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Deformation Characteristics of Leather for Shoe Upper, Filled with Natural Minerals

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Abstract: A promising direction in the tanning industry is the use of natural minerals as environmentally friendly technologically efficient materials that are able to adjust and regulate the efficiency of formation of the dermis structure and the properties of finished leather. The use of finely-dispersed minerals promotes alignment of topographic areas in thickness, increases the yield of leather on the area by avoiding bonding structural elements of the dermis. Changes in the microstructure of the dermis, as a result of mineral filling, contribute to improvement of performance and hygienic properties of finished leather. And the study of the properties of the specified skins should be consistent with the features of operations on their cutting, shoe molding and shoe upper fixing preparations. The most important properties of leather materials, which largely determine the quality of basic technological operations of shoe manufacturing are the deformation properties. Lack of information about relaxation and deformation properties of the leather produced by th e new technologies do not allow to predict their ability to form shapes and save it—indicates the relevance of this study. This paper analyzes relaxation and deformation characteristics of natural leather for shoe uppers, filled with natural minerals montmorillonite and zeolite, and the ability to predict their formation and preservation of shape in service. Features of deformation of the skin with mineral content were assessed by determining single-cycle characteristics when attaching to a complete test cycle "loading-unloading-rest" sample. Correlations of elastic and plastic (permanent) deformation have been established, kinetics of changes in linear characteristics of the samples after removal of the load has been investigated. Introduction of dispersions of mineral to the structure of the dermis contributes to the strength of semi-finished leather, increase of the uniformity of mechanical properties in the longitudinal and transverse directions and rise of shape stability index. It is shown that the direction of this study allows us to offer new competitive ecologically friendly materials to produce shoes.

Key words: Leather for shoe uppers, deformation, relaxation, shape stability, dispersion of mineral, modification.

1. Introduction

Increasing consumer demands for quality of shoes and high competition pose the problem of finding and application of new materials, resource-saving technologies, methods of improving the performance and aesthetic properties of products [1].

Expanding the range of natural leathers manufactured with the help of new technologies creates some prospects for making shoes with improved functional properties.

A promising direction in the tanning industry is the use of technologically efficient ecologically friendly materials based on naturally occurring minerals. There is a lot of information on the use of natural minerals as ion exchangers, sorbents, catalysts for solving environmental problems, wastewater treatment in the literature. This is due to their unlimited quantity, low cost, wide range of structural and sorption properties and ease of use. There is much less information about the use of naturally occurring mining industry as materials that can affect the efficiency of formation properties of the finished leather. In papers [2-6], the

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information is submitted about the modern methods of use of minerals for manufacture of leather that indicate the possibility of creating a high-performance structure of the dermis with predictable performance and hygienic parameters by complex selection of technologically efficient materials based on minerals.

In the papers [7-11], new ecologically friendly leather materials and modern advanced technology of re-tanning processes of leather production that provide the necessary performance properties of finished leather according to their purpose presented. Applied fine minerals of natural origin are able to adjust and regulate the efficiency of formation of the dermis structure and relevant performance properties. In addition, the use of finely-dispersed minerals for semi-finished leather promotes alignment of topographic areas in thickness, increases the yield of leather on the area by avoiding bonding structural elements of the dermis.

However, relaxation and deformation properties of new leather materials are not covered in these works which does not allow to predict their ability to form and retain shape. The study of properties of these skins should be linked to the peculiarities of the process of manufacturing shoes—cutting operations, shaping and fixing shoe uppers, which indicates the urgency of the study.

Deformation properties are the most important properties of leather materials, because they largely determine the quality of basic technological operations of shoes, which in its turn determines the convenience of the product and shape retention during operation. The magnitude and nature of the deformation of the uppers depends not only on the way of shaping, equipment and instruments used, but also on the physical and mechanical properties of materials.

The aim of this research is to establish and analyze relaxation and deformation characteristics of leather, filled with fine naturally occurring minerals during re-tanning processes and to predict their ability of shaping and shape stability.

2. Experiments

2.1 Objects of Research

Natural leather for shoe uppers, modified at the stage of liquid finishing with OMC (organic mineral compositions) has been studied. Instead of expensive synthetic polymer-mineral material “Tanikor FTG” of the firm “Clariant” (Germany) (3% by weight of sliced semi-finished product) modified dispersions of natural MDM (inerals-modified dispersions of montmorillonite) and MDZ (modified dispersions of zeolite) in quantities of 3% and 4% by weight of sliced semi-finished product respectively were used.

Modification of montmorillonite and zeolite was performed with sodium polyphosphate in the amount of 10% by weight of dry mineral. As a compared (control) sample natural leather for shoe uppers, obtained by the functioning technology of tannery JSC “Chinbar” (Kyiv) was used. All processes and operations that precede the process of filling and all subsequent ones were conducted in accordance with the current technology in production, and confirmed by corresponding acts of production testing and implementations.

2.2 Methods of Research

Features of deformation of the skin with mineral content were assessed by determining single-cycle characteristics when attaching to a complete test cycle “loading-unloading-rest” sample.

Identification of the components of strain of modified skins was performed according to the method of study relaxation phenomena with the help of relaxometer “Rack” with accuracy ± 0.1 mm, scheme is shown in Figs. 1 and 2 [12].

Tests were conducted in Analytical and Experimental Testing Laboratory in Institute of Leather Industry, Lodz (Poland). Three groups of samples were formed for research. Each group consisted of 10 samples of semi-finished products, of which 5 samples were cut (shaped) in a longitudinal direction relative to the back bone of hide and 5-to cross.

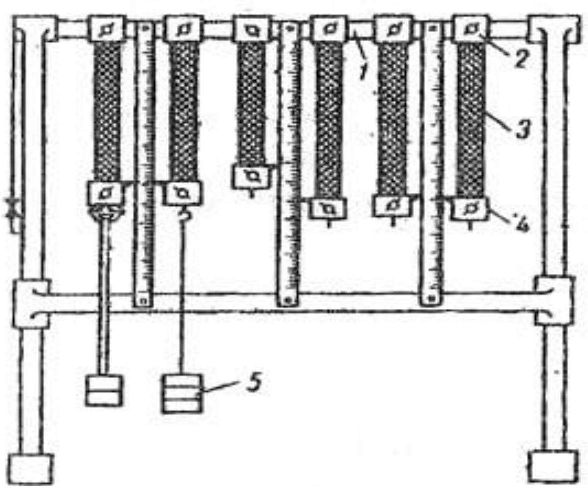

Fig. 1 Scheme of relaxometer type "rack" at constant load: 1—bracket for fixing clamps; 2, 4—clamps; 3—skin samples; 5—load.

To estimate the degree of anisotropy in the skin according to relaxation and deformation properties, uniformity coefficient $K_{unif.}$ of properties of leather in the area was determined—the ratio of the average values of relative elongations in a transverse direction relative to the backbone line, to the average value in the longitudinal direction by Eq. (1).

$$K_{\text{unif.}} = \frac{\varepsilon_{\text{transverse}}}{\varepsilon_{\text{longitudin al}}} \quad (1)$$

It is known that [1, 12], if the test material is mechanically stressed, the full strain caused by it ε_f at time t consists of three components:

$$\varepsilon_f = \varepsilon_{el} + \varepsilon_{fl} + \varepsilon_{pl} \quad (2)$$

where, ε_{el}—instantly caused elastic deformation, ε_{fl}—highly flexible, due to the relaxation process of rearrangement of the structural elements of the polymer, which leads to the appropriate tension of their new equilibrium position and ε_{pl}—plastic, which occurs in case when the structural elements are capable of unlimited displacement.

Calculations of one cycle characteristics of new ecologically friendly leather materials with mineral content were carried out according to methods presented in Ref. [9]. The width and thickness of the standard sample of skin for tensile were measured in five areas and according to mean data its average cross-sectional area was calculated. Cross-sectional area was multiplied on the voltage value of 10 MPa and received steady current load which is necessary to hang on the sample. With set screws relaxometer was installed by level and the samples were inserted so that the distance between the two clamps was L_0 = 50 mm. Then rated load was hung to the lower clamp. After 60 min, length of the sample between the clamps increased to L_1 and by Eq. (3), full (general) deformation was determined.

$$\varepsilon_f = \frac{L_1 - L_0}{L_0} \times 100\% \quad (3)$$

In 5 s, load was removed, sample length L_2 was measured and elastic deformation $\varepsilon_{elastic}$ was calculated using Eq. (4).

$$\varepsilon_{el} = \frac{L_1 - L_2}{L_0} \times 100\% \quad (4)$$

Then, the working length of the sample was measured in 2, 30, 60, 120, 1,440 and 20,160 min after removing the load from the lower clamp and measurements $L_{3(2)}$, $L_{3(30)}$, $L_{3(60)}$, $L_{3(120)}$, $L_{3(1,440)}$ and $L_{3(20,160)}$ were used to calculate the conditional relative flexible deformation $\varepsilon_{flexible}$, which manifests itself in 2 , 30, 60, 120, 1,440 and 20,160 min as follows:

$$\varepsilon_{fl} = \frac{L_2 - L_3}{L_0} \times 100\% \quad (5)$$

Conditional relative plastic deformation $\varepsilon_{plastic}$ was calculated by Eq. (6) in 2 h rest of the sample:

$$\varepsilon_{pl} = \frac{L_{3(120)} - L_0}{L_0} \times 100\% \quad (6)$$

E components of strain—a strain ratio to predict the ability of materials to shaping and form stability of products made of them, the sharotal deformation—were determined:

$$\Delta\varepsilon_{\text{el}} = \frac{\varepsilon_{\text{el}}}{\varepsilon_{\text{f}}} \quad (7)$$

$$\Delta\varepsilon_{\text{fl}} = \frac{\varepsilon_{\text{fl}}}{\varepsilon_{\text{f}}} \quad (8)$$

$$\Delta\varepsilon_{\text{pl}} = \frac{\varepsilon_{\text{pl}}}{\varepsilon_{\text{f}}} \quad (9)$$

Shape stability of skins modified with natural minerals was determined by Eq. (10):

$$S = \frac{L_{\text{permanent}}}{L_{\text{full}}} \times 100\% \quad (10)$$

The reliability of experimental results was measured by traditional methods of mathematical statistics. The standard deviation, the coefficient of variation and parameters that reflect the closeness of the research results—testing accuracy were determined [12].

3. Results and Discussion

Formation of upper is one of the most important phases of shoe production because its appearance and performashape retention nce depend on shape stability of shoes. In the process of forming it is necessary to create conditions that ensure: (1) providing shoe upper with shape and body size that match the shape and size of shoe last; (2) while wearing, given to a shoe in the production process [1].

In the process of shaping materials, undergo deformation that changes shape. With reticulate structure filled skins may exhibit different properties. They may be elastic or flexible (fully recover its original shape and size after removal of loads) and not elastic or plastic (keep the shape and size of shoes after removal of all or part of loads). Due to this materials take the form of shoe last (plastic properties) and keep it in the process of shoe wear (elastic properties).

3.1 Physical and Mechanical Properties of Semi-finished Leather with Mineral Filling

In work [13], a set of physical and mechanical, including deformation, properties of semi-finished leather with mineral filling was identified in the test for uniaxial tensile and bursting ball. It has been found that the physical and mechanical properties of skin are formed on macro level of collagen structure and depend on the type of mineral filler. Changes in the microstructure of the dermis as a result of mineral filling lead to increased strength, reduced elongation of the dermis and increase the coefficient of uniformity of mechanical properties in the longitudinal and transverse directions (Table 1).

In most cases, the nature of the deformation of the material is not determined by the deformation properties of the elements of its “fine” structure, but properties of “large” structure of bundles of skin fibers. In general, the mechanical relaxation phenomena are caused by moving and rotating of the structure elements, while there are mechanical and chemical transformations of macromolecules, destruction and the emergence of supramolecular structures. At the same time, there is a transition of the polymer from the original isotropic state to an anisotropic (approximate condition), or a change in an input indicative state.

3.2 Relaxation and Deformation Characteristics of Modified Skins

In terms of footwear manufacturing technology, elastic and plastic components of filled skins strain are of interest, as they are responsible for the softness, flexibility and elasticity.

The process of elongation of materials under the action of external forces and their reduction after unloading and relaxation (Fig. 2) occur as relaxation processes—processes of change of polymer bodies at the time that are caused by static equilibrium. Relaxation phenomena occur in any static disequilibrium caused by external actions.

The ability of the skin to the shaping and shape retention depends on its ability to stretch and balance of the elastic and plastic (permanent) deformation. The proportion of the components of strain, showing the relationship between strain relaxation processes that occur during stretching of the skin was determined. The magnitude of the components of deformation in the mode of loading and unloading are presented in Table 2.

The emergence of adsorption centers in the form of mineral dispersion particles with high sorption surface promotes deeper diffusion and more uniform

Table 1 Characteristics of the mechanical properties of semi-finished leather under uniaxial tension.

Semi-finished material, filled	Indicator							
	Breaking load (H)	Tensile strength at break (MPa)	Relative elongation (%)		Conditional modulus of elasticity (MPa)	Stiffness (H)	Hygroscopicit (%)	Water yielding capacity (%)
			At 10 MPa	At break				
MDM	487 $K_p = 0.91$	29 $K_p = 0.79$	22.3 $K_p = 0.87$	67.3 $K_p = 0.91$	34.4	468	10.25	8.24
MDZ	428 $K_p = 0.94$	27 $K_p = 0.78$	23.4 $K_p = 0.9$	65.6 $K_p = 0.95$	32.8	492	9.93	9.03
Tanikor FTG (control)	396 $K_p = 0.90$	26 $K_p = 0.77$	24.95 $K_p = 0.73$	65.3 $K_p = 0.90$	32.3	484	8.09	7.55

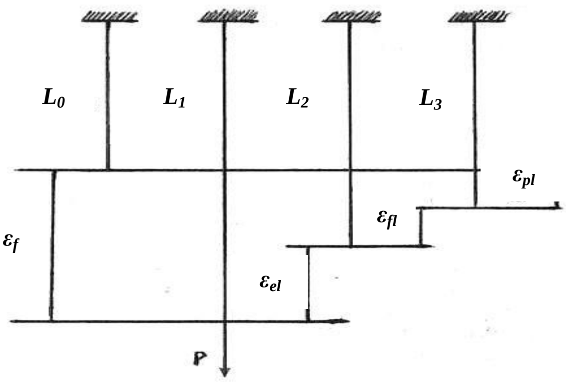

Fig. 2 The scheme of materials samples testing on relaxometer "Rack".

L_0—the initial length of the sample, mm; L_1—length of the working section of the sample at the final measuring under load, mm; L_2—length of working area immediately after unloading, mm; L_3—length of the sample after rest for a certain time, mm.

distribution of them in the structure of semi-finished leather, as evidenced by the increase in the coefficient of uniformity. Interacting with the functional groups of the dermis collagen modified dispersions of montmorillonite and zeolite contribute to its formation and the formation of spatial structures. Penetration of minerals nanoparticles into between fibrillar intervals reduces the ability of the collagen structure to bonding when semi-finished product is dried, promotes the ordering of the elements of the dermis structure and provides the formation of oriented macromolecules and supramolecular structures. So we believe that elastic-plastic properties of experimental skins are characterized by a pronounced deformation compared with unfilled skins.

Fig. 3 presents the chart of impact of the type of mineral filler on the value and size of semi-finished leather components of strain. As it can be seen from the chart, montmorillonite dispersion help to reduce the residual and increase elastic strain of semi-finished leather, and therefore increase the softness, flexibility of the skin. Although the magnitude of the residual strain decreases, the absolute value of the index at 5% provides sufficient shape stability.

When zeolite dispersions are used as a filler, an increase of particles and residual elastic strain is observed, indicating a high ability of skin to shaping and retaining shape during operation, elastic modulus reduced and hardness increased slightly. It can be positively used in the manufacture of footwear with high durable performance.

Curve of linear characteristics of modified skin samples after removal of the load over time (Fig. 4) and the rate of skins shape stability (Fig. 5) show a positive effect of the mineral content of semi-finished leather on the relaxation and deformation characteristics characteristics of the leather for shoe upper .

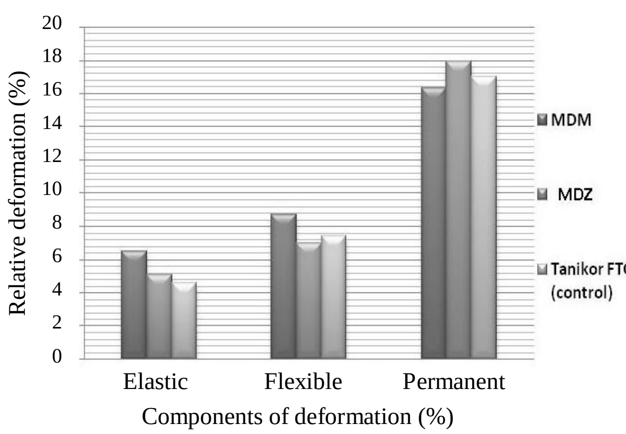

Fig. 3 The ratio of the components of leather deformations filled with variances of natural minerals.

Table 2 Relaxation and deformation characteristics of modified skins.

Filler	Full deformation ε_f (%)	Components of deformation (%)			Share parts of deformation			Plasticity, P (%)	Elasticity, E (%)
		ε_{el}	ε_{fl}	ε_{pl}	$\Delta\varepsilon_{el}$	$\Delta\varepsilon_{fl}$	$\Delta\varepsilon_{pl}$		
MDM	31.5	6.5	8.7	16.3	0.20	0.28	0.52	52	48
MDZ	30.0	5.1	7.0	17.9	0.16	0.24	0.60	60	40
Tanikor FTG (control)	29.0	4.6	7.4	17.0	0.17	0.26	0.57	57	43

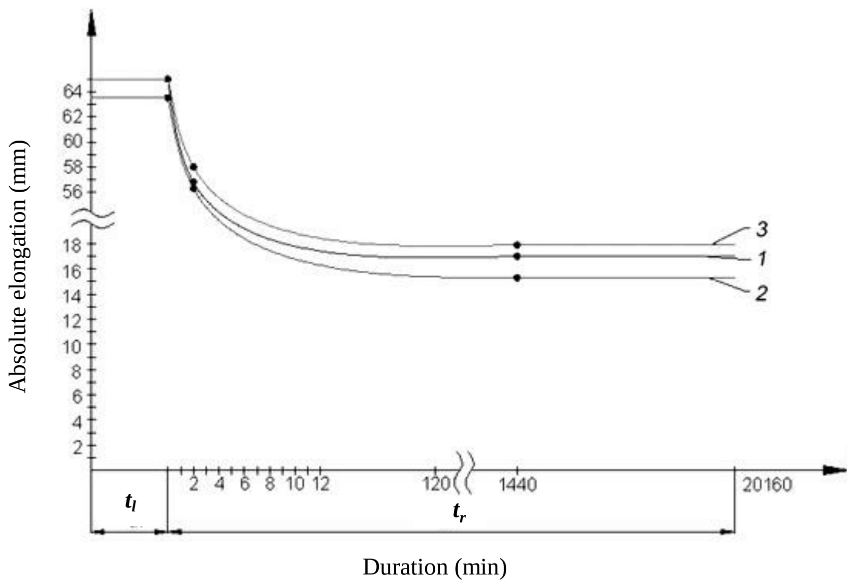

Fig. 4 The dependence of the deformation of tension of filled leather from the time under load (t_l) and at rest (t_r).
1—control, 2—MDM, 3—MDZ.

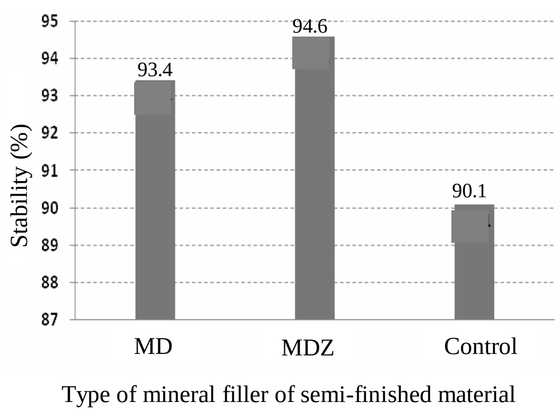

Fig. 5 The dependence of the shape stability of leather on the type of mineral filler.

4. Conclusions

Thus, as a result of the research:

(1) Relaxation and deformation characteristics of leather, filled with fine-naturally occurring minerals and their impact on the performance properties of finished leather have been analyzed;

(2) It has been found that the introduction of dispersions of montmorillonite and zeolite to the structure of the dermis improves the durability of semi-finished leather products, the growth rate uniformity of mechanical properties in the longitudinal and transverse directions and higher rate of shape stability;

(3) Some particle components of deformations that show the relationship between the relaxation processes occurring during the stretching of the skin in full testing cycle "loading-unloading-rest" have been identified;

(4) The results of research can offer new competitive materials for the production of leather shoes for special purpose.

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