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Extraction of Protein from Chrome Shavings, Modification with Acrylic Monomers and Further Re-Utilization in Leather Processing

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Abstract

In this study, four retaining products were synthesized by polymerization of extracted protein from chrome shavings waste with acrylic monomers in the presence of initiators. These products were applied for retanning of goat skins to evaluate their effects on quality of leather. Prepared leather samples were tested according to standard test methods. The results revealed that the proteineous products from hydrolysis of chrome shavings waste had significant improvement in quality without inserting bad effect on leather. The polymer prepared from the redox initiators provided highest yield of polymer. The prepared retanning polymers showed better results of tensile strength, tear strength, etc. In this way, the protein from chrome shavings may be reutilized after chemical modification as a replacement of commercial hazardous retanning products.

Key words: Tanned leather wastes; polymers; retanning products; quality leather.

1. Introduction

One metric ton of salted hides/skins produces about 200kg of final finished leather products leaving behind approximately 250Kg of chromium containing solid waste, 350Kg of chrome free waste and 100 Kg losts in waste water[1]. Chrome tanned leather solid wastes are generated during post tanning operations in the form of shavings, splitting, trimmings, and buffing dust. The classical ways for handling of these chrome tanned solid wastes in most of the countries are land filling, throwing at dumping sites or incineration [2]. The chromium containing leather waste mainly consists of protein and Cr^{+3} complexes which can be additionally treated to give the potential resources of collagen protein as well as chromium [3]. The chrome shaving has directly been utilized for the preparation of high exhaust chrome to minimize the chrome in spent chrome liquor and used for the production of quality leather [4]. Different methods have been reported for the extraction, fractionization and isolation of protein from these leather solid wastes [5-7].

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The isolated protein has been utilized in different products such as animal feed formulations, fertilizers , fillers for paper,etc. [8-11]. Recently, chrome shaving protein has been utilized in the preparation of solvent free adhesive usable for various foot wear industries [12]. However, the purification of protein is very costly which makes it non-feasible for the various products. Therefore, we decided to extract and isolate protein from chrome shavings and reutilization in the leather retanning products by polymerization with potential acrylic monomers.

2. Material and Methods

Chrome shavings were collected from the tannery area of Leather Research Centre, SITE, Karachi.Hydrogen peroxide, sodium metabisulphite, sodium thiosulphate were purchased from Merck, Germany. The commercial acrylic acid and acrylamide purchased from local market and used without further purification. The tannery chemicals were purchased from local market and used with out purification.

Hydrolyzation of chrome shavings

Chrome shavings were first washed with water to remove any dust particles. Then, these were hydrolyzed in autoclave using alkaline mixture to separate the hydrolyzed protein from chrome. The hydrolyzed protein material was separated by filtration after completion of hydrolysis process which was carried out at 100-105^{o}C in a closed vessel with certain amount of water (100-300%) based on selection of initial chrome shavings.

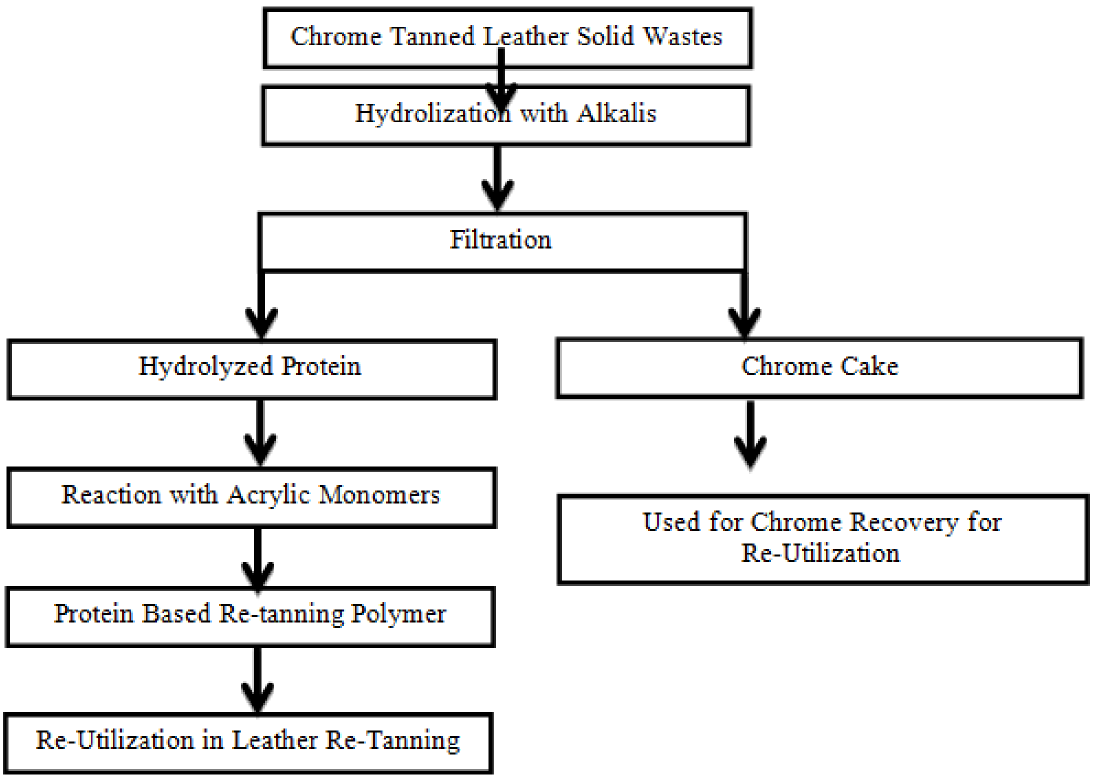

Figure 2: Recovery of Protein and Polymerization with Acrylic Monomers

A commercial acrylic retanning product was used for the comparison of results. Raw goat skins were purchased from local market with full grain and without any defect.

Preparation of Retanning products:

Four retanning polymers were prepared by utilization of alkaline protein isolated from chrome shavings, two monomers and different initiators as shown in table 2. A three necked glass vessel was used for polymerization. Circulation reflux with water was fitted in the central inlet of the flask. The other two inlets were used for the addition of reactants. The flask was charged with protein and heated with continuous stirring. When the temperature reached at 80^0C initiators were added drop by drop in the reaction vessel. The reaction was continued for 2h at same conditions. After complete reaction, the flask was cooled at room temperature. A little amount of inhibitor solution was used to stop the reaction.

Application of Retanning Products

Five goat skins wet blue shaved at 1.0mm $\pm$ 0.3mm processed by Leather Research Centre were retanned with each laboratory prepared polymer and one with commercial acrylic retanning product as under;

Table 1: Tannery Process

Process	**Chemical**	**Control**
Wash	300% Water 35^{o}C	10 minutes
Neutralization	100% Water	60 minutes
	0.8% Sodium Bicarbonate	
	1.0% Sodium Formate	pH 6.0-6.5
Drain & Wash	300% Water	10 minute
Retanning	150% Water 50 ^{o}C	60 minutes
	10% Synthesized Graft Polymer	
	0.25% Formic Acid	20 minutes
		pH 4.4
Drain & Wash	200% Water	10 minute
Fatliquoring	200% Water 65^{o}C	45 minutes
	2% Dye	60 minutes
	6% SR Synthetic Fatliquor	
	6% UPN Fish Oil	
Fixation	1.5% Formic Acid	30 minutes
		pH 3.8

The resulted leathers were, horsed up overnight then set out and dried at room temperature. All chemicals were applied on the base of shaved weight of wet blue.

The physical testing of prepared crust leathers were performed using official methods of analysis for sample cutting, conditioning of leather, distension and strength of grain by ball burst, thickness, tearing load, tensile strength and percentage elongation[13-18]. Universal Testing Machine from Tinius Olsen was used for physical testing of prepared leathers. Leather softness Tester (ST 300) from SATRA was used for the softness test.

3. Results and Discussion

Retanning of leather fills the looser areas of hides and skins and improves the leather properties such as strength, softness, fullness, grain smoothness, etc. Due to multifunctional properties the extracted protein from leather solid wastes is appropriate for the preparation of graft polymer products to improve the above properties of leather. Therefore, we emphasized on the preparation and application of retanning polymers in leather processing.

In the first step, liquid hydrolyzed protein was extracted using alkaline hydrolysis of chrome shavings leaving behind a chromium rich solid residue known as chrome cake. The detailed isolation process is shown in Figure 2 in the material and methods section. The polymeric retanning products were cooled at room temperature and physically characterized as shown in table 2.

Table 2: Reactants and Physical Characteristics of Products

Sample	Reactants Ratio(HP:AM)	Monomer Used	Initiator Used	Colour of Product	Yield (%)
S1	3:1	Acrylic Acid	H_2O_2	Light brown	78.21
S2	3:1	Acrylamide	H_2O_2	Dark brown	89.56
S3	3:1	Acrylic Acid	H_2O_2+ $K_2S_2O_8$	Light brown	77.41
S4	3:1	Acrylamide	H_2O_2+ $Na_2S_2O_5$	Dark brown	90.26

*HP= Hydrolyzed protein, AM =Acrylic Monomer

It was observed that the yield of product from acrylamide was better than acrylic acid.

The rate of reaction is controlled by the ability of amide group of acrylamide to withdraw electrons from the double bond compared to the acid group of acrylic acid. However, colour of product was found dark brown perhaps due to more condensed and long or multi chain polymers due to competitive consecutive reactions.

In this reaction, the grafting of acrylic monomers to the protein was occurred through the covalent bonding. Acrylamide is a conjugated vinyl compound which rapidly goes to the nucleophilic addition reaction with the various functional groups of amino acids of protein such as free NH_2 group, sulfhydryl group (SH) of cysteine, free amino groups of lysine and imidazol group of histidine[19], etc, as shown below;

Protein —SH+ $H_2C{=}CH\ CONH_2$ ⟶ Protein —S— $CH_2CH_2CONH_2$

Protein —NH+ $H_2C{=}CH\ CONH_2$ ⟶ Protein —N— $CH_2CH_2CONH_2$

Protein —NH_2+ $H_2C{=}CH\ CONH_2$ ⟶ Protein —N— $(CH_2CH_2CONH_2)_2$

Figure 1: Polymerization of acrylamide with functional groups of protein.

The highest yield of the polymer was obtained in the sample S4 where a combination of redox initiators was applied. Similarly combined initiators have also been used in industrial process. Due to higher covering of functional groups [20].

The prepared polymers were applied in the retanning of goat skins. The spent liquors obtained after the application of retanning polymer was cleared which showed that the penetration of all the polymers was very good. The leathers were dried as described in material and methods. The procedure for rating of leather for fullness, softness and grain smoothness was adopted to award the points for each functional property by leather experts. The physical testing results of retanning polymers applied in leathers are shown in Table 2.

Table 2: Results of Physical Characteristics of Leather by application of Retanning Products

Product	Elongation (%)	Tensile Strength (N/mm^2)	Tear Strength(N/mm)	Distension at break (mm)	Bursting Load (N)	Fullness	Softness (mm)	Grain smoothness
S1	121.13±2.7*	13.64±1.136	45.70±14.439	58.38±8.750	290.944±71.243	7±1.0	5.70 ± 1.2	7 ± 1.0
S2	132.74±25.69	12.13±3.973	34.91±1.223	63.13±4.941	220.532±5.008	7 ± 1.0	5.8 ± 1.0	7 ± 1.0
S3	148.89±13.091	12.27±0.777	26.79±6.363	51.113±12.141	238.546±40.249	8± 1.0	5.8 ± 1.0	8 ± 0.5
S4	102.49±20.437	14.01±3.799	66.334.244	45.206±1.04	236.545±32.973	8 ± 1.0	6.05± 1.0	7 ± 1.0
S5**	162.48±11.272	10.71±2.693	41.67±3.718	36.340±0.96	237.999±18.25	8± 1.0	6.07± 1.0	8 ± 1.0

*standard deviation is given against each result calculated from three observations of each test

**retanning with commercial Acrylic Retanning (ART-1)

The results as presented in Table 2 showed that the highest elongation was found in the Sample S3 while the lowest was found in sample S4. The highest tensile strength N/mm^2, tear strength N/mm, was found in the Sample S4. The bursting load was found highest in the sample S1. The variation in the results as in the Table 2 was found due to monomer change in retanning polymer composition. The applied protein based polymer has strong affinity with the leather collagen and penetrates easily. Although a small variation was also found in the fullness, softness, and grain smoothness but over all the applied retanning polymer improves the physical characteristics and appearance of leather. The improvement of physical properties of leather with the application of acrylic monomers in the collagen fibers at proper conditions might be due to the formation of an interpenetrating network between the applied acrylic monomers and collagen fibers. The free NH_2 group of acrylamide is found more favourable for the co-ordination of leather fibers and increase the strength, fullness, softness,etc. On the other side, the isolated protein has also played a key role as previously reported as a tanning filler for leather [21].

4. Conclusion

The disposal of chrome shavings from tanneries is a big problem . The valuable protein might be recovered by alkaline treatment of these chrome shavings. The extracted protein from leather solid wastes(chrome shavings) might have potential utilization as leather retanning product after suitable modification with acrylic monomers. Such type of utilization may solve disposition issues of this environmentally restricted waste. The applied leathers were found with improved physical properties and comparable with commercial retanning product.

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5. Recommendations

It is recommended that waste protein from chrome shavings should be extracted and further polymerized with acrylic acid or acrylamide and then used as a retanning agent to obtain required leather.

References

[1]. Taylor, M.M., L.F. Cabeza ,G.L Dimaio , E.M Brown , W.N. Marmer W.N, R. Carrio, P.J Clema and J.Cot. Processing of Leather Waste: Pilot Scale Studies on Chrome Shavings. Part I. Isolation and Characterization of protein products and separation of chrome cake, Journal of American Leather Chemists Association, 93,1998, 61 – 82.

[2]. Alexander K.T.W, Corning D.R, Cory N.J, Donohue V.J and Sykes R.L. Environmental and safety issues—clean technology and environmental auditing, Journal of Society of Leather Technolgists and Chemists, 76, 1991, 17–23.

[3]. Heidemann, E**.** Disposal and recycling of chome-tanned materials, Journal of American Leather Chemists Association, 86,1991, 331-333.

[4]. H.R.Nawaz, B.A Solangi, U.Nadeem , B.Zehra. Preparation of high exhaust chrome from leather shavings and hydrocarbons with its application in leather processing for green tanning technology,Journal of chemical society of Pakistan, 32(4) ,2010, 525-530.

[5]. Imai T., and H. Okamura. Studies on incineration of chrome leather waste. Journal of American Leather Chemists Association 86, 1991, 281-294.

[6]. Cassano, A, Drioli, E., Molinari, R., and Bertolutti, C. Quality improvement of recycled chromium in the tanning operation by membrane processes, Desalination, 108, 1997, 193–203.

[7]. Sivaparvathi,M., Suseela, K., and S.C Nanda . Hydrolytic action of Pseudomonas Aeruginosa on chrome shavings, Leather Science, 33, 1986, 8–11.

[8]. Cabeza, L.F., Mcaloon, A.J and W.C Yee. Process simulation and cost estimation of treatment of chromium containing leather waste, Journal of American Leather Chemists, 93, 1998, 2990-3135.

[9]. Taylor,M.M., W.N Marmer and E.M Brown. Molecular weight distribution and functional properties of enzymatically modified commercial and experimental gelatins. Jounrnal of American Leather Chemists Association, 99, 2004, 133-144.

[10]. Santos, L.M and M Gutteres. Reusing of hide waste for leather fatliquoring, Journal of Cleaner Production, 15, 2007, 12-16.

[11]. Mohamed O.A., and N. F. Kassem. Utilization of Waste Leather Shavings as Filler in Paper Making, Journal of Applied Polymer Science, 118, 2010, 1713–1719.

[12]. A.A Shaikh, A.K Deb, T.Feradous, A.S. Mia. Resource addition to leather industry:adhesive from chrome shaving dust, Journal of Scientific and industrial Research, 6(4), 2017, 138-141.

[13]. BS 3144, IUP-1/EN ISO2419:2006, Sample Cutting , Official Methods of Analysis(1996).

[14]. SLP9 (IUP-9), (International Commission of Chemical Analysis) Ball Burst Test, Official Method of Analysis, SLTC, Northampton (1996).

[15]. SLP,IUP-3;BS3144;method 2, Conditioning, Official Methods of Analysis (1996).

[16]. SLP4, IUP-4, 3144:method3, Thickness, Official Methods of Analysis (1996).

[17]. IUP-6, (International Commission of Chemical Analysis) Determination of Tensile Strength and Elongation at Break, Journal of the Society of Leather Technologists and Chemists, 84, 317 (2000).

[18]. IUP-8, (International Commission of Chemical Analysis) Determination of Tear Strength (Double Edge) from Leather, Journal of the Society of Leather Technologists and Chemists, 84, 327 (2000).

[19]. Jianzhong M A, Lingyun L, ChunhuaX, Wanq W, ZongsuiY. Protein retaining and filling agent from vinyl monomer graft modification of chrome shavings hydrolysate, Journal of the Society of Leather Technologists and Chemists, 88,2004, 1–5

[20]. Nicolas K.S, Pirri R., Asua J.M, Leiza JR, Redox initiator systems for emulsion polymerization of acrylates, Journal of Polymer Science : A polymer Chemistry, 47(11), 2009, 2917-2927.

[21]. W.Xu, J.Zhou, Y.Wang, and B.Shi.Modification of leather split by in situ polymerization of acrylates, International journal of Polymer Science, 2016 http://dx.doi.org/10.1155/2016/7460572.