Optimization of Leather Filling Composition Containing SiO_2 Nanoparticles

by

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Abstract

The global leather industry is looking for a cleaner leather processing technology to overcome its negative environmental impact. As an alternative to conventional processing, an eco-friendly filling composition based on fumed silica was developed and tested for the production of leather materials. Polycriterial optimization of the filling composition containing silica nanoparticles was conducted using the McLean-Anderson method by considering the type of mathematical model of the process "content-properties". For optimization of the experimental conditions a multithreaded program based on calculation of informative and dispersive matrices and their determinants was developed. The optimal formulation of filling composition for the production of flexible leather materials was established and experimentally tested. The developed technology yields leather materials with increased volumetric yield and elasticity and more homogeneous microstructure when compared to the current company technology. The mathematical modelling discussed in the paper can be also used to solve similar problems for other technological processes.

Introduction

While improving existing and developing innovative technologies for the production of high-quality leather materials[1], a prerequisite condition is to find an effective set of eco-friendly reagents for leather production[2,3] and to optimize reagent formulations using mathematical modeling. During multistep processing of leather materials, filling step plays an important role given that final properties of processed materials are determined by the formulation of filling composition. Different mathematical modeling techniques, which consider the peculiarities of the chemical ingredients of the composition, have been used to compute and optimize the filling composition. While solving this problem, significant difficulties arise due to the limited content of ingredient in the composition which is determined by its physical and chemical properties.

In mathematical modeling of technological compositions in form of "content-properties", methods such as simplex-lattice, simplex-centroid, or D-optimal designs are usually used [4,5]. However, sometimes there are compositions in which component fractions cannot be changed continuously in a whole range from 0 to 1, for example, due to the limited solubility of some ingredients. In such cases, methods of imposition of restrictions on the factors are applied. For example, McLean-Anderson method [6], D-optimal design, or pseudo-components method can be used in such situations. However, the well-known McLean-Anderson method for design of the experiment does not consider a type of mathematical model and it often results in getting a degenerate plan when choosing experimental points from a candidate set of points. Direct design of the experiment according to the Fedorov theory does not always allow defining the experimental area/region which indicates a non-optimality of the method.[7]

For experiment optimization of silica-silver nanosupplement content in polypropylene fibers, a simplex-lattice design with pseudo-components using a Harrington criterion was applied.[8] Herewith, a mathematical model of "content-properties" of modified filaments made it possible to compute the optimal content of binary polypropylene-nanosupplement composition which provides high mechanical strength of yarns and their bactericidal capacity. Despite that this method allows displaying an optimal area geometrically, it is not possible to choose the experimental set of parameters (which has to be similar to simplex for a given constrains on mixture ingredients) and due to the loss of a set of points.

A simplex-lattice method is used for modeling the composition of ternary integumentary polymer compositions and composition optimization.[9,10] Herewith, a mathematical model

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of composition of polyvinyl alcohol – urethane fluoropolymers – toluene diisocyanate was obtained using the modified Scheffe design by applying polynomial of the 4th order. An optimized composition of exopolysaccharide-polyacrylate-polyurethane system was computed by using Kiefer D-optimal design. The application of optimized composition results in increased physical and mechanical properties of final leather materials. But despite of mentioned advantageous it was impossible to get the coverage of pure components because the design described in these publications does not include restrictions on the components.

With the help of the linear programming method using a computer program Simplex Win, a composition of the grain and fruit mixture of 9 ingredients was optimized by minimizing cost ratios and caloricity [11]. However, this method cannot be applied to optimize the composition because it does not consider the content condition – a sum of all ingredients must be equal to one. For composite materials based on epoxy resin ED-20 and polyethylene polyamine the content of two-component filler composition based on aluminum oxide and crystalline boron was optimized in order to form a protective coating surface layer with enhanced physical and mechanical properties [12]. The optimal content of filler was determined by mathematical modeling and using orthogonal central composite design [12]. However, this method is only effectively used in "technology-properties" modeling.

Simplex-lattice modeling method can be used as well [13,14]. Studying the degree of soil salinization by natural minerals in sodium chloride – magnesium sulfate – calcium sulfate system, the ratio between the ingredients at which the highest degree of soil salinity is reached was defined.[13] In another study, the authors investigated the selective extraction by natural zeolitic tuff of mixed rare earth elements from its mixtures [14]. The resulting mathematical model gives the opportunity to predict the optimal conditions for extracting of lanthanum, praseodymium, and ytterbium ions.

In paper by Rezanova *et al.* [15] the method of penalty functions and the gradient method for optimization of polymer composition based on four components were used to obtain the ultrathin nanofibers with high exploitational properties. Herewith, only one quality of polymer composition was modeled.

It should be noted that in most studies on content optimization of composite materials with the usage of mathematical modeling, the problem is solved by considering only one property of composite system. However, given a complex and sometimes even contradictory dependence of system properties on the composition, a several output variables (properties) were applied to optimize the filling composition containing silica nanoparticles in order to obtain more reliable data. In this respect, inorganic fillers are very promising to solve the problem during filling stage and develop new innovative and eco-friendly technologies for leather and fur production.

Highly dispersed minerals have been used previously in processing of leather and fur [16,17]. In particular, it has been shown that the application of modified montmorillonite can increase the thickness, volume yield, and improve the physical and mechanical properties of materials compared to the ones processed using existing technology. Among inorganic fillers synthetic silica nanoparticles or fumed silica due to its colloid and physicochemical properties are considered to be a promising reagent for production of elastic leather materials [18]. In a review on recent progress on cleaner preservation of hides and skins [3], one of the discussed sodium chloride less curing method contains silica gel and appears to have environmental advantage over the conventional method by reducing a pollution from chlorides up to 80–85%. Silicon-containing flame retardants are considered as very promising alternatives to halogenated compounds [19] as they do not release corrosive smoke during combustion and at the same time are considered to be an environmentally friendly for its application in coating. Incorporation of silica nanoparticles may also improve mechanical properties and aging- and climate-resistance of final materials.[20] The method of chemical modification of silica nanoparticles by poly(methacrylic acid) was developed by Pan *et al.* [20] and applied as leather finishing agent in leather tanning process. Additionally, silica-based colorant nanoparticles were developed for sustainable dyeing of leather.[21]

Herein we are going to utilize silica nanoparticles as one of the components of leather filling composition. Determination of the optimal formulation of filling composition containing silica nanoparticles by using modified McLean-Anderson method in modelled system "content-properties" will have a significant importance from practical point of view in process intensification. But to achieve this, an optimal design of the experiment with restrictions on ingredients have to be generated and computed first.

Thus, the goal of the study was to improve the physicochemical properties of leather materials by using the optimized formulation of eco-friendly filling composition containing silica nanoparticles. Optimization of filling composition was performed based on McLean-Anderson method by selecting the best experimental points from the candidate set of points according to the D-optimality criterion. To achieve the goal, we (1) developed a computer algorithm which allows calculating automatically plan based on McLean-Anderson method, checking the adequacy of the mathematical model, and carrying out the optimization according to the desirability function; (2) designed mathematical model for the formulation of the filling composition – quality of leather material; (3) determined optimal content of the ingredients of filling composition based on silica nanoparticles; and (4) tested experimentally the developed and optimized formulation for filling the semi-finished leather product and the final properties of leather materials.

Materials and Methods

Filling composition containing silica nanoparticles was studied for improving physicochemical properties and technological quality of semi-finished leather product made of chrome-tanned wet-salted heifer hides. Semi-finished leather product was processed at Chinbar (Kyiv, Ukraine) using an established technology for shoe leather production after spinning and slicing up to 1.4–1.5 mm in thickness. Effect of formulation of the filling composition on the final properties of leather material was studied in 10 batches each containing 8 samples of semi-finished product 8×25 cm. The samples were selected by the method of asymmetric fringe in two rows on both sides of the vertebral column.[22]

The formulations of filling composition contained the following components: nanosized (32.4 ± 1.1 nm for n = 50) **fumed silica A-300** with specific surface area 300 m^2/g (Figure 1) produced by pilot plant (Kalush, Ukraine) of the Chuiko Institute of Surface Chemistry; lightfast resin tanning agent **Relugan D** (BASF, Germany); **Truposol GF** (Trumpler, Germany); and **quebracho extract** (China) as a natural tannin for leather materials.

Filling of semi-finished leather product was carried out after washing and neutralizing with a 1:1 (weight ratio) mixture of sodium formiate and sodium bicarbonate until the pH of a semi-finished product reached 5.8–6.0. The process was carried out for an hour in a drum with the inner diameter of 30 cm and volume 18 L with a weight ratio of technological solution to semi-finished product (hereinafter, the liquid coefficient, LC) fixed to 1. Washing and neutralizing was carried out at 28–30°C with constant rotational speed of 18–20 rpm (Figure 2). The total weight of the filling composition was 11% from the mass of semi-finished leather product. Previously to washing and neutralizing step, semi-finished leather product was incubated for an hour with Trupol RA (Trumpler, Germany) reagent in the amount of 1% of the mass of semi-finished leather product. This fatty reagent was also used for the next fattening of the semi-finished leather product after increasing the volume of the technological solution and temperature to LC 1.5 and 45°C , respectively. For fixation of filling components distributed within the structure of semi-finished product, we added potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$, equivalent to 0.3% Al_2O_3 of the mass of the semi-finished leather product) to decrease pH from 5.8–6.0 to 4.0–4.2. The total duration of the process was approximately 2 hours.

Subsequently, the samples of the semi-finished leather product were vacuum-dried using M1 4025 dryer (Incoma, Italy) to a moisture content of 26% followed by drying at 40–45°C to a moisture content of 16%, and wetting back to 22–24%. The samples were kept for a day under a polyethylene film at 18–22°C and dried again at 40–45°C for 45–50 minutes to a moisture content of 16%. The samples were finally examined after their conditioning for 24 hours at 60% humidity and 20°C .

Physical and chemical properties of the filled leather materials were determined using previously developed methods.[22–24] In particular, for the determination of volume yield

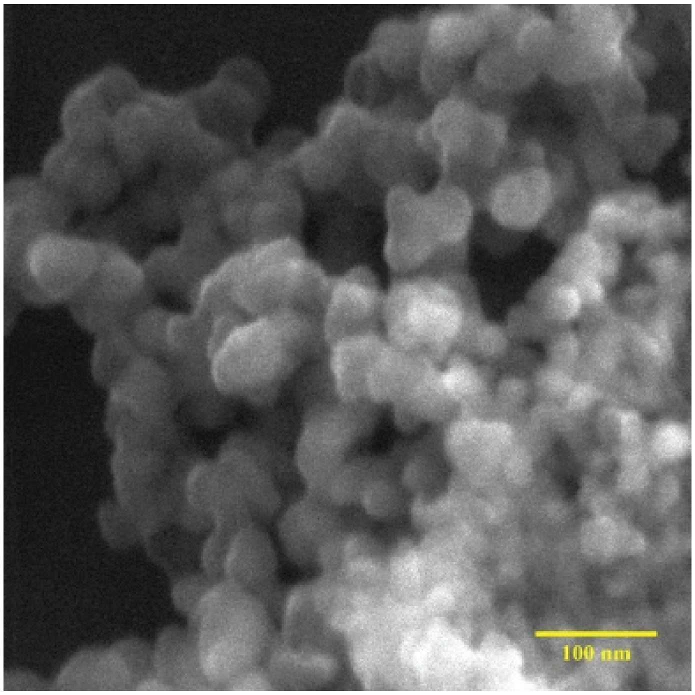

Figure 1. Microphotograph (SEM) of fumed silica A-300.

Figure 2. Photo of the laboratory setup for production of leather material.

[cm³/100 g of proteins], nitrogen content was quantified using Kjeldahl method and converted into protein content. Volume, density, and porosity of leather samples were determined by pycnometry using kerosene. Mechanical properties (tensile stress and elongation) [25] of leather materials were measured using a tensile testing machine RT-250 (range A) at extension rate 80 mm/min. Initial length of the leather samples (10 mm in width) between clamps was 50 mm. Stiffness measurements were carried out using a device PZhM-12M for determination of stiffness and elasticity. Stiffness was characterized by the load in N required to deform the sample (20×160 mm) bent into a ring by 1/3 of its initial diameter.

Scanning electron microscopy (SEM) study was performed on silica nanoparticles, dehaired semi-finished leather product, and final leather materials. The information about topology, morphology, and microstructure of leather samples was obtained from microphotos taken on a high-resolution field emission scanning electron microscope (FE-SEM) Mira 3 LMU (Tescan, Czech Republic). For the microscopical study the leather specimens were attached to standard stubs with conductive graphite paint and coated with Au (20 nm thick) using an ion-sputter coater Gatan Pecs 682. Fields of interest were imaged using secondary electron detector with 10 kV accelerating voltage. For elemental analysis and chemical characterization of surface and cross section of leather samples, energy-dispersive X-ray spectroscopy (EDXS) was carried out using Oxford instruments X-max 80 mm² detector.

All data is presented herein as an arithmetic mean ± standard uncertainty.[25–27]

For the optimization of the formulation of fumed silica filling composition a mathematical model of the incomplete 3rd order polynomial was used:

$$\hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij}\, x_i x_j + b_{ij\ldots k} x_i x_j \ldots x_k, \qquad (1)$$

where $\hat{y}$ – the predicted output variable;
b_i, b_{ij}, $b_{ij\ldots k}$ – the model coefficients;
x_i – the relative weight fraction of component in composition ($i = 1, 2, \ldots, k$);
k – number of factors;
$i, j, \ldots, k$ – factor counters.

The model was normalized using the following condition:

$$\sum_{i=1}^{k} x_i = 1. \qquad (2)$$

From technological point of view restrictions on the numerical values of the ingredients x_i were imposed:

$0 \le \alpha_i \le x_i \le \beta_i \le 1$ (i=1,2,…,k),

where α_i and β_i – are the restrictions of ingredient composition.

Thus, a mathematical model for system composed of three ingredients can be written in the form:

$$\hat{y} = b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3, \qquad (3)$$

where $\hat{y}$ – the predicted output variable;
x_1 – the weight fraction of fumed silica;
x_2 – the weight fraction of mixture of Relugan D and Truposol GF with weight ratio 2:3;
x_3 – the weight fraction of quebracho extract.

The effect of the formulation of filling composition on the final properties of leather materials was evaluated using the following criteria:
y_1 – the volume yield of the leather material [cm³/100 g of proteins];
y_2 – the porosity of samples [%];
y_3 – the stiffness [cN];

In order to get a mathematical model which can describe the properties of system depending on its formulation, it is necessary to compute an experimental plan based on the criterion of the D-optimality with the imposed restrictions on the composition components. After the implementation of the plan and processing of the experimental data, the model coefficients should be determined and checked for its adequacy in the control points. Developed mathematical model will be further used for optimization of the composition using the desirability function.

Results and Discussion

Mathematical Model: Definition

In our previous research we defined the concentration range (as weight ratio) for each component in the filling composition (Table I).[22]

To determine the model coefficients from the candidate set of points (Table II), McLean-Anderson method (without considering the model type) based on maximum distance of candidate point from the center of the design and from each other was used. For generating the design multithreaded computer algorithm developed by authors have been applied.

The *n* points for the design of the experiment were chosen from N candidate points using the D-optimal criterion. To select the points for the experiment the combination was calculated using the following formula:

$$C(N,n) = \frac{N!}{n!\,(N-n)!}, \tag{4}$$

for which the determinant is approaching a minimum value,

where $D = (F^{T}F)^{-1}$ – the dispersion matrix of design (determinant $det\,|I| \to max$ of informational matrix $I = F^{T}F$);
F – the matrix for the design generalized by the type of the model $\bar{f}^{0}(\bar{x})$ with size $n \times l$;
l – the number of model coefficients;
T – the matrix transposition operation.

To determine the coefficients for three-component model an optimal design of the experiment was computed (Table III) in a limited area of simplex (Table I) taking into account the normalization condition.

Note, that the points presented in Table II and in Table III were rounded to 2 decimal places, what caused an apparent deviation in total sum of components for #16 and #7, respectively.

Table I
Concentration range for components of filling composition.

Component	Concentration Restrictions	
	lower limit	upper limit
x_1	0	0.25
x_2	0.14	0.42
x_3	0.22	0.50

Thus, from 16 candidate points (Table II) obtained by using McLean-Anderson method and D-optimal criterion, 7 points (Table III) were selected and tested experimentally. The effect of formulation of filling composition on final properties of leather materials was determined experimentally and corresponding data is presented in Table IV.

The coefficients of three component mathematical model are defined using the method of least squares in a matrix form

$$B = (F^{T}F)^{-1}F^{T}Y, \tag{5}$$

where B – the vector of unknown coefficients; Y – column of values of the dependent variable which were observed in the experiments.

The adequacy of the model was checked using the formula below at each control point of interest:

$$t_p = \frac{|y_i - \hat{y}_i|\sqrt{m}}{s_{exp}\sqrt{1+\zeta}} < t_T\,\{q;\ f\}, \tag{6}$$

where t_p – the calculated critical value of two-tailed *t* distribution;
y_i and $\hat{y}$ – the experimental and calculated output variable at the *i*-control point;
m – number of parallel experiments;
t_T – the theoretical critical value of two-tailed *t* distribution;
q – the level of significance;
$f = z(m-1)$ – the number of degrees of freedom;
z – the number of control points;
s_{exp} – the experimental uncertainty which was calculated using

$$s_{exp} = \sqrt{\frac{1}{z(m-1)}\sum_{i=1}^{z}\sum_{j=1}^{m}(y_{ij} - \bar{y}_i)^2}, \tag{7}$$

$$\bar{y}_i = \frac{1}{m}\sum_{j=1}^{m} y_{ij}\,; \tag{8}$$

Table II
Candidate set for variables , x_1, x_2 and x_3.

Component	Theoretical Points of Experimental Plan															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
x_1	0.20	0.2	0	0.3	0	0.30	0.20	0.25	0.10	0.10	0.25	0	0.15	0.30	0.15	0.17
x_2	0.20	0.50	0.40	0.4	0.50	0.20	0.35	0.20	0.30	0.50	0.45	0.45	0.40	0.30	0.35	0.37
$x_{3.}$	0.60	0.30	0.3	0.3	0.50	0.50	0.45	.55	0.60	0.40	0.30	0.55	0.45	0.40	0.50	0.47

ζ – output variable uncertainty depending on the location of the checkpoints in simplex was calculated as

$$\zeta = \bar{f}^T(\bar{x}) D \bar{f}(\bar{x}), \tag{9}$$

where $\bar{f}(\bar{x})$ – the vector-function depending on the type of the model and coordinates of the checkpoints.

To test the adequacy of the mathematical model, two parallel experiments at three randomly selected control points were carried out (Table V).

Table III
Design of the experiment.

Component	Experimental Points						
	1	2	3	4	5	6	7
x_1	0.25	0.10	0.10	0.25	0	0.30	0.17
x_2	0.20	0.30	0.50	0.45	0.45	0.30	0.37
x_3	0.55	0.60	0.40	0.30	0.55	0.40	0.47

Table IV
Physicochemical properties of leather materials filled with silica nanoparticles.

Technological index	Experimental Points						
	1	2	3	4	5	6	7
y_1	237	243	227	215	203	219	238
y_2	54	60	49	46	42	41	56
y_3	28	31	39	33	36	32	23

Based on the experimental and control data (Table IV and Table V) a nonlinear mathematical model of property dependence of leather materials on the formulation of fumed silica filling

$$\begin{cases} \hat{y}_1 = -111.8828211x_1 + 323.0428301x_2 + 344.450159x_3 \\ \qquad - 372.0384108x_1x_2 + 1.109933603x_1x_3 - 532.5933776x_2x_3 \\ \qquad + 3198.150111x_1x_3x_3; \\ \hat{y}_2 = -463.49878x_1 - 11.12395548x_2 + 63.98313724x_3 + 888.5407893x_1x_2 \\ \qquad + 701.6063908x_1x_3 + 47.73759388x_2x_3 \\ \qquad - 336.0106514x_1x_3x_3; \\ \hat{y}_3 = 899.6635109x_1 + 443.93978861x_2 + 265.4472965x_3 \\ \qquad - 2493.618612x_1x_2 - 1984.054048x_1x_3 - 1251.59158x_2x_3 \\ \qquad + 3762.312302x_1x_3x_3; \end{cases} \tag{10}$$

The results of the validation of mathematical model "formulation of the filling composition – properties of leather materials" at control points are given in Table VI.

As can be seen from Table VI the resulting mathematical model of the formulation of fumed silica filling composition adequately describes the properties of leather materials.

Mathematical Model: Optimization

To optimize the content of the composition $\bar{x} = \|x_1, x_2, x_3\|$ which is characterized by g initial physicochemical characteristics of the resulting mathematical model, the desirability function is used [23]:

$$D_f = \sqrt[g]{d_1 d_2 \ldots d_g} \tag{11}$$

where d_i ($i = 1, 2, \ldots, g$) – the partial function of desirability of the technological index y_i which can take any value in the range from 0 to 1 and it is determined as

$$d_i = \exp[-\exp(-y_i')], \tag{12}$$

where y_i' – dimensionless value of the technological index, defined by a linear correlation:

$$y_i' = b_0^{(i)} + b_1^{(i)} y_i. \tag{13}$$

Table V
Physicochemical properties of leather materials filled with silica nanoparticles at different control points.

Checkpoints	Component			Technological Index					
	x_1	x_2	x_3	y_1		y_2		y_3	
1	0.09	0.46	0.46	227	226	52	51	30	31
2	0.14	0.41	0.46	234	234	55	56	24	26
3	0.18	0.37	0.46	237	239	55	54	23	23

Coefficients $b_0^{(i)}$ and $b_1^{(i)}$ of the above equation are defined from the following system of equations:

$$\begin{cases} y_i'^{worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{cases}, \qquad (14)$$

where y_i^{worse} and y_i^{better} ($i = 1, 2, \ldots, g$) – the worse and the better value of a criterion y_i which is established by the researcher and by the reasons of the technological character cannot be reduced or increased; $y_i'^{\,worse}$ and $y_i'^{\,better}$ ($i = 1, 2, \ldots, g$) – the worse and the better value of the dimensionless quality criterion which can be calculated based on the eq. 12 as follow:

$$\begin{aligned} y_i'^{\,worse} &= -\ln(-\ln d_{worse}), \\ y_i'^{\,better} &= -\ln(-\ln d_{better}), \end{aligned} \qquad (15)$$

where d_{worse} and d_{better} – the worse and the better value of the desirability function (D_f) which are equal to 0.2 and 0.8, respectively [28].

Maximum of the desirability function D_f corresponds to the optimal formulation $\bar{x}^{opt}$ which has the best compromise values of physicochemical properties y_i ($i = 1, 2, \ldots, g$).

Thus, based on the desirability functions an optimal formulation of the filling composition characterized by three best technological indexes are determined.

Table VI

Results of mathematical model validation.[1]

y_{ij}	$\bar{y}_i$	$\hat{y}_i$	ζ	$\lvert\bar{y}_i-\hat{y}_i\rvert$	t_p	*Adequacy*
y_{11}	226.5	227.8	0.6	1.3	2.238	1
y_{12}	234.0	234.7	0.8	0.7	1.179	1
y_{13}	238.0	237.3	1.0	0.7	1.094	1
y_{21}	51.5	51.1	0.6	0.4	0.960	1
y_{22}	55.5	54.7	0.8	0.8	1.666	1
y_{23}	54.5	55.3	1.0	0.8	1.698	1
y_{31}	30.5	31.4	0.6	0.9	1.522	1
y_{32}	25.0	25.6	0.8	0.6	1.003	1
y_{33}	23.0	23.0	1.0	0	0.065	1

[1] All theoretical points presented in Table VI were rounded to 1 decimal place for calculated output variables and its uncertainties, and to 3 decimal places for calculated critical values of *t* distribution.

Table VII

Physicochemical properties of leather materials obtained by developed and current technologies.

Index	**Properties of Leather Materials Obtained by**	
	developed technology	**current technology**
Hydrothermal stability,°C	113.0 ± 0.2	112.0 ± 0.2
Thickness, mm	1.15 ± 0.01	1.09 ± 0.01
Tensile strength, MPa	28.5 ± 0.2	27.0 ± 0.2
Relative elongation at 10 MPa, %	30.0 ± 0.1	27.0 ± 0.1
Relative elongation before fracture, %	62.5 ± 0.1	58.0 ± 0.1

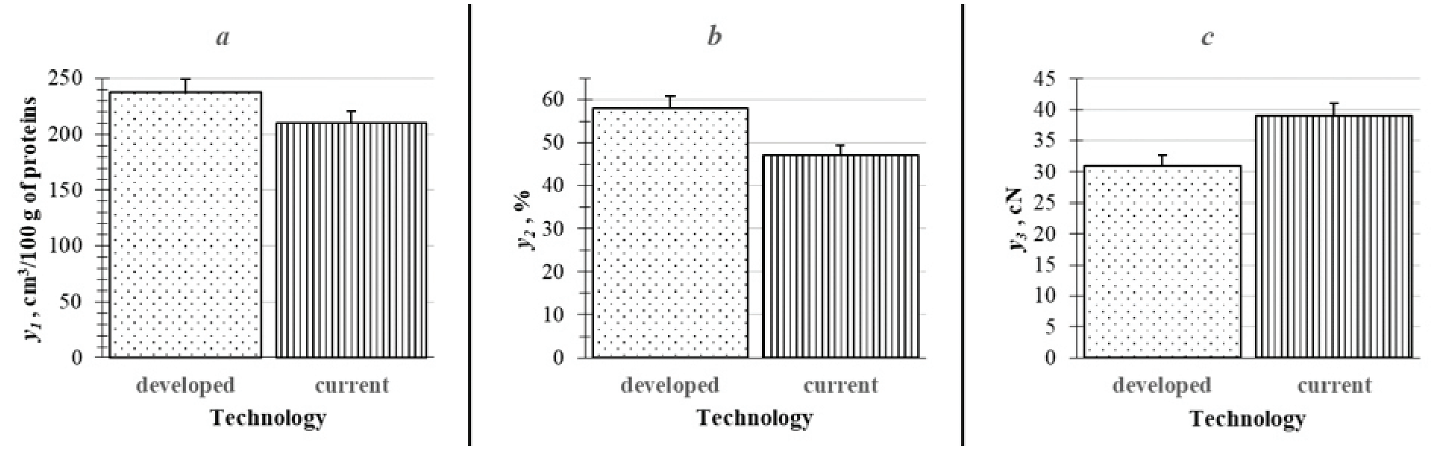

Figure 3. Properties of the leather materials obtained using developed or current technology: a - volumetric yield, b – porosity, c – stiffness.

The resulting regressive equations of the mathematical model are used for a multicriteria determination of the optimal content of the fumed silica filling composition using the generalized functions of desirability. Desirability function are composed based on the resulting equations of the mathematical models in the x-coordinates with the restrictions on the output variables which correspond to the worst and the best values: y_1 – 230 and 243, y_2 – 55 and 60, y_3 – 30 and 23. By the screening using an 0.01 increments, an optimal content of the composition in wt. parts was obtained: $x_1 = 0.165$, $x_2 = 0.340$, and $x_3 = 0.495$ [29]. Herewith, the output variables become: $y_1 = 240.27$ cm^3/100 g of proteins, $y_2 = 57.27\%$, and $y_3 = 22.68$ cN with the desirability function $D_f = 0.6706216$. Thus, to prepare 100 kg of the silica nanoparticle-based filling composition one should take 16.5 kg of fumed silica A-300; 34.0 kg of mixture of Relugan D and Truposol GF with 2:3 weight ratio; and 49.5 kg of quebracho extract.

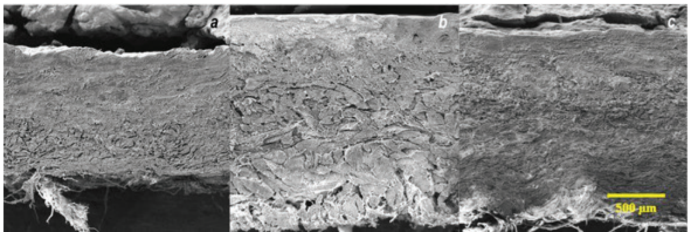

Figure 4. Microphotos (SEM) of cross section of semi-finished leather product (a) and leather materials obtained using current (b) or developed (c) technology at 181× magnification.

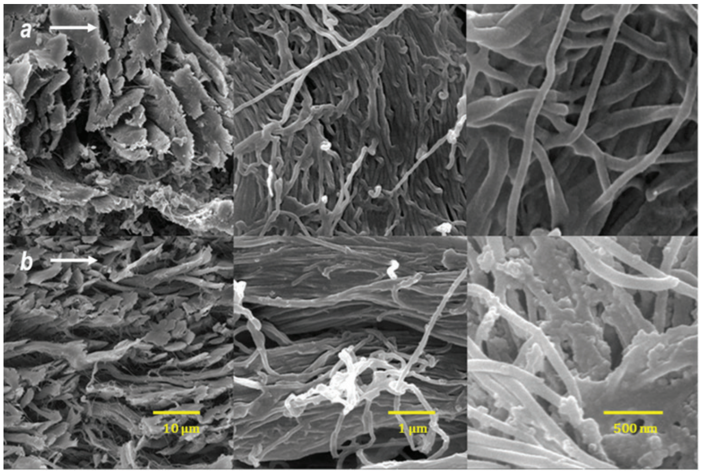

Figure 5. Microphotos of cross section of semi-finished leather product (a) and leather materials obtained using developed (b) technology at three magnifications: 7 220× (column on the left), 90 300× (middle column), and 120 000× (column on the right).

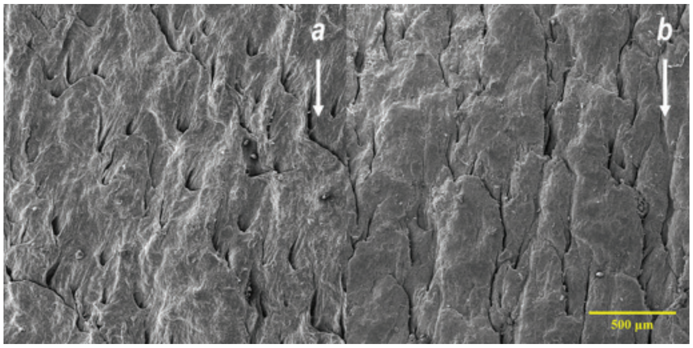

Figure 6. Microphotos of surface of semi-finished leather product (a) and leather materials obtained using developed (b) technology at 181× magnification.

Mathematical Model: Testing

We approbated the developed technology for the production of flexible leather material by filling the semi-finished leather product with optimized formulation of fumed silica-based composition at Chinbar (Ukraine). Using the developed technology 60 m^2 for upper shoe parts were produced.

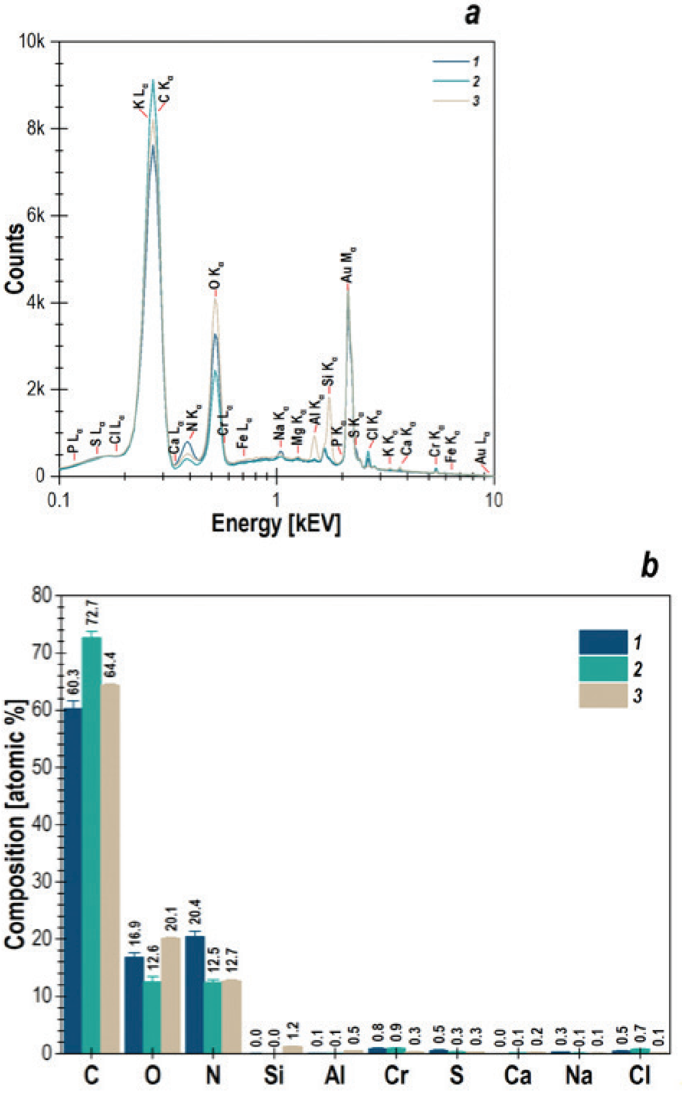

Figure 7. EDXS spectrum (a) and results of elemental analysis (b) of surface of semi-finished leather product (1) and leather materials obtained using current (2) or developed (3) technology. Analysis was performed at 1,810× magnifications (200 µm field of view) for three different areas.

A company current technology was used as a control. It should be noted that the formulation of the company current filling composition differs from the described filling composition containing silica nanoparticles. The former filling composition did not contain nanosized fumed silica and has higher content of quebracho extract (5.1% more). The developed technology was tested by performing the filling in the drum with the volume of 9.2 L. The properties of the resulting leather materials are depicted in Figure 3 and shown in Table VII. As can be seen from the Figure 3 volumetric yield and porosity of leather materials filled with fumed silica composition is increased by 28 cm^3/100 g proteins and 11%, respectively, compared to the control group, while stiffness is decreased by 8%. From SEM photos one can directly see the increase in thickness for both leather materials obtained using current (Figure 4*b*) or developed (Figure 4*c*) technology in comparison to semi-finished leather product (Figure 4*a*). The largest interfibrillar pores have a control sample as a result of agglomeration of collagen fibers during processing. The semi-finished leather product after chrome tanning has a relatively smaller size of collagen fiber bundles (Figure 5*a*). Filling the chrome-tanned leather product with a nanocomposite composition results in more homogeneous and highly dispersed structure of collagen bundles, which is clearly visible at cross section (Figure 5*b*). In general, the microstructure of the leather material obtained by the developed technology is more homogeneous compared to the structure of leather material obtained by current technology.

According to the data listed in Table VII the obtained leather materials have improved mechanical characteristics (tensile strength and elongation), but the difference is not statistically significant.

Figure 5 Microphotographs of cross section of semi-finished leather product (a) and leather materials obtained using developed (b) technology at three magnifications: 7 220× (column on the left), 90 300× (middle column), and 120 000× (column on the right).

The results may be explained by the diffusion of silica nanoparticles deep inside the structure of semi-finished leather product which may help to distribute uniformly other ingredients of filling composition into the microstructure of the leather materials (Figure 5*a*). After removing the water from the leather during the drying-humidifying treatments the presence of silica nanoparticles in the interfibrillar space increases its elasticity and ensures that the mobility of the entire fibrous structure is preserved.

SEM analysis also showed that hair pores were free of any hair residues in dehaired cow pelts after conventional dehairing process (Figure 6*a*). The grain structure of all thee samples was also found clean and without any damages. Silica nanoparticles are found to cover the entire surface homogeneously as well as evenly distributed within the volume of final leather sample (Figure 5).

The filling of the chrome-tanned semi-finished leather product in various degrees changes the atomic ratio between the C, O, and N. This is due to the difference in the chemical formulation of the filling compositions. According to the developed technology filling of semi-finished leather product with composition containing silica nanoparticles and its further fixation with potassium alum results in appearance of Si within leather structure, fivefold increase in Al, and increase in O by 3.2%. The decrease in Cr content may be due to the active interaction of –OH groups of silica nanoparticles [30] with unilaterally bound to collagen ($-COO^- Cr^{3+}-$) or even unbound chromium (III) compounds and it further removing from leather structure during filling.

Summary

The optimal design of the experiment has been generated by using McLean-Anderson method which takes into account the type of mathematical model "content of the filling composition – properties of leather materials" and multithreaded program. The latter one provides the parallel calculations of the informative and dispersive matrices and their determinants for the design of multicomponent system. The described mathematical model can be used to solve similar problems in leather and fur production, or other industries.

The optimal formulation of the composition used in the developed technology of filling the semi-finished leather product was determined as well. The mass ratio between fumed silica A-300, Relugan D, Truposol GF, and quebracho extract corresponds to 1.2:1.0:1.5:3.6. This formulation allows obtaining the leather materials for production of flexible leather materials with enhanced volumetric yield and porosity in comparison to the current company technology.

Besides, industrial testing of the developed technology of filling the semi-finished leather product allows reducing the usage of natural tannins by 5.1%, and results in the leather materials with increased volumetric yield and elasticity by 13 and 25%, respectively, and more homogeneous microstructure. Physicomechanical properties of the obtained leather materials meets the requirements for leather materials for sewing wares (Ukrainian standard GOST 3115-95), international standard for shoe upper leather (GOST 939-88), and quality management systems (ISO 9001:2008).

Conflict of Interest. The authors declare that there's no financial or personal interest or believes that could affect their objectivity.

Authors' Agreement/Declaration. Authors warrant that the article is their original work, hasn't received prior publication and isn't under consideration for publication elsewhere. All authors have seen and approved the final version of the manuscript being submitted.

Authors' contributions. A.P. Danylkovych supervised this work, and together with O.I. Korotych helped in the analysis and interpretation of data. All authors worked on writing and revising the manuscript. Experiments and computation were carried out by A.P. Danylkovych, while scanning electron microscopy study and elemental analysis was performed and analyzed by O.I. Korotych together with A.P. Danylkovych.

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