Встановлено склад наповнювально-пластифікаційних композицій, що включають таніди, білковий гідролізат, монтморилоніт, диспергатор і пластифікатор для формування шкіряних матеріалів. Розроблені технології наповнювання-пластифікації напівфабрикату хромового дублення з шкур овчини і великої рогатої худоби з використанням нових хімічних матеріалів забезпечують ефективну витрату шкіряної сировини у виробництві еластичних шкір для верху взуття, одягових і галантерейних виробів

Ключові слова: шкіряний напівфабрикат, наповнювально-пластифікаційні процеси, таніди, монтморилоніт, технології, фізико-хімічні властивості, мікроструктура

Установлен состав наполнительно-пластификационных композиций, включающих танниды, белковый гидролизат, монтмориллонит, диспергатор и пластификатор для формирования кожевенных материалов. Разработанные технологии наполнения-пластификации полуфабриката хромового дубления со шкур овец и крупного рогатого скота с использованием новых химических материалов обеспечивают эффективный расход кожевенного сырья в производстве эластичных кож для верха обуви, одёжных и галантерейных изделий

Ключевые слова: кожевенный полуфабрикат, наполнительно-пластификационные процессы, танниды, монтмориллонит, технологии, физико-химические свойства, микроструктура

UDC 675.024.9 + 678.046
DOI: 10.15587/1729-4061.2015.65488

IMPROVEMENT OF THE FILLING AND PLASTICIZATION PROCESSES OF FORMING MULTIFUNCTIONAL LEATHER MATERIALS

A. Danylkovych
Doctor of Technical Sciences, Professor*
E-mail: ag101@ukr.net
O. Mokrousova
Doctor of Technical Sciences, Professor, Head of Department*
E-mail: mokrousovaolena@mail.ru
A. Zhygotsky
Candidate of Chemistry Sciences, Senior Research Scientist
Institute of Materials Science Problems named after Frantsevich NAS
Krzyzanowski str., 3, Kyiv, Ukraine, 03142
E-mail: chekhovs@ipms.kiev.ua
*Department of biotechnology, leather and fur
Kyiv National University of Technologies and Design
Nemirovich-Danchenko str., 2, Kyiv, Ukraine, 01011

1. Introduction

Improvement of the existing and development of new technologies of forming multifunctional leather materials especially focuses on the final physicochemical processes – filling and plasticizing of the intermediate product. This is basically caused by completion of the chemical composition changes, the structure compaction, reduction in the moisture content due to its replacement with filler particles and plasticization reagents, levelling the physical and mechanical, sanitary and other performance properties throughout the area of the formed material. The efficiency of these processes is much affected by the conditions of their implementation, the chemical composition of the used reagents, colloid and chemical properties of the latter, and the structural state of the intermediate product that was achieved at the previous stages of treatment.

A scientifically reasonable choice of fillers and plasticizers for further formation of the already structured intermediate products considers that some fillers impregnate, first of all, in relatively large pores, whereas plasticizing requires that some significantly smaller reagents should reach intermicrofibrous and intermolecular spaces that are 2.74 nm and 0.6–0.8 nm in size, respectively [1, 2]. Formation of multifunctional leather materials predetermines, to a large extent, significantly different contents of fillers and plasticizers [1, 3]. Hence, there has been intensive research on developing new chemical reagents to improve the filling and plasticizing technologies of producing leather materials.

2. Analysis of the previous findings and statement of the problem

In the final stages, leather materials of complex hierarchical structures of the dermis collagen are formed with the help of quite a wide range of natural and synthetic reagents. In particular, new technologies of leather manufacturing sometimes apply acrylic polymers and compositions based on them [3–5]. Filling and finishing of a semifinished leather product is combined with its plasticizing, which is called fattening in the relevant technological literature. The use of aqueous dispersions of hydrophilic polyacrylates allows increasing the density, strength and elasticity of leather material as a result of additional structuring of intermediate products. An optimal chemical composition of the copolymer with a flow rate of 2–4 wt % significantly increases the split leather thickness and significantly reduces its unevenness throughout topographic areas [4]. The previous findings [5] show how copolymers that are synthesized from acrylic acid and monomers of various chemical compositions affect the elastic and plastic properties of the filled leather material. It has been found that the use of copolymers, such as ethyl acrylate and butyl acrylate, makes the obtained leather materials more elastic. Water emulsions of copolymers of butyl acrylate and styrene with various-sized particles provide forming leather materials with higher thermal stability as well as improved durability and elasticity [6]. At the same time, the waste water of the enterprise becomes less contaminated.

The processes of filling and finishing the products that are chrome-tanned with Polynex acrylic copolymers of various chemical compositions [7] at a loss of 4.0–5.0 % allow obtaining elastic leather with a dense structure of its finished elements, which facilitates the processing of a fleece surface of a semifinished product when it is polished. The authors recommend using a specific copolymer composition at the stage of filling the semifinished leather for shoes as well as apparel and haberdashery various-thickness leather materials. Acrylic polymer emulsions used as a filling and finishing reagent in the synthesized aminofurazan formaldehyde resin that is modified with the help of isopropyl alcohol allows obtaining leather materials with a drying shrinkage decreased by 1.5–4.0 % [8]. In addition to filling and finishing capacities, the reagent increases the hydrophobicity of semifinished leathers [9]. This effect appears obvious in vegetable and synthetic tanning of hides, for instance in saddler leather materials. It is necessary to note that dimethylformamide resin used as a solvent reduces the hydrothermal stability of chrome-tanned semifinished products and bleaches them. Unlike the modified aminofurazan formaldehyde resin, sulphated melamine formaldehyde oligomers [10] that are used in finishing the chrome-tanned intermediate products enhance their fullness and elasticity and intensify the colour. However, after the finishing, the hides contain up to 10 mg/kg of free formaldehyde.

Studies [11–14] raise an important problem of forming leather material from low-grade raw materials. The authors synthesized sulfoaromatic polymers by means of polycondensation of sulfonated resorcinol as well as a phenol-urea-formaldehyde resin with the aqueous dispersion particle size of 0.7–1.4 mkm at pH 6.0–6.7, which ensures its high diffusibility in the structure of the chrome-tanned intermediate product obtained from hides of medium-size heifers. Despite the increase in the size of copolymer particles in the structure of semifinished leathers to 3.0–3.4 mkm, the formed leather material has higher density and elasticity in comparison with the leather produced with the use of the Ecofix industrial preparation. Application of the designed copolymer can increase the degree of filling as well as elastic and plastic characteristics of the material.

Filling of the semifinished leather product can be efficient with the use of a set of materials the chemical composition of which has optimal colloidal chemical properties. In particular, one study [15] proves that finished leather materials show an improved sustainability to rubbing, better strength and flexibility, as well as a lower shrinkage at trimming with the use of compositions based on nitrogen-containing hydrophilic polymers and acrylic emulsion A.

Scientifically and technologically valuable are studies of the effect of vegetable oil-based polymeric (VOBP) fillers on the formation and properties of leather materials. Thus, still another study [16] synthesizes tanning agents on the basis of acrylamide (AA) and glycidyl methacrylate (GM) used in conjunction with lignosulfonates (LS), a quebracho extract (QE), and chitosan. The degrees of flexibility in the obtained leather materials allow arranging the VOBP fillers in their 5 % consumption in the following sequence: QE>AA-chitosan>GM-LS>AA-LS>AA-QE. Synthesized tanning agents show better results by the criterion of increased thickness: QE>QE-AA>AA-LS. This effect is less pronounced in the case of VOBP tanning agents AA-QE and AA-LS, which is caused by blocking a part of active groups in their molecules, a bigger molecular weight, and a bigger particle size in comparison with a quebracho extract. However, since VOBP fillers GM-LS have reactive functional groups in their molecules, they ensure high physical and mechanical properties in leather materials due to additional structuring of the dermis collagen. Compatibility of aqueous styrene-acrylic dispersions and hydroxyethyl cellulose allowed developing the filler compositions with vegetable tannins [17]. With a use of 8 % of composite reagents, the derived leather materials have better elastic, plastic and durable characteristics.

Filling a semifinished leather with a hydrolyzed protein, glutaraldehyde and vegetable tannins allows deriving high quality leather [18], reducing the production waste and its impact on the environment. A milk-origin whey containing 2.5–5.0 % of proteins alongside gelatin in a ratio of 10:1 [19] can be used in filling semifinished leather for footwear uppers and upholstery where it enhances the physical and mechanical properties of the finished material that has an enhanced colorability.

Hide processing technologies should combine individual technological processes, such as filling-fattening-dyeing, in one operating system by gradually introducing certain chemicals or their compositions. Technical studies view fattening materials as compositions comprising natural and synthetic reagents for deriving leather with high elastic characteristics [20]. In particular, specialists of the TFL company have developed a lecithin-based anionic composition that is characterized by high stability as well as light and heat resistance. The researchers have also synthesized a plasticizing composition based on palm oil. The latter was amidated by means of diethanolamine in the presence of sodium methoxide, which was followed by its modification with silicone oil whose molecules contain terminal hydroxyl groups. It was followed by esterification with the help of maleic anhydride and further sodium bisulfite treatment. The derived plactisizer was used to form a highly elastic leather material.

The combined process of filling-fattening the semifinished material uses a composition, wt %, of stabilized acrylic copolymers – 5, a quebracho extract – 3, a fattening emulsion based on natural and synthetic fats and oils – 8, and addition of a complex-forming emulsifier [21, 22]. Leather obtained in optimum conditions is characterized by a full structure, greater thickness uniformity and the necessary range of performance properties. This decreases the “friable skin” effect to 50 % and reduces the consumption of vegetable and synthetic tanning agents.

The researchers [23, 24] recommend using a phospholipid-based liposome composition with added hydrophobic and hydrophilic reagents in filling leather materials. Researchers have proved a significant impact of target additives – vaseline, castor, linseed, and hemp oils – both on the filling-plasticizing process and the properties of the resulting materials. In particular, the use of vaseline oil ensures hydrophobic properties in the leather, hemp oil – hydrophilic properties with a high vapor capacity, and flaxseed oil allows obtaining a flexible leather with a high vapor permeability. In addition, the use of special liposome fillers with antibacterial properties – essential oils of Monarda fistulosa, tea tree, Tagetes, polyhexamethylene guanidine and others – allows deriving leather with a high resistance to destructive biological effects. The significantly smaller particles that those in the known fattening compositions have a higher diffusion capacity and, therefore, a higher plasticizing effect, which contributes to the strength and elongation at low loads that match the deformation requirements to the material during its performance. The possibility of intensifying the filling-fattening technology by means of the combination of processes and saving chemical materials and energy deserves special attention.

According to the publication [25], members of the Lanxess concern have designed new polymer materials using polyamide-carboxylic acid in filling-fattening different types of leather that are recommended in the production technologies of footwear, apparel, leather goods, furniture, and automotive leather. The advantages of this polymer compared with natural fattening reagents include its heat and light resistance, high colour intensity and resistance to the fogging effect to which leather materials are vulnerable.

The authors of another study [26] show that when a semifinished leather is soaked with dispersions of polymaleinate and polyacrylates of different molecular weights and the particle size is increased from 17 to 562 nm, the porosity and the vapor permeability of the nontreated chrome-tanned bovine leather for footwear uppers decrease when a polymer is injected at the beginning of the process. If polymers are used at the stage of the dyeing completion, the above characteristics slightly increase, and the hygienic properties of such leather materials also rise according to a complex of criteria. Thus, the lining leather of an equine origin has a comprehensive assessment of 98.5 %, and the insole leather of a bovine origin – 46.8 % when the standard natural non-dyed lining leather is of a porcine origin.

Therefore, the analysis of technological studies shows that in most cases synthetic reagents or compositions are recommended as fillers and plasticizers in the formation of leather materials. Regarding the higher environmental requirements for manufacturing processes, the necessity to save energy, improve the quality of leather materials and reduce their cost there should be further research in the development of new efficient filling-plasticizing compositions based on primarily natural reagents for the combined technological processes and obtaining high-quality multifunctional leather materials.

3. The purpose and objectives of the study

The aim of this work is to study the processes of filling and plasticizing at the final stages of manufacturing leather with various ratios of papillary and reticular dermis layers and the use of organic-mineral compositions. To achieve the objective, we have researched the following:

– the technological efficiency of the filling-plasticizing compositions;

– the impact of a filling-plasticizing composition content of physical and chemical properties of semifinished leather;

– the effect of a highly dispersive aluminosilicate on the volume and elastic properties of the resulting leather;

– the structural features of a leather material during its formation.

4. Materials and methods of the study

According to the research objective, the study uses an intermediate 0.9–1.6 mm thick product of chrome tanning made of wet-salted raw material of bovine origin and 1.1–1.2 mm thick sheepskin obtained by a method of producing leathers for footwear uppers. Before the filling and plasticizing processes, raw hides were subjected to a number of technological treatments such as: recovering the hydrophilic state of the dermis structure after its preservation; removing hair and epidermis; dividing the fibrous macrostructure through alkaline processing and simultaneous removal of non-fibrous components; and acid-salt processing followed by chemical structuring with chemical compounds of chromium (III).

In the combined process of filling and plasticizing, the developed technology of forming elastic leathers for footwear uppers involved both natural and synthetic materials. In particular, it included plant tannins of mimosa as an acid hydrolysis product of secondary resources for manufacturing intermediate products of chrome tanning (edge cut and trim): a protein hydrolysate [27, 28] with 41.3 % of solids, with density of 1.21 g/cm^3, a pH of 6.5–7.0, and the molecular weight of collagen destruction products in the amount of (12–14)·10^3. The dynamics of protein oligomers were found to depend on presence of imino acids, hydroxyl amino acids as well as carboxyl and hydroxyl functional groups [29].

The mineral filler that we used is the natural highly dispersive powder of montmorillonite from the Dashukivsk deposit (Cherkasy Oblast, Ukraine); it has the general formula $Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot nH_2O$, modified with sodium concentration of 100 g/l at a flow rate of 10 % of its weight (MAW). The exchange interaction involving sodium cations creates favorable conditions for dispersing montmorillonite aggregates and obtaining a filler of 0.9–1.0 nm in size [30]. Tannins are synthetically dispersed with a condensation product of 2-naphtholsulfonic acid and dioxide phenyl sulfone and a Beta-naphthalene sulfonate formaldehyde condensate (BNS).

The process of filling and plasticizing consists in processing the sliced semifinished product with composite materials of an appropriate chemical structure after its neutralization [3]. Tannins' diffusion and their mixture with the BNS as the modifier in the structure of the intermediate chrome-tanned product were studied at the cuts for determining the filler's diffusion depth by a microscopy method during one hour of processing a 1.6 mm-thick semifinished product. The effect of filling and plasticizing compositions on the formation of leather material was determined by physical, chemical and technological properties of the finished leather by the relevant methods [31]. The substances that are typically extracted with organic solvents (OS) were determined by applying a mixture of 4-hydrocarbon chloride and trichloroethylene in the ratio of 1:1. The contents of the components in the leather material are counted as per absolutely dry substance.

The mechanical properties of the obtained material were studied with the help of a tensile machine of the PT-250M brand at a speed of 90 mm/min^{-1} of the lower clamp. The leather stiffness was studied with the PZhU-12M device. The material thickness was determined by the micrometer TR 25-100 with the point value of 10 microns. The leather output area was measured on an electronic machine of the model 07484/P1 produced by Svit (Czech Republic) after drying and moisturizing processes and operations. The control measure was the material output produced by using the industrial technology.

The microscopy research was performed with the raster scanning microscope REMMA-102 made by Selmi (Ukraine). Leather samples were derived from an intermediate product after its alcohol-ether dehydration. To eliminate electrical charges, the surface of each sample was sprayed with silver film 3–5 nm thick. The depth of the electron beam in scanning the area of a sample according to the method [32] was 3 microns.

5. The effect of organic and mineral compositions on the physicochemical properties of leather material

When studying the filling and plasticizing process in the technology of manufacturing leather materials, it is essential to consider the peculiarities of interaction between reagents and elements of chemically structured dermal collagen at macrofibrous and microfibrous levels. The effectiveness of replacing traditional and scarce fillers with newly developed reagents is determined by a specific mechanism of their dynamics in these processes. The results of studying the influence of the mimosa-BNS composition on the formation of chrome tanning properties of raw bovine hides are shown in Fig. 1 and Table 1.

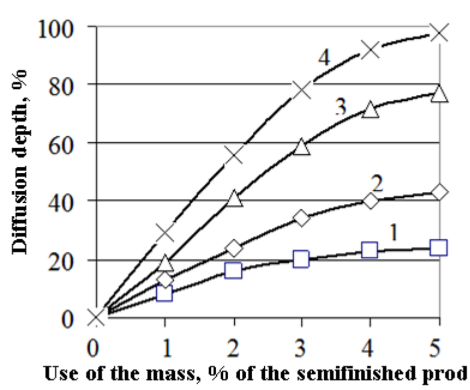

Fig. 1. Dependence of the diffusion depth of the modifier (1 and 3 — mimosa; 2 and 4 — mimosa/BNS) in the ratio of 1:1 in chrome tanning of the intermediate product mass in the following sections: 1 and 2 – saddlecloths; 3 and 4 – skirts

The results of the mimosa and BNS diffusion of tannins in the intermediate product of chrome tanning (Fig. 1) show an acceleration of the filling process if mimosa and BNS are used together. This effect was observed both in loose and dense areas of the samples. The depth of diffusion of reagents in loose areas was close to 100 % with a 5 % use of the mass of the intermediate product; in dense areas even with a bigger use of the mass, it was only 80 % of the thickness of the intermediate product.

At the same time, we observed an increase of the filler content in the dermis of the semifinished product of mineral tanning (Table 1), which facilitates further formation of its structure. The number of organic substances that are extracted by solvents increases alongside the filler content in the structure of the intermediate product. The deformation characteristics of the intermediate product increase, too.

Table 1

Physicochemical properties of the semifinished product of chrome tanning, filled with a complex tanner

Exponent	Semi-finished product of chrome tanning	Mimosa, % of the mass of the semifinished product of chrome tanning	The ratio of mimosa : BNS, % of the mass ofthe semifinished product of chrome tanning		
			1:1		1:2
		1.2	2.4	3.5	3.6
Mass fraction, %, of					
– protein substance	82.2	78.8	74.4	71.7	71.1
– chromium compounds, % Cr_2O_3	3.6/5.6	3.5/5.3	3.3/4.9	3.0/4.2	2.8/4.0
– minerals	5.4/6.9	5.3/6.7	4.9/6.3	4.6/5.7	4.4/5.3
– extracted organic substances	5.6/9.4	6.1/9.9	6.7/10.4	6.9/11.2	7.6/11.8
– organic water-washed substances	0.94	0.81	1.23	1.5	1.38
– tanning composition (filler)	–	3.72	7.51	9.82	10.4
Tensile strength of leather, MPa	18.6	18.1	18.2	17.0	18.3
– front layer	17.4	17.1	15.4	15.7	17.4
Stretch, %, at 9.8 MPa	38.0	34.0	38.0	36.0	29.0
– at the breaking point	63.0	59.0	65.0	60.0	56.0

Note: the data before and after the forward slash correspond to the values of the middle and outer layers

Taking into account the chemical similarity between protein-hydrolyzed and collagen-based semifinished product of chrome tanning, it is expedient to use protein filler while forming the product's structure and properties in the process of filling and plasticizing. Table 2 shows that an increase of the protein hydrolysate content reduces the porosity of the intermediate product and its post-dehydration shrinkage while increasing its thickness.

The ratio variation in the reduction of the area and volume of the intermediate product shows a bigger loss of the leather material area when the content of protein hydrolysate increases. Thus, the filling impact of protein hydrolysate in forming an intermediate leather product is effectively evident when we compare the properties of the material that has been obtained by the developed technique and industrial technology of JSC VOZKO (Ukraine). It should be noted that the use of protein hydrolysate in the composition with BNS-modified tannins reduces the stiffness of the finished leather.

Table 2

Physicochemical properties of the semifinished product of chrome tanning filled with a composition of tannin and protein hydrolysate

Exponent	Filling option			
	Experimental 1	Experimental 2	Industrial technology	Without filling
Use of materials, %, water	150	150	150	–
Protein hydrolysate	2	4	–	–
Mimosa	1	1	3	–
BNS	3	1	3	–
Content of chromium compounds, % Cr_2O_3	5.2	5.4	4.4	4.7
Thickness, mm, saddlecloth/skirt	1.23/1.19	1.29/1.26	1.18/1.07	0.91 / 0.86
Shrinkage of the area/volume, %	5.2/11.0	5.9/10.0	8.2/17.0	13.0 / 28.0
Tensile strength of leather, MPa	19.0	21.0	17.0	14.0
– front layer	17.0	19.0	14.0	13.0
Stretch at 9.8 MPa, %	48.0	45.0	43.0	39.0
Porosity of peripheral sections, %	57.0	55.0	59.0	62.0
Stiffness, SN	21.0	25.0	39.0	28.0

Note: the materials are proportioned to the mass of the intermediate product

More efficient filling of the loose structure of semifinished sheepskin can be observed with an additional use of a highly dispersed montmorillonite at a higher content of chemical reagents. The research findings are presented in Table 3.

Table 3

Physicochemical properties of sheepskin filled with a composition of protein hydrolysate and montmorillonite

Exponent	Use of MDM, %			Industrial technology	Without filling
	1	2	4		
Use of materials, %, water	100	100	100	150	–
Protein hydrolysate	4	4	4	–	–
Mimosa	2	2	2	3	–
BNS	2	2	2	5	–
Thickness, mm	1.23	1.28	1.21	1.17	1.03
Mass fraction, %, minerals	8.7	9.8	10.2	7.9	7.3
– chromium compounds, % Cr_2O_3	4.3	4.3	4.6	4.5	4.9
– extracted organic substances	8.7	8.5	8.1	8.3	7.8
Tensile strength, MPa	14.7	15.3	15.8	13.6	14.0
Stretch, %, at 9.8 MPa	33.8	31.5	32.3	32.0	29.0
– at the breaking point	68.6	72.0	69.4	66.7	63.0
Stiffness, SN	16.0	15.3	15.7	21.5	25.0
Porosity, %	66.3	69.5	67.8	65.4	64.0
Volume output, cm^3/100 g	285	309	296	272	253
Leather output, %, by thickness	102.6	103.9	104.8	100	83.0
– by area	104.3	106.8	105.9	100	86.0

The data show that if the content of montmorillonite increases while the content of protein hydrolysate remains the same, the filling composition results in an extreme change in the physicochemical properties of the semifinished leather product. In this case, the structural and physicomechanical characteristics prevail over the properties of the intermediate leather product that is obtained by the industrial technology of filling sheepskin which is practiced at the public JSC Chinbar (Kyiv, Ukraine). This especially concerns leather porosity and output area. Thus, the technology of using a composition of protein hydrolysate and montmorillonite can be expedient in manufacturing multifunctional leathers.

It is necessary to control interaction between an anion-genetically modified montmorillonite and an intermediate chrome-tanned leather product under intense filling of the product's structure, especially in the papillary layer, on the basis of a preliminary plasticization of the dermis structure. To form elastic leather, the filling and plasticizing processes for footwear uppers are carried out according to the chart presented in Table 4. If the filling process is effective, there can be a lesser interaction between the filling materials and the collagen-based intermediate chrome-tanned product if the process involves use of an alkenyl-carboxylic acid ester addition (ACAEA), which was synthesized by the interaction of monoethanolamine and synthetic fatty acids of the fraction S_{7-9} [33] with a modified dispersion of montmorillonite.

Table 4

The chart of the filling and plasticizing process to form an intermediate leather product

Filling	Fixation processing 1	Plasticization	Fixation processing 2
Reagent – use, % of the intermediate product mass / processing duration, in min.			
Water – 100 Acrylic polymer Targotan 2MB – 1.2/40 ACAEA – 1.0/20 BNS – 4.0/60 Mimosa – 2.0/30 MDM – 4.0/40	Sodium – 0.4+ + potassium aluminum sulfate – 2.5/30	Water – 100 Fattening composition – 6.0 + + ammonia 0.3/60	Formic acid – 1.0/10

Note: after fixation processing procedures 1 and 2, 150 % of water is used to wash the intermediate leather product at temperatures of 54–56 °C and 23–25 °C for 15 minutes and 10 minutes, respectively

Rational use of bovine hides can be achieved by increasing the content of a highly dispersive mineral. ACAEA was involved to optimize the dispersing effect on the dermis structure. An effect similar to the process of filling a semifinished sheepskin product was achieved for bovine hides by increasing the use of montmorillonite, which affected the properties of the intermediate product for leather used in footwear uppers (Table 5).

Processing of the intermediate leather product with ACAEA increases the use of the mineral filler to 4 %. This helps achieve the maximum values of volume and area outputs of the finished leather by the respective 31 cm^3/100 g of the protein substance and by 5.7 % compared to leathers that are obtained by the industrial technology of the public JSC Chinbar (Kyiv, Ukraine), which is a technology that does not involve the use of the ACAEA dispersant and modified montmorillonite.

Table 5

Physicochemical properties of leather for footwear uppers

Exponent	Use of MDM, %				Industrial technology
	1	2	4	6	
Mass fraction, %, of minerals	8.7	9.3	10.1	11.3	7.7
– chromium compounds, % Cr_2O_3	4.3	4.3	4.4	4.3	4.2
– protein substance	75.9	73.4	72.7	71.5	76.8
– extracted organic substances	8.7	8.6	8.6	8.6	8.8
Tensile strength, MPa	20.3	21.7	22.0	20.1	23.0
Stretch, %, at 9.8 MPa	34.6	33.0	31.7	32.4	30.0
– at the breaking point	57.0	54.0	53.0	55.0	59.0
Stiffness, SN	23.0	21.8	21.0	22.5	25.0
Porosity, %	55.3	56.8	57.7	56.4	54.0
Volume output, cm^3/100 g	255.0	268.0	276.0	264.0	245.0
Leather output, %, by thickness	102.3	103.6	104.5	104.2	100.0
– by area	102.8	104.9	105.7	104.6	100.0

The results of the microscopy studying of leathers for footwear uppers made of bovine hides according to the technology that we have developed are listed in Fig. 2. The electron microscopy images (Fig. 2, *a*, *b*) show that the front surface of the leathers that were obtained by the developed technology of using montmorillonite differs from those of the samples that were obtained by the industrial technology and reveals depth and consistency of the filler distribution. This may indicate obtaining leather with a denser papillary layer.

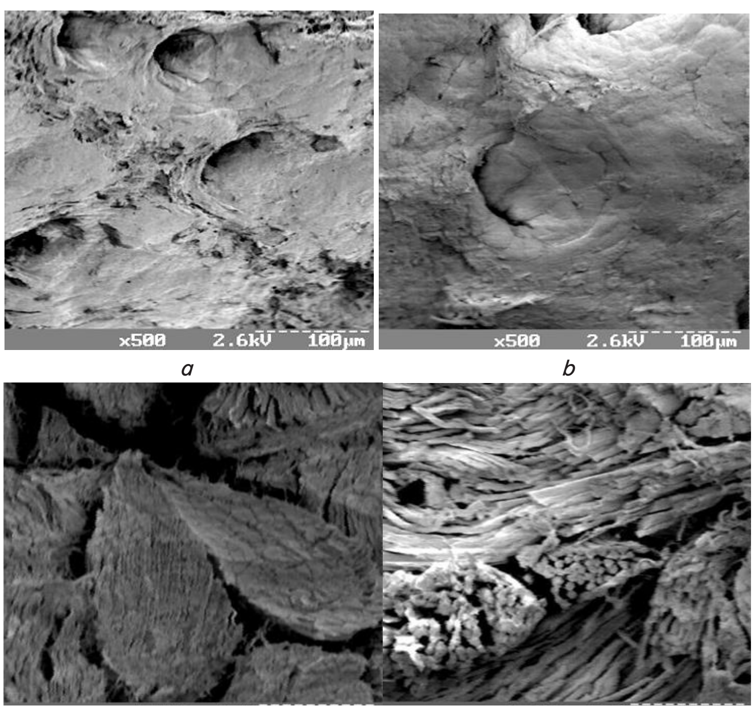

Fig. 2. Electronic microscopy images of the front surface of leather (*a* and *b*) and its cross-section (*c* and *d*): filled without a mineral filler (*a* and *c*) and with montmorillonite (*b* and *d*)

The electronic microscopy images of the internal structure of the dermis in the intermediate leather product without the mineral filler (Fig. 2, *c*) display a dense packing of collagen fibers in bundles, and the cross-bundle intervals are slightly larger than in the samples that were obtained while using montmorillonite (Fig. 2, *d*). In this case, there is some qualitative division of collagen bundles into individual fibers, which indicates uniformity of their distribution throughout the depth of the leather. Thus, the results of the structural research prove a correlation between the obtained data and the properties of the leathers that were formed by the developed technology.

6. Physicochemical characteristics of filling and plasticizing processing of leather materials

An intermediate leather product requires filling with a relevant content in order to form multifunctional leather materials out of various hides that differ by the ratio of the papillary and reticular layers of the dermis as well as by the packing density of fibrillar elements across topographical areas [34, 35]. It is necessary to consider the purpose of the raw materials and the semifinished chrome-tanned product as well as the colloidal and chemical properties of the filler. A leather material with high elastic-plastic properties can be formed by means of dispersing the fibrillar structure of the dermis collagen, which is primarily achievable through using fattening and highly dispersive reagents of high diffusion capacity. Effective filling of a semifinished leather product should also primarily ensure formation of a dense front surface of the leather material, and it should equally distribute the physicochemical properties of the semifinished leather product throughout all topographical areas. The first stage of the process should ensure minimum interaction between tannin particles and dermis collagen so that they could be effectively diffused in the intermediate product structure. This process is implemented at a pH of 5.6–5.8 of the working solution; if the pH is higher, there is an increased interaction between tannin particles and dermis collagen, which leads to concentration of tannins on the surface of the intermediate product. The optimal temperature condition for the process corresponds to 40–45 °C. Higher temperatures reduce the strength of the front layer of the semifinished product due to fixation of tannins in the papillary layer of the dermis, which causes its cracking. Besides, the surface layer of the intermediate leather product gets separated from the reticular layer. This effect is particularly evident in the filling of loose sheepskin.

The second stage of the process is to ensure efficient fixation of tannins in the fibrillar structure; the pH of the technological solution decreases to 4.2. It facilitates interaction between the filling reagents and collagen in the semifinished chrome- tanned product as a result of ionization of amino groups of dermis collagen and tannin molecules.

The process of plasticizing is performed at a temperature of 50–55 °C to increase the mobility of the structural elements as a result of an even distribution of fattening components in the filling and plasticizing composition of the semifinished chrome-tanned product. To maintain the strength of the collagen fibrillar structure of the intermediate product and to ensure the necessary technological characteristics of the plasticizer, the process temperature should be in the range of 50–55 °C. This allows creating a highly elastic leather material of a dense structure at a pH of 7.5–7.8. The fattening particles are destroyed and fixed in the intermediate product structure if the filling and plasticizing process of forming multifunctional leather materials finishes at a pH of 4.0–4.2.

Given the high aggregative capability of tannins, their effective diffusion can be achieved through using 2-naphtholsulfonic acid and dioxide phenyl sulfone as well as modifying the surface of the tannin particles and their dispersion. If the uneven distribution of tannins in the product's layers is reduced, it makes the leather material more elastic, and if tannins are distributed evenly, it increases the rational use of raw leather materials.

A wide range of connections between functional groups of collagen [29] and fewer micropores are possible when the filling composition is supplemented with a reactive oligomeric protein hydrolysate of a chemical nature that is similar to the dermis collagen of the semifinished chrome-tanned product. Increased dispersion and stabilization of the fibrillar structure of dermis collagen result in formation of a dense leather material of high elasticity.

The technological composition was supplemented in the study with a highly dispersive hydrophilic and previously modified montmorillonite in order to form a dense front surface of the intermediate leather product derived from raw sheepskin with deep roots of hair (down to 70 % of the derma thickness). The surface of the aluminosilicate particles was modified to improve the dispersion degree and the diffusion capability. A high degree of absorption of the filling and plasticizing composition depends on how effectively the dispersed particles of montmorillonite influence the processes of screening and dispersion in the dermis structure and how deep their diffusion is in the cross-microfibrillar area. However, an increased content of montmorillonite in the composition reduces the dispersing effect of montmorillonite particles on the dermis structure because the speed of diffusion of anion-genic particles is decreased as a result of a substantial increase in the number of connections between the montmorillonite particles and the positively charged structural elements of the dermis collagen at the beginning of their interaction.

High dispersion and diffusion abilities of the MDM particles in the filling and plasticizing composition help develop elastic leather materials of large volume and area outputs. Preliminary plasticization of the intermediate product of chrome tanning is necessary to ensure an effective degree of filling the structure of a bovine hide, which has a denser packing of collagen fibers bundles, especially in the saddlecloth, compared to sheepskin. If ACAEA is used, the high surface activity of its molecules produces an effect of diffusing the components of the technological composition, especially at the initial stage of the process, which helps achieve a higher degree of dispersing the fibrillar collagen structure and distribute the density of the material throughout all topographical areas. These effects ensure formation of elastic materials for leather uppers with a higher output in terms of thickness and area.

Thus, the laboratory and semi-production research concerned the processes of forming leather materials through using protein hydrolysates and modified montmorillonite. We have determined the technological regimes and composition contents and consequently developed a filling and plasticizing technology of manufacturing multifunctional leather materials from a semifinished chrome-tanned product.

7. Conclusion

The study concerned the processes of a filling and plasticizing technology in manufacturing leathers from raw hides of cattle and sheep origins to create multifunctional products through using new chemical materials. We have determined how to accelerate the process of filling, especially in the loose topographical areas of semifinished chrome-tanned products, by using tannin dispersants of various chemical structures.

An acid hydrolysis product used in the cross-sections of chrome-tanned hides replaces 66 % of natural tannins and synthetic dispersants in the process of filling an intermediate leather material and produces elastic leathers of high-quality peripheral areas of a homogeneous and stable structure. We have obtained an increase of the intermediate product's output area by 2.1–3.0 % in comparison with the industrial technology. The technology of filling and plasticizing semifinished chrome-tanned sheepskin was developed through using a hydrolysis product at the edges of the chrome-tanned material and a modified montmorillonite, which can produce more elastic leather materials for apparel and haberdashery articles as well as increase the efficiency of using raw materials in comparison with the industrial technology.

The undertaken study of the process of filling and plasticizing the semifinished chrome-tanned product involved a modified montmorillonite and an alkenyl-carboxylic acid ester addition, which has helped improve the technology of manufacturing elastic leathers for footwear uppers with the necessary set of physical and mechanical properties, with the volume output of 268–276 cm^3/100 g of a protein substance and the area output that is by 5.7 % larger than through the industrial technology.

The electronic microscopy method was used to study the structure of the semifinished leather product that had been filled with an organic-mineral composition containing a highly dispersive montmorillonite. It has determined a high degree of divisibility of the modified fibrillar structure of the dermis collagen, which ensures its mobility in the deformation processes in forming and using leather products.

The developed technologies have been introduced at industrial enterprises in Ukraine to ensure efficient use of wet-salted hides for manufacturing elastic multifunctional leathers on the basis of environmentally friendly materials.

References

1. Ekolohichno oriyentovani tekhnolohichni vyrobnytstva shkiryanykh ta khutrovykh materialiv dlya stvorennya konkurentospromozhnykh tovariv. In 2 parts. Part I. Ekolohichno oriyentovani tekhnolohiyi vyrobnytstva shkiryanykh ta khutrovykh materialiv [Text] / A. H. Danylkovych (Ed.). – Kyiv: Feniks, 2011. – 437 p.

2. Danylkovych, A. H. Efektyvnist' vykorystannya kolahenu pry yoho strukturuvanni [Text] / A. H. Danylkovych // Visnyk Kyyivs'koho natsional'noho universytetu tekhnolohiy ta dyzaynu. – 2002. – Vol. 1. – P. 182–185.
3. Danylkovych, A. H. Tekhnolohiya i materialy vyrobnytstva shkiry [Text] / A. H. Danylkovych, O. R. Mokrousova, O. A. Okhmat; A. H. Danylkovych (Ed.). – Kyiv: Feniks, 2009. – 580 p.
4. Danilin, D. V. Vlijanie raspredelenija napolnjajushhih polimerov po slojam spilka [Text] / D. V. Danilin, S. Y. Studenikin, N. V. Zykova, V. H. Bohomolov // Kozhevenno-obuvnaja promyshlennost'. – 2009. – Vol. 6. – P. 46–48.
5. Ma, J. Z. Elasticity studies on leather retanned with various types of acrylic polymers [Text] / J. Z. Ma, H. Lu // J. Amer. Leather Chem. Assoc. – 2008. – Vol. 103, Issue 11. – P. 363–369.
6. Nashy, E. H. A. Novel retanning agents for chrome tanned leather based on emulsion-nano particles of styrene/butyl acrylate copolymers [Text] / E. H. A. Nashy, A. L. Hussein, M. M. J. Essa // J. Amer. Leather Chem. Assoc. – 2011. – Vol. 106, Issue 9. – P. 241–248.
7. Vinnickij, B. D. Napolnenie i dodublivanie hromovyh kozh polimerami novogo pokolenija [Text] / B. D. Vinnickij, O. P. Lebedev, Ja. Ja. Makarov-Zemljanskij, S. I. Studenikin, S. V. Gorbatov, A. A. Mazanov // Kozhevenno-obuvnaja promyshlennost'. – 2003. – Vol. 1. – P. 33–34.
8. Giljasov, E. A. Aminofurazanovaja smola kak napolnjajushhij i dodublivajushhij reagent v proizvodstve kozhi [Text] / E. A. Giljasov, A. V. Ostrovskaja. – Novye tehnologii i materialy legkoj promyshlennosti, 2010. –P. 77–81.
9. Chernova, A. V. Modificirovannye aminosmoly kak napolnjajushhie i dodublivajushhie reagenty [Text]: sb. st. mezhdun. nauch.-prak. konf. / A. V. Chernova, I. I. Latfullin, A. V. Ostrovskaja // Novye tehnologii i materialy legkoj promyshlennosti. – Kazan': KGTU, 2010. – P. 120–124.
10. Jaisankar, S. N. Water-based anionic sulfonated melamine formaldehyde condensate oligomer as retanning agent for leather processing [Text] / S. N. Jaisankar, S. Gupta, Y. Lakshminarayana, J. Kanakaraj, A. B. Mandal // J. Amer. Leather Chem. Assoc. – 2010. – Vol. 105. – P. 289–296.
11. Jurasova, O. V. Razrabotka i primenenie dodublivajushhej kompozicii v kozhevennom proizvodstve [Text] / O. V. Jurasova // Kozha i obuv'. – 2008. – Vol. 3. – P. 30–33.
12. Jurasova, O. V. Vlijanie dodublivajushhih i napolnjajushhih preparatov na svojstva kozhi [Text] / O. V. Jurasova // Estestvennye i tehnicheskie nauki. – 2008. – Vol. 3 (35). – P. 382.
13. Jurasova, O. V. Poluchenie dubjashhego preparata dlja kozhevennoj promyshlennosti na baze sul'foaromaticheskih soedinenij [Text] / O. V. Jurasova // Biotehnologija. – 2008. – P. 34.
14. Jurasova, O. V. Vlijanie «RKF-1» na potrebitel'skie svojstva kozhevennogo polufabrikata [Text] / O. V. Jurasova // Kozhevenno-obuvnaja promyshlennost'. – 2010. – Vol. 1. – P. 48.
15. Ramazonov, B. G. Napolnenie kozhazotsoderzhashhimi polimerami [Text] / B. G. Ramazonov, T. Zh. Kadirov, A. Ju. Toshev, U. O. Hudanov, V. N. Ahmedov // Doklady Akademii nauk Respubliki Uzbekistan. – 2008. – Vol. 2. – P. 64–67.
16. Chursin, V. I. Vlijanie ishodnyh komponentov na kozhevenno-tehnologicheskie svojstva polimerrastitel'nyh dubitelej [Text] / V. I. Chursin // Kozha i obuv. – 2009. – Vol. 1. – P. 20–22.
17. Chursin, V. I. Vlijanie biopolimernyh kompozicij na uprugo-plasticheskie i prochnostnye svojstva kozh [Text] / V. I. Chursin, E. V. Bordunova, A. V. Osipov // Kozha i obuv'. – 2008. – Vol. 2. – P. 16–18.
18. Mariliz, G. Leather retanning with hydrolyzed protein [Text] / G. Mariliz, D. Silva, I. Vigannico // J. Amer. Leather Chem. Assoc. – 2010. – Vol. 105. – P. 195–202.
19. Balada, E. H. Whey protein isolate: a potential filler for the leather industry [Text] / E. H. Balada, M. M. Taylor, E. M. Brown, C. K. Liu, E. H. Balada, J. Cot // J. Amer. Leather Chem. Assoc. – 2009. – Vol. 104. – P. 122–130.
20. Wang, C. Preparation of organosilicone modified palm oil fatliquor [Text] / C. Wang, S. Feng, J. Wu // J. Amer. Leather Chem. Assoc. – 2011. – Vol. 106. – P. 161–169.
21. Bajandin, V. V. Intensifikacija krasil'no-zhiroval'nyh processov sovmeshhennym metodom [Text] / V. V. Bajandin, N. V. Klenovskaja, Z. K. Zhivova, T. A. Galushkina, O. I. Chepygova, D. V. Klenovskij, M. A. Tarushina // Kozhevenno-obuvnaja promyshlennost'. – 2003. – Vol. 4. – P. 25–26.
22. Bajandin, V. V. Intensifikacija krasil'no-zhiroval'nyh processov sovmeshhennym metodom (soobshhenie 2) [Text] / V. V. Bajandin, N. V. Klenovskaja, Z. K. Zhivova, T. A. Galushkina, O. I. Chepygova, D. V. Klenovskij, M. A. Tarushina // Kozhevenno-obuvnaja promyshlennost'. – 2003. – Vol. 5. – P. 37–38.
23. Gorjacheva, L. A. Napolnenie kozhi liposomnymi kompozicijami [Text] / L. A. Gorjacheva, N. A. Chirkova, O. I. Chibotarjova // Kozhevenno-obuvnaja promyshlennost'. – 2011. – Vol. 2. – P. 33–34.
24. Chirkova, N. A. Ispol'zovanie liposomal'nyh kompozicij v proizvodstve i jekspluatacii kozhi i meha [Text] / N. A. Chirkova, G. F. Esina, S. A. Chubatova, E. V. Chipilenko // Tehnologii ta dizajn. – 2013. – Vol. 3. – P. 1–8.
25. Tysoe, Ch. Technologie zur Weichmachung von Leder [Text] / Ch. Tysoe, J. Reiners // IDC Leder und Haute Markt. – 2009. – Vol. 1. – P. 26–30.
26. Fordzyun, Yu. Level of comfort: artificial and natural shoe materials. A comprehensive assessment [Text] / Yu. Fordzyun, O. Andreyeva, L. Maistrenko // Key Engineering Materials. – 2013. – Vol. 559. – P. 25–30. doi: 10.4028/www.scientific.net/kem.559.25
27. Glubysh, P. A. Doslidzhennja procesu gidrolizu kolagenvmisnoi' vtorynnoi' syrovyny z oderzhannjam novyh preparativ cil'ovogo pryznachennja [Text] / P. A. Glubysh, O. P. Teslja // Visnyk Kyi'vs'kogo nacional'nogo universytetu tehnologij ta dyzajnu. – 2007. – Vol. 4. – P. 255–259.
28. Kerner, S. M. Kyslotno-luzhni vlastyvosti zoliv kolagenu jak polifunkcional'nogo materialu shkirjanogo vyrobnyctva [Text] / S. M. Kerner, P. A. Glubysh, A. G. Danylkovych, O. G. Zhygoc'kyj // Visti akademii' inzhenernyh nauk Ukrai'ny. – 1995. – Vol. 2. – P. 58–65.

29. Teslja, O. P. ICh-spektroskopichni doslidzhennja vzajemodii' kompozycii' ekonat z kolagenom hromovanoi' dermy [Text] / O. P. Teslja, O. R. Mokrousova, O. V. Kovtunenko, V. J. Buhars'kyj // Visnyk Kyi'vs'kogo nacional'nogo universytetu tehnologij ta dyzajnu. – 2009. – Vol. 6. – P. 95–99.
30. Tarasovich, Ju. I. Adsorbcija na glinistyh mineralah [Text] / Ju. I. Tarasovich, F. D. Ovcharenko. – Kyiv: Naukova dumka, 1975. – 351 p.
31. Danylkovych, A. G. Praktykum z himii' i tehnologii' shkiry ta hutra [Text] / A. G. Danylkovych. – Kyiv: Feniks, 2006. – 340 p.
32. Gouldstejn, Dzh. Rastrovaja jelektronnaja mikroskopija i rentgenovskij mikroanaliz [Text] / Dzh. Gouldstejn, D. N'juberi, P. Jechlin, D. Dzhoj, Ch. Fiori, Je. Lifshin; per. s angl. R. S. Gvozdoverr, L. F. Komolovoj. – Moscow: Mir, 1984. – Vol. 1. – 343 p.; Vol. 2. – 351 p.
33. Danylkovych, A. G. Vlastyvosti nitroceljuloznyh plivok modyfikovanyh alkilkarboksyetanolaminom [Text] / A. G. Danylkovych, N. V. Omel'chenko, A. S. Brai'lko // Problemi legkoj y tekstyl'noj promishlennosty Ukrayni. – 2010. – Vol. 1. – P. 12–15.
34. Stirtz, T. Treatise of Collagen [Text] / T. Stirtz // Leder und Hautemarkt. – 1975. – Vol. 26, Issue 9. – P. 155–168.
35. Mihajlov, A. N. Himija i fizika kollagena kozhnogo pokrova [Text] / A. N. Mihajlov. – Moscow: Legkaja ind., 1980. – 232 p.

УДК 678.747+ 678.76+678:67.08:544.478
DOI: 10.15587/1729-4061.2015.65483

ДОСЛІДЖЕННЯ БІОСТІЙКОСТІ ЗАХИСНИХ ІЗОЛЯЦІЙНИХ ПОКРИТТІВ, МОДИФІКОВАНИХ НАФТОПОЛІМЕРНИМИ СМОЛАМИ

І. Є. Никулишин
Доктор технічних наук, доцент*
E-mail: nk_iren@ukr.net
З. Г. Піх
Доктор хімічних наук, професор, завідувач кафедри*
E-mail: pikh@polynet.lviv.ua
С. О. Гнатуш
Кандидат біологічних наук,
професор, завідувач кафедри
Кафедра мікробіології
Львівський національний університет імені Івана Франка
вул. Михайла Грушевського, 4, м. Львів, Україна, 79005
E-mail: gnatuk88@ukr.net
З. Я. Гнатів
Кандидат технічних наук, асистент
Кафедра хімічної інженерії**
E-mail: zorchyk@gmail.com
Р. Т. Чайківська
Кафедра технології органічних речовин**
E-mail: ruslana.chaikivska.xt2013@lpnu.ua
*Кафедра технології органічних продуктів**
**Національний університет «Львівська політехніка»
вул. С. Бандери, 12, м. Львів, Україна, 79013

Опрацьовано основні закономірності модифікації бітумних композитів нафтополімерними смолами (НПС). Встановлено, що введення НПС до ізоляційного нафтового бітуму покращує протикорозійні характеристики захисного покриття для підземних трубопроводів. Досліджено адгезійну міцність нафтобітумних покриттів. Показано, що створені на основі бітуму ізоляційного БНИ-IV-3 композиції, модифіковані коолігомерними темними НПС, володіють підвищеними протикорозійними характеристиками та проявляють біостійкість до дії корозійно небезпечних ґрунтових сульфатвідновних бактерій роду Desulfovibrio desulfuricans

Ключові слова: нафтополімерні смоли, модифікація, нафтобітумні композити, захисні покриття, адгезія, інгібувальні властивості, ґрунтові бактерії

Установлены основные закономерности модификации битумных композитов нефтеполимерными смолами (НПС). Установлено, что введение НПС в состав изоляционного нефтяного битума улучшает антикоррозионные свойства защитного покрытия для подземных трубопроводов. Исследована адгезионная прочность нефтебитумных покрытий. Показано, что созданные на основе битума изоляционного БНИ-IV-3 композиции, модифицированные соолигомерными темными НПС, обладают повышенными противокоррозионными характеристиками и проявляют биостойкость к действию коррозионно опасных грунтовых сульфатвосстанавливающих бактерий рода Desulfovibrio desulfuricans

Ключевые слова: нефтеполимерные смолы, модификация, нефтебитумные композиты, покрытия, адгезия, ингибиторные свойства, почвенные бактерии

1. Вступ

З метою покращення ізоляційних, механічних і в'язкоеластичних властивостей бітумів, їх застосовують сумісно з поліолефінами (поліетиленом, поліпропіленом) у кількості до 10 % мас. З міркувань здешевлення бітумних композицій спостерігається тенденція використання відходів олефінів [1–6].