Hierarchical Natural Materials: Nanostructured Keratin

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ABSTRACT

Nanotechnology quite certainly will become an important field in the science and technology of the next decades, allowing to manipulate matter at the nanometer scale and to incorporate nanostructures and nanoprocess into working technological innovations. In this important emerging area, natural materials have caused interest due to their interesting nanometric arrangement, which is responsible for many functions and properties of important biological machines and structural materials such as cell, DNA and other natural systems as biofibers. In the mentioned natural structures, organic groups take part in significant manner to develop assembled systems linked by interactions between these chemical groups. Thus, natural biofibers form interesting hierarchical structures which represent an important alternative to develop new nanostructured materials in the field of biomimetic. In this context keratin biofibers are studied and presented in this research.

Keywords: keratin, nanostructure, natural material, hierarchical structures, self-assembly.

1 INTRODUCTION.

The performance and applications of smart materials have been growing in the last years and recently their development near to molecular scale with nanometric structures represents a new challenge in the emerging era of nanotechnology. In this context nature materials have called the attention of research community inasmuch as some of these structures have a clear ability to adapt toward different conditions with slight changes at molecular level. Clear examples of these molecular biomaterials are proteins which have smart response to different conditions depending on their nature. Research on structural proteins such as collagen, keratin, and silk may form the basis for producing a variety of hierarchical structures that are characterized by the ability to undergo biomolecular self-assembling. Research of these structures promises to be an important gate toward the comprehension and develop of novel smart materials at the nanometric level, which could be very useful to control and mimic different nature materials.

In proteins the secondary structure and the organic groups play an important role in this interesting behavior, due to they are directly involved in the self-assembly of the biomolecule. For instance in keratin, α and β conformation change with tensile, chemical or thermal treatment, causing a rearrangement in the hydrogen and sulfur bonds between the main chain of polypeptide and the aminoacids [1].

In this work is studied and discussed the importance of the hierarchical arrangement in nanostructured keratin and the response of this structure towards the knowledge and progress of novel nanosmart and smart nanostructured biomaterials. Figure 1 shows a schematic representation of hierarchical structure in keratin biofibers, where highly organized subcomponents are presented in different levels. This material consists of a cellular component core surrounded by an outer layer with cuticle cells. The core component contains cortical cells arranged in an overlapping way and elongated along the direction of the fiber axis. Cortical cells are composed of microfibrils organized into larger aggregates or macrofibrils, which contain aggregated keratin intermediate filament proteins, surrounded by keratin associated matrix proteins. In spite of their interesting characteristics, a limited number of studies have been dedicated to keratin biofibers such as feathers which present these important features. This kind of hierarchical natural material is analyzed and discussed in this work.

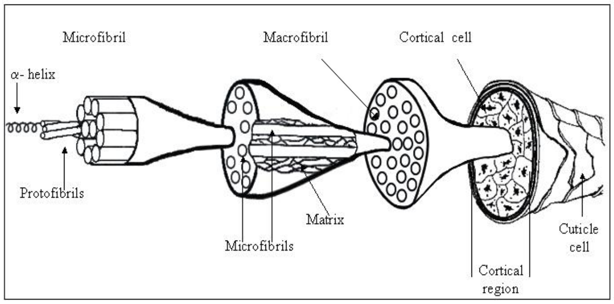

Figure 1. Hierarchical structure in keratin biofibers. [2]

2 HIERARCHICAL NANOSTRUCTURED KERATIN.

In order to analyze keratin biofiber hierarchical structure two electron microscopy techniques were used. Morphological features of surface and microstructure were analyzed by scanning electron microscopy (SEM) and the internal structure was observed through transmission electron microscopy (TEM). Also biofiber morphology and structural changes in secondary structure were studied in these nanostructured biofibers, stimulated by mechanical treatment.

The figure 2 shows some barbs coming from the broad central barb and additionally nodes along each barb are observed in figure 3; it can be assumed that the nodes are comparable to the cuticle scales in wool. The cuticle consists of layers of scales and its role is to protect the fiber's cortex. Nodes and barbs on the feather fiber are related with shape memory properties and improve structural strength, the first property is considered as smart response in materials field. Thus, the comprehension of this kind of systems should be used to modify bulk elastic properties of new bioinspired materials.

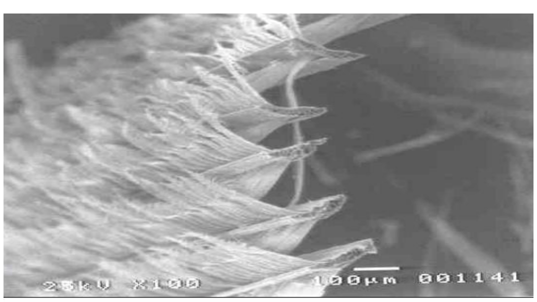

Figure 2. SEM of hierarchical keratin structure in barbs.

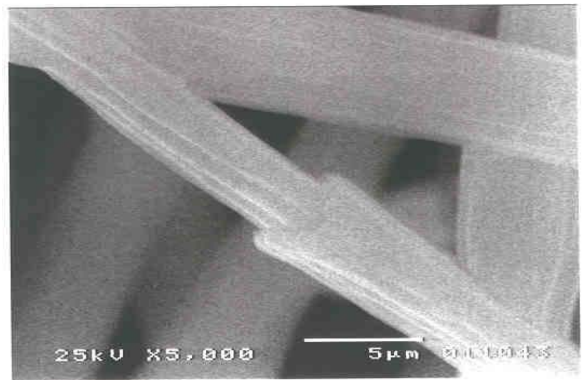

Figure 3. SEM of nodes in keratin structure.

Figure 4 shows TEM images of keratin feather fibers where we can appreciate the complex self-assembled hierarchical structure, also this structure is responsible of the outstanding memory and mechanical properties presented by keratin biofibres [2,3]. In this image microfibrils are observed, these are immersed in the amorphous matrix, identified by its dark color. The microfibrils are twisted forming a helix that is responsible of the fiber's high mechanical strength. In the figure 5 is confirmed the presence of two different structures inside the biofibers: microfibrils and protofibrils. First has order and therefore, crystalline structure. The matrix, is amorphous and with a high content of cystine, revealed by the reaction between the sulphur contained in the aminoacid and the fixation and contrast chemical agents.[2-4]

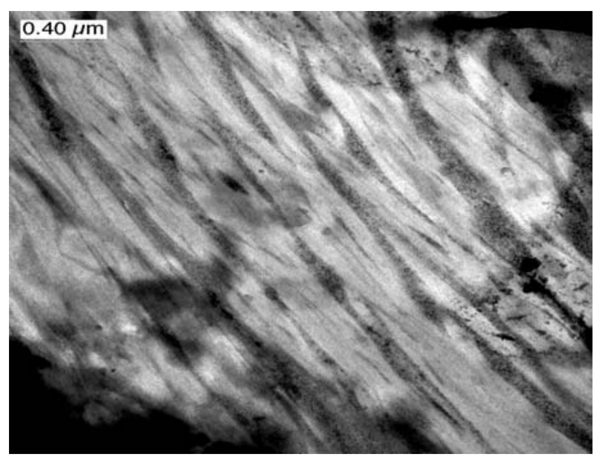

Figure 4. TEM micrograph of longitudinal section of feather keratin fiber.

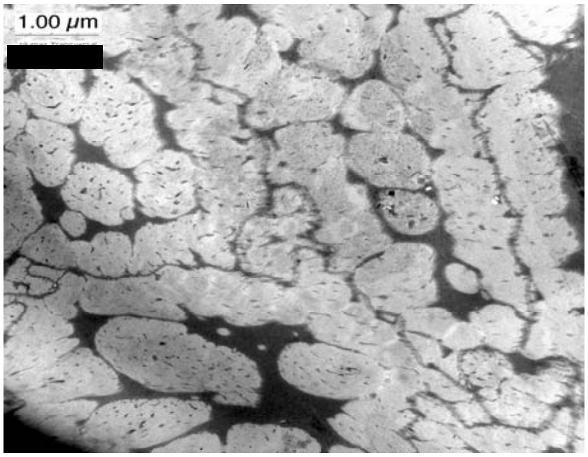

Figure 5. TEM micrograph of transversal section of feather keratin fiber.

As we can observe keratin fiber is made up from a crystalline fiber phase and an amorphous protein matrix phase linked to each other. The crystalline phase consists of α-helical proteins braided into microfibrils where the protein matrix is anchored by means of H bonds and the previously mentionated intermolecular interactions. Thus we can deduced that the hierarchical structural above observed and discussed, form self-reinforced nanocomposite. These molecular interactions that support the analyzed hierarchical structure are sensible to mechanical treatment, which are related with stimuli response at nanometric level and have repercussions on macroscopic behavior. The sensible response corresponds to structural changes in two different secondary structures known as alpha (α)and beta (β). In this context Raman spectroscopy which is a technique is very sensible to structure changes in polymeric materials [5] have been used to corroborate this nanostructured changes where Hydrogen bonds play an important role. More Details about these results can be found elsewhere [4,5]

Thus, the comprehension of hierarchical structures at nanometric level and in this case of hydrogen bonding as one of the most important noncovalent linkages could be the beginning of a new route for the developing of nanomaterials, mimetizing the smart nature materials. As soon as these systems become understood may be able to be produced very reliably because biological systems are capable of manufacturing large molecules in a highly reproducible manner, far more reproducible than any corresponding industrial processes.

As we mentioned, these natural materials present a nanometric smart structure which is sensible to temperature and mechanical force, this principle of nanostructured material could find application in materials field where smart systems are required in order to control the release of molecular structures and the self-assembly. In addition bioinspired materials with these principles of self-assembly might be developing in order to form novel smart materials with sensible nanometric structure where the changes have repercussion at macroscopic level.

This self –assembly features in keratin have been utilized in order to form novel materials such as nanostructured membranes which have found applications in removal of water contaminants [6]. This new material present as base nylon polymer of nanostructured keratin particles. This represents that keratin lie to form nanoforms when chemical conditions are controlled and confirms that some natural materials in controlled environment lie to self-assemble in nanostructured forms. Figure 6 shows SEM image of nanostructured keratin membrane.

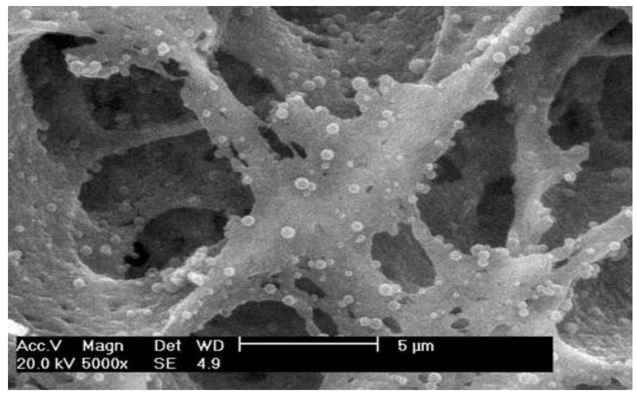

Figure 6. SEM image of nanostructured keratin membrane.

3 CONCLUSIONS

Natural hierarchical structure materials are an important wellspring in order to form bioinspired materials, the understanding of the nanometric functions and smart self-assembly properties, will provide the principles to create ordered structures.

The study of nanostructured transformation in hierarchical natural material can help us to understand their structures and smart responses, in order to mimic and develop new keratin nanomaterials which could be used in other nanoengineering applications such as the mentioned before. In addition this research is useful to understand other important biological systems that undergo similar effects, such as bones [7] and spiders' silks [8], both together with keratin tissues could mean an important key to develop nanostructured smart materials useful in a broad field from medical to environmental applications.

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