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NEW LUBRICATING NATURAL POLYMER FOR WATER-REPELLENT UPPER LEATHER PRODUCTION

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Abstract: *In this study, collagen hydrolysate from bovine shaving wastes of leather production with the alkali hydrolysis reaction was emulsified with amino functional silicone oils to prepare lubricating natural polymer (LNP). Particle size and zeta potential of the LNP were measured. Prepared LNP was used in the fatliquoring step of chromium tanned bovine leathers. Contact angle of the leather surfaces with water were employed to study hydrophobicity of treated leather. The water absorption behavior of leather was determined by dynamic water resistance (penetrometer test) and static water resistance tests (kubelka water up-take). Performance characterizations of leathers were carried out with tensile strength, tear strength, filling efficiency and water vapour permeability (WVP) analyses. The contact angle measurements showed that the hydrophilic property of leather surface decreased after LNP treatment. Both dynamic and static water absorption behaviour was lowered while the WVP of leathers was not significantly affected negatively except of 20% LNP. Only 20% LNP application slightly decreased the WVP of leathers. Moreover, new lubricating agent provided satisfactory strength performance and good filling effect on leathers.*

Key words: Leather, waterproof, collagen hydrolysate, lubricating agent, fatliquoring.

1. INTRODUCTION

The onset of the 21st century has marked great developments in technology and science. However, these developments have come with a price, one of which is aggravated global warming, leading to sudden climatic changes. In order to survive and be productive in such conditions, there is a need for appropriate apparel and shoes for people specifically working in outdoor environments. Waterproof products are engineered with the aim of protecting the wearer from weather conditions like wind, snow and rain as well as preventing excessive loss of body heat [1].

Under normal conditions, the leather has a natural fiber weave structure, so it absorbs water by absorbing certain amount of water. For this reason, leather products used especially in winter get wet when exposed to humid environment. The water absorption feature should be limited in order for the leather to maintain its strength and its shape. For these reasons, the water resistance properties of leathers under dynamic and static conditions are important for the protection of usage hygiene and physiology [2]. During its production, leather is hydrophobed in various ways to meet customer demands [3]. To achieve the required specifications, it is necessary to use an optimized combination of hydrophobic and hydrophilic components in the applications [4]. Lubricants used in leather production are one of the main factors in obtaining hydrophobic leather and reducing the water absorption of leather [5]. Since the production of hydrophobic leather is also done in an aqueous environment, the chemicals used must somehow be dissolved in water, that is, they must contain hydrophilic groups that are compatible with water. At the same time, the chemicals used must have hydrophobic groups because we want to reduce the water absorption rate of the leather [6]. The lubrication emulsions are bounded to the skin with their reactive groups, allowing a certain amount of water to be absorbed into the skin. The oil-in-water emulsion is penetrated into the skin and takes the form of water-in-oil emulsion. The oils cover the leather fibers with a hydrophobic layer with very low surface tension. Water vapor can enter between the fibers; however, hydrophilic water droplets have high surface tension and do not spread to the hydrophobic fiber surface and only wet the inner surface [7]. For these purposes different types of oils, natural and petroleum derivative fatliquors are being used in fatliquoring process [8]. On the other hand, lubricating polymers are a good alternative to provide water-repellent properties to leather as well as their filling effect with softening and retanning features [9].

In recent years there has been an increasing interest in the design of natural polymers for various applications in many industries [10]. Gelatinous products are the subgroups obtained from collagen which is one of the most interesting degradable polymers [11]. Collagen hydrolysates are new forms yielded by hydrolysis of native collagen having lower molecular weight fragments than original structure and including a wide range of sub-categories with differentiated functionalities. Collagen hydrolysates as natural biopolymer exhibits superior properties such as higher enthalpy, the greater network structure of fibrils and strong reactive complex in the leather production [12].

In the present study, it was aimed to develop a novel lubricating emulsion with functional properties using for leather industry by evaluating the waste protein from leather wastes. Collagen hydrolysate emulsified with amino functional silicone oils was investigated for the water-repellent leather production on the way of sustainability of leather industry.

2. EXPERIMENTAL PART

2.1. Materials

In this study, collagen hydrolysate was obtained from low grade by-product of gelatin manufacturing process of bovine shaving wastes with the KOH hydrolysis reaction (Halavet Gelatin Company). Span 60 were purchased from Merck. Amino functional silicone oil was provided from United Chemicals Company, Turkey and LIPSOL LA was provided from Schill+Seilacher GmbH.

2.2. Emulsification with collagen hydrolysate

In the emulsion; amino functional silicone oil and Span 60 were mixed at 90 ^oC. At the same time collagen hydrolysates and water were heated in a separate vessel to about 50 ^oC. Then, the continuous phase was added to dispersion phase while mixing. After adding this mixture, emulsion was stirred for 4 h at 80 °C. pH of the emulsions have been adjusted to 6.5 during homogenization. At the end of the reaction time, the emulsion was cooled to room temperature.

2.3. Particle size of lubricating polymer

Particle size and zeta potential of emulsions were determined with a Malvern Zeta Sizer Nano ZS analyzer. For the analysis, sample were prepared as 0.1 mg/mL concentration by diluting with the ultrapure water. The measurement size range of the instrument was 0.1-10000 nm.

2.4. Application of lubricating natural polymer in fatliquoring process

The process recipe was given in Table 1. The total amount of lubricating natural polymer (given as * in Tables) was 10%, 15%, 20% used in the recipe. For comparison, the one piece was treated with lubricating agent and the other piece was not.

Table 1: *Leather production recipe*

Process	%	Chemicals	Temperature	Time	Remarks
Neutralization	100	Water	30 ºC		
	1	Sodium formate		30 min	
	1	Sodium bicarbonate		60 min	pH:5, drain
Washing x 3	200	Water	30 ºC	10 min	Drain
Fatliquoring- Dyeing	100	Water	40 ºC		
	4	Lipsol LA (modified lecithin)	55 ºC		
	*	LNP		90 min	
	2	Dyeing auxiliary		30 min	
	4	Dye		60 min	
	2.5	Formic acid		60 min	pH:4.1,drain
Washing-Drying					

2.5. Determination of water-repellence properties

Keyence VHX-1000 digital microscope was used to measure the water contact angles on leather. A droplet of deionized water (0.3 ul) was dripped on the leather surface. In order to demonstrate the water-repellent properties of leathers, the dynamic water resistance of the leathers was examined using the Bally Penetrometer 5316 test device according to TS 8541 EN ISO 5403 standard. Determination of the static water absorption of leathers was carried out in the kubelka apparatus according to the TS 4123 EN ISO 2417 method. The amount of water absorbed during immersion of leathers was determined at the end of 30 minutes, 1 hour and 24 hours.

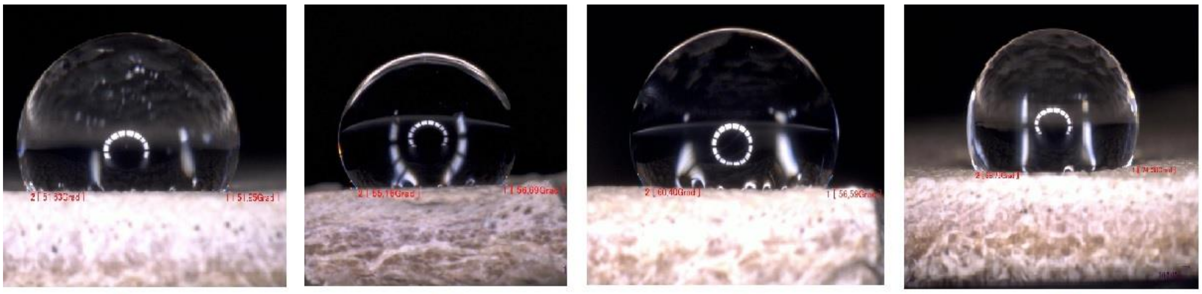
2.6. Pyhsical properties of leather treated with lubricating protein filler

Prior to the tests all leathers were conditioned according to the standard of EN ISO 2419:2012. The tensile strength and tear strength properties of leather was determined according to the standards of TS 4119 EN ISO 3376:2011 and TS 4118-2 EN ISO 3377-2. For the tests, the measurement of the thickness of the samples was performed in accordance with EN ISO 2589:2002. The water vapor permeability analysis was carried out with the Satra STM 473 test device as specified in TS EN ISO 14268. The method was performed in a conditioning room with 20±2 °C temperature and 65±2% relative humidity. The results were calculated in milligrams of water vapor per square centimeter ($mg/cm^2.h$) according to the formula $WVP= m/\pi r^2.h$.

3. RESULTS AND DISCUSSION

Average particle size and zeta potential are important parameters in assessing the stability of emulsions and determining the lubrication efficiency in leather production. As the particle size of the emulsions decreases, there is more surface area in the unit volume of the fatliquors. The increase in the surface area promotes chemical reactions and increases the binding of the fatliquor. If their size exceeds the size of the pores of the leather, their penetration into the leather would become difficult [13]. The average particle size of the emulsion was 1285.3 nm with high stability (ζ= -49.3 mV). During collagen production, a few microfibrils form a fibril with a diameter of 0.2-0.5 µm. Together with the fibrils, a 3 µm diameter collagen strand is formed [14]. When the particle sizes of the emulsions were examined, it was thought that emulsion would penetrate into the collagen matrix.

Contact angle measurement helps in deriving the wettability of the surface. The higher the angle between the surface and water, the higher the water resistance and the lower the wettability. It was observed that the drop of water would seep into the control leather in 5-10 seconds. Hence it was very difficult to measure the contact angle, control leather showed 51.63 contact angle. As shown Fig. 1, after the application of the LNP there was significant increase in the contact angle of the treated leather as 55.16, 60.40 and 67.93, respectively.



(A) (B) (C) (D)

Fig. 1. *The contact angle results of leather: (A) control; (B) 10% LNP; (C) 15% LNP; (D) 20% LNP*

Water repellence properties are achieved by repellent lubricating natural polymer with reducing the free energy at fibre surface. If the adhesive forces between a fibre and a liquid drop are greater than internal cohesive forces in between the liquids, the drop will spread. However, if the adhesive forces between a fibre and liquid drop are less than internal cohesive forces in between the liquids, the drop will not spread [15].

Determination of water resistance properties in dynamic conditions is vital for determining the water absorption properties of leather goods, especially for an out-door walking shoes during usage because the mechanical action during measurement simulates the mechanical action during walking in water. Dynamic and static water absorption of leathers were given in Table 2.

Table 2: *Dynamic and static water absorption behaviour of leathers*

Leather samples	**Dynamic water absorption (%)**	**Static water absorption (%) in 30 minutes**	**Static water absorption (%) in 60 minutes**	**Static water absorption (%) in 24 hour**
Control	152.1	122.4	131.3	135.32
10% LNP treated	101.4	67.75	87.77	89.52
15% LNP treated	73.03	48.11	57.84	74.19
20% LNP treated	56.24	22.14	33.65	57.97

With the increase in the ratio of LNP used in leather production, it is seen that the water absorption characteristics of leathers decreased significantly under dynamic conditions. While the water absorption rates of the control group samples were given as 152.1%, it was observed that this ratio decreased to 56.24% in the leather treated with 20% LNP.

A significant decrease in static water absorption was observed for the experimental leathers after 10, 15 and 20 percent of LNP treatment. Whithout LNP application in control groups, static water absorption ratios were 122.4, 131.3 and 135.32 with the increased duration (30 min to 24 h), respectively. On the other hand, the ratios decreased from 122.4 to 22.14, from 131.3 to 33.65 and from 135.32 to 57.97 after 20% LNP treatment. Furthermore, decreases in absorptions were almost two times more when LNP treatments increased from 10% to 20% for 30 min and 60 min applications. Decreases were comparatively slower when the time reached to 24 h.

Various physical analyses of the leathers were carried out as per standard method. Analyses results were presented in Table 3.

Table 3: *Properties of leather treated with lubricating natural polymer*

Leather samples	Tensile strength (N/mm^2)	Tear strength (N)	Filling coefficiency (%)	Water vapour permeability ($mg/cm^2.h$)
Control	17.82	83.21	3.13	12.46
10% LNP treated	20.26	92.13	8.27	12.24
15% LNP treated	22.97	107.24	12.31	11.78
20% LNP treated	23.42	122.28	14.14	9.56

From the results given in Table 3, it can be seen that mechanical properties of leathers treated by LNP were higher than control groups. It was observed that the increase in the tensile strength of the leather with the increase of the emulsion in the process. The strength value was observed in control group as 17.82 N/mm^2, while the highest strength value was obtained in leathers treated with 20% emulsion with 23.42 N/mm^2. When the tear strength results were examined, there was a significant increase from 83.21 N to 122.28 N. Moreover, LNP emulsion application improved the thickness of skin up to 14.14% when compared to control samples. In the leather production, chemicals with high nitrogen, carbon and amino acid content are highly demanded beacause of the forming crosslink between the leather fiber network [12]. When we evaluate the properties of the LNP, it was thought that collagen hydrolysates in the emulsion can make additional bond to the leather fibers which increase the mechanical properties and the thickness of the leather.

Water vapour permeability or breathability of the materials is one of the key factor in comfort properties of leather. The term “breathable” refers to the ability of materials to diffuse water vapour while preventing the penetration of water. It is important that the products help in passage of sweat from body to atmosphere. This is because, if a person is in a cold climate performing high activity wearing non-breathable clothing, he may suffer from hypothermia, and if he is in a hot, he may suffer from heat stress [16]. From Table 3, it was determined that the increase in the rate of LNP in the production slightly decreased the WVP. WVP and waterproofness are two contrasting abilities. WVP allows the flow of air and water vapour, while waterproof abilities restrict the transfer of water from outside to the inside, protecting the wearer from getting wet. It is therefore a challenge to develop materials that allow the transfer of water vapour from the inside of the materials to the outside and simultaneously restrict the passage of water from the outside to the inside [17]. When the results of the analyses are evaluated, it is determined that when using 20% LNP, the WVP rates of the leathers decreased by approximately 24% compared to control groups. However, it is thought that the significant reduction can be tolerated with the 15% of LNP treatment by providing a 5% decrease.

4. CONCLUSIONS

Demands for products that can impart hydrophobic qualities have increased greatly over the years as their application has become more prevalent in many industries. Water repellency and water vapour permeability of products used in outerwear are of major importance and influence to human comfort. This study focuses on the evaluation of collagen hydrolysates derived from solid tannery waste to produce lubricating natural polymer for processing of leather that would be both water repellent and breathable. Lubricating emulsions have shown that it can be used as a good waterproofing agent in leather production with ensuring lower water absorption rate brought to the leathers with minimal changing of the WVP. In accordance with the proteinic ingredients collagen hyrolysate was used as filler in lubricating agent in order to ensure fullness and some performance characteristics. This study may help to realize a clean, new, renewable leather chemical option from tannery solid waste as an alternative solution to current leather waterproof fatliquoring chemicals.

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