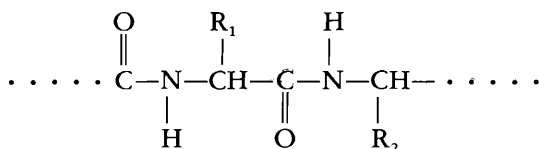# The physical properties of alpha-keratin fibers

PROFESSOR M. FEUGHELMAN, *CSIRO, Division of Textile Physics, 338 Blaxland Road, Ryde, New South Wales 2112, Australia.*

INTRODUCTION

The bulk of the material forming all alpha keratins such as mammalian hair, wools, horns, claws, nails, and quills is a biological polymer consisting of polypeptide chains. These chains, themselves the products of the condensation of amino acids, have the general formula

$$\cdots \cdots \underset{\underset{H}{|}}{\overset{\overset{O}{\parallel}}{C}}-N-CH-\underset{\underset{O}{\parallel}}{\overset{\overset{R_1}{|}}{C}}-N-\underset{\underset{R_2}{|}}{\overset{\overset{H}{|}}{CH}}- \cdots \cdots$$

where R_1, R_2, are the side chains of the amino acids of which twenty different compositions exist in keratin, their proportion varying with the type of keratin. The term alpha refers to the distinct high angle X-ray diffraction pattern (the α-pattern) which differentiates these keratins from others such as feather keratin (1). The distinguishing feature of all keratins, when compared with other proteins, is the presence of a large proportion of the sulphur containing amino acid cystine. This amino acid with two amino and two carbonyl groups can form part of two adjacent polypeptide chains, creating a covalent crosslink via the disulphide group of the cystine residue. These disulphide linkages are associated with some 10% of the amino acid residues of the keratins and confer a high degree of the physical and chemical stability to the keratin fibers. As will be noted further in this review, these disulphide links play a basic role in the process of setting both in the hairdressing and wool textile industries. At the molecular level α-keratin fibers can not only be considered to consist of networks of polypeptide chains crosslinked by the covalent disulphide bonds, but (as with all proteins) a large variety of hydrogen bonds as well as Van der Waals interactions exist both between and within the chains. Of special interest in the physical properties of α-keratin fibers are the Coulombic interactions, also referred to as "salt links," which exist between charged basic side chains of lysine, arginine, and histidine and the acidic side-chains of glutamic and aspartic acids. These basic and acidic side chain groups represent about a quarter of the residues of the α-keratin structure. Hydrophobic bonds, interactions between chains created by the presence of water, have also been detected for α-keratin fibers immersed in water (2).

In considering the physical properties of α-keratin fibers it is necessary to recognize the fundamental role of water in the structure of the fiber. The properties of the fiber change markedly with the amount of water interacting with the structure of the fiber (3) to such a degree that the material may be considered as a keratin-water polymer. The penetration and the interaction of the water molecules depend not only on the existence of hydrophyllic sites within the keratin structure but also on the state of order within the different components of that structure. A high degree of order (crystallinity) as well as the presence of cross links may limit the ability of water to interact at what are chemically hydrophyllic sites. It is the lack of recognition for the role of order, on the sorption of water within the α-keratin structure, that has led to some of the apparently anomalous conclusions, as to the placement of water based purely on the chemistry of the structure (4).

In commercial application, human hair and to a lesser extent finger nails in the cosmetic industry, and wool fibers in the textile industry, are the most important of the α-keratins. The prime physical properties in the application to these fibers are their mechanical properties. Regardless of the treatment that is applied to the fibers, in nearly all instances the result obtained and assessment made are directly related to the mechanical state of the fibers. For this reason the author has considered the mechanical properties of the α-keratin fibers as the central physical properties of these fibers. The other properties such as X-ray diffraction, Infra-red absorption, electrical conduction, dielectric response, birefringence, and other measurements lead to our understanding of the relationship between the molecular and near molecular structure of α-keratin fibers and their mechanical properties. It should be emphasised that the mechanical properties of a fiber are the summation of the properties of the whole fiber involving the molecular units both in the ordered (crystalline) regions of the fiber and the less ordered (amorphous) regions. Many of the physical properties dealt with in this review emphasize mainly one aspect of the fiber structure. High angle X-ray diffraction studies primarily lead to information about highly ordered regions of the fiber structure, whereas calorimetric measurements, being related to the freedom of movement of the molecular components within the fiber, respond more to the less ordered, more mobile regions. This review aims to broadly identify the molecular components and assemblies responsible for the variation of the physical properties of α-keratin fibers with change of moisture content, temperature, and physical and chemical modification. The presence of swelling agents such as concentrated aqueous lithium bromide solutions and formic acid will be examined for their effect on the behavior of the fibers.

Two broad structural features may be identified which control the physical behavior of any polymeric structure. The *equilibrium structural organization* of the fiber, which essentially relates to the equilibrium position of all the components of the fiber, is measured primarily by physical data which do not involve molecular movement. The *structural dynamics* of the system, that is the time dependent component of the physical behavior of the fiber, are measured by physical data which are sensitive to the freedom of movement of molecular groups within the fiber structure. Because molecular movement is mainly confined to the less ordered components of structure, and since the less ordered components are the main regions of absorption of plasticizers such as water and various alcohols, these plasticizers have a major control over the structural dynamics of the fiber. Figure 1 diagrammatically summarizes the relationship between the physical data obtained relevant to the equilibrium structural organization and structural dynamics of a fiber. Known structural modification by chemical and physical
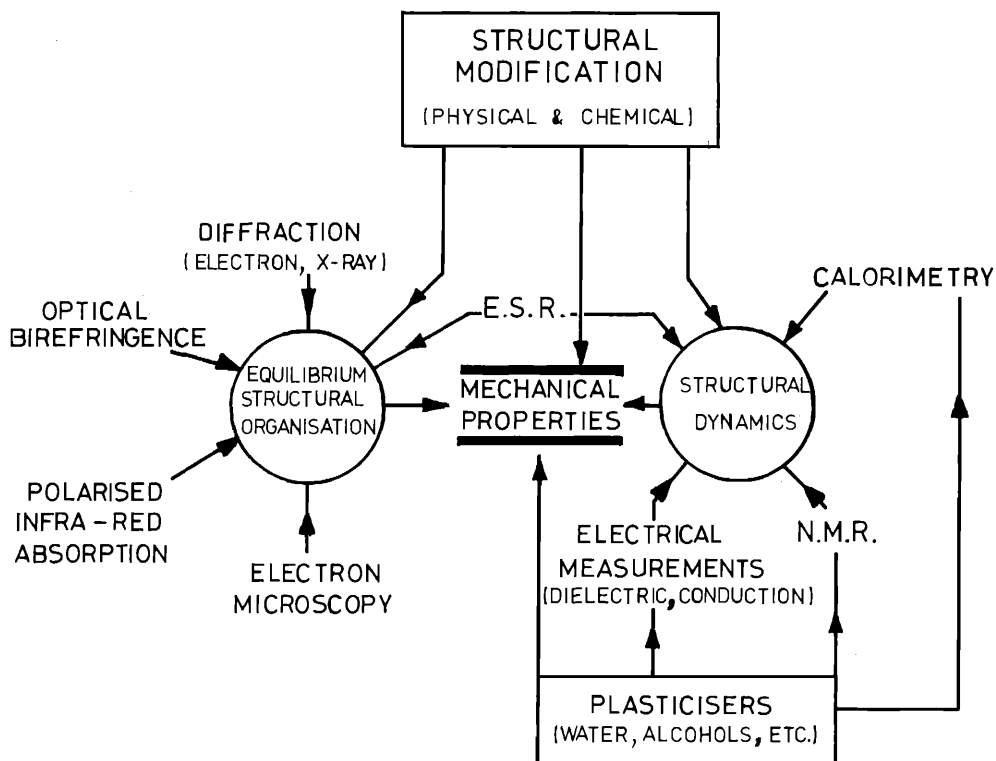
Figure 1. A diagrammatic representation of the typical physical measurements employed in obtaining the data relating the structure of a fiber to its mechanical properties.

techniques, such as reduction of disulphide content of a fiber or swelling in concentrated aqueous lithium bromide solution, can also be assessed in terms of the resultant change in the dynamic and equilibrium properties of the fiber.

Thus, the reviewer proposes to examine the mechanical properties of α-keratin fibers interpreted in conjunction with data obtained with a range of physical techniques. A general introduction has been given to the fibrous protein nature of α-keratins without any indication to the morphology of such fibers, the distribution, size, and role of various components forming such fibers. Obviously the latter factors play their role in the mechanical properties of fibers and a brief discussion follows on this morphology as it relates to hairs, fur and wools.

MORPHOLOGY

Alpha keratin fibers such as hairs, furs, and wools have in common the structural components of cuticle and cortex with a central medulla often present in the coarser fibers. The cuticle covers the whole fiber and consists of layers of scales each about half a micron thick, overlapping to give a ratchet-like profile. The number of scales present in a cross-section of a fiber is dependent on the type of fiber. In human hair these may be as many as ten overlapping scales in one cross-section in a newly formed fiber, whereas in a wool fiber only sufficient scales for barely overlapping the fiber exist. The

ratchet-like effect of the scales of the cuticle give the fibers the directional friction effect and play a vital role in the entanglement of the fibers (5). The mechanical action of disentangling as in combing and brushing of hair also tends to strip the cuticle structure. Microscopic examination of human hair shows a progressive removal of the scale structure from root to tip with a complete removal of scale structure being associated with the splitting and fracture of the hair at the tip end (6). In the undamaged hair a very thin membrane (about 3nm thick), the epicuticle, surrounds the outer surface of the fiber. Beneath this is the exocuticle, a cystine-rich component of each scale cell representing about two-thirds of the cuticle structure. The remainder of the scale structure is the endocuticle, followed by a thin layer of cell membrane complex. The endocuticle is the mechanically weakest part of the cuticle and as a whole has a low cystine content. For futher detail of the cuticle structure the reader is referred to the recent report of R.D.B. Fraser et al. (7). Physically the material forming the cuticle does not display any degree of molecular ordering as indicated by such simple measurements as optical birefringence (8). The cuticle does have a mechanical protective role for the rest of the fiber, and acts as an important barrier to dye sorption by the fiber, but in terms of bulk physical properties such as longitudinal mechanical properties, its role is very secondary. Only in torsional mechanical properties, where the outside of the fiber has a major mechanical role, can one differentiate between the mechanical properties of cuticle and that of the bulk of the fiber. Although some torsional measurements for wool fibers in which fibers were examined with their scale structure intact, and their surface structure removed, do exist, because scale structure represents such a minor component of wool fibers, any positive conclusion with regard to cuticular property would be hazardous (9). Far more significant results should be forthcoming from measurements on human hairs, where the cuticular structure represents a far bigger proportion of the fiber.

The bulk of an α-keratin fiber is the cortex consisting of elongated cortical cells of irregular cross-section of a few microns, packed tightly together and oriented parallel to the fiber axis. The cortical cells when viewed under an electron microscope are seen to consist of long uniform filaments, referred to as microfibrils, of about 7.5n.m in diameter and of the order of 10n.m center to center oriented parallel to the fiber axis. The microfibrils are grouped into units of about 0.5 microns diameter and are known as macrofibrils. The microfibrils are embedded in a cystine rich matrix and within any macrofibril are spatially related to each other by a hexagonally packed or whorl-like configuration as seen in cross-sections under an electron-microscope. Physical evidence on extended samples of keratin fibers suggest that the microfibrils within any one macrofibril extend cooperatively and hence must be closely interacting with each other (10).

The microfibrils within the α-keratin structure contain the α-helical material responsible for the characteristic α-helical X-ray pattern (11). These microfibrils do not appear to differ from one form of α-keratin to another, and the evidence strongly suggests that they are essentially crystalline (12). The dry to wet moisture uptake of a hair or wool fiber results mainly in diametral swelling ($\sim$ 16%) with little change in the fiber direction ($\sim$ 1.2%). This results from the water uptake being confined mainly to the matrix with the microfibrils moving laterally apart. Any tendency to swell in the longitudinal direction is opposed by the microfibrils, whose stability in water appears little affected. It is only when the α-helices in the microfibrils are wholly or in part destablized that it is possible to obtain any major longitudinal change with dry–wet swelling (13).

The medulla present axially in coarser α-keratin fibers may be continuous, discontinuous, or fragmented. Its essential physical characteristic is the presence of large amount of space, which does improve the thermal insulation and economy in weight and material with little loss in the bending characteristics for the fiber. It has a major effect on the optical appearance in particular in low pigmented fiber such as wool. The presence of the medulla causes an increased amount of light scatter especially at the blue end of the optical spectrum, making fibers such as wool with a natural yellowish color appear white. However, in terms of the mechanical properties of an α-keratin fiber its role is that of empty space, and in this review discussion of the medulla will be largely omitted.

LONGITUDINAL MECHANICAL PROPERTIES

Speakman (3,14) first showed that the longitudinal mechanical properties of α-keratin fibers vary markedly with temperature, humidity, and time. The stress-strain behavior of these fibers, he demonstrated, can be considered in terms of three distinct regions of strain. If a fiber is progressively extended under constant temperature and humidity conditions once it is straightened (which depends on the fiber under test, and in the case of a highly crimped Merino wool fiber represents a considerable strain), the stress-strain curve up to a few percent strain has a mechnically stiff, nearly linear region referred to by Speakman as the "Hookean" region (Figure 2). This nomenclature is
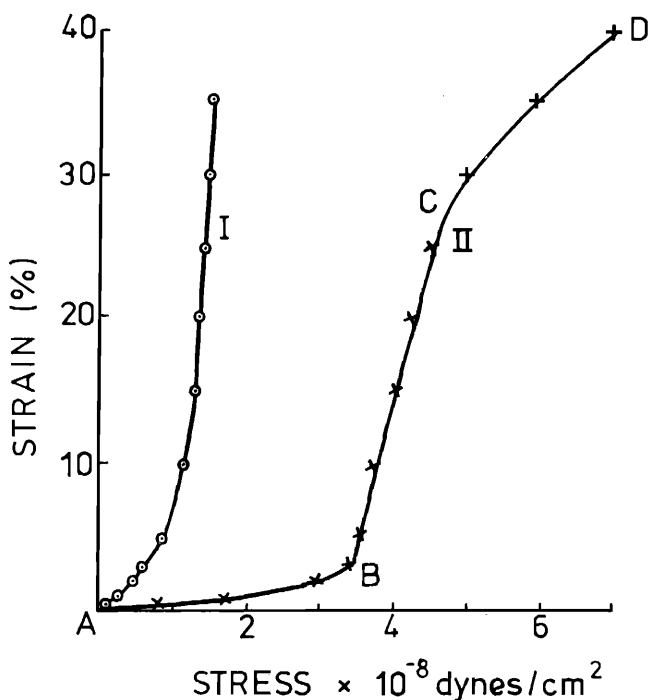

Figure 2. The stress-strain behavior of a keratin fiber (African porcupine quill) in water at 20°C in: (i) the direction perpendicular to growth, (ii) the direction parallel to growth. In the latter case AB corresponds to the "Hookean" region, BC the Yield region, and CD the Post-Yield region.

somewhat misleading as this region of strain is far from spring-like in its mechanical properties. Bendit (15), who has published a discussion of this problem, prefers the term "pre-yield" region. However, due to common usage now for some fifty years in the literature, to prevent confusion the term "Hookean" will be applied in this review.

With further extension of the fiber for strains beyond the "Hookean" region, increase of strain occurs with little increase of stress up to about 25–30% strain. This region of low stress increase with strain is referred to as the Yield region. For further extension of the fiber beyond the Yield region the stress increases more rapidly with increase of strain. This region of increase in fiber stiffness is referred to as the Post-Yield region. Although there are variations in the mechanical properties of α-keratin fibers with variation of both the fiber environment and the type of fiber, all fibers in longitudinal extension have a qualitatively similar stress-stain relationship with the three distinct regions of the "Hookean," Yield, and Post-Yield. These three regions are most distinctly defined for a fiber of uniform cross-section in water (10). In these circumstances the ratio of the moduli of the linear portions of the three regions are approximately 100:1:10. The mechanical behavior of α-keratin fibers in each of the three regions of strain level reflects the state of structure of the fiber and is next discussed in these terms.

THE "HOOKEAN" REGION

MECHANICAL

The linear portion of the Hookean region for α-keratin fibers at room temperature extends up to about 1% strain with the deviation from linearity becoming large as a strain of about 2% is approached. The Young's Modulus for fibers in water at 20°C corresonding to the linear region depends on the rate of straining (16). Typical results quoted for wool fibers at a rate of strain of 0.01% per minute are 1.7×10^9 pascals and at 10% per minute 2.0×10^9 pascals. Up to the strain level of about 1% the behavior of the fibers approximates to linear viscoelasticity, as indicated by the stress-relaxation and creep data (17,18). Progressively as α-keratin fibers are placed in drier environments, that is, as their water content is reduced, the stiffness of the fibers increases. In completely dried fibers ($\sim$ 0% relative humidity environment) the Young's Modulus of the fibers is increased by a factor of about 2.7 relative to the same fiber's modulus in water, the reference cross-section area in both cases being the value for the wet fiber (19). However, this apparent increase in fiber stiffness with the removal of water is completely time dependent. The equilibrium stiffness of the fibers is independent of the moisture content of a fiber, and corresponds to a value of Young's Modulus of 1.4×10^9 pascals in the wet cross-sectional area of the fiber used in all cases as the reference (20). The whole behavior of the fiber corresponds to a fixed Hookean spring contributing 1.4×10^9 pascals to the Young's modulus in parallel with a spring and viscous dashpot in series (10). The viscosity of the dashpot is moisture-dependent and is related to the mobility of the molecular segments, main chains, and side-chains affected by the presence of water. Measurements of Young's Modulus and stress-relaxation data (22) for fibers in water at various temperatures show a progressive reduction of Young's Modulus to a stationary value and disappearance of stress-relaxation between 40° and 50°C. This stationary value of Young's Modulus corresponds to temperature at which the time-related phenomena in the structure are short-lived compared with the experimental time. Hence as expected, the value of Young's modulus of about 1.4 ×

10^9 pascals as the stationary value agrees well with the equilibrium Young's Modulus with which it should correspond.

At the temperature of liquid nitrogen ($-196°C$) no segmental mobility exists in the keratin fiber structure (23), and any mechanical distortion of the structure results in bond deformation only. The Young's Modulus of α-keratin fibers under these conditions is 9.6×10^9 pascals which is a value close to that of ice, indicating the correspondence to the expected stiffness of a hydrogen bonded network (24). Similar values of longitudinal mechanical stiffness were obtained in experiments in which the strain was of very short duration ($\sim$10 microseconds), under which circumstances segmental mobility was again eliminated (25).

The values of Young's Modulus quoted for keratin fibers in water correspond to an aqueous medium at a pH around neutrality. If an α-keratin fiber is tested in aqueous media of varying pH at 20°C it is found that the mechanical stiffness of the fiber (26) remains unchanged from neutrality down to pH 3. Below pH 3 the Young's Modulus decreases by about 40% until a plateau is reached at pH 1. This phenomenon is reversible and indicates the reversible breakdown of Coulombic interactions (salt links) from pH 3 to pH 1 as the increased hydrogen ion concentration neutralizes the side chain carboyxlic acid groups ($-COO^- \rightarrow -COOH$), resulting in a loss of interaction with positively charged groups in the side-chains of the polypeptides in the keratin structure. About 6-7 $\times$ 10^8 pascals of the equilibrium Young's Modulus values of 1.4×10^9 pascals are due to Coulomibic interactions (27,22). Although Coulomibic interactions are present throughout the keratin structure, only those shielded from water molecules, that is not interacting to any degree with water molecules, are involved in opposition to mechanical distortion. These are the interactions producing the stiffness which makes such a major contribution to the Young's Modulus of the fiber (28).

X-RAY DIFFRACTION AND THE α-HELIX

Astbury (29) demonstrated that with extension of an α-keratin fibre in the "Hookean" region the folded molecular structure corresponding to the material responsible for the high angle X-ray diffraction pattern changes by the equivalent amount corresponding to the overall strain of the fiber. This folded structure in α-keratin has been shown by Pauling (30) to correspond to the helical structure designated as the α-helix present in a large proportion of proteins. The mechanical opposition to extension of α-helices has been demonstrated to be due mainly to hydrogen bonds present between the turns of the helices (31). X-ray evidence suggests that water sorbtion in an α-keratin fiber is mainly confined to the non-crystalline regions (32). While the crystalline α-helical structures are intact the stiffness of the α-keratin fibers in water corresponds to a Young's Modulus of the order of 10^9 pascals. However, if the α-helices are randomized (33) (as discussed below) in aqueous solutions of lithium bromide at concentrations greater than 6.4M, the Young's Modulus drops to the value of a material in an elastomeric state (of the order of 10^7 pascals).

OPTICAL BIREFRINGENCE

In keratin fibers the optical birefringence of the fiber is mainly a measure of crystallinity (34). Fibers placed in aqueous solutions of lithium bromide (33) of a progressively increased molarity from pure water to a concentration of 5M, experience a relatively

small change in both birefringence and Young's Modulus. However, from a 6M to 7M concentration of lithium bromide the optical birefringence drops drastically to a value less than 0.2 of the value for the fiber in water. Completely concomittant with this rapid drop of birefringence, the Young's modulus of the fiber as indicated previously drops by a factor in excess of 20 to a value corresponding to a material in the elastomeric state. The α-helices have been transformed to random coils and no longer form crystalline structures. Crystallinity within the α-keratin structure, which involves the ordering of the α-helices within that structure, appears to be the main factor contributing to the stiffness of the fiber in water at extensions within the Hookean region.

INFRA RED ANALYSIS

The infra-red absorption of α-keratin fibers (35) exhibits the characteristics found in protein spectra generally, such as the amide A, I, and II bands. By the application of polarized infra-red and the measurement of absorption with the planes of polarization parallel and perpendicular to the fiber direction (dichroism), it has been shown that the amide NH and CO groups in keratin are preferentially ordered in the fiber direction (36). Further, when the fibers were immersed in heavy water (D_2O) within 24 hours about 70% of the amide hydrogens were replaced by deuterium (37). The remaining amide $-NH$ groups were highly dichroic, the dichroic ratio for $-NH$ groups increasing by the deuteration from about 1.5 to 5.5. This means that the undeuterated NH groups remaining correspond to highly oriented structures. A theoretic estimate from the dichroic ratio (38) shows that the 30% undeuterated groups could be accounted for by 80% perfectly aligned α-helical material with about 20% randomly oriented undeuterated $-NH$ groups. Further, the infra-red data means that this highly organized 30% of the structure of α-keratin fibers in the time range of 24 hours exhibits negligible association with water as far as the amide $-NH$ groups are concerned. Again the evidence points strongly to the lack of interaction of water with the organized α-helical structure within the keratin fibers.

ELECTRICAL CONDUCTIVITY AND THE DIELECTRIC PROPERTIES

The electrical conductivity of an α-keratin fiber is very dependent on the water content of the fiber. The keratin-water system acts as a protonic semi-conductor in which the mechanism of transfer of the proton is similar to that proposed in ice, consisting of a rotation of water molecules and proton jumps between two equilibrium positions between the oxygen atoms of neighboring water molecules.[39] The conductivity requires a continuous hydrogen bonded network of water molecules, and it is the sensitivity to the number of protonic pathways throughout this network that results in an increase of electrical resistivity of wool fibers at 25°C from 6×10^6 ohm-cm at 25% water content to 3×10^{12} ohm-cm at 7% water content based on the mass of dry keratin. The conductivity also depends on the freedom of rotation of the water molecules. The temperature coefficient of the conductivity corresponds to an activation energy barrier of 30K.cal./g. mole for a nearly dry fiber reducing to 15K.cal./g. mole at 25% water content, indicating a freeing within the structure of the movement of protons as the water content of the fiber is increased (40).

With the small extensions corresponding to strain in the "Hookean" region the electrical conductivity of the fibers exhibits an insignificant drop. The network of water

molecules coming under this low level of strain is little affected in terms of its conductivity pathways. Conduction associated with the water present within the keratin structure is essentially a property of the non-ordered component of the structure.

The dielectric properties of the keratin water system (41) are dependent on frequency of the measurement as well as the water content. At high water contents, which correspond to the state of the fibers in a high humidity environment, the dipolar orientational polarization of large segments of the keratin structure is plasticized; that is, it is freed in its movement by water and is responsible for the major component of the total polarization. A contribution is also made by water molecules free to align with the applied field. Because dielectric and dynamic mechanical data are essentially dependent on the mobility of the same elements within the keratin structure, comparison can be made between the mechnical relaxation spectra obtained for fibers extended within the "Hookean" region and the dielectric relaxation spectrum for fibers at the same water content and temperature.

THE TWO-PHASE MODEL

For small distortions of a keratin fiber that exist in the "Hookean" region the fiber's behavior with changes of water content on the basis of much of the foregoing data has been expressed in terms of a two-phase model (42) consisting of a water impenetrable phase of cylindrical rods oriented parallel to the fiber direction embedded in a water penetrable matrix-phase. The matrix-phase is mechanically plasticized and weakened by the presence of water, whereas no mechanical change is expected in the cylindrical rods with water uptake by the fiber. Torsional mechanical data shows that the modulus of rigidity of a dry fiber ($\sim$ 0% relative humidity) is about 1.7×10^9 pascals, falling by a factor of 10–20 to a value of 1–2×10^8 pascals for a wet fiber (43,44). This major change in torsional rigidity for the fiber as the environment is changed from dry to wet occurs in parallel with a much smaller change in the longitudinal stiffness of the fiber by a factor of 3–4. In longitudinal extension in terms of the two-phase model the two phases act in parallel with both equally deformed. This means that in the wet state the unweakened cylindrical rods contribute considerably to the longitudinal stiffness of the fiber. When the structure undergoes twist about the fiber axis, however, if the matrix is weakened by the presence of water the distortion is nearly completely confined to the matrix, and the torsional stiffness depends mainly on the matrix opposition to the torsional distortion. The result would be that on the basis of the proposed model the presence of water in the structure should cause a much greater reduction in torsional rigidity than in longitudinal stiffness of the fiber going from a dry to wet environment, a result borne out by the experimental data.

Ample evidence exists for the presence of a highly ordered structure of low water penetrability within the keratin fibers, containing the organized α-helical material (11). Chemical evidence (45) based on the extraction of proteins from α-keratin fibers after the breaking of the disulphide bonds shows that two major fractions of proteins are obtained, a high and a low sulphur component. The low sulphur component is made up of about 50% α-helical material, and the high sulphur protein extract has no helices. In line with the physical evidence, the microfibrils within the cortex of the α-keratin fibers have been identified with the water impenetrable cylindrical rods of the two-phase model. The microfibrils contain the crystalline α-helical material and hence are the source of the low sulphur protein extracts. However, as has been pointed out by Bendit (46), the low sulphur protein is not completely confined to the microfibrils and

the non-helical "tails" of this protein probably play a vital part in the physical interactions between neighboring microfibrils and the matrix in which they are embedded.

The high sulfur protein extract is confined to the matrix, and with the high glycine-tyrosine protein found in varying quantities in α-keratin fibers forms the non-crystalline protein material of the matrix. The high sulphur and high glycine-tyrosine proteins contain fewer hydrophyllic sites, and the former protein is more crosslinked than the low sulphur protein of the microfibrils. This fact has raised the question, why does the matrix absorb more water than the microfibrils (4). Aside from the crystalline and hence less labile state of the microfibrils, the proteins of the matrix do not have to absorb water within their own structure. The matrix must be considered to consist of water plus the high sulphur and high glycine tyrosine proteins (47). The proteins themselves can form globules, and the water form an enveloping, continuous network of hydrogen bonds with the proteins acting as a filler within this network, interacting with the network, at the globule surface. The existence of protein globules has been indicated by X-ray diffraction measurements (48).

The mechanical properties in water of different α-keratins show a progressive stiffening with increase of the high sulphur plus high glycine-tyrosine content of the fiber, an increase which has been associated with the matrix (49). Further, the dry to wet change in fiber diameter is progressively reduced. This can be understood clearly if we recognize that the matrix consists of water plus these two proteins. Because of the physical limitation of intermicrofibrillar spacing (50,51) set during formation of the fiber in the follicle, an increase of these proteins results in a decrease of water content, and a resultant decrease of mechanical mobility of the matrix structure for the wet fiber. A similar effect can be obtained by introducing into the matrix of a keratin fiber large dye molecules (52). It has been shown that with increase of dye uptake the dry to wet diametral swelling of the fiber is reduced and its mechanical stiffness for small strains, particularly in torsion (51), is increased. With suitable dye molecules this procedure is quite reversible and indicates that the main physical effect of these molecules is to displace water in the matrix structure.

On the basis of the two-phase model regarding the structure as consisting of microfibrils containing the organized α-helical structure, and the matrix, broadly considered as corresponding to the rest of the structure, labile and weakened in water, estimates have been made of the mechanical contribution of each phase to the equilibrium Young's modulus of 1.4×10^9 pascals for α-keratin fibers in water. These measurements (53,54) are based on dynamic measurements at about 10^2 herz and at various humidities, together with conventional mechanical tests at different temperatures in water. All tests show the basic agreement that the contribution of the microfibrils to the equilibrium Young's modulus is close to 1.2×10^9 pascals, and the matrix contribution is of the order of 0.2×10^9 pascals. This latter contribution of the matrix is, as expected, small and is of the order expected from the elastomeric stiffness of an amorphous chains.

SWELLING IN FORMIC ACID, ALCOHOLS, AND UREA SOLUTION

X-ray diffraction evidence shows clearly for both formic acid (33) and the simple alcohols (55) (methanol, ethanol, n-propanol, and n-butanol) that all these solvents swell the crystalline regions of the microfibrils in α-keratin fibers. In the case of the alcohols the range of swelling is 9–11% in the distance between the helices with no

apparent loss of the helical content of the fiber. In the case of the alcohols (56), Speakman obtained a progressive increase of mechanical stiffness of the fibers with increase of molecular size. However, if the tests are carried out to mechanical equilibrium so that the dynamic processes, which are slower for a fiber in the alcohols compared with water, have time to relax, then the fibers indicate a considerable reduction in their stiffness in the "Hookean" region (57). This reduction is the expected consequence of the swelling of the crystalline regions.

Bendit (33) has shown that in 99% formic acid the distance between α-helices in the crystalline region has increased by about 17% above the value in water. For an aqueous solution of formic acid up to 70% (V/V) optical birefringence measurements show no change in the crystallinity of the fibers. However, the "Hookean" Young's Modulus of the fibers up to this formic acid concentration decreases continously to a value of 10^8 pascals, a factor of 20 down on their stiffness in water. This indicates a progressive penetration of the microfibrils by the formic acid with the α-helices intact but certainly weakened by the penetration. The result is in contrast to the effect of immersion of fibres in increasingly higher concentration of lithium bromide solutions, as indicated earlier in this review (33). In the latter case the rapid mechanical weakening of the fiber between 6 and 7 Molar concentrations of aqueous lithium bromide solution results from a randomization of the α-helical structure. Up to just below 6 Molar concentration the mechanical weakening of the fiber was confined to the matrix. In concentrated urea for aqueous solutions as high as 10 Molar the stiffness of the fiber suggests no weakening of the microfibrils (33), with all the change being confined to the matrix. Measurements of optical birefringence also indicate that the crystallinity of the fiber is little changed.

Summarizing the effect of swelling on the physical properties of an α-keratin fiber, we see that three distinct categories of events may occur with three different effects on the mechanical properties of the fiber:

(a) The matrix is the main structure swollen, as in the case of water and urea solutions which results in only a weakening and increased mobility of the matrix with the ordered microfibrils intact.

(b) The matrix and microfibrils swollen with the α-helices intact as in the case of the alcohols and formic acid up to 70% concentration in water (V/V), results in a progressive mechanical weakening of the matrix and microfibrils but has little effect on the optical birefringence, with the X-ray diffraction α-pattern still present but indicating the swelling.

(c) The matrix, microfibrils swollen and the α-helices randomized as for fibers in concentrated aqueous solutions of lithium bromide at molarities greater than 6.6M. The fiber's mechanical stiffness is drastically reduced and its value corresponds to that of a purely elastomeric solid. The high angle X-ray diffraction α-pattern and the optical birefringence have both disappeared in agreement with the structure now consisting of randomized polypeptide chains.

THE YIELD REGION

MECHANICAL

When an α-keratin fiber is extended at a constant rate of straining beyond 2% strain, especially in water, the value of the stress on the fiber does not increase markedly until

about 25-30% strain is reached. This region of extension with little change in stress is the Yield region. Speakman (3) originally demonstrated that for mechanical deformations in this region the properties of the fiber were completely recoverable after relaxation in water in room temperature overnight, provided the deformation had not been maintained too long (< 1 hour) or at a temperature greater than about 50°C. Further work in this field of recovery of mechanical properties after deformation, has shown that this property of recovery is quite sharply limited to the Yield region (58). Extension beyond the Yield region results in a very rapid increase in irrecoverability of mechanical properties accompanied by covalent bond breakdown, as demonstrated by the formation of free radical detected by election spin resonance technique (59).

The behavior of fibers in creep (60) and stress-relaxation (61) for strains in the Yield region is completely non-linear visco-elastic. A complete description for this behavior has been obtained for fibers in water by the application of the Burte-Halsey model (60,62). The fiber can be considered to consist of a continuum of units which can exist in a short state A or an extended state B with an energy barrier between the two states. The description of α-keratin fibers in water in terms of these Burte-Halsey units defines the mechanical properties of the fiber with change of temperature, force, and time (60).

As the fiber is extended from the Hookean into the Yield region, the Burte Halsey units, which are in state A and tensioned when the fiber is in the "Hookean" region, begin to transform into state B units. The whole Yield region corresponds to a phase transition of state A ⇌ state B with the stress remaining constant with the temperature constant as would be expected in such a first order transition. The length of the fiber is defined by the proportion of units in the longer state B as against the proportion in state A. Extrapolation of the fixed stress values for the state A ⇌ state B situation at different temperatures for fibers in water suggests that the transformation of all the state A to state B would occur at zero stress at 160°C. This spontaneous "melt" in water assumes that the fiber is unaffected structurally by any irreversible way. Melting experiments carried out on both hair and wool keratin fibers in water have shown that the melting process is time dependent, occuring at 130°C in minutes and at 120°C in hours (63,64). These latter "melting" processes are irreversible and represent the combination of transformation of units A → units B and the breakdown of the disulphide crosslinks in the structure, which stabilize units A and hence result in a temperature reduction of the melt as this breakdown occurs.

Recent dynamic mechanical measurements (53) using oscillatory displacement techniques at 118hz has shown a clear separation between two major mechanical events at all relative humidities (Figure 3). As the fiber is extended from the "Hookean" to the Yield region there is a rapid loss of dynamic stress as unfolding of units within the structure commences. This unfolding process is quite independent of the moisture content of the fiber and occurs in parallel with a moisture sensitive amorphous thixotropic structure, which during extension of the fiber goes through a gel-sol transformation. The transformation of units from state A to extended state B can be understood as corresponding to the extension of whole cooperative groups of α-helices extending by unfolding into the extended β-configuration. The dynamic data suggests that the units unfolding as the fiber is extended into the Yield region are responsible for a loss of dynamic stress independent of the moisture content of the fiber. Equation of these A units with α-helical units of the microfibrils is therefore
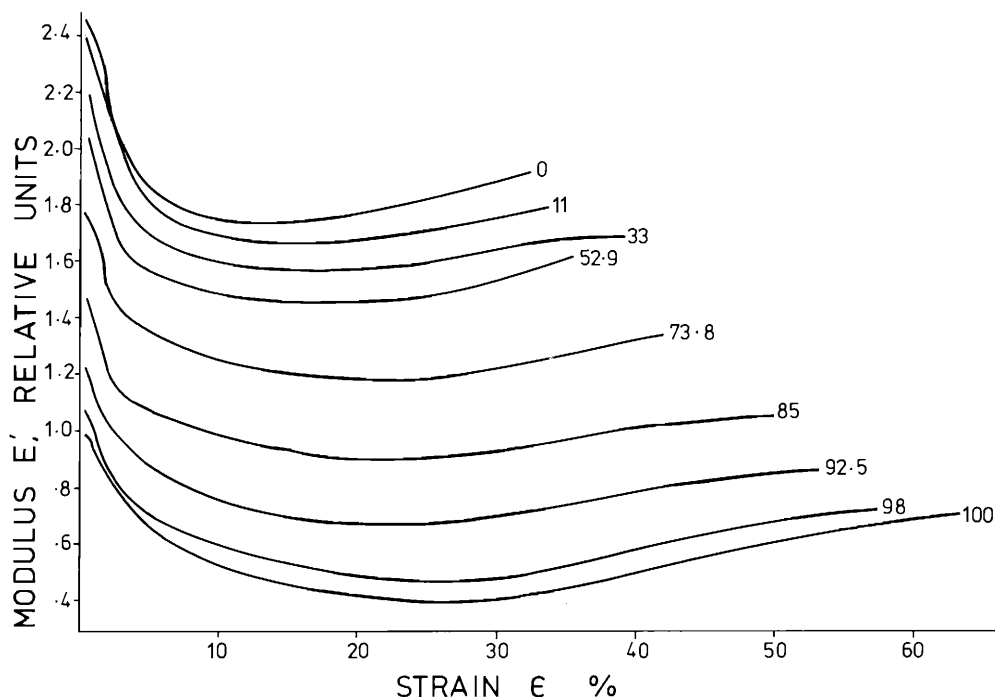
Figure 3. The dynamic modulus E^1 of Lincoln wool fibers against longitudinal strain ϵ for different relative humidities as indicated on each curve. The drop of E^1 as the fiber is extended into the Yield region corresponds to the unfolding of the α-helical structure within the fiber (see text).

particularly appropriate, as is also the moisture sensitive amorphous thixotropic structure with the matrix phase.

Because in longitudinal extension matrix properties act in parallel with microfibrils but in water are relatively weak, they are best observed in the lateral or torsional behavior of the fiber where their effect is dominant. Extension at a constant rate of strain in the direction perpendicular to the fiber direction for rhinoceros horn or African porcupine quill in water (65) results in a hyperbolic relationship between stress and strain with an initial incremental modulus of about 3×10^8 pascals which rapidly drops to the order of 2×10^7 pascals (Figure 2). When extension ceases and the fiber is reextended or contracted at a constant rate the incremental modulus is again high, rapidly dropping to a low value with distortion (65). This behavior can best be described as thixotropic, corresponding to a material on distortion going from a gel to a sol state and (as indicated previously) is the behavior already associated with the matrix.

X-RAY DIFFRACTION AND $\alpha \rightleftharpoons \beta$ TRANSFORMATION

Bendit (66) has shown that for α-keratin fibers extended in the Yield region there is a progressive loss of α-helical content as indicated by the high angle X-ray diffraction pattern. He was able to detect the presence of the extended β-keratin configuration at a few percent strain and a progressive increase of the amount of β-keratin present with further extension of the fiber. At the end of the Yield region about 30% of the original

α-keratin as judged by X-ray diffraction measurement had been unfolded. The process of unfolding the crystalline α-helical structure by extension and forming extended β-keratin had been shown by Astbury (67) to be quite recoverable. When the fiber is returned on release to its original length, provided the temperature at which the extension occurred was not higher than about 50°C for a fiber in water, the β-keratin disappeared and the α-keratin structure returned. The evidence appears clear, that in the Yield region the mechanical transformation of Burte-Halsey units from state A to state B, and units of crystalline α-helical material being unfolded forming extended β-keratin are the same event.

INFRA-RED ANALYSIS AND ELECTRICAL CONDUCTIVITY

Infra-red absorption measurements on the Amide-N-H showed that if α-keratin fibers were immersed in heavy water, exchange of $-NH$ to $-ND$ occurred primarily in the non-helical amide groups. However, when α-keratin fibers in D_2O are extended into the Yield region (and further) the deuteration occurs of the helical amide groups opened up by the extension (68). The unfolding of the α-helices occurs with an apparent absoprtion of water by the opened up microfibrillar structure. Microscopic measurements by Haly (69) have shown that extension into the Yield region for a fiber in water is accompanied by an increase in moisture content for the fiber. Measurements of changes of electrical conductivity with extension into the Yield region also clearly indicate that the process of extension of a fiber is accompanied by moisture uptake into the microfibrils. If in a high humidity environment ($\sim$ 90% Relative Humidity) a fiber is extended to a value of strain in the Yield region and held at this extension, the conductivity of the fiber initially drops markedly, and then recovers to an equilibrium value at a rate determined by the diffusion of water from the environment into the fiber (70). The initial extension opens up the microfibrils so that water is transferred from the matrix. This results in a rapid loss of conduction by the depleted network of water molecules in the matrix responsible for the proton semi-conduction mechanism. Water to replace this depletion must come from the environment, and as shown by Algie this replacement may be hindered by the application of a barrier coating on the fiber surface.

THE POST YIELD REGION

MECHANICAL

The stiffening of α-keratin fibers on extension into the Post-Yield region was shown by Speakman (3) to be independent of the moisture content of the fiber. The increase of the incremental longitudinal modulus was shown to result from a covalently bonded network involving the cystine bond. Torsional data (71) obtained for fibers longitudinally extended to as high as 60% strain indicated no increase in the torsional rigidity of the fiber with strain, thus suggesting that the increased stiffness of the Post-Yield region is produced by material forming a part of the microfibrillar structure rather than the matrix. The sharpness of the onset of irrecoverability (58) of mechanical properties as a fiber is extended into the Post-Yield region also suggests that the change of events from the Yield to Post-Yield region involves highly ordered structures as may be associated with the microfibrils.

It has been shown from mechanical measurements on chemically modified fibers that the Post-Yield region slope is dependent on the cystine content of the fiber (72). This, however, is not the case for fibers in which the cystine content has been modified by a specialized feeding technique applied to the animal producing the fiber (73). An increase of 35% in the cystine content of the same wool fiber obtained by this latter method has negligible effect on the Post-Yield region of that fiber. It was shown for these fibers that the increase of cystine was produced in the matrix protein only, again emphasising the relationship between the Post-Yield region mechanics and the microfibrils of the α-keratin structure.

X-RAY DIFFRACTION

In the Post-Yield region extension of the α-keratin fibers results in an increasing loss of α-helical structure (66). For fibers extended at room temperature at strains of 50–60% all crystalline α-helical material has disappeared as far as X-ray diffraction measurements indicate. This disappearance of the ordered α-helical material with fiber extension is doubtlessly assisted by the association of the α-helices with the covalent bonded network present in the microfibrils and responsible for the stiffening of the fiber structure in the Post-Yield region. The presence of such a network would create steric hindrance to the extension of each α-helical unit to its full β-extended state. This would result in the partial extension of a large proportion of the α-helical units at a strain level lower than that expected if full unhindered extension occurred as in the Yield region.

SUMMARY OF THE STATE OF KERATIN FIBER ON EXTENSION

The evidence reviewed above consolidates the long accepted view of the two-phase nature of α-keratin fibers, when considering their mechanical properties. Mechanically only two distinct phases can be separated out, and when considering the term "matrix" essentially we are taking into account not only the material seen under the electronmicroscope as existing between the microfibrils, but all the material present, whose mechanical properties are indistinguishable from that of the matrix. What is the mechanical "microfibril" also does not necessarily correspond completely with the microfibril visible under the electronmicroscope. Side chains from α-helical components of the microfibrils certainly must interact with the matrix and the distinction of these into one or other phase is difficult. Table I sets out in summary the broad

Table I

A Description of the Major Molecular Events Occurring Within the Microfibrils and Matrix of a Keratin Fiber as Reflected by the Mechanical Properties of the Fiber.

Region of Extension	Microfibrils	Matrix
"Hookean"	α — helices strained	H-bonded water network + globular proteins in "gel" state
Yield	$\alpha \rightarrow \beta$	Structure in "sol" state
Post-yield	$\alpha \rightarrow \beta$ + Covalent network under strain with possible bond breakdown	Structure in "sol" state

distinguishing mechanical events which occur in each of the two phases during the extension of the fiber. These are the events which are compatible with the physical evidence available and lead to an understanding of the mechanical properties of α-keratin fibers.

SET IN α-KERATIN

To obtain set in a fiber it is necessary not only to reduce the forces tending to return the fiber to its native configuration, but also to create new bonds in equilibrium with the setting strain. These latter bonds will oppose on release of the fiber any tendency for the fiber to return to its original state. In the case of "wet setting" of hair and wool fibers, the setting strain is applied to the fiber in a wet state, which assists in the rapid breakdown of weak interactions (hydrogen bonds, Coulombic interactions, etc.). If the fiber is dried while held strained, new interactions are formed between components of the keratin structure by the removal of water and the reduction of swelling. On release dry, the greater part of the fiber strain is retained, the fiber is set. However, if placed in water this set is released, and the fiber returns to its native configuration. This set is referred to as the Cohesive set, and is dependent on the breakdown and reformation of the Cohesive forces within the fiber. In commercial practice, where set in hair or wool textile material must be stable in the presence of moisture, it is necessary for the breakdown and reformation of bonds at the setting strain to involve covalent bonds, which will not be affected by the presence of moisture in the fiber. The disulphide bond formed by the diamino acid cystine present in α-keratins is important in stabilizing the native configuration of the fiber. The breakdown and reformation of this bond via the mechanism of sulfhydryl-disulphide interchange (74) forms the basis of most techniques of "permanent" setting of α-keratin fibers. Disulphide bonds in neutral or alkaline aqueous solutions can undergo a breakdown and reformation mechanism referred to as sulfhydryl-disulphide interchange in the presence of thiol groups by the following scheme:

$$-S_a^- + -S_bS_c- \rightleftharpoons -S_b^- + S_aS_c-$$
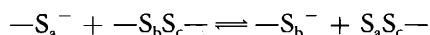
This reaction results in the removal of disulphide bonds opposing the setting strain, the interchange favoring the breakdown of strained bonds, and their reformation in equilibrium, with the set configuration. In normal wool and hair about 0.5% of the amino acid residues are thiols and the above mechanism proceeds in water at temperatures above 50–60°C. If more rapid interchange at lower temperatures is required to obtain this bond breakdown and reformation, it is necessary to form more thiols by reduction of disulphide groups. The review of the chemistry involved, and the various techniques of setting of hair and wool, is beyond the scope of this consideration of the physical properties of α-keratin fibers. However, it is necessary to note the effect of setting under certain conditions on the mechanical properties of the α-keratin fibers and what this reveals with regard to fine structure of the fibers.

If a fiber is set by heating in distilled water at a strain corresponding to the Yield Region, the mechanical properties of the fiber are modified to a varying degree (see Figure 4). The stress-strain curve of the fiber is modified up to a definite strain level dependent on the setting strain, and beyond that level the stress-strain curve reverts to that of the unset fiber (75). The whole behavior of the fiber suggests that only zones
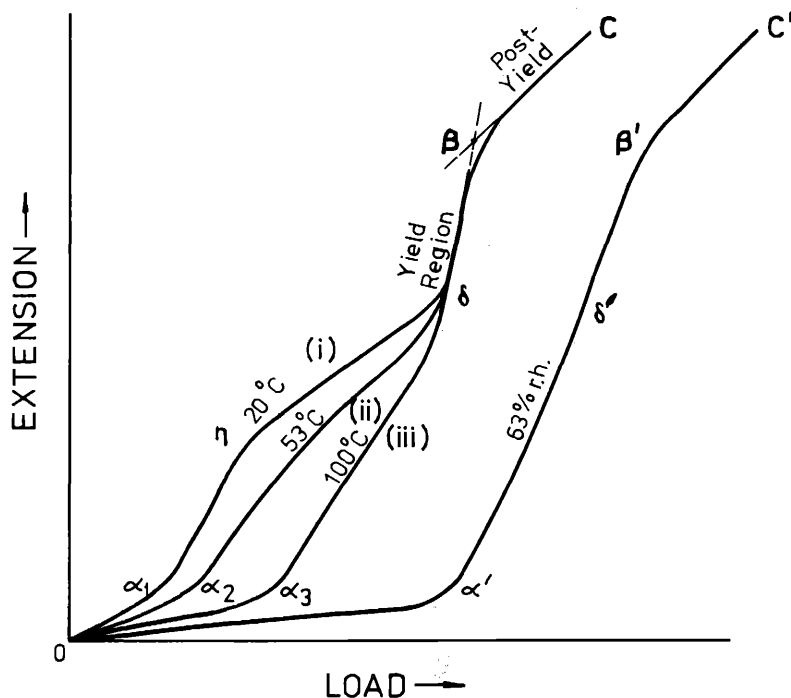
Figure 4. The typical load-extension curve of a wool fiber in water at 20°C after having been held strained 10% for one minute in boiling, distilled water and then released for one hour in water at: (i) 20°C, (ii) 53°C, (iii) 100°C. Also shown is the curve in an environment of 63% relative humidity and 20°C for a fiber set and released as for case (iii). In all cases the modification due to setting mechanical properties of the fiber is limited to the range α to δ, a range defined by the setting strain.

within the microfibrils of the fiber have been modified by the setting treatment, and the zones affected relate to the structure unfolded by the setting strain. The presence of these affected zones has been confirmed by torsional experiments on hair fibers set at various strains within the Yield region (76). These torsional experiments showed a linearly proportional relationship between setting strain and zones present in the set keratin-structure.

SERIES-ZONE MODEL

As a further refinement in our understanding of the mechanical properties of α-keratins, the series-zone model (77) was proposed based on results obtained for longitudinal stress-strain behavior in water and in concentrated lithium bromide of unmodified and of set fibers (75). The model proposes the existence of two varieties of alternating zones along the microfibrils called X and Y, differing in their stability. The α-helices within the X zones are the 30% that unfold in the Yield region of the stress-strain curve of a keratin fiber, and the Y zone α-helices are unfolded with extension into the Post-Yield region. The opening up of the X zones is quite recoverable with no covalent bond breakdown involved, whereas the opening up of the Y zones as the fiber is extended into the Post-Yield region involves the breakdown of covalent interactions (disulphide bonds) which stabilize these zones. This series-zone

model, which is superimposed on microfibrils of the two-phase model, has been successful in explaining many mechanical phenomena for keratin fibers, such as the two-stage contraction behavior in concentrated lithium bromide solution (77).

Recent interpretation of low angle X-ray diffraction data (78) by Fraser *et al.* has led to a suggested model for the microfibrils as shown in Figure 5. In cross section the
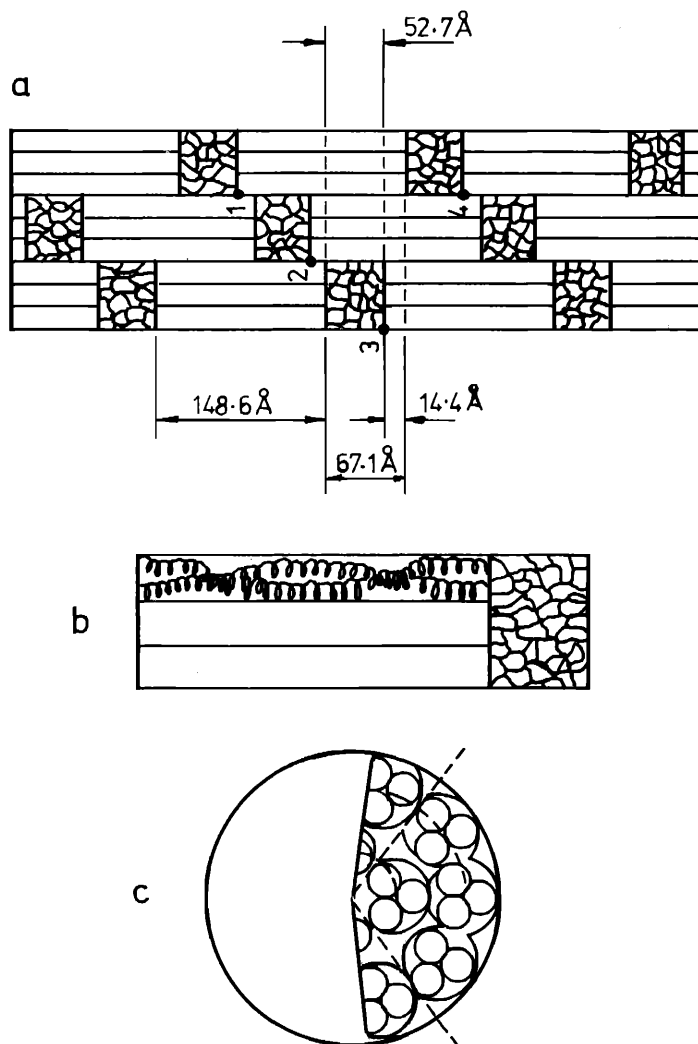

Figure 5. Structure of a microfibril in α-keratin as proposed by Fraser *et al.*(78). The microfibril consists of three units, each containing four protofibrils with three protofibrils on the outside of the microfibril and one protofibril in the core of the microfibril. Each protofibril consists of a coiled rope with segments containing two or three α-helices followed by a nonhelical structure. Within each unit the helical segments come together to form a purely helical component, 148.6 Å long, alternated by nonhelical segments of 52.7 Å. Between the three units the helical components are staggered by 67.1 Å relative to each other. (a) Radial projection of the surface of the microfibril illustrating the nine protofibrils on the outside of the microfibril with the helical segments clear and the nonhelical parts covered with random lines. (b) Portion of a unit on the outside of a microfibril with two α-helices in one of the protofibrils. (c) Cross section of the microfibril with three helices per protofibril, illustrating the relative position of the four protofibrils in the one unit between the dotted radii (1 Å = 0.1 nm).

proposed microfibrils consist of zones of purely α-helices for a longitudinal distance of 1.44 nm in series with zones of 5.27 nm containing 2/3 α-helical material and 1/3 non-helical high cystine material (see Figure 5). The purely α-helical zones may be identified with the X zones, and the others with the Y zones. Calculations can be made on the extensibility of these X zones based on the extension of an α-helix being 125% when transformed to the β state. The amount of strain corresponding to the unfolding of the α-helices of the X zones in the Yield region = 125 × [1.44/(1.44 + 5.27)] = 26.8%, a very reasonable estimate compared with the value of 28% obtained from stress-strain data (75). The proportion for the microfibrils of α-helical material in X zones on Fraser's data = [1.44/(1.44 + ⅔ × 5.27)] = 0.29 is in agreement with the value of 0.30 obtained by Bendit (66) for the number of α-helices unfolded at the end of the Yield Region.

The length of 1.44 nm for the X zones means that the zones consist of short lengths of α-helices, a little less than 3 turns. This would explain why there is no problem in the extension of these units into the β state. Any wrapping around each other of the α-helices due to Pauling's coiled-coiled proposals for the association of α-helices (79) would be negligible over such a short distance.

As already quoted, evidence from torsional data for fibers extended into the Post-Yield region indicates no increase in the stiffness of the matrix with the extension (71). In agreement with this and the "crystalline" sharpness of the change over events such as formation of free radicals (59) and the indication of mechanical irrecoverability (58), the series-zone model has associated the increased stiffness of the extending fibre in the Post-Yield region with the highly ordered microfibrils. Other mechanical models have been proposed to explain the behavior of α-keratin fibers extended into the Post-Yield region (80). These, however, do involve change in the mechanical behavior of the matrix with extension of the fiber beyond the Yield region. The evidence from X-ray diffraction for the zonal nature of the microfibrils, the quantitative agreement of this evidence with the proposed series-zone model and the model's ability to explain the mechanical behavior of fibers modified by setting treatments, the two-stage super-contraction of fibers heated in concentrated aqueous lithium bromide solutions, all emphasize the usefulness of this model in our understanding of the behavior of α-keratin fibers.

ACKNOWLEDGEMENTS

REFERENCES

(1) W. T. Astbury and A. Street, X-ray studies of the structure of hair, wool and related fibres. I. *General Phil. Trans. Roy. Soc.*, **230A**, 75 (1931).
(2) G. Blankenburg, Stress-strain properties and supercontraction of wool keratin in aqueous alcohol media. III Congress International de la Recherche Textile Lainiere (Paris) **Section 2**, 31 (1965).
(3) J. B. Speakman, The intracellular structure of the wool fibre, *J. Textile Inst.*, 18, T431 (1927).
(4) H. Zahn, Wool is not keratin only. *Proc. 6th Quinquennial International Wool Textile Research Conf.*, Vol. I, Pretoria (1980).
(5) R. W. Moncrieff, *Wool Shrinkage and Its Prevention*, (National Trades Press, London, 1953).

(6) S. E. Kelly and V. N. E. Robinson, The effect of grooming on the hair cuticle, *J. Soc. Cosmet. Chem.*, **33**, 203 (1982).

(7) R. D. B. Fraser, L. N. Jones, R. P. Macrae, E. Suzuki, and P. A. Tulloch, The fine structure of the wool fibre. *Proc. 6th Quinquennial International Wool Textile Research Conf.*, Vol. I, Pretoria (1980).

(8) J. H. Bradbury, The structure and chemistry of keratin fibers, *Advances in Protein Chemistry*, **27**, 111 (1973).

(9) M. W. Andrews, M. Feughelman, and T. W. Mitchell, Torsional rigidity of the ortho- and para-cortex of wool, *Textile Res. J.*, **32**, 421 (1962).

(10) M. Feughelman, The relation between structure and the mechanical properties of keratin fibers, *Applied Polymer Symposium*, **No. 18**, 757 (1971).

(11) R. D. B. Fraser, T. P. Macrae, and G. E. Rogers, *Keratins, Their Composition, Structure and Biosynthesis* (Charles C. Thomas, Springfield, Ill., U.S.A., 1972).

(12) R. D. B. Fraser, J. M. Gillespie, and T. P. Macrae, Tyrosine-rich proteins in keratins, *Comp. Biochem. Physiol.*, **44B**, 943 (1973).

(13) M. Feughelman and T. W. Mitchell, The mechanical similarity of "melted" and permanently set keratin fibers, *Textile Res. J.*, **39**, 930 (1969).

(14) J. B. Speakman, The gel structure of the wool fibre, *J. Textile Inst.*, **17**, T457 (1926).

(15) E. G. Bendit, There is no Hookean region in the stress-strain curve of keratin (or other viscoelastic polymers), *J. Macromol. Sci.—Physics*, **B17 (1)**, 129 (1980).

(16) J. Sikorski and H. J. Woods, The effect of rate of extension on the Youngs' modulus of keratin fibres, *Leeds Phil. Soc.*, **5**, 313 (1950).

(17) M. Feughelman, Mechanical properties of wool fibres. I. Creep in the "Hookean" region of wool fibres in water, *J. Textile Inst.*, **49**, T361 (1958).

(18) B. M. Chapman, Bending stress relaxation and recovery of wool, nylon 66, and terylene fibers, *J. Appl. Polymer Sci.*, **17**, 1693 (1973).

(19) H. J. Woods, The effect of humidity and temperature on the Youngs' modulus of keratin fibres, *Proc. Leeds Phil. & Lit. Soc. (Scientific)*, **3**, 577 (1940).

(20) M. Feughelman and M. S. Robinson, Some mechanical properties of wool fibers in the "Hookean" region from zero to 100% relative humidity, *Textile Res. J.*, **41**, 469 (1971).

(21) G. King, The effect of strongly hydrogen bonding agents on some polar polymers, *J. Colloid Sci.*, **2**, 551 (1947).

(22) M. Feughelman and M. S. Robinson, Stress-relaxation of wool fibers in water at extensions in the Hookean region over the temperature range 0°–90°C, *Textile Res. J.*, **39**, 196 (1969).

(23) M. Feughelman and M. S. Robinson, The tensile behaviour of wool fibers in liquid nitrogen, *Textile Res. J.*, **37**, 705 (1967).

(24) N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge University Press, 1970).

(25) M. Chaikin and W. H. Chemberlain, The propogation of longitudinal stress pulses in textile fibres. Part II. *J. Textile Inst.*, **46**, T44 (1955).

(26) J. B. Speakman and E. Stott, The titration curve of wool keratin, *Trans. Faraday Soc.*, **30**, 539 (1934).

(27) M. Feughelman, Mechanical hysteresis in wool keratin fibers, *J. Macromol. Sci. B7 (3)*, 569 (1973).

(28) M. Feughelman, G. D. Danilatos, and D. Dubro, Observations on the property of microfibrils and matrix in α-keratins. In *Fibrous Proteins: Scientific, Industrial and Medical Aspects*, D. A. D. Parry and L. K. Creamer, eds. (Academic Press, London, 1980), Vol. 2, pp. 195–202.

(29) W. T. Astbury and J. W. Haggith, Pre-transformation stretching of the so-called 5.1Å and 1.5Å spacings in α-keratin, *Biochim. Biophys. Acta*, **10**, 433 (1953).

(30) L. Pauling and R. B. Corey, Two hydrogen-bonded spiral configurations of the polypeptide chain, *J. Amer. Chem. Soc.*, **72**, 5349 (1950).

(31) M. Feughelman and M. Druhala, The stability of the α-helix of polypeptides, *Polymer Letters*, **15**, 311 (1977).

(32) R. D. B. Fraser, T. P. Macrae, G. R. Millward, D. A. D. Parry, E. Suzuki, and P. A. Tulloch, The molecular structure of keratins, *Appl. Polym. Symp.*, **No. 18**, 65 (1971).

(33) M. Feughelman, The longitudinal stability of keratin fibres, *Symp. on Fibrous Proteins*, Australia, (1967). W. G. Crewther, ed. Butterworths.

(34) A. R. Haly and O. A. Swanepoel, The physical properties of wool fibers at various regains. Part V. The nature of birefringence, *Textile Res. J.*, **31**, 966 (1961).

(35) E. G. Bendit and M. Feughelman, Keratin. In *Encyclopaedia of Polymer Science and Technology*, Vol. 8, 1 (1968).

(36) E. J. Ambrose and A. Elliott, Infra-red spectra and structure of fibrous proteins, *Proc. Roy. Soc. London, Ser. A.*, **206**, (1951).

(37) K. D. Parker, Infra-red dichroism of fibrous proteins, *Biochim. Biophys. Acta,* **17,** 148 (1955).

(38) R. D. B. Fraser and E. Suzuki, Infra-red dichroism in α-keratin, *J. Mol. Biol.,* **9,** 829 (1964).

(39) J. E. Algie, J. G. Downes, and B. H. Mackay, Electrical conduction in keratin, *Textile Res. J.,* **30,** 432 (1960).

(40) G. King and J. A. Medley, D.C. conduction in swollen polar polymers, Parts I and II. *J. Colloid Sci.,* **4,** 1 (1949).

(41) J. E. Algie, Dielectric constant and conductance changes in wool fiber produced by step changes in the relative humidity, *Textile Res. J.,* **34,** 477 (1964).

(42) M. Feughelman, A two-phase structure for keratin fibers, *Textile Res. J.,* **29,** 223 (1959).

(43) J. B. Speakman, The rigidity of wool and its changes with adsorption of water-vapour, *Trans. Faraday Soc.,* **25,** 92 (1929).

(44) T. W. Mitchell and M. Feughelman, The torsional properties of single wool fibres. Part I. Torque-twist relationships and torsional relaxation in wet and dry fibres, *Textile Res. J.,* **30,** 662 (1960).

(45) W. G. Crewther, R. D. B. Fraser, F. G. Lennox, and H. Lindley, The chemistry of keratins, *Advances of Protein Chemistry,* **20,** 101 (1965).

(46) E. G. Bendit, The distribution of high and low-sulphur fractions in α-keratin, *Textile Res. J.,* **38,** 15 (1968).

(47) M. Feughelman, Intermicrofibrillar linkages in α-keratin fibers, *Textile Res. J.,* **49,** 704 (1979).

(48) R. D. B. Fraser, T. P. Macrae, and G. E. Rogers, Molecular organisation in alpha keratin, *Nature,* **193,** 1052 (1962).

(49) E. G. Bendit, The location and function of the high glycine tyrosine proteins in keratins. In *Fibrous Proteins: Scientific, Industrial and Medical Aspects,* D. A. D. Parry and L. K. Creamer, eds. (Academic Press, London, 1980), Vol. 2, p. 183.

(50) R. D. B. Fraser and T. P. Macrae, Molecular structure and mechanical properties of keratins. In *The Mechanical Properties of Biological Materials* (Society of Experimental Biology, London 1980).

(51) M. Feughelman and I. C. Watt, Torsional properties of chemically modified wool fibers, *Textile Res. J.,* **36,** 849 (1966).

(52) M. Feughelman and I. C. Watt, Wool fibers treated with ninhydrin or formaldehyde: mechanical properties, *Textile Res. J.,* **34,** 643 (1964).

(53) G. Danilatos and M. Feughelman, Dynamic mechanical properties of α-keratin fibers during extension, *J. Macromol. Sci.—Physics,* **B16(4),** 581 (1979).

(54) P. Mason, The viscoelasticity and structure of fibrous proteins. II. Further dynamic measurements of keratin, *Kolloid-Z.,* **218,** 46 (1967).

(55) M. Feughelman and J. W. Snaith, The swelling of crystalline α-keratin by alcohols, *Biochim. et Biophys. Acta,* **79,** 203 (1964).

(56) J. B. Speakman, The elastic properties of wool in organic liquids, *Trans. Faraday Soc.,* **26,** 61 (1930).

(57) F. J. Wortmann and H. Zahn, The influence of water and organic solvents on the rheological properties of single wool fibres, *Proc. 6th Quinquennial International Wool Textile Research Conf.,* Vol. II, 323, Pretoria (1980).

(58) M. Feughelman, A note on the recoverability of mechanical properties in wool fibres, *J. Textile Inst.,* **59,** T548 (1968).

(59) M. Pailthorpe, T. Singhasuwich, and M. Feughelman, Unpublished data.

(60) M. Feughelman, Creep of wool fibres in water, *J. Textile Inst.,* **45,** T630 (1954).

(61) M. Feughelman and B. J. Rigby, A two-energy state model for the stress-relaxation and creep of wool fibres in water, *Proc. of International Wool Textile Research Conference,* D-62, Australia (1955).

(62) H. Burte and G. Halsey, A new theory of non-linear viscoelasticity, *Textile Res. J.,* **17,** 465 (1947).

(63) T. W. Mitchell and M. Feughelman, The phase transition in wet α-keratin fibres above 100°C, *Kolloid Z.u.Z. Polymere,* **229** 124 (1969).

(64) H. Zahn, Alteration of wool by chemical and thermal action, *Melliand Textilber.,* **13,** 481 (1950).

(65) M. Feughelman and M. Druhala, The lateral mechanical properties of alpha-keratin, *Proc. 5th International Wool Textile Research Conf.,* Vol. 2, 340, Aachen (1975).

(66) E. G. Bendit, The α-β transformation in keratin, *Nature* (London), **179,** 535 (1957).

(67) W. T. Astbury and H. J. Woods, X-ray studies of the structure of hair, wool and related fibres. II. *Phil. Trans. Roy. Soc.,* **232A,** 333 (1933).

(68) E. G. Bendit, M. Feughelman, R. D. B. Fraser, and T. P. Macrae, The hydrogen-deuterium exchange reaction in stretched keratin. *Textile Res. J.,* **29,** 284 (1959).

(69) A. R. Haly and M. Feughelman, Stress changes at constant strain and hydrogen bonding in keratin fibres. *J. Textile Inst.,* **51,** T573 (1960).

(70) J. E. Algie, The variation of electrical resistance with strain of keratin fibers with constant water content, *Textile Res. J.,* **34,** 273 (1964).
(71) M. Feughelman, A note on the role of microfibrils in the mechanical properties of α-keratins, *J. Macromol. Sci.—Physics,* **B16(1),** 155 (1979).
(72) M. Feughelman, The mechanical properties of permanently set and cystine reduced wool fibers at various relative humidities and the structure of wool, *Textile Res. J.,* **33,** 1013 (1963).
(73) M. Feughelman and P. J. Reis, The longitudinal mechanical properties of wool fibers and their relationship to the low sulphur keratin fraction, *Textile Res. J.,* **37,** 334 (1967).
(74) R. W. Burley, Some observations on the extension, contraction and supercontraction of wool fibres, *Proc. International Wool Textile Res. Conf.,* Australia 1955, **D88** (1956).
(75) M. Feughelman, The mechanical properties of set wool fibres and the structure of keratin, *J. Textile Inst.,* **51,** T589 (1960).
(76) M. Feughelman, The microfibril-matrix relationships in the mechanical properties of keratin fibers, Part I. The torsional properties of "melted" and permanently set keratin fibers, *Textile Res. J.,* **48,** 518 (1978).
(77) M. Feughelman and A. R. Haly, Structural features of keratin suggested by its mechanical properties, *Biochim. Biophys. Acta,* **32,** 596 (1959).
(78) R. D. B. Fraser, T. P. Macrae, and E. Suzuki, The structure of the α-keratin microfibril, *J. Mol. Biol.,* **108,** 435 (1976).
(79) L. Pauling and R. B. Corey, Compound helical configurations of polypeptide chains. Structure of proteins of the α-keratin type, *Nature* (London), **171,** 59 (1953).
(80) B. M. Chapman, A mechanical model for wool and other keratin fibers, *Textile Res. J.,* **39,** 1102 (1969).