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STUDY ON COMFORT EVALUATION METHODS OF DIFFERENT WOMEN'S HIGH-HEELED SHOES BASED ON ELECTROENCEPHALOGRAPH (EEG) TECHNOLOGY

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STUDY ON COMFORT EVALUATION METHODS OF DIFFERENT WOMEN'S HIGH-HEELED SHOES BASED ON ELECTROENCEPHALOGRAPH (EEG) TECHNOLOGY

ABSTRACT. The 24-27-year-old women with 230-235 mm feet with the similar level of education were selected for the study. During the test, those subjects were tested by SD semantic differential measurement method and BP EEG signal acquisition system. The brain electrical rhythm characteristics and the subjective comfort feelings in the states of static standing and uniform natural walking were tested. The experimental results show that the heel mechanical changes caused by the heel height and the motion states are negatively correlated with the α wave intensity of the brain while the subjective comfort evaluation is negatively correlated with the α wave intensity in the parietal and occipital regions. The research results reveal that EEG technology is used to evaluate the comfort of wearing high-heeled shoes, which can not only make up for the lack of the subjective evaluation method, but also improve the comfort evaluation system of wearing shoes and boots. All these have the important theoretical and practical significance for the footwear comfort evaluation.

KEY WORDS: high-heeled shoe, comfort, plantar pressure, electroencephalograph (EEG)

STUDIU PRIVIND METODELE DE EVALUARE A CONFORTULUI ÎN CAZUL PURTĂRII PANTOFILOR DE DAMĂ CU TOC ÎNALT UTILIZÂND ELECTROENCEFALOGRAFIA (EEG)

REZUMAT. S-au selectat pentru studiu femei în vârstă de 24-27 de ani cu lungimea labei piciorului de 230-235 mm, având un nivel de educaţie similar. Subiecţii au fost supuşi unor teste precum diferenţiala semantică (SD) şi achiziţia semnalului BP EEG. S-au testat caracteristicile activităţii electrice a creierului şi senzaţiile subiective de confort în statică şi în mers natural uniform. Rezultatele experimentale arată că modificările mecanice ale călcâiului cauzate de înălţimea tocului şi de mişcare sunt corelate negativ cu intensitatea undei α a creierului, în timp ce evaluarea subiectivă a confortului este corelată negativ cu intensitatea undei α în regiunile parietale şi occipitale. Rezultatele cercetării dezvăluie faptul că tehnologia EEG este utilizată pentru a evalua confortul în cazul purtării pantofilor cu toc înalt, compensând nu doar lipsa unei metode de evaluare subiectivă, ci şi îmbunătăţind sistemul de evaluare a confortului la purtarea pantofilor şi ghetelor. Toate acestea au o importanţă teoretică şi practică în evaluarea confortului încălţămintei.

CUVINTE CHEIE: pantof cu toc înalt, confort, presiune plantară, electroencefalograf (EEG)

ÉTUDE SUR LES MÉTHODES D'ÉVALUATION DU CONFORT DE DIFFÉRENTES CHAUSSURES À TALONS HAUTES POUR FEMMES BASÉES SUR LA TECHNOLOGIE ÉLECTROENCÉPHALOGRAPHIQUE (EEG)

RÉSUMÉ. Des femmes âgées de 24 à 27 ans avec une longueur de jambe de 230 à 235 mm ont été sélectionnées pour l'étude, avec un niveau d'éducation similaire. Les sujets ont subi des tests tels que le différentiel sémantique (SD) et l'acquisition du signal BP EEG. Les caractéristiques de l'activité électrique du cerveau et les sensations subjectives de confort pendant une démarche naturelle uniforme et en statique ont été testées. Les résultats expérimentaux montrent que les changements mécaniques du talon causés par la hauteur du talon et le mouvement sont corrélés négativement avec l'intensité de l'onde α du cerveau, tandis que l'évaluation subjective du confort est corrélée négativement avec l'intensité de l'onde α dans les régions pariétale et occipitale. Les résultats de la recherche révèlent que la technologie EEG est utilisée pour évaluer le confort de chaussures à talons hauts, compensant non seulement l'absence de méthode d'évaluation subjective, mais aussi en améliorant le système d'évaluation du confort lors du port de chaussures et de bottes. Tous ces éléments ont une importance théorique et pratique dans l'évaluation du confort de la chaussure.

MOTS CLÉS : chaussure à talons hauts, confort, pression plantaire, électroencéphalographe (EEG)

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INTRODUCTION

The comfort of shoes is an important quality factor of shoes, and comfort is currently the subjective feeling of people. Human feet have rich tactile sensations. When wearing shoes, comfort can be described but difficult to quantify. People's subjective feelings cannot be used as a reliable source of comfort evaluation, so relative quantification techniques embody objectively the footwear comfort evaluation.

As an electrophysiological research method, EEG technology has been widely used in the field of comfort evaluation, especially in the research fields of clothing comfort, industrial product comfort and perceptual engineering, and has aroused extensive attention from researchers in the related fields [1].

The comfort evaluation of wearing high-heeled shoes is a comprehensive evaluation process integrating multiple feelings. The related indicators of EEG are related to human physiological and psychological aspects. EEG technology evaluation methods can be used for reference in the related fields [2]. Meanwhile, this technology has a physiological and psychological basis for comfort evaluation.

This study applied EEG technology to the comfort evaluation of high-heeled shoes, and explored the method of EEG technology applied to the comfort evaluation of female high-heeled shoes. In the EEG spectra, the features that can best show the comfort of high heels are screened out, and the quantitative relationship between the spectrum signal of the relevant rhythm of the EEG and the comfort of different high heels is obtained.

EXPERIMENT

Experimental Objects

The subjects undergoing the EEG tests were required to meet the following criteria:

(1) The subjects had no brain mental illness, and the levels of intelligence development were similar, and they were all right-handed.

(2) The subjects were young women at the age of 24-27 with 230-245 mm feet and they didn't have a long history of wearing the high-heeled shoes [3].

(3) The subjects cleaned their hair the day before the tests, and they were forbidden to use oily products, such as hair conditioner and hair oil. The grease and stains would increase the resistance values of the scalps, resulting in the acquisition distortion of the brain waveform.

(4) Empty stomach was prohibited before the tests because studies have shown that hypoglycemia would affect EEG values.

(5) The subjects were revealed the harmlessness of the experiment before the tests so as to eliminate the fear and mental tension of the subjects and reduce the experimental errors.

BP EEG Signal Acquisition System

The EEG acquisition instruments used in the tests were an American Brainvision Recorder with multi-lead neurotic electrophysiological analysis system consisting of an electrode cap amplifier and a computer display. The software in the EEG equipment was prepared with a Pycoder of the acquisition software and an Analyser of the analysis software before the experiment, and the necessary hardware, software and experimental accessories were prepared. The hardware included a display, an amplifier, and electrode caps while the software included an acquisition software (Pycoder), an analysis software (Analyser), a programming software (E-prime). The accessories contained conductive adhesives, blunt syringes, shampoo, washbasins, hair dryers, towels, slippers. Besides, 6 pairs of experimental shoes with different heel heights were required.

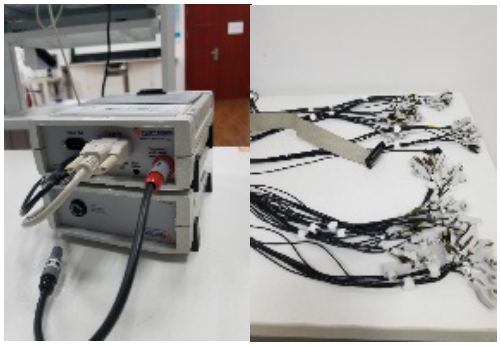


Figure 1. Diagram of the EEG acquisition instrument

Figure 2. Experimental shoes with different heel heights

EEG is a technique for recording spontaneous rhythmic potentials triggered by stimuli. External stimuli caused the brain to generate potential activity, which was recorded by external electrodes through the human tissue to form an electrical signal. The EEG signal amplifier was reached through a junction box. The digital EEG instrument filtered the signals to form the continuous EEG after they were recorded and stored [4].

Experimental Process

EEG Signal Acquisition

Figure 3. Distribution of the electrode cap test points

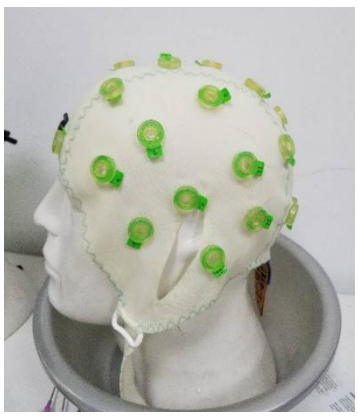


Figure 4. An Electrode Cap

Before starting the formal experiment, a set of pre-experiments should be done first. Prior to the start of the pre-experiment, the subjects should read the instructions of the experiment and were told about the precautions of the test process.

(1) The appropriate type of electrode caps was selected for wearing, and then the electrode was positioned based on the center of the parietal region. The electrode placement position was referred to the Placement System Guide of International 32-lead EEG Electrode. The electrode was comprised of 32-lead locations, wherein the electrode contained a reference electrode, a grounding electrode and 30 position electrodes.

Figure 5. Lead electrodes

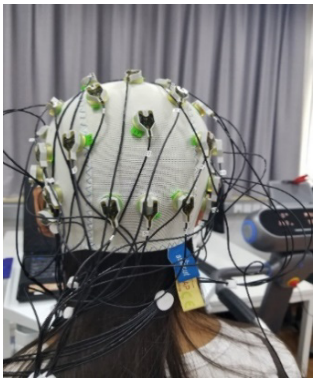


Figure 6. Images of wearing the electrode cap

(2) The experimental shoes were put on, the electrode cap and the amplifier were connected, and the E-prime was connected to the signal acquisition host. The corresponding experimental shoes were put on to start the experiment. The parameters were debugged and the experimental control parameters were input so as to observe whether the electrode impedance was reduced to less than 5 kΩ.

Four states concerned with the experiment settings and wearing the high heels were studied, which included static standing on the ground with both feet, the left foot standing on one foot, the right foot standing on one foot, and walking with two feet. In order to improve the accuracy of the signal acquisition and reduce the interference of the electromyographic (EMG) signals, the intermission time with different lengths were set after each action.

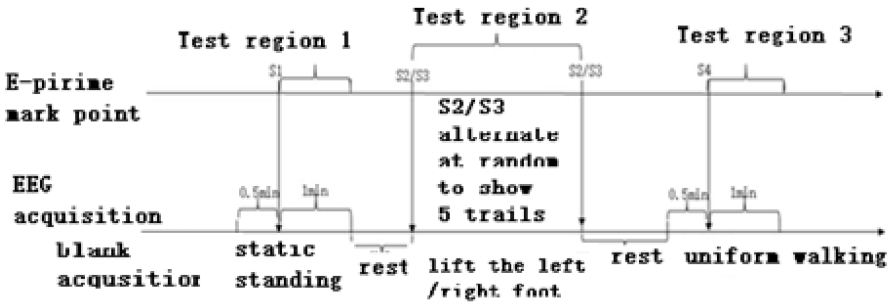


Figure 7. Schematic diagram of test cycle mode

Figure 8. Test image of static standing state

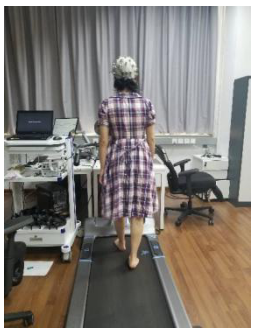
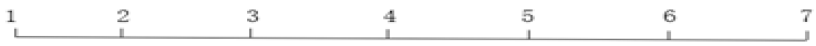


Figure 9. Test image of uniform walking state

The variables in the experiment were 6 types of high-heeled shoes with different high heels, 3 states of different motions and 32-lead electrode acquisition positions [5]. The signals collected from each subject contained 12 segments. After the acquisition, the names of the subjects plus the numbers of the shoes were labelled individually.

Subjective Comfort Evaluation

The most common method for the subjective comfort evaluation of wearing shoes and boots was the semantic differential (SD) scale method. Likert scale was used as the scale in the evaluation and five different points were selected.



1. strongly uncomfortable;
2. much uncomfortable;
3. somewhat uncomfortable;
4. comfortable;
5. somewhat comfortable;
6. much comfortable;
7. strongly comfortable.

Figure 10. Scoring scales of comfort rating

After having finished the EEG test, the subjects were asked the comfort in the wearing process to evaluate the pre-designed comfort and to score the discomfort sites.

EXPERIMENTAL RESULTS AND ANALYSES

The Effects of the Heel Heights on α Wave of EEG

Table 1: Analyses of the effects of the heel heights on α wave power values

α wave power	10 mm	30 mm	50 mm	60 mm	80 mm	100 mm
static standing	17.065 ±0.257	17.339 ±0.311	16.569 ±0.290	16.331 ±0.334	14.314 ±0.395	12.902 ±0.323
uniform walking	16.962 ±0.071	16.10 ±0.425	13.91 ±0.003	12.145 ±0.539	10.05 ±0.022	10.250 ±0.417

The average values of α wave of the subjects wearing women's shoes with 10-100 mm heel heights are statistically analyzed. The experimental results show that both the heel heights and the motion states have the effects on α wave power value. For the 6 different heel heights, all the α power values in the standing state are greater than those in the walking state, which shows that within 1.5 min of the test, the comfort of wearing women's shoes with all the heel heights in the standing state is greater than that in the walking state. The similar effects of the uniform walking within a short time on α wave also show the restraint.

Table 2: T-test of the α-wave paired samples with different heel heights

heel height (I)	heel height (J)	Mean values (I-J)	Standard errors	Sig	95% confidence interval of difference	
					Lower limit	Upper limit
10 mm	30 mm	-0.274	0.079	0.340	0.073	0.578
10 mm	50 mm	0.496	0.026	0.004	0.312	0.680
10 mm	60 mm	0.734	0.096	0.007	-0.485	0.551
10 mm	80 mm	2.751	0.204	0.000	-1.215	0.509
10 mm	100 mm	4.163	1.140	0.000	-1.163	0.088

Through the T tests of the paired samples, the 30-100 mm high-heeled women's shoes are used to compare and analyze those flat shoes with 10 mm heel heights as the most common state of wearing. The results show that there are obvious differences between the four heel heights of 50, 60, 80 and 100 mm and the flat-heel heights of 10 mm. The further analysis of variance shows that there are significant differences in α wave values of wearing different heel heights ($P < 0.001$).

The Impacts of Wearing States on EEG

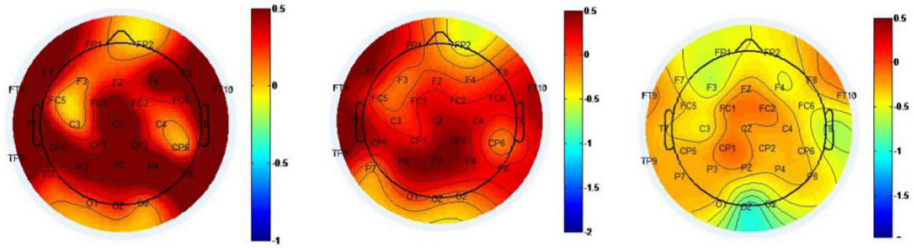


Figure 11. Different BEAMs in the two states

The differential analysis and correlation analysis of the α wave BEAM of wearing the women's shoes with the same height in the standing state and the uniform walking state are respectively performed. In the static standing state and the uniform walking state, the different BEAMs shown in the following are obtained. In the different BEAMs, the deeper the color shows, the greater the differences between the two states are. According to the BEAMs, it can be clearly seen that the differences between the parietal and the temporal regions are most distinct in the following three types of high-heeled shoes in the course of wearing.

After obtaining the visual differential results of the regions from the BEAMs, the further accurate correlation analyses are performed on the different motion states of 30 electrodes. Two states can be found to influence the different electrodes on the specific brain regions.

Some channels of EEG are significantly related to the wearing states of high-heeled shoes, and the significant channels include Channels F2, F3, F7, FT9, FC1, T7, TP9, CP5, P7, O1, Oz, O2, P8, CP2, C4, FT10, FC2 and P4. There are also some channels that have no significant differences with the motion states in this respect. They are Channels FC5, C3, CP1, Pz, P3, P4, TP10, CP6, T8 and FC6. By dividing the brain regions with the electrode channels, it is also found that the electrode channels in the parietal region and a small part of temporal region show a strong correlation with the motion states ($P < 0.001$). In addition, the differences between the standing and walking states after comparison and analyses show that in the parietal region, frontal region, and occipital region, the α value of the standing state is greater than that of the walking state ($t > 0$). Therefore, it can also be concluded that the α wave changes caused by the stimulation of wearing the high-heeled shoes are mainly concentrated on the above-mentioned regions.

RESULTS AND DISCUSSION

Analyses of the Influences of Heel Heights on α Wave of EEG

In the related research fields between EEG and emotions, α wave is the most significant brain rhythm in the parietal and occipital regions when the subjects close their eyes, and is also one of the indicators that can be used to reflect the emotional state of the subjects [6]. With negative emotions, such as fear, excitement, anger and discomfort, α waves are restrained. When the subjects wear the higher heels, α waves in their brains are restrained, which proves that the unbalanced pressure distribution of the soles causes the feet and the body to be in an uncomfortable state. Some scholars have used α waves to characterize the comfort in their studies. The percentages of α waves dominating the brain waves are chosen as the study indexes, which are different from those used in the experiment. Although the selected EEG

indicators are different, the evaluation results on the comfort are consistent [7]. The comfort is related to α waves of EEG. The high-heeled shoes inhibit the appearance of α waves in the course of wearing them, leaving the subjects in an uncomfortable state.

(1) The plantar stress is increased to restrain α waves

The plantar stress under the heels with different heights is different. Some studies have shown that the higher the heel height is, the greater the peak pressure value of the sole is. The peak pressure of the soles in the walking state is stronger than that in the standing state [8, 9]. Therefore, there is a negative correlation between the spectrum energy of α waves and the peak pressure of the plantar stress. That is to say, the greater the peak pressure of the soles is, the lower the spectrum energy of α waves of EEG is. The smaller the peak pressure value of the plantar stress is, the higher the spectrum energy of α waves of EEG is.

(2) Blood circulation is blocked to restrain α waves

Medical research has shown that the blood circulation system may affect the intensity of EEG rhythm. The blood circulation speed is positively correlated with the fast waves (e.g. α wave and β wave) in EEG rhythm [10], but negatively correlated with the slow waves (e.g. γ wave) in EEG rhythm. The stress on the body can affect the blood circulation speed. In particular, when the stress on the surface of the skin is too high, the blood circulation system in the human skin is impeded, so the blood flow is decreased, which causes α waves to be restrained. The human foot is the organ full of the capillaries distributed most densely. Therefore, the excessively high local stress on the sole caused by wearing the high-heeled shoes can affect the blood circulation of the whole body, thus affecting the α wave intensity.

(3) Mental stress from wearing high-heeled shoes restrains α waves

As the height of the heel is increased and the state of wearing the shoes is changed, the mental state continues to strain during the test, causing the mental fatigue. Especially during the process of wearing the heights of 80 and 100 mm, in order to maintain the balance of the body, the subjects are highly stressed to prevent from falling during the test. The constant mental stress may increase the inhibition of the brain's central nervous system to the neuronal activity. Therefore, the thinking activity and complexity in the brain are reduced, and the degree of inhibition of the brain is increased.

Particularly in the standing state of wearing super high heels of 100 mm, although the comfort is reduced, the two feet can still touch the ground so as to keep the body in balance. Once changed in the walking state with this super high heel, the body nervous system is immediately under the state of tension, and the attention is highly concentrated to generate fear. In addition, in order to maintain the body balance, the lower limbs will produce electromyographic signals to interfere the α wave intensity, resulting in the perceived discomfort [11]. In the lower high groups, the difference for this change is not significant. This may be the reason why the mental states of the subjects wearing the lower heels are more stable and the impacts on the brain waves are not obvious.

(4) Mild motion fatigue restrains α waves

Studies have shown that the muscle contraction caused by the motion fatigue brings about the changes of α wave indexes first to rise and then to fall. No matter whether the α wave frequency is increased or decreased, the indexes of α waves are decreased while the energy of α waves is reduced. Therefore, in the course of the experiment of wearing the women's shoes with higher heel heights, the overall experiment shows that the higher height the heels are, the stronger the fatigue of the lower limb muscles is. The muscle fatigue in the walking state is greater than that in the standing state. Changes of the constant muscle contraction affect the degree of excitability of the central nervous system, which reduces the discharge frequency of α waves. The decrease of α wave power values in the course of motion is closely related to the activity between the central neurons. The fatigue caused by walking leads to the brain's inhibitory neurons to be active, which changes the nature of the α-fast wave in EEG into other types of slow waves in EEG.

As the heel height is increased from 30 to 100 mm, α wave intensity presents to decline continuously, which accounts for that the high-heeled shoes are of the restrained type no matter

what state they are in. In the ultra-high heel state, the declining rate is increased, indicating that when the subjects wear the higher heeled shoes, the feelings of "comfort" and "pleasure" are significantly reduced while the feelings of "discomfort" and "tension" are rapidly increased. This is the subject's stress response to his or her body balance, mechanical patterns and mental stress which are beyond their own.

Distribution of Brain Regions Activated by Heel Heights

The differences of α wave power spectra of six different heel heights under the conditions of 32 electrode channels are individually analyzed. If the order of α wave intensities of each electrode channel is sorted from high to low, regarding the cerebral regions of the brain region as the reference, the brain electrodes are divided into six different regions: (O1 O2 Oz CP3 CP4 CPz), (F3 F4 FZ P3 P4 PZ), (FT1 FT2 FT7 F7 F8), (FC3 FC4 FCZ FT8), (C3 C4 CZ T3 TP7) and (T4 TP8 P7 P). The order from low to high can be obtained as follows: central region < frontal region < occipital region < parietal region. From the following BEAMs, the colors used in different shades indicate the different α wave intensities. It can be clearly seen that the different high-heeled shoes and the different motion states have effects on α wave values. The darker the color in the BEAMs, the greater the different α wave intensities in all the channels of the EEG. By comparing the BEAMs of different heel heights and different states, it can be intuitively obtained that the brain stimulation formed from the heel height of the high-heeled shoes and the motion states can activate the brain in the different positions.

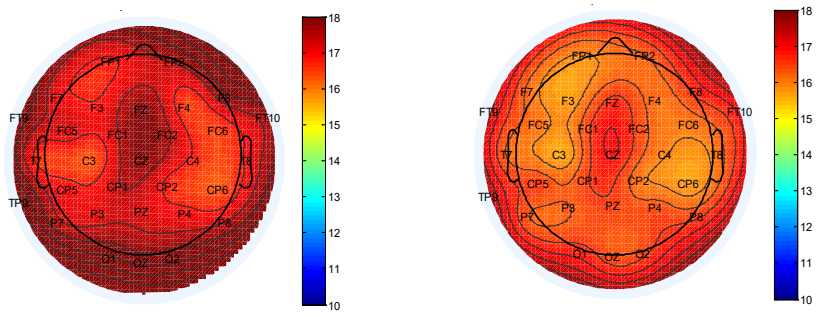


Figure 12. Schematic diagram of α wave intensities in the lead positions

According to the correlation analyses between the BEAMs and the electrode channels in the high activation region, it is considered that the parietal region and the occipital region are the key parts of α wave difference caused by the changes of the heel heights of the women's shoes. The main reasons include three aspects:

(1) The α wave indexes related to the comfort are regarded as a fast wave, which is most obvious in the parietal and occipital regions of the brain. Therefore, the α wave frequency spectrum values collected from these two brain regions are the highest.

(2) The somatosensory stimuli induced by the changes in the plantar mechanics from the variable of heel heights are mainly transmitted through the pressure receptors, while the neural signal transmission analysis and treatment regions of the tactile pressure senses are positioned in the parietal and occipital regions.

(3) As the heel height of the women's shoes is increased, the fatigue caused from the whole test is increased, and the tight nervous system with super high heel of 100 mm makes the mental fatigue from the subjects increase. Some studies have shown that the mental fatigue can inhibit the activity of the central nervous system, and the excitability of the brain is reduced. There is a strong negative correlation between the mental fatigue and the α wave rhythm.

Relationship between α Wave and the Subjective Comfort Evaluation

The analytical method of Pearson correlation coefficient is adopted to analyze the relationship between the subjective evaluation results of the stress comfort and the α wave spectrum energy. The correlation analysis is performed between the subjective comfort evaluation results of six kinds of heel heights

worn by the subjects in the two states, and the α wave intensities of 30 electrode positions. The results show that the α wave intensity of most lead locations is positively correlated with comfort.

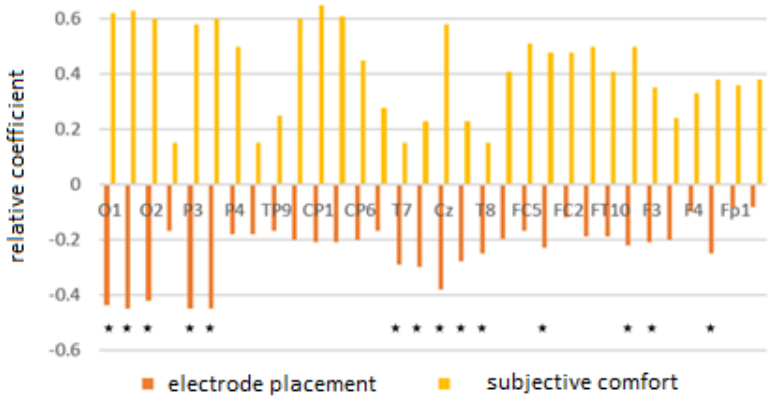


Figure 13. Correlation analyses between the subjective evaluation and the α wave intensity

From the lead position, it can be seen that the α wave intensity measured in most of the brain regions, especially in the occipital region and the parietal region, is much highly correlated with the subjective comfort. The somatosensory stimuli created by wearing the high-heeled shoes include many aspects of psychological feelings, such as comfort on the feet, the stress perception on the soles and the balance of the body. The brain plays an important role in this process.

CONCLUSION

(1) EEG index α wave can characterize the comfort of women shoes with different heels.

(2) The changes in heel heights have effects on EEG. As the heel heights are increased, the α wave intensity is decreased, but the discomfort is increased.

(3) The brain regions activated by the somatosensory stimuli from wearing the different high-heeled shoes are mainly the parietal region and the occipital area.

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OPTIMIZATION OF ALKALINE HYDROLYSIS OF CHROME SHAVINGS TO RECOVER COLLAGEN HYDROLYSATE AND CHROMIUM HYDROXIDE

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OPTIMIZATION OF ALKALINE HYDROLYSIS OF CHROME SHAVINGS TO RECOVER COLLAGEN HYDROLYSATE AND CHROMIUM HYDROXIDE

ABSTRACT. The tanning industry uses skins and hides from cattle, sheep, among others, which are a byproduct of the meat industry. In their production process, they generate wastewater and solid wastes in significant quantities, that require alternatives for their adequate treatment. The present research was developed to optimize the alkaline hydrolysis process of chrome leather shavings to recover collagen hydrolysate and chromium salts, and to identify the relation between the response variables and hydrolysis conditions. For this purpose, a preliminary study was carried out, where alkaline hydrolysis conditions were adjusted, then these were optimized through a factorial design and scaled up the process to a pilot level. The preliminary study of alkaline hydrolysis of the sample was performed, where reaction time and sodium hydroxide concentration were established as factors to adjust the process. The optimization of this method was developed through a factorial design with two response variables: percentage of recovered collagen protein (PRCP) and percentage of residual chromium (PRC) present in the collagen hydrolysate. Thus, the optimum alkaline hydrolysis conditions were obtained: 70°C, 0.47 M NaOH and 90 minutes for the reaction, and the relation between the response variables. Finally, the process was carried out in a pilot scale in which 45 L of collagen hydrolysate was recovered, with 87.16% of recovered collagen protein and 1.17% of residual chromium.

KEY WORDS: waste valorization, chrome shavings, alkaline hydrolysis, tanning process

OPTIMIZAREA PROCESULUI DE HIDROLIZĂ ALCALINĂ A RĂZĂTURII DE PIELE CROMATĂ PENTRU A VALORIFICA HIDROLIZATUL DE COLAGEN ŞI HIDROXIDUL DE CROM

REZUMAT. Industria de pielărie foloseşte piei de bovine şi ovine, printre altele, care sunt un produs secundar al industriei cărnii. În procesul de producţie, acestea generează ape uzate şi deşeuri solide în cantităţi semnificative, care necesită alternative pentru tratarea lor adecvată. Acest studiu de cercetare a fost dezvoltat cu scopul de a optimiza procesul de hidroliză alcalină a răzăturii de piele cromată pentru a valorifica hidrolizatul de colagen şi sărurile de crom şi pentru a identifica relaţia dintre variabilele de răspuns şi condiţiile de hidroliză. În acest scop, s-a efectuat un studiu preliminar, în care au fost ajustate condiţiile de hidroliză alcalină, apoi acestea au fost optimizate printr-un plan factorial experimental şi s-a extins procesul la nivel pilot. S-a efectuat studiul preliminar al hidrolizei alcaline a probei, în care timpul de reacţie şi concentraţia de hidroxid de sodiu au reprezentat factori de ajustare a procesului. Această metodă s-a optimizat printr-un plan factorial experimental cu două variabile de răspuns: procentul de proteine recuperate din colagen (PRCP) şi procentul de crom rezidual (PRC) prezent în hidrolizatul de colagen. Astfel, au fost obţinute condiţiile optime pentru hidroliza alcalină: 70°C, NaOH 0,47 M şi 90 minute pentru reacţie, precum şi relaţia dintre variabilele de răspuns. În cele din urmă, procesul s-a desfăşurat la nivel pilot, recuperându-se 45 L de hidrolizat de colagen, cu 87,16% proteine recuperate din colagen şi 1,17% crom rezidual.

CUVINTE CHEIE: valorificarea deşeurilor, răzătură de piele cromată, hidroliză alcalină, proces de tăbăcire

OPTIMISATION DE L'HYDROLYSE ALCALINE DE COPEAUX DE CHROME POUR RECUPERER L'HYDROLYSAT DE COLLAGENE ET L'HYDROXYDE DE CHROME

RÉSUMÉ. L'industrie de la tannerie utilise des peaux de bovins et de moutons, entre autres, qui sont un sous-produit de l'industrie de la viande. Dans leur processus de production, ils génèrent des eaux usées et des déchets solides en quantités importantes, qui nécessitent des solutions alternatives pour leur traitement adéquat. La présente recherche a été développée pour optimiser le processus d'hydrolyse alcaline des copeaux de cuir chromé afin de récupérer l'hydrolysat de collagène et les sels de chrome, et pour identifier la relation entre les variables de réponse et les conditions d'hydrolyse. À cette fin, une étude préliminaire a été réalisée ; les conditions d'hydrolyse alcaline ont été ajustées, puis optimisées grâce à une conception factorielle et à une mise à l'échelle du processus à un niveau pilote. L'étude préliminaire de l'hydrolyse alcaline de l'échantillon a été réalisée. Le temps de réaction et la concentration en hydroxyde de sodium ont été établis comme facteurs permettant d'ajuster le processus. L'optimisation de cette méthode a été développée selon un plan factoriel avec deux variables de réponse : le pourcentage de protéine de collagène récupérée (PRCP) et le pourcentage de chrome résiduel (PRC) présent dans l'hydrolysat de collagène. Ainsi, les conditions optimales d'hydrolyse alcaline ont été obtenues : 70°C, NaOH 0,47 M et 90 minutes pour la réaction et la relation entre les variables de réponse. Enfin, le processus a été mis en œuvre à une échelle pilote dans laquelle on a récupéré 45 L d'hydrolysat de collagène, avec 87,16% de protéine de collagène récupérée et 1,17% de chrome résiduel.

MOTS CLÉS: valorisation des déchets, copeaux de chrome, hydrolyse alcaline, procédé de tannage

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INTRODUCTION

In recent years, there has been a significant increase in the generation of solid waste globally. For diverse industries, this has provoked a special interest, since most of the times and depending on their characteristics, these residues are not being treated adequately, originating problems that affect the health of the human being and the environment. Facing this situation, an innovative alternative proposed for waste management is the valorization, which allows them to be recovered and reused depending on their composition and characteristics [1].

The tanning industry converts skins and hides into a flexible, non-putrescible and durable leather, necessary for the production of various goods, such as shoes, wallets, clothing, among others. The tanning process generates different waste in large volumes, which is why companies in this sector require alternatives to manage them properly. The wastes that cause more concerns are tanned wastes, especially those that contain chromium in their composition [2]. The largest amount of chrome-tanned wastes is produced in the shaving stage, where the leathers are shaved to give them a uniform thickness, and the waste generated is known as leather shavings or chrome shavings. This residue represents about 10% by weight of the hides that enter the tanning process, for each ton of leather processed, producing about 100 kg of shavings [1, 3, 4].

Chrome shavings contain chromium (Cr) in the +3 oxidation state (Cr_2O_3), and the content can vary between 2.5 and 6% [5, 6], besides that, they have a high calorific value and must be disposed of as a hazardous waste [7]. Traditionally, chrome shavings are disposed of in landfills and mostly, deposited in dumps or around tanneries [1]. Hence, these residues are exposed to conditions that allow Cr as +3 and +6 oxidation states, producing very toxic chemical species with carcinogenic properties [8, 9]. Therefore, its inadequate final disposition shows a risk factor for the health of human beings and environment [10].

Despite the characteristics mentioned above, these residues have a great potential to be valorized, because of their high amount of collagen, which is a natural protein present in the skin and represents most of its composition and provides the leather the characteristics of resistance and durability [1, 5, 11]. In reports before 1970, different researchers have developed alternatives to apply leather shavings, such as insulators, building material, fibrous sheets and shoe soles [12]. Since 1970, a lot of researchers have approached the collagen recovery from chrome shavings through hydrolysis methods. Literature shows projects that aimed to analyze the characteristics of chrome shavings hydrolysis and the applications of the products, Jiang *et al*. [13] applied alkaline hydrolysis with CaO, to extract protein and chrome, the recovered protein was mixed with substrates and used as feed collagen powder, also the behavior of alkaline hydrolysis conditions (pH, temperature and reaction time) were studied. Tahiri *et al*. [11] treated chrome shavings with sodium hydroxide where optimized hydrolysis conditions at NaOH 0,5 M, 15 minutes of reaction time at boiling point, to recover proteins and chrome cake, transform it into basic chromium sulfates and tested it in tanning operations. Beltrán-Prieto and Kolomaznik [14] applied an experimental design to optimize the conditions of chromium oxide recovery in the chromium cake through alkaline hydrolysis with sodium hydroxide, the optimum values identified were 1,58% NaOH concentration, 63,7°C, 3 hours reaction time and solid/liquid ratio 1/70 g/mL. Scopel *et al*. [15] recovered collagen through alkaline hydrolysis; reaction time, temperature, stirring rate and alkali (CaO and MgO) were controlled, to obtain a hydrolysate with high protein content (2,2 g/L NTK) and low chromium content (<0,04 mg/L). Pahlawan *et al*. [16] treated chrome shavings to recover hydrolysate useful for protein binder production, the hydrolysis condition evaluated were sodium hydroxide concentration (1, 2 and 3%), reaction time (1, 2 and 3 hours) reacting at 90°C, after reaction the hydrolysates were characterized on protein content (6,64%), chromium content (47,55 ppm), viscosity (16,9 cp) and types of amino acids. The present study aimed to develop the optimization of alkaline hydrolysis with NaOH, through the simultaneous optimization of both response variables percentage of recovered collagen protein (PRCP) and percentage of residual chromium (PRC) and analyze them. Moreover, the optimized condition was carried out at pilot scale, in a reactor to evaluate the possibility of scaled production.

EXPERIMENTAL

Materials and Methods

Raw Material

Chrome shavings were obtained from a tannery in the district of "San Juan de Lurigancho", Lima. The waste was stored under controlled conditions of moisture (65% RH) and temperature (20°C) for conservation. The shavings were characterized, in a laboratory accredited by ISO 17025, for the parameters of Total Kjeldahl Nitrogen (TKN) by NTP 201.021: 2002 (Revisada 2015) CARNE Y PRODUCTOS CÁRNICOS. Determinación del contenido de proteínas, moisture by NTP ISO 1442: 2006 (Rev 2015) CARNE Y PRODUCTOS CÁRNICOS. Determinación del contenido de humedad, total protein by NTP 201.021: 2002 (Revisada 2015) CARNE Y PRODUCTOS CÁRNICOS. Determinación del contenido de proteínas, ash by AOAC 920.153, On line 20th Ed. 2016 Ash of Meat, fat by NTP 201.016: 2002 CARNE Y PRODUCTOS CÁRNICOS. Determinación del contenido de grasa total, and pH by NTP ISO 4045: 2008 [1, 11].

Hydrolysis Processes

The hydrolysis treatments of chrome shavings were carried out on a laboratory scale. To ensure the homogeneity of the shavings, they were pretreated through grinding by defibrillator method. The hydrolysis system was prepared, comprising a flat-bottomed ball flask, soxhlet equipment, and a magnetic stirring plate. A quantity of pretreated shavings and sodium hydroxide (NaOH) solution was added into the flask, the sample was mixed and according to the concentration of NaOH the pH varied between 10-12.5, then it was heated on a stove to the desired temperature of 70°C, optimum temperature in previous research [15, 17-19], after which the flask was installed in the hydrolysis system, and the reaction time began to be controlled.

After the reaction, the solution was centrifuged to separate the resulting products, collagen hydrolysate and chromium cake, which were stored in glass bottles and Ziplock bags for further analysis. Figure 1 presents the diagram of alkaline hydrolysis processes at laboratory scale.

Preliminary Study

To adjust the variables of the alkaline hydrolysis process, a preliminary study was carried out, in which the levels of NaOH concentration and reaction time were tested. The results were obtained through the measurement of soluble solids expressed in Brix degrees (°Bx) using a refractometer [20], acting as an indirect indicator of the presence of dissolved collagen in the hydrolysate as the collagen is the main dissolved component in the hydrolysate, so it allowed the comparison of recovered collagen between treatments faster than other methods. This method was applied as a recommendation from researchers of Technological Institute of Production laboratory.

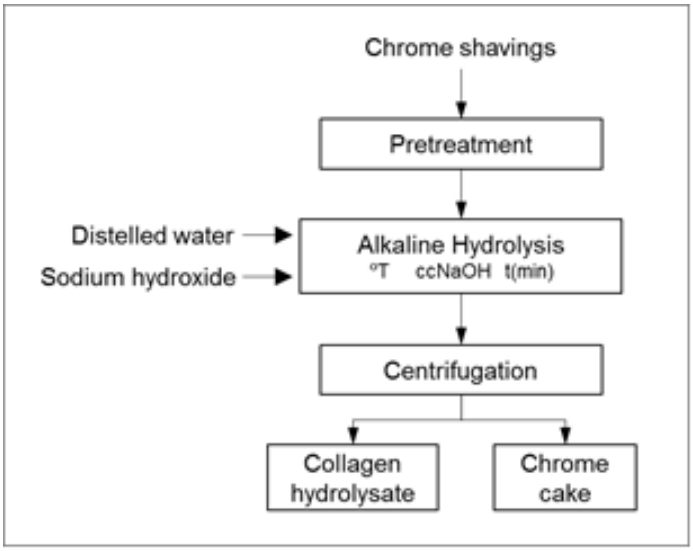

Figure 1. Alkaline hydrolysis process

Experimental Design

To optimize the alkaline hydrolysis process, a 3^2 factorial design was developed in which the factors, concentration of NaOH and reaction time were tested with respect to the response variables: the percentage of recovered collagen protein (PRCP) and percentage of residual chromium (PRC) present in the collagen hydrolysate. The 3^2 factorial design comprised 9 treatments, that were carried out in duplicate. The graphics and analysis were carried out on Statgraphics Centurion XVI.

The PRCP was characterized by determining the total nitrogen content by Kjeldahl method and the PRC by EPA method 200.8, Rev 5.4: 1994. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectroscopy). These results were compared with those obtained in the characterization of the chrome shavings.

Likewise, the levels for the 3^2 factorial design were established using the results of the preliminary study. The model of 3^2 factorial design is presented below.

$$Y_{ijk} = \mu + \gamma_i + \delta_j + (\gamma\delta)_{ij} + \varepsilon_{ijk} \quad (1)$$

with $i = 1, 2, 3$; $j = 1, 2, 3$; $k = 1, 2$

Where:

Y_{ijk} = Effect of the treatment

μ = Overall mean effect

γ_i = Effect of the $_i$th level of factor A

δ_j = Effect of the $_j$ th level of factor B

$(\gamma\delta)_{ij}$ = Interaction effect between factors A and B in levels $_{ij}$

k = Number of replicates

ε_{ijk} = Random error

The hypothesis tests for 3^2 factorial design are used to check whether the effect of the factors investigated is significant or not, as follows:

$H_0 : \gamma_1 = \gamma_2 = \gamma_3 = 0$ *(Main effect of A is absent)*

$H_0 : \gamma_i \neq 0$ *for at least one i*

$H_0 : \delta_1 = \delta_2 = \delta_3 = 0$ *(Main effect of B is absent)*

$H_0 : \delta_i \neq 0$ *for at least one j*

$H_0 : (\gamma\delta)_{11} = (\gamma\delta)_{12} = \ldots = (\gamma\delta)_{33} = 0$ *(Interaction AB is absent)*

$H_0 : (\gamma\delta)_{ij} \neq 0$ *for at least one ij*

These hypothesis are tested in the analysis of variance (ANOVA) through F test. For factorial design, the F test is used to obtain p-value, which is used to test the hypothesis for each factor, at 95% confidence, whether *p-value* is lower than 0.05, the effect of the factor is significant (while lowest the p-value is, the factor presents a more significant effect), or *p-value* higher than 0.05, the effect of the factor is absent.

Scaling to Pilot Level

Once the variables of alkaline hydrolysis at laboratory scale were optimized, the process was carried out on a pilot scale, in a reactor of 60 L. The hydrolysate obtained was characterized by determining the total nitrogen content (Kjeldahl method) and total chromium content by EPA 200.8, Rev 5.4: 1994. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectroscopy).

RESULTS AND DISCUSSIONS

Characterization of Chrome Shavings

The characterization of the shavings allowed to establish the maximum content of recoverable protein and chromium through hydrolysis, the remaining parameters allow identifying the impurities present, which will be part of the chromium cake at the end of the hydrolysis process. Thus, the shavings contain 11.44% of total nitrogen, 21.13% of moisture, 63.52% of collagen protein, 16323.79 mg/kg of total chromium, 3.02% of chromium oxide, 8.34% of ashes, and 0.14% of fats with pH of 3.75. The results match the published reports [1, 11].

Preliminary Study

The working conditions for the treatments evaluated in the preliminary study are presented in Table 1.

Table 1: Alkaline hydrolysis treatments

Chrome shavings (g)		10
Water Quantity (mL)		100
Sample code	Time (min)	cc NaOH (M)
VC-HC-A	30	0.1
	45	0.1
	60	0.1
	90	0.1
	120	0.1
VC-HC-B	30	0.3
	45	0.3
	60	0.3
	90	0.3
	120	0.3
VC-HC-C	30	0.5
	45	0.5
	60	0.5
	90	0.5
	120	0.5

The results in °Bx for each treatment in the preliminary study are shown in Table 2.

Table 2: Results of the preliminary study

Processing code	cc NaOH (M)	°Bx NaOH	ºBx Time (minutes)				
			30’	45’	60’	90’	120’
VC-HC-A	0.1	1.0	0.6	0.6	0.4	0.4	0.4
VC-HC-B	0.3	2.2	7.8	7.8	7.4	7.2	7.0
VC-HC-C	0.5	4.0	6.8	6.6	6.6	6.6	6.6

In the VC-HC-A treatments, carried out with NaOH 0.1 M, low values of soluble solids between 0.4 and 0.6°Bx were obtained after centrifugation of the samples. All treatments presented a colorless supernatant and a chromium cake with a consistency similar to the hydrated shavings (Figure 2), establishing that the reaction time did not influence the concentration of collagen and residual chromium in the solution.

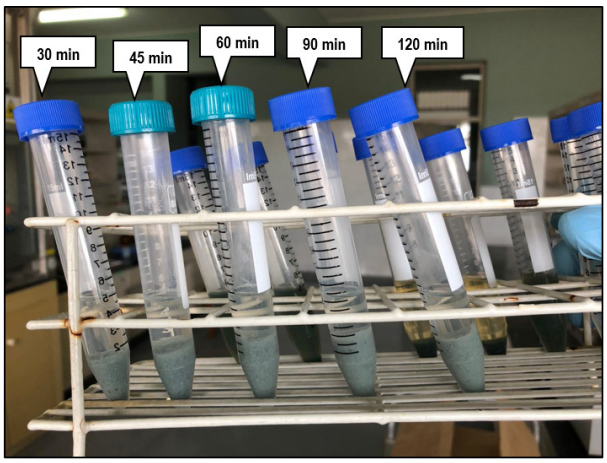

Figure 2. VC-HC-A Treatment

In the VC-HC-B treatments, with NaOH 0.3 M, higher values of Brix degrees were reached, in a range of 7.8 to 7.0°Bx. These levels are due to the effect of hydrolysis of the chrome shavings, resulting in the presence of dissolved chromium in the hydrolysate. However, the values (°Bx) decreased as the reaction time increased. At the longer reaction time, under the established temperature conditions, the chromium concentration decreased while precipitating

into the cake, which was presented as a residue sludge. These conclusions can also be seen in the coloration of the solutions (Figure 3).

Figure 3 shows that after 30 minutes of reaction, the hydrolyzed solution turned into green color, similar to a dissolution of a Cr(III) salt, which indicates the presence of this metal. As the reaction moves, the solution becomes yellowish, a sign of the decrease in chromium concentration in the solution.

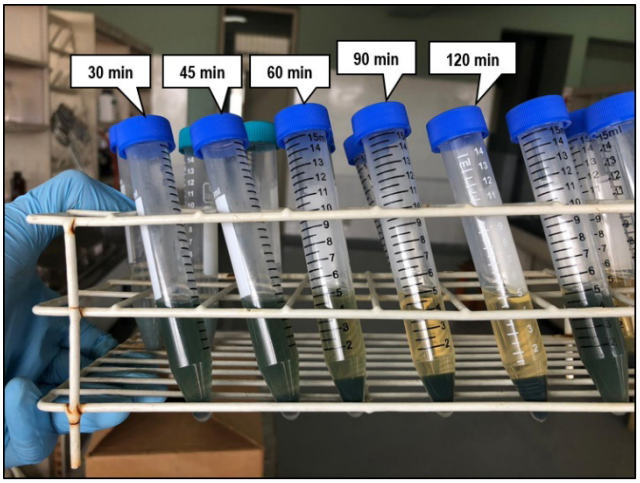

Figure 3. VC-HC-B Treatment

Finally, in the VC-HC-C treatments performed with NaOH 0.5 M, the Brix value at a time of 30 minutes was 6.8° Brix, and 6.6° for the remaining times. It was also observed that for the individual centrifuged treatments, the color of the solution was kept in a yellowish tone, and the cake presented a muddy consistency.

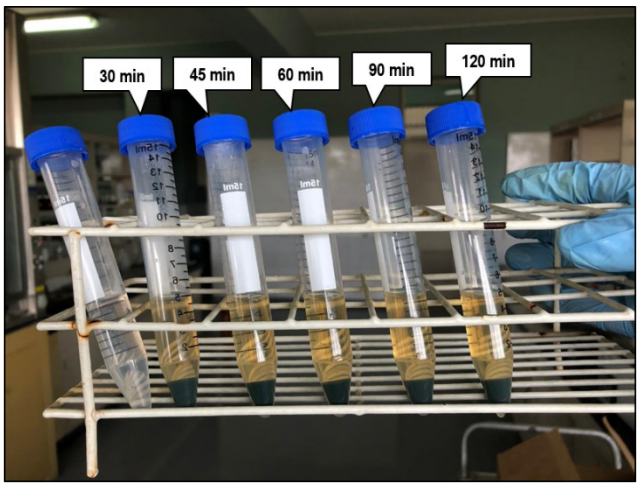

Figure 4. VC-HC-C Treatment

Evaluation of the Experimental Design

Using the results of preliminary study, the levels of variables were established for a 3^2 factorial design, where each treatment was carried out in duplicate. The levels and treatments of 3^2 factorial design are presented in figure 5.

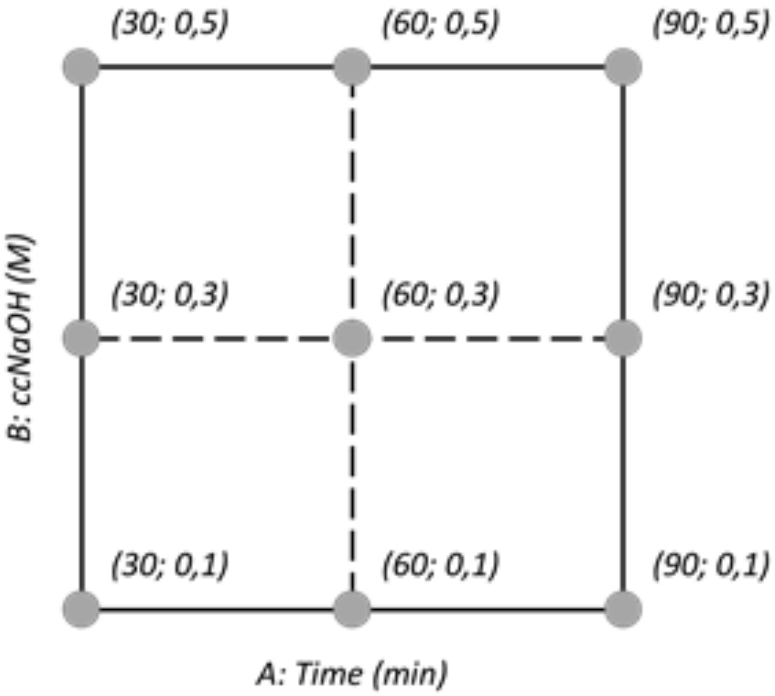

Figure 5. 3^2 factorial design

Table 3 shows the results of PRCP and PRC in the collagen hydrolysate obtained for each treatment.

Table 3: Results of Factorial design treatments

Chrome shavings (g)			10	
Quantity of water			1000%	100mL
Rx temperature (°C)			70°C	
	A	B	R1	R2
Sample code	Time (min)	CC NaOH (M)	PRCP (%)	PRC (%)
VC-HC-01	30	0,1	1,065	0,924
VC-HC-02	60	0,1	0,794	0,129
VC-HC-03	90	0,1	7,577	8,413
VC-HC-04	30	0,3	86,504	84,798
VC-HC-05	60	0,3	78,156	6,936
VC-HC-06	90	0,3	82,733	1,661
VC-HC-07	30	0,5	83,296	4,932
VC-HC-08	60	0,5	85,618	2,200
VC-HC-09	90	0,5	80,088	1,811
VC-HC-10	30	0,1	1,029	2,551
VC-HC-11	60	0,1	0,729	0,370
VC-HC-12	90	0,1	6,287	0,076
VC-HC-13	30	0,3	87,385	88,682
VC-HC-14	60	0,3	75,338	23,757
VC-HC-15	90	0,3	78,502	1,578
VC-HC-16	30	0,5	84,107	2,695
VC-HC-17	60	0,5	80,754	2,186
VC-HC-18	90	0,5	82,776	1,760

*Treatments from VC-HC-01 to VC-HC-09 correspond to the first run, and VC-HC-10 to VC-HC-18 to the second run.

The results obtained were used to analyze variance for each response variable, whose ANOVA results are presented in Tables 4 and 5.

Table 4: ANOVA of the PRCP

Source	Sum of Squares	Degree of freedom	Mean squares	F-Ratio	P-value
A: Time	2.452	1	2.452	0.738	0.4127
B: ccNaOH	19132.738	1	19132.738	5755.932	0.0000
A^2	41.329	1	41.329	12.433	0.0065
B^2	5957.681	1	5957.681	1792.321	0.0000
AB	33.251	1	33.251	10.003	0.0115
A^2B	9.865	1	9.865	2.968	0.1190
AB^2	44.123	1	44.123	13.274	0.0054
A^2B^2	29.181	1	29.181	8.779	0.0159
Error	29.916	9	3.324		
Total	25280.536	17			

In the ANOVA results of the PRCP, the linear and quadratic effects of sodium hydroxide concentration were identified as significant in protein recovery.

Table 5: ANOVA of the PRC

Source	Sum of Squares	Degree of freedom	Mean square	F-Ratio	P-value
A: Time	2388.066	1	2388.066	114.556	0.0000
B: ccNaOH	0.812	1	0.812	0.039	0.8479
A^2	460.291	1	460.291	22.080	0.0011
B^2	4155.442	1	4155.442	199.338	0.0000
AB	10.283	1	10.283	0.493	0.5002
A^2B	3.040	1	3.040	0.146	0.7114
AB^2	4857.499	1	4857.499	233.016	0.0000
A^2B^2	655.645	1	655.645	31.452	0.0003
Error	187.616	9	20.846		
Total	12718.694	17			

From the ANOVA of the PRC, the linear effect of reaction time, the quadratic effect of sodium hydroxide concentration and the interaction effect of both variables were determined as significant in the content of chrome in the hydrolysate.

The behavior of the process variables was also analyzed through the main effects plots shown in Figures 6 and 7.

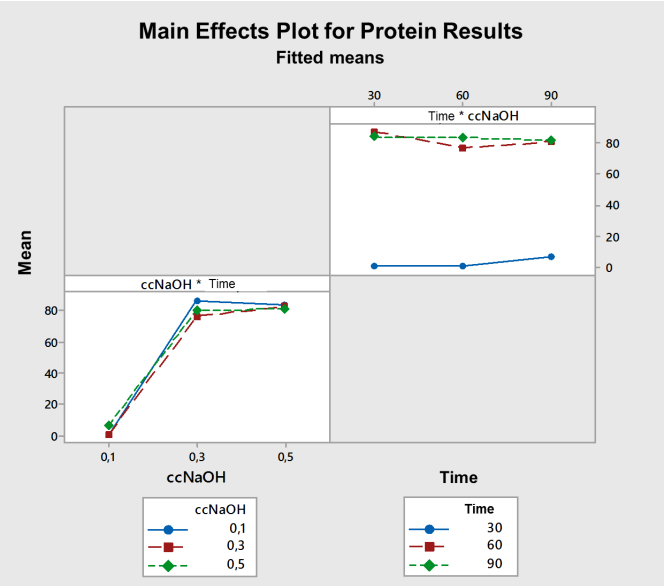

Figure 6. Main Effects Chart for PRCP

Figure 6 presents the behavior of the variable PRCP, where a marked curvature is observed by increasing the concentration of NaOH and producing an increment of the recovered protein. This variation is explained by the rise of the hydrolytic action over collagen fibers as their basicity increases [21]. According to the plot, the reaction time has no effect in PRCP.

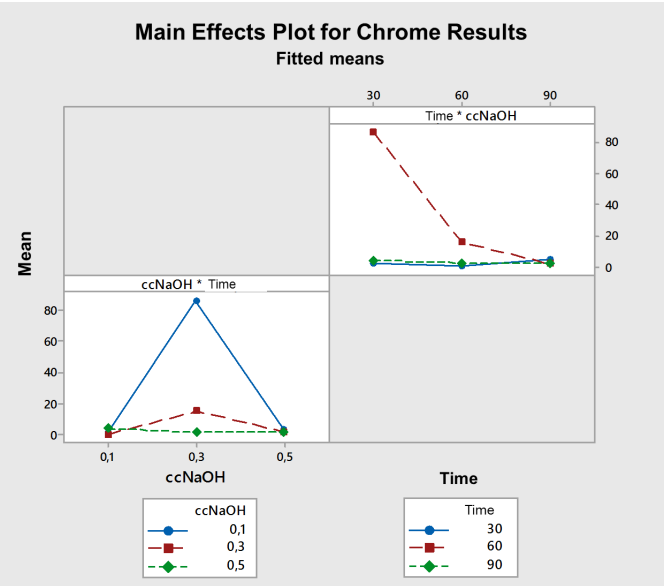

Figure 7. Main Effects Chart for PRC

Figure 7 shows the behavior of the variable PRC in the hydrolysate, observing a curvature in reaction time with the increase in NaOH concentration. At 0,1 M concentration of NaOH, there is a low percentage of residual chromium, due to the low hydrolytic action. At 0,3 M of NaOH, the percentage of residual chromium is above 85% at reaction time 30 minutes, but decreases as reaction time goes by, and at 90 minutes, a low percentage of residual chromium is observed, this behaviour is because a greater hydrolysis of the collagen fibers is achieved, in this case, in contrast with the observed with the variable PRCP, the reaction time plays an important role, weakening the bond between collagen fibers and chromium complexes, and

making it possible to separate them [14, 21]. Finally, at 0,5 M of NaOH, a low percentage of residual chromium was obtained, because the hydrolytic action at this concentration is higher and faster than in other concentrations of NaOH. It is possible to separate chromium from collagen fibers, resulting in a hydrolysate with a low percentage of residual chromium. Another remarkable point is the chromium cake, it is not only composed of impurities and chromium, it also has a small part of collagen protein, so that means chromium precipitates still attached to some amino acids.

The fit model for the experimental design was calculated from the experimental data. For the PRCP, the determination coefficient R^2 = 99.88% and the adjusted determination coefficient R^2_{aj} = 99.77% were obtained, showing a clear variability of the 3^2 factorial design model [22]. Thus, the equation of the adjusted model obtained as:

$$R_1 = -59{,}7905 - 0{,}3417 * A + 798{,}93 * B + 0{,}00357 * A^2 - 0{,}339771 * A * B - 964{,}825 * B^2 \quad (2)$$

Where:

A = Reaction time

B = NaOH Concentration

R_1 = Percentage of recovered collagen protein

For the PRC, the value of the determination coefficient R^2 = 98.52% and the adjusted determination coefficient R^2_{aj} = 97.21%. Hence, 3^2 factorial design model explains well the variability present in the PRC results. The equation of the adjusted model is presented below:

$$R_2 = 22{,}214 - 1{,}84347 * A + 496{,}142 * B + 0{,}011917 * A^2 - 0{,}189167 * A * B - 805{,}811 * B^2 \quad (3)$$

Where:

A = Reaction time

B = NaOH Concentration

R_2 = Percentage of residual chromium

By using the above equations, the estimated response surfaces for each response variables (collagen and chromium) were obtained, as presented in Figures 8 and 9, respectively.

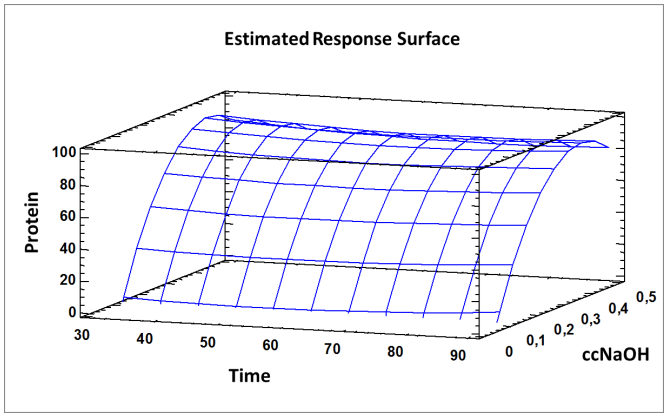

Figure 8. Response surface for PRCP

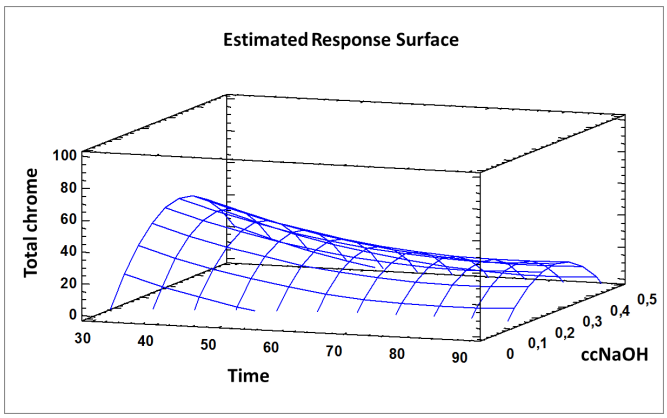

Figure 9. Response surface for PRC

Analyzing the models for PRCP and PRC, and in order to obtain a hydrolysate with the highest amount of recovered collagen protein and the lowest possible content of chromium, both response variables were optimized simultaneously. For that purpose, a desirability function was established, which tested different points of the design and simultaneously optimized both response variables. Figure 10 presents the estimated response surface for the Desirability function.

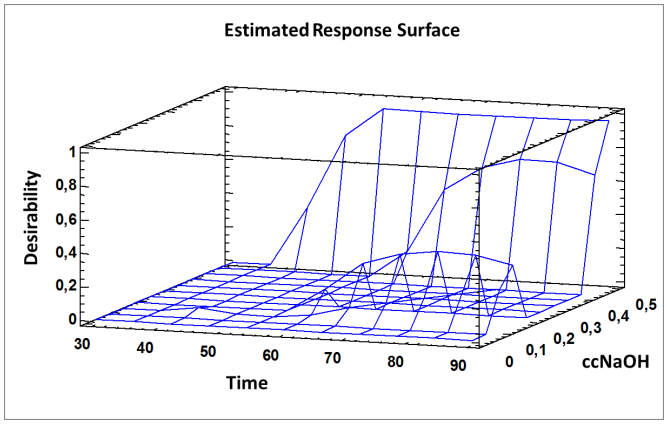

Figure 10. Response surface for the Desirability function

The optimal values for the desirability function were identified as 0.47 M concentration of sodium hydroxide and 90 minutes of reaction time. Under the above conditions, and using the desirability function, it is possible to maximize the percentage of recovered collagen protein as 86.3927% and minimize the percentage of residual chromium as 0.0329%.

The results obtained in the present study are found to be similar to that by Tahiri *et al*. [11]. In those cases, the alkaline hydrolysis was optimized to a concentration of 0.5 M of NaOH. Notably, at a higher concentration of NaOH, the hydrolysate would present an excessive amount of salt [11], hence the lower concentration of NaOH is required to optimize the process. Pahlawan *et al*. [16] reported the concentration of 3% NaOH (equivalent to 0.75 M) with 3 hours of reaction time as the best conditions for the alkaline hydrolysis, resulting in 6.64% protein in the hydrolysate of collagen, and chromium content of 47.55 ppm. Hussien [21] showed that even chromium has amphoteric nature (precipitates in alkaline solution), it can be dissolved in strong alkali concentration, thus maximizing the percentage of chromium recovery in the cake and minimizing it in the collagen solution.

It is necessary to point out that other studies [11, 13, 15] considered to evaluate different reaction temperatures, in the present research it was chosen to work at 70°C because this temperature was optimal in alkaline hydrolysis research [15, 17-19], and in order to evaluate and compare the relation between reaction time and sodium hydroxide concentration, the temperature was set at that level. Besides, the solubility of chromium increases in the high-temperature range, i.e., 80-100°C, resulting in an increase in the difficulty of separating the chromium ions from the hydrolysate. In contrast, at a lower temperature range, i.e., 40-60°, the alkaline hydrolysis reaction could be slower, with reaction times that could vary from 2 to 6 hours [11, 13, 15, 17-19].

Scaling up Results

To scale up the results, the process conditions were adjusted due to the minimum operating capacity of the reactor, as shown in Table 6.

Table 6: Hydrolysis conditions at pilot scale

Chromium shavings (kg)		4.0	
Quantity of Water (%, L)		1250%	50 L
Sample code	Temperature (ºC)	CC NaOH (M)	Time (min)
VC-HP-01	70	0.45	120

In the hydrolysis process on pilot scale, 45 liters of collagen hydrolysate were obtained with PRCP recovered of 87.16% and PRC of 1.17%.

At the pilot scale, the amount of water was higher, so the concentration of NaOH had to be lower than the optimized value for NaOH. About the results, the PRCP and PRC in the hydrolysate were higher than those obtained in the optimized model. However, the variation is within the expected range, as explained before, when chromium precipitates into the chromium cake, it is still attached to a small part of collagen, that would explain why the higher PRC also leads to a slight increase in the PRCP, because a small part of chromium has not precipitated. Therefore, the results satisfy the established model, as these are similar to the optimum values. The chromium content of the hydrolysate is higher than that of the model, but it remains low and is not relevant here, as the hydrolysate is meant to be used as retanning agent in the tanning process. The chromium cake, which has the main component of chromium hydroxide can be converted to form basic chromium sulfate, and the remaining waste, composed by secondary nutrients, can be used as fertilizer.

The application of the alkaline hydrolysis makes the process easier to control compared to others, where it is necessary to control pH and demands higher reactions time. These results show the feasibility to scale up the chrome shavings hydrolysis process, for a higher production of hydrolysate with a high protein amount and low chromium content.

CONCLUSIONS

In the present research, it was possible to identify the relationship between reaction conditions and response variables, where the increase in NaOH concentration allows the hydrolysis reaction to occur, and then the increase in the reaction time allows the separation of chromium adhered to the collagen chain. In addition, to establish the optimal conditions and to carry out the alkaline hydrolysis of chrome shavings, the temperature must be 70°C, the reaction time of 90 minutes and NaOH concentration of 0.47 M. Under these conditions, it is not only possible to recover a high percentage of collagen protein but also to get a hydrolysate with a low percentage of residual chromium. On a pilot scale, it was possible to valorize chrome shavings by recovering hydrolysate with a percentage of recovered collagen protein of 87.16% and a percentage of residual chromium of 1.17% and also obtained 750.80 g of dry chromium cake, reducing the amount of chromium that can be a potential pollutant substance. In addition, the process mainly creates chromium hydroxide, which is the principal component of the chromium cake and can be treated to obtain basic chromium sulfate, which can be reintroduced to the tanning process. Finally, it is recommended evaluate the application of collagen hydrolysate produced in the retanning stage of the tanning process, comparing its effectiveness with a reference commercial re-tanning agent and recover basic chromium salts from the chromium hydroxide recovered from the chromium cake, to evaluate its application in the tanning stage of the tanning process.

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RESEARCH ON THE USE OF TANNED LEATHER FIBRES AS AGGREGATE IN OBTAINING ASPHALT MIXTURES

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RESEARCH ON THE USE OF TANNED LEATHER FIBRES AS AGGREGATE IN OBTAINING ASPHALT MIXTURES

ABSTRACT. The current tendency of road builders and managers is to make asphalt mixtures with improved performance in terms of aging and fatigue resistance, better traffic behavior both in summer and in winter, as well as increased values for dynamic properties: elasticity, tracking, etc. In this sense, there is a permanent concern to find new materials and technologies for the preparation and implementation of asphalt mixtures that convey the desired properties to the layers. In this sense, the addition of microfibres and fibres, with dimensions ranging from 0.01-10 mm when preparing asphalt mixtures, transforms the bituminous binder used into a "composite material", in which the matrix is the bitumen, and fibres are the dispersed phase, leading to the stabilization of the bitumen inside the mix, as well as to the reinforcement of the asphalt mixtures, giving them special properties. The paper presents laboratory experiments for obtaining smart biocomposites (leather fibres-asphalt mixtures) with applications in the field of road infrastructure. The resulting biocomposites were characterized by chemical, physical-mechanical and structural analyses.

KEY WORDS: asphalt mixture, tanned leather fibres, biocomposites, leather waste

CERCETĂRI PRIVIND UTILIZAREA FIBRELOR DE PIELE TĂBĂCITĂ CA AGREGAT ÎN OBŢINEREA MIXTURILOR ASFALTICE

REZUMAT. Tendinţa actuală a constructorilor şi administratorilor de drumuri este de a realiza mixturi asfaltice rutiere cu performanţe îmbunătăţite în ceea ce priveşte rezistenţa la îmbătrânire şi oboseală, comportare mai bună în trafic atât vara, cât şi iarna, precum şi valori crescute pentru proprietăţi dinamice: modul de elasticitate, ornieraj, etc. În acest sens, există o preocupare permanentă de a găsi noi materiale şi tehnologii de preparare şi punere în operă a mixturilor asfaltice, care să confere straturilor realizate proprietăţile dorite. În acest sens, adaosul de microfibre şi fibre, cu dimensiuni cuprinse între 0,01-10 mm la prepararea mixturilor asfaltice, transformă liantul bituminos utilizat într-un „material compozit", în care matricea o reprezintă bitumul, iar faza dispersă fibrele, conducând atât la stabilizarea bitumului în interiorul mixturii, precum şi la armarea mixturilor asfaltice, conferindu-le acestora proprietăţi speciale. În lucrare se prezintă experimentări de laborator de obţinere a biocompozitelor inteligente (fibre de piele-mixturi asfaltice) cu aplicaţii în domeniul infrastructurii rutiere (şosele). S-a realizat caracterizarea prin analize chimice, fizico-mecanice şi structurale a biocompozitelor obţinute.

CUVINTE CHEIE: mixtură asfaltică, fibre de piele tăbăcită, biocompozite, deşeuri de piei

RECHERCHE SUR L'UTILISATION DES FIBRES DE CUIR COMME AGRÉGÉES POUR OBTENIR DES MÉLANGES ASPHALTIQUES

RÉSUMÉ. La tendance actuelle des constructeurs et gestionnaires de routes est de réaliser des mélanges d'asphalte routier avec des performances améliorées en termes de résistance au vieillissement et à la fatigue, un meilleur comportement dans la circulation en été comme en hiver, ainsi que des valeurs accrues pour les propriétés dynamiques : module d'élasticité, orniérage, etc. En ce sens, il y a un intérêt permanent de trouver de nouveaux matériaux et technologies pour la préparation et la mise en œuvre des mélanges d'asphalte, qui confèrent aux couches réalisées les propriétés souhaitées. À cet égard, l'ajout de microfibres et de fibres, avec des dimensions allant de 0,01 à 10 mm lors de la préparation des mélanges d'asphalte, transforme le liant bitumineux utilisé en un "matériau composite", dans lequel la matrice représente le bitume, et les fibres la phase dispersée, conduisant à la fois à la stabilisation du bitume à l'intérieur du mélange, ainsi qu'au renforcement des mélanges d'asphalte, leur conférant des propriétés particulières. L'article présente des expériences de laboratoire pour l'obtention de biocomposites intelligents (fibres de cuir-mélanges d'asphalte) avec des applications dans le domaine des infrastructures routières. Les biocomposites obtenus ont été caractérisés par des analyses chimiques, physico-mécaniques et structurelles.

MOTS CLÉS : mélange d'asphalte, fibres de cuir, biocomposites, déchets de cuir

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INTRODUCTION

In the field of road infrastructure, the current tendency is to make road structures from composite asphalt mixtures, in which, besides the classical materials, fillers or reinforcement materials are added, generally in the form of powders, granules, fibres, yarns. These new materials can be of the most diverse classes of chemical compounds, both inorganic (glass, asbestos, ceramic) and organic (natural and synthetic polymers).

The presence of fibres in an asphalt mix creates a true "interpenetrating network" that allows the distribution of stresses within the matrix and fibres. Therefore, these composite asphalt mixtures are an appropriate solution for preventing the transmission of cracks, increasing the resistance to aging and fatigue and reducing the rapid degradation of road layers [1].

Cracks often occur in the wear layer, having a set of causes, including the low tensile strengths of the constituent mixtures, a phenomenon that can be prevented by different methods and technologies. One of these methods is to use the principle of dispersed reinforcement of asphalt concrete, using different fibres as reinforcement [2, 3].

Selection of the asphalt mixture type from which the bituminous coating is to be made is of great technical and economic importance. Asphalt concretes are mixtures made of chippings, sand, filler, agglomerated with bituminous binder, using an appropriate hot mixing technology. Asphalt concrete can be designed and manufactured in a great diversity, depending on requirements, and with high physical-mechanical characteristics, which will ensure a long operating life for the wear layer [4]. Thus, the most used are asphalt concrete rich in chippings, BA 16-type and called BAA16 (fibre reinforced asphalt concrete). These types of bituminous coatings can be reinforced with fibres and yarns of different classes of chemical compounds.

Another type of mixture used more and more often in the roads abroad, but also in our country, is the asphalt mix with cellulose fibre, MASF 16-type, a mix based on a special SMA - Stone Mastic Asphalt formulation.

SMA is a formulation characterized by the roughness of the crushed aggregates, of high granulation, found in an amount of 70-80%, due to the higher content of bitumen (6.7-7.0%) and stabilizing additive with cellulose fibres [5, 6]. The aggregates are constituted in a framework of resistance in the hollows of which there is a viscous filling of bituminous mastic, additivated with cellulose fibres. Reinforcement using fibres does not allow the bitumen to deteriorate at extreme temperatures, either hot or cold, without compromising on its efficiency [7].

The advantages of using this type of asphalt concrete:

- high stability at permanent deformations;
- the aggregates give the structure of resistance;
- transmission of road loading forces is done from aggregate to aggregate, to the lower layers and then to the ground;
- good resistance to wear, fatigue, aging;
- drainage of water;
- rough surfaces (increases slip resistance and noise absorption by 2-4 dB.

These types of asphalt concrete can be used both on the wear layers, as well as on the connecting layers and the bridge road.

The fibres most used in the establishment/ reinforcement of asphalt mixtures are natural fibres: cellulose, polypeptides, glass fibres, and synthetic polyacrylonitrile (PNA), polypropylene yarns [8]. Generally, the dimensions of these fibres are of the order of microns and their absorption in bitumen (due to the dimensions comparable to the bitumen particles) stabilizes/ stiffens it, transforming it into mastic, and in the case of yarns with millimetric dimensions, they reinforce the mix by creating a discontinuous three-dimensional network. The optimum amount of fibre to be added to the asphalt mixture is between 0.25-0.5% (0.3%).

Asphalt Mixtures Improved by the Use of Modified or Additivated Bitumen

Studying and obtaining of asphalt mixtures with superior mechanical performances are necessary to make road layers with special characteristics and well-defined uses, of which we mention:

- obtaining asphalt mixtures that can be put into operation in thin layers, presenting a great roughness; these will be used especially for the maintenance of existing coatings;

- making asphalt mixtures capable of supporting larger deformations under repeated efforts, which would be used for:

- coating with thin bituminous layers (3 ... 5 cm) of worn coating that shows contraction cracks, crazing due to fatigue of the material, etc.;
- reinforcing existing road structures, especially in cities where it is not possible to apply thick layers to existing coating;
- resistant coating for bridge roads;
- maintenance of the existing coating, by applying asphalt layers of small thickness;

- the application of asphalt layers from special asphalt mixes on cracked cement coating;

- bituminous coatings made from composite asphalt mixtures with additions of natural and synthetic fibres.

The category of special bituminous coatings with superior characteristics includes coatings made of asphalt mixtures with bitumen with rubber and bitumen with polymers as binder. Bituminous coatings made from asphalt mixtures based on bitumen with additives (BA16a) aim to increase the adhesion of bitumen to the natural aggregates and the possibility of using them for ballast aggregates or less processed by crushing.

In conclusion, it is mentioned that the asphalt mixtures with bitumen modified with polymers (Bm) or with additivated bitumen (Ba), due to the high level of their performance, allow the production of efficient bituminous coating under severe stress conditions. The use of BA16a- and BA16m-type asphalt mixtures, which use synthetic fibres and yarns for the purpose of reinforcing and increasing performance at wear, fatigue (BAA16a and BAA16m) is recent, but they tend to expand rapidly, both for the wear layers, but also for the connection ones [7].

EXPERIMENTAL

Making Composite Asphalt Mixtures in the Laboratory

INCDTP - Division: ICPI together with the Technical University of Civil Engineering of Bucharest, the Faculty of Railways, Roads and Bridges, have conducted an experimental study in order to use leather fibre waste in the asphalt mixture for the road layer.

In this sense, at first a formulation for asphalt mixture designed from the point of view of the dosages of the component materials, in the Roads Laboratory of the university was considered.

Thus, the stabilized MAS 16-type asphalt mixture was selected, which can be used in the wear layer of the road structure. This asphalt mixture is composed of aggregates from the Morlaca quarry, filler from the Alesd factory, D50/70 bitumen from Poland, cellulose fibres produced by Iterchimica Italy, and an additive produced by Atica Chemicals was used as a binder.

Starting from this asphalt mixing recipe, cellulose fibre was replaced with enzymatically tanned treated leather fibre. The granularity of the aggregate and the filler in the MAS16 formulation are presented in Table 1, while Figure 1 presents the diagram of the granulometric curve of the MAS 16 asphalt mixture according to AND 605 norm of 2016.

Table 1: Granularity of aggregates and filler according to SR EN 933-1

Aggregate (mm)	Residue on the sieve of ...mm, [%]									
	16	12.5	11.2	8	4	2	1	0.125	0.063	<0.063
Chippings, size 8-16		33.52	22.92	43.55						
Chippings, size 4-8					100.00					
Crushing sand, size 0-4						33.80	21.00	34.80	4.20	6.20
Filler								8.80	14.90	76.30

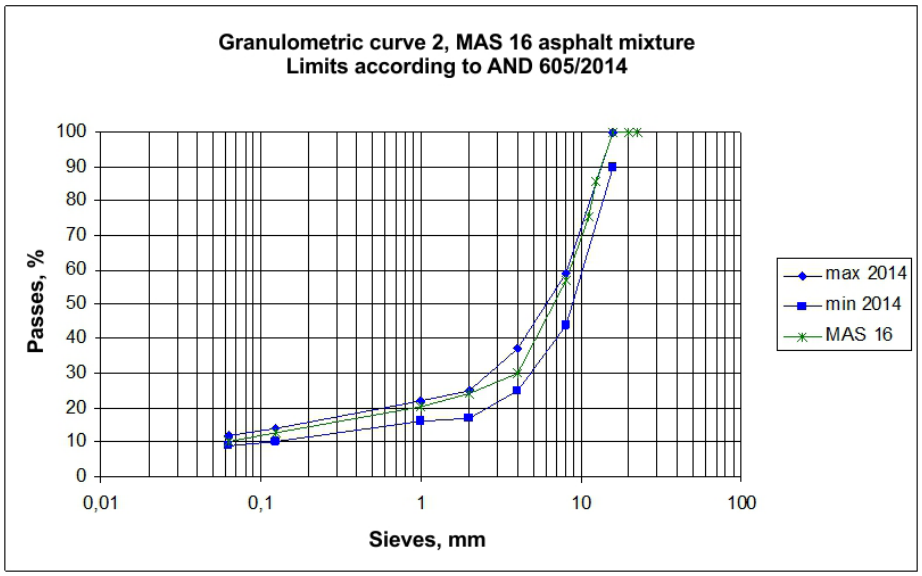

Figure 1. Diagram of the projected curve of the aggregate mixture in the granulometric area according to norm AND 605

In order to establish an optimal percentage of leather fibre and keep the bitumen percentage of the initial recipe unchanged (5.9% - minimum value according to the regulations in force), the Schellenberg binder drainage test was performed, according to the following values: 0%, 0.4 %, 0.5%, 0.6%, 0.7%, 0.8% and 2% (Table 2). The fibre percentage of 2% was chosen, complying with the standard condition, for which a value of 0.1%-0.2% was obtained (minimum value from AND 605).

Table 2: Establishing the optimal percentage of leather fibre in the mixture composition (Schellenberg test)

Formulation	Bitumen, % (M)	Fibre, % (M)	Schellenberg test, D, %	
			Resulting value	Value rounded to 0.1 %, according to SR EN 12697-18
Granulometric curve 2, C2	5.9	0	0.975	1
		0.4	0.82	0.8
		0.5	0.775	0.8
		0.6	0.74	0.7
		0.7	0.72	0.7
		0.8	0.67	0.7
		2	0.075	0.1

Next the maximum density of the mixture, the apparent volume mass (apparent density) on Marshall-type samples (cylindrical samples with h~63.5 mm and F=101 mm, compacted using the Marshall extruder), the volume of holes in the compacted mixture and the volume of holes filled with bitumen (both calculated for Marshall-type samples) were determined.

Figure 2 shows the optimal bitumen content in the leather fibre formulation using the Marshall extruder.

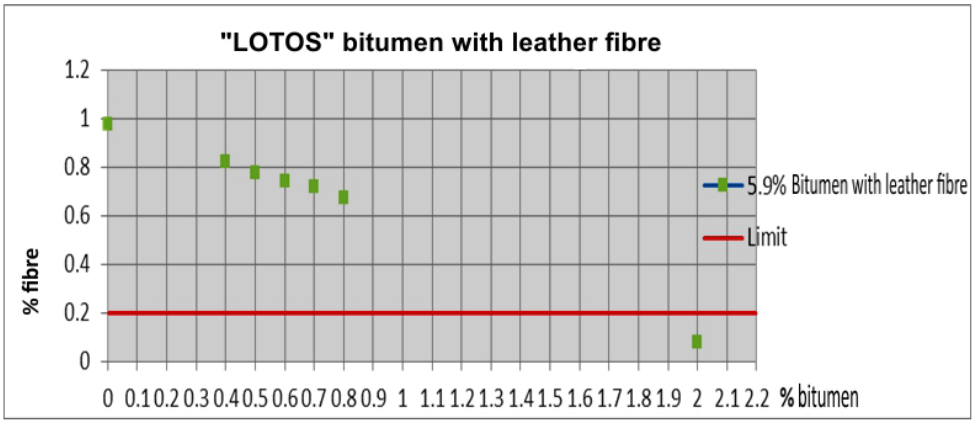

Figure 2. Determining the optimal bitumen content in the leather fibre mixture

The C2-MAS 16 formulation with 5.9% bitumen, containing 0.4% Atica ABR-1 additive (in relation to bitumen) + 2% leather fibre is presented in Table 3.

Table 3: Ingredients of the formulation for asphalt mixture with 2% leather fibre

No.	Material	Dose (%) in mixture
1.	Chippings, size 8-16	39.6
2.	Chippings, size 4-8	24.87
3.	Crushing sand, size 0-4	16.58
4.	Filler	11.05
5.	Bitumen	5.876
6.	Atica ABR-1 additive	0.024
7.	Leather fibre	2
8.	Total	100.00

Table 4 presents the physico-mechanical characteristics of the laboratory-prepared mixture for the formulation selected for experimentation, these complying with the requirements of the standards and norms in force. In addition to the above, determinations were made to establish the stiffness modulus at 20°C, IT-CY and the apparent volumetric mass, on Marshall cylindrical samples, made in the rotary press (gyro-compactor), as well as to determine behaviour to the destructive action of water: ITSR test (water sensitivity) on Marshall cylindrical samples (made using Marshall extruder) according to AND 605 norm.

Table 4: Physical-mechanical characteristics of the asphalt mixture made in laboratory

No.	Formulation	Control	Fibre, 2% (M)	Technical conditions according to AND 605
1.	Maximum density of asphalt mixture, Mg/m^3	2.353	2.452	
2.	Apparent volume mass, kg/m^3	2295	2364	-
3.	Volume of holes in compacted Marshall samples, Vm, %	2.47	3.58	3….4
4.	Volume of holes filled with bitumen, VFB, %	79	83	77… 83
5.	Water sensitivity (method A), %	84	89	min. 80
6.	Stiffness modulus, at 20°C, MPa	5978	3893	min. 4200, class I-II min. 4000, class III-IV

The ICPI asphalt mixture, made in the asphalt station of S.C. Tancrad Galati, is a MASF16 mixture (asphalt mixture stabilized with fibres) using Turcoaia aggregates and ESSO bitumen following an average granulometric curve. The ICPI asphalt mixture formulation was as follows: chippings 8-16 mm - 32.5%; chippings 4-8mm - 23.0%; crushing sand 0-4 mm - 32.0%, filler - 8.8%, bitumen - 5.7%.

Finally, the IT-CY stiffness modulus was

determined, at 20°C on cylindrical samples made using Marshall extruder for two mixtures made in ICPI: one of them without fibres, the second, with 3% leather fibres. Both asphalt mixtures are made of the same materials and have the same granularity and the same percentage of bitumen. A higher value of stiffness modulus is noticed for the mixture with leather fibres.

As shown in Table 5, the ICPI mix has improved Marshall features, from 4200 MPa to 7660 MPa, which shows that it is a flexible mix with low deformability, high workability and a very good compaction compared to a control mix.

Table 5: Physical-mechanical characteristics of ICPI asphalt mixture (average values)

No.	Determination	UM	ICPI asphalt mixture without fibre, control	ICPI asphalt mixture with fibre	Technical conditions according to AND 605
			Trials on Marshall-type cylindrical samples		
1.	Apparent volumetric mass	kg/m^3	2410	2360	-
2.	Stiffness modulus at 20 ºC, 124 ms	MPa	3893	7660	min. 4200, Technical class: road I-II and min. 4000, Technical class: road III-IV

Figure 3 shows the gyratory compactor used to determine the stiffness modulus on cylindrical samples of asphalt mixtures and test diagrams.

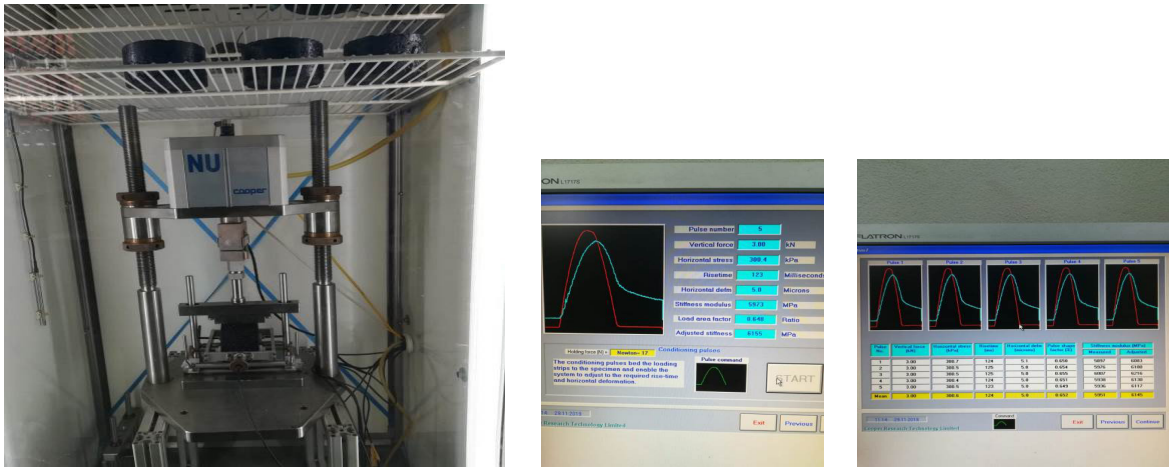

Figure 3. Determination of stiffness modulus on cylindrical samples, IT-CY

a b

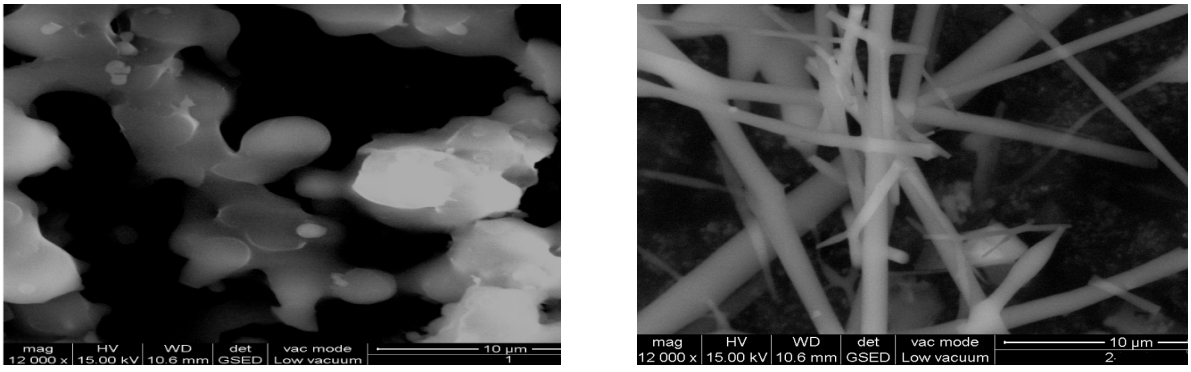

Figure 4. Electron microscopy images of asphalt mixtures - magnitude 12000 x: a) control, b) sample

ICPI asphalt mixtures with and without fibres were studied by SEM electron microscopy (with a magnification of 12,000 x) at the Institute of Atomic Physics, to evaluate the surface morphology and to highlight the leather fibre content (Fig. 4).

The resulting characteristics prove that the solution of an asphalt mixture stabilized with leather fibres is a feasible one, considering that all the results are in compliance with the requirements of the norms in force.

CONCLUSIONS

The paper presents a formulation for asphalt mixture, in which cellulose fibre was replaced with enzymatically treated leather fibre, as well as the granulometric curve of the aggregate and the filler from the MAS16-type formulation.

In order to establish an optimal percentage of leather fibre and keep the bitumen percentage of the initial formulation unchanged (5.9% - minimum value according to the regulations in force), the Schellenberg binder drainage test was performed, for eight samples of asphalt mixture with different percentages of leather fibre content, according to the following values: 0%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 2% and 3%.

Eight asphalt mixtures were obtained with different fibre percentages (0.4-3%), of which, according to SR EN 933-1, two variants were selected by Schellenberg test (with 2% and 3% leather fibre content). For these biocomposites, the IT-CY stiffness modulus was determined, at 20°C on cylindrical samples made using Marshall extruder, obtaining significantly higher results for asphalt mixtures with leather fibre.

In order to evaluate the surface morphology and to highlight the leather fibre content, ICPI asphalt mixtures with and without fibres were studied by SEM electron microscopy.

In conclusion, it can be argued that the solution of an asphalt mixture stabilized with leather fibres is a feasible one, considering that all the technical results are in compliance with the requirements of the norms in force.

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STUDY ON THE CREEP BEHAVIOUR OF NAPPA UPPER PIG LEATHER

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STUDY ON THE CREEP BEHAVIOUR OF NAPPA UPPER PIG LEATHER

ABSTRACT. From viewpoint of creep behavior, the visco-elasticity of nappa upper pig leathers is studied. A series model with three Kelvin models is proposed and has been used to imitate and describe their creep behavior successfully. The Kelvin model is a parallel connection model with a spring model and a dashpot model. The interrelated indexes of the imitation are favorable. It means that the imitation is reliable.
KEY WORDS: nappa upper pig leathers, visco-elasticity, creep behaviour, Kelvin model

STUDIU ASUPRA COMPORTAMENTULUI VISCO-ELASTIC AL PIELII DE PORC NAPPA PENTRU FEŢE ÎNCĂLŢĂMINTE

REZUMAT. Se studiază visco-elasticitatea pielii de porc nappa pentru fețe încălțăminte din punctul de vedere al comportamentului visco-elastic. Se propune o serie de trei modele Kelvin care se utilizează pentru a imita și descrie cu succes comportamentul visco-elastic. Modelul Kelvin este un model de conexiune paralelă cu un model tip arc și un model tip amortizor. Indicii inter-relaționați ai imitației sunt favorabili, ceea ce înseamnă că imitația este fiabilă.
CUVINTE CHEIE: piele de porc nappa pentru încălțăminte, visco-elasticitate, comportament visco-elastic, model Kelvin

ETUDE SUR LE COMPORTEMENT AU FLUAGE DU CUIR PORCIN NAPPA POUR TIGES CHAUSSURES

RÉSUMÉ. Du point de vue du comportement au fluage, la viscoélasticité des cuirs porcins nappa pour tiges chaussures est étudiée. Un modèle de série avec trois modèles Kelvin est proposé et a été utilisé pour imiter et décrire avec succès leur comportement de fluage. Le modèle Kelvin est un modèle de connexion parallèle avec un modèle de ressort et un modèle d'amortisseur. Les indices interdépendants de l'imitation sont favorables, ce qui signifie que l'imitation est fiable.
MOTS CLÉS : cuir porcin nappa pour tiges chaussures, viscoélasticité, comportement au fluage, modèle Kelvin

INTRODUCTION

Visco-elasticity is a physical character that is between the characters of elastic solid and viscous fluid [1]. The visco-elastic behavior of synthetic polymers has been studied thoroughly [2]. These studies may fall into four such classes as stress relaxation, creep, sluggishness and internal consuming [2]. The study on the creep behavior of materials is to study the changing law of strain with the increase of creep duration at a constant stress [2].

Similar to other biological materials, the mechanical behaviors of leathers are very complicated. It depends on the duration of experiment, which means that leathers are visco-elastic materials [3]. The visco-elasticity of leathers is important for the comfortable feeling that leather goods may provide the consumers with and the shape-stability of leather goods. The study on the visco-elasticity of leathers is of great significance both in theory and in application. There are many factors that may affect the visco-elasticity of leathers. Kinds and origins of skins, processing technology, position and orientation of samples, temperature and humidity when the experiment is conducted may affect their visco-elasticity. However, a few studies have been reported in the field before [5].

Leathers are composed of cross networks of collagen protein fibers. There are holes in the collagen fiber network and between collagen molecules, which may vest leathers with good elasticity. Therefore, they are different from the continuous polymers [5]. It is considered that leathers are non-linear visco-elastic materials [6].

From the viewpoint of creep behavior, the visco-elasticity of nappa upper pig leathers is studied. A series model of three Kelvin models is proposed to imitate their creep behavior. The interrelated indexes of the imitation are favorable. It means that the imitation is reliable.

Fundamental Theory

Both spring models and dashpot models are usually used to study the visco-elasticity of materials. The mechanical behaviors of spring models follow the Hooke's elastic law and those of dashpot models follow the Newton's law for viscous fluid [2]. Neither the spring models nor the dashpot models can describe the mechanical behaviors of polymers successfully. So the mechanical behaviors of complicated polymers are located between those of both models.

The Kelvin model, which is a parallel connection of a spring and a dashpot, can describe the creep behavior of linear polymers successfully [2]. The relation between creep compliance (J(t)) and creep duration (t) is according to Equation (1).

$$J(t) = J(0)\left(1 - e^{-\frac{t}{\tau}}\right) \quad (1)$$

where τ is the postponing time, τ=η/E and J is the creep compliance of the Kelvin model.

A series model of some Kelvin models can be used to describe the creep behavior of more complicated polymers. The relation between creep compliance (J(t)) and creep duration (t) is according to Equation (2).

$$J(t) = \sum_i J_i\left(1 - e^{-\frac{t}{\tau_i}}\right) \quad (2)$$

where τ_1, τ_2, …, τ_n are the postponing times of each Kelvin models, respectively, $\tau_i=\eta_i/E_i$, and J_1, J_2, …, J_n are the creep compliance of each Kelvin models, respectively.

Leathers are composed of cross networks of collagen protein fibers. There are differences among the bond length, bond angles, side groups, and chain fragments of collagen chains. The quality and cross length of each fiber bundles are different. There are soft fragments and hard fragments in the peptide chains. There are holes in the network and between collagen molecules, which vest leathers with good elasticity. Therefore, they are different from continuous polymers [5]. It is thought that leathers are non-linear visco-elastic materials [6]. Their creep behaviors are rather complex. Only one Kelvin model cannot describe them successfully. A series of Kelvin models might be able to describe them successfully.

EXPERIMENTAL

Materials and Apparatus

Nappa upper pig leather was provided by a local tannery, produced by the traditional process including soaking, degreasing, unhairing, liming, deliming, bating, pickling, chrome tanning, shaving, retanning, fatliquoring, drying, and finishing. Electronic Materials Testing Machine, WD-1, was from Jinan Zhongchuang testing Co. Ltd, China. Temperature and Humidity Conditioner was from Weifang Anke electronic Co. Ltd., China. Thickness Indicator, GJ9B1, was made by the Zhejiang Yuyao Machinery, China.

Procedures

The samples to be studied were from the center of nappa upper pig leathers. The average thickness t (mm) was determined and calculated. The cross-section area A_0 was obtained as $A_0=10t\times10^{-6}$ m^2 because the sample is 10 mm in width. The samples were placed in the temperature and humidity controller at 18°C, R.H.=65% for more than 48 hours to be air conditioned to reach equilibrium.

A sample was stretched to determine the tensile strength (σmax, the stress at break). Another sample was stretched to the stress of $\sigma_0=\sigma max/2$. Its creep deformation (ΔL) was recorded with its stress unchanged. Its creep elongation (ε) was obtained as $\varepsilon=\Delta L/L_0\times100\%$ and its creep compliance (J(t)) was calculated as $J(t)=\varepsilon/\sigma_0$.

The data processing was completed in computer with Gauss iteration program we had written before. The iteration formula was as equation (2).

RESULTS AND DISCUSSION

Creep Behaviors of Nappa Upper Pig Leathers

Figure 1 and Figure 2 show the relation between creep compliance J(t) and creep duration (t). It can be observed that the sample creep was very quick at the beginning of creep, which turned slow gradually. It could be concluded that there was at least one postponing time that is a few seconds in their postponing time spectrum. This part of creep was completed in a few seconds when the creep experiment began. Their minor creep postponing time means that shoes, or other leather goods, made from them will complete this part of creep when the shoes are dressed. The needs for comfortable feeling in the feet are met and it would be thought that the material (leather) from which the shoes were made is good. The creep compliance does not reach its equilibrium value in a short time, which means that shoes have good shape-stability.

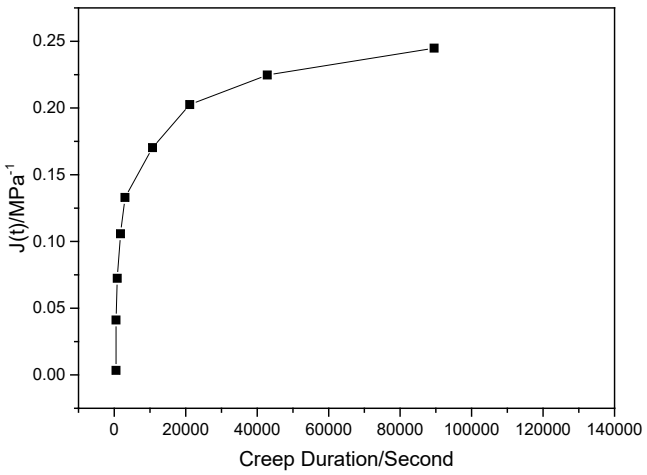

Figure 1. Creep compliance of sample perpendicular to the backbone vs. creep duration

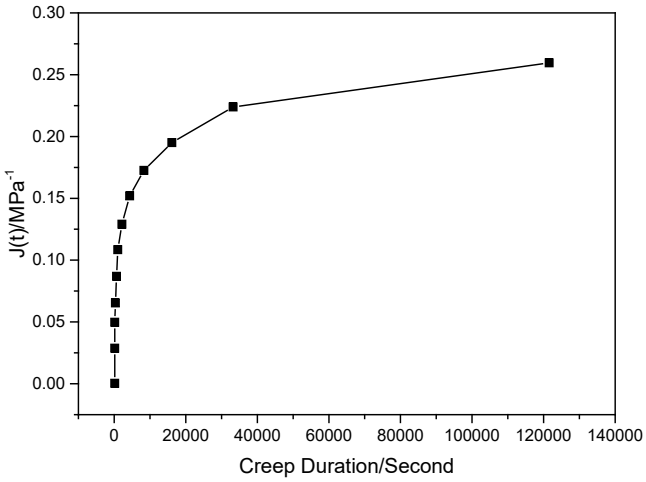

Figure 2. Creep compliance of sample parallel to the backbone vs. creep duration

Model Imitation of Creep Behavior of Nappa Upper Pig Leathers

The relation between creep compliance J(t) and creep duration was imitated with a series of some Kelvin models (equation 2). The imitation results were illustrated in Table 1 and Table 2 for samples of both perpendicular to and parallel to the backbone, respectively. It can be concluded that a series model of three Kelvin models may imitate their creep behavior successfully. The interrelated indexes of the imitation are 0.9971 and 0.9985 for the two samples, respectively. The creep behaviors of nappa upper pig leathers are close to this model. It means that the imitation is rather reliable.

Table 1: Measurement and calculation of creep compliance of sample perpendicular to the backbone

Order	Creep Duration (s)	Measurement of Creep Compliance (MPa^{-1})	Calculation of Creep Compliance (MPa^{-1})	Error
1	0	0.000	0.000	0.000
2	25	0.008	0.010	0.002
3	145	0.041	0.040	-0.001
4	445	0.073	0.073	0.00
5	1045	0.105.	0.106	0.001
6	2455	0.138	0.137	-0.001
7	10030	0.170	0.172	0.002
8	20830	0.203	0.200	-0.003
9	42430	0.225	0.228	0.002
10	89030	0.245	0.245	-0.002

Table 2: Measurement and calculation of creep compliance of sample parallel to the backbone

Order	Creep Duration(s)	Measurement of Creep Compliance (MPa^{-1})	Calculation of Creep Compliance (MPa^{-1})	Error
1	0	0.000	0.000	0.000
2	10	0.029	0.029	0.000
3	165	0.065	0.068	0.003
4	365	0.086	0.082	-0.004
5	873	0.108	0.106	-0.002
6	1983	0.129	0.133	0.004
7	4215	0.151	0.152	0.001
8	8160	0.172	0.168	-0.004
9	15960	0.194	0.192	-0.002
10	33220	0.223	0.225	0.002
11	121420	0.258	0.258	0.000

Rheological Constants of the Model

The rheological constants of the model are illustrated in Table 3. It is indicated that the relation among creep compliance of each Kelvin models is as $J_1<J_2<J_3$. The differences among them are very small.

Table 3: Rheological constants of the creep model

Rheological constants	$J_1(MPa^{-1})$	$\tau_1(s)$	$J_2(MPa^{-1})$	$\tau_2(s)$	$J_3(MPa^{-1})$	$\tau_3(s)$
⊥	0.0329	108.6	0.0985	897.9	0.1134	22637.1
‖	0.0549	14.14	0.0787	956.12	0.1248	25033.2

Where⊥ and ‖ are samples perpendicular to and parallel to the backbone, respectively

It can be calculated that the creep compliance at the beginning of creep (t=0) is 0. When the creep duration t=∞, the creep compliance of samples studied are 0.2448 and 0.2584, respectively. This might be the reason why leather shoes become larger and larger with the increase of dressing duration to fit the shape of the feet.

The relation among postponing times of each Kelvin models is as $\tau_1<\tau_2<\tau_3$. The differences among postponing times of each Kelvin models are considerable. For example, τ_3 is about 200 times of τ_1. It is to say that the creep time distributes in a rather wide range. The first creep time (τ_1) of both samples are a few seconds, which means that the creep starts at the beginning of the experiment. It corresponds to the results in Figure 1 and Figure 2. The contribution to the total creep at the first few seconds of experiment is mostly from the first Kelvin model. It is demonstrated clearly that the cross networks of the collagen fibers are rather complicated.

The contribution of each Kelvin models to the total creep compliance is different in different creep period. Let's suppose that the creep compliance of the i-th Kelvin model is J_i and its postponing time is τ_i. The contribution of this Kelvin model to the total creep compliance is according to equation (2).

When t is much less than τ_i, $J_i(t)=0$. It indicates that no contribution is given by the i-th Kelvin model to the total creep.

When $t \approx \tau_i$, $J_i(t)$ increases with the increase of creep duration obviously. Since the difference among postponing times of each Kelvin models is considerable, the change of the total creep compliance at different period is mainly from different Kelvin models.

When t much more than τ_i, $J_i(t) = J_i$. It is a constant, which means that the contribution of the i-th Kelvin model to the total creep is constant and does not change with the increase of creep duration any more.

The creep rheological constants of samples perpendicular to and parallel to the backbone are different. It indicates that nappa upper pig leathers are anisotropy materials. Although the creep behaviors of the two samples are different, their creep law is the same.

CONCLUSION

Nappa upper pig leathers behave visco-elasticity in creep behavior. A series model of three Kelvin models may describe their creep behaviors successfully. The interrelated indexes of the imitation are favorable, which indicates that the imitation is reliable. The comfortable feeling given to the consumers and the shape-stability of leather goods when their goods are dressed may be described with the creep rheological constants of the model.

Acknowledgments

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EFFECT OF MICROWAVE IRRADIATION ON THE SOLUTION OF AMINO ACID CHROMIUM COMPLEXES

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EFFECT OF MICROWAVE IRRADIATION ON THE SOLUTION OF AMINO ACID CHROMIUM COMPLEXES

ABSTRACT. In recent years, microwave technology has been applied more and more in tanning, however there is still a lack of research on the effect of microwave irradiation on the interaction between chromium complex and amino acids. In the study, the influences of microwave irradiation on the reactions were studied by selecting four kinds of characteristic amino acids in collagen, aspartic acid, hydroxyproline, lysine and glycine, to provide new knowledge on tanning process. The solution of chromium complex reacted with amino acid was heated by microwave as a sample and by water bath heating under the same conditions as a control. During the process, the pH variation and UV-Visible absorption spectrum were used to determine the influence of microwave on the reaction between amino acids and chromium complex. The results demonstrated that both microwave irradiation and water bath could accelerate the reaction rate and promote the stability of the amino acid chromium complex. However, the microwave irradiation had much more obvious effects on these changes than the water bath, indicating that microwave irradiation could promote the reaction between amino acid and chromium complex further and make the formed amino acid chromium complex more stable. In addition, microwave had stronger effect on improving the reaction when the polarity of amino acid was larger. In short, this study would provide some hints for understanding how microwave affects chrome tanning and might be useful to apply microwave in tanning in future.

KEY WORDS: microwave, amino acid, chromium complex, complex stability

EFECTUL IRADIERII CU MICROUNDE ASUPRA SOLUȚIEI DE COMPLECȘI DE CROM ȘI AMINOACIZI

REZUMAT. În ultimii ani, tehnologia cu microunde a fost aplicată tot mai mult la tăbăcirea pieilor; cu toate acestea, încă există lacune privind cercetarea efectului iradierii cu microunde asupra interacțiunii dintre complexul de crom și aminoacizi. În acest studiu s-a examinat efectul iradierii cu microunde asupra reacțiilor prin selectarea a patru tipuri de aminoacizi caracteristici colagenului: acid aspartic, hidroxiprolină, lizină și glicină, pentru a oferi noi cunoștințe cu privire la procesul de tăbăcire. O probă din soluția complexului de crom reacționat cu aminoacid a fost încălzită la microunde și încălzită în baie de apă în aceleași condiții ca proba martor. În timpul procesului, s-au utilizat variația pH-ului și spectrul de absorbție UV-Vis pentru a determina influența microundelor asupra reacției dintre aminoacizi și complexul de crom. Rezultatele au demonstrat că atât iradierea cu microunde, cât și baia de apă ar putea accelera viteza de reacție și promova stabilitatea complexului de crom și aminoacizi. Cu toate acestea, iradierea cu microunde a avut efecte mult mai evidente asupra acestor modificări decât baia de apă, ceea ce indică faptul că iradierea cu microunde ar putea promova reacția dintre aminoacid și complexul de crom și poate face complexul de crom și aminoacizi mai stabil. În plus, microundele au avut un efect mai puternic asupra îmbunătățirii reacției atunci când polaritatea aminoacidului a fost mai mare. Pe scurt, acest studiu oferă câteva indicii pentru înțelegerea modului în care microundele afectează tăbăcirea în crom și ar putea fi util pentru aplicarea microundelor în procesul de tăbăcire în viitor.

CUVINTE CHEIE: microunde, aminoacizi, complex de crom, stabilitatea complecșilor

EFFET DE L'IRRADIATION DES MICRO-ONDES SUR LA SOLUTION DES COMPLEXES DE CHROME ET D'ACIDES AMINÉS

ABSTRAIT. Ces dernières années, la technologie des micro-ondes a été de plus en plus appliquée au tannage, mais il y a encore des lacunes dans l'étude de l'effet de l'irradiation aux micro-ondes sur l'interaction entre le complexe de chrome et les acides aminés. Dans l'étude, les influences de l'irradiation aux micro-ondes sur les réactions ont été étudiées en sélectionnant quatre types d'acides aminés caractéristiques du collagène : l'acide aspartique, l'hydroxyproline, la lysine et la glycine, pour fournir de nouvelles connaissances sur le processus de tannage. Un échantillon de la solution de complexe de chrome ayant réagi avec un acide aminé, a été chauffée par micro-ondes et par chauffage au bain-marie dans les mêmes conditions qu›un échantillon de contrôle. Au cours du processus, la variation du pH et le spectre d'absorption UV-Visible ont été utilisés pour déterminer l'influence des micro-ondes sur la réaction entre les acides aminés et le complexe de chrome. Les résultats ont démontré que l'irradiation aux micro-ondes et le bain-marie pouvaient accélérer la vitesse de réaction et favoriser la stabilité du complexe de chrome d'acide aminé. Cependant, l'irradiation aux micro-ondes a eu des effets beaucoup plus évidents sur ces changements que le bain-marie, indiquant que l'irradiation aux micro-ondes peut favoriser davantage la réaction entre l'acide aminé et le complexe de chrome et peut rendre le complexe de chrome d'acide aminé formé plus stable. De plus, les micro-ondes ont eu un effet plus fort sur l'amélioration de la réaction lorsque la polarité des acides aminés était plus grande. En bref, cette étude fournit quelques conseils pour comprendre comment les micro-ondes affectent le tannage au chrome et peut être utile d'appliquer les micro-ondes dans le tannage à l'avenir.

MOTS CLÉS: micro-ondes, acide aminé, complexe de chrome, stabilité du complexe

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INTRODUCTION

Microwave is an electromagnetic wave with frequency range from 300 MHz to 300 GHz and could act on polar molecules directly, and then causing dipole turning to polarization and interfacial polarization to heat materials. Microwave irradiation has advantages of uniform, selective, energy-efficient and no hysteresis compared with traditional heating methods [1]. It excites the transition of the rotational energy level of the molecule, increases the energy of the molecule and reduces the activation energy of chemical reactions; consequently, some reactions may occur under gentle condition rather than extreme situations [2]. Also, microwave radiation accelerates the rate of chemical reactions [3] and promotes the yield of organic reactions [4, 5].

Hitherto, microwave irradiation had been applied in many tanning processes for improving leather quality. The shrinkage temperature and tear strength of chrome tanned leather could be improved as well as chrome tanning would be finished under lower terminal pH [6, 7]. Microwave had been used to improve tanning agent exhaustion and made products have better thermal stability in aluminium tanning, zirconium tanning and vegetable tanning [8-10]. Besides, the combination between collagen and chemicals could be strengthened during other leather manufacturing processes. The colour fastness of leather could be enhanced when microwave was used in a new dyeing method to fix the dyestuff [11]. Leather softness was improved under microwave drying due to less migration of oil but better uniform distribution [12-15].

Microwave irradiation, as a new technology to increase degree and rate of chemical reactions, might promote the formation of metal complexes. The current researches showed that microwave irradiation could further promote the hydrolysis and olation reaction of chromium tanning solutions compared with water bath [16, 17]. Moreover, microwave irradiation accelerated the reaction rate and improved the stability of chromium complexes in the complexation of carboxylic acids with chromium [18, 19].

The basis mechanism of tanning is the complexation reaction between amino acids and chromium. As a basic structural unit of protein, the amino acid can be used as simplest protein mimicry to study the tanning process for overcoming the impact of the permeation of tanning agent into pelt. The homogeneous reaction is also easier to analyse [20, 21]. Amino acids can be classified into non-polar, polar uncharged, positively charged (basic) and negatively charged (acidic) based on the polarity of the R groups of the amino acid (Figure 1) [22].

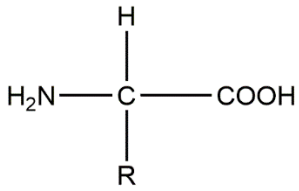

Figure 1. The schematic diagram of amino acid structure

In the study, four kinds of characteristic amino acids in collagen, aspartic acid, hydroxyproline, lysine and glycine, were selected as starting materials to react with chromium. Among them, aspartic acid is an acidic amino acid, lysine is a basic amino acid, glycine is the most abundant amino acid in collagen, and hydroxyproline is the characteristic amino acid of collagen. Microwave was used to heat the reaction between the four kinds of representative amino acids and chromium nitrate; meanwhile, the reactions heated by water bath at same condition were used as control. For keeping consistent with the chrome tanning process, the temperature was 40°C and pH was 4.0 when the amino acids were reacted with chromium nitrate. The results in the study would be a reference for applying microwave in chrome tanning.

EXPERIMENTAL

Materials

Concentrated perchloric acid, sodium bicarbonate, chromium nitrate, lysine, glycine, aspartic acid, and hydroxyproline were analytical grade agents from Chengdu Kelong Chemical Ltd.

Experimental Solutions

0.1 mol/L chromium nitrate solution, lysine solution, glycine solution, hydroxyproline solution and 0.05 mol/L aspartic acid solution were prepared in advance. 2.8% (w/v) dilute perchloric acid solution was prepared as solvent

for subsequent reactions and 0.5% (w/v) sodium bicarbonate solution was used for adjusting solution pH.

The amino acid chromium complex solution was prepared by the molar ratio of amino acid to chromium nitrate solution is 3:2. The pH of the amino acid chromium complex solution was adjusted to 4.0 sodium bicarbonate solution with and then left for 1 hour.

Amino Acid Chromium Complex Solutions Heated for Different Times

50 mL of the amino acid chromium complex solution was put into a 100mL beaker and then heated with an MCR-3C microwave reactor (Xi'an Yuhui instrument Ltd. the frequency of microwave was 2450 MHz,) at 40°C for, 5, 15, 30, 60, 120 and 240 min with stirring. A DF-101S water bath heater (Wuhan Keíer instrument Company) was used to heat control samples at same conditions. The pH meter and UV-Vis spectrometer were used to measure changes the solutions when they cooled down to room temperature.

pH Measurement

pH standard solutions were used to calibrate the PH-3C pH meter (Shanghai Yidian Science Instrument Company), then the pH of the amino acid chromium complex solutions was measured at room temperature, the final result was average of three tests.

Based on the measured pH, the reaction rate of amino acid chromium complex was calculated as following equation [23]:

$$r = \frac{dc}{vdt} = \frac{\Delta c_{H^+}}{\Delta t} \quad (1)$$

where: r = reaction rate, it represents the increasing concentration of product in unit time. Δc_{H}^{+} is the change of H^+ concentration and Δt is the reaction time. $\Delta c_{H}^{+} = 10^{-\Delta pH}$.

UV-Vis Spectrum Measurement

A UV1900 UV-Vis spectrometer (Shanghai Jinghua Instrument Co.) was used to scan the amino acid chromium complex solution from 350 to 650 nm with a scanning rate of 600 nm/min and wavelength (WL) interval of 1 nm. The wavelength of amino acid chromium complex solution at about 420 nm was named λ_1, and the corresponding absorbance was named A_1. The wavelength of amino acid chromium complex solution at about 580 nm was named λ_2, and the corresponding absorbance was named A_2. The R-value was calculated using the following equation [24]:

$$R = \frac{A_1}{A_2} \quad (2)$$

RESULTS AND DISCUSSION

The Influence of Microwave Irradiation on UV-Vis Absorption of Amino Acid Chromium Complex

The absorption peaks and R values of the ultraviolet-visible spectrum of four kinds of amino acids reacted with chromium under different conditions are shown from Table 1 to Table 4.

Table 1: The changes of lysine chromium complex UV-Vis absorption peak and R value

Time (min)	Water bath			Microwave		
	λ_{max1}(nm)	λ_{max2}(nm)	R	λ_{max1}(nm)	λ_{max2}(nm)	R
0	415	568	1.18	415	568	1.18
5	415	568	1.18	415	568	1.18
15	415	568	1.18	415	568	1.18
30	415	568	1.18	415	568	1.18
60	414	567	1.18	414	567	1.17
120	414	567	1.18	414	565	1.17
240	413	566	1.18	413	565	1.17

Table 2: The changes of glycine chromium complex UV-Vis absorption peak and R value

Time	Water bath			Microwave		
(min)	λ_{max1}(nm)	λ_{max2}(nm)	R	λ_{max1}(nm)	λ_{max2}(nm)	R
0	408	546	0.93	408	546	0.93
5	408	547	0.93	408	546	0.93
15	408	546	0.93	408	547	0.92
30	407	547	0.92	407	547	0.92
60	407	547	0.92	408	554	0.92
120	407	547	0.92	407	547	0.92
240	407	547	0.92	407	547	0.92

Table 3: The changes of aspartic acid chromium complex UV-Vis absorption peak and R value

Time (min)	Water bath			Microwave		
	λ_{max1}(nm)	λ_{max2}(nm)	R	λ_{max1}(nm)	λ_{max2}(nm)	R
0	411	567	0.93	411	567	0.93
5	411	566	0.92	411	565	0.90
15	410	564	0.89	410	562	0.87
30	409	561	0.86	409	560	0.85
60	408	558	0.82	408	557	0.81
120	407	555	0.79	407	554	0.78
240	406	553	0.76	405	551	0.75

Table 4: The changes of hydroxyproline chromium complex UV-Vis absorption peak and R value

Time (min)	Water bath			Microwave		
	λ_{max1}(nm)	λ_{max2}(nm)	R	λ_{max1}(nm)	λ_{max2}(nm)	R
0	411	558	1.08	411	558	1.08
5	411	558	1.08	411	558	1.08
15	411	557	1.07	410	557	1.07
30	410	557	1.06	410	556	1.06
60	409	555	1.04	408	554	1.02
120	409	554	1.03	408	553	1.02
240	408	553	1.01	407	552	1.01

The violet shift of the absorption peaks relates to coordination reaction rate between chromium complex and ligands. Generally, larger violet shift means faster reaction rate and greater reaction degree.

As shown in Table 1 to Table 4, the wavelength at about 580 nm decreases and violet shift of the chromium complex reacted with the amino acid is obvious with time prolonging, indicating the coordination reaction rate is faster and the reaction degree is more thorough with the warming time increasing. Under the same conditions, the violet shift of the microwave samples is 1-3 nm larger than the control samples, indicating that the effect of microwave irradiation on promoting the rate and degree of complexation between amino acid and chromium is more significant than water bath.

This additional promoting effect comes from the special effect that microwave irradiation could act on the polar substances directly during reaction to generate more complicated movements and drastic collisions for chromium complexes and amino acid.

It can be seen that the R value of microwave irradiation sample and water bath control sample both decrease during heating process, and R value of all samples is less than 1.19 at any time, showing microwave effect on the complexation between amino acids and chromium might not alter the binding pattern between chromium and amino acids.

Compared with the changes of violet shift and R value of chromium complexes reacted with different amino acids under microwave irradiation and water bath heating, it could be found that aspartic acid results in the most obvious change while glycine leads to the least. The changing tendency from large to small is aspartic acid > hydroxyproline > lysine > glycine. The polarity of these four kinds of amino acids is different because of distinctive R group. The R group of aspartic acid, hydroxyproline, lysine and glycine contain carboxyl, hydroxyl, amino with long aliphatic chain and hydrogen respectively. It is clear that the amino acids with higher polarity bring about smaller R value of chromium complex, indicating microwave affecting the reaction between chromium and amino acid significantly when the polarity of the ligand is larger.

The Influence of Microwave Irradiation on pH Change of Amino Acid Chromium Complex

The pH changes of different amino acids with chromium are shown from Table 5 to Table 8.

Table 5: The pH change and reaction rate of lysine-chromium nitrate reaction

Time: min	pH		Reaction rate: 10^{-7}mol/(L·min)	
	Microwave	Water bath	Microwave	Water bath
0	3.93	3.93	0	0
5	3.87	3.89	34.81	22.60
15	3.85	3.85	15.80	15.80
30	3.82	3.82	11.30	11.30
60	3.74	3.78	10.70	8.070
120	3.67	3.73	8.025	5.725
240	3.53	3.65	7.401	4.429

Table 6: The pH change and reaction rate of glycine-chromium nitrate reaction

Time: min	pH		Reaction rate: 10^{-7}mol/(L·min)	
	Microwave	Water bath	Microwave	Water bath
0	4.00	4.00	0	0
5	3.78	3.78	132.0	132.0
15	3.74	3.76	54.67	49.20
30	3.68	3.72	36.30	30.17
60	3.64	3.67	21.51	18.97
120	3.54	3.65	15.70	9.492
240	3.52	3.64	8.427	5.379

Table 7: The pH change and reaction rate of aspartic acid-chromium nitrate reaction

Time: min	pH		Reaction rate: 10^{-7}mol/(L·min)	
	Microwave	Water bath	Microwave	Water bath
0	3.89	3.89	0	0
5	3.83	3.85	38.17	24.80
15	3.72	3.74	41.13	35.47
30	3.62	3.66	37.03	30.00
60	3.48	3.55	32.05	25.50
120	3.38	3.43	24.01	20.23
240	3.26	3.34	17.53	13.68

Table 8: The pH change and reaction rate of hydroxyproline-chromium nitrate reaction

Time: min	pH		Reaction rate: 10^{-7}mol/(L·min)	
	Microwave	Water bath	Microwave	Water bath
0	3.90	3.90	0	0
5	3.72	3.72	129.2	129.2
15	3.67	3.69	58.60	52.20
30	3.62	3.66	38.00	30.97
60	3.49	3.57	32.95	23.88
120	3.39	3.50	23.46	15.86
240	3.34	3.46	13.80	9.200

Table 5 to Table 8 show that both microwave irradiation and water bath heating affect the pH and rate of the reaction between amino acid and chromium complex. In the microwave experiment, the pH values decrease by 0.48 for glycine, 0.56 for hydroxyproline, 0.63 for aspartic acid and 0.40 for lysine, respectively from beginning to 240 min, while the changes of control are 0.36, 0.44, 0.55 and 0.28 for corresponding samples. Based on the data of Δ pH, the reaction rates can be calculated and the reaction rates between microwave and water bath are compared. The reaction rates between amino acids and chromium under microwave irradiation are faster compared to the control under any corresponding condition.

According to the formula: $[Cr(H_2O)_6]^{3+} \rightarrow [Cr(OH)(H_2O)_5]^{2+} + H^+$ and $[Cr(H_2O)_6]^{3+} + RCOOH \rightarrow [Cr(RCOO)(H_2O)_5]^{2+} + H^+$, the pH of amino acid chromium complex solutions drops during the heating processes as a result of hydrolysis and coordination reaction with temperature rising and time increasing. The molecular thermal motion could result in the carboxyl group of amino acid dissociation which makes H^+ release. The dissociated amino acid carboxyl group enters the inner of the complex to coordinate with the chromium ion, which causes less dissociated amino acid to exist and more amino acid carboxyl groups to dissociate in solution. The processes are promoted by microwave irradiation and water bath, but microwave leads to more significant change. Because the polar amino acids molecules and chromium complex are affected by the microwave directly to generate more collision and rotation at the same temperature compared with water bath heating, the reaction rate is accelerated just microwave could make other chemical reactions much faster.

CONCLUSIONS

In the study, microwave irradiation was used to heat the reaction between chromium complex and four kinds of characteristic amino acids for studying the influence of microwave on its stability and reaction rate, and water bath heating was used as control. The results showed the coordination reaction between chromium

complex and amino acid was accelerated and the stability of the complex was enhanced after heating, but microwave irradiation results in faster reaction rate and better stability beyond thermal. Moreover, microwave had stronger effect on improving the reaction between chromium complex and amino acid when the polarity of amino acid was large just the influence tendency of the reaction from large to small is aspartic acid > hydroxyproline > lysine > glycine. This study would provide some hints for understanding how microwave affects chrome tanning and might be useful to apply microwave in tanning in future.

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FASHION REVOLUTION AS PROMOTER OF SOCIAL INNOVATION AND SUSTAINABILITY IN FASHION

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FASHION REVOLUTION AS PROMOTER OF SOCIAL INNOVATION AND SUSTAINABILITY IN FASHION

ABSTRACT. Fashion Revolution is a global collaborative movement that seeks to increase transparency across industry's production chain and counteract misunderstanding. The movement calls university students around the world to become ambassadors and to become activist designers. Also, students, teachers, businesses, professionals and the community to discuss consumption, sustainable development of fashion and getting millions of people demanding fashion transparency, through brand questioning: #whomademyclothes. This article aims a fashion week revolution, promoting knowledge as social innovation for sustainability when launching a concept as a business value proposition. Authors present a CANVAS and Pestle business model to support future implementation of this conceptual idea. One concludes that design of product-service systems, allied to fashion revolution movement, helps foster social innovation, stimulates circularity, induces behavioural consumption changes, promotes dematerialization of energy consumption, redistribution of idle products, available resources management with social and environmental benefits, through online platform and app.

KEY WORDS: activism design, systems design, social innovation, 2P2 platform

MIŞCAREA FASHION REVOLUTION CA PROMOTOR AL INOVĂRII SOCIALE ŞI SUSTENABILITĂŢII ÎN MODĂ

REZUMAT. Fashion Revolution este o mişcare de colaborare globală care urmăreşte să crească transparenţa în lanţul de producţie al industriei şi să contracareze neînţelegerile. Mişcarea îndeamnă studenţii universitari din întreaga lume să devină ambasadori şi designeri activişti. Se adresează, de asemenea, studenţilor, profesorilor, întreprinderilor, profesioniştilor şi comunităţii, în vederea purtării unor discuţii despre consum, dezvoltarea durabilă a modei şi determinarea a milioane de oameni care să solicite transparenţa în modă, prin punerea mărcii sub semnul întrebării: #whomademyclothes. Acest articol are ca scop o revoluţie a săptămânii modei, promovând cunoaşterea ca inovare socială pentru sustenabilitate la lansarea unui concept ca propunere de afaceri. Autorii prezintă un model de afaceri CANVAS şi Pestle pentru a sprijini implementarea viitoare a acestei idei conceptuale. Se concluzionează că proiectarea sistemelor de servicii-produse, aliată mişcării Fashion Revolution, încurajează inovarea socială, stimulează circularitatea, induce schimbări ale comportamentului de consum, promovează dematerializarea consumului de energie, redistribuirea produselor inactive, gestionarea resurselor disponibile cu beneficii sociale şi de mediu, prin intermediul unei platforme online şi a unei aplicaţii.

CUVINTE CHEIE: design activist, designul sistemelor, inovare socială, platforma 2P2

LE MOUVEMENT FASHION REVOLUTION EN TANT QUE PROMOTEUR DE L'INNOVATION SOCIALE ET DE LA DURABILITÉ DANS LA MODE

RÉSUMÉ. Fashion Revolution est un mouvement collaboratif mondial qui vise à accroître la transparence à travers la chaîne de production de l'industrie et à lutter contre les malentendus. Le mouvement appelle les étudiants universitaires du monde entier à devenir des ambassadeurs et à devenir des designers activistes. Il s'adresse également aux étudiants, aux enseignants, aux entreprises, aux professionnels et à la communauté, pour discuter de la consommation, du développement durable de la mode et amener des millions de personnes à exiger la transparence de la mode, à travers le questionnement de la marque: #whomademyclothes. Cet article vise une révolution de la semaine de la mode, en promouvant la connaissance comme innovation sociale pour la durabilité lors du lancement d'un concept en tant que proposition de valeur commerciale. Les auteurs présentent un modèle commercial CANVAS et Pestle pour soutenir la future mise en œuvre de cette idée conceptuelle. On conclut que la conception de systèmes de produits-services, alliée au mouvement de Fashion Revolution, favorise l'innovation sociale, stimule la circularité, induit des changements du comportement de consommation, favorise la dématérialisation de la consommation d'énergie, la redistribution des produits inactifs, la gestion des ressources disponibles avec des avantages sociaux et environnementaux, via une plateforme en ligne et une application.

MOTS CLÉS: design activiste, conception de systèmes, innovation sociale, plateforme 2P2

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INTRODUCTION

The fashion industry is considered the second most polluting in the world. The textile, clothing and footwear system (fashion industry) operates in a linear fashion: large amounts of non-renewable resources are extracted to produce clothing and shoes that are used for a short time and are subsequently dumped into landfills, incinerated or sent to underdeveloped countries. These problems worsened even further from the 2000s, when fast fashion chains emerged, and production and consumption increased, thereby increasing social and environmental problems [2].

The international activist movement Fashion Revolution [3] was created following the collapse of a garment industry in Dhaka, Bangladesh, on April 24, 2013, in which 1,138 people died and more than 2,500 were injured. Such a tragedy touched a group of people in the UK who decided to found the collaborative Fashion Revolution movement, Carry Somers was the founder and director of global operations. In 2014 in the first edition, the movement was organized in several countries of the world and grew every year.

Fashion Revolution aims to make the production chain more transparent to the eyes of consumers and with that, ensure that a tragedy like the one that happened in Rana Plaza never happens again. According to the organizers the simple question "Who made my clothes?" contributes greatly to a change in this process.

Bringing the protagonists of the industry to the fore, Fashion Revolution aims to change the narrative around clothing, inspiring positive and permanent changes in the fashion industry.

The death of 1,138 people on one terrible day cannot be forgotten. It is imperative to demand changes that prevent such new accidents, wherever they may be. On April 24 of every year, Fashion Revolution mobilizes the entire fashion chain to question the true cost of fashion, and show to the world that changes are possible in the industry segment [3].

The lack of knowledge of the consumers about the production system, the use of natural resources and the exploitation of the labour contributes to the economy of the discard and to the global warming and social degradation [4].

Fashion Revolution, headquartered in the United Kingdom, is a community-based company comprised of nine people in global coordination, from various fields such as politics, communication, branding and education. They work closely with the Global Advisory Committee to plan and implement the Fashion Revolution campaign each year [3].

Members are responsible for organizing and managing the primary groups and overseeing Fashion Revolution globally. They work on communication, policy and strategy and fundraising for events.

The Global Fashion Revolution coordination is also responsible for the governance of the movement in each country, through regional coordinators. Currently, there are over one hundred countries that are part of the Fashion Revolution movement.

Fashion Revolution country coordinators (CCs), as is the case of Salomé Areias in Portugal, work voluntarily assuming the responsibilities of organizing the Fashion Revolution event in their respective countries. Its main tasks are: facilitating and distributing Fashion Revolution campaign materials; defining communication policy and strategy, in accordance with global guidelines; compiling and presenting annual reports on its impact and evaluatng the progress of Fashion Revolution in the country [3].

EDUCATIONAL ACADEMIC FASHION REVOLUTION

The Fashion Revolution movement invites university students to become Fashion Revolution ambassadors at their universities, organizing events and achievements there. Between March 29 and April 1, 2017, the first edition of the event was held at the University of Beira Interior, the first Portuguese university to join the movement. The ambassador and organizers of the event Fashion Revolution Week at the University of Beira Interior, had the collaboration and participation of the course directors, professors and graduation, master's and doctorate students in Fashion Design [5].

The objective was to raise awareness among consumers, designers, industry, artisans about the true cost of fashion, both social, environmental and economic; create relationships with universities, fashion design courses, companies and encourage production,

consumption and circular distribution. Besides, question who made my clothes? [5].

With this, it is expected to sensitize the participants of the event, both regarding social and environmental issues of the fashion industry, in the expectation that they will adhere to the slow fashion, the circular fashion and the change of attitude towards clothing. The first edition was attended by national or international brands that spoke about sustainability in fashion. Brand Natural Cotton Color [6], spoke of the coloured cotton of Paraíba, Brand Away to Mars [7], talked about the creation process open to all. Lala Deheinzelin [8], UNO consultant, spoke on 4D: New and savings to activate the transition. Thomas Echkschmidt [9] talked about Conscious Capitalism, among other important speakers [5].

In the edition of Fashion Revolution at the University of Beira Interior (FRUBI) in 2018, we believed that in order to achieve sustainability in fashion we need to promote a new way of life through social innovation that involves teachers, students, companies, professionals and the local community in the process to accelerate the transition of the circular economy. Thus, the FRUBI of 2018 is divided into three large panels [5]:

- Inner Wellness - Where the sustainable lifestyle is portrayed, from healthy eating habits - avoiding the eating disorders driven by the fashion industry, to the separation and recycling of the garbage generated in the day-to-day;
- Exterior Wellness - Panel based on aesthetics, beauty care and styling, interconnecting internationally renowned cosmetic brands and regional products thought of female empowerment;
- Circular Fashion - After the analysis of consumption and identity established in previous days, the last day focuses on finding established brands in the market that work for a more circular, dynamic, creative and above all transparent fashion industry [5].

In addition, a competition was held to raise awareness of the academic and general community for the development of sustainable fashion, driven by innovation, design and creativity, to stimulate the creative and enterprising capacity of the competitors, as well as, to spread to the community the guidelines of the development of sustainable fashion products. One of the parts of the coordinator must comply with the guidelines of one of the following sustainability concepts:

- The concept of upcycling is simple: it consists of creating new parts from the reuse of other pieces of clothing or leftovers, extending the product life cycle;
- Zero Waste: The "zero waste" design process offers a cleaner production alternative, aimed at minimizing waste already in the design and modelling phases, providing a new approach to product development, making production cleaner and reducing its environmental impacts, aiming at the sustainable concept of slow fashion;
- Modular/Multifunctional Clothing: Modular, multifunctional or convertible clothing consists of dresses and blouses with straps that can be configured in various ways or depending on the modelling, transforming the piece into a skirt, scarf, cape, bag, blouse and dress.

The event ended with the presentation of a parade with about 400 people [5].

The Fashion Revolution Week event at the University of Beira Interior - Bachelor, Master's degree in Fashion Design is a pioneering and unique opportunity to explore, in the interaction between students and community, the many issues of the fashion industry such as: workers' rights, transparency in the production chain, global citizenship, sustainable development and ethical business practices [5].

Together people will question: why a fashion revolution? Who makes our clothes? Where are they made? What is the salary and working conditions? What are the environmental consequences?

From 2015, to 2018 the great differential of

this Movement is the direct interaction with the educational sector of the fashion area, offering material resources to support the participation of the students and the community.

The major challenge of sustainable development is social innovation, which requires a well-informed, participatory and collaborative society that better integrates technical-scientific knowledge for environmental, social and economic sustainability [10].

By connecting design mode courses, these movements also stimulate principals, faculty, and students to rethink the practice of design, designing activism as a tool that can drive transformation throughout the fashion system.

The fashion industry is a global industry with enormous social and environmental impact. The university has a key role in raising awareness of its Fashion Design students and future fashion industry designer. Fashion is not just glamour. It is life and work. Giving students the awareness and the need to reflect on all this with a view to a new model of creating and producing clothes, this being our contribution to sustainability.

Table 1: Sustainable Fashion organizations (In this table are shown only a few of them). For more information visit https://www.fashionrevolution.org/key-organizations and key-organisations at site https://www.fashionrevolution.org [3]

Sustainable Fashion Centre	Clean Clothes Campaign	Ellen MacArthur Foundation [11]	Fairtrade Foundation	Textile Exchange
Sustainable Fashion Centre is a research institute committed to exploring ways to use fashion to drive change through research and collaboration be-tween education and industry.	The Clean Clothes Campaign is a global alliance dedicated to improving working conditions and em-powering workers in the global clothing and sportswear in-dustries.	The Environmental Justice Foundation is working to secure a world where habitats and natural environ-ments can sustain and be sustained by the communities that depend on them for their basic needs and livelihoods.	The Fairtrade Foun-dation's mission is to connect farmers and disadvantaged wor-kers with consumers, promote fairer trade conditions and em-power farmers and workers to fight poverty.	Textile Exchange is a global non-profit or-ganization that works to promote the trans-formation of the in-dustry into sustain-able fibres, integrity and responsible standards and supply networks.

It is growing both by consumers and the brands that have come to answer the questioning about the origin of their productions. A differential of this Movement is the direct interaction with the educational sector, offering material resources to support student participation.

To transform the world, Fashion Revolution believes in the power to work in collaboration with other activist movements.

The way fashion revolution is working and uniting collaborative thinking for the transformation of the garment industry is in the social issues faced by the environmental workers.

For Manzini [10] cultural activists, grassroots organizations and design activities are converging on a variety of initiatives whose purpose is not to provide immediate solutions to problems, but to arouse interest in these scenarios and to show, in general and in a paradoxical or provocative way that exist different ways of looking at them and solving them. Social innovation in design may be one of them because of the natural need or desire to design supported by digital tools and new social networks. This is the case of the fashion revolution platform with guidelines, blog and materials available for downloads. And it works collaboratively in more than 100 countries. The country coordinators always give support on the site during Fashion Revolution week. The movement encourages, do it yourself, upcycling, swap market production, and conscious consumption of fashionable product with value together for all.

FACTORS	ATUAL (consollidated)	FUTURE (emergent)	INSIGHTS LIST
POLITICAL **Regulations** **Regional Regimes and Taxation** **Government Grants Financing & Fundings**	Universities internal policies; Design/platform maintenance fees; Municipal, State Incentives Incubators / Investors Crowdfound;	Prevent or hinder the implementation of the model; High competition, great app offer, strong competitive differential;	Possibility to use other infrastructures, including digital (app); Partners, take the project to startups fairs;
ECONOMIC **Cost of labor** **Economic scenario** **Demand for raw materials**	Maintenance of the platform; Increasing need and awareness of people in saving;	Make updates on the platform / service users; People will look for other ways to save money;	Outsourced or personal encountered or partnered with students with any advantage offered; Use economics as a marketing call to win over people who are not yet into the collaborative lifestyle;
SOCIAL **Changes in expectations** **Specific pressure and interest groups** **Cultural changes** **Role of media** **Social responsibility**	Circular Economy and collaborative support groups; Fashion Revolution Movement pressing fast fashion companies and raising the awareness of the population (alternative media) about the economic, social and environmental impacts; International Learning Network of networks on Sustainability (LENS);	Universities adhere to a teaching with more application of the circular and collaborative economy; Fashion Revolution Movement in expansion which will impact more and more the consumption habits of people; International Learning Network of networks on Sustainability;	Actions with students of fashion design to encourage the application of circular economy in projects; To count on the support / partnership of the Fashion Revolution Movement and other pressure groups to actions, publicize and maintain the system; Massive presence in social media; LENS;
TECHNOLOGIC **New technologies** **Effects of internet** **P2P platforms** **Need for infrastructures** **Availability to adopt innovations**	Impact of the internet on the organization of people; Strong positioning of facilitating applications / platforms; Existing faculty infrastructure; Young audience at university (Millenius) with ease of adopting novelties;	Collaborative economy on the rise which will redefine people's lifestyles; Need to adapt existing infrastructure and a lot of bureaucracy to be feasible to implement;	Use the internet to publicize the system; Create an online platform p2p; Use online platforms to reach more people and avoid the need for physical and bureaucratic infrastructure; Strategies to initially reach young people who are more willing to adopt novelties;
LEGAL **Guidelines** **Variation in laws by country, state or region**	PERSU 2020 (Strategic Plan for Urban Waste);		
ENVIRONMENTAL **Carbon footprint** **Emission reduction** **Waste Disposal Regulations** **Social pressure for social responsibility**	Agendas for compliance with municipal and regional goals; Stronger pressure groups;	Agendas delayed; Increasing and higher visibility charges;	Seek support for companies and agencies that have a late compliance agenda; Maximize use and delay the disposal of parts in nature; Conscious designers.

Figure 1. PESTLE analysis. Adapted from Sampaio, 2017 [12]

According to Fuad-Luke [13] design activists make their "moves" create a critical mass. This can significantly impact the transformation of the clothing industry and our consumption habits.

Fashion Revolution is seen as a promoter of the social innovation of Fashion library P2P UBI, is in the process of development together with the Informatics Department of UBI.

Manzini [10] states that design for social innovation is service design (to design and develop solution ideas that take into account the quality of the interactions involved) and strategic design (to promote and support partnerships between the different actors involved). It also produces significant social innovations, that is, solutions based on new social forms and new economic models.

Social design deals with all types of social change geared to sustainability: changes that can reduce its environmental impact, regenerate common goods and strengthen the social community.

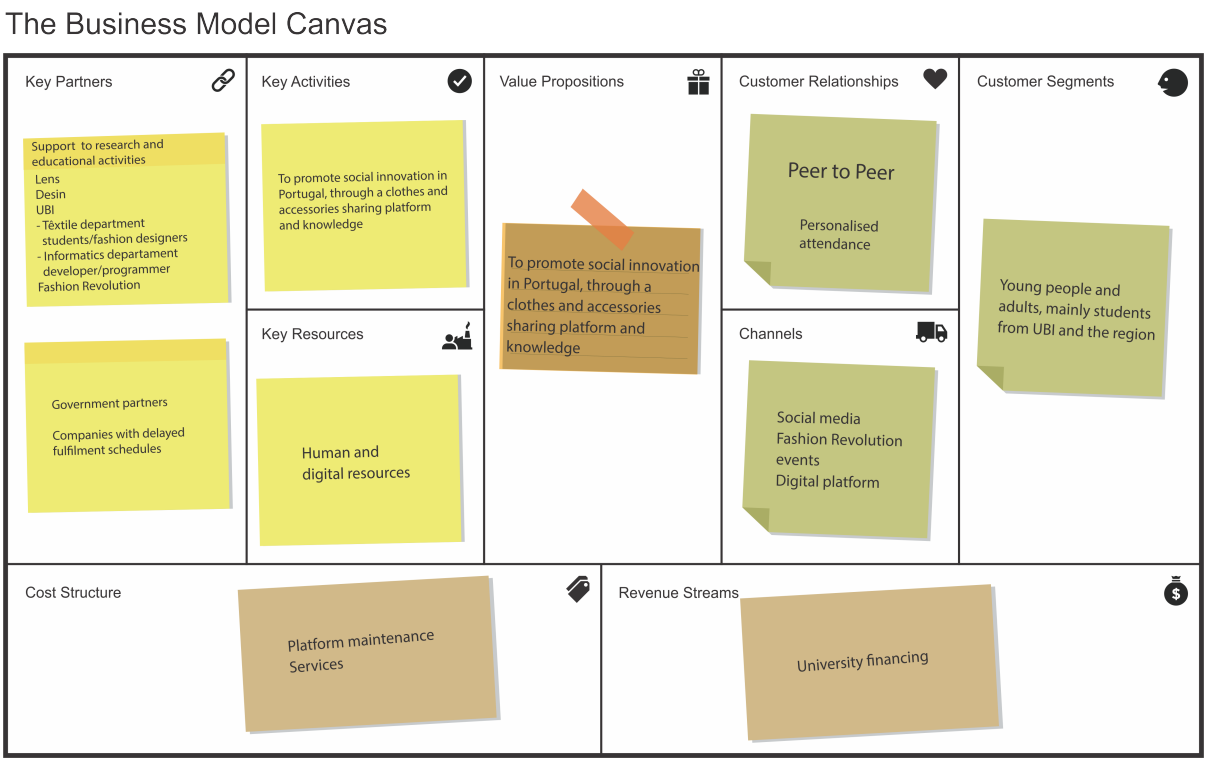

Figure 2. The Business Model Canvas, adapted from Sampaio [12]

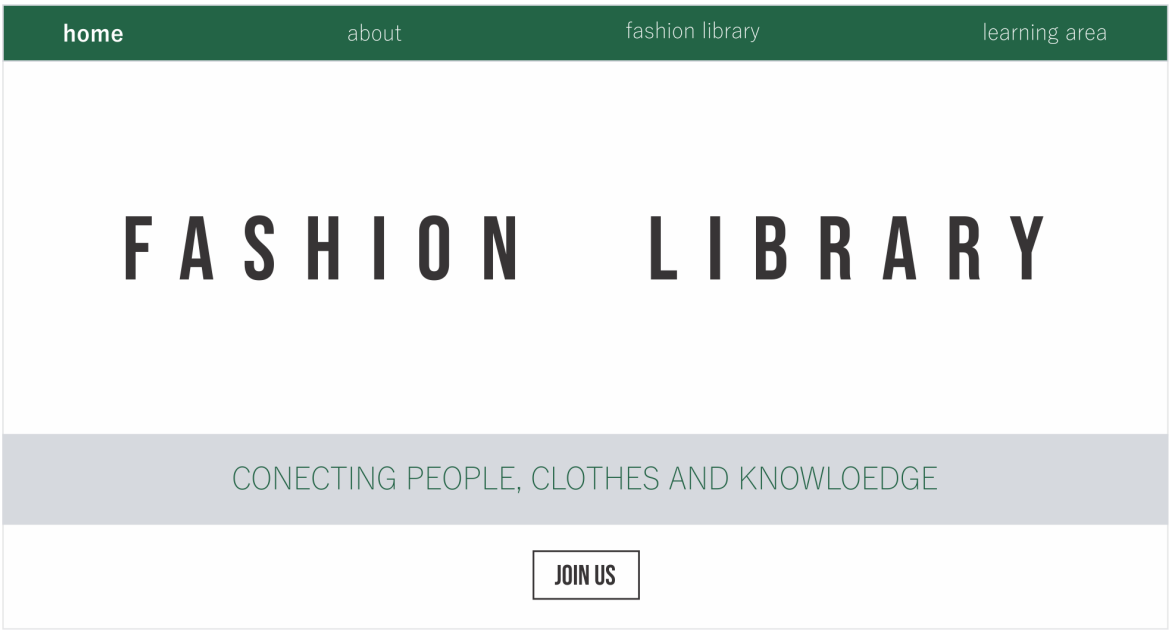

Figure 3. Landing page “Home”. Adapted from Solange *et al*. [14]

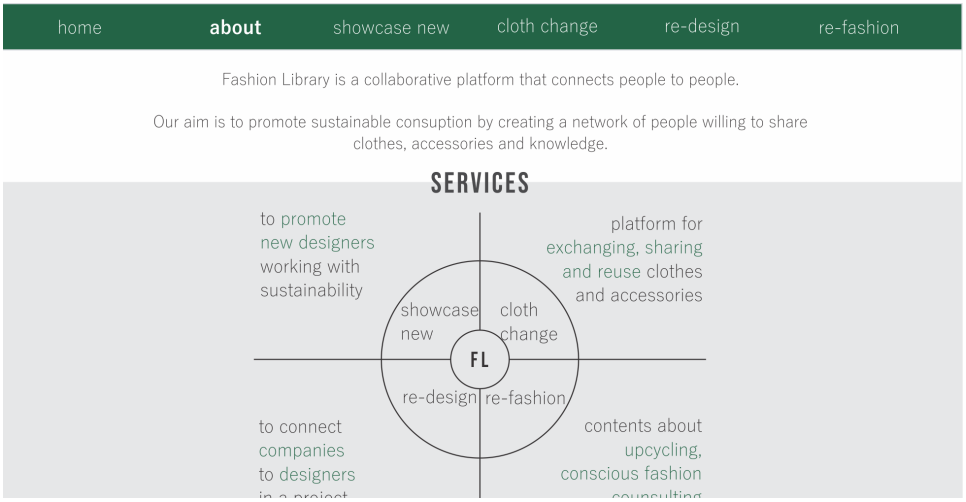

Figure 4. Landing page "About". Adapted from Solange *et al*. [14]

Figure 5. Landing page "Cloth change". Adapted from thenuwardrobe, 2018 [15]

FINAL CONSIDERATIONS

Initially, the perceived obstacles were the behaviour of Portuguese consumers, who are not accustomed to access business models that replace the property. There is a lack of awareness and mobilization of citizens and economic agents.

Its implementation is proposed in Covilhã, Portugal, with the provision of eco-efficient, collaborative and sustainable services in fashion products, which can be replicated in its entirety, or by parts, in other places and contexts, adopting, for this, modularity as an adaptive resource. Adoption of the system will depend heavily on the culture to which it is embedded.

It will be an online P2P platform to connect source and demand promoting access to clothing, without the need to buy, will thus help change the perception of disposable article apparel to a reusable product. The cleaning will be done by the home user who lends the clothes. "Increasing the number of times clothes are worn may be the most powerful way to capture value, reduce resource pressure and reduce negative impacts" [13].

Accelerating sustainable development requires a paradigm shift in terms of the productive process in order to migrate from a linear to a circular economy: it is about changing habits, the mentalities and methods rooted in society.

According to 2030 agenda the future of research and innovation for the Circular Economy in Portugal depends on a collective

approach, along with the collaborative economy, involving the Academy in the first place, with multidisciplinary models of interaction in civil society [16].

This project has as target audience the generation Millennials, also known as generation or the "generation Uber" or "Airbnb" that use the collaborative economy.

Rifkin [17] has published a book called "The Age of Access", in which presented the future transitions of economic activities based on access to goods and services through the shared use. The shared consumption will cause a real revolution of behaviours for the sake of sustainability, pointing to the replacement of products for services. The shared practices are ways of optimizing the lifetime of the products, reducing the need for new products, leading to less environmental impact. This is to say that it reduces the amount of discarded products which can reduce up to 50% the environmental impact as compared with the single use. And the footwear and accessories industry is also discussing this topic, preparing new solutions and approaches [18].

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PRODUCTION OF MULTIFUNCTIONAL FOOTWEAR FOR PRISON POLICE OFFICERS

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PRODUCTION OF MULTIFUNCTIONAL FOOTWEAR FOR PRISON POLICE OFFICERS

ABSTRACT. There is a close connection between the comfort in wearing footwear and the quality of this product. When we refer to the quality of footwear, we must start from the analysis of materials used to make the upper and lower shoe assembly, the analysis of how the joints between the different elements of the assembly behave and finally we must consider the behavior of the shoes as a whole. The footwear must create a climate where temperature, humidity, air circulation and their action on the foot, and on the whole body are correlated. Even at a rapid change of internal or external influences, the wearer must feel good. The so-called triple physiological agreement - temperature, humidity and air circulation - must be adaptable to various requirements during a working day such as: rest, movement, physical effort and climatic conditions. The design of a product is not only related to the aesthetic, artistic aspect, but more to its functionality and engineering (from the correct choice of materials, construction and technological concept, to prototyping). A good example in this regard is the design of multifunctional footwear, for soldiers and police officers. Therefore, designing the right footwear is a big challenge not only for designers, but also for engineers. The paper presents the way in which footwear as a component of the work uniform of prison police officers was made.

KEY WORDS: multifunctional footwear, materials, specifications

DEZVOLTAREA ÎNCĂLŢĂMINTEI MULTIFUNCŢIONALE PENTRU POLIŢIŞTII DE PENITENCIARE

REZUMAT. Există o strânsă legătură între confortul pe care purtarea unui produs de încălțăminte îl conferă utilizatorului şi calitatea acestui produs. Când ne referim la calitatea unui produs de încălțăminte trebuie să pornim de la analiza materialelor destinate confecționării ansamblului superior şi inferior al încălţămintei, analiza modului în care se comportă îmbinările dintre diferitele elemente ale ansamblului şi în final trebuie să avem în vedere comportarea produsului de încălţăminte în ansamblu. Încălțămintea trebuie să creeze un climat unde să fie corelate temperatura, umiditatea, circulația aerului şi acțiunea lor asupra piciorului, respectiv a întregului organism. Chiar la o schimbare rapidă a influenţelor interioare sau exterioare, purtătorul trebuie să se simtă bine. Așa numitul acord triplu fiziologic - temperatura, umiditatea şi circulația aerului - trebuie să fie adaptabil cerințelor diverse din timpul unei zile de lucru cum ar fi: odihnă, mișcare, efort fizic şi condițiile climatice. Proiectarea unui produs nu este legată doar de aspectul estetic, artistic, ci mai mult de funcționalitatea și ingineria sa (de la alegerea corectă a materialelor, construcției și conceptului tehnologic, până la prototipare). Un bun exemplu în acest sens este proiectarea încălțămintei multifuncționale, încălțăminte pentru soldați, polițiști. Prin urmare, proiectarea încălțămintei adecvate reprezintă o provocare mare nu numai pentru designeri, dar și pentru ingineri. Lucrarea prezintă modul în care a fost realizată încălțămintea din componenţa uniformei de serviciu a polițiștilor de penitenciare.

CUVINTE CHEIE: încălţăminte multifuncțională, materiale, specificații

DÉVELOPPEMENT DE CHAUSSURES MULTIFONCTIONNELLES POUR DES AGENTS DE POLICE DES PRISONS

RÉSUMÉ. Il existe un lien étroit entre le confort des chaussures et la qualité de ce produit. Lorsque nous nous référons à la qualité des chaussures, nous devons partir de l'analyse des matériaux destinés à fabriquer l'ensemble supérieur et inférieur de la chaussure, l'analyse du comportement des combinaisons entre les différents éléments de l'ensemble et enfin nous devons considérer le comportement des chaussures dans son ensemble. Les chaussures doivent créer un climat où la température, l'humidité, la circulation de l'air et leur action sur le pied, et respectivement sur le corps entier sont corrélées. Même lors d'un changement rapide d'influences internes ou externes, le porteur doit se sentir bien. Le soi-disant triple accord physiologique - température, humidité et circulation de l'air - doit être adaptable à diverses exigences au cours d'une journée de travail telles que: repos, mouvement, effort physique et conditions climatiques. La conception d'un produit n'est pas seulement liée à l'aspect esthétique, artistique, mais plus à sa fonctionnalité et à son ingénierie (du choix correct des matériaux, de la construction et du concept technologique au prototypage). Un bon exemple à cet égard est la conception de chaussures multifonctionnelles pour les soldats et les agents de police. Par conséquent, la conception des chaussures appropriées est un grand défi non seulement pour les concepteurs, mais aussi pour les ingénieurs. Le document présente la façon dont les chaussures pour l'uniforme de service des agents de police des prisons ont été fabriquées.

MOTS CLÉS : chaussures multifonctionnelles, matériaux, spécifications

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INTRODUCTION

Footwear protects human feet against harsh conditions, such as cold or hot environments, wet surfaces, etc. Over time, there have been many changes in design, materials and technologies used, all of these in order to meet the needs of end users, from fashion to comfort and protection. That is why, today, there are a lot of types of footwear on the market, each with its own specific characteristics, e.g. sports shoes, trekking/hiking shoes, summer shoes, safety shoes, work shoes, etc. A special type of footwear is for soldiers and police officers, which is used in different environmental conditions (for cold and/or hot weather).

Military footwear has to fulfill many specific requirements, from maintaining and improving mobility to maximizing protection and eliminating or minimizing the risk to the wearer (protection against ballistics, low temperatures, heat, degradation of human perspiration or microbiological agents, insects and snake bites etc.). Therefore, designing proper military footwear represents a major challenge not only for designers, but also for engineers.

When developing new products, considerable efforts must be made in designing the process, from the correct choice of materials, construction type and technological concept, to prototypes and consumer preferences (Figure 1) [1]. Only in this way the new product will be designed and functionalized according to the needs and requirements of the end user.

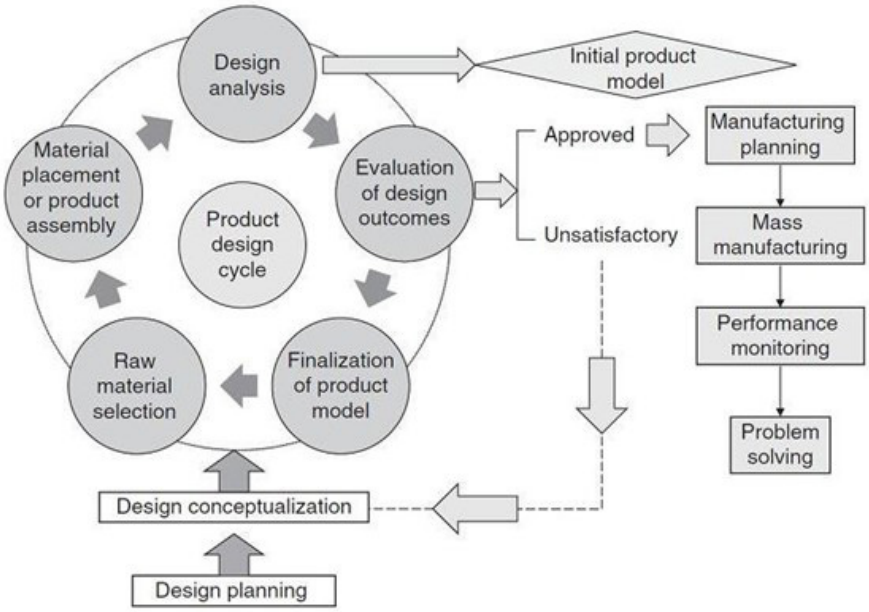

Figure 1. Product design concept

The process of designing specific products (for example, protective clothing or footwear) includes the entire design activity for the development of new products with high technological content, from the initial idea and the first project concept to the feasibility analysis, taking into account the materials to be tested during design, prototyping and manufacturing [2]. Designing specific products means balancing design requirements with function, performance, protection and comfort [3, 4]. This paper presents the development of boots for hot and cold climatic conditions, specifically for the work uniform of police officers working in prisons.

EXPERIMENTAL

The purpose of the study is to develop multifunctional footwear for prison police officers, which can be worn in different climatic conditions, both during hot and cold weather. According to the common product design cycle (Figure 1), the design analysis, the material

selection, the product assembly mode, the evaluation of the design results, the prototyping, the prototype testing in real environment and the prototype corrections were performed according to the preferences and recommendations of the end user. As a result of such an integrated and iterative process of product development, a multifunctional product is developed for hot and cold weather conditions.

RESULTS AND DISCUSSIONS

As a result of a survey on functionality, ergonomics, comfort, protection, shape, weight, etc. conducted among the end users the sketch of the boots that are part of the work uniform was made (Figure 2).

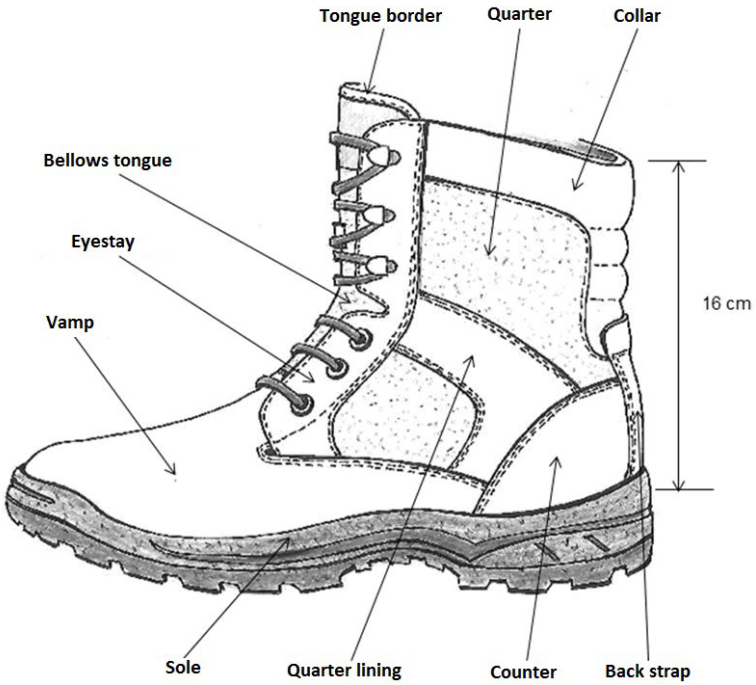

Figure 2. Sketch of the boots used as part of work uniform

Because there are many different component parts that make up the product, it is very important to choose the right materials that meet all end-user requirements regarding tensile strength, flexural strength, hardness, abrasion, etc., while ensuring adequate comfort for the wearer, both in hot and cold environments. In addition, the materials for all 70 component parts must be able to be combined together, ensuring aesthetic and functional value, as well as comfort.

Thus, the shoe uppers are made of natural black bovine leather (vamp, counter, back strap, collar, quarter lining, eyestay, eyestay lining), but also of textile material (quarters and tongue). Both leather and textile material are chemically waterproofed.

The upper leather must be waterproof, with a thickness of 1.8 to 2 mm, so that it can meet the parameters related to tear strength and load resistance. These parameters influence the quality, strength, elasticity and plasticity during the manufacturing process and on the final product - the boots. Also, according to environmental standards, the chromium content should be undetectable. Other parameters (water permeability, water absorption, water vapor permeability) are closely related to foot comfort when wearing boots.

The textile material for uppers is a Cordura-type fabric and must be resistant to water penetration.

The inner linings are made of pig basan (counter lining), but also of textile material (quarter lining, vamp and tongue). The linings are stitched in a zig zag pattern and the seams are heat sealed.

The intermediate linings are made of a thermo-adhesive textile material (vamp reinforcement and quarter reinforcement), a self-adhesive material (eyestay) and a self-adhesive sponge (intermediate collar lining and intermediate tongue lining).

The sole is bicomponent (rubber + polyurethane), directly injected into the double density system. The outer layer has a high density which ensures increased wear resistance. The inner layer has a lower average density than the outer layer, which ensures an elasticity that takes over the mechanical shocks and allows an efficient distribution of body weight. The outsole has a non-slip appearance with regular shapes on the outer surface. No bumps or irregularities are allowed on the visible side of the sole.

The locking system is stitching with eyelets and a black cotton lace.

The boots are made using the injection system (shoes with soles directly injected on the uppers).

No metallic elements are allowed in the boots, in order not to elicit a false alarm during antiterrorist and specialized control, when accessing the penitentiary.

Table 1 presents the characteristics of the materials used to make the boots as part of the work uniform of prison police officers.

Table 1: Characteristics of materials used to make the boots for prison police officers

No.	Material	Size (mm)	Nature of material	Use
1.	Natural bovine black leather, smooth grain, chemically waterproofed	1.8-2 (thickness)	Bovine leather	Vamp, counter, back strap, collar
2.	Natural bovine black leather, smooth grain, chemically waterproofed	1.2-1.4 (thickness)	Bovine leather	Quarter lining, eyestay, eyestay lining
3.	Double layer Cordura waterproof fabric	3 (thickness)	Synthetic	Quarters
4.	Simple Cordura waterproof fabric	0.5 (thickness)	Synthetic	Bellows tongue
5.	Textile material doubled with polyurethane foam	1.6 (thickness)	Synthetic	Inner lining for quarters, vamp and tongue
6.	Self-adhesive sponge	8 (thickness)	Synthetic	Intermediate lining for collar
7.	Self-adhesive sponge	6 (thickness)	Synthetic	Intermediate lining for tongue
8.	Thermoadhesive fabric	0.4-0.5 (thickness)	Cotton	Reinforcement for vamp and quarters
9.	Self-adhesive reinforcement	0.4-0.5 (thickness)	Non-woven textile	Reinforcement for eyelets
10.	Cotton strap	12 (width)	Cotton	Tongue border
11.	Self-adhesive strap	10 (width)	Synthetic	Sealing the stitches
12.	Thermoadhesive reinforcement	1.7 (thickness)	Thermoplastic material	Toe-cap
13.	Thermoadhesive reinforcement	2 (thickness)	Thermoplastic material	Rigid counter
14.	Tubular cotton laces	1300 (length)	Cotton	Lacing
15.	Expanded EVA doubled with textile material, preformed	2.2 (thickness)	EVA + synthetic	Insole cover
16.	Synthetic thread	30/3 Nm 40/3 Nm	Synthetic	Sewing uppers and linings
17.	Black round eyelets	Ø 5 mm	Plastic / composite material with high hardness	Lacing, 12 pcs/pair

18.	Hooks for lacing	Plastic / composite material with high hardness	Lacing, 12 pcs/pair
19.	Adhesives	Manual solution	Upper gluing
20.	Injected sole	Rubber + Polyurethane	Sole
21.	Colourless wax		Finishing
22.	Dye for upper retouching		Retouches

Table 2 presents the requirements that must be met by materials used for the boots and the finished product.

Table 2: Physical-mechanical parameters required for the materials and the finished product

Specifications	Standard	U/M	Imposed values
Leather			
Tensile strength	SR EN ISO 3376:2012	N/mm^2	min. 24
Water resistance of flexible leather - absorption after 3h - amount of water passed through the leather	SR EN ISO 5403-1:2012	% g/h	max. 45 max. 2.5
Water vapour permeability	SR EN ISO 14268:2013	mg/cm^2h	min. 0.8
Flexural strength	SR EN ISO 5402-1:2012	cycles	250000
Sole			
Hardness - outer layer - inner layer	SR ISO 7619-1:2011	°ShA	70±5 60±5
Abrasion strength	SR EN 12770:2002	mm^3	max. 250
Flexural strength	SR EN ISO 17707:2005	cycles	100000
Material for quarters			
Resistance to water penetration	SR EN 811:2018	mm col. water	min. 10000
Bellows tongue material			
Moisture resistance (Spray-test)	SR EN ISO 4920:2013	note	min. 4
Lining			
Tear strength	SR EN ISO 13937-3:2002	N	min. 20
Abrasion strength	SR EN ISO 12947-2:2017	no. of cycles	min. 25000
Finished product			
Leather upper and sole peel resistance	SR EN ISO 17708:2004	N/mm	min. 4

In accordance with the specified materials and the chosen technology, the prototypes were made and offered to the volunteers for real field tests in hot and cold environment. The feedback was positive from almost all users, which meant that all their requests and expectations were met, although some suggested that the size of the boots could be better adjusted to the type of foot (narrower, wider, etc.). Based on these results, the final shape of the multifunctional boots for hot and cold weather conditions (Figure 3) was established. They will be standard equipment for prison police officers, as they are comfortable and durable boots.

Figure 3. Multifunctional footwear for hot and cold weather

CONCLUSIONS

The production of a type of footwear that can be worn even in hot and cold weather conditions, intended for use during service by the penitentiary police officers, proved to be possible by the multifunctional design of a new product, made through the interdisciplinary team work of engineers and designers, in accordance with the requirements and suggestions of end users.

Acknowledgements

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AGE-RELATED INFLUENCE OF OBESITY ON PLANTAR PRESSURE IN CHILDREN AGED 7-14

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AGE-RELATED INFLUENCE OF OBESITY ON PLANTAR PRESSURE IN CHILDREN AGED 7-14

ABSTRACT. Obesity is an important factor influencing foot geometry and function, especially for children whose musculoskeletal system are experiencing growth and maturation. The objective of this study was to examine the development of plantar pressure for the obese and normal-weight children aged 7-14 years, and the difference between the two groups in this developing duration. Totally 288 children (138 normal-weight and 150 obese) were included into the data analysis. Plantar pressure measurements were performed during barefoot walking in a self-selected speed. Contact areas, pressure-time integrals (PTI) and force-time integrals in ten plantar regions were obtained to calculate the arch index (AI) and the relative force-time integral (relFTI). Results showed that: the AI and PTI were evidently higher for obese children compared to the normal-weight group. The AI seemed to be even with age for both groups. PTI values of both groups elevated with increasing age and significance appeared from the age of 11. RelFTI values were significantly higher in lateral forefoot (M3-5) and midfoot (MF) for obese children. And the age-related changes of relFTI were different in obese children compared with normal weight ones. Obesity would obstruct normal age-related development of plantar pressure distribution.

KEY WORDS: obesity, children, footwear design

INFLUENȚA OBEZITĂȚII ÎN FUNCȚIE DE VÂRSTĂ ASUPRA PRESIUNII PLANTARE LA COPIII CU VÂRSTELE DE 7-14 ANI

REZUMAT. Obezitatea este un factor important care influențează geometria și funcția piciorului, în special pentru copiii al căror sistem musculo-scheletic crește și se maturizează. Obiectivul acestui studiu a fost de a examina dezvoltarea presiunii plantare la copiii obezi și cu greutate normală cu vârste cuprinse între 7 și 14 ani și diferența dintre cele două grupuri în această perioadă de dezvoltare. În analiza datelor au fost incluși 288 de copii (138 cu greutate normală și 150 obezi). Măsurătorile de presiune plantară au fost efectuate în timpul mersului desculț cu o viteză la alegere. S-au obținut zonele de contact, integralele presiune-timp (PTI) și integralele forță-timp în zece regiuni plantare pentru a calcula indicele plantar (AI) și integrala relativă forță-timp (relFTI). Rezultatele au arătat că AI și PTI au fost evident mai mari în cazul copiilor obezi în comparație cu grupul de copii cu greutate normală. AI părea să se echilibreze odată cu vârsta pentru ambele grupuri. Valorile PTI ale ambelor grupuri au crescut odată cu vârsta, având o semnificație crescândă de la 11 ani. Valorile RelFTI au fost semnificativ mai mari în zona laterală a antepiciorului (M3-5) și la nivelul zonei de mijloc (MF) în cazul copiilor obezi. Modificările relFTI în funcție de vârstă au fost diferite la copiii obezi în comparație cu cei cu greutate normală. Obezitatea împiedică dezvoltarea normală a distribuției presiunii plantare în funcție de vârstă.

CUVINTE CHEIE: obezitate, copii, proiectarea încălțămintei

L'INFLUENCE DE L'OBÉSITÉ LIÉE À L'ÂGE SUR LA PRESSION PLANTAIRE CHEZ LES ENFANTS DE 7 À 14 ANS

RÉSUMÉ. L'obésité est un facteur important qui influence la géométrie et la fonction du pied, en particulier pour les enfants dont le système musculo-squelettique connaît une croissance et une maturation. L'objectif de cette étude a été d'examiner le développement de la pression plantaire chez les enfants obèses et de poids normal âgés de 7 à 14 ans, et la différence entre les deux groupes dans cette durée de développement. Au total, 288 enfants (138 de poids normal et 150 obèses) ont été inclus dans l'analyse des données. Des mesures de pression plantaire ont été effectuées lors de la marche à pieds nus à une vitesse auto-sélectionnée. Les zones de contact, les intégrales pression-temps (PTI) et les intégrales force-temps dans dix régions plantaires ont été obtenues pour calculer l'indice de la voûte plantaire (AI) et l'intégrale force-temps relative (relFTI). Les résultats ont montré que l'AI et le PTI ont été évidemment plus élevés chez les enfants obèses que pour le groupe des enfants au poids normal. L'AI semblait s'équilibrer avec l'âge pour les deux groupes. Les valeurs de PTI des deux groupes ont augmenté avec l'âge et une signification est apparue dès l'âge de 11 ans. Les valeurs de relFTI ont été significativement plus élevées à l'avant-pied latéral (M3-5) et au milieu du pied (MF) pour les enfants obèses. Les changements des relFTI liés à l'âge ont été différents chez les enfants obèses par rapport à ceux de poids normal. L'obésité empêche le développement normal de la répartition de la pression plantaire selon l'âge.

MOTS CLÉS : obésité, enfants, conception de chaussures

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INTRODUCTION

Obesity has been associated with orthopedic problems due to the increasing joint stress and overload on the musculoskeletal structures, especially for the children and adolescents whose musculoskeletal system are experiencing maturation [1-3]. Children obesity is commonly related to a flatter foot pattern and a lower postural stability, resulting in bad performance in some weight bearing activities and higher risks of injuries [2, 4-8]. Foot is the medium between human body and the environment (ground) [9] and therefore the excess weight, laying more burden on children's muscles and bones of lower extremities, will affect the plantar pressure distribution in some way. Studies have found larger contact areas and increased plantar pressure for the obese children while walking or running [10, 11]. Similar difference was reported by Yan *et al*. [2, 12], and their data also showed an increase in the arch index of the obese children's left feet. Therefore, special shoe lasts are needed in footwear design for children with obesity.

Children's musculoskeletal system is subject to complex developmental processes of bony and muscular structures [13], making it a typical gait pattern and foot geometry as well as its special developmental changes different from the adults [14]. Researchers have studied the development of gait in normal children and adolescents, involving both the cross-sectional studies and the longitudinal investigations [13, 15-19]. It was reported that children's plantar peak pressure increased with age, and the relative maximum force in the midfoot decreased accompanied by a higher foot arch [13]. Furthermore, the area, in which the highest peak pressure appeared, turned from rearfoot to forefoot with increasing age [19]. Therefore, some reference data were exhibited for normal children's gait recognition regarding plantar pressure and foot arches [13, 16, 20-23].

While most previous cross-sectional and follow-up literature was focused on the normal children, data of gait development for obese children are lacking. According to a deep literature review, Mueller *et al*. [24] discussed the influence of obesity on foot loading for consecutive years, and found that obese children showed greater difference with increasing age in midfoot loading (FTI) compared to normal-weight ones. Obese children would have higher incidences to become obese adults [25], and the effect of obesity on the children's gait might be long-term. Therefore, it's imperative to figure out the development of the special gait for obese children during childhood, to establish a reference database of gait pattern like that of the normal weight children. Analysis of more foot function parameters and larger age ranges need to be conducted.

The purpose of this study was two-fold: first, to investigate the influence of obesity on plantar pressure through childhood to early adolescence. Second, it aimed to investigate the age-related changes in plantar pressure of obese children ranging from 7 to 14 years. It can expectedly provide a better understanding of age-related plantar pressures in children with obesity. It was anticipated that this may enable the adaptation and improvement of materials of shoe components and structures and sizes of shoe lasts when designing footwear for children with obesity.

METHODS

Participants

This study involved 734 children, recruited from randomly selected local primary school and middle school in Yantai city, China. Children were excluded if they had any history of lower extremity injuries, gross gait abnormalities, neuromusculoskeletal condition or cardiovascular diseases. Furthermore, to avoid gender difference [26], we focused on plantar pressure in obese boys in this study. Finally 138 normal-weight (NW) and 150 obese (OB) boys aged 7 to 14 years old were screened according to the Chinese body mass Index reference norm [27]. Basic information of the participants is detailed in Table 1. Written informed consent was received from parents of all potential participants prior to the test. The study was approved by the Ethics Committee of Sichuan University.

Table 1: Basic information of the participants

Age	NW				OB			
	N	Height/cm	Body mass/kg	BMI/(kg/m²)	N	Height/cm	Body mass/kg	BMI/(kg/m²)
7	19	126.8 ± 3.6	24.4 ± 2.8	15.2 ± 1.1	13	134.5 ± 6.2	41.0 ± 7.9	22.5 ± 2.7
8	46	130.6 ± 4.1	27.1 ± 2.8	15.8 ± 1.2	33	138.0 ± 5.3	44.6 ± 7.2	23.3 ± 2.7
9	16	135.4 ± 5.0	30.4 ± 4.1	16.6 ± 1.6	21	142.6 ± 5.9	51.1 ± 7.8	25.0 ± 2.4
10	15	143.0 ± 6.5	34.5 ± 5.9	16.7 ± 1.8	20	148.2 ± 6.6	58.0 ± 8.7	26.3 ± 2.6
11	14	147.7 ± 6.3	39.3 ± 5.5	17.9 ± 1.6	15	152.4 ± 7.3	65.4 ± 10.6	28.0 ± 2.7
12	15	155.0 ± 7.6	42.2 ± 6.4	17.5 ± 2.1	24	163.6 ± 7.0	75.7 ± 8.6	28.3 ± 2.9
13	9	162.8 ± 7.3	50.4 ± 7.9	18.9 ± 1.5	14	169.3 ± 8.3	84.8 ± 12.9	29.4 ± 2.6
14	4	164.9 ± 6.5	54.0 ± 6.2	19.8 ± 1.0	10	171.5 ± 6.2	88.8 ± 4.2	30.2 ± 1.5

Plantar Pressure Measurements

Plantar pressure data were collected using a Footscan® plate system (RSscan Inc., Belgium; 7.7kg; 1068mm×418mm×12mm; 4 sensors/cm²) with a sampling rate of 250Hz. The plantar pressure plate was mounted in the middle of a 6-m rigid rubber track of same height, to estimate a natural walking condition. After a familiarization with the plate and the experimental procedure, participants were asked to walk through the plates barefoot at a self-selected speed, using a "two-step" initial protocol, which confirmed two complete footprints on the plate (Figure 1). Five successful footprints of each foot were recorded.

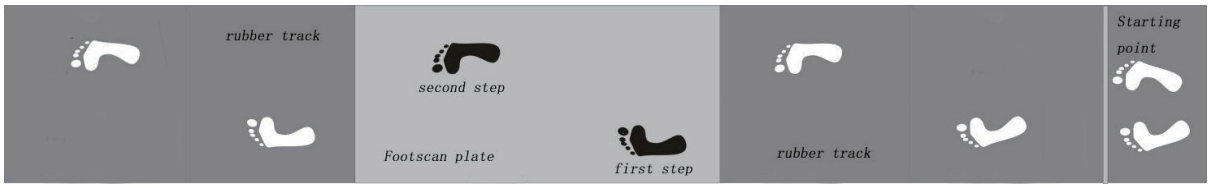

Figure 1. "Two-step" initial protocol

Data Analysis

Foot was divided into ten regions by Footscan® software and artificial adjustments according to the anatomical principal: Toe 1 (T1), Toes 2-5 (T2-5), the first to fifth metatarsal (M1, M2, M3, M4, M5), Midfoot (MF), Heel medial (HM), Heel lateral (HL).

Only the pressure data of the right foot were analyzed in this study [28]. Data of related parameters from three relative stable measurements of each subject were averaged for each participant. The parameters included arch index (AI), pressure-time integral (PTI, N·s/cm²) and relative force-time integral (relFTI, %) of ten regions. A high arch would result in a small AI according to Cavanagh's definition [29], and the relFTI (the FTI in one region divided by the FTI of all regions) would indicate the plantar pressure distribution to some extent [30]. The AI described by Cavanagh *et al*. [29] and the relFTI were calculated as follows:

$$AI = \frac{CA_{Midfoot}}{CA_{forefoot} + CA_{midfoot} + CA_{hindfoot}} \quad (1)$$

$$relFTI = \frac{FTI}{\sum FTI} \times 100\% \quad (2)$$

Statistical Analysis

Normality of the data for every group was assessed using Frequencies analysis and Kolmogorov-Smirnov test, and all data were found to be normally distributed (skewness<1, kurtosis<1; p>0.05). Differences between NW and OB in each age stage were tested by Independent Samples T Test. One-way ANOVA test was applied to evaluate differences among 8 age stages (7-14 years old), separately for either

body type group, with a Bonferroni correction and post-hoc test.

RESULTS

Higher AI values were found in the obese children through the ages during 7 and 14 years old. No systematic increase or decrease was observed with the increasing age in either of the two groups (Figure 2).

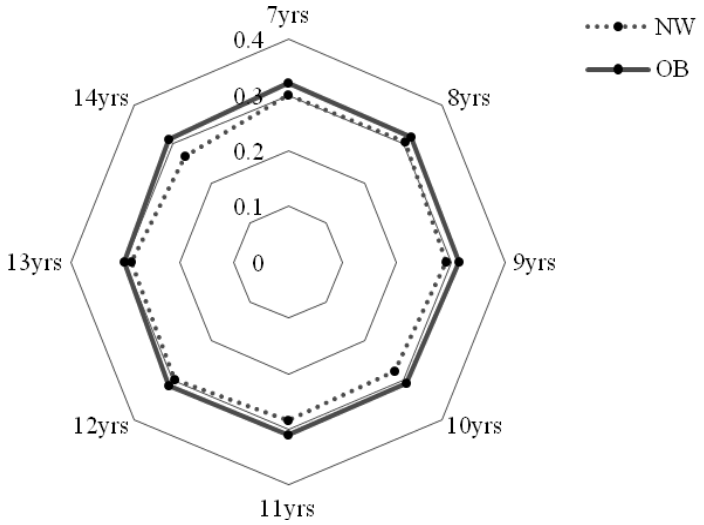

Figure 2. The AI in obese and normal-weight participants aged 7-14

Obese children showed relatively higher pressure-time integrals than their normal-weight counterparts in all plantar regions (Table 2). And the significance was found in almost all the foot regions except for T1 and T2-5, in which the significances were only found in 7 year-old children.

The pressure-time integral (PTI) for both of the BMI groups showed a continuous increase with age in almost every foot region. Significances were found in forefoot, midfoot and heel areas between age groups for obese children. The PTI in normal weight children were in the same conditions, but for the midfoot (p=0.052). Significantly higher PTI values were observed in most areas at the age of 12-14 compared to those at the age of 7-9.

Table 2: The pressure-time integral (PTI, N·s/cm²) for the participants aged 7-14

		7	8	9	10	11	12	13	14	p
T1	NW	**0.6 (0.4)**	0.7 (0.6)	0.7 (0.3)	0.9 (0.4)	0.7 (0.4)	1.1 (0.7)	1.0 (0.5)	1.1 (0.3)	0.101
	OB	**1.2 (0.8)**	1.2 (0.8)	1.2 (0.7)	1.3 (0.8)	1.1 (0.6)	1.5 (0.8)	1.4 (0.8)	2.1 (1.4)	0.068
T2-5	NW	**0.2 (0.1)**	0.2 (0.2)	0.2 (0.1)	0.2 (0.1)	0.2 (0.1)	0.2 (0.1)	0.6 (0.2)	0.2 (0.1)	0.729
	OB	**0.3 (0.2)**	0.2 (0.2)	0.2 (0.1)	0.3 (0.2)	0.3 (0.3)	0.3 (0.2)	0.2 (0.1)	0.5 (0.2)	0.099
M1	NW	**0.7 (0.5)**	**0.9 (0.6)**	**1.0 (0.5)**	1.3 (0.6)	1.1 (0.5)	**1.1 (0.6)**	1.6 (0.6)7	1.9 (1.0)[7 8]	0.000*
	OB	**1.5 (1.1)**	**1.6 (1.1)**	**1.6 (0.7)**	1.5 (0.6)	1.5 (0.8)	**1.7 (0.8)**	2.4 (1.2)	2.4 (1.3)	0.022*
M2	NW	**1.4 (0.8)**	**1.8 (1.1)**	**2.2 (0.9)**	**2.7 (0.8)**[7]	**2.6 (1.3)**	**2.7 (1.3)**[7]	**3.8 (0.9)**[7-9]	**3.9 (1.0)**[7 8]	0.000*
	OB	**3.2 (2.2)**	**3.2 (1.4)**	**3.5 (0.9)**	**3.6 (1.0)**	**3.7 (1.6)**	**5.0 (2.1)**[8]	**5.9 (2.4)**[7-11]	**6.0 (1.4)**[7-11]	0.000*
M3	NW	**1.6 (0.9)**	**1.9 (1.3)**	**2.2 (0.8)**	**2.5 (0.6)**	**2.8 (1.7)**	**3.3 (1.3)**[7 8]	**3.8 (1.0)**[7-9]	**4.1 (1.9)**[7 8]	0.000*
	OB	**3.6 (1.9)**	**3.6 (1.4)**	**4.0 (1.3)**	**4.2 (1.5)**	**4.8 (1.8)**	**6.0 (2.2)**[7-10]	**6.6 (2.1)**[7-10]	**7.0 (1.0)**[7-10]	0.000*
M4	NW	**1.3 (0.9)**	**1.5 (1.0)**	**1.7 (0.8)**	**1.7 (0.5)**	**2.4 (1.9)**	**2.6 (0.9)**[7 8]	**2.9 (0.7)**[7 8]	**2.7 (1.4)**	0.000*
	OB	**2.9 (1.2)**	**3.0 (1.2)**	**3.3 (1.1)**	**3.8 (1.2)**	**4.4 (2.6)**	**5.3 (2.0)**[7-9]	**5.2 (1.7)**[7-9]	**5.4 (1.1)**[7-9]	0.000*
M5	NW	**0.4 (0.3)**	**0.5 (0.5)**	**0.6 (0.4)**	**0.6 (0.3)**	**1.0 (0.6)**[7 8]	**1.1 (0.7)**[7 8]	**1.4 (0.7)**[7-9]	**0.8 (0.5)**	0.000*
	OB	**1.2 (0.8)**	**1.2 (0.6)**	**1.6 (0.8)**	**1.8 (0.7)**	**2.3 (2.0)**[8]	**2.8 (1.4)**[7-9]	**2.2 (0.9)**	**2.7 (0.8)**[7 8]	0.000*
MF	NW	**0.4 (0.3)**	**0.5 (0.3)**	**0.5 (0.3)**	**0.5 (0.3)**	**0.5 (0.4)**	**0.6 (0.4)**	**0.9 (0.4)**[7 8]	**0.4 (0.2)**	0.052
	OB	**1.0 (0.7)**	**0.9 (0.5)**	**1.2 (0.5)**	**1.2 (0.4)**	**1.2 (0.7)**	**1.3 (0.6)**	**1.7 (0.9)**[8]	**1.5 (0.7)**	0.002*
HM	NW	1.5 (0.9)	**1.7 (1.0)**	**1.7 (0.7)**	**2.1 (0.7)**	2.0 (1.1)	**2.1 (0.7)**	**2.6 (1.1)**	2.7 (0.8)	0.028*
	OB	2.2 (1.2)	**2.2 (1.0)**	**3.2 (1.0)**	**2.9 (0.7)**	2.9 (1.4)	**3.0 (1.3)**	**4.1 (1.8)**[7 8]	3.9 (1.3)[7 8]	0.000*

HL	NW	**1.1 (0.8)**	**1.4 (0.8)**	**1.6 (0.8)**	**1.8 (0.7)**	1.8 (1.2)	**2.1 (0.8)[7]**	**2.30 (0.8)[7]**	**2.1 (0.5)**	0.002
	OB	**2.0 (1.2)**	**1.9 (1.0)**	**2.7 (0.7)**	**2.6 (0.7)**	2.6 (1.5)	**2.9 (1.2)[8]**	**3.6 (1.5)[7 8]**	**3.6 (1.1)[7 8]**	0.000

Figures in bold indicate significant difference between obese participants and the normal-weight counterparts ($p<0.05$). [n] significantly different from PTI at age of n, e.g. [7-11] in M2 area of 13 year-old OB group indicates that significant differences for PTI were found for children with obesity between age of 13 and 7. 8, 9, 10, 11, respectively; *$p<0.05$, significantly different between age groups, by One-way ANOVA test.

The relative force-time integral data were illustrated in Table 3. Higher values of the relFTI were found for the 7-14 years obese children in lateral forefoot (M3, M4 and M5) and the midfoot. Conversely, the obese cohort showed lower relFTI in the Toes (T1, T2-5), medial forefoot (M1 and M2) and the heel (HM and HL). Significance of the difference nearly disappear from age of 11.

Rare significantly regular changes were found between and within age groups in relFTI values of both obese and normal weight children. RelFTI in midfoot for normal weight participants kept decreasing with aging, but those of obese children kept a relatively even trend.

Table 3: The relative force-time integral (relFTI, %) for the participants aged 7-14

		7	8	9	10	11	12	13	14	p
T1	N	6.7 (3.5)	7.3 (4.6)	6.7 (3.3)	6.9 (3.1)	7.0 (5.6)	7.9 (5.2)	5.8 (3.2)	7.5 (1.5)	0.960
	O	6.9 (3.3)	6.5 (3.5)	5.6 (3.0)	5.5 (2.8)	4.6 (3.0)	5.5 (2.7)	5.2 (3.1)	6.4 (4.3)	0.474
T2-5	N	2.9 (2.4)	2.3 (1.9)	2.1 (1.4)	3.2 (3.6)	1.6 (1.3)	1.8 (1.3)	**2.2 (1.2)**	2.1 (1.1)	0.409
	O	1.9 (1.0)	2.0 (2.0)	1.5 (1.1)	1.8 (1.2)	1.9 (1.8)	1.4 (0.9)	**1.1 (0.7)**	2.2 (1.2)	0.309
M1	N	10.6 (7.6)	11.3 (6.7)	11.5 (5.8)	**11.0 (5.0)**	10.5 (5.8)	9.0 (5.7)	9.6 (3.8)	12.4 (5.9)	0.929
	O	9.4 (4.0)	11.7 (6.7)	8.7 (4.2)	**7.7 (3.2)**	8.1 (4.2)	7.1 (3.4)	8.9 (3.3)	8.8 (5.1)	0.017*
M2	N	12.0 (5.2)	12.2 (6.1)	**14.4 (6.4)**	13.8 (5.4)	14.5 (4.7)	12.4 (5.9)	12.7 (2.3)	14.1 (1.3)	0.744
	O	12.5 (4.5)	13.0 (4.8)	**10.9 (2.5)**	11.0 (2.7)	12.2 (4.8)	13.4 (5.4)	12.7 (3.6)	12.2 (2.5)	0.428
M3	N	**11.2 (3.4)**	**10.5 (4.4)**	11.6 (4.0)	11.8 (4.3)	12.6 (4.1)	13.5 (2.6)	12.8 (3.9)	13.9 (3.0)	0.162
	O	**13.9 (4.0)**	**13.4 (3.9)**	11.5 (3.0)	12.2 (3.6)	13.3 (3.3)	14.7 (3.4)	13.6 (2.6)	13.3 (2.1)	0.203
M4	N	8.3 (4.7)	**7.5 (3.3)**	8.4 (3.1)	**8.1 (2.7)**	9.8 (4.8)	10.3 (3.1)	9.7 (2.8)	8.9 (3.5)	0.149
	O	11.0 (3.5)	**10.0 (3.1)**	9.3 (2.6)	**10.8 (3.3)**	11.1 (4.1)	12.5 (4.5)	10.2 (2.2)	10.0 (2.5)	0.076
M5	N	**2.2 (1.8)**	**2.5 (2.2)**	**3.3 (2.0)**	**3.6 (1.6)**	4.5 (2.3)	4.5 (2.9)	4.7 (2.4)	**2.8 (2.0)**	0.002*
	O	**3.9 (1.6)**	**4.1 (2.1)**	**4.9 (2.4)**	**6.0 (2.8)**	6.6 (4.1)	6.1 (2.8)	4.6 (1.7)	**5.4 (1.4)**	0.007*
MF	N	12.9 (8.5)	11.8 (6.5)	**10.7 (5.6)**	**10.4 (6.0)**	**8.4 (5.8)**	9.5 (6.5)	12.0 (5.6)	5.7 (2.8)	0.317
	O	15.2 (6.8)	14.2 (7.5)	**15.9 (7.4)**	**14.8 (6.0)**	**14.4 (5.5)**	13.4 (5.8)	15.0 (7.5)	14.1 (7.5)	0.963
HM	N	**20.7 (11.4)**	**20.4 (9.9)**	17.7 (4.7)	16.8 (4.7)	17.4 (7.0)	16.3 (5.8)	17.3 (6.1)	19.0 (1.2)	0.536
	O	**13.8 (4.0)**	**14.3 (4.0)**	18.4 (5.2)	16.8 (5.2)	16.1 (5.8)	14.2 (6.2)	16.2 (4.1)	15.49 (4.8)	0.063
HL	N	12.6 (4.8)	**14.3 (6.6)**	13.8 (3.4)	14.3 (3.8)	13.7 (6.8)	14.7 (5.8)	13.2 (3.8)	13.63 (3.7)	0.959
	O	11.6 (4.1)	**10.7 (4.1)**	13.4 (3.1)	13.2 (3.8)	11.8 (4.5)	11.8 (4.6)	12.5 (3.8)	12.13 (3.4)	0.322

Figures in bold indicate significant difference between obese participants and the normal-weight counterparts ($p<0.05$), by Independent Samples T Test; *$p<0.05$, significantly different between age groups, by One-way ANOVA test.

DISCUSSION

Since BMI (obesity) and age are both important factors for children' gait and foot function [2, 4, 13, 15, 31], the study purposed to examine the different development of the plantar pressure distribution (PTI, relFTI) and foot geometry (AI) between the obese and the normal weight children across their body growth and maturation (7-14 years old).

Although obese children generated a higher arch index than the normal-weight ones, no evident increasing or decreasing trends were found in the AI parameters, suggesting that the longitudinal arches have finished developing before 7 years old for both of the BMI groups. The findings are partly consistent with the results from Mueller *et al*. [24], who established AI data in 1-12 years old normal-weight, overweight and obese children and found that the arch indexes for the three groups decreased with age until about 7 years old. Bosch *et al*. [13] also gained similar AI trend for normal children in a longitudinal investigation. However, the AI values in the two studies seemed lower than those in

the same BMI categories of this study, which may be resulted from different plantar divisions and regional differences between China and Germany. The relatively even development of arch index in the obese cohort may indicate that a "maturation" stage similar with the normal-weight children would occur before the age of 7, which meant that the influence of obesity did exist on the longitudinal arch, but it would not accumulate with age after 7 years old.

Significant differences in pressure-time integral of obese and normal weight children found in the present study agree with the previous research [21, 32]. Distinctly higher PTI was observed in the 7-14 years old obese children except the toes regions after age of 8. Both the obese and normal weight participants generated elevated pressure impulses with aging due to the increasing body mass and BMI values. PTI in most plantar regions were found to be significantly different between age groups. Furthermore, significance began to appear at age of 12-14 compared to age of 7-9, even 10 and 11 years old in several regions (M2, M3). It could be concluded that age is a substantial factor considering about plantar pressures, as a potential result of maturation development and appearance of secondary sexual characteristics in the early adolescence.

The relative force-time integral in the present study indicated a disproportional foot loading distribution in obese children, with lower relFTI in toes (T1 and T2-5), medial forefoot (M1 and M2) and heel (HM and HL) and higher relFTI in lateral forefoot (M3-5) and midfoot (MF). This kind of imbalance can also be partly found in the study of Mueller *et al*. [24], who examined the influence of obesity on FTI for children aged 1 to 12 years. Some studies identified highly elevated FTI in the midfoot and the lateral forefoot for obese children [32, 33]. Therefore, in the context of higher plantar loads compared to the normal-weight counterparts, load transferences to the lateral forefoot and the midfoot would happen in obese children. However, few significances in relFTI difference of obesity were found after 11 years old. So, obesity would make a difference on plantar pressure distribution and the degree of the impact is partially dependent on age.

It is interesting to find that relFTI values in midfoot of obese children nearly kept unchanged with age, while in midfoot of normal children, relFTI decreased with aging, resulting from the development of longitudinal arch and a natural pressure distribution. One reasonable explanation is that the excess weight laying on the longitudinal arch will cause some collapse, which could also be supported be the larger AI values in the present study. As a result, obesity impedes normal distribution, caused by body development with age, of plantar pressure.

CONCLUSION

Overall, although obese children have lower foot arches and take larger plantar pressures, the arch development got into maturation before 7 years old for both groups in this study. Foot pressures increased with age and difference showed significance between early-adolescence (12-14 years old) and late-childhood (7-10 years old) stage. Foot loading for obese children would transfer to lateral forefoot and the midfoot compared to the normal weight ones. And the plantar pressure distribution in midfoot of obese children cannot change normally with age, which may be caused by collapse of foot arch. Therefore, special footwear design for obese children is necessary and it would be better to consider about different age stages.

Limitation and Suggestion

As the time the children have become obese was unknown and inconsistent in this cross-sectional study, further research is needed to examine the long- and short-term influence of obesity during children's development. And due to our limited experiment equipment, our results and discussion could only involve plantar pressure and potential relevance. Further studies combining kinematic data, direct clinical measures, radiographic measures and physical examination would contribute towards a better understanding of the age-related foot function of children with obesity.

Conflict of Interest

There are no conflicts of interest associated with this research.

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MODIFICATION OF WATERBORNE PU FINISHING AGENT WITH HYDROXYL SILICONE

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MODIFICATION OF WATERBORNE PU FINISHING AGENT WITH HYDROXYL SILICONE

ABSTRACT. In the present paper, a waterborne polyurethane (PU) finishing agent was synthesized with isophorone diisocyanate (IPDI), polytetrahydrofuran (PTMG), dimethylol propionic acid (DMPA) and n-butylamine, in which hydroxyl-terminated polydimethylsiloxane (OH-terminated PDMS) was added in three different ways, i.e., one-step, two-step and as a chain-extension agent. The PU was characterized using FT-IR and DSC and the water resistance and dry/wet rubbing resistance of the PU films were studied and compared. It was found that the chain segments by the reaction with OH-terminated PDMS and IPDI act as hard segments, and the elongation at break and water resistance of PU with OH-terminated PDMS as chain-extension agents are better than those with OH-terminated PDMS in both ways of one-step and two-step. The elongation at break could reach 1300% with the water absorption of only 1/4 of the latter PU films, when the same amount of OH-terminated PDMS is added in the system. It is better that OH-terminated PDMS is added in the top layer than added in the middle layer. The dry rubbing resistance could reach grade 5 with the wet rubbing resistance of grade 4.5.

KEY WORDS: waterborne polyurethane, polyurethane (PU), finishing agent, hydroxyl-terminated polydimethylsiloxane (Hydroxyl silicone)

MODIFICAREA UNUI AGENT DE FINISARE POLIURETANIC PE BAZĂ DE APĂ CU SILICON HIDROXIL

REZUMAT. În lucrarea de față, s-a sintetizat un agent de finisare poliuretanic (PU) pe bază de apă, cu diizocianat de izoforonă (IPDI), polietetrahidrofuran (PTMG), acid dimetilol propionic (DMPA) și n-butilamină, în care s-a adăugat polidimetilsiloxan cu hidroxil terminal (PDMS cu OH terminal) în trei moduri diferite, adică, într-o singură etapă, în două etape și ca agent de extensie a catenei. PU a fost caracterizat prin analiza FT-IR și DSC și s-au studiat și comparat rezistența la apă și la abraziunea uscată/umedă a peliculelor PU. Prin reacția cu PDMS cu OH terminal și IPDI, s-a constatat că segmentele de lanț acționează ca segmente dure, iar alungirea la rupere și rezistența la apă a PU cu PDMS cu OH terminal ca agenți de extensie a catenei sunt mai bune decât valorile PU cu PDMS cu OH terminal într-o singură etapă și în două etape. Alungirea la rupere poate ajunge la 1300% cu absorbția de apă a numai 1/4 din peliculele PU în varianta de sinteză în două etape, atunci când se adaugă aceeași cantitate de PDMS cu OH terminal. Este mai bine să se adauge PDMS cu OH terminal în stratul superior decât în stratul de mijloc. Rezistența la abraziune uscată poate atinge gradul 5, iar rezistența la abraziune umedă, gradul 4.5.

CUVINTE CHEIE: agent poliuretanic pe bază de apă, poliuretan (PU), agent de finisare, polidimetilsiloxan cu hidroxil terminal (silicon hidroxil)

MODIFICATION D'UN AGENT DE FINITION PU À BASE D'EAU AVEC DU SILICONE HYDROXYLÉ

RÉSUMÉ. Dans cet article, on a synthétisé un agent de finition polyuréthane (PU) à base d'eau avec du diisocyanate d'isophorone (IPDI), du polytétrahydrofurane (PTMG), de l'acide diméthylol propionique (DMPA) et de la n-butylamine, dans lesquels on a ajouté le polydiméthylsiloxane à terminaison hydroxyle (PDMS à terminaison OH) de trois manières différentes, c'est-à-dire en une étape, en deux étapes et comme agent d'extension de chaîne. Le PU a été caractérisé en utilisant l'analyse FT-IR et DSC et la résistance à l'eau et la résistance au frottement sec / humide des films PU ont été étudiées et comparées. On a constaté que, par la réaction avec PDMS à terminaison OH et IPDI, les segments de chaîne agissent comme des segments durs, et l'allongement à la rupture et la résistance à l'eau de PU avec PDMS à terminaison OH comme agents d'extension de chaîne sont meilleurs que ceux avec PDMS à terminaison OH ajouté en une seule étape et en deux étapes, également. L'allongement à la rupture peut atteindre 1300% avec l'absorption d'eau de seulement 1/4 de ces derniers films PU, lorsque la même quantité de PDMS à terminaison OH est ajoutée dans le système. Il est préférable que le PDMS à terminaison OH soit ajouté dans la couche supérieure plutôt que dans la couche intermédiaire. La résistance au frottement à sec peut atteindre le grade 5 et la résistance au frottement humide, le grade 4,5.

MOTS-CLÉS : agent polyuréthane à base d'eau, polyuréthane (PU), agent de finition, polydiméthylsiloxane à terminaison hydroxyle (silicone hydroxylé)

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INTRODUCTION

The present waterborne polyurethane cannot reach the level in the properties of solvent-based polyurethane [1,2]. However, only by changing the monomer ratio to improve the properties of polyurethane usually cannot meet the needs for excellent properties of polyurethane. So attempts have been done to modify the polyurethane in molecular level.

The internal rotation of the -Si-O-Si-bonds in silicone oil is very easy. So the materials with silicone are good in some physical properties and silicone oil has found a wide application in many fields. The use of organic silicone oil in the modification of polyurethanes should be a good way to prepare finishing agent for leather making. In the preparation of waterborne polyurethane modified with amino silicone, Chen *et al*. [3] found that with increasing the silicone oil content in the polyurethane film, the Young's modulus of the polyurethane decreased, while the tensile strength and elongation at break increased gradually. Similar results had been obtained by Zhu *et al*. [4] in their studies on the modification of polyurethane with hydroxyl silicone. In the study on the modification of polyurethane with amino silicone by Chen *et al*. [5], however, a different conclusion was obtained. They found that with increasing the amino silicone content, the elongation at break increased in the first period of stretching, followed by a decrease. The maximum elongation at break appeared at the silicone amount of 10%, an increase of 52%, compared with that of the unmodified polyurethane. At the same time, many studies had shown that the surface properties of polyurethane were changed by the addition of silicone. Chen *et al*. [3] found that the polarity of the polyurethane surface was changed when the silicone was added in the synthetic process of polyurethane. Zhu *et al*. [4] found that the surface tension of polyurethane decreased gradually with the increase of the amount silicone used. Silicone has a low surface tension and a high surface activity. With the increase of the silicone amount, the polysiloxane block content in the polyurethane molecular chain will increase, the polar intensity of the molecular chain will decrease, and the aggregation capacity of the molecules will be weakened. So the surface tension of the polyurethane emulsion was decreased. In short, the use of silicone is an effective way to increase the elongation at break of polyurethane, and the water resistance of waterborne polyurethane may be improved to a certain extent. However, from viewpoint of the low surface tension of polyurethane, silicone modification is not a very good choice, because the surface polarity is decreased and the adhesive force between polyurethane and the basis materials is weakened.

In the present work, with hydroxyl silicone as modifying agent, the polyurethane was modified by hydroxyl silicone to improve the flexibility and water resistance of polyurethane finishing agent. Three different ways were tried, i.e., one-step way, two-step way, and hydroxyl silicone chain-extension way. The elongation at break, FT-IR, DSC, water absorption and other properties of the polyurethane finishing agent were applied in the study. The final product was used in the finishing of leathers with the finishing results compared. It was indicated that the chain-extension way is the best in the three ways, indicating a potential application in the modification of PU finishing agent in leather making.

EXPERIMENTAL

Main Materials and Apparatus

Isophorone diisocyanate (IPDI, 95%), dimethylol propionic acid (DMPA), and poly tetrahydrofuran (PTMG, Mn=2000) were from Yantai Wanhua Polyurethane Co., Ltd, China. Hydroxyl silicone and n-butylamine were from Tianjin Chemical Reagent Factory, China. The dibutyltin dilaurate (AR) was from Chengdu Silicone Research Center, Ministry of Chemical Industry, China. Both triethylamine and acetone were analytical agent and purchased from Tianjin Chemical Reagent Factory, China. Thermal analyzer was made by the NETZSCH company, Germany. The FT-IR-8700-type variable temperature Fourier transform infrared spectrometer was made by Shimadzu, Japan. The CMT6000 universal electronic testing machine was from the New Sans Co. Ltd., Shenzhen, China. The MCJ-01A friction testing machine was from the Labthink technology development center, Jinan, China.

Synthesis of the Waterborne Polyurethane Finishing Agent

One-step

IPDI and PTMG were weighed with the -NCO/-OH ratio of 1.1:1. The DMPA was 8% in weight of the reaction mixture and the dibutyltin dilaurate was 3‰ in weight of the reaction mixture. The hydroxyl groups of the silicone were controlled at 5%, 10%, 15% and 20% of the total hydroxyl content in the polymerization. The DMPA, PTMG, and hydroxyl silicone were added to a four-necked bottle, and with dibutyltin dilaurate as catalyst, the mixture was allowed to react at 80°C for 3 hours to yield the prepolymer. In the prepolymerization process, some acetone was added to dissolve the pre-polymer. Some triethylamine was added for neutralization according to the amount of DMPA, and the mixture was rapidly cooled to 25°C. The n-butylamine, 10% of the amount of isocyanate groups in weight, was added for chain-extension at 80°C. The reaction time was 5 min. After being stirred for water dispersion at the speed of 500r/min, light blue translucent polyurethane emulsion was obtained.

Two-step

The procedure and the amount of all reagents were the same as that of the one-step except that the hydroxyl silicone was added when the pre-polymerization lasted for 2 hours.

Chain Extension

IPDI and PTMG were weighed with the -NCO/-OH ratio of 1.1:1. The DMPA was 8% in weight of the reaction mixture and the dibutyltin dilaurate was 3‰ in weight of the reaction mixture. The DMPA and PTMG were added to a four-necked bottle, and with dibutyltin dilaurate as catalyst, the mixture was allowed to react at 80°C for 3h to yield the pre-polymer. In the pre-polymerization process, some acetone was added to dissolve the pre-polymer. According to the amount of DMPA added, some triethylamine was added for neutralization, and the mixture was rapidly cooled to 25°C. The n-butylamine, 10% of the amount of isocyanate groups in weight, was added for chain-extension at 80°C. The reaction time was 5 min. After being stirred for water dispersion at the speed of 500r/min, light blue translucent polyurethane emulsion was obtained.

Film Forming of the Polyurethane

The waterborne polyurethane emulsion was poured in a PP film mold. After being dried at 50°C for 72 hours, the films were then dried at room temperature for another 48h to yield the polyurethane film for subsequent study.

Characterization of the Properties

Mechanical Properties

The mechanical properties of the polyurethane films were obtained according to GB/T 508-1998, with the thickness of 1mm (± 0.4mm) of standard, dumbbell-shaped samples. The minimum force was 0.01N and the stretching speed was 500mm/min.

FT-IR Analysis

The FT-IR spectra of the polyurethane films were obtained on a Fourier transforming infrared spectroscopy from Shimadzu Corporation, Japan.

Thermal Analysis

The glass transition temperature (Tg) of the PU films were determined by DSC. The work was done at the 10°C/min of heating and cooling speed from -100°C to 200°C temperature range. The samples were cooled from room temperature to -100°C, and then heated to 200°C to obtain the glass transition temperature of the polyurethane films.

Water Absorption of the PU Films

The polyurethane films were placed in a vacuum oven with the vacuum degree of 0.91MPa at 70°C to constant weight, about 5 h was needed. The polyurethane films were weighed, noted as m_1. The films were then immersed into distilled water for a certain period and weighed again, noted as mass m_2. The water absorption was calculated according to equation (1).

$$Water\ absorption = \frac{m_2 - m_1}{m_1} \times 100\% \qquad (1)$$

The water absorption was plotted against water soaking time to yield the relationship between water absorption and soaking time.

Finishing

In this study, three layers named bottom, middle, and top were conducted with the pigment paste only in the middle layer. In the middle finishing, the ratio of pigment paste to polyurethane emulsion was 1:2. After the finishing mixture was carefully and evenly brushed on the surface of leathers, the samples were removed in the constant temperature drying oven to be dried at 70°C.

Dry/Wet Rubbing Resistance [6]

The rubbing head was wrapped with white lining, and used to rub the samples with determined pressure, back and forth on the surface of the samples. In the rubbing process, the color on the surface of the samples was transferred on the lining of the rubbing head. Grey card was used to compare the color of the white lining to determine color level. The technical indicators are as follows: pressure load: 80g.cm^{-2}; rubbing speed: 43 cycles/min; rubbing length: 60mm; dry rubbing: 25 back and forth; wet rubbing: 20 back and forth; the water content of white lining was 70%-75%. The white lining was the national standard (GB/T406) and the grey card was the national standard (GB250-1995) one.

RESULTS AND DISCUSSION

Influence of Hydroxyl Modification on the Mechanical Properties of Polyurethane Films

In this study, three different ways of adding hydroxyl silicone to modify polyurethane was employed: one-step, two-step, and chain-extension. In both ways of one-step and two-step, the amount of hydroxyl silicone was calculated as the ratio of hydroxyl groups to total hydroxyl content in percentage. Figure 1 shows the curves of the elongation at break of polyurethane films vs. hydroxyl silicone content. In Figure 1, the elongation at break of the polyurethane films decreases with increasing the amount of hydroxyl silicone, no matter whether the one-step way or two-step way was used. This phenomenon is different from those by Zhu and Chen [4, 5]. In their work, they found that the elongation at break of polyurethane films increased gradually with increasing the amount of silicone to reach a maximum. This may be related to the length of the silicone chain. The molecular chain of the hydroxyl silicone is small, which might increase the hard segment content in the synthesis process of polyurethane, resulting in an increased interaction between hard segments. Similar to the performance of pure PU, the hydrogen bonds or crystallization of polyurethane should account for the decrease in the elongation at break.

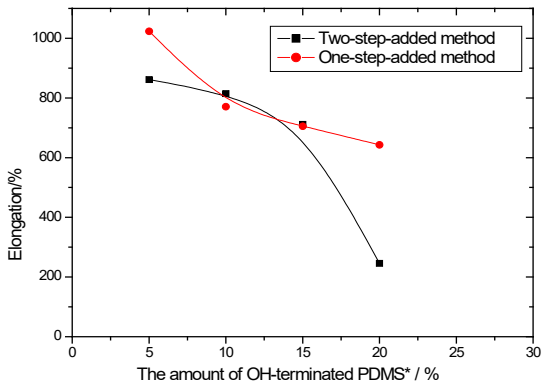

Figure 1. Relationship between the elongation at break and the hydroxyl silicone
*the hydroxyl ratio of OH-terminated PDMS to total –OH in the system

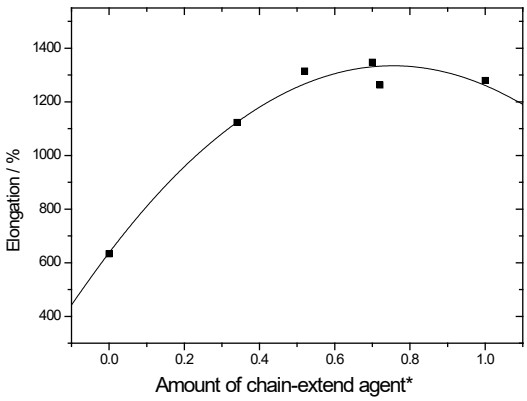

Figure 2. The elongation at break vs. amount of chain-extension agents
*the molecular ratio of chain-extension agent and dissociative –NCO

Figure 2 shows the relationship between elongation at break and the amount of chain-extension agent when the hydroxyl silicone was applied as chain-extension agent. When the amount of chain-extension agent accounts for 60% of the dissociative –NCO, a maximum was reached in elongation at break. Furthermore, hydroxyl silicone leads to a decrease in elongation at break again. The maximum elongation at break is 1300%. Compared to those by one-step and two-step, the way of chain-extension is the best to improve the elongation at break.

FT-IR Spectra of Hydroxyl Silicone Modified Waterborne Polyurethane

Figures 3-7 are the FT-IR spectra of hydroxyl silicone modified polyurethane films at different IR wave number ranges. The samples were obtained with different silicone contents by two-step way. In Figure 3, the peak at 802 cm^{-1} increases with increasing the content of hydroxyl silicone to form an obvious peak gradually. The absorption peak represents the oscillating vibration of Si-CH_3, indicating the reaction between hydroxyl silicone and the polyurethane molecule. The peak at 1240 cm^{-1} of the waterborne polyurethane film in Figure 4 was the absorption of the C-O-C. Although the bending vibrations of Si-CH_3 are also in the region, because the amount of hydroxyl silicone is too small compared to that of the polyurethane, the peak should be the strong absorption of C-O-C in the polyurethane. Figure 5 indicated the changes in absorption of the single bond of N-H in the modified polyurethane [7]. The absorption of N-H single bond appeared in the range from 3447 to 3600 cm^{-1} without hydrogen bonds. When hydrogen bonds are formed, the absorption peak moves to lower wave number, in the range of 3300 to 3380 cm^{-1}. Hydrogen bonds may be formed between the H atom in N-H and the O atom in C-O-C or C=O. A shoulder peak appeared in 1047 cm^{-1} in Figure 6. The emergency of the shoulder peak might be because the absorption peak of the Si-O-Si was covered for the little amount of hydroxyl silicone in the system. The changes of C=O in the waterborne polyurethane were shown in Figure 7. The absorption of C=O of polyurethane without hydrogen bonds usually occurs in the range from 1730 to 1745 cm^{-1} and that with hydrogen bonds moves to lower wave number [8]. The absorption of C=O appeared in 1712 cm^{-1} and no obvious shoulder peak was found at a higher wave number. Therefore, most of the C=O groups take part in the formation of hydrogen bonds. Besides, the obvious broad peak at 1654 cm^{-1} indicated the formation of urea. In short, there are Si-O-Si bonds and hydrogen bonds between the hard segments in the hydroxyl silicone modified polyurethane.

In Figures 6 and 7, the area of the shoulder peak of the hydrogen bonded C-O-C increases with increasing the hydroxyl silicone content, indicating an increased bonding degree of C-O-C. The higher the hydrogen bonding degree between the soft segment and the hard segment, the more difficult for the soft segment molecules in the polyurethane to move, which will decrease the elongation of polyurethane. The decrease

in the elongation at break with increasing the hydroxyl silicone content in the polyurethane (Figure 1) was consistent to the changes in the absorption area of hydrogen bonded C-O-C in polyurethane, indicating that the elongation at break of polyurethane is related to the hydrogen bonds and the movements of the soft segments.

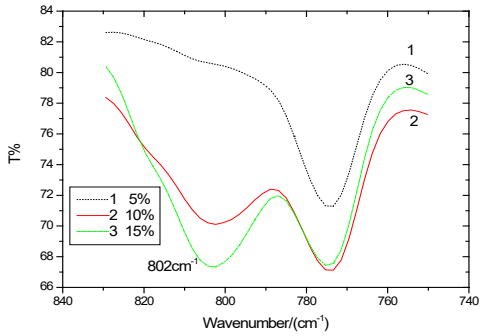

Figure 3. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (840-740 cm^{-1})

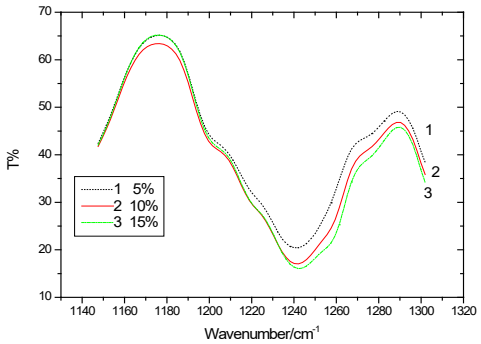

Figure 4. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1140-1320 cm^{-1})

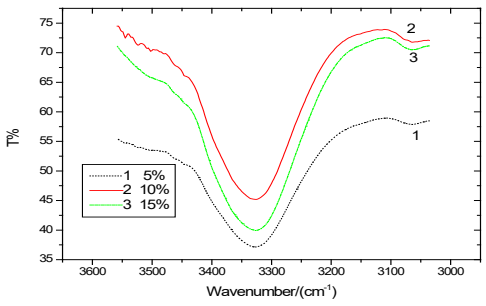

Figure 5. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (3600-3000 cm^{-1})

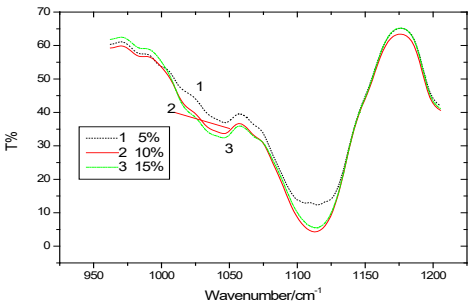

Figure 6. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (950-1200 cm^{-1})

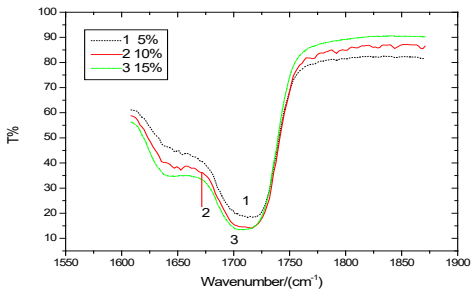

Figure 7. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1550-1900 cm^{-1})

DSC Analysis of the Hydroxyl Silicone Modified Polyurethane [9,10,11]

The DSC curves of the hydroxyl silicone modified polyurethane by two-step way were shown in Figure 8 and Figure 9. Step endothermic was found at both low temperature range and high temperature range, suggesting the glass transition in the polyurethane sample. The temperature range in Figure 8 was from -100°C to -30°C. When the amount of hydroxyl silicone is 5%, no obvious glass transition was found. At the amount of 10%, the Tg was -79°C with the endothermic of 0.0706 J/mg. At the amount of 15%, the Tg was -81°C and the endothermic was 0.1246 J/mg. The results for the 20% sample were

similar to the 15% one. The movement of the soft segment for the samples with 15% and 20% of hydroxyl silicone is easier than that with 10% hydroxyl silicone, which may be good to increase the elongation at break of the PU finishing agent. The DSC curves of the hydroxyl silicone modified polyurethane in the temperature range from -50°C to 200°C were shown in Figure 9. At the amount of hydroxyl silicone of 5%, Tg was 19°C with the endothermic of 1.079 J/mg. When the amount of hydroxyl silicone was 10%, the Tg was 31°C and the endothermic was 0.3964 J/mg. For the 15% sample, the Tg was 6°C and the endothermic was 0.3023 J/mg. The Tg was -14°C and the endothermic was 0.2886 J/mg for the sample with the hydroxyl silicone of 20%. It was indicated that the maximum interaction between hard segments appears at the amount of hydroxyl silicone of 10%. The interaction between the hard segments decreases with increasing the hydroxyl silicone amount above 10%.

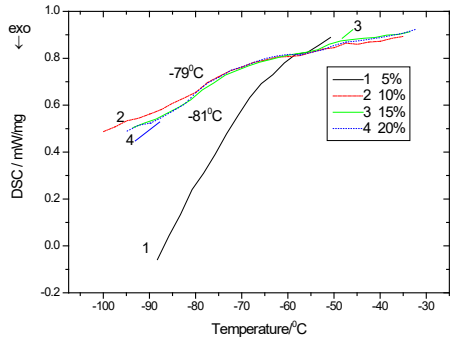

Figure 8. DSC curves of the hydroxyl silicone modified PU films by two-step way (-100~-30°C)

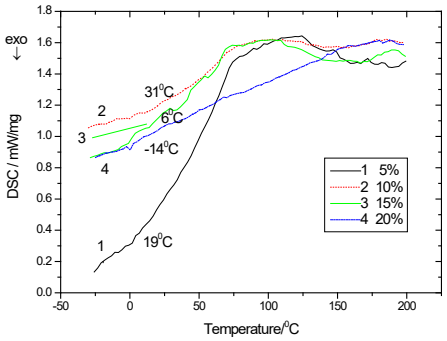

Figure 9. DSC curves of the hydroxyl silicone modified PU films by two-step way (-50~200°C)

The DSC curves of the modified polyurethane films with hydroxyl silicone as chain-extension agent are shown in Figure 10-11. The same results as Figure 8-9 were obtained: step endothermic was found both at low temperature range and high temperature range, suggesting the glass transition in the polyurethane sample. The temperature range in Figure 10 was from -100°C to -30°C. When the amount of hydroxyl silicone is 52%, the Tg of the polyurethane is -82°C with the endothermic of 0.2913 J/mg. 67% of hydroxyl silicone gave a polyurethane with the Tg of -81°C and endothermic of 0.1934 J/mg. At the amount of 75%, the polyurethane presented a Tg of -81°C and an endothermic of 0.244 J/mg. At the hydroxyl silicone amount of less than 75%, the endothermic decreases with increasing the hydroxyl silicone amount, while in 75%, the endothermic increases. By comparing with the result Figure 2, a change in the elongation at break appeared at the hydroxyl silicone amount of 75%. The DSC curves of the hydroxyl silicone chain-extended polyurethane in the temperature range from -70°C to 125°C were shown in Figure 11. At the hydroxyl silicone amount of 52%, the Tg of the polyurethane was 5°C with the endothermic of 0.4054 J/mg. The 67% of hydroxyl silicone yielded the PU with a Tg of -1°C and an endothermic of 0.3388 J/mg. When the hydroxyl silicone was 75%, the Tg was 1°C with the endothermic of 0.3757 J/mg. With increasing the amount of hydroxyl silicone as chain-extension agent, the endothermic decreases gradually, which does good for the hard segments to move. The elongation at break of the hydroxyl silicone chain-extended polyurethane films increases with increasing the amount of hydroxyl silicone, suggesting that the elongation at break of the polyurethane is related to the intermolecular interactions in it.

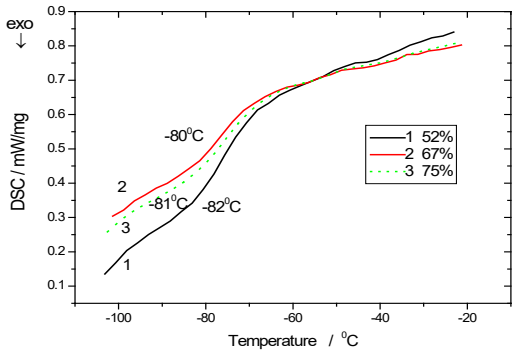

Figure 10. DSC curves of PU film chain-extended by hydroxyl silicone (-100~-20°C)

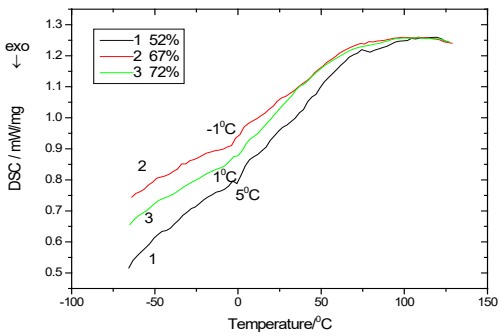

Figure 11. DSC curves of PU film chain-extended by hydroxyl silicone (-70~150°C)

In summary, for the polyurethane chain-extended by hydroxyl silicone, there appeared both the glass transitions of the soft segment (at -80°C or so) and the hard segments (around 0°C), indicating the phase separation between the hard segments and the soft segments. It was also indicated that the reaction between the hydroxyl silicone and the isocyanate takes place in the hard segments. This may be the reason why, for the one-step way and the two-step way, the elongation at break of the polyurethane films decreases with increasing the amount of hydroxyl silicone.

Water Absorption of the Hydroxyl Silicone Modified Polyurethane

The waterborne polyurethane without hydroxyl silicone modification will be dissolved when being soaked in water for a long time. For example, the weight of waterborne polyurethane chain-extended by ethylene diamine decreases when being soaked in water for 6 hours, indicating the hydrolysis of the product. In the present study, for the polyurethane chain-extended by hydroxyl silicone, no weight loss was found even after being soaked in water for 24 hours. The water absorption curves of the polyurethane films by the ways of one-step, two-step, and chain-extension were shown in Figure 12. For the samples by both ways of one-step and two-step, when being soaked in water for 24 hours, the water absorption decreases with increasing the amount of hydroxyl silicone. At a small amount of hydroxyl silicone, the water absorption of the two-step sample decreases faster than that of the one-step one. For the chain-extended sample, the water absorption increases and then decreases with increasing the amount of hydroxyl silicone. The water absorption of the chain-extended sample is much less, compared with those of the samples by the other two ways. At the same amount of hydroxyl silicone, the polyurethane of the chain-extended one shows the smallest, only 1/4 of those by the other two ways, indicating that the way of chain extension with hydroxyl silicone is a more efficient way to modify polyurethane.

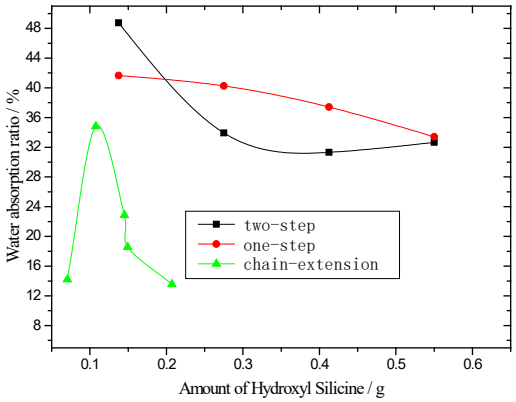

Figure 12. Water absorption of PU modified by hydroxyl silicone in different ways

Dry/Wet Rubbing Resistance

The PU finishing agents chain-extended with hydroxyl silicone were applied in the finishing of leathers. The bottom finishing was the traditional finishing agent, while the hydroxyl silicone was used only in the finishing of both layers of middle and top. The dry/wet rubbing resistance of the samples was studied with the results shown in Table 1.

Table 1: Dry/wet rubbing resistance of the finished samples

Samples	Amount of hydroxyl silicone in finishing coat (g)	Wet rubbing resistance grade	Dry rubbing resistance grade
1 (Top finishing)	0.02	3.5	5
2 (Top finishing)	0.05	4	5
3 (Top finishing)	0.08	4.5	5
4 (Middle finishing)	0.05	2.5	5
5 (Middle finishing)	0.08	2	5

In Table 1, the synthesized waterborne polyurethane finishing agent is good at dry rubbing resistance and the wet rubbing resistance is related to the amount of hydroxyl silicone used in the finishing. When the hydroxyl silicone modified polyurethane is used in top finishing, the wet rubbing resistance of the leathers increases gradually with increasing the amount of hydroxyl silicone in it. No obvious improvement in wet rubbing resistance was found when the hydroxyl silicone modified polyurethane was used in middle finishing. So top finishing is a good choice for hydroxyl silicone modified polyurethane to improve the dry/wet rubbing resistance of coatings.

CONCLUSIONS

The reaction between hydroxyl silicone and isocyanate takes place in the hard segments in polyurethane. The elongation at break of hydroxyl silicone modified polyurethane films is related to the location of hydrogen bonding. The polyurethane chain-extended with hydroxyl silicone showed a better elongation at break and water resistance, compared with those by ways of one-step and two-step. When being used in top finishing, hydroxyl silicone modified polyurethane may provide the dry rubbing resistance of 5 and the wet rubbing resistance of 4.5.

Acknowledgments

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EUROPEAN RESEARCH AREA

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, and were also published in the 2019 issues of Leather and Footwear Journal. The three newsletters issued in 2020 are given below.

NEWS 1/2020

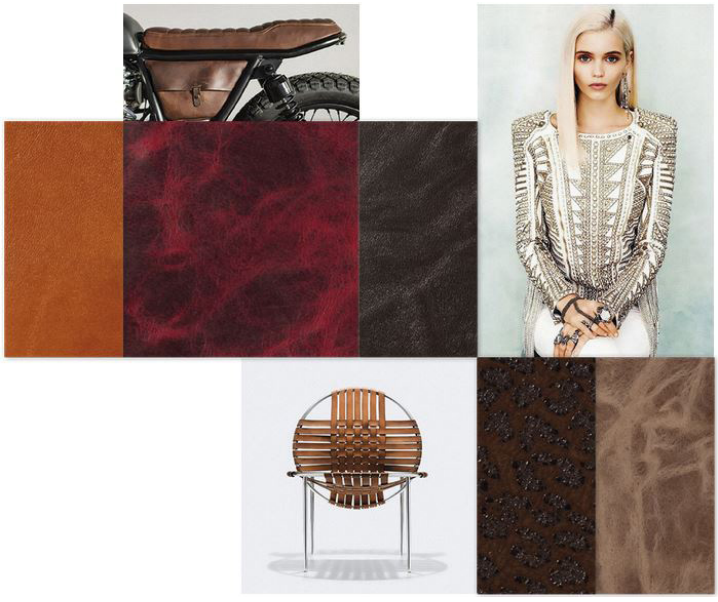
Leather: Traditional and Trendy!

Leather is one the oldest and most traditional materials used by mankind.

When people think about leather, they think about **tradition, durability, luxury**… they think about a classic material. Typically, they will picture a brown or black leather, used in jacket, a pair of shoes or a doctor's brief case.

This traditional image of leather arises from the fact that the most ancient tanning operations were based on vegetable tanning, using extracts of trees such as quebracho, tara, mimosa, oak and others.

Although traditional vegetable tanning is still used today, for leather articles such as horse saddles, the soles of shoes, belts and many others, modern **tanning technologies enable an enormous variety of colours for the finished leather.**



The final phase of leather production, known as finishing, has evolved greatly providing a plethora of colours, patterns and textures. This makes leather **attractive for consumers and meets the needs of designers and creators for a material that combines tradition, good physical and chemical features and which can be fashionable and trendy**. Leather production processes are undertaken in a such way as to ensure that the finished leather is free of dangerous chemical substances and are continuously evolving to further any reduce environmental impact and increase sustainability.

Together with the chemical industry, tanners have made great strides in product development to make leather one of the preferred materials for designers, creators and brands in the fashion and luxury industries.

For this reason, the **main international leather fairs**, especially in Europe are held every 6 months to meet the demands of the fashion seasons.

To be ahead of fashion trends, the industry's agents prepare information on leather trends ahead of each season to be used by designers, creators and brands.

The international trade fairs then prepare a trends preview for each season, to guide the leather companies to develop finished leather in line with the fashion trends.

In Portugal, the PT Leather InDesign Project – www.ptleatherindesign.com – a pilot project on trends deployment in the leather industry, provides a global approach to leather trends, by creating a Trend Book, covering colour, patterns and textures. This has five inspiration themes for each season, developing finished leathers according to identified trends and closing the circle to the finished product by producing prototypes of shoes and bags.

As well as making the finished leathers to meet design and fashion needs, the leather industry has also committed to the development of the tools for use by designers, creators and brands to make leather an easy and attractive material to work with.

Leather a wonderful natural and renewable material that combines its innate properties, good physical and chemical performance, with the ability to be trendy and meet the consumers preferences.

edited by COTANCE

in collaboration with APIC

All you need to know about vegetable tanned leather

Vegetable tanned leather is currently finding favour among certain circles.

Vegetable tanned leather is a leather in its own right produced with tanning agents of certain barks, fruits or leaves which transform the hide or skin of an animal into a durable material with many attractive properties. New formulations have appeared, with those from grape seeds, olive tree leaves and rhubarb showing great promise.

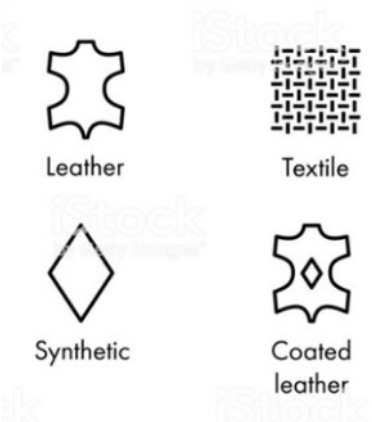
This process makes it possible to obtain leathers that are firm, highly resistant to abrasion, technical and hypoallergenic. They also have antibacterial advantages and are breathable, with good absorption and evacuation of moisture. With its characteristic scent, warm shades that deepen over time and "ability to age well", **vegetable tanned leather** embodies the very essence of this material.

Vegetable tanned leather can be called "vegetable leather" for convenience and some have seized on this to court a new audience, shaped by the growing trend for veganism. However, the confusion between "vegetable leather" and "vegan *leather*" was quickly flagged up as unacceptable.

In fact, there is no such thing as "*vegan leather*" – it is more appropriate to talk about vegan

materials, whether they are of petroleum, synthetic or vegetable origin.

Some European countries have decrees and regulations on the use of the term *leather* and/or the labelling of leather articles (France, Italy, Spain, Belgium, Greece, Estonia). However, only Footwear enjoys uniform labelling legislation in the EU, but even this does not prevent misleading descriptions and deceptive promotion or marketing practices affecting the term *leather*.



However, there are not yet any specifications for other leather products, applicable at European level to protect leather from misleading oxymorons where the word leather is associated to pineapple, mushroom, etc.

Together with COTANCE, Europe's leather industry organisations are working hard to lobby for protection for the term *leather* within the European Union.

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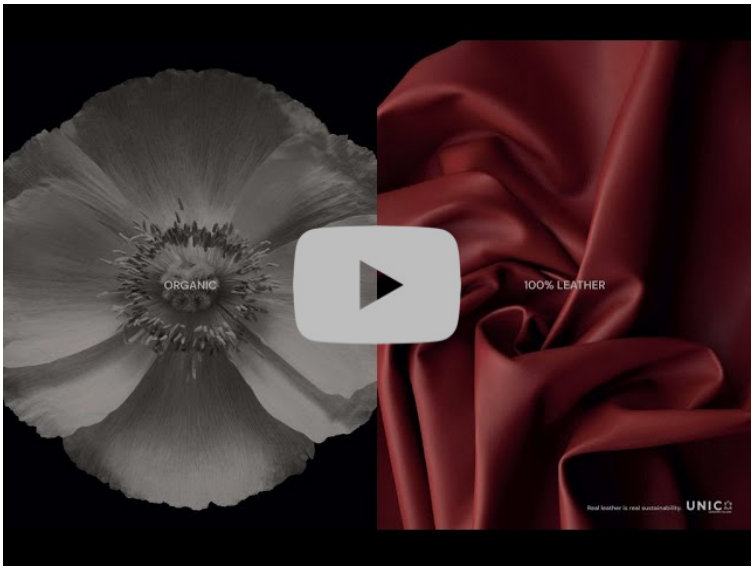
Supported by CTC

Only real leather is real sustainability

Most consumers are full of praise for leather, its performance, its versatility and the sensations it gives. However, a recent survey commissioned by UNIC Concerie Italiane, revealed the existence, in a number of interviewees, of a certain **scepticism about the sustainability of leather** and the tanning process through which it is obtained. Many even wrongly believe that animals are bred and then slaughtered specifically to obtain leather or even tortured to improve the quality of leather.

In order to overturn these false assumptions and misleading information, the Italian tanners' association (UNIC) has decided to carry out a communication campaign that focuses on the real sustainability of leather, entitled, **"Real leather is real sustainability"**.



The purpose is to show consumers that **only real leather is synonymous with naturalness, circularity, durability and creativity**. Leather is in fact, a by-product of the food industry, otherwise destined to be disposed of with a high impact on the environment. Instead, the tanning industry recovers it, ennobles it and transforms it into a material with a very high added value and multiple uses; fashion (leather goods, footwear, clothing), automotive, furniture and design.

Think about it. Real leather is #realsustainability.

edited by COTANCE

in collaboration with UNIC ITALIAN TANNERIES

NEWS RELEASE FROM THE IULTCS

February 09, 2020

Winners of Three 2020 IUR Research Grants Announced

The Executive Committee of the IULTCS is pleased to announce the winners of the 2020 IUR research grants to be awarded to three young scientists, under the age of 35. The monetary awards help support the work of young talent in the leather sector.

This is the sixth year of the grants which have been generously supported by industry and IULTCS alike. The Selection Committee of the IULTCS Research Commission (IUR), chaired by Dr Michael Meyer, is pleased to announce the following recipients:

Young Leather Scientist Grant 2020 Basic Research

Dr Megha Mehta, PhD, AMRSC from New Zealand Leather and Shoe Research Association (LASRA), Palmerston North, New Zealand. IULTCS has provided the monetary sponsorship for a single sum of €1,500 grant to Basic Research. The title of her project is "Investigating the Structural Differences of Hides, Skins and Leather Throughout the Different Processing Stages".

Dr Mehta's project's main objective is the utilisation of two non-destructive techniques – Raman and ATR-FTIR spectroscopy - to investigate the structural profiles of hides or skins throughout the stages of leather processing. This will enable investigation of the changes that take place in the microstructure of leather. The structural basis of these changes at the level of collagen cross-links is poorly understood.

Young Leather Scientist Grant 2020 Machinery Award

Nilay Ork Efendioglu, Ege University, Leather Engineering Department, Turkey. Machinery manufacturer ERRETRE has again generously provided the monetary sponsorship for a single sum of €1,000 grant for machinery / equipment research. The title of the project is "Determining Leather Properties Required for 3D Simulation Programs and Obtaining Realistic Visualizations".

The major objective of this project is to apply or adapt the leather material options in 3D visualization and simulation program as including many different properties of leathers, especially for the garment leathers. The benefit of this research will be to define a path to build up a leather material database for 3D simulation programs. This will enable production of final realistic visuals of the leather garment in the form of a sample, or in the form of production variations, without mistakes. Also, visuals will be as per customer request at a point where the leather cost is not existing, which will increase the competitiveness of the leather apparel sector.

Professor Mike Redwood Young Leather Scientist Grant 2020 Sustainability / Environmental Award

Wenkai Zhang, also from New Zealand Leather and Shoe Research Association (LASRA) will be the beneficiary of the generosity of Leather Naturally who have sponsored the €1,000 grant for the project entitled "Fate of Biocides used in Leather Industry and Their Environmental Impact".

The objective of this project is to investigate the fate of biocides used in the leather industry and their degradation products. It aims to quantify the distribution of the applied biocides in the processing skin/leather, the pickling liquor and the processing float, to identify and quantify the degradation products of the biocides and to understand the condition at which the degradation happens during leather processing.

Dr Michael Meyer, the IUR Chair of the Selection Committee, stated "All three project proposals show technological knowledge at a very high level and demonstrate the competitiveness of the leather industry with other industries worldwide." The IULTCS looks forward to seeing the outcomes of the projects and wishes all the Award recipients every success as they contribute to expanding our industry knowledge.

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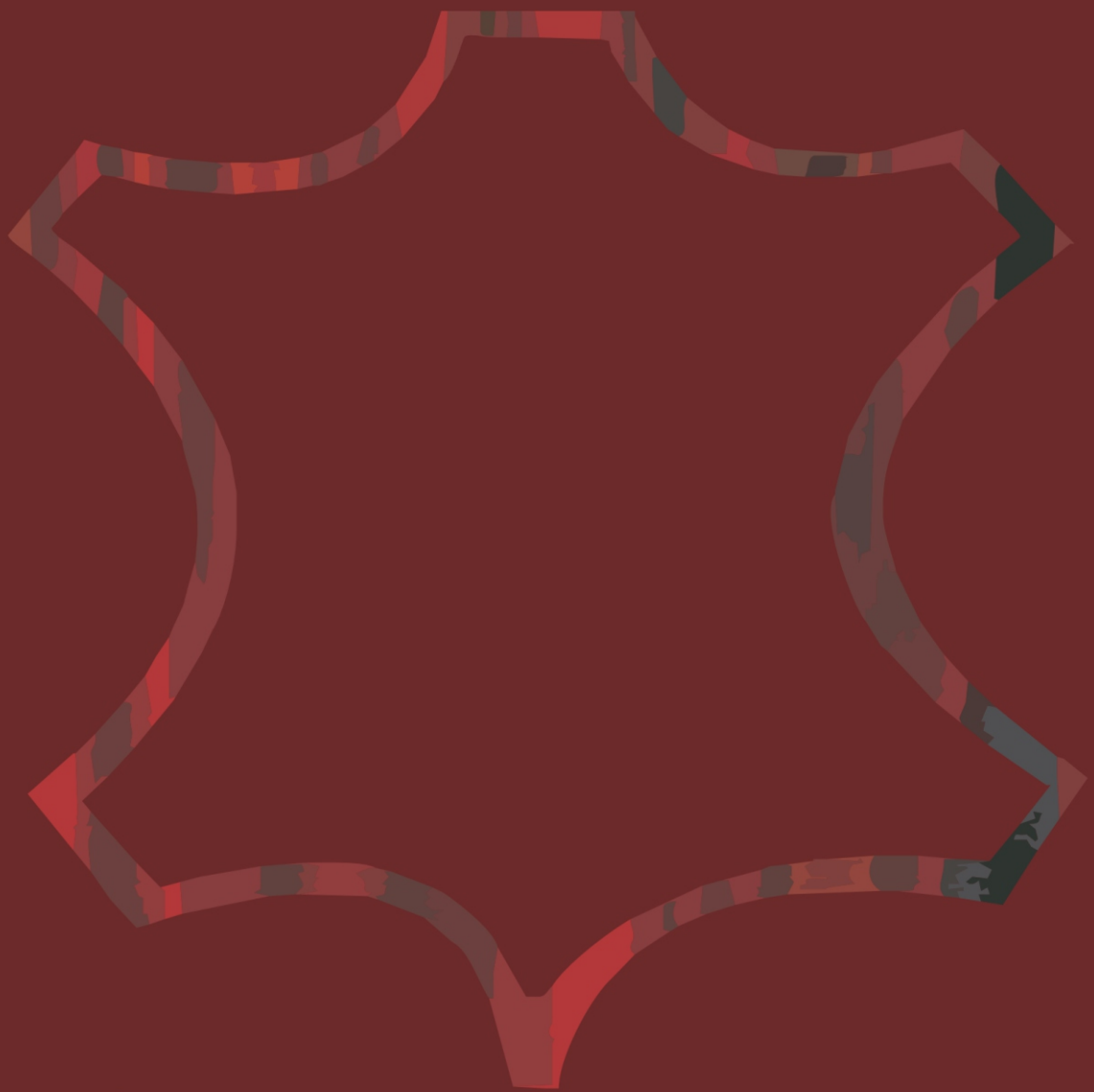

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