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A NOVEL SHOE COMFORTABILITY EVALUATION METHOD TO REFLECT RECOGNITION IN NURSING OF DIABETIC FOOT AMONG DIABETES PATIENTS IN SOUTHWEST CHINA

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A NOVEL SHOE COMFORTABILITY EVALUATION METHOD TO REFLECT RECOGNITION IN NURSING OF DIABETIC FOOT AMONG DIABETES PATIENTS IN SOUTHWEST CHINA

ABSTRACT. Effective footwear and offloading interventions were recommended in the official guidance for diabetic foot (DF) management, where unfortunately the detail of shoes' definition was still unclear; meanwhile, in China, 0.1 billion population has been diagnosed with diabetes mellitus, but what kind of shoes worn by Chinese diabetic patients was unknown. Therefore, the aim of this study was to establish a system to quantify the comfortability of shoes among DF patients, and based on this method conduct a random survey of shoe wearing situation in diabetes population in Sichuan province. 472 participants joined in this study and their shoes were defined as structure of shoes, upper materials, status of welt, heel height and thickness of sole. Each part of shoes was first quantified into scores; and then aggregated scores were calculated as the final assessment result for the shoes. Three levels reflecting the recognition of shoes from patients were classified into: discomfort; moderate comfort; comfort. Finally, a univariate analysis with least significant difference (LSD) was exerted in shoe wearing comfort for variables of age, gender, BMI, occupation, history of diabetes mellitus and Michigan score. Results show that numbers of elder and male patients wear comfort shoes were more than that of female and younger ones; meanwhile, those findings were recorded to be significant. Overall, comfortability quantification system was established and both gender and age factors determined the consciousness and knowledge in shoe wearing; thereby, our system was valid and shoes wearing education for female and younger diabetic patients are urgent.
KEY WORDS: diabetic foot, diabetic shoes, comfortability evaluation, foot nursing, ulceration

O NOUĂ METODĂ PENTRU EVALUAREA CONFORTULUI ÎNCĂLȚĂMINTEI CARE SĂ FIE RECUNOSCUTĂ ÎN ASISTENȚA PACIENȚILOR CU DIABET DIN SUD-VESTUL CHINEI

REZUMAT. În ghidul oficial pentru îngrijirea piciorului diabetic se recomandă încălțăminte eficientă și intervenții de reducere a presiunii, însă, din păcate, definiția detaliată a încălțămintei este încă neclară; între timp, în China, 0,1 miliarde de persoane au fost diagnosticate cu diabet zaharat, dar nu se cunoaște ce fel de încălțăminte poartă pacienții diabetici chinezi. Prin urmare, scopul acestui studiu a fost de a stabili un sistem de cuantificare a confortului încălțămintei în rândul pacienților cu diabet și, pe baza acestei metode, să se efectueze un sondaj aleator privind încălțămintea purtată de populația de diabet din provincia Sichuan. În acest studiu s-au alăturat 472 de participanți, iar încălțămintea acestora a fost definită în funcție de structură, materialele pentru fețe, starea ramei, înălțimea tocului și grosimea tălpii. Fiecare parte a pantofilor a fost mai întâi cuantificată în scoruri; iar scorurile agregate au fost calculate ca rezultat final al evaluării încălțămintei. S-au stabilit trei niveluri care reflectă nivelul de confort al încălțămintei pacienților: disconfort; confort moderat; confort. În cele din urmă, s-a efectuat o analiză univariată cu testul celei mai puțin semnificative diferențe (LSD) privind confortul încălțămintei pentru variabilele de vârstă, sex, IMC, ocupație, istoricul diabetului zaharat și scorul Michigan. Rezultatele arată că numărul de pacienți vârstnici și bărbați care poartă încălțăminte confortabilă a fost mai mare decât cel al pacienților mai tineri și de sex feminin; aceste constatări au fost înregistrate ca fiind semnificative. În ansamblu, a fost stabilit sistemul de cuantificare a confortului, iar factorii de gen și de vârstă au determinat nivelul de sensibilizare și de cunoaștere privind purtarea încălțămintei; prin urmare, sistemul nostru este valid, iar educația privind purtarea pantofilor comozi în cazul pacienților cu diabet zaharat de sex feminin și mai tineri este imperioasă.
CUVINTE CHEIE: picior diabetic, pantofi pentru diabetici, evaluarea confortului, asistență medicală la nivelul piciorului, ulcerație

UNE NOUVELLE MÉTHODE D'ÉVALUATION DU CONFORT DE CHAUSSURES RECONNUE DANS LES SOINS DES PATIENTS DIABÉTIQUES DU SUD-OUEST DE LA CHINE

RÉSUMÉ. Dans le guide officiel sur les soins des pieds pour diabétiques, des chaussures et des interventions efficaces sur le soulagement de la pression sont recommandées, mais malheureusement, la définition détaillée des chaussures n'est toujours pas claire ; en Chine, 0,1 milliard de personnes ont été diagnostiquées avec le diabète, mais on ne connait pas quel type de chaussures portent les diabétiques chinois. L'objectif de cette étude était donc d'établir un système permettant de quantifier le confort des chaussures chez les patients diabétiques, et à partir de cette méthode, de mener une enquête aléatoire sur la situation des chaussures portées par la population diabétique de la province du Sichuan. 472 personnes ont participé à cette étude et leurs chaussures ont été définies comme suit: structure des chaussures, matériaux de la tige, statut de la trépointe, hauteur du talon et épaisseur de la semelle. Chaque partie de chaussures a d'abord été quantifiée en scores; et ensuite, les scores agrégés ont été calculés comme résultat final de l'évaluation des chaussures. Trois niveaux reflétant la reconnaissance des chaussures par les patients ont été classés en: inconfort; confort modéré; confort. Enfin, une analyse univariée avec le test de différence significative minimale (LSD) a été réalisée en ce qui concerne le confort des chaussures pour des variables d'âge, de sexe, d'IMC, de profession, d'histoire du diabète sucré et de score de Michigan. Les résultats montrent que le nombre de patients âgés et d'hommes portant des chaussures de confort était supérieur à celui des femmes et des patients plus jeunes ; ces résultats ont été jugés significatifs. Dans l'ensemble, le système de quantification du confort a été mis en place et des facteurs liés au sexe et à l'âge ont déterminé le degré de sensibilisation et de connaissance en ce qui concerne les chaussures ; par conséquent, notre système est valable et une éducation sur les chaussures confortables pour les femmes et les patients diabétiques jeunes est impérative.
MOTS CLÉS : pied diabétique, chaussures pour les diabétiques, évaluation du confort, les soins du pied, ulcération

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INTRODUCTION

Loss of tactile sensation, deformities, ulceration and even the amputation in the foot are usually observed in diabetes patients. Those symptoms are the clinical manifestation of diabetes foot (DF) [1] and they have significantly increased the risk of morbidity and mortality for patients. Critical point in DF daily care is the ulcer prevention, where abnormal high plantar pressure, excessive loads on metatarsal heads or toes, and cracks of skin are main management targets [2, 3]. Currently, around 2% yearly incidence rate of ulceration was reported in diabetes group but recurrence rates was between 30%-40% during the first twelve months after rehabilitation [4-8]. Since, occurrences and reoccurrences of ulcers increase both the economical and physical burden of patients, efficient nursing and management for ulcer prevention were required among diabetes patients, [9] which was also important to reduce amputations [10].

Among the approaches of DF management, the pressure relieving is the priority. Varied pressure reliving methods have been reported in literatures. Usually, shoes or socks were prevalent. Waaijman *et al*. [11] used custom-made footwear in off-loading of foot pressure to avoid ulceration; preventive foot care socks were also beneficial in increasing the contact area of foot to decrease the plantar foot pressure [12]. Unexpectedly, a low cost of running shoes was also reported as a very minimally acceptable choice for patients without deformities [13]. While nursing of ulcers, felted foam applied in toe ulcers and wound healing, flexor tenotomies in healing ulcers were also effective and safe approaches [14, 15]. Further, L. Uccioli *et al*. designed special manufactured shoes to prevent relapses of ulceration in DF [2]. Officially, the international working group on the diabetes foot (IWGDF) has published a guidance on the clinical nursing and management for diabetes foot. This guidance indicated that effective footwear and offloading interventions shall be recommended to diabetes patients [11]. However, in this guidance, the detail of shoes' definition was failed to achieve. Unfortunately, in majority Asia countries, including China, DF intensive care following the IWGDF's guidance is still a tough mission, as lacking professional podiatric services and well-trained foot-care medical centers [12]. Moreover, although more than 0.1 billion population has been confirmed as diabetes mellitus in China; how the current situation of those patients in wearing shoes in China is also a blank zone. It was insisted that correct shoes wearing are the first-step to the ulcer prevention. Purpose of this study was to establish a comfortability quantification system to quantify the comfortability of shoes among DF patients, and then conduct a random survey on the shoe wearing in diabetes population in Sichuan province to know the general situation of daily shoe wearing of Chinese diabetes. According to the literature, hypothesis: 1. a criterion to quantify the shoes comfortability could be established; 2. shoe wearing situation was only related to the social experience, where elder people care more about their shoes in daily life.

EXPERIMENTAL

Material and Method

Subjects

In this study, totally 472 participants from outpatient service of West China Hospital of Sichuan university in Chengdu during 2015-2017 were randomly recruited. The criteria of inclusion were: (1) patients were diagnosed with diabetes mellitus; (2) no amputee or ulcers in the foot or history; (3) wearing the daily usual-used shoes. Parameters such as age, gender, height, weight, BMI, history of diabetes mellitus, occupation (Heavy (frontline worker at heavy industry), Moderate (general manual workers), Light (civilian and design workers) and Other relaxed work (freelance and unemployed)), shoe information were recorded. Following the principle of Helsinki Declaration, the whole process of test was introduced to participants and their formal approvals were authorized.

Quantify Assessment for Shoes

Five key factors of shoes were measured: structure of shoes (*Ss*), upper materials (*Um*), status of welt (*Ws*), heel height and thickness of sole, where a clean height of shoes (*Ch*) was calculated by heel height minus thickness of sole. Referring the guidance of IWGDF, in which thin bottom, soft, breathable, loose and delicate structure and materials were recommended [13]. Moreover, in this study, a quantification system was established to quantify each factor of shoe by a certain score (Table 1) and the aggregated suitable score (S) represents the final assessment result. It can be explained by the following formula (Eq 1). Range of S valued from -8 points to 7 points. The whole assessment was completed by an experienced footwear engineer.

$$Ss+Um-Ch-Ws=S \quad (1)$$

Table 1: Quantification system for each factor of shoes

Parameter	Point	Category
Structure (Ss)	1	Single shoes
	2	Cloth shoes
	3	Sandal shoes
	4	Leather shoes
	5	Sports shoes
Upper materials (Um)	1	Others
	2	Artificial leather
	3	Textile
	4	Leather
Clean heel height (Ch)	1	0mm to 10mm
	2	11mm to 20mm
	3	21mm to 30mm
	4	31mm to 40mm
	5	41mm to 50mm
	6	Above 51mm
Welt (Ws)	1	Open status
	2	Close status

Diabetes Foot Inspection

Michigan Neuropathy Screening Instrument (MNSI) which contains fifteen questions was first filled in by patients themselves; appearance and deformities of foot, dryness, infection and cleft of skin, as well as ulcers were then checked by the physician [16]. Ankle reflex, toe vibration sensation and tactile sensation were tested by reflex hammer, 128 Hz tuning fork and 10-gram filament, respectively [17]. At last, overall scores were calculated and this score indicated the DF severity, where, previous study reported that score 4 was a threshold for DF risk alert [18].

Data Processing and Statistical Analysis

Shoe's quantification scores (S) were classified into three levels: discomfort (-8 to 0); moderate comfort (1 to 4); comfort (5 to 7). Discomfort (G1), moderate comfort (G2) and comfort (G3) indicated the recognition from the patient to the shoe. The higher comfort scores implied that the patient has a high recognition on the effect of shoes on the ulcer prevention and vice versa. Participants also divided into three age groups, as youth group (A1; aged 1 to 39), middle-aged group (A2; aged 40 to 59), old group (A3; aged above 60).

In the process of statistical analyses, one-sample K-S test was first exerted to all parameters and all parameters followed the normal distribution; then descriptive analysis was applied to all the quantized indexes. At last, a univariate analysis with Least—Significant Difference (LSD) was exerted to explore the differences in shoe wearing comfort for variables of age, gender, BMI, occupation, history of diabetes mellitus and Michigan score. Statistical analysis was operated under software SPSS (V22, IBM, USA), with significant level of 0.05 and confidence interval of 95%.

RESULTS

Demographic information showed that the gender ratio is 205:267 (Male: Female), mean age is 59.7 (SD:11.0), mean BMI is 24.2 (3.6), mean MNSI score was 5.4 (2.7), mean history of diabetes mellitus were 7.00 (6.35) years, occupation distribution result was in table 2. Further, 9 subjects were diagnosed with type 1 diabetes and others were type 2 diabetes.

Table 2: Number and ratio of each classification

Gender	Suitable	Numbers	Ratio in total (%)	Ratio in gender (%)	Occupation	Numbers	Ratio in total (%)	Ratio in gender (%)
Female	G1	32	6.78	11.99	Heavy	2	0.42	0.75
					Moderate	8	1.69	3.00
					Light	8	1.69	3.00
					Others	14	2.97	5.24
	G2	162	34.32	60.67	Heavy	23	4.87	8.61
					Moderate	53	11.23	19.85
					Light	45	9.53	16.85
					Others	41	8.69	15.36
	G3	73	15.47	27.34	Heavy	12	2.54	4.49
					Moderate	23	4.87	8.61
					Light	18	3.81	6.74
					Others	20	4.24	7.49
Male	G1	11	2.33	5.37	Heavy	1	0.21	0.49
					Moderate	5	1.06	2.44
					Light	4	0.85	1.95
					Others	1	0.21	0.49
	G2	121	25.64	59.02	Heavy	17	3.60	8.29
					Moderate	29	6.14	14.15
					Light	45	9.53	21.95
					Others	30	6.36	14.63
	G3	73	15.47	35.61	Heavy	5	1.06	2.44
					Moderate	18	3.81	8.78
					Light	33	6.99	16.10
					Others	17	3.60	8.29

In terms of shoes wearing, totally 43 diabetes patients (9.11%) wear G1-kind shoes, in which the number of males was 11 (ratio in total: 2.33%) and that of females was 32 (6.78%); particularly, 1 man (0.21%) and 2 women (0.42%) participants engaged on heavy work; 5 men (1.06%) and 8 women (1.69%) were working on moderate physical jobs. 238 participants (59.60%) wear G2-kind shoes, where male participants were 121 (25.64%) and female ones were 162 (34.32%). Meanwhile, 146 participants (30.94%) wear G3-kind shoes during their daily life and men's wearing numbers were the same to their female counterparts. (see Table 2).

Table 3: Number and ratio of each classification

Age	Numbers	Suitable	Numbers	Ratio in total (%)	Ratio in each age group (%)	Occupation	Numbers	Ratio in total (%)	Ratio in each age group (%)
A1	24	G1	5	1.06	20.83	Heavy	0	0.00	0.00
						Moderate	2	0.42	8.33
						Light	2	0.42	8.33
						Others	1	0.21	4.17
		G2	13	2.75	54.17	Heavy	0	0.00	0.00
						Moderate	4	0.85	16.67
						Light	3	0.64	12.50
						Others	6	1.27	25.00
		G3	6	1.27	25.00	Heavy	0	0.00	0.00
						Moderate	1	0.21	4.17
						Light	4	0.85	16.67
						Others	1	0.21	4.17

		G1	23	4.87	12.71	Heavy	2	0.42	1.10
						Moderate	6	1.27	3.31
						Light	4	0.85	2.21
						Others	11	2.33	6.08
A2	181	G2	112	23.73	61.88	Heavy	18	3.81	9.94
						Moderate	34	7.20	18.78
						Light	31	6.57	17.13
						Others	29	6.14	16.02
		G3	46	9.75	25.41	Heavy	7	1.48	3.87
						Moderate	16	3.39	8.84
						Light	12	2.54	6.63
						Others	11	2.33	6.08
		G1	15	3.18	5.62	Heavy	1	0.21	0.37
						Moderate	5	1.06	1.87
						Light	6	1.27	2.25
						Others	3	0.64	1.12
A3	267	G2	158	33.47	59.18	Heavy	22	4.66	8.24
						Moderate	44	9.32	16.48
						Light	56	11.86	20.97
						Others	36	7.63	13.48
		G3	94	19.92	35.21	Heavy	10	2.12	3.75
						Moderate	24	5.08	8.99
						Light	35	7.42	13.11
						Others	25	5.30	9.36

Patients in three age groups (Table 3) were 24 people (5.08%) from A1, 181 people (38.34%) from A2 and 267 people (56.57%) from A3. With the age increasing, the number of wearing G1-kind shoes decreased, while the number of G2 and G3 increased. Ratio of wearing for G1, G2 and G3 kind shoes in A1 group was G1:G2:G3=20.83%: 54.17%: 25.00% (ratio in all age group = 1.06%: 2.75%: 1.27%), and in A2 group was G1:G2:G3=12.71%: 61.88%: 25.41% (ratio in all age group = 4.87%: 23.73%: 9.75%), and in A3 group was G1:G2:G3=5.62%: 59.18%: 35.21% (ratio in all age group = 3.18%: 33.47%: 19.92%).

Univariate analysis results showed that model of age, gender and their mix have significant influence on the suitable score (age factor: $p=0.001<0.05$, gender factor: $p=0.000<0.05$; age*gender factor: $p=0.024<0.05$). LSD result indicated that G1 to G2 was 0.498, and G1 V.S. G3: $p=0.040<0.05$, G2 V.S. G3: $p=0.003<0.05$. No significances were founded in variables of occupation, BMI, history of diabetes mellitus and Michigan score.

DISCUSSION

In terms of demographic findings, average BMI of diabetes patients were reported as 25.0 in China [19]; while that of this study was 24.2 (3.6), which is very close to the guidelines. Those two close results improved that participants recruited in this study were generalizable enough. Although, Golmohammadi [20] indicated that occupational stress is an important factor induce to the diabetes mellitus, factors such as occupation were not found significant in selection of shoe wearing.

In this study, a quantification system was established to quantify the comfort of shoes. According to each part of shoe structure, criterion of rating for their level of suitability for diabetic patients was following literature stated by IWGDF. Then the sum of scores were calculated and the result implied a general comfort level of particular shoes, or a kind of consciousness on the suitability of shoes. For instance, discomfort illustrated that no attention or no correct knowledge in wearing shoes; moderate comfort explained that although patients paid attention to the shoe's suitability, they were lacking knowledge of what a pair of suitable shoes should be; comfort indicated that both two aspects were applied in wearing shoes. Unfortunately, there were no similar studies in current database. Nevertheless, our first hypothesis is proved to be available.

In comprehending our findings, only 30.94% of patients wear suitable shoes during their daily life, which suggested that the diabetes patients in China have a low consciousness on shoes in terms of foot protection, in contrast with their Europe counterparts [5]. Two-ways ANOVA assessed the joint-effects of gender and age, and significant findings were obtained. In terms of age factor, with the social experience increasing, patients are gradually aware the importance of foot nursing and they know how to wear suitable shoes for foot protection. Meanwhile, significant differences between discomfort-moderate comfort and discomfort-comfort groups were also observed. Hence, those clues proved that shoes wearing education to the younger diabetes patients were necessary. In terms of gender, female patients wearing discomfort shoes were doubled than that of male group and the gender variation was significant. This revealed that women are easy to omit the important of shoes wearing. The high-heeled shoes which are harmful for their gait and posture though, this kind of shoes have prevalent centuries. Our finding was accordance with literature [21]. So, our second hypothesis was manifested to be real.

LIMITATIONS

Although significant outcomes illustrated general status of shoes wearing in Chinese diabetes patients, Limitations existed and should be declared: (1) The time of this report lasted in three years, some particular shoe stylish such as sheepskin boots etc., was not included in this survey; (2) Since our study was the first to quantify the shoe, so no previous studies on shoes can be referred, but our idea might inspired more people to focus on the comfortability evaluation work.

FUTURE RESEARCH AND IMPLICATIONS

Our comfortability quantification system accomplished quantified the comfortability of shoes and this was used to disclosed that factors of age and gender have a strong influence on the consciousness and knowledge in shoes wearing of diabetes patients, where male and elder ages showed a better consciousness and knowledge of shoe wearing. So, the consciousness and knowledge education of shoes wearing for female and younger diabetes patients are urgent. And our idea of quantifying comfortability of shoes might inspire more research to focus on the comfortability evaluation work.

CONCLUSION

Qualification system was useful when quantifying the comfortability of shoes among DF patients; male and older populations paid more attention to their shoes.

Conflict of Interest

All authors declare that they have no conflict of interest.

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FATLIQUORING POTENTIALS OF SULPHONATED *Hura crepitans* L. SEED OIL

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ABSTRACT. Fatliquors are oil-in-water emulsions required in leather processing for the purpose of leather lubrication. They ensure that the collagenic fibres do not stick together on drying and as a consequence make the leather flexible. In this work sulphonated oil with negligible inorganic salt content has been synthesised from *Hura crepitans* L. seed oil. Both the unsulphonated and sulphonated oils were characterized by DSC, FT-IR, ^{1}H NMR, ^{13}C NMR, and ^{13}C NMR DEPT. The sulphonated oil and its blend with 7.5 % raw castor oil were applied onto light leather and compared with commercial fatliquor in the processing of shoe upper leather. The characteristics of the processed trial leathers were comparable with similar leathers made with commercially available fatliquors. This work raises the possibility of increasing the range of commercially viable, sustainable fatliquors in the leather industry.
KEY WORDS: *Hura crepitans* L., fatliquor, leather, lubrication, sulphonated

POTENŢIALUL DE UNGERE AL ULEIULUI SULFONAT DIN SEMINŢE DE *Hura crepitans* L.

REZUMAT. Agenţii de ungere sunt emulsii de tip ulei-în-apă necesare la prelucrarea pieilor pentru ungerea acestora. Aceştia împiedică lipirea fibrelor colagenice la uscare şi, prin urmare, fac pielea flexibilă. În această lucrare s-au sintetizat uleiuri sulfonate cu conţinut neglijabil de săruri anorganice din uleiul de seminţe de *Hura crepitans* L. Atât uleiurile nesulfonate cât şi cele sulfonate au fost caracterizate prin DSC, FT-IR, RMN ^{1}H, RMN ^{13}C şi RMN DEPT ^{13}C. Uleiul sulfonat şi amestecul său cu 7,5% ulei de ricin brut au fost aplicate pe piele uşoară şi au fost comparate cu grăsimile comerciale utilizate la prelucrarea pielii pentru feţe de încălţăminte. Caracteristicile probelor de piele prelucrate au fost comparabile cu cele ale pieilor similare fabricate utilizând agenţi de ungere disponibili în comerţ. Această lucrare prezintă posibilitatea lărgirii gamei de agenţi de ungere sustenabili şi viabili din punct de vedere comercial pentru industria de pielărie.
CUVINTE CHEIE: *Hura crepitans* L., ungere, piele, lubrifiere, sulfonat

LE POTENTIEL DE L'HUILE SULFONÉE DE GRAINES DE *Hura crepitans* L. COMME LIQUEUR GRASSE

RÉSUMÉ. Les liqueurs grasses sont des émulsions huile dans eau nécessaires pour la nourriture du cuir. Elles empêchent les fibres de collagène de coller pendant le séchage et rendent donc le cuir souple. Dans cet article, des huiles sulfonées avec une teneur négligeable en sels inorganiques de l'huile de graines de *Hura crepitans* L. ont été synthétisées. Les huiles non sulfonées et sulfonées ont été caractérisées par DSC, FT-IR, RMN ^{1}H, RMN ^{13}C et RMN DEPT ^{13}C. L'huile sulfoné et son mélange avec 7,5% d'huile de ricin brute ont été appliquées sur un cuir léger et ont été comparées aux liqueurs grasses commerciales utilisées dans le traitement du cuir pour les chaussures. Les caractéristiques des échantillons de cuir traités étaient comparables à celles de peaux similaires fabriquées avec des liqueurs grasses disponibles dans le commerce. Cet article présente la possibilité d'élargir la gamme de liqueurs grasses durables et commercialement viables pour l'industrie du cuir.
MOTS CLÉS : *Hura crepitans* L., liqueur grasse, cuir, lubrification, sulfoné

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INTRODUCTION

Hura crepitans L., also known as the sandbox tree, possumwood, or jabillo, is an evergreen perennial tropical plant belonging to the family *Euphorbiaceae* [1]. In Africa, these trees are usually planted as shade trees for roadsides and are also widely used to provide shade in front of residential, public buildings and parks. The trees are about 9 metres tall on the average. The bark is covered with lots of short spines; the woody fruits bear a resemblance to small pumpkin pods in which the seeds are housed with about 10-13 seeds in a pod. The seeds of these trees, when mature and dried, usually explode mechanically, littering the environment - thereby constituting a waste. These brown seeds have average diameters of about 1-5 cm [2].

These seed kernels contain a very high percentage of non-edible, golden yellow coloured oil [3]. Although several attempts have been made by researchers to proffer uses of this oil, such as metal soap production [4], biodiesel [5], it presently has no known commercial use. Other means of turning these oils into wealth are being researched; this work on sulphonation and subsequent use as a fatliquor in the leather industry is one example.

The leather industry makes use of a process that converts animal hide (or skin) into a non-putrescible substrate. During this process natural fat from the animal hide is removed to aid penetration of water born chemicals. When tanned leather without fatliquor is dried it produces a hard, intractable material which is difficult to work with; this is due to the collagen fibres sticking together. The inclusion of fatliquor (oil-in-water emulsion) into leather is often the last of the wet processing stages of leather manufacture and lubricates the leather fibres preventing this sticking and producing softer leather. It also reduces the frictional forces between the leather fibres thereby making them slide over one another easily, improving the flexibility, tensile strength and other mechanical /physical properties of leather [6].

Most natural oils (from animal and plant sources) used in fatliquor production have major food uses and this unhealthy competition affects a nation's total available reserve [7-9].

This paper describes the use of *H. crepitans* seed oil for the preparation of a sulphonated leather fatliquor and its consequent use in the processing of a leather shoe upper. This research gives a possible commercial application for this abundant, underutilized, non-edible oil.

EXPERIMENTAL

Materials and Methods

Mature and dried *H. crepitans* pods were collected from Fatilami Park in Abakaliki, Ebonyi State, Nigeria. Wet blue goat skins were obtained from the tannery at the Institute for Creative Leather Technologies (ICLT), The University of Northampton (UoN), Northampton, United Kingdom. Reagents used in the laboratory for synthesis and analysis were of analytical grade while those used for leather processing were of commercial/industrial grade. The samples of pods, seeds and leaves were identified in the Biology unit of the department of Biology/ Microbiology and Biotechnology of the Alex Ekwueme Federal University Ndufu-Alike, Ebonyi State, Nigeria and voucher samples kept. The pods were cut open and the seeds removed. The seeds were manually decorticated and the endocarp gently removed to get the creamy white cotyledons. These creamy white cotyledons were sun dried for five days and the cotyledons were coarsely ground (approximately 2 mm) using the kitchen hand grinder before extraction [3]. The extraction of the oil from the seeds was carried out in a soxhlet apparatus using n-hexane as a solvent.

Characterisation of H. crepitans Oil

Physicochemical properties of *H. crepitans* oil (HCO) were determined according to the methods recommended by the Society of Leather Chemists and Technologists (SLTC, 1996). Fatty-acid composition of HCO was determined using its methyl ester prepared with the method described by Adewuyi *et al*. [5] on an Agilent 19091S-433HP-5MS gas chromatograph attached to a mass spectrometer. The injection and detection temperatures were 280 and 300°C respectively. Helium was used as the carrier gas at a flow rate of 20 ml/min. The area percentages were recorded with a standard Chemstation Data system. For the mass spectrometry, an ACQ mode scanner (with scan range of 15-500 atomic mass unit and voltage of 2094) was used and the mass spectra were compared with the NIST11 mass spectral library.

Differential scanning calorimetry (DSC) of the oil was performed using a DSC 2 Star System (Mettler Toledo). The purge gas (nitrogen) had a flow rate ~60 ml/min. Samples of oil, of between 5-7 mg, were weighed into low pressure aluminium crucibles, and sealed hermetically. The sealed crucibles were pierced prior to analysis [10]. An empty, hermetically sealed aluminium crucible with a pinhole was used as a reference. A temperature profile of -80 to 180°C was run using the following temperature program: -80°C isotherm for 3 min; dynamic ramp at -80°C to 180°C (at 10°C min^{-1}), isotherm at 180°C for 3 min; isotherm at 30°C for 2 min. The resulting DSC data was analysed for peak temperature, onset temperature and melting temperature for comparison. All DSC experiments were carried out in triplicate and average values are reported. Melting temperature was considered to be the temperature at the end of the melting transition [11].

Sulphonation Process

Concentrated sulphuric acid (45 ml) was added dropwise into 150 g of *H. crepitans* seed oil (with constant stirring at 20°C for 2 h). The crude mass was dissolved in 450 ml of ethanol, and neutralised using 15% NaOH (solubilised in methanol). The salts were filtered off under vacuum. The solvent was removed and recovered using a rotary evaporator. The resulting sulphonated oil was ready for use.

Characterisation of the Sulphonated Oil

To investigate the presence of H-C-S and H-C-O-S group in the sulphonated fatliquor, the oils were characterised by FT-IR measurement (600-4000 cm^{-1}), normal resolution of 4 cm^{-1} using a Shimadzu 8400S FT-IR instrument (Shimadzu, Milton Keynes, UK). ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR and distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR, spectra of both the unsulphonated and sulphonated oils were acquired on a Bruker Biospin® AV500 – 5mm BBO probe with Z axis gradient, TOPSPIN v 2.1, ^{1}H=500.13 MHz, ^{13}C=125.76 MHz (Brucker, Coventry, UK). The thermal behaviour of the unsulphonated and sulphonated oils was determined using the Mettler DSC 2 Star System in temperature range of -80 to 180°C.

Physicochemical Tests on the Sulphonated Oil

The specific gravity, pH, stability of the emulsion, total organic SO_3 and percentage ash were determined according to the standard methods recommended by the Society of Leather Chemists and Technologists [12].

Fatliquoring Process

Wet blue goat skin, shaved at 1.2-1.3 mm was divided into four quarters such that the sampling positions (BS EN ISO 2418:2002) [13] were uniformly represented in all the four quarters. Further treatments on each of the four quarters of the wet blue goat skins labelled NC, PC, A1 and A2 respectively were simultaneously carried out (with the aid of four separate tanning drums/ baths) using a conventional shoe upper manufacturing process (fatliquoring process) (ICLT SR 15/31) [14].

A negative control (designated NC) was processed without any fatliquor; a positive control (designated PC) was processed using a commercial fatliquor, Trupon DXV (Trumpler Gmbh, Worms, Germany, an imported fatliquor commonly used in the Nigerian leather industry). Sample A1 was processed using pure sulphonated *H. crepitans* oil; Sample A2 was processed using a blend of pure sulphonated *H. crepitans* oil and 7.5% raw castor oil. Leather dyeing was omitted to enable the Sudan IV staining (for fatty substances) to be carried out effectively after the leather manufacture.

The chrome tanned leather was wet back by the addition of water (300%) and wetting agent-Bermanol WAU (0.2%) in the drums at a temperature of 30°C. After 20 minutes run, the water was drained. It was then neutralised by addition of water (100%), sodium formate (1%) for 5 minutes and sodium bicarbonate (0.25%) for 30 minutes at 35°C, drained, washed with water (200%) and drained. On addition of water (100 %) and replacement syntan (Trupotan GDL) (6%) in the drum, it was run for 15 minutes and vegetable tannin added at 30°C and allowed to run for 30 minutes. Water (200%) and Acrylic resin (3%) were added and allowed to run for another 30 minutes at 35°C before drainage. It was further washed with water (200%) for 5 minutes at 50°C and drained. Sulphonated *Hura crepitans* oil, labelled A2 mixed with water (1:3) (8%) was added and allowed to run for 50 minutes at 50°C. Formic acid (1%) was added and allowed to run for 20 minutes, washed for 10 minutes twice and horse dried.

Mechanical / Physical Properties of Leather

All leather samples: NC, PC, A1 and A2 were conditioned according to BS EN ISO 2419:2002 [15] prior to staking twice using a Cartigliano PAL 160 leather staking machine (Cartigliano) and subsequent mechanical testing.

The mechanical properties of leather samples were all determined using standards; softness (BS EN ISO 17235:2015) [16], tensile strength (BS EN ISO 3376:2011) [17], elongation at break and tear strength of leather (BS EN ISO 3377-2:2011) [18] and grain strength (BS EN ISO 3379:2015) [19]. Thin cross sections (50 µm) of the leather samples were cut with a Leica 1850 cryostat microtome (Leica, Wetzler, Germany) (set at -20°C) and used in the Sudan (IV) stain test for the determination of extent of penetration of the fatliquors between the leather fibrils.

RESULTS AND DISCUSSIONS

Characterisations

Fatty Acid Composition

The fatty acid composition of unsulphonated *H. crepitans* oil (HCO) is shown in Table 1.

Table 1: Fatty acid profile of the extracted oil

Fatty acid	Percentage composition
Palmitic acid	27.54
Oleic acid	27.24
Linoleic	33.06
Linolenic	7.45
∑ Saturated fatty acids	27.54
∑ Unsaturated fatty acids	67.75
Others	4.71

It was observed that linoleic acid (33.06%) which is an unsaturated fatty acid is the main fatty acid present in *H. crepitans* oil. Other major fatty acids present are oleic acid (27.24%) and palmitic acid (27.54%). The iodine value of the unsulphonated oil (Table 2) is consistent with the total unsaturated fatty acids (67.75%). The double bonds present in the unsaturated fatty acid were targets in the sulphonation process.

Physico-chemical Properties

The physico-chemical properties of unsulphonated *H. crepitans* oil (HCO) and sulphonated *H. crepitans* oil (SHCO) are shown in Table 2. A high percentage of oil clearly indicates that *H. crepitans* seed contains a sufficiently large quantity of oil which can be chemically modified for the synthesis of fatliquor via sulphonation. The oil yield value of 52.76% is in close agreement with what is obtained for the seed (53.61%) as reported by Okolie *et al*. [20], (53.81%) by Abdulkadir *et al*. [2] but higher than what was reported by Adewuyi *et al*. [5] (37.75%). Variations in properties of oil maybe due to the differences in variety of plant, cultivation, climate, ripening stage, the harvesting time of the seeds and the extraction methods used [21].

The golden colour possessed by *H. crepitans* oil is the colour of most vegetable oils and would not be detrimental to the final colour of the article produced. Its smell which is inoffensive conveys the likelihood of the oil not influencing the odour of the finished leather product. The specific gravity of the oil is in line with the density of most vegetable oils [22]. The oil has an iodine value of 117, which signifies a high quantity of unsaturated fatty acids [22]. The decreased iodine value observed in the sulphonated product signifies a low level of unsaturation as most of the C=C bonds in the unsulphonated oils have been used up in the sulphonation reaction. The sulphonated oil produced from the oil has a high percentage of SO_3 (5.87%). High percentage of SO_3 in a fatliquor is an indication of a deeper penetration prospect of sulphonated *H. crepitans* oil when used in leather fatliquoring [6]. The very pale brown colour of the 10% solution did not affect the colour of the finished leather product and suggests that the finished leather product could be dyed to any choice of colour by the tanner.

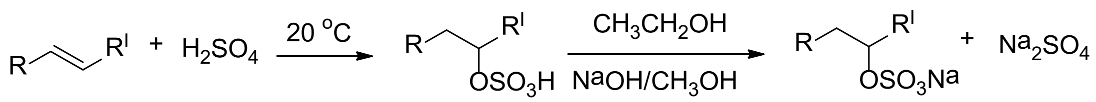
Similarly, the sulphonated oil which is odourless, has no influence on the final odour of the produced leather unlike most leather products with a unique fishy smell.

Contrary to previous published works [23-25], the fatliquor detailed in this work is virtually free from inorganic salts; a disparity likely caused by differences in the method of production.

Table 2: Physicochemical properties of both unsulphonated and sulphonated *H. crepitans* oils

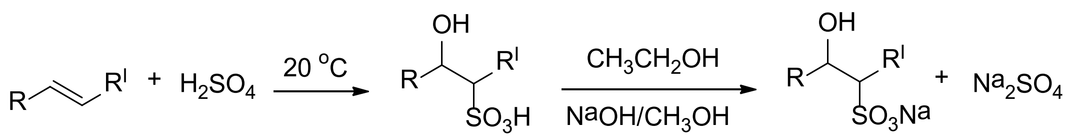
Parameter	Unsulphonated oil (HCO)	Sulphonated oil (SHCO)
Percentage Yield (w/w%)	52.76	74.86
Colour	Golden yellow	Brown red
Odour	Inoffensive	Odourless
Appearance of 10% Solution	-	Translucent
Colour of 10% solution	-	Very pale brown liquid
pH of 10% Solution	-	7.36
Stability of 10% solution	-	Stability > 24hrs
% Ash Content	-	Trace
% SO_3	-	5.87
Specific gravity (at 20°C)	0.920	0.942
Acid Value (mg KOH g^{-1})	6.17	5.93
Free fatty acid (% oleic acid)	3.09	2.97
Iodine value (g/100)	117	27
Saponification value (mg KOH g^{-1})	210	196

Sulphonation Process



Scheme 1. Sulphonation of *H. crepitans* oil to produce sulphonated (Sulphated) oil

The side reaction can be found below:



Scheme 2. Side by side reaction of the sulphonation of *H. crepitans* oil

Apart from the sulphated and true sulphonates, the reactions (as shown in schemes 1 and 2) also yielded a large quantity of Na_2SO_4 (a drying agent), which was vacuum filtered, thus making the sulphonated *H. crepitans* free from water.

Fourier Transform Infra-Red (FT-IR) Results

The FT-IR spectra of unsulphonated HCO and the corresponding sulphonated SHCO are shown in Figure 1a and 1b. In Figure 1b, the absence of the peak at 3009 cm^{-1} (C-H stretching frequency of non-conjugated unsaturation) as found in Figure 1a depicts the attack of H_2SO_4 on the –C=C- to form the sulphonated product. In Figure 1b the peak at ~1198 cm^{-1} (S=O stretching) is absent in Figure 1a. This confirms the formation of sulphonation reaction. Other prominent peaks found in both samples are at (2853 cm^{-1}) C-H stretching frequency of alkene, (1744 cm^{-1} (C=O stretching frequency of ester), 1464 cm^{-1} (bending frequency of unsaturated alkene), 721 cm^{-1} (bending frequency of saturated carbon atom). The wide peak in the range at 3200-3600 cm^{-1} is the OH stretching of alcohols and could be attributed to traces of alcohol left in the sulphonated product.

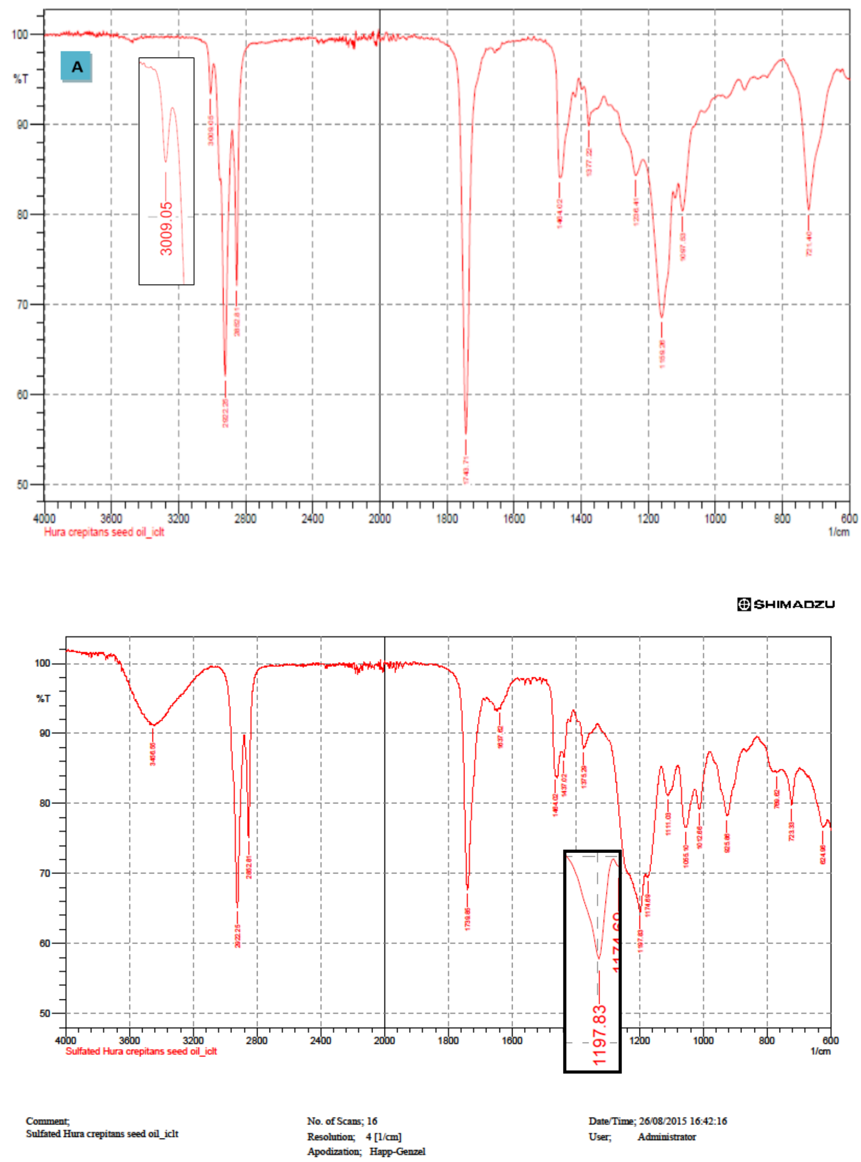
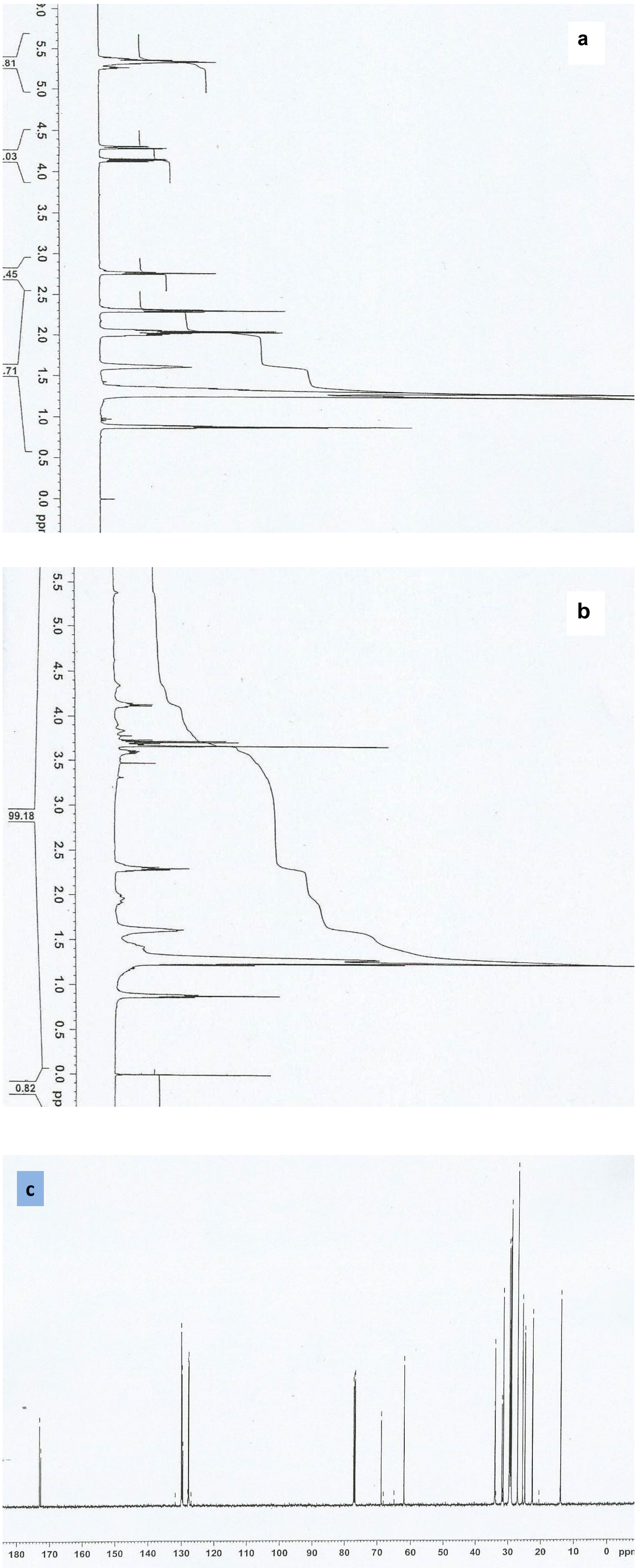


Figure 1. FT-IR spectra of unsulphonated *Hura crepitans* seed oil (A) (insert: expanded section of signal showing 3009.06 cm^{-1}) and sulphonated *Hura crepitans* seed oil (B) (insert: expanded section of signal showing 1197.83 cm^{-1})

Nuclear Magnetic Resonance (NMR) Spectroscopy Results

The ^{1}H NMR of HCO and SHCO are shown in Figures 2a and 2b respectively while the ^{13}C NMR and ^{13}C NMR DEPT spectral diagrams are found in Figures 2c, 2d, 2e and 2f, respectively.


a
b
99.18
0.82
c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

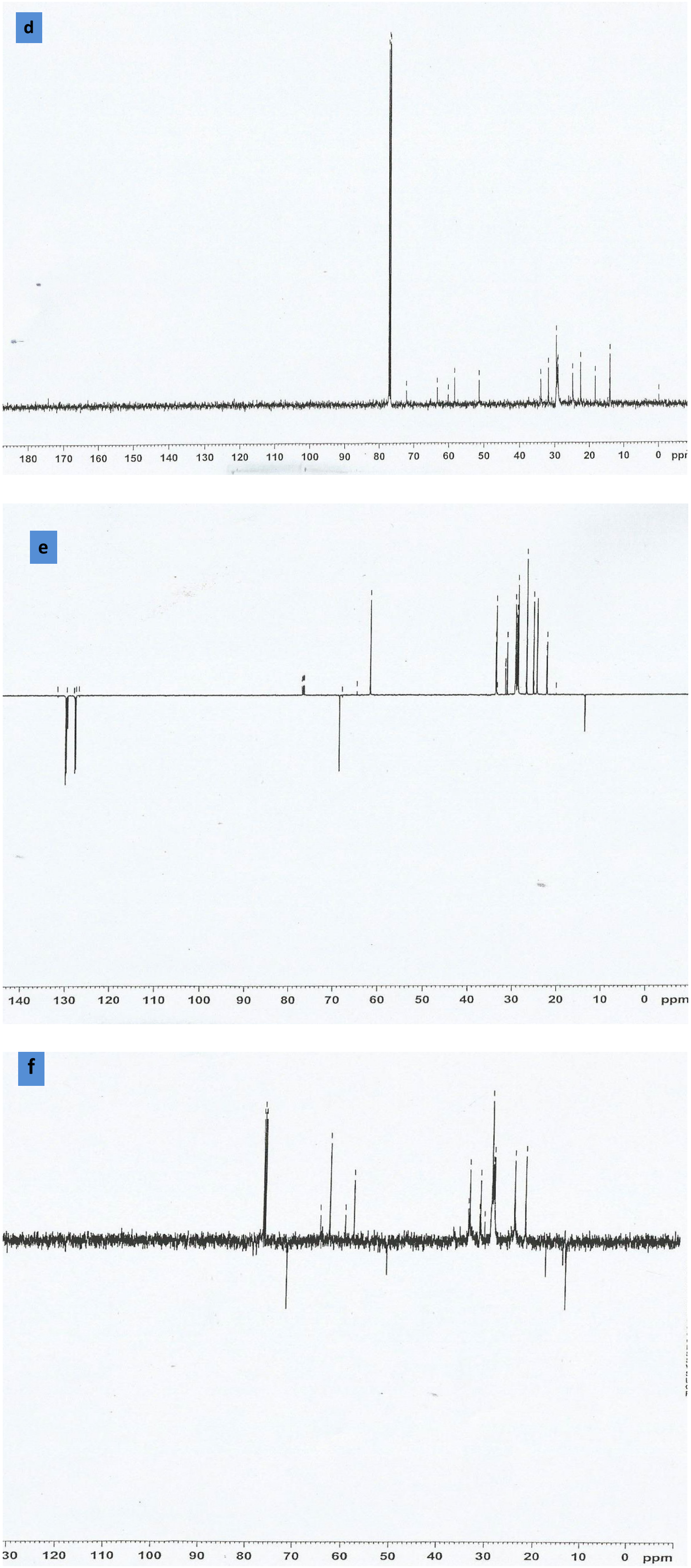


Figure 2. NMR spectroscopy results: (a) ^{1}H NMR of HCO (b) ^{1}H NMR of SHCO (c) ^{13}C NMR of HCO (d) ^{13}C NMR of SHCO (e) ^{13}C NMR DEPT of HCO (f) ^{13}C NMR DEPT of SHCO in deuterated chloroform

In the ^{1}H NMR, the multiplet observed at δ 5.29 (Figure 2a), in the unsulphonated oil are due to the olefinic protons attached to the C=C double bond. These protons are sp^2 hybridized and as such their NMR signals are deshielded by the influence of the diamagnetic anisotropy of the π system. Sulphonation / sulphation and sulphitation usually lead to the saturation of the double bond. The sp^3 hybridized protons formed are thus expected to be shielded relative to the sp^2 olefinic protons. The newly formed protons (H-C-S or H-C-O) in the two reactions formed (scheme 1 and scheme 2) showed signals at δ 3.6 and 3.73 ppm (Figure 2b). It is important to note that the slight deshielding observed for these protons relative to the rest of the protons in the sulphonated oil (Figure 2b) is due to the inductive effect of the electronegative sulphur and oxygen atoms. The inductive effect, however, causes less deshielding than diamagnetic anisotropy.

Similar explanation can be used to explain the differences in carbon chemical shifts observed in the ^{13}C NMR for the unsulphonated and sulphonated oils. In the ^{13}C NMR spectra of the unsulphonated oil, (Figure 2c), the methyl group at the end of the acyl chains in glyceride moiety give one signal at around 14.1 ppm. It is well separated from other signals and hence easily recognized. The same values have been reported in literature [22, 26, 27]. In the ^{13}C spectrum the signals associated with the olefinic carbons appear highly deshielded at δ 127.09 to 131.85 ppm due to the diamagnetic anisotropic effect of the π system. Upon sulphonation, (Figure 2d), these signals disappeared completely due to loss of the double bonds. The new signals which appeared at 52 and 72 ppm belong to the sp^3 hybridized carbons (C-S and C-O) formed after the sulphonation reactions. The slightly deshielded position of these signals is also due to the influence of the inductive effect of the electronegative sulphur and oxygen atoms.

From the ^{13}C NMR DEPT spectra diagrams (Figure 2 (e) and (f), the two samples (unsulphonated and sulphonated oils) studied had similar results except for some slight differences observed as a result of the reactions underwent by the sulphonated oils. The terminal CH_3 could be seen phased down in both results at δ 14 ppm. The C-H-O of the glycerol backbone could be seen phased down at δ 68 ppm. In like manner the two CH_2O of the glycerol backbone phased up and were seen at δ 64 ppm and 62 ppm. The -$(CH_2)_2$ of the fatty acid chains phased up an were seen at various positions δ 20-30 ppm. The evidence of the formation of C-O-S and C-S bonds by the reaction with H_2SO_4 was shown by the absence of the HC=CH previously found phased down in unsulphonated oils δ 127 ppm and 131.87 ppm in the sulphonated oils. The C-O-S was observed phased up δ 65.27 ppm in the sulphonated oils and C-S bonds were equally observed phased up at various positions δ 60.16 ppm and 58.38 ppm. These C-O-S and C-S bonds were completely absent in the unsulphonated oils. Also, the additional signals at 51.44 ppm, 58.38 ppm which represent the –C-S peaks and the signal at 72.17 ppm which represent the –C-O-S peak are completely absent in the starting HCO.

Characterisation of the Sulphonated Oil

The stability test results (Table 3) show that 10% fatliquor emulsions of sulphonated *H. crepitans* oil is generally stable in various salt solutions used in leather manufacturing processes like deliming and pickling solutions. As soon as a stable emulsion particle hits the fibre structure, the sulpho fraction interacts electrostatically with it, causing the emulsion to lose its emulsifier and the neutral oil will be deposited (Fixation) [6].

The sulphonated oil had good emulsion stability towards pickle liquor and hard water but unstable when in contact with formic acid. Anionic fixation takes place only in acid medium. This is because collagen at a pH < IEP becomes cationic and therefore anionic fatliquors are fixed. Addition of 10% emulsion of sulphonated oil (pH of 7.36) brings about an increase in the pH of 5% Chromium sulphate (pH of about 3) to a higher pH of about 3.8 to 4.2. This leads to the destabilisation of the emulsion and phase separation occurs thereby making it stable after about an hour. The table also shows that the prepared fatliquor can be used in the retanning and fatliquoring steps.

Table 3: Stability of 10% fatliquor emulsion towards pickle liquor, tan liquor and hard water

Solution added	Stability Status
5% Basic chromium sulphate (tan liquor)	Stable (1 hour)
5% $MgSO_4$ (hard water)	Stable
5% NaCl (found in pickle liquor)	Stable
5% Formic acid	Unstable

Differential Scanning Calorimetry (DSC)

Table 4: The thermal behaviour of HCO and SHCO

Oil Sample	Onset Temperature (°C)	Peak Temperature (°C)	Endset Temperature (Melting Point) (°C)
Unsulphonated	-30.85 + 0.40	-23.88 + 0.08	-15.21 + 0.53
Sulphonated	-10.17+ 1.05	3.48 + 0.25	11.91 + 0.12

A higher melting point found in the sulphonated oil signifies a phase transition and could be an indication that most of the unsaturated fatty acids have been used up in the sulphonation reaction; leaving behind saturated fatty acids (which have a higher melting point) than unsaturated fatty acid [28]. The DSC results also show that the oils are very stable within the temperature range studied.

Mechanical Properties of the Leather Samples

Mechanical properties of the leather samples were shown in Table 5.

Table 5: Mechanical properties of the leather samples

Properties	NC	PC	Pure	Blend
Average Softness	25.8	32.6	32.2	33.4
Average tear load (N)	352.5	409.2	505.5	613.3
Average Tensile strength (N/mm^2)	15.66	20.62	23.51	26.13
Average elongation at break (%)	34.79	41.86	36.40	45.02
Average grain crack strength (N)	200	330	410	370
Average Ball burst strength (N)	380	435	500	480

Note: NC = Negative control (without fatliquor), PC = Positive control (with commercial fatliquor), Pure = with pure sulphonated *H. crepitans* oil, Blend = a blend of pure sulphonated *H. crepitans* oil and 7.5% raw castor oil

It is evident from the strength or mechanical properties results that the leather fatliquored using sulphonated *H. crepitans* seed oil has better properties than the commercial fatliquor. The value of the mean tensile strength of the negative control (leather processed without fatliquor) was very low (15.66 N/mm^2) when compared with that of the fatliquored leather samples - PC (20.62 N/mm^2), A1 (23.51 N/mm^2). This can even be improved by the addition of 7.5% castor seed oil A2 (26.13 N/mm^2). (Castor oil is normally used in the tanning industry as a source of lubrication because of its humectant property). These enhancements in the strength properties of the leather from prepared fatliquors result from good lubrication of the leather fibres [29].

Stain Test Results

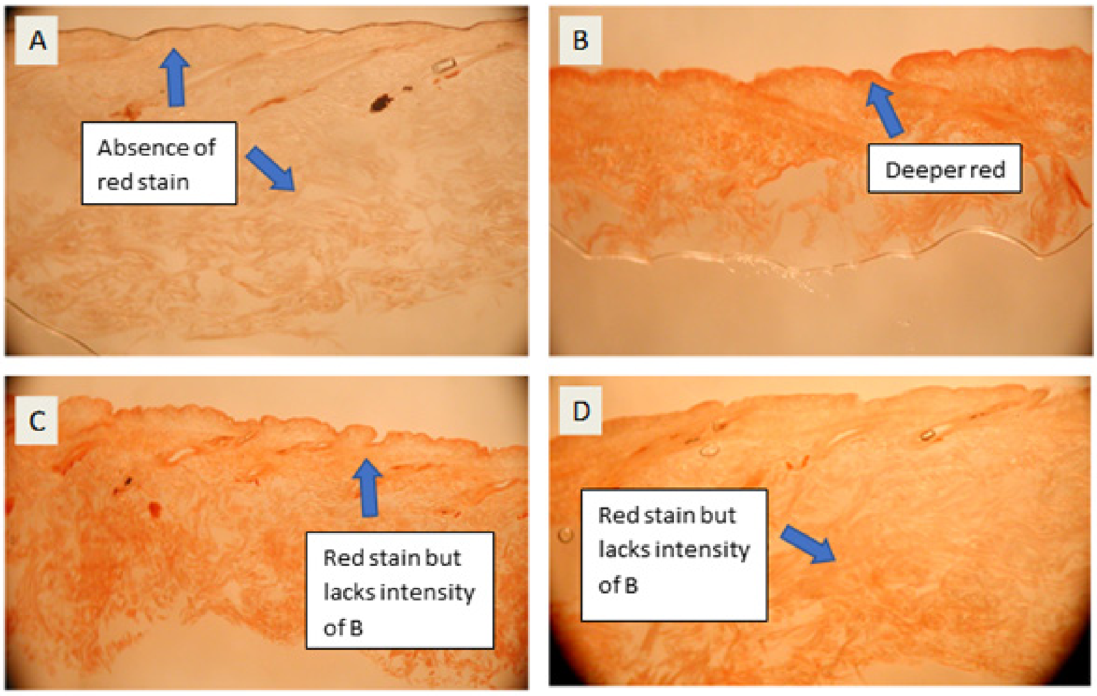


Figure 3. Staining test results showing cross section of goatskins fatliquored with: A) without fatliquor; B) with pure sulphonated *H. crepitans* fatliquor; C) with a blend of pure sulphonated *H. crepitans* fatliquor and 7.5% raw castor oil; D) with commercial fatliquor

The development of a deepening red colour in the stain as the figures move from Figure 3a to 3b signifies that the Sudan stain confirms the penetration of the sulphonated oils into the leather fibre structure [30].

Figure 3b, 3c, and 3d all show a deep penetration of fatliquor. The intensity of the red colour seen in Figure 3b-d indicates that the Sudan stain is detecting the presence of fats. Figure 3a indicates that no fat is present in the material. Figure 3c and 3d indicate that fatliquor is present, but the grain layer is not as deep in red colour as can be seen in Figure 3b. Surface lubrication is vital for grain strength when a leather is placed on the shoe last.

CONCLUSIONS

The sulphonation of *H. crepitans* seed oil (oil from underutilized seeds of no known market value), has been confirmed by the structural characterizations performed by FT-IR, ^{1}H NMR and ^{13}C NMR analysis. The sulphonated oil has no odour which will affect the smell of the finished leather product and is quite stable in pickle liquor and hard water. The leather processed by the sulphonated *H. crepitans* fatliquor had better tensile strength, double edge tear, and grain strength than that processed with commercial/imported fatliquor. This provides evidence that the sulphonated *H. crepitans* fatliquor is comparable and could even outperform commercial products for the production of leather shoe upper. It highlights the suitability of sulphonated fatliquor made from *H. crepitans* – a quite sustainable source.

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METHOD OF SKETCH PROFILING WITH SPLINE CURVES FOR FOOTWEAR DESIGN

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METHOD OF SKETCH PROFILING WITH SPLINE CURVES FOR FOOTWEAR DESIGN

ABSTRACT. The method of profiling sketches with spline curves with curvilinear guide paths is proposed in the work. The variants of possible combinations of types of spline sections are considered, all necessary variants of point positions for detection of a spline curve are given. The advantages of the developed method are the simplification of the design procedure of the proposed type of curves while providing more accurate representation of the real details, the mobility in controlling the shapes of curvilinear curves of sketch parts with a decrease in the order of the curve, including the curvature of different directions, which is in particular of first importance for all curves of the characteristic of shoe last sketches and conditional unfolding of the shoe last.

KEYWORDS: method of profiling, sketch, spline, designing, footwear

METODĂ DE TRASARE A SCHIȚELOR UTILIZÂND CURBE SPLINE PENTRU PROIECTAREA ÎNCĂLȚĂMINTEI

REZUMAT. În lucrare se propune o metodă de trasare a schițelor utilizând curbele spline cu traiectorii curbilinii. Sunt luate în considerare variante ale posibilelor combinații de tipuri de secțiuni spline și sunt date toate variantele necesare ale pozițiilor punctelor pentru detectarea unei curbe spline. Avantajele metodei dezvoltate sunt: simplificarea procedurii de proiectare a tipului de curbe propus oferind în același timp o reprezentare mai precisă a detaliilor reale, mobilitatea în controlul formelor curbelor de tip curbiliniar ale părților schiței cu o scădere în ordinea curbei, inclusiv curbarea în direcții diferite, care are o mare importanță pentru toate curbele specifice schiței calapodului și desfășurarea condițională a calapodului.

CUVINTE CHEIE: metodă de trasare, schiță, spline, proiectare, încălțăminte

PROCÉDÉ DE TRACER LES CROQUIS AVEC DES COURBES SPLINES POUR LA CONCEPTION DE CHAUSSURES

RÉSUMÉ. Dans cet article on propose un procédé de tracer les croquis avec des courbes splines avec des chemins de guidage curvilignes. Les variantes de combinaisons possibles de types de sections splines sont considérées et toutes les variantes de positions de point nécessaires à la détection d'une courbe spline sont indiquées. Les avantages de la méthode développée sont la simplification de la procédure de conception du type de courbes proposé, tout en fournissant une représentation plus précise des détails réels, la mobilité dans le contrôle des formes des courbes curvilignes des pièces du croquis avec une diminution de l'ordre des courbes, y compris la courbure des différentes directions, ce qui est notamment de première importance pour toutes les courbes caractéristiques pour les croquis de la forme des chaussures et du développement conditionnel de la forme.

MOTS-CLÉS : procédé de tracer, croquis, spline, conception, chaussures

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INTRODUCTION

The necessary condition for increasing the efficiency of the organization of manufacturing and quality assurance of products of footwear industry is the introduction of innovative technologies, namely, the development of manufacturing, scientific, technical and innovation activities of enterprises using the latest achievements. The advancement of footwear industry is aimed at the development of the concept of footwear design automatisation, which provides a continuous connection of design processes, which include the development, the design, the implementation and use of footwear products.

Modern methods of application of applied and analytical geometry bases allow to simulate objects of rather complex forms and footwear products are among these objects. At the same time tasks that are being solved are directed on the search of analytical description and further modeling of objects using curves of different orders. Methods of simulating curves according to the way of their description can conditionally be divided into: using arrays of points; using equations. Firstly, the application of arrays of points is bulky, because it involves the use of significant numerical computational methods, and secondly, found in this way characteristics may not meet the requirements which had been set and do not contain an analytical basis [1]. They also do not solve the problem fully because they do not take into account the geometric characteristics appropriate to curves. There is also a certain number of methods for finding the dependences for curve equation descriptions in the form of various functions, polynomials, etc.

As it is known, the processes of modeling and designing products are largely associated with the creation and use of geometric models of surfaces or contours of surfaces. Objects with a complex curvilinear surface (foot, shoe last, shoe uppers), are of the greatest difficulty in designing because in order to ensure the appropriate quality of the products the structure of the foot should be taken into account.

Therefore, the creation of methods for processing the received source information of analytical modeling is an integral part of the research and shows the way for information footwear design.

RESEARCH METHODS

In the practice of design work for the simulation of curve lines certain approaches and methods are used [1-11]. The basis of these methods is the use of geometric techniques and the formation of a curves description model using complex mathematical techniques and transformations.

In works [12-14] the main principles of the use of spline curves for the design of sketches of details of footwear industry. Theoretical principles and algorithms for the solution of the inverse problem of a lineation design, which means to find the position of control points of the spline at known positions of points of sketch parts are presented there. The corresponding software for the practical realization of the inverse problem algorithms has been developed.

RESEARCH RESULTS

It is proposed to use Bezier spline curves to develop an analytical model. This spline category is most commonly used in automated design systems and in many graphical packages. The advantages of using these curves include the relatively simple mathematical apparatus, the description of bodies of any complexity with the necessary accuracy.

In the first instance, it is necessary to define some specific issues related to the classification and terminology of splines in general and splines with curvilinear guides in particular. Spline or spline curve is a smooth line, that is a line at any point which the derivative is determined monosemantically. A straight line (a first-order spline, defined by two control points i.e. the ends of this line) can be a spline in a specific case. Basically, the lineation of a part can have a lot of bends, but it should be borne in mind that each bend requires a separate control point, and the order of the curve per unit is greater than the number of these bends, respectively, the number of control points per unit is greater than the order of the curve.

In the article [14] it is shown that the use of splines with curvilinear guides can greatly complicate the shape of the curve without increasing its order. It is known [1] that the further a certain section from a certain control point is located, the less the position of this point affects the shape of this spline area.

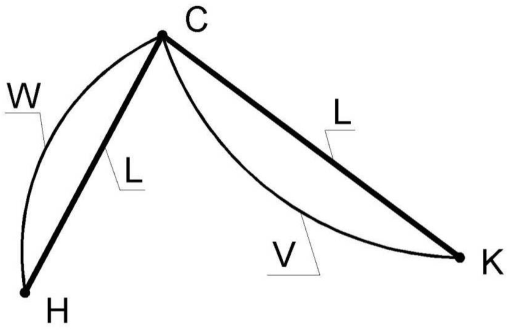

Figure 1. Scheme of symbols in the EU

So, from this point on, to simplify the presentation, it is enough to investigate the analyst of its element which is the simplest component of the spline curve. The spline element (EC) is considered to be the least complicated section (excluding the first order spline), which is a spline of the second order and is determined by three control points. We also conditionally set the sequence of these points by bypassing them clockwise (the direction for analytics has no principal importance), so the point H will be the point of the beginning of the EC, the point C - the middle, and the point K - the final (Fig. 1). Accordingly, HC sections are called the initial section of the EC, and the segment CK - the final. Usual HC and CK splines are straight lines, which we denote by the letter L. The ordinary EC of L type is inside the corner formed by the guides, and its ends coincide with the points of the beginning and the end of the EC (H and K respectively) (these properties are reserved for EC of all types).

Curvilinear guidance (KH) is any curve that connects the ends of the initial or final sections. The simplest of them can be circle arcs, ellipses etc. From this point on, curvilinear guides in the form of circle arches are under consideration. If the center of KH curvature is inside the angle formed by the EC guides, then this KH is called convex (type W), if outwardly it is called curved one (V type). Obviously, the center of the circle will always be symmetric relatively to the ends of the corresponding section.

LL option has been considered in details from the standpoint of analytics in [1], and the construction principle in [5]. It should be noted that the basis for all calculations needed to construct splines of different types is the parameter t, because the oscillation of the position of any point on the segment is determined by multiplying this parameter by the length of the segment.

WL Option

In this combination the initial guide is curvilinear convex, the finite is rectilinear one. The calculation scheme is shown in Fig. 2.

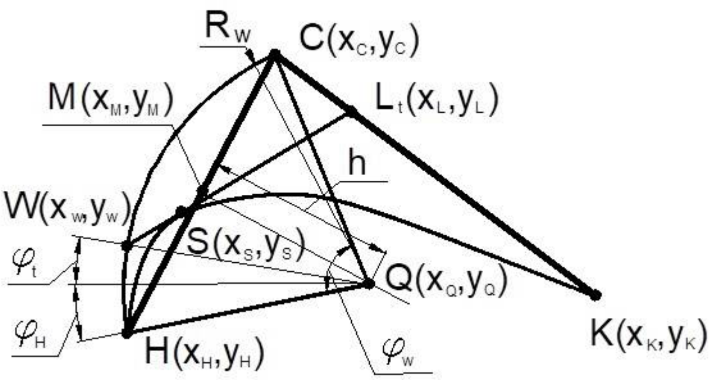

Figure 2. The scheme of construction of WL spline type

The position of the control points of H(x_H, y_H), C(x_C, y_C), K(x_K, y_K) spline is specified by the spline control points coordinates, the radius of the curvilinear guide RW is chosen selectively. The task is to determine the coordinates of the spline point at a certain value of the parameter t (the current S point with the coordinates x_S, y_S).

$$x_S = x_W + t(x_L - x_W).$$

$$y_S = y_W + t(y_L - y_W).$$

Coordinates of L point

$$x_L = x_C + t(x_K - x_C)$$

$$y_L = y_C - t(y_C - y_K)$$

Coordinates of W point

$$x_W = x_Q - R_W \cos\varphi_t,$$

$$y_W = y_Q + R_W \sin\varphi_t$$

The position of the center of the curvilinear guide circle is determined from the following construction. From the middle of M point of the initial segment HC, which coordinates are

$$x_M = x_H + 0{,}5(x_C - x_H),$$

$$y_M = y_H + 0{,}5(y_C - y_H)$$

a perpendicular is made, the distance is set on it

$$h = \sqrt{R^2 - (0{,}5\ HC)^2}.$$

If we take into account that the angular coefficient of inclination of HC guide is $k_{HC} = (y_C - y_H)/(x_C - x_H)$, then the perpendicular angle coefficient $k_h = -(1/k_{HC})$, which is numerically equal to the inclination angle tangent of the perpendicular. Then

$$x_Q = x_M + h\cos(arc\ tg\ k_h),$$

$$y_Q = y_M - h\sin(arc\ tg\ k_h).$$

Angle φ_t, which is required to determine the coordinates of the current point W (x_W, y_W),

$$\varphi_t = t \cdot \varphi_W - \varphi_H,$$

where the secondary angle is

$$\varphi_H = arc\ tg((y_Q - y_H)/(x_Q - x_H)),$$

and the angle of the curvilinear guide is

$$\varphi_W = 2\,(arc\sin(0{,}5 HC/R)).$$

Length of the segment

$$HC = \sqrt{(x_C - x_H)^2 + (y_C - y_H)^2}.$$

The given analytics is the basis for automated calculations of coordinates of a spline curve points with a circular convex initial guideline.

Let's consider other options.

VL Option

In this case, the initial guide is a concave circular guide, the terminal guide is a straight guide. A scheme of such combination of guides is shown in Fig. 3. The system of symbols used in the previous scheme has been saved as much as possible.

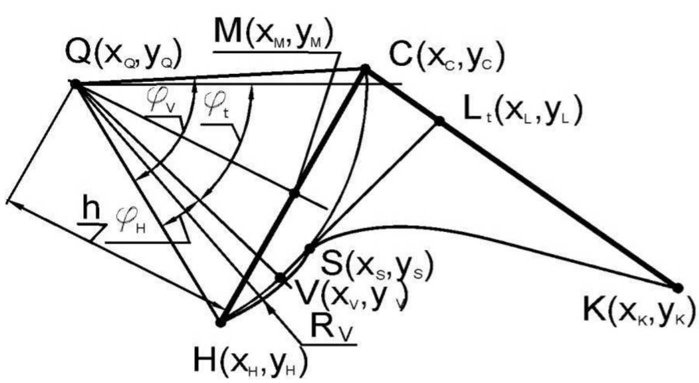

Figure 3. The scheme of construction of VL spline type

The task is to determine the coordinates of the spline point at a certain value of the parameter t (the current point S with the coordinates x_S, y_S).

$$x_S = x_W + t(x_L - x_W),$$
$$y_S = y_W + t(y_L - y_W),$$
$$x_L = x_C + t(x_K - x_C),$$
$$y_L = y_C - t(y_C - y_K),$$
$$x_W = x_Q + R_W \cos \varphi_t,$$
$$y_W = y_Q - R_W \sin \varphi_t.$$
$$x_M = x_H + 0{,}5(x_C - x_H),$$
$$y_M = y_H + 0{,}5(y_C - y_H)$$
$$h = \sqrt{R^2 - (0{,}5\ HC)^2}.$$

Angular coefficient of the guide HC inclination

$k_{HC} = (y_C - y_H)/(x_C - x_H)$, then the perpendicular angle coefficient $k_h = -(1/k_{HC})$, which is numerically equal to the tangent of the angle of perpendicular inclination. Then

$$x_Q = x_M + h\cos(arc\ tg\ k_h),$$
$$y_Q = y_M + h\sin(arc\ tg\ k_h).$$
$$\varphi_t = \varphi_W - \varphi_H - arc\sin((y_C - y_Q)/(x_C - x_Q)).$$
$$\varphi_W = 2\ (arc\sin(0{,}5HC/R)$$
$$\varphi_H = t \cdot \varphi_W,$$
$$\varphi_W = 2\ (arc\sin(0{,}5HC/R).$$
$$HC = \sqrt{(x_C - x_H)^2 + (y_C - y_H)^2}.$$

WV Option

The corresponding scheme of this combination is shown in Fig. 4.

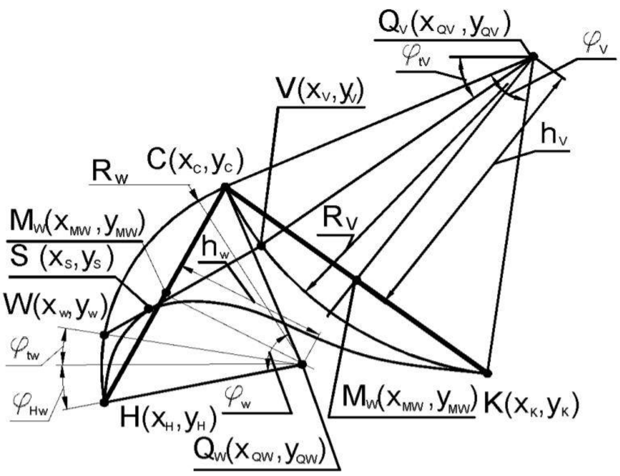

Figure 4. Scheme of spline construction of WV type

In fig. 4 the following indexing system is used: the parameters relating to the convex curvilinear direction include W index, concave - V index. Parameters concerning the convex curvilinear direction are similar to analog analyst in Fig. 2 taking into account the specifics of the designations, the study material has been presented without comments and explanations.

$$x_W = x_{QW} - R_W \cos \varphi_{tW},$$
$$y_W = y_{QW} + R_W \sin \varphi_{tW}$$
$$x_{MW} = x_H + 0{,}5(x_C - x_H),$$
$$y_{MW} = y_H + 0{,}5(y_C - y_H)$$
$$h_W = \sqrt{R_W^2 - (0{,}5\ HC)^2}.$$
$$k_{HC} = (y_C - y_H)/(x_C - x_H),$$
$$k_{hW} = -(1/k_{HC})$$
$$x_{QW} = x_{MW} + h_W \cos(arc\ tg\ k_{hW}),$$

$$y_{QW} = y_{MW} - h_W \sin(arc\ tg\ k_{hW}).$$

$$\varphi_t = t \cdot \varphi_W - \varphi_H .$$

The angle φ_W is determined by

$$\varphi_{tW} = t \cdot \varphi_W - \varphi_{HW} ,$$

$$\varphi_{HW} = arc\ tg((y_{QW} - y_H)/(x_{QW} - x_H)),$$

$$\varphi_W = 2\ (arc \sin(0{,}5HC/R_W)).$$

$$HC = \sqrt{(x_C - x_H)^2 + (y_C - y_H)^2} .$$

V point coordinates are determined in the following way

$$x_V = x_{QV} - R_V \cos \varphi_{tV} ,$$

$$y_V = y_{QV} - R_V \sin \varphi_{tV}$$

$$x_{MV} = x_C + 0{,}5(x_K - x_C),$$

$$y_{MV} = y_C + 0{,}5(y_C - y_K)$$

$$h_V = \sqrt{R_V^2 - (0{,}5\ KC)^2} .$$

$$k_{KC} = (y_K - y_C)/(x_K - x_C),$$

$$k_{hV} = -(1/k_{KC})$$

$$x_{QV} = x_{MV} + h_V \cos(arc\ tg\ k_{hV}),$$

$$y_{QV} = y_{MV} + h_V \sin(arc\ tg\ k_{hV}).$$

$$\varphi_{tV} = t \cdot \varphi_V + arc \sin((y_{QV} - y_C)/R_V).$$

$$\varphi_V = 2\ (arc \sin(0{,}5KC/R_V)).$$

$$KC = \sqrt{(x_C - x_K)^2 + (y_C - y_K)^2} .$$

VW Option

The variant scheme is shown in Fig. 5. Analytics to Fig. 5, as it was done previously for other schemes, is given without comments.

The coordinates of V point are determined in the following way

$$x_V = x_{QV} + R_V \cos \varphi_{tV} ,$$

$$y_V = y_{QV} - R_V \sin \varphi_{tV}$$

$$x_{MV} = x_C - 0{,}5(x_K - x_H),$$

$$y_{MV} = y_C - 0{,}5(y_C - y_H)$$

$$h_V = \sqrt{R_V^2 - (0{,}5\ HC)^2} .$$

$$k_{KC} = (y_C - y_H)/(x_C - x_H),$$

$$k_{hV} = -(1/k_{KC}).$$

$$x_{QV} = x_{MV} - h_V \cos(arc\ tg\ k_{hV}),$$

$$y_{QV} = y_{MV} + h_V \sin(arc\ tg\ k_{hV}).$$

$$\varphi_{tV} = \varphi_V - t \cdot \varphi_V - arc \sin((y_C - y_{QV})/R_V$$

.

$$\varphi_V = 2\ (arc \sin(0{,}5HC/R_V)).$$

$$HC = \sqrt{(x_C - x_H)^2 + (y_C - y_H)^2} .$$

$$x_W = x_{QW} + R_W \cos \varphi_{tW}$$

$$y_W = y_{QW} + R_W \sin \varphi_{tW} .$$

$$x_{MW} = x_K + 0{,}5(x_K - x_C),$$

$$y_{MW} = y_K + 0{,}5(y_C - y_K).$$

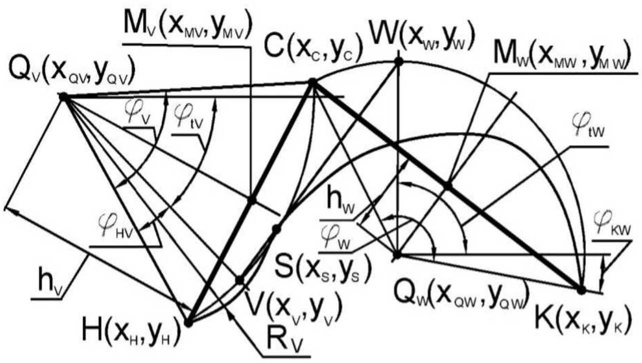

Figure 5. The scheme of construction of VW spline type

$$h_W = \sqrt{R_W^2 - (0{,}5\ KC)^2} .$$

$$k_{HC} = (y_C - y_K)/(x_C - x_K),$$

$$k_{hW} = -(1/k_{HC}).$$

$$x_{QW} = x_{MW} - h_W \cos(arc\ tg\ k_{hW}),$$

$$y_{QW} = y_{MW} - h_W \sin(arc\ tg\ k_{hW}).$$

φ_W angle is determined in the following way

$$\varphi_W = 2\,(arc \sin(0{,}5KC/R_W)$$

$$\varphi_{tW} = \varphi_W - t \cdot \varphi_W - \varphi_{KW},$$

$$\varphi_{KW} = arc\ tg((y_{QW} - y_K)/(x_{QW} - x_K)),$$

$$KC = \sqrt{(x_C - x_K)^2 + (y_C - y_K)^2}.$$

All other possible combinations (LW, LV, WW, VV, etc.) are individual cases of the above mentioned and the analyst for them can be developed based on the one given above.

It should be noted that in each of the drawings, despite the same position of control points, the shape of the spline is changing constantly, which one more time shows the advantages of splines with curved guides, the main advantage is the more flexible fitting of real lineation of parts. Another important fact to be taken into account is that the radius of the circular curvilinear guide should be greater than half of the length of the corresponding straight guide.

Profiling of parts of the lineations was done, using spline curves with curvilinear guides. The spline curve (for example, of the second order) is given by three points: apart from starting PS (x_S, y_S) points and PE (x_E, y_E) ending points an intermediate point P_1 (x_{P1}, y_{P1}), is required and while these points are connected by straight guides (Fig. 6).

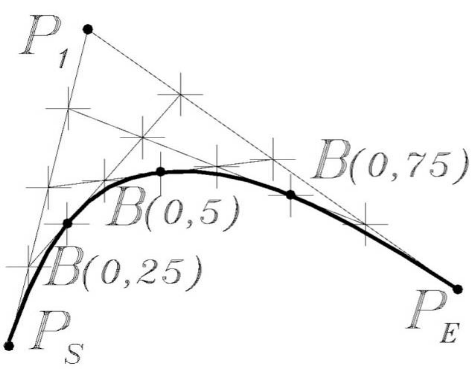

Figure 6. Formation of a spline curve with straight guides

On each sections of the guides additional points 1 (on the P_S-P_1 section) and 2 (section P_1-P_E) are moving synchronously. At any time the distance to points 1 and 2 from the beginning of the corresponding section is determined as the product of the parameter t (this is the parameter (time-iterator) which varies within 0 ... 1, assuming that $t_i=1$ when $i=1$ and $t=0$ when $i=0$) and its length. The point B(t) is on the segment which connects points 1 and 2 whereas its distance from point 1 is also determined as the product of the parameter t and the length of the segment 1-2. In Fig. 6. in order to simplify its perception, the construction of a spline curve is shown on the example of only a few points with values of the parameter t 0; 0.25; 0.5; 0.75; 1. However, the drawback of this method is the one-valuedness of the curve shape and the need of large number of control points for the complex curvatures of the lineations since straight-line guides are used for the control system. One more possible option for construction of complex sketches is to make use individual Bezier curves which can be sequentially connected with one another in Bezier spline. In order to ensure the smoothness of the line at the junction of two curves, the adjacent points of both curves must lie on the same line, which requires additional operations.

Taking into account the above-mentioned imperfections, it is proposed to perform profiling of parts of the lineations using spline curves with curvilinear guides.

Fig. 7. shows the variant of construction of the sketch curve with the use of a curvilinear guide in the form of an arc of a circle between the points P_S-P_1, and Fig. 8. shows the variant of construction of the sketch curve with the additional use of the guide in the form of the arc of the circle P_1-P_E, with the opposite sign of curvature. Further construction is made following the above-mentioned principles.

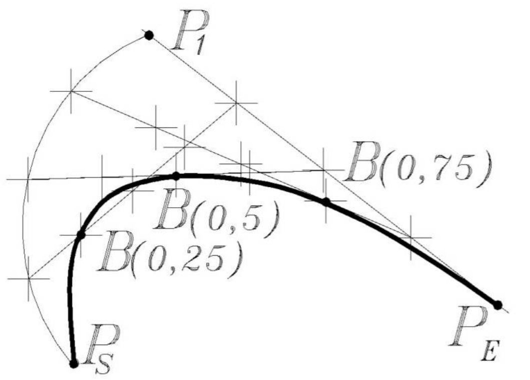

Figure 7. Construction of a spline curve with curvilinear guides

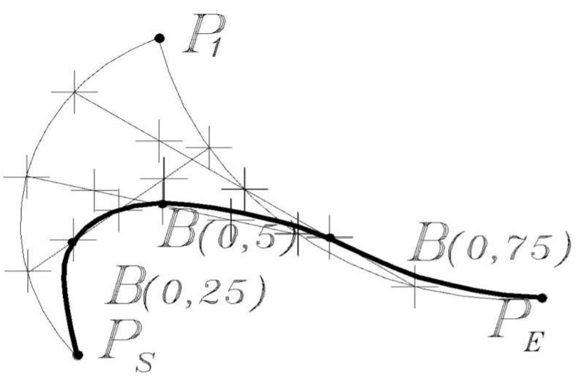

Figure 8. Construction of a spline curve with curvilinear guides (two arcs)

The given examples allow to obtain the curves of lineations of any form with the same control points P_S, P_1, P_E.

An extremely important advantage of the method of constructing curves of the sketches is that the curve in Fig. 7 if it had been built using straight-line guides could be obtained only with the third order of the spline curve, the curve in Fig. 8 - the fourth, respectively it would require four and five control points, which would greatly complicate the construction process. It should also be mentioned that the shape of the curvilinear guide can be omniform which also increases the polyvariability of the spline curves.

Thus, presented examples demonstrate the advantages of using curvilinear guides which simplify the construction of complex sketches.

The presented properties and principles of construction of spline curves allow to solve the inverse problem of profiling the contours of the longitudinally vertical section of the inner mold line tool (Fig. 9), namely, at given points, where it is necessary to pass the curve through, to determine the exact position of the coordinates (saying more accurately to determine the matrix

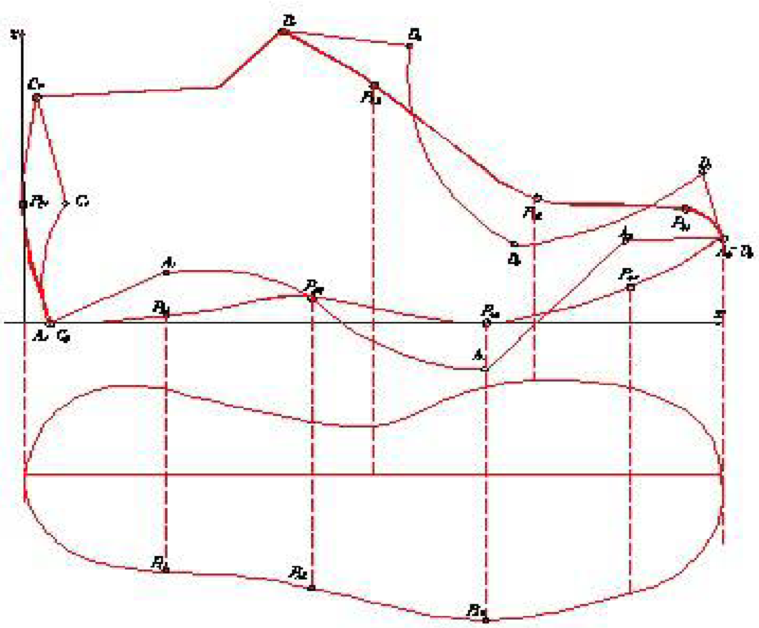

Figure 9. Principle of construction of the main contours of the longitudinal and vertical section of the inner mold line tool of shoes

of coordinates) of the control points, which allows to describe the curves analytically which are assumed to be used to form contours with.

The mathematical apparatus of spline curves allows to reproduce a function with a predetermined accuracy (within 5% for footwear industry) deviation from the original curve.

CONCLUSIONS

The method of profiling parts of sketches with spline curves with curvilinear guides has been proposed, which provides the flexibility of control of the shape of the curvilinear sections of the parts, reducing the order of the curve of considerable complexity, including the curvature of a different sign.

The analytical bases of determination of coordinates of spline curve points with circular curvilinear guides for the basic combinations of section types have been developed.

Profiling of sketch contours of the longitudinally vertical cut of the inner mold line tool of shoe using spline curves with curvilinear guides has been proposed.

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METHODS USED TO MANAGE DEFECTS RELATED TO VEGETABLE TANNED LEATHER

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METHODS USED TO MANAGE DEFECTS RELATED TO VEGETABLE TANNED LEATHER

ABSTRACT. Leather surface quality is vital when it comes to leather artifact production. Users of the locally produced vegetable tanned leather adopt various methods to manage and improve on the poor surface quality of leather produced in Ghana. Students from the various secondary schools and local craftsmen who often depend on the vegetable tanned leather for it inherits unique properties such as flexibility, resilience, breathability, perspiration, durability and mechanical strength adopt various methods to improve on the surface quality and also meet the market standard. The necessity for quality leather surface in leather artefact production has called for the need for corrective measures to manage defects associated with vegetable tanned leathers produced in Ghana. Stains, cuts, holes, grain loosing, creases, wrinkles, scratch marks, bacterial and viral infections are common defects which affect the quality of vegetable tanned leathers produced in Ghana. Defect managing methods such as dyeing, painting, screen printing, stamping, appliqué, and scorching adopted by leather users to manage surface defects were examined for their viability in this current study.

KEYWORDS: vegetable tanned leather, defects, managing methods, viability

METODE PENTRU GESTIONAREA DEFECTELOR PIEILOR TĂBĂCITE VEGETAL

REZUMAT. Calitatea suprafeţei pielii este vitală atunci când vine vorba despre producția de artefacte din piele. Utilizatorii pieilor tăbăcite vegetal produse la nivel local adoptă diverse metode de gestionare şi îmbunătăţire a calității slabe a suprafeței pieilor produse în Ghana. Elevii din diferite licee şi meşteşugarii locali care depind adesea de pielea tăbăcită vegetal care are proprietăți unice, cum ar fi flexibilitatea, rezistența, respirabilitatea, permeabilitatea la vapori de apă, durabilitatea şi rezistența mecanică, adoptă diferite metode de îmbunătăţire a calității suprafeței, pentru a se conforma standardelor pieții. Necesitatea pielii cu suprafață de calitate înaltă în producția de artefacte din piele a impus luarea unor măsuri corective pentru a gestiona defectele pieilor tăbăcite vegetal produse în Ghana. Petele, tăieturile, găurile, curgerea feței, cutele, încreţiturile, zgârieturile, infecțiile bacteriene şi virale sunt defecte comune care afectează calitatea pieilor tăbăcite vegetal produse în Ghana. În acest studiu s-a examinat viabilitatea metodelor de gestionare a defectelor, cum ar fi vopsirea, pictarea, serigrafierea, ştanţarea, aplicarea cusăturilor şi pirogravura, adoptate de utilizatorii de piele pentru a gestiona defectele de suprafață.

CUVINTE CHEIE: piele tăbăcită vegetal, defecte, metode de gestionare, viabilitate

MÉTHODES POUR GÉRER LES DÉFAUTS DU CUIR TANNÉ VÉGÉTAL

RÉSUMÉ. La qualité de la surface du cuir est essentielle pour la production d'artéfacts en cuir. Les utilisateurs de cuir tanné végétal produit localement adoptent diverses méthodes pour gérer et améliorer la qualité de surface médiocre du cuir produit au Ghana. Les étudiants des différentes écoles secondaires et les artisans locaux qui dépendent souvent du cuir tanné végétal aux propriétés uniques telles que la souplesse, la résilience, la respirabilité, la perméabilité à la vapeur d'eau, la durabilité et la résistance mécanique adoptent diverses méthodes pour améliorer la qualité de la surface et s'adaptent également aux normes du marché. La nécessité d'une surface en cuir de qualité dans la production d'artéfacts en cuir a nécessité de mesures correctives pour gérer les défauts associés aux cuirs à tannage végétal produits au Ghana. Les taches, les coupures, les trous, la fleur creuse, les plis, les rides, les égratignures, les infections bactériennes et virales sont des défauts communs affectant la qualité des cuirs à tannage végétal produits au Ghana. Les méthodes de gestion des défauts telles que la teinture, la peinture, la sérigraphie, l'estampage, les appliqués et la pyrogravure adoptées par les utilisateurs de cuir pour gérer les défauts de surface ont été examinées dans la présente étude pour déterminer leur viabilité.

MOTS-CLÉS : cuir tanné végétal, défauts, méthodes de gestion, viabilité

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INTRODUCTION

All skins and hides have natural defects which attest to the genuineness of leather though not desirable on the finished leather product [1]. Quality is a crucial factor in leather product consumption. Defect on leather surfaces affect the quality of the leather product and furthermore, restrict the development of the leather industry [2]. These defects occur during life and death of the animal [3, 4]. Defects that occur when the animal is still alive include, cuts resulting from barbed wire, in-fighting among male members, thorn scratches and cuts; brand marks made for ownership purposes using hot iron; holes and spots from infestations and infections caused by ticks, horn flies, mange and bot-flies; abscesses resulting from wrong vaccination techniques and wrinkles resulting from natural growth marks or excess weight related problems [4]. Defects which occur at the death of the animal may result from improper handling of various techniques during skin transportation and production. According to [4], defects which occur during skin production are much less common as they are controlled by tanneries which have quality leather production as their main business. Leathers go through treatment operations to control such defects and also improve on the final appearance of the leather [5, 6].

In Ghana, leather is obtained from the southern and Northern part of the country. Leather from these areas are often of show defects with little or no surface treatment [3]. The leather shows defect such as abscess, blind warble wholes, brand mark, dung damage, eczema, scar mark, grain break, blisters, holes, flay cuts and grain peeling [7, 8]. According to [3], observations made in the various leather shops in Kumasi, Accra and Takoradi show that the vegetable tanned leather is not a material of choice due to various surface defects associated with the leather. Significance of the leather is very limited for products such as footwear, sofas, bags, jackets, gloves, car seats, car seat backs and spare tyre covers which are commonly used by Ghanaians. Imported leather and leatherette are bought at high cost although most of these materials lack the imperative properties of vegetable tanned leather such as resilience breathability, perspiration, durability, tooling and ability to model and form to shape as emphasized by [9].

Since leather is mostly used for visually appealing products like upholstery, footwear, bags, jackets and car seats, excellent optical properties of materials is a great requirement [10]. Users of the vegetable tanned leather in Ghana adopt several methods to manage and improve on the quality of leather and its products to meet market standards. Students of leather in various institutions in Ghana who are required by curriculum [11] to use vegetable tanned leather for their course work adopt various managing methods to manage defects and improve on the quality of leather products [12]. Leather craftsmen who produce leather products for market supply also adopt various methods to manage defects and improve on the quality of the leather products produce on the Ghanaian market. The research examines the methods implemented by users of locally produced vegetable tanned leather and the viability of the methods by identifying their strengths and weakness.

MATERIALS AND METHODS

Users of the locally produced vegetable tanned leather were students from the second and tertiary education institutions in the Kumasi metropolis of Ghana and leather craftsmen from Bolgatanga in the Northern part of Ghana. The research adopted the purposive and the convenience sampling technique to sample a population of 20 students who make use of locally produced vegetable tanned leather from the department of Integrated Rural Art and Industry in the Kwame Nkrumah University of Science and Technology (KNUST). 31 visual Arts students from second cycle institution in the Kumasi metropolis of Ghana and 5 local craftsmen from Bolgatanga Craft Village. Face to face interview were conducted with the respondents on methods they adopt in managing locally produced vegetable tanned leather surface defects. Observation of products are made to further analyze the methods used in situations where samples of works were available.

RESULTS

The local leather craftsmen adopt two methods to manage locally produced vegetable tanned leather surface defects. Defects may be ignored or occasionally leather be discarded when these two methods are unable to manage defects. This affect the aesthetic appearance of the leather products produce on the market by the local leather craftsmen. The following methods are adopted by leather craftsmen to manage defect with vegetable tanned leather.

Tack Patching

Tack patching is a leather defect management method used by some local leather craftsmen to repair defects like open cuts and larger holes on surfaces of vegetable tanned leathers. In tack patching, a strip of leather or plastic yarn is used to join an open cut or hole in a leather by means of hand stitching. Though tack patching ensures closure of open cuts and holes, stitch lines which are formed on the leather surface after patching remain as another form of defect as shown in Figures 1 and 2. Leather users trim Patched areas during leather artefact production because the presence of the stitch lines interrupt with the leather's surface grain structure and reduce the aesthetic appearance of the leather and artefacts produced from the leather.

Figure 1. Patched leather with strip of leather
Source: Field photograph, February-May, 2017

Figure 2. Patched leather with plastic yarn
Source: Field photograph, February-May, 2017

Dyeing

The local leather craftsmen manage dark brown spots which may result from stains and parasitic infections by changing the original khaki colour of the leather to red, coffee brown or black. Colour is much dependent on the intensity and nature of the defect. Leathers with less intense defects are often dyed red or coffee brown whereas the very intense leathers are dyed black.

When dyeing red colour, the local craftsmen use the stalk of a sorghum plant. The sorghum stalk is boiled in water to extract colour. The leather is also soaked in water between three to four days and later pounded to soften and open the pours of the leather fiber to enable penetration of the dye into the fibres of the leather. The leather is soaked in the boiled sorghum stalk solution for five to seven days depending on the intensity of red colour needed. The leather is removed from the solution and stretched under a shed to dry.

For black and coffee brown colour, the dye is obtained by rusting metals with iron content in a lime or lemon solution. The lime or lemon solution facilitates the rusting of the iron metals to obtain a dark brown or black chemical for changing the khaki or red leather to coffee brown or black colour. The leather to be dyed is first soaked in water and transferred into the rusted iron solution after two to three days. The length of the time the leather is soaked in the rusted solution is dependent on the shade of coffee brown colour required. For black colour, the leather is soaked in the solution for a very long time that is for about three weeks to a month. When the right colour is obtained, the leather is removed from the colorant and dried under shade. Black colour dyeing according to the craftsmen is best at hiding different kinds of stain defects and parasitic infections than red colour dyeing. Black colour dyeing also reduces the intensity of grain peeling and scratch marks defects.

Figure 3. Cream dyed leather
Source: Field photograph,
February-May, 2017

Figure 4. Red leather
Source: Field photograph,
February-May, 2017

Figure 5. Coffee brown leather
Source: Field photograph,
February-May, 2017

Figure 6. Black leather
Source: Field photograph,
February-May, 2017

Students of leather adopt more methods than the local leather craftsmen who produce on the market. Students adopt the following methods to manage various defects on vegetable tanned leather surfaces to enable them produce leather products with outstanding surface appearance.

Dyeing is done in two ways by students. Dyeing by immersion which involves submerging the whole leather into a dye solution called dye bath. Dye bath is prepared by mixing vat dye of their preferred colour with warm water, sodium hydroxide (caustic soda) and sodium hydrosulphite (hydros) in the ratio, 3:1:3. The caustic soda and hydros in dye bath ensure colour fastness and brightness. With this method, the brightness of the colour after dyeing is dependent on the concentration of the dye in the solution. In the process of dyeing, Leather is wet with water to open up fibers and immersed into a dye bath. The leather is allowed to stay in the bath for about 10 to 15munites and spread out under a shade to oxidize or change colour. The leather is washed in clean water to remove excess dye after colour change and finally dried.

Figure 7. Leather dyed by immersion
Source: Department of Integrated Rural Art and Industry Leather Studio, KNUST

Marbling is the second technique students adopt in dyeing their leather to manage defects. In marbling, leather is soaked in water and beaten in mortar with pestle to soften the leather and open up its fibers to ensure effective penetration of dye into the fibers. The leather is spread out on a clean large table and gently gathered by pulling it with the fingers bit by bit towards the center. With the help of a table-spoon, prepared dye is fetched and spread evenly all over the leather. The leather is left to stand under a shade for about 10 to 15 minutes to oxidize or change colour. The leather is washed in clean water and allowed to dry under a shade.

Figure 8. Marbled leathers
Source: Kumasi Technical Institute Visual Arts Department

According to leather users, the marbling technique is a more effective method in managing leather surface defects such as stains, grain peelings, parasitic infections, wrinkle marks, hair remains and shallow cuts than dyeing by immersion. This is because the different shapes, lines and shades of colour produced on the leather surface after dyeing (Figure 8) mingles and subdue defects making them less visible.

Despite the effectiveness of dyeing as a method of managing locally produced vegetable tanned leather surface defects like stains, grain peelings and parasitic infections, the following weaknesses were shared by students who adopt these methods.

According to leather users, it takes at least a whole day to dye and get leather dried for use on a normal sunny day. In a situation where the atmosphere is humid and leather is dense, leather can take more than a day to dry depending on its thickness. In view of this, it becomes a great challenge for the student to adopt this method when they do not have the luxury of time.

Painting

In painting, colour is applied on leather surfaces with brushes to manage surface defects such as stains, scratch marks, parasitic infections and sometimes minor cuts. Painting, allow students to express various ideas on surfaces of vegetable tanned leather which do not only manage surface defects, but also contribute to the value of the aesthetic appearance of the leather and products produced from them. Because vegetable tanned leather is highly absorbent, colours which are applied on their surfaces are able to fix well. According to users, though painting is an effective way of managing leather surface defects, there are some challenges students face when adopting this method.

In order to produce good painting a special skill is required. Good painting contributes beauty and quality to work. When painting is poor, the entire work become less attractive. In order to produce leather works with outstanding surface appearance, leather users who lack good painting skills but desire to produce good paintings employ professionals who render the services to them at a fee which adds to the cost of production.

Painting becomes time consuming when leather surface is large or when scenes, motifs and images to paint are comprehensive. According to users, it is difficult to rectify mistakes when painting on vegetable tanned leather surfaces. Once the leather receives paint, cleaning the paint when a mistake occurs becomes impossible because of the high moisture absorbency rate of the vegetable tanned leather. Painting is not the right surface defect managing method for locally produced vegetable tanned leather when a single colour or the usual cream, red, coffee brown and black colour is desired by the consumer as shown in Figure 9.

Figure 9. Painted leather
Source: Department of Integrated Rural Art and Industry, KNUST

Screen Printing

Just like painting, screen printing is the application of colour onto a leather surface but with a different application method. With screen printing, print paste is forced through a mesh with a design to be printed from a mesh but in a reversed form so that when printed the colour can be obtained in the positive side of the leather surface. The negative areas of the design to be printed from mesh onto leather surfaces are blocked by making blocked areas impermeable to colour. Using a squeegee (a flat pallet knife for forcing paint through holes of mesh), colour is forced through the open areas of the mesh whiles it rest on the leather surface to be printed. Screen printing, just like painting, is able to manage stains and subdue defects like minor cuts, parasitic infections and sometimes hair remains. Screen printing unlike painting is less time consuming especially when the same design is required for a mass production. Screen printing becomes much expensive and time consuming when variations are required in mass production. Screen printing unlike painting gives room for less mistakes because prints are defined by the mesh. Challenges associated with screen printing as a leather surface defect managing method is the management of different leathers with defects messily spread on their surfaces with the same design frame. While some defects may be covered by colour spread through the mesh, other defects may also hide under blocked areas of the mesh making them visible after the screen printing. Just like painting, screen printing cannot be the right leather surface defects management method when the usual colour of the locally produced vegetable tanned leather is desired by the consumer. Figure 10 shows screen print made on vegetable tanned leathers to manage leather surface defects.

Figure 10. Screen printing on black leather
Source: Department of Integrated Rural Art and Industry, KNUST

Scorching

Scorching is the use of hot metal rod or soldering iron to burn designs on vegetable tanned leather surfaces with the purpose of managing defects. Scorching creates varying shades and tones on vegetable tanned leather surfaces. Scorching manage defects like parasitic infections, stains, scratches, hair remains and scars by mingling with the defects and subduing their clarity. Scorching according to users of the leather best manages these defects when scorching design forms texture on the leather surface.

According to leather users, the ability to create interesting scorched designs on the leather is dependent on the one handling the scorching tool. Right control of temperature and the ability to choose the right soldering iron tips is paramount. Lack of these skills contributes additional damage to the leather instead of managing defects on them. Scorching is effective on cream and red leathers than on black and coffee brown leathers. The dark appearance of black and coffee brown leather is unable to bring out shades and tones burned on the leather surfaces.

Stamping

Stamping is the use of pressing tools in the form of metal rod with motif at one end of the rod to produce a repetitive pattern on leather surfaces. In stamping, leather is placed on a punching board or any hard resilient surface and with a mallet, a stamping tool is striked to print pattern on leather surfaces. According to users, stamping reduces the surface glossiness of leather and leaves the leather surfaces rough and matt. When stamping, as the number of patterns increases or repeated, they fuse together and reduce the visual clarity of the leather surface as well as defects by obscuring the defects.

Defects like creases, wrinkles and minor scratches according to users of this method are best concealed when stamping patterns are small, numerous and closely parked on the surface.

Although according to leather users, stamping is an effective method for reducing the intensity of leather surface defects like creases, wrinkle marks and scratches, the method is labour intensive and time consuming, more especially when the stamping surface area is large. Again, producing patterns with same depth is less assured since the method is manual and for that matter the striking force may differ (Figure 11 shows a leather belt with a varying stamped depth). The users of this method also reported that, there is always the danger of injuring themselves when striking the stamping tools with mallet.

Figure 11. Stamped leather belt with varying depth
Source: Department of Integrated Rural Art and Industry, KNUST

Appliqué

Appliqué is a method employed in controlling leather surface defects by fixing a second leather or a different material over a defected leather's surface area to mask defects and also create design on the leather surface. A leather or a different material with a colour different from the working leather is often fixed to the working leather's surface to mask defects as showed in Figure 12. Leather may be attached to a defected leather surface by either gluing or stitching it manually or with machine. This method is effective because defects are completely masked.

Appliqué becomes an expensive and tedious method to use when the defect spreads on a large surface area of the leather. This is because leather users require a lot of time combined with effort and skill to mask all defects. In addition, when the entire surface area of the leather is defected, this method cannot be adopted because masking the entire surface area of the leather will result in bonded leather instead of an appliqué work. Again the beauty of an appliqué work is much dependent on the leather user's skill to produce an appliqué which conform perfectly to the work.

Figure 12. Appliqué leatherwork for masking defects
Source: Prempeh College Leather Studio

CONCLUSION

Leather users adopt patching of holes and open cuts, dyeing, painting, screen printing, scorching, stamping and appliqué for managing various leather defects. The research revealed that these methods which are employed by leather users in managing leather defects have their own strengths and weaknesses. In the case of painting, dyeing and screen printing, methods hide stains, minor scratches and grain peeling defects but in situations where the actual colour of the leather is required of a work, these methods become less feasible. Though stamping is an effective method for reducing the intensity of leather surface defects like creases, wrinkle marks and scratches, the method is labour intensive and time consuming, more especially when the stamping surface area is large. Again, producing pattern with same striking force is less assured since the method is manual and for that matter, the striking force may vary. In the case of appliqué, scorching and painting, special expertise is required of the vegetable tanned leather user to be able to effectively employ the methods. Users who lack the skills rely on professionals who render the service to them at a fee which add to their cost of production.

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RIGID ANTIMICROBIAL POLIMERIC COMPOSITE WITH PVC MATRIX AND ZnO AND TiO_2 FUNCTIONALIZED NANOPARTICLES

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RIGID ANTIMICROBIAL POLYMERIC COMPOSITE WITH PVC MATRIX AND ZnO AND TiO_2 FUNCTIONALIZED NANOPARTICLES

ABSTRACT. In this paper, rigid antimicrobial polymeric nanocomposites were developed - polymeric material based on chemically functionalized nanoparticles with polydimethylsiloxane (PDMS) – dispersed in a plastomer matrix. By dispersing them in plastomer matrix (polyvinyl chloride - PVC), hybrid TiO_2/ZnO nanoparticles (50:50) (fillers) functionalized for good compatibility have led to the development of an advanced polymeric material with antibacterial, multifunctional and processing properties specific to plastics. Experimental polymeric materials are adapted to biomedical and food applications, therefore, they were tested for stability and long-term antimicrobial activity. The combined effects of functionalised nanoparticles and polymer on the structure and properties of new experimental materials were studied. Experimental nanocomposites were morpho-structurally, microbiologically and physico-mechanically characterized.

KEY WORDS: nanocomposite, antibacterial, functionalized, rigid

COMPOZIT POLIMERIC RIGID ANTIMICROBIAN ÎN MATRICE DE PVC ŞI NANOPARTICULE DE ZnO ŞI TiO_2 FUNCŢIONALIZATE

REZUMAT. În această lucrare s-au realizat nanocompozite polimerice antimicrobiene rigide – material polimeric bazat pe nanoparticule funcţionalizate chimic cu polidimetil siloxan (PDMS) – dispersate într-o matrice de plastomer. Prin dispersarea lor în matrice de plastomer (clorură de polivinil - PVC), nanoparticulele hibride TiO_2/ZnO (50:50) (materiale de umplere) funcţionalizate pentru o bună compatibilizare au condus la obţinerea unui material polimeric avansat cu caracteristici antibacteriene, multifuncţionale şi proprietăţi de prelucrare specifice materialelor plastice. Materialele polimerice experimentate sunt adaptate aplicaţiilor biomedicale şi alimentare, prin urmare, au fost testate din punct de vedere al stabilităţii şi activităţii antimicrobiene pe termen lung. Au fost studiate efectele combinate ale nanoparticulelor funcţionalizate şi ale polimerului asupra structurii şi proprietăţilor materialelor noi experimentate. Nanocompozitele experimentate au fost caracterizate morfo-structural, microbiologic şi fizico-mecanic.

CUVINTE CHEIE: nanocompozite, antibacterian, funcţionalizat, rigid

COMPOSITE POLYMÉRIQUE ANTIMICROBIEN RIGIDE EN PVC ET NANOPARTICULES DE ZnO ET TiO_2 FONCTIONNALISÉES

RÉSUMÉ. Dans cet article, on a développé des nanocomposites polymères antimicrobiennes rigides – matériau polymérique à base de nanoparticules chimiquement fonctionnalisées avec du polydiméthylsiloxane (PDMS) – dispersés dans une matrice de plastomère. En les dispersant dans une matrice de plastomère (polychlorure de vinyle - PVC), les nanoparticules hybrides de TiO_2/ZnO (50:50) fonctionnalisées pour une bonne compatibilité ont conduit au développement d'un matériau polymère avancé doté de propriétés antibactériennes, multifonctionnelles et propriétés de traitement spécifiques aux plastiques. Les matériaux polymères expérimentaux sont adaptés aux applications biomédicales et alimentaires. Ils ont donc été testés pour déterminer leur stabilité et leur activité antimicrobienne à long terme. On a étudié les effets combinés de nanoparticules fonctionnalisées et de polymères sur la structure et les propriétés de nouveaux matériaux expérimentaux. Les nanocomposites expérimentaux ont été caractérisés du point de vue morpho-structurel, microbiologique et physico-mécanique.

MOTS CLÉS: nanocomposite, antibactérien, fonctionnalisé, rigide

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INTRODUCTION

At the global level, the trend of obtaining new advanced polymeric structures based on nanopowder reinforced elastomers offers possibilities for obtaining new materials and expanding their range of applications. In the past 5-7 years, fillers with a particle size of 1 to 10 nanometers, referred to as nanostructures, [1] are of particular interest. Nanoparticles have a high specific surface, and their antimicrobial, physical, mechanical, thermal, optical and other properties are superior compared to similar material obtained from structural elements with micron and submicron dimensions. Among the nanoscale filling materials, the most popular are the modified organic clays [2, 3], carbon nanofibres and nanotubes, nano silicon oxide, calcium, and magnesium carbonate, aluminum and titanium nanoparticles, zinc and titanium oxides, graphite, silver, etc. Therefore, new materials can be found in a wide variety of different applications, such as biomedical applications, consumer goods, health, medical or food technology, automotive and transport [4, 5]. Antibiotic resistance of bacteria increased rapidly in recent decades, especially in the hospital setting. Among hospital-acquired infections, medical device-related infections (MDIs) have been recognized as one of the rapidly growing and significant issues, especially for some permanent devices that come in intimate contact with the human body. The bacterial colonization of the medical device not only precedes the infection but can also negatively affect the function of a device [6, 7]. Polymeric materials for medical applications have a long history, leading to the fact that currently more than 50% of all medical devices are made of polymers. The polymers used are mainly polyethylene, polypropylene, polyvinyl chloride, polyester or polycarbonate, which share the fact that most surface and/or volume modifications are necessary to achieve outstanding properties [8-10]. Being one of the largest polymers, polyvinyl chloride (PVC) is widely used and essential in almost all fields. The optimal ratio of properties and costs makes PVC a material capable of competing with both natural materials and other polymers in many areas of science and engineering. Polyvinyl chloride (PVC) is one of the most used types of polymers (40% of dedicated polymeric materials) for biomedical and food applications. Although much has been done to replace PVC in medical applications, it remains the most used polymer in medical device manufacturing. PVC applications include blood bags and tubes, intravenous containers and components, dialysis equipment, inhalation masks, examination gloves, etc. [11]. PVC-based polymeric materials are subject to continuous research for new modifications and improvements [12, 13].

Polymer composite materials are systems consisting of one or more discontinuous phases dispersed in a continuous phase. Thus, at least two different materials, which are completely immiscible, are mixed to form a composite. Additives such as compatibilizers, plasticizers, pigments, temperature and UV stabilizers, nanoparticles are frequently added to improve certain properties. The type and geometry of the dispersed phase gives the composite optimized properties such as high specific strength, stiffness and hardness, antimicrobial, etc. [14].

There are different types of nanoparticles that can be incorporated into the polymer matrix, depending on their properties and their application. ZnO has found various applications in everyday life such as the rubber and plastics industry, packaging of medicines, cosmetics, medical devices, dentistry and orthopedics, antibacterial coatings, textile industry [15, 16], etc. It is an antibacterial and antifungal agent and is one of 5 zinc compounds currently accepted by the US Food and Drug Administration (21CFR182.8991). Antibacterial activity has been demonstrated on various bacterial strains (*Staphylococcus aureus*, *Staphylococcus epidermidis*, *E. coli*, *Listeria monocytogenes*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Salmonella enteritidis*, *Salmonella typhimurium* etc). Particles normally have a higher surface/volume ratio, which provides more efficient antibacterial activity. ZnO nanoparticles even have antibacterial activity against spores resistant to high temperatures and high pressure. The rubber industry is the area where ZnO is used extensively due to its antibacterial and antifungal activity. TiO_2 is used for countless applications in everyday life, such as building materials, medical devices, dental implants, textile industry, plastics, antibacterial coatings [17, 18]. Having antibacterial, antifungal and antiviral properties similar to ZnO, the medical industry is a field where TiO_2 is used intensively. The use of TiO_2 offers several advantages due to its antibacterial and UV protection. PVC is not compatible with ZnO/TiO_2. The properties of composite materials depend on the compatibility method. For this purpose, the external surface of the nanoparticles can be modified with different agents, the most common functionalizing agents being organo-functional siloxanes or sodium oleate. Functionalizing agents are used to improve adhesion between the polymer matrix and nanoparticles, protect surfaces from internal stresses that can cause cracks, stabilize the interface layer, improve humidity and increase hydrophobicity. The silanolic groups present on the surface of the nanoparticle will interact with polar groups on the surface of the polymer substrate to form primary bonds. In this way, such a molecule is bifunctional, it contains polar silanolic groups capable of adhering to the surface of the nanoparticles and an R-group designed to interact with the polymeric matrix. Functional ZnO and TiO_2 nanoparticles offer flexibility in adapting superficial chemistry and molecular structure to the polymer/nanoparticle interface [19, 20]. These nanosize molecules form the "molecular bridges" between individually dispersed compounding agents and the continuous phase polymer matrix resulting in a maximized performance of the composite material by optimized interfacial compatibility and bonding.

EXPERIMENTAL

Materials and Methods

Materials

Materials used to obtain the polymer composites based on plasticized polyvinyl chloride and ZnO/TiO_2 (50:50) nanoparticles are as follows: PC with a 70K-wert value, Diisononyl phthalate (DINOF) (density 0.984 g/cm^3, pH 7, 99.5% purity), non-toxic plasticizer, mainly used by the pharmaceutical, food and cosmetics industries, PVC stabilizer - Calcium stearate (Ca content 11%, melting point 127°C), Antioxidant Irganox 1010 (pentaerythritol tetrakis (3-(3,5 di-tert-butyl-4-hydroxy-phenyl)propionate) was produced by BASF Schweiz AG (active ingredient 98%, melting point of 40°C). Functionalizing agent – polydimethylsiloxane-PDMS. ZnO, white powder, with particle size 20 nm, molecular mass – 98,87 g/mol, specific surface area – 23 m^2/g, density – 4,26 g/ml, and concentration – 99,5% and TiO_2 white powder, with particle size 21 nm, molecular mass – 79,87 g/mol, specific surface area – 23 m_2/g, density – 4,26 g/ml, and concentration – 99,5%, by Sigma Aldrich.

ZnO and TiO_2 Nanoparticle Surface Modification by Ultrasonication

The ZnO and TiO_2 (50:50) nanoparticles were functionalized in the laboratory with PDMS using an ultrasonic bath, as follows: 1 g of ZnO and TiO_2 (50:50) powder was introduced into 50 mL centrifuge plastic tubes, 10 mL of isopropanol (role of reaction/dispersion medium) was added. The tubes were placed in a plastic holder and immersed in the ultrasonic bath, thermostated in advance at 40°C. After a period of contact/mixing of the nanoparticles with isopropanol for about 5 minutes, 1 mL of PDMS is introduced into each tube, and allowed to react for 2h. The tubes were covered with caps to avoid alcohol evaporation during the reaction, and to maintain an equal amount of solvent for all powders. After 2 h, the centrifuge tubes were removed from the ultrasonic bath, left to rest at room temperature for about 10-15 min, filtered and washed 3 times with alcohol in abundance to remove the unreacted functionalizing agent. Afterwards it was dried in an oven with warm air at 80°C for about 4-6 hours, followed by grinding. In order to confirm the functionalization, morphological and structural characterization (SEM, EDAX, DSC-TG) was performed.

Morpho-structural Characterization of ZnO and TiO_2 Nanoparticles with Modified Surface

TG/DSC – To highlight the thermal changes of the ZMO nanoparticles functionalized with PDMS, the new material, was analyzed with Pyris Diamond DSC equipment – Perkin Elmer, calibrated with Indium (99% purity), both temperature and energy. Figure 1 shows that the sample is stable up to 365°C (losing only 0.35% of the mass). There is only one decomposition stage, between 365-530°C, with an onset at 395.7°C, when a mass loss of 5.51% occurs, accompanied by a slight exothermic effect, with a maximum of 411°C. The residual mass is 93.96%.

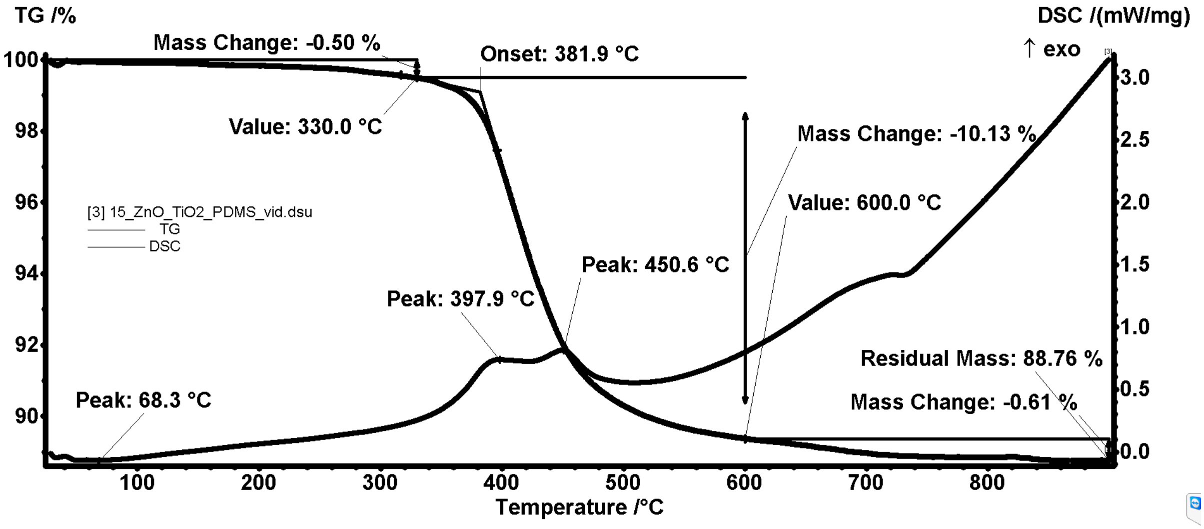
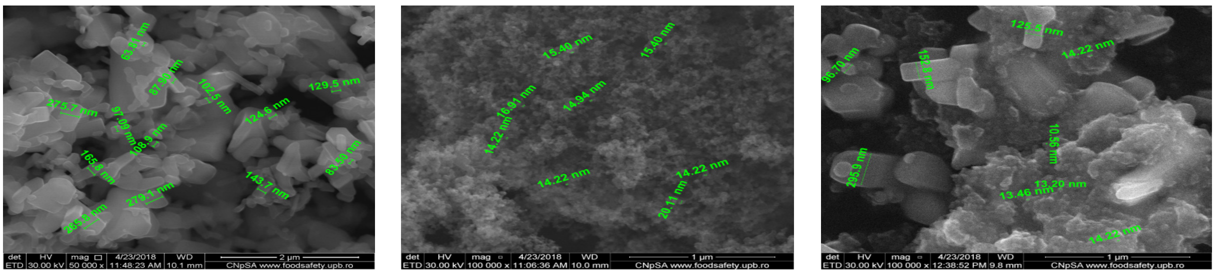


Figure 1. Thermal DSC-TG analysis for ZnO and TiO_2/PDMS powder obtained by ultrasonication

SEM. Simple and functionalized nanoparticles were analyzed by SEM using an ESEM QUANTA 200 instrument operating in a low vacuum equipped with an LFD detector.



A) ZnO B) TiO_2 C) ZnO/TiO_2/PDMS, ultrasonication

Figure 2. SEM images of simple and functional ZnO and TiO_2 powders

Scanning electron microscopy (SEM) images were recorded on ZnO and TiO_2 particles both simple and modified with PDMS. As it can be seen from Figure A and B, recorded on unmodified ZnO and TiO_2 particles at 50000x magnification, the particle size varies between 63.81 and 279 nm, with an extremely varied shape: acicular, canes, rectangular, etc., and very well separated between them (monodisperse without agglomeration). In the case of ZnO and TiO_2 particles functionalized with PDMS (Figure C), it is observed that the presence of organosilane does not significantly affect the shape and size of the particles. Moreover, there are clear contours between ZnO and TiO_2 particles. In Figures 3, 4 and 5 are presented EDAX spectra, recorded on simple ZnO, TiO_2 and ZnO/TiO_2 (50:50) nanoparticles and functionalized with PDMS. For the ZnO and TiO_2 functionalized with PDMS spectrum the presence of silicon beside Zn, Ti and O is observed. This indicates that the functionalization occurred.

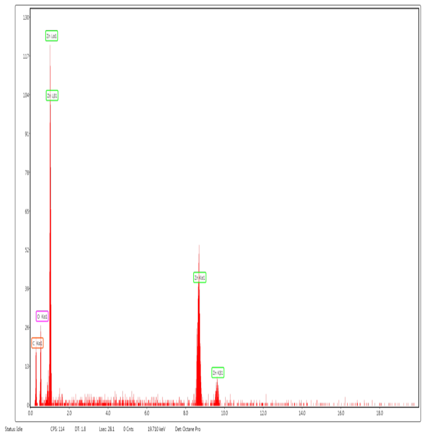


Figure 3. The EDAX spectrum recorded on the ZnO powder

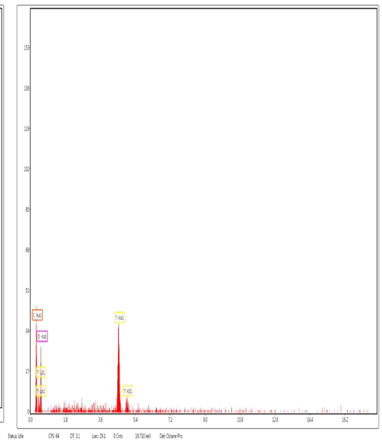


Figure 4. The EDAX spectrum recorded on the TiO_2 powder

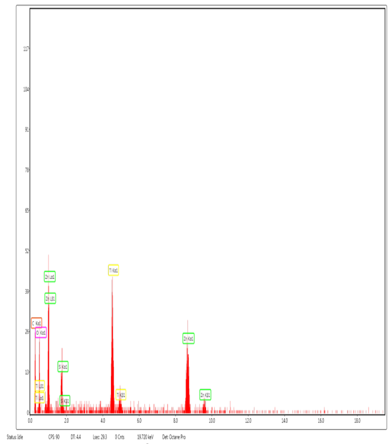


Figure 5. The EDAX spectrum recorded on the ZnO/TiO_2/PDMS, ultrasonication

The EDAX spectrum in Figure 5 shows the following elements: Zn, Si, TiO_2 and O. It is noted that the relative intensity between the peaks varies significantly, and is the most intense in Zn and Ti. The appearance of an extra peak of Si, compared with Figures 3 and 4, confirms once again the results obtained by SEM and DSC-TG, namely, demonstrates that the functionalization of the surface of ZnO and TiO_2 nanoparticles was successfully achieved by ultrasonication. The percentage of atomic, and weight content between the three elements (O: Si: Zn) is shown in Table 1.

Table 1: Quantitative analysis of ZnO/TiO_2/PDMS powder, ultrasonication

Element	Weight content, %	Atomic content, %	Error, %
O K	27.97	56.87	19.49
Zn K	51.47	25.61	14.93
SiK	7.42	8.59	23.59
TiK	13.14	8.93	8.79

Preparation of Polymer Nanocomposites based on Plasticized Polyvinyl Chloride and ZnO/TiO_2 (50:50)

PVC, ZnO and TiO_2 functionalized with PDMS, plasticizer – Diisononyl phthalate, calcium stearate, and antioxidant – Irganox 1010 were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 30-100 rotations/min, for 5 min. at 178°C to melt the plastomer and 2 min. at 170°C for homogenisation. The total processing time was 7 minutes. Table 2 shows tested formulations. Remove the composition from the mixer and press into specimen molds for physico-mechanical characterizations.

Table 2: Polymeric composites based on PVC plasticized with 25% diisononyl phthalate, and 50:50 ZnO and TiO_2 nanoparticles, PDMS functionalized

Compound	B1	B31	B32	B33
PVC	240	240	240	240
ZnO/TiO_2/PDMS (50:50)	-	2.4	7.2	12
Diisononyl phthalate	60	60	60	60
Calcium stearate	3	3	3	3
Irganox 1010	3	3	3	3
Total	306	308.4	313.2	318

The Brabender mixing diagrams, Figure 6, show the following: chamber temperature increases from 178 to 205°C for the control sample – B1, with a maximum mixing force of 182 N/mm in 48s. When adding nanoparticles, the mixing force decreases (158 N/mm for 1-3% mixture of ZnO and TiO2 (samples B31 and B32) and 145 N/mm for 7% ZnO and TiO_2 – B33 mixture). The time need to reach maximum force, increases proportionally to the amount of ZnO and TiO_2 mixture, from 48s –control sample to 52s – B31, 58s – B32, and 63s – B33. The temperature in the chamber decreases, at the maximum force, from 190°C – B1 control sample to 205°C – B31, 210°C – B32 and 221°C – B33. The chamber temperature increases, at the maximum force from 190°C – B1 control sample to 205°C – B31, 210°C – B32 and 221°C – B33.

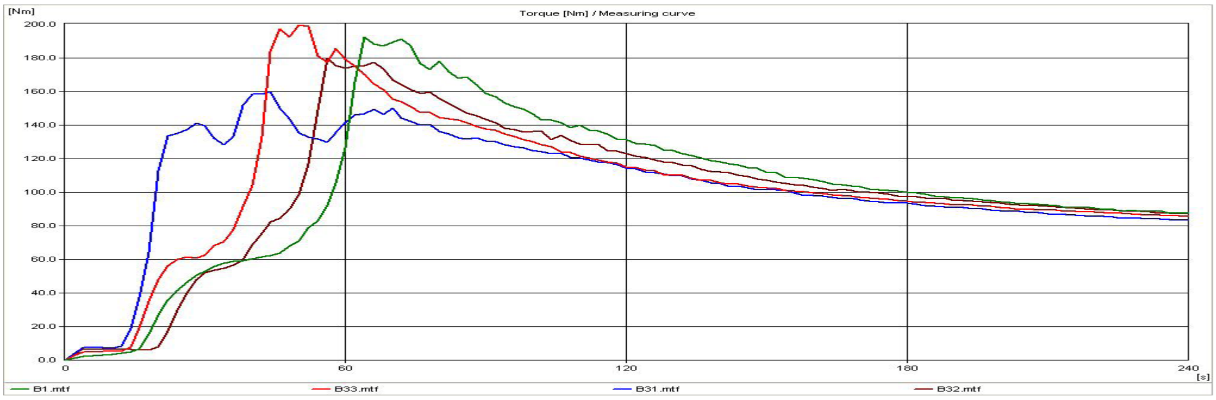


Figure 6. The overlapping Brabender mixing diagrams of control sample and PVC-based polymeric composites plasticized with 25% diisononyl phthalate – DINOF, and 1, 3, 7% ZnO and TiO_2 nanoparticles (50:50)

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN; temperature 170°C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore "A" Durometer according to SR ISO 7619-1:2011.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Melt flow index was determined at 180°C and a pressure force of 5 kg, with Melt Flow Index – Haake equipment.

FT-IR spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm^{-1}.

The method for control of antibacterial activity is in accordance with SR EN ISO 20645/2005-Textiles materials.

RESULTS AND DISCUSSIONS

The polymer structures obtained, in initial state and after accelerated ageing were characterized in terms of their physical-mechanical properties, and results are presented in Table 3. Analyzing the values of physical-mechanical tests reveals the following:

Hardness

In the initial state of the control sample, B1, is 61°Sh D, when adding nanoparticles, it grows with a unit, up to 62°Sh D. This is demonstrated by the fact that the hardness increases with the amount of filler. The amount used in the mixture, being very small (max. 7%) the increase is small. At the same time, the degree of plasticization being small, the samples show a high degree of stiffness. The type of plasticizer influences very little the degree of hardness.

Table 3: Normal physico-mechanical characterization for PVC-based polymeric composites plasticized with 25% diisononyl phthalate – DINOF, and 50:50 nano ZnO and TiO_2 mixture functionalized with PDMS

Samples	B1	B31	B32	B33
Initial State				
Hardness °Sh D, SR ISO 7619-1:2011	61	62	62	62
Elasticity %, ISO 4662:2009	16	16	16	16
Tensile strength, N/mm^2, SR ISO 37:2012	23.0	24.1	24.8	25.2
Elongation at break, %, SR ISO 37:2012	260	260	300	340
Residual elongation, %, SR ISO 37:2012	84	110	116	110
Tear strength, N/mm, SR EN 12771:2003	160	142	147	149
Density, g/cm^3, SR ISO 2781:2010	1.3	1.3	1.3	1.3
Abrasion resistance, mm^3, SR ISO 4649/2010	97	96	99	100

Tensile Strength

The tensile strength is in the 23-25.2 N/mm^2 range, in the initial state. It is worth noting the high values of this parameter, which are not found in plastics mixtures with hardness values of 60-70°Sh D.

Elasticity

High elasticity values (16%) are observed for high values of hardness, a characteristic feature of these materials not influenced by the addition of mixed nanoparticles.

Tear Strength

The tear strength decreases by several units proportional to the amount of nanoparticles introduced in the composite from 160 N/mm to 142 N/mm for the composite with 7% ZnO/TiO_2 nanoparticle.

Abrasion Resistance

The values of abrasion resistance increase slightly from 97 mm^3 for the control sample up to 100 mm^3 for the sample with the largest quantity of nanoparticles, respectively 7%. The values fall within the requirements imposed by the standards.

Density

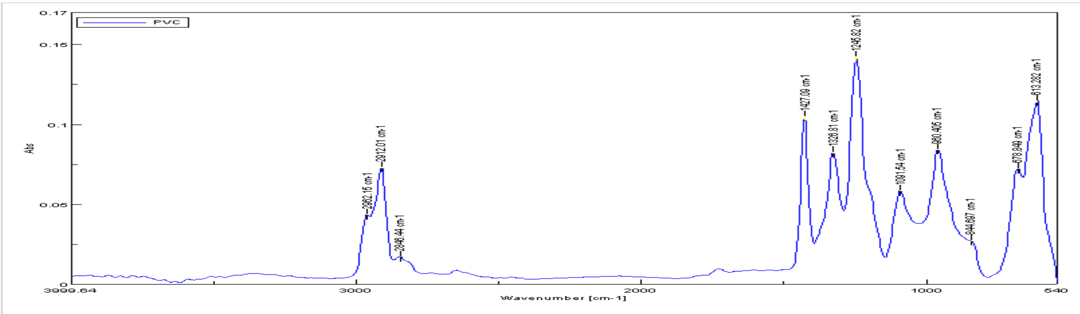
Density values do not change when the nanoparticles are added to the mixture.

FT-IT Spectroscopy

IR spectrum represent the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm. IR domain for usual organic chemistry is between 2.5 and 25 μm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm^{-1}, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the pure elastomer spectrum.

After the tests were carried out, the following were found:

Figure 7 shows the FTIR spectra recorded on the single PVC powder and shows numerous characteristic bands associated with this type of polymer. The bands of 2962, 2912, 2846 cm^{-1} can be attributed to the elongation vibration of asymmetric CH_3 groups, asymmetric CH_2 and respectively symmetric CH_3 groups of PVC. The band at 1427 cm^{-1} is attributed to the planar deformation vibration of the CH_2-Cl bond, the band at 1326 cm^{-1} is attributed to outside the plane (balance) deformation bonds of the -CH_2 groups. The band at 1245 cm^{-1} is attributed to deformations outside the plan (balance) of Cl-CH bonds, the 960 cm^{-1} band is attributed to outside the plane deformation of C-Cl bonds, and those of ~ 844, 678, and 613 cm^{-1} can be attributed to C-Cl stretch groups. The band at 1091 cm^{-1} is attributed to stretching bond of the C-C group of PVC.



Fgure 7. FTIR spectrum of pure PVC powder

The spectra obtained on the plasticized PVC mixture with 25% diisononyl phthalate (B1), composites based on DINF plasticized PVC reinforced with varying amounts (1, 3, and 7%) of nanoparticles mix (ZnO/TiO_2 50:50) functionalized with PDMS (Figure 8), it can be observed that the type of nanoparticle used does not induce significant change in the structure of the spectra, probably because they are deeply embedded in the polymer matrix – PVC, and therefore cannot be identified neither on the basis of the characteristic bands derived from the nanoparticle structure nor on the basis of the functional bonds existing in the organosilane structure. Compared to the spectrum recorded on the PVC powder, we can observe the presence of functional groups derived from the plasticizer structure, namely the carbonyl group (from about 1720 to 1121 cm^{-1} for the mixture B1), and those from 1724 and 1126 cm^{-1} for blends containing ZnO/TiO_2 nanoparticle mixture. The presence of carbonyl functional groups shows that plasticization of PVC has been optimally achieved. Also, the bandwidth characteristic of methylene groups increases as the percentage of PDMS functionalised nanoparticles increases.

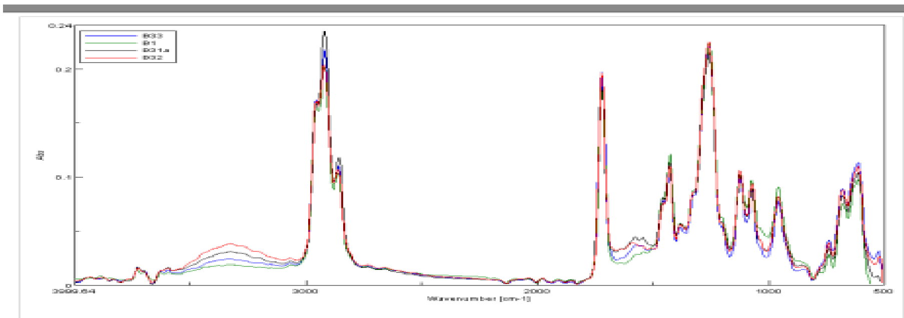


Figure 8. The FTIR spectra of composites B1 (PVC + plasticizer DINF), B31 (PVC + DINF + 1% ZnO/TiO_2/PDMS), B32 (PVC and DINF + 3% ZnO/TiO_2/PDMS), B33 (PVC and DINF + 7% ZnO/TiO_2/PDMS)

Control of Antibacterial Activity

Test of diffusion on the gelose plate. The result is considered to have a "satisfactory effect" unless bacterial propagation is observed. The analyzed samples do not allow the development of aerobic germs for the tested bacteria (*Staphylococcus aureus*), the major inhibitory effect being presented by the samples with ZnO:TiO_2 – 50:50 nanoparticle mixture.

Method

- subculturing of the bacteria used in the test: *Staphylococcus aureus*. The culture used was pure, freshly subcultured;

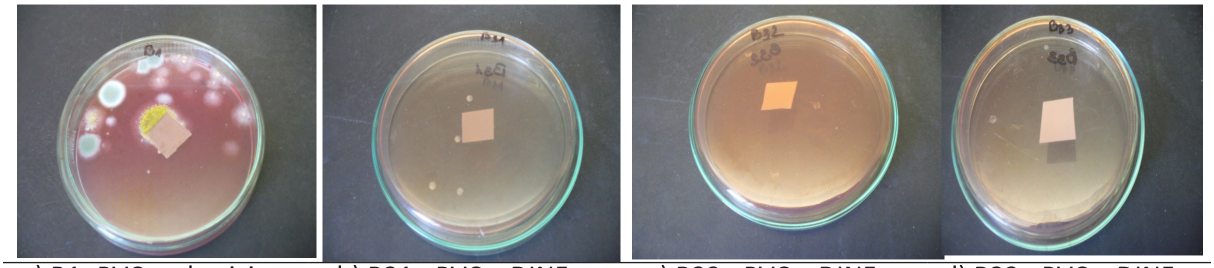
- dry sterilization of the laboratory glassware in the oven at 180°C;

- preparation of the culture medium, characteristic of the test bacteria used, namely: Mannitol Salt Agar for the genus *Staphylococcus aureus*; wet sterilization, autoclave and Erlenmayer glass with culture media;

- the test specimens were collected from the 2 mm thick elastomer plates and 2 cm squares, were cut into squares.

The Test

The amount of gelose for the lower layer without bacteria is prepared. An amount of (10 ± 0,1) ml is added to each sterilized Petri dish and the gelose is allowed to solidify. The amount of gel is prepared for the upper layer and cooled to 45°C in a water bath. 150 ml of gelose is inoculated with 1 ml of bacterial working solution (1-5 x 10 8 ufc/ml). The container is vigorously stirred for the uniform distribution of bacteria. An amount of (5 ± 0,1) ml is introduced into each Petri dish and the gelose is allowed to solidify. The specimens are placed on the surface of the nutrient medium and then incubated at 37°C between 24h and 48h.



a) B1- PVC + plasticizer DINF	b) B31 - PVC + DINF + 1% ZnO/TiO_2/PDMS	c) B32 - PVC + DINF + 3% ZnO/TiO_2/PDMS	d) B33 - PVC + DINF + 7% ZnO/TiO_2/PDMS

Figure 9. Effect of antibacterial treatment

The result is considered to have a "satisfactory effect" if no bacterial proliferation is noticed. Nanocomposite samples based on PVC did not allow development of aerobic germs for the tested bacterium (*Staphylococcus aureus*), exhibiting a major inhibition effect visible in samples with 50:50 ZnO:TiO_2 nanoparticle mixture, both around the sample and in its vicinity; the most intense effect was found in the sample with 7% ZnO/TiO_2 mixture – B33 (Figure 9, d), while no effect was found in the control sample – B1 (Figure 9, a).

CONCLUSIONS

The paper presents the study of the new nanostructured polymer composites based on chemically functionalized nanoparticles dispersed in the plastomer matrix. Hybrid ZnO/TiO_2 (50:50) nanoparticles (filler) dispersed in PVC matrix resulted lead to a high performance polymeric material with multi-functional antibacterial, and polymorphic processing properties. The materials are adapted for biomedical and food applications and have been tested in terms of physico-mechanical properties, spectrometry and antibacterial activity. Prototypes of biomedical applications will be obtained from nanocomposites, and will be microbiologically tested for a further examination.

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THE COLLAGEN STATE WITHIN THE PARCHMENT AFTER INFLUENCE OF ARTIFICIAL AGING

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THE COLLAGEN STATE WITHIN THE PARCHMENT AFTER INFLUENCE OF ARTIFICIAL AGING

ABSTRACT. The study examines the influence of artificial aging on the stability of collagen within the parchments. Aging of the parchments was generated by heating at 70°C in a dry oven for 72 h as well as by keeping the parchment samples in the solution of artificial sweat. Sodium dodecyl sulfate polyacrylamide gel electrophoresis and size-exclusion chromatography were utilised to investigate the state of proteins within the parchment samples after exposure to heating and artificial sweat. The study has shown that the accelerated aging of the parchment results in marked change of protein and peptide concentrations, release of collagen chains, as well as leads to the alteration in the peptide compositions.

KEY WORDS: parchment, collagen, accelerated aging, electrophoresis, chromatography

STAREA COLAGENULUI DIN PERGAMENT SUB INFLUENŢA ÎMBĂTRÂNIRII ARTIFICIALE

REZUMAT. Studiul examinează influenţa îmbătrânirii artificiale asupra stabilităţii colagenului din pergamente. Pergamentele au fost îmbătrânite prin încălzirea la 70°C într-un cuptor uscat timp de 72 de ore, precum şi prin menţinerea probelor de pergament în soluţia de transpiraţie artificială. S-au utilizat electroforeza în gel de dodecil sulfat de sodiu-poliacrilamidă şi cromatografia de excludere a mărimii pentru a investiga starea proteinelor din probele de pergament după expunerea la încălzire şi transpiraţie artificială. Studiul a arătat că îmbătrânirea accelerată a pergamentului are ca rezultat o schimbare vizibilă a concentraţiilor de proteine şi peptide, eliberarea lanţurilor de colagen, precum şi modificarea compoziţiilor peptidice.

CUVINTE CHEIE: pergament, colagen, îmbătrânire accelerată, electroforeză, cromatografie

L'ETAT DE COLLAGENE DANS LE PARCHEMIN SOUS L'INFLUENCE DU VIEILLISSEMENT ARTIFICIEL

RÉSUMÉ. L'étude examine l'influence du vieillissement artificiel sur la stabilité du collagène dans les parchemins. Les parchemins ont été vieillis par chauffage à 70°C dans un four sec pendant 72 heures, ainsi que par conservation des échantillons de parchemin dans la solution de transpiration artificielle. L'électrophorèse en gel de polyacrylamide contenant du dodécysulfate de sodium et la chromatographie d'exclusion stérique ont été utilisées pour étudier l'état des protéines dans des échantillons de parchemin après une exposition au chauffage et à la transpiration artificielle. L'étude a montré que le vieillissement accéléré du parchemin entraînait un changement visible des concentrations de protéines et de peptides, la libération de chaînes de collagène et une modification des compositions de peptides.

MOTS CLÉS: parchemin, collagène, vieillissement accéléré, électrophorèse, chromatographie

INTRODUCTION

Parchment is an important biomaterial that has been used for cultural artifacts and household objects [1, 2]. Although parchment is an incredibly stable material it inevitably changes over time which can cause alteration in its physical properties. Aging of parchment can be accelerated by a range of environmental (temperature, humidity), biological (bacterial, fungal growth) as well as physical (mechanical, radiation damage) factors [3]. All of these factors, alone or synergistically, are capable of altering the chemistry of the collagen molecules that leads to destabilization of the native conformation of parchment objects and generates different types of deteriorations over time. Heat-induced aging and action of artificial sweat are among the factors that imitate the influence which the parchment can undergo during extensive exploitation.

For today, some destructive and non-destructive techniques are applied for investigation of parchment state [4-6]. However, development and implementation of new simple methodological approaches based on analysis of the structure of protein component within the parchment might be useful for more complete characteristic of parchment state. This paper examines the application of biochemical techniques with the purpose to improve diagnostic tools for estimation collagen integrity within the parchment. The long-term heating and artificial sweat action were applied as agents for acceleration wear of parchment samples.

EXPERIMENTAL

Materials and Methods

Materials

Our experiments were carried out on sheep parchments that were manufactured by several methods of liming. There were 4 experimental groups based on the method used for the parchment preparation: the group 1 - the parchment for restoration work was manufactured according to the method [7], which involves two-stage liming with consumption of calcium hydroxide up to 35 g/L; the group 2 - the parchment for writing was manufactured according to the method [8], which involves two-stage liming with consumption of calcium hydroxide up to 26 g/L; the group 3 - the transparent parchment was manufactured according to the ancient method [9] by sulphide-limy method; the group 4 - the parchment for general purpose was manufactured by accelerated method of oxidative liming [10]. The finishing processes and operations for experimental groups of parchments was executed by drying, surface grinding as well as plasticization; in addition, the bleaching was carried out in the groups 2 and 3 while the filling with potassium aluminum salt was performed in the group 3 [11-12]. The artificial aging of the parchments was done as described below. Heat-induced aging was imitated by keeping the parchment samples in the laboratory chamber at 70°C, 0% rH for 72 h. Sweat resistance test was carried out by keeping the parchment samples in the solution of artificial sweat (NaCl 0.2% (w/w), $(NH_4)_2CO_3$ (0.07%), Na_2HPO_4 (0.02%), carbamide (2.4%), lactic acid (0.13%) at 25°C for 72 h [13]. Afterwards, the samples were dried at room temperature for 24 h. After been dried, the parchment was cut into small pieces (0.3x0.3cm) with scissors. A piece was put into distilled water (1:10 weight/volume) and left for 2 h at 90°C in a thermostat. Then the solution was centrifuged at 600 rpm for 15 minutes. The residue was discarded and obtained solution was used for further analysis.

Protein Concentration Determination

The concentration of protein was determined according to the method described by [14] using crystalline bovine serum albumin as the standard protein and measuring the absorbance at 595 nm.

Peptide Fractions Isolation

The peptide fractions were obtained according to [15]. The aliquot of the solutions after soaking of the parchment fragments were mixed with 1.2 M $HClO_4$ at 1:1 (v/v) ratio in order to precipitate the proteins. After centrifugation (20 min, 5000 g, 4°C) the supernatants were neutralized by 5 M KOH to pH 7.0 and the samples were subjected to centrifugation step again. Ethanol was added to the final concentration of 80%, the samples were kept at 4°C for 30 min and after final centrifugation the concentration of peptides was determined in the supernatant by measuring the absorbance at 210 nm.

Size-exclusion Chromatography

The peptide fraction was applied to size exclusion chromatography on Sephadex G-15 column (Bio Rad, USA) pre-equilibrated with 0.05 M Tris-HCl, pH 7.4 containing 0.13 M NaCl. The samples were loaded and the peaks were collected at a flow rate of 30 mL per hour. The areas under the peaks of chromatographic curves were calculated using the OriginLab (v 9.1). The molecular weight of peptides was estimated using calibration curve. For this purpose, the column was previously calibrated with standard marker solution (lysozyme, 14.3 kDa; insulin, 5.7 kDa; vitamin B12, 1.35 kDa) [16].

Sodium Dodecyl Sulfate Polyacrylamide Gel Electrophoresis (SDS-PAGE)

SDS-PAGE was done using the Laemmli system as described by [17]. The stacking and separating gels were 4 % (w/v) and 8 % (w/v), respectively. Samples were concentrated by trichloroacetic acid; the obtained precipitates were twice washed with acetone, dried at 37°C and then dissolved in SDS-PAGE buffer (5 mM Tris-HCl, pH 8.3 containing 2% SDS, 5% sucrose, and 0.02% bromophenol blue). SDS-PAGE was performed using Mini-Protean Tetra System (Bio Rad, USA) at 19 mA for stacking gel and 36 mA for separating gel. The amount of protein applied to the gel was 20 µg per line. After electrophoresis was done, the gels were stained with 2.5% Coomassie brilliant blue R-250 in 10% (v/v) ethanol, 10% (v/v) acetic acid, 15 % (v/v) isopropanol and the background of the gel was destained with 7% (v/v) acetic acid for 30 min. The electrophoregrams were analyzed using the program TotalLab (v 2.01). The molecular weights of proteins were estimated based on MW standard (myosin, 200 kDa; β-galactosidase, 116.2 kDa; phosphorylase b, 97.4 kDa; bovine serum albumin, 66 kDa; ovalbumin, 45 kDa; carbonic anhydrase, 31 kDa; trypsin inhibitor, 21.5 kDa (Bio Rad, USA)).

Statistical Analysis

The results were reported as mean±SEM (n=5). Statistical analysis was performed using one-way analysis of variance (ANOVA). Differences were considered to be statistically significant when $p < 0.05$.

RESULTS AND DISCUSSIONS

Parchment is predominantly composed of collagen type I that is a heterotrimeric molecule consisting of three polypeptide chains, namely two α1-chains and one α2-chain [18]. These chains are organized into fibrils, which are, in turn, grouped into fibers. Over time, collagen molecules could lose their structural stability, which is accompanied by decreasing of mechanical properties of the parchment objects [19]. Similar to other biomaterials parchment is sensitive to the environmental conditions which in case of sudden and significant changes accelerate aging of the parchments. In the current study we have investigated collagen integrity of the parchment samples after the influence of both long-term heating and artificial sweat using methods of protein biochemistry.

At first, we determined the concentration of protein in solution obtained after soaking of the parchment samples. It has been shown the least concentration of protein in the group 2 under control condition (Table 1) which is most likely mediated by higher stability of protein molecules within the parchment. The highest concentration of protein has been detected in the control sample of the group 3. This result might indirectly indicate the partial destruction of proteins during the manufacturing process.

The influence of heating and artificial sweat leads to multidirectional change of the protein concentration. The significant increase of protein concentration (the group 1 under long-term heating and artificial sweat action; the group 2 under artificial sweat action; the group 4 under long-term heating) as well as the decrease of protein concentration (the group 3 and the group 4 under artificial sweat action; the group 2 under long-term heating) was shown.

Table 1: Protein concentration ($mg \cdot mL^{-1}$) in the solution obtained after soaking of the parchment samples

Condition	Group 1	Group 2	Group 3	Group 4
Control	5.50±0.38	3.75±0.26	8.00±0.56	7.00±0.49
Long-term heating	13.25±0.92*	1.62±0.11*	7.37±0.51	9.37±0.65*
Artificial sweat action	10.37±0.72*	4.50±0.31*	6.25±0.43*	3.62±0.25*

Values are expressed as mean±SEM (n=5); *p<0.05 significantly different from the control

The changes of protein concentration can be explained by destabilizing of collagen structure and releasing collagen chains or/and collagen fragments into solution. In order to analyze the qualitative composition of proteins with respect to the presence of collagen fragments, the SDS-PAGE technique was applied. The results of electrophoretic analysis of the solution obtained after soaking of the parchment samples are presented in Table 2.

Table 2: Results of electrophoretic analysis of the solution obtained after soaking of the parchment samples

	Condition	Dimmer of α-chains of collagen (>200 kDa), %	α1-chains of collagen (110 kDa), %	α2-chains of collagen (100 kDa), %	Fragments of collagen (<100 kDa), %
Group 1	Control	25	73	2	-
	Long-term heating	27	73	-	-
	Artificial sweat action	59	37	2	2
Group 2	Control	13	54	7	26
	Long-term heating	20	63	3	14
	Artificial sweat action	30	48	9	13
Group 3	Control	22	64	6	8
	Long-term heating	26	64	7	3
	Artificial sweat action	58	33	3	6
Group 4	Control	14	84	2	-
	Long-term heating	15	83	2	-
	Artificial sweat action	4	47	19	30

SDS-PAGE analysis has revealed the presence of α1-chains of collagen, the content of which was much higher comparing to the content of α2-chains. The appearance of both α-chains might be due to disorder of native structure of the parchment and extraction of collagen fragments into solution. In general, the influence of artificial sweat on parchment samples was more damaging as it provoked the release of big collagen fragments, namely dimmers of α-chains. The accumulation of dimmers is an unfavorable sign as it indicates the changes at the level of collagen triple helix. Moreover, loss of big fragments would potentially lead to decrease of mechanical properties of the parchment during its intensive exploitation in the future. In contrast, the influence of artificial sweat provoked significant disturbances in ordered collagen structure in the group 4. As a result, collagen chains were disintegrated into fragments with molecular weights less than 100 kDa.

Taking into account that the structure of collagen is stabilized by hydrogen bonds [20], long-term heating might provoke break down of collagen molecules into individual chains by affecting hydrogen bonds within collagen fibers. Changes of water content caused by long-term heating of the parchment samples also might provoke the structural alteration of the arrangement of collagen chains at molecular and supramolecular levels. This finding is based on well-known fact that integrity of collagen triple helix is in part due to the formation of water bridges, which act as a stabilizing factor in holding collagen chains together [21].

Depending on the strength and type of damaging agent, the destruction of collagen molecules could be accompanied not only by releasing of individual chains, long protein fragments but also the appearance of peptides. In order to clarify the possible mechanisms of collagen disruption the solution obtained after soaking of the parchment samples was analyzed on the presence of peptides. According to the data, the significant increase of the peptide fraction level has been observed in the group 1 and 4 under experimental conditions (Table 3). We suppose the accumulation of peptides could be considered as by-effect of release of dimmers (the group 1) or cleavage of collagen into lower molecular weight fragments (the group 4).

Table 3: Level of peptides (r.u · mL^{-1}) in the solution obtained after soaking of the parchment samples

Condition	Group 1	Group 2	Group 3	Group 4
Control	1.19±0.09	2.16±0.14	3.29±0.22	0.32±0.02
Long-term heating	3.76±0.25*	0.19±0.01*	2.00±0.16*	0.71±0.04*
Artificial sweat action	2.38±0.16*	1.28±0.08*	1.86±0.13*	2.77±0.19*

Values are expressed as mean±SEM (n=5); *p<0.05 significantly different from the control

On the other hand, the changes in the peptide content might be the result of action of lipid radicals. It is well-known that additionally to collagen fibres, the parchment includes lipids [22], the qualitative and quantitative composition of which depend on the method of processing the skin at the stage of parchment manufacture. It has been established [23] that lipids presented in the parchment samples, might interact with the collagen possibly contributing to the degradation of parchment. Lipids influence the collagen structure, probably via autoxidation of lipids and accumulation of highly reactive peroxidation products.

The decrease of the peptide level in the groups 2 and 3 under long-term heating and artificial sweat action has been found (Table 3). This observation is fully consistent with our previous data regarding the protein concentration in these groups.

The analysis of the qualitative composition of peptide fraction could be useful to provide additional information about the collagen integrity and as a consequence about the mechanical resistance of the parchment. The more long-size peptides are released from the parchment, the less the parchment will be persistent to the damages. Size-exclusion chromatography was applied to estimate the presence of peptides of different molecular weights. The comparison of the results of chromatographic analysis of peptide fractions obtained after exposure of the parchment samples to long-term heating and action of artificial sweat (Table 4) has revealed that they were similar in terms of number of peaks and distribution of peptides among the peaks. In general, the influence of these factors has resulted in the increase of peak numbers as well as the appearance of low-size peptides compared to the control samples.

As can be seen from Table 4, the majority of peptides detected after influence of long-term heating and artificial sweat action were molecules with molecular weight up to 1 kDa which correspond to peptide length less than the 10 amino acids.

Table 4: Results of chromatographic analysis of the peptide fractions

		General area under peaks (r.u)	Number of peaks	Molecular weight (Da)	Area under peak (r.u)
Group 1	Control	1.4	1	1881	1.4
	Long-term heating	16.9	1	1202	3.3
			2	1016	5.1
			3	780	4.9
			4	635	1.2
			5	567	1.3
			6	482	1.1
	Artificial sweat action	8.4	1	1166	1.8
			2	973	3.1
			3	755	2.4
			4	622	0.7
			5	558	0.4
Group 2	Control	4.3	1	2951	1.6
			2	1140	1.7
			3	951	0.8
	Long-term heating	3.1	1	1114	0.6
			2	987	1.6
			3	945	0.9
	Artificial sweat action	9.5	1	1162	1.9
			2	957	3.7
			3	712	2.2
			4	611	0.5
			5	547	1.3
Group 3	Control	10.0	1	1116	5.8
			2	1003	4.4
	Long-term heating	6.9	1	1257	1.0
			2	1010	2,4
			3	745	1.7
			4	625	0.4
			5	567	1.3
	Artificial sweat action	7.5	1	1596	3.7
			2	1172	0.8
			3	975	1.8
			4	728	1.2
Group 4	Control	5.9	1	1140	0.6
			2	963	0.7
			3	758	3.5
			4	561	0.3
			5	463	0.8
	Long-term heating	6.0	1	350	6.0
	Artificial sweat action	5.2	1	1017	2.5
			2	690	1.0
			3	556	0.7
			4	444	0.6

CONCLUSIONS

Using the parchment samples obtained by several preparation methods (modern and ancient) we investigated the influence of accelerated aging on protein component of the parchment. The structural integrity of collagen molecules was estimated applying the SDS-PAGE and size-exclusion chromatography. We can state that these techniques may be employed as additional tools to monitor the degradation of proteins within the parchments. In our findings we have revealed that the most suitable manufacturing technique to maintain the collagen structure was the two-stage method with the use of calcium hydroxide in the concentration up to 26 g/L (the group

2). We have also shown that the damaging effect of long-term heating and artificial sweat action strongly depended on the method of parchment obtaining. Most of the times, the damage of collagen structure produced by action of artificial sweat on parchment was more pronounced. Obtained data contribute to better understanding of the mechanisms of the parchment degradation and could be useful to improve manufacturing process.

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EUROPEAN RESEARCH AREA

Program: LIFE
Agreement Number: LIFE17 ENV/PT/000337
Duration: 01.10.2018 - 30.09.2022

PARTNERS

The **LIFE GreenShoes4All** project sets out to provide clear information and accurate measurements on the environmental impact of footwear products, as set out in Commission Directive 2013/179/EU on the use of common methods to measure and communicate the life cycle environmental performance of products and organisations.

The project consortium involves 10 organizations with complementary expertise and competences such as research organisations, training centres, national & European footwear associations and manufacturers of footwear and components from Belgium, Portugal, Romania and Spain.

The project Coordinator is Centro *Tecnológico do Calçado de Portugal - Portuguese Footwear Technology Centre (CTCP), Portugal.*

Romanian partners involved in this project are: *The National Research and Development Institute for Textiles and Leather (INCDTP) - Division Leather and Footwear Research Institute (ICPI)* and *PESTOS PRODUCTION SRL*.

OBJECTIVES

Implement a Footwear Environmental Footprint Category Rules (FEFCRs) methodology:

- Establish innovative eco-design concepts and eco-processes for shoes manufacturing with great transfer potential to other sectors (i.e. leather goods, clothes, etc.)
- Test new recycling routes in the EU footwear value chain to reduce raw materials needed and wastes discarded
- Contribute to building a Single Market for Green Products by demonstrating the great added value of the footwear PEFCRs methodology for producers, retailers and consumers
- Allow beneficiaries to acquire experience and knowledge resulting in new services and products to market.

PROJECT DESCRIPTION

The project aims to implement and disseminate a Footwear Product Environmental Footprint (PEF) methodology and to develop efficient eco-design, recycling and manufacturing solutions, in order to obtain performing shoes with a lower PEF.

In particular, **LIFE GreenShoes4All** intends to achieve a Single Market for Green Products by promoting the great added value of the innovative PEF Category Rules (PEFCRs) methodology. The project is also intended to test and demonstrate new recycling routes in the EU footwear value chain and to establish and compare, through demonstrative experimentations, innovative eco-design concepts and eco processes for shoes manufacturing.

The project will support the Single Market for Green Products by implementing a new method to measure environmental performance throughout the lifecycle, the Product Environmental Footprint (PEF) for footwear. The overall objective is to reduce the problems and costs companies are facing and to give a better understanding to the consumers regarding the labels used. Consumers indeed tend to be confused by the flow of green misleading terms and labels.

The PEF methodology will help manufacturing companies reduce the CO_2 and greenhouses gases emissions, aiming at a low carbon economy. Through the development of innovative eco-design concepts and eco-processes, natural resources will be used in a more efficient manner encouraging the reduction of PEF, to obtain performing shoes. The **LIFE GreenShoes4All** is also directed to create new green jobs, services and products thanks to the new recycling routes and business models towards a Circular Economy.

EXPECTED OUTCOMES

Application of FEFCRs' demonstration pilot to different footwear styles produced in the EU:

- Reports on PEFCRs' applicability to selected shoe styles and recommendations to reduce the environmental footprint
- Development of innovative sustainable green shoes and components, as well as Eco-design, recycling and manufacturing methodologies for low Footwear Environmental Footprint (FEF) & sustainable footwear
- A strategy to ensure sustainability, replicability and transferability of the project to other sectors

NEWS AND EVENTS

In order to be permanently informed and to benefit by the project results, please visit our **LIFE GreenShoes4All** page at: http://www.greenshoes4all.eu/

DISCLAIMER

LIFEGREENSHOES4ALL (LIFE17 ENV/PT/000337) project is been co-funded with support from the European Commission under the LIFE + programme. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

PARTNERS

Co-funded by the
Erasmus+ Programme
of the European Union

LEATHUB

Establishment of Leather Hubs in Russia and Mongolia

Programme: ERASMUS+ _ Key Action 2: Capacity Building in the field of higher education
Agreement Number: 598715-EPP-1-TR-EPPKA2-CBHE-JP
Duration: 36 Months (15.01.2019 – 14.01.2022)

PARTNERS

LEATHUB project concentrates on strengthening and enhancing the role of higher education institutes and universities in innovation capacity building, technology transfer, commercialisation of applied scientific research outcome and brokerage of R&D services in the leather industry from Russia and Mongolia.

The project involves a complex consortium of **13 organisations** with complementary expertise and competences from **8 countries:** Turkey, Greece, Italy, Lithuania, Mongolia, Poland, Romania and Russia.

The project Coordinator is ***EGE University from Izmir, Turkey***.

The Romanian partner involved in this project is *The National Research and Development Institute for Textiles and Leather (INCDTP) - Division Leather and Footwear Research Institute (ICPI) from Bucharest.*

The Consortium is designed to provide a combination of outstanding teaching and academic resources along with knowledge and experience in the field of R&D services. All of the universities have extensive experience of EU and wider international cooperation, both in terms of academic/ educational expertise and technical capacity/experience in project management, required to carry out all aspects of the project work programme. They have extended capacity in terms of staff and equipment in order to meet the programme development needs, as well as financial resources to handle and manage the project and its budget.

AIMS & OBJECTIVES

LEATHUB project responds to one of specific needs of the region in promoting innovation and R&D to boost leather industry in an eco-friendly approach. Thus, it responds to the need for a professional profile able to work with an interdisciplinary approach that integrates knowledge and expertise in R&D in the leather sector on one hand, and in innovation-driven business on the other hand. Currently, the region appears to lack integration in these fields, resulting in difficulties in bridging the gap between the HEIs and the leather industry.

The aim of the project is to bridge the gap between the leather industry and the universities by enhancing the collaboration on a research and development base in schemas where industry will be the innovation seeker. Within an industry's value chain, an innovation seeker is a company searching for innovation solutions beyond its boundaries. The intense collaboration between industries and universities will:

- Accelerate the pace of applied research in advanced industries in leather sector;
- Drive down the cost of advanced industries technologies and accelerate their deployment;
- Contribute to workforce development, not just at the Ph.D. level, but at all levels;
- Boost exports and enable the specific regions in Russia and Mongolia to compete effectively in global markets, which in turn will ensure a vibrant national economy.

In order to achieve the aforementioned aim **the main general objective** of the project is the **establishment and operation of 4 training and innovation centres (Leather Hubs)** which will act as intermediary between innovation seekers (industry) and the innovation providers (research teams in the universities, laboratories, spin-offs).

A further general objective is the provision from the Leather Hubs of a holistic bouquet of services that will meet the actual need of companies for fast and effective R&D. The Leather Hubs will seek to accelerate technology deployment, operate demonstration facilities and test beds, support education and training, and perform applied research on new manufacturing processes - all unlikely activities for private industry on its own.

The specific objectives of the collaborative relationships that Leather Hubs will build with the industry of various sectors are:

- ✓ the creation of the ability to identify and respond to the needs of local client companies in the leather sector;
- ✓ the effective matching among technology providers and user industries;
- ✓ their active involvement through the whole leather value chain;
- ✓ the animation of their networks – both local and further afield – as a coherent ecosystem;
- ✓ the provision of links to other hubs and competence centers around Europe for a wider exploitation of available knowledge in leather sector

LEATHUB project will be among the first projects that private business and public academic institutions work together to bridge the gap between them in the leather sector. The creation of the 4 Leather Hubs in Universities from Russia and Mongolia that is proposed through LEATHUB is totally new for the region. Such structures and facilities exist in Europe and they have been proven very successful and supportive for the growth of regional economies. The international dimension that Universities in the region strongly promote as well as the need of changing the traditional functioning of leather economy in the region has led them to the acknowledgment of the urgent need for the establishment and development of such facilities.

PROJECT DESCRIPTION

The leather industry of the Russian Federation and Mongolia reached its high rate of development in the 1980s. However, with the transition to market economy there was a significant reduction in tanneries, in assortment of products and a shortage of qualified personnel.

To date, the main problems in the development of the leather industry in Russia and Mongolia are:

- shortage of leather raw materials;
- ecological problems;
- recycling of collagen-containing subproducts;
- lack of qualified staff.

Currently, the production of leather industry, both in Russia and in Mongolia, is slowly but steadily growing. Prospective directions of development of this segment are:

- the ecologization of leather production and the use of chromium-free tanning methods;
- transition to a new technological approach, based on the development of low-waste and non-waste technological processes.

The main solutions of the problems in this segment are:

- stimulation of the development of the domestic raw materials production, in particular, the increase in the number of livestock and the improvement of the quality of hides and skins;
- stimulation of processing leather production wastes;
- introduction of innovative technologies to improve the environmental safety of production processes;
- closer and advanced integration and cooperation of industrial enterprises with educational institutions.

To solve the above tasks, in the frame of LEATHUB project, four training and innovation centers (Leather Hubs) will be set up in four universities from Russia and Mongolia.

The **LEATHUB** project shall approach its methodology with an aim to ensure that the project will be carried out in a disciplined, well managed and consistent manner, one that will ultimately deliver quality project results, on time and within budget.

LEATHUB is a multinational project that will span a period of 3 years. The project comprises a set of implementation activities that will materialise the project objectives, supported by preparation, management, quality and dissemination activities that will ensure the propagation of its results even after the project has ended.

All of the project activities are depicted in the **Logical Framework Matrix** - a set of Work Packages, Objectives, Indicators of progress and Outputs.

ENVISAGED RESULTS & TARGET GROUPS

The main outcomes of **LEATHUB** project will be the establishment of four training and innovation centers in four participating universities from Russia and Mongolia, which will provide training services for tanneries, support the design and the implementation of research and development services from the university according to the specific needs of the companies, and also implement research on the use environmentally friendly technologies for tanning raw materials and recycling of collagen-containing waste. The centers established will solve the problems that are acute for the leather industry community of the EU, Russia and Mongolia.

Furthermore, to meet the aforementioned challenges, the established centers will be equipped with modern analytical and testing equipment, professional literature, journals, and regulatory documents in force in Russia, Mongolia and the EU. These centers will act also as technology brokers for local leather industry.

One basic activity, which sustains the LEATHUB project outcomes, is the transfer of European experience to the staff of Leather Hubs and other organisations from Russia and Mongolia.

As a result of this project, the main goal - **the establishment of 4 Leather Hubs in Russia and Mongolia** - will be achieved, so the leather industries of Russia and Mongolia will have access to:

- new technologies that will minimise the negative impact on the environment;
- new ways of using chemicals;
- reviving traditional technologies for processing leather and fur raw materials;
- new management approaches focused on the creation of value through clusters and networks.

All of these will allow the creation of conditions for broad mutually beneficial cooperation between the educational community and the industrial enterprises of the leather and fur sector of the EU, Russia and Mongolia.

The target groups to which LEATHUB will be addressed are:

- staff and trainers of the Leather Hubs, who will benefit from the acquisition of know-how about the services that Leather Hubs should provide to the end-users. The improvement of their skills will include among others the usage of an R&D facilitation platform with a database, the consultation with EU partners, mobility activities, training events and study visits;
- researchers and post graduate students, who will benefit from the enhancement of innovation and entrepreneurship programmes in the leather sector;
- entrepreneurs from the leather industry who will benefit from innovation training, technology agreements with R&D centres for joint projects, testing and demonstration activities.

The Leather Hubs' staff will get better conditions to facilitate the access of companies to research results. This will improve the innovation capacity building (both technical and managerial) of local communities, because through clustering models (tanneries, producers of leather products, quality assurance providers, academia-industry partnerships) innovation ecosystems in leather sector will be supported, new business investments will be encouraged and the whole territorial system will become more stable, dynamic and mature, thus slowing the brain drain process.

In general terms, within a global framework in which the speed of the connection between knowledge and market is decisive to sustain innovation, the LEATHUB project intends to give a contribution to how to implement an efficient and effective use of knowledge for the successful integration of local producers from the leather industry into regional and global value chains (RVCs and GVCs), as well as, towards the exploitation of the necessary knowledge regarding technologies, methods and tools for sustainable development of their businesses.

Sustainability of the project outcomes after the end of EU funding will depend on the assumption of an operational/business model through which the 4 Leather Hubs and their network can provide. They will also attract talents and catalyze innovative processes and will definitely create economic value for local leather supply chains.

The consultation with policy makers will allow, during and at the end of the project, to maximise mainstreaming and integration of project results into national and regional policy frameworks.

NEWS AND EVENTS

In order to be permanently informed and to benefit by the project results, please visit our **LEATHUB** page at: www.leathub.eu.

DISCLAIMER

The European Commission support for the production of this publication does not constitute an endorsement of the contents which reflects the views only of the authors, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

LEATHUB PARTNERSHIP

Coordinator:

EGE University, Turkey

Partners:

Coordinator: EGE UNIVERSITY – **EGE, Turkey**

C.G.S. DI COLUCCIA MICHELE & C. S.A.S. – **CGS, Italy**

CREATIVE THINKING DEVELOPMENT - **CRE.THI.DEV, Greece**

INSTITUTUL NATIONAL DE CERCETARE-DEZVOLTARE PENTRU TEXTILE SI PIELARIE - **INCDTP – ICPI, Romania**

ANOTATO EKPAIDEYTIKO IDRIMA PEIRAIA TECHNOLOGIKOY TOMEA – **PUAS, Greece**

INSTYTUT PRZEMYSLU SKORZANEGO W LODZI – **IPS, Poland**

KAUNO TECHNOLOGIJOS UNIVERSITETAS – **KTU, Lithuania**

Partners:

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THE FEDERAL STATE EDUCATION INSTITUTION OF HIGHER PROFESSIONAL – **BSAA, Russia**

CHAMBER OF COMMERCE OF THE REPUBLIC OF BURYATIA - **TPP RB, Buryatia**

MONGOLIAN UNIVERSITY OF LIFE SCIENCES – **MULS, Mongolia**

MONGOLIAN UNIVERSITY OF SCIENCE AND TECHNOLOGY – **MUST, Mongolia**

MONGOLIAN LEATHER INDUSTRY ASSOCIATION - **MLIA, Mongolia**

COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council will issue a monthly ***COTANCE Newsletter*** with the purpose of **promoting an improved image of leather** to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at https://www.euroleather.com/index.php/newsletter. The first three newsletters were also published in the first 2019 issue of *Leather and Footwear Journal*. The April and May newsletters are given below.

NEWS 4/2019 - April 2019

Why you shouldn't worry about chromium

Hides and skins are by-products from the meat and dairy industry. Once they are generated, man has only two options: to let them go to waste or recycle them; and he has never failed to recycle them into leather. Tanners eventually took up that mission. Thanks to tanning, the hide or skin doesn't rot, withstands mechanical and thermal stress, can be dyed and becomes fit for various uses.

Typically, there are three tanning techniques: vegetable, mineral and synthetic tanning. The technique that conquered the market relies on mineral trivalent chromium (Cr III). About 85 - 90% of all leathers in the world are chromium III tanned. There must be a reason for that!

Indeed, Cr III is extremely versatile; it can be used with all typologies of hides and skins; its use is simple, precise, secure; the process time is shortened; the amount of chemicals reduced. In short, it is the market's most demanded processing technique, and tanneries listen to their customers.

Moreover, the trivalent form of chromium is an essential trace element which the human body needs in small quantities. It contributes to the normal metabolism of carbohydrates, lipids and proteins. In fact, a lot of alimentary supplements are dedicated to this. Chromium III naturally exists in food like bread yeast, meat, potatoes, cheese, molasses, spices, wholemeal bread, cereals, fresh fruits and vegetables.

So, why are people concerned? This mineral has become a kind of scapegoat for negative influences on human health or the environment, although the corresponding EU-Legislation (REACH dossier) has redeemed its image. The only relevant issue concerns people sensitive to chromium, a tiny fraction of the population, far less than those allergic to nuts or to the hair of cats… and far less risky as well, as it is limited to contact dermatitis.

Leather has also been associated with hexavalent chromium (Cr VI). This other form of Chromium is not as benign as its trivalent form, but it is not used for tanning, as it has no tanning properties. How can it be, then, that traces of Cr VI have been found in certain leathers? That occurs in leather of doubtful origin, where the process and the process chemicals used are not state of the art; in such cases, unfixed Cr III can oxidise into Cr VI. However, appropriate technologies and reputable chemicals, as well as quality control, provide a high level of safety.

The use of trivalent chromium salts can be traced back to over 150 years in the leather industry and no major public health problem has ever been reported. Only vegetable tannins have a longer history of safe use. Also, in spite of all scientific developments, no alternative with equivalent performances has been found so far.

Chromium III, correctly and responsibly used in tanneries, is perfectly OK!

Dear reader, rest assured chromium-tanned leather from reliable sources presents no danger to the average consumer. Don’t eat your shoes like Charlie Chaplin (because they do not taste really good), but enjoy their long-lasting comfort and beauty! And… always ask where the leather is coming from!

edited bv COTANCE

in collaboration with APPBR

Leather and climate change

The tanning and leather industry is no stranger to the sustainable mindset. As mentioned in previous newsletters, the entire concept of making leather goods is based on recycling industrial waste of the food sector. The hides and skins of slaughtered animals are residues of meat production, which is necessary for a balanced diet. We don't waste resources! In fact, tanning is probably the world's most efficient recycling industry, as virtually all hides and skins generated at global level are recovered and recycled. Tanners cooperate with stylists and designers as well as other industries to make the most out of our raw materials.

According to the UN Food & Agriculture Organisation, 7.2 million tonnes of skins and hides are generated every year. Without the tanning and the leather industry, they would have to go to landfill or incineration, producing greenhouse gases. I hear you say, livestock production also contributes to emissions. Indeed, but by substituting the need for synthetic textiles or plastic, made with unsustainable petrochemicals, tanning precludes that impact and generates more added value, all from renewable resources.

Leather is not fast fashion! It is durable and repairable and becomes even more beautiful while ageing. You can enjoy a leather product all your life and even pass it on to your children.

Look at substitutes for leather. They are often made of polymers, like polyurethane or PVC, and often carry a heavy petroleum-based coating. Have you thought about microplastic pollution? Plastics are being found everywhere, from mountaintops to the deepest depths of the ocean. They also take significantly longer to biodegrade after disposal– a few hundred years, for sure.

Tanners in Europe have made a big step towards sustainability. They are not yet there with zero pollution, but that is the ambition. This is why after a successful first edition in 2012, European tanners will produce a new European Social and Environmental Report. Data on social accountability and environmental performance of tanneries is currently being collected from all over Europe. We want to see how far we have progressed towards our goal!

To sum up, European tanners are continuously improving their manufacturing processes with state-of-the-art technologies, to make their leather products every time more sustainable – because with sustainability comes more efficiency, durability and high-quality processes and products.

So, you can wear and use our leather products with a good conscience: through recycling and sustainable development of manufacturing, European tanners contribute to a cleaner and greener environment.

edited by COTANCE

in collaboration with ASSOCIATION OF HUNGARIAN LIGHT INDUSTRY

NATIONAL AND INTERNATIONAL EVENTS

eseia INTERNATIONAL SUMMER SCHOOL
1-12 JULY 2019, ZAGREB, CROATIA

Join the eseia International Summer School 2019 from 1 to 12 July at University of Zagreb, Croatia, to find a novel approach to smart energy system integration and utilisation of non-conventional biomass.

The eseia International Summer School 2019 will tackle topics such as:

- The integration of products and processes based on non-conventional bio-resources into buildings and smart cities,
- The identification of optimal bio-fuel integration into sustainable mobility systems,
- Policy and economic instruments for mobilising non-conventional bio-resources.

Additional focus will be given to the implementation of the research knowledge, including the creation of a successful EU funding proposal, project management best practices, and the development of International Strategic Partnerships.

Deadline for registration has been extended until **28 June 2019**.

More information: http://www.eseia.eu/

21st INTERNATIONAL CONFERENCE ON ADVANCED ENERGY MATERIALS AND RESEARCH
11-12 JULY 2019, ZURICH, SWITZERLAND

Advanced Energy Materials 2019 provides platform for world-wide Researchers, Scientists, Professors, Engineers, and CEO's of Energy Materials and Materials Science companies to share their research experience and indulge in interactive discussions on all aspects of Energy Materials, Solar Energy, Hydrogen Energy, Carbon Materials, Batteries and fuel cells. Join us for two intensive and interesting days of discussion on contemporary Energy Materials research.

Advanced Energy Materials provides wide range of sessions that discourse the current innovations and novel approaches for the expansion of energy materials to meet the global desires. Advanced Energy Materials 2019 covers major subjects such as fuel cells, organic and inorganic photovoltaic, batteries and super capacitors, Piezoelectronics, hydrogen generation and storage, thermoelectric, photo catalysis, solar fuels and thermosolar power.

More information: https://energymaterials.materialsconferences.com/

THE 5th INTERNATIONAL CONGRESS ON WATER, WASTE AND ENERGY MANAGEMENT (WWEM-19)
22-24 JULY 2019, PARIS, FRANCE

The 5th International Congress on Water, Waste and Energy Management (WWEM-19) is organized by academics and researchers belonging to different scientific areas of the University Complutense of Madrid, University Carlos III of Madrid, University of Extremadura and University of Las Palmas de Gran Canaria with the technical support of Sciknowledge European Conferences.

The event has the objective of creating an international forum for academics, researchers and scientists from worldwide to discuss worldwide results and proposals regarding to the soundest issues related to Water, Waste and Energy Management.

This event will include the participation of renowned keynote speakers, oral presentations, posters sessions and technical conferences related to the topics dealt with in the Scientific Program as well as an attractive social and cultural program.

More information: https://waterwaste-19.com

THE 2019 INTERNATIONAL CONFERENCE ON GREEN ENERGY AND ENVIRONMENTAL TECHNOLOGY (GEET19)
24-26 JULY 2019, PARIS, FRANCE

The 2019 International Conference on Green Energy and Environmental Technology is organized by academics and researchers belonging to different scientific areas of the University Complutense of Madrid, University Carlos III of Madrid, University of Extremadura and University of Las Palmas de Gran Canaria with the technical support of Sciknowledge European Conferences.

The event has the objective of creating an international forum for academics, researchers and scientists from worldwide to discuss worldwide results and proposals regarding to the soundest issues related to Green Energy and Environmental Technologies.

This event will include the participation of renowned keynote speakers, oral presentations, posters sessions and technical conferences related to the topics dealt with in the Scientific Program as well as an attractive social and cultural program.

More information: https://geet-19.com/

14th INTERNATIONAL CONFERENCE ON MICROBIAL INTERACTIONS & MICROBIAL ECOLOGY
19-20 AUGUST 2019, VIENNA, AUSTRIA
"Addressing New Challenges and emerging issues in Microbiology"

Microbial Interactions 2019 is the premier event that brings together a unique and international mix of experts, researchers and decision makers from both academia and industry across the globe to exchange their knowledge, experience and research innovations. The scope of Microbial Interactions 2018 is to bring the advancements in the field of microbiology and different microbial cooperation with other organisms or within themselves. Microbial Interaction processes include coupling across a large range of scales and linkage between a numbers of factors of different nature.

Microbial Interactions 2019 will be the best platform for all the Microbiologist, Scientists, Research Scholars, Students, Technologists who are working in this field to exchange their knowledge related to microbial interactions its evolution, diversity and role.

Microbial Interaction 2019 is an exciting opportunity to showcase the new technology, the new products of your company, and/or the service your Industry may offer to a broad international audience.

More information: https://microbialinteractions.expertconferences.org/

EUROPEAN RESEARCH AND INNOVATION DAYS
24-26 SEPTEMBER 2019, BRUSSELS, BELGIUM

Register for one of the three main components of the European Research and Innovation Days: the high-level Policy Conference, the Innovative Europe Hub and the 'Science is Wonderful' exhibition of EU-funded projects.

The Policy Conference will cover vital areas of science, engineering, medicine and wider social and environmental concerns. The Innovative Europe Hub is a unique meeting and matchmaking space for innovators, investors, entrepreneurs and the whole range of services, businesses and organisations. The 'Science is Wonderful' exhibition is free and open to everybody and brings the world of science to the public.

More information: https://ec.europa.eu/info/research-and-innovation/events/upcoming-events/european-research-and-innovation-days_en

THE 10th INTERNATIONAL CONFERENCE AND EXHIBITION ON 3D BODY SCANNING AND PROCESSING TECHNOLOGIES - 3DBODY.TECH 2019
22-23 OCTOBER 2019, LUGANO, SWITZERLAND

The past nine international conferences from 2010 to 2018 were all largely attended with 200-250 participants from different countries, different technical fields and different industries. The rich technical programs of the past events included a wide variety of works related to applications, developments and research on 3D body scanning and processing from all over the world.

The conferences were accompanied by parallel exhibitions featuring live demonstrations of 3D body scanning equipment and solutions. Various manufacturers had chosen our events for presenting and announcing world and international premieres.

The success of the 9th edition of 2018 with about 250 attendees, with over 80 presentations and with more than 20 exhibitors confirmed again 3DBODY.TECH Conference & Expo as the most important international event for the sectors related to 3D body scanning and processing technologies. With the 10th conference and exhibition of 2019, we will continue the role as the world leading technical and scientific platform dedicated to these specific fields.

3DBODY.TECH Conference & Expo provides a platform of eminent professionals, entrepreneurs, academicians and researchers across the globe to present, learn and discuss the latest in 3D body scanning and processing technologies. The multidisciplinary character of 3DBODY.TECH makes it unique and not comparable to any other meeting related to 3D body technologies.

More information: https://www.3dbody.tech/2019/

1st INTERNATIONAL CONFERENCE ON ADVANCED JOINING PROCESSES 2019 (AJP 2019)
24-25 OCTOBER 2019, PONTA DELGADA, AZORES, PORTUGAL

The 1st International Conference on Advanced Joining Processes 2019 will take place in Ponta

Delgada, Azores (Portugal) on 24-25 October 2019. The focus will be on all advanced methods of joining such as friction stir welding, joining by plastic deformation, laser welding, advanced mechanical joining, adhesive bonding, hybrid joining, etc.

Deadline for submission of abstracts: 7 June 2019.

More information: https://web.fe.up.pt/~ajp2019/

1st INTERNATIONAL CONFERENCE ON INDUSTRIAL APPLICATIONS OF ADHESIVES 2020 (IAA 2020) 5-6 MARCH 2020, FUNCHAL, MADEIRA, PORTUGAL

The 1st International Conference on Industrial Applications of Adhesives 2020 will take place in Funchal, Madeira (Portugal) on 5-6 March 2020. The focus will be on applications of adhesive bonding in the industry such as automotive, aeronautic, railway, marine, energy, electronics, etc. The idea is to bring together the adhesive makers and the adhesive users to exchange experiences and facilitate potential synergies and partnerships.

Deadline for Submission of Abstracts: 8 November 2019.

More information: https://web.fe.up.pt/~iaa2020/

INTERNATIONAL CONFERENCE ON NANO RESEARCH AND DEVELOPMENT (ICNRD-2020) 12-14 MARCH 2020, SINGAPORE

The International Conference on Nano Research and Development (ICNRD-2020) is going to be held in Singapore from March 12-14, 2020. With the theme "Breakthrough and Innovation in Nano Science and Technology", ICNRD-2020 is aiming to bring you the latest research progress and innovation on Nano science and technology. ICNRD-2020 will be the best platform for the leading academicians, scientists, researchers, engineers, practitioners to share their research achievement and indulge in interactive discussions and technical program at the event. There will be also a space for companies and institutions to present their technology, service, products and innovations.

More information: http://www.istci.org/ICNRD2020/

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Introduction. Should include the aims of the study and results from previous notable studies.

Materials and Methods. Experimental methods should be described clearly and briefly.

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Conclusions. The general results of the research are discussed in this section.

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