

Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather

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The change of tanning parameters reflects on leather chemical and physical properties. The standardized determination methods of more important for customers leather indexes do not allow absolutely clear to conclude about suitability of developed tanning method for leather processing. Due to this DSC analysis and IR spectroscopy were employed as additionally analyses methods for the clarification of tanning process influence on leather qualitative properties.

During research established structural characteristics of variously tanned leather show how differently tanning materials join to derma collagen and prove that content of linked tanning materials is not most important factor, which ordains the thermo stability of collagen, in the case of chrome-free tanning. The results of DSC and IR-spectroscopy clarify the data obtained by other investigation methods and allow more exactly estimation of the tanning method suitability for leather processing. It was established that variation of vegetable tannins in tanning recipe influences on leather properties and best results are obtained using mimosa tannins.

Keywords: leather, chrome-free tanning, tannin, shrinkage temperature, thermo stability.

INTRODUCTION

Natural leather is processed from hides and skins of animals. There is a need to understand the properties of processed natural leather to select proper material for an application. During the past 20 years, leather researchers have used experimental and theoretical approaches to investigate several methods for stabilizing collagen structure. Insight gained from these studies and those of leather and biomaterials scientists will be evaluated as steps toward a still elusive, comprehensive mechanism for stabilization of collagen in leather and other biomaterials.

The main process of skin or hide converting into leather is tanning. Chromium has been used as primary tannage for many leathers for over 100 years. In the early days the tanning form, Cr(III), was produced from Cr(VI) by reduction of the chrome by sugars at low pH. When basic chrome sulphate was introduced as a product ready to be used for tanning, tanneries changed to the use of these products either as an aqueous solution or a dry product [1]. During the last 20 years new tanning methods, which allow avoidance of toxic chromium compounds, have been developed. Although such tanning methods enable the avoidance of chromium compounds, it does not mean that the leather is free from inorganic salts (aluminium, silicon, titanium etc.). Due to increasingly strict requirements for leather and with regard to recycling of leather wastes, the manufacture chromium-free leather becomes very important [2]. Developing of environmentally friendly tanning technologies, most perspective is the combination of inorganic (aluminium, silica, zinc etc.) and organic (vegetable tannins, resins, aldehydes etc) chrome-free materials [3–6]. On the other hand, mostly researches limit the investigation evaluating those leather properties, which are most important for consumers such as shrinkage

temperature and strength properties, and few chemical indexes like as content of chromium in leather, content of volatile or extractable with dichloromethane materials. Of course, these indexes also are very important, but their values are determined by changes in derma structure which are occurred during leather processing. Any change of leather manufacture process reflects on derma structure and influences the final properties of leather. Development of new and more environmentally friendly technologies of leather processing leads to markedly differences in leather structure comparing with leather processed under conventional technologies.

The aim of this research was the investigation of leather structural properties dependence on chrome-free materials used for tanning process and estimation of chrome-free tanning method suitability in conformity with physical and chemical properties of leather.

EXPERIMENTAL PROCEDURES

Parameters of processes

Salted cattle hide was used as a raw material. The samples for the investigation were taken from lower part of the hide. The parameters of hide processing are presented in Table 1.

The pelt after preparation to tanning process was cut into pieces (5 × 10) cm and 7 equal series of samples were formed from these pieces. Also, the solution drained after the preparation to tanning (“weak pickle”) was divided into 7 equal parts and used for tanning, which was carried out in the following ways (material amount, % on pelt mass):

Variant 1 – a) the solution from the preparation to tanning stage was diluted with H₂O 160 %, temperature 25 °C, Na₂SiO₃ 1 % (reckoned as SiO₂), duration 2 h, run continuously;

b) Quebracho (Tanac S.A, Brasil) vegetable tannins 30 %, duration 24 h, run continuously;

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Table 1. Processes before tanning

Process title	Process parameters		
	Material title and amount, % on hide (pelt) mass	Temperature, °C	Duration and regime
Washing	H ₂ O – 200	23–25	1 h run continuously
Soaking	H ₂ O – 200, Na ₂ CO ₃ (100 %) – 1.35	23–25	1.5 h run continuously; later 5 min. every 1 h. Total – 12 h.
Liming and opening up of derma structure	H ₂ O – 100, non-ionic surfactant – 0.1; Ca(OH) ₂ (100 %) – 2.3, Na ₂ S (100 %) – 2; Ca(OH) ₂ (100 %) – 2.3; H ₂ O – 100	25–27	30 min run continuously; 1.5 h run continuously; 1 h run continuously; 17 h run continuously.
Washing	H ₂ O – 400	25–27	1 h run continuously
Delimiting and bating*	H ₂ O – 40, CH ₃ COOOH (peracetic acid) (100 %) – 0.75; Enzyme preparation Novo Bate WB – 0.30	35–37	1 h run continuously; 1 h run continuously.
Washing	H ₂ O – 200	20–25	0.5 h run continuously
Preparation to tanning “weak pickle”**	H ₂ O – 40, NaCl – 5.5; HCOONa – 1; H ₂ SO ₄ (98 %) – 0.5	20–22	20 min run continuously; 15 min run continuously; 5.5 h run continuously.

* Delimiting, bating and preparation to tanning were carried out under conditions described in literature [7, 8].

c) KAl(SO₄)₂ · 12H₂O 1.5 % (reckoned as Al₂O₃), duration 6 h, run continuously;

d) Na₂CO₃ 1 %, duration 15 min, run continuously;

e) Na₂CO₃ 1 %, duration 15 min, run continuously;

f) Na₂CO₃ 1 %, duration 45 min, run continuously;

Variant 2 – as (1), replacing Quebracho by Mimosa (Tanac S.A, Brasil) vegetable tannins 30 %;

Variant 3 – as (1), replacing all Quebracho by Quebracho 15 % and Mimosa 15 %;

Variant 4 – as (1), replacing all Quebracho by Quebracho 21 % and Mimosa 9 %;

Variant 5 – as (1), replacing all Quebracho by Quebracho 9 % and Mimosa 21 %;

Variant 6 – as (1), replacing Quebracho by Chestnut (Tanac S.A, Brasil) tannins 9 % and Mimosa 21 %;

Variant 7 (control) – a) temperature 20 °C–22 °C, Chromeco Extra (Gruppo Chimico Dalton, Italy) 1.5 % (reckoned as Cr₂O₃), duration 12 h, run continuously;

b) Neutragene MG-120 (Codyeco s.p.a., Italy) 0.25 %, duration 2 h, run continuously;

c) Neutragene MG-120 0.25 %, duration 2 h, run continuously;

d) H₂O 40 %, temperature 55 °C, duration 1 h, run continuously.

All samples after tanning were stored during 48 h.

Commercial products used in the processes

a) Enzyme preparation Novo Bate WB (Novozymes, Denmark) is a bacterial protease produced by submerged fermentation of a *Bacillus* micro organism, which is commonly applied in the re-bating process of wet-blue stock.

b) Quebracho, Mimosa and Chestnut (Tanac S.A, Brasil) vegetable tannins are commonly applied in vegetable tanning or retanning.

c) Chromeco Extra (Gruppo Chimico Dalton, Italy) is chroming material having 33 % basicity.

d) Neutragene MG-120 (Codyeco s.p.a., Italy) is a material applied for increasing of chromium compounds

basicity, high chrome fixation and uniform distribution, containing magnesium oxide.

Chemicals

Chemically and analytically pure chemicals without any additional preparation were used carrying out analyses.

Methods and analyses

The shrinkage temperature of leather was measured using special equipment [9].

Content and exhaustion of organic and inorganic matter in leather were determined according to the methods described in literature [9]. Content of chromium compounds in leather was determined by method described in [10].

The physical and mechanical properties were determined according to standard [11].

An infrared (FTIR) reflection spectrum was obtained using a Perkin-Elmer FTIR Spectrum GX (USA) spectrometer using KBr pellets. The resolution 1 cm⁻¹, scan rate 0.2 cm/s and scan number 16 times. The software “Spectrum 5.0.1” was used calculating the area of peaks in spectra ΔS (T%·cm⁻¹).

Differential scanning calorimetry (DSC) analysis was performed with the Netzsch Gerätebau GmbH (Germany) thermal analyzer in nitrogen atmosphere at the heating rate of – 10 °C/min.

Statistical analysis

All data were expressed as the mean indicating standard error of triplicate measurements. Confidence limits were set at P < 0.05. Standard deviations did not exceed 5 % for the majority of the values obtained.

RESULTS AND DISCUSSIONS

The knowledge of the character of crosslinking bonds is of great importance to the tanning chemistry. The formation of such bonds decreases the solubility of collagen, which increases the shrinkage temperature and influences many other properties.

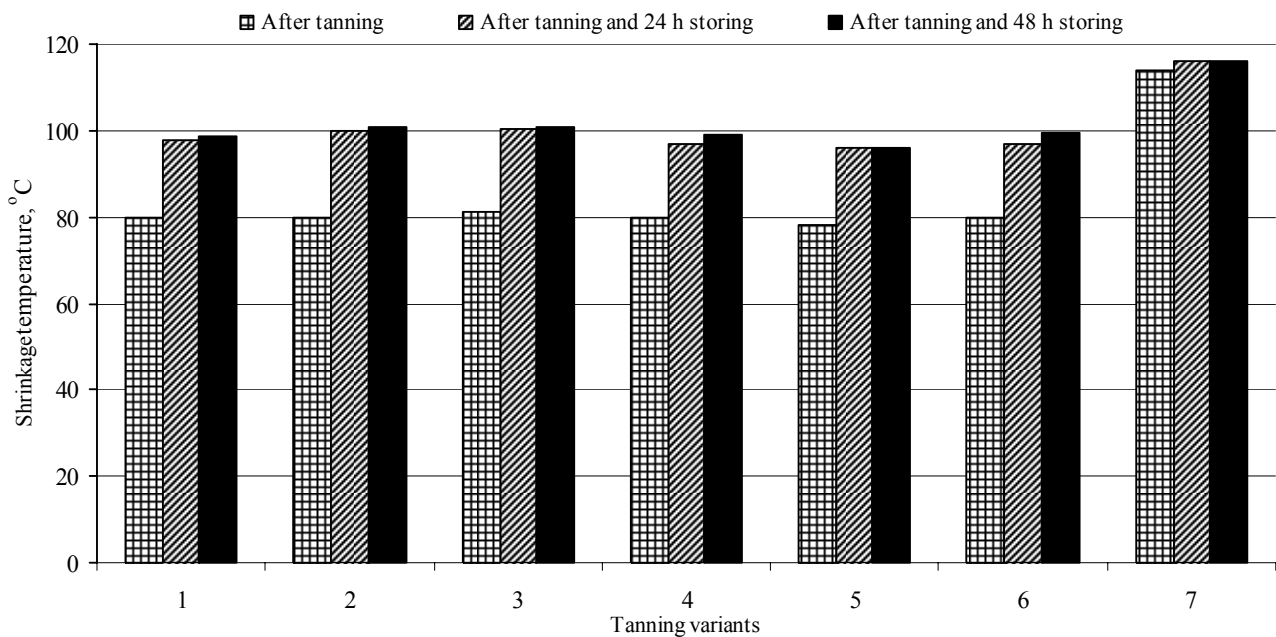


Fig. 1. Dependence of leather shrinkage temperature on tanning method

The change from the soluble to the insoluble fibrous state is an essential biological requirement for crosslinking [12]. Due to this, the shrinkage temperature remains as important index, which reflects quantity of new bonds formed in collagen and quality of tanning and tanned leather. Usually, users of leather, as raw material for shoes, garment or other, require the shrinkage temperature of leather to be not less than 100 °C. Such temperature is reached lightly when chrome compounds use in tanning process. On the other hand, the reaching of such shrinkage temperature using chrome free tanning materials is more complicated due to different crosslinking abilities of various tanning materials. Only combining different chrome free tanning materials for tanning the needful thermal stability can be obtained [13–15]. It is the reason why the combinations of inorganic and organic chrome free agents was used in experiment.

The determination of leather shrinkage temperature has shown (Fig. 1, tanning variants correspond to the methods described in chapter Experimental procedures) that varying combinations of chrome free tanning materials can be achieved even 100 °C shrinkage temperature. On the other hand, there are some differences between chrome and chrome-free tanning.

The chrome tanning allows reaching high shrinkage temperature during tanning. The increase of shrinkage temperature during 24 h of chromed leather storing is negligible: only 2.3 °C. During next 24 h of storing the shrinkage temperature does not change more. Due to the high crosslinking ability of chromium compounds the formation of cross links goes on fast and qualitative.

Different image we have using chrome-free materials. Independently on tanning combination the shrinkage temperature after tanning process reaches only 77 °C–81 °C. However, the process of crosslinking does not stop after ending of tanning and intensive goes on when leather is storing. The shrinkage temperature increases 17 °C–20 °C during first 24 h of storing and

additionally 0.5 °C–2.3 °C during next 24 h up to 96 °C–101 °C. Authors suppose that when storing tanned by chrome-free materials leather the formation of links goes on not only between tanning agents and collagen active groups. The additionally linking between tanning complexes, which are joined to the collagen by one link, takes place and forms new cross links joining adjacent chains of collagen like as in the case of combination tanning with aluminium-phosphonium-vegetable tannins [2].

The highest shrinkage temperature was reached using Mimosa or mixtures of Quebracho and Mimosa vegetable tannins (tanning variant 2 and 3) but, summarising, could be noted that other chrome-free tanning variants allowed to reach sufficiently high shrinkage temperature.

The evaluation of organic and inorganic matter was second step making the image of crosslinking process in leather more perspicuous. Data in Table 2 show that there is no direct dependence between exhaustion of tanning materials and amounts of linked organic and inorganic matter in tanned leather. It means that part of tanning materials, which gets into leather, is not linked overall or is linked weakly and removes during washing with water. On the other hand, the bigger amount of linked tanning materials either organic or inorganic does not decide higher shrinkage temperature of leather. This once more confirms the proposition that somewhat tanning complexes are linked to the collagen by one link without joining of adjacent chains of collagen and, consequently, has not influence on the increase of shrinkage temperature.

Due to this better tanning effect can be obtained not by increasing of initial amounts of tanning materials but through the change of tanning process conditions, which necessitates better linking of tanning materials.

The strength properties of leather are almost most important deciding about quality of manufactured leather. We can process the leather with good chemical properties but it is not suitable for customers if strength properties are not sufficiently good.

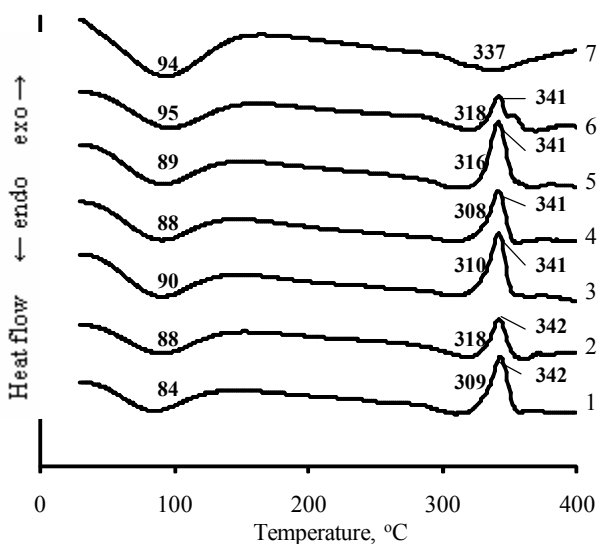
Table 2. Content of organic and inorganic matter in tanned leather

Index	Tanning variants						
	1	2	3	4	5	6	7
Amount of linked organic matter, %*	23.5	22.2	26.2	29.6	25.5	21.9	–
Exhaustion of tannins, %	72.9	77.6	74.3	75.8	76.4	70.3	–
Amount of linked inorganic matter, %*	2.7	3.0	3.1	3.3	3.2	3.0	5.4
Exhaustion of inorganic tanning materials, %	57.5	62.3	58.6	57.0	55.8	58.0	82.5

* Percentage is counted on absolutely dry leather.

Table 3. Dependence of strength properties of leather on tanning method

Index	Tanning variants						
	1	2	3	4	5	6	7
Tensile strength, N/mm ²	15.2	12.8	11.9	12.3	13.3	12.6	18.3
Strain when grain layer breaks, N/mm ²	14.5	12.0	11.2	12.2	13.3	12.6	15.5

**Fig. 2.** DSC curves of various tanned leather (number of curve corresponds to tanning method)

As shows review of literature, usually the chromed leather has higher strength properties comparing with the chrome-free tanned one [16, 17]. Leather strength indexes established in this research are presented in Table 3.

The obtained results were not exception because the chrome-free leather yielded in strength to conventional one. The less crosslinking in collagen determines less tensile strength of leather and less grain strength. Comparing chrome-free leather obtained by different tanning methods it can be said that using Quebracho tannins only (tanning variant 1) the best tensile strength is reached despite the fact that such leather has not highest shrinkage temperature (Fig. 1). This means that not only the crosslinking has influence on tensile strength of leather but, also, individual properties of material used for tanning. The replace of all or part of Quebracho by other tannins determines lower tensile strength of leather and grain strength as well.

DSC and IR spectroscopy were employed to ascertain the structural characteristics of differently tanned collagen. The DSC curves are presented in Fig. 2.

The comparison of these curves shows that behaviour of chromed leather is different from chrome free one, especially, when begins the thermal destruction. On the other hand, DSC curves have only three distinct thermal effects (exception is DSC curve of chrome tanned leather: there are only two distinct endothermic effects).

As is written in literature [18, 19], first effect can be associated with removal of hydration water from derma, which leads to change of collagen structure. Also it is known [13] that mentioned effect can be associated with shrinkage of native collagen. However, the shrinkage of collagen treated by acids or alkalies, as a rule, does not coincide with maximum of this thermal effect.

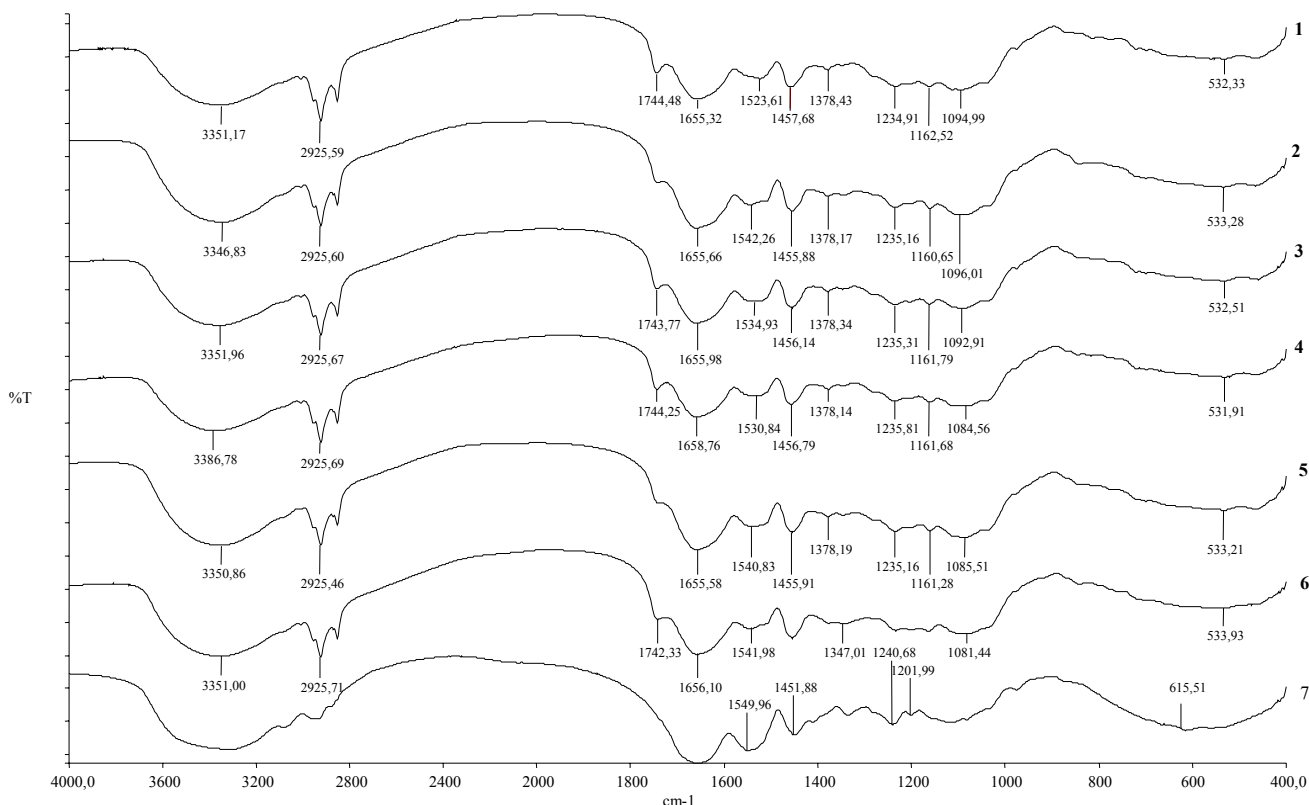
This endothermic effect allows following how differently goes on change (shrinkage) of leather. The comparison of DSC curves shows that maximum of mentioned effect is related to shrinkage temperature: samples after tanning by 2nd, 3rd and 6th method have high values of shrinkage temperature and, consequently, higher temperature of first thermal effect maximum.

According to [18], interval of first thermal effect is more narrow when the collagen is stronger affected by acids and alkalies. Does it is true in our case? All samples till tanning were treated by the same way and all samples were affected equally. But the intervals of first thermal effect are different. This means that influence of acids and alkalies on width of this thermal effect should be rejected. The treatment by acids and alkalies leads to breaking of links in collagen. The tanning process has opposite aim: to form new links in collagen. It allows us to suppose that bigger amount of cross links formed during tanning reflects more wide interval of first thermal effect.

Comparing the results presented in Table 4, the relation between width of first thermal effect and tanning effect, which is confirmed by values of shrinkage temperature, is noticeable: higher shrinkage temperature determines larger interval of thermal effect. This means that bigger amount of cross links in collagen and higher shrinkage temperature leads to higher temperature of first thermal effect maximum and larger interval of this effect. Especially it is observable in the case of chromed leather: it has highest shrinkage temperature, highest temperature of effect maximum and mostly wide effect interval.

Table 4. Delimitation of thermal effects in DSC curves

Tanning variants	First endothermic effect, °C			Second endothermic effect, °C			Third exothermic effect, °C		
	start	finish	Δt	start	finish	Δt	start	finish	Δt
1	46	120	74	287	330	41	330	352	22
2	46	130	84	295	334	39	331	351	20
3	45	126	81	295	329	35	329	350	21
4	46	126	80	294	329	34	329	351	22
5	46	129	83	287	327	40	329	351	22
6	49	132	83	290	334	44	330	349	19
7	38	140	102	326	372	46	–	–	–

**Fig. 3.** IR spectra of chrome-free and chromed leather (number of curve corresponds to tanning method)

Second endothermic effect allows deciding about thermal stability of collagen [20–24]. The effects start in higher temperature when collagen is more thermo stable.

The data in Table 4 show that higher initial temperature of this effect is in cases of chrome-free tanning by 2nd, 3rd, 4th and 6th method and in case of chrome tanning (7th method).

Because the thermal stability of collagen depends on crosslinking quality, that lets to suppose that more cross links in collagen are formed in mentioned cases. Comparing these results with data presented in Table 2 it can be seen that there is not directly dependence between thermal stability of collagen and content of inorganic and organic matter.

This situation once more proves the supposition that quality of cross links formation by organic and inorganic tanning materials decides higher thermal stability of collagen and the content of mentioned materials in collagen is less important factor in the case of chrome-free tanning.

Third exothermic effect is specific to chrome-free tanned collagen only. Unfortunately, any explanation of this effect in literature was not found.

Usually, the structural changes, which are occurred in collagen structure, reflect in IR spectrum (Fig. 3). Comparison of values of peaks areas allows concluding about formation of functional groups and degrading or formation of bonds during leather processing.

The data in Table 5 show differences between areas of peaks in range (3319–3356) cm^{-1} and (2925–2935) cm^{-1} . The vibrations in range (3300–2500) cm^{-1} are attributed to hydrogen bond of associated functional groups O–H, N–H and C–H [25–28]. In cases of 2nd and 7th tanning method the biggest area of peaks in range (3319–3356) cm^{-1} was obtained. It shows that during tanning, as mentioned, the maximum of hydrogen bonds was formed. Because the amount of hydrogen bonds has influence on the system stability the leather having most stability is produced in mentioned cases of tanning. This supposition coincides

Table 5. Data of IR-spectrum quantitative analysis

Functional group or bond, to which the vibration is attributed	Tanning variants													
	1		2		3		4		5		6		7	
	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS	ν , cm^{-1}	ΔS
N-H; O-H	3351	6510	3346	10908	3351	7000	3356	6340	3350	10684	3351	8710	3319	9496
C-H	2925	745	2925	761	2925	584	2925	634	2925	679	2925	570	2935	334
=C=O „amide band I“	1655	1038	1655	1594	1655	1090	1658	1026	1655	1488	1656	1152	1658	2573
„amide band II“	1523	272	1542	413	1534	319	1530	260	1540	417	1541	258	1549	986
-OH; R-COO ⁻	1457	471	1455	434	1456	323	1456	323	1455	378	1455	39	1452	357
„amide band III“	1235	72	1235	99	1235	63	1235	61	1235	78	1235	59	1240	59
(SO ₄) ²⁻ ; R-SO ₃ ⁻ ; R-SO ₃ H	1162	378	1160	615	1160	376	1161	390	1163	589	1163	489	1118	1117
	1094		1096		1092		1084		1085		1081		1082	

with conclusion obtained after evaluation of shrinkage temperature and DSC data.

Comparison of chrome and chrome-free leather spectres shows the differences of peaks intensity in range (2925–2935) cm^{-1} .

It can appear due to tannins, which get into collagen matrix during chrome-free tanning. The area of the peak in spectres of chrome-free tanned leather is about 2 times bigger than in spectrum of chromed one. Under this characteristic the biggest area of the peak in this range has leather tanned according to 2nd method.

Peaks in ranges (1655–1658) cm^{-1} ; (1523–1549) cm^{-1} and (1235–1240) cm^{-1} are attributed to I, II and III amide bands respectively. The area of peaks in the range (1655–1658) cm^{-1} depends on amount of carboxyl carboxyl groups.

Due to the fact that chromium and aluminium basic sulphates quantitative differently join to ionized carboxyl groups of collagen [12], it can be reflected in IR-spectrum. The peak intensity in this range is 1.6–2.5 times bigger for chromed leather (7th method) comparing with chrome-free one (1st–6th methods).

Peaks in range (1082–1163) cm^{-1} are typical to collagen but there is not one opinion which groups are reason of that peak. Nakamoto [29] supposes that peaks in such range can be attributed to the vibration of sulpho groups. It seems to be true, because the biggest area of peak in this range is in the spectrum of chrome tanned leather. Exactly, the biggest amount of sulphates containing chromium compounds is linked to the collagen in this case. Accordingly, the biggest amount of ionised amide groups remains in chromed collagen and this fact reflects on area of peak in range (1655–1658) cm^{-1} .

Carrying out chrome-free tanning the aluminium sulphate is used and area of peaks in spectrum of chrome-free leather depends on the amount of linked aluminium compounds. Under this feature it can be proposed that highest level of linked with collagen aluminium compounds is in leather tanned correspondingly to 2nd tanning method. On the other hand, the data in Table 3 show that mentioned leather has not highest content of inorganic matter. This lets to suppose that more aluminium

compounds and less silica compounds are linked to the collagen in this case.

Summarising the IR spectroscopy analysis results it can be supposed that such analysis enlarges understanding about effect of tanning method on the collagen super molecular structure. Of course, it lets to make absolutely practical conclusion: the data obtained by IR spectroscopy analysis show that chrome-free leather having comparatively best properties is obtained under 2nd chrome-free tanning method conditions.

CONCLUSIONS

The study of structural characteristics of variously tanned leather by physical analyses, especially DSC and IR-spectroscopy allows detecting structural characteristics in derma structure, which can not be found by standard methods of investigation, such as chemical and strength indexes determination. Mentioned characteristics show how differently tanning materials join to derma collagen and prove that content of linked tanning materials is not most important factor, which ordains the thermostability of collagen in case of chrome-free tanning. The results of DSC and IR-spectroscopy clarify the data obtained by other investigation methods and allow more exactly estimation of the tanning method suitability for leather processing. It was established that variation of vegetable tannins in tanning recipe influences on leather properties and best results are obtained using mimoso tannins.

Acknowledgments

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