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HYDROLYSATES FROM CHROMED SHAVINGS FOR LEATHER FINISH

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Leather's finishing coatings were produced using collagen hydrolysate (CH) obtained from chromed shavings by alkali and enzymatic hydrolysis. 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 worse mechanical properties of the films.

Introduction

Chrome shavings, one of the major proteinous solid wastes of leather industry are posing a pollution threat[1]. Nearly $0.8x10^6$t of chrome shavings are produced from leather industries annually[2].

The most 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[3]. Another trend[3] 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 is limited by chromium present in the products[4]. The residues of chromium has 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. 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[6]. The alkali-enzyme two step hydrolysis methods are commonly utilized for improved protein recovery efficiency. Sasia et al.[7] studied a method of treatment which involves a first-step 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.[8] investigated protein extraction by protease mixed with a-amylase and found that there was significant change in the protein extraction by protease in the presence of a-amylase.

Probably, the best decision is to apply the hydrolysates for the processing of leather again. Zarlok et al. demonstrated that CH produced from waste chromium-tanned hide by means of acid hydrolysis in the finishing mixes improved the hygienic properties of finished leathers[9]. Pahlawan et al. hydrolysed the scraps with NaOH in 90^{o}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^{o}C –1400 units/g. Chromed shavings from calf leather obtained from tannery “Kedainiu oda” (Lithuania) contained 3.7% Cr_2O_3 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[11] described by Cantera et al.: 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; 4% EP Vilzim PRO Conc and mixing 6 hours. Temperature of the treatment 50^{o}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[12]. The content of chromium in shavings and CH was determined according standard[13]. 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

After hydrolysis according to conditions described in the Experimental the properties of the obtained liquid CH were determined: amount of Cr_2O_3 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 1 and Table 2.

Table 1 – properties of films formed from first composition mixtures.

Composition, %				Mechanical properties	
CH	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 in 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 2 – properties of films formed from second composition mixtures

Composition, %					Mechanical properties	
CH	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 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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