Evaluation of Collagen Hydrolysate on the Performance Properties of Different Wet-White Tanned Leathers

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Summary

Tanning with basic chromium sulphate is the most commercially favoured process in the manufacture of a variety of high quality leathers. Environmental restrictions to the disposal of chromium containing solids and effluents, as well as speculations concerning the presence of toxic and carcinogenic chromium(VI) traces in leather products, have already directed the industry towards using alternatives. Wet-white tannages which consist of zirconium (IV) and aluminium (III) salts with high durability and resistance and organic alternatives which use phosphonium, aldehydes and some syntans both types with more eco friendly and biodegradable characteristics seem to be the main options for industry. However, properties like high hydrothermal stability, tensile strength, and thickness cannot be achieved by any alternative single tanning method. In this study, collagen hydrolysates derived from gelatin manufacture were used to improve wet-white leather performance properties through combination with tanning agents comprising zirconium and aluminium salts, phosphonium salts and aldehydes. The result shows that the apparent density, shrinkage temperature, denaturation temperature and strength properties of differently tanned leathers increased with the addition of collagen hydrolysates. SEM analyses show that collagen fibres are dispersed after tanning. Besides, collagen hydrolysates make the fibres loosen and the fullness of leather is increased.

INTRODUCTION

Tanning of skins or hides is one of the most ancient arts of humankind, making the raw material resistant to putrefaction, heat and chemical effects.[1] Today, chrome tanning is the common process and is used in the global industry.[2] The reason for versatility of the method is based on the high stability and superior skin characteristics. Whilst this preference is sustained by hydrothermal, heat and light stability and good dyeability, some drawbacks of the method like heavy metal accumulation, high discharge parameters in terms of chloride, sulphate, total suspended solids, chromium and other metal salts are considered to be the main obstacles for the sustainability of this versatile method.[3] In particular, the amount of effluents ,sludge quality and the possibility of the formation of hexavalent chromium compounds in products and sludge wastes over time are indicators that the sustainability of chromium tanning could no longer be foreseen. Increased interest in avoiding certain chemicals and industrial products that are harmful to our environment may indicate that chromium tanning is not able to meet the green approach and it’s not surprising that many brands are becoming ingenious in pointing out attributes that play to this script. So, we hereafter will be hearing the claims for ‘chrome free’ leathers.[4]

The stringent norms set by regulations as well as the deep interest in clean technologies have led tanners to increase their efforts to develop chrome-free tanning agents. Chromium-free leathers have advantages, like the lack of chromium in the effluents, giving recyclable shavings and end-products for agricultural applications, no risk of Cr (VI) formation, improved sorting in the pre-tanned stage, and white and light coloured brilliant leathers. Different markets thus, require the manufacture of chrome-free leather to have properties comparable to those of chrome tanned leather such as feel, fullness, softness, and hydrothermal stability.[5]

Due to the lack of predictability of the future in chromium tanning, wet-white technology seems to be ecologically better without foregoing any of the the distinct properties of mineral tannage.[6] A wide variety of different types of leather can be produced using wet-white system, including automotive, upholstery, garment and shoe upper leathers. At the same time, different market requirements might possibly be overcome by wet-white technology to have comparable properties to chrome tanned leather such as feel, fullness, softness, and hydrothermal stability.[7] This technology also suggests that the environmental impact of chromium could be alleviated or eliminated by substituting the other metal tanning salts, such as Al(III), Ti(III)/(IV), Fe(II)/(III), Zr(IV), and La(III) due to the offer required.[8] Because cross-linking agents play an important role in the physical properties of collagen, wet-white procesing is carried out by methods using the agents capable of reacting with functional groups

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to enhance the properties. A number of alternative tanning agents[9] like zirconium,[10] aluminium,[11] titanium,[9] zinc,[12] vegetable tannins,[13] glutaraldehyde,[14] oxazolidine,[15] starch,[16] silica,[17] syntans,[18] resins[19] and polymers[20] have been investigated by many researchers during the last few decades.

It is well-known that wet-white leathers have lower fastness properties compared to wet-blue leathers including lower thermal stability, tensile strength and fullness. Depending on these properties, the performance of wet-white leathers is lower.[8] Moreover, considering that both chrome and other inorganic pollutants may contaminate air and water and also that vegetable- and organic-tanned leathers are also known to be poorly biodegradable which results in high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), combination tanning systems were considered as suitable to overcome these problems arising from single tanning systems.[21]

In this study, it was aimed to produce improved wet-white leathers with physical and physico-mechanical properties by using collagen hydrolysates having a strong reactivity in the combined tanning process with different wet-white tannages. Thanks to the filling ability of hydrolysates, we aimed to increase the softness and to enhance the biodegradibility by increasing the organic component.

EXPERIMENTAL PROCEDURES

Materials

In this study, collagen hydrolysates obtained by enzymatic hydrolysis from gelatine production were used and and such low grade by-products were intended to generate added value for re-use in wet-white tanning processing. Collagen hydrolysates used in the study were supplied from Halavet Gelatin Co., Turkey. The properties of hydrolysates are given in Table I.

TABLE I
Properties of collagen hydrolysates

Properties	Collagen hydrolysates
Total organic matter	89.81%
Total nitrogen	14.74%
Organic nitrogen	14.60%
pH	4.87
Particle size	1.651μm
Free amino acid content	15.76%,
Colour	White
Form	Powder

When we evaluated the collagen hydrolysate properties, it was concluded that this hydrolysate would increase thermal stability by forming stable bonds with collagen and would be a good filler depending on the organic carbon content and would also act as a good tanning aid by complexing with wet-white tanning agents. The water soluble collagen hydrolysates portions were added directly into the drums and dissolved during the process. The trials were carried out on pickled cattle hides.

Determination of self-tanning action of collagen hydrolysates

In the self-tanning tests the wet-blue leathers were treated with a standard basic tanning procedure, starting with a depickle to pH4.0 and running with additions of 3%, 5%, 7%, 10% and 15% hydrolysate. The time was 4 hours and overnight and subsequently 10% synthetic oil was added and the final pH value was adjusted to 3.2. After rinsing, leathers were taken out for sammying and horsing up overnight and dried properly.

Tanning performance of collagen hydrolysates with wet-white tannages

After the optimisation of collagen hydrolysates proportion for acceptable tanning properties, the experimental process design was composed using the properties obtained by hydrolysates in wet-white tannages. The total amount of hydrolysates (given as X in tables) was 7%, 10%, 15% used in each of four tanning recipes. Each procedure indicated herewith was considered to be easily applicable and appropriate for conventional process equipments and infrastructures. Full cattle hides with the same characteristics were used in trials. Recipes are given in the following Tables II to V.

Analyses

The manufactured leathers were subjected to the tests for shrinkage temperature, denaturation temperature, tensile strength, extension set, apparent density and softness. A Shimadzu AG-IS brand tester was used for tensile strength and extension set. Prior to the tests all leathers were conditioned according to the EN ISO 2419:2012 standard and the sampling was in accordance with the EN ISO 2418:2002 standard The measurement of the thickness of the samples was performed in accordance with EN ISO 2589:2002, tensile strength with TS 4119 EN ISO 3376:2011, extension set test with EN ISO 17236:2002, shrinkage temperature (Ts) with IUP 16, nitrogen contents with

TABLE II
Aluminium tanning

Chemicals	%	Time (min)	Temp. (°C)	pH	Remarks
Water	50		25		6-7°Be’
Collagen hydrolysates	X/2	30			
Sulphited oil	5	60			
Formic acid	0.8	60		2.9	
Collagen hydrolysates	X/2	30			
Aluminium triformate	5	30			
Aluminium triformate	5	90			
Sulphited oil	5	30			
Sodium bicarbonate	0.5	30			
Neutral syntan	1.5	45		4	
Lecithin	3.0	40			
Sodium bicarbonate	0.5	30		4.2	

TABLE III
Phosphonium tanning

Chemicals	%	Time (min)	Temp. (°C)	pH	Remarks
Water	50		25		4-5°Be’
Phosphonium sulphate	5	120			
Collagen hydrolysates	X/2	60			
Sodium bicarbonate	0.5	60		4.0	
Collagen hydrolysates	X/2	30			
Tara	5	60			
Phosphate ester oil	5		40		
Sulphited fish oil	5	30			
Sodium bicarbonate	0.3	30			
Acrylic polymer	4	30			
Lecithin	3	60			
Formic acid	0.7	60			

TABLE IV
Zirconium tanning

Chemicals	%	Time (min)	Temp. (°C)	pH	Remarks
Water	50		25		6-7°Be’
Collagen hydrolysates	X/2	30			
Sulphited oil	5	60			
Formic acid	0.8	60		2.9	
Collagen hydrolysates	X/2	30			
Sodium citrate	5	30			
Zirconium sulphate	10	30			
Sulphited oil	5	60			
Sodium bicarbonate	0.5	30			
Neutral syntan	1.5	45		4	
Lecithin	3	40			
Sodium bicarbonate	0.5	40		4.2	

TABLE V
Aldehyde tanning

Chemicals	%	Time (min)	Temp. (°C)	pH	Remarks
Water	50		25		4-5°Be’
Glutaraldehyde	3	60			
Collagen hydrolysates	X/2	60			
Sodium bicarbonate	0.5	60		4.0	
Collagen hydrolysates	X/2	30			
Oxazolidine	5	60			
Phosphate ester oil	5		40		
Sulphited fish oil	5	30			
Sodium bicarbonate	0	45			
	0.3				
Lecithin	3	60			
Formic acid	0.7	60			

TS 4134 and apparent density with ASTM D 2346-13. The analyses of structural characterisation of the tanned leather samples were carried out with a Hitachi TM-1000 Tabletop Electron Microscope.

Differential scanning calorimetry (DSC) measurements were carried out on the tanned leathers to determine the denaturation temperatures (Td) using a Shimadzu DSC-60 Plus instrument. To investigate the denaturation temperature of tanned leather, each sample, typically weighting 3-4mg, was placed in an aluminum pan, which was covered with an aluminum lid with three small holes. The reference was a similar empty crucible. The analysis was performed in a nitrogen flow (purity 99.99%; 20ml min^{-1}). Leather samples were heated from 25 to 200°C at a heating rate of 10°C/min. The peak temperature of the DSC curve was taken as the denaturation temperature of leather.

RESULTS AND DISCUSSION

Determination of self-tanning action

Collagen hydrolysate is a white and transparent straight chain structural protein which has attractive properties such as biodegradability, weak antigenicity and biocompatibility.[22] Hydrolysis of collagen from the leather waste is not only a solution to the disposal of solid wastes, but also a novel approach to utilise hide collagen. Collagen hydrolysates have a tendency to complex any other chemical due to having reactive hydroxyl, carboxyl and amino groups.[23] Moreover, the interaction forces between peptide chains containing electrovalent bonds, hydrogen bonds, Van der Waals forces and hydrophobic bonds provide many cross links between hydrolysate and other complexes such as with leather or tannages.[24] In the study, the self-tanning action of collagen hydrolysate was investigated. The following parameters were tested after production trials; shrinkage temperature, denaturation temperature, tensile strength, filling effect, total organic nitrogen content. Analysis results are given in Table VI.

TABLE VI
Properties of leather tanned with collagen hydrolysates

Percentage of collagen hydrolysates	Denaturation temperature (°C)	Shrinkage temperature (°C)	Tensile strength (N/mm^2)	Filling effect (%)	Total organic nitrogen (%)
0%	51.17	39.50	20.90	21.17	12.62
3%	53.40	40.00	14.86	25.86	12.06
5%	54.57	40.00	24.61	33.42	13.21
7%	55.03	41.00	24.85	45.58	13.26
10%	54.36	41.00	25.89	43.78	14.20
15%	56.10	42.00	32.45	47.86	15.14

A steady increase of the nitrogen concentrations was observed in the studies. This corresponds to the increase of the organic matter content as nitrogen is increased. This data will be used in the later stages of leather processing with auxiliary substances which increases the capacity for bonding with the skin of other chemical substances. The increase in shrinkage temperature, denaturation temperature and tensile strength properties were determined against the increased amount of collagen hydrolysate used. The filling effect is a parameter representing the skin firmness. The highest enhancement in the trial was provided by the filling effect values. Leather treated without collagen hydrolysate had 21.17% and results after 15% collagen hydrolysate applications were 47.86% with 127% betterment ratio. Self-collagen hydrolysate tanned material was uniform in grain quality, appearance and colour. The tanned leather was full, firm, slightly boardy and white on the grain and flesh sides. Leather treated without collagen hydrolysate was a slightly transparent, thin, dry, bony similar in appearance and texture to parchment and dry raw pelt. Following the evaluation of the results obtained by the analysis and organoleptic assesments in the percentage of use of tanning extract collagen hydrolysate it has been optimised. Accordingly use of the hydrolysate in the concentration range 7-15%, hide collagen hydrotermal stability temperature strength was identified as being the optimum level.

Microscopic observations

Isolation of the fibres was monitored by SEM images as shown in Fig. 1.

When Fig. 1 is examined, images of different sizes in the leather cross-section revealed collagen fibres of the leather in the papillary and reticular layers. It was

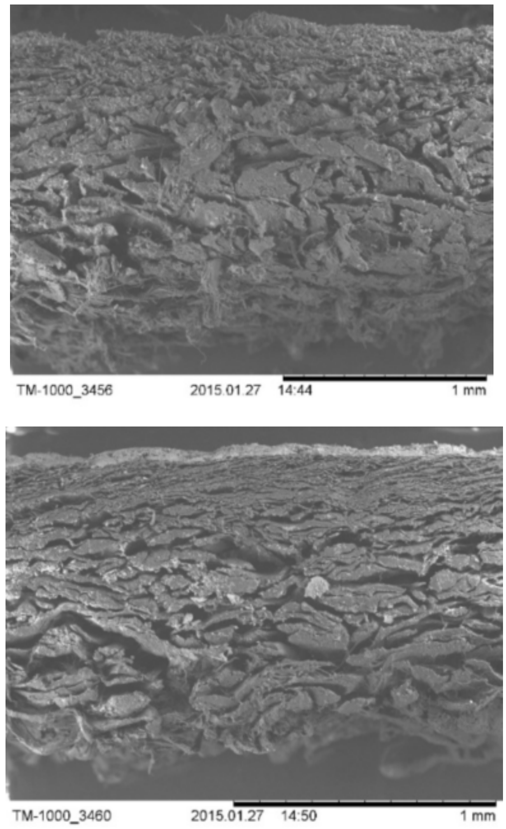

Figure 1. SEM images of hydrolysate self- tanned leather

determined that the fibre bundles were well dispersed and isolated from each other in the samples tanned with collagen hydrolysates. In tanning and after tanning operations; the isolation is expected to improved by the additional additions and auxiliaries which are capable of interacting with the reactive groups to fill up the gaps. As can be seen from the images, it was determined that the isolation of collagen fibres in the ratios of 7%- 15%

TABLE VII
Physical properties of wet-white tanned leathers

	Aluminium-tanned leather				Zirconium-tanned leather			
	0%	7%	10%	15%	0%	7%	10%	15%
Shrinkage temp. (°C)	44.00	45.83	49.16	57.50	53.00	52.50	55.83	56.00
Denaturation temp. (°C)	58.26	59.10	63.25	65.22	57.00	65.09	71.15	72.91
Filling effect (%)	18.44	39.15	43.85	45.67	27.00	45.06	41.18	42.12
Softness (mm)	1.070	1.20	0.85	1.15	0.68	1.75	1.83	1.56
Apparent density (g/cm^3)	0.621	0.859	0.781	0.884	0.684	0.820	0.863	0.809
Elongation (%)	27.03	57.89	40.19	33.66	30.97	37.37	42.96	35.49
Tensile strength (N/mm^2)	18.62	18.08	18.98	19.73	18.08	24.11	19.98	18.13
	Phosphonium-tanned leather				Aldehyde-tanned leather			
	0%	7%	10%	15%	0%	7%	10%	15%
Shrinkage temp. (°C)	72.50	71.66	74.16	75.33	65.33	70.33	74.50	74.66
Denaturation temp. (°C)	59.14	68.16	74.26	76.00	54.00	61.18	72.21	73.36
Filling effect (%)	29.00	48.08	53.76	55.49	28.00	31.78	32.67	33.64
Softness (mm)	0.85	1.15	1.13	1.07	1.15	1.60	1.17	1.17
Apparent density (g/cm^3)	0.551	0.661	0.686	0.700	0.631	0.632	0.633	0.687
Elongation (%)	29.40	41.86	41.99	47.47	22.34	43.18	36.33	30.51
Tensile strength (N/mm^2)	21.23	18.51	19.31	20.52	14.42	13.09	11.01	13.82

collagen hydrolysate offers, which was chosen as the optimum hydrolysate ratio as a result of the evaluation of stability and mechanical properties, is sufficient to provide mechanical strength and can be evaluated as auxiliary tanning agent in wet-white leather production.

Determining the physical properties of wet-white tanned leathers

The tensile strength, extension set, apparent density, softness, fiilling effect, denaturation temperature and shrinkage temperature of leathers are presented in Table VII.

The knowledge of the character of cross-linking bonds is of great importance to tanning chemistry. The formation of such bonds decreases the solubility of collagen, which increases the shrinkage temperature and influences many other properties such as thickness, tensile strength, apparent density and elongation.[25] Table VII shows the increase in the apparent density of the leather with increasing offer of collagen hydrolysate in the tanning process with different wet-white tanning agents. The lowest density value of the leathers was observed in phosphonium tanned leather which does not contain collagen hydrolysate, while the highest density value was obtained in aluminum-tanned leathers containing 7% hydrolysate.

When the tensile strength results are examined; the lowest tensile strength values of the leathers were obtained in the aldehyde-tanned leathers and the highest tensile strength values were obtained in phosphonium-tanned leathers. As a result of tensile strength evaluation, it has been determined that collagen hydrolysates used as tanning auxiliaries in different tanned leathers do not significantly affect the tensile strength values.

Elongation results showed that the usage of collagen hydrolysate in the tanning process, reduces the expansion rate of leather. The expansion of the skin is a parameter representing the skin firmness. The tanning process means that due to the fixing of the collagen protein, after completing tanning a marked decrease in elongation it is expected to occur. The results obtained from tanned leather, show that a decrease in the elongation corresponds to the amount of collagen hydrolysate offered. The lowest elongation value was obtained in aldehyde-tanned leathers which did not contain collagen hydrolysate and the highest elongation value was obtained in aluminum-tanned leathers containing 7% collagen hydrolysate.

When the results of determining the effect of collagen hydrolysates on the leathers were examined; the lowest thickness increases of the leathers were obtained in the tanned leathers and the highest thickness increase values were obtained in phosphonium-tanned leathers. The highest thickness was found in phosphonium-tanned leathers with a collagen hydrolysate of 15% with a value of 55.49%. On the other hand the highest filler effect was determined by aluminum salts and 15% hydrolysate with 147.7 % betterment ratio.

The effects of chemical modifications to collagen results in an alteration to the denaturation temperature which is the main tanning effect.[7] According to Covington *et al.*, recent studies on unmodified and chemically modified collagen indicate that the observed hydrothermal stability is dependent on the moisture content: reducing the water content causes the fibres to approach more closely, preventing them from collapsing into the interstices and which is correlated with elevated denaturation temperature.[26] Therefore, a reduced ability to shrink is the related to the increased hydrothermal stability. Consequently, reducing the ability of collagen to shrink by chemical modification results in higher observed denaturation temperature. The hydrothermal stability of collagen can be modified by many different chemical reactions which is tanning action; thereby, increases the performance as per the demands.[2] Examining Table VII, it can be seen that leather samples with the lowest shrinkage temperature were obtained in aluminum-tanned leathers and the samples with the highest hydrothermal stability were taken from the phosphonium-tanned leathers. The reason for this situation can be explained by the tanning power of the agents. While aluminium salts can set up only electrostatic attraction with a bonding energy of less than 40kj/mol, phosphonium salts can be able to form strong covalent bonds between collagen amino groups with high bond energy.[11,27] When the effects of collagen hydrolyzates on hydrothermal stability were examined, it was found that 10% and 15% percent of hydrolysates increased the shrinkage temperature of the leathers. Denaturation temperature measured by the DSC method is an alternative way for determining hydrothermal stability.[28] DSC analyses showed that 10% and 15% percent of collagen hydrolysates enhanced the denaturation temperature of different tanned leathers. Among the samples, the highest denaturation temperature (Td) was observed in phosphonium-tanned leathers (76°C), followed by aldehyde (73.36°C), zirconium (72.91°C), and aluminum-tanned leathers (65.22°C), respectively. The denaturation temperatures obtained by DSC were in accordance with the values obtained from conventional shrinkage temperature test.

CONCLUSIONS

Wet-white tanning procedure is a method developed for avoidance of possible chromium tanning risks for both humans and the environment. However, the fact that leather performance characteristics are weaker for wet-whites than for chromium-tanned leathers is the biggest obstacle to the spread of this technology. Depending on the regulations and orientations related to the production of chrome-free leather in the leather sector, intensive studies will increase in order to meet the leather specifications and expectations.

In our study; considering the recent concerns about ecological issues, collagen hydrolysates obtained by enzymatic hydrolysis from gelatine production were used to enhance different tanned wet-white leather properties. To improve wet-white product qualities.

Collagen hydrolysates having a strong reactivity were used in combination trials with mineral tannages such as aluminium and zirconium salts, organic alternatives such as aldehydes and phosphonium salts. The wet-white tanning of cattle hides was successfully performed using the optimised collagen hydrolysates ratio. The application of hydrolysates is simple and convenient to use and would slot into any conventional tanning process with relative ease.

Thanks to the filling ability of hydrolysates, their application increased the softness and fullness of leather. Collagen hydrolysate also provided transformation of hides to leather by diminishing the environmental impacts of tannages used in he industry and also enhanced the final leather properties as well as improving the biodegradability. Moreover, it has been determined that these hydrolysates provide a notable improvement in the mechanical and thermal stability of leather. Collagen hydrolysates proved to be instrumental in the generation of an effective tanning auxiliary and the tanned leathers produced were physically and aesthetically comparable to the conventional-tanned material. According to the study, wet-white leather qualities seem obviously to be convertable to the versatile demands which are needed for many types of consumer goods. At the same time; leather properties with ecologically compatibility were obtained with increased proportion of hydrolysates.

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