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CORRESPONDENCE

Editor-in-Chief – Dr. Viorica Deselnicu

INCDTP – Division: Leather and Footwear Research Institute (ICPI), 93, Ion Minulescu Street, Bucharest, sector 3, postal code 031215, Romania, Europe; tel./fax: + 40 21 323 52 80, e-mail: jlfjournal@gmail.com

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ON THE RELATIONSHIP BETWEEN FOOT PRESSURE DISTRIBUTION AND SOLE HARDNESS DURING LONG-TIME STANDING

Xintao XIE

Physical Education College of Xi'an Technological University, Xi'an 710032, China, xxtyy2004@163.com

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ON THE RELATIONSHIP BETWEEN FOOT PRESSURE DISTRIBUTION AND SOLE HARDNESS DURING LONG-TIME STANDING

ABSTRACT. For people like soldiers, doctors and traffic police who need to stand for a very long time at work, their feet are under long-time pressure; thus, their foot health affects their work and life. Based on the foot pressure sensing system Footscan. This paper studies the foot pressure distribution during long-time standing. According to the subjects' subjective assessment and experimental results, the author carries out statistical analysis on how different sole hardness can relieve the foot pressure during long-time standing. The conclusions are of great guiding significance to help people who need to stand for a long time at work scientifically relieve their foot pressure and select suitable footwear.

KEY WORDS: long-time standing, Footscan, sole hardness, subjective assessment, experiment

CONSIDERAŢII PRIVIND RELAŢIA DINTRE DISTRIBUŢIA PRESIUNII PICIORULUI ŞI DURITATEA TĂLPII ÎN TIMPUL STAŢIONĂRII ÎNDELUNGATE

REZUMAT. Pentru soldaţi, medici şi poliţişti rutieri, care trebuie să stea foarte mult în picioare la locul de muncă, picioarele acestora se află sub presiune îndelungată; astfel, sănătatea piciorului le afectează munca şi viaţa. Pe baza sistemului Footscan de detectare a presiunii piciorului, această lucrare studiază distribuţia presiunii piciorului în timpul staţionării îndelungate. Conform evaluării subiective a subiecţilor şi a rezultatelor experimentale, autorul efectuează analize statistice asupra modului în care diferite durităţi ale tălpii pot ameliora presiunea piciorului în timpul staţionării îndelungate. Concluziile sunt semnificative în a-i ajuta pe cei care sunt nevoiţi să stea mult timp în picioare la locul de muncă să-şi amelioreze presiunea piciorului pornind de la principii ştiinţifice şi să aleagă încălţămintea potrivită.

CUVINTE CHEIE: staţionare îndelungată, Footscan, duritatea tălpii, evaluare subiectivă, experiment

CONSIDÉRATIONS SUR LA RELATION ENTRE LA DISTRIBUTION DE LA PRESSION DES PIEDS ET LA DURETÉ DE LA SEMELLE PENDANT LA STATION DEBOUT PROLONGÉE

RÉSUMÉ. Pour les personnes comme les soldats, les médecins et les agents de la circulation qui doivent rester debout longtemps au travail, leurs pieds subissent une pression de longue durée; ainsi, la santé de leurs pieds affecte leur travail et leur vie. Basé sur le système Footscan de détection de pression du pied, cet article étudie la répartition de la pression du pied pendant la station debout prolongée. Selon l'évaluation subjective et les résultats expérimentaux des sujets, l'auteur effectue une analyse statistique de la mesure dans laquelle différentes duretés de la semelle peuvent soulager la pression du pied pendant la station debout prolongée. Les conclusions ont une grande importance pour aider les personnes qui ont besoin de rester debout longtemps au travail à réduire la pression exercée sur leurs pieds sur de bases scientifiques et à choisir des chaussures appropriées.

MOTS-CLÉS : station debout prolongée, Footscan, dureté de la semelle, évaluation subjective, expérience

** Correspondence to: Xintao XIE, Physical Education College of Xi'an Technological University, Xi'an 710032, China, xxtyy2004@163.com*

INTRODUCTION

Medically speaking, standing for longer than 40 minutes is identified as long-time standing. Occupations involving long-time standing include teachers, doctors, nurses, traffic police and guards [1]. During long-time standing, the feet are under pressure for a long time. The over-concentration of pressure on foot will cause foot muscle soreness and affect people's working status and physical and mental health. Researches on foot protection for these groups of people are still in the preliminary stage. Some shoe factories are already selling foot-protection footwear, but due to lack of scientific design guidance, there are many deficiencies in footwear design, and those who need to stand for a long time at work also do not know how to choose footwear scientifically [2]. Besides, few researches have explored the relationship between foot comfort and different sole hardness during long-time standing from the theoretical perspective. As people are getting more concerned about their foot comfort and health, it becomes very necessary to scientifically analyse the relationship between foot pressure changes during long-time standing and sole hardness. Sole hardness is the key parameter of shoe comfort, and studies have shown that plantar pressure distribution is closely related to sole hardness [3]. In this paper, through both subjective assessment and objective test, we provide two ways of evaluation – quantitative and perceptual evaluation – for footwear comfort. Subjective assessment is mainly to measure shoe wearers' subjective feelings through questionnaire survey; objective evaluation is to test the foot pressure changes over the standing time with pressure measurement equipment [4]. With the help of the foot pressure test system - Footscan gait analysis system, the author conducted a foot pressure experiment with 15 young men within the same age group involved. Through reasonable experimental design and scientific scheme, the author collected statistics of foot pressure changes, foot fatigue start time and test shoe comfort of subjects on bare foot and wearing test shoes of different sole hardness and conducted comprehensive analysis on the experimental results based on the subjective assessment of the subjects. This study offers scientific guidance to improving the footwear of people who stand for a long time at work and provides shoe factories with relevant data basis and theoretical support. At the same time, it is of great significance to promoting plantar pressure and comfort research.

OVERVIEW OF THE THEORETICAL CONCEPT OF FOOT PRESSURE

Static Mechanical Behaviors of Foot

A human body stands with his/her two feet against the ground. The weight of the human body is transferred through muscles and bones to the feet. Through the spine and waist and then the legs, the body weight is divided into three pressure forces in each foot – one force is transferred to the heel, one to the forefoot and one to the buffer zone between the arch and the ground. Figure 1 shows the foot area map [5]. In the weight transfer process, foot pressure distribution is affected by various factors. Physiological factors include gender, weight, age, walking velocity and height, etc. Environmental factors include different footwear. For example, if a person wears high-heeled shoes, the pressure will increase on the medial side of the forefoot, while the pressure on the heel and the arch is relatively small [6]. Foot pressure measurement site, occupation of the subject and different sports are the external factors to the static pressure distribution of foot.

Figure 1. Foot area map

Biomechanics of Foot Movement

The research object of foot movement biomechanics is the pattern of foot movement when the human foot is under both internal muscle control and the action of an external force [7]. In the biomechanics of foot movement, in addition to the physiological conditions related to human body, footwear is also a key element. Footwear and human foot are an interactive whole. In different standing and movement postures, human body can adjust the posture to gain maximum comfort [8], and footwear design can help human body change the stress conditions of feet and ground [9].

The physiological characteristics of foot are basically fixed, but footwear can be designed and purchased according to demand, so adjusting foot pressure distribution mainly relies on footwear design. Foot pressure distribution and footwear design affect and improve each other. In this paper, the author recorded and analysed the plantar pressure distribution data of testees wearing shoes of different materials, hardness and heights and obtained the relationship between pressure distribution and shoe comfort, in an effort to help people design more suitable shoes for human.

EXPERIMENTAL DESIGN FOR PLANTAR PRESSURE DISTRIBUTION DURING LONG-TIME STANDING

Experiment Apparatuses and Test Shoes

Experiment apparatuses and testing instruments for foot pressure distribution mainly include Footscan gait analysis system, three pairs of test shoes with different hardness and hardness testing device.

The heights of the test shoes are around 2cm. To eliminate the impacts of shoe last, all test shoes are made by one manufacturer. The data of the test shoes measured by the hardness testing device and other apparatuses are listed in Table 1.

Table 1: Data of the test shoes

Shoes	Sole hardness	Heel-height(cm)	Shoe size	Shoe type
Test shoe 1	55	2.0	42	casual shoes
Test shoe 2	64	1.9	42	casual shoes
Test shoe 3	72	2.1	42	leather shoes

Test Subjects

1. Age and gender. For persons of different age groups, the physiological characteristics of foot pressure and subjective assessment on the shoe comfort will also be different. In order to eliminate the impacts of age on the test results, this research selected 15 young men aged 23-25 as the test subjects [10].

2. Height and weight

Body height and weight also affect the comfort during long-time standing. In order to eliminate the impacts caused by these factors, the 15 young testees all had a height of 170-172cm and a weight of around 65Kg [11].

3. Illustration

All participants in the test are college students who were invited to the test through part-time invitation released in the campus network. All participants in the test are volunteers and will be compensated after the test.

Experimental Design

In this research, the author measured the plantar pressure distribution of individual subjects standing for a long time on bare foot and in different test shoes and recorded their subjective assessment [12].

Figure 2 shows the foot pressure distribution percentages of the test subjects during the static standing test measured by Footscan.

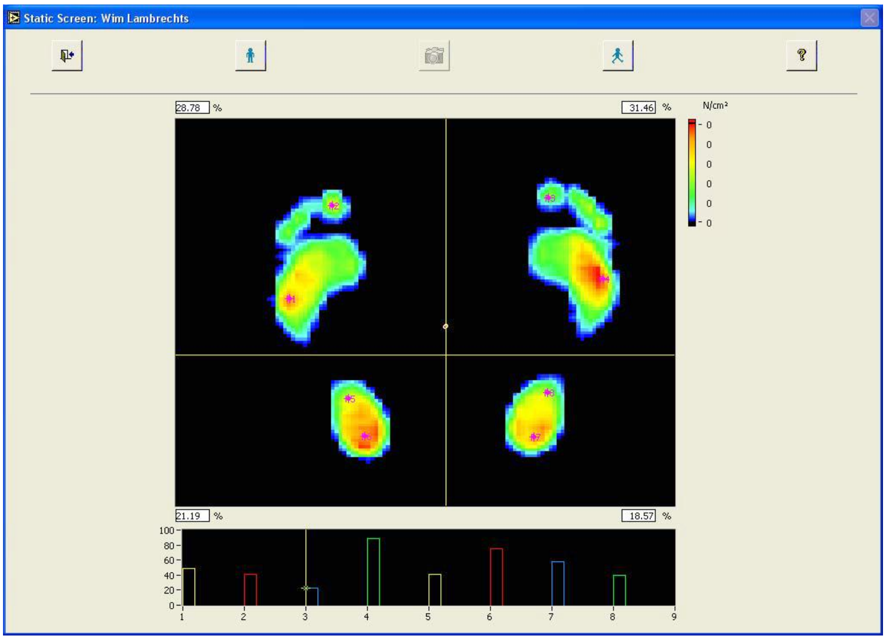

Figure 2. Static test pattern

The author designed the standing time to be 40min and the pressure data sampling time to be 5min/time [13]. Before the test, the testees had a rest for 30min with their feet off the ground so that their foot conditions would be the same before the test started.

In order to reduce the impact of standing posture on the experimental results, the foot spacing should be between 40~60cm provided that it satisfied the testees' usual standing habits.

Through a questionnaire survey on footwear comfort, the author recorded the testees' subjective assessment [14]. The author designed 4 levels in the pressure assessment: 1. Too much pressure, causing pain – 4 points; 2. Too much pressure – 3 points; 3. A little too much pressure – 2 points; 4. Pressure comfort – 1 point. For footwear assessment, there were 4 levels as well. Testees could rate the footwear as excellent, good, qualified and poor according to the comfort degree [15].

In this section, the author conducted preliminary analysis of the main experiment, collected information about the testees, carried out a preliminary experiment to determine the duration of the main experiment, provided preliminary training for testees and advised them of things to pay attention to. After that, the author completed the whole experiment, designed an objective assessment data system and subjective test table and completed the collection of experimental data and preliminary analysis.

Experimental results and analysis of plantar pressure distribution during long-time standing

According to the requirements of the experimental design, the author used Footscan to test the plantar pressure distribution, and at the same time conducted subjective assessment survey on footwear comfort. The experimental data and analysis results are as follows.

Long-time Standing on Bare Foot

First, the author collected statistics of plantar pressure distribution of 15 testees after they stood for 1 min to understand how different regions of a foot carried body weight. Table 2 shows the percentages of foot pressure of 15 testees.

Table 2: Foot stress test results

	Left forefoot (%)	Left rear (%)	Right forefoot (%)	Right rear (%)	Forefoot total (%)	Rear total (%)	Left foot total (%)	Right foot total (%)
A	24.97	25.95	22.53	26.55	47.5	52.5	50.92	49.08
B	27.37	24.87	24.92	22.84	52.29	47.71	52.24	47.76
C	26.54	27.57	25.92	19.97	52.46	47.54	54.11	45.89
D	29.13	20.91	27.68	22.28	56.81	43.19	50.04	49.96
E	18.99	31.53	23.46	26.02	42.45	57.55	50.52	49.48
F	29.53	20.71	28.35	21.41	57.88	42.12	50.24	49.76
G	25.62	21.22	26.75	26.41	52.37	47.63	46.84	53.16
H	24.85	25.72	28.22	21.21	53.07	46.93	50.57	49.43
I	21.58	27.63	21.8	28.99	43.38	56.52	49.21	50.79
J	26.91	18.57	27.27	27.25	54.18	45.82	45.48	54.52
K	27.56	23.89	27.48	21.07	55.04	44.96	51.45	48.55
L	21.45	25.14	27.31	26.1	48.76	51.24	46.59	53.41
M	23.48	28.67	24.1	23.75	47.58	52.42	52.15	47.85
N	19.57	26.39	28.39	25.65	47.96	52.04	45.96	54.04
O	23.05	23.55	26.04	27.36	49.09	50.91	46.6	53.4

From the data in the table, it can be seen that, out of the 15 testees, 8 had a forefoot pressure percentage of over 50%; 7 had a rear foot pressure percentage of over 50%; 9 had a total left foot pressure percentage of over 50% and 6 had a total right foot pressure percentage of over 50%. This indicates that the pressure conditions of forefoot and rear foot during standing vary from person to person, and that there is no big difference between the pressure on the right and left feet. In the case of bare foot, the right forefoot bears the greatest pressure [16].

Then, the author collected the statistics of foot pressure distribution of one testee on bare foot at different time. Table 3 shows the pressure percentage of each part of the foot and the changes therein.

Table 3: Plantar pressure percentages of a testee on bare foot

Time	Percentage of stress (%)				Percentage of change (%)			
	Left forefoot	Left rear	Right forefoot	Right rear	Left forefoot	Left rear	Right forefoot	Right rear
2	25.78	24.9	23.13	26.19	0.81	1.05	0.6	0.36
7	25.12	25.12	23.75	26.01	0.62	0.6	0.62	0.6
12	24.85	25.24	22.98	26.93	0.5	0.26	0.47	0.71
17	25.74	22.76	24.61	26.89	1.01	1.14	0.15	0.28
22	24.14	26.07	23.04	26.75	0.72	0.53	0.09	0.1
27	25.12	24.73	25.38	24.77	0.78	0.72	0.36	0.42
32	25.48	25.93	24.48	24.11	0.47	0.28	0.5	0.69
37	26.76	22.06	26.86	24.32	0.98	1.61	0.8	0.17

The table shows data that were collected every 5 min. From the data, it can be seen that, after 12min, the testee started to feel fatigue in his feet. Through self-adjustment, the foot pressure was relieved. Over time, the fatigue came more frequently. Other 15 testees felt fatigue for the first time within 8~13min. The comfortable time that could be maintained after self-adjustment became shorter and shorter.

Test on Shoes with Different Sole Hardness

One Testee Wearing Different Test Shoes

According to the experimental design, 15 young testees participated in the foot pressure distribution test by wearing shoes with different hardness.

Figure 3 shows the plantar pressure distribution of the testee D in test shoes 1 in the first minute.

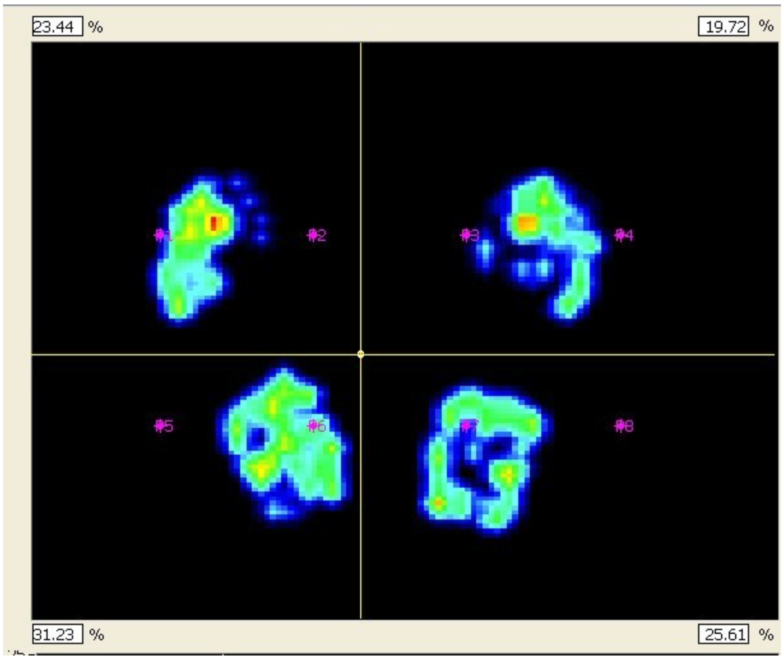

Figure 3. State of Testee D with shoes 1 in the first 1 minute

As shown in Figure 3, the foot pressure was mainly concentrated in the forefoot and the heel. The local pressure was too large while the regional coverage was small (the orange parts).

Figure 4 shows the plantar pressure distribution of the testee D in test shoes 2.

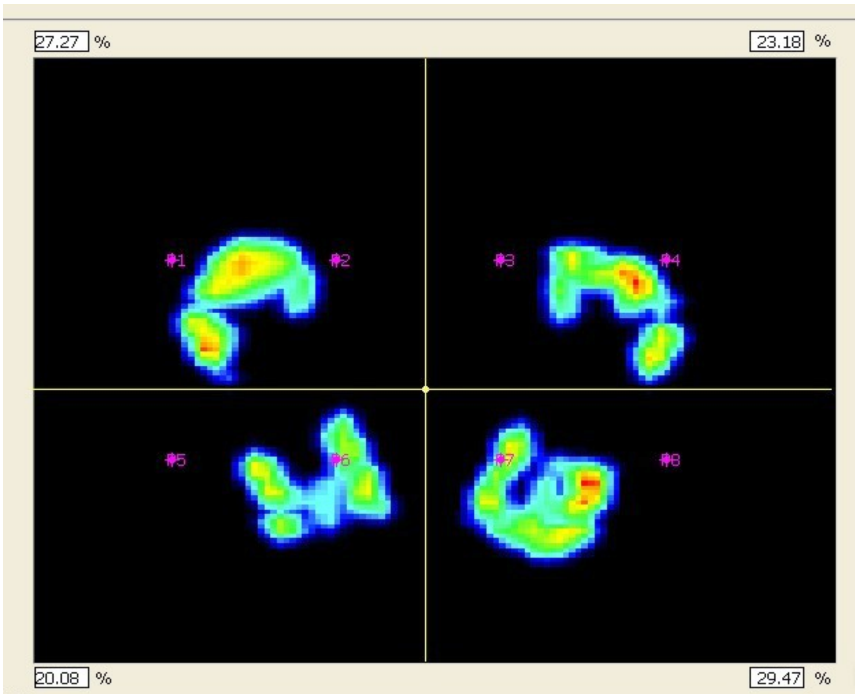

Figure 4. Testers D with shoes 2 for the first 1 minute state experiments

As shown in Figure 4, compared with shoes 1, in the shoes 2 case, the pressure was too large and the area coverage was expanded – the orange parts were expanded, indicating the feet carried more pressure.

Figure 5 shows the plantar pressure distribution of the testee D in test shoes 3.

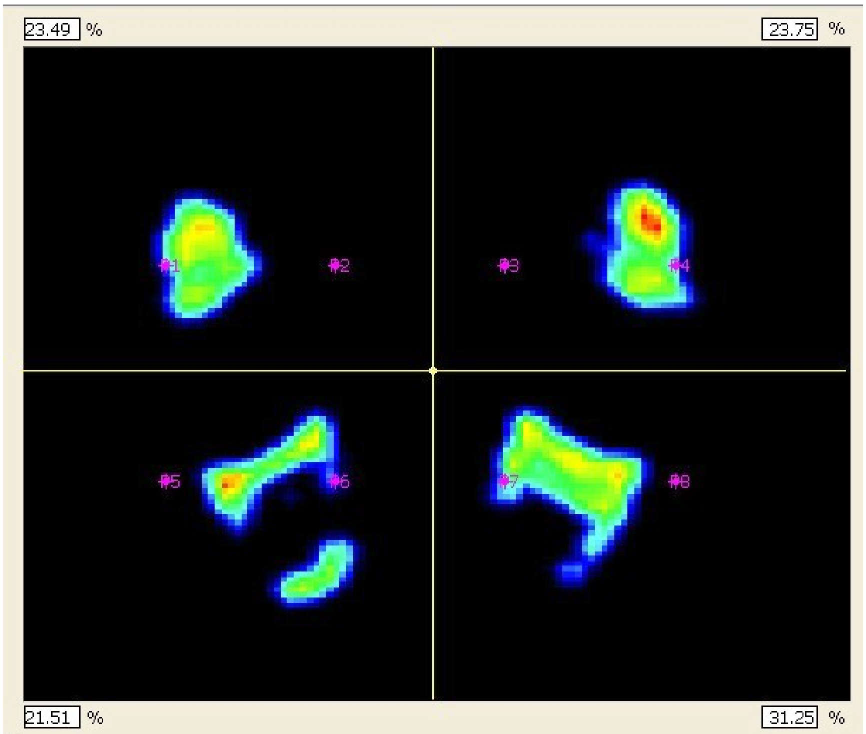

Figure 5. Testers D with shoes 3 for the first 1 minute state experiments

Figure 5 shows the foot pressure distribution when the testee wore the test shoes 3. The hardness of the test shoes is: test shoes 3> test shoes 2> test shoes 1. By comparing and analyzing the experimental results of the three pairs of test shoes, it can be seen that the higher the sole hardness is, the less the shoes can do to adjust foot pressure.

Different Testees Wearing Different Test Shoes

The test was to find out the first foot fatigue time for different testees wearing different test shoes. Table 4 shows the foot fatigue time for 15 young testees.

Table 4: Testee's foot fatigue time point

Tester	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
							Shoe 1								
Time	15	12	13	13	10	14	16	13	5	16	7	14	8	15	11
							Shoe 2								
Time	25	22	23	20	20	12	23	19	12	17	14	17	11	18	19
							Shoe 3								
Time	21	19	19	16	15	17	19	13	11	14	10	13	8	19	22

From the data in the table, it can be seen that the average time after which the testees felt fatigue in their feet when wearing test shoes 1 was 12.1min; that the fatigue start time for test shoes 2 was 12~25min, with an average of 18min; and that the fatigue start time for test shoes 3 was 15.3min on average.

Subjective Assessment by Subjects

Subjective Assessment for Barefoot Test

In the survey, testees on bare foot believed that it was the least comfortable to stand on bare foot. During the 40-min barefoot test, the feet were under too much pressure for over 20min and that caused pain. The average rating given by the 15 testees on pressure was nearly 3, indicating that the subjective perception of the testees standing on bare foot for a long time was too much pressure.

This is consistent with the experimental results - when standing on bare foot, the human body was poor at making self-adjustments and the pressure on feet was more concentrated.

Subjective Assessment Given by Testees Wearing Different Test Shoes

People's subjective assessment on footwear comfort was always lagging. After the end of the shoe test, the author collected the opinions of the 15 testees on the shoes with three different hardness. 14 interviewees rated test shoes 2 as good, shoes 1 as qualified and shoes 3 as poor.

Judging from the objective test data and subjective assessment, the test shoes 2 (casual shoes with a sole hardness of 64) are the best.

Discussion of Research Results

The main innovations of this paper are to explore foot comfort and different sole hardness during long-time standing. From the perspective of the change of plantar pressure, combined with the hardness of the sole and the standing time, the comfort of the shoes is studied. The comprehensive evaluation method was adopted which combines subjective and objective evaluation method to study the comfort of long-term standing shoes. The experimental results obtained from the objective test results of the sole pressure distribution and the subjective evaluation of the test subject have certain guidance, but the experimental test subjects do not consider the industry and age factors and do not consider the flat foot and the specific foot shape due to the limitations of the experimental object and time. The impact of these factor can be considered in later research.

CONCLUSIONS

In order to study the actual distribution of foot pressure during long-time standing and the effects of sole hardness in pressure cushion and adjustment, this paper first introduces the basic theories about foot and then describes the experimental design and process. It uses Footscan to carry out the experiment on testees under different conditions and also conducts subjective assessment survey. After the experiment and the subjective assessment, this paper analyses the results and obtains the following conclusions:

(1) On bare foot, the feet have the poorest ability to adjust themselves. Footwear is the main buffer for foot pressure.

(2) During long-time standing, sole hardness has a great impact on the shoe comfort. Considering self-adjustment and fatigue resistance, medium hardness is the best.

(3) People who need to stand for a very long time at work should choose shoes that have heels and appropriate sole hardness.

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HIGH BLOOM GELATIN STRENGTH FROM WHITE LEATHER SHAVINGS

Hamed M. ELSAYED[1]*, Rasha Z. ATTIA[1], Ola A. MOHAMED[1], Nabil H. EL-SAYED[1], Saber A. IBRAHIM[2]*

[1]Chemistry of Tanning Materials and Leather Technology Department, National Research Centre, Dokki, Cairo 12622, Egypt

[2]Packaging Materials Department, National Research Centre, Dokki, Cairo 12622, Egypt

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HIGH BLOOM GELATIN STRENGTH FROM WHITE LEATHER SHAVINGS

ABSTRACT. Leather making process is recognized as one of the highly polluting extensive industries which generate huge amounts of solids and liquid tannery wastes. These wastes effect in severely way on the surrounding environment and human health if these polluting not well treated. The aim of this article is to obtain high bloom gelatin from white leather shavings (untanned hide shavings, WLS) via alkaline hydrolysis for improved utilization of leather waste. This research introduces a system of reusing technologies for WLS wastes including preparing gelatin, isolating collagen protein by extracting method then characterization of extracted gelatin. This article recognized to determine efficiency of the thermal and chemical treatments on the white leather waste in recovering the largest amount of gelatin with high bloom strength and a smallest amount of residue. Chemical treatments of white solid wastes by partial hydrolysis of wastes using different factors affecting on hydrolysis such as alkalis concentration, temperature and contact time were discussed. The method verified that the leather wastes can be successfully processed to the powder like leather gelatin products. It was found that the optimum conditions to obtain high bloom gelatin strength from white shaving leather wastes around 150 bloom are 4 % w/v NaOH, 4 hours contact time, 250 rpm at 50 °C.
KEY WORDS: alkaline hydrolysis, gelatin, high bloom strength, SEM, white leather shavings

OBŢINEREA GELATINEI CU PUTERE GELIFIANTĂ MARE DIN DEŞEURI DE PIELE NETĂBĂCITĂ

REZUMAT. Industria de pielărie este recunoscută ca fiind una dintre industriile care poluează foarte mult, care generează cantităţi uriaşe de deşeuri solide şi lichide. Aceste deşeuri au efecte adverse asupra mediului înconjurător şi asupra sănătăţii umane dacă nu sunt tratate cum trebuie. Scopul acestui articol este de a obţine gelatină cu putere gelifiantă mare din deşeuri de piele netăbăcită prin hidroliză alcalină pentru o utilizare mai bună a deşeurilor de piele. Această cercetare introduce un sistem al tehnologiilor de reutilizare a deşeurilor de piele, inclusiv prepararea gelatinei, izolarea proteinei de colagen prin metoda de extracţie, apoi caracterizarea gelatinei extrase. Acest articol a avut scopul de a determina eficienţa tratamentelor termice şi chimice asupra deşeurilor de piele netăbăcită în vederea recuperării unei cantităţi mari de gelatină cu o putere gelifiantă mare şi cu o cantitate mică de reziduuri. S-au discutat tratamente chimice ale deşeurilor solide de piele netăbăcită prin hidroliza parţială a deşeurilor utilizând diferiţi factori care afectează hidroliza, cum ar fi concentraţia de baze, temperatura şi timpul de contact. Metoda a verificat faptul că deşeurile de piele pot fi prelucrate cu succes sub formă de produse din piele gelatină pulbere. Condiţiile optime pentru a obţine gelatină din deşeuri de piele netăbăcită cu putere gelifiantă mare, de 150 grade Bloom, au fost: 4% NaOH w/v, timp de contact 4 ore, 250 rpm la 50°C.
CUVINTE CHEIE: hidroliză alcalină, gelatină, putere gelifiantă mare, SEM, deşeuri de piele netăbăcită

OBTENTION D'UNE GÉLATINE À HAUTE RÉSISTANCE À L'ENFONCEMENT À PARTIR DE DÉCHETS DE PEAU NON TANNÉE

RÉSUMÉ. L'industrie du cuir est reconnue comme l'une des vastes industries qui polluent beaucoup, générant d'énormes quantités de déchets solides et liquides. Ces déchets ont des effets néfastes sur l'environnement et la santé humaine s'ils ne sont pas traités correctement. Le but de cet article est d'obtenir une gélatine à haute résistance à l'enfoncement à partir de déchets de peau non tannée par l'hydrolyse alcaline pour une meilleure utilisation des déchets de cuir. Cette recherche introduit un système de réutilisation des technologies de traitement des déchets de cuir, notamment la préparation de gélatine, l'isolement de protéines de collagène par une méthode d'extraction, et puis la caractérisation de la gélatine extraite. Cet article a eu le but de déterminer l'efficacité des traitements thermiques et chimiques sur les déchets de peau non tannée afin de récupérer une grande quantité de gélatine à haute résistance à l'enfoncement et une faible quantité de résidus. Les traitements chimiques des déchets solides de peau non tannée ont été discutés par l'hydrolyse partielle des déchets en utilisant divers facteurs qui influent sur l'hydrolyse, tels que la concentration des alcalis, la température et le temps de contact. La méthode a permis de vérifier que les déchets de peau pouvaient être traités avec succès sous forme de produits à base de poudre de peau en tripe. Les conditions optimales pour obtenir de la gélatine à 150 degrés Bloom à partir de déchets de peau non tannée ont été: 4% NaOH poids/volume, temps de contact 4 heures, 250 tr/min à 50°C.
MOTS CLÉS : hydrolyse alcaline, gélatine, haute résistance à l'enfoncement, MEB, déchets de peau non tannée

** Correspondence to: Hamed M. ELSAYED, Chemistry of Tanning Materials and Leather Technology Department, National Research Centre, Dokki, Cairo 12622, Egypt, hamed_sci@yahoo.com; Saber A. IBRAHIM, Packaging Materials Department, National Research Centre, Dokki, Cairo 12622, Egypt, saberam2000@yahoo.com*

INTRODUCTION

Leather industry generates a huge amount of solid and liquid tannery wastes during the hide tanning process that produces leather as a supply for shoes, automotive and furniture markets. Environmental risk challenges arise from the nature and the wastes discharged from leather processing. The main part of leather wastes is the hide collagen structure. The leather making process generates large quantities of solid and liquid wastes, one metric ton of rawhide produces on an average 200-400 kg of tanned leather and a range of 600-800 kg of solid wastes and an average consumption of 45-50 m3 of waste liquors. In these process stages, solid wastes generated from leather industry are classified as 1st wastes from untanned hides or skins (white shavings, fleshing wastes) 80% of solid wastes (500-600 kg), 2nd wastes from tanned leather (chrome shaving, buffing dust) 150 kg, 3rd wastes from finished and dyed leather (trimmings) 20-30 kg [1, 2].

The problems, solid protein wastes, have admittedly received more attention however; these have been mostly disposed until now to landfill or glue production. Many cleaner processing approaches aimed at reduction of liquid and solid wastes proved to be economically and environmentally beneficial [3-6]. Leather wastes divided into leather waste from tanneries, trimmings from leather goods factories and trimmings from the old leather products. The leather wastes from tanneries are divided into white leather wastes, chrome-containing leather wastes and dyestuff-containing leather wastes. The major part of leather wastes is protein. If protein and other unspent chemicals not utilized or treated correctly they cause severe environmental problems threatening the sustainability of leather making. Various useful products (glue, gelatin, artificial fibrous leathers, and collagen hydrolysate) can be extracted from leather wastes. The best way for their removal is to recover soluble proteins that may have a commercial use. A number of authors have reported about chemical and enzymatic treatment of leather waste [7-9].

Approximately 80 % of dry matter of the hide or skin is made up of complex nitrogenous organic compound known as proteins. Collagen is the ultimate plentiful insoluble protein of animal origin, comprising about 29 % of total protein. It is the major protein of skin, tendon, cartilage, bone, and white fibrous connective tissue in mammals. Collagen extracted from the previous materials is used for clarifying beverages, in cosmetics, in casing for meat products and in a host of biomedical applications. Medical applications of collagen include use in drug delivery systems, sponges for burns and wound and in tissue engineering [10].

Gelatin is a high molecular weight polypeptide derived from collagen; it is obtained by denaturation and solubilization of collagen [11, 12] which is derived from pigskins and bovine hides, bones and fish skin. To produce gelatin, collagen is heated in either acidic or basic solutions to break the covalent bonds between the rods and solubilize the protein. The treatment also separates the polypeptides and hydrolyzes some of the polymer chains. Gelatin quality is measured by Bloom units [13, 14].

There are three methods of gelatin production: acid, alkali, enzymatic processes due to soaking and autoclaving processes. The most widespread methods are acid and alkaline processing followed by heating in water. Acid and base processes produce gelatins commonly point as Type A and Type B, respectively. Following these extraction processes [15-18], gelatin is dried to form coarse granules, fine powders, or thin sheets, which are odorless, tasteless, and yellowish in color. Over many years, gelatin has been an important biopolymer used widespread in food pharmaceutical industries. Commonly, it is used as transparent dessert jelly, but it is widely used in pastry, dessert, factories of meat products and dairy products [19-22].

The best way for their removal is to recover soluble proteins that may have commercial use. This paper deals with one of the major environmental problems of the huge manufacture in Egypt (leather industry). Approximately 80 % of leather solid wastes is generated during pretanning processes in beam house operations. Untanned trimmings and white leather wastes have negative effects on soil and water resources of the surroundings due to the bad smell produced during their putrefaction and their dangerous chemical contents. In Egypt, production of glue is the only use for white leather shavings. In this research article, production of gelatin with high bloom strength from white leather shavings by different alkalis is our target. Alkali treatment is suitable for more complex collagen as in bovine hides, the purpose of the alkali treatment is destroying chemical crosslinks fiber bundle present in collagen.

Alkali chemical treatments of WLS by partial hydrolysis of wastes using different alkalis (NaOH, KOH, LiOH) and different factors affecting hydrolysis such as alkalis concentration (2-10 % w/v), contact time (1-6 h) and temperature (40-90 °C) were studied.

EXPERIMENTAL

Materials and Methods

Materials

White leather wastes were supplied by tannery from Misr-El-Kadima, Cairo, Egypt. Sodium hydroxide, lithium hydroxide and potassium hydroxide are used as received. All reagents were analytically pure according to the grade of national reagent purity standards.

Methods

The purpose of this research is to recover gelatin from the white leather waste to be used in many applications [21-26]. The study also aimed at evaluation of the different parameters affecting on white leather shavings hydrolysis. White shavings with a pH of 3.8 after basification were obtained from a commercial tannery. The shavings were soaked in 5x their weight of water for cleaning.

Factors Affecting on the Hydrolysis of White Leather Shavings (WLS)

There are different factors affecting on hydrolysis process of WLS by different alkalis (NaOH, KOH, LiOH) have been studied systematically such as concentration of different alkalis, contact time and temperature.

Effect of Different Concentration of Alkalis (Optimum Condition of Alkalis)

The effect of concentration of different alkalis on the hydrolysis of WLS studied as follows: White shavings (20 g) were put into a 250 mL flask and 80 mL of water was added, together with 2-10 % w/v of alkalis (LiOH, NaOH, KOH) equivalent to (1-2.5 mol/L). Then, the flask was put into a water bath at 70 °C and 200 µL surfactant, 250 rpm, for 6 h, the solution was then left to cool down.

Effect of Time on the Hydrolysis (Optimum Condition of Time)

The effect of time on the hydrolysis of WLS studied as follows: white shavings (20 g) were put into a 250 mL flask and 80 mL of water was added, together with optimum condition of concentration of alkalis. Then, the flask was put into a water bath at 70 °C and 200 µL surfactant, 250 rpm, different shaking time from 3 h up to 8 h, the solution was then left to cool down.

Effect of Temperature on the Hydrolysis (Optimum Condition of Temperature)

The effect of temperature on the hydrolysis of WLS studied as follows: white shavings (20 g) were put into a 250 mL flask and 80 mL of water was added, together with optimum condition of concentration of alkalis. Then, the flask was put into a water bath at different temperature from 50-90 °C and 200 µL surfactant, 250 rpm, optimum condition of time, the solution was then left to cool down.

Separation of Gelatin

After hydrolysis of white leather shavings in each of parameters used (conc. of alkali, hydrolysis time, temperature), the extracted gelatin poured into sintered glass filter grade 4 for filtration. The residual solid white cake was washed twice with water for adjusting pH at 7 and then the cake was put into a Teflon mold in a drying oven for complete dryness. The dried gelatin was ground for obtaining gelatin powder for further characterization.

Determination the Properties of the White Leather Wastes and Extracted Gelatin

Determination of Moisture

Osborne punch was used to cut samples for moisture. The samples were weighed into dry, tared porcelain dishes. The samples were dried for 17 h at 105 °C. The samples were cooled in a desiccator, weighed and the percent moisture determined. 5 g of sample were accurately weighted in a tared dish, and then heated at 105 °C for three hours in air-oven at which the temperature was as uniform as possible; the dish was allowed to cool in a desiccator, and then weighted. The process of heating, cooling and weighting was repeated till constant weight, the moisture content is defined as the percentage loss in weight of the sample.

% moisture = (W1 - W2) x 100/W1 (1)

Where: W1 = weight of the sample before drying.

W2 = weight of the sample after drying.

Determination of Ash

The dried samples were ashed at 600 °C for two hours then cooled in a desiccator and weighed to determine ash content and percent volatile substance calculated on a moisture-free basis. In a burnt platinum crucible about 5 g of sample was accurately weighted, the sample was carefully ignited in a muffle furnace at about 600 °C for about 2 hours. Finally the crucible with its contents was cooled in a desiccator and weighted. The ignition, cooling and weighting were repeated till constant weight.

% ash = Wt. of residue × 100/ Wt. of original fat (2)

Determination of Total Kjeldahl Nitrogen (TKN)

TKN was determined by the semi-micro Kjeldahl method. Solid samples weighed to the nearest 50 mg and liquid samples measured to 1 mL and transferred to a 30 mL digestion flask. Digestion catalyst (1.2 g), a few boiling chips and sulfuric acid (2 mL) added. The samples were digested for two hours. The samples were carefully transferred to the filling funnel and NaOH solution (10 mL) will be added. The mix was distilled to a 125 mL Erlenmeyer flask containing boric acid saturated solution (10 mL). The samples were titrated with standardized HCI to the gray endpoint.

Determination of Fat

For fat determination, samples were weighed into appropriate flasks and 6N HCI (75 mL) added. The samples were hydrolyzed for 2 h. The hydrolysate was transferred to a separating funnel and the fat was extracted with chloroform or petroleum ether. The chloroform layer was put in dry, tared crystallizing dishes, the chloroform evaporated and the samples were held at 60 °C for 16 h. The samples were cooled in a desiccator and then weighed.

pH Measurement of Leather Waste

The tests for the determination of the initial pH value were accomplished as follows: 5 g of white shavings sample was placed in 100 mL of distilled water at room temperature during two hours with agitation. After decantation without filtration of soluble matter, proceed to the determination of the pH of the prepared liquor using the pH-meter.

pH Measurement of Gelatin

The British Standard was adapted and one gram of gelatin sample was dissolved in 100 mL warm distilled water. The solution was cooled to 25 °C and the pH was measured with a standard pH meter.

Yield of Gelatin

The yield of extracted gelatin obtained was determined as follows:

Yield (%) = (dry weight of the gelatin/dry weight of white leather shavings) x 100 % (3)

Characterization

Determination of Gel Strength

The gel strength (Bloom) was determined according to British Standard 757:1975 method (BSI, 1975), by using a texture analyzer (CT3 Brookfield, USA). A solution containing 6.67 % (w/v) gelatin was prepared by mixing 7.50 g of gelatin and 105 mL of distilled water in a Bloom bottle with stopper. The mixture was swirled and left to stand at room temperature for 3 h, allowing the gelatin to absorb water and swell. The Bloom bottles were then transferred to a water bath maintained at 65 °C and held for 25 min with occasional swirling to dissolve the gelatin. The bottles were taken out of the water bath, allowed to cool for 15 min at room temperature and then placed in a cold-water bath (Brookfield gelatin bath system, model TC-550MX refrigerated bath) maintained at 10 °C and held at this temperature for 18 h before the determination of the gel strength. The Bloom bottle was placed centrally under the plunger (Delrin probe, which is clear acrylic AOAC and GMA cylinder with sharp edge; TA10, 12.7 mm diameter) of the instrument. The Bloom strength was determined with a load cell of 10 kg and crosshead speed of 0.5 mm/s. The maximum force (g) was determined when the probe penetrated to a depth of 4 mm into the gel.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were taken with a Nexus 670 FTIR spectroscopy (Nicolet, United States) over the range of 400–4000 cm-1 with a resolution of 4 cm-1; the KBr disk technique was applied.

Dynamic Light Scattering (DLS)

The particle size investigation of the aqueous dispersions was carried out with Zetasizer Nano S (Malvern Instr., UK) equipped with a monochromatic He-Ne laser lamp (λ = 633 nm) as light source (ALV GmbH, Germany) at an angle of 173°. All measurements of dispersed samples were carried out in disposable cuvettes.

X-Ray Fluorescence (XRF)

It used to identify and determine the concentrations of elements in solid, powdered and liquid samples. XRF is capable of measuring all elements from Beryllium to Uranium and beyond levels often below one part per million. X-ray fluorescence was carried out using Axios, WD-XRF sequential spectrometer. Sample was crushed then ground in Herzog mill to powder, then sieved through 0.063 mm sieve. The samples were prepared as pressed disks, through mixing 7 g of fine powder of each sample with 1.6 g of binding wax in small mill, at 380 rpm, for one minute. Sample was kept in standard aluminum cup, pressed in automatic machine less than 130 KN, the yield disk spacemen was used in qualitative and quantitative analysis of elements.

High Performance Liquid Chromatography, HPLC Amino Acid Analyzer

HPLC consists of pump for pumping of mobile phase (liquid), Octocatyl silica column (C18-column). It provided with photodiode UV detector. It is used for determination of bulky organic compounds. Liquid chromatography 300, amino acid analyzer - Eppendorf, Germany, and flow rate: 0.2mL\min, pressure of buffer from 0-50 bar, pressure of reagent to 0-150 bar, reaction temp 123 °C, was used for amino acid analysis.

Preparation of sample to amino acids analysis:

1 - 1g of gelatin was weighed in a hydrolysis tube, then 1 mL of 6 N HCL.

2 - The solution was frozen and evacuated from the tube with vacuum pump.

3 - The hydrolysis tube was closed by melting the glass with a suitable gas-burner.

4 - Depending on original material, hydrolysis was carried out in an oven with a uniform temperature distribution of 110 °C for 24 hours, then the tube was cooled down in an ice-bath after hydrolysis. Afterwards, the solution was centrifuged in order to precipitate insoluble components.

5 - Centrifuged solution was evaporated at approximately 40 °C in a rotary evaporator.

6 - The sample was dissolved with 1-2 mL of sample diluting buffer; then the sample was ready for analysis.

Thermal Gravimetric Analysis (TGA)

Thermal analysis was studied with a Perkin Elmer thermogravimetric analyzer (rate=10 °C/min) from room temperature to 600 °C at the National Research Center of Egypt.

Differential Scanning Calorimetry (DSC)

DSC was carried out in a TA Instruments Q100 to determine glass transitions (Tg), crystallization temperatures (Tc) and melting points (Tm). The thermal history was erased during the first run at a high heating rate up to 200 °C, followed by cooling cycle to -50 °C. After that, the heating rate was modulated ± 1.0 °C min-1 with heating rate 5.0 °C min-1 to 200 °C. According to ASTM D 3418, Tg was calculated as the midpoint temperature.

Scanning Electron Microscopy (SEM)

SEM is thus a useful technique for evaluating the effects of various treatments on the leather surface and it can be used to assess the penetration of the copolymer through leather and onto the hierarchy of the structure. Leather samples (1cm2) were subjected to sputter coating with gold ions which acted as a conducting medium during scanning, and observed using a Philips Quanta 250 electron microscope.

RESULTS AND DISCUSSION

Characterization of White Leather Shaving (WLS)

It is very important to characterize the WLS before hydrolysis for obtaining extracted content was in the range 0.39-0.5 %. All the percentage represented in a dry basis except for moisture.

Table 1: Properties of white leather shaving

Characteristic	Mean Value*
pH	4 ± 0.3
Ash content	2.8 ± 0.2 %
Moisture content	11 ± 2 %
Nitrogen content	14 ± 1 %
Fat content	0.55 ± 0.2 %

Mean Value* ± SD triplicate analysis

Chemical Hydrolysis of White Leather Shavings (WLS)

Effect of Different Concentration of Alkalis

The effect of concentration of different alkalis on the hydrolysis of WLS was studied, for obtaining optimum conditions of conc. of alkalis which is a step growth for further parameters. Table 2 showed the effect of different concentrations on the gelatin extraction from WLS. The experimental results proved that as the percent of conc. of alkalis increases, the percent of the hydrolysable protein increases, where at 2 % w/v conc. of alkalis the WLS were not completely hydrolyzed and at 4 % w/v, 6 % w/v conc. of alkalis is adequate and enough for obtaining gelatin with good bloom strength but at 8 % w/v and 10 % w/v conc. of alkalis waste is completely hydrolyzed to hydrolysable protein.

Table 2: The effect of different concentrations on the gelatin extraction from white leather shavings (WLS)

Conc. %	NaOH			KOH			LiOH		
	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %
2	-----	-----	-----	-----	-----	-----	-----	-----	-----
4	160 ±5	120 ±4	80 ±2	140 ±5	163 ±4	79 ±3	135 ±4	160 ±2	79 ±3
6	100 ±4	80 ±5	70 ±3	110 ±6	150 ±6	70 ±2	111 ±4	120 ±3	71 ±2
8	80 ±6	65 ±3	50 ±2	70 ±3	90 ±8	52 ±4	76 ±6	60 ±1	55 ±4
10	40 ±7	55 ±6	20 ±4	30 ±7	50 ±4	27 ±6	35 ±8	40 ±4	25 ±5

-----Not enough hydrolysis
Mean Value ± SD triplicate analysis

From Table 2, it is obvious that, 4 % w/v conc. of alkalis is the best concentration for gelatin extraction and it gives good viscosity and bloom values. At 2 % w/v conc. of alkalis there is not enough hydrolysis to the shavings. Over 6 % w/v conc. of alkalis there is a decrease in the bloom and viscosity values, due to the hydrolysis of the collagen fibers, yielding mixture of free amino acids and hydrolysable protein. High concentration of alkaline materials decreased the gelatin yield and gel strength [27, 28]. In conclusion, 4 % w/v conc. of all alkalis is the best concentration for gelatin extraction because it gives good viscosity and high bloom values which is very important in case of application in the further part of the research especially in biodegradable packaging.

Effect of Extraction Time on the Hydrolysis of White Leather Shavings (WLS)

The time of extraction is a very important parameter for studying the hydrolysis of WLS for saving money for industrial application. The data was recorded in Table 3. The experimental results proved that as time increased the gel strength increased up to 4 h after that it tends to decrease.

From Table 3 it is obvious that, 4 h extraction time is the optimum time required for gelatin extraction, besides high viscosity and good bloom values. At 3 h extraction time is not enough time to yield acceptable bloom and viscosity. However, over 5 h the extracted gelatin was hydrolyzed resulting in weak bloom and viscosity, longer extraction times give very low yield. Extracted gelatin has low gel strength and viscosity due to excessive damage and breaking down the collagen fractures with longer heating and possibly extraction of hydrolysable proteins. In conclusion, 4 h is the best time for gelatin extraction because it gives good viscosity and bloom values.

Table 3: Effect of time on the hydrolysis of white leather shavings (WLS)

Extraction time Hours	NaOH			KOH			LiOH		
	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %
3	-----	-----	-----	-----	-----	----	-----	-----	-----
4	155 ±6	140 ±7	78 ±6	160 ±3	135 ±4	77 ±4	140 ±6	150 ±6	78 ±4
5	125 ±5	100 ±5	77 ±5	130 ±5	100 ±8	65 ±4	120 ±5	89 ±7	66 ±3
6	80 ±6	90 ±4	34 ±4	90 ±7	80 ±6	26 ±3	70 ±7	65 ±4	27 ±4
7	40 ±8	30 ±8	13 ±7	30 ±6	40 ±4	10 ±6	30 ±6	20 ±7	15 ±5

--- = Not enough hydrolysis
Mean Value ± SD triplicate analysis

Effect of Temperature on the Hydrolysis of White Leather Shavings (WLS)

The thermal effect is very efficient parameter in case of studying the hydrolysis of WLS. Table 4 show the effect of temperature on the hydrolysis of white leather shavings.

Table 4: Effect of temperature on the hydrolysis of white leather shavings (WLS)

Extraction temperature °C	NaOH			KOH			LiOH		
	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %	Bloom G	Viscosity Poise	Yield weight %
40	----	----	----	----	----	----	----	----	----
50	160 ±4	120 ±4	79 ±3	140 ±4	163 ±7	78 ±2	130 ±6	160 ±5	76 ±2
60	130 ±3	100 ±5	61 ±4	120 ±6	117 ±5	60 ±3	99 ±3	120 ±4	84 ±3
70	100 ±6	80 ±3	40 ±5	100 ±8	83 ±5	43 ±4	74 ±4	90 ±3	63 ±4
80	50 ±7	56 ±5	23 ±7	80 ±5	62 ±8	24 ±6	60 ±4	66 ±7	46 ±2
90	40 ±7	34 ±7	13 ±8	50 ±7	30 ±6	12 ±8	40 ±4	36 ±8	20 ±8

---- Not completely hydrolyzed
Mean Value ± SD triplicate analysis

The experimental results proved that as temperature increased there will be an extensive increase in the hydrolysable protein up to 90 °C. From Table 4, it is obvious that 50 °C is the optimum extraction temperature required as it gave high viscosity and good bloom values. At temperature lower than 50 °C solubility of gelatin decreases, so the yield was decreased. However over 60 °C the extracted gelatin was affected by increasing temperature and hydrolyzed to free amino acids. Different temperatures are used in extraction of gelatin but most of them are in the range from 50 °C to 60 °C. Temperatures from 45 °C to 60 °C can enhance bond formation within molecules between strands and therefore gelatin with stronger crystallization ability can be obtained. However, temperatures above 60 °C lead to broken chains within the particles giving weaker gelatin ability. Lower extraction temperatures, on the other hand, lead to low yields. The higher yield percent of the gelatin is obtained at moderate temperature.

In conclusion, the optimum condition for obtaining higher bloom strength around 150 bloom with an average molecular weight of 20000 - 25000 g mol^{-1} or 20-25 kilo Daltons was 4 % w/v NaOH, 4 hours contact time, 250 rpm at 50 °C. After that, characterization of the extracted gelatin was investigated chemically and instrumentally to check suitability for industrial or biomedical application.

Characterization of Extracted Gelatin

There is increasing attention in the extraction process of gelatin and its derivatives due to the rising tendency to use gelatin to replace synthetic agents in various industrial processes, which results in a greater approval of the by-products from animal slaughter. Gelatin's characteristics depend on the raw material and the extraction conditions, which subsequently determine its application. Gelatin has a wide range of applications in the food, pharmaceutical, cosmetic and photographic industries, among others; also gelatin quality is highly affected by physico-chemical characteristics, not only by species and tissue extract, but also by processing methods [27].

The properties of extracted gelatin samples from different alkalis are showed in Table 5.

Table 5: The properties of extracted gelatin

Extraction Material	Color	Moisture Content %	Ash Content %	Nitrogen Content %	Fat Content %	Turbidity
NaOH	Brown	5.5 ±0.5	4.5 ±0.6	13.5 ±0.8	0.45 ±0.03	72
KOH	Brown	5.1 ±0.4	5.4 ±0.4	11.6 ±0.5	0.40 ±0.02	45
LiOH	Brown	4.7 ±0.6	5.3 ±0.5	10.9 ±0.7	0.42 ±0.03	101

Mean Value ± SD triplicate analysis, All the percentage represented in a dry basis except for moisture.

From Table 5 it is clear that the moisture content of all extracted gelatin from three alkalis was from 4 to 5.5 % with the highest value for NaOH and lower value with LiOH. The ash content was in the range from 4-6 %. However the nitrogen content has a high value 14 % in case of NaOH and lower value in case of 11 % in case of LiOH. The gelatin extracted from the LiOH is more turbid than the others extracted gelatin from NaOH and KOH and the fat content from all the extracted gelatin was in range 0.39 -0.45 %.

FTIR Analysis of Extracted Gelatin

Figure 1 and Table 6 show a typical FTIR spectrum for extracted gelatin at 50 °C using 4 % w/v of different alkalis which completely resemble each other, taking NaOH and KOH solution with bloom 150 g as example. It displays three major peak regions noticeable as 1st region (3600-2700 cm^{-1}), 2nd region (1900-900 cm^{-1}), and 3rd region (400-900 cm^{-1}). The regions are specifying to the bonds as amide A and B; also amide I, II and III; and amide IV, V and VI.

The FTIR spectrum shows characteristic transmittance peaks of the chemical functional groups of the gelatin in Figure 1 and Table 6. The gelatin fibril found to be broadening and a slight shift to lower wave number of the amide A peak, so associated with increased inter-molecular interactions of gelatin. The absorbance bands are identified as follows: a strong and broad overlapping band in the range of 3600-3300 cm^{-1} was assigned to NH bond in the peptide group of collagen and protein and for the OH of carboxylic group in the protein, the bands at 2938, 2877 cm^{-1} are from -CH3 and -CH2 stretching vibrations for the gelatin. The strong band at 1646,1652 cm^{-1} is due to C=O overlapping between carbonyl groups of gelatin, the bands at 1335 cm^{-1} and 1433 cm^{-1} are due to -CH3 and -CH2 bending vibration. The band at 1225 cm^{-1} was assigned to NH bending vibration of the amide group and the band at 1174, 1051 cm^{-1} is attributed to the strong C-O-C of amide bond in gelatin stretching vibrations, the bands at 987 cm^{-1}, 969 cm^{-1}, 695 cm^{-1} are the skeletal stretch C-C- and CH out off plane. For the region from 750 to 500 cm^{-1} especially for extracted gelatin by KOH, the C-S stretching mode is generally was observed related to cysteine and cystine [29]. Also, another characteristic skeletal deformation is due to the C-S-H and O=C-S out of plane bending appears at 400-500 cm^{-1}.

Table 6: FTIR spectra and assignments of extracted gelatin

Region	Extracted gelatin	
	Peak wave number cm^{-1}	Assignment
Amide A	3500	NH stretch
	3422	OH stretch
	2936	CH2 asymmetrical stretch
	2850	CH2 symmetrical stretch
Amide I	1647	C=O stretch coupled with COO-
Amide II	1524	NH bend coupled C-N stretch
	1455	CH2 bend
	1331	CH3 bend, CH2 wagging of proline
Amide III	1246	NH bend
	1047	C-O stretch
Amide IV	863	-C-C-, Skeletal stretch
Amide V	687	CH out off plane, skeletal stretch
Amide VI	611	CH out off plane, skeletal stretch

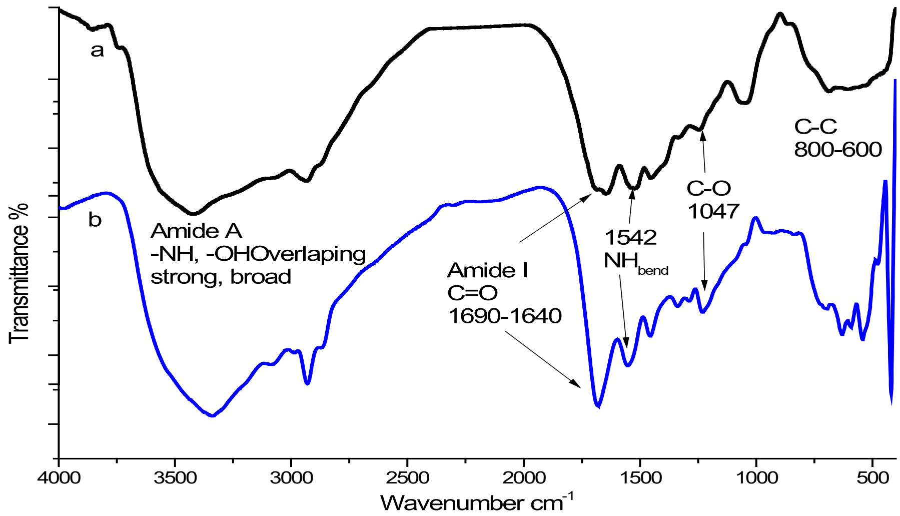


Figure 1. FTIR spectra of extracted gelatin with different alkalis: (a) NaOH, (b) KOH

All the previous detected peaks confirmed the structure of the extracted gelatin. The results obtained are in similarity in the literature [30].

Dynamic Light Scattering (DLS)

DLS can be considered a main tool to understand and verify models pertaining to the dynamics of biopolymers (gelatin) in dilute solution. It allows determining the size and hydrodynamic radius of biopolymers molecule in solution. As shown in Figure 2, the particle size distribution of gelatin which dispersed in aqueous medium presence relative particle diameter measurement distribution over narrow range from 0.45-1.6 µm with percentage more than 90 % of particles by volume distribution. Low polydispersity, narrow distribution of particle size (870 nm) of gelatin indicated to the ability to form homogenized distribution of blended film gelatin, which gives gelatin film a range of application from few µm as packaging films.

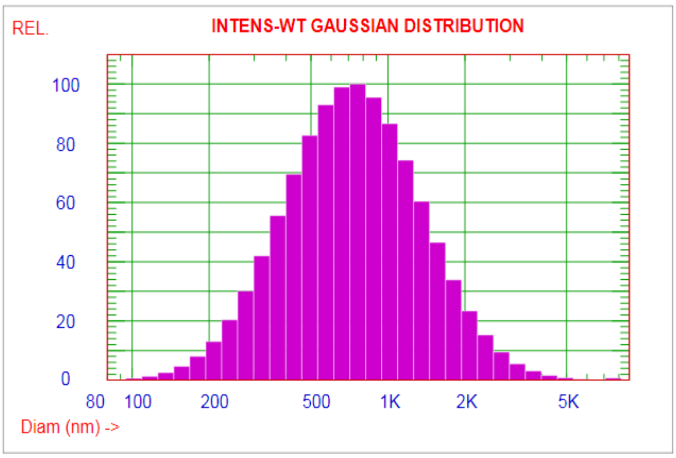


Figure 2. DLS image of particle size distribution of extracted gelatin with different ratios

Amino Acids of Extracted Gelatin at Optimum Condition

The amino acid composition of the gelatin extracted from white leather shavings (WLS) were presented in Table 7. The experimental results showed that under the conventional acidic hydrolysis conditions, complete hydrolysis of the white leather shavings (WLS) was proceeded with yield of 16 amino acids as revealed in Table 7. It was observed that, all of asparagines and glutamine are completely hydrolyzed to aspartic and glutamic acids, respectively. It is difficult to determine cysteine by acid hydrolysis and also tryptophan is completely damaged. Glutamic acid reaches the maximum amount of 20% while, aspartic acid and lysine reach to 10%. Tyrosine is partially hydrolyzed and trace amounts are present in the hydrolysate, low amount of serine and threonine due to partial hydrolysis of about 3 and 4 %, respectively. The results obtained match with the literature [31].

Table 7: Amino acids composition (%) of the extracted gelatin

Amino Acids	%	Amino Acids	%
Aspartic Acid	10.35	Leucine	3.54
Threonine	3.93	Isoleucine	6.57
Serine	3.72	Phenylalanine	2.57
Glutamic Acid	19.78	Tyrosine	4.04
Glycine	3.86	Histidine	3.78
Alanine	3.76	Lysine	10.56
Valine	4.63	Arginine	4.66
Methionine	2.82	Proline	9.06
NH_4^+	2.16		

X-Ray Fluorescence Spectrometric Analysis of Extracted Gelatin

XRF study was carried out to determine the elemental constituents of extracted gelatin from white leather shavings by 4 % w/v of different alkalis.

Table 8: XRF analysis of extracted gelatin at 4% w/v of different alkalis

Main constituents	(NaOH), Wt.%	(KOH), Wt. %	(LiOH), Wt. %
Si	0.154	0.139	0.186
Al	0.123	0.134	0.322
Fe	0.234	0.314	0.386
P	0.118	0.089	0.127
S	1.35	0.98	1.168
Ca	1.166	1.120	1.230
Mg	0.048	0.050	0.039
Br	--	0.030	0.003
Cu	--	----	----
K	0.175	0.248	0.230
Na	0.256	0.129	0.316
Sr	-	---	---
Cl	1.333	1.230	1.654
Li	--	----	0.123
Co	--	0.001	----
Loss On Ignition, LOI	93.88	95.14	94.21

From Table 8, it is obvious that, the percent of sulfur are (1.35, 0.98 and 1.168) for different alkalis NaOH, KOH, LiOH, respectively. It is one of the highest values of element percent in gelatin. This is due to the cleavage of S-S bonds in cystine and cysteine by the different alkalis. Other elements have few contributions with minor percentages. The higher value of Na in case of using LiOH is not logical but it may be related to apparatus analysis error. The higher value of Loss On Ignition related to the organic part of the extracted gelatin (N, C, O, H) with percent 94% - 96%.

Thermal Gravimetric Analysis (TGA) of Extracted Gelatin

TGA is a thermoanalytical technique that follows the change in weight of gelatin as a function of temperature. The response to thermal treatment depends on the structure and morphology of gelatin at each step. Thermal behaviours for gelatin extracted by NaOH, KOH and LiOH from white shaving leather waste completely resemble and are presented in Figure 3.

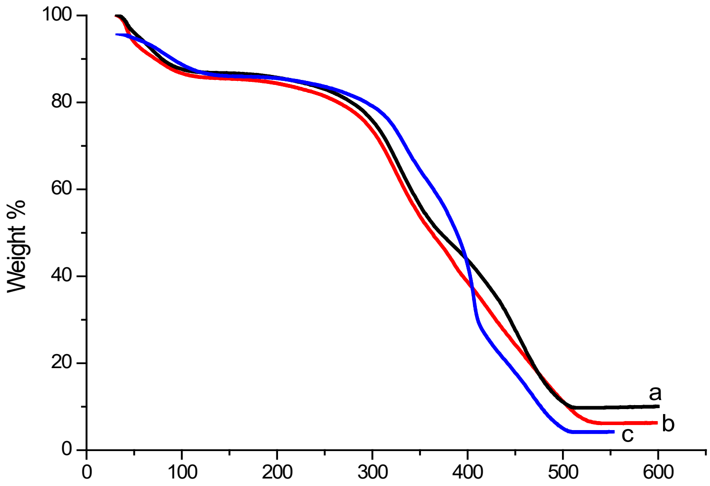


Figure 3. TGA of gelatin extracted by different alkalis (a) NaOH, (b) KOH (c) LiOH

It is clear that there are three main degradation stages: 1st stage represents dehydration volatilization of low molecular weight substances and moisture. The 2nd stage is the main degradation stage and the third stage is the carbonization stage. The gelatin sample extracted by different alkalis from WLS has an initial weight loss of about 12 % at temperature between 50-127 °C due to the evaporation of water included in gelatin. There is a gradually decreased in the weight loss of the gelatin which reaches to 60 % at temperature between 130-440 °C due to burning of hydrocarbon chain of the gelatin chain. The 3rd peak at 440-600 °C included the degradation of the rest of gelatin with a weight loss 19 %. After 600 °C, the ash formed with about 9 % of the initial weight. The results obtained are comparable and similar with the literature [32, 33].

Differential Scanning Calorimetry (DSC)

DSC analysis gives information about the glass transition behavior, T_g of the extracted gelatin. Commonly, If T_g of gelatin lies below room temperature, the gelatin films be more flexible and good elastomers. If T_g of gelatin above room temperature the gelatin films takes rigid and brittle behavior. Thus, known information of T_g is important in the selection of materials for various applications.

The slow traditional DSC scan at 10 °C/min gives broadening endothermic peak that is observed from almost -100 °C up to 200 °C in extracted gelatin samples (Figure 4). For regularity, the three thermal transitions of gelatin experimental in increasing order of temperature and will be referred to as T_g (glass transition) \ T_m (melting) \ T_i (isomerization), T_g in the range of 40–50 °C and a melting peak (T_m) in the range of 133–144 °C and melting enthalpy (normalized per unit mass) of 33 J/g. The results obtained match with the literature [34].

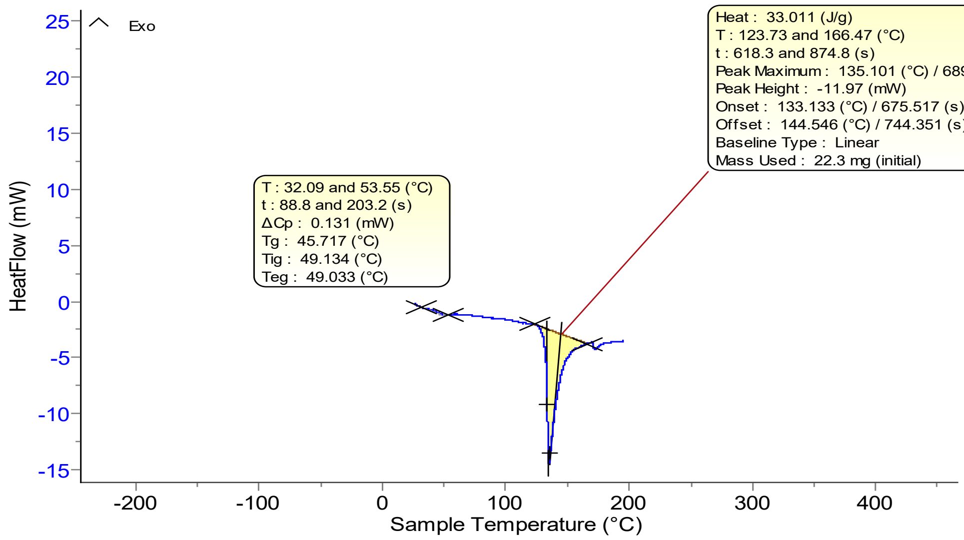
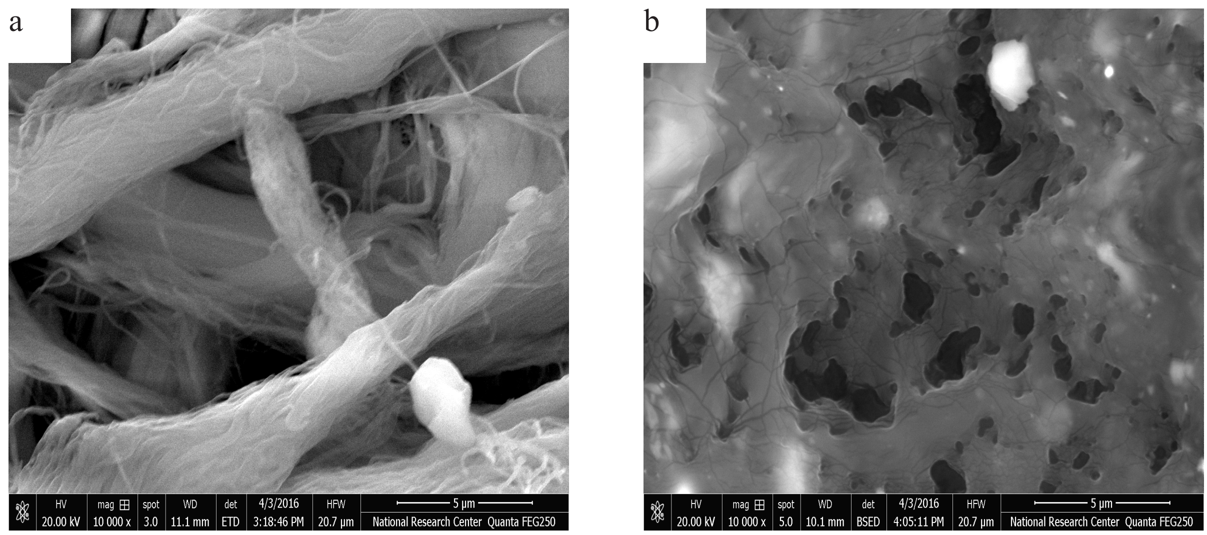


Figure 4. Differential scanning calorimetry (DSC) thermograms of extracted gelatin

Scanning Electron Microscope (SEM) for White Leather Shaving and Extracted Gelatin with Different Alkalis

Surface area morphology and microstructure of gelatin are recognized as vital tools for understanding its industrial, chemical and biomedical applications [35]. Figure 5 shows SEM images of white leather shavings, extracted gelatin with different alkalis at 10000 x magnifications. The white leather shavings had a striped fiber bundle with irregularly filamentous shape Figure 5(a), while the extracted gelatin from different alkalis showed pores with flake shape Figure 5(b-d). The collagen extracted from alkalis had a complex fibril form, related to the higher wet-ability, i.e. the ability to be adsorbed and be soluble in water [36, 37]. Therefore, extracted gelatin is used as a hydrating agent in field of cosmetics. As described by the comparatively well-distributed pore structure might be suitable for biomedical application as mentioned by many researchers [38].



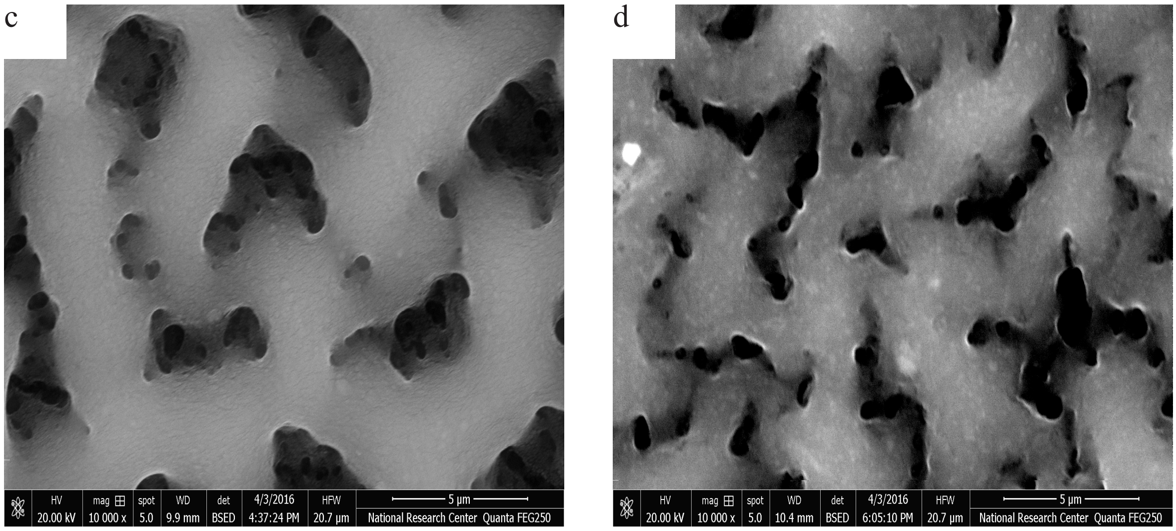


Figure 5. SEM images of a) white leather shavings; and extracted gelatin with different alkalis: b) NaOH; c) KOH; d) LiOH

CONCLUSION

The aim of our article is to obtain high bloom gelatin from white leather shavings via combining the fields of leather technology and waste management technology for enhanced utilization of leather waste. Chemical treatments of white solid wastes by partial hydrolysis of wastes using different alkalis and different factors affecting hydrolysis such as alkalis concentration, contact time and temperature were studied. The system included preparing gelatin from white leather waste, isolating collagen protein from white leather waste by extracting method and characterization of extracted gelatin. The method verified that the leather wastes can be successfully processed to the powder gelatin products. It was found that the optimum conditions to obtain high bloom gelatin strength from white shaving leather wastes around 150 bloom are 4% w/v NaOH, 4 hours contact time, 250 rpm at 50 °C. FTIR spectra show the presence of functional groups of gelatin with different alkalis. TGA of extracted gelatin reaching to higher temperature 440 °C, and glass transition temperature at 45 °C. SEM of the extracted gelatin from different alkalis showed pores with flake shape with the comparatively well-distributed pore structure that might be suitable for biomedical application especially in biodegradable packing materials.

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THE EFFECT OF BACKPACK LOAD ON MOTION COORDINATION OF SCHOOLCHILDREN

Nan ZHOU[1,2], Wuyong CHEN[1*], Jin ZHOU[1], Luming YANG[1]

[1]National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, 610065, China

[2]Guangzhou Shiling Leather& leather products investigation center, No.6 Yangguang Road Shiling Town, Huadu district, Guangzhou city, Guangdong province, 510850, China

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THE EFFECT OF BACKPACK LOAD ON MOTION COORDINATION OF SCHOOLCHILDREN

ABSTRACT. The aim of this study was to explore the influence of the load of a backpack on the coordination of motion of healthy children aged 7 to 12. 100 healthy schoolchildren were recruited and they were quantified with the normal BMI, no foot deformities or injuries, no abnormal gait patterns. Coda Motion System was used to record the angle of walking with backpack loads of 0%, 5%, 10%, 15%, 20% and 25% of their body weight (BW) randomly. Vector angles between angle of head, body, knee and ankle were first calculated and then the phase angle (PA) and continuous relative phase (CRP) including their standard deviations (SD) were figured out. Distinctions within six load condition were evaluated by covariance univariance with significance level of 0.05 and a confidence interval of 95%. Our results show that significant effect loading on the CRP of head and body was found (p=0.005<0.01), where 0%BW (p=0.002<0.05), 5%BW (p=0.001<0.05) and 10%BW (p=0.008<0.05) were recorded with smaller CRP values than those of 20%BW. However, no significant distinctions were found between 20%BW and 25%BW. Although significant differences were not found for all PA variables, their decreased simultaneously with the weight of backpack increasing, particularly in the body and ankle. Overall, coordination in motion of schoolchildren was partially influenced by an increasing load of the backpack, as significant body tilt was performed by the children to overcome the backwards drag, while other body parts were not affected.

KEY WORDS: backpack loading, continuous relative phase, phase angle, coordination of motion

INFLUENŢA GREUTĂŢII RUCSACULUI ASUPRA COORDONĂRII MIŞCĂRII LA ŞCOLARI

REZUMAT. Scopul acestui studiu a fost de a explora influenţa greutăţii rucsacului asupra coordonării mişcării la copii sănătoşi cu vârste cuprinse între 7 şi 12 ani. Au fost recrutaţi 100 de elevi sănătoşi cu IMC normal, fără deformări sau leziuni la nivelul picioarelor, fără mers anormal. S-a utilizat sistemul Coda Motion pentru a înregistra unghiul de mers la o greutate a rucsacului de 0%, 5%, 10%, 15%, 20% şi 25% din greutatea corporală (BW) în mod aleatoriu. Au fost calculate mai întâi unghiuri vectoriale între unghiurile capului, corpului, genunchiului şi gleznei şi apoi s-au calculat unghiul de fază (PA) şi faza relativă continuă (CRP), inclusiv abaterile standard (SD) ale acestora. Diferenţele dintre cele şase condiţii de încărcare au fost evaluate prin analiza univariată şi determinarea covarianţei cu un nivel de semnificaţie de 0,05 şi un interval de încredere de 95%. Rezultatele noastre arată că s-a observat o încărcare semnificativă a CRP la nivelul capului şi corpului (p=0,005<0,01), unde s-au înregistrat 0%BW (p=0,002<0,05), 5%BW (p=0.001<0.05) şi 10%BW (p=0.008<0.05) cu valori CRP mai mici decât cele obţinute în cazul 20%BW. Cu toate acestea, nu s-au constatat diferenţe semnificative între 20%BW şi 25%BW. Deşi nu s-au găsit diferenţe semnificative între variabilele PA, acestea au scăzut simultan cu creşterea greutăţii rucsacului, în special la nivelul corpului şi gleznei. În ansamblu, coordonarea mişcării elevilor a fost parţial influenţată de greutatea crescândă a rucsacului, pe măsură ce copiii şi-au înclinat semnificativ corpul pentru a nu fi tras înapoi, în timp ce alte părţi ale corpului nu au fost afectate.

CUVINTE CHEIE: încărcarea rucsacului, faza relativă continuă, unghiul de fază, coordonarea mişcării

L'EFFET DU POIDS DU SAC À DOS SUR LA COORDINATION DU MOUVEMENT DES ÉCOLIERS

RÉSUMÉ. Le but de cette étude était d'explorer l'influence du poids du sac à dos sur la coordination des mouvements chez les enfants en bonne santé âgés de 7 à 12 ans. On a recruté 100 étudiants en bonne santé avec un IMC normal, sans déformations ni lésions des pieds sans marcher anormalement. Le système Coda Motion a été utilisé pour enregistrer l'angle de marche à 0%, 5%, 10%, 15%, 20% et 25% du poids corporel de manière aléatoire. Les angles de vecteur ont d'abord été calculés entre les angles de la tête, du corps, du genou et de la cheville, puis l'angle de phase (PA) et la phase relative continue (CRP), y compris leurs écarts-types (SD), ont été calculés. Les différences entre les six conditions de poids ont été évaluées par analyse univariée et détermination de la covariance avec un niveau de signification de 0,05 et un intervalle de confiance de 95%. Nos résultats montrent qu'une charge de CRP significative dans la tête et le corps a été observée (p=0,005<0,01), où on a enregistré 0% de poids corporel (p=0,002<0,05), 5% de poids corporel (p=0,001<0,05) et 10% de poids corporel (p=0,008<0,05) avec des valeurs de CRP inférieures à celles obtenues pour 20% de poids corporel. Cependant, il n'y avait pas de différence significative entre 20% de poids corporel et 25% de poids corporel. Bien qu'il n'y ait pas eu de différences significatives entre les variables PA, elles ont diminué simultanément avec l'augmentation du poids du sac à dos, en particulier du corps et de la cheville. Dans l'ensemble, la coordination du mouvement des élèves a été en partie influencée par l'augmentation du poids du sac à dos, car les enfants se penchaient de manière significative pour éviter d'être tirés vers l'arrière, alors que d'autres parties du corps n'étaient pas affectées.

MOTS CLÉS : poids du sac à dos, phase relative continue, angle de phase, coordination du mouvement

* *Correspondence to: Wuyong CHEN, National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, 610065, China, tel.: 86-28-85405237; fax: 86-28-85405237, email address: wuyong.chen@163.com*

INTRODUCTION

Backpack load is an important issue for the health of primary students. Trevelyan and Legg stated overloading of backpacks may cause several problems [1], like pain in the spine, shoulders, and back, etc. Consequently, problems with loading will directly or indirectly affect the growth and development of students. Singh *et al*. assessed 17 pupils walking on a treadmill under different weights of backpacks and suggested that with an increasing weight of the backpack [2], the body gradually leaned forward, and an increase of weight would lead to a change in body posture. Pau *et al*. reported that with an increasing of weight of the backpack [3], the longitudinal track of the center of pressure (COP) became longer and moved forward, and the lateral displacement of the COP became smaller. These increased discomfort and structural damage to the feet. Thus, the load has been demonstrated to change the posture of walking; but how it affects coordination has unfortunately seldom been studied.

Clark and Phillips stated walking continues to develop as the higher cortical and subcortical centers mature and gain control of the spinal level CPGs [4]. The task of walking is more difficult considering that such coordination is composed both within one leg and also between both legs. They also found that toddlers must not only be able to coordinate their two legs in order to attain upright stability and forward mobility, but also develop coordination between the joints of the knee and ankle for each individual leg [5]. Hence, by quantifying intra-limb coordination in walking, we could study the maturation of the neuro-musculo-skeletal system. Clark and Truly first quantified the motion of lower limbs and introduced a variable relative phase representing how these two (thigh and shank) limit cycle attractors are coupled [6]. After Clark, Miller *et al*. normalized the angle and velocity into timeless parameters and suggested that the continuous relative phase (CRP) was more suitable to quantify the coordination of motion [7]. Chiu *et al*. contrasted differences of coordination between young and elderly adults in walking at various speeds [8], and Continuous Relative Phase was used to study the joint coordination. Ryan Chang used Continuous Relative Phase for quantitative analysis of the coordination between the back foot and the front foot while walking [9].

Therefore, the aim of this research is to explore the influence of the load of a backpack on the coordination of motion of healthy children aged 7 to 12. Since the load would affect the gait in the stance phase, one hypothesis was proposed that with an increasing load, coordination in the stance phase would be influenced.

EXPERIMENTAL

Methods

Subjects

In total, 100 healthy schoolchildren, ages 7 to 12, were recruited in this study. The mean age of subjects is 9.6±1.4 years, the mean weight is 28.4 ±6.0 Kg and the mean height is 134.5±8.8 cm. Criteria for inclusion are shown below: (1) a body mass index (BMI) consistent with the BMI standard for normal Chinese children according to Force's study; (2) no foot deformities or injuries; (3) no abnormal gait patterns, such as a crouching gait or equinus. All the measures were done after the details of this study were introduced to children's parents and their formal approvals were obtained. Moreover, all the measurements and procedures were in accordance with principles of Helsinki Declaration.

Motion Capture of Children's Lower Limbs

The Coda Motion System (Coda Motion CX1, Charnwood Dynamics Ltd., United Kingdom) was used in this study to obtain the temporal-spatial parameters of children's lower limbs in normal walking. All the key points of subjects including the ear, shoulder, trochanter, knee, lateral malleolus and the fifth toe, which were marked in turn (Figure 1). The vector angle (θ) and velocity (ω) of ∠D1DE, ∠O1OD, ∠OAB, ∠ABC in the sagittal plane were calculated. ∠D1DE describes the motion of the head; ∠O1OD describes the relative motion of the body; ∠OAB and ∠ABC indicate the posture of knee and ankle. Test instrument area was shown in Figure 2.

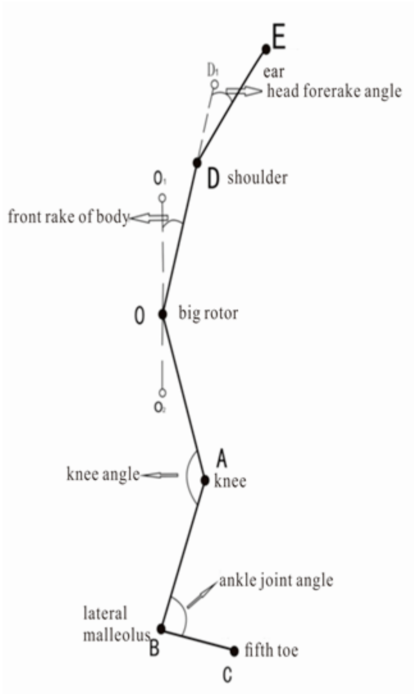

Figure 1. Graph of Key Points of Codamotion

All subjects were asked to change into tight clothing when they arrived; and then markers were set by a researcher. A three to five minute warm-up was provided for their familiarization. Afterwards, subjects walked at their own selected speed on the 6 meters track while the data recording was on (Figure 3a). All subjects were guided walking with backpack loads of 0%, 5%, 10%, 15% and 25% of their body weight (BW) randomly. Three successful measures for CODA test were required. The backpack used in the study was provided by Guangzhou Nuohu Company (Figure 3b).

Data Processing

Mathematical models of a continuous relative phase (CRP) were utilized (EQ 1-4) for coordination analysis. The calculation procedure is shown below: θ (Degrees) and ω (arc/s) were first normalized into and (EQ 1 and EQ 2); and then the point phase angle (PA) was determined according to EQ 3; finally, the CRP (degrees) of body-knee and knee-ankle was resolved (EQ 4). In-phase indications were within the range of 0 to 30 degrees; while those of anti-phase were 150 to 180 degrees; other angles were classified as out-phase.

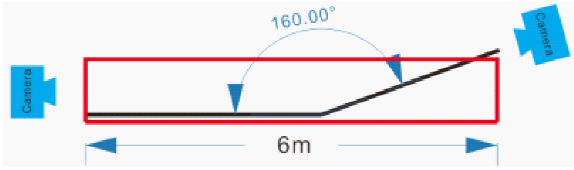

Figure 2. Graph of test instrument area

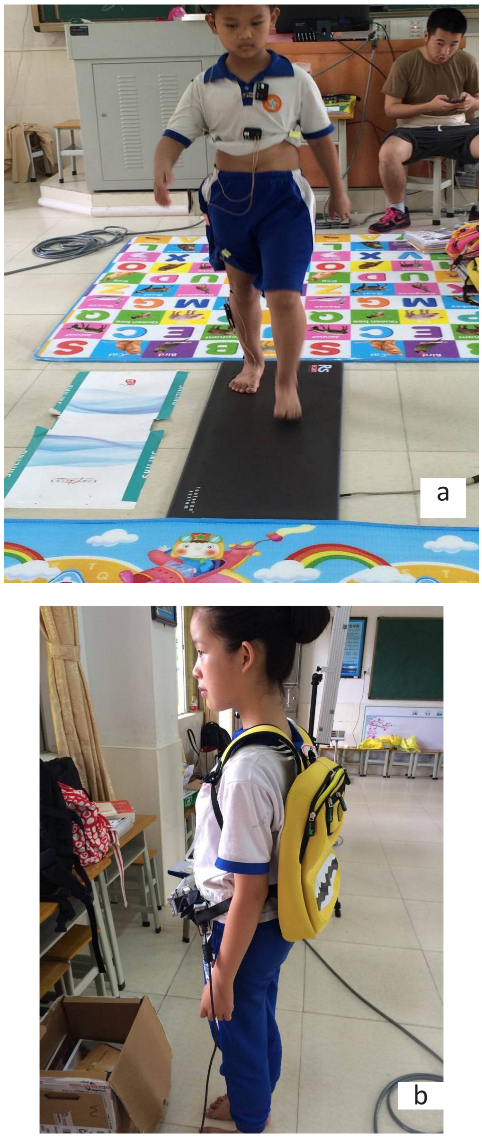

Figure 3. The backpack used in the study

$$\bar{\theta} = 2\left[\frac{\theta - min(\theta)}{max(\theta) - min(\theta)}\right] - 1 \qquad \text{(EQ 1)}$$

$$\bar{\omega} = \left[\frac{\omega}{\max(|\omega|)}\right] \qquad \text{(EQ 2)}$$

$$\varphi\,(i) = tan^{-1}\left[\frac{\bar{\omega}\,(i)}{\bar{\theta}\,(i)}\right], \quad i = 1,2,\dots,n \qquad \text{(EQ 3)}$$

$$\theta_{CRP}(i) = |\varphi_1(i) - \varphi_2(i)| \qquad \text{(EQ 4)}$$

Statistical Analysis

All the time series data was first filtered by a 6Hz cut off to reduce the influence of other factors on experimental results and then the time period of a complete gait cycle was selected; further a quintic spline procedure was used to create a 100-point time-normalized gait cycle (GC). Intra-subject data was first averaged and then inter-subject data. One sample K-S model was used to test for a normal distribution and all data was found to be following a normal distribution. Variables of PA and CRP were chosen for further analysis, so the relationship between the angle (θ) and its velocity (ω) was first determined; then their consistencies were quantified in terms of standard deviations (SD). Distinctions within six load condition were evaluated by univariance with covariance of body weight. All the statistical models were executed under SPSS 16 with a significance level of 0.05 and a confidence interval of 95%.

RESULTS

The Relationship between the Angle of Joints and Velocity

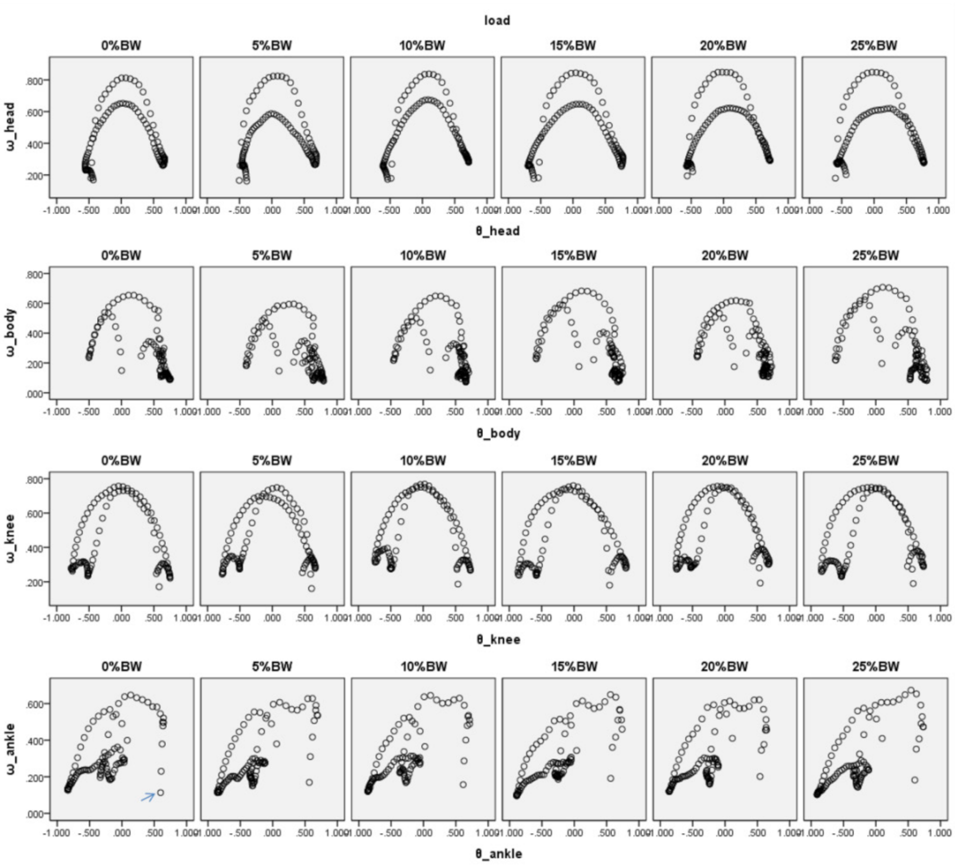

Figure 4. The relationship between the angle and velocity of the head, body, knees and ankles in the six load conditions

From Figure 4, relationships between the angle of joints and velocity were determined as the load increased. Similar track patterns were found from the load of 0%BW to 25%BW; while their standard deviations in terms of θ and ω in the head, body, knees and ankles were close - within the six load conditions. (SD ranged 0.29-0.36 degrees for θ-ankle, 0.47-0.54 degrees for θ-body, 0.46-0.51 degrees for θ-head, 0.35-0.43 degrees for θ-knee; SD ranged 0.18-0.20 arc/s for ω-ankle, 0.22-0.25 arc/s for ω-body, 0.23-0.24 arc/s for ω-head, 0.22-0.25 arc/s for ω-knee).

Phase Angle Across the Walking Cycle

In terms of the PA of the head, it is located in the neutral position in the initial contact with the ground. Further, the PA of the head increased while the body pivoted with the heel. Then it became stable during the stance phase. After that, it moved backwards as the body again led the head in the swing phase. As the load increased, there were no significant differences were found in the PA of the head. Its SD was distributed in a narrow range of 39.2-40.2 degrees (Figure 5). The PA of the body remained stable between gait cycles of 31-99%; it fluctuated during heel contact and flattening of the foot. The SD of the PA of the body was between 24.3 and 26.2 degrees, in which 0%BW was 26.3 degrees and 25%BW was 24.3 degrees. A similar tendency was also recorded in the ankle: with the load increasing, the PA in the whole stance phase became stable, while its SD decreased as well (32.0 degrees for 25%BW, 35.8 degrees for 0%BW). In the lower limbs, as the knee quickly extended after heel contact, the PA of the knee decreased dramatically around 10%GC. Then it kept stable for the whole stance phase. In the toe lift, it again fluctuated and its PA increased significantly.

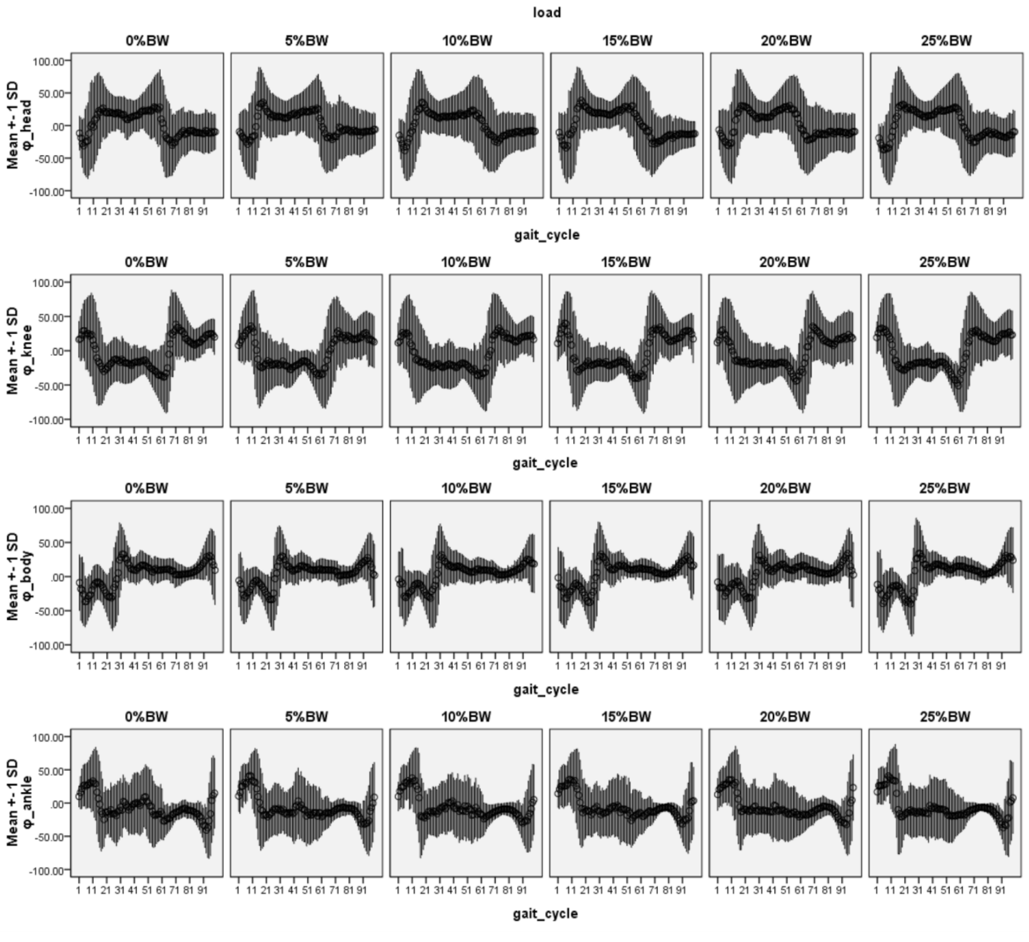

Figure 5. Phase angles of the head, body, knees and ankles in the six load conditions

Relative Phase Angles between Two Joints

In the 0%BW condition, the CRP of the head-body was about 30 degrees in the initial contact, and increased to around 80 degrees when the heel contact finished (Figure 6); then it gradually fell until 35%GC and then raised back and peaked at the toe lift. In the swing phase, it fluctuated between the 30 and 60 degrees. Significant effects of load on the CRP of head and body were found (p=0.005<0.01), where 0%BW (p=0.002<0.05), 5%BW (p=0.001<0.05) and 10%BW (p=0.008<0.05) were recorded with a smaller CRP value than that of 20%BW.

There were vibrations during the entire gait cycle, but it remained stable with a slightly increasing tendency while supporting the body weight (21-51% gait cycle). The tendency of

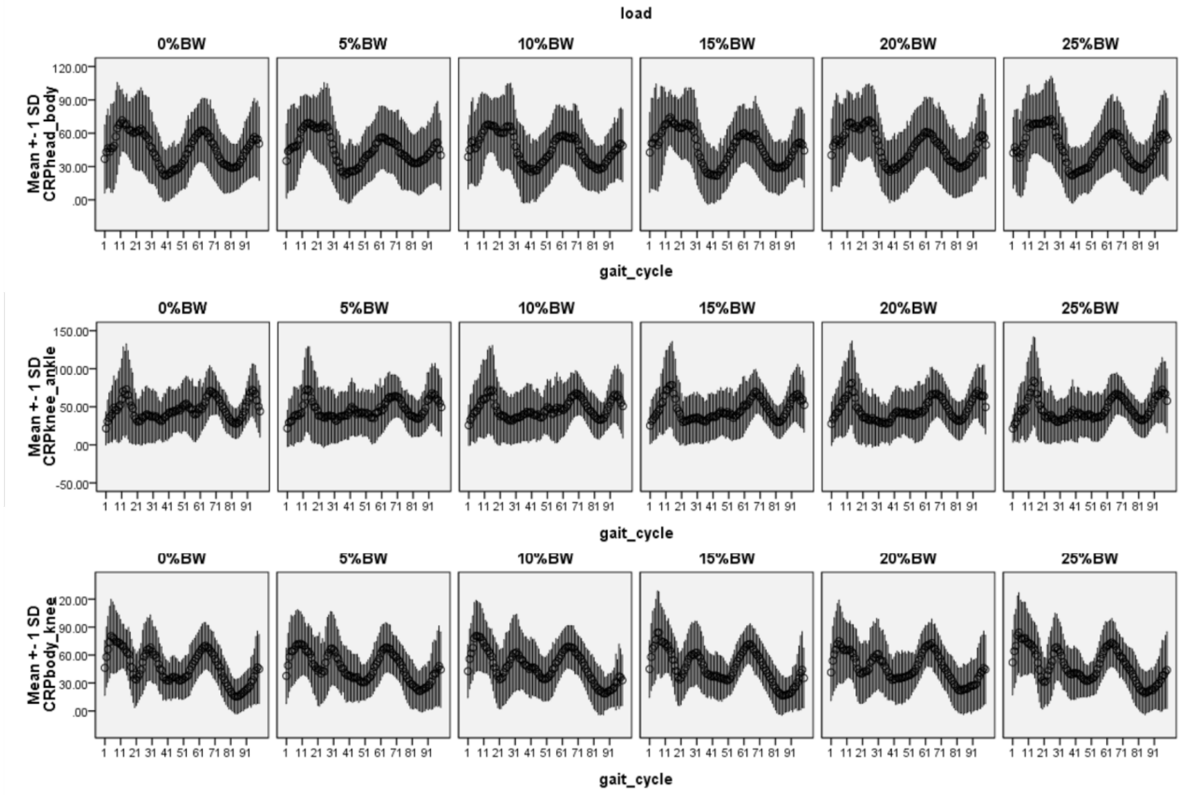

Figure 6. The relative phase angle of head-body, body-knee and knee-ankle while walking

increase was attenuated as the load increased, experiencing three peak values while walking. However, significant influences were not found for the CRP of body-knee (p=0.069>0.05) and knee-ankle (p=0.727>0.05).

DISCUSSION

The backpacks covered an area from the neck to the sacrum and directly affected the center of body (COB). When the backpack was loaded, the COB shifted backward. Hence, backwards moments were generated and changed the posture of the upper body. In order to overcome this deficit, a forward tilt of the body and head was usually observed. Hong *et al*. showed that an increasing backpack load increased the front rake angle of body significantly, especially the comparison between 15-20%BW and 0-10%BW [10]. The load changed the posture of the body and affected motion and balance. Meanwhile, Pascoe *et al*. indicated there was a significant difference in forerake angle of body when comparing the 17%BW backpack loading with 0%BW [11].

Our outcomes were consistent with the above literature; significant effect loading on the CRP of head and body was found (p=0.005<0.01), where, 0%BW (p=0.002<0.05), 5%BW (p=0.001<0.05) and 10%BW (p=0.008<0.05) were recorded with smaller CRP values than those of 20%BW. This higher CRP indicated a large relative motion between the two joints. So with the additional load, the body tilt increased. However, no significant distinctions were found between 20%BW and 25%BW; we assumed that young schoolchildren aged between 7 and 12 can quickly adapt to a gait with an increased backpack load.

In terms of PA, although significant differences were not found for all PA variables, their SD showed that with the weight of backpack increasing, the SD decreased simultaneously, particularly in the body and ankle. This phenomenon implied the load diminished the vibration while walking and made the gait more stable to some extent. This could also be observed by the greater influence of the body and ankle in the stance and swing phase.

In this study, limitations existed and they need to be declared before understanding our findings: (1) children chose their preferred walking speed during measurement; although the walking speed affected the amplitude of motion, in this study, normalization was made to diminish the influence of speed; (2) markers were set on tight clothing rather than skin, which would cause movement of the marker while walking; in order to overcome these defects, a 6Hz cut off strategy was applied in the period of data processing.

CONCLUSION

Coordination in motion of schoolchildren was partially influenced by an increasing load of the backpack, as significant body tilt was performed by the children to overcome the backwards drag, while other body parts were not affected.

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EFFECT OF CRUSTING OPERATIONS ON THE PHYSICAL PROPERTIES OF LEATHER

Kallen Mulilo NALYANYA[1], Ronald K. ROP[1], Arthur ONYUKA[2], Zephania BIRECH[3], Alvin SASIA[2]

[1]Department of Physics, Faculty of Science, Egerton University, Nakuru, Kenya, kallenmulilo@ymail.com

[2]Kenya Industrial Research and Development Institute, Nairobi, Kenya

[3]Department of Physics, School of Biological and Physical Sciences, University of Nairobi, Kenya

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EFFECT OF CRUSTING OPERATIONS ON THE MECHANICAL PROPERTIES OF LEATHER

ABSTRACT. Physical properties of leather form vital quality parameters that determine the performance characteristics in their areas of applications. However, the transformational processing of hide to leather involves a series of both chemical and physical/mechanical changes that affect these mechanical properties. Many researches have been published regarding the effect of processing on the mechanical properties of leather. However, the effect of entire crusting operations (post tanning) on the mechanical properties is not documented. This study reports the findings of the effect of crusting operations (retanning, dyeing and fatliquoring) on the mechanical properties of the final leather. Results have shown that retanning process improves tear and tensile strengths, distensions at crack and burst, and shrinkage temperature. An improvement in the organoleptic properties such as fullness was recorded in retanned crust leather. However, the uniformity coefficient and percentage elongation significantly decreased after retanning. Dyeing raises the elongation at break, distensions at crack and burst, shrinkage temperature and uniformity coefficient whereas both tensile and tear strengths decreased after dyeing. Similarly, fatliquored samples recorded higher elongation at break values, and distension values. Conversely, tensile and tear strengths, shrinkage temperature and uniformity coefficient decreased as a result of fatliquoring process. All the samples tested at tanning, retanning, dyeing and fatliquoring processes indicated no damage at 50,000 flexes. The study discussed these effects using transmission of fracture and damage mechanics in leather, structural implication of the resulting leather and existing models of materials.

KEYWORDS: physical properties, crusting operations, leather anisotropy and uniformity, fracture and damage mechanics, micromechanical deformation, stress concentration

EFECTUL OPERAȚIUNILOR DE FINISARE UMEDĂ ASUPRA PROPRIETĂȚILOR MECANICE ALE PIELII

REZUMAT. Proprietățile fizice ale pielii constituie parametri de calitate importanți care determină caracteristicile de performanță ale pielii în domeniile în care vor fi utilizate. Cu toate acestea, transformarea pieii crude în piele finită implică o serie de modificări chimice şi fizico-mecanice care afectează proprietățile mecanice ale pielii. Au fost publicate multe cercetări privind efectul prelucrării asupra proprietăților mecanice ale pielii. Cu toate acestea, efectul ansamblului de operațiuni de finisare umedă (post-tăbăcire) asupra rezistenței mecanice nu este documentat. Acest studiu prezintă constatările privind efectul operațiunilor de finisare umedă (retăbăcire, vopsire şi ungere) asupra proprietăților mecanice ale pieii finite. Rezultatele au arătat că procesul de retăbăcire îmbunătăţeşte rezistența la rupere şi la sfâșiere, alungirea la crăpare şi rupere şi temperatura de contracție. S-a înregistrat o îmbunătăţire a proprietăților organoleptice, cum ar fi plinătatea, la pielea retăbăcită şi finisată umed. Cu toate acestea, coeficientul de uniformitate şi alungirea procentuală au scăzut semnificativ după retăbăcire. Vopsirea crește alungirea la rupere, alungirea la crăpare şi rupere, temperatura de contracție şi coeficientul de uniformitate, în timp ce rezistența la rupere şi la sfâșiere scad după vopsire. În mod similar, eșantioanele unse au înregistrat valori mai mari ale alungirii la rupere şi ale alungirii la crăpare şi rupere. Dimpotrivă, rezistența la rupere şi la sfâșiere, temperatura de contracție şi coeficientul de uniformitate au scăzut ca rezultat al procesului de ungere. Nicio probă testată după tăbăcire, retăbăcire, vopsire şi ungere nu a prezentat deteriorare la 50.000 de flexiuni. Studiul a prezentat aceste efecte prin propagarea fracturii şi deteriorările mecanice ale pielii, proprietățile structurale ale pielii rezultate şi modelele de materiale existente.

CUVINTE CHEIE: proprietăți fizice, operațiuni de finisare umedă, anizotropia şi uniformitatea pielii, fracturi şi deteriorări mecanice, deformare micromecanică, concentrație de stres

L'EFFET DES OPÉRATIONS DE FINITION HUMIDE SUR LES PROPRIÉTÉS MÉCANIQUES DU CUIR

RÉSUMÉ. Les propriétés physiques du cuir forment des paramètres de qualité vitaux qui déterminent les caractéristiques de performance dans leurs domaines d'application. Cependant, le traitement de la peau en cuir implique une série de modifications tant chimiques que physiques/mécaniques qui affectent les propriétés mécaniques du cuir. De nombreuses recherches ont été publiées concernant l'effet du traitement sur les propriétés mécaniques du cuir. Cependant, l'effet de l'ensemble des opérations de finition humide (après tannage) sur la résistance mécanique n'est pas documenté. Cette étude présente les résultats de l'effet des opérations de finition humide (retannage, teinture et nourriture) sur les propriétés mécaniques du cuir final. Les résultats ont montré que le processus de retannage améliore les résistances à la déchirure et à la traction, l'extension à la gerçure et à l'éclatement, la température de rétraction. Une amélioration des propriétés organoleptiques telles que la plénitude a été enregistrée dans le cuir retanné et fini humide. Cependant, le coefficient d'uniformité et le pourcentage d'allongement ont significativement diminué après retannage. La teinture augmente l'allongement à la rupture, l'extension à la gerçure et à l'éclatement, la température de rétraction et le coefficient d'uniformité, tandis que les résistances à la traction et à la déchirure diminuent après la teinture. De manière similaire, les échantillons nourris ont enregistré des valeurs plus élevées d'allongement à la rupture et d'extension. Inversement, les résistances à la traction et à la déchirure, la température de rétraction et le coefficient d'uniformité ont diminué à la suite du processus de nourriture. Aucun des échantillons testés lors des processus de tannage, de retannage, de teinture et de nourriture n'indiquent aucun dommage après 50 000 flexions. L'étude a examiné ces effets en utilisant la transmission de la rupture et les dommages mécaniques dans le cuir, les propriétés structurelles du cuir résultant et les modèles de matériaux existants.

MOTS CLÉS : propriétés physiques, opérations de finition humide, anisotropie et uniformité du cuir, rupture et dommages mécaniques, déformation micromécanique, concentration de stress

** Correspondence to: Kallen Mulilo NALYANYA, Department of Physics, Faculty of Science, Egerton University, Nakuru, Kenya, P.O. Box 536, Egerton-20115, Phone: +254712627620, Fax: 254 51 22178257, email: kallenmulilo@ymail.com*

INTRODUCTION

Leather is an important intermediate industrial product in the down-stream sectors of the consumer products industry [1]. The conventional applications include footwear, clothing, upholstery, and furniture [2, 3]. Physical properties in this case play an important role of determining the specific field of applications since they determine the required performance characteristics [1, 4, 5]. However, the transformational journey of bovine hide to leather involves a sequence of chemical and mechanical operations that greatly alter these properties [6]. The operations can be categorized into beam house (pretanning), tanning, post-tanning (crusting or wet-finishing) and dry-finishing operations [7]. Beam house operations prepares the hide for tanning by removing the hairs, flesh and fats that accelerate the degradation and opening up the pelt structure for tanning agents [8]. Among the leather making operations, tanning is the most outstanding operations that entirely transforms hides' putrescible proteins into physically and chemically stable collagen, known as leather [9]. Crusting operations involve retanning, dyeing and fatliquoring processes [4, 7].

A number of studies have investigated the effect of pretanning and tanning operations on the physical properties of leather [9-12]. Publications on the effect of retanning, fatliquoring and dry-finishing operations on the chemical and organoleptic properties of leathers are available [13-18]. Theoretically, retanning process imparts fullness into the leather. This involves the structural crosslinking within and among the collagens in the leather which consequently increases the mechanical stability [9]. Dyeing process gives the leather the base of the desired color. The dyes components interact with collagens in leather chemically and physically by electrostatic attraction. Therefore the interaction is expected to modify the structural and hence the mechanical integrity of the final leather. By the time of tanning, the pelt does not contain sufficient lubricants to prevent it from drying into a hard/stiff material [19]. For this reason, after tanning, proper lubrication is needful [20]. Lubrication is done through the incorporation of oils and fats into leather matrix in finely dispersed form in a water medium (emulsion) in the process referred to as fatliquoring. The oils and fats safeguard the leather against cracking or sticking together of its collagen fibres and becoming hard and stiff during drying [21]. This step results to hydrophobic leather [22]. Although fatliquoring is known to impart softness and a certain degree of water repellency, little is known about its effect on the structural and physical properties of leather. Since there are many polar functional groups in collagen such as –OH, -COOH, $-NH_2$ and –CONH-, then the processes of crusting operations that involve hydrophilic chemical compounds will be absorbed and affect structural bonds of the leather matrix [22]. Any effect on the structural or molecular bond impacts the structural and hence the physical properties [23]. Hence in this study, the effect of retanning, dyeing and fatliquoring processes on the physical properties have been investigated using tensile tester (Instron 1011). The physical properties investigated includes tensile strength, tear strength, elongation at break, flexing endurance, ball burst distension, shrinkage temperature and uniformity coefficient.

EXPERIMENTAL

Materials

Fresh cowhide, procured from the slaughterhouse, was processed to chrome tanning stage using conventional procedure as described in [12]. The wet blue leather was fixed using formic acid and cut into two identical pieces along the backline as shown in Figure 1.

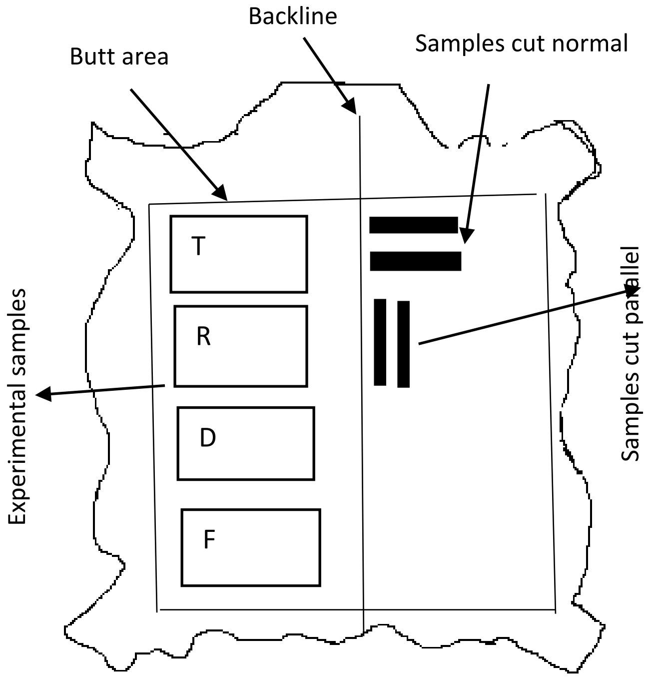

Figure 1. Representation of sample preparation and sample location

One quarter of one piece was cut out within the butt area and coded tanned sample (T). The remaining three quarters proceeded to retanning stage using chromium sulphate in a drum. Before this stage, the wet blue was wetted in water, basified using sodium bicarbonate and then neutralized using ammonium bicarbonate. 1% of antimould and 2% of the sodium formate were also added during neutralization stage to prevent fungal growth and as a complexing agent to further improve chrome exhaustion after chrome tanning, respectively. Retannage was carried out using 150% water at 45°C and 6% retanning agent (chromium sulphate-Cromogenia Retanal BD Polvo) in a drum running moderately slow for 45 minutes. After penetration check, 1.5% formic was added to fix the crust. The crust was then drained, washed and toggled overnight prior to dyeing. A third of the crust was cut out within the butt area as retanned sample (R). To prepare the crust for dyeing, the remaining piece was basified using ammonium bicarbonate to adjust the pH to 6.5. Dyeing involved 100% water at 50°C and 2% of acidic HLC Novolene HC black dye, added through the axle as the drum runs. The crust was then fixed using formic acid before it was drained, washed and toggled overnight. Half of the crust was cut out within the butt area as dyed sample (D). The remaining crust was fatliquored using sulphited vegetable cromogenia Fosfol 51 oils. Water (100% at 50°C) and 2% fat liquor was run in a drum for 45 minutes. After fixing, the fatliquored crust was drained, washed in 200% water, and toggled overnight. The crust was cut out and sample labeled as fatliquored (F).

Sampling, Sampling Location and Sample Conditioning

The specimens for mechanical tests were kept in a standard atmosphere of temperature 25±2°C and relative humidity of 65%±2% for at least 48 hours according to ISO 2419: 2012. Sampling was done in accordance with the standard ISO 2418 (2005). In this procedure, the samples were cut within the “official sampling position (OSP)” within which, the variation in strength properties and anisotropy are gradual and minimal [1]. Cutting samples from the same hide also helped to minimize the variations of strength properties that arise due to differences in animal age, sex and breed [16]. For tensile strength, tear strength, percentage elongation and flexing endurance, eight (8) samples were cut; 4 sampled parallel while 4 sampled perpendicular to the backline.

Methods

Determination of Tensile Strength and Elongation at Break

Tensile strength (also known as ultimate tensile strength) is the capacity of a material or structure to withstand loads tending to elongate it. Tensile strength determines the maximum tensile stress/tension that the leather can sustain without fracture [24]. Quantitatively, this can be expressed as the force required to rupture a material specimen of unit cross sectional area. In leather, this strength is thus the combined breaking strength of all the fibers which are taking part to fight against the applied load. For most leather end uses or applications, this strength must be adequate; the acceptable minimum tensile strength for chrome tanned is 20 Nmm^{-2} (MPa) [24, 25].

Elongation refers to the ability of a material to lengthen/stretch when stress is applied to it and represents the maximum extent the material can stretch without breaking. In leather, this is an important quality parameter to be considered, especially when choosing garment leathers, because a low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even lose usability [4]. Good quality leathers should have a percentage elongation of at least 40% [24-26].

For tensile strength and elongation, eight dumbbell-shaped (dog-bone shaped) test pieces (four from each principal direction) were cut from the crusts using special steel press knife in template according to ISO 3376: 2002 as described in [8]. The thickness of each specimen and mean thickness was measured in accordance to ISO 2589. These tests were carried out using tensile tester (Instron machine 1011) according to ISO 3376:2012 at a cross-head speed of 100 mm/min at room temperature.

Determination of Baumann Tear Strength/ Slit Tear Resistance

Tear strength (also known as tear resistance) is a measure of how well a material can withstand the effects of tearing. It specifically measures a material's resistance to the growth of any cuts when under tension, measured in N/mm [9]. In the leather fracture behavior, deformation and crack growth, this strength measures the resistance to the formation of a tear (tear initiation) and its corresponding expansion or growth (tear propagation within the structure). The least recommended tear strength for chrome-tanned shoe upper side leathers is 40 N/mm [24-26]. In this test, the specimens were cut and tested in accordance to ISO 3377:2002.

Measurement of Shrinkage Temperature

Shrinkage temperature gives the temperature at which the leather starts to shrink in water or over a heating media [15]. This property is used to characterize the thermal stability of leather. It provides information about the degree of tanning, because the better the crosslinking reactions between the collagen fibres and the tannins, the higher the shrinkage temperature [27]. Good quality leather should have a minimum shrinkage temperature of 75°C [24]. In this study, the shrinkage temperature was measured using SATRA STD 114 test apparatus according to the official method (ISO 3380:2002) at a heating rate of 2°C/min.

Measurement of Distension of Grain by the Ball Burst Test

This is a property for testing quality of leathers intended to indicate the grain resistance to cracking during top lasting of the shoe uppers. The threshold recommended values for grain crack and grain burst for upper leathers is 6.5 mm and 7.0 mm, respectively [26]. In this study, the ball burst test was measured using a Lastometer according to the official method (ISO 3379:1976).

Flexing Endurance

Bally flex or flexing endurance is an indication of the finishing resistance to crack and crease when repeatedly flexed, emulating the flexing of the actual use of the shoe. It's a very good indication of the ability of leather grain to withstand lasting operation during shoe making without cracks. Flexing endurance of the prepared leather crust was measured using SATRA STM 701 Bally flexometer according to the official method (ISO 5402:2002). The leather samples were subjected to pre-determined 100,500, 1,000, 5,000, 10,000, 20,000, 50,000 flexes/cycles and it was observed periodically for any signs of crack on the grain surface of the leather. Results were defined by observing tendency of cracking with the help of an illuminated lens (10 x magnifications).

Statistical Analysis of Data

Results were evaluated statistically by using One-Way ANOVA, descriptive statistical and represented as mean for four independent measurements. Comparison of means was analyzed and differences were considered as significant when $p<0.05$. Every value reported here is an average of four samples.

RESULTS AND DISCUSSION

The mean values of tensile strength, tear strength, percentage elongation and distension at crack and burst are reported in Table 1.

Table 1: Physical properties of tanned, retanned, dyed and fatliquored leather

Physical Properties	Direction	Tanned	Retanned	Dyed	Fatliquored
Tensile Strength (N/mm^2)	Normal	20.05±0.21	22.34±2.01	19.7±1.79	18.16 +1.80
	Parallel	21.28±1.03	24.15±2.08	22.28 ±2.40	19.04 + 1.67
Tear Strength (N/mm)	Normal	88.20±5.73	106.14±7.31	75.04±19.49	86.87±9.69
	Parallel	74.60±3.08	98.18±5.39	70.10±13.88	84.51±13.87
Elongation (%)	Normal	60.38±4.06	50.67±3.43	56.92±6.95	69.25±6.83
	Parallel	52.75±6.53	45.5±2.88	47.17±3.62	67.58±2.23
Ball Burst Distension (mm)	Crack	8.26±0.42	13.09±0.22	13.77±0.96	17.66±0.06
	Burst	9.19±0.67	16.4±0.23	16.38±0.48	17.77±0.03
Flexing Endurance	Normal	No damage @ 50,000 flexes	No damage @ 50,000 flexes	No damage @ 50,000 flexes	No damage @ 50,000 flexes
	Parallel	No damage @ 50,000 flexes	No damage @ 50,000 flexes	No damage @ 50,000 flexes	No damage @ 50,000 flexes
Shrinkage temperature (℃ °C)		108	115	118	115
Uniformity coefficient (K_{unif})		1.1446	1.1136	1.206699	1.024

Anisotropic Effect on Physical Properties of Leather

Tensile strength values for samples cut in parallel to the backline were higher than for perpendicular samples. Structurally, for the samples cut along backline, majority of their fibres are already aligned in the same direction as the applied strain, hence they have little scope to orientate towards the strain axis [9]. This therefore means that the fibres themselves are directly strained at low levels of nominal strain and the process of fibre orientation is limited. For samples cut perpendicularly, many fibres are aligned normal to the direction of the applied strain, therefore, the fibres orientate towards the strain axis. This orientation minimizes levels of nominal strain and deformation occurs by straining themselves. Further deformation is associated with straining of the fibres themselves. Since tensile strength is proportional to the number of fibres aligned in that direction, its value is higher in the parallel orientation because the strain is being applied to a more orientated network of fibres than the case for perpendicular sampling. Fibre orientation will cause frictional damage to the fibres, and therefore increases the tensile strength. In perpendicular sampling, more fibre orientation thereby increasing the possibility of fibre damage and reducing tensile strength.

Tear strength and percentage elongation values for specimens sampled along the backline were less than the value for specimen sampled perpendicular to the backline. When specimens are oriented parallel to the backbone, the general fibre direction is assumed to be in the same direction as the strain axis. Under these conditions, the specific work of fracture is higher because the tear does not propagate through fibre diameters. Instead, the fibres bridge the advancing tear and are subject to more of a straightforward rupturing process. In addition, when specimens are oriented in a direction perpendicular to the backline, the general fibre direction is assumed to be nearer 900 to the strain axis. Therefore, the specific work of fracture is lower because the tear is able to propagate directly through the felt work of fibres and tear strength is higher. In addition to the above explanation, when the samples for tear analysis are taken in parallel, the direction of tearing is in perpendicular and vice versa [9]. This explains the higher tear strength and elongation for samples cut in perpendicular, a negative trend, compared to tensile strength.

Effect of Retanning on the Physical Properties of Leather

Retanned samples were observed to be structurally more compact and full and its grain surface was mechanically tighter compared to others. Retanning slightly increased tensile strength, tear strength, distension at crack and burst and shrinkage temperature. On the other hand, percentage elongation decreased after retanning. For all the tanned and retanned specimens tested for flexural endurance, there was no observable damage at 50,000 flexes. Results from this study show that leathers at both tanned and retanned stages of processing are appropriate for most of the leather applications. The margins of the results and patterns reported in this study are comparable to other related publications [28-32]. An increase in flexural endurance after retanning has also been observed by [33]. References [34, 35] reported an increase in tensile strength and shrinkage temperature after retanning process. Retanning using chromium salts imparts extra crosslinks into the crust. These alkali salts form hydrogen bonds with hydroxyl components from the carboxyl units present in the aspartic and glutamic acids from the collagen of the crust [36]. Kinetic theory predicts increase in strength as the degree of crosslinking increases [37-39]. This explains the increase in tensile strength, tear strength, shrinkage temperature, and distension properties. Extra crosslinks reduces fibrillar (molecular) mobility and increased rigidness of the leather matrix between fibrils and within fibre bundles which impose mechanical restraints. These additional crosslinks act as rigid particulate fillers to a leather polymer matrix which decreases the elongation at break. Similarly, tanning induces bonding between the basic fibres. Mechanically, the bonds formed inhibit the realignment and straightening process of the fibres which slightly weakens the extensibility of the retanned leather.

Effect of Dyeing on Mechanical Properties of Leather

The chemical nature and intrinsic poly-functionality of dyes allows the formation of chemical bonds, van der Waals interactions and additional hydrogen bonds. Although these functionalities were expected to improve the physical properties, dyeing process was observed to decrease both tensile and tear strengths while it increased elongation, shrinkage temperature and distensions at grain crack and burst. The bonds or links formed are weaker [40]. Decrease in shrinkage temperature after dyeing has been reported by [30]. The authors attributed the decrease in tensile strength and tear strength to poor adhesion between the dye and leather matrix. In our present study, the claims can be refuted because the dye bath was slightly acidic, facilitating the swelling of the leather substrate especially in the presence of water. Similarly, the temperatures of the dyeing processes were slightly higher than room temperature hence there is an increased mobility of the molecule segments in the polymer [40]. The two factors work together to improve the dispersion and distribution of dye molecules in the leather substrate and suitable adhesion between the substrate and molecules. On the other hand, the very penetration of the dye particles into leather matrix decreases the energy of the intermolecular interaction and therefore destroys a significant portion of the already stable intermolecular bonds. Additionally, increased segmental mobility due to the said temperatures favours the disorientation of the collagen fibres. Modeling dyed crust as the heterogeneous composite, the mechanism of micromechanical deformations and macroscopic properties depend on local stress distribution around the fillers/inclusions. Poor adherence of the filler to the crust implies that the fillers are unable to carry any load, making it weak body. This is because stress concentrations will be created around the particles, reducing the composite strength. We also hypothesized the mechanism whereby the oily nature of dyes in collagen imparts water retention ability. The polar or amphoteric nature of dyes has also been associated with level of hydration which also increases collagen's D-spacing [41]. The increased D-spacing leaves more free volume for water attachment. The water retention alters the collagen's structure at the fibrillar scale. The water attached disrupts hydrogen bonds which provide structural integrity to the molecular backbone of collagen and therefore decreases the strength properties of leather.

Effect of Fatliquoring on Organoleptic and Physical Properties of Leather

Fatliquored samples were softer, loose in structure and more pliable compared to other samples. Our observations agree with results in [41]. Reference [42] observed that penetration of fatliquors into leather increases its looseness. It was also observed in this study that fatliquoring modifies mode of break; induced both fibre rupture and pull-out (fine break). Fatliquored samples tore instead of snapping abruptly. This is fine break, which is normally dominant where collagen distribution is uniform and there are many fine wrinkles per unit length, and it usually indicates good quality leather [43]. Although it has been argued by [24] that any tannery processes that prevent the fibrils from sticking together tightly on the grain surface definitely produces fine break, the tanned, retanned and dyed samples (fatliquor-free hide) were almost brittle and snapped at break. This type of break is a result of snapping of individual fibres themselves. This deformation behavior can be explained by using fibre recruitment model by [44]. In this model, we hypothesized that fatliquoring effectively lubricates the crust weave which opens up its structure allowing its collagen fibres to align along the direction of the applied stress at low strains before the fibres themselves get elongated at high strains. Since there are different degrees of tautness of the collagen fibres in the weave, only few fibres get taut at the beginning of the strain but as the strain increases, more fibres get taut and the strength increases [45]. During break, some of the fibres pull apart while some get taut before others and break. However, in the unfatliquored (tanned, retanned and dyed) crusts, where the higher degree of fibre adhesion makes the material to have closed compact and solid structure. In such a weave, the constituent fibres do not slide but extend on their own during elongation. This means that no fibre gets taut at low strains due to fibre adhesion. At break, some fibres get taut before others and rupture making the weave to snap. For this reason, fatliquoring can be recommended since this type of break is desirable for majority of today's customers.

Fatliquored samples recorded lower tensile strength and shrinkage temperature as compared to dyed samples. The same pattern was observed by [46] and [31]. The range of our results for fatliquored samples is comparable to other studies [47-49]. The tear strength, percentage extension and distensions at crack and burst of fatliquored crust were significantly greater than those for dyed crusts (p=0.01267). This indicates that fatliquoring increases tear strength, elongation at break and distension of leather. This trend resonates with results reported by [46] and [31]. The results for elongation of fatliquored leather agree with those previously published by [20, 48, 50]. The increase in elongation was attributed to the sliding effect of the fat liquors in the fibres [46]. The trend for tensile strength and shrinkage temperature contradicted our hypothesis. It's expected that fatliquored crust permits the easy sliding of fibres against each other and aid in the stress distribution during the extension, a fact that ought to raise tensile strength and shrinkage temperature [51]. Be it as it may, the authors explained the decrease of tensile strength and shrinkage temperature and increase of tear strength, elasticity and distension, in three ways. The explanations modeled fatliquors in the collagen network as primary plasticizers, secondary plasticizers and humectants [41, 52-53]. As primary plasticizers, the synthetic sulphated oils used in this study are anionic colloids with large molecules carrying a negative charge. Usually, after chrome tanning, the wet blue crust are neutralized, making them slightly acidic and cationic in nature. This ensures that the anionic oil molecules penetrate into the gaps of collagen fibres, their polar groups being attracted to the crust fibres through the cross section; forming a lubricant film around the collagen fibres. This ionic interaction of the two polar groups neutralizes the attractive forces between crust matrixes, weakening the Van der Waals forces between adjacent polymer chains. Hence in aqueous environment, it's accurate to model fatliquors as primary plasticizers. As secondary plasticizers, the inert molecules of fatliquors disperse within the leather matrices like fillers, providing mechanical spacers that separate adjacent collagen chains hence reducing Van der Waals forces. This reduces the number of fibre adhesion in the weave [54]. Low or poor adhesion between the crust matrix and fatliquors can explain the decrease in tensile strength and shrinkage temperature while supporting the explanation for increase in extensibility and tear strength [54-55]. As humectants, findings from Synchrotron scattering experiments have shown that fatliquors enhance water-retention capacity in the collagen [41]. The high hydration level which is the reason for increased d-spacing of collagen also affects the physical properties. Therefore, the decrease in elasticity and increase in tensile strength are consequence of the increased d-spacing. In all the three explanations above, the leather structure weakens as a result of decreasing Van der Waals forces. The decrease consequently reduces the resistance of the crust to deformation [20]. Reference [56] termed the weakening as destabilizing the crust and reversing the crosslinking action of the chrome tanning. Reversing crosslinking action definitely reduces the tensile strength and shrinkage temperature [6, 9, 12]. This also explains why the fibre bundle allows the constituent fibres to straighten up and align themselves in the direction of the deforming force before the fibres actually get to be stretched and hence elongation at break, softness and pliability. Some differences can also be attributed to the difference in the sample locations although minimal since all samples were cut within the official sampling location where anisotropic variations are minimal.

Effect of Crusting Processes on Leather's Anisotropy and Uniformity

It was anticipated in this study that some features of the collagen structure can purposefully change and transform its fibrous structure during the crust processing, and this influences the deformation properties of the resulting leather. The degree of anisotropy in the leather was estimated according to relaxation and deformation properties. The uniformity coefficient Kunif of the physical properties of leather was determined as the ratio of the average values of the elongations in transverse directions to the average values in the longitudinal direction. The changes in the coefficient were employed to infer dermal microstructural changes due to the underlying crust process. The coefficients of the crusted leathers were calculated using equation 1.

$$K_{unif} = \frac{\epsilon_{normal}}{\epsilon_{parallel}} K_{unif} = \frac{\epsilon_{normal}}{\epsilon_{parallel}} \quad (1)$$

It found out that retanning decreases the coefficient by 2.7%. This implies that retanning disrupts the hierarchy of collagen hence disrupting the uniformity. Dyeing increased the coefficient by 8.36% which means that dyeing stabilizes the structure of collagen. Fatliquoring decreased the coefficient by 15.14%. This is the greatest decrease among the three processes considered. This implies that fatliquoring is the most destructive crusting process to the leather uniformity. This observation corroborates the results by Sizeland *et al*. [41] and Dutta [42]; penetration of fatliquors into leather increases looseness, softness and pliability.

CONCLUSIONS

All the samples tested showed enough strength properties according to the recommended minimum tear strength, tensile strength, percentage elongation, distension at crack and burst and flexing for garment leathers, linings, and shoe upper leathers. Apart from the minimal effect of sampling the specimens from the same cowhide and hence variation in location, retanning improves tear and tensile strengths, distensions at crack and burst, and shrinkage temperature. It also improves the organoleptic properties such as fullness. However, the uniformity coefficient and percentage elongation decreased after retanning. Dyeing increased the elongation at break, distensions at crack and burst, shrinkage temperature and uniformity coefficient whereas both tensile and tear strengths decreased after dyeing. Similarly, fatliquoring increases elongation at break values, and distension values while decreases tensile and tear strengths, shrinkage temperature and uniformity coefficient. All the samples tested at all stages of processing indicated no damage at 50,000 flexes. Among the other beneficial effects of fatliquoring, induction of tearing type of break instead of the undesirable snapping makes it a necessary process, since this type of break is desirable for majority of today's customers.

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Conflict of Interest

The authors of this manuscript declare that no conflict of interest exists regarding its publication.

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INTEGRATING ANTHROPOMETRY APPROACH AND KANSEI ENGINEERING IN THE DESIGN OF CHILDREN SHOE

Annisa Dwi NOVIANI, Ari WIDYANTI[**]

Department of Industrial Engineering, Bandung Institute of Technology (ITB), Indonesia, Labtek 3 Ganesa 10 Bandung 40132 Indonesia, email: widyanti@mail.ti.itb.ac.id

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INTEGRATING ANTHROPOMETRY APPROACH AND KANSEI ENGINEERING IN THE DESIGN OF CHILDREN SHOE

ABSTRACT. Shoes play an important role in human life. For children in particular, shoes also support the development of their feet. This study is aimed to integrate anthropometric approach with Kansei Engineering in designing shoes for Indonesian children. Eighteen dimensions of foot anthropometry for 331 Indonesian Sundanese children ages 6-10 were measured and presented, a shoe size chart for Indonesian children is proposed as well. Moreover, Kansei Engineering was applied to capture consumers' 'emotion' toward children's shoe design and was evaluated both for Indonesian parents and children. The result shows that emotion related to children's shoe design are comfort and appearance. The implication of the results is further discussed.

KEY WORDS: Indonesian, children, shoe, anthropometry, Kansei, engineering

INTEGRAREA ABORDĂRII ANTROPOMETRICE ŞI A INGINERIEI KANSEI ÎN PROIECTAREA ÎNCĂLŢĂMINTEI PENTRU COPII

REZUMAT. Încălţămintea joacă un rol important în viaţa oamenilor. În special în cazul copiilor, încălţămintea susţine dezvoltarea picioarelor acestora. Acest studiu are ca scop integrarea abordării antropometrice şi ingineria Kansei în proiectarea încălţămintei pentru copiii indonezieni. S-au măsurat optsprezece dimensiuni antropometrice ale piciorului la 331 de copii sundanezi din Indonezia cu vârstele cuprinse între 6 şi 10 ani şi s-a propus o diagramă a dimensiunilor încălţămintei pentru copii indonezieni. În plus, s-a aplicat ingineria Kansei pentru a capta „impresia" consumatorilor faţă de designul încălţămintei pentru copii, evaluând atât percepţia părinţilor, cât şi a copiilor din Indonezia. Rezultatul arată că impresiile legate de designul încălţămintei pentru copii sunt confortul şi aspectul. Se discută implicaţiile rezultatelor obţinute.

CUVINTE CHEIE: indonezieni, copii, încălţăminte, antropometrie, Kansei, inginerie

L'INTEGRATION DE L'APPROCHE ANTHROPOMETRIQUE ET L'INGENIERIE KANSEI DANS LA CONCEPTION DES CHAUSSURES POUR LES ENFANTS

RÉSUMÉ. Les chaussures jouent un rôle important dans la vie humaine. Pour les enfants en particulier, les chaussures favorisent également le développement de leurs pieds. Cette étude vise à intégrer l'approche anthropométrique et l'ingénierie Kansei à la conception de chaussures pour les enfants indonésiens. On a mesuré 18 dimensions anthropométriques du pied chez 331 enfants indonésiens sundanais âgés de 6 à 10 ans, et on a proposé un tableau des pointures des chaussures pour enfants indonésiens. De plus, l'ingénierie Kansei a été utilisé pour capturer « l'émotion » des consommateurs à l'égard de la conception de chaussures pour les enfants et l'on a évalué à la fois pour les parents et les enfants indonésiens. Le résultat montre que les émotions liées à la conception des chaussures pour les enfants sont le confort et l'apparence. L'implication des résultats est discutée plus en détail.

MOTS CLÉS : indonésien, enfants, chaussure, anthropométrie, Kansei, ingénierie

[*] *Correspondence to: Ari WIDYANTI, Department of Industrial Engineering, Bandung Institute of Technology (ITB), Indonesia, Labtek 3 Ganesa 10 Bandung 40132 Indonesia, email: widyanti@mail.ti.itb.ac.id*

INTRODUCTION

Shoes play a crucial role in human activity. Originally, shoes were worn for human protection from the environment, particularly from injury and infection [1]. However, shoes have evolved to be a form of social status, and more recently have even emerged as a fashion trend. Later, shoes also have been developed as a part of medicine, known as the corrective shoe [1]. It is not surprising, therefore, that research in shoes has been conducted for decades, for example in relation with aspects of the foot [2, 3], design elements of the shoes [4, 5] and technology of the shoes' design [6, 7].

In designing shoes, some considerations are applied such as the foot shape and dimensions, manufacturability and consumer preference [8]. Foot shape and dimensions in particular are closely related to shoe size. Shoe size is crucial when the shoe is used to support the foot in its physiological function and development [1, 9]. Failure to consider foot dimensions leads to negative consequences [10] such as foot problems and pathologies in childhood and adulthood [1, 11] as well as strain in foot muscles and tendons [12].

Shoe size is an important feature of the shoe, not only to avoid negative consequences of an ill-fitting shoe, but also to satisfy a wide range of consumers with a vast choice of footwear sizes applicable to multiple individual and group needs [13]. Thus, research in shoe size system or shoe size standards have been often conducted [3, 14].

In most shoe systems, shoe sizes are pre-determined by the last, a mechanical form of a human foot that have been made from various materials, such as hardwoods and high-density plastics [15]. It is usually used by shoe makers or shoe designers. The shoe last corresponds with foot dimensions through all parts of the last such as foot length, ball, instep, and heel [16]. Therefore, the same foot length can vary in regards to the position of the ball-of-foot, instep height, or heel width which are important features for a well-fitting shoe. In general, within one size, values for these dimensions are set to be fixed.

Several methods have been used in determining shoe size. One commonly used method in shoe size system is the mondopoint system. This method/system is based on the mean foot length and width for which the shoe is suitable (in millimeters). This method is used as a base of ISO 9407:1991 [17]. The mondopoint has an advantage for better fit than most other systems since it takes the foot width into account. The mondopoint has been applied in the USA shoe size system and generally most army shoes. Other shoe size systems are available and have been used in different countries. For examples, shoe sizing in the United Kingdom (British size) is based on the length of the last and the formula is [(3 x last length in inch) – 12] or [(3 x heel to toe length in inch) – 10]. The Continental European system, used in most continental European countries, considers the length of the last for the shoe size with the formula being (3/2 x last length in cm) or (3/2 x foot length in cm (+ 1.5)) [15].

Children's shoes have been gaining attention for years in several countries (e.g., in Malaysia [18] and Srilangka [19]. It should be underlined that most shoe size systems differentiate adult and children shoes. For children, shoes are not just used to protect the wearer from the environment nor for fashion. Children must wear proper shoe sizes according to their foot measurement and shape because ill-fitting shoes can influence the normal development of a maturing foot [11]. Parents who have children aged 5 and 6 years old reportedly also face problems in finding correct footwear sizes for their children [8].

As stated earlier, not only is the shoe size system important in the design of children's shoes, but also other aspects of design regarding the preference or perception of consumers are important as well [8]. The study of perception in shoe design is of great interest to designers.

Perception will influence consumers when making decisions about the different types of shoes they purchase [20].

In general, several techniques can be used to translate consumer or user needs and preferences into product design characteristics [21]. The techniques include Quality Function Development (QFD) - which can be used to identify the relationship between consumer needs and engineering characteristics [22] and Kansei Engineering - which can be used to translate consumers' feelings and image for a product into design elements [23]. In other words, Kansei Engineering is a method of consumer-oriented product development based on the consumer mind.

Indonesia is a developing country with a large number of children which make Indonesians a potential market for children's shoes. Unfortunately, the Indonesian children shoe market is dominated by imported shoes. As a matter of fact, the number of imported shoes in Indonesia is increasing yearly [24]. Regrettably, most Indonesian footwear manufacturers lack adequate knowledge on the requirements for designing and producing footwear. Moreover, children's shoes in the Indonesian market are based on foreign sizing such as US and UK standard sizes [20] which are not suitable for Indonesian children. This condition is similar to that of children clothing in Indonesia [25]. Coupled with the increase of the middle class population in Indonesia, parents' attention to children's shoes is elevating. Therefore, more attention should be given to the shoe design particularly in relation with parents' perception about shoes that suit the environment and the purpose.

The aim of this study is to integrate anthropometric approach with Kansei Engineering in the design of Indonesian children's shoes. Anthropometric approach is crucial in determining shoe size system whereas Kansei Engineering is important in capturing the feelings and preferences of shoes for Indonesian children and parents. The integration of anthropometry and Kansei Engineering in the design of Indonesian children's shoes will ensure the creation of shoes that are functional as well-fitting to the current trends and lifestyle of the target market.

EXPERIMENTAL

Anthropometry Measures

Subjects

Three hundred and thirty-one Sundanese Indonesian elementary school students, aged 6 – 10 years old, were voluntarily involved in this study. They were recruited from three elementary schools in the West Java area. Permits were obtained from the school principals with a prior request letter from the Laboratory for Work System Design and Ergonomics of Bandung Institute of Technology. Ethical guidelines have been followed and measurement procedures have been approved by an ethical committee. The participants were instructed to be barefooted during the foot measurement.

Procedure

Eighteen foot anthropometry data were measured: 1) foot length, 2) arch length, 3) heel to medial malleolus, 4) heel to lateral malleolus, 5) heel to 5th toe, 6) foot width, 7) heel width, 8) bimalleolar width, 9) mid-foot width, 10) medial malleolus height, 11) lateral malleolus height, 12) height at 50% foot length, 13) ball girth, 14) instep girth, 15) long heel girth, 16) short heel girth, 17) ankle girth and 18) waist girth. The anchor point of measure for each dimension can be seen in Figure 1. The eighteen foot anthropometry dimensions were chosen since these dimensions are the most commonly used in footwear design.

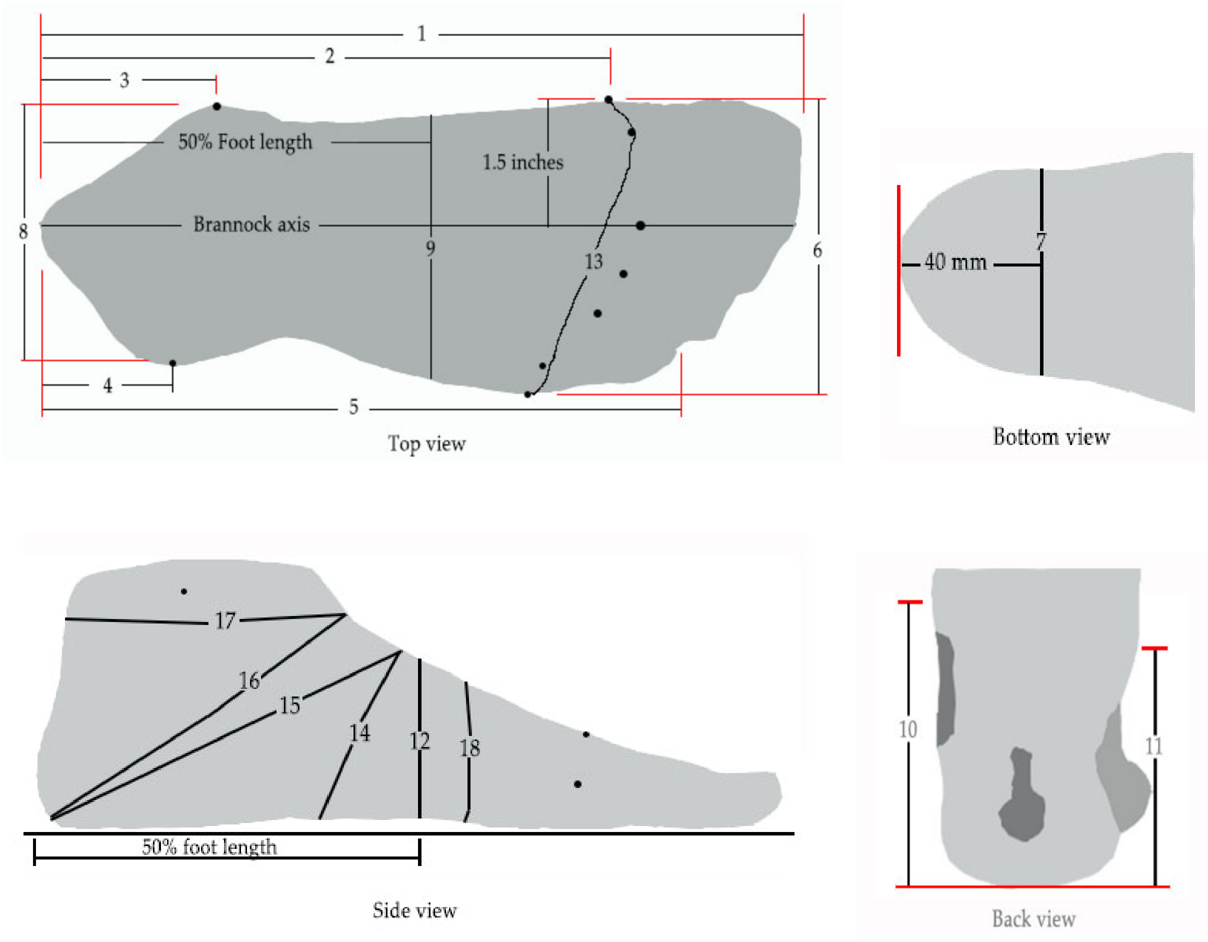

Figure 1. The anchor point of measures of foot anthropometry

The measurement was conducted using a manual method due to restriction on research budget and technical constraint. Subjects were barefooted during measurement with a time measurement for each subject of around 10 minutes. First, participants were instructed to stand on a piece of white paper with a landmark of heel touching the background wall. A pattern of the foot was drawn out on the paper using a pencil based on the foot contour. This pattern was used as a base to measure all length of foot dimensions. In addition, the calliper was used to measure height dimensions and measuring tape was used to measure girth.

The measurement was conducted by 10 student research assistants who received prior knowledge and training regarding the foot measurement. The training was intended to avoid intra-observer error (i.e., error when repeated measurements were taken by the same observer [26]) and inter-observer error (i.e., error when repeated measurements were taken by different observers [25, 27, 28]). To ensure correct measurements and valid data were obtained, authors performed random checks during measurement.

Kansei Engineering

Kansei Engineering is used to capture consumers' feelings and images towards a product and used it in design elements. The steps in Kansei Engineering used in this study are explained as follows. First, kansei words for children's shoes were generated based on literature study and consumer perception. The kansei words were separated for boys and girls' shoes. 53 subjects consisting of 22 parents with 6-10 year old children (all female) and 31 children (14 boys and 17 girls) participated voluntarily in the study by filling out a questionnaire with one only question "what are the words or sentences that can describe boys' and girls' shoes". As stated by Nagamachi [23], kansei word identification is stopped when no new kansei words are identified.

Second, kansei words were restructured using confirmatory study and expert opinion. In the confirmatory study, the previously identified kansei words proposed in the first questionnaire and another sample of participants (n = 30, 20 female) were asked their agreement upon the identified kansei words in relation with children's shoes. Next, expert opinion from one linguistic expert was obtained to avoid bias or duplications in resulted kansei words from the confirmatory study.

Third, a second questionnaire was developed to observe the importance of the restructured kansei words with a Likert scale ranging from 1 (not important at all) to 5 (very important). Six samples of favorite children's shoe products were used as base of evaluation. The samples of the product can be seen in Figure 2.

Figure 2. Example of shoe product to be evaluated, upper for girls' shoe and lower for boys' shoe

Participants were asked to give a rating for each sample of product based on the kansei words with scale ranging from 1 (very bad) to 5 (very good). 112 participants were involved in completing the second questionnaire. Higher structurization of kansei words was conducted through Principal Component Analysis on the final score of the multiplier of the importance of the attributes and ratings of each sample product. Lastly, a synthesis of product attributes based on Kansei Engineering was conducted through an interview with children's shoe manufacturer.

RESULTS AND DISCUSSIONS

Foot anthropometry

Foot anthropometry data of Indonesian children can be seen in Table 1.

Table 1: Foot anthropometry of Indonesian children (in cm)

No	Foot anthropometry dimensions	Boys				Girls			
		Mean	SD	P5	P95	Mean	SD	P5	P95
1	Foot length	19.70	1.65	17.19	22.41	19.49	1.43	17.30	22.00
2	Arch length	14.18	1.31	12.10	16.20	14.06	1.24	12.10	16.20
3	Heel to medial malleolus	4.54	.83	3.20	5.90	4.40	.78	3.10	5.70
4	Heel to lateral malleolus	3.76	.87	2.30	5.20	3.70	.79	2.30	5.10
5	Heel to 5th toe	16.21	1.31	14.05	18.26	16.10	1.07	14.40	17.70
6	Foot width	8.05	.48	7.20	8.90	8.10	.53	7.20	9.00
7	Heel width	5.02	.50	4.25	6.00	4.97	.48	4.10	5.90
8	Bimalleolar width	6.35	.71	5.15	7.56	6.29	.71	5.20	7.60

9	Mid-foot width	6.41	.68	5.22	7.56	6.35	.62	5.30	7.40
10	Medial malleolus height	5.52	.49	4.76	6.36	5.42	.55	4.50	6.30
11	Lateral malleolus height	4.86	.93	3.07	6.20	4.78	.98	3.20	6.30
12	Height at 50% foot length	3.77	.36	3.20	4.40	3.84	.37	3.20	4.40
13	Ball girth	19.22	1.95	16.34	22.50	19.08	1.71	16.50	22.00
14	Instep girth	20.48	2.27	17.35	24.72	20.84	2.40	17.50	25.30
15	Long heel girth	25.78	2.78	21.78	30.61	25.67	2.57	22.00	30.20
16	Short heel girth	24.80	2.39	21.50	28.78	24.52	2.11	21.50	28.50
17	Ankle girth	18.37	2.03	15.59	22.11	18.48	1.93	15.50	21.80
18	Waist girth	18.48	1.48	16.00	20.80	18.36	1.24	16.50	20.50

Principal Component Analysis (PCA) was applied to observe the foot anthropometry dimensions that correlate with the principal dimensions of shoe size (i.e., foot length). The result of the PCA can be seen in Table 2.

Table 2: Principal Component Analysis of foot anthropometry dimensions

Foot anthropometry data	Component		
	1	2	3
Foot length	.816		
Arch length	.812		
Heel to 5th toe	.767		
Bimalleolar width		.809	
Height at 50% foot length			.735
Ball girth	.874		
Instep girth	.791		
Long heel girth	.800		
Short heel girth	.881		

It can be seen that the foot length is in a similar component with arch length, heel to 5th toe, ball girth, instep girth, long heel girth and short heel girth. In addition, it should be underlined that the shoe size standard most commonly found in Indonesia is European Union (EU) standard. Incorporating the EU shoe size system and the result of the PCA analysis above, the suggested shoe size chart, which include the most commonly measured anthropometry data, are similar with the PCA result (i.e., foot length, foot width, toe length). The values of foot length, foot width and toe length are calculated from the regression analysis based on the foot length. The proposed shoe size chart can be seen in Table 3.

Table 3: Shoe size chart and the corresponding dimensions for Indonesian children

Euro shoe size	Corresponding foot dimensions for Indonesian children (in cm)			
	Length	Width	Ball girth	Toe length
15.5	8.3	5.1	11.4	4.4
16	8.9	5.3	11.7	5.3
16.5	9.2	5.5	11.9	5.7
17	9.5	5.6	12.1	6.1
17.5	10.2	5.9	12.5	7.1

Euro shoe size	Corresponding foot dimensions for Indonesian children (in cm)			
	Length	Width	Ball girth	Toe length
18	10.5	6.0	12.7	7.5
18.5	10.8	6.1	12.9	7.9
19	11.4	6.3	13.3	8.7
19.5	11.7	6.4	13.5	9.1
20	12.1	6.5	13.7	9.6
21	12.7	6.7	14.1	10.3
22	13	6.8	14.3	10.6
22.5	13.3	6.9	14.5	11.0
23	14	7.1	15.0	11.7
23.5	14.3	7.2	15.2	12.0
24	14.6	7.2	15.4	12.4
24.5	15.2	7.4	15.8	12.9
25	15.6	7.5	16.1	13.3
26	15.9	7.5	16.3	13.6
27	16.5	7.7	16.8	14.1
27.5	16.8	7.7	17.0	14.3
28	17.1	7.8	17.2	14.6
29	17.8	7.9	17.7	15.1
30	18.1	7.9	18.0	15.3
30.5	18.4	8.0	18.2	15.5
31	19.1	8.1	18.7	16.0
31.5	19.4	8.1	19.0	16.2
32	19.7	8.1	19.2	16.3
33	20.3	8.2	19.7	16.7
33	20.6	8.2	19.9	16.8
34	21	8.2	20.2	17.0
34	21.6	8.3	20.7	17.2
35	21.9	8.3	21.0	17.4
36	22.2	8.3	21.2	17.5
36	22.9	8.3	21.8	17.7
37	23.2	8.3	22.1	17.8
37	23.5	8.3	22.3	17.9

Kansei Engineering

In the first step - kansei words identification - for parent participants, no more kansei words were found after the 19th participant, indicating a sufficient number of participants for kansei word identification. In total, 114 and 107 kansei words for both boys and girls' shoes were obtained from all participants - both parents and children - in addition to literature study as well. Examples of the identified kansei words include "simple", "casual" and "comfort".

Restructurization of kansei words using confirmatory study and expert opinion resulted in 21 groups and 18 groups of kansei for girls and boys' shoe respectively. Higher kansei restructrurization conducted using PCA with varimax rotation resulted in 4 dimensions for girls' shoes and 3 dimensions for boys' shoes. For those dimensions, the 1st dimension for girls and boys' shoes is related with the comfort aspect of the shoe. Whereas the 2nd, 3rd, and 4th dimensions for girls' shoes and 2nd and 3rd dimensions for boys' shoes are related with the appearance of the shoe. The dimensions and the related variable can be seen in Table 4.

Table 4: Result of kansei engineering in Indonesian children's shoes

Girls shoe Dimension	Kansei words	Boys shoe Dimension	Kansei words
Comfort	Flexible	Comfort	Flexible
	Light		Light
	Not slippery		Not slippery
	Simple		Simple
	Comfort		Comfort
	Strong		
	Non formal		Non formal
	soft		Soft
	Suit with the age		Suit with the age
	Sporty		Sporty
	Fit size		Fit size
	casual		Casual
Appearance	Girly design	Appearance	Boys design
	Funny		Funny
	Girly / neutral color		Boys / neutral color
	Unique/ Classic		Up to date
	Up to date		

Synthesis of the dimensions to find significant attributes of children's shoes design was conducted through an interview with Indonesian children's shoe manufacturer and can be seen in Table 5 and Figure 3.

Table 5: Synthesis of kansei words into shoe attribute

	Comfort											Appearance				
Kansei words / Product Attribute	Flexible	light	Not slippery	simple	Comfort	strong	Non formal	Soft	Suit with children age	*Sporty*	Fit size	Casual	Design	Funny	Color	Classic/up to date
Upper pattern/design				v	v							v				
Upper material	v					v							v			
Sole pattern	v		v			v			v	v			v			
Sole material		v	v			v										
Toe box pattern											v			v		
Lining material					v			v								
Toe cap										v						
Heel													v			
Vamp											v					

Color									v			v		v	v	v
Accessories				v						v	v	v		v		v
Model	v						v		v	v			v	v		v
Shoe tongue					v			v		v						

Figure 3. Attribute of the children shoe

The aim of this study is to integrate anthropometry and Kansei Engineering in the design of Indonesian children's shoes. From the view of anthropometry data, there are no significant differences between boys and girls in Indonesian children's foot anthropometry data. Although it is well established that gender-specific differences in foot shape exist in adults (see [29] for an example), some research did not discover the differences in their findings [30]. It should be noted that the gender differences in children's foot anthropometry is observed after puberty and may be a contributing factor for no anthropometric variations between the boys and the girls in this study. The result of this present study also supports race difference in anthropometry data [9], in which the Indonesian foot anthropometry data is smaller than Caucasian ones (for example Spanish children foot anthropometry data [31]).

The result of PCA shows that foot length highly correlates with arch length, heel to 5th toe, ball girth, instep girth, long heel girth and short heel girth. This result supports previous studies in corresponding foot length with other dimensions of foot anthropometry such as ball girth [17] and toe length [32]. It should be underlined, however, that the differences in the corresponding dimensions of foot length varies due to the different numbers of data and the different foot structures among samples of these studies [33].

The importance of suitability of shoe size with foot development in children have been realized by Indonesian parents [20]. The negative consequences of huge variation in shoe size system in Indonesian children's shoes have been underlined by the shoe manufacturer and consumers as well. Therefore, study about Indonesian children's shoe size is of utmost importance. In this present study, instead of developing a new shoe size system for Indonesian children, we prefer completing the shoe size chart available in the market. The consideration for the completion of the chart is since the effort to develop a new standard of shoe size system in Indonesia has failed [34]. The additional anthropometry references (i.e., ball girth) is due to consideration of the different structure of foot [33]. In addition, a small interview with a shoe manufacturer reveals the difficulties of the shoe manufacturer in adapting a possible new shoe size system.

Kansei Engineering applied for Indonesian children's shoes in this present study shows that Indonesian consumer preference for children's shoe design falls in the category of comfort and appearance. The "comfort" and "appearance" were synthesized into the attributes of the product such as sole and vamp, which give guidance for the shoe manufacturer in the design process of Indonesian children's shoes. As stated by Penkala *et al*. [8], shoe-fitting practices were affected not only by the available shoe size, but also by shoe style (i.e., related with comfort and appearance).

Kansei Engineering used in this study has some advantages. Kansei Engineering establishes a suitable framework for working with symbolic attributes and user perceptions, expressed in their own words. It also establishes a framework for quantifying the relationships between design characteristics and emotional responses [23, 35]. These contributions are very meaningful in areas such as shoe design, where emotional impressions can explain a significant part of the variance associated with the purchase decision. Two levels of kansei word restructurization were applied, instead of only one level of kansei word restructurization, since the two levels provide less number of kansei words per groups and in return gives more focused result.

This study has several limitations worth noting. First, the sample of participants in anthropometry measurement is limited to Sundanese children only. Considering the ethnic differences in Indonesian anthropometry data [27], further study covering other ethnicity in Indonesia is needed. Second, the foot anthropometry measures were conducted using manual measurement. Although the validity of such measures is often questionable compared to advanced measurements such as using foot scanner, due to restriction of research budget and technical limitation, the manual measure was used. Furthermore, since the observers received prior training in relation with the measurement, it can be argued that inter and intra-observer error in this study are minimized. However, further study comparing result of manual and foot scanner measurements should also be conducted. Third, the participants of Kansei Engineering approach are limited to parents and children in Bandung as a representative of big cities in Indonesia. Further research involving participants from small cities or rural areas is suggested.

CONCLUSIONS

In conclusion, the present study gives valuable contribution in the initial step of providing foot anthropometry data of Indonesian children as well as a rigorous children shoe size chart in Indonesia. Not only related with the shoe size system, this study also shows the preferences of Indonesian consumers in relation with children's shoes. The result of this present study will help Indonesian children's shoe manufacturers to design marketable children's shoe design. For consumers, result of this present study could minimize error in choosing shoe sizes as well as give more choices in children's shoe design. It should be underlined that shoes of the future should be designed to support function and protection while retaining comfort and appearance.

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BINDINGS OF RARE BOOKS FROM THE COLLECTIONS OF THE ROMANIAN ACADEMY LIBRARY - A MULTIDISCIPLINARY STUDY

Cristina CARȘOTE[1], Luminița KÖVARI[2], Carmen ALBU[2], Emanuel HADÎMBU[3], Elena BADEA[3,4*], Lucreția MIU[3], Gabriela DUMITRESCU[2]

[1]The National History Museum of Romania, 12 Calea Victoriei Street, 030026 Bucharest, Romania

[2]Department of Manuscripts and Rare Books, Romanian Academy Library, 125 Calea Victoriei Street, 010071 Bucharest, Romania

[3]INCDTP - Division: Leather and Footwear Research Institute, 93 Ion Minulescu Street, 031215 Bucharest, Romania

[4]Department of Chemistry, Faculty of Sciences, University of Craiova, 107 I Calea București Street, 200512 Craiova, Romania

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BINDINGS OF RARE BOOKS FROM THE COLLECTIONS OF THE ROMANIAN ACADEMY LIBRARY - A MULTIDISCIPLINARY STUDY

ABSTRACT. This paper presents an overview of the conservation state of the tawed white leather, parchment and reused parchment bookbindings from the Rare Book Collection of the Romanian Academy Library. The transdisciplinary study was jointly conducted by the researchers of INCDTP-ICPI and Manuscripts and Rare Book Department of the Romanian Academy Library. Over 50 bindings in alum-tawed (white) leather, parchment and reused parchment were analyzed *in situ* using specific non-invasive or micro-invasive analysis methods such as visual and microscopic analyses, thermal microscopy (imageMHT method), attenuated total reflection (ATR), Fourier transform infrared spectroscopy (FTIR), and X-ray Fluorescence Spectrometry (XRF). Based on these results, conservation sheets have been drawn up including damage status, threats and conservation recommendations for each investigated bookbinding. Two conservation sheets are illustrated for alum-tawed and re-used parchment bindings. This is the first Romanian study dedicated both to the artistic and material aspects of rare book bindings so far.
KEY WORDS: bookbinding, alum-tawed leather, parchment, damage status, conservation reccommendations

LEGĂTURI DE CARTE RARĂ DIN COLECȚIILE BIBLIOTECII ACADEMIEI ROMÂNE - STUDIU MULTIDISCIPLINAR

REZUMAT. Această lucrare prezintă o imagine de ansamblu asupra stării de conservare a legturilor de carte din piele albă argăsită, pergament și pergament reutilizat din Colecția de Carte Rară a Bibliotecii Academiei Române. Studiul transdisciplinar a fost realizat în comun de către cercetătorii din cadrul INCDTP-ICPI și din cadrul Departamentului de Manuscrise și Cărți Rare al Bibliotecii Academiei Române. Peste 50 de legături din piele argăsită cu alaun (albă), pergament și pergament refolosit au fost analizate *in-situ* utilizând metode specifice de analiză neinvazivă sau microinvazivă, cum ar fi analize vizuale și microscopice, microscopie termică (metoda imageMHT), reflexie totală atenuată (ATR), spectroscopie în infraroșu cu transformată Fourier (FTIR) și spectrometrie de fluorescență de raze X (XRF). Pe baza acestor rezultate, au fost întocmite fișe de conservare, care includ starea de deteriorare, riscuri și recomandări de conservare pentru fiecare legătură de carte studiată. Două fișe de conservare sunt ilustrate pentru legături din pergament argăsite cu alaun și reutilizate. Acesta este primul studiu românesc de până acum dedicat atât aspectelor artistice, cât și aspectelor materiale ale legăturilor de carte rară.
CUVINTE CHEIE: legătură de carte, piele argăsită cu alaun, pergament, stare de deteriorare, recomandări de conservare

RELIURES DE LIVRES RARES DES COLLECTIONS DE LA BIBLIOTHÈQUE DE L'ACADÉMIE ROUMAINE - ÉTUDE MULTIDISCIPLINAIRE

RÉSUMÉ. Cet article présente une vue d'ensemble de l'état de conservation des reliures en cuir blanc tanné à l'alun, en parchemin et en parchemin réutilisé de la Collection de Livres Rares de la Bibliothèque de l'Académie Roumaine. L'étude transdisciplinaire a été menée conjointement par les chercheurs de l'INCDTP-ICPI et du Département des Manuscrits et des Livres Rares de la Bibliothèque de l'Académie Roumaine. Plus de 50 reliures en cuir (blanc) tanné à l'alun, en parchemin et en parchemin réutilisé ont été analysées *in situ* à l'aide de méthodes d'analyse non invasives ou micro-invasives telles que les analyses visuelles et microscopiques, la microscopie thermique (méthode imageMHT), la réflexion totale atténuée (ATR), la spectroscopie infrarouge à transformée de Fourier (FTIR) et la spectrométrie de fluorescence des rayons X (XRF). À partir de ces résultats, des fiches de conservation ont été élaborées, indiquant notamment l'état de détérioration, les menaces et les recommandations de conservation pour chaque reliure explorée. Deux fiches de conservation sont illustrées pour les reliures en parchemin tanné à l'alun et réutilisé. Cet article est la première étude roumaine consacrée à la fois aux aspects artistiques et matériels des reliures de livres rares.
MOTS CLÉS : reliure, cuir tanné à l'alun, parchemin, l'état de détérioration, recommandations en matière de conservation

THE RARE BOOK COLLECTION OF THE ROMANIAN ACADEMY LIBRARY

The Rare Book Collection, established since 1958, by the selection of volumes from the General Book Fund of the Academy Library, brings together 11626 copies of Romanian and foreign prints, grouped chronologically and by bibliophilia criteria, such as the rarity of editions, the richness and quality of the illustrations, the special materials on which they were printed, the trademarks of different types, the precious bindings. The collection reflects the entire evolution of book printing, from the beginning to the present day, for the entire European space and its most important printing centers. The Rare Book Fund is also a collection of bindings, with notable examples for each epoch, reflecting both the artistic and ideological vision of the moment. Over 50 white leather and parchment bindings have been the subject of this study. They make up a distinctive group, with its own physical, structural and ornamental characteristics, in the valuable rare book collection of the Academy Library.

BOOKBINDING

The main function of a binding is to keep together the sheets/bundles of a manuscript or a book. In addition, the binding provides protection against mechanical stresses. Not seldom the binding fulfills an aesthetic, beautifying role, being a distinctive feature of the owner. By the nature of the materials and the ornamentation techniques used, the bindings are equally the expression of socio-cultural tendencies and of the artistic vision of each age. Moreover, a detailed analysis of the binding can reveal exceptional information about the material processing technologies, contributing to the improvement and expansion of dating and localization studies. The material elements of the covers, long undervalued, represent an invaluable source of information, with an exceptional potential to complement knowledge and understanding of history in all its aspects. For conservators and restorers, knowledge about the nature of materials and manufacturing technologies are essential tools, in the absence of which changes due to conservation conditions or a determined treatment over the general "balance" of the "book system" cannot be assessed.

The disregard of the material elements of the covers has led to the loss of most of the old bindings due to the campaigns of rebinding and restoration made during the first half of the 20th century. In Europe, massive restoration interventions, during which curators' attention focused exclusively on text or decorative portions of the cover, allowed restorers to eliminate parts without text or decorations. Thus, in the case of so-called artistic covers, fragments were preserved, while the covers lacking textual or graphic components were almost totally lost. A modern and responsible approach to surviving bindings must therefore start from the identification of the constituent materials of the structural elements of bindings, their *in situ* characterization by non-invasive techniques (where micro-sampling is possible, micro-destructive analyses can contribute with very useful quantitative information), assessing the degree of deterioration, drawing up the conservation sheet and developing a long-term monitoring program. The conservation sheet is the starting point for any decision regarding the selection of the optimal conditions (temperature, relative humidity, illumination, maximum concentration allowed for atmospheric pollutants and volatile organic substances) for preservation, exposure, consultation and manipulation, as well as the choice of conservation or restoration treatments based on the specific characteristics and damage of each binding. It is important to emphasize that not all bindings require conservation or restoration interventions, let alone radical treatments with a high risk of damaging both the information contained therein and the longevity of the binding.

In Romania, there are very few studies dedicated to bookbindings, whose main objective is the study of ornamental schemes (*Studite* project - *Study and Creation on Byzantine Bookbindings* [1], 2011-2013, coordinated by the Book Conservation Center of Arles, within which the Byzantine bindings of Greek [2] and Slavic manuscripts from the collection of the Romanian Academy Library were identified and studied, and 10 replica bindings were made, respecting the elements of structure, technique and ornamentation of the Byzantine bindings) or medieval book fastenings [3] in the archaeological discoveries of Transylvania. This is the very first study dedicated both to the artistic and material aspects of rare bookbindings so far.

Ornaments for White Leather Bookbinding

White leather bindings are made of pig, sheep or calf skin treated with aluminum salts, on wooden boards, and more rarely on cardboard bark, wooden supports being used until late in the 17th century, especially on German territory. This is where plate-decorated bindings largely come from (a technique that appeared in the 13th century in Holland), with which portrait ornaments are made, depicting personalities of the time: great figures of the Reformation era, such as Martin Luther, Philip Melanchton, Erasmus of Rotterdam, Jan Hus (for example, in the binding of some New Testament editions, printed in Hagenau in 1521, in Geneva in 1590, a 1591 edition of the Bible, published in Frankfurt, or in the binding of the work *Thomae Linacri Britanni De emendata structura Latini sermonis*, Leipzig, 1545 - Figures 1-3); historical personalities such as Charles V (*Chronicon Carionis*, Wittenberg, 1580, Figure 4, *Florilegium diversorum epigrammatum veterum*, Genevae, 1566, *Vita Jacobi despotae*, Wittenberg, 1587), Maximilian II (*Florilegium diversorum epigrammatum veterum*, Geneva, 1566), or German princes of the various Länder, among which Johann Friedrich I, Prince of Saxony, is distinguished by his numerous appearances: *Commentariorum C. Iulii Caesaris De bello gallico*, Frankfurt, 1584, *Chronicon Carionis*, Wittenberg, 1580, *M. T. Ciceronis Orationum volumen tertium*, Strasbourg, 1574 (Figure 5).

Portraits placed on the back covers sometimes correspond to the blazons of the historical character, the noble family, the Land or city of origin. The borders of these bindings also have a historical character, made with *Reformer Roll* ornaments, an enclosed frame, comprising miniature portraits of representatives of the Reformation Age (*P. Ovidii Nasonis Opera quibus in omnes Metamorphoseos* ..., Basel, 1556, Figure 6).

Figure 1. *New Testament*, Hagenau, 1521

Figure 2. *New Testament*, Geneva, 1590

Figure 3. *Bible*, Frankfurt, 1591

Figure 4. *Chronicon Carionis*, Wittenberg, 1580

Figure 5. *M. T. Ciceronis Orationum…*, Strasbourg, 1574

Figure 6. P. *Ovidii Nasonis Opera ... Metamorphoseos ...*, Basel, 1556

The theme of central rectangular panels, as well as of the segmented borders, may be the allegory of Christian or celestial virtues established by the ideology of the epoch, but taking on elements from the vision of Plato or other classical thinkers: cardinal virtues among which prudence (*prudentia*), temperance (*temperantia*), courage (*fortitudo*), justice (*justitia*), and theological virtues, among which faith (*fides*), hope (*spes*), love/charity (*caritas*). These moral traits, defining the profile of the perfect Christian, are allegorically portrayed as feminine characters, accompanied by canonical symbolic objects and therefore easily decipherable, such as the scales and sword for Justice (*Homērou Odysseia*..., Strasbourg, 1572, Thucydides, *De bello peloponnesiaco* ..., Wittenberg, 1562), the wheel of Fortune (Ulpianus, *Iustiniani Institutionum*, Geneva, 1578), hands clasped together in prayer for Hope and Faith, or are suggested by situations of clear significance, such as offering bread to an old man to symbolize Charity or Mercy (Euripide, *Tragōdiai oktōkaideka* ..., Basel, 1551).

However, to represent these qualities, characters from the biblical text or from ancient history, which have become emblematic for a certain character trait, are used: the wife of Lucius Tarquinius Collatinus, Lucretia, is a symbol of moral purity, fidelity and dignity (*De Philippi Melanchthonis ortu, totius vitae curriculo*, Leipzig, 1566, *Nicodemi Frischlini Balingensis, Hebraeis. Continens duodecim libros* ..., Strasbourg, 1610), while Judith, a veterotestamentary character who decapitates Holofern, is the incarnation of courage, strength and faith, in the service of the community.

The great iconic Christian themes, from the Christic and Marianic cycles, are also found in the ornamentation of the time: Crucifixion and Resurrection (*P. Ovidii Nasonis Opera quibus in omnes Metamorphoseos* ..., Basel, 1556), Annunciation and Resurrection (Alessandro Guagnini, *Rerum Polonicarum* ..., Frankfurt, 1584). There are also Old Testament themes in combination with the novotestamentary ones: Adam and Eve in Heaven, Moses and the Tablets of the Law.

However, there are many bookbindings with non-figurative ornamentation, whose inventory includes only varied phytomorphic and geometric elements, from the phytomorphic network border to small individual elements representing stylized inflorescences placed in the center panel.

Another feature of the white leather bookbindings on wooden boards, especially German ones, is the printing of the binding year and the initials of the owner, essential items for dating and volume circulation.

Ornaments for Parchment Bookbindings

Among the specific features of parchment bindings is the use of cardboard barks or even the lack of any support, which gives them a lower weight and greater maneuverability, being called *limp binding* (*reliure flexible*) or Dutch bindings, for the place where they were established, at the end of the sixteenth century and the beginning of the seventeenth century, although they had been known since the previous centuries.

Ornamentation is often sober and simple, but elegant and refined using the golden leaf process. Many of the parchment bindings are decorated with a single central polylobate medallion with oriental geometric motifs (arabesques) with phytomorphic or heraldic motifs. From this last subtype the binding with the coat of arms of Louis-Antoine de Noailles, archbishop and cardinal of Paris (Anastasius Bibliothecarius, *Historia Ecclesiastica* ..., Paris, 1649, Figure 7) or the binding with the emblems of Maximilian Erasmus von Hacklberg Gallois, *Traité des plus belles bibliothèques de l'Europe*..., Paris, 1685) stand out. Bindings with the heraldic emblems of some cities, such as Rotterdam and Regensburg can also be found.

Spectacular through the richness and polychromy of the decor, made by pressing and then painted, are the bindings of the *Bauern Einbände* (*peasant binding, reliure folklorique allemande / de paysan*) originating in Hungary and then spread to Germany, the Netherlands and the northern countries, in the 17^{th}-18^{th} centuries. The folk-style motifs are mostly floral and plant, filling the entire space of the covers and drawing attention through the vivid color of the pastels. They are often the framework in which the fundamental religious scenes, Crucifixion and Virgin Mary with the Child, are integrated, also placed in compositions with geometrical motifs, in which the bands serving as borders or arcs marking the corners are highlighted by different colors. Many of the volumes that keep these bindings are New Testament editions (two editions printed at Leyda, 1765 and 1785, an edition published in Halle in 1710, of this last edition the library contains two copies, Figures 8a and 8b).

Figure 7. Anastasius Bibliothecarius, *Historia Ecclesiastica* ..., Paris, 1649

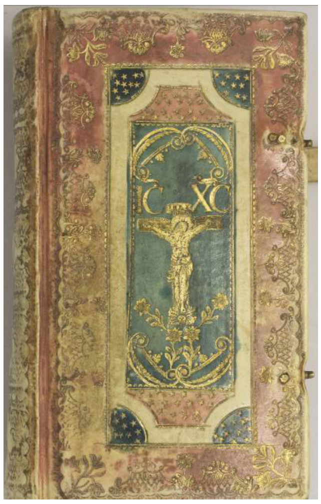


Figure 8a. *New Testament*, Leyda, 1765 (copy 1)

Figure 8b. *New Testament*, Leyda, 1785 (copy 2)

Reused Parchment Bookbindings

The third type of binding analyzed was that of the reused parchment bindings, valuable for the age of the parchment, the variant of the text, or the graphs used. Among the most important ones are a sheet with a fragment of St. Augustine's texts, originally included in a Homiliarium or a Breviary (binding for an edition of Lambert Daneau's work, *Elenchi ereticorum*, printed in 1560 in Geneva), another parchment sheet taken from a copy of the lexicon made by Giovanni Balbi (link to *Vindiciae contra tyrannos*..., published in Basel in 1579) or a parchment sheet with a fragment from *Vita Sancti Petri*, in Carolingian writing (dressing a volume of *Annales Sultanorum Othmanidarum*, printed in Frankfurt in 1596, Figure 9).

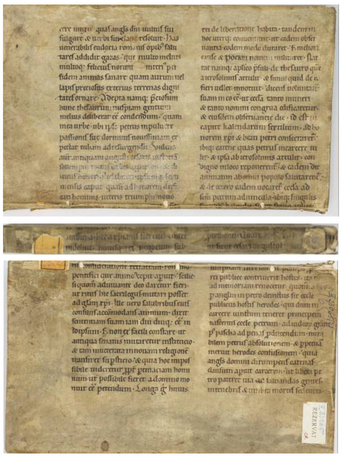


Figure 9. *Annales Sultanorum Othmanidarum*, Frankfurt, 1596

The white alum-tawed leather and parchment bindings represent a well-defined corpus of the rare books collection, in terms of leather appearance, manufacturing techniques, combining with the other structural elements of the book, and inventory and ornamentation techniques.

***In situ* Analysis of Bookbindings**

Over 50 bindings in white leather, parchment and reused parchment from the Rare Book Collection of the Romanian Academy Library were analyzed *in situ* using specific analysis methods. Based on the results obtained conservation sheets were drawn up. The *in situ* analysis performed and two selected conservation sheets are presented below.

The visual analysis was based on the macroscopic and microscopic analysis protocol for both surfaces of the leather or parchment (corium - flesh side and grain - hair follicle side) developed in the Improved Damage Assessment of Parchment (IDAP) European project [4, 5]. The protocol seeks to gather information on (i) the animal species used for the manufacture of leather or parchment; (ii) aspects concerning the skin processing technique; (iii) damage caused by physical, chemical and biological factors or improper handling; (iv) the types of inks and pigments applied to the support, and (v) the ink and pigment conservation state [6-8]. The microscopic observations were made with a Dino-Lite digital microscope, model AD7013MZT, 1.3 Megapixel resolution.

Attenuated Total Reflection Infrared Spectroscopy (FTIR-ATR) is one of the most widely used methods of analysis in modern conservation and restoration laboratories, being non-destructive, versatile and fast. The technique is based on vibration-rotation transitions that occur at the molecular level by infrared radiation absorption. The recorded spectrum contains information on the main characteristic frequencies of specific functional groups in the molecule to be analyzed, and by its interpretation substances can be identified and structural changes at the molecular level can be detected. In the case of leather and parchment, FTIR-ATR allows the detection and quantification of structural changes in molecular collagen as well as the identification of materials added in the manufacturing process or subsequently formed in deterioration and/or aging processes [6-9].

FTIR-ATR analyses were performed in a non-destructive manner, directly on the cover, using an Alpha portable spectrometer (Bruker Optics) equipped with the Platinium diamond ATR accessory. The spectra were recorded in the spectral range 4000-650 cm^{-1} at a resolution of 4 cm^{-1} using 32 scans. OPUS 7.0 software was used for spectra processing and evaluation.

Thermal microscopy known as the *Micro Hot Table (MHT) method* is a combined technique based on the microscopic analysis of collagen fibers subjected to controlled heating (heating speed: 2°C/minute) in the temperature range (20-100)°C. Collagen materials have an intrinsic property of shrinking when subjected to heating in an aqueous medium, reducing their length to a quarter of the original. The temperature at which the shrinking begins, the one at which the fibers contract simultaneously and the one at which shrinking is completed are indicators on the basis of which the hydrothermal stability and structural heterogeneity of the collagen fibers [10-13] are evaluated.

Microsamples (0.05-0.1 mg) of the material taken from the damaged areas of the bookbindings (where sampling was possible) were analyzed in the Advanced Cultural Heritage Research Laboratory (ARCH Lab) using a system consisting of a heating microplate LTS 120 (Linkam Scientific Instruments) equipped with an automatic heating rate control system and a Nikon 1000 SMZ 745 stereomicroscope equipped with a Nikon D90 digital camera. Image acquisition and interpretation was done with imageMHT software.

X-ray Fluorescence Spectrometry (XRF) is an elemental, non-destructive and rapid analytical technique that is used to determine the elemental composition of materials. A major advantage of this technique is the availability of portable systems and the possibility of *in situ* analysis of objects of interest without any prior training.

XRF measurements were performed to identify pigments and precious materials in the decorations of the bookbindings as well as the materials added to the manufacturing process. For the detection of chemical elements with atomic number Z>12, an ED-XRF Elio (XGLab) portable spectrometer with a 1 mm analysis spot size, equipped with an excellent resolution SDD (Silicon Drift Detector), integrated video camera and laser-based alignment.

Conservation Sheet for a White Leather Bookbinding

Call number: **C. R. II 46586**

Author: Francofurdi (Frankfurt), Impensis Samueli Selfischii & Bechtoldi Rab

Editors: Selfisch, Samuel // Rab, Bechtold

[11], 981 [-992] f., 2 h.; il.; in 4° (20 cm)

Title page: Bibliorum codex sacer et authenticus, Testamenti utriusque Veteris & Novi, ex Hebraea & Graeca veritate, quàm proximè ad literam quidem fieri potuit, fidelissimè translatus in linguam Latinam...

Dating: 1591

Pagnino, the Saint 1470-1541, trad. // Bèze, Théodore de 1519-1605, trad.// Baduel, Claude 1491-1561 trad.

Bookbinding type: wooden bark covered in alum-tawed leather (Figure 10), dyed

Microscopic and Macroscopic Characteristics

-Microscopic identification of the animal - pigskin

-Microscopic view (Figure 11): yellow-brown color with areas showing discoloration, mechanical damage, flaking, fraying, dirt adhesion to the surface and various dark spots; the clasps are missing

-Microscopic view (morphology) of water-dispersed fibers, most of the fibers exhibit good cohesiveness, the tendency to lose the helical character and to be flattened is reduced.

Figure 10. Overview of the leather bookbinding: recto (left image) and verso (right image)

Figure 11. Macroscopic details illustrating mechanical damage of the bookbinding in the area of the spine and clasp

Hydrothermal Stability of Leather Determined by MHT Method

MHT parameters indicating hydrothermal stability (*T_s* - shrinkage temperature, *T_f* – the temperature when the first fiber shrinks, *T_l* - the temperature when the last fiber shrinks) and structural heterogeneity (*C* - the main shrinkage interval, Δ*T* - total shrinkage interval) for a white leather micro-sample taken from a damaged area of the bookbinding are shown in Table 1.

Table 1: MHT parameters for a white leather sample taken from the bookbinding and for a new alum-tawed leather

Sample / Parameters	Hydrothermal stability T_s / °C	T_f / °C	T_l / °C	Structural heterogeneity C/ °C	ΔT / °C
New leather	63.8 ± 0.3	53.2 ± 0.4	79.8 ± 0.4	5.3 ± 0.2	31.6 ± 0.6
II 46586	55.4	47.0	88.3	7.3	32.9

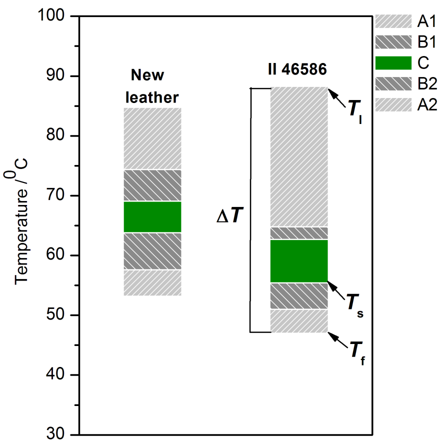


Figure 12. Graphic illustration of shrinkage intervals (A1, B1, C, B2, A2), highlighting MHT parameters for the leather sample taken from the cover and for a new alum-tawed leather. Assessment of deterioration degree [12]: undeteriorated parchments, $T_f > 45\ ^0C$; $T_s > 50\ ^0C$; parchments with minor deterioration degree, $40\ ^0C < T_f < 45\ ^0C$; $45^0C < T_s < 50\ ^0C$; parchments with medium deterioration degree, $35\ ^0C < T_f < 40\ ^0C$; $40\ ^0C < T_s < 45\ ^0C$; parchments with major deterioration degree, $T_f \leq 35\ ^0C$; $T_s \leq 40\ ^0C$

According to the criteria for classification of the deterioration degree based on T_s and T_f parameters [12], the bookbinding shows a minor degree of deterioration. However, the structural heterogeneity of the leather is quite high compared to that of the new leather, suggesting the presence of several collagen populations with distinct thermal stability: collagen "stabilized" by reaction with aluminum salts, "free" collagen, resulting from the "detanning" process and "destabilized" collagen, resulting from hydrolytic and oxidative processes. The thermally unstable, pregelatinized and gelatinized fractions of collagen are susceptible to being affected by high and/or oscillating relative humidity (RH) in the storage, consultation or exposure space, as well as wet conservation or restoration treatments.

Risk of exposure to wet treatments: solubilization of unstable fractions, formation of sticky appearance areas, loss of collagen material.

Risk of exposure to oscillating RH: crack formation, superficial cracks (*craquelé* appearance), loss of collagen material.

Molecular Changes and Added Materials Identified by FTIR-ATR - Figure 13

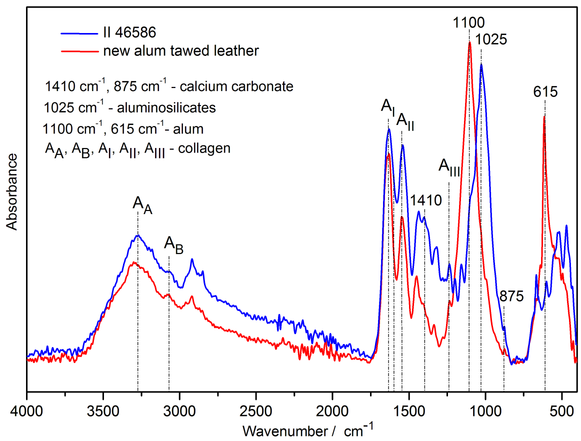


Figure 13. FTIR-ATR spectrum of the leather cover (II 46586) compared to that of new alum-tawed leather. The main absorption bands of collagen are highlighted (AA, AB, AI, AII, AIII), as well as those attributed to calcium carbonate, alum and aluminosilicates

- *calcium carbonate*: comes from the manufacturing process
- *alum*: the tanning agent
- *aluminosilicates*: dust (dirt) adhering to the surface of the cover
- *low A_I/A_{II} ratio*: indicates the hydrolytic cleavage of peptide bonds of collagen

Materials Added to Leather Identified by XRF - Figure 14

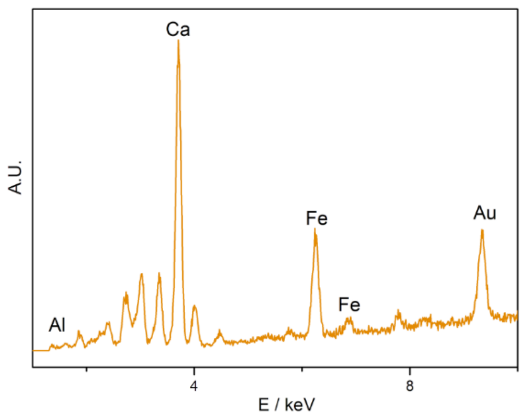


Figure 14. XRF spectrum of leather cover (II 46586). Goethite (Fe) – yellow-brown pigment used in cover decoration; Gold – letters applied to the leather cover. The presence of calcium carbonate and alum is confirmed.

Conservation Sheet for a Reused Parchment Bookbinding

Call number: **C. R. I 39622**

Author: Daneau, Lambert 1530 – 1595/ Vignon, Eustache 1530 - 1588 |4 tip.

Editor: Genevae, Apud Eusthatium Vignon 1580 [4] f., 162[-167] p. in 8° (180 x 117 mm)

Title page: Elenchi haereticorum. Ubi facili et singulari methodo explicatur qua ratione haereticorum paralogismi deprehendi et solui possint. Liber omnibus Evangelicae veritatis studiosis valde necessarius |f Lamberto Danaeo authore, a quo nunc primum auctus que recognitus cum Indice locupletissimo

Dating: 1580

Polemic theology// dialectics

Bookbinding type: reused parchment, written in black, red and blue ink (Figure 15)

Figure 15. Overview of the reused parchment cover: recto (left image) and verso (right image)

Macroscopic and Microscopic Characteristics

-Microscopic identification of the animal species: calfskin

-The macroscopic view shows mechanical damage, marginal fraying, dirt adhering to the surface, spots of different nature (water or other liquids, lime) and foxing (Figures 16a and 2b)

-Microscopic view (the morphology) of water-dispersed fibers, the majority of fibers exhibit good cohesiveness, the tendency to lose their helical character and to flatten is minimal. No gelatinous fibers and no fragmented fibers are observed.

-Microscopic view of inks: black ink is slightly discolored, blue ink is exfoliated, while red ink is well preserved (Figures 16c and 2d).

(a) (b)

(c)

(d)

Figure 16. (a) Macroscopic image illustrating adherent dirt and various stains on the parchment surface. Microscopic images illustrating: (b) lime spots on the parchment surface; (c) slightly discoloured black ink; (d) exfoliated blue ink and well-preserved red ink.

Hydrothermal Stability of Parchment Determined by MHT Method

MHT parameters indicating hydrothermal stability (T_s - shrinkage temperature, T_f – the temperature when the first fiber shrinks, T_l - the temperature when the last fiber shrinks) and structural heterogeneity (C - the main shrinkage interval, ΔT - total shrinkage interval) for a parchment sample taken from a damaged area of the cover are presented in Table 2 in comparison with those corresponding to a new parchment.

Table 2: MHT parameters for a parchment sample taken from the cover and for a new parchment

Sample / Parameters	Hydrothermal stability			Structural heterogeneity	
	T_s / °C	T_f / °C	T_l / °C	C/ °C	ΔT / °C
New parchment	58.4 ± 0.4	52.8 ± 0.5	72.0 ± 0.4	5.4 ± 0.9	19.2 ± 0.9
I 39622	46.9	35.3	79.0	10.1	43.7

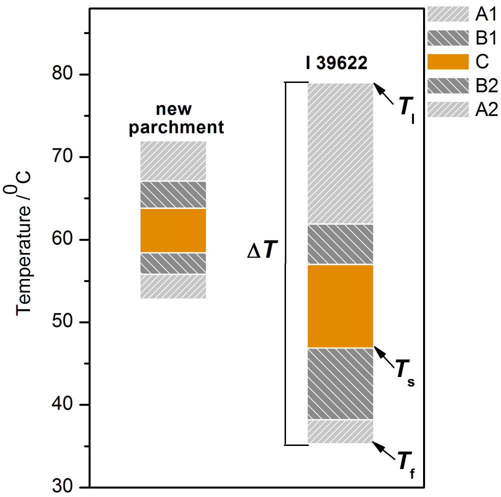


Figure 17. Graphic illustration of shrinkage intervals (A1, B1, C, B2, A2), highlighting MHT parameters for the parchment sample taken from the cover and for a new parchment. Assessment of deterioration degree [12]: undeteriorated parchments, $T_f > 45$ °C; $T_s > 50$ °C; parchments with minor deterioration degree, 40 °C < T_f < 45 °C; 45°C < T_s < 50 °C; parchments with medium deterioration degree, 35 °C < T_f < 40 °C; 40 °C < T_s < 45 °C; parchments with major deterioration degree, $T_f \leq 35$ °C; $T_s \leq 40$ °C

According to the classification criteria for the degree of deterioration according to the parameters T_s and T_f, the cover of the parchment presents a minor degree of deterioration. However, the structural heterogeneity of the parchment is very high compared to that of a new parchment (Figure 17), indicating the presence of several collagen populations with distinct thermal stabilities, including thermally unstable, pregelatinized and gelatinized collagen fractions [14].

Keeping it under controlled temperature and relative humidity conditions is recommended. Conservation or restoration interventions, especially wet treatments, are not recommended.

Molecular Changes and Added Materials Identified by FTIR-ATR - Figure 18

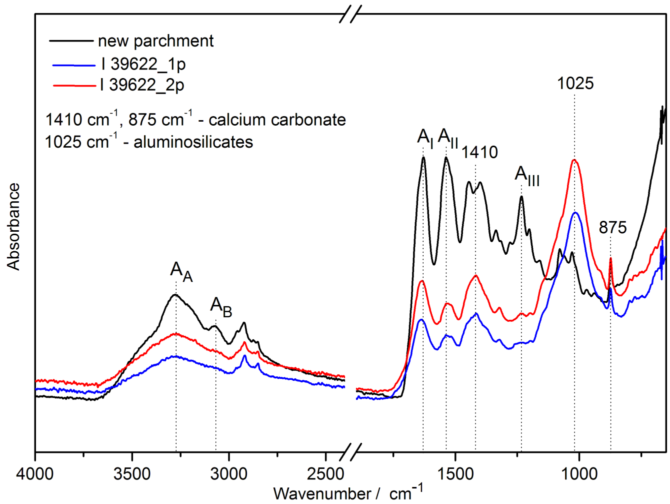
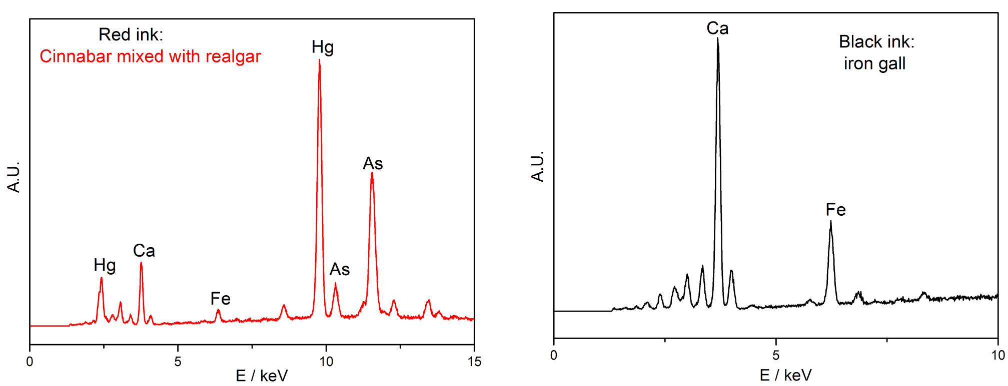


Figure 18. FTIR-ATR spectra recorded for 2 parchment samples taken from the cover and for a new parchment. The main absorption bands of collagen are highlighted (A_A, A_B, A_I, A_{II}, A_{III}), as well as those attributed to calcium carbonate, alum and aluminosilicates.

- *calcium carbonate*: originats from the manufacturing process
- *aluminosilicates*: dust (dirt) adhering to the surface of the cover
- *low A_I/A_{II} ratio*: indicates the hydrolytic cleavage of peptide bonds of collagen
- *A_{III} band completely disappears*: indicates the presence of collagen populations with disorganized structure.

Materials Added to Parchment Identified by XRF - Figure 19



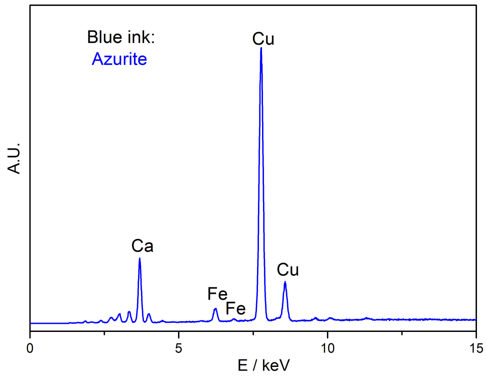


Figure 19. XRF spectra of inks applied to the parchment cover (I 39622). Red ink: mixture of cinnabar (HgS) and realgar (As_4S_4); blue ink: based on Cu (probably azurite); black ink: ferogallic (identification based on the presence of Fe in the XRF spectrum). The presence of calcium carbonate on the parchment surface is confirmed.

CONCLUSIONS

Over 50 bindings in alum-tawed (white) leather, parchment and reused parchment were analyzed in situ using specific non-invasive or micro-invasive analysis methods such as visual and microscopic analyses, thermal microscopy (imageMHT method), attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) spectroscopy and X-ray Fluorescence Spectrometry (XRF). Based on these results, conservation sheets have been drawn up including damage status, threats and conservation recommendations for each investigated bookbinding. The main findings of the study refer to the ornaments for white leather and parchment bindings as well as identification of materials, inks and pigments and evaluation of damage status of parchment and leather.

For both alum-tawed leather and parchment, the structural heterogeneity is quite high suggesting the presence of several collagen populations with distinct thermal stability: collagen “stabilized” by the reaction with aluminum salts or by dehydration and consequent crosslinking, “free” collagen resulting from the “detanning” process, “destabilized” collagen from hydrolytic and oxidative processes and pregelatinized and gelatinized collagen fractions in case of parchments. The thermally unstable, pregelatinized and gelatinized fractions of collagen are susceptible to being affected by high and/or oscillating RH in the storage, consultation or exposure spaces, as well as by wet conservation or restoration treatments. Such inappropriate storage/exhibition/use conditions and/or conservation treatments represent a high risk of solubilization of unstable fractions, appearance of sticky areas or crack formation (craquelé appearance), loss of collagen.

ATR-FTIR parameters such as A_I/A_{II} ratio were used to characterize the molecular alterations of collagen structure. For example, low A_I/A_{II} ratio indicates the hydrolytic cleavage of peptide bonds of collagen, while the reduction or disappearance of A_{III} band indicates the presence of collagen populations with disorganized structure.

Alum was identified by both ATR-FTIR and XRF techniques. Identification of black ferogallic ink was based on the presence of Fe in the XRF spectrum. Red, blue and gold inks were also identified. In most cases red ink was a mixture of cinnabar (HgS) and realgar (As_4S_4), blue ink was a copper-based pigment (most probably azurite), while golden ink was liquid gold. Calcium carbonate originating from the manufacturing process, aluminosilicates from the dust (dirt) adhering to the surface of the covers are also present on the surface of all bindings.

Two conservation sheets are included at the end of this paper as exemplifying material.

Acknowledgements

The study was funded by the Ministry of Research and Innovation and UEFISCDI within the project: Natural leather for contemporary design, LeatherCoDe, Contract no. 176CI/2018, PN-III-CERC-CO-CI-2018.

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LEATHER AS A POTENTIAL LINER FOR THE PROSTHETIC LEG USERS

Arife Candaş ADIGÜZEL ZENGIN*, Nilay ÖRK, Ümitcan YIĞIT, Behzat Oral BITLISLI

Ege University, Engineering Faculty, Leather Engineering Department, 35100, Bornova, Izmir, Turkey,

candas.adiguzel@ege.edu.tr

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LEATHER AS A POTENTIAL LINER FOR THE PROSTHETIC LEG USERS

ABSTRACT. Wear comfort and hygiene is responsible for the significant improvement in the life quality of many amputees and in this regard liners have an important role for the prosthetic leg users. They are protective materials used as covers and worn over the residual limb before the socket to prevent the discomfort occurred during the movements of the patients. Liners are made of different synthetic flexible materials and designed with specific features for different suspension systems. Selecting a correct liner depends on the activity level and needs of the users in addition to the suspension system of the prosthetic leg. Although liners ensure wearing comfort to the users, feeling uncomfortable occurs due to perspiration and lack of evaporation. In this context, leather has advantages due to its triple helix collagen fibers and seems to be a perfect alternative natural material to synthetic liners. For this purpose, the production of a leather liner as an alternative to synthetic liners was aimed to perform for the prosthetic leg users. Chromium free leathers were manufactured based on the properties of the synthetic liners found in the market and the physical, mechanical and comfort properties of the liners in terms of water vapor permeability, static water absorption, tensile strength, elongation at break, tear strength, rubbing fastness and thickness were determined. The results revealed that leather could be used as an alternative natural liner for the use of prosthetic legs and has become prominent due to its wear comfort, hygiene and mechanical properties.
KEY WORDS: leather, prosthesis, liner

PIELEA CA POTENȚIALĂ CĂPTUȘEALĂ PENTRU PROTEZE

REZUMAT. Confortul în purtare și igiena sunt responsabile pentru îmbunătățirea semnificativă a calității vieții multor persoane cărora li s-au amputat membre și, în acest sens, căptușelile au un rol important pentru utilizatorii de proteze. Acestea sunt materiale de protecție folosite ca înveliș și purtate peste membrul rezidual înainte de a pune proteza pentru a preveni disconfortul care apare în timpul mișcării pacienților. Căptușeala este fabricată din diferite materiale sintetice flexibile și proiectate cu caracteristici specifice pentru diferite sisteme de suspensie. Selectarea unei căptușeli corecte depinde de nivelul de activitate și de nevoile utilizatorilor, pe lângă sistemul de suspensie al piciorului protetic. Deși căptușeala asigură confortul purtătorilor, senzația de disconfort apare din cauza transpirației și a lipsei de evaporare a acesteia. În acest context, pielea are avantaje datorită fibrelor de colagen cu structură de triplu helix și, fiind un material natural, este o alternativă perfectă pentru căptușelile sintetice. În acest scop, s-a propus căptușeala din piele ca alternativă la căptușelile sintetice, funcțională pentru utilizatorii de proteze. Pieile fără crom s-au fabricat pe baza proprietăților căptușelilor sintetice găsite pe piață și s-au determinat proprietățile fizice, mecanice și de confort ale căptușelilor în ceea ce privește permeabilitatea vaporilor de apă, absorbția statică a apei, rezistența la tracțiune, alungirea la rupere, rezistența la sfâșiere, rezistența la frecare și grosimea. Rezultatele au arătat că pielea poate fi utilizată pentru căptușeli naturale alternative utilizate în proteze și este importantă datorită confortului în purtare, igienei și proprietăților sale mecanice.
CUVINTE CHEIE: piele, proteză, căptușeală

LE CUIR COMME DOUBLURE POTENTIELLE POUR LES PROTHÈSES

RÉSUMÉ. Le confort et l'hygiène sont responsables de l'amélioration significative de la qualité de vie de nombreuses personnes amputées d'un membre, à cet égard, les doublures ont un rôle important à jouer pour les utilisateurs de prothèses. Ce sont des matériaux de protection utilisés comme couvertures et portés sur le membre résiduel avant la pose de la prothèse pour éviter l'inconfort survenu lors des mouvements des patients. Les doublures sont fabriqués à partir de différents matériaux synthétiques flexibles et conçues avec des caractéristiques spécifiques pour différents systèmes de suspension. Le choix d'une doublure appropriée dépend du niveau d'activité et des besoins des utilisateurs, en plus du système de suspension de la jambe prothétique. Bien que les doublures assurent le confort des utilisateurs, le sentiment de malaise survient en raison de la transpiration et du manque d'évaporation. Dans ce contexte, le cuir présente des avantages en raison de ses fibres de collagène à triple hélice et semble constituer un matériau de remplacement naturel idéal pour les doublures synthétiques. À cette fin, la production d'une doublure en cuir en tant qu'alternative aux doublures synthétiques a été destinée aux utilisateurs de prothèses. Des cuirs sans chrome ont été fabriqués sur la base des propriétés des doublures synthétiques disponibles sur le marché, et on a déterminé leurs propriétés physiques, mécaniques et de confort, la perméabilité à la vapeur d'eau, l'absorption statique d'eau, la résistance à la traction, l'allongement à la rupture, la résistance au déchirement, la résistance au frottement et l'épaisseur. Les résultats ont révélé que le cuir pourrait être utilisé comme une doublure naturelle alternative utilisée dans les prothèses et il est devenu une priorité en raison de son confort, de ses propriétés hygiéniques et mécaniques.
MOTS CLÉS : cuir, prothèse, doublure

* *Correspondence to: Arife Candaş ADIGUZEL ZENGIN,Ege University, Engineering Faculty, Leather Engineering Department,Bornova, İzmir, candas.adiguzel@ege.edu.tr*

INTRODUCTION

The lack of prostheses comfort occurred due to the heat and perspiration are the main problems of the amputee people and till now no correlation has been found with the prosthesis type, amputation cause, and amputated limb [1-3]. The heat inside the prosthetic socket leads to perspiration and many complaints have arisen about health, discomfort, odor as well as the use of prostheses [3]. Up to now, aesthetic and biomechanical properties of the prostheses have the major attention and prostheses are produced without taking into consideration the heat, perspiration, discomfort and cold stress problems [3, 4]. In recent years, a liner company has introduced a new type of liner with a phase change material as a potential solution for heat and perspiration discomfort [3, 5] and a prototype with air-based helical cooling channel is designed for the prosthetic socket [6]. Besides, Ghoseiri *et al*., 2016, have studied the prototype of a thermoregulatory system for measurement and control of temperature inside prosthetic socket as well as the evaluation of the prototype functionally [3, 7]. However, further studies are needed to confirm the efficiency of the systems to resolve the discomfort complaints of the users [5], although measuring and quantifying the comfort is difficult [1].

Liners are covers worn over the residual limb before the prosthetic sockets and have an important role in terms of wear comfort and hygiene. They are produced by different synthetic materials such as silicone, polyurethane and copolymer and designed for different suspension systems. Although liners ensure wearing comfort to the users, discomfort occurs due to the perspiration and lack of evaporation. Although there are some studies on resolving the thermal discomfort [3-7], no study has been published about manufacturing a leather liner for the amputees. From the point of wear comfort and hygiene, leather has advantages due to its triple helix collagen fibers and seems to be a perfect alternative natural material to synthetic liners.

In this study, the manufacturing of a leather liner as an alternative to synthetic liners was aimed for the prosthetic leg users. Chromium free leathers were manufactured based on the properties of the synthetic liners (gel and silicone based) found in the market and the performance properties in terms of water vapor permeability, static water absorption, tensile strength, elongation at break, tear strength, rubbing fastness and thickness were determined.

EXPERIMENTAL

Materials

The synthetic commercial liners based on gel and silicone material were obtained from Deva Orthopedics in Izmir, Turkey. Gel (2 with socks and 1 without sock) and silicone liners were used in the study to compare the physical, mechanical and comfort properties with the produced chromium free leathers.

In the study, four pickled domestic sheepskins were used for the chromium-free tanning procedure. Zirconium and aluminum were used as the main tanning materials and the conventional leather chemicals were used in the production processes. The pickled sheep skins used in tanning trials were supplied from Güvener Company in Izmir, Turkey.

Methods

Tanning Procedure

Depickling, bating and degreasing processes were performed to pickled sheepskins with conventional formulation and the pelts were tanned with 4% zirconium and 4% aluminum over skin weight. After the tanning process, leathers were converted into crust leathers by retanning and fatliquoring processes, using synthetic sulphited and combination fatliqours. No finishing application was performed and the recipe of the leather manufacturing is given in Table 1.

Table 1: Tanning procedure of the chromium free leathers

Process	Amount (%)	Product	Temp(°C)	Time(Min.)	pH
Depickle	150	Water 6°Be	28-30	10	
	2	HCOONa		30(15*2)	
	1	$NaHCO_3$		90	4.5-5
Bating	100	Water	35		

	2	Acidic bating enzyme		60	
Washing	100	Water	25-28	15	
Degreasing	5	Degreasing agent	35	90	
Washing	200	Water 3°Be		10	
Washing	200	Water 3°Be		10	
Pickling	50	Water 7°Be		20	
	2	Synthetic fatliquor (electrolyte stabile		40	
	2	Modified aldehyde		30	
	2	HCOOH		45	
	1	H_2SO_4		60	1.5-2
Tanning	4	Zirconium	30	60	
	4	Aluminum triformate		60	
	+50	Water	10		
	1	HCOONa		30	
	1	$NaHCO_3$		30(10*3)	4
		Mechanical Processes			
		Washing & Draining			
Neutralization	100	Water	30		
	2	Neutral syntan		30	
	2	Synthetic fatliquor (electrolyte stabile		60	5
Retanning	80	Water	35		
	3	Formaldehyde free syntan		30	
	5	Tara		45	
	3	Synthetic fatliquor (electrolyte stabile		30	
	3	Acrylic syntan		30	
	2	Modified aldehyde		45	
	+50	Water	65		
	5	Synthetic fatliquor			
	5	Combination fatliqour			
	2	Sulphited fatliquor		60	
	3	HCOOH		90	3.8-4

Later, the half of the chromium-free crust leathers was laminated with spandex fabric to increase the elasticity of the crust leathers for the use in prosthetic legs as a liner [8].

Determination of Physical, Mechanical and Comfort Properties of the Liners

The physical, mechanical and comfort properties of the synthetic and leather liners were determined in order to compare the properties of the liners and to produce an alternative leather liner for the prosthetic legs.

Subsequent to sampling of the synthetic liners and leathers (TS EN ISO 2418), the samples were conditioned at 23±2°C and 50±5% relative humidity for 48 h in accordance with the standard of TS EN ISO 2419 prior to the tests [9, 10].

The comfort properties of the liners were determined in terms of water vapor permeability and static water absorption in accordance with the standards of TS EN ISO 14268 (2004) and TS 4123 EN ISO 2417 (2005) respectively [11, 12].

Mechanical resistance of the liners were investigated by performing the tests of tensile strength, and elongation at break (TS EN ISO 3376) and tear strength (TS EN ISO 3377-2) with reference to standard methods respectively [13, 14].

The thickness of the samples was determined with SATRA Thickness Gauge with the standard of TS EN ISO 2589 [15].

The rubbing fastness properties of the samples were examined with a Bally Finish Tester 9029 according to TS EN ISO 11640 standard (100 rubs dry and 25 rubs wet) [16]. The tests were done in duplicates and the results were given as mean values and the standard deviations.

RESULTS AND DISCUSSIONS

The physical, mechanical and comfort properties of the gel, silicone and leather liners were determined and comparatively evaluated.

The thickness values of the gel, silicone and leather liners are given in Figure 1. Crust chromium free leathers were found the thinnest material compared to other liners including stretched leathers. By the lamination of the leather with spandex fabric, an increase was found in thickness values, however the leather liners were found still thinner than the commercial liners (Figure 1). The thickness values of the gel liners were determined between 5.9 and 6.1 mm due to the incorporation of the cotton material. To have a high thickness value seems to have an advantage because thick and soft materials could help to prevent the feeling of discomfort occurred during the movements of the prosthetic leg users.

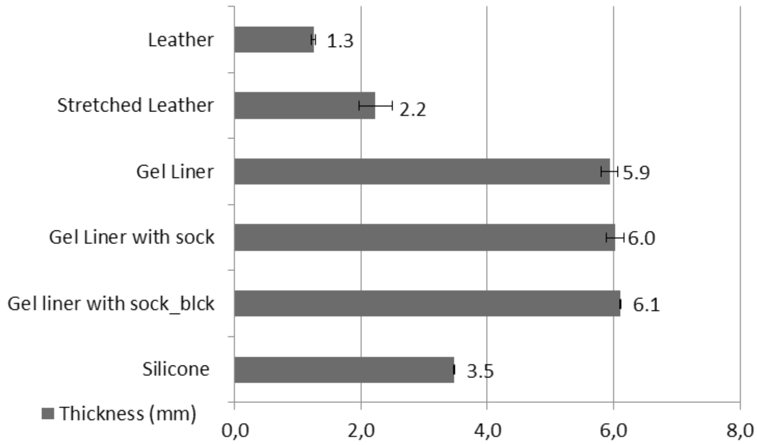

Figure 1. Thickness results of the liners

Comfort Properties of the Liners

Silicone based liner had the lowest water vapor permeability with the result of 0.08±0.01 mg/cm^2h. Gel liners with socks had higher results compared to silicone, however lower results were obtained in comparison to gel and leather liners. The highest result was determined from the gel liner among the common used synthetic liners. However, it does not seem sufficient from the point of wear comfort and hygiene due to the complaints of the patients [3-7]. The natural character of the leather, also in the form of with and without stretched, provides a considerably high water vapor permeability compared to gel and silicone liners and leather could be manufactured in the view of the required qualifications from the liners and be used as an alternative natural liner (Figure 2).

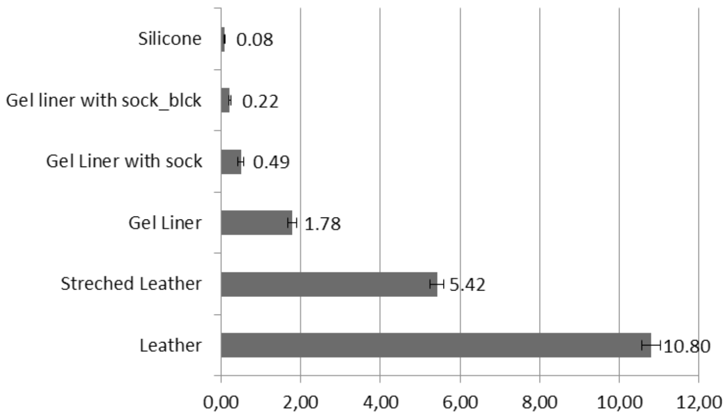

Figure 2. Water vapour permeability results of the liners

The static water absorption (Kubelka) test results at six different time interval are shown in Table 2. In contrast to the results of water vapor permeability, the minimum water uptake was determined from the gel liner and the increase in water uptake was due to the cottons that incorporated to the gel liners. Although silicone based liner had very low water vapor permeability, the water uptake capacity was found higher than the gel liners. The different Kubelka results of the leathers were due to the lamination of spandex fabric on the suede side of the chromium free leathers. This spandex fabric prevented the water uptake into the leather and resulted 10% decrease in water absorption results of the stretched leathers (Table 2).

Table 2: Static water absorption results of the liners

	1/12h	1/4h	1/2h	1h	2h	24h
Silicone	16.17±0.16	30.74±2.60	33.95±1.94	35.57±0.36	37.18±1.91	46.83±1.81
Gel liner with sock_blck	4.49±1.27	4.49±1.27	4.49±1.27	4.49±1.27	6.29±1.27	8.98±2.54
Gel Liner with sock	10.95±1.43	12.94±1.44	12.94±1.44	12.94±1.44	13.94±0.03	16.93±1.45
Gel Liner	0±0	0±0	0±0	1.78±0.02	1.78±0.02	6.25±1.33
Stretched Leather	154.21±29.32	161.93±32.15	166.01±29.82	169.65±34.98	174.25±38.78	179.54±38.18
Leather	177.89±31.58	181.82±37.13	189.28±37.68	189.28±37.68	193.01±37.96	198.31±30.46

Comfort properties of the liners showed that leathers with high water vapor permeability and static water absorption characteristics could be one of the reasons to be used as a potential liner for the prosthetic leg users. Leather liners could absorb the sweat generated during the movements and help to evaporate the sweat which provides wear comfort and hygiene to prosthetic leg users.

Mechanical Resistance of the Liners

The mechanical resistance of the liners in terms of tensile and tear strength are given in Table 3. The tensile and tear strengths of the leathers were found higher than the synthetic liners. Although the lamination process with spandex fabric caused a decrease in tensile strength, no significant difference in tear strength values was observed.

Tear strength values of the gel and silicone liners were determined higher than the tensile strength values and the strengths of the gel and silicone liners were found considerably lower than those of the leathers.

In contrast to strength values of gel and silicone liners, the elongation at break (%) values were found nearly 4 times higher than the leather liners. This is the expected result that generates because of the raw material of the liners. And the lamination of the leathers with spandex fabric was performed to improve the percentage of elongation at break values. And positive results were achieved (Table 3). The tensile and tear strength properties of the leathers were found adequate in accordance with UNIDO [17] acceptable leather qualities.

Table 3: Mechanical resistance of the liners

	Tensile strength (N/mm^2)	Elongation (%)	Double edge tear strength (N)/(mm)
Silicone	1.15±0.0	325.7±0.0	25.42±0.48
Gel liner with sock_blck	0.96±0.0	456.4±0.0	6.98±0.0
Gel Liner with sock	1.09±0.28	350.94±61.24	16.36±1.08
Gel Liner	0.36±0.04	500±0.0	3.24±0.0
Stretched Leather	17.51±0.25	97.3±0.65	68±0.06
Leather	31.82±0.51	80.4±3.47	70.24±1.72

The mechanical results of the leather liners showed that the main advantage for the users is the long-term use of leather liners compared to the gel and silicone liners due to their high mechanical properties.

Table 4: Rubbing fastness results of the liners

	Dry		Wet	
	Felt	Material	Felt	Material
Leather liners	5	5	4/5	4/5
Synthetic liners	5	5	5	5

Rubbing fastness values of the liners are shown in Table 4. The rubbing fastness values of synthetic and leather liners were found similar except from the leathers rubbed in wet condition.

CONCLUSIONS

In the study, leather liners as an alternative to synthetic liners were produced for the prosthetic leg users based on the properties of the synthetic liners (gel and silicone based) found in the market and following conclusions have been drawn:

a. Leather liners had considerably high water vapor permeability and static water absorption values compared to gel and silicone liners.
b. The high mechanical resistance of the leather liners provides a long-term use to the prosthetic leg users.

c. Leather liners gain advantages over synthetic liners in terms of wear comfort, hygiene and long-term use and could be a perfect potential natural liner compared to synthetic liners.
d. To eliminate the discomfort feeling of the patients during the movements, leather liners could be produced as multilayer liners.
e. The findings of the study are important because new field of application for leather industry is found and the production of high performance leathers for the liners of the prosthetic users has a considerable potential needed to be strengthened by the cooperation of orthopedic device companies.

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BIO-COMPOSITES WITH LEATHER FIBERS AND CEMENT - PHYSICO-MECHANICAL AND STRUCTURAL CHARACTERIZATION

Gabriel ZĂINESCU[1], Viorica DESELNICU[1*], Roxana CONSTANTINESCU[1], Claudiu CIULACU[2]

[1]National R&D Institute for Textiles and Leather - Division: Leather and Footwear Research Institute, 93 Ion Minulescu st., 031215, Bucharest, Romania, e-mail: icpi@icpi.ro

[2]S.C. PROCEMA - Cercetare SRL, 6R Preciziei st., sector 6 Bucharest, Romania, e-mail: office@procema-cercetare.ro

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BIO-COMPOSITES WITH LEATHER FIBERS AND CEMENT - PHYSICO-MECHANICAL AND STRUCTURAL CHARACTERIZATION

ABSTRACT. Circular economy systems keep the added value in products for as long as possible and eliminate waste. Resources are kept within the economy when a product has reached the end of its life, so that they can be productively used again and again and hence create further value. In this context, the specialists from leather and footwear sector look for innovative solutions for utilization of leather wastes for obtaining of new bio-composites with application in construction industry. This paper presents utilization of leather wastes for obtaining construction materials for pedestrian walkways (paving blocks) containing leather fibers obtained from leather waste and their physical-mechanical and structural characterization.
KEY WORDS: leather waste, leather fibers, concrete, bio-composite

BIO-COMPOZITE CU FIBRE DE PIELE ȘI CIMENT - CARACTERIZARE FIZICO-MECANICĂ ȘI STRUCTURALĂ

REZUMAT. În economia circulară, sistemele mențin valoarea adăugată a produselor cât mai mult timp posibil și elimină deșeurile. Resursele se păstrează în cadrul economiei atunci când un produs a ajuns la sfârșitul vieții sale, astfel încât să poată fi folosit din nou și din nou și, prin urmare, să creeze o valoare suplimentară. În acest context, specialiștii din sectorul pielăriei și încălțămintei caută soluții inovatoare pentru utilizarea deșeurilor de piele pentru obținerea unor noi bio-compozite cu aplicații în industria construcțiilor. Această lucrare prezintă utilizarea deșeurilor de piele pentru obținerea materialelor de construcție pentru pavele pietonale care conțin fibre de piele obținute din deșeurile de piele și caracterizarea fizico-mecanică și structurală a acestora.
CUVINTE CHEIE: deșeuri de piele, fibre de piele, beton, bio-compozite

BIO-COMPOSITES AVEC DES FIBRES DE CUIR ET DE CIMENT - CARACTÉRISATION PHYSICO-MÉCANIQUE ET STRUCTURELLE

RÉSUMÉ. Les systèmes d'économie circulaire conservent la valeur ajoutée des produits le plus longtemps possible et éliminent les déchets. Les ressources sont conservés dans l'économie lorsqu'un produit est en fin de vie, de sorte qu'il peut être utilisé encore et encore, créant ainsi une valeur ajoutée. Dans ce contexte, le spécialiste du secteur du cuir et de la chaussure recherche des solutions innovantes pour l'utilisation des déchets de cuir afin d'obtenir de nouveaux bio-composites destinés au secteur de la construction. Cet article présente l'utilisation des déchets de cuir pour obtenir des matériaux de construction pour les chaussées piétonnes contenant des fibres de cuir dérivées de déchets de cuir et leur caractérisation physico-mécanique et structurelle.
MOTS CLÉS : déchets de cuir, fibres de cuir, béton, bio-composites

* *Correspondence to: Viorica DESELNICU, National R&D Institute for Textiles and Leather - Division: Leather and Footwear Research Institute, 93 Ion Minulescu st., 031215, Bucharest, Romania, e-mail: icpi@icpi.ro*

INTRODUCTION

European Leather Sector

Europe is an important player in the international leather trade. With some 25% of the world's leather production and one of the largest and most dynamic consumer markets for leather articles, Europe stands out as the leading force in international business circles in relation to leather and tanning.

With a turnover of nearly € 8 billion, over 3000 companies and some 50000 people directly employed in the sector, Europe's tanneries demonstrate their competitiveness on the global market. Their products are renowned and appreciated by manufacturers worldwide for their quality and fashionable designs. European leathers are exported all over the world to satisfy the highest standards, the most stringent ecological regulations and the increasing expectations of quality aware consumers [1].

Tanners in Europe have a long tradition of producing all kinds of leather, from bovine and calf leather to sheep and goat leather, from sole and exotic specialities to double-face garment leather. Their expertise contributes to the success of leading footwear, garment, furniture and leather goods manufacturers (Figure 1). This solid experience and the outstanding know-how of European tanners and dressers is displayed at major international fairs. All this explains the continuously strong demand for their products on international markets.

The European leather industry is committed to a socially and environmentally sustainable development.

Figure 1. The current use of finished leather [2]

The depollution task associated to leather processing activities falls into the range of medium to high difficulty. Solid wastes (wastes from tanned and not tanned hides and sludge resulting from waste water treatment) represent a big problem of the leather sector. In tanneries, only about one third of the total mass of starting materials (hides and skins) is converted into leather, while the two thirds occur either as dissolved or solid wastes [3].

From the total mass of hides and skins, nearly 4.4 mill tons (EU 700 000 tons) of solid waste (moisture content 70-80%) with a content of over 1.2 mill tons (EC 190 000 tons) of utilizable dry proteins will occur. Only a part of these proteins have been utilized so far, especially for animal nutrition, but the EC – legislation (due to BSE – crisis) has closed this line (except few still permitted applications). Since the utilization of the mentioned solid tannery wastes is, so far, only possible to a limited extent, the problem of disposal is already evident in EU [4], in USA [5] or will arise in the near future for the developing countries as Romania. A pure incineration is not feasible due to an insufficient energy yield (high drying costs) and the formation of Green House Gases (CO_2, NOx). On the other hand, collagen (main component of fleshings, trimmings and shavings) is a protein with several functional groups (-CO-NH-, -OH, $-NH_2$ and -COOH) and shows – after treatment – excellent reactivity and glueing properties. Large European tanneries and clusters already perform a separation of fleshings into fat and protein [6] or transfer their wastes to specialized companies (e.g. SICIT S.p.a., Chiampo/ Vicenza, Italy), where they produce from the resulting hydrolysates various fertilizers, some (low-value) auxiliaries for leather [7] and textile. All these treatments lead to rather heterogeneous hydrolysates, and so their further application is limited. The major share of fleshings is still incinerated (in EU).

The footwear industry is a diverse manufacturing sector that utilizes a wide variety of materials to manufacture products ranging from different types and styles of footwear to specialized shoes. Leather, synthetic materials, rubber, and textiles are among the most commonly used basic materials in footwear manufacturing, each material having its own characteristics. Materials significantly affect not only the life of footwear, but also treatment at the end of product life. About 40 different materials are used in footwear manufacturing [8]. Of these, leather has the highest percentage (25%) [9].

In recent years the footwear industry has made significant efforts to improve the efficiency of energy and material consumption, as well as to eliminate the use of hazardous materials in the manufacturing phase. However, the advantages gained in production in terms of environmental protection and improving efficiency of energy use are outweighed by the significant increase in demand for footwear products, the so-called "boomerang" effect [10].

To meet customer needs and to be competitive at the same time, footwear companies have to face two key challenges: to respond quickly to market changes and remain interested in changes in order to identify or establish new trends in consumption. These lead to a shorter life cycle of shoes, and even to a shorter product development cycle for the footwear industry. A lower life cycle for shoes means a higher yield over time, resulting in an increased amount of waste from the footwear sector.

The worldwide footwear production resumed growth in 2017 reaching 23.5 billion pairs, 2% more than in the previous year. Although this is still far from the fast growth pace registered between 2010 and 2014 (+15.4%), it represents a return to a positive dynamic. In terms of its geographic distribution, production continues to be heavily concentrated in Asia where 87% of all pairs of footwear are manufactured. China remains in pole position at the head of the table of the 10 largest footwear consumers where 3 other Asian countries also appear: Pakistan, Japan and Indonesia. These 5 Asian countries represent almost 40% of world consumption. Two thirds of the total European footwear production is focused on three countries, namely: Italy, Spain and Portugal. Italy alone is responsible for approximately 50 percent of production. [11].

Circular Economy

The European Commission adopted in 2016 an ambitious Circular Economy Package**,** which includes measures that will help stimulate Europe's transition towards a circular economy, boost global competitiveness, foster sustainable economic growth and generate new jobs [12-15].

The Circular Economy Package consists of an EU Action Plan for the Circular Economy that establishes a concrete and ambitious programme of action, with measures covering the whole cycle: from production and consumption to waste management and the market for secondary raw materials and a revised legislative proposal on waste. The proposed actions will contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy.

In a circular economy [16], products and the materials they contain are valued highly, unlike in the traditional, linear economic model, based on a 'take-make-consume-throw away' pattern. In practice, a circular economy implies reducing waste to a minimum as well as re-using, repairing, refurbishing and recycling existing materials and products. What used to be considered as 'waste' can be turned into a valuable resource.

Moving towards a more circular economy could deliver benefits, among which reduced pressures on the environment, enhanced security of supply of raw materials, increased competitiveness, innovation, and growth and jobs. However, it would also face challenges, among which finance, key economic enablers, skills, consumer behaviour and business models, and multi-level governance.

The revised legislative proposals on waste [17, 18] set clear targets for reduction of waste and establish an ambitious and credible long-term path for waste management and recycling. One of key element of the revised waste proposal include: Concrete measures to promote re-use and stimulate industrial symbiosis - turning one industry's by-product into another industry's raw material.

Circular economy systems keep the added value in products for as long as possible and eliminate waste. They keep resources within the economy when a product has reached the end of its life, so that they can be productively used again and again and hence create further value. Transition to a more circular economy requires changes throughout value chains, from product design to new business and market models, from new ways of turning waste into a resource to new models of consumer behaviour (Figure 2)

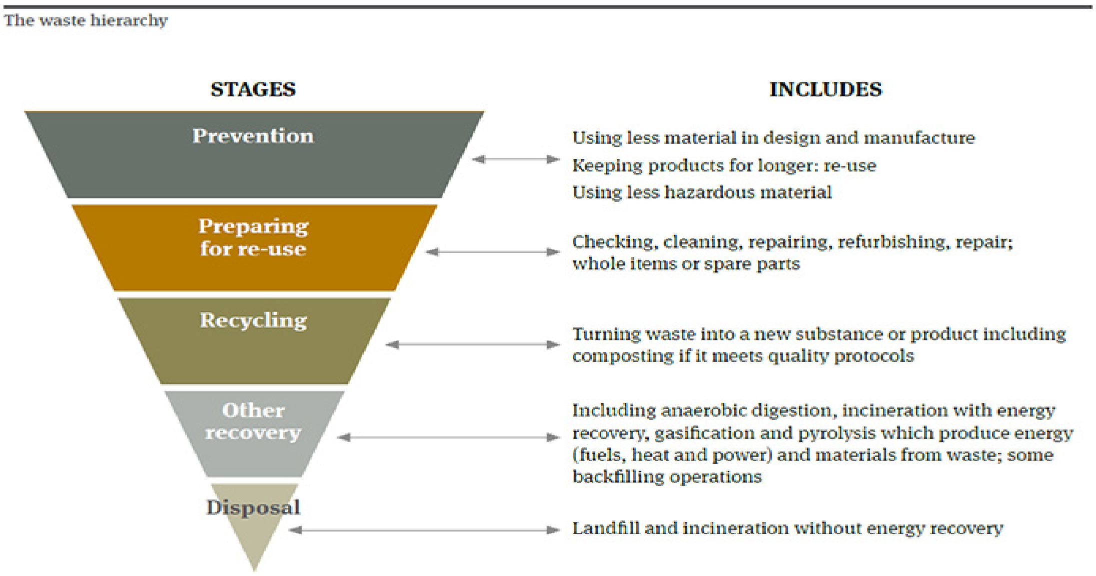


Figure 2. The waste hierarchy [19]

Natural leather fiber reinforced polymers are commonly used in the automotive and construction industry because natural fibers exhibit many advantageous properties such as low weight, low cost, low density, high specific properties and availability from renewable resources [20].

In the same research line, leather fibers can be easily modified with different kinds of polymeric resins. These modified leather fibers can be used in cement based matrices for improvement of tensile strength, toughness and multi-cracking behavior. Because of its natural properties and especially thermal efficiency, leather is an excellent insulation and reinforcing material. The physical properties which make leather a unique and valuable material for different purposes includes: high tensile strength; resistance to tear; high resistance to flexing; good heat insulation; resistance to heat and flame; resistance to mildew; resistance to chemical attack (the atmosphere of modern cities is polluted from the burning of carbon fuels with sulphur dioxide gas, which can accelerate the deterioration of leather; modern leathers are tanned and dressed to resist these harmful chemicals).

Many studies relates utilization of leather waste as raw material for construction materials. In the project TAIMEE (2012-2015) [21], the production and market implementation of an innovative leather composite material which has thermal insulation properties in addition to acoustical isolation properties for immediate application in building sector have been produced and market implemented. Other studies [22-31] relate utilization of leather waste to make light weight concrete and biocomposites for use in construction.

The aim of this paper is to present an innovative production model in the context of the Circulation Economy concept. The main objective is to re-evaluate leather waste from the leather sector by turning it into value-added raw material and use it in the construction materials industry by developing new technologies.

EXPERIMENTAL

Materials

Preparation of Leather Fibers

The leather shavings used in this work as raw material for obtaining of paving blocks were obtained from Pielorex-SA Jilava-Ilfov tannery.

The leather waste was cut using a knife mill equipped with a metal sieve with meshes of 6-9 mm in diameter, resulting in pieces of waste with a surface area of max. 0.5-0.6 cm^2, transported to the storage room, where they are loaded into bags. The leather wastes before grinding were hand-picked with a permanent magnet. An amount of 1500 g of leather fibers was dispersed in 2L water and was subjected to hydrolysis with 1-2% concentrated sulfuric acid solution based on the weight of the leather fibers, at a temperature of 30-50°C for 60 minutes. Then 0.4-0.9% organic polymer binder used in the field of synthetic foil and fiber is poured over leather fibers. This polymer has the role of encapsulating the fibers in a polymeric "shirt". The leather fibers (PFA) are obtained with physical-chemical characteristics presented in Table 1.

Table 1: Physical- chemical characteristics of leather fibers treated with acid (FPA)

Characteristics	UM	FPA	Standard Method
Dry substance	%	8.53	SR EN ISO 4684 : 2006
Ashes	%	18.29	SR EN ISO 4047 : 2002
Total nitrogen	%	12.66	SR ISO 5397 : 1996
Dermal substance	%	71.15	SR ISO 5397 : 1996
Chromium oxide	%	5.16	SR EN ISO 5398/1 :2008
pH	pH units	1.78	STAS 8619/3 :1990
Calcium Oxide	%	0.23	

Values for ash, total nitrogen and dermal substance are reported as free from volatile matter

Production of Paving Blocks

Paving blocks for use in pedestrian walkways have been obtained by utilization of 1% and 3% respectively of treated leather fibers (FPA) following technological process scheme presented in the Figure 1 to obtain high-density concrete (vibrating concrete), based on receipt of S.C. PAV-Consult SRL-Glina-Popesti Leordeni factory [28, 30].

A quantity of 20 m^2 of paving blocks containing 1% and 3% leather fibers were made. Paving blocks with FPA have the dimensions of 280 x 230 x 25 mm.

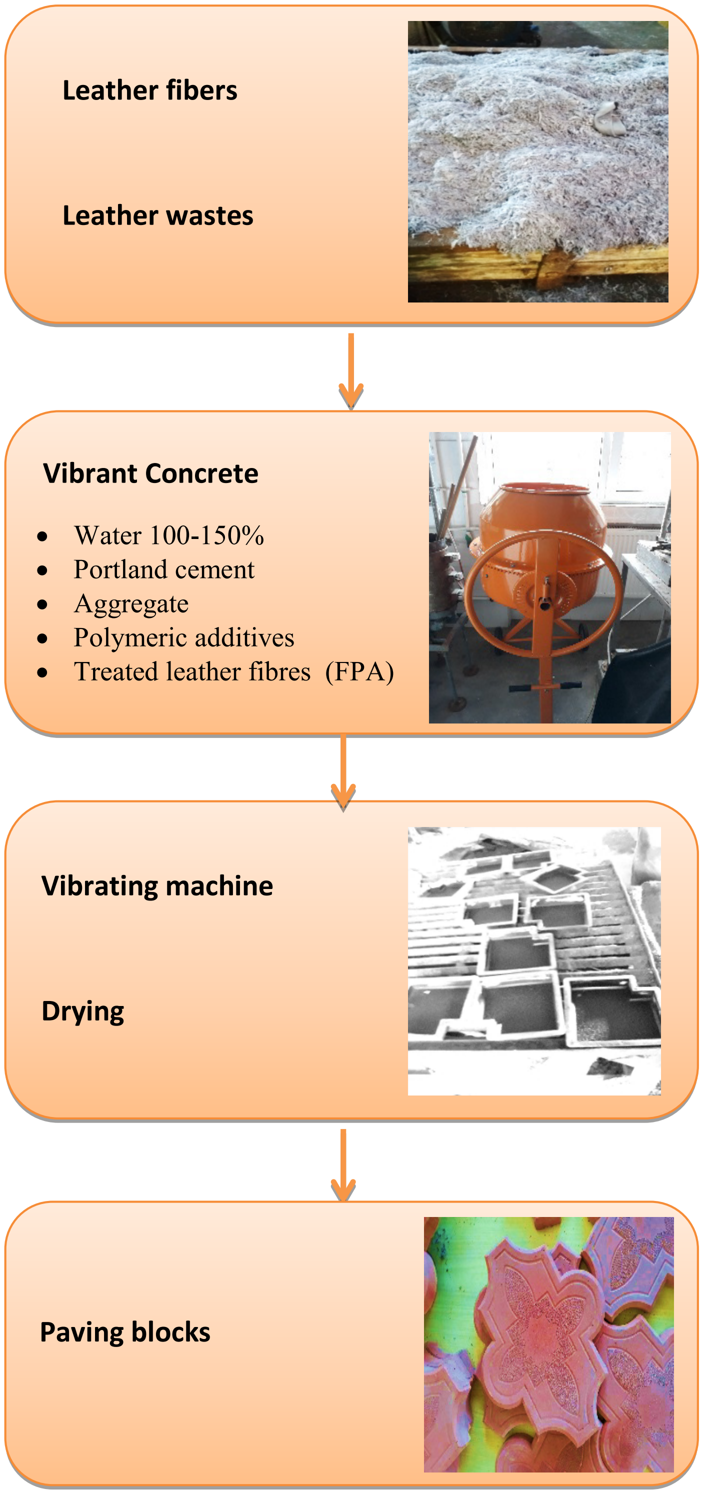


Figure 3. Technological process scheme for obtaining paving blocks with leather fibers (FPA)

Methods

The paving blocks with leather fibers (FPA) made by the technological process of making concrete with vibrating compaction (for pavements) were compared with production of low-density concrete (fluid).

Physical-Mechanical Characteristics

Paving blocks with FPA were analyzed by a specialized laboratory, PROCEMA Cercetare SRL Bucharest (www.procema-cercetare.ro), for physical-mechanical characteristics.

The tensile strength and resistance to action of climatic factors, namely the determination of water absorption, have been measured according to SR EN 1338:2004/AC:2006 - Concrete pavements. Test conditions and methods - according to the procedure: PS-LI 01.

The equipment used for measuring the tensile strength was CONTROLS 04074755 Type: 50 - C56W2 - a compression-bending test system for concrete with compression measuring ranges of 1: 150 kN and another of 0: 3000 kN.

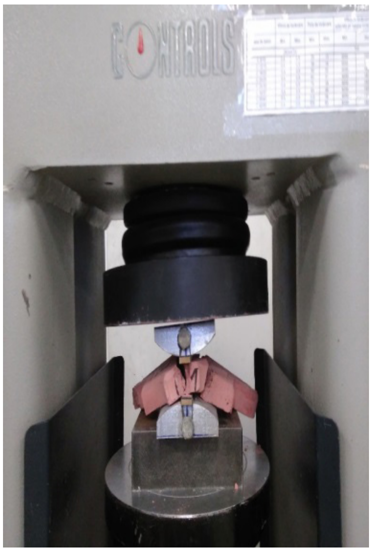


Figure 4. Determination of tensile strength by splitting with CONTROLS 50 - C56W2 system

Microstructural Characterization of Paving Blocks

Microstructural characterization was performed by SEM-EDAX scanning electron microscopy. The samples were analyzed at the Institute for Macromolecular Chemistry "Petru Poni" in Iasi using a Zeiss DSM 940-A scanning electron microscope, with a voltage of 25 kV and a distance of 15 mm.

RESULTS AND DISCUSSIONS

Organoleptic Analysis

As far as the visual aspect is concerned, all analyzed samples of paving blocks have no visible defects (cracks, material detachments), and the texture is uniform of both exposed and tear sections after the splitting test. Also the samples have no color variation on each sample or between different samples.

Tensile Strength by Splitting

Physical-mechanical analysis of paving block samples with FPA fiber, labeled 729 PB-4 (containing 1% FPA), 729 PB-7 (containing 3% PFA) and with 729 PB-M2 (without leather fiber FPA) were performed.

Table 2 presents the results of tensile strength by splitting for the samples with leather fibers compared with control sample without leather fibers. The results obtained by the splitting test indicate a good behavior for the samples with the addition of leather waste (especially for sample 729 PB - 4).

Figure 3 presents images of the specimens after measurement of tensile strength by splitting. Small pieces of leather fibers can be observed in cross section of specimens.

Table 2: Results obtained for tensile strength by splitting

Characteristics	U.M.	Results	Method
Sample Code: 729PB - M2			
Tensile strength by splitting - T	N/mm	3,5	
Load /unit of length - F	MPa	230	
Sample Code: 729PB - 4			
Tensile strength by splitting - T	N/mm	5,0	SR EN 1338:2004/ AC:2006 Annex F PS-IF-06
Load /unit of length - F	MPa	332	
Sample Code: 729PB – 7			
Tensile strength by splitting - T	N/mm	3,3	
Load /unit of length - F	MPa	221	

Figure 5. Images of the specimens after measurement of tensile strength by splitting

Resistance to Action of Climatic Factors (Water Absorption)

Table 3 presents the results of resistance to action of climatic factors (water absorption).

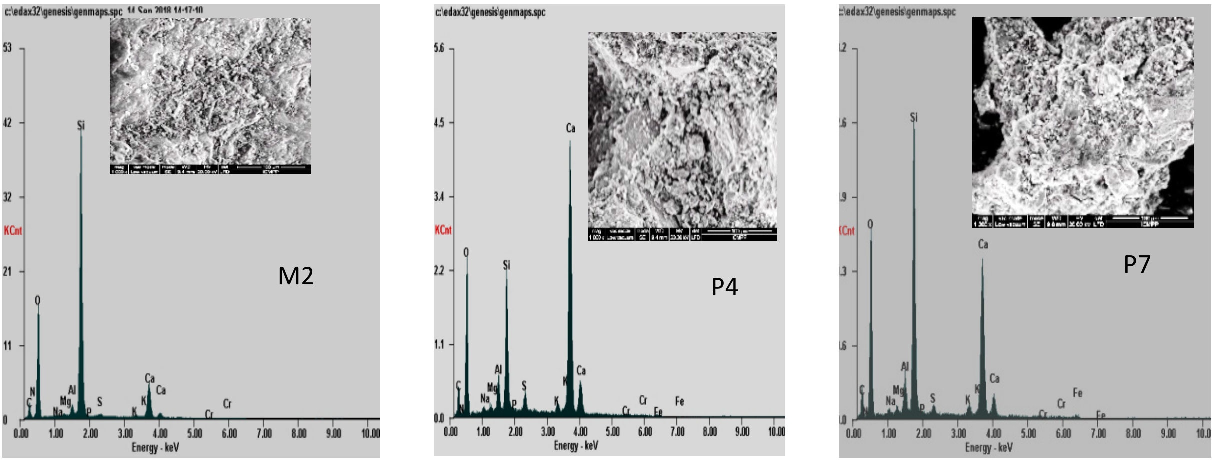
Table 3: Resistance to action of climatic factors (water absorption)

Characteristics	Water absorption, %	Method
Sample Code: 729PB - M2	8,1	SR EN 1338:2004/ AC:2006 Annex E PS-IF-06
Sample Code: 729PB - 4	7,1	
Sample Code: 729PB - 7	7,2	

With regard to the physical characteristics of the climatic factors, namely the determination of the water absorption, a uniform behavior is observed in the two samples with leather fibers FPA compared to the control sample. This characteristic, i.e. determination of the water absorption, is very important because the small values denote that they will be more resistant to the action of climatic factors and especially to the action of the frost-thaw phenomenon.

SEM-EDAX Microscopy

By analyzing the specimens by SEM-EDAX (Figure 4) it is observed that the images of the samples with content of leather fibers (P4 and P7) show surfaces' structure with a large number of portlandite plates (silicon and calcium), reducing the amount of silicified water crystals and consequently, it results in an increase of splitting resistance - a main characteristic of concrete pavements.



6. SEM-EDAX microscopy for control (M2) and samples P4 and P7 of biocomposites

CONCLUSION

This paper presented a new production concept in order to develop bio-based composites with improved properties with application in construction materials. This transformation of an actual waste into new value-added products will lead to remarkable life-cycle-improvements of the starting materials and will close loops in terms of sustainable utilization of former wastes, increasing the eco-efficiency and economic efficiency of leather and footwear sector.

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NATIONAL AND INTERNATIONAL EVENTS

FOLLOW-UP OF THE 7TH INTERNATIONAL CONFERENCE ON ADVANCED MATERIALS AND SYSTEMS - ICAMS 2018

18-20 OCTOBER, BUCHAREST, ROMANIA

The International Conference on Advanced Materials and Systems has become a traditional multi- and inter-disciplinary event that facilitates the exchange of knowledge in the area of advanced experimental or computational environmental technologies to structurally characterize materials and technological systems.

The seventh edition of ICAMS Conference was organized under the patronage of the Romanian Ministry of Research and Innovation, on October 18th-20th, 2018, at Capital Plaza Hotel, Bucharest, featuring in total 100 scientific papers from 233 authors and co-authors from 15 countries (Albania, Algeria, Bulgaria, China, Egypt, Germany, Greece, Israel, Italy, Jordan, Lithuania, Portugal, Turkey, Ukraine and Romania). This edition of the Conference has marked 100 years from the Great Union, and a special session was dedicated to promoting Romanian cultural identity and heritage in the European context by presenting papers on the conservation of heritage leather and parchment objects.

The exciting plenary lectures, oral presentation and poster sessions provided a comprehensive view on issues of great interest related to advanced materials and systems.

After a short introduction made by Dr. Luminiţa Albu as President of the Organizing Committee and Dr. Carmen Ghiţuleasa, General Director of INCDTP, the conference opened with the special session dedicated to the celebration of 100 years from the Great Union, titled “100 Years from the Great Union-Promoting Cultural Identity and Heritage”, where Dr. Octaviana Marincaş, the representative of the Ministry of Research and Innovation, presented the paper “Cultural Identity and Heritage - Romanian Contribution to the European Culture”, highlighting the most significant contributions of notable Romanian people to the cultural development of Europe.

Opening ceremony and the special session dedicated to the celebration of 100 years from the Great Union

The second plenary lecture was presented by Dr. Carmen Ghiţuleasa, titled “The Textile and Leather Industry - from Tradition to Sustainability through Research, Development and Innovation”, comprising a short history of INCDTP in the context of the industrial sector and highlighting its role of research and innovation promoter through representative international projects and results achieved by the institute over the last years as coordinator or partner.

The third plenary lecture, titled "Beyond the Shape and Size Control of Nanoparticles: on the Importance of the Knowledge of Surface Property at a Molecular Level", was held by Prof. Dr. Gianmario Martra from the University of Turin, Italy, revealing the importance of knowing in detail, as well as designing and controlling surface properties of nanoparticles, in order to develop nanoparticles used particularly in biomedical applications, falling into the topical theme of smart materials.

Plenary lectures

The conference thematic constituted one of the most important and topical fundamental and applicative research problems, justified by both the necessities of practice, and the requirements to clarify the effect of the action of multiple factors that favour and influence the development of advanced materials and systems. Conference papers were divided into 10 sections, to which a special session was added dedicated to circular economy, each section chaired by two national or international experts in those fields: **Advanced Functional Materials & Biomaterials, Nanotechnology and Nanomaterials, Emerging Techniques, Smart Materials, Materials Engineering and Performance, Materials Processing and Product Manufacturing, Modelling and Simulation, Materials Characterization, Non-destructive Testing, Advanced Materials & Systems Innovation and a Special Session - Towards a Circular Economy.**

Oral presentation sessions

Participants to the ICAMS International Conference had the opportunity to attend two plenary lectures on major topics of the Horizon 2020 program of the European Commission – smart materials with applications in the biomedical field and responsible research for sustainable development of society. In addition, during the conference were organized 3 workshops dedicated to ERASMUS+ projects (Fit 2 Comfort, LEAMAN and INNOLEA) and one workshop dedicated to InSuLA Manunet project.



Workshops held during the conference

With a participation of 100 Romanian authors and 50 foreign authors from representative institutions, the conference provided a valuable opportunity to communicate, promote and disseminate results of research. The exhibition of product samples and scientific literature gave participants the possibility to directly come into contact with concrete results of research activity in the leather and footwear field.

Exhibition of product samples and scientific literature

The Proceedings of the seventh edition (ICAMS 2018) are published by CERTEX under ISSN 2068-0783; the 604-page volume comprises 95 full papers in English and was submitted for indexing in databases such as SCOPUS, Crossref, Chemical Abstracts Service, Web of Science and other international databases.

More information: http://www.icams.ro/

12TH INTERNATIONAL SYMPOSIUM ON FLEXIBLE ORGANIC ELECTRONICS (ISFOE19)
1-4 JULY 2019, THESSALONIKI, GREECE

ISFOE is the biggest world-class scientific & technology event on Flexible Organic Electronics (OEs), promoting Research, Technology and Innovation in OE nanomaterials, Manufacturing Processes, Devices, Applications and Solutions. ISFOE19 provides an interdisciplinary forum for front-line scientists, engineers, people from industry and policy makers to discuss and exchange ideas on the hottest topics and progress in the field of OEs.

More information: http://www.nanotexnology.com/index.php/isfoe

4TH INTERNATIONAL CONGRESS ON BIOMATERIALS AND BIOSENSORS (BIOMATSEN)
12-18 MAY 2019, OLUDENIZ, TURKEY

BIOMATSEN intends to be a global forum for researchers and engineers to present and discuss recent innovations and new techniques in Biomaterials and Biosensors. In addition to scientific seminars, a wide range of social programs including boat cruises and visits to historical places will be available. Topics include Biomaterials, Sensors using recognition elements, Sensors with transducers, New Trends in Sensor Development.

More information: http://www.biomatsencongress.org/

4TH WORLD CONGRESS ON RECENT ADVANCES IN NANOTECHNOLOGY (RAN’19)
APRIL 14-16, 2019, ROME, ITALY

RAN’19 is composed of 5 conferences, while each conference consists of an individual and separate theme, they share considerable overlap, which prompted the organization of this congress. The goal of this undertaking is to bring together experts in each of the specialized fields, and at the same time allow for cross pollinations and sharing of ideas from the other closely related research areas. Interested authors, researchers, and industrial experts are invited to register for the conference that best resonates with their technical background. At the same time, attendees are permitted, and even encouraged, to attend talks from co-located conferences.

More information: http://rancongress.com

7TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT
26-29 JUNE 2019, MUNICIPALITY OF HERSONISSOS, CRETE ISLAND, GREECE

The Conference aims to address the significant issue of sustainable solid waste management through the promotion of safe practices & effective technologies. The Conference focuses mainly on modern solid waste technologies. It aims to stimulate the interest of scientists and citizens and inform them about the latest developments in the field of municipal solid waste management. Separation at source, Biological Treatment, the treatment at central facilities, waste prevention, biowaste utilization, recycling promotion, Waste-to-energy technologies & energy recovery, smart technologies for waste management, sludge management, agricultural and livestock waste, management of specific waste streams (construction & demolition waste, waste from electrical and electronic equipment, etc.), biotechnology, Best Available techniques, symbiosis networks, energy consumption and saving, carbon footprint and water footprint, zero-waste initiatives, plastics and bioplastics, marine litter constitute main conference subjects. Special attention will be drawn to the valorization prospects & the products from solid waste, such as: biofuels, compost, materials, etc. It is also our ambition to strengthen the link of the applied research with industry. Hazardous waste & Household hazardous waste also constitute target area of the conference. Emphasis will be placed on circular economy in all key action areas (production, consumption, waste management, secondary raw materials, innovation, investment & monitoring) and all priority sectors (food waste, plastics, biomass and bio-based-products, construction & demolition waste, critical raw materials), as well as waste management issues and resource efficiency in islands and generally isolated and remote areas.

More information: http://www.heraklion2019.uest.gr/

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