

Utilisation of Phenolsulphonic Acid to Hydrolyse Chrome Shavings in Preparation of Composite Condensates for Leather Retanning

JUNQING ZHANG¹, LIMING DONG², MIN CHEN^{1,3} and HAIMING CHENG^{1,3*}

¹ Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu, 610065, China

² Key Laboratory of Cleaner Production and Integrated Resource Utilization of China National Light Industry, Beijing Technology and Business University, Beijing, 100048, China

³ National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, 610065, China

Abstract

The treatment and utilisation of chromium containing tannery waste has been of increasing concern because of the environmental pressure for safe disposal. The aim of this work is a development of the intermediate acids of the syntan to hydrolyse chrome shavings, then the hydrolysed mixtures were condensed with formaldehyde and urea to obtain a composite condensation retanning agent by the one-pot method. The effects of hydrolysis temperature, hydrolysis duration and the amount of chrome shavings were investigated. The molecular weight of the hydrolysate was controlled. The prepared composite condensations were applied for retanning bovine upper leather. The results showed that the prepared composite condensates have an excellent thickening [substance increase], filling and good level-dyeing effect on bovine upper leather. Furthermore, two benefits exist in this development, one is that no extra acid need to be added in the hydrolysis step and the other is that the chromium present does not need to be separated since the final composite product contains Cr(III).

摘要：制革工业含铬废弃物的处理和利用由于面临着严格地安全处置压力而越来越得到关注。本论文旨在采用一锅法利用芳香族合成鞣剂的中间体酚磺酸来水解含铬革屑，所得的水解混合物再与甲醛、尿素缩合制备获得含铬的复合复鞣剂。考察了水解温度、时间以及含铬革屑对水解过程及水解产物分子量的影响。将所制备的复合物用于牛皮鞋面革的复鞣发现该产品具有优异的增厚性、填充性和良好的染色均匀性。本论文所报道的一锅法处理和利用含铬革屑方法再水解过程中无需另外添加酸，而且制备过程中铬无需分离。

INTRODUCTION

In leather making, one ton of salted hide will produce approximately 200kg of finished leather, however over 600kg of by-product and solid wastes are also generated.^{1,2} There are restrictions in many countries on direct discharge of tannery waste, especially the chromium-tanned waste because of the potential risk of the conversion of Cr(III) to acute toxic Cr(VI).³ In China, chromium-tanned waste has been listed as a hazardous industrial waste and must be treated following the special management rules for hazardous materials. Therefore, the treatment and utilisation of tanned waste has been of increasing concern to researchers.

However, chrome shavings containing both Cr(III) and collagenous protein, are a source of materials which could be used in many fields. The material has found application (without separation of Cr(III) and protein) in manufacturing rubber, bonded leather, leather boards, insulators and building materials.⁴⁻⁸ More often, Cr(III) would be effectively removed by various methods and the recovered collagenous proteins are then, mostly used as feeds, fertilizers, fillers in tanneries and gelatins in many industrial fields.⁹⁻¹³

Alkalis and the combination of alkali with enzymes are mostly used for removing the chromium from the tanned wastes.¹⁴⁻¹⁷ Acids have also been used to hydrolyse chrome shavings into a chromium-containing protein hydrolysate, which could be used as a retanning agent for leather manufacture.^{18,19}

The condensate of an aromatic sulfonic acid and formaldehyde makes a typical syntan and such has been marketed for over one hundred years.²⁰ During the synthesis, there is an intermediate with the mixture of aromatic sulfonic acid and sulphuric acid which has the potential to hydrolyse chrome shavings. In this study, phenolsulfonic acid and sulphuric acid were used to hydrolyse chrome shavings, then the hydrolysed mixtures were reacted with formaldehyde and urea to obtain a retanning agent by the one-pot method. The prepared composite was applied for retanning cattle hide upper leather. The composite shows an excellent thickening [increase in substance], filling and good dyeing effects. Furthermore, two benefits exist in this development, no excessive acid need to be added in the hydrolysis step and there is no need to separate the chromium present since the final composite product contains Cr(III).

* Corresponding author: E-mail: chenghaiming@scu.edu.cn

MATERIALS AND METHODS

Materials

Chrome shavings were obtained from local tannery (Cr_2O_3 3.6%, moisture 21.7%). Wet-blue cattle hide was obtained from local tannery. All the chemicals used for the preparation of the hydrolysis and condensation process are of analytical grade and used as received.

Phenolsulphonic hydrolysis of chrome shavings

Step 1: Phenolsulphonic reaction. The reaction was carried out at 130°C with the mole ratio of phenol and sulphuric acid at 1:1.2 for 4 hours. The sulfonation degree was determined according to literature.²¹

Step 2: Hydrolysis of chrome shavings. When the temperature had decreased to 55-90°C, a certain amount of chrome shavings were added for hydrolysis for 0.5-4.0 hours. The amount of chrome shavings, temperature, and hydrolysis duration were investigated. The hydrolysis yield and molecular weight of the hydrolysate were evaluated periodically.

Step 3: Condensation. The temperature of the hydrolysis system was adjusted to 70-80°C, and then 14.4g of urea were added with mixing to dissolve. 35.7g of formaldehyde was added dropwise over 30 minutes. The reaction was kept at constant temperature for 1- 8 hours. After reaction, the system was cooled down and neutralised with 40% NaOH solution to pH5-6 and then the solid content was adjusted to 50% by deionised water. The obtained composite product was assigned as C-PUF.

Retanning applications

The wet-blue samples were split and shaved to 1.2mm with the sample size at 30 x 20cm. The application process of C-PUF for retanning is listed in Table I.

Determination of the hydrolysis yield

The hydrolysis yield was calculated by the centrifugation method. The hydrolysed mixture was centrifuged at 8000rpm for 10 minutes. The unhydrolysed part was in the pellet, which was weighed and used for calculating the hydrolysis yield.

$$\text{Hydrolysis yield \%} = \frac{W_0 - W_1}{W_0} \times 100\%$$

In which W_0 is the weight (g) of the dry chrome shavings used, W_1 is the weight (g) of the dry unhydrolysed part remained.

SDS-PAGE analysis

The molecular weight distribution of the hydrolysate was determined by SDS-PAGE. The hydrolysate was dialysed in deionised water overnight. The samples were then applied on SDS-PAGE of 10% running gel and stained with Coomassie Blue R250, and then de-stained by the mixture of methanol and acetic acid.

Determination of free formaldehyde content

The free formaldehyde content was tested by acetylacetone assay (GB/T2912.1-1998). Briefly, for the prepared C-PUF, 1g of the sample was diluted and

TABLE I
Retanning process

Process	Chemical	%	Temp.°C	Duration min	Remarks
Wetting back	Water	150	35	90	Drain
	Non-ionic Detergent	0.2			
	Formic acid	0.2			
Retanning	Water	150	B	C	Adjust pH=D
	Sodium bicarbonate	X			
	C-PUF A				
	Glutaraldehyde	1			
Washing	Water	200	35	15	O/N Drain
	Sodium bicarbonate	0.8-1.0			
Neutralising	Sodium bicarbonate	0.8-1.0		60	pH5.5
Washing	Water	200	45	15	Drain
Dyeing and fatliquoring	Water	150		30	
	Dye	2		60	
	Fatliquor mixtures	6			
Fixing	Formic acid	1.0		30	pH3.8-4.0
Washing	Water	200	25	15	Horse up, drying and staking

A: the dosage of C-PUF was set at 4%, 6%, 8%, 10%, 12% and 14%.
 B: the retanning temperature was set at 25, 30, 35, 40, 45 and 50°C.
 C: pH value of the process was set at 2.5, 3.0, 3.5, 4.0, 5.0, and 6.0.
 D: the retanning duration was set at 30, 60, 90, 120 and 150 minutes.

adjusted to a constant volume of 100mL, while for the retained crust, 2g of the shared samples were extracted by 50mL of distilled water at 40°C for 2 hours, and then transferred and made up to 100mL. 1mL of the solution was mixed with 1mL of 0.5% acetylacetone and then made up to 10mL. The solution was put in boiling water for 3 minutes to react. The optical density of the supernatant was measured by a UV9100 UV-vis spectrophotometer (Ruili Analytical Instrument, China) at 412nm to determine the concentration of formaldehyde based on a previously established calibration curve from standard solution.

Determination of total chromium content and Cr(VI) in C-PUF

The total chromium content of the prepared C-PUF was analysed by a 2100DV inductively coupled plasma-atomic emission spectrometry (ICP-AES) (PE, USA). The samples were digested by HNO₃-HCl solution in an oven to exhaust its organic components before determination. Cr(VI) in the prepared C-PUF was quantified in accordance with Chinese National Standard (GB/T 19940-2005), which is based on the reaction with diphenylcarbazide and subsequent quantification by colorimetry. The detection limit of the method is 3ppm of Cr(VI).

Morphological observation

The SEM morphologies of the samples were observed by using a JSM 7500F scanning electron microscope (JEOL, Japan) operating the SEM at an accelerating voltage of 15kV. The grain morphologies of the finished leathers were observed using an Olympus SZX12 stereomicroscope (Olympus, Japan) at 75x magnification and recorded with a digital camera.

Softness assessment

The leather samples were conditioned at 20°C and 65% relative humidity for 48 hours. The softness of samples was measured using GT-303 leather softness tester (Gotech Testing Machines, China) by loading a 500g weight on 35mm leather samples.

Physical properties testing

The shrinkage temperature of the leather was tested using a standard shrinkage temperature recording instrument. The leather samples were conditioned at 20°C and 65% relative humidity for 48 hours, and then their physical properties such as tensile strength, elongation at break and tear strength were determined according to ASTM standard method.

RESULTS AND DISCUSSION

Hydrolysis of chrome shavings by phenolsulphuric acid

Before hydrolysis of chrome shavings, phenol was sulphonated by sulphuric acid at 130°C for 4 hours, reaching a 95% degree of sulfonation. Then, chrome shavings were hydrolysed by the mixture of

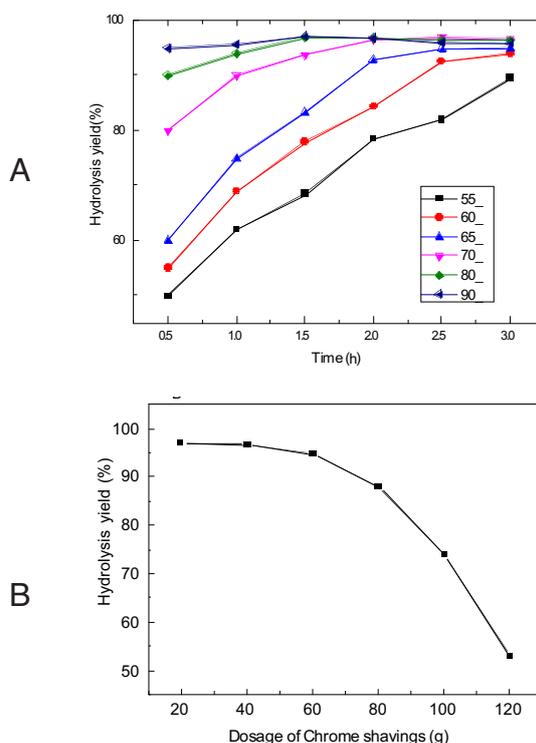


Figure 1. The effect of temperature, hydrolysis duration and dosage of chrome shavings on hydrolysis yield.

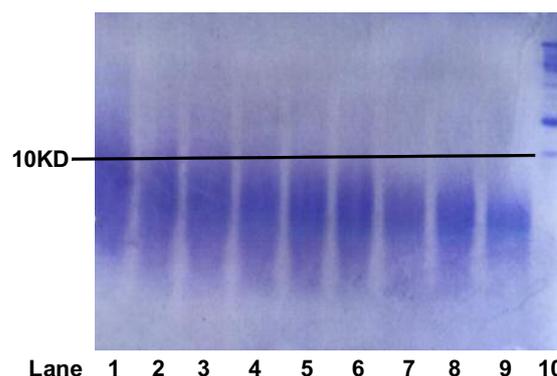


Figure 2. The SDS-PAGE of hydrolysates of chrome shavings by phenolsulphuric acid under 80°C. Lane 1-9, 0.5h; 1.0h, 1.5h, 2.0h, 2.5h, 3.0h, 3.5h, 4.0h, 4.5h; Lane 10 protein marker.

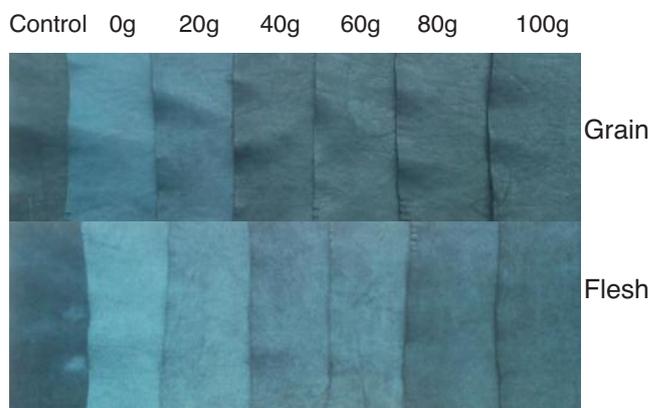


Figure 3. The colour of the crust retained by the hydrolysates with different dosages of chrome shavings. phenolsulphuric acid and sulphuric acid. The amount of chrome shavings, hydrolysis temperature and hydrolysis duration were investigated.

The hydrolysis process was performed by varying the temperature from 55 to 90°C and duration from 0.5 hours to 3 hours to evaluate the effect of temperature and hydrolysis time on hydrolysis. The hydrolysate yield was determined periodically. The results are shown in Figure 1A. It was obvious that the hydrolysate rate increased with increasing hydrolysis temperature. When the hydrolysis process was carried out for 3 hours at 55°C, the hydrolysate yield was 83%. When the temperature was raised to 80°C, the hydrolysate yield reached 95% in just 90 minutes, after which no further increase was observed. We set the hydrolysis temperature at 80°C for the following hydrolysis experiments.

The molecular weight and distribution of the hydrolysates at 80°C with various durations was determined by SDS-PAGE. The results are shown in Figure 2. It shows that extending the hydrolysis time not only causes the molecular weight of the hydrolysates to decrease but also narrows its polydispersity. When the hydrolysis time was 3 hours, the molecular weights of the main components in the hydrolysates are far below 10KD. Although the hydrolysis yield had already reached above 90% for 3 hours at 80°C, to ensure that the hydrolysate maintained a small molecular weight and narrow polydispersity, we chose the hydrolysis performed for 4 hours at 80°C.

The effect of the amount of chrome shavings on hydrolysis process was investigated by adding various amounts of chrome shavings into 100g of the mixtures of phenolsulphonic acid and sulphuric acid treated for 4 hours at 80°C. The hydrolysate yield was determined. The results showed that the hydrolysate yield decreased while increasing the amount of the chrome shavings (Fig. 1B). We all know that the phenolsulphonic syntans show obvious shade weakening effect in leather dyeing, therefore, a higher ratio of the hydrolysates of chrome shavings in the system causes a darker shade dyeing effect on the leather (Fig. 3). Herein, when 60g of chrome shavings is added in the system, the hydrolysis yield could reach 92% in 4 hours at 80°C and the crust shows a good dyeing effect. As a result, in the following investigation, the hydrolysate of chrome shavings prepared using phenolsulphonic acid and sulfuric acid was prepared using 60g of chrome shaving (water content 20%) with 100g of acid for 4 hours at 80°C.

Condensation process

The condensation process was carried out at different temperatures and times. The content of free aldehyde was determined to evaluate the extent of condensation. It showed that, the longer the condensation duration and the higher the condensation temperature, the smaller the amount of free aldehyde remaining in the product (Fig. 4). When the condensation was carried out at 70°C, the free formaldehyde content in the product was maintained at 500mg/kg even when reacted for 8 hours. When the reaction was performed at 90°C, the free formaldehyde

content in the product is about 200mg/kg after 6 hours condensation. To ensure the content of free aldehyde was at a safe level, the condensation process was performed at 90°C for 6 hours. We found that after vacuuming the reactor for 30 minutes after condensation that neutralisation is likely to lead to a further decrease of the free formaldehyde content to less than 100mg/kg.

The characteristics of the prepared synthetic product are shown in Table II. It should be noted that there is no Cr(VI) released during the whole process.

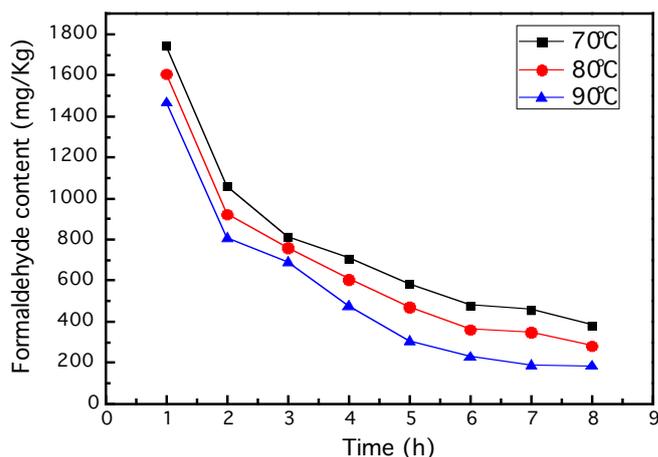


Figure 4. Free formaldehyde content under various condensation temperature and duration.

Solid content (%)	50
Cr ₂ O ₃ content (g/kg)	6.33
Formaldehyde (mg/kg)	85.8
Cr(VI) content	Not detected
pH	5.0-6.0

Retanning application on bovine upper leather

The prepared C-PUF was applied in retanning the bovine upper leather. The effects of C-PUF dosage, pH, temperature and duration to the thickening of leather were investigated. The results are shown in Figure 5.

The retanning process was carried out at 35°C and pH5.0 for 90 minutes by varying the dosage of C-PUF from 4% to 14%. The thickening of the leather was determined (Fig. 5A). The results showed that the thickening increases with increase of the amount of C-PUF from 4% to 12%, reaching the maximum at 23%. Therefore the dosage of C-PUF was used as 12% in the following experiments.

The process was performed at pH5.0 for 90 minutes at temperatures from 25°C to 50°C. It could be observed that the thickening of the leather increases with increasing temperature up to 45°C, reaching a maximum thickening of 27% (Fig. 5B). After that, the thickening of the leather decreases with increase of temperature.

The effect of retanning pH on thickening was investigated by varying the pH from 2.5 to 6.0 adjusted

by sodium bicarbonate. The results are shown in Figure 5C. The thickening reached a maximum when the process pH was 5.0.

The retanning was performed by varying process duration from 30 minutes to 150 minutes at pH5.0 and 45°C to evaluate the effect of process time on thickening. The results (Fig. 5D) showed that extending the process time increases the thickening of the leather up to 90 minutes, after that the thickening is constant at

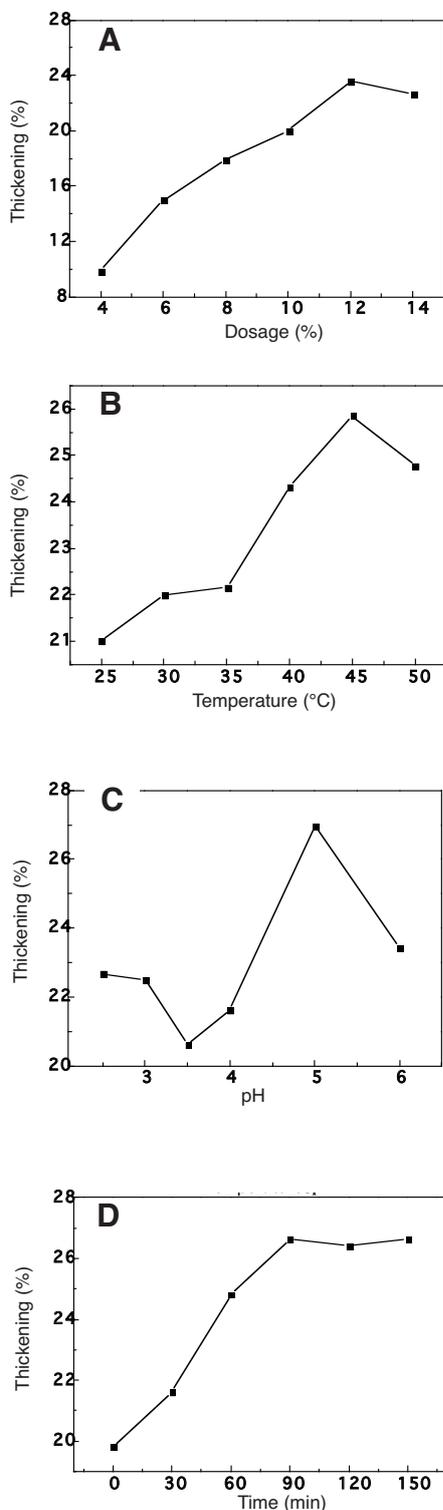


Figure 5. The effect on thickening of the leather. **A**, amount of C-PUF; **B**, Temperature; **C**, pH; and **D**, duration.

approximately 27%. These results indicate that the prepared composite condensation is a potential retanning agent for leather manufacturing.

The physical properties of the C-PUF retanned leather are shown in Table III. It shows that the tensile strength, tear strength and elongation at break of the leather retanned by C-PUF are higher than those of the control sample, suggesting that C-PUF can improve the mechanical properties of the leather. The softness of the C-PUF retanned leather was 5.50mm which is almost same as that of the control sample (5.52mm). It indicates that C-PUF will not influence the softness of the leather. It could be noted that, after retanning by C-PUF, the Ts of the leather increases by 2.4°C, which may due to the existance of chromium in C-PUF.

As a result, The bovine upper leather retanned at 45°C and pH5.0 with 12% of C-PUF for 90 minutes was used for the following analysis.

Samples	Control	C-PUF
Tear strength (N/mm)	60.03 ± 0.84	69.89 ± 0.54
Tensile strength (N/mm ²)	11.36 ± 0.77	13.67 ± 0.79
Elongation at break (%)	88.55 ± 0.42	93.01 ± 1.2
Softness (mm)	5.52 ± 0.03	5.50 ± 0.03
Thickening (%)	0	2814 ± 0.72
ΔTs	0	2.4 ± 0.3

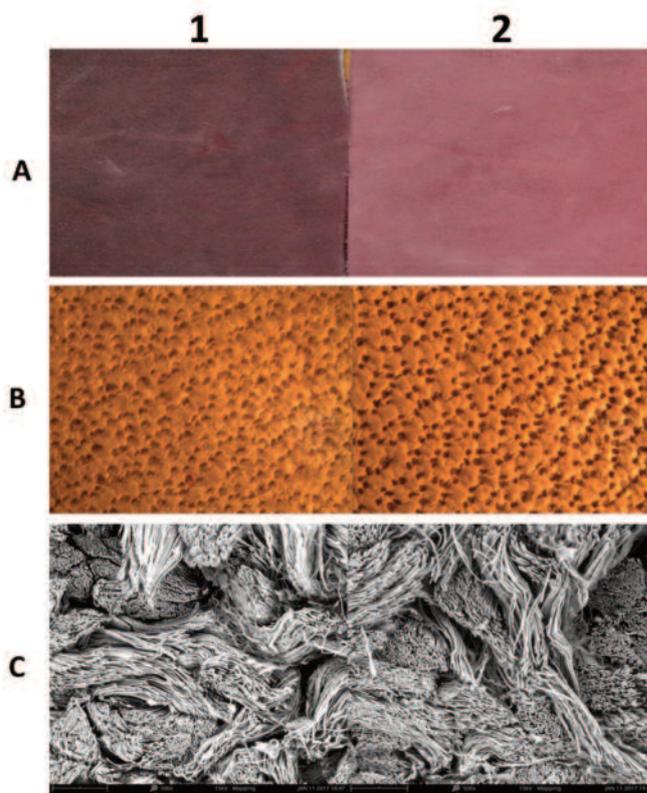


Figure 6. The morphologies of the leather. (1 – control; 2 – C-PUF).

A, Digital camera profiles; **B**, stereomicroscope profiles (75x); **C**, SEM profiles.

CONCLUSIONS

Chrome-tanned wastes have been listed as hazardous industrial materials in China. Due to increasingly serious environmental pressure, how to utilise chrome-tanned wastes is a problem faced by the tanneries and researchers. This study focused on hydrolysing chrome shavings using the immediate product of aromatic syntans made with the mixture of phenolsulfonic acid and sulphuric acid. Then, the hydrolysate was condensed with urea and formaldehyde to prepare the aromatic syntan modified collagen hydrolysates. The chrome containing products were applied in a leather manufacturing process as a retanning agent. The product showed a synergistic effect with aromatic syntan, protein filler and chrome tanning effect. The preparation process could be carried out by a concise one-pot method without excess acid for hydrolysis or a chrome removing step.

ACKNOWLEDGEMENTS

The authors are grateful for the financial aid provided by the Key Research Program of Sichuan Province of China (2017GZ0268, 2017TD0010) and by the Open Research Fund Program of the Key Laboratory of Cleaner Production and Integrated Resource Utilization of China National Light Industry (CP-2018-YB03).

(Received 24 February 2018)



in association with
China Leather

References

1. Cabeza, L. F., Taylor, M. M., DiMaio, G. L. *et al.*, Processing of leather waste: pilot scale studies on chrome shavings isolation of potentially valuable protein products and chromium. *Waste Management*, 1998, **18**, 211.
2. Erdem, M., Chromium recovery from chrome shaving generated in tanning process. *J. Hazardous Mats.*, 2006, **129**, 143.
3. Rao, J. R., Thanikaivelan, P., Sreeram, K. J. *et al.*, Green route for the utilization of chrome shavings (chromium-containing solid waste) in tanning industry. *Environmental Sci. & Technol.*, 2002, **36**, 1372.
4. Sundar, V. J., Gnanamani, A, Muralidharan *et al.*, Recovery and utilization of proteinous wastes of leather making: a review. *Rev. Enviro. Sci. and Bio/Technol.*, 2011, **10**, 151.
5. Rajaram, J., Rajnikanth, B. and Gnanamani, A., Preparation, characterization and application of leather particulate-polymer composites (LPPCs). *J. Polymers and Environment*, 2009, **17**, 181.
6. El-Sabbagh, S. H. and Mohamed, O. A., Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber. *J. App. Polymer Sci.*, 2011, **121**, 979.
7. Ruiz, M. R., Budenberg, E. R., Cunha, G. P. D. *et al.*, An innovative material based on natural rubber and leather tannery waste to be applied as antistatic flooring. *J. App. Polymer Sci.*, 2015, **132**, 1002.
8. Liu, Y., Wang, Q. and Li, L., Reuse of leather shavings as a reinforcing filler for poly(vinyl alcohol). *J. Thermoplastic Composite Mats.*, 2016, **29**, 327.
9. Kolomazník, K., Adámek, M., Andel, I. *et al.*, Leather waste – potential threat to human health, and a new technology of its treatment. *J. Haz. Mats.*, 2008, **160**, 514.
10. Liu, N., Gao, L. F., Ding, Z. W. *et al.*, Preparation of amino acid fertilizer with chrome shavings. *China Leather*, 2015, **44**, 27.
11. Sedliacik, J., Application of collange colloid from chrome shavings for innovative polycondensation adhesives. *J. Amer. Leather Chem. Ass.*, 2011, **106**, 332.
12. Beltrán-Prieto, J. C., Veloz-Rodríguez, R., Pérez-Pérez, M. C. *et al.*, Chromium recovery from solid leather waste by chemical treatment and optimisation by response surface methodology. *Chem. & Ecology*, 2012, **28**, 89.
13. Shanthi, C., Banerjee, P., Babu, N. K. *et al.*, Recovery and characterization of protein hydrolysate from chrome shavings by microbial degradation. *J. Amer. Leather Chem. Ass.*, 2013, **108**, 231.
14. Zhao, J. H., Wang, Q. and Shan, Z. H., Exploration of chrome shavings dechromed by composite alkali. *Leather Sci. Eng.*, 2016, **26**, 68.
15. Wionczyk, B., Apostoluk, W., Charewicz, W. A. *et al.*, Recovery of chromium(III) from wastes of uncolored chromium leathers. Part I. Kinetic studies on alkaline hydrolytic decomposition of the wastes. *Separation and Purification Technol.*, 2011, **81**, 223.
16. Pati, A., Chaudhary, R. and Subramani, S., Biochemical method for extraction and reuse of protein and chromium from chrome leather shavings: A waste to wealth approach. *J. Amer. Leather Chem. Ass.*, 2013, **108**, 365.
17. Zhou, W., and Dan, W. H., Extraction of collagen hydrolysate from chrome shavings with Enzymes. *China Leather*, 2012, **41**, 25.
18. Gonçalves, M. A., Resende, J. E., Oliveira, L. C. A. *et al.*, Use of ethylenediaminetetraacetic acid as a scavenger for chromium from “wet blue” leather waste: thermodynamic and kinetics parameters. *J. Chem.*, 2014, **2014**, 1.
19. Malek, A., Hachemi, M. and Didier, V. New approach of depollution of solid chromium leather waste by the use of organic chelates: economical and environmental impacts. *J. Haz. Mats.*, 2009, **170**, 156.
20. Huang, W. and Shi, B., Tanning mechanisms for aromatic syntans. *China Leather*, 2000, **29**, 17.
21. Liu, X. Y., Li, J. and Liu, W. T., Measuring methods and principle of sulfonation degree of polymer. *Fine and Specialty Chems.*, 2011, **19**, 51.