are used for sound absorption. Metal threads, including *Lurex*, which sandwiches metal foil between plastic films, are used for decorative purposes. Optical fibres, either from glass or from transparent amorphous plastics, now have a major role in communication. Fibres for medical uses must have biological compatability and may be required to degrade after new growth of tissue. Hollow fibres are used for drug release.

'Smart fibres' [87, 88] have special electrical, magnetic, radiation-absorbing, diffusion, biological or other properties. They may be used as transducers, as wearable electronics, as actuators, or for thermal regulation and other adaptive responses. Some of these fibres depend on additives, such as carbon for electrical conduction. Others are made from particular polymers, such as the piezoelectric material, polyvinylidene fluoride, —$(CH_2 \cdot CF_2)_n$—.

1.10 Some concluding views

1.10.1 Levels of structure

The complexity of fibre structure, and of the means of achieving particular properties, comes in large measure from the number of levels of structure. To bring these various levels into relation, Table 1.8 indicates the dimensions of typical fibre features.

Wool is the extreme example of complexity, with structure at a large number of levels, as shown in Figs 1.42 and 1.43. Other fibres are less complex. At the level of fine structure, states intermediate between a perfect crystal and random disorder are difficult to define and often easy to manipulate into other forms.

1.10.2 Thermodynamic stability

The ultimate state of lowest free energy for most fibre-forming polymers would be a single crystal of extended polymer chains, but the barriers that stand in the way of reaching that state are insurmountable. The fibre states with which we are concerned are metastable states, with a local minimum of free energy. With all the possible arrangements of polymer chains, there are a vast number of local minima defining

Table 1.8 Dimensions of fibre features (approximate levels)

10 cm	
	Fibre lengths
1 cm	
1 mm	Spacing of crimps in wool
0.1 mm	Spacing of convolutions in cotton
10 µm	Fibre diameters
1 µm (10^{-4} cm)	Major structural features
	Molecular length
0.1 µm	Laminae
10 nm	Micro-fibrils
	Crystalline and non-crystalline regions
1 nm	Molecular width
1 Å (10^{-8} cm)	Atoms C,N,O H

different, reasonably stable, but metastable states. The minimum free-energy states are defined by many parameters, and could be regarded as represented by troughs in a multidimensional landscape. By the action of heat, stress and chemical changes, it is possible to shift from one metastable state to another. This is another reason for the complexity of fibre structure problems. It also has the effect that care needs to be taken in applying thermodynamics, because the thermodynamic equalities apply strictly only to reversible changes between true equilibrium states.

The situation can be illustrated by considering nylon fibres. On cooling from the melt, a partly crystalline structure will form, but important details of the structure, such as the extent of spherulitic material, will depend on the temperature at which crystallisation occurred because of its influence on the number of nuclei present. There is thus a collection of possible states of the undrawn fibre; storage may lead to further changes as thermal vibrations shake the structure down to a slightly lower energy state. Drawing causes a major rearrangement to another collection of metastable states. Subsequent heat-setting and mechanical treatments cause further changes. If the fibre has been partially or fully oriented by high-speed spinning, there will be other structures. In many important respects, these different metastable forms will have different properties; and thus the mode of formation and history of the fibre, which determine the fibre structure, in turn determine the physical properties of fibres and hence their practical utility.

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2
Testing and sampling

2.1 Test procedures

2.1.1 Evolution

The development of electronics in the middle of the 20th century and of digital processing at the end of the century led to major changes in the methods and instruments used for testing the physical properties of fibres. This is particularly important in the evolution of procedures for evaluating (classing or grading) natural fibres, which has gone through three main stages, though these are not totally distinct from one another.

At first, there was subjective evaluation by sellers and buyers viewing and handling the material. For cotton, this became somewhat more objective by skilled classers estimating fibre length on hand-stapled fibre tufts and comparing quality against sets of standard samples [1]. The cotton was described by terminology such as American middling, 5/16 inch (8 mm), with added information on colour and trash content. With the growth of fibre research in the first half of the 20th century, painstaking slow direct methods for measuring fibre dimensions were developed.

In the 1950s, there was a move to develop new test procedures, which were semi-automatic and gave objective measurements, even though these were not always directly related to specific fibre properties. Air-flow methods, which, for cotton, gave a *micronaire* value dependent on both fineness and maturity (fibre shape), are a typical example. These methods reflected the electromechanical and electronic technology of the time. After 1980, developments in robotics, sensors and computers enabled these methods to be combined with automatic handling, which fed samples through a series of tests. For cotton, HVI (high-volume instrumentation) is 'an integrated, automatic or semi-automatic system of cotton fibre measurement hardware, software and calibration for the rapid estimation of several fibre properties in a single sample' [2]. Typically, HVI covers micronaire, fibre length and length distribution, fibre bundle strength and elongation, colour (reflectance and yellowness), and trash content. One HVI line can test over 800 samples for length, length uniformity, short fibre content, strength, extension, micronaire and colour in a single shift [3]. Another method in current use is the Uster Advanced Fibre Information System (AFIS), which reports length and length distribution, fineness and maturity, neps, trash and dust. A 0.5 gram sample is hand-drawn into a 25 cm sliver. The results are influenced by operator technique and a test takes 3 minutes, so that the method is not suitable for routine commercial testing, but can be used in laboratory testing [4].

By the end of the century, the IT revolution had led to further advances in digital imaging and information processing. New methods, which were faster and gave more direct information on fibre dimensions, have been introduced. As the 21st century continues, these methods are likely to replace older methods. Because the move to *sale-by-specification* came later to wool than to cotton and because the fineness of the near-circular fibres was the major defining quality parameter, digital techniques, such as the CSIRO *Laserscan* and the OFDA technology described in the next chapter, have been adopted sooner.

The commercial practices are designed to provide sufficient information at minimum cost. The test methods for dimensions, strength and other properties will be described in later chapters. It is beyond the scope of this book to give full instructions on test methods, but the basic principles will be presented. Further information on procedures can be obtained in publications of the International Committee for Cotton Test Methods, the International Wool Textile Organisation, and national and international standards. A selection of these standards is included in Appendix III.

2.1.2 Material for testing

For research purposes, individual fibres can be selected and mounted for examination or testing. However, each operation is time-consuming and, with the variability of natural fibres, a very large number of fibres must be examined to get statistically useful results. In order to get the benefit of automated high-speed testing, provision of the test sample is as challenging a problem as the test method itself. After the initial preparation of a suitably aligned tuft of material, a way must be found of selecting a representative selection of the fibres. For transverse dimensions, this has been solved by cutting snippets, which can be dispersed on a slide for microscopic examination. For fibre length measurement and for tensile testing, the problem is more difficult and tufts of fibres are examined. The data may then need processing to obtain the required information.

Account must also be taken of variability in fibre dimensions and physical properties, which means that appropriate sampling procedures from the bale or other source are needed, particularly for natural fibres.

2.2 Variability and sampling

2.2.1 Quality control in manufactured fibres

With a few exceptions, such as melt-blown non-wovens and stretch-broken tows, manufactured fibres are made to controlled specifications. Chemical composition and manufacturing operations are controlled to give constant dimensions and physical properties. Standard deviations are small, though they may be significant. The scientific researcher has no difficulty in taking test samples from a package. However, it is important to specify the source and designation. One manufacturer's nylon or polyester is not the same as another's.

Nevertheless, faults can occur in manufacturing, so that quality control is needed to maintain standards. This can be done by a programme of sampling production at intervals and sending material to the test laboratory. However, there is an increasing use of on-line testing.

2.2.2 Natural fibres

For natural fibres, the situation is different. There is always appreciable variability and often great variability. Even the product of a single farm in a single season will show variations along fibres, between fibres in a cotton boll or a lock of wool, between neighbouring bolls on a cotton plant or parts of a fleece, and between different plants or animals. A typical example of variability in a consignment of cotton is shown in Table 2.1. Sources of variation are discussed by Steadman [6]. There are similar variations in other natural fibres.

The value of a source of fibre depends on the dimensions and other qualities, which have to be evaluated. There have been major changes since the mid-20th century and the evolution from subjective to objective assessment is described in Section 2.1. However, sampling is always necessary. As an example, before about 1960 the commercial procedure was for skilled buyers to view wool in bales, which had been opened up in a wool-broker's store before an auction [7]. Although the whole lot was available to them, inevitably the buyers only looked at small portions of opened bales. This was subjective sampling. Now, representative *grab samples* are displayed in viewing boxes and *core samples*, produced by punching a sharp tube into the bale, are sent to a test-house for objective testing. In the cotton industry, samples of cotton were taken from the bale after ginning for cotton classing. This procedure is still widely used, but there is a move towards samples being taken for objective testing [4]. For sampling at a later stage, Steadman [6] comments: 'As cotton is the most homogeneous of the natural fibres, when the fibre reaches the mill the usual practice is simply to cut off a sample from each side of the bale and discard the cut edges.' For routine evaluation of the wool and cotton crop, speed and cheapness of sampling are important factors, provided the information generated is adequate to determine price and expected performance. For research studies, more care may be

Table 2.1 Coefficient of variation (%) in a consignment of cotton [5.0].

Property	Between bales	Within bales
Micronaire	14.2	2.6
Upper half mean length	1.3	1.1
Strength	4.6	4.6
Extensibility	5.7	6.2
Reflectance	1.1	4.4
Yellowness	5.7	4.9
Colour grade	34	41
Trash area	99	112
Short fibre content	15.5	15

needed to obtain representative samples for detailed testing, which may be used to calibrate or validate quicker test methods or for scientific investigations.

With little alteration, the account written by W. E. Morton for the 1st and 2nd editions of this book brings out the principles and problems of sampling. Practical information on sampling is given by Saville [8].

2.2.3 Sampling requirements

Practically every measurement made on textile materials must of necessity be restricted to only a small fraction of the bulk. Where testing is carried out for commercial purposes, and especially when it is destructive, as in strength-testing, the reason for this is obvious, but in the general case the bulk is nearly always so large that to test it completely would be quite impracticable, even if any material advantage were to be gained by doing so. It is therefore almost invariably the practice to measure a sample only.

Whether and how far the results obtained from a sample may be relied upon to characterise the bulk, or, in statistical parlance, the ‘population’, from which it is drawn, depends on two things: the size of the sample and the manner in which it is taken.

As regards the size of the sample, little need be said here. Naturally, the larger the sample, i.e. the greater the number of individuals it contains, the more closely do the results obtained from it agree with those which would be obtained from the entire population. How large the sample should be to raise the confidence in the results to any desired level can be readily determined by the application of elementary statistical method. All that is needed is an estimate of the variability of the character measured, and this may be obtained from the sample itself or assumed as a result of past experience[1]. Unfortunately, the properties of textile materials are generally characterised by such great variability that samples must nearly always be relatively large if useful reliability is to be assured. Except in special circumstances, which will be noted later, no matter how large a sample may be, it is useless unless it is also representative.

In any attempt to take a truly representative sample, or what is termed a ‘numerical’ sample, the guiding principle is simple to state: the technique should be such that every individual in the parent population has the same chance of being included in the sample. It is not so simple, however, to follow this precept in practice. The requirement would be met completely if we were free to take, absolutely at random and without conscious selection, any individual whatsoever, regardless of where it is to be found in the population. In fact, our freedom to do this is commonly limited, and sometimes severely limited, either by the amount of labour that would be involved or because of other, and even more practical, considerations. In commercial yarn- and cloth-testing, for example, a perfectly random sample is never possible because the bulk to be characterised would be spoilt by the taking of the individuals. The sampling of fibrous raw materials in bulk form may also suffer from limitations of a

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[1] Useful data are included in BS EN 12751:1999.

similar kind, though not so acutely. In all cases where such limitations apply, it must be recognised that, to the extent that a sample is not a perfectly random one, so will the results from it be less reliable than as indicated by the experimentally determined standard errors.

In fibre testing, however, uncertainty arising from restrictions on random selection can generally be reduced to small proportions without much difficulty. On the other hand, unless special precautions are taken, a much greater source of error may be introduced, which arises from the essential nature of a fibre, namely, that it is very much longer than it is thick. Because of this, it is only too easy to take a sample in such a way that it contains far more long fibres than it should; this is true whatever form the population of fibres may take, whether bale, top, roving, yarn or cloth. The nature and avoidance of this bias in favour of the longer fibres will be discussed in succeeding sections, but at this point two observations should be made.

The first is that length bias is not only of importance when fibre length is the quantity to be measured. It is also important when the test is for any fibre property associated with length. Thus with wool, for example, where there is a strong correlation between fibre length and fibre diameter, any sample biased in favour of length will also be biased in favour of coarseness. Again, in cotton, bias for length may be accompanied by a bias for strength [9] (see Section 13.5.2).

The second is that there are some circumstances in which the taking of a biased sample is convenient and desirable, or even essential. In such cases, it almost goes without saying that the quantitative nature of the bias must be known. If not, the results of any measurements made can never tell us anything useful about the population we desire to characterise. For the relation between biased and numerical samples to be known, certain conditions must be satisfied. These will be discussed in the sections that follow.

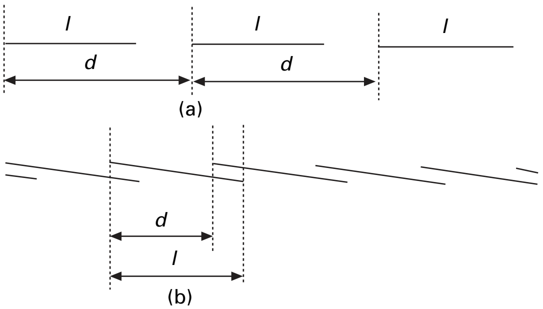
2.3 Numerical and biased samples

2.3.1 Numerical proportions

Consider first a highly idealised, homogeneous strand of overlapping straight, and parallel fibres. Since it is homogeneous, its composition is the same at all parts along its length. There are no concentrations of long fibres in some parts or short fibres in others; the short fibres are spread out evenly throughout its length, and so also are the long fibres or fibres of any other designated length. The different lengths of fibres present may, in fact, be mixed thoroughly together, but no invalid assumptions are involved if, for our present purpose, we imagine the strand to be made up of a large number of superimposed streams of fibres, each stream consisting of fibres all of a particular length.

If we take any one of these streams characterised by a length l, then, since the fibres composing it are spread out evenly, the displacement of one with respect to the next is constant, as shown in Fig. 2.1.

Let the displacement be denoted by d, the number of fibres in the stream by n, and the length of the strand by L. If n is small, then d is large compared with l and there are gaps between the individuals, as at (a). If, on the other hand, n is large enough,



2.1 Fibre displacement.

d is less than l and there is overlapping, as shown at (b). In either event and in the general case, the number of whole fibres in any stream is given by:

$$n = \frac{L}{d} \tag{2.1}$$

Let the quantities referring to the several streams be denoted by the suffixes 1, 2, 3 … etc. Then the total number of fibres in the complete strand is:

$$n_1 + n_2 + n_3 + \ldots = \Sigma n$$

and the numbers of fibres in the several streams, expressed as fractions of the total for the strand, are

$$\frac{n_1}{\Sigma_n}; \frac{n_2}{\Sigma_n}; \frac{n_3}{\Sigma_n}; \ldots \tag{2.2}$$

This, then, is the pattern of the numerical proportions (frequencies) of the various fibre lengths present in the strand as a whole.

2.3.2 Length bias

In taking a sample from such a strand, the most natural procedure would be to take a pair of tweezers and pick out a few fibres here and there at random all over the strand until a sample of sufficient size has been obtained. Let us examine the consequences of such action.

Consider first the stream of fibres at (a). Since the points of the tweezers are applied entirely at random, it is by no means certain that any fibre at all will be taken from the stream. The probability of one being taken at each attempt is obviously l/d. If k attempts are made, then in the long run of experience the number taken will be $kl/d = knl/L$, since $n = L/d$, from equation (2.1).

Consider next the stream at (b). The probability of taking a fibre here is greater than 1, i.e. at least one will be taken every time and sometimes two. If $l = 2d$, it is a certainty that two would be taken every time. Thus, in k attempts, the number taken is still $kl/d = knl/L$. This relationship, in fact, holds good whatever the values of l or d, and the numbers of fibres taken from the various streams are:

$$\frac{kn_1l_1}{L}; \frac{kn_2l_2}{L}; \frac{kn_3 3}{L}; \ldots \tag{2.3}$$

or, expressed as fractions of the number of fibres in the entire sample:

$$\frac{n_1l_1}{\Sigma nl}; \frac{n_2l_2}{\Sigma nl}; \frac{n_3l_3}{\Sigma nl}; \ldots \tag{2.4}$$

It is thus seen that, in the sample, the proportionate frequency of occurrence of fibres of any particular length is determined, not only by n, the number of them occurring in the strand as a whole, but also by how long they are. For example, if equal numbers of 50 mm and 25 mm fibres are present in the strand, the 50 mm fibres will be twice as numerous in the sample as the 25 mm fibres. Every fibre does not have an equal chance of being included in the sample, and we have not, therefore, obtained a representative, or numerical, sample. What we have instead is a length-biased sample, sometimes referred to as a Wilkinson tuft [10, 11].

2.3.3 Frequencies, length proportions and mass proportions

It will be noted that the quantities, n_1l_1, n_2l_2, n_3l_3, etc., give the total lengths of fibre of lengths, l_1, l_2, l_3, etc., respectively, in a numerical sample and that Σnl is the total length of fibre in a numerical sample as a whole. Thus the terms in equation (2.4) above, which represent the *frequencies* in a length-biased sample, also represent the proportions by length, or *length proportions*, in a numerical sample.

Furthermore, if the fibre mass per unit length is the same for all lengths, length proportions are equivalent to mass proportions (often referred to as weight proportions). Hence, under these conditions, the frequencies in a length-biased sample are also equivalent to the mass proportions in a numerical sample.

In practice, there are some circumstances in which the proportions by length or the proportions by mass are the quantities in which we are really interested, for example, in studies of fibre breakage in carding or of length fractionating in combing. In such cases, if a numerical sample is taken, the desired quantities must be calculated from the frequencies by multiplying the latter by the corresponding lengths. If, on the other hand, a length-biased sample is taken, the frequencies obtained from it give the desired quantities directly.

Length-biased samples have their uses also in other contexts. For example, suppose that we wish to determine the mean diameter of a sample of wool by a method in which the diameter is measured at one point only on each fibre examined. If the sample taken were a numerical one, long fibres would be given no greater weight than short fibres, and, the relation between length and fineness of wool being what it is, the resultant mean would be too low. Clearly, in such a case, the results should be weighted for length, and the only way of doing this is to work with a length-biased sample. It cannot be too strongly emphasised, however, that, in taking a sample of this kind, the population to be sampled must consist of fibres that are straight and parallel: otherwise the bias, or weighting, for length is indeterminate (see Section 3.5). Length-biased sampling is therefore only practicable when the material to be examined is in the form of well-drawn slivers, tops, rovings or yarns.

2.3.4 Tong sampling for length bias

In the procedure already described, which resulted in a length-biased sample, it will have been noted that, at each application of the tweezers, only those fibres were taken that *passed through a cross-sectional area* of the strand, the section being that normal to the fibres and lying in the plane between the points of the tweezers. This basic principle of sampling for length bias is utilised in the tong-sampling method [12], where two pairs of narrow clamps or surgical tongs with leather-lined jaws are used for defining the section.

A portion of the top, sliver, roving or yarn is clamped at right angles by one pair of tongs, and the fibres at one side are combed so as to remove those not gripped. The resulting combed tuft projecting from the side of the tongs is now clamped by the second pair of tongs, which are placed parallel to, and in contact with, the first pair. The first pair is then removed and the fibres not gripped by the second pair combed out on the side not hitherto combed. The fibres retained in the second pair are thus all those that crossed a plane perpendicular to the length of the sliver, and these constitute the sample.

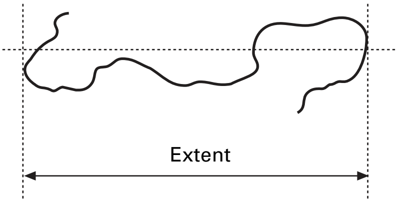
This method has been found satisfactory for wool materials [13], but according to Hertel [14] it is not very suitable for cotton because fibre breakage is excessive if the combing is to be effective.

2.3.5 Extent bias

In the foregoing, we have considered only the special case where all the fibres are assumed to lie straight and parallel in the strand, and where those fibres are taken that pass through a plane at right angles to the axis of the strand. In card webs and card slivers, and especially in bulk samples of unprocessed raw materials, however, the arrangement of the fibres is anything but regular. The fibres may be crimped and distorted, they may be bent over into a hooked form at one or both ends, and they may vary very greatly in their orientation. Even in uncombed, but otherwise well-drafted, slivers, perfect straightness and orientation of the fibres cannot be assumed with certainty. It is, therefore, necessary to introduce the notion of *fibre extent*.

Fibre extent may be defined as the length of the projection of a fibre on any chosen axis of orientation. With slivers, rovings and yarns, the direction in which extent is measured is usually parallel to the axis of the strand. With card webs, it is usually parallel to the card sides. With samples of loose raw materials, it may be anything one chooses. As will be clear from Fig. 2.2, the extremities of the projection are not necessarily determined by the ends of the fibre under consideration.

Under conditions such as these, if fibres are taken which pass through a given cross-section, the sample is biased for extent, and, unless the ratio of fibre extent to fibre length is constant for all fibres, the degree of bias is indeterminate. Apart from bast and leaf fibres, nearly all fibres are crimped in some degree, and it could thus be argued that, in practice, a length-biased sample is an impossibility. However, provided that the population to be sampled is not a blend of materials having different crimp characteristics, and provided that, except for the crimp, the fibres are straight, the



2.2 Fibre extent.

extent/length ratio can be assumed to be constant. Under any other conditions, an extent-biased sample is of no use whatever.

2.3.6 Avoidance of extent bias

The object is to take fibres of the different lengths present in numerical proportions determined solely by their several frequencies of occurrence in the entire population.

We have seen from equation (2.1) that, in a strand of length L, the number of fibres n of any length l is inversely proportional to d. What we have to ensure is that this also holds good for the sample.

From Fig. 2.1, it is evident that the probability of any chosen *point* on a fibre occurring within any short length δL of the strand is strictly proportional to the ratio $\delta L/d$. If, then, we take one or other of the fibre ends as our chosen point, we see that the solution of our problem is to take *all fibres that terminate within a given volume*, i.e. within any chosen length δL of the strand, since δL is the same for all fibres.

The size of the sample taken depends on what we choose for our δL, but the composition of the sample reflects truly, on a reduced scale, the composition of the entire population, and we have an unbiased sample. Selection is made according to the occurrence of fibre ends, of which every fibre has two, whatever its length. Length therefore plays no part in the selection. This remains true whether we are dealing with fibres that are straight or fibres that are crimped and disarranged, as is clearly demonstrated in Section 2.4.2.

2.4 Sampling techniques

2.4.1 Squaring and cut-squaring

Squaring and cut-squaring are two related methods that are applicable to slivers, rovings or yarns in which the fibres are in a reasonably ordered state and give a numerical sample. In what follows, it will be assumed that the material to be sampled is in the form of a sliver.

In the simplest form of this operation [15], the sliver is opened out, without disturbing the fibres, into a flat ribbon, and one end is roughly squared by hand. It is then placed on a black velvet-covered board, and a sheet of glass, of suitable size and weight, is laid on top of it, leaving a short fringe projecting. The projecting fibres are now removed in *small* groups with tweezers until the edge of the glass is reached, whereupon the glass plate is moved back a short distance to expose a new fringe, which is similarly treated. This is repeated until a succession of fringes have been squared back a distance at least equal to the length of the longest fibre present. Only then is the actual sample taken for measurement by moving the plate back a further short distance and withdrawing *all* the fibres that now project beyond its edge. These fibres are those that terminated in a given volume and so constitute an unbiased sample provided that the precautions mentioned are observed.

The succession of preparatory squarings, before the sample is taken, is absolutely essential because the fringe formed at the broken edge of any fibrous strand naturally contains a predominance of longer fibres, and this initial bias can be eliminated only in the manner described.

The pressure of the glass plate on the velvet board effectively controls the fibres during squaring and during the taking of the sample, while the thickness of the glass can be chosen so as to give optimum control without breakage. Since the control is by friction, and not by positive grip, looped and even slightly tangled fibres can be withdrawn, though, with cotton fibres at least, the possibility of the breakage of some fibres is always present.

In the withdrawal of fibres from the fringes, long or somewhat tangled fibres sometimes drag out with them other fibres initially lying wholly behind the edge of the glass. This is minimised by drawing the fibres almost singly, but, in any case, no bias is introduced provided this form of disturbance occurs equally in the final drawing of the sample as during the preparatory squarings. Hence the manner of withdrawal must be the same at all stages, and so also must the distance by which the plate is moved. The latter, of course, determines the size of the sample taken.

Cut-squaring is a modification of the squaring technique, designed to minimise the labour of preparatory squaring [12, 15]. Here the strand is cut to a straight edge instead of being broken and is then covered with a glass plate, as before. In theory, only one preparatory squaring of the fringe is now necessary because all the cut fibres are removed at this one stage, and the fibres whose ends project beyond the glass, when next moved back a short distance, should constitute a numerical sample. It has been shown [16], however, that in practice this is not the case and that a series of at least three preparatory squarings is necessary. The reason for this is probably to be found in the fact that the conditions under which the cut fibres are withdrawn in the first stage are not the same as those prevailing when the fibres forming the second fringe are extracted to form the sample. In the first stage, the fringe is dense, and it is inevitable that the fibres must be drawn in rather large bunches, thus giving rise to a greater degree of fibre disturbance than when the much thinner second fringe is dealt with. Hence errors due to disturbance during the taking of the sample are not cancelled out by corresponding errors during the preparatory squaring. In general, short fibres are the ones that are most easily dragged forward out of turn, and consequently, with only one preparatory ‘fringing’, the observed mean length is too high, the sample being deficient in short fibres.

The reason why *all* projecting fibres in the final fringe must be taken is that, if any attempt at random selection is made, bias is almost certain to be introduced by an unconscious preference for thick fibres. Thickness may be, and with wool certainly is, correlated with length.

2.4.2 Dye-sampling

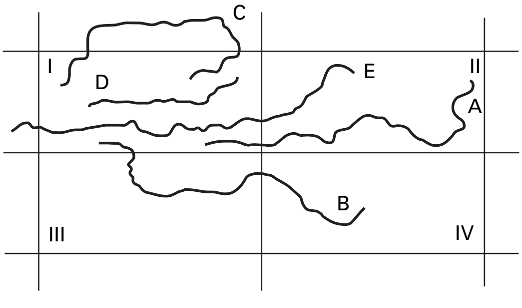
This method was evolved [16] primarily for the sampling of wool fibres in the form of card web with the object of reducing to negligible proportions the risk of fibre breakage, which is considerable if a card sliver is sampled by the squaring method. In general, it is applicable only to thin layers of fibre, as in card or comber webs, or to tops or slivers that can be opened out into thin-web form.

As required for the taking of a numerical sample, the fibres are to be identified by the occurrence of their ends in a given volume. Accordingly, the web is coloured over a small rectangular area by means of a brass or wooden block covered on one face with filter paper uniformly wetted with a suitable dye. Fibres passing through the coloured patch, and therefore having undyed ends, are neglected. Those terminating within the patch, and thus having one or both ends stained, are taken as the sample. The only proviso is that, in the final computations, fibres having only one end stained should be accorded half the weight of those having both ends stained. Thus the lengths of those with one end dyed and with two ends dyed are recorded separately. The true fibre-length distribution is then given by adding half the number of one-enders to the number of two-enders in each length group.

The necessity for this is readily seen by noting the requirement that taking fibres from the stained patch should not alter the composition of any possible adjoining patch. Let rectangle I in Fig. 2.3 be the dyed patch. Fibre E has neither end stained and is neglected. Taking A and B for patch I deprives patches II and IV of fibres to which they have an equal claim. Fibres C and D, on the other hand, cannot be claimed by any other patch, and hence, if these are given a weight of unity, A and B must each be counted as half-fibres.

There is an optimum size and shape of patch for each material to be sampled. If the patch is too small, or too long and narrow and placed transversely to the general orientation of the fibres, a large number of them pass right through the defined area and have to be handled even though they do not contribute to the sample. There is thus waste of time and effort.

For wool card webs, a patch 1.5 cm square is recommended [13], but for shorter fibres a somewhat smaller area would probably be more suitable. As regards shape, there are some circumstances in which the patch should preferably be oblong and lie



2.3 Dye-sampling.

along the direction of general fibre orientation. The more oriented the fibres, the longer and thinner the oblong should be [16].

In taking the fibres for measurement, the portion of web containing the dyed patch (when dry) is covered with a microscope slide, which has rounded edges. The fibres are then removed with forceps by drawing them one by one from under the slide, which the operator is free to move about at his or her convenience. It will be observed that the method is only suitable in cases in which the fibres are to be measured individually.

2.5 Zoning

2.5.1 The problem of heterogeneity

An individual sample obtained by any of the methods so far described represents the population under examination only if the composition of the population is the same at every point. In fact, this is very rarely, if ever, true of textile populations, and, in the absence of definite knowledge to the contrary, it should be assumed that the population is heterogeneous, i.e. that its composition varies from one part to another. This being the case, a sample draw taken from any one part must be regarded as no more than a sub-sample; the sample representative of the entire population should consist of several such sub-samples taken at random from different parts in such a way that all the elements of heterogeneity are represented in due proportion. Such an operation is referred to as zoning.

The extent to which a population must be zoned depends, of course, on how and to what extent it varies in composition from place to place, which must be found from experiment if it is not known from experience. Considering the sampling technique as a whole, including zoning, the method adopted should satisfy the requirement that replicate samples should all yield results between which the differences are statistically insignificant.

Quoting from a standard:

> When carried to the limit, zoning consists in taking the required number of individuals singly from the same number of selected parts or zones. Due representation with any desired degree of accuracy is then obtained with the minimum number of individuals. However, the saving in time secured by reducing to a minimum the number of measurements that have to be made may be more than offset by the extra time required to prepare the extra zones.

If the between-zone variance is small by comparison with the within-zone variance,

> it is common practice to take a relatively large number of individuals from a relatively small number of zones, even if in so doing it is necessary to maintain the accuracy by taking a rather larger number of individuals all told [17].

Sampling from slivers, rovings and yarns is comparatively simple because the fibres have been fairly well mixed in the processes through which they have passed, and the material is reasonably homogeneous. Zoning on a modest scale is therefore all that is required. In dealing with masses of fibre in a loose state, however, it is quite otherwise, and, furthermore, special difficulties are encountered.

2.5.2 Sampling from raw materials in a loose state

Ideally, as already indicated, the required number of fibres should be taken one at a time from a corresponding number of places distributed at random all over the bale, bag or whatever other form the population assumes. This, of course, would be impracticable because of the amount of labour involved. Of greater importance is the fact that it would be impossible in this way to obtain a sample free from extent bias. The reason is that each fibre would have to be extracted with tweezers and would therefore be a fibre passing through a selected cross-sectional area.

The same objection would still hold good if a wisp of, say, ten or a dozen fibres at a time were taken. Extent bias can, in fact, only be avoided if we take, not small wisps, but quite large tufts of fibre from each zone. Preferably, these tufts should be natural units. In cotton, for example, they might be discrete clusters of fibre from single seeds, while in wool they might be natural locks.

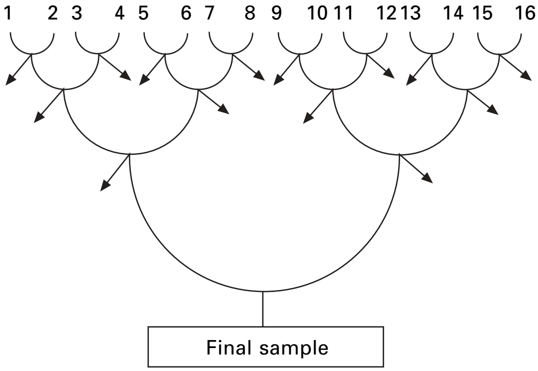
In any event, if zoning is to be carried out on any reasonable scale commensurate with the heterogeneity present, we are faced with an initial sample of very considerable size, in most cases, far greater than can be used for subsequent measurement. For some purposes, the final sample has to be of 1000 fibres or fewer, a mere fraction of the quantity, for instance, that is to be found on a single cotton seed. If m tufts have been taken, averaging w grams each, then somehow the whole mw grams of material must be reduced in size so that the final sample of the required size contains, in due proportion, representative fibres from all the original m tufts.

One method is to proceed by a process of successive halvings. Each of the m tufts is divided into two approximately equal parts, care being taken to avoid fibre breakage, and one half discarded. The retained half is again divided into two and one half discarded. This is repeated until the remnants of all the tufts taken together provide a sample of the required size.

If the fibres in the portions being divided are substantially parallel, the portions should be split lengthwise. This is important because, if the projecting fibres at the two ends of such a tuft are held, and the tuft is drawn into two parts by separating the hands, it is almost certain that one part will be greater than the other. The smaller part will be deficient in short fibres, and the larger in long; whichever part is discarded, that remaining will no longer represent the original tuft. The plane of cleavage should therefore be parallel to the fibres.

In order to reduce still further the possibility of introducing any systematic bias, it was at one time thought desirable that the choice of which half should be discarded should be made at random, but in practice this is not easy to do. An alternative procedure therefore commonly employed is to discard with the right hand and left hand alternately [18]. However, so long as lengthwise splitting is resorted to when conditions require it, the question is probably unimportant.

A somewhat different procedure, suitable for manufactured staple fibres, is as follows. The initial sample obtained by zoning is formed into 16 tufts, and, by a



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process of doubling, drawing, halving and discarding, these are reduced to the representative sample for measurement as indicated in Fig. 2.4. Here, the tufts are taken in pairs and repeatedly drafted by hand and recombined before being divided into two parts. Since the fibres are thereby not only thoroughly mixed together but also effectively parallelised, lengthwise splitting is essential.

For cotton and other fibres of similar length, mechanical blenders are available, capable of reducing an aggregation of zonal tufts to a homogeneous batt or sliver from which the final test sample can be taken by any of the methods appropriate to material in that form.

The earliest of such mechanical devices was the Balls drawbox [19], a miniature drawframe consisting of two pairs of rollers and a special collecting device. A zoned sample weighing about 0·5 g is roughly formed by hand into a sliver about 20 cm long. This is then drafted between the drawbox rollers, which are set at a distance apart appropriate to the length of the fibres. On emerging from the delivery rollers, the fibres are deposited on a small revolving drum covered with 'one-way' hatter's plush, where they form a lap. The lapping of the fibres in successive layers on the drum mixes them effectively, and the lap may be split off and redrawn as often as desired[2].

Later machines, which are useful in preparing samples for fineness testing by air-flow methods or for other tests, are the SDL *Shirley Analyser*, developed for measuring trash content in cotton, and the SDL *Fibreblender*. Samples prepared by this and other such devices are thoroughly well mixed, but there is always danger of fibre breakage unless great care is taken to adjust the settings of the instrument in accordance with the maker's instructions.

2.6 References

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