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Modified Fibrous Mass of Leather and Paper Waste for the Production of Packaging Paper and Cardboard

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ABSTRACT
Recycling leather waste, which accumulates in large quantities in tanneries, and producing packaging paper with improved properties reduces the environmental burden and is at the same time economically efficient. A modified fibrous mass of waste from tanned and untanned leather scraps, waste paper, and acrylic emulsion was obtained and packaging paper based on them was produced. Alkaline modification of tanned leather waste - chrome shavings - leads to an increase in the electrokinetic potential and, accordingly, the stability of the fibrous suspension, partial hydrolysis of skin collagen occurs with the formation of new polar groups, and at the same time, the degree of cross-linking of the skin increases. In the paper composition, new intermolecular bonds are formed between cellulose and skin collagen. The microstructure, elemental composition, morphology, thermal and physical-mechanical properties of modified chrome shavings and composite paper were determined. A significant improvement has been achieved in the main parameters of paper: surface density (decrease by 16-25%), breaking load and breaking length (increase by 15-23%), number of double bends (increase by 2-6 times) in comparison with paper obtained from pure waste paper, and also to a greater extent compared to paper obtained from unmodified leather waste.

KEYWORDS
leather, paper, waste, packaging paper, cardboard, alkaline modification, collagen

INTRODUCTION

Paper and cardboard, including packaging paper, is a composition consisting of fibrous, polymer, mineral, binders and other components. The main fibrous raw material for the production of paper products is wood or cotton pulp. The extreme limitation of primary cellulose raw materials forces manufacturers to use secondary raw materials in the form of waste paper, cotton linters, fluff, and textile waste to produce paper products. There are objective reasons that limit the proper processing of waste, as a result of which the environmental load on the environment and economic losses increase [1]. Currently, packaging paper and cardboard are almost entirely produced from waste paper. A systematic review of the literature reflects an increasing trend in the number of publications and citations showing interest in this area [2]. Waste paper is the main component of industrial and municipal waste, and its annual generation is about 400 million tons, which has only been recycled 50–

65% due to the poor quality of fibres and other waste mixed with it [3]. Paper waste contains primarily cellulose, with lower levels of hemicellulose, lignin, and inorganic materials analyzed by ash content. The remains of pulp and paper waste are combined with mineral fillers [4].

To prepare recycled paper pulp, it is proposed to grind the fibre, add sizing and fill it with kaolin. However, this method disrupts the stability of sizing [5]. To increase strength when processing cellulose pulp, more polymers are introduced and their retention is ensured. However, it has been found that polymer processing according to this method has a negative effect on the bulk of the paper, i.e. the paper density becomes undesirably high [6]. Increasing the strength of paper and cardboard without negatively affecting bulk is a challenge. To increase the strength of paper while maintaining biodegradability, it is proposed to apply a polymer film made from natural products to its surface [7]. Thus, at present there is an acute shortage of environmentally friendly fibrous mass for the production of paper and cardboard; it is necessary to find new sources of raw materials. In our opinion, such a source could be tannery waste in the form of tanned and untanned hides.

Leather, footwear, and clothing industries produce significant quantities of chromium-containing proteinaceous wastes [8]. Leather production is divided into three main processes: the elementary or preparatory stages, tanning and crust formation. When processing raw leather, the most widely used method is chrome tanning using trivalent chromium salts. In this case, approximately 60-70% of the salts react with the collagen of the skin, and tanned leather is formed. The unreacted part of the salts is discharged into tannery wastewater, and leads to environmental pollution, especially in developing countries [9]. Leather is stabilized during the tanning process, but it produces far more by-products and waste than the leather itself. Each ton of hide produces only 200 kg of leather, while simultaneously generating more than 600 kg of solid waste or by-products [10]. It has been estimated that approximately 600 000 tons of solid waste is generated each year worldwide by the leather industry, and approximately 40-50% of hides are lost to shavings and trimmings. Tanned waste is leather or chrome shavings [11] and sawn trimmings, as well as dust generated during planing, sawing, and grinding semi-finished products, which have structural formations due to the interaction of collagen with chromium (III) salts and many other tanning compounds [12]. During the tanning process, and especially with improper disposal of waste, trivalent chromium is oxidized to hexavalent, which turns it into a toxic compound [13]. The main waste product of leather production remaining after splitting bleached hides before tanning is the bottom layer of leather along with the underlying fatty tissue. This layer consists of up to 87% water; the protein content is 40 - 60 g and fat 10 - 20 g per 1 kg of dry weight, as well as small amounts of carbohydrates and inorganic salts. The method of processing waste into target products includes the following processes: washing of salts, separation of fat, enzymatic hydrolysis of proteins using protease, and extraction of hydrolyzed collagen into hot water [14]. The most common component of the hide is collagen [15]. It is proposed to use untanned collagen-containing tanning waste as a component of sizing compositions. Positive results were achieved when using protein hydrolyzate from cattle hide waste [16] and its graft copolymers [17] when sizing cotton yarn. Recycling tanning waste can help improve the environmental situation due to its almost complete recycling. The problem becomes more obvious when you keep in mind that the leather tanning process uses harmful chemicals. Thus, finding eco-sustainable and innovative alternatives for the management and disposal of these wastes is becoming a huge challenge for tanneries and researchers around the world [18].

One of the directions for processing chromium-containing waste is the production of artificial leather by mixing leather fibres with a melt of a thermoplastic polymer binder [19]. Artificial leather or "pressed leather" has reduced strength, and the use of a significant amount of synthetic resins that impregnate the entire structure produces a material with reduced hygienic properties. It is known to use tanning dust for filling rubber mixtures based on various rubbers. It was revealed that the introduction of tanning dust as filler into the composition of rubber mixtures affects the properties of the vulcanizing reagent [20]. The tensile strength of leather and rubber waste fibre composites is increased to 25 parts per hour, and tensile and elongation at break are reduced within the acceptable range to 12.5 parts per hour for styrene-butadiene rubber and 15 parts per hour for acrylonitrile butadiene rubber [21]. For rubbers based on natural, nitrile, chloroprene and butadiene rubbers, when unmodified leather dust is introduced into them, a decrease in tensile strength and hardness was noted [22]. However, no research has been carried out on the modification of leather waste. A mixture of solid leather waste and waste paper binder is used to make fuel briquettes [23]. There is the prospect of improving the fire safety of paper by adding fire-resistant leather [24]. Composite dust-proof boards are made based on leather dust with the addition of cotton and jute fibres [25]. Various methods are known for modifying and dechroming waste chrome-tanned leather. Modification of the skin with iron significantly improves the adsorption of hexavalent chromium, the adsorption capacity increases to 51 mg of chromium (VI) per gram of skin. Organically stabilized skin was used as an adsorbent to remove the colour from wastewater depending on the concentrations of dye and neutral salt, pH [26]. A known method includes washing the waste with water, modification with a mixture of reagents that form coordination complexes with trivalent chromium ions, washing with water, modification with an oxidizing mixture to transform Cr^{3+} into a soluble form Cr^{6+}, additional washing water, purification and deionization from Cr^{6+} [27]. According to another method, after washing the waste with water, acid modification is performed, then modification with an oxidizing mixture consisting of a 2% solution of caustic soda and perhydrol, washing with running water until the chromium oxide content in the waste is 0.4% [28]. Processing of chrome chips in an oxidizing solution is carried out at a temperature of 18-20 ^{o}C, liquid coefficient equal to 5, for 15-20 minutes of periodic stirring [29]. It has been discovered that the hydrolysis of chrome shavings, which occurs mainly in certain places of collagen fibres, makes it possible to reuse them, for example, for the production of synthetic tanning agents [30]. One of the advantages of this direction of processing chromium-containing collagen waste is the possibility of using hydrolysates without preliminary purification from chromium compounds. On the contrary, the presence of a tanning agent in the final product helps to increase the heat resistance of the semi-finished product and makes it possible to obtain a material with high elastic-plastic characteristics [31]. When using scraps of chrome leather, the crushed waste is mixed and, under the influence of temperature and pressure, their thermoplastic properties are increased. Next, the resulting plates are used to form inserts for the bottom of shoes in the production of polyurethane soles [32].

Replacing primary cellulose fibres when producing paper with waste paper and other fibrous waste makes it possible to obtain a fundamentally different material compared to traditional paper [33]. The formation of sheets from a composition of cellulose, waste paper, polymers and fillers can be carried out using the traditional method of paper production or the injection moulding method for processing polymers [34]. Thus, tanning waste is used in the production of shoes, leather, rubber, construction and composite materials. Despite this, a huge amount of waste accumulates at tanneries, occupying useful space, and causing damage to the ecology of the environment. To date, the processes of preliminary modification of waste and processes at the interface, which significantly affect the structure and properties of polymer materials including skin waste, have not been sufficiently studied. The issues of using leather waste in the production of environmentally friendly, biodegradable packaging paper and cardboard have not received due attention from researchers; these issues remain unresolved. Meanwhile, targeted recycling of tanned leather waste can help solve an important environmental and economic problem. The purpose of this work is to study the possibility of obtaining a modified fibrous mass of tanned and untanned leather waste, and waste paper for the production of packaging paper and cardboard with improved properties. To achieve the goal, an alkaline modification of chrome shavings was carried out, a modified fibrous mass was obtained based on waste-tanned, untanned leather and waste paper, the electrokinetic properties of the fibrous suspension, microstructure, morphology and physical and mechanical properties of paper were determined.

EXPERIMENTAL

Materials

Crushed chrome-tanned cattle leather waste (chrome shavings) was provided by a tannery in Tashkent (Uzbekistan). Chrome shavings are a plate-dispersed mass of light green colour (small scales), which are obtained during the production of leather tanned using various methods and salts. Particle sizes on average do not exceed 4 - 6 mm in width, 12 - 15 mm in length, and thickness usually ranges from 0.5 to 1 mm. MS-6 class waste paper was obtained from cardboard waste by grinding to a fineness of 60 - 65 degrees Schopper-Riegler (°SR). Acrylic emulsion (AE), a product of emulsion polymerization of methyl acrylate, is a milky-white liquid, miscible with water in any proportions, produced at the Navoiazot JSC enterprise (Uzbekistan).

The collagen-containing solution is obtained from raw cattle hide waste [16,17]. Untanned leather waste, cleared of wool, was also provided by a tannery in Tashkent. Pieces of peeled skin measuring 3-4 mm were placed in a container, and a 3% sodium hydroxide solution was poured on top at a mass ratio of 1.2:2. After the skin had swollen for 12 - 24 hours, the container with the solution was placed in a thermal cabinet at a temperature of (50 ± 1) °C, and the contents of the container were stirred from time to time. After the formation of a homogeneous mass, the solution was sifted through a sieve with mesh sizes of 0.05 - 0.1 mm, and neutralized with acetic acid to pH = 6.8 ± 0.2.

Obtaining a modified fibrous mass

To impart elasticity and resilience to the fibres, chrome shavings were subjected to alkaline modification. Alkaline modification is carried out in a 1 - 5 per cent solution of sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3). The waste is immersed in an alkaline solution with a bath modulus of 1:10 and kept at room temperature for 2.0 - 2.5 hours. Leather fibres were removed from the alkali solution and washed in water until neutral. The fibres were separated from the solution on a sieve, placed in a container with water and left for a day. The fibres were then taken out of the water again and dried. 300 g of leather fibres are mixed with 10 litres of water and ground in a laboratory mill - hydro thinner “YANTE 23L” (China) to a grinding degree of 60 - 65 °SR. Primary conclusions about the effect of modification on the properties of chrome shavings were made by the organoleptic method. Chromium shavings modified in a 2-3% NaOH solution became more resilient and elastic than the sample modified in a Na_2CO_3 solution. After modification in a 4 - 5% NaOH solution, a cotton wool-like mass was obtained, which after drying turns into a hard plastic mass. A modified fibrous mass of chrome shavings, waste paper and sizing polymer was used to cast packaging paper on a laboratory paper-making machine “CYEEYO-2.2” (China). An acrylic emulsion or collagen-containing solution is introduced as a sizing polymer. The acrylic emulsion has high adhesive properties concerning cellulose [35], collagen combines well with both cellulose and chrome shavings. The paper sheet is formed from a 3% fibrous suspension, dried at a temperature of (105 ± 5) °C, and then calenderer using a roller press.

Characterizations

The degree of grinding of the fibrous mass was determined using the Schopper-Riegler laboratory complex (China). The electrokinetic potential of the fibre suspension was measured by the percolation potential method using a zeta potential system (SZP 06 BTG Mtek Gmbh). The assay suspension had a fibre concentration of less than 3%. If the concentration was above 3%, dilution was made with the filtrate of the analyzed suspension. The samples for zeta potential measurements were kept at a constant temperature. The structure of the samples was determined using infrared spectroscopy with Fourier transform (FT-IR) Nicolet IN10 Company Thermo Fisher Scientific (USA) in the scanning range of 500 - 4000 cm^{-1}. The pH of the solutions was determined using an automatic titrator "EasyPlus™ Titration". The study of surface morphology and elemental analysis of samples of fibrous mass was carried out using a scanning electron microscope "JSM-IT200LA InTouchScope™" (Japan) with an application for recording an energy-dispersive spectrum (SEM-EDS). The thermal properties of the samples were studied by thermogravimetry (TGA) and differential thermal analysis (DTA). The studies were carried out on a Netzsch Simultaneous Analyzer 409 PG (Germany), equipped with K-type thermocouples and aluminium crucibles. All measurements were carried out in an inert nitrogen atmosphere, in the range of 0 - 600 °C, with a heating rate of 10 K/min. The mass of the samples is 20 - 30 mg, the measuring system is calibrated against a set of standard substances KNO_3, In, Bi, Sn, Zn, CsCl. Sampling, preparation of an average sample and determination of the physical and mechanical properties of paper were carried out in accordance with GOST 13525.1-79 (ISO 1924) "Semi-finished fibrous products, paper and cardboard. Methods for determining tensile strength and tensile elongation." The number of double bends was determined according to the ISO 5626 standard. The surface density was determined according to the ISO 534 standard. Test specimens (strips) are cut in one of the directions in accordance with the instructions in the relevant product standards. The width of the strips should be in millimeters: for paper – 15 ± 0.1; The length of the strips is 150 mm with an allowance for strengthening in the clamps.

RESULTS AND DISCUSSION

Chemistry of modification processes

Electrokinetic properties

The formation of a paper sheet is largely determined by the colloidal chemical properties of the fibrous suspension. One of the parameters that determines these properties is the electrokinetic potential of dispersed particles. Electrokinetic or ζ (zeta) potential (EP) is the potential that arises at the interface between the adsorption and diffusion layers in dispersed systems during their relative movement in an electric field. EP reflects the properties of the electrical double layer (EDL) and is determined experimentally from electrokinetic phenomena [36]. The value of EP is significantly influenced by the nature, molecular weight, and concentration of the dispersed phase – the polymer [37]. When particles have a strongly positive or strongly negative charge, there is also a strongly repulsive electrostatic interaction between the particles. This prevents the particles from approaching each other and forming agglomerates. According to the DLVO theory, when particles are close to each other, van der Waals forces, which are based on dipole-dipole interactions, come into play. These forces have an attractive effect. If the EP is close to zero, the repulsive effect of the EDL is small, and the coagulation of dispersed particles is more likely. EC is not a direct measure of variance stability, but it provides a good prediction of stability. Because EP analysis is much easier and faster to perform than stability measurements, its value is often used to assess the quality of variance. An EP value of 30 mV (positive or negative) can be considered a characteristic value for the conditional separation of low-charged and highly-charged surfaces. The more EP, the more stable the colloid. If the potential is between 0 and ±30 mV, the system has poor stability (coagulation or flocculation is possible). If the system potential is greater than ±30 mV, it has good stability.

A change in the composition and concentration of the electrolyte leads to a shift in the EP [38]. As the measurement results showed, after the alkaline modification of skin waste, the electrokinetic properties of the fibrous suspension changed significantly (Table 1).

Table 1. Electrokinetic properties of a suspension of chrome shavings

Properties	Suspension of unmodified chrome shavings	Suspension of modified chrome shavings at a concentration of NaOH/Na_2CO_3, %				
		1	2	3	4	5
Electrokinetic potential, mV	54.6	120.8/98.3	142.1/98.9	145.4/106.6	148.3/110.8	129.1/109.5
Electrical conductivity, µS/cm	14.2	1.13/0.48	2.07/0.55	2.15/0.67	2.21/0.79	1.64/0.87

As can be seen from Table 1, after modification with an alkali solution to a concentration of 4%, the EP increases, and at an alkali concentration of 5%, it begins to decrease. A suspension of unmodified chrome shavings has greater electrical conductivity compared to a suspension of modified chrome shavings. The unmodified chrome shavings retain the electrolytes used in the pre-modification and tanning processes of raw leather. During washing of the modified chrome shavings, these electrolytes are removed from the sample. Judging by the values of electrokinetic parameters, a solution of 2% sodium hydroxide turned out to be sufficient for alkaline modification. At an alkali concentration of 5%

and higher, the properties of the suspension deteriorate. Modification of chrome shavings with a solution of Na_2CO_3 does not lead to a significant change in the organoleptic properties of chrome shavings and the electrokinetic properties of the suspension. The pH value of the used NaOH solution is within pH=12.7 - 13.0 (strongly alkaline environment), and the Na_2CO_3 the solution is within pH=10.8 - 11.5 (weakly alkaline environment). To change the microstructure of chrome shavings, a highly alkaline environment is required; the alkalinity of the Na_2CO_3 solution turned out to be insufficient for the expected changes. The change in the electrokinetic properties of the suspension is due to a change in the microstructure of chrome shavings as a result of alkaline modification, which was recorded using FT-IR.

FT-IR of chrome shavings

The FTIR of shavings (Figure 1) shows a typical spectrum of collagen [39]. In the FT-IR of chromium shavings, absorption bands characteristic of stretching (ν) and bending (δ) vibrations of bonds of protein substances were detected: at 3292 cm^{-1} – ν_{N-H}, ν_{O-H}; at 3076 and 2987 cm^{-1} – ν_{C-H}, at 1628 cm^{-1} – $\nu_{C=O}$ (amide I band); at 1539 cm^{-1} – δ_{N-H} (amide II band); at 1446 cm^{-1} – ν_{C-H}; at 1335 and 1235 cm^{-1} – ν_{C-N}+δ_{N-H} (amide III band); at 1202-973 cm^{-1} – ν_{C-N}, ν_{C-O}.

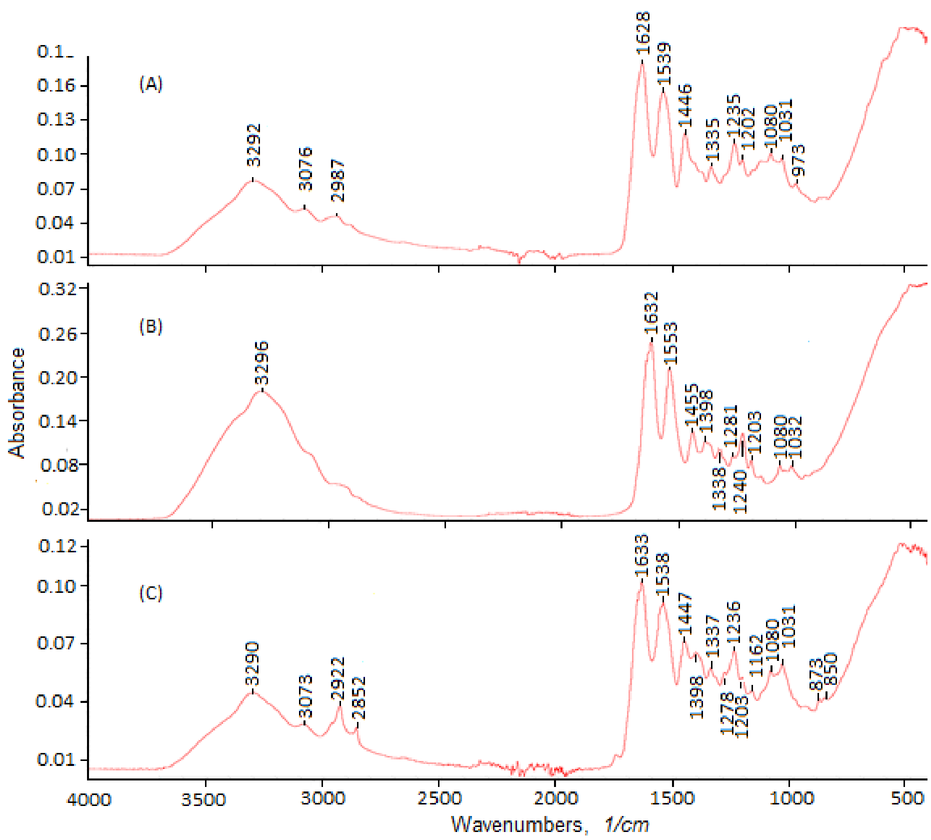


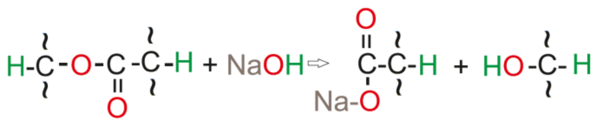
Figure 1 FT-IR of chrome shavings: unmodified (A), modified in 2% caustic solution (B), modified in 5% caustic solution (C)

The following changes were detected in FT-IR of chromium shavings modified with a 2% alkali solution:

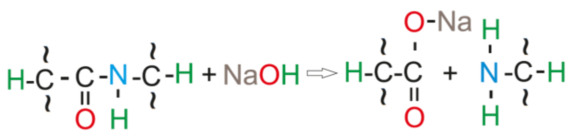
1. An increase in the intensity and width of the absorption bands of stretching vibrations ν_{N-H}, ν_{O-H}, which is a consequence of an increase in the number of hydroxyl and amino groups, as well as intermolecular hydrogen bonds;
2. The absorption bands shift mainly to the high-frequency region;
3. The appearance of new absorption bands at 1398 and 1281 cm^{-1}.

The detected changes confirm the values of electrokinetic parameters and indicate the formation of new polar functional groups as a result of partial hydrolysis of skin collagen. An increase in the number of charged groups leads to an increase in the electrokinetic potential on the surface of the suspension particles. In a sample of chrome shavings modified with a 5% alkali solution, the degree of change in the FT-IR spectrum decreases, i.e. this spectrum is close to the spectrum of the unmodified sample. As the alkali concentration increases, the hydrolysis of skin collagen increases, and, firstly, closely located opposite charges begin to be neutralized. Secondly, due to an increase in particle dispersion, the specific surface area and, accordingly, the total surface energy of the particles increases. All this leads to a decrease in EP and stability of the fibre suspension. During the modification of lame shavings with an alkali solution, partial hydrolysis of the cross-linked structure of the protein macromolecule occurs; the skin becomes looser, with smaller particle sizes. Sodium hydroxide leads to the rupture of bonds of a protein macromolecule according to the following schemes.

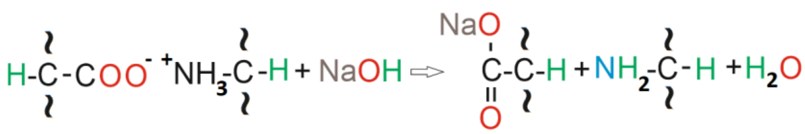
Hydrolysis of ester bonds:



Hydrolysis of peptide bonds:



Hydrolysis of salt bridges:



As a result of such processes, the adsorption of potential-determining ions on the surface of dispersed phase particles increases. A change in the ionic density of the adsorption layer with a simultaneous decrease in particle size contributes to an increase in the EC of the system. At the same time, the total number of ions in the diffusion layer decreases, because chrome shavings after alkaline modification are thoroughly washed. This leads to a decrease in the electrical conductivity of the system.

TGA and DTA of chrome shavings

The thermal properties of chrome shavings samples were studied. The DTA method provides information not only on the thermal properties but also on the nature of the modification processes of composites. Figure 2 shows the TGA and DTA dependences of chrome shavings samples.

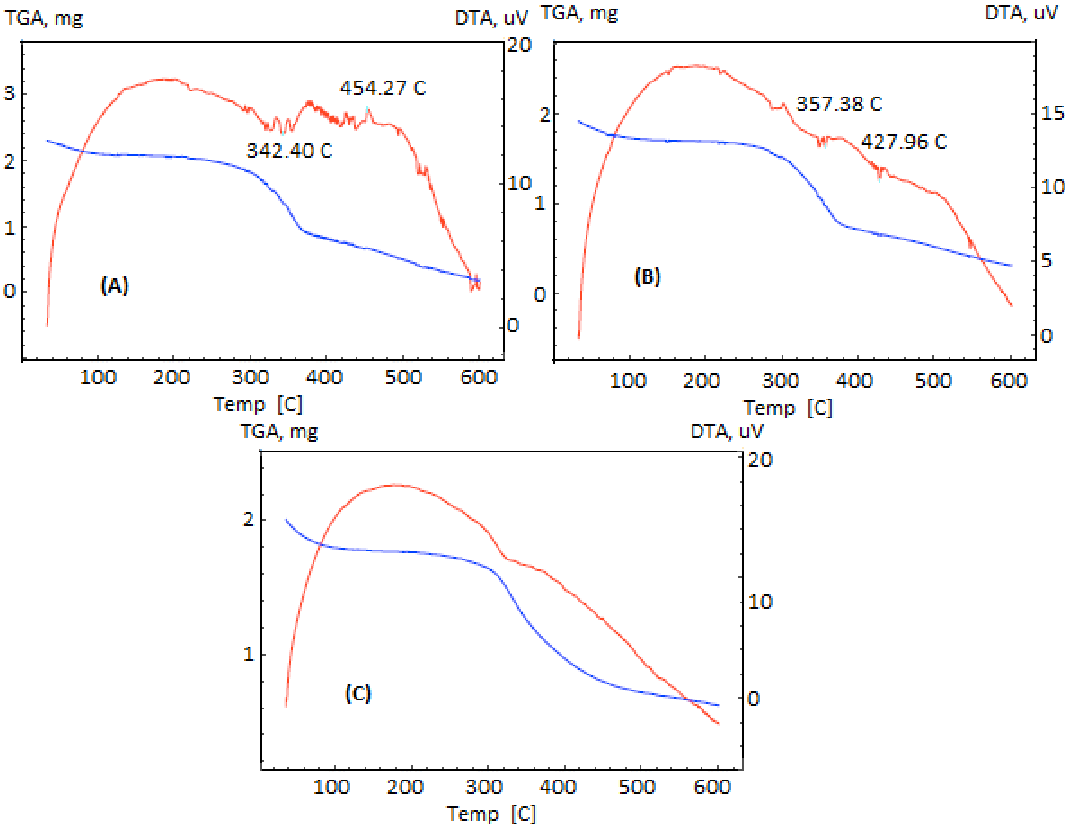


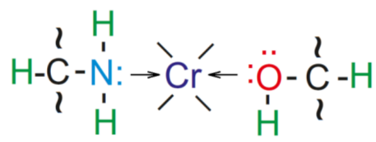
Figure 2. TGA and DTA curves of chrome shavings unmodified (A), modified in 2% solution (B) and 5% solution (C) of sodium hydroxide

The TGA and DTA curves of three samples of chrome shavings have approximately the same shape. The DTA curve of the unmodified sample contains peaks of endothermic and exothermic heat effects. In the modified samples, the magnitude of heat effects decreases, then disappears at an alkali concentration of 5% (Table 2). The first stage of the process of thermal decomposition of an unmodified chrome shaving sample begins at room temperature and ends at 227 °C; the modified chrome shavings end at a higher temperature of 243 - 247 °C. The loss of mass in the first stage in the range of 12 - 13.5% occurs, apparently, due to the release of absorbed water from the samples. The second TGA stage is characterized by intense mass loss as a result of the processes of thermochemical decomposition and chemical condensation. The total weight loss of samples up to 600 °C decreases in the following series: unmodified shavings (92%), modified in a 2% (84%) and 5% (69%) alkali solution. Judging by the data obtained, the alkali modification process improves the thermal properties of chrome shavings. The process of collagen hydrolysis reported in previous studies does not lead to a significant decrease in molecular weight and a corresponding deterioration in the properties of chrome shavings.

Table 2. TGA and DTA parameters of chrome shavings

TGA processes				DTA processes		
Unmodified						
Start, °C	33.29	226.89	382.46	Start, °C	301.74	350.41
End, °C	226.89	382.46	601.38	Peak, °C	342.40	354.27
Weight Loss, %	-12.10	-50.56	-29.23	End, °C	371.48	364.20
		-91.89		Heat effect, J/g	-184.28	13.56
Modified in 2% solution of sodium hydroxide						
Start, °C	33.69	247.34	388.76	Start, °C	343.36	426.02
End, °C	247.34	388.76	601.39	Peak, °C	357.38	427.96
Weight Loss, %	-13.42	-48.67	-22.39	End, °C	360.89	431.06
		-84.48		Heat effect, J/g	-15.49	-7.83
Modified in 5% solution of sodium hydroxide						
Start, °C	35.99	242.88	388.51	Start, °C	-	
End, °C	242.88	388.51	601.75	Peak, °C	-	
Weight Loss, %	-13.44	-35.44	-20.31	End, °C	-	
		-69.19		Heat effect, J/g	-	

Peaks were found in the DTA curves of unmodified chrome shavings: the first at 342.4 °C with a rather large endothermic effect (-184.28 J/g), the second at 354.27 °C with an insignificant exothermic effect (13.56 J/g). The DTA curve of chrome shavings modified in a 2% alkali solution reveals two minor endothermic heat effects. On the DTA curve of a sample modified in a 5% alkali solution, heat effects are almost not noticed. In this case, the presence of heat effects indicates the incompleteness of the crosslinking reactions during the tanning of the hide. These reactions continue in unmodified chrome shavings when exposed to high temperatures. Alkaline modification contributes not only to the appearance of new polar groups but also to an increase in the degree of cross-linking of the product. This is confirmed by the TGA results: the less weight loss, the more coke residue, i.e. a cross-linked product that does not decompose even at high temperatures. New functional groups on the macromolecules of modified chromium shavings turn out to be spatially accessible to chromium ions and new coordination bonds are formed between them:



FT-IR of composite paper

To clarify the nature of the interaction of modified chrome shavings with waste paper cellulose and sizing agent, FT-IR spectra of composite paper were taken (Figure 3).

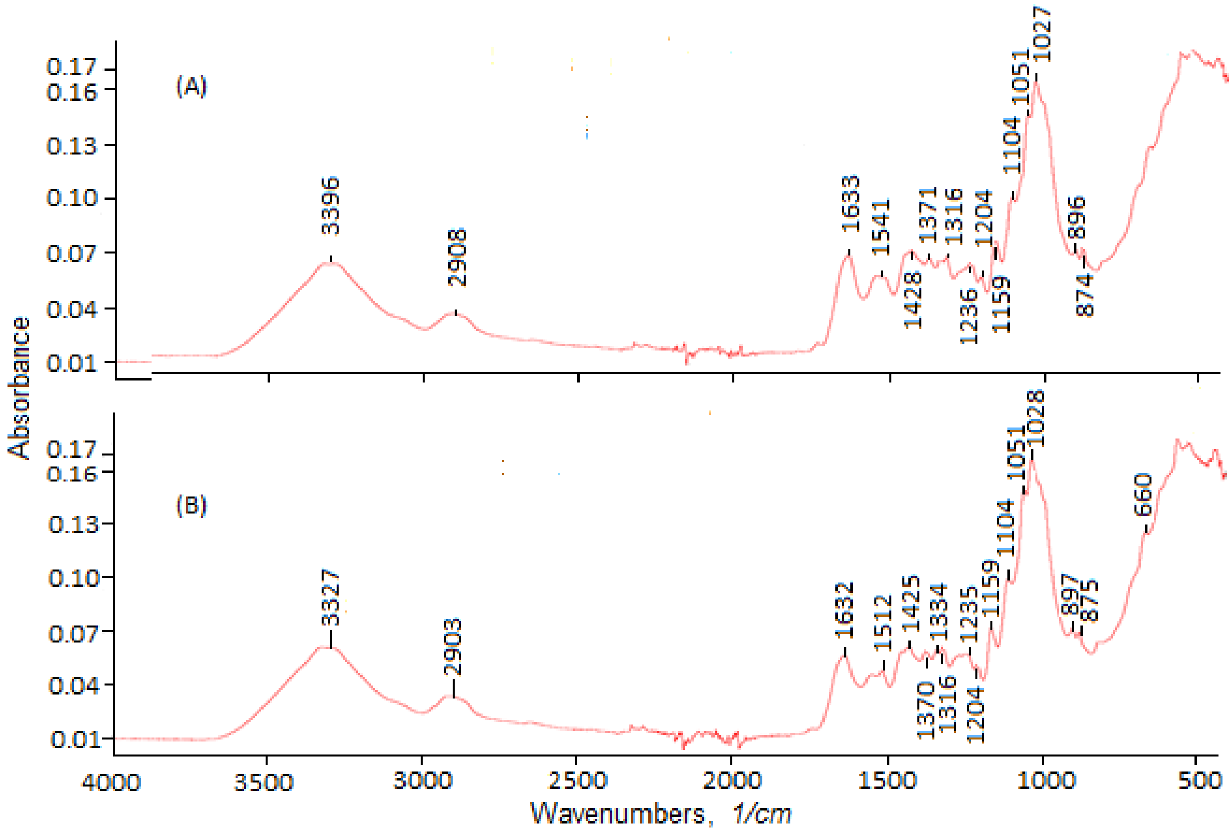


Figure 3. FT-IR of a composite paper made from waste paper and modified chrome shavings at a mass ratio of 50:50, using an acrylic emulsion (A) and a collagen-containing solution (B)

The presence of hydroxyl, methylene groups and ether bonds in the cellulose molecule should lead to the similarity of the spectra of composite paper with the spectra of chrome chips. As expected, the spectrum of the paper revealed approximately the same absorption bands as those found in chromium shavings, except for some changes. In the wavenumber region of 1630 - 850 cm^{-1}, the number of absorption bands increases and several new bands appear, which relate to vibrations of the bonds between cellulose and the sizing agent. Judging by the FT-IR between the modified chromium shavings and waste paper cellulose, interaction occurs at the level of intermolecular hydrogen bonds, and not covalent or ionic bonds.

TGA and DTA of composite paper

TGA and DTA studies of composite paper were carried out (Figure 4, Table 3).

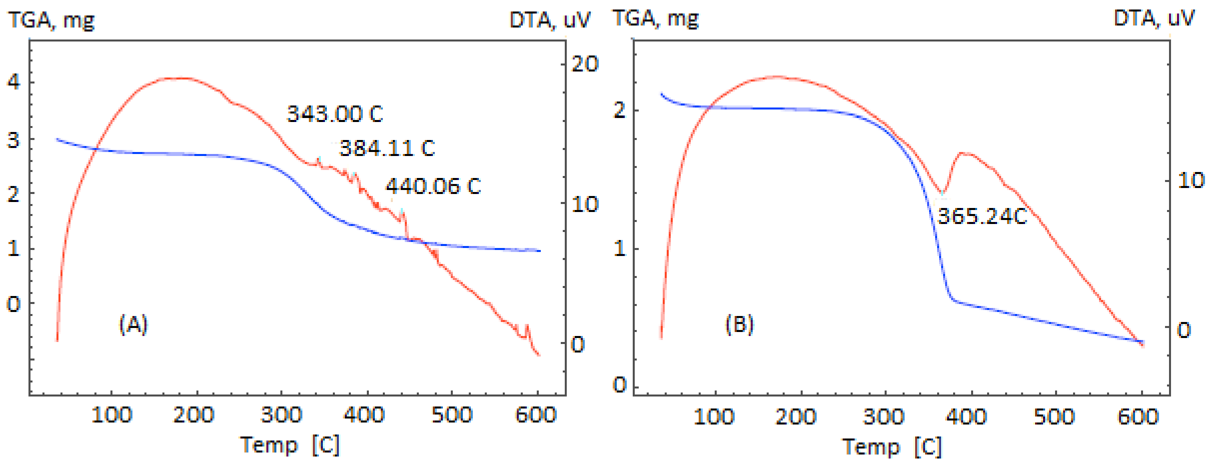


Figure 4. TGA and DTA curves of composite papers obtained from a mixture at a mass ratio of waste paper: modified chrome shavings = 50:50: with acrylic emulsion (A), with collagen-containing solution (B)

Table 3. TGA and DTA parameters of composite papers obtained from a mixture with a mass ratio of waste paper: modified chrome shavings = 50:50

TGA processes				DTA processes			
			Sizing agent – acrylic emulsion				
Start, °C	35.10	225.24	380.26	Start, °C	337.93	380.72	437.71
End, °C	225.24	380.26	601.20	Peak, °C	343.00	384.11	440.06
Weight Loss, %	-10.06	-42.31	-15.35	End, °C	347.57	392.66	448.36
		-67.72		Heat effect, J/g	4.21	9.85	13.15
			Sizing agent – collagen-containing solution				
Start, °C	35.54	234.65	388.78	Start, °C		258.41	
End, °C	234.65	388.78	601.66	Peak, °C		365.24	
Weight Loss, %	-6.11	-65.35	-13.16	End, °C		388.23	
		-84.62		Heat effect, J/g		-451.60	

In the paper with an acrylic emulsion up to 225.24 °C, about 10% of the mass is lost, while with a collagen-containing solution up to 234.65 °C the weight loss is much less - about 6%. In the second stage of decomposition, the bulk of the samples are lost, especially paper with collagen: up to a temperature of 388.78 °C, the mass decreases by another 65.35%. In general, the weight loss of paper with collagen is greater than that of the first. These data are somewhat consistent with the DTA results. The DTA curve of paper with acrylic emulsion revealed minor exothermic effects, which most likely characterize the process of adhesion of the sizing agent to the fibres of chrome shavings and cellulose. The DTA curve of collagen paper has a peak at 365.24 °C with a large endothermic effect of -451.6 J/g. Here not only adhesion takes place, but to a large extent chemical condensation with the release of low molecular weight products. Hence, there is a significant loss of sample mass in this temperature range. Thus, TGA and DTA provide fairly complete information about the interaction of packaging paper components during the process of alkaline modification, paper production and thermal exposure.

Morphology and elemental composition

During alkaline modification, the surface morphology of chrome shavings changes significantly (Figure 5).

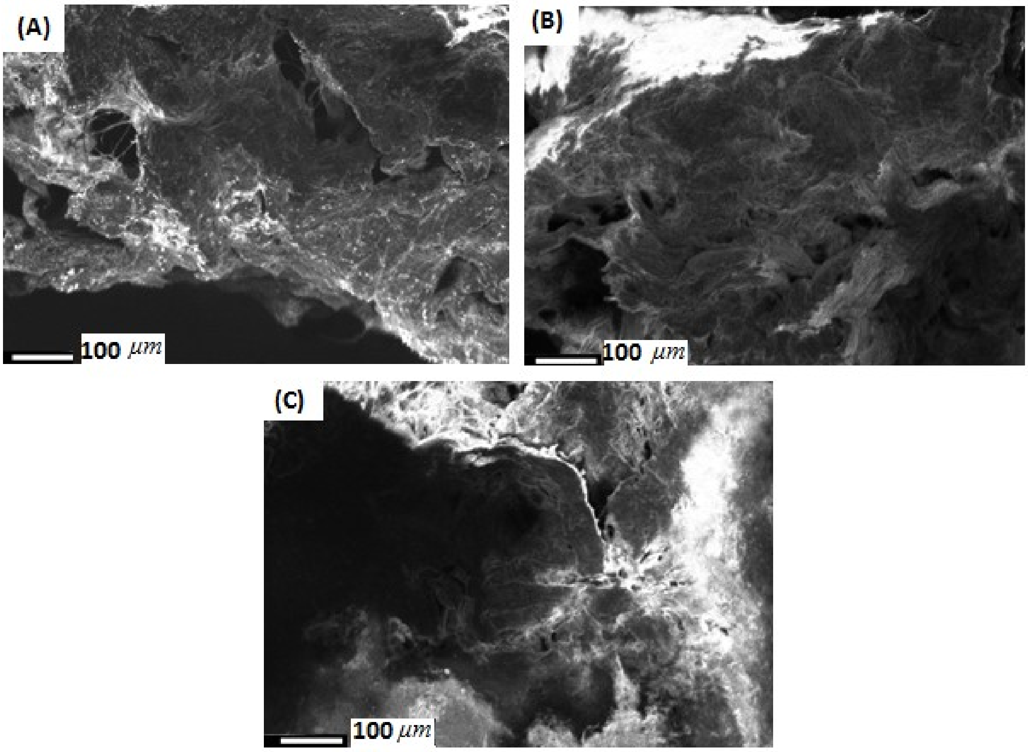


Figure 5. SEM images of the surface of chrome shavings particles: unmodified (A), modified in a 2% alkali solution (B) and a 5% alkali solution (C)

As can be seen from Figure 5, pieces of unmodified chrome shavings have a rough surface with micropores of uncertain shape and size, and the presence of by-products is noticeable. The higher roughness of the top side stems from the sheet-forming process [40]. After modification in a 2% alkali solution, the surface of the pieces is smoothed, and by-products are almost completely removed. After modification in a 5% alkali solution, the pieces are flattened, the surface takes on a tortuous shape, and the chrome shavings themselves become harder and more brittle. Deeper destruction with a 5% alkali solution worsens the surface morphology and properties of chrome shavings.

Figure 6 shows the SEM-EDS spectra of the scanned surface of chromium shavings samples.

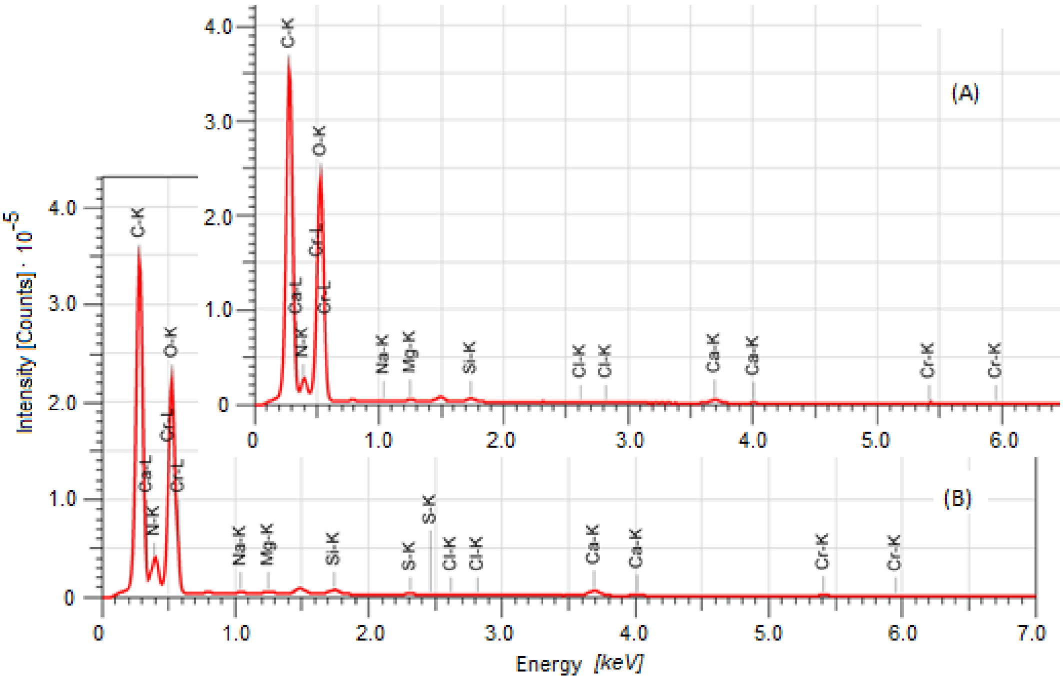


Figure 6. SEM-EDS of chrome shavings: unmodified (A), modified in 2% alkali solution (B) and 5% alkali solution (C)

Mainly three elements were found in chrome shavings: carbon (37.05 ± 0.02%), oxygen (36.71 ± 0.04%) and nitrogen (22.21 ± 0.03%); sodium (1.54 ± 0.01%), chlorine (1.32 ± 0.00%), chromium (0.59 ± 0.00%) and sulfur (0.52 ± 0.00%) were found in smaller quantities; and traces were also found magnesium, potassium, calcium and silicon. As a result of alkaline modification with a 2% solution, the percentage of carbon, oxygen and nitrogen increases slightly, while at the same time, sodium and chlorine are almost completely removed from the surface of the sample. After modification in a 5% alkali solution, the percentage of carbon increases significantly, oxygen decreases slightly, and nitrogen decreases significantly. This once again confirms the deeper hydrolysis of chrome shavings with the release of nitrogen in the form of ammonia and oxides. At this time, the surface of the shavings is "bare" and minor signals of secondary elements appear. Samples of experimental papers were obtained by mixing chrome shavings and waste paper modified with a 2% alkali solution at their different mass ratios. SEM-EDS studies of paper obtained with a mass ratio of chips:waste paper = 50:50 were carried out. Two samples of paper were studied, in the first of them an acrylic emulsion was used as a sizing agent, and in the second a collagen-containing solution of unduplicated hide waste was used. At first glance, a paper sheet is formed by entangling waste paper cellulose fibres and chrome shavings (Figure 7).

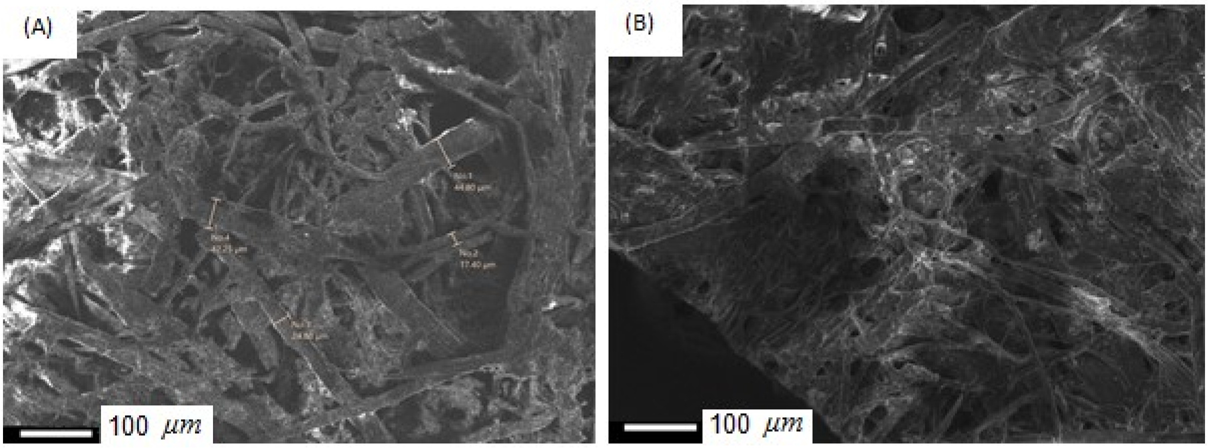


Figure 7. SEM images of the surface of composite papers obtained from a mixture with a mass ratio of waste paper: modified chrome shavings = 50:50: with acrylic emulsion (A), with collagen-containing solution (B)

As can be seen from Figure 7, when acrylic emulsion is introduced as a sizing agent, individual cellulose fibres and shavings are visible. Chromium reacts with collagen in stages, beginning with the interaction of the collagen carboxylic groups with the chromium salt [41]. When a collagen-containing solution is introduced, the boundary between the fibres and the sizing agent is smoothed out, and cellulose fibres can be distinguished, but the chrome shavings fibres are combined with collagen. This was to be expected; the collagen-containing solution and the chrome shavings contain the same polymer – collagen protein. Paper samples differ in the percentage composition of carbon, oxygen, and especially nitrogen (Figure 8).

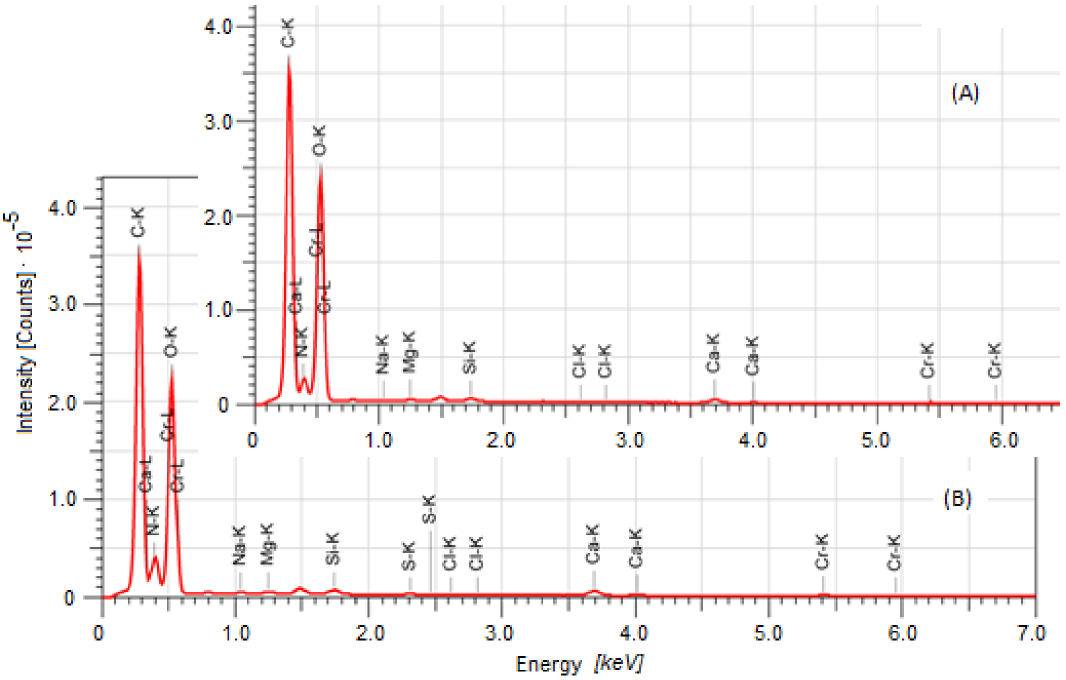


Figure 8. SEM-EDS spectra of papers obtained from a mixture with a mass ratio of waste paper: modified chrome shavings = 50:50: with acrylic emulsion (A), with collagen-containing solution (B)

It is noteworthy that in paper with collagen-containing solutions, the amount of nitrogen is almost twice as high (11.99 ± 0.03%) than in paper with acrylic emulsion (6.13 ± 0.03%). It must be borne in mind that, unlike acrylic emulsion, collagen contains nitrogen (approximately 15-20%). It follows that the protein from the collagen-containing solution covers the surface of the fibres, both processed chrome shavings and waste paper and perfectly performs the function of a sizing agent. The following studies will show whether this will affect the physical-mechanical properties of composite paper.

Physicomechanical properties

Typically, alkaline modification of the fibrous mass improves the mechanical properties of products, while acid modification leads to deterioration [42]. The physical-mechanical properties of paper are assessed primarily by the breaking length and fracture index or the number of double bends, but other characteristics are also important. Figure 9 shows the dependence of these indicators on the composition of the manufactured versions of experimental papers using an acrylic emulsion and a collagen-containing solution as a sizing agent. As expected, based on the data in Figure 9, it can be stated that in all respects, the alkaline processing of chrome shavings has a clear advantage. When using unmodified chrome shavings in composite paper, the introduction of a sizing agent does not contribute to achieving satisfactory strength results. When using modified chrome shavings, both in the presence of an acrylic emulsion and a collagen-containing solution, a significant and approximately equal improvement in surface density, breaking load and breaking length is observed. In terms of the number of double bends, the collagen-containing solution has some advantages over the acrylic emulsion. This is facilitated by the complete chemical compatibility of the nature of the chrome shavings polymer and the sizing agent.

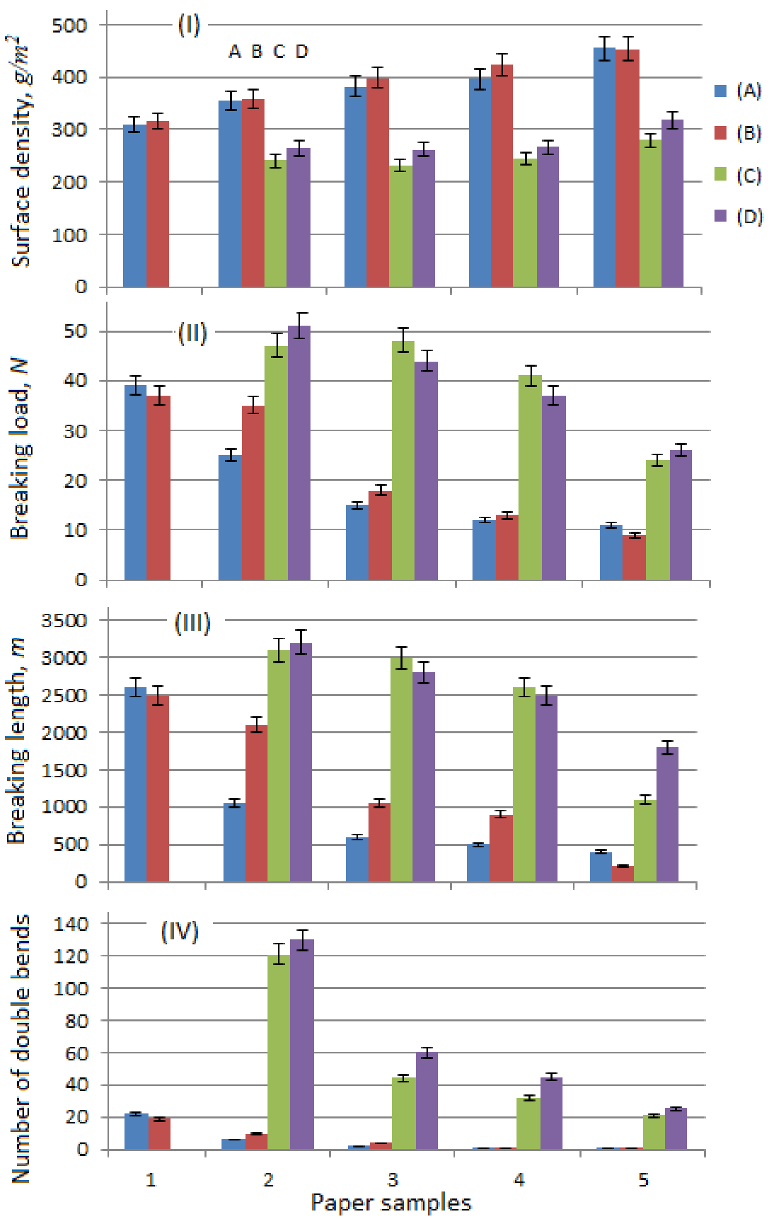


Figure 9. Dependence of surface density (I), breaking load (II), breaking length (III) and number of double bends (IV) of paper obtained from unmodified (A, B) and modified (C, D) chrome shavings with the introduction of acrylic emulsion (A, C) and collagen-containing solution (B, D) on the ratio of fibrous components: waste paper: chrome shavings = 1) 100:0; 2) 75:25; 3) 50:50; 4) 40:60; 5) 25:75

CONCLUSIONS

An effective method for alkaline modification of untanned and chromium-containing tanned leather waste is proposed. By dissolving the rawhide in a 2-3% sodium hydroxide solution, a collagen-containing sizing solution was obtained. Chromium-tanned leather waste modified in an alkaline solution can be a significant raw material base for the production of packaging paper and cardboard. The high electrokinetic potential of a fibrous suspension of modified leather and waste paper ensures not only its stability but also improved surface morphology and high physical and mechanical properties of packaging paper obtained. Alkaline modification of chrome shavings promotes the appearance of new polar groups, while simultaneously increasing the degree of cross-linking of the product. Thermal effects during heating of the leather-waste paper-acrylic emulsion composite characterize the process of adhesion of the sizing agent to the fibres. When a collagen-containing solution is used as a sizing agent, not only adhesion occurs, but to a large extent chemical condensation with the release of low-molecular-weight products. The intermolecular interaction of the modified protein with cellulose, new coordination bonds of chromium ions with the nitrogen and oxygen atoms of the fibres, and sizing the fibrous mass with an acrylic emulsion or collagen-containing solution leads to improved performance properties of packaging paper: an increase in strength up to 23%, bending resistance up to 6 times, with a decreased mass (surface density) by at least 16%.

Author Contributions

Conceptualization – Rafikov A, Kadirova N and Jurayeva G; methodology – Kadirova N and Jurayeva G; formal analysis – Rafikov A; investigation Rafikov A; resources – Kadirova N; writing-original draft preparation – Rafikov A; writing-review and editing – Kadirova N and Jurayeva G. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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