Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Hierarchy of α-Keratin Fibers with a glance at Skin and Ötzi

Hartwig Höcker[a]
[a] Lehrstuhl für Textilchemie und Makromolekulare Chemie, Deutsches Wollforschungsinstitut an der RWTH Aachen, Aachen, Germany

To cite this Article Höcker, Hartwig(1996) 'Hierarchy of α-Keratin Fibers with a glance at Skin and Ötzi', Journal of Macromolecular Science, Part A, 33: 10, 1437 — 1446
To link to this Article: DOI: 10.1080/10601329608014918
URL: http://dx.doi.org/10.1080/10601329608014918

J.M.S.—PURE APPL. CHEM., A33(10), pp. 1437–1446 (1996)

HIERARCHY OF α-KERATIN FIBERS WITH A GLANCE AT SKIN AND ÖTZI

HARTWIG HÖCKER

Lehrstuhl für Textilchemie und Makromolekulare Chemie
Deutsches Wollforschungsinstitut an der RWTH Aachen
Veltmanplatz 8, D-52062 Aachen, Germany

INTRODUCTION

Hierarchy is usually an organization with grades of authority from lowest to highest, e.g., in the civil service, in organized priesthood, or in enterprises where efficiency is essential. An extremely high degree of efficiency, however, is realized in all kinds of life, from the life of microorganisms up to that of human beings. Therefore, we expect hierarchical structures, particularly in life sciences.

An impressive example of a hierarchical structure is a eucaryotic chromosome which consists of spirals of spirals. The chromosome is the ordered system; in the amorphous state the material is called chromatin and consists of histones (50%) and DNA (50%). The DNA double helix is associated with the proteins to form a pearl string; the pearl strings are arranged to form a filament with 30 nm diameter. These organize themselves into loops with 50×10^6 base pairs; 6 loops result in a rosette, and 30 rosettes in a spiral. 2×10 spirals form a pair of two chromatides [1].

These structures have intrigued polymer chemists, particularly because of two reasons: the self-organizing potential of the natural structures and the functionality and efficiency of the resulting supramolecular material.

Supramolecular structures are known to be formed by surfactants which organize themselves into micelles in equilibrium with the monomers. Phospholipids are known to form liposomes. More elaborate structures, e.g., *N*-octyl- and *N*-dodecyl-D-gluconamide, form intertwinning quadrupole helices which reorganize themselves into a tubular helix. Some polymerizable phospholipids form two interpenetrating unconnected water channels separated by phospholipid surfaces and stabilized by polymerization [2].

Nature has a large variety of self-organizing molecules that do not use covalent bonds or make use of extrusion of bulk material. An impressive example is the structural elements of eucaryotic cells which consist of filaments of proteins which,

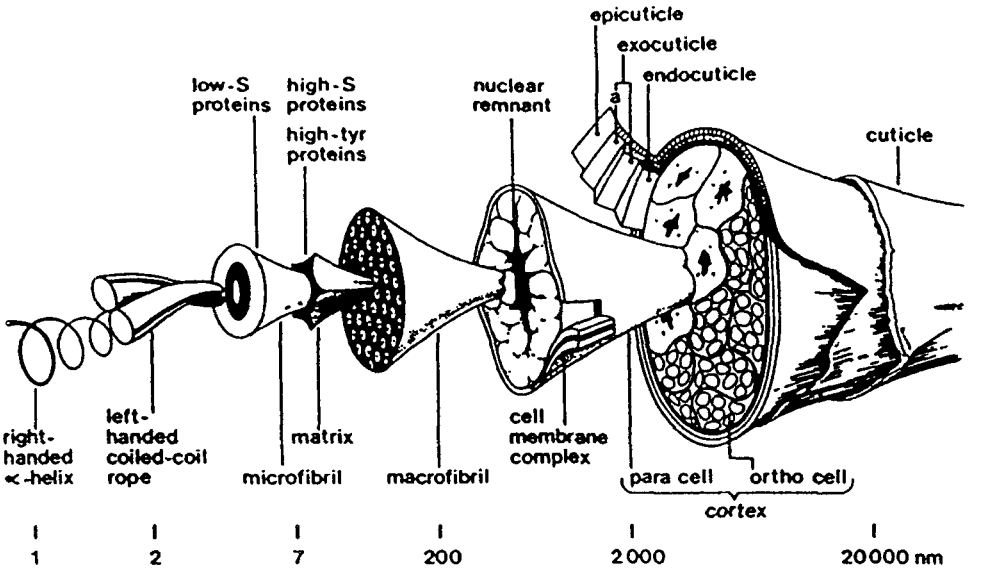

FIG. 1. Schematic diagram of the morphological components of a fine wool fiber [5].

in a dynamic process of polymerization and depolymerization/association and dissociation of polypeptides ("treadmilling process"), not only organize themselves into static structures but are able to move through the cell [3].

These filament structures can also be expected in dead or keratinized cells such as wool and hair.

HIERARCHICAL STRUCTURES IN KERATIN FIBERS

There is a large variety of keratin fibers (wool, hair) originating from sheep and goats (cashmere, angora), camels and cameloids (alpaca, guanaco, llama), rabbits and a large variety of animals from the forest, and last, but not least, human beings.

Keratin fibers have remarkable physical properties [4]. They show a water regain of up to 35 wt%, which exceeds that of cotton by more than 15% (absolute) and that of nylon and polyester by 25% (absolute). In addition, wool fibers are characterized by the "wettability paradox," a hydrophobic surface and a hygroscopic interior. Young's modulus is much less influenced by water regain than the torsional modulus, and the longitudinal swelling is much less influenced than the radial swelling.

The glass transition temperature of the amorphous material in wool varies between 175 and -15°C from dry to wet.

This intriguing physical behavior may be explained by the complex morphology of wool fiber (Fig. 1). The fiber shows a typical core/mantel structure. The mantel, i.e., the cuticle, is composed of an epicuticle which consists of a fatty acid

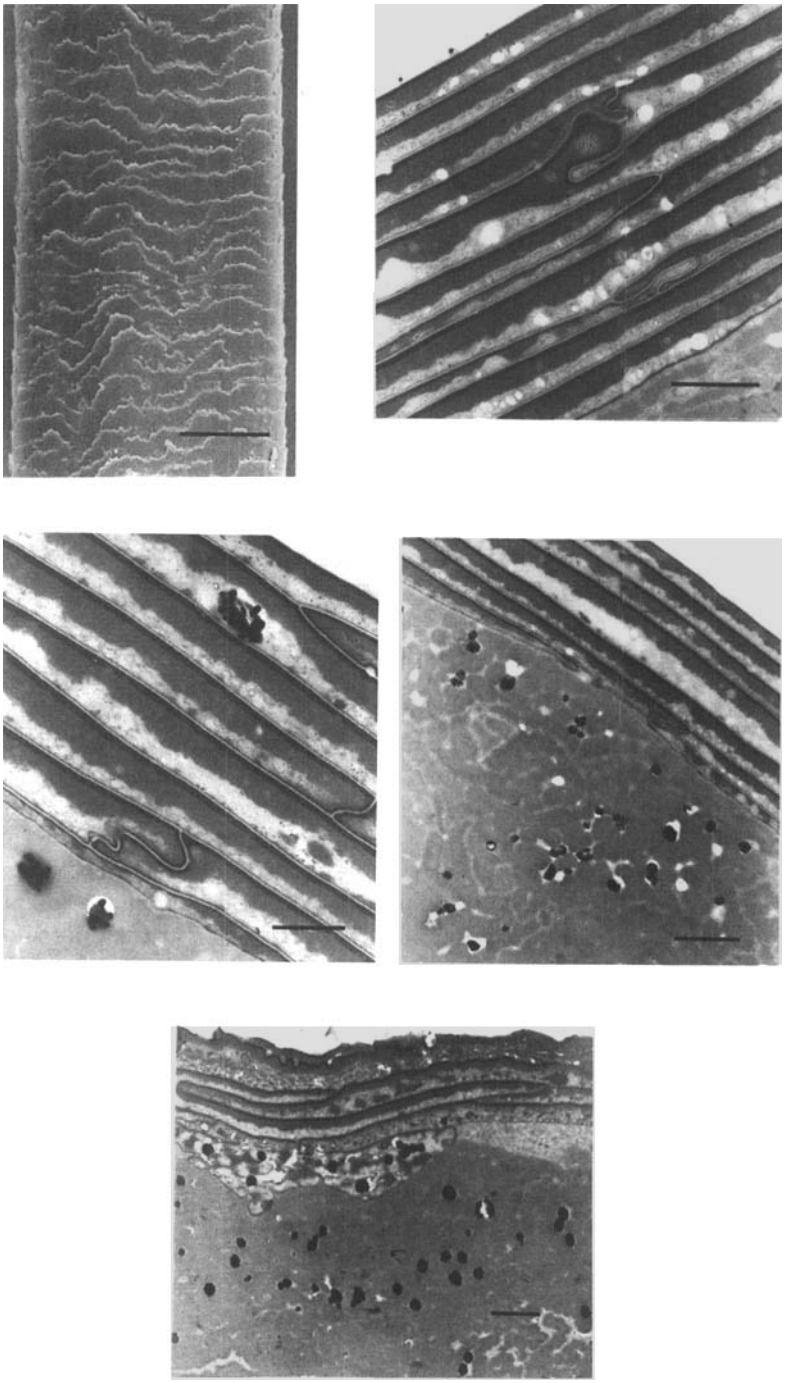

FIG. 2. Upper left: Human hair surface (SEM), bar = 20 μm. Upper right: Cuticle (TEM), bar = 1 μm. Center left: African-American hair, bar = 1 μm. Center right: European hair (TEM), bar = 1 μm. Bottom: Hair of the iceman "Ötzi," more than 5000 years old, bar = 1 μm.

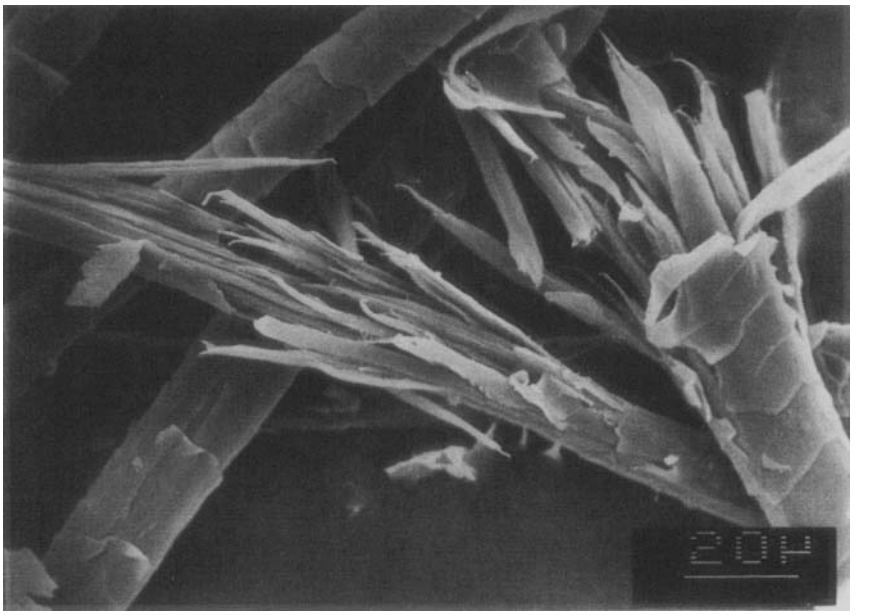

FIG. 3. Spindle cells of the cortex after destructive enzymatic treatment [8].

layer covalently bound to the protein material of the A-layer of the exocuticle. The A-layer shows the highest content of cystine residues (35%), followed by the B-layer of the exocuticle with 15 mol% residues and the almost cystine-free endocuticle. The cuticle is composed of cuticle cells which cover the cortex cells. The cortex cells are roughly divided into para- and orthocortex cells, the paracortex being richer in cystine residues than the orthocortex and showing nuclear remnants. Each cell is surrounded by the cell membrane complex. The cortex cells are composed of macrofibrils which are embedded in a intermacrofibrillar material; the macrofibrils consist of microfibrils embedded in high sulfur and high tyrosine proteins as a matrix material. The microfibrillar material has a low cystine content and is composed of an ensemble of helices or keratin chains.

The cuticle scale edges display different topologies for different keratin fibers. The height of the scale edges, however, is around 0.4 μm in all cases except for sheep's wool where it is roughly twice as large, i.e., 0.8 μm [6].

A typical human hair has up to 10 cuticle layers. The cuticle is therefore extremely stable, as may be seen from a cross section of the hair of the ice-man ("Ötzi") who lived more than 5000 years ago (Fig. 2) [7]. Cosmetic treatment, both mechanical and chemical, may remove all cuticle cells from the hair surface so that the cortical cells become visible. This also may be achieved by enzymatic treatment. Figure 3 shows the spindle cells of the cortex after destructive enzymatic treatment [8].

Wool shows a typical bilateral structure of the cortex, one-half of the fiber cross-section being characterized by the paracortex and the other half by the orthocortex. The bilateral structure can be seen by means of transmission electron microscopy and staining with silver nitrate or by means of x-ray fluorescence spectroscopy

Relationship between ortho/para segmentation and fibre crimp

FIG. 4. Schematic representation of the bilateral structure of a wool fiber (top) and TEM of a cross section (bottom).

of the cross section in conjunction with the scanning electron microscope. In both cases a high concentration of sulfur is indicated in the paracortex compared to the orthocortex (Fig. 4) [9].

The borderline between the ortho- and paracortex along the fiber axes shows a helical structure which produces a fiber crimp with the paracortex cells situated on the inside of the curvature and the orthocortex cells on the outside.

As mentioned above, the cortex cells may be separated from the fiber when the cuticle is removed and the cell membrane complex separating the different cells is destroyed. Note, however, that the cortex cells are not only glued together by the cell membrane complex, they show an intriguing kind of interpenetration (Fig. 5) [9].

The cell membrane complex is composed of residual material of plasma membranes, intercellular material, and part of the intracellular material, i.e., the cytoplasma (Fig. 6). The continuous fiber tenacity is due to the cell membrane complex

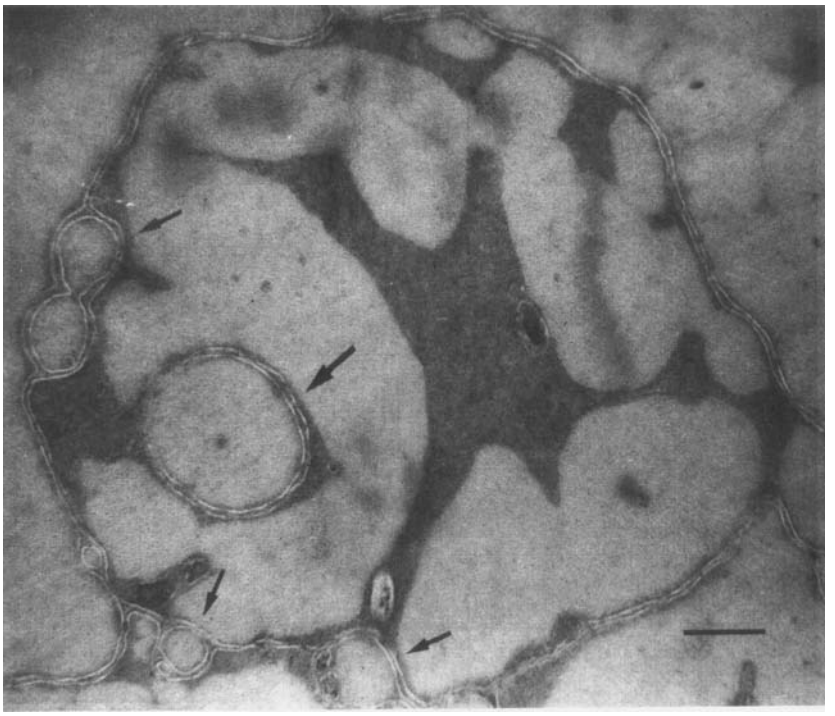

FIG. 5. Cross section of a wool fiber with interpenetrating cortex cells (TEM), bar = 200 μm [9].

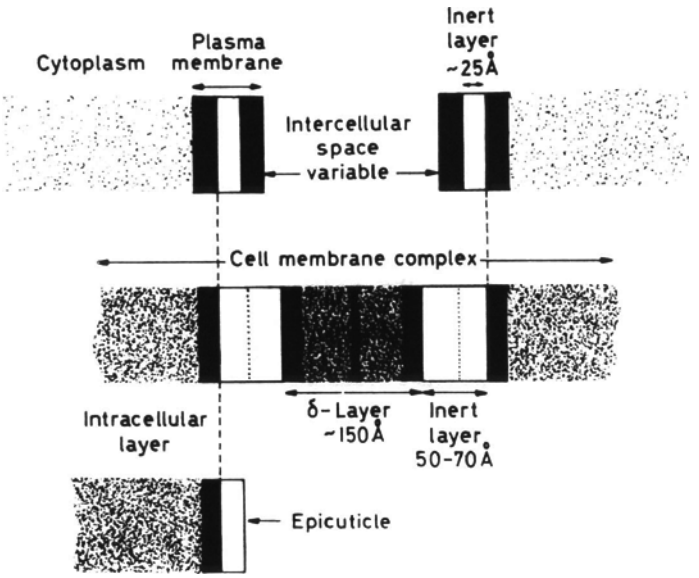

FIG. 6. The relationship between the plasma membranes of living cells and the cell membrane complex of keratinized tissues (according to Fraser et al. [10]).

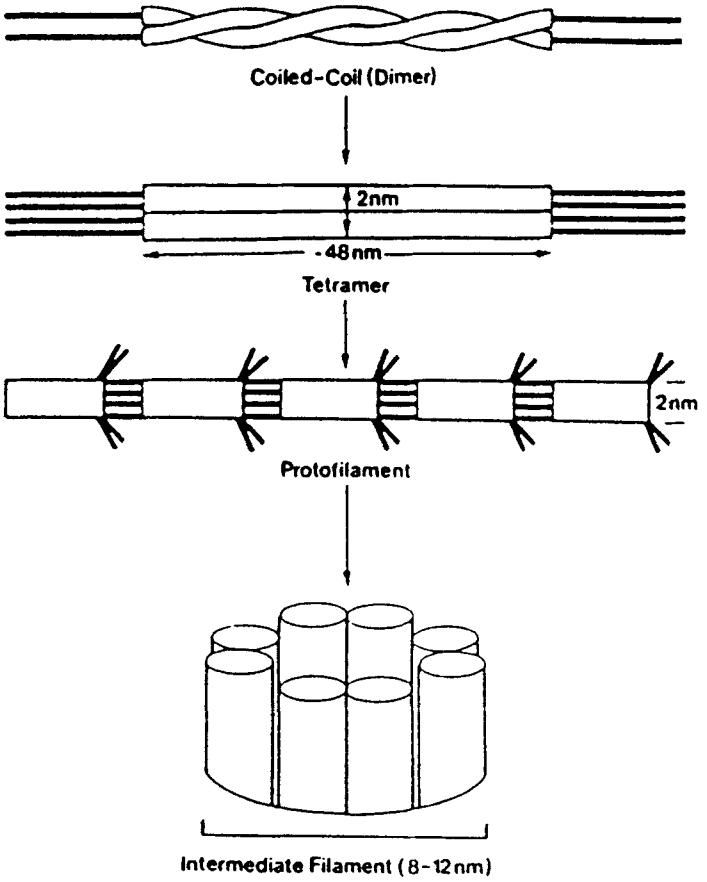

FIG. 7. Hierarchical order in the intermediate filament structure (according to Francke et al. [11c]).

comprising proteins which mechanically communicate between neighboring cortex cells.

While the cortex cells usually are 100 μm long and 1 μm wide, their components, the macrofibrils, are 10 μm long and 100 nm wide, and the components of the macrofibrils, the microfibrils or intermediate filaments, are 1 μm long and 10 nm wide. The microfibrils are composed of the so-called α-keratins. All other material is considered to be nonkeratinous material. The base molecule of the microfibril or the intermediate filament is an α-keratin molecule, major parts of which are present in the helical conformation. Two different α-keratin chains, one more basic and the other more acid in character, form a heterodimer (coiled coil) with a length of ca. 50 nm. Two heterodimers form a tetramer with a width of 2 nm. The tetramers are combined to form a protofilament by increasing their length, not their diameter. About 8 protofilaments are considered to be packed together to form an intermediate filament with a diameter of 8–12 nm, the microfibril of keratin fibers (Fig. 7).

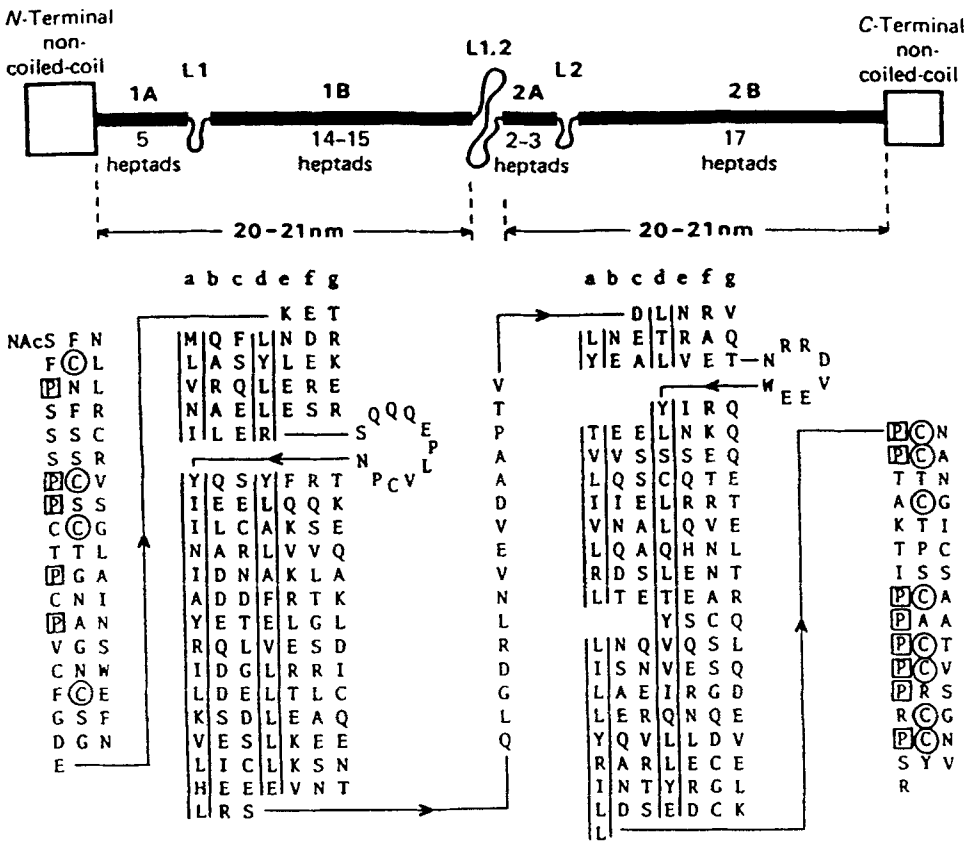

FIG. 8. Primary and predicted secondary structure of component 8c-1. Coiled-coil segment (1A, 1B, 2A, 2B) are indicated by heavy lines, terminal non-α-helical segments rich in cystine and proline are indicated by boxes, and linker segments (L1, L1,2, L2) are indicated by irregular lines. In the terminal non-α-helical segments, proline and cystine residues that lie on the three-residue grid are boxed and circled, respectively. Residues in the *a* and *d* positions in the coiled-coil segment are outlined [12].

We have now arrived at the molecular level, and the chemical nature and the conformation of the α-keratin chain will be discussed.

The α-keratin molecule (Fig. 8) is characterized by two terminal segments, which are considered to be in the amorphous state, and four helical segments (1A, 1B, 2A, 2B), which are organized in heptades of amino acid residues and are connected by linkers (L1, L1,2, and L2); the linker sequences are considered to be in a statistical coil conformation.

The terminal segments are rich in proline and cysteine residues, and hence have a strong capability of crosslinking. The first and fourth amino acid residues of the heptades are of a nonpolar character, i.e., each third/fourth residue is Leu, Ile, Tyr, or Val. The hydrophobic effect originating from this structure as well as the polar interactions originating from the amino acids Asp and Glu in the residual positions of the heptades are the reasons for the superhelix formation.

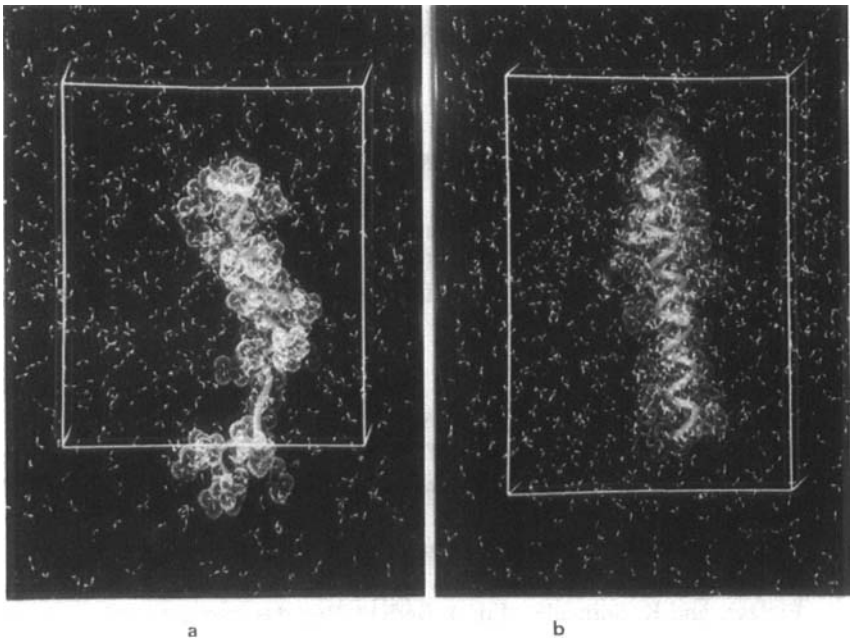

FIG. 9. Molecular dynamics simulation with CFF 91 at 300 K. (a) Segment L1,2/water, after 400 ps. (b) Segment 1A/water, after 300 ps [13].

There is no x-ray structure of an α-keratin molecule or an assembly of molecules available. The assumption of helical and nonhelical domains is based on the specific amino acid composition. Molecular modeling investigations, however, clearly show that the linker segment L1,2, starting from the helical conformation, readily transforms to a rather coiled conformation while the helical conformation of segment 1A under comparable conditions remains stable over long periods of simulation (Fig. 9) [13].

CONCLUSION

The chemical and morphological nature of keratin fibers is the source of their particular mechanical and chemical properties. The high strength of the fiber is due to intermediate filaments organized along the fiber axis, the interpenetration of cortex cells, and the cell membrane complex which acts as a glue. Crosslinking is an extremely important structural element. It results in a cuticle which has to be considered to be a duromer. Crosslinking is also one reason for the close contact between intermediate filament material and matrix material. The interactions between the reinforcing intermediate filaments and the matrix, however, are additionally enforced by the entanglement of linker segments with matrix segments. Last but not least, the chemistry between the intermediate filament and the matrix is very favorable for the formation of hydrogen bridges.

Thus, keratin fibers are an extremely instructive example of natural hierarchical morphology resulting in significant physical/mechanical and chemical properties.

REFERENCES

[1] A. L. Lehninger, D. L. Nelson, and M. M. Cox, *Prinzipien der Biochemie*, 2. Aufl., Spektrum Verlag, Heidelberg, 1994, p. 922.

[2] Reported in J. G. Tirrell, M. J. Fournier, T. L. Mason, and D. A. Tirrell, *Chem. Eng. News*, 1994, p. 40.

[3] Reference 1, p. 45.

[4] H. Zahn, U. Altenhofen, and F.-J. Wortmann, *Ullmanns Enzyklopädie der Technischen Chemie*, Vol. 24, 4. Aufl., 1983, p. 489.

[5] R. D. B. Fraser, J. M. Gillespie, T. P. MacRae, and R. C. Marshall, *International Report of CSIRO, Division of Protein Chemistry*, Parkville, Vic., Australia, 1981.

[6] F.-J. Wortmann and W. Arns, *Text. Res. J., 56*, 442 (1986).

[7] M. Wittig and G. Wortmann, in *Der Mann im Eis*, Bd. 1 (F. Höpfel, W. Platzer, and K. Spindeler, Eds.), Bericht über das internationale Symposium 1992 in Innsbruck, Eigenverlag der Universität Innsbruck, 1992, pp. 273–298.

[8] E. Heine, *Schriftenr. DWI, 105*, 57 (1990).

[9] K.-H. Phan, Dissertation, RWTH Aachen, 1994.

[10] R. D. B. Fraser, T. P. MacRae, and G. E. Rogers, *Keratins—Their Composition, Structure and Biosynthesis*, Charles C. Thomas, Springfield, IL, 1972.

[11] (a) D. A. D. Parry and R. D. B. Fraser, *Int. J. Biol. Macromol., 7*, 203 (1985). (b) L. G. Sparrow, L. M. Dowling, V. Y. Loke, and P. M. Strike, in *The Biology of Wool and Hair* (G. E. Rogers et al., Eds.), Chapman & Hall, London, 1988, p. 145. (c) W. F. Franke, T. M. Magin, and H. Herrmann, in *Verhandlungen der Gesellschaft Deutscher Naturforscher und Ärzte, 115. Versammlung, Freiburg FRG, 1988*, Wissenschaftl. Verlagsgesellschaft, Stuttgart, 1989, p. 153.

[12] L. M. Dowling, W. G. Crewther, and D. A. D. Parry, *Biochem. J., 236*, 705 (1986).

[13] B. Knopp, Dissertation, RWTH Aachen, 1995.