

## **14. Wool**

### **14.1. Introduction**

Today, wool accounts for only ca. 4 wt% of world textile-fiber production. However, if the value added by dyeing and printing is included, the share in monetary terms is considerably higher. The importance of wool is due to its unique physiological properties as a clothing material and the wide range of techniques for converting it into textiles, including felts and finishing processes.

Some important methods and discoveries in modern biological sciences had their origins in wool research (partition and paper chromatography, the structure of  $\alpha$ - and  $\beta$ -keratin, intermediate filaments).

The production of wool and woolen textiles and the trade in these commodities have played an important role in political and economic history.

### 14.1.1. Definition

The natural fiber wool, like other types of fine and coarse animal hair and also silks ( $\rightarrow$  Silk), is an animal fiber [54], and although the term “wool” can be used in conjunction with the names of various animals, e.g., “angora wool”, it is here understood to include only the hair of the various breeds of domesticated sheep (*Ovis aries*).

### 14.1.2. Historical Aspects [55]–[57]

The wool of the sheep was the first textile raw material used by humans for clothing purposes. The development of clothing began when people first dressed themselves in the skins of mammals. Felts, which are more easily shaped, were produced later from hairs plucked or cut from the animal. The development of spinning and weaving to produce fabrics was a still later development.

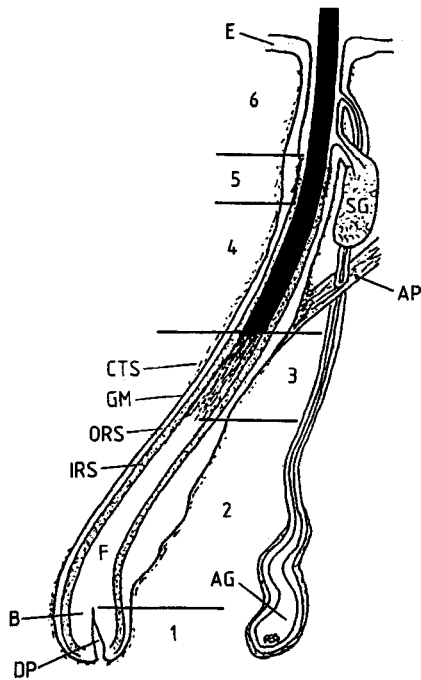
The first country to process and trade in wool was Babylon (Babylonia = land of wool). The oldest known wool fabrics, dating from the second half of the second millennium B.C., were found in Danish tree coffins.

Sheep rearing reached a high point in the Middle Ages and the renaissance. The merino sheep, bred in Spain, produced wool of very fine quality, and in the late 1700s Saxon merinos were exported via England and South Africa to Australia, where the climate proved to be very favorable for rearing this breed.

### 14.1.3. Biology

Wool fibers and other animal hairs, including human hair, are formed in follicles—sheath-like formations of the epidermis, at the base of which are papillae of mesodermal cells (Fig. 1).

Follicles are dynamic organs in which various processes occur simultaneously: cell division, cell differentiation, upward movement of the keratinocytes, biosynthesis of wool proteins as gene products, self-assembly of the proteins to form supramolecular structures, and finally keratinization (cornification) by formation of cross-linked disulfide and isodipeptide bridges. At the same time, cells of the inner and outer root sheath are catabolized [58].



**Figure 1.** Diagram of fully developed wool follicle (not to scale) [58].

The six zones are: 1) Bulb; 2) Keratogenous zone; 3) Zone of final hardening of the fiber; 4) Zone of inner root sheath degradation; 5) Zone of sloughing of inner and outer root sheath cells; 6) Pilary canal.

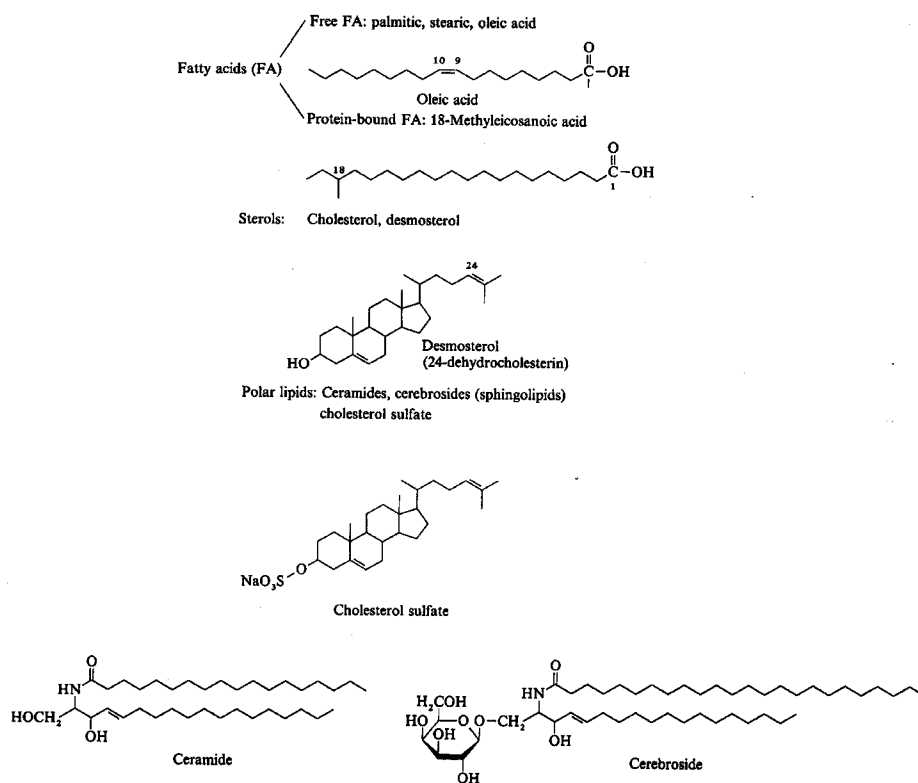
AG = apocrine gland; AP = arrector pili; B = bulb; CTS = connective tissue sheath; DP = dermal papilla; E = epidermis; GM = glassy membrane; IRS = inner root sheath; ORS = outer root sheath; SG = sebaceous gland.

The various stages of development of the growing wool fiber in the follicle can be divided into six zones (Fig. 1). In the upper part of Zone 1, fine keratin intermediate filaments (KIF) and trichohyalin granules are already forming. Between Zones 1 and 2, filaments aggregate to form macrofibrils, in which keratin-associated proteins (KAP) are deposited. In Zone 2, amorphous protein aggregates, ca. 30 nm in diameter, form in the fiber cuticle cells. By the end of Zone 2 the cuticle cells are hardened, while the final keratinization of the entire wool fiber occurs in Zone 3.

#### 14.1.4. Chemical Composition [27], [31]

The protein fiber wool consists of carbon, hydrogen, oxygen, nitrogen, and sulfur. The elemental analysis of wool (free of water) is as follows:

Carbon	50.5 wt %
Hydrogen	6.8 wt %
Oxygen	22.0 wt %
Nitrogen	16.5 wt %
Sulfur	3.7 wt %
Ash	0.5 wt %



**Figure 2.** Structural lipids

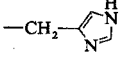
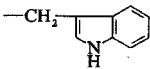
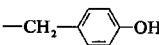

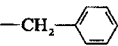
Except for the sulfur content, this composition is typical for all proteins. The high sulfur content is due to the high content of cystine, a double amino acid containing two sulfur atoms in a disulfide bond:  $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{S}-\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ .

The ash contains potassium, sodium, calcium, aluminum, iron, silica, sulfate, carbonate, phosphorus pentoxide, and chloride. Water-free wool consists mainly (ca. 97%) of wool proteins, the remainder being made up of ca. 2% structural lipids (Fig. 2) [59]–[62], ca. 1% mineral salts, nucleic acids [63], [64], and carbohydrates.

Industrially scoured wool has only small residual amounts of woolgrease (ca. 0.5%). The structural lipids, in contrast, are components of the cell membrane complex which binds together the cuticle and cortex cells.

A characteristic of the structural lipids of the cuticle is the presence of a covalently bound branched-chain  $\text{C}_{21}$  fatty acid 18-methyleicosanoic acid [65]–[67].

**Table 1.** Amino acid composition of fine merino wool \* [49]

Group	Name	Side chain	Concentration, $\mu\text{mol/g}$
"Acidic" amino acids and their $\omega$ -amides	aspartic acid	$-\text{CH}_2-\text{COOH}$	200
	glutamic acid	$-(\text{CH}_2)_2-\text{COOH}$	600
	asparagine	$-\text{CH}_2-\text{CONH}_2$	360
	glutamine	$-(\text{CH}_2)_2-\text{CONH}_2$	450
"Basic amino acids and tryptophan	arginine	$-(\text{CH}_2)_3-\text{NHC}(\text{NH}_2)=\text{NH}$	600
	lysine	$-(\text{CH}_2)_4-\text{NH}_2$	250
	histidine	$-\text{CH}_2-$ 	80
	tryptophan	$-\text{CH}_2-$ 	40
Amino acids with hydroxyl groups in the side chain	serine	$-\text{CH}_2-\text{OH}$	900
	threonine	$-\text{CH}(\text{OH})-\text{CH}_3$	570
	tyrosine	$-\text{CH}_2-$ 	350
Sulfur-containing amino acids	cysteine	$-\text{CH}_2-\text{SH}$	10
	thiocysteine	$-\text{CH}_2-\text{S}-\text{SH}$	5
	cystic acid	$-\text{CH}_2-\text{SO}_3\text{H}$	10
	cystine	$-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$	460
	lanthionine	$-\text{CH}_2-\text{S}-\text{CH}_2-$	5
	methionine	$-(\text{CH}_2)_2-\text{S}-\text{CH}_3$	50
Amino acids without reactive groups in the side chain	glycine	$-\text{H}$	760
	alanine	$-\text{CH}_3$	470
	valine	$-\text{CH}(\text{CH}_3)_2$	490
	proline		520
	leucine	$-\text{CH}_2-\text{CH}(\text{CH}_3)_2$	680
	isoleucine	$-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$	270
	phenylalanine	$-\text{CH}_2-$ 	260

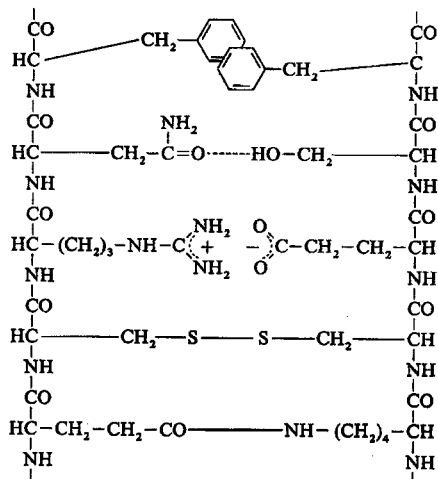
Total hydrolysis of the peptide bonds in wool proteins yields 24 amino acids. The data given in Table 1 were obtained by combining data from acidic and from enzymatic hydrolyses of wool.

The amino acids are classified in five groups: "acidic" amino acids, "basic" amino acids, amino acids with hydroxyl groups, sulfur-containing amino acids, and amino acids with no reactive groups in the side chain. The total amount of amino acids with reactive side chain groups is 5395  $\mu\text{mol/g}$ , and of amino acids without reactive side chain groups 3450  $\mu\text{mol/g}$ . The sum of these two figures, after subtraction of the concentration of C-terminal amino acids (10  $\mu\text{mol/g}$ ), gives a figure of 8835  $\mu\text{mol/g}$  for the concentration of peptide groups in the peptide chains of wool.

Like all proteins, wool contains both cationic and anionic groups, and is therefore amphoteric. The cationic character is due to the protonated side chains of arginine,

lysine, and histidine, and to the small number of free amino groups at the ends of the peptide chains. The amino groups of lysine, histidine, the amino end groups, and the thiol groups of cysteine are important sites for the covalent attachment of reactive dyes [68]. Anionic groups are present as dissociated side chains of aspartic and glutamic acids and as carboxyl end groups.

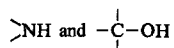
The side chains, which in wool account for a considerable proportion (50%) of the protein material, interact with each other, thereby stabilizing the peptide by forming links between the chains and rings within a chain:



This structural formula is a schematic representation of five such links between segments of two hypothetical peptide chains. From the top downwards it shows interactions between phenyl rings (for the role of aromatic rings as hydrogen bond acceptors see [69]), hydrogen bonds between an asparagine residue and a serine residue, a salt bridge between an arginine residue and a glutamic acid residue [70], a disulfide bridge between two cysteine residues, and an isodipeptide bridge between glutamic acid and lysine [71], [72].

The disulfide bridge plays an important part in stabilizing the wool fiber, leading in particular to its relatively high wet strength, moderate swelling, and insolubility. A second covalent bridge is provided by the isodipeptide  $N_\epsilon$ -( $\gamma$ -glutamyl)lysine, which provides an additional stabilizing effect in the cornified cell envelopes of the cortex and cuticle.

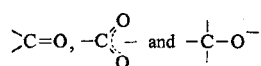
The so-called salt bridge is due to the electrostatic interaction between cationic and anionic side-chain groups. Hydrogen bonds are formed in proteins between



as donors and

**Table 2.** Proteins of the wool fiber [78]

Type of protein	Number of proteins	Range of molecular mass, kDa
<i>Keratins</i>		
Acidic keratins (Type I)	4	40–50
Basic keratins (Type II)	4	56
<i>Keratin associated proteins (KAP)</i>		
High-sulfur proteins	80–100	11 16 19 23
Ultrahigh-sulfur proteins		16
High glycine–tyrosine proteins (Type I)	10	6–9
High glycine–tyrosine proteins (Type II)	5	6–9



as acceptors, especially in the helical rod domains of the keratin filaments.

Hydrophobic effects stabilize the aggregation of nonpolar side chains, so reducing the area of the interface with water.

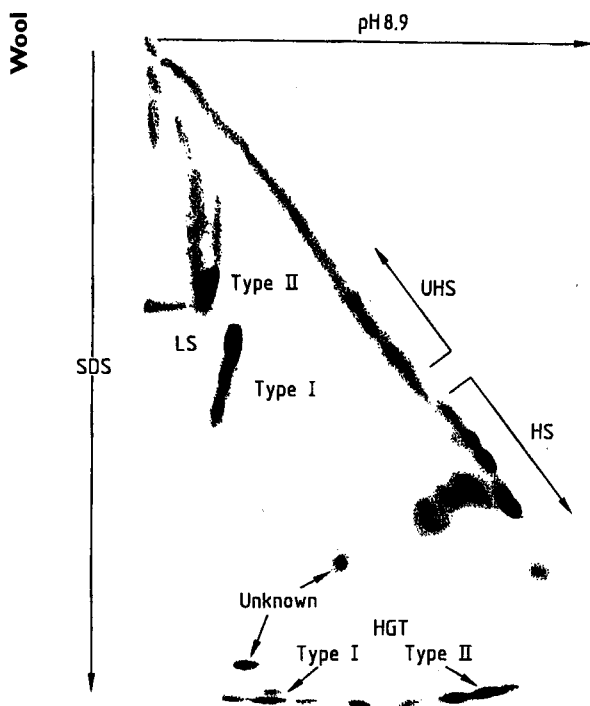
The three-dimensional structure of the wool proteins is stabilized both by the hydrophobic effect and by a wide variety of electrostatic interactions between amino acid constituents [73].

Eight *N*-terminal amino acids have been analyzed by means of 2,4-dinitrofluorobenzene: cystine, glycine, threonine, valine, alanine, serine, and glutamic and aspartic acids. Other *N*-terminal amino acids are present in *N*-acetylated form. Thus, the acid hydrolysis of wool liberates 50  $\mu\text{mol/g}$  acetic acid [74].

*S*-Carboxymethylated soluble wool proteins can be obtained by exhaustive mercapto-lysis and carboxymethylation of the resulting SH groups [75]–[77].

The dissolved *S*-carboxymethylated wool proteins can be separated into the main groups listed in Table 2, and these fractions can be separated into definite proteins, some of which have been sequenced [78]. In two-dimensional polyacrylamide gel electrophoresis [79], the proteins are first separated according to charge, and, in the second dimension, in the presence of sodium dodecylsulfate (SDS), according to molecular mass (Fig. 3). The heterogeneity of this class of proteins can thus be demonstrated by a relatively simple analytical process. The keratins are well separated from the sulfur-rich proteins because of their high molecular mass, and the high glycine–tyrosine proteins are nearly at the front of the SDS dimension because their molecular mass is very low. Some of the heterogeneity of the keratins is caused by phosphorylation [80].

The keratins in wool come from the microfibrils, which like some other protein filaments are classified as intermediate filaments [81]–[84]. Intermediate filaments



**Figure 3.** Two-dimensional polyacrylamide gel electrophoretic separation of wool proteins [79].

The proteins were extracted from merino wool and subjected to electrophoresis at pH 8.9 in one direction and in the presence of SDS in the other.

LS = low sulfur; HS = high sulfur; UHS = ultra-high sulfur; HGT = high glycine-tyrosine.

form an important filamentary system in the cytoplasm of higher eukaryotic cells. They have a diameter of 8–10 nm, and are thus larger than actin filaments and smaller than the microtubuli [41] of the cell.

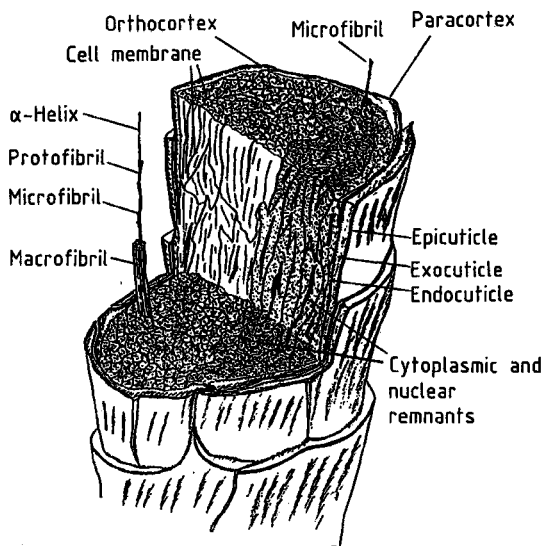
## 14.2. Structure

### 14.2.1. Morphology [85]–[89]

Wool fibers consist of two cell types: cuticle and cortex cells. In coarse fibers, there is also a central medulla (Fig. 4).

The cuticle [87] consists of plate-shaped cells (“scales”) that overlap longitudinally and peripherally, with the 1  $\mu\text{m}$  thick edges of the scales pointing in the direction of the tip of the fiber. Each cuticle cell consists of three layers with different cystine and isodipeptide contents: the outer a-layer or epicuticle, the exocuticle, and the endocuticle. Between overlapping cuticle cells is the cell membrane complex. The extreme outer layer of the cuticle consists of fatty acids (principal component 18-methyleicosanoic acid, Fig. 2) covalently anchored in the a-layer (epicuticle).





**Figure 4.** Longitudinal and cross section of a fine merino wool fiber [86]

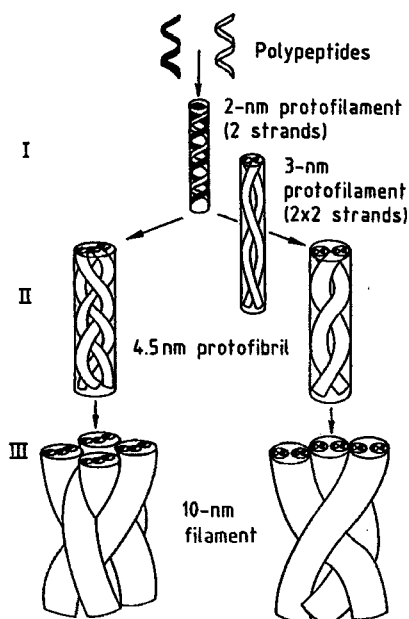
The cortex consists of spindle-shaped interdigitated cells [88]. These consist of ortho, para, and more rarely meso cells, all differing in their cystine content and staining behavior with silver salts. A cortex cell of wool contains around 5–8 macrofibrils with a diameter of 300 nm at their widest point. Between the macrofibrils are cytoplasmic and nuclear remnants of the keratinocytes. This intermacrofibrillar material swells in water more than the macrofibrils. A macrofibril is a bundle of 500–800 keratin intermediate filaments (microfibrils). Keratin-associated proteins (KAP) are intercalated, enveloping individual microfibrils and their aggregates. An individual microfibril consists of protofibrils, which in turn consist of protofilaments (Fig. 5) [89].

The medulla in coarser wool fibers consists of hollow cells with a skeleton of amorphous proteins and fine filaments.

The natural color of brown wool is caused by pigment granula of black to brown eumelanin and yellow to red pheomelanin.

### 14.2.2. $\alpha$ - and $\beta$ -Keratin

The microfibrils are partly crystalline, and on X-ray structural analysis give reflections on the meridian (0.51 nm) and equator (0.98 nm), as well as many long-period reflections on the meridian and some on the equator. ASTBURY [90] designates the modification that gives this fiber diagram (Fig. 6 A) as  $\alpha$ -keratin. Wool that has been stretched by ca. 50% in water and then dried gives a new fiber diagram with a meridian reflection at 0.34 nm and equatorial reflections at 0.465 nm and 0.98 nm. This X-ray diffraction pattern is due to the modification known as  $\beta$ -keratin (Fig. 6 B). After relaxation of the stretched wool fiber in water, X-ray analysis again shows the  $\alpha$ -keratin



**Figure 5.** Schematic representation of the three distinct levels of fibrillar organization in keratin filament assembly and architecture [89].

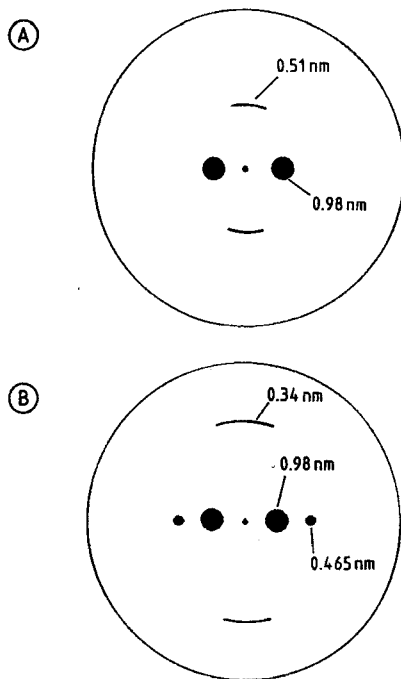
I) The 2-nm protofilament consists of two coiled-coil keratin polypeptides, presumably one acidic (white) and one basic (black) species; II) The 4.5-nm protofibril may be a six-stranded subunit composed of three 2-nm protofilaments (shown on left), or, alternatively, may be an eight-stranded subunit formed by the lateral aggregation of two four-stranded 3-nm protofilament intermediates (shown on right); III) The 10-nm filament may comprise four (left) or three (right) protofibrils, depending upon protofibril substructure. The number of protofibrils (four or three) per 10-nm filament is not unique but just represents one possible polymorphic form.

pattern. This reversible change from the  $\alpha$ -modification (unstretched) to the  $\beta$ -modification (stretched in water) explains the good stretching and recovery properties of wool. The  $\alpha$ - $\beta$  transformation begins even with small amounts of stretching ( $> 2\%$ ).

In  $\alpha$ -keratin [91], the peptide chains are twisted like a right-handed screw ( $\alpha$ -helix, Fig. 7). The stability of the  $\alpha$ -helix is due to intramolecular hydrogen bonds between the  $>C=O$  groups of the peptide bonds and adjacent  $>N-H$  groups of amino acid units located on the next turn of the  $\alpha$ -helix.

The  $\alpha$ -helix contains 18 amino acid units in five turns, i.e., 3.6 amino acid units per turn. To give the distance between successive turns of the helix that leads to the observed meridian reflection (0.51 nm), the helical chain must itself be slightly coiled (superhelix, coiled coil). Two superhelices combine to form a left-handed, two-stranded, rope-like assembly in which the superhelices are arranged such that the hydrophobic side chains on the outside of the helix interlink to form a stable "buttonhole" structure. These dimers are the actual physical structural elements of the intermediate filaments (microfibrils), and can be termed "molecular twins."

In the  $\beta$ -keratin structure [92], the peptide chains are considerably stretched, as in silk fibroin ( $\rightarrow$  Silk). The chains form so-called pleated sheet structures (Fig. 8). The sheet is formed by cross-linking of the chains by hydrogen bonds between peptide groups of opposing chains. The sheet is folded at the  $-CHR$  groups of the chains to such an extent that the meridian reflection of the  $\beta$ -keratin X-ray diffraction pattern at 0.34 nm corresponds with the geometry of the model.



**Figure 6.** Diagnostic X-ray reflections [9]  
A)  $\alpha$ -Keratin pattern; B)  $\beta$ -Keratin pattern

**Table 3.** Morphology of wool as a combination of two-component structures (see also Fig. 4)

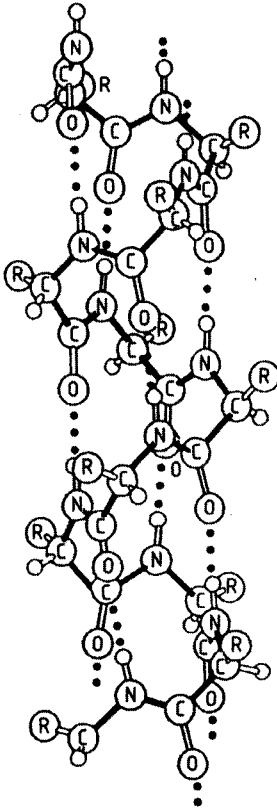
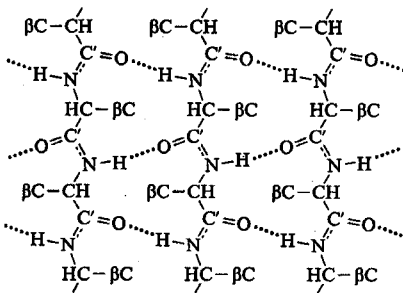
Composite system	Type *	Component 1	Component 2
Wool fiber	r/c	cuticle	cortex
Cortex	f/m	cortex cell	cell membrane complex
Cortex cell	f/m	macrofibrils	cytoplasm and cell nucleus remnants
Macrofibril	f/m	keratin intermediate filament	keratin-associated proteins

\* r/c = ring/core structure; f/m = filament in matrix.

### 14.2.3. Two-Phase Model

The complex morphological and molecular structure of wool (Fig. 4) echoes the construction principle of all biological composite structures and many man-made materials, combining components with different properties in one material so as to maximize suitability for its purpose. Table 3 shows the stepwise differentiation of the morphological structure of the wool fiber into the most important two-phase structures.

With regard to elastic properties, the essential difference between the components is in their degree of order. If only the  $\alpha$ -helical central rodlike domains in the microfibrils (intermediate filaments) are regarded as microcrystalline, the crystalline phase accounts for 30% of the fiber [93]. The other components make up the “matrix” phase, which includes the cuticle, the cell membrane complex, the intermacrofibrillar material, the

Figure 7.  $\alpha$ -Helix structure of  $\alpha$ -keratin [91]Figure 8. Pleated sheet structure of  $\beta$ -keratin [92]

interfilament material, and 40% of the microfibrils, i.e., the nonhelical ends of the keratin molecules or of the dimers.

On stretching the fiber in the linear-viscoelastic region ( $\epsilon < 0.8\%$ ), the behavior of the crystalline phase is linearly elastic and that of the noncrystalline matrix phase is linearly viscoelastic.

The modulus of elasticity of the helices is [94]

$$E_{\text{hx}} = 7.8 - 9.6 \text{ GPa}$$

This value is remarkably close to the modulus of elasticity of crystalline ice, which is also stabilized by hydrogen bonds (ice I, 0 °C:  $E = 10 \text{ GPa}$ ). This fact emphasizes the ideal arrangement and cooperation of the short  $\alpha$ -helical segments in the microfibrillar crystal. The time-dependent modulus of elasticity of the dry (d) and wet (w) matrix are calculated to be

$$E_{\text{m}}^{\text{d}} = 6.1 - 6.6 \text{ GPa}; \quad E_{\text{m}}^{\text{w}} = 0.5 \text{ GPa}$$

$$E_{\text{m}}^{\text{d}}/E_{\text{m}}^{\text{w}} \approx 13$$

The ratio of the moduli of elasticity of the matrix is in good agreement with the ratio of the corresponding torsion moduli ( $G^{\text{d}}/G^{\text{w}} = 10$ ) [94]. In a filament–matrix composite, the torsion behavior is mainly a property of the matrix. The small difference between the values for the viscoelastic modulus of the matrix in the dry state and the modulus of elasticity of the helical filaments is due to the fact that both components are stabilized mainly by strong hydrogen bonds which are broken under the influence of water in the amorphous, glassy matrix phase, while they continue to exist in the crystalline region.

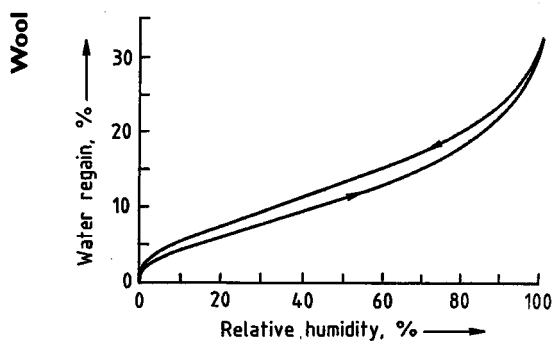
For small amounts of longitudinal strain in the linear-viscoelastic region, the relaxation behavior of a wool fiber shows no fine structure ascribable to individual morphological components. This fact can be explained by the low contents of individual components and their chemical and structural similarity. For small deformations, all amorphous components behave as constituents of a homogeneous mixture, whereby the effect of each component is proportional to its volume fraction. The elastomechanical behavior is satisfactorily represented by the simple Feughelman two-phase model [95]. The elastic and viscoelastic properties of the fiber largely determine the crease resistance, dimensional stability, drape, and handle of a fabric.

## 14.3. Properties [2], [6], [17], [48]

### 14.3.1. Physical and Mechanical Properties [17]

Wool fibers with no medulla have a density of  $1.31 \text{ g/cm}^3$  at 25 °C and 65 % relative humidity. The mean fiber diameter varies between 16 and 40  $\mu\text{m}$  and the mean fiber length between 2.5 and 25 cm, depending on type and origin.

**Water Absorption.** Wool is hygroscopic, and the amount of water taken up depends on the relative humidity of the air, temperature, and the history of the wool (Fig. 9) [96]. The adsorption and desorption curves exhibit hysteresis. At average relative



**Figure 9.** Moisture absorption of wool as a function of relative atmospheric humidity at 25 °C [96]

humidities, the difference between the two curves is ca. 2%. As with all textile fibers, the moisture uptake of wool is accompanied by liberation of heat.

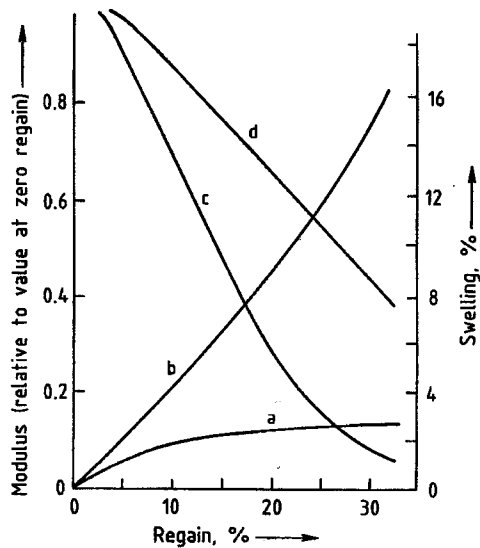
Although wool is hygroscopic, its surface is hydrophobic towards liquid water and is therefore difficult to wet. This apparently contradictory behavior, which is an important factor in the physiological effects of wool as a clothing material, is due to the fact that the interior of the fiber absorbs water vapor, whereas liquid water is repelled by the hydrophobic outer surface of the cuticle.

Water absorption results in swelling, whereby wool shows considerable swelling anisotropy, i.e., longitudinal and radial swelling are different (Fig. 10) [10].

An increase in the amount of absorbed moisture from 0% to 33% leads to a longitudinal swelling of ca. 2% and a radial swelling of 16%. The extent of swelling depends on the pH and composition of the swelling medium.

The degree of fiber swelling is least at the isoelectric point (pH 4.9), where there is no excess of ionic groups. Above and below this point, the number of stabilizing salt bridges decreases, and the wool carries excess negative or positive charges which cause electrostatic repulsion of the peptide chains, thereby increasing the swelling [97]. Many physical and mechanical properties of wool depend on its moisture content. Thus, for example, dry undamaged wool has an ultimate tensile strength of ca. 150–200 N/mm<sup>2</sup> in its initial state and a wet ultimate tensile strength of only 70–80% of this value. Whereas the tensile strength of wool decreases with increasing moisture content, the fracture strain increases. In the dry state, it is 35–55%, and in the wet state 40–60%.

**Stress–Strain Behavior.** Figure 11 shows the stress–strain behavior of a wool fiber in a standard climate of 65% relative humidity at 20 °C compared with that in water at 20 °C. The stress–strain curve can be divided into three regions which are affected to different extents by increasing humidity. After decrimping (not shown in Fig. 11), the tension in the fiber increases very rapidly and almost linearly up to a strain of 1–2%. This so-called initial region (A–B) is often incorrectly referred to as the “Hookean region”. Above this, the elongation increases rapidly for small increases in stress. This section of the curve (B–C) is known as the yield region. Point C lies between 25 and 30% elongation. The third region of the stress–strain curve is known as the post-yield



**Figure 10.** Effect of moisture adsorption on swelling and moduli [10]  
 a) Length swelling; b) Radial swelling; c) Torsional modulus; d) Extensional modulus

region (C–D), and is terminated by rupture of the fiber (D). In this section of the curve, the increase in tension that accompanies a given increase in elongation is larger.

The three characteristic regions of the stress–strain curve are very distinct in water at 20 °C, and the transitions at points B and C are sharp. The slopes in the initial, yield, and post-yield regions are in the approximate ratio 100 : 1 : 10.

Noteworthy is that when the wool fiber is stretched in water to point C at room temperature, i.e., by ca. 30 %, there is complete reversibility of mechanical properties if the time in the stretched state does not exceed ca. 1 h. If the fiber is then relaxed and kept in water at room temperature overnight or at ca. 50 °C for 1 h, not only does the fiber return to its original length, but, on repeating the test, gives the same stress–strain curve as in the first cycle. This high degree of reversibility is not exhibited by any other fiber.

In addition to this simple tensile test, tensile elasticity testing can provide further information about the behavior of the fiber. Here the fibers are stressed several times between constant elongation limits or constant tension limits. The test enables the permanent elongation and the elastic elongation to be determined. In this way, the elastic behavior of fibers over the whole range of elongation up to the point of rupture can be determined.

**Glass-Transition Temperature.** Knowledge of the glass transition temperature  $T_g$  of wool [98] as a function of water content is of central importance for understanding its viscoelastic fiber properties, especially under the varying conditions of moisture content and temperature that can exist during the manufacture and wearing of woolen fabrics, and also for an understanding of the aging and tempering processes of these fabrics.

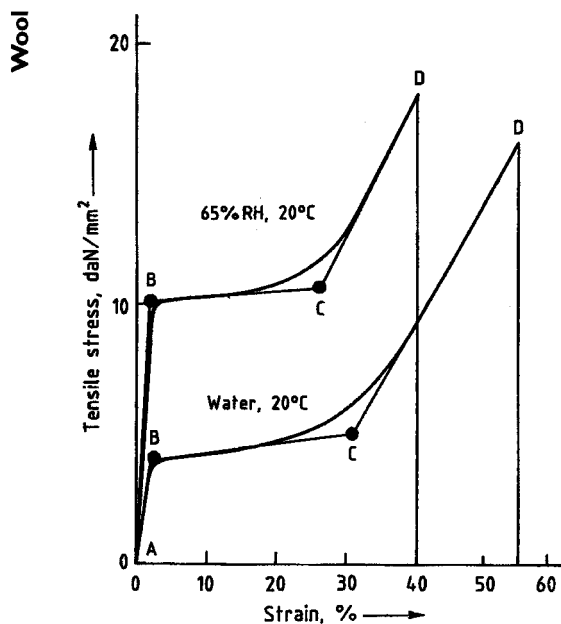


Figure 11. Tensile stress–strain diagrams

A simple equation due to Fox [99] represents the relationship between the glass-transition temperature of wool and its water content:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

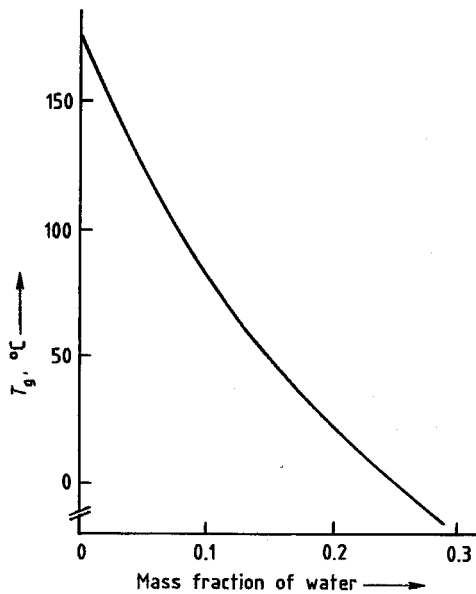
The mass fraction of each component is represented by  $w$ , the indices 1 and 2 denoting dry wool and pure water respectively. By replacing  $w_1$  by  $(1-w_2)$ , the Fox equation becomes

$$\frac{1}{T} = w_2 \left[ \frac{1}{T_{g2}} - \frac{1}{T_{g1}} \right] + \frac{1}{T_{g1}}$$

If the reciprocal of the glass-transition temperature of the wool–water system is plotted against the mass fraction of water, a straight line is obtained, confirming the validity of the Fox equation [99]. The glass-transition temperatures of the pure components can be calculated from the slope and the intersection of this line with the axis. The time-dependent recovery of wool fibers after a fixed torsional deformation as a function of temperature and water content has been measured. For dry wool, this gave  $T_{g1} = 447 \text{ K}$  ( $174^\circ \text{C}$ ), and for water  $T_{g2} = 125 \text{ K}$  ( $-148^\circ \text{C}$ ) [98]. Figure 12 shows the glass-transition temperature of wool as a function of water content in the fiber.

The temperature dependence of the physical properties of wool–water systems has been investigated by many authors using a variety of methods. Wool in water has a  $T_g$





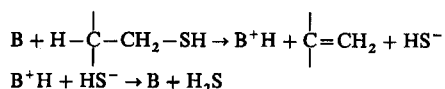
**Figure 12.** Glass-transition temperature of wool as a function of mass fraction of water in the fiber [98]

of  $-5^\circ\text{C}$ , significantly below room temperature. Thus water in wool eliminates aging and tempering effects because the thermal history of the wool is erased when  $T_g$  is exceeded, in analogy with the behavior of other glassy polymers.

#### 14.3.2. Chemical Reactivity [5], [13], [27], [31]

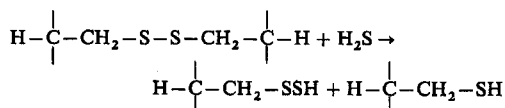
**Dry Heat.** Dry wool free of chemicals is stable for hours at  $150^\circ\text{C}$ . Short heating periods, e.g.,  $185^\circ\text{C}$  for 30 s, produce tolerable changes in the fibers.

**Moist Heat.** Depending on the temperature, pH of the liquor, and duration of heating, heating with water can lead to degradation of wool. Heating with water at  $130\text{--}140^\circ\text{C}$  leads to the disappearance of the  $\alpha$ -keratin X-ray diffraction pattern with chemical decomposition. Wool is most stable near the isoelectric point (pH 4.9), but chemical degradation occurs even below  $100^\circ\text{C}$ . The cysteine in the wool proteins is decomposed first, liberating hydrogen sulfide which then attacks the cystine in the wool and accelerates the decomposition autocatalytically [100]. This is the cysteine–cystine self-degradation and self-cross-linking mechanism (thiol–disulfide degradation reaction).

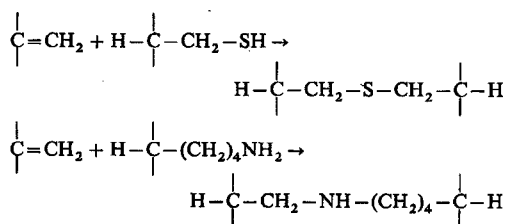


B = amino groups of histidine or lysine residues and main-chain end groups.

First step: self-degradation of cysteine residues by heat-induced  $\beta$ -elimination. Formation of dehydroalanine residues and hydrogen sulfide.

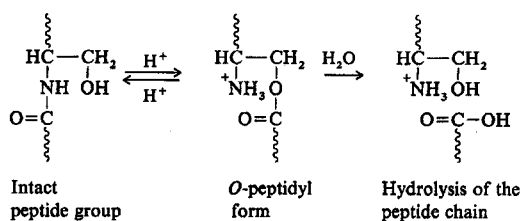


Second step: self-degradation of cystine residues by reduction of disulfide bonds with hydrogen sulfide. Formation of S-thiocysteine and cysteine residues.



Third step: Self-cross-linking by reaction of cysteine and lysine residues with dehydroalanine residues. Formation of lanthionine and lysinoalanine cross-links.

**Acid Degradation.** Mineral acids can degrade wool proteins to an extent that depends on pH, temperature, duration of reaction, and the presence of salts and surfactants. Sensitive sites in the wool proteins include the side chains of asparagine and glutamine, from which ammonia is released, and the peptide bonds formed by serine, threonine, cysteine, aspartic and glutamic acids, and tryptophan. The liquors from acid-degraded wool contain ammonium salts, free amino acids, and peptides ("wool gelatins"). The hydrolysis of peptide bonds leads to weight losses and the liberation of end groups in the wool proteins. Carbonizing by heating wool impregnated with sulfuric acid produces an N  $\rightarrow$  O peptidyl shift in the serine and threonine units of the peptide chain. The reaction is reversible if the acid is removed after the process, but if the wool is stored in moist air in the O-peptidyl form, the peptide chain is slowly and irreversibly hydrolyzed:



**Degradation by Alkali.** Wool is sensitive to alkali. In alkaline solution, the alkali binds to the wool proteins with swelling and simultaneous degradation. Even at low hydroxide concentrations, the reversible binding is accompanied by fiber damage. The alkali binds to the wool so firmly that it cannot be completely removed by washing with water alone. The alkali salts of the wool proteins must first be decomposed by reaction with stronger acids. Wool containing alkali residues undergoes decomposition on heating in a stream of dry air, the most important degradation reactions being the decomposition of cysteine and cystine. Alkalis hydrolyze the primary carbonamide bonds of asparagine and glutamine, cleave peptide bonds in the main chains, and cause racemization of the amino acid residues:

Cysteine → dehydroalanine + hydrogen sulfide

Cystine → dehydroalanine + thiocysteine

Dehydroalanine + cysteine → lanthionine

Dehydroalanine + lysine → lysinoalanine

Dehydroalanine + ammonia →  $\beta$ -aminoalanine

Glutamine → glutamic acid + ammonia

Asparagine → aspartic acid + ammonia

Isoleucine → alloisoleucine.

Some of the wool proteins become soluble on degradation. The solubility of wool in alkali under standard conditions is used as an indicator of chemical changes in the fiber. Wool that has been damaged by acids, reducing agents, or oxidizing agents becomes sensitized to alkali, and its solubility in a standard solution of alkali increases.

Degradation reactions are also revealed by yellowing of the wool.

The decomposition reactions depend on the type of alkali, the temperature and duration of the reaction, the pH, and added salts and auxiliaries. Cationic surfactants increase the decomposition of cysteine and cystine and formation of lanthionine catalyzed by alkali. Nonionic surfactants have no effect on alkali damage to wool [101].

### 14.5.5. Dyeing and Finishing [37], [40], [45], [50]

**Dyeing and Printing.** Dyeing is the most important wet finishing process for wool. Wool can be dyed in most stages of its manufacture, i.e., as flock, slubbings, yarn, or piece. The dyeing of flock is only of importance in the production of woollen yarn consisting of blends of wool with other types of fiber. The dyeing of sliver is useful for the production of large batches of completely uniform color. Color discrepancies can usually be leveled by mixing slivers without additional dyeing. Dyeing of wool blends is described in [45, Chap. 9].

Chrome dyes continue to fulfill a high proportion of wool dyeing capacity, particularly as a cost effective, high-wetfastness system for slubbing and loose wool. Residual chrome creates a problem in dyehouse wastewater. This has been minimized by the use of modified chrome dyeing techniques [113]–[115].

Reactive dyes represent an alternative method of achieving the high wetfastness of chrome dyes whilst eliminating the problem of heavy metal contamination of dyehouse or scouring liquors.

The tenacity of wool is often reduced in stock-dyeing processes. As a result of this, many fibers are broken in the card. Most of the reduction in fiber strength is due to setting of bends or curvatures of the packed fibers by the hot water treatment. Such set fiber bends are nonuniformly strained by tensions and thus resist smaller loads than fibers set in the straight state [120].

In addition to the minimum wool damage exerted due to their optimum application pH in the isoionic region, reactive dyes further enhance wool quality by chemical reaction with thiol groups, H<sub>2</sub>S, and histidine side chains, and by acting as antisetting agents [116]–[119].

#### **Protection from Moths and Beetles [129]–[132].**

Permethrin-based insect-resist (IR) products account for ca. 90% of the European market, based on the volume of treated wool. Permethrin-treated wool has poor fastness to moisture and light, so that treatment with these products is recommended mainly for carpets and for storage protection.

Conventional wool-specific protection agents based on Sulcofuron are Mitin FF h.c. (80% AS, Ciba-Geigy), and Mitin FF liquid (Ciba-Geigy). Wool treated with Mitin FF has very good fastness towards moisture and light, and is therefore suitable for articles from which high standards of colorfastness are demanded.

### 14.10. Uses [32]

Merino and crossbred wools are mainly used in clothing and home textiles [158]–[160]. According to [161], the wool fiber can now be found in applications as diverse as thermal insulation, weed mats, and as a means to soak up oil spills. Wool has been used for thermal insulation in houses in Switzerland for many decades and is being increasingly used for both homes and commercial buildings [162]–[164]. Wool is naturally fire resistant, and the increased use is being driven by consumer demand for natural products in their homes. The moisture absorbing and de-sorbing properties of wool can also contribute to passive heating and cooling effects. L-Cystine can be isolated from hydrolysates of hair or wool.

## 14.11. Trademarks

In 1937, the International Wool Secretariat (IWS) was founded by the Wool Boards of Australia, New Zealand, and South Africa. Since then, Uruguay has joined and New Zealand has broken away. Finance is provided by the sheep farmers of the member countries. Its tasks include the promotion of research, the development of products, and the marketing of virgin wool products. The woolmark was introduced in 1964 (Fig. 14). Textiles with this mark must consist of 100 % virgin wool. Admixtures of wool recovered by mild methods from the skins of slaughtered sheep are permitted. Equal status is given to fine animal hair from the alpaca, llama, vicuna, guanaco, camel, angora, rabbit, angora-mohair, cashmere and cashgora goats, and yak, provided that here also it is obtained by a mild process. The woolmark covers all areas of use, e.g., hosiery, outer clothing, underwear, hand-knitting yarns, upholstery cloth, carpets, floor coverings, and industrial protective clothing. The license for using the woolmark can be bought from the IWS under certain conditions (maintenance and monitoring of quality) [165].

In 1970, the designation “pure new wool” (Reine Schurwolle) was included in the textile labeling law (TKG) of the Federal Republic of Germany, and became valid in the European Community in 1972. The “combi” woolmark was introduced in 1971 for products consisting of virgin wool blended with other fibers, e.g., synthetic fibers (minimum virgin wool content 60–90 %; minimum wool content in cotton blends 55 %).

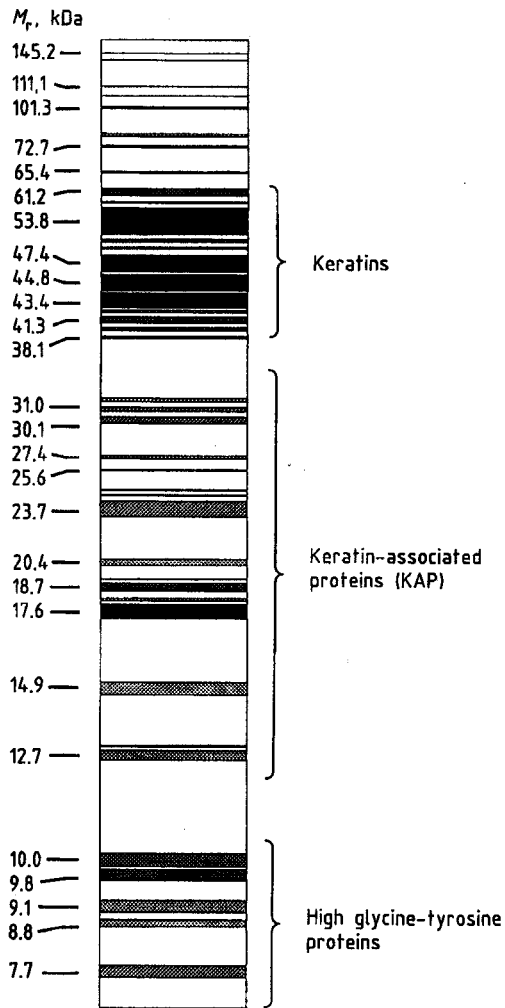
In 1973, the woolmark label “Machine Washable up to 30 °C was introduced.

The Wool plus Lycra label was launched by IWS and DuPont in 1995 for knitwear manufacturers and to producers of men's and ladies' wear fabrics as a new woven-textile quality control label. “Wool plus Lycra” fabrics must contain at least 60 % wool and 2–8 % Lycra [166].

## 14.12. Economic Aspects

**Wool Production.** Table 5 gives world wool production figures for the major producing countries during the period of the shearing seasons from 1991/92 to 1994/95; Figure 15 shows percentage shares of world production. The top half of the table shows actual weights of raw wool or lime wool, with calculated corresponding weights of pure scoured wool shown below. Raw wool is traded internationally on this basis.

Wool production has grown only slowly over recent decades, as grazing land for sheep cannot be increased indefinitely. A decline has even occurred since 1990/91 for reasons of climate, price (lucrative alternatives for farmers), and political economy (economic decline in Eastern Europe). A reversal in this trend, i.e., an increase in wool production, is forecast for the 1996/97 season.



Sheep rearing and hence wool production exist in almost all parts of the world, although at widely varying levels of intensity. In most countries, home-produced wool is processed and consumed internally, and therefore is not available on the international market. This also applies to important wool-producing countries such as China and the countries of the former Soviet Union. The suppliers of the raw material to the international wool textile industry are those countries that produce and export amounts of wool in excess of their own requirements. These principally comprise Australia, New Zealand, Argentina, Uruguay, and South Africa.

Australia is the world's largest producer and exporter of garment wools (merinos), exporting ca. 60% of its wool production as raw wool, and thus being the most important supplier for the wool combers of the industrialized countries. New Zealand

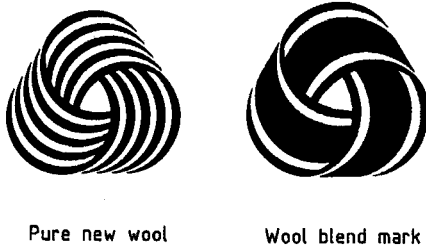


Figure 14. Woolmarks for pure new wool and new wool with other fiber

Table 5. World wool production by the major producing countries (in  $10^6$  kg)

	1991/92	1992/93	1993/94	1994/95
<b>Raw wool weight</b>				
Australia	875	869	829	753
New Zealand	296	256	284	272
Former Soviet Union	441	414	376	298
China	240	238	220	260
Argentina	121	114	98	90
Uruguay	87	90	93	87
South Africa	83	75	75	68
Others	879	860	840	833
World	3022	2916	2815	2661
Merinos	1377	1319	1243	1129
Crossbreds	708	711	691	656
Carpet wools	937	886	881	876
<b>Scoured wool weight</b>				
Australia	569	566	540	490
New Zealand	221	193	214	205
Former Soviet Union	198	186	169	134
China	120	119	110	130
Argentina	73	68	59	54
Uruguay	57	59	61	57
South Africa	49	44	44	42
Others	463	448	436	432
World	1750	1683	1633	1544
Merinos	813	778	737	674
Crossbreds	409	406	396	378
Carpet wools	528	499	500	492

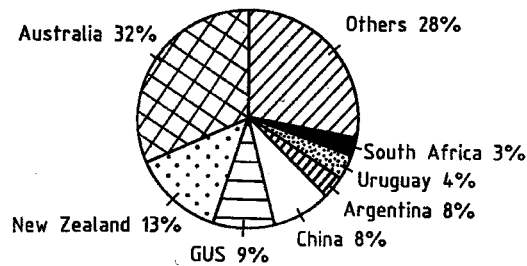
produces mainly scoured coarse wools that are exported for use in the production of home textiles, especially carpets. Argentina, Uruguay, and South Africa have also built their own wool scouring and combing plants, and export wool either in scoured loose form or as tops (scoured and combed wool). Table 6 lists wool export figures, for the five most important exporting countries for the seasons 1989/90 to 1993/94.

**Wool Prices.** The price differences between the various wool qualities are considerable. The most important factors determining quality and therefore price are the fineness and staple length of the fiber. Not only the mean fineness and length, but also

**Table 6.** Wool exports (raw wool, scoured wool, and sliver) by the five major exporting countries (in 10<sup>6</sup> kg scoured wool)

	1989/90	1990/91	1991/92	1992/93	1993/94
Australia	430	390	531	485	491
New Zealand	184	182	217	174	218
South Africa	29	31	27	19	20
Argentina	38	33	27	32	40
Uruguay	29	21	21	16	24
Total	710	657	823	726	793

\* Source: IWTO, Table 28.

**Figure 15.** World wool production (1994/95)

the uniformity of distribution are of great importance. Other quality and price parameters are the content of vegetable matter and pigmented fibers, tensile strength, color, elasticity, crimpiness, and many others.

Since the collapse in early 1991 of the minimum price system which imposed a lower limit on wool prices for 17 years in Australia, New Zealand, and South Africa, prices have been determined by the market forces of supply and demand. Figure 16 shows the development of the average auction price of Australian raw wool, the so-called market indicator (i.e., the weighted average of the qualities) in the sales seasons 1992/93, 1993/94, and 1994/95. The market indicator during this period fluctuated between 3.89 A\$/kg (April 1993) and 8.43 A\$/kg (March 1995).

However, the price differences between two given qualities can vary greatly over time with supply and demand. This is illustrated in Figure 16, which also shows the price curve for 19  $\mu$ m wools. The difference in price between this and the market indicator varied between 0.50 A\$/kg (February 1993) and 7.85 A\$/kg (September 1994). The reasons for the relatively low prices for fine wools may be an increased supply of "hunger-fine" wools after a drought, and the lack of interest in such low-quality, albeit fine wools. A high price is evidence of a strong, fashion-induced demand accompanied by a restricted supply.

**Wool Consumption.** Table 7 lists world wool consumption. Europe has the highest consumption of wool (43% of the world total). This underscores the world importance of the European woolen industry. The 15 EU countries account for 23%, the rest of Western Europe 6%, and Central and Eastern Europe 14% of total world consumption





**Figure 16.** Price development of Australian raw wool a) Average auction price (market indicator); b) 19 µm indicator

for spinning mills. In second place is the Far East, with 32% of the total world industrial demand for wool. For German wool imports, see Table 8.

The comparatively minor importance of the wool textile industry in the United States, i.e., 4% of the world's consumption of virgin wool, is remarkable.