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Mechanical properties of lining leathers finished with the addition of oregano essential oil*

1. Introduction

Leather is a valuable raw material for manufacturing goods used by humans in different areas of life. After stripping from the body of an animal the hide is delivered to a tannery where it is subjected to various treatments and operations to get features desired by customers. Depending on its intended use the leather is given specific properties, e.g. garment leathers should be very soft and flexible, while gloving leathers should have appropriate extensibility and sweat resistance, while sole leathers are required to be wear resistant and have a low absorbability [Duda and Marcinkowska 2001].

For lining leathers, due to their close and, fairy often, prolonged contact with the user body, an important feature is their hygienic properties. Hygienic properties of materials used for sock linings, linings and uppers decide on convenience referred to as comfort of use. They include at first place water vapour permeability and sweat absorbability [Skrzyńska *et al.* 2006]. Hygienic properties of shoes are also connected with providing appropriate microbiological purity, thus also health and safety of users. The studies conducted by E. Bielak [2016] and E. Bielak [*et al.* 2016] confirmed that fatliquoring leathers with oregano oil of the antiseptic action allows leather to get antimicrobial properties, thus it can improve hygienic properties of shoes, internal parts of which are made of such enriched raw material.

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Product standards give requirements to be meet by leathers of specific intended use. The requirements related to mechanical strength belong to the basic ones. Mechanical properties of leathers are influenced by many factors, such as kind of leather, tanning and finishing methods used as well as water and fat content. The place from which a specimen has been taken plays an important role, as there are large differences in tensile strength and extensibility between various parts of the leather [Raabe and Kornaś 1965].

The aim of this paper is to present research targeted at determining a possible effect of oregano oil (3%) introduced into the leather during finishing phase on basic mechanical properties of cowhide lining leather, i.e. tensile strength, elongation and tear load. Tests were performed according to methodology specified in PN-EN ISO 3376:2012 *Leather - Physical and mechanical tests - Determination of tensile strength and percentage extension* and PN-EN ISO 3377-1:2012 *Leather - Physical and mechanical tests - Determination of tear load - Part 1: Single edge tear.* The obtained results were subjected to statistical analysis by using the chi-squared, Hartley and Fisher-Snedecor tests.

2. Materials and methods

2.1. Lining leather enriched with oregano oil

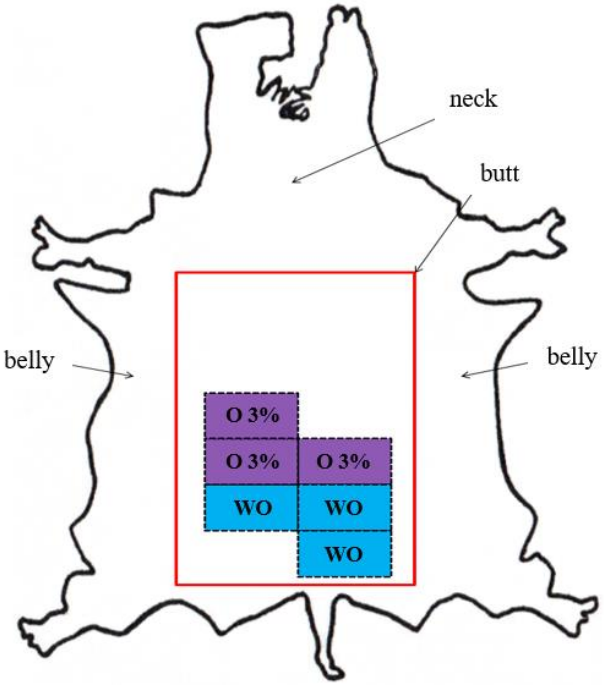
The tests were carried out on cowhide leather designed for shoe lining. In a tannery this hide was chrome tanned and shaved to a thickness of 1.4 to 1.6 mm. The semi-processed product, "wet-blue" purchased from PPHU "TECHNO-SKÓR" was bath finished with and without the addition of Portuguese essential oil derived from *Origanum vulgare* plants. The oil has been gained from the Industrial and Experimental Laboratory at the PWSZ Krosno.

2.1.1. Leather bath finishing

Original samples (rectangles in size of 150 x 250 mm (±10 mm) were taken from "wet-blue" butt according to a schematic presented in Figure 1, weighed and placed in triples in Wacker type drums for bath finishing.

The following operations were performed in sequence: soaking, retanning I, rinsing, retanning II, fixation, and rinsing. During retanning II oregano oil at concentration of 3% (w/w) [Bielak 2016] was added to give the leather antimicrobial properties. After the 8-hour finishing cycle the original samples were allowed to dry in hanging position for 1 day, and then they were kept in horizontal position for 10 days to remove excess

moisture. Afterwards, the material was placed in paper envelopes and stored at room temperature. The control samples were leathers fatliquored according to the indicated procedure without the essential oil and emulsifying agent.



O 3% – samples to be fatliquored with the addition of 3% oregano oil;
WO - samples to be fatliquored without addition of the oil.

Figure 1. Places from which original samples were taken
Source: own research, cowhide leather shape based on [*Mięso – podstawy…* 2011].

2.1.2. Preparing laboratory specimens

The original samples subjected to bath finishing were cut into laboratory specimens by using a hand press and steel punching dies of shape and size specified in applicable standards.

The specimens for tensile strength and percentage elongation testing (Figure 2A) were prepared according to PN-EN ISO 3376:2012. As lining leathers belong to soft leathers, the specimen width was 10 mm according in compliance with this standard. For each kind of leather (fatliquored with or without the addition of oregano oil) 9 specimens cut parallel and perpendicularly to the backbone. This number was thrice larger than that recommended by the standard [PN-EN ISO 3376:2012]. This could enable statistical analysis to improve accuracy and reliability of the obtained results. Thickness was measured with a thickness gauge according to PN-EN ISO 2589:2016-05 *Leather - Physical and mechanical tests - Determination of thickness*.

To measure tear load it was necessary to prepare rectangular test pieces with incision (Figure 2B), according to the schematic presented in PN-EN ISO 3377-1:2012. For each kind of leather (fatliquored with or without the addition of oregano oil) 3 specimens cut parallel and perpendicularly to the backbone [PN-EN ISO 3377-1:2012]. Thickness was measured with a thickness gauge [PN-EN ISO 2589:2016-05].

Before testing the samples (Figure 2) were conditioned at 20±2˚C and 65±5% RH for 48 hours according to PN-EN ISO 2419:2012 *Leather - Physical and mechanical tests - Sample preparation and conditioning.*

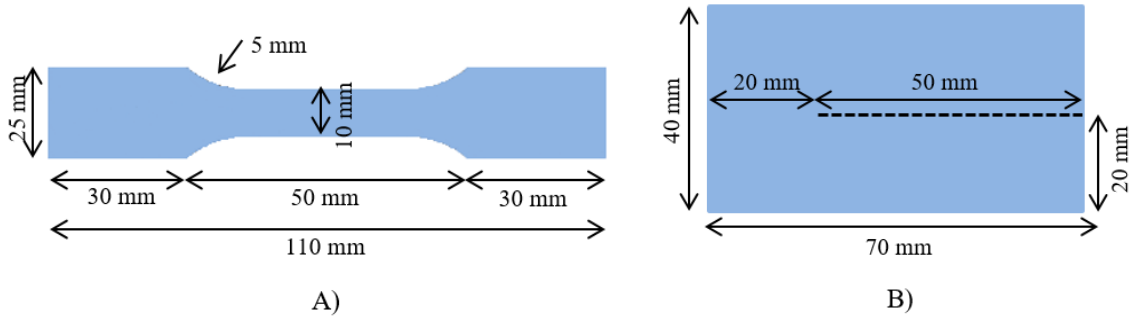


Figure 2. Shapes and sizes of tensile strength and percentage elongation test specimens (A), tear load, single edge tear test pieces (B)
Source: own research based on [PN-EN ISO 3376:2012, PN-EN ISO 3377-1:2012].

2.2. Mechanical properties test methods

The tests were carried out at the Strength Testing Laboratory at the Faculty of Commodity Science, Cracow University of Economics by using an Instron 5544 universal tester equipped with a measuring head of force capacity up to 1000 N. The specimens of leather (Figure 2) fatliquored without and with the addition of oregano oil at concentration of 3% per leather weight were tested.

2.2.1. Tensile strength and percentage elongation

Tensile strength and percentage elongation tests were carried out according to guidelines outlined in PN-EN ISO 3376:2012. The method consists in stretching a leather specimen at a speed of 100±20 mm/min until it eventually breaks (the instrument is stopped when tensile force drops by 20% within 100 ms). Tensile force acting on a leather specimen at break as well as gauge section elongation are measured and recorded.

Leather specimens (Figure 2A) were clamped in the instrument jaws separated by a distance of 50±1 mm. After starting the tester was allowed to run until the tested specimen breaks. Based on the obtained results tensile strength in MPa and percentage elongation of gauge section were calculated.

2.2.2. Tear load (single edge tear)

Tear load (single edge tear) was tested according to PN-EN ISO 3377-1:2012.The methods consists in stretching a rectangular test piece on the shorter side so that tear begins from the end of incision. Tear load is recorded.

The gripping jaws of the Instron 5544 tester were 50±1 mm from each other. In the lower jaw a 20 mm section of one specimen tongue (Figure 2B) was gripped, while the another one after bending to 180° was clamped in the upper jaw. After starting the testing machine was running until the test piece was torn completely. Based on the recorded measurements tear load in N was determined.

2.3. Methods of statistical analysis

For statistical analysis with the *Statistica 12* software package [Dobosz 2001, Mynarski 2003] the results of tensile strength and elongation tests as well as tear load tests carried out on the leather fatliquored without and with the addition of oregano oil (3%) were used. At first stage the values of basic statistical measures were calculated: arithmetic mean ($\bar{x}$) and standard deviation (s_d), and then at second stage – variance analysis was carried out. Initially, two assumptions in variance analysis were verified, i.e. two hypotheses:

- on compliance of empirical distributions with a hypothetical (normal) distribution that was verified by using chi-squared test;
- on homogeneity of variance, checked with Harley's test.

After confirming the hypothesis on compliance of empirical distributions with normal distribution and the hypothesis on variance equivalence, a substantive hypothesis on differentiation of the selected indices depending on the addition of oregano essential oil at concentration of 3% per leather weight was verified with one-way analysis of variance and by using Fisher - Snedecor test. Statistical inference was drawn at a significance level $\alpha = 0.05$.

3. Results and discussion

The results of tensile strength and percentage elongation tests for specimens of leather fatliquored without and with the addition of oregano oil at concentration of 3% per leather weight are presented in Table 1-2. For each specimen the values of thickness, breaking force, tensile strength and percentage elongation are given. The arithmetic means and standards deviations for mentioned parameters were computed both for specimens cut parallel and perpendicularly to the backbone.

Table 1. Tensile strength and percentage elongation for the leather fatliquored without the addition of oregano oil

Specimen No. and its orientation to the backbone	**Thickness mm**	**Breaking force N**	**Tensile strength MPa**	**Elongation %**
	parallel			
1	1.83	254.72	13.92	55.00
2	1.67	252.65	15.13	57.34
3	1.54	208.45	13.54	58.00
4	1.56	212.02	13.59	52.00
5	1.61	216.08	13.42	47.34
6	1.67	221.80	13.28	51.66
7	1.65	219.82	13.32	55.66
8	1.65	219.20	13.28	53.34
9	1.59	215.48	13.55	53.34
$\bar{x}$ [a/]	1.64	224	13.7	53
s_d [b/]	0.09	17	0.6	3.3
	perpendicularly			
1	1.53	157.38	10.29	64.66
2	1.57	169.96	10.83	65.00
3	1.56	162.14	10.39	64.66
4	1.59	171.38	10.78	61.00
5	1.63	172.18	10.56	76.34
6	1.67	178.85	10.71	71.66
7	1.79	210.04	11.73	66.66
8	1.74	195.02	11.21	68.66
9	1.72	179.83	10.46	69.34
$\bar{x}$ [a/]	1.64	177	10.8	67
s_d [b/]	0.09	16	0.5	4.6

[a/] arithmetic mean, [b/] standard deviation.

Source: own research.

The test specimens of leather fatliquored without and with the addition of oregano oil at concentration of 3% per leather weigh cut along the backbone were characterized by

higher tensile strength (13.7 MPa and 16.6 MPa, respectively), than those cut crosswise (10.8 MPa and 11.8 MPa, correspondingly) (Table 1-2), that is consistent with the literature [Raabe and Kornaś 1965].

Table 2. Tensile strength and percentage elongation for the leather fatliquored with the addition of oregano oil

Specimen No. and its orientation to the backbone	**Thickness mm**	**Breaking force N**	**Tensile strength MPa**	**Elongation %**
	parallel			
1	1.77	325.54	18.39	52.00
2	1.69	277.77	16.44	50.34
3	1.60	235.41	14.71	52.34
4	1.65	271.01	16.42	50.66
5	1.61	250.99	15.59	46.34
6	1.63	270.16	16.57	56.00
7	1.71	289.46	16.93	45.66
8	1.61	262.41	16.30	41.00
9	1.71	307.59	17.99	52.34
$\bar{x}$ [a/]	1.66	276	16.6	50
s_d [b/]	0.06	27.7	1.1	4.5
	perpendicularly			
1	1.69	224.73	13.30	72.00
2	1.67	224.39	13.44	62.34
3	1.56	158.54	10.16	60.00
4	1.59	174.26	10.96	63.00
5	1.67	186.83	11.19	71.34
6	1.57	170.63	10.87	63.34
7	1.56	168.54	10.80	66.00
8	1.62	174.83	10.79	66.66
9	1.75	252.68	14.44	69.34
$\bar{x}$ [a/]	1.63	192	11.8	66
s_d [b/]	0.07	32.7	1.5	4.2

[a/] arithmetic mean, [b/] standard deviation.

Source: own research.

An inverse relationship was recorded for percentage elongation. The specimens of leather fatliquored without the addition of oregano oil and cut along the backbone were characterized of percentage elongation of 53%, while for those cut crosswise the elongation was higher and reached 67% (Table 1). For specimens of leather fatliquored with the addition of oregano oil (3%) percentage elongation of specimens taken parallel and perpendicularly to the backbone was 50% and 66%, accordingly (Table 2). The thickness of specimens of leather fatliquored without and with the addition of oregano

oil was comparable. The average thickness of specimens varied between 1.63-1.66 mm (Table 1-2).

The values of mean and standard deviation of tensile strength and percentage elongation for individual kinds of leather are listed in Table 3. Based on the obtained test results a higher tensile strength was found for leather enriched with oregano oil (14.2 MPa), compared to leather fatliquored without the addition of oregano oil (12.2 MPa) (Table 3). When referencing the results of tensile strength tests to the requirements for lining leathers specified in PN-P-22218:1986 *Light leather – lining leathers* it has been found the tested leathers meet these requirements (tensile strength for lining leathers - whole cowhide leather, half-hide leather, hide without bellies, and butts or necks should not be less than 9 MPa).

For percentage elongation the larger value of this parameter was recorded for leather without oregano oil (61%). The leathers with the oil addition were characterized by percentage elongation at a level of 58% (Table 3). For leaning leathers percentage elongation should not be less than 30% [PN-P-22218:1986]. The obtained results indicate that the leathers under investigation meet this requirement.

Table 3. Comparison of tensile strength and percentage elongation for individual kinds of leathers

Leather	**Tensile strength**		**Elongation**	
	$\bar{x}$ [a/] MPa	s_d [b/]	$\bar{x}$ [a/] %	s_d [b/]
fatliquored without oregano oil	12.2	1.6	61	8.1
fatliquored with the addition of oregano oil (3%)	14.2	2.8	58	9.4
[a/] arithmetic mean, [b/] standard deviation.				

Source: own research.

The tensile strength and percentage elongation tests carried out on lining leathers with and without the addition of oregano oil at concentration of 3% per leather weight have shown that leather enriched with this natural substance meets requirements for lining leathers related to its tensile strength and percentage elongation.

The results of tear load (single edge tear) tests for specimens of leather fatliquored without and with the addition of oregano oil at concentration of 3% per leather weight are presented in Table 4-5. For each specimen the values of thickness and tear load are given. The arithmetic means and standards deviations for mentioned parameters were computed both for specimens cut parallel and perpendicularly to the backbone.

For leathers fatliquored without and with the addition of oregano oil (3%) higher tear loads were recorded for test pieces cut parallel to the backbone (40 N and 44 N, correspondingly) compared to specimens cut crosswise (34 N and 27 N, accordingly). The thickness of specimens of leather fatliquored without and with the addition of oregano oil (3%) was comparable. The average thickness of specimens varied between 1.58-1.68 mm (Table 4-5).

Table 4. Tear load for the leather fatliquored without the addition of oregano oil

Specimen No. and its orientation to the backbone	**Thickness mm**	**Tear load N**	**Thickness mm**	**Tear load N**
	parallel		**perpendicularly**	
1	1.85	41.88	1.63	38.02
2	1.56	38.37	1.54	28.77
3	1.62	39.29	1.60	34.53
$\bar{x}$ [a/]	1.68	40	1.59	34
s_d [b/]	0.15	1.8	0.05	4.7
[a/] arithmetic mean, [b/] standard deviation.				

Source: own research.

Table 5. Tear load for the leather fatliquored with the addition of oregano oil (3%)

Specimen No. and its orientation to the backbone	**Thickness mm**	**Tear load N**	**Thickness mm**	**Tear load N**
	parallel		**perpendicularly**	
1	1.67	43.37	1.60	27.53
2	1.69	57.06	1.61	31.36
3	1.58	30.15	1.53	23.56
$\bar{x}$ [a/]	1.65	44	1.58	27
s_d [b/]	0.06	13.5	0.04	3.9
[a/] arithmetic mean, [b/] standard deviation.				

Source: own research.

The mean values of tear load along with standard deviations for leathers fatliquored without and with the addition of oregano oil (3%) are listed in Table 6. The obtained values of tear load for individual kinds of leather were very close. For leather fatliquored without oregano oil a slightly higher tear load (37 N) was recorded compared to that of leather fatliquored with the addition of natural substance (36 N).

The results of tensile strength, percentage elongation and tear load for individual kinds of leather were subjected to statistical analysis. The results of statistical analysis confirming the hypothesis on compliance of empirical distribution with normal

distribution by using chi-squared test are presented in Table 7. The values of χ^2 indicated that all empirical distributions under investigation are close to normal distribution ($p > \alpha$, where $\alpha = 0{,}05$).

Table 6. Comparison of tear load for individual kinds of leather

Leather	Tear load	
	$\bar{x}$ [a/] N	s_d [b/]
fatliquored without oregano oil	37	4.6
fatliquored with the addition of oregano oil (3%)	36	12.5
[a/] arithmetic mean, [b/] standard deviation.		

Source: own research.

Table 7. The results of testing the hypothesis on normal distribution of test results

Leather	Tensile strength		Elongation		Tear load	
	χ^2	p	χ^2	p	χ^2	p
fatliquored without oregano oil	11.25	0.277	3.59	0.999	1.67	0.989
fatliquored with the addition of oregano oil (3%)	10.52	0.310	3.87	0.998	7.49	0.824

Source: own research.

The results related to the hypothesis on homogeneity of variation checked by using Hartley F_{max} test are shown in Table 8. The hypothesis on homogeneity of variation has not been rejected, because the values of F_{max} were less than the limit value F_{max} ($\alpha = 0.05$) = 5.39.

Table 8. Results of testing the hypothesis on homogeneity of variation

Leather	Tensile strength	Elongation	Tear load
	s^2_d		
fatliquored without oregano oil	2.48	65.23	21.12
fatliquored with the addition of oregano oil (3%)	7.83	88.89	75.72
	Calculated values of F_{max}		
	3.15	1.36	3.58
	Limit value F_{max} ($\alpha = 0.05$) = 5.93		

Source: own research.

Afterwards, the substantive hypothesis on differentiation of the levels of selected parameters depending on the kind of leather (fatliquored without and with the addition of oregano oil (3% w/w) was verified with one-way analysis of variance by using Fishera-Snedecor F test. The results of analysis are presented in Table 9. The values of

test probability p indicated a significant differentiation of tensile strength depending on the kind of leather ($p < 0.05$) and that both percentage elongation and tear load do not depend on the kind of leather ($p > 0.05$).

Table 9. Differentiation of tensile strength, percentage elongation and tear load depending on the kind of leather - results of analysis of variance

Leather	Tensile strength MPa	Elongation %	Tear load N
	$\bar{x}$		
fatliquored without oregano oil	12.22	60.65	36.81
fatliquored with the addition of oregano oil (3%)	14.18	57.82	35.51
	Analysis of variance		
F	6.71	0.94	0.05
p	0.014	0.340	0.815

Source: own research.

4. Conclusions

The research on an effect of the addition of oregano oil on the selected mechanical properties of cowhide lining leathers enabled the following conclusions to be drawn:

1) Lining leather enriched with oregano oil (3%) meets the requirements for lining leathers specified in the product standard regarding to tensile strength and percentage elongation.
2) Tensile strength for leather fatliquored with the addition of oregano oil (3%) is significantly higher than that of leather fatliquored without the addition of oregano oil.
3) Percentage elongation for leather fatliquored with the addition of oregano oil (3%) does not differ significantly from that obtained for leather fatliquored without the addition of oregano oil.
4) Tear load for leather fatliquored with the addition of oregano oil (3%) does not differ significantly from that obtained for leather fatliquored without the addition of oregano oil.
5) Introducing the oil derived from *Origanum vulgare* into the leather bath finishing process has an advantageous effect of tensile strength of leather, while the addition of this oil has no effect, neither advantageous nor adverse, on percentage elongation and tear load.

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