COLLAGEN HYDROLYSATE FROM CHROMED SHAVINGS FOR LEATHER FINISH

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Chrome shavings are posing a pollution threat. An alkali-enzymatic hydrolysis method was utilized to get collagen hydrolysate (CH) as possible constituent for leather finishing formulations. The new enzyme preparation Vilzim PRO Conc was exploited for the hydrolysis. The dependence of CH properties on conditions of hydrolysis was explored. The direct addition 5% CH into finishing compositions increases tensile strength and relative elongation of films obtained from the compositions. Further increase of the collagen hydrolysate content in the films leads to worse mechanical properties of the films.

Keywords: leather, chromed shavings, collagen hydrolysate, coating.

INTRODUCTION

Chromium has been used as primary tannage for many leathers for over 100 years (Musa and Gasmelseed, 2013). Despite the fact that many chrome-free technologies were developed (Plavan *et al.*, 2009), nevertheless chromium is considered as the best mineral-tanning. Unfortunately, the chromium gets into leather production wastes like shavings, cuttings, dust and a removal of the chromium from them is very complicated.

Chrome shavings are formed during shaving, which is performed to give the leather the desired thickness. Chrome shavings, one of the major proteinous solid wastes of leather industry are posing a pollution threat (Shakilanishi *et al.*, 2017). Nearly 0.8×10^6 t of chrome shavings are produced from leather industries annually (Rao *et al.*, 2002).

The most common method of disposal for chromed leather shavings is depositing them in landfill (Brown *et al.*, 1996). Unfortunately, there is a risk that trivalent chromium in landfills can oxidize to a more dangerous form.

The next often proposed technological solution to the problem of waste shavings utilization is the production of secondary or artificial leathers designed for footwear elements, fancy goods or non-woven fabrics as substrates for leather-like materials (Prepiorkowska *et al.*, 2007). Another trend (Prepiorkowska *et al.*, 2007) of utilization consists in detanning to recover chromium (III) compounds and processing the recovered collagen into gelatin, adhesives or protein hydrolysate (fodders, modified polymers, film-forming agents). Of course, various products can be obtained from the chromed waste shavings but usually the application of such products as fodders, fertilizers, cosmetic preparations are limited by chromium present in the products (Chaudhary and Pati, 2016). The residues of chromium have less importance when the products are used as fillers for rubber or are reused for leather processing.

Usually, removal of chromium from chromed shavings takes place after detanning of the waste. Depending on a kind of the applied detanning agent, three fundamental means of chromium removal are known chemical and enzymatic methods (Pati *et al.*, 2014). Usually, chemical and enzymatic methods are combined. Firstly, the removal of chromium by chemical materials is carried out and, after that, the enzymatic hydrolysis of treated shavings is executed (Adeoye *et al.*, 2014). The alkali-enzyme two step hydrolysis methods are commonly utilized for improved protein recovery efficiency. Sasia *et al.* (2019) studied a method of treatment which involves a first-step

<https://doi.org/10.24264/icams-2020.IV.10>

denaturation and degradation with alkali followed by inoculation with bating enzyme. Accordingly, hydrolysis using conventional bating enzyme could offer a low-cost alternative for the reuse of chrome-tanned shaving solid waste. Pati *et al.* (2013) investigated protein extraction by protease mixed with α -amylase and found that there was significant change in the protein extraction by protease in the presence of α -amylase.

Probably, the best decision is to apply the hydrolysates for the processing of leather again. Zarlok *et al.* (2015) demonstrated that CH produced from waste chromium-tanned hide by means of acid hydrolysis in the finishing mixes improved the hygienic properties of finished leather. Pahlawan *et al.* (2019) hydrolysed the scraps with NaOH in 90°C and the hydrolysis resulted in two forms of substance, liquid and solid. The liquid substance, as protein binder has the potential to replace the common binder. It is important to know the quality of leather finished using the protein binder.

The aim of the current research was to explore the possibility to use the CH obtained from chromed shavings as constituent of composition for leather finishing.

EXPERIMENTAL

Materials

All chemical materials used for experiments were of analytical grade. Proteolytic enzyme preparation (EP) Vilzim PRO Conc “Baltijos enzymai” (Lithuania) having proteolytic activity at pH 11 and temperature 50°C –1400 units/g. Chromed shavings from calf leather obtained from tannery “Kedainiu oda” (Lithuania) contained 3.7% Cr₂O₃ were used for hydrolysis. Acrylic resin RA-2312 (“Stahl”, Netherlands); polyurethane acrylate mix polimerisate PU-Binder 5954 (“DLH LEDERTECHNIC”, Austria) and polyurethane mix Filler 150 (“EstCo”, Slovakia) were used for coating films formation.

Procedure

Hydrolysis of the shavings was carried out according to the method described by Cantera *et al.* (1994): 10g of shavings; 2% (% here and further from mass of shavings) Ca(OH)₂; distilled water (1200%) and mixing for 30 minutes; NaOH 10% and mixing 2 hours; EP Vilzim PRO Conc and mixing 6 hours. Temperature of the treatment 50°C. After treatment, the liquid hydrolysate was filtrated from solid part.

Analysis and Testing

The enzymatic activity of EP was determined according to Anson method (Standard USSR, 1988). The content of chromium in shavings and CH was determined according standard (Standard ISO, 2007). Dynamic viscosity of CH was determined using Ubbelohde viscometer. The tensile strength and elongation of films were determined using dynamometer Zwick/Roell BDO-FBO.5TH (“ZwickRoell GmbH&Co” Germany).

RESULTS AND DISCUSSION

The exploration of the activity of the EP Vilzim PRO Conc has shown that optimal conditions for action of the EP are: pH 11 and 50°C (activity 1420 units per gram).

The next step was to establish an influence of EP on properties of CH. Accordingly, various amounts of EP were used in the hydrolysis process: 0 (control), 2, 4 and 6%. (Table 1).

Table 1. Properties of collagen hydrolysate dependently on enzyme preparation Vilzim PRO Conc amount used for hydrolysis.

Enzyme preparation amount, %	Collagen hydrolysate qualitative indexes		
	Cr ₂ O ₃ concentration, mg/l	Nitrogen content, g	Dynamic viscosity, Pa·s
0	9.3	0.74	-
2	5.4	0.75	2.1
4	4.8	0.79	1.6
6	8.8	0.69	1.4

Assessment of the presented data allows conclusion that 4% EP is appropriate amount to obtain qualitative CH.

After hydrolysis according to conditions described in the Experimental the properties of the obtained liquid CH were determined: amount of Cr₂O₃ 3mg/l; dynamic viscosity 1.49 Pa·s.

The CH was mixed with other film forming materials used in leather industry in various proportions, films from mixtures obtained and mechanical properties of the films evaluated. The results are presented in Table 2 and Table 3.

Table 2. Properties of films formed from first composition mixtures.

CH	Composition, %			Mechanical properties	
	RA-2312	PU-Binder 5954	Water	Tensile strength, N/mm ²	Relative elongation, %
0	12	23	65	6.36	463
5	12	23	60	9.15	482
10	12	23	50	9.6	444
21	12	23	44	10.6	385

The addition 5% of CH into the first composition (Table 1) improves the tensile strength of the film. Further increasing of CH amount in the composition leads to decreasing of relative elongation of the film.

Table 3. Properties of films formed from second composition mixtures.

CH	Composition, %				Mechanical properties	
	RA-2312	PU-Binder 5954	Filler 150	Water	Tensile strength, N/mm ²	Relative elongation, %
0	11	22	6	61	4.44	582
5	11	22	6	56	5.27	645
9	11	22	6	52	4.17	508
18	11	22	6	43	4.22	529

The investigation of the properties of films obtained using the second composition (Table 2) shows similar results: the addition of 5% of CH into composition improves mechanical properties of the film.

CONCLUSIONS

The collagen hydrolysate obtained from chromed shavings after alkali and enzymatic hydrolysis using enzyme preparation Vilzim PRO Conc is suitable as constituent for leather finishing coatings. The addition 5% collagen hydrolysate into finishing compositions increases tensile strength and relative elongation of films obtained from the compositions. Further increase of the collagen hydrolysate content in the films leads to their worse mechanical properties.

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<https://doi.org/10.24264/icams-2020.IV.10>