Reutilization of skin fleshing-derived collagen hydrolizate in the re-tanning/ dyeing/fatliquoring phases

Domenico Castiello [(1)]

Monica Puccini [(2)]

Maurizio Salvadori[(1)]

Sandra Vitolo [(2)]

(1) PO.TE.CO. Scrl – Polo Tecnologico Conciario
Via Walter Tobagi, 30 56022 Castelfranco di Sotto Pisa, Italy

(2) Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali –
Università di Pisa, Via Diotisalvi, 2 56126 Pisa, Italy

Abstract

The investigation conducted assess the feasibility of the reutilization, in the re-tanning/dyeing/fatliquoring phase, of the collagen hydrolizate as it is obtained by alkaline hydrolysis of fleshings, one of the most important by-product of the leather compartment. The hydrolizate has been used both in a vegetable-chrome re-tannage dyeing/fatliquoring and in a vegetable re-tannage dyeing/fatliquoring to obtain bovine upper leather. Following a semi-industrial scale screening of the optimal operating conditions, crust leather have been obtained on industrial scale. The hydrolizate solution may be used as it is obtained by the industrial alkaline hydrolysis process currently adopted in the Santa Croce sull'Arno tanning district. Both in a vegetable-chrome re-tannage and in a vegetable re-tannage, the final leather show similar properties in terms of physical and technical properties. The salt content of the solution is not damaging of the physical and technical properties of the final leather, or rather the introduction of the hydrolizate in the skin structure produces better technical qualities, particularly in terms of better quality of the dyeing that results more intense and homogeneous.

An elevate exhaustion of the hydrolizate was observed, so that a minimal fraction is discharged through the exhaust floats.

The results obtained indicate the reutilization of the collagen hydrolizate in the re-tanning/dyeing/fatliquoring phase as an interesting route for recovering the fleshing.

Introduction

Leather industry is constantly under threat from the pressure of legislation and ever-tightening restrictions has resulted in tanners coming under pressure to minimize the production of wastes. Research interest has thus centered on the development of processes to valorize the by-products by finding suitable industrial uses either in the tanning or in other industrial sectors.

Fleshing represent one of the most important by-product of the leather compartment. They are obtained in the fleshing phase of the unhaired hide and are mainly constituted of raw collagen. A measure of its environmental impact is given by the wastes from fleshing of the industrial tannery district of Santa Croce sull’Arno (Italy), whose production is close to 80,000 tons/year.

In Santa Croce, the fleshing of the whole district is collected and processed in a centralized plant where, through an alkaline hydrolysis, a raw collagen hydrolizate solution is obtained. The high content of salts of the raw collagen hydrolizate, whose separation is cost effecting, is the obstacle that makes difficult its reutilization.

Following the promising results reported in a previous study (1) in which the hydrolizate was used in the tanning phase, we have conducted an experimental investigation to verify the feasibility of recycling the salted collagen hydrolizate in the re-tanning/ dyeing/fatliquoring phases of bovine upper leather production cycle.

In order to assess the feasibility of the use of the collagen hydrolizate for a wide range of final products, the re-tanning/ dyeing/fatliquoring has been developed both after a standard chrome tannage and after a standard vegetable tannage. Besides, the collagen hydrolizate has been inserted into the recipe either in total/partial substitution of filler/fatliquoring agents or in addition of the traditional components.

The procedures, investigated and set up on pilot scale, has been validated on an industrial scale. The quality of the final leathers obtained has been assessed through their organoleptic and physical-mechanical properties. On the basis of the results previously obtained, specific attention has been focused on the dyeing performances.

Experimental procedures

The raw collagen hydrolizate solution was supplied by S.G.S. S.p.A. of Santa Croce sull’Arno (Italy), a centralized plant that treats the wastes from fleshing of all the Tuscany leather district. The hydrolizate solution is obtained through alkaline hydrolysis, degreasing and concentration.

All the process steps were conducted on semi-industrial scale in a stainless steel drum (1.2 m diameter, 0.8 m length) by using heavy calf skins (12-16 kg).

The skins were processed using a standard formulation up to the pickling step; after pickling, some skins were chrome tanned and the rest was vegetable tanned (by using a mix of chestnut and tara) according to standard procedures. A chrome-vegetable re-tanning/dyeing/fatliquoring step followed the chrome-tannage (recipe in Table 1), while a vegetable re-tanning/dyeing/fatliquoring step was provided for the vegetable tanned skins (recipe in Table 2).

The collagen hydrolizate was inserted into the chrome-vegetable re-tanning/dyeing/fatliquoring recipe in total/partial substitution of filler/fatliquoring agents, while in the vegetable re-tanning/dyeing/fatliquoring it was simply added to the standard recipe.

After tannage, each skin, previously sammed and shaved (1.1 or 1.4 mm), was divided into two sides: one side was re-tanned/dyed/fatliquored according to the standard recipe, the other side by introducing the hydrolizate.

After retanning, the crust leathers obtained were characterized by their main physical and technical properties. Physical testing were conducted according to Italian standards (UNI 10594) for upper leather by measuring the extension and load at tear (electronic dynamometer Pegasil Mod. Marte) and the extension and load at grain crack (Pegasil lastometer) according to the Methods ISO 3377-2 and ISO 3379, while technical properties were assesses by the technical personnel of PO.TE.CO. The dyeing performances were assessed by UV-visible spectophotometry on the crust leather samples (UV 2100 Shimadzu spectrophotometer).

The exhausted floats after re-tanning and after fatliquoring were sampled; their dry matter and ash contents were determined by drying in oven at 105°C and by heating in furnace at 800°C, respectively.

The crust leather was also characterized by their ash content by heating in furnace at 800°C.

Results and discussion

The composition of the collagen hydrolizate solution used in this study is reported in Tab. 3. The salt content appears quite elevated and it is due mainly to the presence of NaCl, used in the conservation of the hides. Besides, the protein phase is characterized by a quite low molecular weight and by the presence of a significant percentage of free amino acids. This composition is due to the high degree of hydrolysis of the polypeptides induced by the strong alkaline treatment.

Use of the collagen hydrolizate in the re-tannage/dyeing/fatliquoring of crome-tanned leather: semi-industrial scale runs (RUNS 1-3)

The runs were performed by varying the modality of the introduction of the collagen hydrolizate in the recipe reported in Table 1:

- RUN 1. the collagen hydrolizate was introduced in total substitution the re-tanning agents of the anionic re-tannage (quebracho, diciandiaminic resin and acrylic resin, global dosage 14%, were substituted with collagen hydrolizate at 14% dosage) and in total substitution of the fatliquoring agents (global dosage 6%);
- RUN 2. the collagen hydrolizate was introduced in partial substitution of the re-tanning agents of the anionic re-tannage (quebracho, diciandiaminic resin, acrylic resin, global dosage 7%, were dosed with collagen hydrolizate 7%) and in total substitution of the fatliquoring agents (substituted with a 6% collagen hydrolizate dosage);
- RUN 3. the collagen hydrolizate was used in total substitution of the filler (3% dosage).

Each run was conducted by using correspondent sides of the same whole skin: one side was re-tanned/dyed/fatliquored according to the standard recipe (blank runs), the other according to the same recipe, modified with the total/partial substitution with the collagen hydrolizate.

In order to observe the degree of exhaustion of the collagen hydrolizate, the exhausted floats after re-tannage and after fatliquoring were analysed by their dry and ash content (Table 4).

As expected, in Run 3, where the collagen hydrolizate was used only in the fatliquoring step in total substitution of the filler, non significant increase of the dry matter and of the ash content of the exhaust floats after re-tannage was observed. On the contrary, after fatliquoring, the exhaust float shows an increase of the dry matter and of the ash content. The higher dry matter may be explained by a lower exhaustion of the collagen hydrolizate, while the higher ash content by the salt present in the hydrolizate.

In the RUNS 1 and 2, where the collagen hydrolizate was used also in the re-tanning step, the dry matter and ash content increase both after re-tannage and after fatliquoring and result as higher as the collagen hydrolizate dosage increases. The exhaustion of the hydrolizate appears thus to decrease as the dosage is increased.

The determination of the ash content of the crust leathers (Table 5) shows a decrease of the ash content when the collagen hydrolizate is used. The decrease is more evident when the hydrolizate is used in higher dosages. Since the collagen hydrolizate is characterized by an elevated salt content, the lower value of the ashes of the crust leather indicates that a preferential exhaustion of the proteins occurs and that the salts remain prevalently in the exhaust float.

Results of the physical tests, conducted on the re-tanned, dyed and fatliquored samples, are given in Figure 1. The physical performances of the crust leathers seem to slightly improve when the collagen hydrolizate is used. All samples show good physical properties; the extension to crack test gives a result of between 7.8 and 10 mm (well above the lower limit of 7 mm established by the norm UNI 10594). The tear load test gives a result of between 40 and 77 N, that comply with the requirements. The best performance is obtained when the hydrolizate is used in substitution of the filler.

The technical performance was based on handling and tactile evaluations made upon the crust leather by the expert personnel of PO.TE.CO., expressed numerically. A rating for each property was awarded on a scale of 1 to 5. The results are reported in Table 6. It may be observed that the use of the hydrolizate improves significantly the dyeing performances; the dyeing results more intense and homogeneous.

Despite the good result in terms of uniformity and yield of colour, the crust leather obtained in RUN1 does not complies with the standards required for high-quality leathers. Also RUN 2, even if showing slightly better performances, does not reach the high quality displayed by the blank crust leather. An acceptable performance is given by RUN3, when the hydrolizate is used in substitution of the filler.

The colour yield was also quantitative assessed by UV-spectrophotometry, where each side produced according to the standard recipe was compared with the correspondent side produced by the introduction of the collagen hydrolizate. Table 7 reports the standard evaluation parameters that quantify the colour tonality deviation and the colour yield. In all runs, a higher colour yield is observed with respect to the blank run; the colour yield increases as the dosage of hydrolizate increases. Deviations of the tonality are also observed and they increase as the hydrolizate dosage increases.

Following the results obtained, it may be concluded that the optimal use of the collagen hydrolizate may be found in the total substitution of the filler. In this case, a significant increase of the colour yield and of the physical properties is achieved with respect to the standard recipe, being the technical properties practically identical. Besides, a good exhaustion of the floats is achieved as well.

Use of the collagen hydrolizate in the re-tannage/dyeing/fatliquoring of vegetable-tanned leather: semi-industrial scale runs (RUN 4)

Following the same procedures reported in the previous section, in this case the re-tannage/dyeing/fatliquoring was conducted, according to the recipe reported in Table 2, by simply adding the collagen hydrolizate to the re-tanning agents. In the case of a vegetable-tanned leather, the technical standard required (fullness, roundness, feel) imply the use of specific re-tanning and fatliquoring agents that cannot be eliminated from the recipe. Since the collagen hydrolizate has shown the capability of improving the physical and dyeing performances, it was added to the recipe to verify if this capability is displayed also in the vegetable tannage and re-tannage.

Results of the physical tests, conducted on the re-tanned, dyed and fatliquored samples, are given in Figure 2. Also in this case, the physical performances of the crust leathers seem to slightly improve when the collagen hydrolizate is used. All samples show good physical properties; the extension to crack test gives a result of 8.7 and 9.2 mm (well above the lower limit of 7 mm established by the norm UNI 10594). The tear load test gives a result close to 50, that comply with the requirements.

The technical performance results are reported in Table 8. It is confirmed the improvement of the dyeing performances when the hydrolizate is added to the recipe; the other technical parameters appear comparable or, in some cases, better than the blank crust leather.

The spectrophotometric analysis confirm the technical evaluations about the dyeing improvements due to the presence of the hydrolizate (Table 9).

Use of the collagen hydrolizate in the re-tannage/dyeing/fatliquoring of chrome-tanned leather: industrial scale runs (RUN 5)

Following the results obtained in the semi-industrial scale runs, an industrial run was performed to assess on real scale the total substitution of the filler with the collagen hydrolizate in the chrome-vegetable re-tannage/dyeing/fatliquoring (recipe in Table 1). Due to the good results obtained in the preliminary semi-industrial scale runs, the dosage of the hydrolizate was increases from 3 to 6%.

The skins were processed using a standard formulation up to the chrome tannage according to standard procedures. After tannage the skins, previously sammed and shaved (1.4 mm), were divided into two sides, re-tanned and dyed. After dyeing, ten sides, extracted from the drum, were separately fatliquored in the semi-industrial drum by substituting the filler with the hydrolizate, while the other were fatliquored in the industrial drum according to the standard recipe.

Table 10 reports the determination of the dry matter and ash content of the fatliquoring exhaust floats, as well as the ash content of the crust leathers. Similarly to the semi-industrial RUN 3, after fatliquoring, the exhaust float shows an increase of the dry matter and of the ash content. The higher dry matter may be explained by a lower exhaustion of the collagen hydrolizate, while the higher ash content by the salt present in the hydrolizate. The higher percentage increases are due to the higher dosage of the hydrolizate.

The determination of the ash content of the crust leathers shows a decrease of the ash content when the collagen hydrolizate is used. In comparison with RUN 3, the decrease is more evident and this is due to the higher exhaustion of the hydrolizate used in higher dosage.
The physical tests (Fig. 4), the technical evaluations (Table 11), and the spectrophotometric analysis (Table 12) confirm the results obtained on semi-industrial scale.

Conclusions

The investigation conducted assess the feasibility of the reutilization, in the re-tanning/dyeing/fatliquoring phase, of the collagen hydrolizate obtained by alkaline hydrolysis of the offal, one of the most important by-product of the leather compartment. The hydrolizate has been used both in a vegetable-chrome re-tannage dyeing/fatliquoring and in a vegetable re-tannage dyeing/fatliquoring to obtain bovine upper leather. In the vegetable-chrome re-tannage the best results are obtained when the hydrolizate is used in total substitution of the filler in the fatliquoring step up to a dosage of 6% of solution (68% dry content) on the shaved skin weigh. In the vegetable re-tannage/dyeing/fatliquoring the best results are obtained when the hydrolizate is used in addition to the standard components in the re-tanning step up to a dosage of 6% of solution on the shaved skin weigh. Following a semi-industrial scale screening of the optimal operating conditions, crust leather have been obtained on industrial scale. The hydrolizate solution may be used as it is obtained by the industrial alkaline hydrolysis process currently adopted in the Santa Croce sull'Arno tanning district. Both in a vegetable-chrome re-tannage and in a vegetable re-tannage, the final leather show similar properties in terms of physical and technical properties. The salt content of the solution is not damaging of the physical and technical properties of the final leather, or rather the introduction of the hydrolizate in the skin structure produces better technical qualities, particularly in terms of better quality of the dyeing that results more intense and homogeneous.
An elevate exhaustion of the hydrolizate was observed, so that a minimal fraction is discharged through the exhaust floats.
The results obtained indicate the reutilization of the collagen hydrolizate in the re-tanning/dyeing/fatliquoring phase as an interesting route for recovering the fleshing.

References

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Tab.1. **Chrome tanned skins: procedures for re-tanning/dyeing/fatliquoring (dosages: % on the shaved wt.).**

Washing	**300**	**Water**	**40**		
	0.5	**Oxalic acid**			
	0.2	**Surface active agent**			**Turn 20'**
	150	**Water**	**40**		**Drain**
	200	**Water**	**40**		**Drain**
Cationic re-tannage and basification	**150**	**Water**	**40**		
	1	**Formic acid**		**2.6**	**Turn 10'/pH control**
	10	**Basic chromium (III) sulfate (16% Cr_2O_3)**			
	1.5	**Cationic fatliquor**			**Turn 60'**
	4	**Masking agents**			**Turn 60'**
	Basification with sodium bicarbonate until pH 3,7/3,8				
					Drain
	200	**Water**	**40**		**Drain**
De-acidifica	**100**	**Water**	**40**		
	Neutralization with sodium until pH 5				**Drain**
	300	**Water**	**40**		**Drain**
	100	**Water**	**40**		
	7/14	**Anionic Retanning Agents (vegetable tannins, and resins)**	**and/or**	**7/14**	**Collagen hydrolizate**
					Turn 90'
	0.8	**Formic acid**			**Turn 20'/Drain**
Dyeing	**300**	**Water**	**60**		
	1	**Acid dye**			**Turn 20'**
	0.5	**Formic acid**			**Turn 20'/drain**
	150	**Water**	**55**		**Drain**
Fatliquoring	**150**	**Water**	**40**		
	6	**Mix of fatliquoring agents**	**or**	**6**	**Collagen hydrolizate**
	3	**Filler**	**or**	**3**	**Collagen hydrolizate**
					Turn 120'
	1	**Formic acid**			**Turn 20'/drain**
					Drain/cool/horse up overnight/set out/ vacuum drying 45°C/210 sec (air drying overnight/stake)

Tab.2**. Vegetale tanned skins: procedures for re-tanning/dyeing/fatliquoring (dosages: % on the shaved wt.).**

	%	PRODUCT	T (°C)	pH	Operations & controls
Washing	200	Water	35		
	1	Oxalic acid (solution 1:10 w/w)			Turn 30'/drain
	300	Water	35		Turn 10'/drain
Re-tannage	100	Water	35		
	4	Vegetable tannin (chestnut)			
	2	Diciandiaminic resin			
	2	Naphtalenic syntan			
	2	Phenolic syntan			
	0/6	Collagen hydrolizate			Turn 90'
	0.5	Formic acid			Turn 30'/Drain
	200	Water	35		Turn 10'/Drain
Dyeing	50	Water	20		
	3	Acid dye			Turn 40’
	100	Water	50		Turn 5’
	2	Formic acid			Turn 40'/Drain
	200	Water	55		Drain
Fatliquoring	200	Water	45		
	16	Mix of fatliquoring agents			Run 90’
	0.5	Oxalic acid			Run 30’/drain/cool/horse up overnight/set out (air drying overnight/stake)

Table 3. Composition of the collagen hydrolizate and main chemical-physical properties.

Dry matter (wt.%)	68		
Ashes (800°C)	14		
Nitric nitrogen (wt.%)	0.4		
Organic nitrogen (wt.%)	6.5		
Organic carbon (wt.%)	23.5		
Free amino acids (wt.%)	7.9		
Total amino acids (wt.%)	54		
	Amino acids speciation (wt.%):	Aspartic acid	1.7
S (as SO_2, mg/kg)	385	Glutamic acid	3.9
P (as P_2O_5, mg/kg)	33.6	Glycine	16.4
K (mg/kg)	990	Hydroxyproline	3.1
Ca (as CaO, mg/kg)	853	Leucine	2.4
Na (wt.%)	9.9	Lysine	3.2
Cl (wt.%)	6.1	Methionine	4.6
Density (g/cm^3)	1.25-1.28	Proline	7.3
pH	7.0-7.5	Other	11.4
Mean molecular weigh (kDa)	1.84		
Cinematic viscosity (25°C, cSt)	360		
Dynamic viscosity (25°C, Pa·s)	0.17		

Table 4. Dry matter content and ash content of the exhaust floats of the vegetable-chrome re-tannage.

	Dry matter (wt. %)		Ash content (wt. %)	
RUN	after re-tannage	after fatliquoring	after re-tannage	after fatliquoring
RUN 1	3.81	1.40	1.28	0.32
RUN 1- blank	3.34	1.17	1.20	0.25
Percentage increase	+ 14.1	+ 19.6	+ 6.67	+ 28.0
RUN 2	2.65	1.40	1.12	0.46
RUN 2 - blank	2.43	1.15	1.05	0.40
Percentage increase	+ 9.05	+ 21.7	+ 6.67	+ 15.0
RUN 3	2.84	1.26	1.35	0.41
RUN 3 - blank	2.80	1.13	1.32	0.33
Percentage increase	+ 1.43	+ 11.5	+ 2.27	+ 24.2

Table 5. Ash content of the vegetable-chrome crust leathers.

RUN	Ash content (wt. %)	Percentage decrease
RUN 1	6.28	- 8.32
RUN 1- blank	6.85	
RUN 2	6.85	- 3.52
RUN 2- blank	7.10	
RUN 3	6.92	- 0.86
RUN 3- blank	6.98	

Table 6. Technical evaluation of the vegetable-chrome crust leathers.

Parameter	Blank	RUN 1	RUN 2	RUN 3
Uniformity of colour	3	4	4	4
Intensity of colour	3	5	4.5	4.5
Roundness	3	2	3	4
Fullness	4	3	3.5	3.5
Feel	4	4	4	4.5
Lightness	5	4	5	5
Softness	4	3	3.5	4

Table 7. Comparative spectrophotometric analysis of the vegetable-chrome re-tanned crust leather.

Parameter	RUN 1	RUN 2	RUN 3	Notes
Luminosity	-11.21	-6.74	-2.19	darker than blank sample
Red/Green deviation	3.68	2.43	1.25	+ red
Yellow/Blu deviation	1.38	1.55	1.75	+ yellow
Global Deviation	2.17	1.55	0.85	
Yield	133%	120%	108%	

Table 8. Technical evaluation of the vegetable re-tanned crust leathers.

Parameter	Blank	RUN 4
Uniformity of colour	4	4
Intensity of colour	3	4.5
Roundness	4	4
Fullness	4	4
Feel	4	4
Lightness	5	5
Softness	4	4

Table 9. Comparative spectrophotometric analysis of the vegetable re-tanned crust leather.

Parameter	RUN 4	Notes
Luminosity	-1.27	darker than blank sample
Red/Green deviation	1.21	+ red
Yellow/Blu deviation	1.03	+ yellow
Global Deviation	0.61	
Yield	105%	

Table 10. Dry matter content and ash content of the exhaust floats of the vegetable-chrome re-tannage on industrial scale and ash content of the crust leathers.

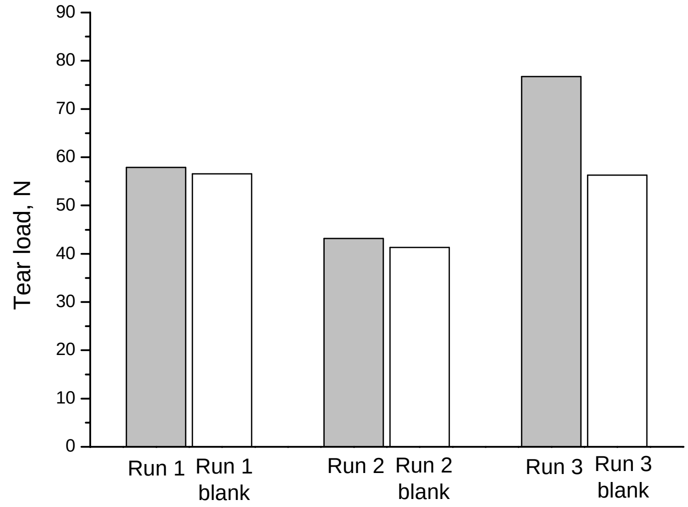
	Exhaust float		Crust leather
	Dry matter (wt. %)	Ash content (wt. %)	Ash content (wt. %)
RUN	after fatliquoring	after fatliquoring	
RUN 5	1.72	0.71	6.60
RUN 5- blank	1.16	0.44	7.08
Percentage increase/decrease	+ 48.3	+ 61.4	- 6.77

Table 11. Technical evaluation of the vegetable-chrome re-tanned crust leathers on industrial scale.

Parameter	Blank	RUN5
Uniformity of colour	3	4
Intensity of colour	3	4.5
Roundness	4	4
Fullness	4	4
Feel	4	4.5
Lightness	5	5
Softness	4	4

Table 12. Comparative spectrophotometric analysis of the vegetable re-tanned crust leather on industrial scale.

Parameter	RUN 5	Notes
Luminosity	-3.09	darker than blank sample
Red/Green deviation	1.28	+ red
Yellow/Blu deviation	0.59	+ yellow
Global Deviation	0.73	
Yield	108%	



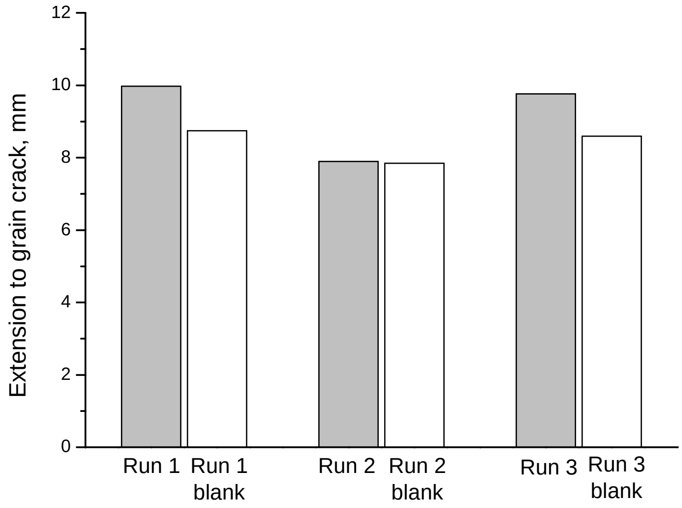


Fig. 1. Tear load and extension at crack of the vegetable-chrome re-tanned crust leathers.

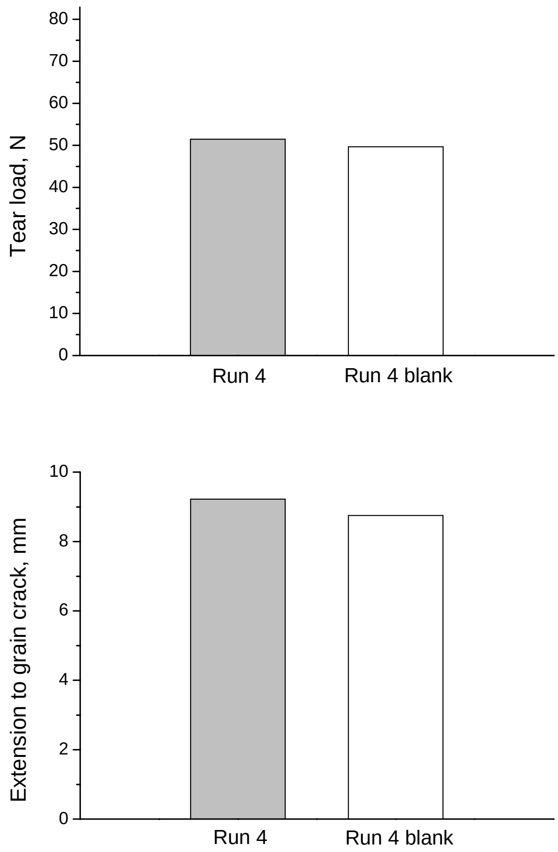


Fig. 2. Tear load and extension at crack of the vegetable re-tanned crust leathers.

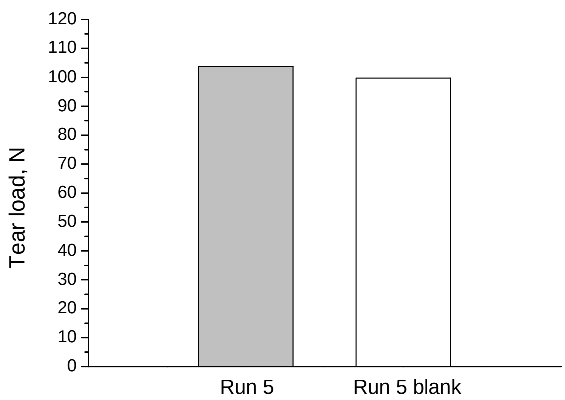


Fig. 3 Tear load and extension at crack of the chrome vegetable re-tanned crust leathers on industrial scale.