



Molecular structure of fibers

Supermolecular structure of fibers, models

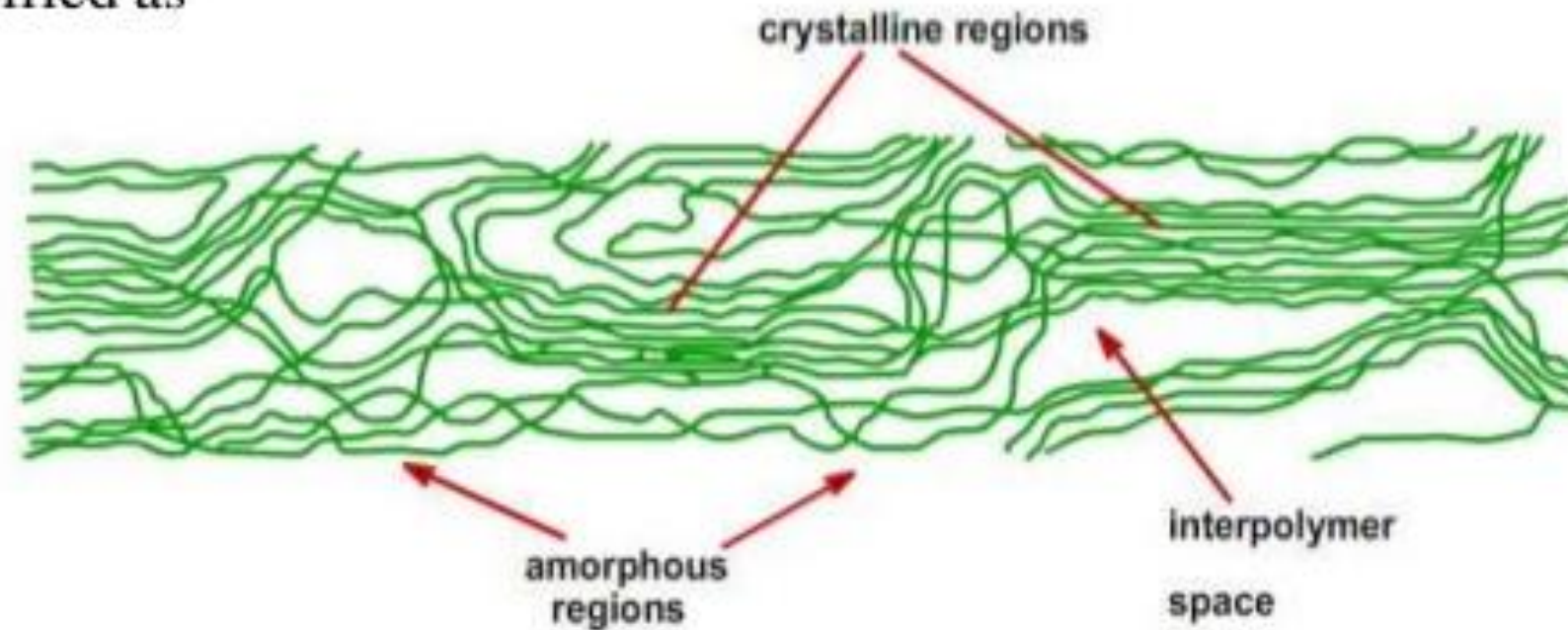
Evaluation of supermolecular structure



FIBRE STRUCTURE

- Properties of fibers are reflections of their structure.
- Fiber properties, and indeed the properties of any substance, may be conveniently classified as

- chemical,
- physical and
- Mechanical

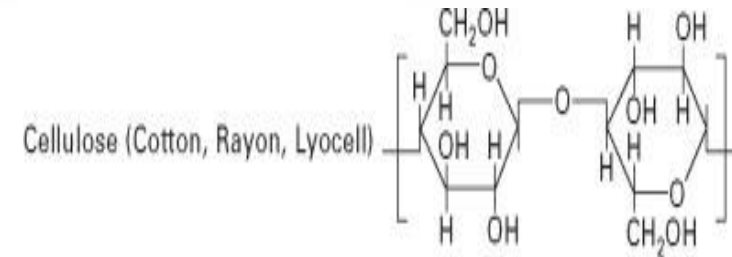


- In order to relate these varied properties of fibers with their structure it is desirable to define the level of structure to be considered.

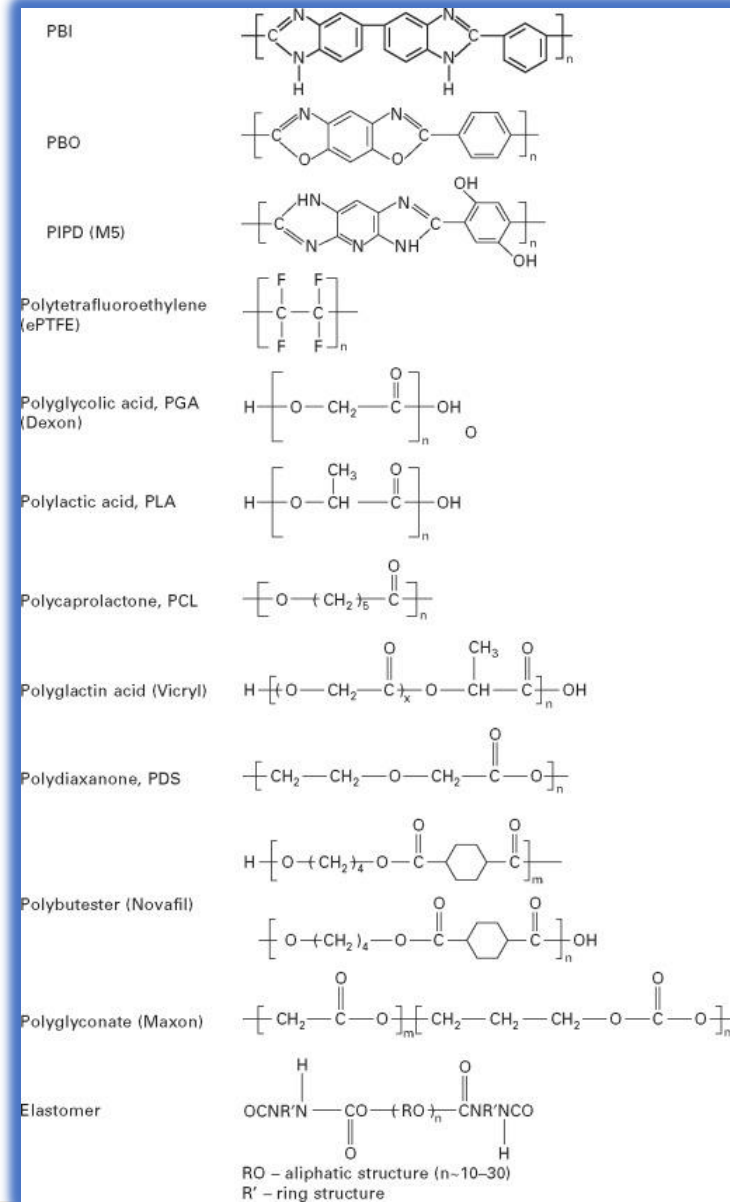
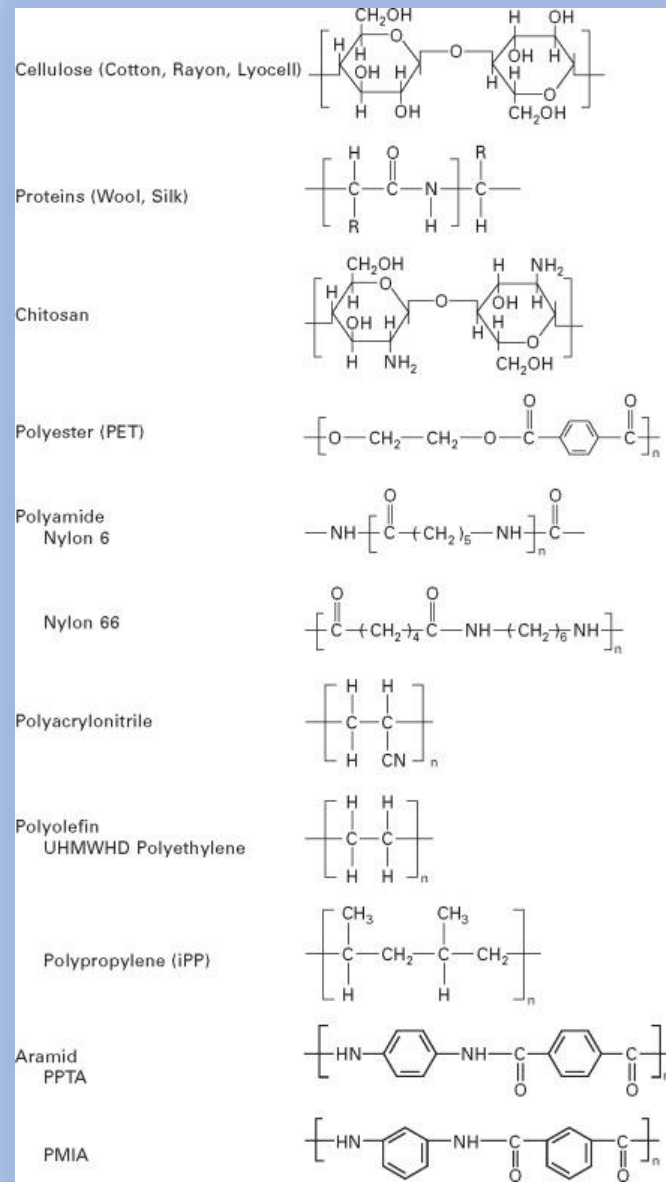
- For this purpose it seems appropriate to define three levels of organization.

- **Organo chemical structure,**
- **Macro molecular structure, and**
- **Supra molecular structure**

- **Organo chemical structure:** describes quite simply the chemical structure of the repeating unit in the base polymer from which the fiber is made, and is not a unique feature of the fiber.



- **Macromolecular structure:** describes the entire polymer molecule in terms of chain length, chain length distribution, chain stiffness, molecular size, and molecular shape.
- **Supra molecular structure:** To find structural features that become characteristic of fibers.
 - The arrangement of the polymer chains in three-dimensional space,
 - The extent and nature of interactions between individual polymer chains and between certain aggregates of these chains, may be defined as the **Supramolecular structure.**



Organo Chemical Structures

Chemical constitutions of the primary repeat units of fibres.





- Determines unique features of fibers.
- It is at this super molecular level of structure that one introduces the concept of lateral or three-dimensional order, and such terms as
 - crystallinity,
 - orientation,
 - crystallite perfection,
 - crystallite size,
 - defects,
 - packing,
 - micelles, and fibrils.

THEORIES OF FIBER STRUCTURE

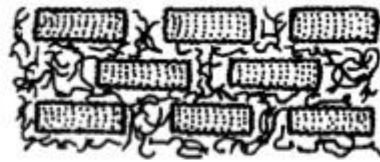
- Micellar theory,
- Continuous theory,
- Fringed micelles theory,
- Fringed fibrils theory,
- Modified fringed micellar theory





MICELLAR THEORY

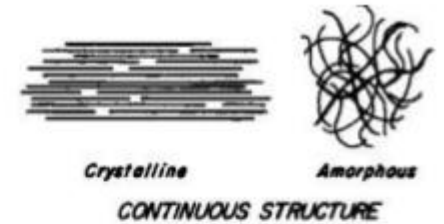
- Originated in the 19th century.
- Non homogeneity of polymer and fiber structure.
- The original micellar theory, as formulated by Nügeli, envisaged the existence of
 - **crystalline micelles embedded in an intermicellar material or substance of an unspecified nature.**
- The discovery that fibers and other plant materials were able to diffract x-rays provided great support for the micellar concept.

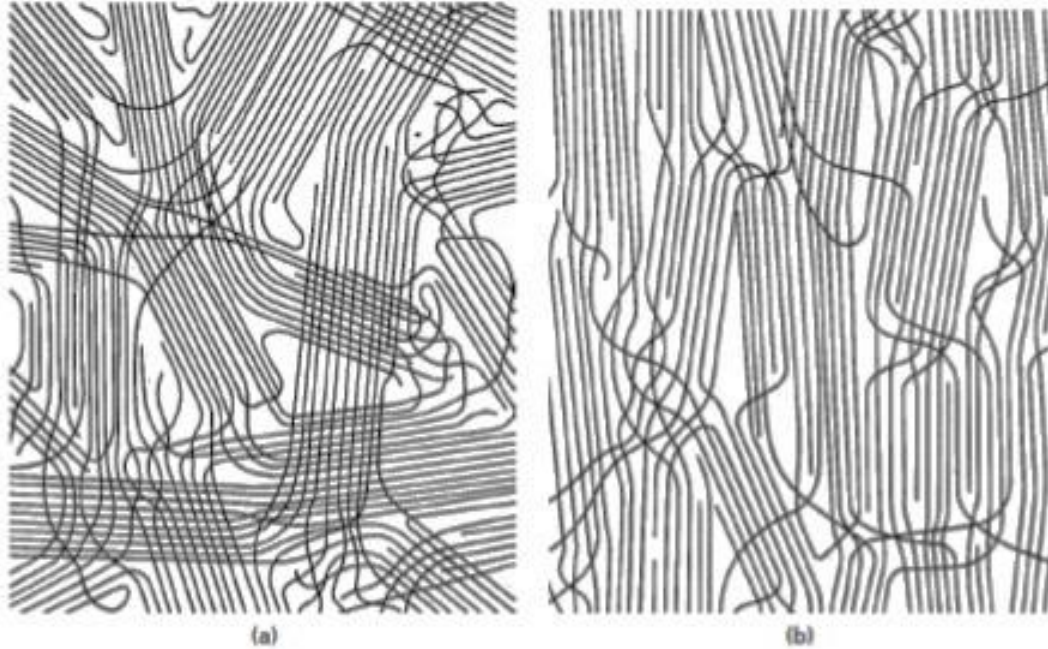


MICELLAR STRUCTURE

CONTINUOUS THEORY

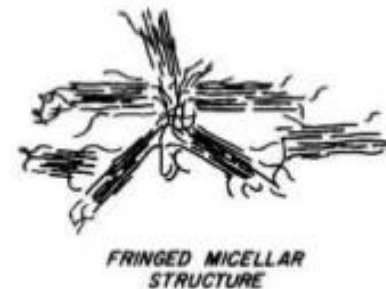
- In the early part of the 20th century
- Length of the polymer molecules was much greater than previously envisaged and that could be accommodated in the Nügeli micelles.
- This led to the postulation of a theory of **continuous structure.**
- Polymer was considered as
 - **A large continuous imperfect crystal,**
 - **with the crystalline imperfections being associated with the ends of the molecular chains.**
- An amorphous polymer
 - **consisted of a random network of intertwined polymer molecules with no three-dimensional order or structural regularity.**





Fringed Micelle Structures (a) Unoriented (undrawn) fibre
(b) in oriented (drawn) fibre

- As molecular dimensions became better established by both chemical and physical methods, the Niigeli micelle had to be abandoned.
- Most polymer and fiber scientists, however, were not willing to accept the continuous model,
- Polyphase concept was so successful in interpreting many chemical, physical, and mechanical properties of fibrous polymers.
- A solution was found in the proposal of fringed micelles
- In this model crystalline micelles were still embedded in amorphous regions;
- Individual polymer chains were able to pass through several crystalline micelles and amorphous regions in a more or less alternating manner.
- The crystalline micelles were interconnected by primary molecular forces orientation with respect to the fiber axis.
- In addition to accommodating the large molecular dimensions, the fringed micellar concept was able to interpret
 - Mechanical properties,
 - x-ray diffraction,
 - Optical birefringence, and
 - such physical properties as density, sorption, and swelling.

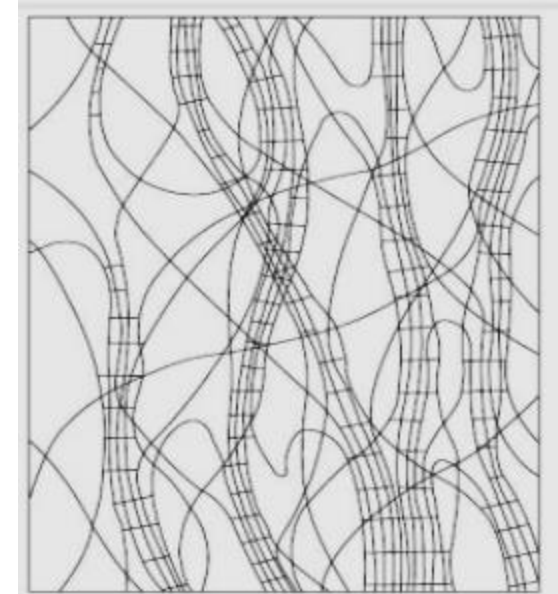


FRINGED FIBRILS THEORY



FRINGED FIBRILLAR
STRUCTURE

- **Fringed fibrillar theory** of fiber structure which replaces the dimensionally discrete micelle of the **fringed micellar theory** with a continuous fibril was proposed.
- In this concept, essentially crystalline fibrils run along the length of a fiber, with some polymer chains traversing from one fibril to another.
- Thus forming the fringed, imperfectly ordered, or amorphous regions.



Fringed-Fibril Structure

Parameters needed for specification of fibre structure

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.

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



Degree of Order

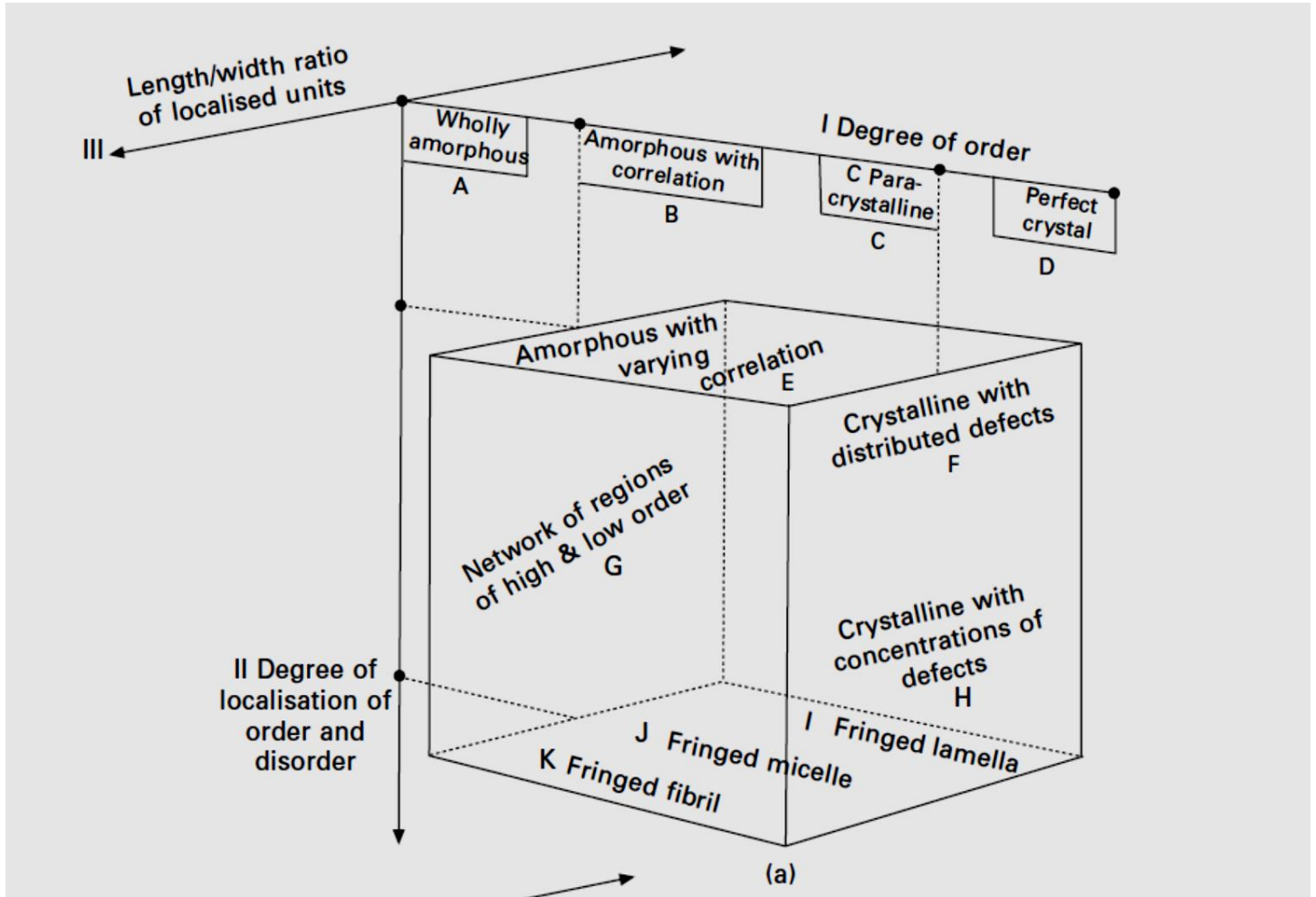
- *Degree of order* would be theoretically defined as the mean value of some correlation function relating the position of neighbouring chains. Practically, it could be defined in terms of density by the expression:
- degree of order =
$$\frac{\rho - \rho_{am}}{\rho_{cr} - \rho_{am}}$$
- where ρ is the 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. Alternatively, estimates of degree of order could be obtained by other methods, such as X-ray diffraction, accessibility, infrared absorption or NMR studies.



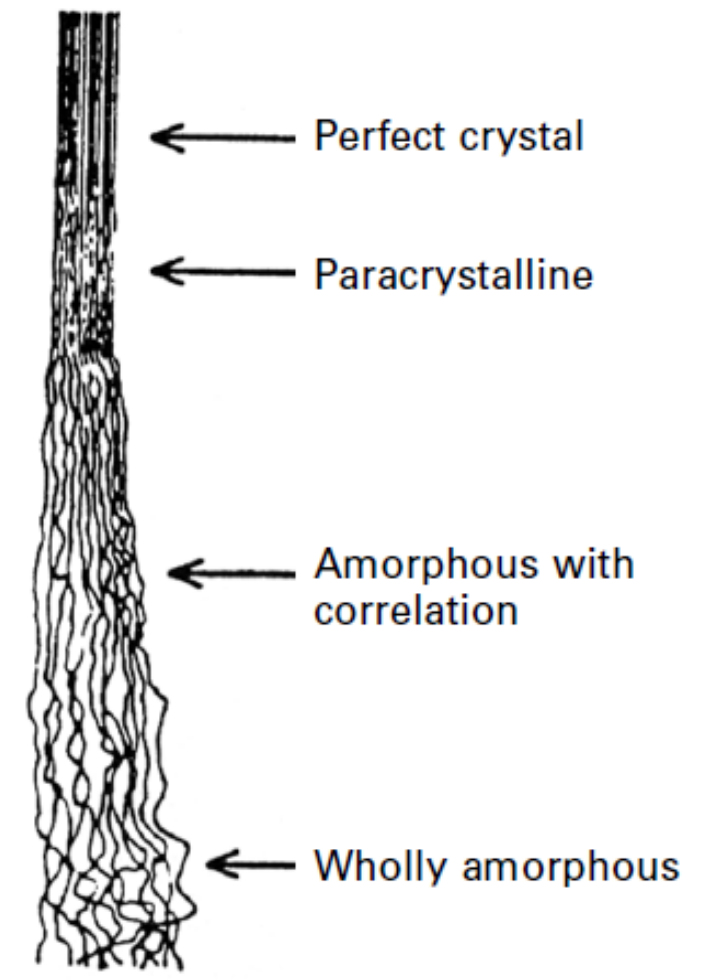


- ***Degree of localisation of order*** would be theoretically defined by some measure of the spread of values of degree of order taken over zones a few molecules wide. The uniform distribution A would have a low value, B would be larger, and C would have the largest value, since it represents a split 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.





Schematic representation of fibre structure in terms of three major variables.



Range of degrees of order of packing of chain molecules



- 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 from the Figure 1.
- 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 Figure 2, molecular extent approximates to fold length. With few folds, fibre length is more important.



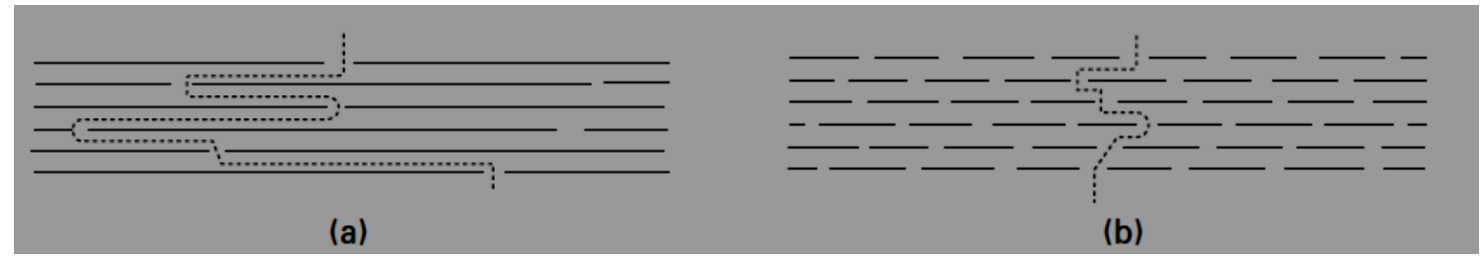


Figure 1

Analogy - 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 Figure 1.
- a more or less parallel arrangement of the molecules.
- lateral forces to hold the molecules together and give cohesion to the structure.

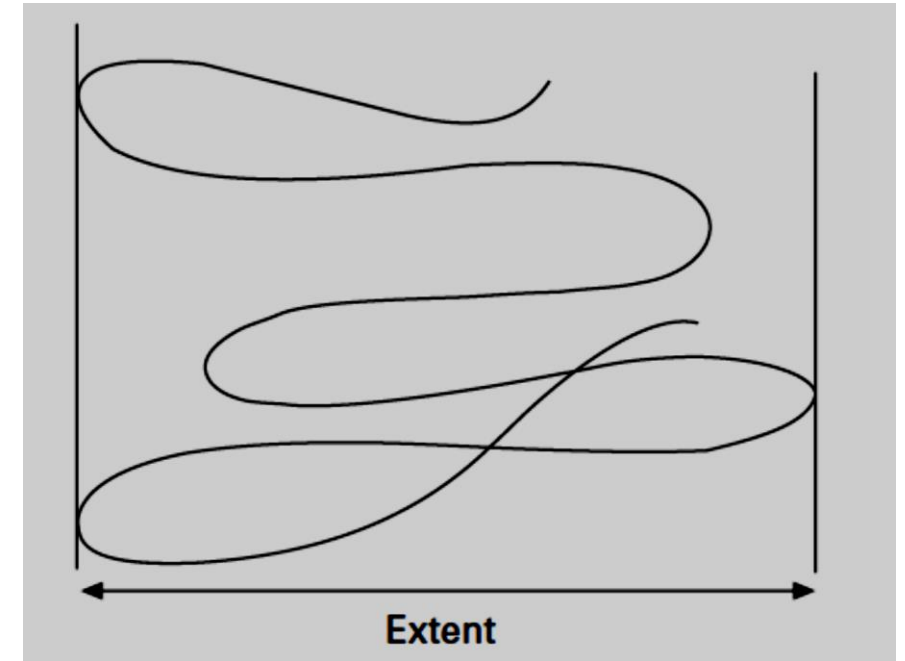


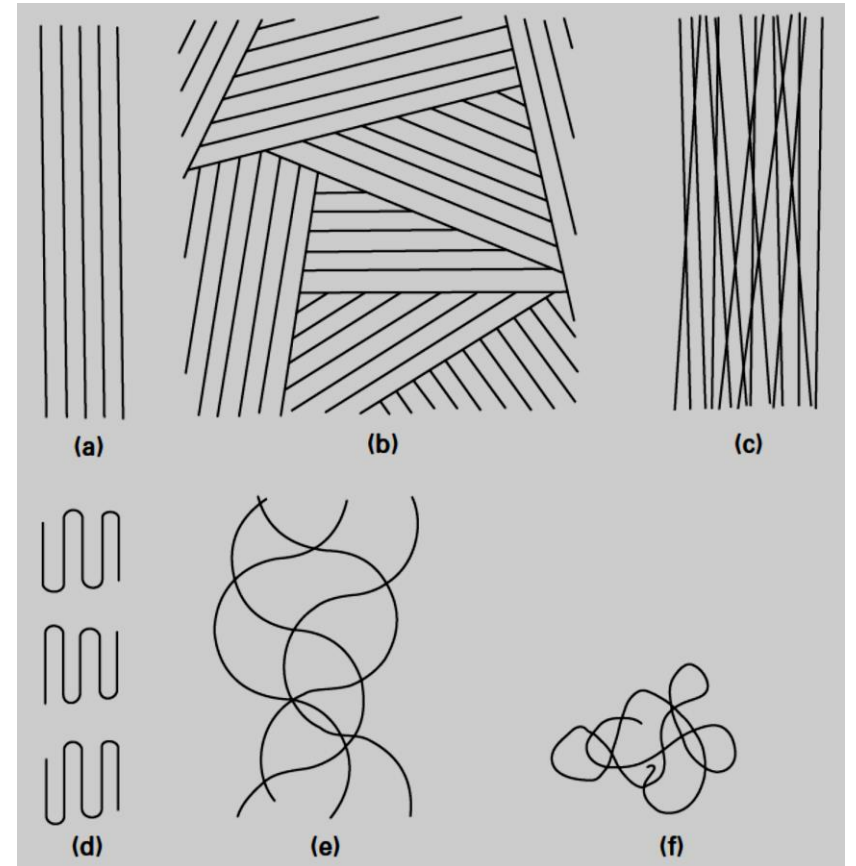
Figure 2



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.

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.



(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.

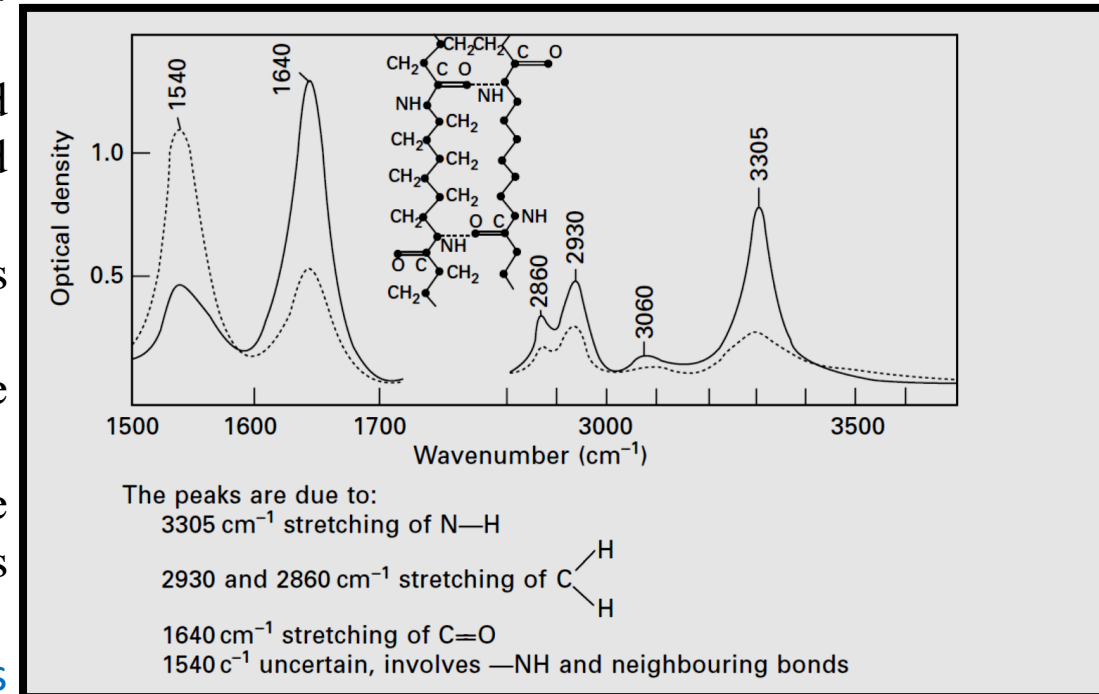
Evaluation of molecular structure

- chemistry of the fibre material – its preparation, composition, molecular formula and reactions
- 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



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.
- 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.

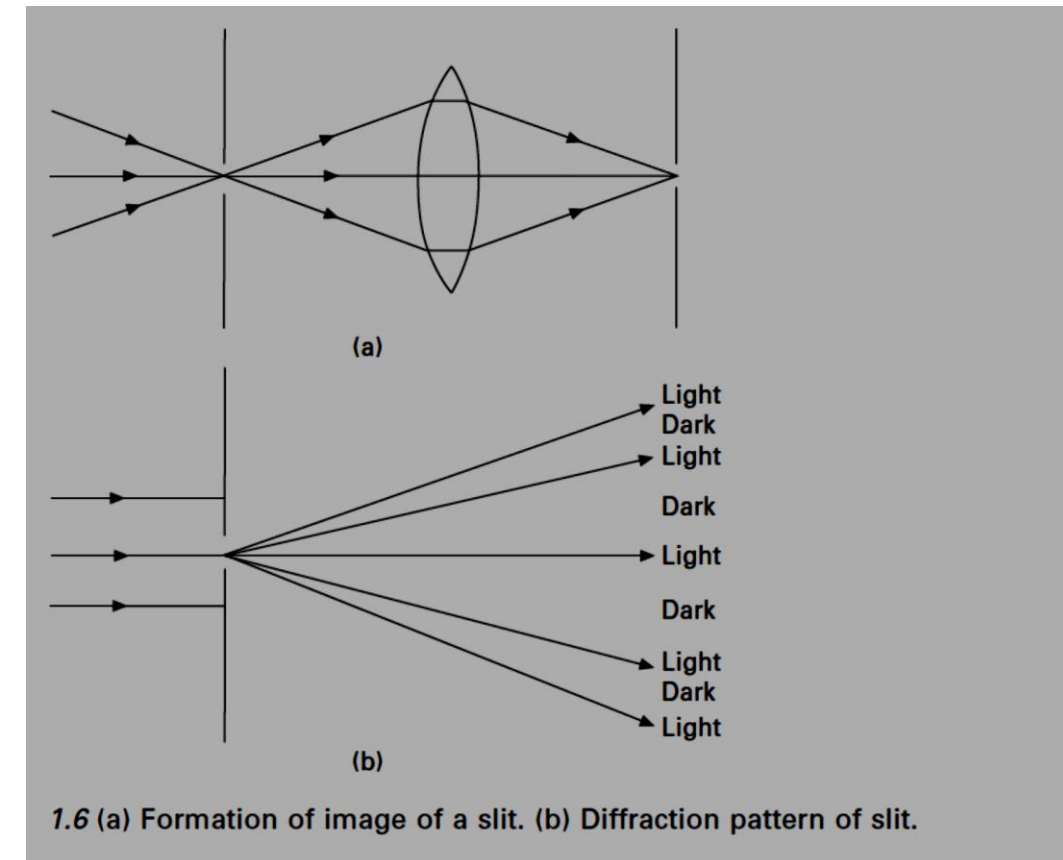


Infrared absorption spectrum of nylon (solid line: electric vector perpendicular to fibre axis. Dotted line: electric vector parallel to fibre axis. Inset: Crystal structure of nylon 6.6.



- 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 Figure.
- 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.
- 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, which may be related to fibre structure. The X-ray diffraction photographs of fibres may be used for various purposes.

Optical and X-ray diffraction

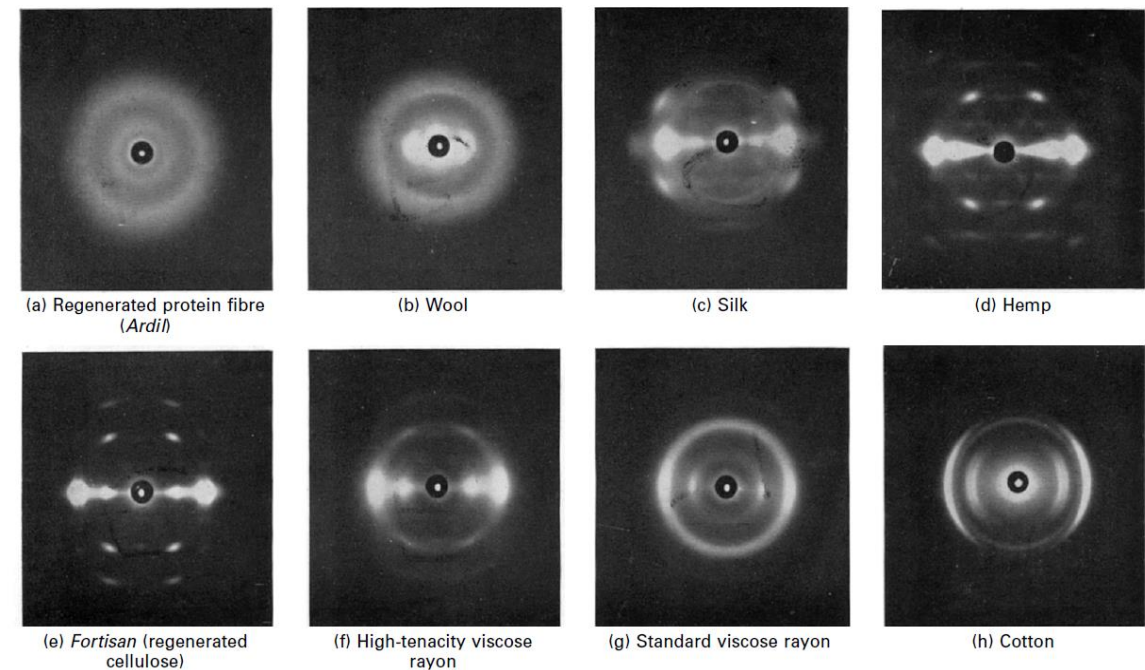


- (a) Formation of image of a slit.
- (b) Diffraction pattern of slit.



Since the patterns for each type of fibre are different, as illustrated in Figure, 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.

- 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 $0.1 \mu\text{m}$. Indeed, optical microscopy becomes very difficult as soon as one approaches $1 \mu\text{m}$, which is not much less than typical fibre diameters.
- 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.

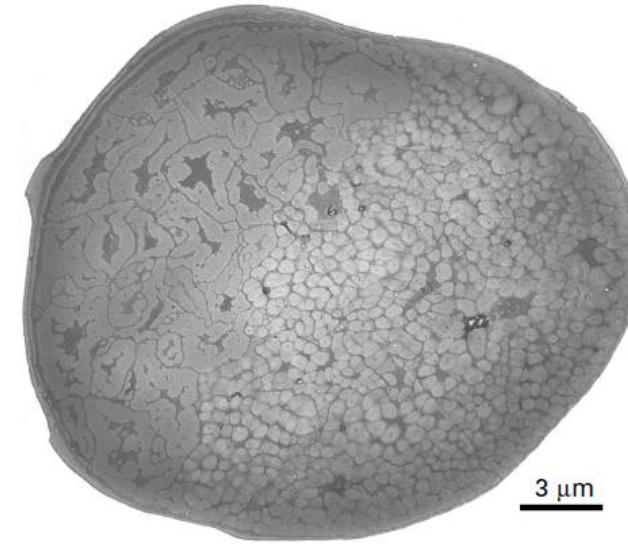


X-ray diffraction photographs of fibres

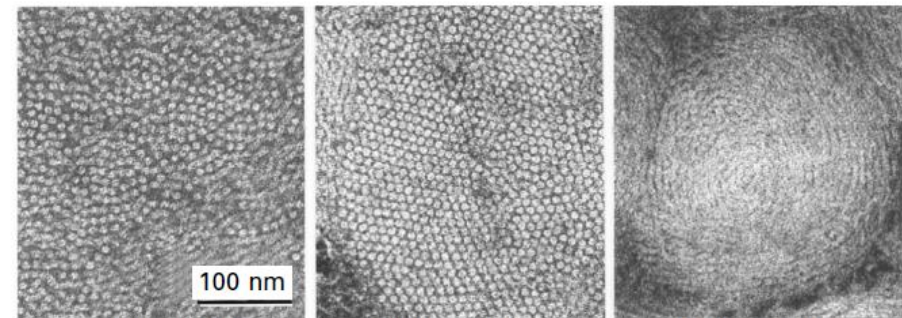
Although they were made around 50 years ago, the various X-ray diffraction patterns found in fibres are well illustrated in Figure by a set of comparative pictures. It is an example of a pattern of a completely crystalline, completely oriented fibre, namely, asbestos.



- 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 $0.1 \mu\text{m}$ 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.
- 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.
- 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.



(a)



Para-cortex

Meso-cortex

Ortho-cortex

(b)

Electron microscope picture of transverse section of high-crimp wool

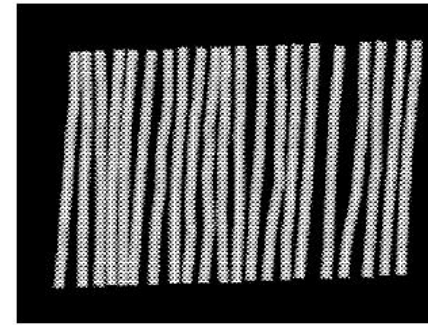
(a) Whole fibre

(b) Macrofibrils

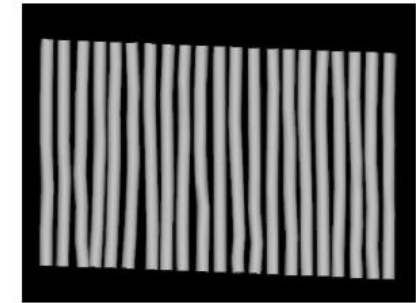


Reconstructed tomograms of macrofibrils in wool showing orientation of microfibrils

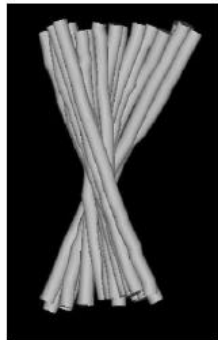
- (a) In para-cortex
- (b) Meso-cortex
- (c) Ortho-cortex



(a)



(b)



(c)

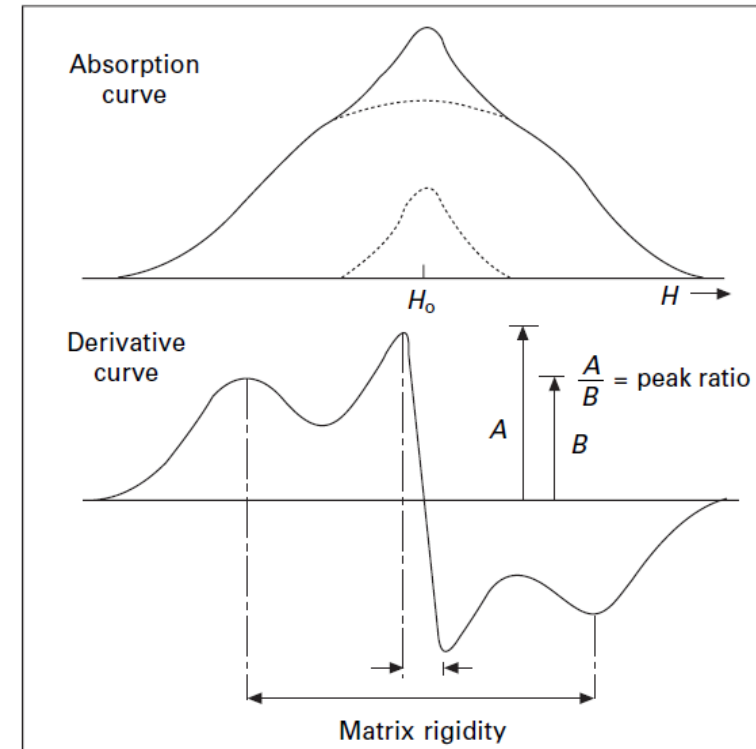
- Atomic force microscopy is a useful way of examining fibres. In its simplest form, a probe with a minute tip mounted on a cantilever arm rests on the surface of the specimen. As it moves across the surface, the tip rises and falls and the deflection of the cantilever is a measure of force. This can 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.
- An order of magnitude increase in voltage has enabled high-voltage electron microscopes to be used with thicker specimens. Researchers 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 Figures. If a specimen is observed at a series of tilt positions, a three-dimensional tomographic reconstruction can be produced. Computer graphics then enables this to be viewed at any angle and measurements to be made.

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.

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 Figure. 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.
- The figure 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.



Nuclear magnetic resonance curve for a solid polymer

