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STUDYING CHEMICAL TRANSFORMATIONS OF THE MODIFIED DERMA COLLAGEN

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Досліджено хімічні трансформації модифікованого колагену для прогнозування ефективного формування та стабілізації структури дерми з використанням дисперсій монтморилоніту, що оброблені різними модифікаторами. Ідентифікацію хімічних взаємодій оцінювали за допомогою ІЧ-спектроскопічних досліджень на желатині, амінокислотний склад якого близький до колагену.

Наявність в структурі колагену активних до взаємодії карбоксильних, аміно-, пептидних та водневих груп сприяє ефективному структуруванню дерми. Під час переробки шкур в натуральну шкіру відбувається трансформація зв'язків у колагені. При цьому хімічні матеріали взаємодіють із функціональними групами білка та утворюють нові хімічні зв'язки. Це сприяє стабілізації структури дерми. В результаті формується об'ємна капілярно-пориста структура з необхідним рівнем експлуатаційних та гігієнічних властивостей шкір.

ІЧ-спектроскопічний аналіз виявив ефективну фізико-хімічну взаємодію між колагеном та модифікованими дисперсіями монтморилоніту. Це підтверджено утворенням чисельних зв’язків за участю функціональних груп желатину та активними центрами мінералу. Найбільші зміни спостерігаються у високочастотній та низькочастотній областях. Відповідно, спектри характеризують валентні коливання, які беруть участь в утворенні водневих, іонних і ковалентних зв’язків. Це дозволяє стверджувати, що попередньо хромований желатин, і в подальшому оброблений алюміній-модифікованою дисперсією монтморилоніту, має більше координаційних зв’язків. Це зумовлено гідроксокомплексними іонами Cr (III) та Al (III), які знаходяться між силікатними шарами. Водночас присутність попередньо хромованого желатину забезпечує утворення додаткових міжмолекулярних зв’язків, що може позначатись на стабільності властивостей та структуруванні колагену дерми.

Таким чином, є підстави стверджувати про можливість більш ефективного використання сполук хрому під час процесу дублення. За рахунок введення композиції на основі модифікованого сполуками алюмінію монтморилоніту буде досягнуто зменшення витрат хромових сполук. Це надасть можливість вирішити завдання екологізації виробництва та підвищення безпечності натуральних шкір для дитячого взуття

Ключові слова: хімічна взаємодія, дисперсія, монтморилоніт, дублення, хромові та алюмінієві сполуки, виробництво шкір

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1. Introduction

Quality formation of structure and properties of leather is the result of the implementation of the tanning process. A series of compounds of organic and inorganic nature, which are capable to interact with derma collagen are applied for this. The existence of active in interaction carboxylic, amino-, peptide and hydrogen groups in the collagen structure makes it possible to make the bonds with tanning compounds of different nature and contributes to the effective structuring of derma. These actions provide the formation of a complex of functional properties of finished leather, which include physical and mechanical resistance to breaking, stretching, deformation, wear and tear, etc., as well as stabilization of the capillary-porous structure with the required level of hygienic properties.

An innovative direction of effective tanning of leather is the use of tanning compositions based on montmorillonite dispersions [1]. This contributes to the complex formation of the structure of derma via formation of bonds not only between collagen and tanning compound, but also between the mineral, tanning compound and collagen. To enhance the effectiveness of the above-mentioned method of tanning, it is important to establish and identify chemical interactions both for the modified mineral, and for derma collagen after treatment with obtained tannic compositions.

Accordingly, it is necessary to consider that research, aimed at the application of modified montmorillonite dispersions for the effective structuring of collagen of derma, is relevant. In this case, the application of the infrared spectroscopic studies will allow evaluating the chemical nature of the bonds between the basic groups of atoms both in the modified mineral and in the collagen of derma after the treatment with designed compositions. At the same time, it will offer an opportunity to identify the changes in the properties of modified montmorillonite dispersions by analyzing the changes in intensity of the vibration bands of absorption.

2. Literature review and problem statement

In recent years, a large number of studies have focused on the implementation of environmentally-oriented technologies, aimed at the use of the compositions based on bentonite clays for the production of leather for different purposes. According to the results of the presented studies [2], this is caused by the special colloid-chemical properties of the basic mineral of bentonite clays – montmorillonite. Thus, research [3] proved the enhancement of physical-mechanical indicators of finished leather, improvement of state of waste water of leather producing enterprises and improvement of ecological safety of production, indicating the prospects of the application of montmorillonite and compositions on its basis for treatment of skins. The results of the presented papers [2–4] note the possibility of creation of modern materials for the production of leather, however, the problems devoted to structuring and formation of collagen of derma remain unresolved.

In paper [5], the interaction of chromed gelatin with active groups of acrylic emulsion and modified montmorillonite was studied based on the IR-spectroscopic analysis. We will note that the conducted studies involve the use of the polymer-mineral composition only for filling the leather semi-finished product. Accordingly, the results of the study do not substantiate the general problems of stabilization of the collagen structure of derma during the technological process.

In addition, article [6] contains the results of research into the interaction of chromium compounds with collagen and their influence on structuring of derma. The more thorough research results are given in paper [7], which analyzed physical and chemical interaction between chromed gelatin and chrome-modified dispersion of montmorillonite that was the basis for the creation of the composition for the tanning process. Despite the practical relevance of these results, the change of the modifier of the mineral with the aim of reducing the number of chromium compounds requires further development. To solve this problem, in papers [8, 9], the studies of the interaction of aluminum sulfate with collagen of derma were carried out, based on which it is possible to argue that Al (III) forms complexes with carboxylic groups in collagen. As a result, aluminum compounds can act as a modifier of montmorillonite dispersions for further efficient use as auxiliary tanning compositions. However, no IR-spectroscopic studies on detecting the interaction between collagen and montmorillonite dispersions treated with aluminum compounds were conducted to prove this hypothesis.

In addition, in paper [10], the impact of Al (III) and Cr (III) during leather tanning was explored, while the interaction of aluminum and chromium compounds with montmorillonite dispersions and their influence on structuring of collagen of derma were not. That is why all this gives grounds to assert that it is important to carry out IR spectroscopic studies and analysis of the interaction between the basic groups of atoms in both the modified mineral, and collagen of derma after its treatment with the developed compositions based on montmorillonite.

3. The aim and objectives of the study

The aim of this study is to investigate chemical interactions in the structure of modified montmorillonite dispersions and the compositions on their basis with collagen of derma. This would make it possible to predict the effective formation and stabilization of the collagen structure of derma using tanning compositions based on modified montmorillonite dispersions.

To achieve the set aim, the following tasks have been solved:

– to explore a change in the intensities of light absorption of the characteristic montmorillonite bands, treated with different modifiers in order to substantiate the chemical interactions in its structure;

– to explore the nature and effectiveness of chemical transformations in the structure of gelatin, treated with compositions based on modified montmorillonite;

– to analyze different types of H-bound gelatin water and gelatin, treated with compositions based on modified montmorillonite;

– to substantiate the influence of modified montmorillonite dispersions on the effectiveness of structuring of collagen of derma.

4. Materials and methods to study the chemical interactions of montmorillonite dispersions with modifiers and collagen of derma

Bentonite clays from Dashukivsky deposit (Cherkasy oblast, Ukraine) were used for the research. The content of montmorillonite in bentonite clays was 85 %. Modification was carried out stage by stage by sodium carbonate, basic chromium sulfate or potassium aluminum sulfate. At the first phase, sodium carbonate in the amount of 6 % of the weight of dry mineral in the form of 10 % solution was introduced into aqueous dispersion of montmorillonite of the concentration of 100 g/l and thoroughly stirred. The resulting montmorillonite dispersion was kept for one day at room temperature after being treated with sodium salts (MMT_{Na}).

The next stage included the modification of the dispersion (after multiple washing with distilled water) of MMT_{Na} with the solution of basic chrome $Cr_2(SO_4)_n(OH)_{6-2n}$ with basicity OH/Cr=1.5 (TU 645PK5604173OAO-001-2001, Kazakhstan, Aktiubinsk plant of chromium compounds) in the amount of 6.0 % in conversion for Cr_2O_3 of the weight of dry mineral (montmorillonite). The third stage of the modification implied the modification of dispersion of MMT_{Na} with the solution of potassium aluminum sulfate ($AlK(SO_4)_2.12H_2O$) in the amount of 10 % in conversion for Al_2O_3 of the weight of dry mineral (montmorillonite). Subsequently, all samples of dispersions were thoroughly stirred and left for a day to complete ion exchange processes [11]. As a result, dispersions (MMT_{Cr}) modified with chrome compounds and montmorillonite dispersions (MMT_{Al}) modified with aluminum compounds were obtained.

To study the interactions of the resulting montmorillonite dispersions and their constituents with collagen of derma, technical quickly soluble gelatin obtained by acid method, amino acid composition of which is close to collagen, was applied. 5 % solution of gelatin was prepared to evaluate the chemical interaction of montmorillonite with collagen of derma.

The identification of the characteristic bands was performed for gelatin (G) and gelatin treated with different tannic compounds and compositions based on modified montmorillonite. Sequential introduction of tanning substances and compositions based on montmorillonite was applied to identify the effectiveness of the tanning action. After treating with tanning compounds and compositions, the modified gelatin solutions were poured on Teflon substrates and dried at room temperature for 72 hours to obtain films. The obtained films were taken off and stirred into a powdered state. The studied samples had a different kind of a tanning compound, consumption and sequence of their introduction. According to the options of treatment, the following was introduced into the gelatin solution:

– tanning compounds of chrome in the amount of 5 % of chrome oxide of the weight of dry protein; the G+Cr sample was obtained;

– tanning compounds of aluminum in the amount of 8 % of aluminum oxide of the aluminum of the weight of dry protein; the G+Al sample was obtained;

– modified dispersion of MMT_{Cr} in the amount of 6 % of the mineral of the weight of dry protein; the G+MMT_{Cr} sample was obtained;

– modified dispersion of MMT_{Al} in the amount of 8 % of the mineral of the weight of dry protein; the G+MMT_{Al} sample was obtained;

– tanning compounds of chrome in the amount of 5 % of chromium oxide, followed by the introduction of modified dispersion of MMT_{Al} in the amount of 8 % of the mineral of the weight of dry protein, the G+Cr+MMT_{Al} sample was obtained.

IR-spectroscopic research was carried out on the modern universal Fourier – IR-spectrometer TENSOR-37 (BRUKER, Germany) within 4,000–400 cm^{-1}. The character and effectiveness of the interactions of functional groups of montmorillonites with active gelatin groups were evaluated by the change of intensity of light absorption of the corresponding absorption bands. According to sources [12–15], the analysis of vibration bands of absorption in the IR-spectra of resulting substances and the products of their interaction according to frequencies of vibration of characteristic groups of atoms was performed.

Indicators of areas of peaks of relative indicators of light absorption were determined from the Gauss equation [15]. Assessment of the changes in the absorption bands and their shift makes it possible to identify chemical interactions in the treatment of collagen by different tanning agents.

5. Results of research into chemical interaction of montmorillonite dispersions with collagen of derma

5. 1. Research into chemical interactions in the structure of modified montmorillonite dispersions

IR-spectroscopic analysis of modified montmorillonite MMT_{Na} (Table 1, Fig. 1) is characterized by the intensive band of 1,077–1,034 cm^{-1}, which is characteristic of silicic acid structures, less intensive – 783 cm^{-1} and strong bands– 531 and 463 cm^{-1}.

According to sources [14, 16], the spectrum of the MMT_{Na} sample is characterized by a wide band (Table 1, Fig. 1) with the frequency of vibration of 1,038 cm^{-1}. This band corresponds to valence fluctuations of tetrahedrals of silicic acid groups Si–O–Si in the structure of the mineral, which indicates the perfection of the crystalline lattice of montmorillonite.

Table 1

Characteristic bands of absorption bands of modified montmorillonite and a change of their light absorption

Frequency of vibration in maximum peak, cm^{-1}	Group of atoms	Light absorption, A/A_o (for peak areas)		
		MMT_{Na}	MMT_{Cr}	MMT_{Al}
3,639; 3,640; –	νOH_{free}	448	92	–
3,452; 3,435; 3,394	νOH_{bound}	1023	703	651
–; 3,031; 3,163	νOH	–	882	221
–; 2,924; 2,982	H_2O, νOH	–	8	239
–; –; 2,905	H_2O, νOH	–	–	210
–; –; 2,475	H_2O, νOH	–	–	37
1,937; –; –	δOH	16	–	–
1,643; 1,641; 1,658	Si–O, $\delta(H–O–H)_{bound}$	14	93	308
1,451; 1,459; –	δAlO_3 OH	8	23	–
–; –; 1,094	ν(Si–O–Si) Al–O–Al, S=O	–	–	2,246
1,077; 1,074; 1,071	ν(Si–O–Si) Al–O–Al	1,177	2,299	711
1,038; –; –	ν(Si–O–Si), AlO_4 – tetrahedrals	76	–	–
1,034; 1,029; –	ν(Si–O–Si)	475	274	–
–; –; 904	δ(Al–O–H)	–	–	105
783; 784; 781	SiO_4, AlO_4	46	65	38
–; –; 695	ν(Al-O) ν(Al–O–Si)	–	–	137
–, –, 610	Si–O, S–O	–	–	49
–, –, 598	δ(O–Si–O), SO_4^{2-}	–	–	165
–, –, 572	Al–O–Si	–	–	69
531, 528, 520	δ(O–Si–O), Me–O	249	352	177
463, 462, 429	δ(O–Si–O), Me–O	162	218	56

Characteristic bands of 531 cm^{-1} and 463 cm^{-1} are typical for dioctahedral minerals of the montmorillonite type and indicate the vibration of bonds (O–Si–O) and (Me–O). The band in the interval 783 cm^{-1} corresponds to SiO_4, vibrations of rings from AlO_4 tetrahedrals. The band in the region of 1,451 cm^{-1} is characteristic of deformation vibrations of the structural hydroxylic groups of the mineral, which are bound by Al^{3+} cations.

The intensive band with vibration frequency of 3,452–3,639 cm^{-1} and the band of 1,937 cm^{-1} belongs to OH-valence and deformation vibrations of free and bound water. Peaks of 3,639 cm^{-1} and 3,452 cm^{-1} should be referred to valence fluctuations of structural hydroxylic groups Al^{3+}-OH, which indicates the existence of inter-layer exchange cations that are formed after the treatment of montmorillonite with a modifier. A weak band in the MMT_{Na} sample with vibration frequency of 1,643 cm^{-1} is characteristic for deformation vibrations of H–O–H groups.

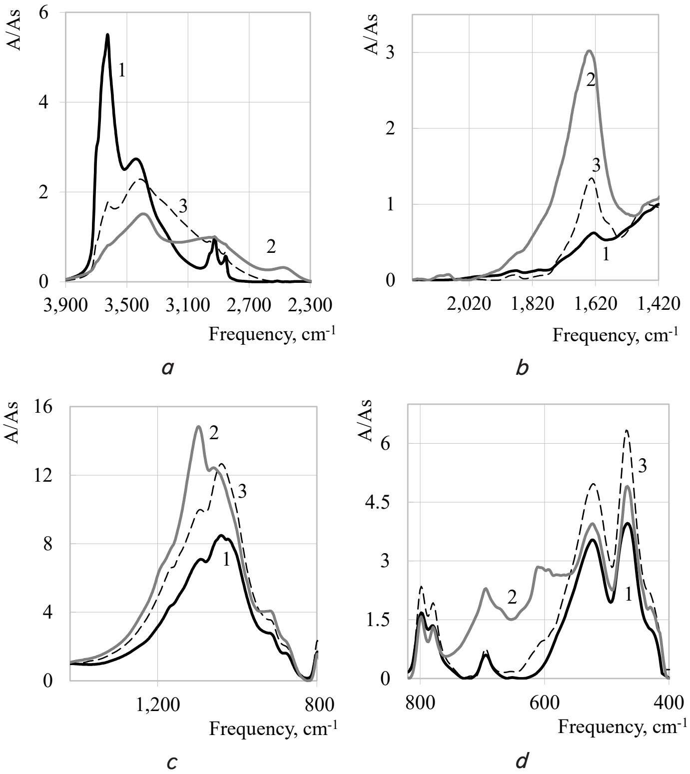


Fig. 1. Spectra of absorption of different intervals of montmorillonite before (1) and after (2) modifications by potassium aluminum sulfate or basic chromium sulfate (3) in the intervals of frequencies: *a* – 3,900–2,300 cm^{-1}; *b* – 2,020–1,420 cm^{-1}; *c* – 1,300–800 cm^{-1}; *d* – 840–400 cm^{-1}

Analysis of the spectra of the MMTCr sample reveals that absorption bands are very close to basic MMTNa (Table 1, Fig. 1). The exception is small changes in magnitudes of absorption frequencies that belong to fluctuations of covalent bonds of Si–O–Si and Al–O–Si in the region of 800–1,074 cm^{-1}.

The area after the peak of 3,640 cm^{-1}, which belongs to free inter-package molecular water, decreased almost by 5 times in comparison with the MMT_{Na} sample (Table 1). Absorption at frequencies of 3,435 cm^{-1} and 3,031 cm^{-1} is referred to bound absorbed water in volume phase [14].

The absorption band at the frequency of 3,435 cm^1 of the MMT_{Cr} sample is shifted to the low-frequency region with a decrease in its area as a result of the compaction of OH-groups and emergence of an intensive band at 3,031 cm^{-1} (Fig. 1, *a*), which indicates the redistribution of intra-molecular bonds.

Deformation vibrations of bound water in the region of frequencies of 1,641 cm^{-1} for MMT_{Cr} have the area of peaks that is 7 times larger in comparison with the MMT_{Na} sample (Table 1, Fig. 1, *b*). This was caused by the fact that water molecules in the MMT_{Cr} crystal are bound by much stronger hydrogen bonds in comparison with the basic sample [17, 18].

Bands of 528 and 462 cm^{-1}, which correspond to valence fluctuations of the bond Cr–O and deformation vibrations of O–Si–O, have the area that is at least 1.5 times larger in comparison with the spectrum of MMT_{Na} (Table 1).

The essential difference of the spectrum of MMT_{Al} sample from the MMT_{Na} sample is an increase in the intensity of the absorption band in the region of 1,658 cm^{-1}, appearance of intensive bands in the region of 1,094 and 598 cm^{-1}, appearance of peaks in the region of 3,163; 2,982; 2,905; 2,475; 904; 695; 610 and 572 cm^{-1} and disappearance of absorption bands at 3,639; 1,937; 1,451 and 1,038 cm^{-1}.

Deformation vibrations of H_2O in the MMT_{Al} sample are observed in the region of higher frequencies of 1,658 cm^{-1}, in addition, they are characterized by the intensity that is by 22 times higher in comparison with the MMT_{Na} sample. This is explained by the fact that water molecules in the MMT_{Al} crystal are bound by stronger bonds, and at an increase in concentration of molecular water, the inter-package distance in the crystalline lattice of MMT_{Al} increases.

The bands at 2,982 and 2,905 cm^{-1} (Fig. 1, *a*) belong to silanolic groups of micropores bound by H-bond, but not for molecular-adsorbed water, which is indicated by the absence of the absorption band of δ-vibrations in the region of 1,600–1,618 cm^{-1} (Fig. 1, *b*).

The disappearance of the absorption band at the frequency of 3,639 cm^{-1} and appearance of the new peaks at frequencies of 3,394; 3,163; 2,982; 2,905; 2,475 cm^{-1}, which are referred to bound adsorbed water in the volume phase, testify to the creation of hydrogen bonds. An increase in distinct maximum at 1,658 cm^{-1} is overlapping the spectra of capillary-condensed water in wide pores and monomolecular water adsorbed in micropores of silicate [19].

The appearance of the intensive band for the MMT_{Al} sample at 695 cm^{-1} Si–O(Al) (Fig. 1, *c*), and an increase in the intensity of the band at 1,094 cm^{-1} of vibrations of the Si–O–Si framework of the mineral and its shift to the high-frequency region in the spectrum, indicates that hydroxyls characterized by these bands take part in the reaction of the cation exchange (Fig. 1, *d*).

According to the literary data [20], the existence of the surface OH-groups only at the “peripheral: areas of the plates of the mineral is characteristic of montmorillonite. The typical result of the formation of H-bond is the shift of the band to the long-wave region along with an increase in its width and total area of the peaks. Hydroxyls that are responsible for H-bonds with cations of Al^{3+}, characterized by the bands with the frequency of vibration of 3,394 cm^{-1} and 904 cm^{-1}, have weak acidic properties; the proton of these hydroxyls is an exchange proton in the interaction with the metal cation.

The disappearance of the absorption band at the frequency of 3,639 cm^{-1} and the appearance of new peaks at frequencies of 3,394; 3,163; 2,982; 2,905; 2,475 cm^{-1}, which are referred to bound adsorbed water in volume phase, testify to the formation of hydrogen bonds. An increase in distinct maximum at 1,658 cm^{-1} is overlapping of spectra of capillary-condensed water in wide pores and monomolecular water adsorbed in micropores of silicate [19].

5. 2. Research into chemical interactions in the structure of gelatin, treated with compositions based on modified montmorillonite

When evaluating the absorption bands in the spectrum of gelatin (G) (Table 2, Fig. 2), it is possible to separate the most characteristic spectra that are located in the intervals of frequencies of 3,500–3,100 cm^{-1} and

1,640–900 cm^{-1} and less intensive in the interval of 900–400 cm^{-1} [21, 22].

The peaks within the absorption band of 3,500–3,200 cm^{-1} characterize valence fluctuations of associated NH_2^-, NH^- and OH-groups that take part in the formation of hydrogen bonds. The peak of 3,413 cm^{-1} is referred to bound valence NH-groups that take part in the formation of internally molecular hydrogen bonds. The absorption in the range of the spectrum of 2,955 cm^{-1} and 2,834 cm^{-1} is referred to asymmetric and symmetric valence fluctuations of the CH_2 groups.

For sample G, it is possible to observe the deformation vibrations of bonds NH (Amide I) and (Amide II) in the region of spectrum 1,645–1,532 cm^{-1}, deformation vibrations of bond of O–H in the region of peaks of 1,333–1,201 cm^{-1} and valence fluctuations of C–N-groups in amides (Amide III).

The interval of the spectrum for sample G in the range of 1,161–922 cm^{-1} combines the set of bands that indicate the pendulum vibrations of NH_3^+ groups (1,161 cm^{-1}), characteristic for valence fluctuations of groups CN, C–O and C=C (1,082 cm^{-1} and 1,032 cm^{-1}) and the bands that are characteristic for bound NH groups (922 cm^{-1}) (Fig. 2, *c*).

In spectrum (G), the wide and less intensive band is manifested in the range of 873–550 cm^{-1}, which characterizes deformation vibrations of bound NH-groups with peaks of 873 cm^{-1} (Amide V) and 550 cm^{-1} (Amide VI).

The band of 1,448 cm^{-1} characterizes scissor vibrations of CH_2 groups, the band of 2,834 cm^{-1} indicates the valence symmetric vibrations of $-CH_2-$ chains, the band of 2,955 cm^{-1} indicates the valence asymmetric vibrations of CH_2 groups [23, 24].

After the treatment of gelatin with chromium tanning agent (G+Cr) (Table 2, Fig. 2), the most characteristic absorption is observed in the interval of frequencies of 3,500–3,200 cm^{-1} in the spectrum region of 1,654–1,037 cm^{-1} and less intensive in the region of the spectrum of 685–537 cm^{-1} [25].

The band in the frequency range of 3500–3200 cm^{-1} (Fig. 2) is characterized by the regions of valence vibrations of associated amino-, imino- and hydroxyl groups that are involved in the formation of hydrogen intermolecular bonds [23].

The bands of carbonyl absorption are manifested somewhat stronger than the band of Amide II that occurs as a result of valence vibrations of CN-groups, at the time when bond C–N to a greater extent shows the nature of the double bond due to the resonance with carbonyl group [24].

The existence of residues of amino acids in the structure of the G+Cr sample is proved by bands of 1,659 cm^{-1} (Amide I) and 1,536 cm^{-1} (Amide II). These bands characterize carbonyl absorptions and deformation vibrations of NH-groups and valence fluctuations of CN-groups (Fig. 2, *b*).

Vibrations in the range of 1160–1034 cm^{-1} also demonstrate active interaction of gelatin with chromium tanning agent (G+Cr). The band of 1,160 cm^{-1} indicates the pendulum vibrations of NH^{3+} groups, the band of 1,081 cm^{-1} is characteristic of SO_4^{2-}-groups, the band of 1,034 cm^{-1} indicates the valence groups of CN, C–O and C=C. The formation of the collagen structure at tanning occurs due to participation of finished carboxyl and amino groups of protein, which is proved by disappearance of the band at 1,201 cm^{-1} and appearance of the band at 1,122 cm^{-1} [23].

The appearance at 685-604 cm^{-1} (Fig. 2) of the frequencies, which are observed for Amide V, for the G+Cr sample, characterize deformation vibrations of the complex ether fragment and the chrome complex, at the same time, the frequency of 537 cm^{-1} (of Amide VI) is characteristic of deformation vibrations of C=O groups and deformation vibrations of the NH-groups, which may indicate the interaction of chromium with active groups of gelatin.

Table 2

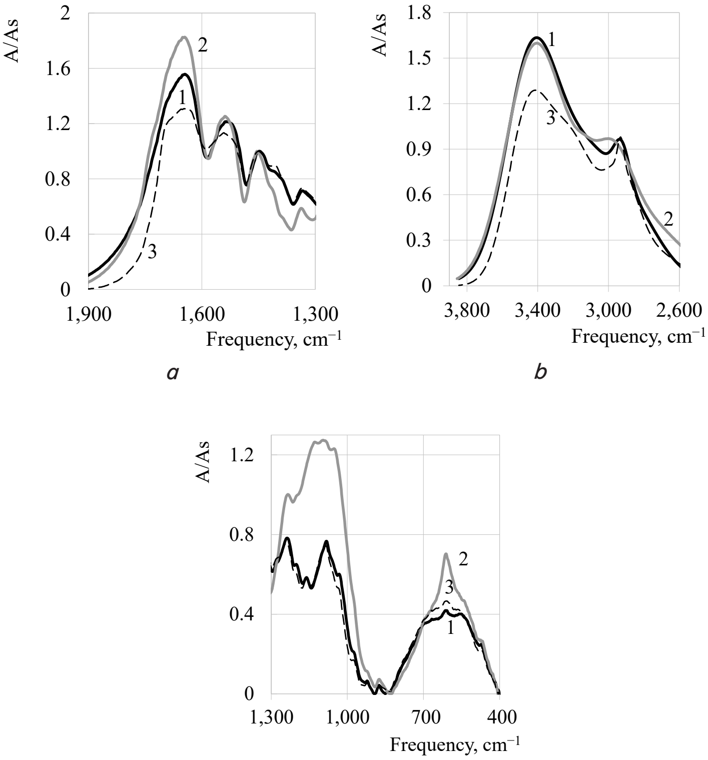
Characteristic bands of absorption gelatin and chromed gelatin

G		G+Cr	
Vibration frequency, cm^{-1}	Group of atoms	Vibration frequency, cm^{-1}	Groups of atoms
3,413; 3,200–3,500	νNH_{bound}, νOH	3,337; 3,200–3,500	νNH bound., νOH
3,082	νNH_{bound}, νCN	3,072	νNH bound., νCN
2,955	νCH_2 asym.	2954	νCH_2 asym.
2,834	νCH_2 sym.	2,813	νCH_2 sym.
1,645	Amide I, nC=O	1,654	Amide I, νC=O
1,532	Amide II, δ NH, νCN	1,547	Amide II, δNH, νCN
1,448	CH_2 scissor	1,454	CH_2 scissor
–	–	1,398	C=O val. (COO-)
1,333	Amide III, νCN+δNH	1,337	Amide III, νCN+δNH
1,237	νCN, δNH	1,245	νCN, δNH
1,201	Amide III, νCN, δNH	–	–
1,161	NH_3^+	1,160	NH_3^+
–	–	1,122	S=O, NH_3^+, $SO4^{2-}$
1,082	νCN, dOH	1,081	νCN, δOH, SO_4^{2-}
1,032	νC–O, νC=C	1,034	νC–O, νC=C
922	νC=C, νNH	973	νC=C, νNH
873	ν(C–O–C), dNH	685	δNH, Amide V, Cr^{+3}
550	Amide VI, δNH, δC=O	604	Amide V, δNH, Cr^{+3}
471	δ(C–C)	537	Amide VI, δ NH

On the spectrum of (Fig. 2), like on the initial spectrum of gelatin, at 3,422 cm^{-1} we observe a wide band that is characteristic of all proteins, caused by valence fluctuations of the N–H bond in groups NH_2, which take part in the formation of hydrogen bonds. Valence fluctuations of the bonds in OH groups at 3,500–3,200 cm^{-1} are also characteristic. Absorption bands of 3,158–3,089 cm^{-1} and 1,663 cm^{-1} corresponds to valence fluctuations and deformation vibrations of N–H bond in NH^{3+} groups.

The appearance of the absorption band in the spectra of the G+Al sample of valence fluctuations at 2,951 cm^{-1} indicate the formation of H-bonds of the “bridge” type. The bands formed in this region point out the existence of weakly bound moisture [24].

The existence of the intensive band of valence vibrations for the sample G+Al of associated carbonylic groups C=O (Amide I) at 1,663 cm^{-1} is explained by the interaction of the functional groups of gelatin with sulfate complex of aluminum. The band Amide is somehow weaker than the bands of carbonyl absorption. Absorption bands at 1,532 cm^{-1} are caused by deformation vibration of NH-groups of amino acids in the composition of the protein part of gelatin.



a *b*

c

Fig. 2. Spectra of absorption of different intervals of gelatin before (1) and after (2) modification of potassium aluminum sulfate or basic solutions of chromium sulfate (3) in the intervals of frequencies: *a* – 3,800–2,600 cm^{-1}; *b* – 1,900–1,300 cm^{-1}; c – 1,300–400 cm^{-1}

The band for the G+Al sample in the region of 1,234 cm^{-1} characterizes deformation vibrations of NH-groups (Amide III). Vibrations within the band of 1,128–1,053 cm^{-1}, which point out pendulum vibrations of NH^{3+} groups, SO_4^{2-} groups and valence groups CN, C–O and C=C are more intensive in comparison with sample G. It is probably the result of the interaction of carboxylic and amino groups of gelatin with hydroxo-complex ions of Al, in the internal sphere of which there are sulfate-ions.

Analysis of the IR-spectrum of the G+Al sample indicates that the interaction of tanning compounds of aluminum results into the formation of the complexes with sulfate-ions in the internal sphere, and binding of the complex with protein occurs with the help of the bond of aluminum and amino groups of gelatin [21].

Changes in relative indicators of light absorption in spectra G and in modified G+Cr, G+Al, G+MMT_{Al} and G+Cr+MMT_{Al} are represented in Table 5. Analysis of IR spectra (Table 3, Fig. 2, 3) made it possible to determine the bands of absorption and enables determining the set of bands which is more sensitive to the influence of tanning compounds on collagen.

Spectra of G+MMT_{Al} (Table 3, Fig. 3) are different from the spectra of the G+Al sample in the region of valence –NH fluctuations of nitrogen-containing groups of gelatin and valence vibrations of structuring hydroxyl groups $Al(OH)_3$. The band of 3,462 cm^{-1} is related to OH-vibrations of the molecules of absorbed water that take part in hydrogen bonds. The specified band shifted to low-frequency region by 23 cm^{-1} has smaller area under the peak. Appearance of the medium peak at 3,387 cm^{-1} and more intensive at 3,354 cm^{-1} for the sample G+MMT_{Al} indicate the inter-layer exchange cations and are proved by the existence of the pronounced maximum in the IR-range at 3,080 cm^{-1}.

The bands of valence fluctuations of Amides I, II and III for the G+MMT_{Al} sample reveal a certain influence on the structure of gelatin in comparison with the spectrum of G+Al. In this case, the area under the peaks of 1,663 cm^{-1}, 1,532 cm^{-1} and 1,241 cm^{-1} decreases in comparison with maxima in the spectrum of the G+Al sample.

In the spectral range of 1,161–1,016 cm^{-1}, valence fluctuations of CN-groups, sulfogroups and NH_3^+ vibrations of gelatin, valence fluctuations of Si(OH)AI, as well as vibrations of free surface deformation of OH-groups of SiO vibrations are manifested for the sample G+MMTAl. There is a significant increase in the area of the peak of 1,088 cm^{-1}, for the sample of G+MMTAl, as well as the shift of the band of 1,161 cm^{-1} by 33 cm^{-1} to the region of higher frequencies (Fig. 3, *c*) [1].

In the region of spectrum of 780–615 cm^{-1} for the G+MMTAl sample, there are the bands of valence fluctuations and deformation vibrations of peptides (Amide V and Amide VI) and the aluminum complex. In the spectrum of the G+MMTAl sample, the wide absorption band is divided into four maxima at 780 cm^{-1}, 699 cm^{-1}, 659 cm^{-1} and 615 cm^{-1}, unlike one-layer peak at 611 cm^{-1} in the G+Al sample (Fig. 3, *d*). This can indicate the participation of OH-groups in the formation of hydrogen interaction Si–OH···O–C.

Appearance of peaks of 525 and 426 cm^{-1} for the G+ MMTAl sample, which characterize deformation vibrations of C=O-groups, O–Si–O and valence fluctuations of Al–O may indicate the formation of hydrogen bonds between the functional groups of gelatin and MMTAl of the Si–O....H–N type with NH-groups of protein and Si–O....H–C with CH-groups of protein [20].

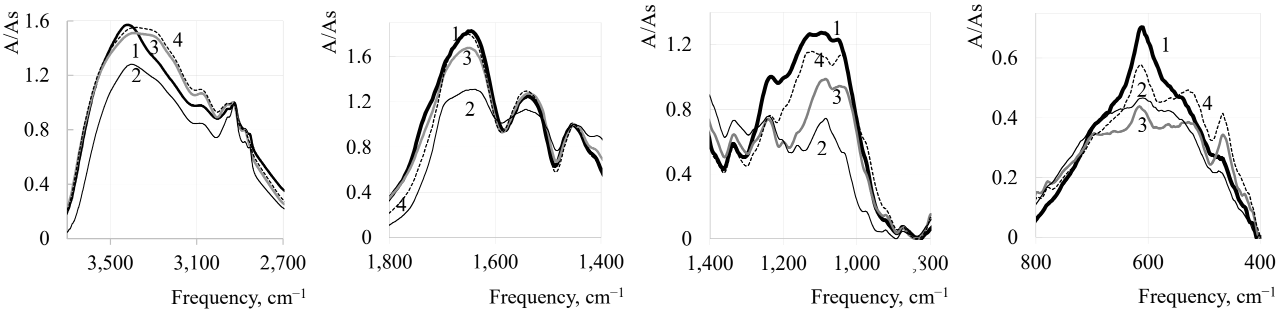
For the spectrum of the sample of G+Cr+MMTAl (Table 3, Fig. 3), valence fluctuations of OH-groups in the region of 3,400 cm^{-1} are the most sensitive to the presence of hydrogen bonds. Their location depends on the concentration of water, conditions of obtaining the spectra that are easily separated from the absorption bands of other groups [22].

In the IR-spectrum of the G+Cr+MMTAl sample, adsorption moisture is characterized by wide absorption bands in the interval of 3,500–3,000 cm$^{-1.}$ A wide adsorption band with two peaks at 3,391 and 3,379 cm^{-1} shifted to the low-frequency region, but with a larger area in comparison with the G+MMTAl sample, is caused by valence vibrations of H-bound OH-groups and their compactness. This fact is proved by a decrease in the sample of weakly bound moisture, characterized by the peak maximum at 3,077 cm^{-1} (Fig. 3, *a*).

Table 3

Characteristic bands of absorption of modified gelatin and a change in their light absorption

Group of atoms	Vibration frequency in the maximum of peak, cm^{-1}	Light absorption, A/Ao (for areas of peaks)				
		G	G+Al	G+MMTAl	G+Cr	G+Cr+MMTAl
νNH_{bound}	3,436; 3,422; 3,399 3,462; 3,391	525	584	388	287	554
νOH_{bound}	–; –; 3,387; –; 3,379	–	–	93	–	156
νSi(OH)AI	–; –; 3,354; 3,216; –	–	–	247	332	–
νSi(OH)AI	3,137; 3,158; –; –; –,	261	4	–	–	–
νNH_{bound}, NH_3^+	–; 3,089; 3,080; –; 3,077	–	73	106	–	66
ν (CH_3), νOH	–; 2,951; –; –; –	–	58	–	–	–
ν (CH_3), νOH	2,926; 2,927; 2,931; 2,926; 2,937	26	370	24	112	318
H_2O, νOH	2,894; –; 2,879; 2,882; –; –	204	–	202	282	–
Amide I,						
νC=O,	1,670; 1,663; 1,663; 1,659;1,667	184	256	226	147	177
δ(H–O–H)	1,638; –; –; –;1,649	14	–	–	–	41
Amide II, δNH+ νCN	1,531; 1,532; 1,532; 1,536; 1,537	43	41	42	62	65
Amide III, νCN, δ NH	1,234; 1,234; 1,241; 1,243; 1,242	14	26	10	12	10
Amide III, νCN, δ NH	1,200; –; –; –; –	10	–	–	–	–
Amide III, NH_3^+	1,159; 1,128; 1,161; 1,150; 1,119	10	38	36	17	122
νCN, δOH, νSi(OH)AI	1,080; 1,097; 1,088; 1,084; 1,097	25	38	77	28	15
SO_4^{2-}, NH_3^+, νSi(OH)AI	1,032; 1,053; 1,016; 1,030; 1,041	20	34	27	13	89
νC–O, νC=C	976; –; –;974; –	6	–	–	2	–
δSiOH,	–; –;780; 732; 754	–	–	14	29	27
ν(C–O–C), νNH,	662; –; 699; –; –	47	–	35	–	–
δ (Al–OH), AlO_4,	652; –; –;659; 637; –	51	–	15	47	–
COO^-, Me–O	–; 611; 615; 592; 609	–	127	14	8	53
δC=O, (C–C–C), Me–O, Al–O–Si	584; 586; –; –; – 544; –; 561; –; – –; –;525; 534; 522	2 11 –	12 – –	– 10 36	– – 27	– – 20
δ(C–C), Me–O	478; 472; 463; 464; 462	21	14	12	10	10
Me–O, δ(O–Si–O)	–; –; 426; –; –	–	–	6	–	–



a *b* *c* *d*

Fig. 3. Spectra of absorption of difference intervals of gelatin modified by potassium aluminum sulfate (1), basic chromium sulfate (2), MMT_{Al} (3) or basic chromium sulfate and MMT_{Al} combined (4) in the frequency range: *a* – 3,500–2,700 cm^{-1}; *b* – 1,800–1,400 cm^{-1}; *c* – 1,400–800 cm^{-1}; *d* – 800–400 cm^{-1}

Analysis of the spectra of the G+Cr and G+Cr+MMT_{Al} samples indicates that chromed gelatin has more active coordination bonds between chrome and OH-groups of protein. It is also proved by the interval of the spectrum of 1,667–1,242 cm^{-1}, which characterizes the existence of valence groups of Amides I, II and III (Fig. 3, *b*). At the same time, bands of 1,119–1,041 cm^{-1} correspond to vibrations C–N of valence groups, NH and NH_3^+ deformation vibrations, as well as sulfogroups of chromium and aluminum complexes. The band of 1,119 cm^{-1} has the area that is by 3.4 times larger and shifted by 42 cm^{-1} to the low-frequency region in comparison with the G+MMT_{Al} sample (Fig. 3, *c*).

The shift of the peak of 1,041 cm^{-1} by 25 cm^{-1} to the high-frequency region, as well as the shift of the bands of 754 and 609 cm^{-1} and an increase in their area, which is characteristic of COO^-, Me–O groups (Fig. 3, *d*), can indicate the formation of coordination bonds mainly between the ions of chromium and carboxylic groups –COOH of the side chains of gelatin.

5. 3. Analysis of different types of H-bound water of gelatin and gelatin, treated with compositions based on modified montmorillonite

Analysis of the spectra of the studied samples in the area of the absorption of water and hydroxyl groups allows arguing that the molecules of adsorption moisture are on the surface of gelatin and the mineral. Their location is also possible in empty crystalline lattices, in channels-capillaries, in the internal coordination sphere of hydrated metal, where they are bound by the weak van der Waals forces, sometimes by hydrogen bonds. At the same time, in some samples, water molecules in the crystal are bound by stronger hydrogen bonds in comparison with others. This leads to an increase in the inter-package distance in the crystalline lattice of the mineral.

That is why in order to study various types of H-bound water for the samples of gelatin and those of modified gelatin, relative intensity of light absorption bands was calculated using the indicators of strongly bound (R_1) and weakly bound moisture (R_2).

The band of 1,530 cm^{-1}, which was caused by deformation vibration of NH-groups of amino acids (Table 3, Fig. 3, *b*) that objectively describes a change in the state of water in the studied samples, was selected as the calculation standard.

Calculation of R_1 and R_2 from formulas (1), (2) is presented below as an example:

$$R_1 = \frac{S_{1670} + S_{1640}}{S_{1530}}, \qquad (1)$$

$$R_2 = \frac{S_{2950} + S_{2930} + S_{2890}}{S_{1530}}, \qquad (2)$$

where R_1 is the indicator of strongly bound moisture; R_2 is the indicator of weakly bound moisture; S is the sum for the areas of peaks at the corresponding frequency of vibrations [26].

According to the above results of calculations (Tables 4, 5), relative intensity of absorption bands of gelatin and gelatin modified by potassium aluminium sulfate, basic chromium sulfate, MMT$_{Al}$ and sequential treatment by basic chrome sulfate and MMT$_{Al}$ characterizes the largest existence of free and bound groups of water in the G+Al sample, and least – in the G+Cr sample.

In this case, the least number of free groups of water is in the G+Cr+MMT$_{Al}$, sample, which indicate strengthening of the structure of the studied sample, caused by hydroxo-complex ions of Cr (III) and Al (III), which are located between silicate layers.

Table 4

Relative intensities of bound water in studied samples

Studied samples	S1670	S1640	Σ	S1530	Indicator of strongly bound moisture (R1)
G	184	14	198	43	4.6
G+Cr	147	–	147	62	2.37
G+Al	256	–	256	41	6.24
G+MMTAl	226	–	226	42	5.38
G+Cr+MMTAl	177	41	218	65	3.35

Table 5

Relative intensities of free water in studied samples

Studied samples	S_{2950}	S_{2930}	S_{2890}	Σ	S_{1530}	Indicator of weakly bound moisture (R_2)
G	–	26	204	230	43	5.35
G+Cr	–	112	282	394	62	6.35
G+Al	58	370	–	428	41	10.44
G+MMT$_{Al}$	–	24	202	226	42	5.38
G+Cr+MMT$_{Al}$	–	318	–	318	65	4.89

6. Discussion of results of studying the chemical interaction of montmorillonite dispersions with modifiers and their influence on structuring of collagen of derma

The results of IR-spectroscopic studies of montmorillonite revealed that the spectra of the mineral modified by sodium carbonate indicate the perfection of the crystalline lattice of montmorillonite.

Montmorillonite dispersions modified by chromium compounds are characterized by strengthening of the role of hydrogen and valence bonds Si–O–Si and Al–O–Si. In addition, there are Cr–O and O–Si–O bonds, indicating the formation of the systematized crystalline structure of chromium ions on the surface of the mineral.

Considering that in solutions of Cr (III salts), there occur complexing phenomena [16–18], accompanied by a change in the charge of hydroxo-complex ions and an increase in molecular weight, it is possible to argue about strengthening of the structure of the MMT$_{Na}$ sample with an increase in siloxane groups in MMT$_{Cr}$ due to the role of the hydroxocomplex ions of Cr (III).

Montmorillonite modified by aluminum compounds is characterized by substantial changes of deformation vibrations of free and bound water, which is proved by the intensity that is by 22 times higher in comparison with the MMT$_{Na}$ sample and the area of peaks that is by 3 times larger in comparison with MMT$_{Cr}$. Besides, the analysis of the spectra in the region of absorption of water and hydroxylic groups allows arguing that MMT$_{Al}$ is in the conditions of higher activity of water than in the MMT$_{Na}$ sample. This conclusion is based on the fact that there are fewer weakly bound hydroxylic groups in the MMT$_{Al}$ sample than in the MMT$_{Na}$ sample, and more water in the inter-layer space.

However, we cannot but note that replacement of Na^{+} cation with Al^{3+} cation for the MMT$_{Al}$ sample in the Si–OH-groups must lead to an increase in frequency of Si–O(Al). It is proved by an increase in vibrations of Si–O–Si of the mineral framework and its shift to the high-frequency range in the spectrum. At the same time, a shift of Si–O bands can indicate an increase in "hardness" of the system. In this case, there is a redistribution of hydroxyl groups on the surface of MMT$_{Al}$, which is characterized by weak acid properties and caused the formation of the strong H-bond with Al^{3+} molecules. This phenomenon points out the possibility of more effective formation of the derma structure in case of using MMT_{Al} for leather tanning.

After the treatment by chromium gelatin or by aluminum tanning agent, the most significant changes are observed in the regions characteristic for absorption of OH-groups, carboxylic or amino groups. These changes indicate a possibility of formation of additional intermolecular bonds through the interaction with the Cr (III) or Al (III) ion, respectively, displacing sulfate ion from the inner coordination sphere.

Gelatin treated with modified montmorillonite dispersions is characterized by the existence of nitrogen-containing and hydroxylic groups. This is proved by the formation of hydrogen bonds between the nitrogen atoms of gelatin and protons of inter-package water. In addition, the existence of valence fluctuations of amine groups shows that hydrogen bonds are formed between the nitrogen atoms of gelatin aminogroups and protone of water in the inter-layer space of the G+Al sample with the cations in the exchange complex.

Existence of valence fluctuations of the CN-groups and sulfogroups for gelatin treated by MMT_{Al} allow arguing about the formation of electrovalent bonds between the active groups of protein component and the charged surface of the MMT_{Al} and hydrogen bonds with the surface hydroxyl groups of montmorillonites.

Gelatin, sequentially treated by chromium compounds and modified montmorillonite dispersions, is characterized by the existence of active coordination bonds between chromium and OH-groups of protein. The predicted strengthening of the structure of treated gelatin can also be the manifestation of an increase in siloxane groups, which is caused by hydroxo-complex ions of Cr (III) and Al (III), located between the silicate layers of the mineral as a result of compression by OH-groups.

Thus, sequential treatment of collagen by chromium compounds and montmorillonite dispersions modified by aluminum compounds can contribute to most effective protein structuring and ensure higher hydrothermal resistance of the collagen structure of derma as a result of technological treatments.

7. Conclusions

1. The identification of chemical interactions in the structure of montmorillonite dispersions treated by different modifying agents revealed the existence of the inter-layer exchange cations after the modification of montmorillonite by sodium salts. It was discovered that the role of hydrogen and valence bonds after the modification of the mineral by chromium compounds strengthened. At the same time, for montmorillonite, modified by aluminum compounds, we detected substantial changes of deformation vibrations of free and bound water, which indicated the possibility of more efficient formation of the structure of derma in case its use for leather tanning.

2. The conducted research found that changes of the properties of collagen during leather tanning can be characterized by different phenomena. The formation of the aluminum-involving transversal bonds between the lateral chains of collagen and hydroxyl groups of molecules of already bound peptides of previously chromed gelatin was discovered. The totality of interactions ensures formation of hydrogen, ionic and covalent bonds, which can influence the stability of properties and collagen structuring.

3. Different types and H-bound water for the samples of gelatin and modified gelatin were analyzed. Calculations of relative intensity of light absorption bands indicate the existence of the least amount of weakly bound water in the $G+Cr+MMT_{Al}$, which will consequently contribute to most effective protein structuring and ensure higher hydrothermal stability of collagen structure of derma.

4. It was substantiated that the introduction of modified montmorillonite at the stage of tanning ensures creation of additional bonds in the structure of derma, which will cause more effective interaction of compounds of chromium and aluminum with collagen and, respectively, will contribute to more effective derma structuring. In this regard, it is possible to predict more rational use of chromium compounds for tanning due to the introduction of the composition based of montmorillonite modified by aluminum compounds. This will solve the task of making production ecologically friendly and enhancing the safety of leather for children's footwear.

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