A NEW MODERN THEORETICAL VIEW OF THE STRUCTURAL MODEL OF THE STRUCTURE OF NATURAL LEATHER

Mykola Skyba[1], Oleg Synyuk[1], Borys Zlotenko[2], Tetiana Kulik[2] and Svitlana Natroshvili[2]

[1]*Khmelnytskyi National University, Instytuts'ka str. 11, Khmelnytskyi 29016, Ukraine*
[2]*Kyiv National University of Technologies and Design, Nemyrovycha-Danchenka Street 2, Kyiv 01011, Ukraine*
rector@khnu.km.ua; synoleg@ukr.net; zlotenco@ukr.net; t-81@ukr.net; friit@knutd.edu.ua

Abstract: *The article presents approaches to the processing of waste from natural leather to artificial leather while preserving the beneficial properties of natural leather. It is proposed not to grind, but to defiber leather waste, i.e. before the destruction of the material you need to weaken its structure so that the fibers are easily separated at loads less than the breaking point of a single fiber. As a result of the analysis it is established that the structure and properties of leather materials form the basis of the processes of their defibering. A structural model of the structure of natural leather has been developed, which makes it possible to determine the change in the properties of leather fibers under the action of loads in the process of defibering natural leather waste and to establish a relationship with the properties of artificial leather obtained from recycled natural leather. It is established that the fibers, joining in bundles that look like strands or ribbons, and intertwining in all directions form a structural element of the natural leather. Elastic fibers, when combined with tannins and glycoproteins, which are unbound between the structural elements of the natural leather, form a macroscopic element of the natural leather.*

Keywords: *waste, leather, fibrils, collagen, fibers, material, properties.*

1 INTRODUCTION

Over the last century, humanity has made such progress in its own development that it has not been able to achieve during the previous two thousand years. Great scientific discoveries, the invention of new technologies and substances have increased many times the human need for raw materials, energy and water resources. Of course, no production is waste-free. All of Europe and America have long spoken of the great damage done to the environment by urban landfills, polluting not only the air but also the soil and groundwater that humans eventually consume. This is the law of the great terrestrial water cycle. It should also be noted that the areas where landfills are located, even after their elimination will be unsuitable for any use for many decades.

Waste incineration is also not an option. Toxic gases come to us again in the form of rain. And what is to say about large industrial enterprises, because they are the biggest polluters. It is their work that has given rise to such a term as "global environmental problems".

Most developed countries are already quite successful in combating these problems, using the latest processing technologies, repeated cycles of raw materials. Of course, the efficient and rational use of technological waste and secondary material resources received from enterprises and the population affects the intensity of economic development and, most importantly, requires a new approach to saving production and raw materials. However, this does not completely solve this problem, which is faced by many manufacturers. Today, special attention is paid to solving this problem. Many companies have long included in their production programs specialized machines for processing secondary material resources and various technological wastes. These machines are characterized by a high degree of automation, automatic control systems and versatility of design. Automated lines for the processing of secondary material resources and waste include various technological processes (for example, the production of shoe cardboard, nonwovens, yarn and fibers for various purposes). Nowadays, such machines are produced that can process technological waste from mixtures of different materials into high-quality products with high waste content or from pure secondary raw materials.

Waste of footwear and leather goods production is about 25-40% of all raw materials for leather and fur. Of course, workers in these industries can help reduce production costs by maximizing the use of leather, as well as employing its proper processing using advanced production methods. As a result, the production and processing of natural leather will expand, although the amount of waste will also increase. On the other hand, the growing tendency to chemicalize leather and footwear production will reduce the use of natural leather.

Waste generated in the process of preparation and processing of leather raw materials can be divided into sold, which can be used for the manufacture of various products and semi-finished products, and those that are taken to landfill. The fully used wastes include wool as well as core, scrap and chips of leather obtained by the chrome tanning method [1, 2].

Waste subjected to dechromization can be used not only for the manufacture of core glue, household soap and feed protein additives, but also for the production of synthetic rubbers, fiberboards, foaming agents.

When processing leather waste, more attention should be paid to preserving the valuable properties characteristics of natural raw materials. Therefore, when defibering waste, it is necessary to preserve the structure of fiber bundles, as well as their original length. The presence of short fibers in the future in the production of artificial leather such as cardboard requires the use of binders for their bonding, in some cases in an amount of more than 100% by weight of the fiber [3, 4]. At the same time, the hygienic properties of cardboard type artificial leather significantly deteriorate [5].

The use of existing technologies and equipment for defibering leads to the destruction of the material due to excessive crushing of fiber bundles. This is due to the strong fibrous-mesh structure of natural leather. As a result of the mutual pressure, twisting and looping of the fibers, they are clamped in volume, just as individual strands are clamped in a complex rope, and therefore the strength of the weave is greater than the natural strength of the fiber bundles. The works [6-8] are devoted to the study of physical and mechanical properties of leather and the nature of connections between fibers, where it is confirmed that when fibrous materials such as leather, felt, cardboard and artificial leather are tested for rupture, the tensile strength decreases with decreasing stripe width; a decrease in the tensile strength is observed when the stripe size is less than 5 mm.

To preserve in the artificial material made of recycled leather waste, the useful properties characteristics of natural leather, this waste must not be ground, but defibered. To do this, you need to find a way to weaken the structure of the leather before defibering so that the fibers can be easily separated without grinding.

2 DISCUSSION AND ANALYSIS

Before proceeding to the development of technologies for the defibering of leather waste, let's focus on general issues of its structure and microstructure in order to establish how the properties of leather fibers change under the influence of individual production processes, and how they affect the properties of the finished products. As noted in studies [5, 8, 9], the produced leather retains the natural fibrous structure inherent in animal skin.

2.1 General ideas about the structure of leather

In the animal skin there are three layers (Figure 1) [5, 8]: 1) a relatively thin upper cell layer - the epidermis;
2) the thickest dense fibrous layer - the dermis;
3) porous-fibrous layer that connects the skin with the body of the animal that is called subcutaneous tissue.

In the process of leather production, the epidermis, hair, sebaceous and sweat glands, as well as subcutaneous tissue are completely removed. The finished leather is only the middle layer of the skin - the dermis, treated accordingly.

The main histological elements of the dermis are fibrils, which are the thinnest threads up to 0.5 μm in diameter. Fibrils form fibers. The fiber can contain up to 10,000 fibrils. The fibers, in turn, are connected in bundles that have the form of strands or ribbons that intertwine in all directions and form a tissue.

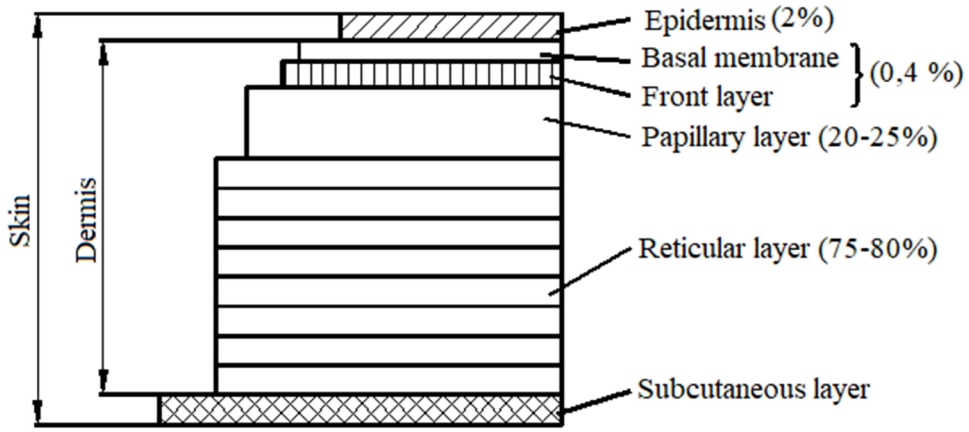


Figure 1 Scheme of layers in the dermis of cattle [5]

It is possible to compare the sizes of structural elements of a derma tissue on their transverse sizes [8]: a bunch 50-100 μm; fiber 20-40 μm; fiber 2 μm; fibril 0.5 μm.

The main component of the dermis fibers is a protein - collagen. Along with collagen fibers, the dermis also contains elastin and reticulum fibers. Elastin fibers are positioned in different directions and create a grid that serves as a framework for different structural elements. Reticulum fibers in the upper part of the dermis also form a dense network. Intertwined, the bundles of collagen fibers form a tissue in which the network of the bundles of collagen fibers changes depending on the species of animal, and in animals of the same species - depending on the topographic area of the skin.

At transition from intermediate levels of formation of skin collagen to the final one – the dermis – the principle of parallelism of structural elements (polypeptides, molecules, subfibrils, microfibrils, fibrils, primary and secondary fibers) packing is lost. Within the dermis, the fibers intertwine in different directions, forming a network. The size of the gaps between the collagen fibers of the dermis was determined by the parametric method [5, 6]. Thus, it was found that the average pore diameter in the dermis of cattle is 5 μm, i.e. almost 10 times smaller than the diameter of the secondary fibers.

To characterize the interfiber spaces of the dermis, as well as the products of its processing in leather production, in addition to porosity, the values are used: the volume of the dermis, which contains 100 g of collagen [9, 10]. Table 1 shows the ratio of these indicators of the dermis.

Table 1 Porosity, bulk density and bulk yield of air-dry dermis (humidity 15%, density excluding pore volume, 1.35 g/cm^3) [8]

Porosity [%]	Bulk density [g/sm^3]	Bulk yield [sm^3/100 g]
20	1.08	88.90
40	0.81	123.45
60	0.54	176.00
80	0.27	370.35

Using an optical microscope on the incisions of the dermis, you can see the secondary fibers located in the plane of intersection at different angles to the surface of the dermis. Schematically, this is shown in Figure 2 [5].

By measuring the angle of inclination of a large number of secondary fibers, you can calculate its average value, which depends on the topographic area of the skin.

The largest average angle of inclination of the fibers has the dermis in the back (about 50°), the smallest - in the abdomen (about 17°). Between themselves, the secondary collagen fibers of the dermis in the plane of its incision form rhombic shapes [8]. It seems that the fibers inside the dermis form a network of spirals, diamonds like threads in artificial nonwovens [5, 8, 11]. The sides of the rhombuses found in the incisions of the dermis are projections of the turns of the spirals, part of which are these fibers.

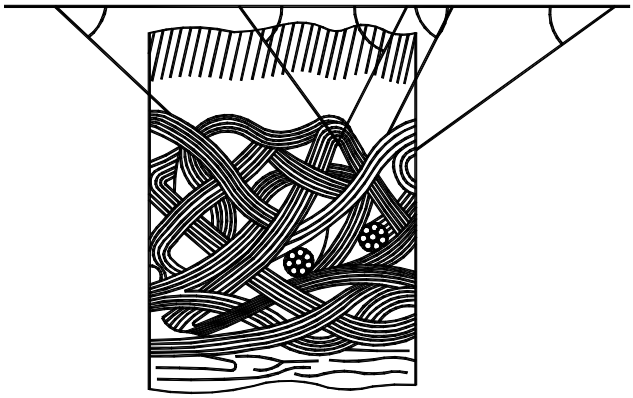


Figure 2 Layout of secondary fibers in the dermis [5]

It is always necessary to take into account the possibility of fluctuations in the indicators values of the cattle skin dermis structure. In particular, its density in different layers of the skin and in different topographic areas is not the same (Figure 3).

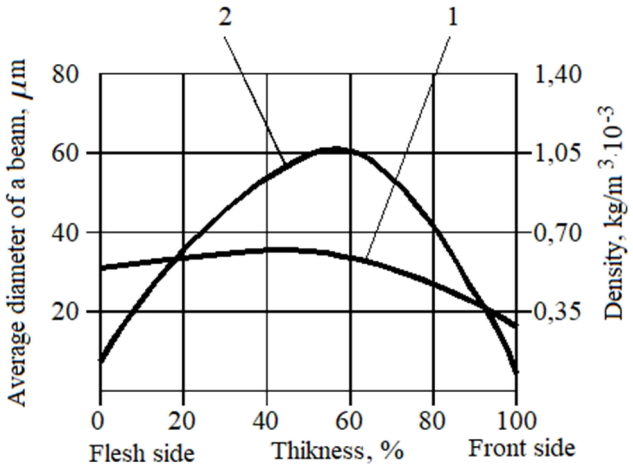


Figure 3 Density (1) and cross section of fibers (2) in the layers of the dermis of cattle

In the papillary layer of the cattle dermis the secondary fibers are twice as thin as in the reticular one, and are very close to each other. Even thinner elements of the structure are located in layers in contact with the epidermis, in which the fibrils are not combined into fibers. In the skin of sheep skin, the papillary layer accounts for up to 66% of its thickness, and in the skin of goats, this share is 33-50%. In the skin of pig skins it is impossible to distinguish papillary and reticular layers. Another feature of the dermis of pig skins is

the strong branching of secondary fibers. The thickness of the epidermis of the skin of pigs reaches 5%, while in cattle, sheep, goats and horses it does not exceed 2%.

2.2 Structural levels of the fibrous structure of collagen

Skin collagen can be considered as a complex composite of fibrous structure at all levels of its structure. Consideration of the levels of collagen structure of the skin should start with the molecular level and go to larger structures [8]. Collagen is a fibrous protein that contains glycine, proline and oxyproline as the main components, and other amino acids in different proportions. The chains have a uniform length - 290 nm. Three such chains form a triple helical element called tropocollagen (Figure 4a). As noted in recent studies [5, 8, 9], five such tropocollagen elements form a microfibril (Figure 4b). These elements are located on the ledges along the longitudinal axis of the microfibrils in a section of fixed length (about 1/4 of the length of the molecule).

It is assumed that such a ledge together with the distance between the ends of the following tropocollagen is responsible for the characteristic period of the structure with a step of 65 nm, visible both in the electron microscope and at low-angle diffraction. It is also assumed that the five tropocollagens are intertwined in an elongated triple helix.

Microfibrils are enclosed in tetragonal or hexagonal lattices, which have a period of 3.8 nm (Figure 4d). They form a known fibrous element of collagen - collagen fibril (Figure 4d), which has a structure period of 65 nm and visible in an electron microscope. The diameter of these fibrils varies between 100-500 nm in mature animals.

There are a number of indications that fibrils may not be homogeneous throughout their cross section. Proof of this is the nature of the color of the interfibrillar carbohydrate matrix [5, 12], visible under an electron microscope. References to the subfibrillar region have appeared in other works [8]. When considering micrographs of strongly deformed fibers, the splitting of fibrils into separate subfibrils - fibrous elements with a diameter of 15 nm is visible (Figure 4d).

Collagen fibrils are surrounded by an interfibrillary matrix, which consists mainly of mucopoly-saccharides and to a lesser extent of structural glycoproteins, and it has been found that this structure spreads in width, forming collagen elements with a diameter of several hundred μm.

These elements, connecting with elastic fibers and fibroblasts, form a macroscopic element of the skin. The element of collagen with a smooth outer surface is presented in Figure 5a.

The cross section of such collagen is not round – the ratio of its main diameters is in the range of 0.5-1.0. This shape is closer to the shape of a flattened cylinder than to what could be called a stripe. The diameter varies from 100 to 500 μm. With the appropriate orientation, the element considered in polarized light shows periodically fading bands with a period of about 100 μm along the fibers. This stripe character is due to the periodicity of the change in the orientation of the element of birefringence (Figure 5a). In separation experiments, it was found that these optical effects are characteristic of the structure of small beams of fibrils. When considering sections of collagen in polarized light, it is seen that all the stripes are corrugated in phase, and the planes of the stripes are parallel throughout the thickness of the skin (Figure 5b).

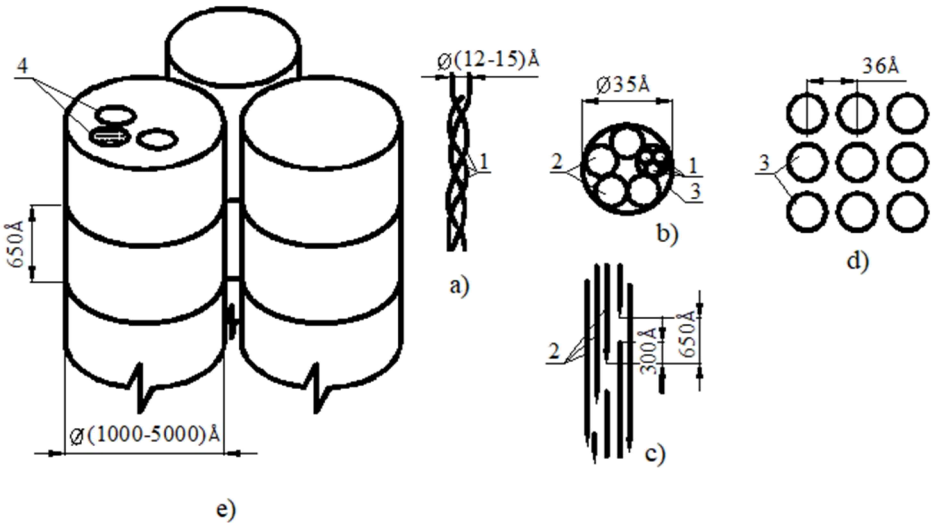


Figure 4 Scheme of structural levels of collagen, starting from the molecular level: a) triple helix of tropocollagen; b) cross section of microfibrils; c) longitudinal section of microfibrils; d) tetragonal packaging of microfibrils; e) collagen fibrils. 1 - peptide chains; 2 - tropocollagen; 3 - microfibrils; 4 - a separate subfibril formed by a lattice of microfibrils

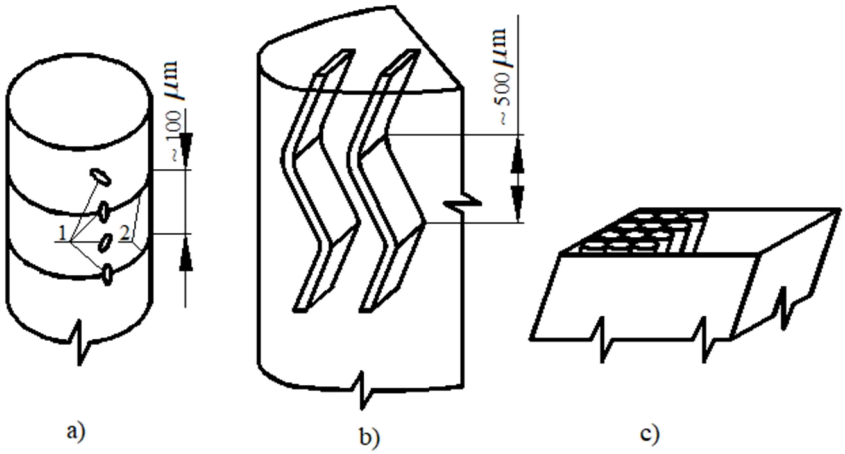


Figure 5 Scheme of the structure of collagen fiber at the macroscopic level: a) element of collagen fiber; b) the location of flat corrugated stripes in the fiber element; c) axonometric view of the cross section of the stripe, consisting of collagen fibrils. 1 - optical indicators, 2 - attenuation bands

To date, the dimensions of the cross section of these stripes are not precisely defined. It is believed that they vary from 2-3 to several tens of μm. Large elements are split into smaller ones until the smallest element with a noticeable stripe structure remains (Figure 5c). This condition corresponds to the structure of collagen fibrils shown in Figure 4d.

The nature of the relationship of structural levels depends on the mechanical behavior of the entire system. Larger elements of the structure have the properties of the tissue as a whole. Stretching in the area of small deformations leads to the reversible removal of the periodicity and the corresponding straightening of the folds. The mechanical model allows analyzing structures of smaller sizes. As mentioned earlier, the diameter of the load-bearing element cannot be measured on a macroscopic sample. To comply with experimental data, it is required that it be within the size of collagen fibrils (Figure 4d).

Mechanical behavior, obviously, reflects the relationship between different elements. When determining the structural level of the connecting elements, it should be borne in mind that there may be further splitting of the elements into smaller ones - depending on whether the collagen of the skin is in a state of growth (before obtaining leather) or in aging (after obtaining leather). After reaching the maturity of collagen, the modulus of its elements does not change; the increase in strength can be attributed to the possible connections between the fibrils: since large deformations cause flow and fracture, including sliding of adjacent elements, the bonds that connect the sliding elements will create the necessary reinforcement. In young skin, the fibrils in the matrix do not touch each other, in mature - begin to touch, and then, perhaps, they are fused [8]. In the latter case, the effective diameter of the fibrils is increased, and a direct chemical bond may occur between the fibrils. Despite the fact that the fibrils are separated by an interfibrillar matrix, there may be a direct mechanical connection between them (Figure 4d). In the electron microscope, the consistency of the internal structure of the fibrils is noticeable [4], which allows us to make assumptions about the similar nature of the striation. Thread-like structures that branch and connect groups of fibrils over long distances are described in [5].

Non-collagen components should also be considered in the block diagram. It has been established that mucopolysaccharides and, to a lesser extent, glycoproteins are associated with fibrils [3, 9]. They form a matrix surrounding the fibrils. However, mucopolysaccharides and glycoproteins may be at other structural levels. Thus, in [3] it was noted that saccharides are located between microfibrils, forming an interfibrillar space.

3 RESULTS AND DISCUSSION

The use of polarization optics has shown that periodically fading bands in the collagen structure are due to the presence of corrugated elements [4]. When collagen fibers are stretched, this "stripe character" gradually disappears. Analysis of the deformable properties of collagen showed that the load is mainly carried by a fiber whose diameter is several orders of magnitude smaller than that of the fiber visible in an optical microscope ($d \geq 2$ μm). The best model describing straightening of folds is based on the idea of stretching folds with rigid hinges. This model assumes the existence of the main load-bearing element, the diameter of which increases with age from 100 to 500 nm. The behavior of the material at high deformation rates indicates that the load-bearing fibrils themselves are fibrous composites and break down into smaller elements during fracture.

Consider the relationship between different structural levels of collagen fibers, in particular, the interaction of individual components of collagen fibers. For satisfactory modeling of the stress-strain behavior of collagen, it is necessary to determine the role of fibrils with a diameter smaller than visible in an optical microscope (d > 2 μm). The existence of such fibers is confirmed by electronic micrographs of individual parts [8]. One part of the samples was examined before loading, and the other - after cyclic deformation or failure.

In the cross section of undeformed collagen fibrils, stained areas of 3.0-3.5 nm in size are visible, which are identified as individual microfibrils [5, 8]. In animals of any age, except newborns, fibrils in the thickness of the skin are located regularly. In this distribution, the smaller fibrils fill the cavities between the larger ones, creating an interfibrillar matrix with a high volume content of fibrils. The close proximity of fibrils obviously leads to their fusion or germination into each other.

When the structure of the skin is subjected to mechanical impact, the formation of cavities and subsequent splitting of the fibrils of the interfibrillar space, it seems to us, are the main and general mechanism of deformation. The splitting of fibrils increases with increasing mechanical impact. Initially, in some fibrils there are random cavities; with a further increase in the mechanical impact the cavities spread throughout the fibril. By the time of destruction, the fibril completely decomposes into subfibrils with a diameter of about 15 nm, each of which contains several sections of 3.5 nm. A longitudinal section of a split fibril shows that subfibrils with a diameter of 15 nm are individual longitudinal elements with an unstable length. The characteristic periodicity (65 nm) visible in undeformed collagen fibrils is absent in subfibrils, which indicates the deformation that occurs in these elements.

The main age effect is a change in the number of splits that occur before destruction. It is highest at a young age of collagen (1.5 months), and decreases with age. Since fibril cleavage is the main mechanism of destruction at any age, the observed change in the number of cleavages may be the result of increased adhesion between subfibrils and microfibrils. This is consistent with the aging hypothesis based on the fact of increasing the density of cross-links at such structural levels, where these links can effectively reduce the possibility of slipping between subfibrils and microfibrils.

As noted, the crystalline interferences on the collagen radiograph revealed that the proportion of crystalline zones depends on the content of amino acid residues (proline and oxyproline) in the collagen polypeptides. The degree of crystallinity of the structure can be judged by determining the intensity of interference on radiographs and the half-width of reflexes [5, 8]. The results of these experiments are shown in Table 2.

In the initial stages of the study of supramolecular aggregates, the object of study was only one level of ultrastructure - fibrillar. Thinner filaments formed by the cleavage of fibrils by enzymes and certain chemical compounds were considered as random packets of molecules of different diameters. As a result of further experiments, the existence of structural additional protofibrillar levels was established.

Table 2 Crystallinity of tropocollagen with different content of amino acid residues [5]

Tropocollagen	The content of amino acid residues in the polypeptide	The proportion of the crystalline phase [%]
Mammal dermis	214	35
Pike dermis	189	30
Cod dermis	155	26

The analysis of spatial structures based on the principle of shear led to the finding of another additional level of collagen ultrastructure - microfibrillar. In the cross section of the fibrils there are five collagen molecules, which, depending on the humidity, form a hollow cylinder with a diameter of 3-5 nm. The scheme of such cylindrical collagen microfibrils is shown in Figure 6.

Another, related, scheme of microfibrils with four collagen molecules in cross section has been proposed in [5]. Experimental confirmation of the fact that collagen fibrils are aggregates of microfibrils of the same diameter is electronic microphotographs of negatively contrasted samples, on which it is clearly visible at high magnification.

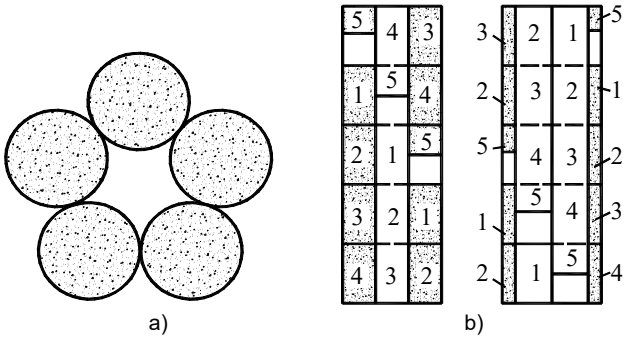


Figure 6 Scheme of collagen microfibrils: a) cross section; b) longitudinal section [5]

Data on the density of fibrous collagen, as well as gelatin of collagen-like conformation, can be a strong proof of the tubular nature of microfibrils (Figure 6b). Examination of air-dry collagen and gelatin preparations or after drying without special

precautions reveals that their density usually does not exceed 1.4 g/sm^3, which corresponds to a specific volume of 0.71 sm^3/g. This value is much higher than the atomic volume of the same proteins, which does not exceed 0.5 sm^3/g. This indicates that in collagen the principle of dense packing of atoms in the crystal structure is not maintained. Thoroughly dehydrated collagen preparations, as well as collagen-like gelatin, have a density of about 2.0 /sm^3.

The above experimental data and considerations can be used to substantiate the scheme of self-assembly of microfibrils, which is subject to different laws than the ordered aggregation of protofibrils. The mechanism of fibrillation proposed in [9] can be considered the most substantiated. A very significant addition to the views expressed by these authors is the inclusion in the scheme of fibril formation of collagen molecules of two structural intermediate levels - protofibrillar and microfibrillar. Measurements of electron microscopic images of the filaments in the thickness of negatively stained fibrils indicate that they have a diameter of 3-4 nm, which corresponds to the diameter of the microfibrils. In this regard, there is every reason to use the idea of combining microfibrils into fibrils to consider the process. According to this scheme, in the collagen microfibrils, which are mistakenly identified with protein molecules, the areas of autogenesis of adjacent elements of structures and intermediate areas alternate. This alternation of areas of autogenesis and intermediate areas is fully consistent with the scheme of microfibrils, in which each period D contains areas of fusion. In their cross section there are five protofibrils, thickened with a layer of glycosaminoglycans (GAG), and intermediate sections consisting of only four molecular strands, on the surface of which there are fewer carbohydrates.

Possible types of interaction between microfibrils, leading to aggregates of the following supramolecular, i.e. fibrillar level, are: a) oriented, multilayer adsorption at the phase boundary; b) self-assembly in the interstructural fluid, i.e. in the absence of contact with the pre-formed phase boundary; c) fibril formation in jells.

Elements of the superfibrillary structure of the dermis of various mammals, as well as collagen fibers, of which it is mainly composed, have many features. In addition to the type of organism, the properties of the fibers and the dermis are influenced by the topographic features of the sampling site, as well as other factors (age of the mammal, sex, layer of the dermis, conditions of development of the organism, etc.). The anatomy and histology of the skin are mainly descriptive [8]. Some histological parameters of the dermis of a number of mammals are given in Table. 3.

Secondary fibers, or collagen bundles, are bundles of primary fibers (Table 4). The most common objects of study are secondary fibers that are plucked from the skin. The easiest way to achieve adefibering of the scalp of cattle. The thickest and longest bundles are located in this area.

Contacts between the fibers, which complicate the defibering of the dermis, occur as a result of pre-dehydration of the skin by air drying. In this case, between the elements of the structure of the fibers, as well as between the fibers in the dermis, there is an additional interaction that remains after dehydration.

Table 3 Basic structural parameters of the mammalian dermis [8]

Animal	Dermal thickness [μm]	Reticular layer thickness [% of dermis thickness]	Diameter of secondary fibers [μm]
Cattle	4000-6600	60-80	20-100
Pig	2500-5000	100	5-10
Sheep	2800	42	11.5
Goat	400-600	10-35	3.0-6.6
Squirrel	860	60-65	–
Hare	270	47	–
Mole	270-630	35-50	3.6-5.3
Fox	460	55	6.0

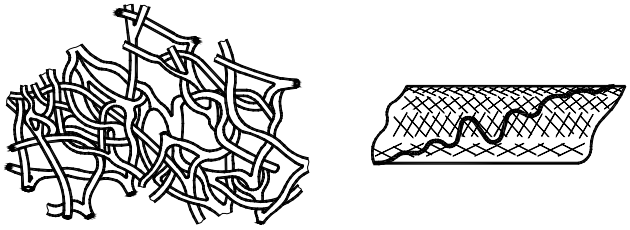
Table 4 The tortuosity and length of secondary fibers in different areas of the cattle skin dermis [5, 8]

№	Indicators	The area of the dermis	
		back	*head*
1	Dermis thickness [mm]	4.75	6.60
2	The average length of the secondary fiber [mm]	24.50	110.60
3	Fiber tortuosity:total (2:1)	5.20	16.80
4	The tortuosity of the fiber:per 1 mm of its length (2:3)	4.70	6.60

In the formation of primary and secondary collagen fibers of the dermis, the effect of mutual orientation and interaction of fibrils with a diameter of hundreds of nanometers is manifested. Therefore, it is worth noting the comparison of some elementary processes of obtaining artificial fibers by the spin method and the method of aggregation of collagen fibrils in the dermis of mammals. The deformations that the fibrils accumulate can be compared with those to which the spinning solutions of polymers are subjected as a result of forced syneresis during the formation of fibers by the spin method.

In the dermis, the parallel orientation of collagen particles is completed at the level of the secondary fibers that have the greatest length and diameter in the neck. The skin in this area of the dermis has greater mobility than in the back, abdomen and other areas. By cutting pieces of dermis of cow skin into horizontal layers, it was possible to determine the length of secondary collagen fibers in different topographic areas of the skin [5, 8]. The average lengths of secondary fibers in dense areas of the dermis reach 24.8 mm and in loose areas 109.7 mm. The number of branched fibers is 4- 9% of their total number. The length of the tortuous fibers significantly exceeds the thickness of the dermis (Table 4).

Most of the secondary fibers of the cattle dermis (70-80%) do not branch at all. Others have one branch. The difference between the tortuosity divided by the thickness of the dermis and tortuosity per 1 mm of fiber length is partly due to its unequal average slope relative to the surface. An important feature of the secondary fibers of the cattle dermis is that their ends, which have a diameter of 5-10 μm, are usually located in the surface layers of the dermis. In its middle layer, they thicken to up 20 μm [5]. Each of them combines 20-1000 primary fibers with a diameter of about 5 μm, in the cross section of which are 200-800 fibrils. The scheme of fibers branching in a derma and an arrangement of secondary fibers is given in Figure 7.

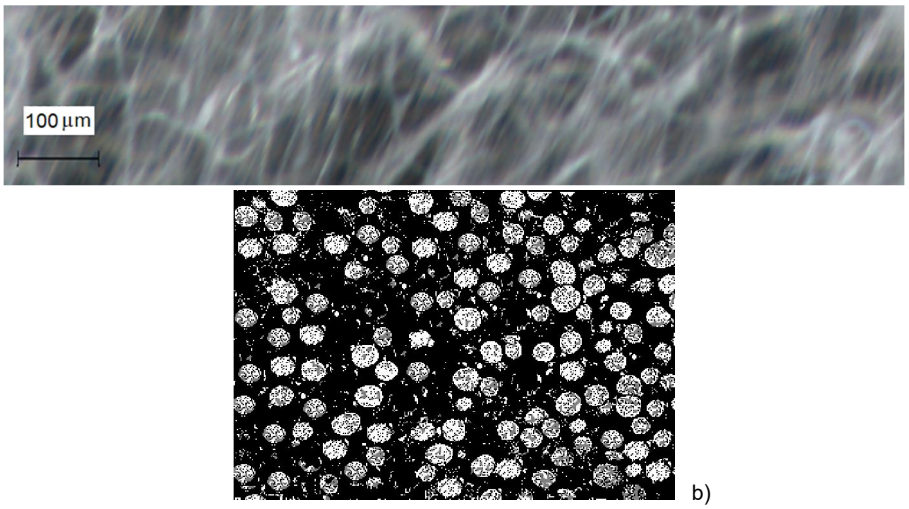


a) b)

Figure 7 Scheme of branching fibers in the dermis of pigs (a) and the location of secondary fibers (b)

The source of fiber formation can be considered the primary fiber that occurs in the layer of the dermis close to the epidermis. It is a rod to which the primary fibers formed in the middle layer of the dermis join without merging. Differences in the change in the diameter of the primary fibers along their length, in contrast to the secondary, are not observed. In the primary fibers, along with the equally directed stacking of adjacent fibrils, there is also a multidirectional stacking, which can be seen by analyzing the cross-sectional pattern [3]. Collagen fibers, compared to other fibrous materials, in the air-dry state contain more interstructural gaps. This confirms the electron microscopic image of their cross section (Figure 8).

The consequence of the "porosity" of the structure is the difference between the true and imaginary density of the fiber. It was found that the density of the protein substance of collagen, which was not subjected to complete dehydration, is equal to 1.4 [5]. The apparent density of protein fibers is 1.096 kg/m^3 [8]. Thus, the interfibrillary troughs occupy approximately 22% of their volume. As a result of intensive compression, the diameter of the fibers decreases by 20-40%.



a)

b)

Figure 8 Photomicrographs of leather sections parallel (a) and perpendicular (b) to the fibers

4 CONCLUSION

Today, equipment for processing natural leather waste into various products is widely produced. But when using existing technologies and equipment, leather waste is ground, i.e. the destruction of the material is carried out through excessive crushing of fiber bundles. The production of artificial leather from small fibers requires the use of binders to bind them, sometimes in the amount of 100% by weight of the fiber. At the same time hygienic properties of artificial leather considerably worsen.

The grinding of the fibers is due to the fibrous-mesh structure of natural leather. As a result of the looping of the fibers, they are twisted into a certain volume, and the strength of the intertwined bundle of fibers is much greater than the strength of a single fiber.

The article presents approaches to the processing of waste from natural leather to artificial leather while preserving the beneficial properties of natural leather. It is proposed not to grind, but to defiber leather waste, i.e. before the destruction of the material you need to weaken its structure so that the fibers are easily separated at loads less than the breaking point of a single fiber.

As a result of the analysis it is established that the structure and properties of leather materials form the basis of the processes of their defibering.

The main histological element of the dermis is fibrils, which form fibers. The main component of the fibers of the dermis is a protein - collagen. Skin collagen can be considered as a complex composite of fibrous structure at all levels. Along with collagen fibers, the dermis also contains elastin and reticulum fibers. Elastin and reticulum fibers are positioned in different directions and create a grid that serves as a framework for different structural elements.

Fibrils enclosed in a hexagonal or tetragonal lattice form the main fibrous element of skin collagen. Collagen fibrils are surrounded by an interfibrillary matrix, which consists more of tannins and to a lesser extent of structural glycoproteins, which are also unbound between the structural elements of the skin. These elements of structural levels, connecting with elastic fibers, form a macroscopic element of the skin.

5 REFERENCES

1. Laing R.M.: Natural fibres in next-to-skin textiles: current perspectives on human body odour, SN Appl. Sci. 1, 2019, pp. 1329, https://doi.org/10.1007/s42452-019-1388-1
2. Danylkovych A., Bilinskiy S., Potakh Yu.: Plasticification of leather semifinished chrome tanning using biocatalitic modifier, EUREKA: Physics and Engineering No. 1, 2018, pp. 12-18, http://dx.doi.org/10.21303/2461-4262.2018.00527
3. Maruhlenko M.O., Palamar V.A., Mokrousova O.R.: Stabilizing derma collagen structure with modified dispersions of montmorillonite, IOP Conf. Ser.: Mater. Sci. Eng., Baltic Polymer Symposium, Sigulda, Latvia, 16-18 September 2015, IOP Publishing, Vol. 111, 2016, 012023, http://dx.doi.org/10.1088/1757-899X/111/1/012023
4. Bhushan B., Chen S., Ge Sh.: Friction and durability of virgin and damaged skin with and without skin cream treatment using atomic force microscopy, Beilstein J. Nanotechnol No. 3., 2012, pp. 731-746, https://doi.org/10.3762/bjnano.3.83
5. Skyba M.E.: Technological processes and equipment for defibering leather and fibrous materials, Monograph, Khmelnytsky: PP Kovalsky V.V., 2003, 135 p. (in Ukrainian)
6. Pahlawan I.F., Griyanitasari G.: Physico-mechanical properties of cattle hide leather for working gloves with flame retardant addition, Livest. Anim. Res. 18(2), 2020, pp. 151-159, https://doi.org/10.20961/lar.v18i2.42937
7. Sudha T.B., Thanikaivelan P., Aaron K.P., Krishnaraj, K., Chandrasekaran B.: Comfort, Chemical, Mechanical, and Structural Properties of Natural and Synthetic Leathers Used for Apparel, J. of Applied Polymer Sci. 114(3), 2009, pp. 1761-1767, https://doi.org/10.1002/app.30589
8. Montelli S., Corain L., Cozzi B., Peruffo A.: Histological analysis of the skin dermal components in bovine hides stored under different conditions, J. of the American Leather Chemists Association 110(2), 2015, pp. 54-61, https://journals.uc.edu/index.php/JALCA/article/view/3594
9. He L., Lan W., Zhao Yu., Chen Sh., Liu Sh., Cen L., Cao Sh., Dong L., Jin R., Liu Ya.: Characterization of biocompatible pig skin collagen and application of collagen-based films for enzyme immobilization, RSC Advances No. 10, 2020, pp. 7170-7180, https://doi.org/10.1039/C9RA10794K
10. Meyer M.: Processing of collagen based biomaterials and the resulting materials properties, Biomedical engineering online 18(24), 2019, pp.1-74, https://doi.org/10.1186/s12938-019-0647-0
11. Bereznenko S., Bereznenko N., Skyba M., Yakymchuk D., Artemenko T., Prybeha D., Synyuk O., Kalinsky E.: Novel equipment for making nanocomposites for investigating the antimicrobial properties of nanotextiles, International Journal of Clothing Science and Technology 33(1), 2020, pp. 25-34, https://doi.org/10.1108/IJCST-07-2019-0107
12. Skyba M.Ye., Synyuk O.M., Zlotenko B.M.: Model of changing the stressed-deformed state of a polymer sheet during stretching, Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu No 1, 2019, pp. 83-89, https://doi.org/10.29202/nvngu/2019-1/4