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A Technical Study on the Effect of Hydrothermal and Dry Heat Shrinkage of Different Shoe-Upper Leathers Used in Pakistan

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Abstract—The shrinkage of leather becomes a problem when leather is used in the form of leather shoes or other products and is heated at a high temperature. This technical study addressed shrinkage occurring in most leather shoes used in Pakistan during the shoe manufacturing process. The chemical testing results revealed fat content (4.0-4.5%), chromic oxide (2.3-2.5%), ash content (1.3-1.6%), and pH (3.5-3.7) under significant limits. The effects of hydrothermal and dry heat shrinkage were investigated in selected shoe-upper leathers. The leather samples showed (18-41%) shrinkage in all 03 samples. The results revealed that an extensive change in various physical tests, such as tensile strength, % elongation, tear strength, had been found with heat induction. The temperature and time of heat contact significantly affect the destruction of bonding in shoe upper leather after being converted into shoes.

Keywords— Leather shoe; Physical testing; Shrinkage.

1. INTRODUCTION

Hides/skins of animals are converted into a value-added imputrescible product known as leather. Tanning is the fundamental process for converting raw hide/skins into leather form. This tanning process is completed after different tannery processes. Leather processing is divided mainly into three distinct stages; the earliest is the pre-tanning process. This process includes some operations in the tannery area known as soaking, fleshing, unhairing, and bating. The second is the tanning process, including tanning with chromium sulfate, sammying, sorting, splitting, and shaving. The third stage converts wet blue into finished leather after many operations, such as neutralization, retanning, dyeing, fat liquoring, drying, and finishing with finishing auxiliaries [1].

Leather is the most widely used material for making various products, such as automotive, buildings, upholstery, personal safety items, handbags, and other domestic items [2]. The chromium-tanned leather is usually used for long climbing shoes made of Cowhide upper and Buffalo shoe-upper leather. Chrome-tanned leathers show better stability and flexibility as well as good feeling and comfort. Therefore, chrome-tanned upper leathers are widely used in manufacturing [3-5]. Shrinkage occurs when the skin or leather is heated to a certain temperature [6]. Raw skins may shrink approximately at 60 °C while the shrinkage temperature of fully chrome-tanned leathers may reach higher than 120 °C. When thermal shrinkage occurs, the area of the leather is reduced, and the service performance is lost. High thermal stability is consequently crucial and needed for leathers, as per their wide application. However, studies of the changes in the mechanical behavior of skins or leather due to thermal shrinkage has been conducted but not extensively.

Leather is a fast-growing industry in Pakistan, having leather processing units at different locations. Thus far, the main export markets of Pakistani leather are Italy, Portugal, Spain, South Korea, France, Germany, the USA, the UK, and UAE. The manufacture of leather products passes through various steps and environmental conditions, especially leather shoes, where the attachment of the sole to the leather position through molding machines requires at least 150-200 °C contact heat for 3-4 min. Recently, a dispute has arisen between leather shoemakers and their customers, who have reported a significant decrease in the shrinkage and mechanical properties of leather after shoe manufacturing. The impact of dry heat and hydrothermal shrinkage on shoe-upper leather has

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been investigated by our team at the Leather Research Centre, Karachi to overcome disputes between suppliers and clients.

2. EXPERIMENTAL SECTION

2.1. Material and Methods

The three different types of samples were tested in this technical study. Sample 01 was a supplied leather shoe made from buffalo shoe upper leather. Sample 02 was a commonly available shoe in the local market from shoe upper leather. Sample 03 was shoe-upper leather prepared at Leather Research Centre, PCSIR, Karachi. The three samples were prepared in equal size in a rectangular shape (**Fig. 1a-1b**) according to the standard method ISO-3380-2015 and conditioned to ISO 2419-2012. Sampling and conditioning of leather samples was carried out by Society of Leather Technologists and Chemists (SLTC) IUP-2 and IUP-3. The dry heat of the three leather samples was examined according to IUP-35 to examine the loss of area percent of samples in a calibrated oven from Gallen Kamp. These samples were stored at room temperature till testing time.

The shrinkage test was carried out on a shrinkage tester, SATRA STD 114 apparatus England (SLTC-IUP-16) using a standard method. The principle of the apparatus is to immerse a strip of leather sample into the water with slow heating until visible/rapid changes in the leather sample occur which shows the tanning characteristic (stability). The physical testing sample was cut by (BS-3144 IUP-1/EN ISO 2419:2006), conditioning of leather (SLP3, IUP 3; BS 3144: method 2, 2001), thickness by SLP4, IUP4; BS 3144: method 3), and tensile strength and elongation at the break by (BS-3144, IUP-6/EN ISO 3376: 2002). Universal Testing Machine model H5KS was used for physical testing of the prepared leathers. Flexing Endurance was checked on Bally Flexometer T 4086 by SATRA. The leather samples were also tested using various chemical tests for fat content using the ISO 4048 method, chromic oxide using ISO 5396, ash content using ISO 4047, and pH value using ISO 4045. **Fig. 1a** and **Fig. 1b** show the sampling area cut from the shoe.

(a) **(b)**

Fig. 1. (a) Shoe sample; (b) Shoe sample cut area.

3. RESULT AND DISCUSSION

Hides and skins are mainly composed of water, protein substances, and fatty materials [6]. Hides or skins are natural proteins that are easily attacked by organisms and prone to decay. Tanning is the treatment of raw hides and skins with tanning chemicals to turn them into material against bacterial attack, i.e., to provide a stable fiber structure called leather. In simple, the tanning operation is a permanent stabilization method when hide protein come into contact with organic or inorganic tanning agents under the appropriate conditions. In chrome tanning, water molecules were removed from the collagen of the skin/hide and then replaced with chromium ions of the applied chromium salt. This reaction is mostly between trivalent chromium ions and carboxyl groups of collagens. Chrome tanning compared to other metal tanning has various advantages, namely stable covalent bonds. These bonds lead to hydrothermal stability (also known as hydrothermal shrinkage). The shrinkage of leather is an important characteristic that determines the inner stability of collagen. Raw skins may shrink approximately at 60 °C, while the shrinkage temperature of fully chrome-tanned leathers may reach even higher than 120 °C [7]. The chromium sulfate percentage applied for tanning is an important factor to increase the shrinkage of leather as described earlier [5]. The reaction can be seen in **Fig. 2.**

Table 1. Chemical testing of shoe upper leather samples

Sample	Fat content (%)	Chromic oxide (%)	Ash content (%)	pH value
1	4.0±0.50	2.5±0.01	1.6±0.05	3.75±0.05
2	4.2±0.05	2.3±0.01	1.3±0.04	3.69±0.01
3	4.5±0.06	2.8±0.02	1.4±0.03	3.59±0.02

In this study, leather samples were selected as described in the materials and methods. The samples were also tested for various chemical tests. The results are summarized in **Table 1**. These results were found to be satisfactory chemical parameters.

Table 2. Shrinkage % of shoe upper leather samples

Sample	Before shrinkage (mm)	After shrinkage (mm)	Shrinkage (%)
1	50 × 3.0	46 × 2.3	29.46
2	50 × 3.0	40 × 2.2	41.33
3	50 × 3.0	47 × 2.5	20.00

After chemical testing of leather samples, the samples were tested for shrinkage. In leather shoe manufacturing, moist heat was applied to the leather. Therefore, the shrinkage behaviour of leather samples is very useful for determining the quality of different shoe-upper leathers. All the samples were tested for shrinkage. The results are presented in **Table 2**. The highest shrinkage occurred in sample 02, while the lowest shrinkage was found in sample 03. The highest dose of chromium sulfate was applied in sample 03.

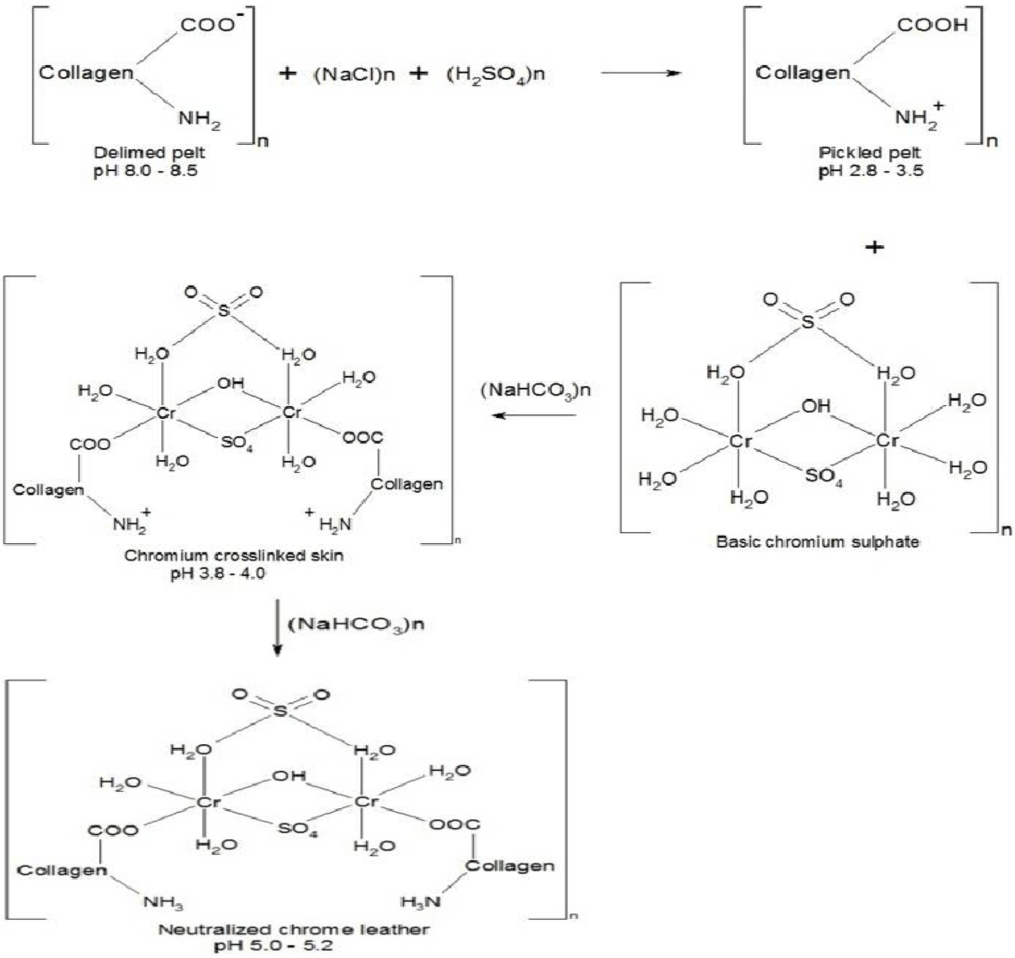

Fig. 2. Reaction of collagen with basic chromium sulphate

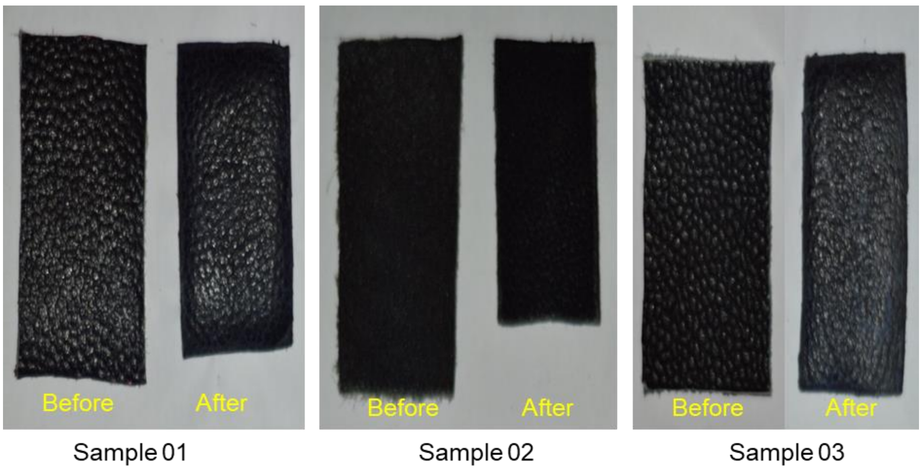

Fig. 3. Physical appearance of dry heat effect on leather samples

The samples showed better stability against moist heat. These samples were also tested for dry heat resistance to determine the dry heat effect on shrinkage characteristics. The images of samples 01-03 before and after dry heat were presented in **Fig. 3.** The area loss presented in sample 01, 02, and 03 were 27%, 38%, and 18%, respectively.

In the shrinkage phenomenon, changes occurred in the collagen structure of the leather. These changes in the functional groups were investigated using the FTIR spectrum. The shrinkage of leather depends on the tanning type as earlier reported [8]. The shrinkage of leather might occur up to 35% of the calculated area from various initial samples by breaking the internal bonds of leather and different contraction stages of samples [9]. In the shoe vulcanization process, the leather patterns are attached through the

Table 3. Effects on leather physical characteristics (before and after dry heat shrinkage)

Sample	Before shrinkage				After shrinkage			
	Tensile strength (N/mm^2)	Elongation (%)	Tear strength (N/mm)	Flexing endurance for 50,000 flexes	Tensile Strength (N/mm^2)	Elongation (%)	Tear Strength (N/mm)	Flexing endurance for 50,000 flexes
01	27.66±1.8	97.0±3.0	55.16±4.14	No change	21.17±0.7	80.1±0.7	44.83±2.34	No visible change
02	24.16±2.0	104.0±5.0	47.66±3.31	Slightly wrinkles were seen	19.50±1.5	91.7±7.0	39.50±3.02	Slightly wrinkles were seen and finish also damage
03	31.33±3.0	115.0±6.0	59.33±4.83	No significant change at finish side	27.33±2.5	101.0±5.0	49.33±3.83	Slightly wrinkles were seen and a visible change in damage of finish

rubber/polyurethane soles by induction at high temperatures above 150 °C for a required specific time.

This heat reduces the moisture content of the leather and structural changes/modifications occur. As a result, new bonds are formed. Thus, the shoe upper leather shrank, which is a reversible phenomenon. Furthermore, the shrinkage temperature of leather collagen is different in each region, and the amount of shrinkage is different in chrome-tanned leather and chrome-free leather. Thus, in leather shoe manufacture resistance to shrinkage will be more beneficial. Beside the shrinkage, the leather samples were tested for various physical parameters (**Table 3**). The highest tensile strength and tear strength were found in sample 03. This is due to the chrome tanning effect. The results revealed that a slight change in all physical parameters was found in all three samples before dry heating and after providing the dry heating.

CONCLUSION

The shoe leather should be selected after standardized testing procedures and quality testing. The leather shoe should be made according to environmental conditions, such as resistance to high or low temperatures. The shrinkage due to leather heat depended on the tanning material concentration (mostly tanning was carried out using different percentages of basic chromium sulfates), while the chromium-free leathers did not show such type of shrinkage. Thus, this study was beneficial for solving the problem of shrinkage for tanners. The wet leather shrunk rapidly through a slight heat source. Dry heat reduced the leather's physical properties. Therefore, heat should be minimized in the shoe-making process.

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CONFLICT OF INTEREST

The authors have no conflict of interest to disclose.

AUTHOR CONTRIBUTIONS

BAS, UZ, and MZ participated in the technical results compilation through standard procedures. HRN, MKP, BZ edited and revised the manuscript. All authors agreed to the final version of this manuscript.

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