

A STUDY ON USABILITY OF COLLAGEN HYDROLYSATE ALONG WITH OXAZOLIDINE IN LEATHER PROCESSING

KOLLAGEN HİDROLİZATLARI İLE OKSAZOLİDİNİN DERİ İŞLENTİSİNDE BİRLİKTE KULLANILABİLİRLİĞİ ÜZERİNE BİR ARAŞTIRMA

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ABSTRACT

In this study, it is aimed to find out usability of collagen hydrolysate along with oxazolidine in retanning process to achieve an enhanced over all strength and fullness properties of leathers and to reuse hazardous chromed shaving wastes from leather industry as well. Those wastes were hydrolyzed with commercial enzyme preparation in an alkali medium. This collagen hydrolysate was used along with oxazolidine in retanning process. Strength and fullness properties of leathers were evaluated after applying varying ratios of collagen hydrolysates (7.5-10.0-12.5-15.0 %) along with oxazolidines (4-6-8%). As a result it is determined that all applied combinations had enhanced expected properties of leather. The highest strength and fullness properties were found to be achieved in the samples which were processed with the combination of 15 % hydrolysate and 6 % oxazolidine.

Key Words: Chromed shaving waste, Collagen hydrolysate, Oxazolidine, Retanning, Tensile strength, Fullness, Tear load, Leather.

ÖZET

Bu projede, derilerin dayanım ve dolgunluk özelliklerini geliştirmek için retenaj prosesinde kollagen hidrolizati ile oksazolidinin birlikte kullanım ve deri endüstrisinin zararlı tıraş atıklarını değerlendirme olanakları araştırılmıştır. Bu atıklar, alkali bir ortamda ticari bir enzim preparatı ile hidrolize edilmiştir. Elde edilen kollagen hidrolizat, oksazolidin ile birlikte retenaj işleminde kullanılmıştır. Farklı oranlarda uygulanan kollagen hidrolizati (% 7,5, 10,0, 12,5 ve 15,0) ile oksazolidinin (% 4,0, 6,0 ve 8,0) deriye verdiği dayanım ve dolgunluk özellikleri tespit edilmiştir. Sonuçta, uygulanan tüm kombinasyonların deride istenilen özellikleri geliştirdiği saptanmıştır. En iyi değerler ise % 15 hidrolizat ve % 6 oksazolidin kullanılması ile elde edilmiştir.

Anahtar Kelimeler: Kromlu tıraş atığı, Kollagen hidrolizati, Oksazolidin, Retenaj, Kopma dayanımı, Dolgunluk, Yırtılma dayanımı, Deri.

Received: 11.07.2008

Accepted: 17.09.2008

1. INTRODUCTION

Chromium salts have been used commonly as a tanning agent due to its excellent tanning property, low cost, easy application and wide supply. Approximately 25% of chrome tanned leathers are discarded based on their weight in the processes like trimming, shaving and buffing (1, 2). As a result a world total of 540.000 tonnes of chrome tanned solid waste is produced each year. This collagen based waste consists of 4.5% three valenced chrome on average (3).

Interest on this waste has increased in recent years due to its volume and oxidation risk of Cr(III) to Cr(VI) which is carcinogenic for human and more toxic

for environment. Discharging of the solid waste to restricted areas is a problem for tanners due to the high cost.

There are some researches related to use of alternative tanning agents and/or modified processes of leather production which is aimed to decrease the amount of solid waste and pollution load (4).

In recent years, various methods were developed to separate chromium and collagen (5, 6). Possibilities of using collagen hydrolysates which produced by those methods were the main topic of the studies. Collagen hydrolysates have been used in various industries like artificial leather, plywood, fertiliser and nutritional products (7,8). The

noxious wastes from the tanning industry such as chrome-tanned leather shavings were used as filler of rubber mixes containing carboxylated butadiene-acrylonitrile rubber (XNBR) or butadiene-acrylonitrile rubber (NBR), to improve the mechanical properties: tensile strength (Ts), elongation at break (9).

Products which are produced by modification of collagen hydrolysate with acrylate and glutaraldehyde have been used as filler in retanning process (10,11). Lime fleshing wastes were hydrolysed with a proteolytic enzyme and further broken down to the amino acids prior to combining with the corresponding aldehyde, which will act

as a cross-linking agent in tanning (12). A research made on collagen hydrolysates from chromed leather wastes showed that it is possible to modify them with epoxy resins to be used in leather processing (13). To increase the chrome uptake of leather, unmodified hydrolysates were used at the end of chrome tanning or chrome retanning as well (14,15). Possibilities of using collagen hydrolysate along with oxazolidine, which is generally applied with vegetal tannins in combinations are researched to develop strength and fullness properties of leather (16,17,18).

Our study apart from the above mentioned literatures is exclusively focused on the use of oxazolidine as a crosslinking agent for collagen hydrolysate which produced from chromed shaving waste in retanning to enhance the physical properties of leather.

2. MATERIALS AND METHODS

2.1. Materials

In this research pickled sheep skins and chromed shaving wastes were supplied from a tannery. Chemicals were also supplied as follows: Oxazolidine (100 %), Münzig Chemie; MgO (GR grade), Merck; alkaline protease Rodazym ML, Rohm&Haas.

2.2. Method

First of all, collagen hydrolysates were produced from the chromed shaving wastes to be used as filler in retanning for removal of looseness in leather structure. Pickled skins were processed according to a regular garment leather production recipe (Table 1). In the retanning phase of the process 12 different collagen hydrolysate-oxazolidine combinations were used. The physical properties of the processed leather groups were tested according to the related standards which the application was capable of enhancing.

2.3. Preparation of Collagen Hydrolysate

Shaving wastes of sheep leathers, that had pH of 3.8 were soaked by 500 % water of their weight. Then they were treated with 4 % MgO for 30 minutes at 65 °C. In the following step, the enzyme Rodazym ML was added to the solution at a ratio of 1 %, and the mixture was shaken for 4 hours. The solution obtained was then filtered to separate chromium cake and liquid collagen hydrolysate (3). The pH of the separated liquid collagen hydrolysate was adjusted to 7,0 by adding 0.1 N

HCl. Then, liquid hydrolysate was used in a concentration of 40 % after a partly evaporation.

2.4. Processing of Skins

The pickled skins were divided as sides through their backbone due to increase of research material quantity and uniformity (19).

Pickled skins at pH 2,5 were depickled to increase the pH value. Depickled skins were bated to loose structure and degreased to reduce natural fat content. Research materials were randomly divided into 13 batches according to the application quantities of hydrolysates and oxazolidines then each lots were weighted. The groups

of leathers were retanned with combinations of 7.5-10.0-12.5-15.0 % collagen hydrolysate and 4-6-8 % oxazolidine. And one batch is kept as blank. Then leathers were dried and treated with some mechanical processes as in conventional systems up to finish.

For the physical tests the following Official Standards were used: IUP/1 and IUP/3 for sample preparation and conditioning; IUP/2 for sampling location; IUP/4 for measurement of thickness; IUP/6 for tensile strength and percentage elongation; IUP/8 for tear load (20). The results were statistically evaluated using Microsoft Excel program.

Table 1. The leather production recipe

Process	Chemical Additives	Temp. (°C)	Prop. (%)	Time (min.)	Remarks
Weight					weight + % 30
Depickle	Water	25	200		
	Sodium chloride		11	15	
	Sodium formate		1	45	
	Sodium bicarbonate		1	60	pH:5,5
Bating	Acidic enzyme		0.5	60	drain
Degreasing	Alkyl polyglycoside		2	30	
Washing	Water	35	200	20	drain
Washing	Water	35	200	20	drain
Pickle	Water	25	100		
	Sodium chloride		7	15	
	Formic acid		1	45	
	Sulfuric acid		0,8	60	pH:3,2
Tanning	33 % Basic chromium sulphate		8	240	
Basification	Sodium formate		1	45	
	Sodium bicarbonate		0,8	60	pH:4,2. horse up and shaving
Washing	Water	25	200	20	
Neutralization	Water	35	100		
	Sodium formate		1	40	pH:5,5, drain
Retanning	Water	40	150		
	Collagen hydrolysate		X*		X*:7,5;10,0;12,5;15,0
Fat liquoring	Oxazolidine		Y*		Y*:4;6;8
	Combined fat liquor		5		
	Sulphite fat liquor		1		
	Formic acid		1	20	drain
Washing	Water	25	200	20	horse up

3. RESULTS AND DISCUSSION

Almost all of the skins and hides are processed through a secondary tanning step to enhance the physical properties, remove the looseness and to increase the useful area of the skins which is called retanning.

Collagen fiber structure formation and its modification degree with tanning agents have a significant effect on leather strength (21) It is pointed out that the **main effect on the strength properties of leather is mostly based on papillar and reticular layers the reticular layer is more effective than other** (22).

In this study, collagen hydrolysate which produced by chromed shaving waste was used along with oxazolidine as a cross-linking agent in retanning to enhance the physical properties of leather.

3.1. Tensile Strength

A good tensile strength value is desired in all leather types and this characteristic is an important indicator about leather quality (23). In this study, tensile strength values were found to be between 3,43 N/mm² and 9,63 N/mm² (Table 2). Sample 12 was given the highest tensile strength with a value of 9,63 N/mm². It was shown that tensile strength of leathers had been positively effected with increasing quantities of collagen hydrolysate and oxazolidine usage .in retanning.

A research made on lamb skins showed that the value of tensile strength was 12,94 N/mm² (24). UNIDO declared that chrome tanned leathers must have minimum 10 N/mm² tensile strength (25).

When we compare the results of the tensile strength tests of the leather processed with collagen hydrolysate-oxazolidine combinations with the value on the above mentioned literatures it is obvious that the values are lower. In a routine retanning process, some retanning agents like chromium, aluminium, vegetal tannins, syntans and resins are used to increase the crosslinkage between the collagen fibers which were lacking after tanning, too. By this way, strength and fullness properties of leathers can sufficiently be developed. However, in our study, as it is aimed to find out usability of collagen hydrolysate along with oxazolidine in retanning process,

only combinations of hydrolysates and oxazolidines were used. Due to the known lack of the crosslinkage among the collagen fibers, expected weakness on this properties were determined.

3.2. Elongation at Break

The elongation at break of the leather gives an idea about the fullness property. In general lower values referee to a less elastic leather character. When the elongation at break values on Table 2 are considered it is seen that the highest value belongs to the sample No.1 with %40,32 while sample No.12 scored the lowest with %11,60. According to these results, the increasing amount of the applied collagen hydrolysate-oxazolidine combinations is affecting the fullness on leather positively and prevents from over elongation.

Afsar in 1984 had given %48,58; %51,36 and %59,0 values for different type of double-face lamb leathers (26). Sharhouse 1989 found out that vegetal tanned goat leather must have elongation at break value of minimum 40,0. % UNIDO declared that chromed tanned garment leather must have elongation at break value of maximum 60 % (27).

The reason why the results in our research are lower than the ones in the literatures above is that the retanning process was only made by using collagen hydrolysate-oxazolidine combinations.

3.3. Tear Load

One of the other strength parameters of the finished leathers which they will show during their usage is tear load. The results of the tear load tests applied on the samples which were retanned with various collagen hydrolysate and oxazolidine combinations has given values between 16,8 N/mm and 53,1 N/mm. The values achieved clearly point out that the increasing quantity of collagen hydrolysate and oxazolidine combinations ratios in retanning is enhancing the tear load property of leather.

Sample No.12 has given the highest tear load with a value of 53,1 N/mm. It is found out that the tear load value for garment sheep leathers is 23,0 N/mm (28) For the vegetal tanned ship skins the same value is mentioned to be 42,42 N/mm (29). UNIDO declared the

minimum tear load value for chrome tanned garment leathers as 15 N/mm (27). According to those data, it is determined that tear load of our leathers were found better then the mentioned values.

Tensile strength, elongation and tear load values characteristics of leathers retanned with collagen hydrolysates and oxazolidines combinations are given in Table 2.

In this research, chromed shaving wastes from leather industry were hydrolyzed with commercial enzyme preparation in an alkali medium and collagen hydrolysate was used along with oxazolidine at various ratios in retanning process. As a result, it is determined that all applied combinations had enhanced the evaluated properties for leather. Highest values were given by the sample No.12. However, there is no significant difference at the values between sample No.11 and No.12. It would be more cost effective to use the sample No.11 due to the less oxazolidine consumption.

As a result it is determined that collagen hydrolysate and oxazolidine combinations could be effectively used as retanning agent along with the other well known retanning materials. Although some values of the physical properties is seen to be lower when compared with the above mentioned literatures, it can be predicted that the usage of collagen hydrolysate-oxazolidine combinations together with the other regular retanning agents will lead us to achieve standard values.

In the hard competition world, low cost production has a great importance also for the leather industry as for the others. In this sense, reevaluation of the hazardous solid wastes originated from leather industry is of great importance for both ecological and economical aspects.

ACKNOWLEDGMENT

The authors wish to thank to Ege University Research Fund Accounting Office for financial support under Project 05 MUH 003.

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Bu araştırma, Bilim Kurulumuz tarafından incelendikten sonra, oylama ile saptanan iki hakemin görüşüne sunulmuştur. Her iki hakem yaptıkları incelemeler sonucunda araştırmannın bilimselliği ve sunumu olarak "Hakem Onaylı Araştırma" vasfıyla yayımlanabileceğine karar vermişlerdir.
