INFLUENCE OF DIFFERENT TANNING AGENTS ON THERMAL RESISTANCE OF LEATHER

Franka Žuvela Bošnjak; Dragana Kopitar & Jadranka Akalović

Abstract: *Leather owns its unique property of breathability through porous structure. Leathers structure and their pores connectivity influence on heat transport processes. All leather treatments, including tanning process and different tanning agents, significantly change leather structure. There are more tanning agents used in leather production, where chromium, vegetable and synthetic tanning agents are most common. The same type of bovine leather was tanned with different tanning agents, respectively chromium and synthetic. The thermal resistance of the leathers was tested on Sweating Guarded Hot Plate according to the standard ISO 11092:2014. Influence of chromium and synthetic tanning agents on thermal resistance of the leather under standard condition was investigated. Quite often, leather intended for footwear is used for protection against cold environment where the total comfortability of the footwear made up of leather depends on many factors. Thermal comfort of footwear made up of leather is accomplished by balancing three factors: insulation value (of the leather), rate of heat transfer (heat rate from the human body to its surroundings) and present environment temperature. A human body must maintain a skin temperature of 34°C and to be in thermal balance with present environment so that a person would feel comfortable. Considering above listed factors, insulation value of leather is important parameter to provide footwear thermal comfort. Measuring a leather insulation values can provide information for prediction final product performance. The second objective of the paper is to study one of the main comfort parameters, thermal resistance (m^2 K W^{-1}), of chromium and synthetic tanned leathers.*

Key words: *Leather, Tanning agents, SGHP, Thermal resistance*

1. Introduction

Man and his early ancestors have exploited the unique properties of skin and leather for millennia and almost all human cultures have developed specialist techniques to utilize this raw material for a wide variety of purposes. Tanning has been described as man’s first manufacturing process [1]. The aim of leather making is to make pelt durable, soft, porous, and opaque when dry, whilst retaining such properties, together with good dimensional stability, over a wide range of physical and chemical conditions, extremes of pH value, temperature and relative humidity. To bring about this conversion many processes are needed, of which the most important is process of tanning [2]. The tanning process is the stabilization of the collagen matrix to retain a separated fiber structure and to increase the hydrothermal stability. This is the stage at which the pelt becomes 'leather' and is then resistant to putrefaction or rotting. Organic or inorganic based materials which are able to crosslink with reactive groups of the collagen are used in the tanning process [3]. The only strict definition of tanning is the conversion of a putrescible organic material into a stable material that resist putrescible by spoilage bacteria. Changes as appearance, handle and smell will typically accompany a tanning process. Rise in hydrothermal stability typically observed as a rise in shrinkage/denaturation temperature is also expected [4].The chemical nature of collagen allows it to react with a variety of agents, often resulting in its conversion to leather, of the changes in appearance and properties that are a consequence of tanning, one of the more important is the increase in hydrothermal stability. Modern tanning chemistry can be classified by mineral, vegetable, oil, aldehyde, and organic tanning and syntans [5]. Chrome tanning is one of the most popular mineral tanning materials because of the excellent qualities of chrome tanned leather such as high hydrothermal stability, good dyeing characteristics and softness. Chrome tanning provides better leather characteristics than other tanning materials such as high thermal stability, light weight and high strength properties [6, 7].

This term syntan refers to the range of synthetic tanning agents. An abbreviation of synthetic tannins, was created to cover substances which were manufactured in order to replace, partially or completely, the natural vegetable tanning extracts. The main advantage which use of these products can give is independence from overseas sources of vegetable tannins, but the possession of desirable properties, such as good color, resistance to light, solubility and dispersing power, has enabled the syntans to become commodities in their own right. The manufacture of almost all syntans involves formaldehyde, which is itself a tanning agent [2]. The leather matrix goes through changes the pore structure during processes of production: from raw material to finished leather. Structure and connectivity of pores in skin influence the heat and mass transport processes associated with the thermoregulatory function of the organ. Leather derives its unique property of breathability through its porous network [8].

Physical-mechanical properties of leather and thermal conductivity depend not only on the properties of their fibers, but also on the relative position and structure, i.e. the leather microstructure. The basic indicators of the microstructure of the leather are: the regularity of the fibers splice, the angle of their overlap, the density of the splice, the bend of the fibers, the degree of separation and the thickness of the fibers. The microstructure of the leather depends on the quality of raw skin, some topographic parts of the same leather and on the production process. Compared to vegetative tanned leather, chromed and synthetic tanned leather is lighter, the fibers are thinner, and the leather is porous structure and contains less bound tanning materials. More porous leather tissue contains more air between the fibers resulting in lower thermal conductivity values. Leathers which finishing is stopped after process of tanning have a usage value and it is ready for market under the name of crust nature or dyed crust depending on the degree of technological processing. The natural front side (face) of crust leather is sensitive to external influences. Crust leather can be processed with the finishing technological operations, depending on the use of the leather. Leather apparels and footwear are generally used for protection against cold weather conditions. Major role in providing thermal comfortability of garments have different kind of processing and designing of leather. Expectation from the leather garments is increasing every year because of the rise of people's living standards. Not only aesthetic comfort but also thermal properties and interaction with the body also become to the forefront. Although one of the aims of leather garments is to protect from the cold, there is only few research on this subject. However thermal properties of the leathers for garments and shoes are as important as other quality characteristics.
The effect of the tanning materials on the leather properties were researched by many researcher but a few researches were found about the thermal properties of the leathers [9]. H. Özgünay et. al. investigated the influence of different tanning agents on dyeing properties of leather. Pickled sheep skin were used as material. Chromium and aluminium from mineral tanning agents, and tara, valonea and gambier representing 3 different chemical subgroups of vegetable tannins were used for tanning. Each dyeing experiment was performed with two repetitions. 1 red and 1 black colored dyestuff both from acid dyes and 1:1 metal complex dyes were selected for dyeing of leather samples tanned with various tanning materials. It was shown that as the type of tanning material change, the sites available for reaction with dyestuffs may also vary, and resulting different dyeing properties for the same dyestuff. Acid dyestuffs are very suitable for dyeing of mineral tanned leathers, they have consumption and fastness problems in dyeing of vegetable tanned leathers. Metal complex dyes are adviseble to use for better dyeing properties for vegetable tanned leather [3]. In the study of N. Örk et. al. physical and fastness properties leather tanned with various tanning agents, for leather skirt production were investigated. Physical test including: Tensile, Double edge tear, Single edge tear, Stitch tear, Extension set and Softness. Fastness test including: color fastness to cycles of to-and-fro rubbing, color fastness to water spotting, color fastness of crocking of leather, color fastness to water test, color fastness to perspiration test. 10 samples of vegetable tanned leather, 10 semi-vegetable tanned leather and 10 chromium tanned leather from two companies (60 leather samples all together) were tested. After statistically evaluation physical test results of leathers tanned with different tanning types, it was concluded that, even from the same origin, tanning type has important effect on the physical properties of leathers. Physical properties of the leather were varied due to the tanning material used in their production. From the evaluation of the fastness test results, it was concluded to use synthetic fabrics for lining in manufacture of skirts from these leathers and dry fastness properties of the leather samples were better than wet (water and perspiration) fastness properties [7]. S. M. Çolak et.al. investigated thermophysiological comfort properties on sheep leather tanned with chrome, zirconium, vegetable, phosphonium, and glutardialdehyde tanning materials. The thermal comfort properties of the leathers were measured on Alambeta instrument (hot plate). Thermal conductivity (λ), thermal resistance (R), thermal absorptivity (b) values of the leathers were obtained from the instrument. Also scanning electron micrographs of the cross section of the leathers was taken, with x100 magnification. It was reviled that different tanning agents have significant effect on thermal and vapor permeability properties of the leather. Different thermophysiological properties can be achieved by using different tanning agents for the leathers. Suitable tanning agents and processes should be applied, depending on use of the leather [9]. Therefore, in this study influence of differently tanned bovine leathers, chrome and synthetic, on thermal resistance under standard conditions was investigated. Standard conditions of thermal resistance measurement is the plate temperature of 35 °C, air temperature at 20 °C, relative humidity of 65 % and air speed at 1 m s^{-1}.

2. Materials and methods

2.1. Materials

Five samples of bovine leather obtained from garment leather manufacturing factory were used. Two of them were tanned with synthetic and three with chromium tanning materials. Description of the samples is given in Table 1.

Table 1: Marks and description of the samples

mark sample	description of the sample
BLS1	synthetic tanned, Cr-free bovine leather, basic turquoise dyed and hydrophobic
BLS2	synthetic tanned, Cr-free bovine leather, basic dyed in beige color
BLCr3	chrome tanned bovine crust, basically dyed in black and hydrophobic
BLCr4	chrome tanned bovine nature crust, hydrophobic
BLCr5	chrome tanned bovine nature crus, split leather, hydrophobic

2.2. Methods

Sampling of leathers according to HRN EN ISO 2419:2012 were done. [10]. Thicknesses of test samples were measured according to HRN EN ISO 2589:2016. [11].
Thermal resistance was determinate using the Sweating Guarded Hot Plate equipment according to the standard ISO 11092:2014. For the determination of thermal resistance (R_{ct}) the air temperature is set at 20 °C, relative humidity of 65 % and air speed at 1 m s^{-1}. Test sample is placed on the heated plate at 35 °C temperature with the conditioned air ducted to flow along and parallel to its upper surface with speed of 1 m s^{-1}. Determining the value can begin after the test conditions and steady-state is reached. Measuring procedure mentioned above is repeated without leather sample, to obtain bare plate resistance. The result of leather thermal resistance is subtracted off the bare plate resistance value. The thermal resistance of the fabric is calculated according to the following equation:

$$R_{ct} = \frac{(T_m - T_a) \cdot A}{H - \Delta H_c} - R_{ct0} \quad (1)$$

where: R_{ct} is the thermal resistance [m^2 °C W^{-1}], T_m is temperature of measuring unit [°C], T_a is the air temperature during testing [°C], A is the area of the measuring unit [m^2], H is the heating power supplied to the measuring unit [W], ΔHc is the correction term for heating power for the measurement of thermal resistance and R_{ct0} is the apparatus constant for the measurement of thermal resistance [m^2 °C W^{-1}] [12]. Arithmetic mean of three individual specimens was taken to determine thermal resistance R_{ct} of the leather samples.

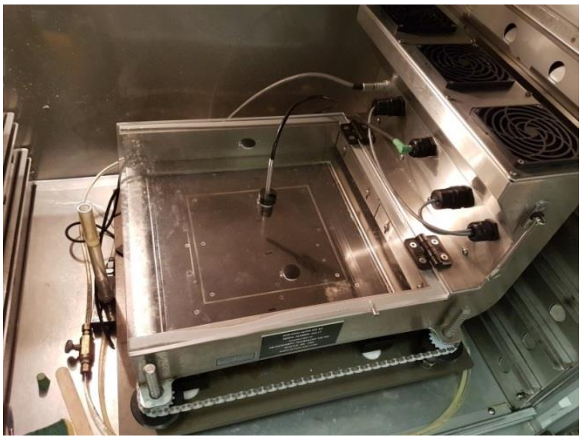


Figure 1. Sweating guarded hot plate

3. Results and discussion

Table 2 shows the results of thickness (M_T) and the thermal resistance (R_{ct}) with statistic parameters (SD and CV), which indicate the deviations from the mean values. The sampling from the neck and back of the bovine leathers were done (N is neck; B is back, croupon). The highest values of standard deviation and coefficient of variation for thickness are in the neck part of sample BLCr4 (SD: 0.13 mm; CV: 10.44 mm) while for BLS1 (SD: 0.04 mm; CV: 2.04 %) and BLCr3 (SD: 0.04 mm; CV: 2.41 %) in the back part, these indicators have the lowest values. Thickness values in all samples are higher in the neck part than in the back part of leathers.

The highest values of standard deviation and coefficient of variation for thermal resistance are in the neck part of sample BLCr3 (SD: 0.0066 m^2 °C W^{-1}; CV: 27.6761 %). The lowest values have also sample BLCr3 in back part (SD: 0.0003 m^2 °C W^{-1}; CV: 1.8211 %).

Table 2: Thickness and thermal resistance of chrome and synthetic tanned bovine leathers

Sample mark		T, mm	M_T, mm	SD_T, mm	CV_T, %	R_{ct}, m^2 °C W^{-1}	M_{Rct}, m^2 °C W^{-1}	SD_{Rct}, m^2 °C W^{-1}	CV_{Rct}, %
BLS1	1N	1,81	1.80	0.10	5.65	0.0319	0.0372	0.0056	14.9269
	2N	1,75				0.0449			
	3N	1,83				0.0349			
	1B	2,13	2.11	0.04	2.04	0.0243	0.0249	0.0014	5.5163
	2B	2,10				0.0268			
	3B	2,10				0.0236			
BLS2	1N	1,30	1.24	0.09	7.11	0.0252	0.0265	0.0013	4.7259
	2N	1,19				0.0277			
	1B	1,31	1.35	0.05	3.43	0.0205	0.0222	0.0017	7.4492
	2B	1,39				0.0238			
BLCr3	1N	1,50	1.45	0.09	6.28	0.0273	0.0238	0.0066	27.6761
	2N	1,47				0.0146			
	3N	1,39				0.0296			
	1B	1,58	1.56	0.04	2.41	0.0182	0.0187	0.0003	1.8211
	2B	1,59				0.0188			
	3B	1,53				0.0190			
BLCr4	1N	1,22	1.24	0.13	10.44	0.0277	0.0229	0.0040	17.4649
	2N	1,10				0.0179			
	3N	1,39				0.0232			
	1B	1,30	1.27	0.10	7.93	0.0227	0.0189	0.0030	15.6777
	2B	1,13				0.0155			
	3B	1,37				0.0184			
BLCr5	1B	0,85	0.87	0.05	5.53	0.0173	0.0147	0.0019	12.6899
	2B	0,89				0.0140			
	3B	0,87				0.0129			

where: T is thickness, mm; M_T is mean value of thickness, mm; SD_T is standard deviation of thickness, mm; CV_T is thickness coefficient of variation, %; R_{ct} is thermal resistance, m^2 °C W^{-1}; M_{Rct} is mean value of thermal resistance, m^2 °C W^{-1}, SD_{Rct} is standard deviation of thermal resistance, m^2 °C W^{-1}; CV_{Rct} is thermal resistance coefficient of variation, %

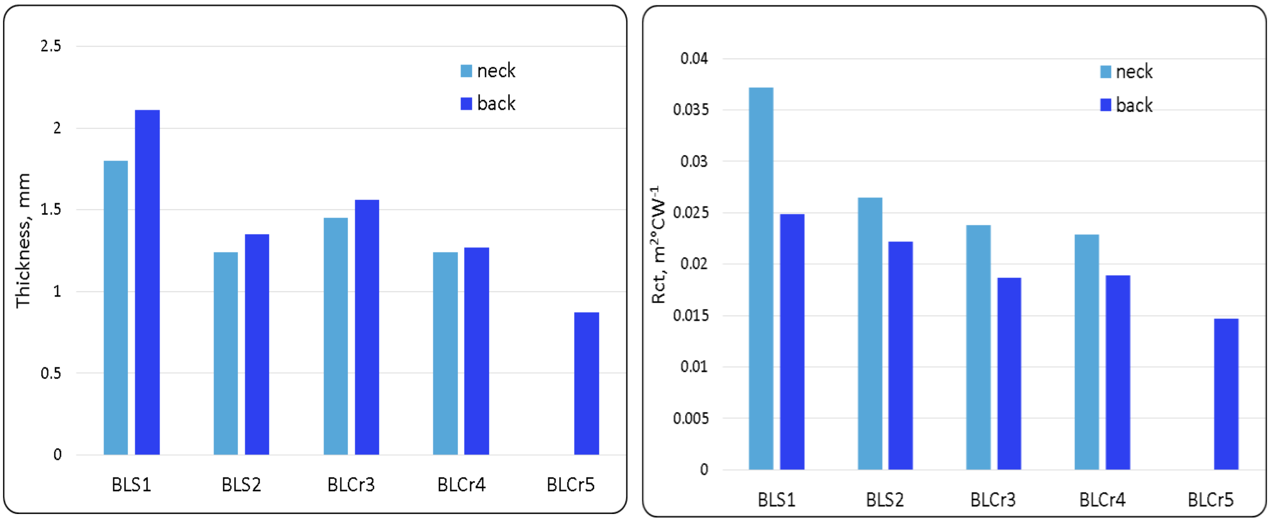
Figure 1 and figure 2 shows graphic results of thermal resistance and thickness of neck and back parts of leathers.

All samples have higher thermal resistance of neck part than those taken from the back part of the leathers.

Synthetic tanned samples have a higher thermal resistance than chromium tanned samples in the neck and in the back parts. The highest thermal resistance have BLS1 sample at the neck (0.0372 m^2 °C W^{-1}) and the back (0.0249 m^2 °C W^{-1}). Sample BLS1 is also the thickest sample: on the neck (1.80 mm) and on the back (2.11 mm). The lowest thermal resistance (0.0147 m^2 °C W^{-1}) provides a sample BLCr5, chromium tanned crust nature, split leather, and hydrophobic whose back part is also the tiniest (0.87 mm). The thermal resistance values measured on samples of dyed crust leather, synthetic tanned BLS1 (neck 0.0372 m^2 °C W^{-1}, back 0.0249 m^2 °C W^{-1}) and chrome tanned BLCr3 (neck 0.0238 m^2 °C W^{-1}; back 0,0187 m^2 °C W^{-1}) are higher on synthetic tanned, thicker sample (BLS1) on neck and back parts.

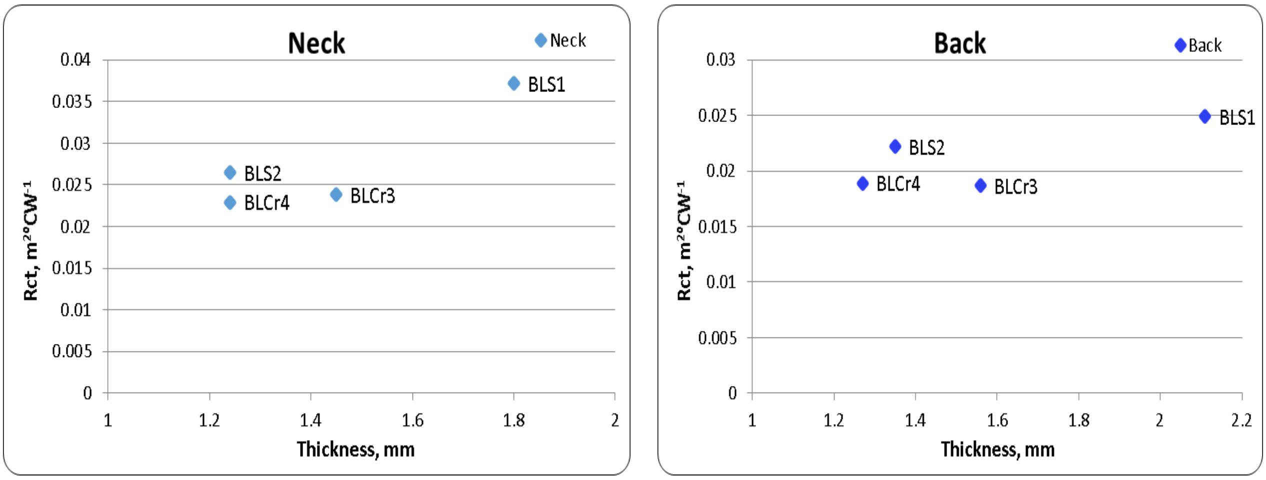
The thermal resistance measured on the hydrophobic sample BLS1 (neck 0.0372 m2 °C W-1, back 0.0249 m2 °C W-1) is higher than on BLS2 sample. BSL2 sample don’t have hydrophobic treatment and has a final coating on the natural face (neck 0.0265 m2 °C W-1, back 0.0222 m2 °C W-1).

The BLS2 sample and BLCr4 sample have the same thickness in neck part (1.24 mm), but thermal resistances have higher value for BLS2 (0.0265 m2 °C W-1) then for BLCr4 (0.0229 m2 °C W-1).



a. b.

Figure 1 Graphical view of results measured on the samples from neck and from back parts of the leather: a) thickness, b) thermal resistance



a. b.

Figure 2 Graphical view dependence of thermal resistance on the thickness: a) samples from neck parts, b) samples from back parts

4. Conclusions

According to the obtained thermal resistance values of the tested samples differently processed bovine leather taken from the neck and back parts, we can conclude the following:

1. The dispersion values for thickness of neck parts are higher than the value of the dispersion of the back parts for all samples, which is expected, as the structure of the neck part is les uniform than the structure of the back part of the leather. Dispersion values for thermal resistance are also higher for neck parts for all samples except BLS2 sample, which can depend on structure of raw leather. Leather is natural material, this difference is not unusual. The lower value of thermal resistance dispersion in the

neck part synthetic tanned leathers can also be related to the specific properties of synthetic tanning agents.
2. The higher values of leather thickness in the neck part compared to the thickness of the back part are related to the technological process of leathers and their purpose.
3. The measured thermal resistances of all the samples have higher values on the neck parts than those of the back parts of the same leather sample. That is result of the specificity of the porous structure of the neck part of the leather whose basic indications are the angle of fiber interlacing, their thickness, and the density of fiber curl.

4. Thermal resistance values of different tanned samples, but the equal stage of processing (BLS1 and BLCr3) are higher on a synthetic tanned sample (BLS1) due to differences in structure.
5. On BLS2 and BLCr4 samples, despite the same thickness of the neck part, different thermal resistances were measured. There is a higher thermal resistance of a synthetic tanned sample, so it can be concluded that the thermal resistance depends on the type of tanning process rather than on the thickness of the sample.
6. A higher thermal resistance value of the hydrophobic, synthetic tanned leather (BLS1) in comparison to the sample of the non-hydrophobic synthetic tanned leather (BLS2) can be associated with a significantly higher thickness of hydrophobic sample. Process of hydrophobic, may reduce thermal resistance and increases thermal conductivity of leathers. Final coating applied to the leather may also increase thermal resistance.
7. Sample BLCr5 is chrome tanned and have the lowest thermal resistance. The low thermal resistance values of this sample in addition to the chrome tanning process, can also be related to the lowest thickness. It is important to consider the structure of the spit leather without face, which also additionally reduces the thermal resistance.
According to points 3, 4 and 5 it can be concluded that the thermal resistance of the leathers depends on the type of tanning agents and that synthetic tanned leathers has higher thermal resistance than chrome tanned leathers. The higher values of thermal resistance of synthetic tanned samples compared to the chromium tanned samples are result of specificity and the difference in the chemistry of knitting of collagen fibers with synthetic and chromium tanning agents. Chrome-tanned leathers have higher thermal conductivity.
According to points 3, 4, 5, 6 and 7 it can be concluded that the thickness of the leathers samples is not directly proportional to the measured values of thermal resistance. Thicker leathers don't have higher thermal resistance. For samples of the same tanning and different processing, the thickness of the sample affects the value of thermal resistance.

Acknowledgments

This work has been fully supported by the Croatian Science Foundation under the project number IP-2016-06-5278.

References

[1] Thomson, R.; & and Kite, M.: Conservation of leather and related materials, *Elsevier Linacre House,* Jordan Hill, Oxford, (2006), pp.1
[2] Reed, R.: *Science for students of leather technology,* (1969)
[3] Hasan Özgünay, H. et al: Dyeing Properties of Simple Acid and Metal-Complex Dyestuffs on the Leathers Tanned with Various Tanning Materials, *Tekstil ve Konfeksiyon*, Vol. 4, pp. 312-3154 (2009)
[4] Covington, T.: *Tanning Chemistry, The science of leather*, The Royal Society of Chemistry, ISBN: 978-0-85404-170-1, The University of Northampton, Northampton, UK, (2009)
[5] Covington, A.:, Modern tanning chemistry, *Chemical Society Reviews*, Northampton, UK, pp. 111-126 (1997)
[6] Örk, N. et al: ; Sewability properties of garment leathers tanned with various tanning materials, *Annals of the University of Oradea, Fascicle of textiles, Leatherwork, (2016)*
[7] Örk N. et al: Comparative Determinatıon of Physical and Fastness Properties of Garment Leathers Tanned With Various Tanning Materials for Leather Skirt Production, *Tekstil ve Konfeksiyon*, 24(4),pp. 413-418. (2014)
[8] Fathima N. N. et al: A DSC investigation on the changes in pore structure of skin during leather processing, *Thermochimica Acta*, Vol. 501, pp.98–102, (2010) *Thermochimica Acta* 501 (2010) 98–102
[9] Çolak S. M. et al: Thermophysiological comfort properties of the leathers processed with different tanning agents, *Tekstil ve Konfeksiyon* 26(4), pp. 436-443 (2016)

[10] HRN EN ISO 2419: 2012.:Leather - Physical and mechanical testing - sample preparation and conditioning
[11] HRN EN ISO 2589:2016.: Determination of thickness
[12] ISO 11092 Textiles – Physiological effects – Measurements of thermal and water-vapour resistance under steady-state conditions (sweating guarded-hotplate test)

B.SC. Franka Žuvela Bošnjak, Assistant
University of Zagreb, Faculty of Textile Technology, Study in Varaždin
Hallerova aleja 6, 42000 Varaždin, Croatia
Phone: +(385) (42) 330 676 Fax: +(385) (42) 330 450 E-mail: franka.zuvela.bosnjak@ttf.hr

Ph. D. Dragana Kopitar, Assistant Prof.
University of Zagreb, Faculty of Textile Technology, Department of Projecting and Management of Textiles
Prilaz baruna Filipovića 28a, HR-10000 Zagreb, Croatia
Phone: +(385) (1) 3712 574 Fax: +(385) (1) 3712 599 E-mail: dragana.kopitar@ttf.hr

B.Sc. Jadranka Akalović, Lecturer
University of Zagreb, Faculty of Textile Technology, Study in Varaždin
Hallerova aleja 6, 42000 Varaždin, Croatia
Phone: +(385) (42) 330 676 Fax: +(385) (42) 330 450 E-mail: jadranka.akalovic@ttf.hr