Do Leather Anisotropic Properties Have an Effect on Shrinkage Temperature?

by
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Abstract

Herein are the results of studies of mechanical properties and shrinkage temperature of cowhide leather tanned with modified glutaraldehyde and chrome. The tests were carried out on samples cut from both kinds of leather parallel and perpendicular to the backbone. The aim of these studies was determining whether the sample orientation to the backbone, thus leather anisotropic properties defined by its tensile strength and ultimate extension, has an effect on shrinkage temperature and kinetics of this process.

Mechanical properties were tested according to PN-EN ISO 3376:2012 Leather – Physical and mechanical tests – Determination of tensile strength and percentage extension. The conditions for shrinkage temperature measurements were set according to guidelines specified in PN-EN ISO 3380:2015-11 Leather – Physical and mechanical tests – Determination of shrinkage temperature up to 100°C. The experiment was carried out by using an instrument of our own design enabling automatic recording of leather specimen length changes during measurement.

The results of mechanical tests allowed the determination of the degree of differentiation of obtained tensile strength and ultimate extension values depending on test sample orientation to the backbone. For leather tanned with modified glutaraldehyde the coefficient of variation with respect to tensile strength in both directions was 0.31, while for chrome tanned leather was 0.44. The coefficient of variation for ultimate extension calculated for both directions was 0.55 and 0.42 for glutaraldehyde and chrome tanned leathers, respectively.

The slope of obtained regression lines was compared to find any statistically significant differences in leather shrinkage rate depending on orientation to the backbone. The results of analyses performed for two differently tanned leathers show no statistically significant differences in shrinkage rate depending on cut orientation. Thus, anisotropy of mechanical properties of leather samples under investigation does not affect both shrinkage temperature and the rate of this process.

Introduction

A number of different factors have an effect on shrinkage temperature of leather heated in water. One of the basic factors deciding on the behavior of leather immersed and heated in water is type of tanning and tanning degree. The structure of chemical compounds such as tannins determines its cross-linking ability, thus also the number and durability of additional bonds formed between polypeptide chains in the structure of collagen. Thus, the chemical nature of tannins affects the amount of kinetic energy necessary to break the formed bonds and transit between bent and extended states[1].

Also, factors promoting protein dehydration influence thermal resistance of leather are expressed by its shrinkage temperature. This causes that polypeptide chains approach each other, thus increasing the force of attraction between them and in consequence increasing the leather shrinkage temperature.[2] Also, pH of tanned leather effects its thermal resistance. It has been found that an increase in the pH value decreases leather shrinkage temperature.[3,4] This could be explained as follows: strong bases are chemical compounds that decrease the number of hydrogen bonds in the structure of collagen, thus promoting lower shrinkage temperatures.

When considering individual factors determining thermal resistance of leathers, a question arises whether anisotropic properties, for example, differentiated mechanical properties depending on orientation to the backbone, characteristic of any leather, have an effect on leather shrinkage temperature and shrinkage rate. It is known that leather heated in water shows thermal expansion that depends on fiber orientation with respect to the backbone.[2]

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The aim of this study is to find whether there exist statistically significant differences between leather shrinkage temperature and the kinetics of this process for samples oriented parallel and perpendicular to the backbone. The tests were carried out by using an instrument of our own design enabling not only the determination of leather shrinkage temperature but also kinetics of the process under examination.

Materials and Methods

Material

The tests were carried out on two cowhide leathers designed for shoe uppers of similar thickness of approx. 1.5 mm. One of leathers was chromium tanned and uncolored. The second leather was tanned with modified glutaraldehyde and drum dyed black.

Methods

Mechanical Properties Test Method

Mechanical properties were tested according to PN-EN ISO 3376:2012.[5] For each leather described above three specimens for the tensile strength and percentage extension tests were cut parallel and perpendicularly to the backbone according to guidelines in PN-EN ISO 3376:2012. The width of these test specimens was 10 mm.

The strength tests were carried out on the Instron 5544 testing machine equipped with a measuring head of force capacity up to 1000 N. According to recommended methodology the specimens were clamped in gripping jaws spaced 50±1 mm apart, and then after starting the testing machine, were stretched at a speed of 100±20 mm/min until break. The measurements made allowed the maximum force and break strength as well as gauge section length increments to be recorded. Tensile strength σ_{max} was computed from the following formula:

$$\sigma_{max} = F / S, \text{ MPa}$$

F – maximum force, N

S – specimen cross-sectional area, mm^2

Ultimate extension E_b was computed with the following relationship:

$$E_b = (L_2 - L_0) / L_0 \; 100, \%$$

L_2 – the gripping jaw separation at break, mm

L_0 – initial gripping jaw separation, mm

Method to Measure And Analyze Leather Shrinkage Temperature

Shrinkage temperature was measured in compliance with PN-EN ISO 3380:2015-11.[6] To determine leather shrinkage temperature three specimens were cut parallel and crosswise to the backbone from both tested leathers. As the thickness of all leather specimens did not exceed 3 mm, the strips of 50 mm ± 2 mm x 2.0 mm ± 0.2 mm were prepared. The cut specimens were placed in 5.5 ml ± 0.5 ml of distilled water. The specimens immersed in water were placed then in the desiccator from which the air was removed with a vacuum pump and absolute pressure below 4 kPa was maintained. The deaerated specimens were soaked in water for not longer than 6 hours. Such prepared materials were used to measure leather shrinkage temperature and to analyze kinetics of the process.

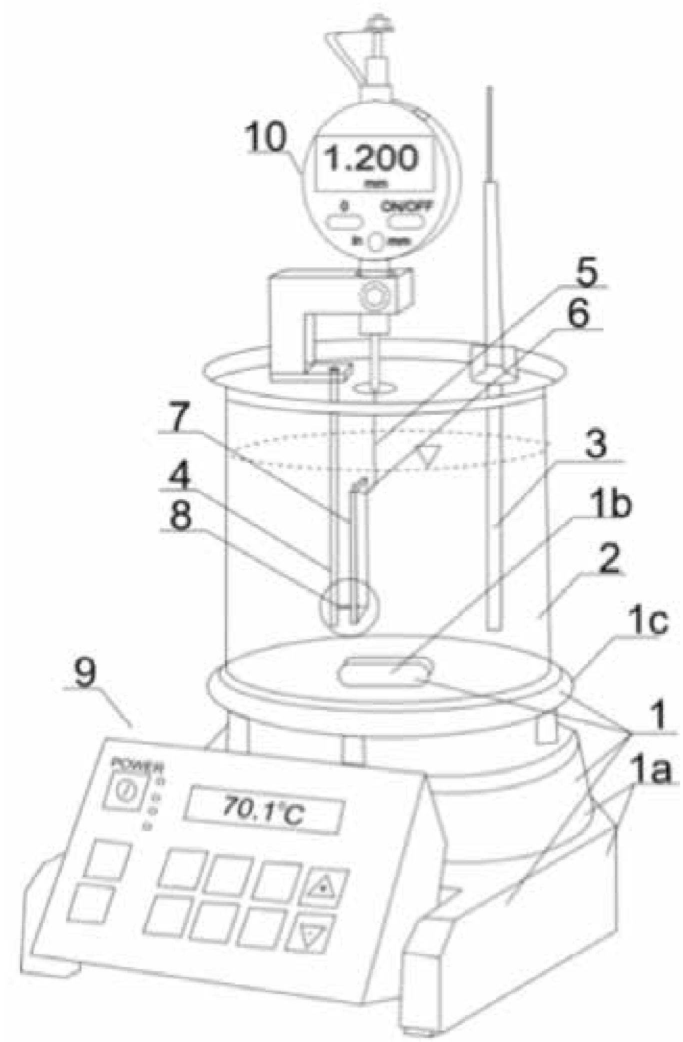

Figure 1. Schematic of instrument for leather shrinkage temperature measurement.
1 - heating and mixing unit: 1a – magnetic stirrer, 1b – magnetic dipole, 1c – hot plate, 2 – working liquid tank, 3 – temperature gauge, 4 – bracket, 5 – tie, 6 – movable specimen upper clamping, 7 - specimen, 8 – fixed specimen lower clamping, 9 – control panel, 10 – specimen length gauge.

The measurement of leather shrinkage temperature was made by using an instrument of our own construction (Figure 1) enabling automatic recording of leather specimen length changes during measurement.[7,8] The instrument is equipped with a heating and mixing unit, temperature gauge and specimen length gauge as well as control panel that facilitates manual operation of the apparatus.

A vessel containing working liquid, here water, was placed on the magnetic stirrer housing. The magnetic dipole as a stirring element was located on the bottom of the vessel. The instrument was equipped with a lower fixed element enabling specimen clamping, and an upper movable clamping element. The magnetic heating and mixing unit is connected to a computer to record working liquid temperature and specimen length changes.

To determine leather shrinkage temperature and kinetics of the process, leather specimens were placed vertically one at a time in the vessel and fixed from the bottom with a stationary element. The specimen was secured from the top with a movable element that connected the leather specimen to the length gauge through a tie. After fastening the specimen, the tank was filled up with water in such quantity so that the water level was above the upper end of the specimen. Before commencing measurement, the specimen length gauge was reset (zeroed) and stirring was started to provide uniform temperature distribution in the entire volume of water. Water was heated at a constant rate of (2^0C/min) provided by a temperature controller. The relationships between working liquid temperature and time, and specimen length changes vs. temperature, and leather shrinkage temperature were recorded in tabular and graphic forms.

According to the procedure contained in the patent application[9] the value of shrinkage temperature can be read out either graphically or analytically. When using the graphical method equations of tangents to straight line segments of the graph corresponding to times before and during specimen shrinkage. In analytical method equations of tangent lines are determined by using the least squares method. After solving a system of equations of these tangent lines it is possible to find a common point T_S that represents shrinkage temperature being sought (Figure 2).

It has been assumed that at the beginning of the measurement no shrinkage occurs (y=0), thus initially the straight line crosses the origin of the coordinate system and coincides with the temperature axis 0T (Figure 2). While expressing the straight line after shrinkage with a linear equation y = at+b, shrinkage temperature T_s is:

$T_s = -b/a$

where:

$$a = \left(\sum_{i=k}^{n} t_i y_i - \bar{t}\sum_{i=k}^{n} y_i\right) / \left(\sum_{i=k}^{n} t_i^2 - \bar{t}\sum_{i=k}^{n} t_i\right)$$

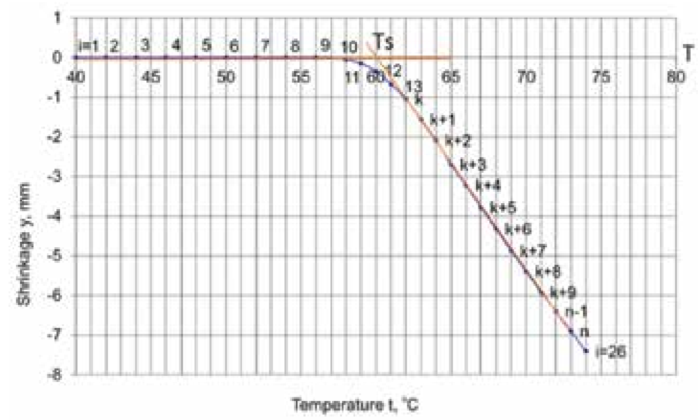

Figure 2. The way of determining leather shrinkage temperature based on empirical data

$$b = \bar{y} - a\bar{t}$$

$$\bar{t} = \left(\sum_{i=k}^{n} t_i\right) / m$$

$$\bar{y} = \left(\sum_{i=k}^{n} y_i\right) / m$$

i - measuring point number,

k - initial index of measuring point adopted for computation,

n - final index of measuring point adopted for computation,

m – number of measuring points used for computing, m = n-k

The kinetics of leather shrinkage was computed by determining the slope coefficient of the straight line obtained by linear regression based on measuring data recorded during shrinkage.

Methods of Statistical Analysis

Statistical analysis was performed by using the *Statistica 13* software package. The results of leather tensile strength and extension measurements for chrome and modified glutaraldehyde tanned leathers were analyzed. Based on the gathered measuring data the arithmetic mean ($\bar{x}$), standard deviation (S_d) and coefficient of variation (v) were computed.

The values of shrinkage temperature T_S obtained for leathers under examination were also averaged. Standard deviation and coefficients of variation were computed to find a statistically significant difference between the value of shrinkage temperature for specimens cut parallel and perpendicularly to the backbone.

Based on the data derived from measurements of time dependence of leather shrinkage the slope coefficients of straight lines obtained by linear regression and using the least squares method and the results of fitting a model proposed at $\alpha = 0.05$. Then statistical inferences about statistically significant differences between regression coefficients determined for both specimen cutting directions of two leather under investigation were made. The inference was made based on the calculated coefficients of variation.

Results and Discussion

The results of tensile strength and percentage extension measurements obtained for modified glutaraldehyde and chrome tanned leathers are presented in Tables I and II. Based on the results obtained the mean values, standard deviations and coefficients of variation were calculated for specimens cut parallel and crosswise to the backbone. For aldehyde-tanned leather specimens cut perpendicularly to the backbone tensile strength was 8.9 MPa, while for specimens cut parallel to the backbone this figure was 14 MPa. The coefficient of variation for tensile strength calculated for both specimen cutting directions was 0.31.

The values of percentage extension were also diversified depending on specimen orientation with respect to the backbone. For specimens cut perpendicularly to the backbone the percentage extension was 106%, while for parallel direction this value was 47%. The calculated coefficient of variation for this parameter was 0.55.

The obtained values of coefficients of variation for aldehyde-tanned leather indicate a high directional diversification depending on specimen orientation to the backbone. The diversified values of tensile strength and ultimate extension for both directions confirm the data given in the specialized literature.[10]

For the chrome-tanned leather the values of tensile strength and ultimate extension determined for both orientations with respect to the backbone also confirm anisotropic properties of leather structure. The specimens cut perpendicularly to the backbone

Table I

Tensile strength and ultimate extension for the modified glutaraldehyde-tanned leather.

Specimen number	Thickness mm	Maximum strength, N	Extension at break, mm	Tensile strength MPa	Ultimate extension, %
	perpendicular direction				
1	1.53	124	54	8.1	108
2		141	51	9.3	102
3		142	54	9.2	107
$\bar{x}$		136	53	8.9	106
	parallel direction				
1	1.53	214	22	14.0	43
2		213	25	13.9	50
3		218	24	14.2	48
$\bar{x}$		215	24	14.0	47
	perpendicular and parallel direction				
S_d				3.61	41.72
v				0.31	0.55

$\bar{x}$ - average, S_d –standard deviation, v- variation coefficient.

Table II

Tensile strength and percentage extension for the chrome-tanned leather.

Specimen number	Thickness mm	Maximum strength, N	Extension at break, mm	Tensile strength MPa	Ultimate extension, %
	perpendicular direction				
1	1.66	135	36	8.2	72
2		120	32	7.3	65
3		133	34	8.0	68
$\overline{x}$		129	34	7.8	68
	parallel direction				
1	1.66	228	18	13.8	36
2		257	22	15.5	43
3		249	16	15.0	33
$\overline{x}$		245	19	14.8	37
	perpendicular and parallel direction				
S_d				4.95	21.92
v				0.44	0.42

$\overline{x}$ - average, S_d –standard deviation, v- variation coefficient.

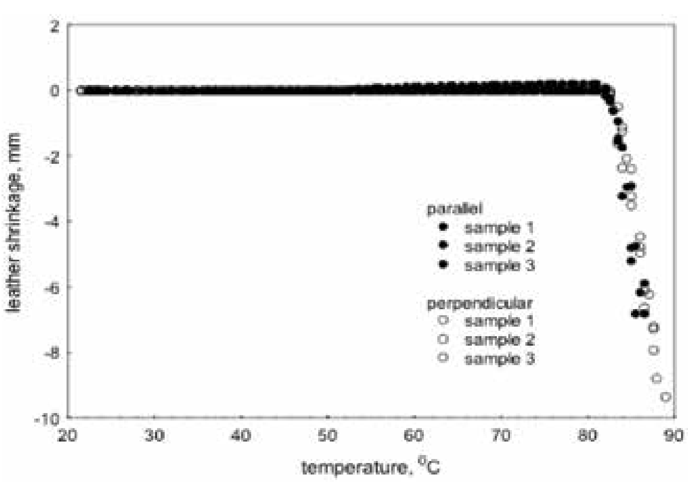

Figure 3. The dependence of shrinkage on temperature for the modified glutaraldehyde-tanned leather. Specimens parallel and perpendicular to the backbone.

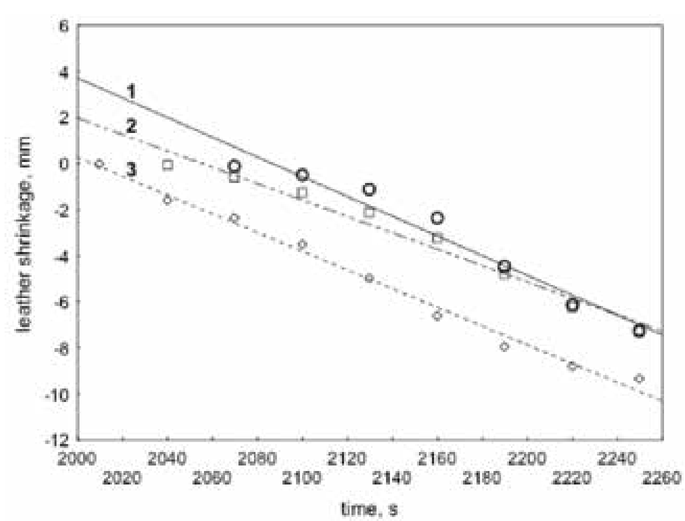

Figure 4. Kinetics of shrinkage for the leather tanned with modified glutaraldehyde. The results for specimens oriented perpendicularly to the backbone.

show lower values of tensile strength than those of specimens cut parallel to the backbone. The calculated coefficient of variation for this parameter was 0.44. In turn, the mean values of percentage extension were 68% and 37% for specimens cut perpendicularly and parallel to the backbone, respectively. The calculated coefficient of variation for this parameter for both directions was 0.42. Based on the results obtained one may conclude that the chrome-tanned leather also showed diversified mechanical properties depending on the orientation of collagen fibers with respect to the backbone.

The results of shrinkage temperature measurements for the leather tanned with modified glutaraldehyde for specimens cut perpendicularly and parallel to the backbone are presented in Figure 3. Shrinkage temperature for these specimens was 82,5^{0}C, while the coefficient of variation for both cutting directions was 0,003. Thus, the obtained value of this coefficient indicates that for this leather the specimen orientation has no effect on shrinkage temperature.

The results of the estimation of data related to kinetics of shrinkage for the leather tanned with modified glutaraldehyde are presented in Figure 4 and Figure 5. An analysis of kinetics of the leather shrinkage process was made by determining the slopes of straight lines by using linear regression with the least squares method. The results obtained for specimens cut perpendicularly to the backbone are presented in Figure 4. The parameters of model fitting to experimental data at a significance level α = 0.05 are presented in Tables III and IV.

Table III

Summary results of fitting a model y=A*x+B at α = 0.05.

Specimen No.		Assessment	Standard error	Correlation coefficient r
	perpendicular direction			
1	A	-0.0429	0.0041	0.978
	B	89.4	8.8	
2	A	-0.0407	0.0015	0.995
	B	81.6	3.3	
3	A	-0.0356	0.0024	0.987
	B	73.1	5.1	

Table IV

Summary results of fitting a model y=A*x+B at α = 0.05.

Specimen No.		Assessment	Standard error	Correlation coefficient r
	parallel direction			
1	A	-0.0483	0.0048	0.995
	B	97	10	
2	A	-0.0418	0.0039	0.983
	B	88.2	8.4	
3	A	-0.038	0.0034	0.985
	B	75.1	6.9	

The results of the estimation of data (Table III) related to leather shrinkage with time indicate that for the aldehyde-tanned leather cut parallel to the backbone the slope of straight lines determined by the least squares method was -0.040. It has been found that fitting a model y=A*x+B is statistically significant at a significance level $\alpha = 0.05$. The mean correlation coefficient for this estimation was 0.987, thus indicating a strong linear relationship in the analyzed data.

The results of regression analysis for specimens cut parallel to the backbone are presented in Figure 5. The results of the estimation of source data (Table IV) related to leather shrinkage measurements with time indicate that for the aldehyde-tanned leather cut parallel to the backbone the mean value of the slope of straight lines was -0.043. A statistically significant fitting a model y=A*x+B, at significance level $\alpha = 0.05$ was found. Based on the average correlation coefficient of 0.988 a linear relationship between analyzed data was established.

The results of shrinkage measurements for the chrome-tanned leather vs. temperature for specimens cut perpendicularly and parallel to the backbone are presented in Figure 6. For tested specimens the mean value of shrinkage temperature was 92.8°C, while the coefficient of variation was 0.001 when considering both specimen cutting directions. The value of this coefficient indicates that the specimen orientation with respect to the backbone has no effect on shrinkage temperature.

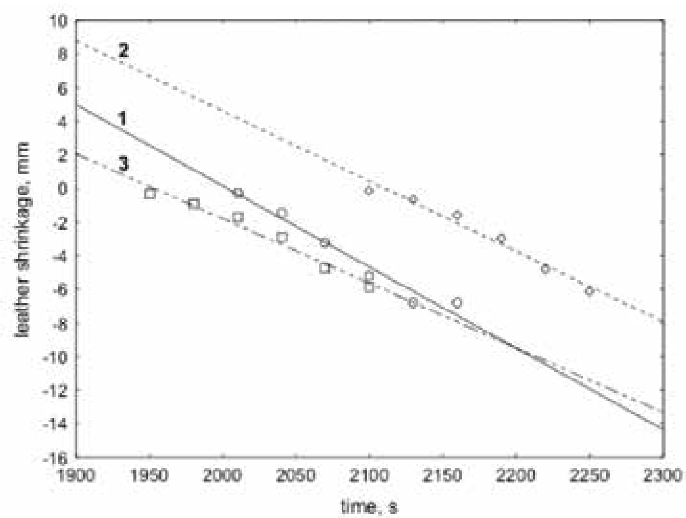

Figure 5. Kinetics of shrinkage for the leather tanned with modified glutaraldehyde. The results for specimens oriented parallel to the backbone.

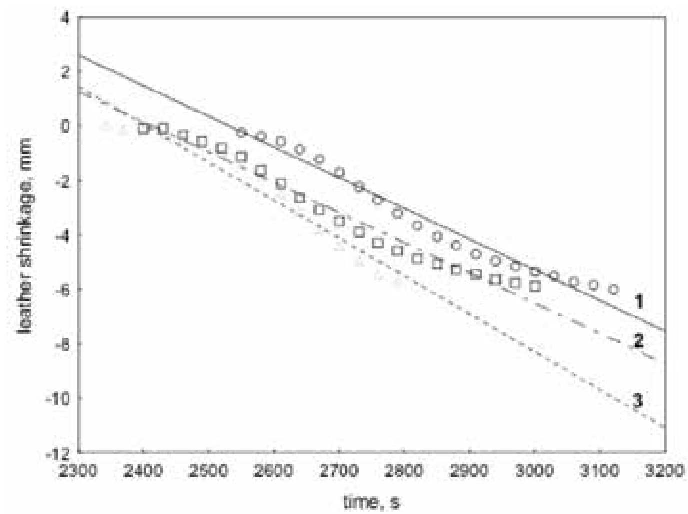

Figure 7. Kinetics of shrinkage for the chrome-tanned leather. The results for specimens oriented perpendicularly to the backbone.

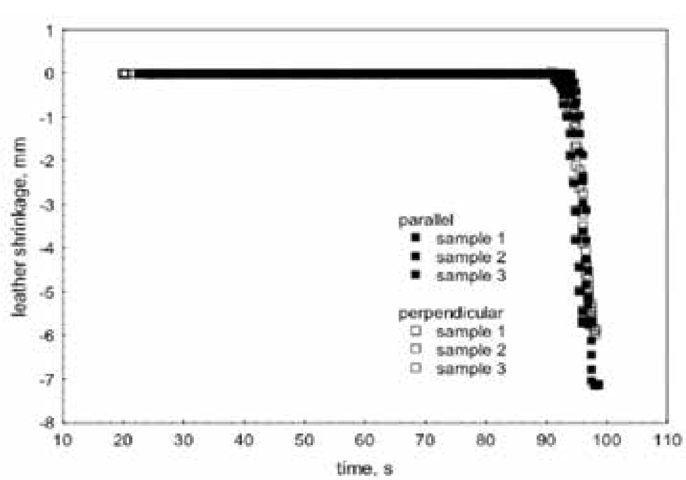

Figure 6. Linear relationship between leather shrinkage and temperature – chrome-tanned leather.

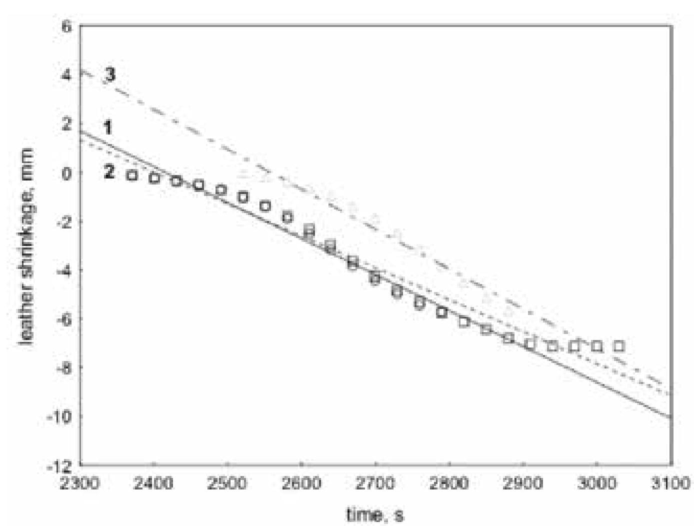

Figure 8. Kinetics of shrinkage for the chrome-tanned leather. The results for specimens oriented parallel to the backbone.

The results of the estimation of data related to leather shrinkage with time for the chrome-tanned leather are presented in Figures 7 and 8. Like in the case of aldehyde-tanned leather the slopes of straight lines were determined by using linear regression with the least squares method. The results obtained for specimens cut perpendicularly to the backbone are presented in Figure 7. The parameters of fitting for a model y=A*x+B at $\alpha = 0.05$ are listed in Tables V and VI.

The results of analysis of data related to the measurement of leather shrinkage with time are presented in Table V. It has been found that for chrome-tanned leather specimens cut perpendicularly to the backbone, the mean value of the slope of straight lines was -0.012 and fitting with the model of y=A*x+B was statistically significant at significance level $\alpha = 0.5$. Based on the average correlation coefficient of 0.982 it has been found that the mentioned relationship between analyzed data is linear. The results of regression analysis for specimens cut parallel to the backbone are presented in Figure 8.

The results of the estimation of source data (Table VI) related to leather shrinkage with time indicate that for the chrome-tanned leather cut parallel to the backbone the mean value of the slope of straight lines was -0.013.

A statistically significant fitting with the model of y=A*x+B at significance level $\alpha = 0.05$ was found. The average correlation coefficient of 0.980 indicated a linear relationship between analyzed data.

Table V

Summary results of fitting a model y=A*x+B at $\alpha = 0.05$.

Specimen No.	Assessment		Standard error	Correlation coefficient r
	perpendicular direction			
1	A	-0.01	0.00	0.986
	B	29	1.28	
2	A	-0.01	0.00	0.987
	B	27	1.05	
3	A	-0.01	0.00	0.972
	B	33	2.32	

Table VI

Summary results of fitting a model y=A*x+B at $\alpha = 0.05$.

Specimen No.	Assessment		Standard error	Correlation coefficient r
	parallel direction			
1	A	-0.014	0.00088	0.977
	B	35.6	2.3	
2	A	-0.011	0.00056	0.982
	B	31.4	1.5	
3	A	-0.015	0.00096	0.982
	B	41.8	2.6	

The calculated values of slope of straight lines determined by linear regression allowed an analysis of kinetics of shrinkage for the leather tanned with modified glutaraldehyde and chrome-tanned leather. This provided basis for conclusions on an effect of leather specimen orientation with respect to the backbone on the run of shrinkage with time. The coefficient of variation calculated for regression coefficients pertaining to both leather specimen orientations was 0.051 and 0.057 for the leather tanned with modified glutaraldehyde and chrome-tanned leather, correspondingly. Based on the obtained values of this coefficient it has been assumed that analyzed statistical features, namely regression coefficients determined for two specimen cutting directions showed an insignificant diversification.[11,12]

Conclusions

The performed tests related to an effect of specimen orientation with respect to the backbone on leather shrinkage temperature led to the following conclusions:

The values of tensile strength and percentage extension for the leather tanned with modified glutaraldehyde and chrome-tanned leather indicate, in compliance with the source literature, a statistically significant diversification depending on the orientation of tested specimens with respect to the backbone. The coefficient of variation of tensile strength was 0.31 and 0.44 for aldehyde-tanned and chrome-tanned leather, correspondingly. Similarly, large values of variation coefficient were obtained for ultimate extension, namely 0.55 and 0.42 for aldehyde-tanned and chrome-tanned leather, respectively.

The shrinkage temperatures for the leather tanned with modified glutaraldehyde and chrome-tanned leather were insignificantly diversified depending on specimen cutting direction with respect to the backbone. The value of variation coefficients for this parameter was: 0.003 for the leather tanned with modified glutaraldehyde and 0.001 for the chrome-tanned leather.

The kinetics of shrinkage for both leathers showed insignificant diversification in both specimen orientations to the backbone. The coefficient of variation of regression coefficients determined for both leather specimen cutting directions was: 0.051 for the leather tanned with modified glutaraldehyde and 0.057 for the chrome-tanned leather.

The presented instrument of our own design to measure shrinkage temperature allowed a large number of measurements to be made and gathered. Automatic recording of the course of the process in graphic form enabled an analysis of the time course of leather shrinkage. The results of measurements obtained by using the new instruments are characterized by repeatability confirmed by small values of variation coefficients for analyzed parameters.

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