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	CONTENTS	CUPRINS	SOMMAIRE	
Ilda KAZANI Stelios MITILINEOS Majlinda HYLLI Aulon SHABANI Savvas VASSILIADIS Genti GUXHO	Electromagnetic Shielding Properties of Polypyrrole Treated Leather: A Comparative Study	Proprietățile de protecție electromagnetică ale pielii tratate cu polipirol: un studiu comparativ	Propriétés de blindage électromagnétique du cuir traité au polypyrrole : une étude comparative	99
Maria SÖNMEZ Laurenția ALEXANDRESCU Mihai GEORGESCU Dana Florentina GURĂU Maria Daniela STELESCU Denisa FICAI Anton FICAI Roxana TRUȘCĂ Ioana Lavinia ARDELEAN Doina CONSTANTINESCU Cristina Elisabeta PELIN George PELIN Adriana ȘTEFAN	Influence of Compatibilizer and Short Hemp Fibres on the Mechanical, Rheological and Morphological Properties of Recycled Polyethylene Terephthalate	Influența compatibilizatorilor și a fibrelor scurte de cânepă asupra proprietăților mecanice, reologice și morfologice ale tereftalatului de polietilenă reciclat	Influence des compatibilisants et des fibres courtes de chanvre sur les propriétés mécaniques, rhéologiques et morphologiques du polyéthylène téréphtalate recyclé	109
Dwi WULANDARI Thoyib Rohman HAKIM SUGIYANTO	Use of Gelatin Binder as a Base Coat in the Finishing Process of Tanned Rabbit Skin	Utilizarea gelatinei ca liant în stratul de bază aplicat în procesul de finisare a pielii de iepure	L'utilisation de la gélatine comme liant dans la couche de base appliquée dans le processus de finition de la peau de lapin	131
Tong Zhan CUI Rafiu King RAJI Jian Lin HAN Yuan CHEN	Review of Avant-Garde Concept in Footwear Research and Design and Application Trends	Trecere în revistă a curentului avangardist în cercetare și design în domeniul încălțămintei și tendințe de aplicare	Revue du courant d'avant- garde dans la recherche et la conception de chaussures et tendances d'application	141
Van-Huan BUI Duy-Nam PHAN	Research on Foot Anthropometry and Complications of Women with Diabetes in Vietnam	Cercetări privind antropometria piciorului și complicațiile apărute la femeile cu diabet din Vietnam	Recherche sur l'anthropométrie du pied et les complications chez les femmes diabétiques au Vietnam	157
	European Research Area	Spațiul european al cercetării	Espace Européen de la Recherche	169

ELECTROMAGNETIC SHIELDING PROPERTIES OF POLYPYRROLE TREATED LEATHER: A COMPARATIVE STUDY

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ELECTROMAGNETIC SHIELDING PROPERTIES OF POLYPYRROLE TREATED LEATHER: A COMPARATIVE STUDY

ABSTRACT. Due to the increase in electromagnetic waves emitted by the electrical and electronic equipment surrounding us, protection from electromagnetic waves has become a very important subject. It is thereby proposed that conductive textiles and fabrics are used for protection of sensitive equipment and personnel from electromagnetic interference. Conductive textiles are considered to be a particular sub-genre of technical textiles and exhibit favourable electromagnetic shielding properties together with a list of other attributes that make them suitable for such applications. In more detail, conductive textiles exhibit light weight and low volume while being comfortable to wear, conforming to different shapes of surfaces and everyday objects (thus being easily integrated within the surrounding environment), being aesthetically appealing, etc. In this context, most of the literature-available shielding textiles or fabrics used are either conventional or conductive fabrics that are further coated with metal layers for extra conductivity and shielding. However, metal shielding exhibits certain disadvantages: it is prone to corrosion while corrosion-resistant materials (such as silver or gold) are extremely expensive; it is difficult to process; and it compromises the comfortability and aesthetic appeal of the final product. Herein, we propose the usage of electrically conductive leather for efficient shielding from electromagnetic interference. The motivation for this work is twofold: first, leather materials are seldom if not at all used for electromagnetic shielding and we wanted to close that gap for an industry sector (leather clothes and garments) that is thriving. Second, we are using one or more layers of polypyrrole treatment (PPy) to inherit conductivity to leather surfaces. We show that PPy is sufficient treatment for inheriting very satisfactory electromagnetic shielding properties all the while maintaining the comparative advantages of a non-metal-processed fabric surface (e.g. comfortability, aesthetic appeal etc.). We demonstrate a variety of different PPy treated leather samples and illustrate that electromagnetic shielding is proportional to the number of PPy layers used for leather processing. The measurements results are obtained using RF and microwave high-frequency equipment in a controlled laboratory environment within the X-microwave band (8-12 GHz).

KEY WORDS: electromagnetic shielding, X-band, microwave shielding, leather materials, polypyrrole treatment

PROPRIETĂȚILE DE PROTECȚIE ELECTROMAGNETICĂ ALE PIELII TRATATE CU POLIPIROL: UN STUDIU COMPARATIV

REZUMAT. Datorită creșterii undelor electromagnetice emise de echipamentele electrice și electronice din jurul nostru, protecția împotriva undelor electromagnetice a devenit un subiect foarte important. Prin urmare, se propune utilizarea textilelor și țesăturilor conductoare pentru protecția echipamentelor sensibile și a personalului împotriva interferențelor electromagnetice. Textilele conductoare sunt considerate a fi o subcategorie specială de textile tehnice și prezintă proprietăți favorabile de ecranare electromagnetică, împreună cu o serie de alte atribute care le fac potrivite pentru astfel de aplicații. Mai în detaliu, textilele conductoare prezintă greutate redusă și volum redus, în timp ce sunt confortabile de purtat, se conformează diferitelor forme ale suprafețelor și obiectelor de zi cu zi (fiind astfel usor de integrat în mediul înconjurător), fiind atractive din punct de vedere estetic etc. În acest context, majoritatea textilelor de ecranare întâlnite în literatură sau țesăturile utilizate sunt fie țesături convenționale, fie conductoare, care sunt acoperite cu straturi metalice pentru conductivitate și ecranare suplimentare. Cu toate acestea, ecranul metalic prezintă anumite dezavantaje: este predispus la coroziune, în timp ce materialele rezistente la coroziune (cum ar fi argintul sau aurul) sunt extrem de scumpe; acesta este dificil de procesat și compromite confortul și atractivitatea estetică a produsului final. În această lucrare propunem utilizarea pielii cu proprietăți de conductivitate electrică pentru o ecranare eficientă împotriva interferențelor electromagnetice. Motivația pentru această muncă este dublă: în primul rând, pielea este rareori sau chiar deloc folosită pentru ecranarea electromagnetică și am vrut să reducem acest decalaj pentru un sector industrial (haine și confecții din piele) care este înfloritor. În al doilea rând, folosim unul sau mai multe straturi de tratament cu polipirol (PPy) pentru a conferi conductivitate suprafețelor din piele. Demonstrăm că tratarea cu PPy este suficientă pentru conferirea unor proprietăți de ecranare electromagnetică foarte satisfăcătoare, menținând în același timp avantajele comparative ale unei suprafețe de țesătură neprelucrată cu metal (de exemplu, confort, atractivitate estetică etc.). Demonstrăm o varietate de mostre diferite de piele tratată cu PPy și ilustrăm faptul că ecranarea electromagnetică este proporțională cu numărul de straturi PPy utilizate la prelucrarea pielii. Rezultatele măsurătorilor sunt obținute folosind echipamente de frecvență radio (RF) și de înaltă frecvență și microunde într-un mediu de laborator controlat, cu microunde în banda X (8-12 GHz).

CUVINTE CHEIE: ecranare electromagnetică, banda X, ecranare cu microunde, piele, tratament cu polipirol

PROPRIÉTÉS DE BLINDAGE ÉLECTROMAGNÉTIQUE DU CUIR TRAITÉ AU POLYPYRROLE : UNE ÉTUDE COMPARATIVE

RÉSUMÉ. En raison de l'augmentation des ondes électromagnétiques émises par les équipements électriques et électroniques qui nous entourent, la protection contre les ondes électromagnétiques est devenue un sujet très important. Il est ainsi proposé que des textiles et des

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tissus conducteurs soient utilisés pour protéger les équipements et le personnel sensibles contre les interférences électromagnétiques. Les textiles conducteurs sont considérés comme un sous-genre particulier de textiles techniques et présentent des propriétés de blindage électromagnétique favorables ainsi qu'une liste d'autres attributs qui les rendent adaptés à de telles applications. Plus en détail, les textiles conducteurs présentent un poids léger et un faible volume tout en étant agréables à porter, s'adaptant à différentes formes de surfaces et d'objets du quotidien (s'intégrant ainsi facilement dans l'environnement), étant esthétiquement attrayants, etc. Dans ce contexte, la plupart des textiles ou tissus de blindage rencontrés dans la littérature utilisés sont des tissus conventionnels ou conducteurs qui sont en outre recouverts de couches métalliques pour une conductivité et un blindage supplémentaires. Cependant, les blindages métalliques présentent certains inconvénients : ils sont sujets à la corrosion alors que les matériaux résistants à la corrosion (comme l'argent ou l'or) sont extrêmement coûteux ; ils sont difficiles à traiter, et cela compromet le confort et l'attrait esthétique du produit final. Nous proposons ici l'utilisation de cuir électriquement conducteur pour un blindage efficace contre les interférences électromagnétiques. La motivation de ce travail est double : premièrement, les matériaux en cuir sont rarement, voire pas du tout, utilisés pour le blindage électromagnétique et nous voulions combler cet écart pour un secteur industriel (maroquinerie et vêtements en cuir) en plein essor. Deuxièmement, nous utilisons une ou plusieurs couches de traitement au polypyrrole (PPy) pour conférer de la conductivité des surfaces en cuir. Nous montrons que le PPy est un traitement suffisant pour conférer de propriétés de blindage électromagnétique très satisfaisantes tout en conservant les avantages comparatifs d'une surface de tissu non traitée en métal (par exemple confort, attrait esthétique, etc.). Nous démontrons une variété de différents échantillons de cuir traités au PPy et nous illustrons que le blindage électromagnétique est proportionnel au nombre de couches de PPy utilisées pour le traitement du cuir. Les résultats des mesures sont obtenus à l'aide d'équipements RF et haute fréquence et microondes dans un environnement de laboratoire contrôlé, avec des micro-ondes en bande X (8-12 GHz).

MOTS CLÉS : blindage électromagnétique, bande X, blindage micro-ondes, cuir, traitement au polypyrrole

INTRODUCTION

Electromagnetic pollution is known to be harmful for both human health and sensitive electronic devices. Therefore it is essential to be protected from the hazardous effects of electromagnetic radiation. As electric and electronic devices and also the accessories are increasing rapidly, transmitting electromagnetic power through the different frequency bands used on the markets, restricting and preventing electronic equipment from all sources of interference has become important. Electromagnetic shielding materials are used for protection from electromagnetic waves. Since most of the electromagnetic shields are materials including metals, they have several disadvantages such as poor handle properties, difficulties in processing, high cost, high weight, sensitivity to corrosion and so on. On the antipode, our garments cannot protect us due to the fact that they are not conductive. The smart garments need to be made conductive in order to provide shielding effects.

In order to achieve these electrical properties, from the traditional textiles, different methods can be used, such as incorporating conductive fibres/yarns, or treating them with conductive coatings, polymers or inks. Moreover, several techniques that can be used to integrate conductive fibres/yarns into a textile structure such as knitting, weaving, embroidering, sewing and needle felting, conductive textiles can be obtained also by treating the surface of the traditional textiles. This last method can be achieved by coating them with a conductive layer, by coating with conductive polymers, deposited onto the surface of textile substrates or by printing with conductive inks [1-13].

In this study we propose the chemical treatment of the leather, in order to be conductive. This can be achieved by coating it with different processes such as: electroless deposition, electroplating, Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), sputtering and coating with conductive polymers, where the last one is more used on textiles, and this paper focuses on this technique to make it conductive, but on leather [14-18].

This study focuses on the development of electrically conductive leather for electromagnetic shielding applications and investigation of their properties. Different groups have worked on leather shielding materials. Shen et al. has prepared natural composites based on leather and high-Z elements, which were used as gamma-ray shielding materials. They showed low density, high strength and wearable behaviours [19]. Gao et al. [20] developed a three-step procedure to produce flexible nanofibers films as shielding materials against electromagnetic interference (EMI), based on hydrolysate of waste leather scraps. The nanofiber films that they produced showed a high EMI shielding efficiency. Zeng et al. has fabricated a novel foldable leather solid waste conductive paper,

which has offered a new avenue toward recycling of leather waste and displayed promising potential for applications in flexible shielding materials or wearable clothing [21]. While Zhao *et al.* propose a green chrome-free tanned electromagnetic shielding leather using *in situ* poly method with polyaniline. They were able to improve leather tanning and electromagnetic shielding performance to a large extent [22].

To the best of our knowledge this is the first time to report on electromagnetic shielding performance of electroconductive leather coated with polypyrrole, as alternatives to metals. Polypyrrole was chosen because it has a wide thermoelectric application and it is easy to be prepared, besides it is a low-cost polymer. Furthermore, intrinsically conducting polymers are able to absorb as well as reflect electromagnetic waves, exhibiting a significant advantage over metallic materials, which cannot be used as electromagnetic wave absorbers since high conductivity corresponds to a high reflection coefficient and very small penetration depth [23-24].

MATERIALS AND EXPERIMENTAL SETUP

Materials

The leather samples selected for conductivity treatment were white sheep crust Albanian leather chosen according to standard method [25]. Sheep crust leather samples have undergone the same preparation stage. They are tanned, dried, but not fully finished. The leather thickness varies from 0.9-1.1 mm.

Five samples were analysed in this study, sample number 0 is the reference sample which is not treated with PPy, while the other four samples, S1, S2, S3 and S4, are treated with PPy, as described in Table 1. All the reagents used, such as pyrrole (PPy), ferric chloride, (FeCl₃) anthraquinone-2- sulfonic acid sodium salt monohydrate [(AQSA), were purchased by Sigma-Aldrich].

Chemical Preparation of PPy-treated Leather Samples

Leather samples were treated using two chemical oxidative polymerization techniques:

single *in situ* polymerization and double *in situ* polymerization. In order to obtain conductive leather, polypyrrole was chosen as a conductive polymer. The leather samples (10 x 10 cm) were prepared and conditioned before the treatment according to ISO standards [25-26], while after the thickness was measured based on the ISO standard [27].

The polymerization on leather samples was carried out using pyrrole monomer, ferric chloride as oxidant and AQSA as a dopant. The concentration of all the reactants, pyrrole, AQSA and FeCl₃ were used with different concentration and optimized in order to give maximum conductive properties to leather samples. In some cases, in order to raise the conductivity of the leather samples one parameter is changed, the others are kept constant [16].

Final experiments for *in situ* polymerization treatment were performed using pyrrole concentrations (0.15 M), AQSA concentration was 10 wt % based on the weight of pyrrole and ferric chloride concentration (0.4 M).

polymerization For single *in situ* treatment, first a mixed solution is prepared of 0.15 M pyrrole and AQSA (10 wt % based on the weight of pyrrole) by dissolving pyrrole in AQSA solution with vigorous stirring for 30 min. Then, the white sheep crust leather samples were first soaked in the mixed solution pyrrole/AQSA and are rotated in a rotating mixer for 1 hour at 10 rpm to uniformly mix. After the treatment, 0.4 M ferric chloride solution is added to the mixture as an oxidant to initiate the polymerization. The polymerization was carried out for 2 h at 5°C in 10 rpm. Treated leather samples were rinsed 4 times with distilled water and dried at 35 °C.

Experiments for double *in situ* polymerization were performed following all the procedures like the single *in situ* polymerization, but after the first bath the leather was treated again in a second bath containing the same concentrations of reactants, following the same procedure to obtain double *in situ* PPy coated leather. At the end the coated leather was washed 4 times with distilled water and dried at 35°C, as it is shown in Figure 1.

This polymerization method produces conductive and black coloured leather sample

only by using the chemical polymerization treatment in a bath.



Figure 1. Scheme of the double in situ polymerization of pyrrole [18]

Resistance Measurements

The resistance of square shape leather samples was measured by using Van Der Pauw method [14]. The method consists of placing four probes along the circumference of the sample (in this case in four corners), two adjacent corners are used to apply a current by a DC power source and then by placing a multi meter into two opposite corners we measure the voltage drop. The procedure is repeated four times by changing corners one by one in clockwise direction. Then we calculate two resistances called horizontal and vertical resistances by using Ohm's law. After that we solve the equation (1) regarding surface resistance.

$$e^{-\pi \frac{R_{vertical}}{R_S}} + e^{-\pi \frac{R_{horizontal}}{R_S}} = 1$$
(1)

Microwave Testbed and Electromagnetic Shielding Measurements

The microwave characterization of the shielding properties of the provided leather

samples was performed in the premises of the Department of Electrical and Electronic Engineering, University of West Attica, Athens, Greece. We used a R&S ZVA24 Vector Network Analyzer (VNA) that is suitable for measurements up to 24 GHz, as well as appropriate cables, connectors and waveguides. The waveguide equipment consisted of type WR-90 waveguides operating in the X-band (8.20 to 12.40 GHz) thus limiting the frequency range of the final setup. The testbed included two straight waveguide components and two end-launchers for connection to the VNA. Initially, we calibrated the waveguide testbed by connecting the straight parts together without any sample in between. An overview of the one end of the testbed with an end-launcher and a straight waveguide component is illustrated in Fig. 2(a), while the calibration testbed is illustrated in Figs. 2(b) and 2(c) below. The careful reader may discriminate the characteristic cutoff frequency displayed in the attached monitor in Fig. 3(c).



Figure 2. Waveguide testbed setup and VNA connections for initial calibration; (a) end-launcher and straight waveguide; (b) waveguide testbed; (c) final measurements setup

Subsequently, all the provided leather samples (reference samples and samples #1 through 4) were sequentially attached in the gap between the straight waveguide components and held together by applying gentle force through the supporting endlaunchers. For each sample, the VNA display was photographed, printed to .jpg figures and the measurements were stored through the VNA user interface into .csv files. Photos of a leather sample attached to the testbed is illustrated in Figs. 3(a) and (c) below, while a close-up of the VNA display is provided in Fig. 3(b).



Figure 3. Waveguide testbed setup and VNA connections for initial calibration; (a) end-launcher and straight waveguide; (b) waveguide testbed; (c) final measurements setup

RESULTS

All leather samples were then measured with respect to their electromagnetic shielding

properties using the testbed and methodology described in Section II above. The leather samples used and their measurements results are provided in Table 1.







Figure 4. Shielding measurements results of conductive leathers (a) reference, and (b) through (e) samples #1 through #4, respectively

First, the reference sample with no PPy treatment whatsoever was measured and the transmission coefficient (known as " S^{21} ") through the VNA and waveguide apparatus is displayed in Fig. 4(a). The horizontal axes of all sub-figures within Fig. 4 are in Hz units for the signal frequency, whereas the vertical axes are in dB. Since S^{21} refers to the transmission coefficients (output voltage to input voltage), the vertical axes in dB are calculated as 20*log (S^{21}), where S^{21} the transmission coefficient in linear scale.

Furthermore, please note that the nominal frequency range of operation for WR-90 waveguides is from 8.20 to 12.40 GHz. From Fig. 4(a) it can be deduced that there is a slight

fluctuation of shielding vs. frequency; this is expected and attributed to the surface roughness and imperfections of the sample body. The transmission coefficients correspond to an attenuation of ~3 dB, which is rather small; this is also expected since the untreated leather does not inherently possess significantly high conductivity.

Then, all leather samples were also measured. The respective transmission coefficients are illustrated in Fig. 4(b) through (e) for the samples #1 through #4, respectively. Furthermore, Table 1 tabulates the average shielding effectiveness per sample for the entire 8.20-12.40 GHz frequency range. It can be seen that for samples #1 and #2, with single *in situ* PPy polymerization, the shielding effectiveness is in the order of 25 dB. This represents a satisfactorily large number meaning that a single layer of PPy polymer on top of the reference sample is able to provide

a significant attenuation since the output signal is in the order of ~17,8 times lower than the input signal; this corresponds to a power of the output signal that is ~ 300 times lower than the input signal.

No.	Leather samples	Thickness (mm)	Chemical treatment	Electrical resistance Ω/sq	Average Shielding effectiveness 8.20- 12.40 GHz (dB)		
0	Reference (white sheep	1.015	Not Applicable	8			
	crust leather (not treated)				-3.82		
1	S ₁	0.974	single <i>in situ</i>	23.90			
			polymerization		-25.35		
2	S ₂	0.982	single <i>in situ</i>	21.42			
			polymerization		-25.27		
3	S₃	1.034	double <i>in situ</i>	7.27			
			polymerization		-32.68		
4	S ₄	0.988	double <i>in situ</i>	8.43	-35.06		
	polymerization						

Table 1: Measurements results of leather samples shielding effectiveness

On the other hand, samples #3 and #4, with double in situ PPy polymerization exhibit a shielding effectiveness in the order of 34 dB, which corresponds to an output signal in the order of ~50 times lower than the input signal; this corresponds to an output signal power that is ~2500 times lower than the power of the input signal. It is also worth noting that the attenuation of samples #3 and #4 is almost 10 dB lower than in the case of samples #1 and #2. This attenuation corresponds to a significantly high level of shielding effectiveness and demonstrates our motivation in using the proposed approach for electromagnetic shielding using PPy conductive layering. It should be also noted that the higher shielding effectiveness of double polymerized samples is expected since double polymerization with a conductive layer corresponds to higher conductivity and, thus, higher microwave signal attenuation and electromagnetic shielding.

CONCLUSIONS

In this research we have studied the electrically conductive leather for efficient shielding from electromagnetic interference. The leathers were prepared with two different chemical treatments, single *in situ* polymerization and double *in situ* polymerization, by using polypyrrole (PPy) to inherit conductivity to leather surfaces. We have shown that PPy is

sufficient treatment for inheriting verv satisfactory electromagnetic shielding properties all the while maintaining the comparative advantages of a non-metal-processed fabric surface (e.g. comfortability, aesthetic appeal etc.). Measurements results were obtained by using RF and microwave high-frequency equipment in а controlled laboratory environment within the X-microwave band (8-12 GHz). In this study was presented that electromagnetic shielding is proportional to the number of PPy layers used for leather processing, by increasing the number of treatments the shielding effectiveness is increased as well. This is due to double polymerization with a conductive layer, which corresponds to higher conductivity and, thus, higher microwave signal attenuation and electromagnetic shielding.

The shielding effectiveness of samples treated with single *in situ* polymerization, show to have a shielding effectiveness in the order of 25 dB, while those treated with double *in situ* polymerization have a shielding effectiveness in the order of 34 dB, almost 10 dB lower than the first ones. We may conclude that 2500 times attenuation is a satisfactory result, which corresponds to a significantly high level of shielding effectiveness and demonstrates our motivation in using the proposed approach for electromagnetic shielding using PPy conductive layering.

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INFLUENCE OF COMPATIBILIZER AND SHORT HEMP FIBRES ON THE MECHANICAL, RHEOLOGICAL AND MORPHOLOGICAL PROPERTIES OF RECYCLED POLYETHYLENE TEREPHTHALATE

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INFLUENCE OF COMPATIBILIZER AND SHORT HEMP FIBRES ON THE MECHANICAL, RHEOLOGICAL AND MORPHOLOGICAL PROPERTIES OF RECYCLED POLYETHYLENE TEREPHTHALATE

ABSTRACT. The purpose of the paper is to evaluate the influence of maleic anhydride grafted polyethylene (PE-g-MA) and untreated/treated hemp fibers on the properties of recycled polyethylene terephthalate (PETr). Blends based on PETr, PETr/PE-g-MA (70:30wt%) and composites (67.30:28.85:3.85wt%) based on PETr/PE-g-MA/untreated/treated short hemp fibres with 1-5wt% TiO₂ were obtained. Composites were processed using Brabender Plasticorder mixer at 240°C for 7min and pressed to fabricate test specimens. The decoration of hemp fibres with oxide nanoparticles followed by embedding in PETr leads to the fabrication of composites with improved mechanical and thermal properties, this technology being suitable to reuse PET and to develop added-value products.

KEY WORDS: polymer blend or composite, hemp fiber, torque, TiO₂, polyethylene wax, flexural and impact properties

INFLUENȚA COMPATIBILIZATORILOR ȘI A FIBRELOR SCURTE DE CÂNEPĂ ASUPRA PROPRIETĂȚILOR MECANICE, REOLOGICE ȘI MORFOLOGICE ALE TEREFTALATULUI DE POLIETILENĂ RECICLAT

REZUMAT. Scopul lucrării este de a evalua influența polietilenei grefate cu anhidridă maleică (PE-g-MA) și a fibrelor de cânepă netratate/tratate asupra proprietăților tereftalatului de polietilenă reciclat (PETr). S-au obținut amestecuri pe bază de PETr, PETr/PE-g-MA (70:30% în greutate) și compozite (67,30:28,85:3,85% în greutate) pe bază de PETr/PE-g-MA/fibre scurte de cânepă netratate/tratate cu 1-5% TiO₂ în greutate. Compozitele au fost prelucrate cu ajutorul malaxorului Brabender Plasticorder la 240°C timp de 7 minute și presate pentru a realiza eșantioane de testare. Decorarea fibrelor de cânepă cu nanoparticule de oxid urmată de încorporarea acestora în PETr duce la fabricarea de compozite cu proprietăți mecanice și termice îmbunătățite, această tehnologie fiind potrivită pentru reutilizarea PET-ului și pentru dezvoltarea de produse cu valoare adăugată.

CUVINTE CHEIE: amestec sau compozit polimeric, fibră de cânepă, moment de torsiune, TiO₂, ceară de polietilenă, proprietăți de încovoiere și de impact

INFLUENCE DES COMPATIBILISANTS ET DES FIBRES COURTES DE CHANVRE SUR LES PROPRIÉTÉS MÉCANIQUES, RHÉOLOGIQUES ET MORPHOLOGIQUES DU POLYÉTHYLÈNE TÉRÉPHTALATE RECYCLÉ

RÉSUMÉ. Le but de l'article est d'évaluer l'influence du polyéthylène greffé à l'anhydride maléique (PE-g-MA) et des fibres de chanvre non traitées/traitées sur les propriétés du polyéthylène téréphtalate recyclé (PETr). On a obtenu des mélanges à base de PETr, PETr/PE-g-MA (70:30% en poids) et composites (67,30:28,85:3,85% en poids) à base de PETr/PE-g-MA/fibres de chanvre courtes non traitées/traitées avec 1-5% du TiO₂ en poids. Les composites ont été traités à l'aide du mélangeur Brabender Plasticorder à 240°C pendant 7 minutes et pressés pour fabriquer des éprouvettes. La décoration des fibres de chanvre avec des nanoparticules d'oxydes suivie de leur incrustation dans du PETr conduit à la fabrication de composites aux propriétés mécaniques et thermiques améliorées, cette technologie étant adaptée pour réutiliser le PET et développer des produits à valeur ajoutée.

MOTS CLÉS : mélange ou composite de polymères, fibre de chanvre, couple de torsion, TiO₂, cire de polyéthylène, propriétés de flexion et d'impact

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INTRODUCTION

In recent decades, a particular emphasis has been placed on recycling plastic materials and the development of new or partially biodegradable composite materials by incorporating compounds from renewable sources (cellulose fibers, chitosan, starch, or other derivatives) [1-3] was found suitable for a sustainable development. The addition of natural ligno-cellulosic fibers in polymers can improve mechanical properties, flexibility and toughness, provided there is good interaction between the phases [4]. The replacement of conventional synthetic fibers (carbon, glass, etc.) with natural fibers (hemp, wood, bamboo, kenaf, flax) in various polymeric composites is a priority and has multiple advantages due to their renewable nature, biodegradability, corrosiveness, recyclability, low energy processing, etc. [5-8]. However, most plant fibers, prior to blending and compounding with various polymeric matrices, are subjected to a pre-drying treatment, which leads to fiber agglomeration due to the formation of oxygen bonds. This fiber agglomeration, together with the percentage of fiber used and the generally high viscosity of the polymers, leads to a poor dispersion, to the formation of the voids and to the reduction of the mechanical properties of the composite. Natural fibers derived from plants contain cellulose as a major structural component [9]. Due to the hydrophilic character of the cellulose and the hydrophobic nature of the thermoplastic matrix, the interaction between the phases is limited [10]. The most commonly used method for improving the polymeric wettability of the fiber surface and, implicitly, the mechanical properties is the treatment with hydroxide (NaOH) [11]. Other treatments focus on physical modification (corona, plasma treatment), chemical modification (esterification-based treatments using silane coupling agents, graft copolymerization, isocyanates, etc.) [12-14]. Hemp fibers are lignocellulose-based fibers and contain ~57-77 wt% cellulose, ~14-22 wt% hemicellulose, ~3.7-13wt% lignin, and waxes in their chemical structure [15].

Particular attention should be paid to the selection of the polymer matrix used for fiber reinforcement as it provides the barrier against

adverse media, protects the surface of the fibers from mechanical abrasion and transfers the loads applied to the fibers [16]. A major limitation in the selection of the matrix used for natural fiber reinforcement is related to the thermal instability of the fibers at temperatures higher than 200°C. For this reason, only those polymers that soften under this temperature, PE, PP, PVC, polystyrene, and thermoactive compounds can be used as matrices [17]. However, some engineering applications require the development and use of composite materials based on high temperature melting thermoplastics reinforced with natural fibers. Obtaining such materials is difficult because engineering thermoplastics have a melting point > 200°C, above the degradation temperature of natural fibers [18, 19]. In addition to these temperature differences, fiber reinforcement is influenced by other factors: fiber type, configuration, composition, length, harvest season, post-harvest treatment, humidity, etc. [20, 21]. These factors, together with thermal stability, drastically influence the properties of the composites during the development process, thus limiting their use in various applications [22]. Thus, for the obtaining of high temperature thermoplastic composites, it is necessary to modify the surface of the fiber in order to avoid degradation during processing.

One of the engineering thermoplastic polymers, widely used for the manufacture of beverage bottles, is polyethylene terephthalate (PET). Due to the short usage period and the very high annual consumption, over millions of tons, it makes recycling a problem both ecologically and economically [23]. Recycling is the most cost-effective method for removing PET waste, thus offering cheaper material than virgin. Physical recycling by reprocessing PET in the melt is considered the simplest method because it requires minimal investment due to the high volume and availability of PET, can be achieved on ordinary processing equipment and is also environmentally friendly. However, during recycling, PET undergoes a number of chemical, mechanical, thermal and oxidative degradations that lead to lower intrinsic viscosity / molecular mass and implicitly lower thermal and mechanical properties [24]. From this point of view, many studies have focused on blending PET with other polymers: polycarbonate [25], HDPE [26], polypropylene [27-29], polyvinyl chloride (PVC) [30]. Unfortunately, these polymers are incompatible with PET and require the use of an interface compatibilizer, the most used being maleic anhydride graft polymers. Other methods have focused on the use of compounds known as chain extenders to improve viscosity and limit PETr degradation processes. The most commonly used is the multifunctional epoxy-based oligomeric chain extender (Joncryl), mainly added at the start of / during PET melt processing [31, 32]. Another study focused on the addition of styrene and ethylene / butylene (SEBS) triblock copolymer as impact modifier, and PE-g-MA as interface compatibilizer, in the blend containing recycled polymers (HDPE and PET). 4,4'-methylenebis (phenyl isocyanate) (MDI) was investigated as a chain extender. The chain extension reaction of the carboxyl or hydroxyl groups of PETr with the isocyanate groups in MDI and the reaction of the hydroxyl groups of R-PET with anhydride groups of PE-g-MA was observed. The study found that the reaction between anhydride and hydroxyl groups led to the formation of esters, and that urethane linkage is formed between the hydroxyl and isocyanate groups. Interactions between the carboxyl group and the isocyanate lead to the formation of amide linkages. The flexural strength and modulus obtained with the PETr / HDPEr / SEBS / PE-g-MA / MDI blend (70: 30: 5: 2: 0.5) was 23.2MPa, 0.7 GPa, respectively. For recycled HDPE (27.1MPa, 0.64 GPa), and for PETr (83.3 MPa and 2.83 GPa). The impact resistance in the PETr / HDPEr / SEBS / PE-g-MA / MDI blends was 12.16 KJ/m², and the one obtained for HDPEr (13.35 KJ/m²) and PETr (3.89 KJ/m²) [33]. Another study focused on the addition of hemp fibers (1%, 5%, 10%, 15%, and 20%) to limit thermal degradation of PET. The mixtures were processed in a torque batch mixer at 240, 250 and 260 °C. Heavy thermal degradation of hemp fibers was influenced by the amount and processing time that were higher [19]. Pereira et al. [34] studied the effect of the addition of poly(ethylene methylacrylate) (EMA) and cotton linter (CL) on the properties of recycled

poly(ethylene terephthalate) (PETr). То improve compatibility between EMA and PETr, ethylene / methyl acrylate / glycidyl methacrylate terpolymer (EMAGMA) and maleic anhydride grafted polyethylene (PE-g-MA) were used. The rheological results showed that the torque value measured after 30 minutes, in the case of the non-compatibilized mixture – PETr / EMA (ratio 70:30) was 1.6 Nm versus 1.0 Nm obtained for PETr. The addition of 1% CL in the PETr / EMA / CL mixture decreases the torque value to 0.9 Nm, indicating that viscosity decreases and, implicitly, degradation phenomena are favored. In the case of PETr / EMA / EMA-GMA / CL and PETr / EMA / PE-g-MA / CL mixtures containing compatibilizer, the torque values increase to 1.2 and 1.3 Nm, however, to a rather low extent relative to PETr. The tensile strength obtained in these blends is, however, inferior to PETr. İzgi et al. [35] obtained different mixtures based on Cynara scolymus / polyethylene terephthalate fibers (72/25, respectively 25/75%) and investigated their influence on the mechanical properties. The tensile strength of the mixture (75/25% Cynara scolymus / PET) was 11.84 and for the mixture (25/75% Cynara Scolymus / PET) of 9.87 N/mm² relative to PET (3.77 N/mm²). The most common methods for obtaining lingo-cellulosic fiber reinforced composites are: vacuuminfusion process [36], hand-layup technique [37], pultrusion, melt mixing, etc. [38, 39].

The purpose of this paper is to evaluate the influence of the addition of polypropylene grafted with maleic anhydride and untreated / treated hemp fibers on PETr's physicomechanical, thermal, rheological and morphological properties.

MATERIAL AND METHODS

Materials

Polyethylene terephthalate in the form of flakes was obtained by the industrial partner SC MONOFIL SRL by recycling of municipal waste bottles using a knife mill; Maleic anhydride modified mLLDPE (PE-*g*-MA) - Bondyram TL4109E, MFI 190°C/2.16 Kg: 2, density g/cm³: 0.905, melting point °C/F: 117/243, Vicat softening point °C/F: 85/185, maleic anhydride %: high, from Polyram, Israel; 2.2; hemp fibers of 3-5 mm; Isopropanol – molecular weight: 60.10, assay ≥99.7%, Sigma-Aldrich; Titanium(IV) isopropoxide – molecular weight : 284.22, assay: ≥97.0%, density: 0.96 g/mL at 20 °C(lit.), acquired Sigma Aldrich; Non polar polyethylene wax – Deurex E11K, drop point, °C: 110-120, viscosity, mPas ≤80, density, g/cm³: 0.94-0.96, acquired from Deurex AG, Germany.

Obtaining Composites

In order to obtain composite materials, the hemp fibres were functionalized according to the following two routes:

Route 1 – The first synthesis route involves the spraying of the titanium isopropoxide (1 and 5%wt in anhydrous isopropanol) onto the surface of the cotton fibers, followed by precipitation of the TiO_2 by spraying water, the precipitation of the TiO_2 nanoparticles happening very fast.

Route 2 – The second synthesis route consists in treating the cotton fibers with water followed by the spraying of titanium isopropoxide (1 and 5%wt in anhydrous isopropanol) onto the surface of the wet cotton fibers while TiO_2 are obtained.

In both cases, the functionalized fibres were dried in vacuum oven at 50°C before compounding with the polymeric blends.

All blends/ composites were obtained in the presence of compatibilizer - PE-g-MA, introduced in an amount of 30wt% (relative to the amount of PETr) and in the presence of 4 wt% treated/untreated natural fibers (relative to the total amount of PETr/PE-g-MA). Formulations presented in Table 1, were processed in a 350 E Brabender mixer, with maximum mixing capacity of 370 cm³. Prior to processing, PETr flakes were dried in a hot air oven for 24 hours at 150°C. Dried PETr flakes were used to obtain the mixture (P1) or the (P11-P14). When composites adding untreated/treated natural fibers to the blend, due to the density difference between PETr and fibers, PE-based wax is used. In these blends, dry and warm PETr flakes were initially mixed with 10 wt% PE-based wax (relative to the amount of fibers) in order to adhere to and disperse the fibers as homogeneously as possible on the surface of the PETr granules. All formulations presented in Table 1, were processed in the Brabender mixer, under similar conditions of temperature, screws speed, mixing time and amount, to limit experimental errors as much as possible. It is important to mention that even if both routes of hemp functionalization involved two concentrations (1 and 5% wt of titanium isopropoxide in anhydrous isopropanol) only two of these functionalized fibres will be presented because the other two composites led to low mechanical properties. During the mixing, the influence of compatibilizer and treated/untreated natural fibers on torque and temperature was monitored, depending on the mixing time. The temperature set for all samples on the three Brabender mixing zones was 240°C, a total mixing time of 7 minutes (of which 1 minute at 30 rpm and 6 minutes at 110 rpm), in order to obtain a more homogeneous dispersion of the compatibility agent and hemp fibers in the molten PETr mass. From the processed blends, physico-mechanical test specimens were obtained in an electric heated press, by the compression method, using the following parameters: the temperature of the plates – 243°C; pre-heating time – 3 minutes; pressing time – 4 minutes, cooling – 10 minutes, force - 300 kN. The specimens for physical, mechanical and thermal properties (flexural, elongation, modulus, Charpy shock, density, hardness, Vicat) had the following dimensions: length - 80 mm, width - 10 mm and thickness -4 mm. Subsequently, fractured specimens after Charpy shock resistance determination were subjected to morpho-structural determinations (SEM, FTIR microscopy).

Raw materials/ Sample symbol	PETr	P1	P11	P12	P13	P14
PETr flakes	100	70	70	70	70	70
PE-g-MA	-	30	30	30	30	30
Hemp fibers	-	-	4	-	-	-
Hemp fibers immersed in isopropanol	-	-	-	4	-	-
Hemp fibers functionalized with 1% titanium isopropoxide, according to route 1*	-	-	-	-	4	-
Hemp fibers functionalized with 5% titanium isopropoxide, according to route 2**	-	-	-	-	-	4
PF-based way	_	_	10	10	10	10

Table 1: Formulations of processed blends/composites, wt%

* the composites obtained using hemp fibres functionalized with 5% wt titanium isopropoxide in anhydrous isopropanol, according to route 1, exhibited low mechanical properties and are not presented in this manuscript

* the composites obtained using hemp fibres functionalized with 1%wt titanium isopropoxide in anhydrous isopropanol, according to route 2, exhibited low mechanical properties and are not presented in this manuscript.

Tests and Analysis

Torque rheometry – mixtures / composites were processed in a Brabender type 350E mixer equipped with a temperature measurement sensor in the mixing chamber. It also features temperature, torque, and speed measurement and control elements. These parameters can be controlled / set up and recorded in real-time by specialized software, with the possibility of data interpretation and statistical analysis, at various points of interest.

The 3-point *flexural tests* were performed according to the SR EN 178 standard with a minimum of 6 specimens, at a speed of 2 mm/min, at conventional deflection (1.5 x specimen thickness) and the distance between supports of 16 x specimen thickness. Flexural strength, elasticity modulus, and flexural elongation were determined.

The impact resistance of the mixtures / composites was determined using INSTRON (CEAST 9050) hammer-pendulum equipment. Charpy resistance was determined on notch specimens, using a hammer with a maximum energy of 2J. The determinations were carried out according to ISO 179, method A, the Charpy test type, at a 150° angle, support span 62, using a number of 10 specimens with a length of 80 mm and a thickness of 4 mm.

Density, g/cm³ – mixtures / composites were determined according to SR ISO 2781: 2010.

Hardness, **°ShD** was determined according to the SR ISO 7619-1:2011 standard.

FTIR microscopy and FTIR spectra were performed to determine the individual components found in the sample (at specific

wavelengths) and to determine the degree of compatibility between the phases. The images were obtained with a Thermo iN10 MX microscope operated in reflection mode.

Scanning Electron Microscopy (SEM) was used to study the morphology of untreated / treated hemp fiber surface, deposition rate, TiO₂ particle size measurement, fiber distribution in PETr mass, interface between fiber / polymer matrix and type of mechanism involved in composite failure. SEM images were recorded on a Quanta Inspect F scanning electron microscope (FEI-Philips, Hillsboro, OR, USA) with a field emission gun at an accelerating voltage of 30 kV with a resolution of 1.2 nm.

Vicat Softening temperature was determined according to the ISO 306 standard.

RESULTS AND DISCUSSION

Torque/Temperature/Time Analysis

Figure 1 and Figure 2 show temperature and torque versus time registered by the Brabender laboratory mixer for PETr, PETr/PEg-MA (P1) and PETr/PE-g-MA composites reinforced with untreated / treated short natural fibers (P11-P14), processed in similar conditions (time, temperature, screw speed, etc.) to limit the experimental errors. As can be seen, when PETr is being processed, due to its high hardness, torque increases to 222 Nm in just 4 seconds at the time of loading, then drops to about 110 Nm after a 60-second mixing time. Upon increasing the mixing speed to 110 rpm, the torque increases to about 140 Nm, then decreases progressively to 30 and

24.8 Nm in the 224 and 416 seconds respectively. A sudden rise in temperature at 258°C is observed, in the range of 4-224 seconds, after which the temperature remains constant until the end, Figure 2. This clearly demonstrates that PETr is completely melted in 224 seconds, also taking into account that the torque remains constant. At first glance, it can be deduced that the PETr melt processability is excellent, taking into account the torque, and temperature, during the last processing step. However, in the last stage of processing, the torque drops by approximately 17%, which could be attributed to PETr degradation (decrease in molecular weight, reflected in decreased intrinsic viscosity). It is known that the viscosity reduction is directly proportional to torque. These observations are in very good

agreement with studies conducted by other researchers [32, 40]. For PETr, mainly due to the higher hardness than the other mixtures (P1 or P11-P14), the initial torque corresponds and plastic to the friction dissipation, deformation. The torque is directly proportional to the rate of mechanical energy dissipation inside Brabender's mixing chamber. In this way, the mechanical energy is dissipated in the form of heat and leads to the temperature rise, resulting in the melting of the PETr matrix. Instead, if PETr and lower hardness polymers are used, the initial torque moment decreases because the viscous energy dissipation mechanism is different from the dissipation mechanism which takes place between solid particles of high hardness [1].



Figure 1. Torque versus time for PETr, P1, and P11-P14 samples





Therefore, in the case of the mixtures P1 and P11-P14, a decrease in the initial torque as well as the temperature, as compared to the values obtained in PETr, is observed. In order to be able to demonstrate that the addition of PE-*g*-MA improves the torque value and implicitly the viscosity, due to the limitation of PETr degradation

processes, a detailed analysis of point D was performed. Evaluation of point D, recorded at the end of the mix (7 minutes), provides very important information regarding the influence of PE-g-MA and untreated / treated fibers on the torque value. The values obtained for all samples are presented in Table 2.

Tests	Time [s]	Torque [41]	St. temp. [°C]	Speed [1/min]	Energy [kJ]
PETr	416	24.8	258.2	110.0	170.4
P1	410	32.5	264.2	110.0	223.3
P11	416	28.0	260.8	110.0	215.8
P12	416	28.2	260.3	110.0	228.4
P13	416	30.6	261.4	110.0	219.3
P14	416	31.3	261.4	110.0	227.9

Table 2: Statistical Evaluation – Point: D of PETr, P1 and P11-P14 samples

Analyzing the results presented in Table 2, for PETr, it is found that the torque and energy values are only 24.8 Nm and 170.4 kJ at the end of the mixing process. That demonstrates the viscosity of the PETr mixture is low. Instead, mixtures containing PE-*g*-MA and / or untreated / treated fibers with varying percentages of TiO₂ show improved torque values by 30% (P1), 12.9% (P11), 13.7% (P12) 23% (P13), and 26% (P14) compared to PETr. Also, for all mixtures, there is a substantial increase in temperature, and energy required for mixing, compared with PETr.

Although the torque value is improved for samples P1 and P11-P14, compared to PETr, it should be noted that there is a fairly substantial influence of the addition of unfunctionalized / functionalised fibers. For P11 and P12 samples containing nonfunctional fibers and immersed only in isopropanol, the torque value decreases to 28 and 28.2, respectively, compared to 32.5 for P1 (PETr / 30% PE-g-MA). This decrease can be attributed to the fact, that in these cases, the interaction between the OH- (fiber) group, the PETr terminal groups and the PE-g-MA anhydride group is weak, such as Van der Waals, hydrogen. These bonds do not have the same strength as the covalent bond and as such they fail to maintain viscosity in the same parameters as the P1 sample (where the reaction is of a chemical nature, between the

terminal PETr group and the PE-g-MA anhydride group). In contrast, for samples P13 and P14, the torque value is very close to that obtained with the P1 sample due to the formation of strong chemical bonds / strong interactions between the of TiO₂ surfacecoated fibers, the anhydride group of PE-g-MA, and the terminal groups from PETr (-COOH or OH). It is also noted that as the amount of TiO₂ deposited on the surface of the fibers is higher, the viscosity is more pronounced. Pereira et al. [34], Zimmerman and Zattera [42] note that the presence of anhydride-terminal coupling agents promotes the formation of hydrogen or covalent chemical bonds between polymeric and fiber phases, leading to higher molar mass. Moreover, in the SEM one can see a very good compatibility between the phases, especially the mixture (P1) and the P13 and P14 composites, which demonstrates the good interaction between the components in the system, similar to the observations made by Chiu and Hsiao [27].

Physico-Mechanical Determinations

Hardness and Density

The hardness values obtained for the processed blends are presented in Figure 3. It can be seen that the highest hardness of 81 °Sh D is presented by PETr, which also demonstrates the high values of the initial

torque moment recorded in the Brabender mixing chamber. For sample P1, due to the addition of a high 30% PE-g-MA, the hardness value is substantially reduced to 75 °Sh D. In the case of P11 and P12 mixtures containing untreated fibers, the hardness values did not change significantly, relative to sample P1. The samples P13 and P14, however, show hardness values increased proportionally with increasing of the TiO₂ percentage, present on the fiber surface, up to 76 and 78 °Sh D respectively. This was to be expected because the addition of inorganic particles in the polymer mass increases the hardness and substantially improves the mechanical properties provided it is homogeneously dispersed in the polymer mass and there is a good interaction with the components in the system.



Figure 3. Hardness values obtained for PETr, P1 and P11-P14 samples



Figure 4. Density values obtained for processed samples

As can be seen from Figure 4, the density of all mixtures decreases relative to the value obtained on PETr. The lowest density value is obtained for the P1 mixture followed by the P12 mixture. If TiO_2 treated fibers are added, a slight increase in density is observed. Density is an important parameter in many areas (and especially automotive, aeronautics, etc.), where materials with improved mechanical properties, environmentally friendly but also with low density are increasingly required (taking into account economic considerations, and in particular fuel economy).

Flexural Properties

The flexural properties of the blends / composites were determined using a 3-point flexural test. All blends / composites subjected to this type of test were obtained under similar conditions of temperature, time, pressure, etc. (in the Brabender mixer followed by obtaining the test specimens in an electric heated press) in order to be able to accurately determines the influence of compatibilizer addition and untreated / treated natural fibers on PETr properties. The flexural strength for PETr shows the lowest value – only 17.72 MPa, of all the tested mixtures, which demonstrates that repeated cycles of heating / cooling at high temperatures / pressures lead to massive PETr degradation. The PETr flexural modulus, and elongation are significantly lower than the values obtained for PE-g-MA and / or fiber mixtures. Moreover, visually, PETr specimens obtained showed very high, both hardness and friability. It is also important to mention that PETr flakes used to obtain blends were not pure because they contained materials from caps, especially polypropylene.



Figure 5. Flexural properties (resistance, modulus, and elongation) of PETr, P1 and P11-P14 samples

In the case of the P1 mixture, it is observed that the addition of PE-g-MA in PETr significantly improves bending properties. It is noted that flexural strength increases by 106% relative to the value obtained in the case of PETr. Moreover, Young's modulus and elongation improved by 31 and 187% respectively compared to PETr. These results demonstrate that the addition of PE-g-MA is beneficial, being able to greatly limit the PETr degradation due to the bonds formed between the PE-g-MA anhydride group and the PETr terminal groups, thus increasing the molecular mass of PETr and implicitly the bending properties. Furthermore, PE-g-MA used in

blends has a high viscosity due to the high percentage of maleic anhydride – 30% – grafted on the PE surface. Increasing the number of anhydrous groups allows the formation of a high number of chemical bonds with the existing PETr groups, bonds that lead to an increase in molecular weight, similar to the observations made by Pereira *et al.* [34]. Visually, it can be seen that the addition of PE*g*-MA significantly improves PETr friability. The obtained specimens were also subjected to bending by hand, observing a very good deformability compared to the PETr specimens that were instantly breaking. Moreover, the films obtained from this mixture could be subjected to a rather high number of flexions, until the cracks appeared/material failure.

In the case of the P11 and P12 mixtures, it is observed that bending properties increase relative to PETr but are inferior to those obtained in the case of P1 mixture. Thus, flexural strength decreases by 10 and 3% in the case of P1 and P12 mixtures relative to P1. Young's modulus decreases by 4.7% for P11, but increases by 2% for P12 as compared to P1. Similar behavior is observed in the case of the elongation values; for P11 mixture, the elongation decreases by 21.5%, but increases by 7% in the case of the P12 mixture. As noticed, the addition of untreated natural fibers or just immersed in alcohol reduces flexural strength, probably due to slight agglomerations in PETr mass and limited compatibility between phases.

Very good flexural strength values were obtained, however, in the case of adding fibers whose surface was treated with 1% and 5% TiO₂ respectively, samples P13 and P14. As it can be seen, the flexural strength increases by 75 and 23% respectively for samples P13 and P14 relative to sample P1. Young's modulus improves by 23% for P13 but decreases by 4% for P14 composite compared to P1. Bending elongation shows a substantial increase of 140 and 38% for P13 and P14 mixtures compared to those obtained for P1. The reduced elongation of P14 composite compared to P13 may be attributed to the 2°ShD hardness increase. The results show a significant improvement in PETr bending properties, both by the addition of PE-g-MA (improves the ductility and phase compatibility) and the addition of treated fibers. Furthermore, a very high influence of the treatment applied to the surface of the fibers on the bending properties is noticed, because the presence of the TiO₂ groups improves the interactions with the polymeric components in the system, limits to a higher extent the agglomeration of the fibers and protects their surface against thermal degradation, due to high processing temperatures.

Impact Resistance

Impact resistance is a very important property of composite materials because it provides information on the maximum energy to which a material may be subjected before it breaks. In general, polyesters both recycled and virgin have low impact resistance, mainly due to their very high hardness. To improve their strength, numerous research studies have focused on the addition of flexible (especially elastomeric) chains to improve ductility. The mixtures / materials obtained in this work, Figure 6, show very different shock resistance values and are strongly influenced by the composition. All Charpy impact resistance determinations were carried out in similar conditions using a number of 10 notch specimens and a pendulum with 2J energy. In PETr, a very low shock resistance of only 1.02 kJ/m² is observed, due to, in particular, very high friability and thermal degradation that occurred during processing. A very pronounced improvement in resistance of up to 7.09 kJ/m² was observed in the P1 mixture, which demonstrates that the addition of PE-q-MA, due to its very good compatibility with PETr and its elasticity, reduces friability and absorb applied mechanical energy. In the case of P11 and P12 mixtures, the shock resistance is less than just 4.48 and 6.7 kJ/m² respectively, compared to those obtained with the P1 mixture due to poor interactions / adhesions between the fibers and the polymers in the system, these findings are supported by the SEM microscopy. In these cases, the failure of the material occurs predominantly by pulling out the fibers. Generally, this is the main mechanism for failure of fiber-reinforced materials, in the case of impact assessments, phenomenon also observed by other authors [37, 43]. Substantial increases in impact strength values of 13.78-14.67 kJ/m² were obtained for P13 and P14 mixtures containing titanate-treated fibers. The SEM images obtained confirm the deposition of a generous polymer layer on the surface of the fibers and a very good insertion of these in the PETr mass. In these cases, could not be seen areas where the fibers were pulled or fractured from the matrix. Therefore, the addition of an optimal amount of PE-g-MA has the ability to improve Charpy impact because it improves PETr ductility by acting as a stress transfer agent, limiting phase debonding and allowing for strong interactions between components [44]. It is known that, the higher the interfacial adhesion between fibers and matrices, the higher the impact resistance [26, 37, 45].



Figure 6. Impact resistance for PETr, P1 and P11-P14 samples

Thermal Analysis

Vicat Softening Point

The Vicat temperature reflects the softening point and is an important parameter with regard to the maximum temperature at which the material can be used in a given application. Table 3 presents the Vicat temperatures obtained for the PETr, P1 and P11-P14 mixtures. It can be seen that PETr has the highest softening point, 210°C. The introduction of PE-*g*-MA into the PETr (P1) mixture decreases the Vicat temperature by

almost 85°C. This was to be expected because PE-g-MA has a softening point of about 85°C, much lower than PETr. If TiO₂-functionalised hemp fibers are used in 5% (P14) and 1% (P13), the Vicat temperature increases bv approximately 7 to 5°C compared to P1 but is maintained at low values compared with PETr. These results clearly indicate that PE-g-MA greatly decreases the thermal properties, and in applications requiring high temperatures, it is necessary to compensate for these losses, either by the addition of stable thermal oxides in higher quantities or by the addition of synthetic fibers (glass, carbon, etc.).

Table 3: The softening temperature of the processed mixtures

Determination/Samples	PETr	P1	P11	P12	P13	P14
Vicat softening point, °C	210	125	127	129	130	132
Softening interval, °C	230-240	140-150	135-145	140-150	142-152	145-155

Morpho-Structural Characterisations

Scanning Electron Microscopy and EDS Spectra

Scanning electron microscopy was used to study the morphology of untreated / treated hemp fiber surface, TiO_2 particle size measurement, PETr mass distribution, interface between the fiber / polymer matrix, and the type of mechanism involved in composite failure. In Figure 7, SEM images obtained on untreated / treated hemp fibers with different amounts of TiO_2 are shown. For the images recorded on non-functional hemp fibers, fine layers with the non-cellulosic structure deposited on the surface (wax, pectin) and impurities can be seen. In the case of 1% TiO₂ modified fibers, a uniform deposition of the powder on the fiber surface is observed. Also, for fibers treated with 5% titanium isopropoxide, the thickness of the deposited layer is much higher compared to that obtained with 1% titanium isopropoxide. In this case, a relatively uniform deposition of TiO₂ on the surface of the fiber is observed, which shows that the chosen modification method is suitable. At 20000x magnification, it is observed that the TiO_2 particle shape is

Untreated hemp fibers, 500x

spherical, and the size falls within the nanometer range.

1% TiO₂ treated fibers, 500x



5% TiO₂ treated fibers, 500x







Figure 7. SEM images of untreated / 1 and 5% TiO₂-treated hemp fibers

The SEM microscopies recorded for the P1 mixture and the P11-P14 composites were tested in the fracture section, resulted after Charpy resistance determination. As shown in Figure 8, for all the blends / composites obtained, the degree of dispersion of PE-g-MA and the untreated / treated fibers is relatively homogeneous. No areas with poor or fibrous agglomeration areas could be seen in PE-g-MA. In the case of the P1 mixture, a very good dispersion of PE-g-MA in the PETr mass (in the form of spherical particles with dimensions between 46-66 nm) is observed. As a result of the material failure, no voids could be seen, due to a high interaction between the polymeric phases. This demonstrates that PEg-MA improves PETr ductility and adsorbs much of the applied energy. In the case of the P11 mixture, a good dispersion of untreated fibers in the mass of polymers, and the

deposition of a substantial layer of polymer on the surface of the fibers can be observed. However, due to poor interactions, the adhesion between the matrix and the fiber is weak, and leads to the separation of the fibers, following the applied energy. In the case of the P12 mixture, a good coating of hemp fibers with polymers, as well as the presence of voids in the material due to fiber pulling, is observed, which shows a poor interaction between the components. However, the fibers remaining after the impact do not show the debonding phenomenon, as in the case of P11. In the case of P13 mixture, which contains TiO₂ modified hemp fibers, a very good adhesion between the phases is observed, and the fibers are virtually completely embedded in the polymer matrix. The failure of the composite takes place predominantly at the fiber / matrix interface and not by fracture the fibers or pulling out. This behavior confirms with certainty the very good resistances obtained by bending and impact. In case of P14 mixture, hemp fibers can not be viewed, probably due to the deposition

of a more generous polymer layer on their surface, which confirms the very good shock resistance of the hemp.





Figure 8. SEM images for P1, P11-P14 samples, at various magnifications, 10000, 80000 and/or 40000x

EDS analysis is a useful method of identifying the constituent elements existing in a sample. In this case, EDS analysis was performed to identify the distribution of TiO_2 from P13 and P14 samples containing TiO_2 as a consequence of the functionalization of the

hemp fibres with 1 and 5% titanium isopropoxide. As can be seen from Figure 9, the presence of Ti, could be identified in the sample, but in a small amount, if we relate to the relative intensity of C.





Figure 9. EDS spectra for P13 samples

The EDS spectra of sample P14 shown in Figure 10 highlights a substantial amount of TiO_2 present at the failure surface which can be explained based on the higher amount of TiO_2 deposited onto the surface of the hemp fibres. Also, combining EDS data with the SEM data it can conclude that SEM images of P14 do not

reveal any fibres extremity at the fracture surface which could be explained if accepting that over certain content of TiO_2 the detaching appear at the TiO_2 layer allowing in fact the pulling out of the hemp fibres partialy coated with TiO_2 while another part remain at the PET mass.



Figure 10. EDS spectra for P14 sample

FTIR Microscopy

The reference as well as the short fibers reinforced composite materials were analysed by FTIR and found similar spectra (Figure 11). All the spectra were overlaid such as the most intense peak appearing at 724cm⁻¹ to have the same intensity for all the spectra. The reference sample (P1) containing only PET and PE-*g*-MA can be considered a first reference sample and comparing with the P11 which additionally contains 4% hemp fibres, a strong water adsorption as well as the splitting of the band from 1092cm⁻¹ can be seen. According to FTIR database the main peaks of PET appears at 1721, 1270, 1129, 1107, 1020, 872 and

728cm⁻¹ while the main peaks of hemp fibres appear at 2917, 2850, 1734, 1426, 1368, 1315, 1202, 1159, 1107, 1055, 1030, 897, 704cm⁻¹. Also, for all the samples, the intensity of the bands corresponding to CH_2 decreased significantly as a consequence of the functionalization, the samples obtained with functionalized hemp fibres (P13 and P14) exhibiting the lowest peaks at about 2850 and 2920cm⁻¹ being shielded by the TiO₂ layer. Based on these data, the distribution of the components is highlighted in Figures 11-16 at 1130 cm⁻¹ (strong peak corresponding to PET), 1265cm⁻¹ (strong peak corresponding to hemp fibres) and 3430cm⁻¹ free OH groups. Based on the analysis of the spectra, it can be seen that only the peaks of PET and PE-*g*-MA appear which means that hemp fibres are well covered by the polymeric blend.



Figure 11. FTIR spectra of the reference / short fibres reinforced composite materials



Figure 12. FTIR and video image of the P1 mixture (PETr/30%PE-g-MA)

In microscopy, certain important differences can be highlighted. In the case of P11 (Figure 13), it can be observed that all the components are homogeneously distributed which means that water absorption mainly occurs at the level of hemp fibres. The distribution of the short fibres within the composite materials is very good, in fact there are no significant heterogeneities (very good similarity between the four representative maps recorded at 1130, 1265, 3429 and 2850cm⁻¹). The same conclusion was obtained for the sample P12, Figure 14, obtained in similar conditions with P11 but maintaining hemp fibres in isopropanol before drying and use for obtaining the composite materials.



Figure 13. FTIR and video images of P11 sample (PETr/30%PE-g-MA/ Untreated hemp fibers)



Figure 14. FTIR and video images of P12 sample (PETr/30%PE-g-MA/ Hemp fibers immersed in isopropanol)

When functionalised hemp fibres are used, some important changes appear. First of all, the peaks of hemp as well as the peaks corresponding to adsorbed water decreases because of the presence of TiO₂ nanoparticles which cover the hemp fibres. Also, because of the surface modification of the hemp fibres, the peaks corresponding to CH₂ decrease because they are shielded by the oxide layer. Two spectra corresponding to two different areas of the samples, marked with 1 and 2 are presented below, Figure 15, and based on these spectra the FTIR maps are presented in Figure 16. Based on these spectra as well as on the different distribution of the main peaks it can be concluded that a heterogeneous structure is obtained because of the heterogeneous fracture through the material. Similar results are obtained also for the P14 samples, Figure 17 but in this case, the differences between the maps recorded at the three selected wavelengths are much more evident because the fracture is preferential.



Figure 15. The FTIR spectra of the P13 sample recorded in the 1 and 2 area (PETr/30%PE-g-MA/4% hemp fibres/1% titanium isopropoxide)





Figure 17. FTIR and video images of P14 sample (PETr/30%PE-g-MA/4% hemp fibres/5% titanium isopropoxide)

CONCLUSIONS

The main objective of the paper was to study the effect of the addition of compatibilizer - PE-g-MA and untreated / treated hemp fibers on the mechanical, morphological and rheological properties of PETr. Also, the use of PE-g-MA, can limit the thermo-oxidative degradation processes to which PETr is subjected during reprocessing. The formation of bonds between the polyester terminal groups and the PE-g-MA anhydride groups increases the viscosity of the mixture and, implicitly, the molecular weight. These findings are supported by the torque values obtained with PETr / PE-g-MA (P1), which are clearly superior to those recorded for PETr. It was found that if non-functionalized hemp fiber or only immersed in isopropanol is introduced into the PETr / PE-g-MA mix, the torque decreases compared to the one obtained for the P1 sample but increases compared to that obtained for PETr, due to poor interactions between components. Instead, the addition of modified hemp fibers with 1 or 5% TiO₂ improves the torque value to close to that obtained for the P1 sample. Mechanical properties (flexural, modulus, elongation, shock) are greatly improved by simply adding PE-g-MA to PETr, due to the reduction of PETr fragility. However, the Vicat temperature is clearly below PETr. In the case of composites containing untreated fibers, mechanical properties are reduced due to poor interface interactions. The best mechanical properties were obtained in the case of adding functionalized fibers, due to very strong interactions developed at the interface. SEM and FTIR microscopy confirm a good coverage of the fibers with polymer, a very good dispersion of both PE-g-MA and PETr mass. In the case of composites containing untreated fibers, the main material failure mechanism is by debonding and pulling out. Instead, in the case of treated fibers, due to a very good interface between the components (the fibers are fully embedded in the matrix), failure occurs exclusively by fibers fracture to the interface. Areas associated with fiber pullouts cannot be viewed. FTIR spectra and FTIR microscopy confirm a very good polymer

coating of fibers. Based on the results, it can be concluded that the PETr processing by the addition of suitable components leads to the achievement of some high-performance properties and offers the premises for the use of these low-cost materials in various applications in automotive, construction industry, etc. Moreover, these materials can successfully replace conventional composites, based on virgin polymers, reinforced with synthetic fibers in various applications, with some more environmentally friendly, more cost-effective (due to the abundance and the lower price of recycled polymers and natural fibers) materials, and with a lower impact on human health.

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USE OF GELATIN BINDER AS A BASE COAT IN THE FINISHING PROCESS OF TANNED RABBIT SKIN

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USE OF GELATIN BINDER AS A BASE COAT IN THE FINISHING PROCESS OF TANNED RABBIT SKIN

ABSTRACT. Research on the use of bovine split hide gelatin protein binder for the finishing process of rabbit crust skin has been carried out. This research aimed to study the use of gelatin as a protein binder as a substitute for patent binders for finishing tanned rabbit crust skin and to obtain the best percentage of using gelatin as a protein binder in the finishing process of tanned rabbit skins. The materials used in this study were 20 sheets of Rex rabbit skin with an area of 21.25 square feet (sqft), bovine split hide gelatin, casein, and tanning agents. The research treatment was T1 base coat solution plus 50 parts of gelatin, T2 plus 70 parts, T3 plus 90 parts and TK using casein binder as much as 70 parts with five repetitions. Data were analyzed using a one-way completely randomized design, if there were differences between treatments it was continued with Duncan's Multiple Region tests. The results showed that there were significant differences in each parameter except for the drop test before the base coat. The results for the drop test before base coat ranged from 12-14 seconds, after base coat 18-33 seconds, tensile strength around 9.31-13.72 kgf/m², elongation 41.27-60.28%, water absorption after 2 hours 206.15-228.81%, water absorption after 24 hours 212.43 -241.43%, wet rubbing resistance slightly fading (3/4), dry rubbing resistance not fading (4) and ring 25 flexibility between 4.6-5.2 cm. Gelatin from bovine split hide can replace casein as a binder in finishing solutions. The use of gelatin up to 70 parts can be used in the finishing solution for rabbit crust skin and can replace casein. KEY WORDS: finishing solution, gelatin, protein binder, rabbit skin

UTILIZAREA GELATINEI CA LIANT ÎN STRATUL DE BAZĂ APLICAT ÎN PROCESUL DE FINISARE A PIELII DE IEPURE

REZUMAT. S-au efectuat cercetări privind utilizarea liantului proteic din gelatină din piele șpalt de bovine pentru procesul de finisare a pielii crust de iepure. Această cercetare și-a propus să studieze utilizarea gelatinei în calitate de liant proteic ca înlocuitor al lianților comerciali pentru finisarea pielii de iepure tăbăcite și să obțină cel mai bun procent de utilizare a gelatinei ca liant proteic în procesul de finisare a pielior de iepure. Materialele utilizate în acest studiu au fost 20 de piei de iepure Rex cu o suprafață de 1,974 m², gelatină din piele șpalt de bovine, cazeină și agenți de tăbăcire. Tratamentul a constat într-o soluție pentru strat de bază T1 plus 50 de părți gelatină, T2 plus 70 de părți, T3 plus 90 de părți și TK folosind liant de cazeină până la 70 de părți cu cinci repetări. Datele au fost analizate folosind un design unidirecțional complet randomizat, dacă au existat diferențe între tratamente, s-a continuat cu testul Duncan pentru intervale multiple. Rezultatele au arătat că au existat diferențe semnificative pentru fiecare parametru, cu excepția testului de permeabilitate la apă înainte de a aplica stratul de bază. Rezultatele testului de permeabilitate la apă înainte de a aplica stratul de bază au variat între 12-14 secunde, după aplicarea stratului de bază 18-33 secunde, rezistența la tracțiune a fost în jur de 9,31-13,72 kgf/m², alungirea 41,27-60,28%, absorbția de apă după 2 ore 206,15-228,81%, absorbția de apă după 24 ore 212,43-241,43%, rezistența la frecare umedă cu ușoară decolorare (3/4), rezistența la frecare uscată fără decolorare (4) și rigiditatea inelară 25 între 4,6-5,2 cm. Gelatina din pielea șpalt de bovine poate înlocui cazeina ca liant în soluțiile de finisare. Se poate utiliza gelatina în proporție de până la 70 de părți în soluția de finisare a pielii crust de iepure și poate înlocui cazeina.

CUVINTE CHEIE: soluție de finisare, gelatină, liant proteic, piele de iepure

L'UTILISATION DE LA GÉLATINE COMME LIANT DANS LA COUCHE DE BASE APPLIQUÉE DANS LE PROCESSUS DE FINITION DE LA PEAU DE LAPIN

RÉSUMÉ. Des recherches ont été menées sur l'utilisation de liant protéique gélatine provenant de la croûte de bovin pour le processus de finition du cuir en croûte de lapin. Cette recherche visait à étudier l'utilisation de la gélatine comme liant protéique en remplacement des liants commerciaux pour la finition des peaux de lapin tannées et à obtenir le meilleur pourcentage d'utilisation de la gélatine comme liant protéique dans le processus de finition des peaux de lapin. Les matériaux utilisés dans cette étude étaient 20 peaux de lapin Rex d'une superficie de 1 974 m², de la gélatine de croûte de bovin, de la caséine et des agents tannants. Le traitement consistait en une solution de couche de base T1 plus 50 parties de gélatine, T2 plus 70 parties, T3 plus 90 parties et TK utilisant un liant caséine jusqu'à 70 parties avec cinq répétitions. Les données ont été analysées à l'aide d'un plan unidirectionnel entièrement randomisé. S'il y avait des différences entre les traitements, elles ont été suivies par le test à plages multiples de Duncan. Les résultats ont montré qu'il y avait des différences significatives pour chaque paramètre, à l'exception du test de perméabilité à l'eau avant l'application de la couche de base de 18 à 33 secondes, la résistance à la traction était d'environ 9,31 à 13,72 kgf/m², l'allongement de 41,27 à 60,28 %, l'absorption d'eau après 2 heures 206,15-228,81 %, l'absorption d'eau après 24 heures 212,43-241,43 %, la résistance au frottement humide avec légère décoloration (3/4), la résistance au frottement à sec sans décoloration (4) et rigidité annulaire 25 entre 4,6-5,2 cm. La gélatine de la croûte de bovin peut remplacer la caséine.

MOTS CLÉS : solution de finition, gélatine, liant protéique, peau de lapin

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INTRODUCTION

The leather tanning industry is an industry that manages raw animal skins that easily rot or break down into tanned leather or also called finished leather. Tanned leather can be processed into various products that have a higher economic value than raw leather.

Leather finishing is the final stage of the leather tanning process, and is responsible for the final properties and characteristics of the leather, such as hydrophobicity, fastness, abrasion resistance, gloss, and color evenness. The composition of the finishing formulation determines these properties. Finishing formulations include film-forming materials which can be divided into protein-based or resin-based formulations. Standard properties such as color fastness, hydrophobicity, binding to skin pigment particles, providing adhesion to the skin, providing flexibility so that the final product can be stretched with the skin, and also to protect the skin surface are provided by resin-based formulations [1], while protein-based formulations provide a more natural appearance [2, 3]. Protein binders provide a fine grain pattern, good air circulation, and a natural feel [4].

Coloring, oiling, and drying are the final stages of the rawhide (hide and skin) process to become finished leather, while dyeing is the final stage of refinement after the skin is tanned. A topcoat on tanned leather will determine consumer appeal. This finishing process aims not only to cover the damage to the grain by dyeing it but also to improve quality, even out the color, handling, fastness, reduce stickiness and add beauty so that the skin surface becomes more attractive [5].

Binder or adhesive in leather tanning is often used in leather finishing processes or top coat. The purpose of this cover painting is to enhance the attractiveness and durability of the finished skin, namely the appearance of the grain like the original, for example, glacé goat skin, python skin, lizard skin, chicken claw skin, fish skin, and crocodile skin and rabbit skin. Almost all glacé and reptile skins use protein/casein binder top coat. Acrylic, polyurethane, butadiene, and protein binders are binders for creating natural finishing processes with various particle sizes and degrees of hardness to achieve the desired final result (glossy, matte), as well as physical and mechanical characteristics such as tensile strength, elongation, tear strength, and paint rub resistance [6].

There are two kinds of binders, namely natural binders (proteins) and synthetic binders. Protein binders can be made from egg white, milk, cow blood, and gelatin, while synthetic binders are made from ethyl cellulose, polyvinyl alcohol, and poly acrylic acid [7]. Binder from gelatin is obtained by extracting animal skin or bones using hot water. Gelatin can be made from bovine split hide, which is a by-product of the leather tanning industry in the form of split leather of the flesh resulting from liming [8]. The skin of this split still contains collagen, which when hydrolyzed produces gelatin. It was explained further, that the characteristics of gelatin from the bovine split hide are almost the same as commercial gelatin, so bovine split hide gelatin can be used as a substitute for commercial gelatin, which means it can be used in various usage applications.

The functions of gelatin include as a stabilizer, thickening agent, gelling agent, emulsifier, forming a thin film, a suspension, increasing the elasticity, consistency, and stability of the product. Film-forming polymers play an important role in the physical performance of leather finishes. However, the practical use of gelatin as a binding polymeric material may be limited by its relatively poor mechanical properties. Binders are often used in finishes to improve the properties (such as stability, water resistance, and molecular weight) of the polymer binders used in the topcoat [9].

Research related to protein binders for leather finishing includes: using waste which was hydrolyzed with NaOH as a protein binder [10]; the use of vegetable peel waste which is extracted with enzymes as a protein binder [11]; comparison of protein binders and acrylic binders as color binders [12]; comparison of various protein binders in finishing chicken claw skin [3]; examining the effect of egg white protein binder on tilapia skin finishing [13].

This research will be conducted to apply gelatin from bovine split hide which is used in

the finishing of rabbit crust skin with different concentrations, compared to commercial gelatin binder (casein) by measuring its physical properties parameters. Many rabbit breeders do not use their rabbit skins, most rabbit skins are just thrown away or stored in a preserved salt form whenever someone needs it. This research utilizes rabbit skin to become tanned leather to increase its usability and apply gelatin as a binder in the finishing process to improve the appearance of rabbit skin as a tanned leather product and have a higher selling value.

EXPERIMENTAL

Materials and Methods

Instruments

The tools used in this study were tanning drums, compressors, spray guns, digital scales, glass beakers, measuring cups, Petri dishes, stirrers, filters, crock meters, grayscale, Mechanical Universal Testing Machine (Zwick/Z 0.5), softness leather test ST 300 and stopwatch.

Materials

The material used in the study was 20 sheets of rabbit skin with an area of between 1-1.5 sqft each, type A gelatin from a bovine split hide (which is extracted using the acid

method) as a film-forming agent or adhesive. The physical and chemical properties of the gelatin used are water content 6.28%, protein 69.07%, fat 0.32%, ash 0.3%, viscosity 3.83 cP and gel strength 153.53 bloom. Tanning agents and finishing materials such as direct paint as a coloring agent, silicone emulsion, glycerin, 10% formaldehyde solution as a fixative and water as a solvent, ammonia, thinner, and lacquer.

Experimental Design

Statistical analysis was used using a Completely Randomized Design (CRD) with 5 replications where the percentage of gelatin binder was used as a treatment: 50, 70, and 90 parts and 70 parts casein binder as a control.

The Process of Tanning Rabbit Skin

The tanning process uses 20 pieces of fresh Rex rabbit skin which are selected without defects due to disease and cleaned of remaining meat and fat, then weighed to determine the wet weight of 21.25 kg as a chemical calculation. Tanning is done with a combination of chrome and vegetable tanning agent based on quebracho powder. The tanning process formula is presented in Table 1.

		Product		Control				
Process	%	Chemical	patent	Time (minutes)	рН	Other		
Sorting and						Fresh skin selection		
Measuring						and measurement		
Weighing						As fresh weight		
Soaking	400	H2O	Water			diluted 1:10		
	1	Wetting agent	Peramit MLN			Wet conditions		
	0.05	Disinfectant	Preventol ZL					
Green fleshing	200					The remains of flesh		
	4					and blood were		
	0.5					cleaned		
De-hairing		H2O	Water	60		Stir slowly		
		Na ₂ S		30		Continued		
		Ca(OH)₂	Lime			intermittently:		
						run 5' of 15'		
Fleshing								

Table 1: Formulation of Rabbit Skin Vegetable Chrome Tanning Process

Revista de Pielărie Încălțăminte 24 (2024) 2

			Product		Contr	rol
Process	%	Chemical	patent	Time (minutes)	рН	Other
Scudding						
Weighing						
Deliming	300	H2O	Water			
5 6	4	(NH₄)SO₄	ZA	60	Bloten	
	0.5	НСООН	Formic Acid	30	weight	
	1	Degreasing	Gelon PKN	45	- 0 -	
		agent				
Drain. Wash.						
Drain						
	200	H ₂ O	Water			Minimum 6º Be
Pickling	18	NaCl	Salt			
	1.5	HCOOH	Formic Acid			
	0.5	H_2SO_4	Sulfuric Acid			
	100	Pickle water				6-8º Be
Tanning	8	Chrome tanning	Chromosal B			Translucent check
	0.45	agent	Mgo			
Ageing Sammying						
Saving						1 mm
Trimming						
Weighing						
Watting back	200	ЦО	Water	60		
Wetting Dack	200	H2U Wotting agont	Piramid MIN	60		
	0.5	wetting agent				
Drain						
Neutralisation		H ₂ O	Water	6 x 10		
	200	NaHCO ₃	Natrium			
	1.5		bicarbonate			
Retanning		Acrylic resin	Tergotan ESN	20		
-	2	Vegetable	Quebracho	20		
	5	Vegetable	Mimosa	60		
	5					
Drain						
Fatliquoring	100		Temperature			
			water 80°C			
	3		Peramid SLW —		5-5.2	
	5	Sulphited oil	Derminol OCS	60		
	2	Lecithin oil	Trianol LC 60 🔔			
	1	Emulsifier	Peramit MLN			
	3	НСООН	Formic acid			
	0.02	Antifungal	Preventol C			
Setting out						
Tacking wet						
Drying						
Finishing						

Preparation of Base Coat Solution

To gelatin with variations of 50, 70, and 90 parts, were added 20 ethyl glycol, 100 acrylic, 150 acrylic medium, 50 parts wax, and water up to 1000 ml volume. pH should be 8– 9; if not reached, ammonia is added. The base solution formula is shown in Table 2.

ТК	T1	T2	Т3
70	-	-	-
-	50	70	90
610	630	610	590
20	20	20	20
100	100	100	100
150	150	150	150
50	50	50	50
1000	1000	1000	1000
	TK 70 - 610 20 100 150 50 1000	TK T1 70 - - 50 610 630 20 20 100 100 150 150 50 50 1000 1000	TK T1 T2 70 - - - 50 70 610 630 610 20 20 20 100 100 100 150 50 50 1000 1000 1000

Table 2: Rabbit Skin Base Coat Formula

Preparation of Top Coat Solution

Laq water 200 parts, silicone emulsion 20 parts, and water were added to a volume of 1000 ml and stirred until homogeneous.

Preparation of Clearing Solution

Wetting agent 20 ml, ammonia 10 ml were mixed and added water to a volume of 1000 ml and stirred until homogeneous.

Application to the Skin

Rabbit crust skin is sprayed with clearing solution, was left to stand until dry then coated with base coat, allowed to dry, then coated with top coat solution using a spray gun, and after drying fixed with 10% formalin.

Measurement of Rub Fastness (INS ISO 20433:2013) [14]

The parameters observed were testing the rub fastness of rubbing paint on a wet cloth and a dry cloth. The paint's rubbing resistance was tested using a Crock meter equipped with a Gray Scale.

Measurement of Tensile Strength (INS ISO 3376:2012) [15]

Tensile strength values were measured using a Mechanical Universal Testing Machine. The sample was cut according to the pattern in the ISO 3376. The tensile strength value is calculated based on the maximum force (N) with the skin area (mm²) that is applied until the skin breaks.

$$TS = (F max)/A$$
(1)

F max = The force needed until it breaks (N) A = The cross-sectional area of the film (mm²) (Axl)

S = Tensile Strength (kgf/m²)

Measurement of Elongation (INS ISO 3376:2012) [15]

The measurement of elongation is carried out simultaneously with tensile strength. Elongation is an increase in the length of the skin that is pulled from the length of the first to the maximum length.

EL = (Lc-Lo)/Lo x 100%	(2)
Lc = Maximum film length	
Lo = The length of the first film	
EL = Elongation (%)	

Measurement of Drop Test (EN ISO 5404:2021) [16]

Done by dripping a drop of water to the surface of the skin and then calculating with a stopwatch how many seconds it takes the water to be absorbed perfectly into the skin.

Measurement of 2 and 24 Hours of Water Absorption with the Petri Dish Method (SNI ISO 17229:13) [17]

Water absorption is done by making a circular skin sample with a diameter of 7 cm. The skin sample is soaked in a Petri dish at

room temperature for 2 hours and 24 hours. After the desired soaking, the sample was removed and drained and then weighed.

Water Absorption = (W2-W1)/W1 x 100% (3) W1 = Initial sample weight W2 = Sample weight after soaked for 2 or 24 hours.

Measurement of Skin Softness (ISO 17235:2015) [18]

Standard Testing Skin softness was carried out according to ISO 17235. Standards Using Softness Leather Test ST 300. Softness Leather Test ST 300 was used to read data.

Statistical Analysis

Data obtained from treatment were analyzed with ANOVA (Ko variant analysis) based on a completely random design. If there is a difference, it was followed by Duncan's new Multiple Range Test [19]. The level of statistical significance was set at P<0.05. The statistical software package SPSS 15.0 (SPSS, Inc., Chicago, IL, USA) was used for these data analyses.

RESULTS AND DISCUSSIONS

Data on the results of research on the use of gelatin protein binder for the finishing

process of rabbit crust skin can be seen in Table 3.

Drop Test

The drop test is used to determine the quality of water penetration into the skin. Drop test before being given a layer of base coat (crust skin) is not significantly different between treatments. This is because the samples have not been treated with a finishing layer, so there is no effect of binder on the absorption of skin water. The drop test value before the base coat ranges between 13-14 seconds. A drop test with an absorption time of under 20 seconds shows that the level of penetration and surface tension of the skin is good so that it can be continued for the finishing stage, namely the base coat [20].

Table 3 shows the addition of gelatin in the base coat solution, the increase in the amount of gelatin causes the longer absorption of water into the skin. This is because the addition of gelatin which acts as a binder in the base coat solution will form a layer of film on the skin so that the layer of the film can inhibit or hold the water into the skin. Protein binder coating will reduce air permeability [21]. Binder is the main ingredient in forming a film in finishing leather. The more additional binder will form a layer of film that is thicker and the longer the water seeps into the skin [7].

Table 3: Research Data on the Use of Protein Binders for the Finishing Process of Rabbit Crust Skins

Parameter	Treatment							
	T1	Т2	Т3	ТК				
Drop test before base coat (second)	12.50±0.71	13.50±0.71	13.50±0.71	13.50±0.71				
Drop test after base coat (second)	18.50±0.71ª	22.50±0.71 ^b	32.50±0.71 ^d	24.50±.71 ^c				
Tensile strength (kgf/m ²)	9.89±0.81ª	12.10±0.81ª	13.13±0.76 ^b	12.97±1.06 ^b				
Elongation (%)	57.83±0.50°	43.96±0.57 ^b	41.89±0.88ª	59.83±0.64 ^d				
2 hours of water absorption (%)	206.76±0.86ª	212.67±0.90 ^b	215.11±0.55 ^b	227.975±1.18 ^c				
24 hours of water absorption %)	212.60±0.23 ^a	217.79±0.30 ^b	224.95±0.47 ^c	240.66±1.09 ^d				
Dry rub fastness	4 (No fade)	4 (No fade)	4 (No fade)	4 (No fade)				
Wet rub fastness	¾ (A little faded)							
Softness ring 25 (cm)	5.1±0.00c	4.85±0.07b	4.6±0.00a	5.15±0.07c				

Note: Values followed by different letters in the same row indicate a significant difference (P<0.05). T1 = 50 parts gelatin binder, T2 = 70 parts gelatin binder, TK = 70 parts casein binder (control)

Tensile Strength

The increase in the addition of gelatin as a binder in the base coat solution also increases the tensile strength of rabbit skin. Statistics show that there are real differences between T1 and T2 and T3 and TK. This shows that the addition of gelatin in the base coat solution causes a layer that covers the surface of the skin, and the greater the addition of gelatin, the thicker and stronger layers become to increase the tensile strength. The final layer must have a degree of bonding to the skin surface which will be used to improve the physical properties of the skin [4]. When using egg white binder in the finishing process of tanned tilapia skin, with an increase in the concentration of egg whites, tilapia skin tensile strength also increases [13].

The tensile strength test results ranged from 9.31 to 13.72 kgf/m², these results are below INS 06-4586 [22]. Quality requirements for tanned leather with a minimum tensile strength value of 1.500 N/mm² (152.97 kgf/m²). This is because the INS standard uses goat leather, where the thickness of the leather is different from rabbit leather. One of the factors that determines the size of the tensile strength is determined by the thickness of the skin, length of the sample, type of skin and type of tanning agent.

Elongation

The elongation of the skin is related to the softness or elasticity of the resulting skin. The elongation value of the rabbit skin as a result of the test is presented in Table 3. With the increased use of gelatin in the base coat solution, the elongation value of the rabbit skin decreased and was lower than the control treatment using a casein binder. The elongation is inversely proportional to the tensile strength, if the elongation is low, the tensile strength will be high. This value is following the results of a study, who used egg white binder in the finishing process of tilapia skin; with increasing egg white concentration the elongation of tilapia also decreased [13]. The role of the gelatin binder is to fill the empty spaces in the rabbit's skin so that the skin becomes dense and filled which causes low elongation.

The elongation of rabbit skin ranged from 41.27%-60.28%, this result exceeds the INS 06-4586-1998 standard, which is a maximum of 30%. High elongation can be caused by the tanning agent used. The research rabbit skin tanning process uses chromium as a tanning agent with vegetable retanning materials. The explanation is that in chrome tanning, the final product becomes soft and supple to the touch, the color remains the same throughout life, high quality and high hydrothermal stability [23].

Two and 24 Hours of Water Absorption

Water absorption was carried out at 2 and 24 hours, intended to determine the ability of the skin to absorb water. With the increase in the use of gelatin in the base coat solution, the water absorption value of the rabbit skin at 2 and 24 hours of the rabbit skin increased, but it was lower than the control treatment using casein binder. This is because the film that is formed is thicker, and the film that is formed from protein binders is hydrophilic, so the thicker the film layer, the more it absorbs water when immersed in water.

The results of the variance calculation in Table 3 show that water absorption at 2 and 24 hours is significantly different (P<0.05) in each treatment. This is because the nature of gelatin when it becomes a sol is hygroscopic, and will absorb water when soaked in water, so that the film layer formed becomes gel and the skin absorbs more water.

The results of water absorption in rabbit skin for 2 hours ranged from 206.15%-228.81% and 24 hour absorption ranged from 212.43% -241-43%. This result exceeds the standard INS 0234 [24], which requires water absorption for 2 hours a maximum of 80%, and 24 hours for a maximum of 100%. The high water absorption exceeds the SNI standard because gelatin is a protein binder that absorbs water.

Rubbing Fastness

The rubbing fastness of leather is a physical test to determine the color fastness of finished leather. Rubbing fastness is an organoleptic assessment by comparing the color change after the skin is rubbed with a crock meter with a standard color change (Grayscale). The results of the rub fastness test are shown in Figure 1. The average dry rub fastness of rabbit skin is 4 (good enough/does not fade). Casein and protein as the adhesive power of the binder and lacquer solvent emulsion for the top layer are strong enough to adhere to the surface of the skin [25].

The addition of gelatin to the dry rub fastness base coat solution showed no fading. This is because the binder as a film-forming material has the function of binding the materials in the finishing process so that the material will stick to the surface of the skin [26]. Discoloration can also be corrected by adding a top coat [27]. The higher the amount of binder used, in this case, gelatin, the stronger the ability to bind the finishing materials so that the skin does not experience discoloration. The top coat solution determines the final appearance and grip of the leather surface [4].

Plating treatment with 90°C heat treatment also affects the skin and does not fade. Heat in the plating treatment helps to flatten the formed film layer, so that the film layer becomes compact and permanent and is resistant to rubbing [28]. The rubbing fastness of the wet cloth was the same for all

treatments including the control, which was 3/4 (medium/slightly faded). This could be because the binder used is a water-soluble protein binder. When rubbed with a wet cloth, the film layer that is formed is wet so that the bonded finishing material is not tightly bound and does not stick to the skin surface. This condition causes the skin to experience discoloration when tested with a crock meter. The rub fastness resistance for wet fabrics is because the biopolymer film may experience swelling, which tends to open and weaken the polymer structure causing the pigment to diffuse out [9].





Figure 1. Test results for rubbing fastness of tanned rabbit skin TK wet = Addition of 70 parts casein to wet rubbing fastness TK dry = Addition of 70 parts casein to dry rubbing fastness T1 wet = 50 parts addition of gelatin on wet rubbing fastness T1 dry = 50 parts addition of gelatin on dry rubbing fastness T2 wet = 70 parts addition of gelatin on wet rubbing fastness T2 dry = 70 parts addition of gelatin on dry rubbing fastness T3 wet = 90 parts addition of gelatin on wet rubbing fastness T3 wet = 90 parts addition of gelatin on dry rubbing fastness

Softness

The addition of different gelatin to the base coat solution had a significant effect on the softness of the tanned rabbit skin (P<0.05). Table 3 shows that the more gelatin is added to the base coat solution, the lower the laxity. This is because the more gelatin is added the thicker the finishing layer will be, causing the skin to stiffen and reduce its flexibility. According to Smiechowski et al. (2014), skin laxity depends on skin thickness to a small extent [29]. These results indicate that the addition of gelatin to the base coat solution affects the thickness of the finishing layer. The role of gelatin in this case is as a binder that binds chemicals to the finishing solution so that the finishing material can adhere firmly to the skin and this will affect the skin's elasticity. A mixture of binders and finishing materials including pigments has a supple and flexible effect on the skin [30, 31]. Meanwhile, a combination of binders and finishing materials can provide adhesion, softness, and flexibility to the skin [32]. Control treatment (TK) using casein 70 gave almost the same or not significantly different (P>0.05) with T1 using 50 parts gelatin. This shows that gelatin can replace casein with a smaller amount and can produce the same parameter values as casein. Softness is directly proportional to elongation, the higher the percentage of elongation, the higher the softness. The results of the rabbit skin elongation test showed that the more gelatin was added to the base coat solution, the lower the elongation, as well as the lower the skin softness test results.

CONCLUSIONS

Gelatin as a protein binder added to the base coat solution in the finishing process of rabbit skin can be used to replace casein. The use of gelatin up to 70 parts as a protein binder in a rabbit skin finishing solution has been able to replace casein as a control treatment. Variation in the amount of gelatin used as a binder in the finishing process showed a significant effect on all parameters, namely drop test after base coat solution, tensile strength, elongation, water absorption 2 and 24 hours, rubbing fastness, and skin softness with a 25 cm ring and had no effect on the drop test before the base coat.

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REVIEW OF AVANT-GARDE CONCEPT IN FOOTWEAR RESEARCH AND DESIGN AND APPLICATION TRENDS

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ABSTRACT. Whether originating from a deliberate intention or emerging from subconscious, spontaneous doodling, design concepts perform the crucial role of demonstrating the vision of a final product. Even though academic discourse on design concepts is prevalent in all fields of design, the same cannot be said about footwear design. Academic discussion about footwear design concept is usually rooted in comfort and functionality. This paper aims to enhance the academic conversation on footwear design concepts by exploring the avant-garde concept in footwear design, its impact and significance. Avant-garde describes a French medieval military lexicon that literally translates to vanguard, or advanced guard, referring to the frontline of the army. However, the applicative meaning of the term is an intellectual, artistic and cultural movement characterized by experimental, radical and unorthodox approaches to the arts. Therefore, in actuality, for a product or idea to be considered avant-garde is to dwell outside of the established norms and confines of a discipline. Despite the widespread usage of the terminology in contemporary fashion circles, academic discussing the concept of avant-garde in fashion generally, some notable avant-garde designers/artists and their contributions, important avant-garde concepts in footwear design and finally the areas of avant-garde footwear applications. The study contends that although avant-garde fashion and for that matter footwear is thought to satisfy a specific niche, its impact is significantly observable in the trends of mainstream fashion. KEY WORDS: design concept, fashion design, co-branding, design innovation, brand perception

TRECERE ÎN REVISTĂ A CURENTULUI AVANGARDIST ÎN CERCETARE ȘI DESIGN ÎN DOMENIUL ÎNCĂLȚĂMINTEI ȘI TENDINȚE DE APLICARE

REZUMAT. Fie că provin dintr-o intenție deliberată, fie că provin din mâzgălirea spontană, subconștientă, conceptele de design îndeplinesc rolul crucial de a demonstra viziunea unui produs final. Chiar dacă discursul academic asupra conceptelor de design este predominant în toate domeniile designului, nu se poate spune același lucru despre designul încălțămintei. Discuția academică despre conceptul de design de încălțăminte se concentrează de obicei pe confort și funcționalitate. Această lucrare își propune să contribuie la conversația academică asupra conceptelor de design de încălțăminte prin explorarea curentului avangardist în designul încălțămintei, a impactului și semnificației acestuia. Termenul de "avangardă" provine din lexiconul militar francez medieval și se traduce literalmente prin "care merge în frunte", referindu-se la prima linie a armatei. Cu toate acestea, sensul aplicativ al termenului este o mișcare intelectuală, artistică și culturală caracterizată prin abordări experimentale, radicale și neortodoxe ale artelor. Prin urmare, în realitate, ca un produs sau o idee să fie considerat de avangardă în seamnă să se situeze în afara normelor și limitelor stabilite ale unei discipline. În cuida utilizării pe scară largă a terminologiei în cercurile modei contemporane, discursul academic despre încălțămintea de avangardă în modă în general, despre unii designeri/artiști avangardiști de seamă și contribuțiile acestora, despre conceptul de avangardă în modă în general, despre unii designeri/artiști aconsiderat a satisface o anumită nişă, impactul acesteia este observabil în mod semnificativ în tendințele modei mainstream. CUVINTE CHEIE: concept de design, design de modă, co-branding, inovație în design, percepția mărcii

REVUE DU COURANT D'AVANT-GARDE DANS LA RECHERCHE ET LA CONCEPTION DE CHAUSSURES ET TENDANCES D'APPLICATION

RÉSUMÉ. Qu'ils proviennent d'une intention délibérée ou qu'ils émergent d'un gribouillage subconscient et spontané, les concepts de design jouent le rôle crucial de démontrer la vision d'un produit final. Même si le discours académique sur les concepts de design est répandu dans tous les domaines du design, on ne peut pas en dire autant du design de chaussures. Les discussions académiques sur le concept de conception de chaussures sont généralement fondées sur le confort et la fonctionnalité. Cet article vise à enrichir la conversation académique sur les concepts de conception de chaussures, son impact et sa signification. Avant-garde décrit un terme militaire médiéval français qui se traduit littéralement par « ce qui est précurseur », faisant référence à la ligne de front de l'armée. Cependant, le sens applicatif du terme est un mouvement intellectuel, artistique et culturel caractérisé par des approches expérimentales, radicales et peu orthodoxes des arts. Par conséquent, en réalité, pour qu'un produit ou une idée soit considéré comme avant-gardiste, il faut vivre en dehors des normes et des limites établies d'une discipline. Malgré l'usage répandu de cette terminologie dans les cercles de la mode contemporaine, le discours académique sur les chaussures d'avant-garde notabler set de leurs contributions, des concept d'avant-garde importants dans la conception de chaussures et enfin des domaines d'applications de chaussures d'avant-garde. L'étude affirme que même si la mode d'avant-garde, et donc les chaussures, est censée satisfaire une niche spécifique, son impact est significative.

MOTS CLÉS : concept de design, design de mode, co-branding, innovation dans la conception, perception de la marque

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INTRODUCTION

Undoubtedly there has been consistent prevalence of avant-garde movements emergence within every field of creativity, ranging from the fine arts to music [1]. Contemporary utilization of the term "avantgarde" has been touted to have emanated France. from revolutionary Avant-garde originates from a medieval French military term that literally translates to "vanguard," or "advanced guard [2]" and refers to the frontline of the army. 19th-century French strategist General Henri Bonnal is credited for the invention of the term. For over a century, the concept of "avant-garde" has possibly been the most significant and influential force in modern art and culture, dominating the critical appraisal of the significance of an artist or a work of art.

A host of stakeholders including, critics, journalists and academicians often utilize the term avant-garde when evaluating, interpreting, and scrutinizing art, architecture, film, and fashion. However, the meaning of the term avant-garde is often ambiguous [3]. Hence, the direct interpretation and application of the term avant-garde to mean "ahead of the guard" are somewhat misleading. In the realm of the arts, being avant-garde does not necessarily mean staying ahead of trends. Instead, it signifies existing beyond the established norms and boundaries of a particular discipline [1]. Avant-garde artists or practitioners are generally in opposition to dominant social values or established artistic conventions [4].

Be it apparel or footwear, the object of a designer is to create both aesthetically pleasing and comfortable fitting products for the end user by manipulating design elements based on design concepts and principles. elements and principles Design are fundamental guidelines for designers in all fields [5]. A design concept serves as the portrayal of a designer's abstract ideas for ultimate entities, such as garments in the context of apparel design [5]. A design concept thus performs the crucial role of demonstrating the vision of a final product [6]. Whether originating from a deliberate intention or emerging from subconscious, spontaneous doodling, design concepts evolve through a process in which the designer navigates perception and concepts by assimilating information [7].

Even though the discourse on design concept is prevalent in all fields of design, ranging from fashion, architecture to user interface, the same cannot be said about footwear design. Academic discussion about footwear design concept is usually rooted on comfort and functionality [8-10]. This paper seeks to contribute to the discourse on footwear design concepts by discussing the avant-garde concept in footwear design and its significance.

Avant-garde footwear design has undergone a fascinating evolution, marked by its innovative and unconventional approach over the periods. Avant-garde footwear design finds roots in avant-garde art movements of the late 19th and early 20th centuries. In the Mid-20th century, Designers like Salvatore Ferragamo of Italy [11] and Roger Vivier of France introduced novel materials and shapes, pushing the boundaries of conventional shoe design [12]. The rise of pop art and youth in the 1960s further fueled culture experimentation in fashion, including footwear.

The punk movement in the 1970s-1980s and the Post-Punk Era had a significant impact on avant-garde design, with DIY aesthetics and rebellious themes influencing footwear. Designers like Vivienne Westwood and Malcolm McLaren played a key role in translating punk culture into avant-garde fashion, including shoes [13].

Advancements in materials and manufacturing technologies in the 1990s allowed designers to explore futuristic and [14]. unconventional designs Alexander McQueen, known for his intriguing and innovative designs, emerged as a prominent figure in avant-garde footwear during this era. In the 21st Century, collaboration between fashion designers and technology experts became more prevalent, leading to avant-garde designs that merge fashion with cutting-edge technology. High-profile collaborations showcase avantgarde elements in mainstream fashion [15].

In terms of cultural significance, avantgarde footwear has come to serve as a form of artistic expression, challenging societal norms and pushing the boundaries of what is considered wearable [16]. Recent avant-garde designs increasingly incorporate sustainability principles and address social issues, reflecting a broader societal awareness in the fashion industry. Designers use avant-garde footwear as a platform for social commentary, addressing topics like gender, identity, and environmental impact [17].

The concept of avant-garde tends to play a significant role in the design of contemporary footwear and even though avant-garde footwear design is thought to remain in a niche market, its influences in mainstream footwear trends are very much evident. From oversized silhouettes to funky color schemes, massive soles, and elevated commonplace. heels are now This demonstrates that the avant-garde concept in footwear extends beyond advancing the frontiers of footwear design; however, it possesses the influence to shape the broader landscape. It continues to shape and be shaped by cultural, technological, and societal changes, offering a unique perspective on the intersection of art, fashion, and innovation.

Contributing to the literature of this concept relative to footwear design, this study discusses avant-garde concepts applied in footwear design. Also discussed are some prominent avant-garde footwear designers and brands and their impact on the contemporary footwear design landscape, and the various areas in which avant-gardeconcept-designed footwear are applied. The objectives of this study are as follows:

1. To investigate the concept of avantgarde as pertains to footwear design.

2. To investigate prominent avant-garde designers and brands and their impact on contemporary footwear design.

3. To investigate the areas of application of avant-garde-concept-designed footwear.

METHODOLOGY

The method adopted involves the selection of search criteria, selection of relevant databases and search engines, and manual sifting of collated data for analysis. The framework is shown in Figure 1. The following databases and search engines were used for the collection of data: Web of Science Core Collection, Google Scholar, and Bing academic. There was no period restriction for the documents consulted. The types of documents consulted in the study were research papers, conference papers and proceedings, books, and patents.



Figure 1. Framework of the research

FINDINGS AND DISCUSSIONS

The findings of this paper are partitioned as follows: a brief discussion on the avantgarde concept in fashion, deliberations on prominent avant-gardists and their contribution to footwear research and design, avant-garde footwear concepts and the areas of avant-garde footwear applications.

Concept of Avant-Garde in Fashion

Since the early 20th century, there has been ongoing debate among critics and scholars regarding the origins, definitions, and enduring relevance of the term avant-garde and its practices. Theoretical discussions have even suggested the demise of the avant-garde. However, according to Cardullo [18], the avantgarde has rather experienced significant changes in the latter part of the twentieth century, and that continues to be a pertinent and practical concept as it exemplifies a pervasive drive to challenge aesthetic limits.

While everyday clothing typically serves utilitarian purposes, from the introduction of jeans to dual-sided zippers, avant-garde apparel leans more towards artistic expression, consistently aiming to challenge our conventional notions of what actually constitutes clothing. Avant-garde fashion has a rich history of pushing boundaries and challenging traditional norms in the industry.

The concept of avant-garde in fashion is not restricted to runway fashion only; however there exist other subsets such as street avant-garde, museum avant-garde and so on. Street style avant-garde fashion depicts the distinctive street-wear fashionable dresses that are extravagant and eye-catching and worn by a few people to make their presence known in public [19]. Museum avant-garde entails works of renowned avant-gardists.

Prominent Avant-Garde Footwear Designers and Brands

as the definition Inasmuch and attributes of the term avant-garde tend to be equivocal and diverged, a number of researchers have frequently studied artists and designers and described them as avantgarde [3]. Groundbreaking shoe designs have emerged continually but it has never been so exciting thanks to a number of audacious footwear designers' willingness to abolish the traditional archetype. In no special order, the succeeding discussion presents some prominent avant-garde footwear designers and brands of the 20th century and beyond.

Maison Margiela is an avant-garde fashion brand established in 1988 by Belgian designer Martin Margiela and creative partner Jenny Meirens [20]. The Paris-based luxury brand is famous for its experimental, deconstructive and unconventional designs.



Figure 2. (a) Tabi leather Mary Jane pumps [21]; (b) Yeezy Foam RNNR MX Sand Grey [22]; (c) Crocs Pollex Clog [23]

The split-toe Margiela tabi is a signature of Maison Margiela, featuring various versions every season since spring 1989 and beyond. The Margiela tabi was inspired by the Japanese 'jika-tabi', a functional shoe or boot which features a flexible rubber sole and an upper formed traditionally from a hardwearing canvas textile from the late 19th century. Figure 2(a) shows Tabi leather Mary Jane pumps crafted from black calf leather and designed with the iconic Tabi toe – that features a split between the big toe and the rest of the toes to promote flexibility and provide extra security, comfort, and stability.

Kanye West introduced the world to some novel, extremely noticeable footwear. Yeezy has popularized the sort of pioneering and innovative design work that defines the avant-garde. Kanye West's Yeezy brand portrayed obvious avant-garde elements in footwear design. His designs often incorporate minimalist aesthetics, unique silhouettes, and unconventional materials. The Yeezy Boost series, for example, featured distinctive shapes and a focus on comfort through innovative materials like Primeknit. Additionally, West has experimented with earthy tones and neutral colors, contributing to a distinct avant-garde style within the realm of sneaker design. Yeezy Season is a project of Kanye's collaboration with sportswear giant Adidas, releasing fashion collections since 2013 [24]. Figure 2(b) shows one of his iconic creations by way of the collaboration with footwear giant Adidas, the Yeezy Foam Runner. The Yeezy Foam Runner is a one-piece sneaker with a porous EVA foam upper and a contoured outsole.

Salehe Bembury is an independent footwear designer whose futuristic design vision has achieved broad influence in the worlds of street-wear and high-end sneakers. Salehe Bembury is known for his work with major footwear brands like Yeezy, Versace, Crocs, New Balance and so on. He was an integral part of the men's footwear task force for Yeezy Season 3 and Season 4 [25]. Bembury is celebrated for his avant-garde designs, blending creativity with functionality in the realm of footwear fashion. His contributions to the footwear industry have garnered attention for shifting boundaries and redefining the aesthetics of contemporary shoe design. One of his impressive creations -Crocs Pollex Clog - is an exploration of form and function that balances Crocs' heritage and nostalgia. The model's curved ridges provide exceptional multi-directional grip while the iconic perforations work around the grooves to provide enhanced breathability [23]. A translucent rubber panel wraps around the front of the shoe for added protection. Figure 1(c) shows the Pollex Clog.

Rick Owens – No discussion of avantgarde footwear is complete without Rick Owens [26]. Rick Owens is an American fashion designer based in Paris, well-known for avant-garde luxurious grunge fashion and interior pieces. Rick Owens is widely regarded as an avant-garde fashion designer known for his unconventional and distinctive approach. His work often features dark, dramatic aesthetics with oversized silhouettes and asymmetrical designs. Owens' avant-garde style challenges traditional fashion norms, making a significant impact on the industry. Figure 3(a) shows one of his signature avantgarde footwear models known as the quad sole pentagram jumbo lace boot.

Lee Alexander McQueen was born on March 17, 1969 in London, England. He dropped out of school at a young age to learn tailoring. In a bid to further his clothes-making career, McQueen departed London briefly and spent some time in Milan, serving as a design assistant to the Italian fashion designer Romeo Gigli. After coming back to London, McQueen joined Central Saint Martin's College of Art & Design, earning his M.A. in fashion design. Following that, he was appointed as the Chief Designer for Givenchy, a prestigious French haute couture fashion house owned by Louis Vuitton [27]. While known as Lee to friends and acquaintances, McQueen opted to exclude his first name and chose Alexander McQueen as the brand's title [28].

(b)

Figure 3. (a) Rick Owen's quad sole pentagram jumbo lace boots [29]; (b) A version of McQueen's armadillo boot [30]

According to Kwon and Keum [31], McQueen's designs are marked by unstructured expressive techniques that disrupt the fundamental principles of design, such as harmony and balance. His creations showcase disordered visuals, breaking away from traditional design forms. Recognized for his inventive and artistic shoe designs, Alexander McQueen is famed for the avantgarde Armadillo boot, a truly iconic footwear creation. The eponym of the boot is due to its form and armour-like appearance, the boots transform from the leg to create the visual effect of a ballerina standing on pointe. Figure 3(b) shows a version of armadillo boot. **Nicholas Kirkwood** is renowned for his sculptural and unconventional shoe creations. He became famous courtesy a collection made up of statement shoes which mix elements of architectural design, sex appeal and avant-garde fashion [32]. His designs, however, are perfect and very unique, beautiful, to the polished wood heel and platform he adds many other sophisticated elements. He focuses on the silhouette, works with negative spaces and abstract forms. Decorative elements, when used, are integrated into the architecture of the shoe, rather than just placed on the surface.

United Nude – Based in Amsterdam, United Nude is a luxury footwear brand renowned for its innovative designs, architecturally-inspired and cutting-edge style [33]. The brand was founded by Rem D. Koolhaas and Galahad Clark in 2003. United Nude is celebrated for its unconventional and avantgarde approach to footwear, often incorporating geometric shapes and unusual materials.

One of the brand's most iconic designs is the "Möbius" shoe shown in Figure 4(a), which features a single strip of material that forms both the sole and upper in a continuous loop, creating a visually striking and unconventional look. United Nude's shoes often blur the line between art and fashion, and they have collaborated with various designers and artists to create unique and cutting-edge footwear collections. United Nude's commitment to pushing the boundaries of traditional shoe design has made it a distinctive and influential brand in the world of fashion and footwear.

Iris van Herpen is a Dutch fashion designer and couturier renowned for her futuristic, darkly fantastical aesthetic. As a fashion designer, she has collaborated with shoe designers to create unique and avant-garde footwear [34]. Embellished with stone spikes and 7.5-inch heels, the "Thorn" boots shown in Figure 4(b) are regarded as one of her great footwear creations.

Thom Browne – originally from Pennsylvania, initially explored a career in acting before finding his true calling in the field of design. Browne's creations are known for their unique proportions, precise tailoring, and a fusion of traditional menswear with surrealistic elements. Thom Browne crafts avant-garde footwear with a distinctive and playful flair. Undoubtedly, he is also a leading figure in avant-garde menswear, he established his self-named brand in 2001, swiftly gaining acclaim for his unique aesthetic [41].

Figure 4. (a) United Nude's "Möbius" shoe [36]; (b) Iris van Herpen's thorn boots [37]; (c) High-heel Nike sneakers [38]; (d) Play Comme des Garçons chuck Taylor [39]; (e) Warrior 2 sneaker by Ruthie Davies and Disney [40]; (f) Dolce & Gabbana's Keira Leaf Applique Bejewelled Sandals [41]

Comme des Garçons refers to a Japanese clothing outfit established by Rei Kawakubo in Tokyo in 1969 [42], now situated in Tokyo, Japan, and in Place Vendôme in Paris, France. The brand is famous for extending the limits of traditional shoe design. Famously known for its avant-garde aesthetic, Comme des Garçons introduced a collaboration with Nike featuring a sneaker/ankle boot hybrid with a high heel [37]. The footwear shown in Figure 4(c) looked like weirdly tall soccer shoes. Also in their collaborative work with converse, Comme des Garcons released a classic style of Converse with a modern twist as shown in Figure 4(d). The sneakers featured bold and playful patterns which made them the statement piece of any outfit.

Ruthie Davis is an American female shoe designer with a penchant for the empowering bodycon style, seamlessly blends sensuality and strength in her innovative silhouettes. She combines high fashion with futuristic elements in her shoe designs. Skyhigh heels and platforms, super structural features and bright pops of color are signature details of the brand. Notable avant-garde pieces are in the collaboration with Disney to create a line of seven shoes inspired by Mulan (movie). Figure 4(e) shows one of the seven "warrior" branded heels [39].

Dolce & Gabbana is a famous fashion house in Milan, Italy. The company was founded in the year 1985 by two designers, Domenico Dolce and Stefano Gabbana. Domenico Dolce and Stefano Gabbana are known for their unique style and look. They are known for incorporating avant-garde elements into their footwear collections. Figure 4(f) shows one of the brand's footwear – Keira Leaf Applique Bejewelled Sandals, featured in New York Fashion Week (NYFW spring '20) 2020.

Issey Miyake was born Kazunaru Miyake 1938 in Hiroshima. After completing his education at Tama Art University in Tokyo, Miyake relocated to Paris in 1965 and pursued studies at the prestigious Ecole de la Chambre Syndicale de la Couture Parisienne. During his early career as a designer, he gained experience under Guy Laroche and Givenchy. Additionally, his perspective was shaped by the significant student-led uprising of May 1968.

In 1970, he founded the Miyake Design Studio in Tokyo and shortly thereafter opened his maiden boutique in Paris. During the 1980s, his career reached its zenith as he explored various materials, ranging from plastic and metal wire to traditional Japanese paper [43]. Typically avant-gardist, Issey Miyake rather desired neither to be referred to as an artist nor to be labeled a 'Japanese' fashion designer [44]. Issey Miyake has consistently shown a keen interest in environmental concerns and is recognized as a designer who prioritizes practicality and universality in his clothing designs [45]. At the beginning of the century, he stepped back from creating his Paris collections and has since provided numerous talented young designers with significant opportunities.

Renowned for his minimalist approach to footwear design, Issey Miyake's shoes embody a Japanese design aesthetic characterized by simplicity. They skillfully blend Eastern and Western influences, resulting in a remarkably modern and international style. Just like most prominent avant-garde footwear designers, Miyake had a number of collaborations with brands such as New Balance.

Yohji Yamamoto - born in Tokyo in 1943, started his career by studying English and law at Keio University before ultimately obtaining a fashion degree from Bunka Fashion College in 1969 [46]. Yamamoto's creations defy straightforward associations with gender, nationality, or artistic categorizations. He dismantled and challenged clothing norms, reconsidering established notions of beauty, age, gender, and the human body [47]. The blended nature of his creations, along with abundant references to both Japanese tradition and Western culture, can be characterized as an avant-garde manifestation of postmodernism that resonates with a worldwide audience [46].

In addition to his work as a designer for his own fashion house, Yamamoto collaborated with other outfits. One of such notable collaborations is the one with Adidas which began on October 7, 2002 [48]. Adidas and Yohji Yamamoto continue their industry defining partnership with a triumphant offering of audacious sportswear, reimagined through a distinctly avant-garde lens. Yamamoto and Adidas took their collaboration to new heights with the launch of Y-3. Symbolizing the union of Yamamoto ("Y") and the Three Stripes ("3"), Y-3 is a designer sportswear line that has been walked at Paris Fashion Week since 2003. Notable sneaker models of this collaboration include Qasa High, Super Zip, Pro Zip, Stan Zip, Noci High, and Noci Low, there are also new Ryo High and Ayero sneakers.

Figure 5. Brand positioning of the 14 brands discussed

A brand market position analysis was carried out on the fourteen brands and designers presented and shown in Figure 5. The chosen parameters are luxury against mass market, independent against co-brand. Luxury pertains to whether the brand is significantly a luxury brand or mas market brand. Independent brand in the sense as to whether the brand largely operates on its own, or predominantly engages in cobranding or other collaborative arrangements. The perceptual mapping constructed suggests that most of the brands are luxury brands. Therefore, none of the brands is effectively a mass market brand; therefore, the first guadrant of the map is empty. Potential mixes of mass market and luxury offerings only pertains to Yeezy, United Nude and Ruthie Davies and also with Salehe Bembury depending on the collaboration. Due to the similarities of the brands, there are overlaps in the positions shown on the maps.

The authors thus contend that this presents an opportunity for further studies to ascertain the feasibility of mass market footwear brands' ability to tap into this luxury market by adopting avant-garde design concepts. It is however instructive to note that co-branding has been prescribed as one of the effective means to achieve this end as captured under the section of avant-garde footwear applications areas.

Avant-Garde Footwear Design Concepts

The avant-garde concept in footwear design represents a departure from traditional or conventional shoe styles, pushing the boundaries of creativity, innovation, and artistic expression. Avant-garde footwear designers and brands explore new materials, shapes, and technologies to create shoes that are often regarded as wearable art. Figure 6 presents some key aspects and applications of the avant-garde concept in footwear design.

Figure 6. Overview of Avant-garde in footwear design, research and applications

Artistic Expression

Artistic expression describes the utilization of art and artistic methods to explore, communicate, and express the psychic content of an individual [49]. Usually, products of avant-garde are seen as obstinate, nonfunctional and awkward pieces of art. However, some avant-garde footwear is not necessarily constrained by functionality. Avant-garde footwear is a form of artistic expression conveying creativity bv experimenting with materials, techniques and the form a shoe can take [50].

Some avant-garde creations take inspiration from everyday objects and combine it with pure imagination. Others seem to find inspiration within, creating pieces unlike anything we could have imagined. Designers use shoes as a canvas to convey unique and thought-provoking ideas. These creations often blur the lines between fashion and art. A typical example is McQueen's armadillo boot shown in Figure 3(b), the side view showing the use of iridescent paillettes to imitate the scales of the armadillo.

Unconventional Materials

Avant-garde footwear designers experiment with unconventional materials such as plastics, metals, glass, and even organic materials like wood and flowers. They may also experiment with texture by incorporating ruffles, frills, or other structural elements. Avant-garde fashion also often plays with proportions and shapes, using voluminous or oversized silhouettes to create dramatic effects [51].

These materials challenge traditional perceptions of what shoes can be made of. Manila-based designer Kermit Tesoro have demonstrated that horns, tentacles, hooves, skulls are materials capable of being formed into footwear. Figure 7(a) shows Kermit Tesoro's famous Polypodis footwear made up of bones. Kermit Tesoro is noted to have used various mediums in his shoes such as wood, plaster, steel, leather, industrial resin, coral, and human bones and teeth, all of which have been inspired from natural environs and things found in specific environments.

Figure 7. (a) Kermit Tesoro's Polypodis [50]; (b) Minimalist slippers [52]; (c) Rem D. Koolhaas architectural shoes designed for United Nude [53]; (d) Energy harvesting sneaker for mobile device charging [54]; e) Yeezy 450 [62]; (f) The bat [36]

Minimalist and Maximalist Aesthetics

The minimalist aesthetic focuses on the principle that less is more. As a design style, it involves simple design formats, scarcity and visual peace [52]. In terms of footwear design, there seem to be two schools of thought on the definition of minimalist footwear. One school of thought which seems the most popular describe it as, basically, footwear designed to replicate the sensation of being barefoot while offering a sufficient level of insulation and protection, typically in the soles, can be categorized as "minimalist". Figure 7(b) shows an example of a minimalist slipper. Contrarily, there is also the concept of maximalist footwear. This type of footwear is characterized by an enlarged midsole and is intended to offer extra cushioning and shock absorption compared to typical running shoes [53].

Other description of minimalist footwear design is that it focuses on simplicity, emphasizing clean lines, a limited color palette, and a reduction of unnecessary elements. It often involves using basic shapes and highquality materials to create a streamlined and functional look. This class of minimalist shoes aims to provide essential features without excessive ornamentation, offering a design that is both aesthetically pleasing and practical. This style is characterized by a less-is-more philosophy, promoting simplicity and elegance in shoe design.

Structural Form Concepts

Avant-garde shoes often feature sculptural and architectural elements. They may have exaggerated shapes, intricate structures, or asymmetrical designs that defy conventional shoe forms. Rem D. Koolhaas teamed up with British shoemaker Galahad Clark to create a line of architectural shoes for their brand United Nude. United Nude designs have also been inspired by other art forms, like furniture [57]. Figure 7(c) shows Rem D. Koolhaas architectural shoes designed for United Nude. Other notable examples featured famous architect Zaha Hadid's works with Brazilian brand Melissa, Adidas, Pharrell Williams and United Nude and Lacoste [58]. Issey Miyake and United Nude's 'rock' and 'wrap' shoes and so on [59].

Technology Integration / Futuristic Concept

For a long time, the craft of creating footwear has been predominantly done by hand. Increasingly technology has seen pervasive application in the creative and experimental environment of the avant-garde fashion runway, particularly in relation to its garments [60] and to a much lesser degree, footwear. Technology is an essential element of futuristic design. Futuristic design aims to craft a visually impactful and distinctive setting that captures the sensation of being in a future era. Integration of smart fabrics, 3D printing, and wearable technology opens up new avenues for experimentation and innovation. Figure 7(d) shows Energy harvesting sneaker for mobile device charging [56].

3D printing is being incorporated into more and more industries, and footwear design and manufacture is no exception to this. Avant-garde footwear often incorporates advanced technologies, such as 3D printing, to achieve complex and innovative designs. These technologies expand the possibilities of shoe design. Even though complete shoes have been produced using 3D printing technology, the majority of the applications are for prototyping.

Shih-Hung Cheng also investigated the impact of Generative artificial intelligence (GAI) on footwear design creativity and feasibility [61]. Using a text-to-image GAI tool called Midjourney, 17 prompts were tested to generate footwear concepts. Interesting avant-garde effect footwear designs such as what they described as kimono-style high heeled shoes, lady running shoes with futuristic style and football shoes with mutation style were generated.

Functionality Concept

pertains Functionality the to effectiveness of a design in assisting users in achieving their objectives and fulfilling their needs. When creating high-end fashion footwear, the focus typically revolves around innovating and introducing novel shapes for the shoes, unique sole and heel designs, fresh cuts, material combinations, variations, as well as distinctive trimmings and decorations [62]. However, some avant-garde footwear also has functionality as part of the objective. This may include fit, ample protection and comfort, ease of wear, materials with functional qualities such as anti-microbial properties. Proper fit of footwear stands as a crucial factor for the wearer, impacting comfort, and its absence can result in foot injuries [63]. Figure 7(e) shows an image of the Yeezy 450. The elaborate web-like pattern on the upper not only functions as a design element but also guarantees a secure and supportive fit. Footwear made of antimicrobial treated materials tends to improve sanitary properties as well as protecting the wearer from detrimental impact of the environment, actions of microorganisms [62]. The use of high-quality materials enhances the durability and, for that matter, the functionality of the footwear.

Deconstruction Concept

Deconstruction is part of modern philosophy that regards the process of understanding as a breakdown of stereotypes and the creation of a new context [64]. Mainly, it emphasizes the stereotypical thinking that provides standardized explanations and meanings for the context. Applied to the fashion phenomenon, the deconstructivist method creates new fashion representations and interpretations, overcomes fashion stereotypes and fashion attitudes, and crosses typical borders. Japanese designers like Rei Kawakubo, Issey Miyake, and Yohji Yamamoto innovatively applied the deconstructivist method to their fashion collections [64]. Martin Margiela is also categorized under the avantgardists whose works showed significant deconstructivist tendencies [65].

Areas of Avant-Garde Footwear Applications

Apart from the special group of people who gravitate towards avant-garde fashion as a means of expressing their unique personal style. Avant-garde footwear has seen application in a number of areas including but not limited to high Fashion and Runway Shows, limited edition collectibles, museum displays and so on. The succeeding discussions take a close look at some of these areas.

High Fashion and Runway Shows

A number of high-end brands utilize fashion shows as a platform to unveil their interpretations and presentations of new

collections for both clothing and accessories. High-fashion shows therefore tend to serve as conduits for high fashion or established designers conveying new fashion design ideas, while the mass market and fast fashion subsequently adopt and adapt these trends [66]. The contention therefore is that, Runway fashion should be considered as an art gallery where most items are not ready to wear. Instead, their purpose lies in showcasing creativity and imagination, conveying an underlying statement or message that spearheads a specific design campaign for the brand [67]. Avant-garde footwear is frequently showcased in high-fashion runway shows. It is an integral part of avant-garde fashion presentations and couture collections. Haute involves meticulous couture handmade craftsmanship and is conceived by highly skilled designers and artists. Practicality is not the primary objective; many runway looks are worn in their most artistic forms during their debut to accentuate the designer's vision. Today, fashion shows frequently, but not always, are held in the context of fashion weeks in cities like Paris, Milan, London, New York, and an increasing array of other fashion hubs [68].

Limited Edition and Collectibles

Many avant-garde shoe designs are produced in limited quantities and are considered collectibles. They can be highly sought after by collectors and enthusiasts. Figure 5(f) shows limited edition footwear dubbed The Bat created by two companies, Suicoke and Vibram. The footwear is an integration of faux-fur lining and bat-eared toe design elements cratering for a visually striking aesthetic product. Vibram is a company named after its founder, Vitale Bramani, who is credited with inventing the first rubber lug soles, while Suicoke is a Japanese footwear brand founded in 2006. Suicoke specializes in functional, yet casual outdoor footwear. Works such as McQueen's armadillo boots are all limited-edition collectibles.

Editorial and Fashion Photography

A fashion editorial is a photographic collection that tells the story of a clothing collection, including its references and

inspirations. The purpose of editorials is to literally create the most artistic fashion visuals humanly possible with photographic techniques, weird models, and a mixture of clothing. Avant-garde footwear is often featured in editorial spreads and fashion photography. These shoes can serve as focal points in fashion campaigns, creating striking and memorable imagery.

Costume and Theatrical Design

The realm of theatrical costume design relies not just on the need to physically dress performers but also on recognizing the communicative power of clothing [69]. Certainly, it has been observed that theatrical costumes are likely the most overt utilization of clothing for communication [70]. Costumes usually afford viewers an idea of the story unfolding before them, offering them a way to get into the story. Avant-garde shoes are used in costume and theatrical design to create unique and otherworldly looks for performances, films, and artistic productions. Even though some theoretical arguments have and continue to speculate that avant-garde is dead, Cardullo [18], contends that the avantgarde has just undergone radical changes in the second half of the twentieth century, and for that matter it still remains a viable, practical concept in theater as it demonstrates an unhindered impetus to extend aesthetic limits.

Conceptual Fashion

Across a broad spectrum of relevant literature, clear definition as to what constitutes conceptual fashion is lacking [71]. In certain quarters, it has been described to feature exploration of innovative and abstract ideas, pushing the boundaries of traditional design to create garments that often prioritize artistic expression and storytelling over conventional wearability. Jackie Mallon suggests that it is synonymous with Avantgarde and describes garments that raise eyebrows and questions, and expand our perception of clothing [72].

The designers of such works are often perceived as disinterested in mass production, scalability, traditional beauty norms, directing their attention toward deconstruction, unconventional materials, technology, and the liberation of creative expression. Avant-garde footwear thus may be thought to imbibe or feature a broader conceptual fashion movement as designers use shoes to explore social, cultural, or political themes, making statements and challenging norms.

Gordana Vrencoska cites an example of works by greats such as Alexander McQueen and Hussein Chalayan of exemplifying conceptual fashion due to the use of their personal histories, cultural identities and political concerns as a self-referent standing point for the conceptual frame of their seasonal fashion collections [73]. The significance of conceptual fashion has gained recognition primarily through the evolution of fashion studies in recent times. This has varied introduced а more arrav of perspectives on fashion compared to the conventional linear narratives of the past [74].

Cobranding / Collaboration

Co-branding is a form of cooperation between two brands with significant consumer recognition that results in the creation and introduction of a new product on which both brands are visible [75]. Designers often collaborate with artists, architects, and other creative professionals to bring avant-garde footwear concepts to life. These collaborations result in truly unique and boundary-pushing designs. Avant-garde designers are able to fuse their unconventional ideas into mainstream fashion. Many success stories in the footwear industry include the collaboration between Adidas and Yohji Yamamoto (Y-3) [48]. The collaboration enabled the fusion of sports and avant-garde designs. Martin Margiela and Comme des Garçons have both designed for H&M [76]. Also, Rick Owens and Raf Simons have created successive shoe collections for Adidas, and Kris Van Assche has likewise collaborated repetitiously with brands such as Lee and Eastpak.

CONCLUSIONS

In conclusion, we contend that the incorporation of avant-garde elements into footwear design symbolizes a bold exploration of creativity and artistic expression. While

certain designs might not be suitable for daily use, they stimulate our understanding of what footwear can be while at the same time inspiring innovation within the fashion industry. Avant-garde footwear serves as a testament that fashion extends beyond mere clothing; it serves as a potent form of communication and artistic expression.

Considering the numerous successes attained by major brands in terms of collaborations with avant-garde artists or designers, it will suffice to state that the application of avant-garde art in the field of footwear has become a marketing strategy for many fashion brands to enhance their popularity. The outlook for avant-garde fashion appears promising, as anticipation grows for more designers to persist in pushing limits and erasing the distinction between fashion and art.

The brand perception analysis of the fourteen designers and brands studied, however, points to domination by the luxury market. Nevertheless, potential mixes of mass market and luxury only pertain to Yeezy, United Nude, and Ruthie Davies and also with Salehe Bembury depending on the collaboration.

It is undoubtedly clear that the various avant-garde concepts outlined feature predominantly in even the mass footwear market, especially with regards to sneakers. We thus opined that avant-garde footwear is gradually becoming mainstream if not already.

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154

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RESEARCH ON FOOT ANTHROPOMETRY AND COMPLICATIONS OF WOMEN WITH DIABETES IN VIETNAM

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RESEARCH ON FOOT ANTHROPOMETRY AND COMPLICATIONS OF WOMEN WITH DIABETES IN VIETNAM

ABSTRACT. Diabetes is a dangerous, chronic disease that frequently causes foot complications. Diabetes patients are at risk for amputation due to the serious complications of foot ulcers. Shoes made specifically for people with diabetes might greatly reduce this issue. It is crucial to wear shoes that are specifically made for the patient based on their anthropometric measurements and the evaluation of foot damage. The foot anthropometric and foot damage study results of 295 female diabetic patients at Khoai Chau District Medical Centre, Hung Yen Province, and the National Hospital of Endocrinology of Vietnam are presented in this research. The results showed that there were differences in measurements of height, width, and foot circumference between the two groups of patients. This discrepancy, which is independent of age, is caused by the level of problems or injuries to the feet. Women with diabetes often experience worsening foot injuries over the course of the illness. According to the level of foot complications, up to 96.69% of female patients with diabetes require "Extra Depth Diabetic Shoes"; 17.9% of patients needed "Custom Molded Inlays/insoles"; 3.1% of patients need to use "Custom Molded Inlays".

KEY WORDS: diabetic foot, foot anthropometry, therapy shoes, custom diabetic shoes

CERCETĂRI PRIVIND ANTROPOMETRIA PICIORULUI ȘI COMPLICAȚIILE APĂRUTE LA FEMEILE CU DIABET DIN VIETNAM

REZUMAT. Diabetul este o boală cronică periculoasă, care provoacă frecvent complicații la nivelul picioarelor. Pacienții cu diabet sunt expuși riscului de amputare din cauza complicațiilor grave ale ulcerului piciorului. Încălțăminte fabricată special pentru persoanele cu diabet ar putea reduce foarte mult această problemă. Este esențială purtarea de încălțăminte fabricată special pentru pacient, pe baza măsurătorilor antropometrice și a evaluării leziunilor piciorului. În această cercetare sunt prezentate rezultatele studiului antropometric și de evaluare a leziunilor piciorului la care au participat 295 de femei cu diabet, paciente ale Centrului Medical Districtual Khoai Chau, provincia Hung Yen și ale Spitalului Național de Endocrinologie din Vietnam. Rezultatele au arătat că au existat diferențe în măsurătorile înălțimii, lățimii și circumferinței piciorului între cele două grupuri de pacienți. Această discrepanță, care este independentă de vârstă, este cauzată de gradul leziunilor la nivelul picioarelor. Femeile cu diabet se confruntă adesea cu leziuni care se agravează pe parcursul bolii. În funcție de nivelul complicațiilor piciorului, până la 96,69% dintre pacienții de sex feminin cu diabet au nevoie de "Încălțăminte pentru diabet cu adâncime suplimentară"; 17,9% dintre pacienți au avut nevoie de "Inserții/Branțuri personalizate"; 3,1% dintre pacienți trebuie să folosească "Încălțăminte personalizată pentru diabetici" și "Inserții personalizate".

CUVINTE CHEIE: picior diabetic, antropometria piciorului, încălțăminte ortopedică, încălțăminte personalizată pentru diabetici

RECHERCHE SUR L'ANTHROPOMÉTRIE DU PIED ET LES COMPLICATIONS CHEZ LES FEMMES DIABÉTIQUES AU VIETNAM

RÉSUMÉ. Le diabète est une maladie chronique dangereuse qui entraîne fréquemment des complications au niveau des pieds. Les patients diabétiques courent un risque d'amputation en raison des complications graves des ulcères du pied. Des chaussures spécialement conçues pour les personnes diabétiques pourraient réduire considérablement ce problème. Il est essentiel de porter des chaussures spécialement conçues pour le patient en fonction de ses mesures anthropométriques et de l'évaluation des lésions du pied. Les résultats de l'étude anthropométrique du pied et des lésions du pied portant sur 295 patientes diabétiques du centre médical du district de Khoai Chau, province de Hung Yen, et de l'Hôpital National d'Endocrinologie du Vietnam sont présentés dans cette recherche. Les résultats ont montré qu'il existait des différences dans les mesures de taille, de largeur et de circonférence du pied entre les deux groupes de patients. Cet écart, indépendant de l'âge, est dû au niveau de problèmes ou de lésions du pied. Les femmes atteintes de diabète subissent souvent des lésions aux pieds qui s'aggravent au cours de la maladie. Selon le niveau de complications du pied, jusqu'à 96,69 % des patientes diabétiques ont besoin de « chaussures pour diabétiques avec une profondeur supplémentaire » ; 17,9 % des patientes avaient besoin de « inserts/semelles moulées sur mesure »; 3,1 % des patientes doivent utiliser des « chaussures pour diabétiques moulées sur mesure » et des « inserts moulées sur mesure ».

MOTS CLÉS : pied diabétique, anthropométrie du pied, chaussures orthopédiques, chaussures sur mesure pour les patients diabétiques

157

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INTRODUCTION

According to data from the Ministry of Health of Vietnam [1], in Vietnam, there will seven million diabetics by 2023. be Remarkably, more than 55% of patients experienced complications; 34% were cardiovascular complications, 39.5% were ocular and neurological complications, and 24% were kidney complications. Over 17% of people have prediabetes [1].

Diabetics usually have dangerous complications such as coronary artery disease, cardiovascular diseases, neurologic diseases, kidney diseases, blindness diseases, etc. The feet of people with diabetes are very susceptible to damage due to a reduction in or loss of feelings, poor blood flow, etc. Dry skin, cracked skin, calluses, and ulcers are the most common complications. An extremely high risk of amputation results from foot injuries, particularly ulcers, which are extremely difficult to cure because of a lack of oxygen, nutrition, and lowered antibodies [1-3]. Different results for the types of foot damage in individuals with diabetes have been shown in previous published publications [4-15]. This is dependent upon the location, attributes, and quantity of patients under investigation. According to Abbas and Archibald [4], 40% of diabetic patients in Africa experience foot issues like blisters, sores, ulcers, and scrapes. According to Ahmed, O. et al., the risk of foot ulcers rises with disease duration, more than ten years, for up to 18.1% of diabetic patients in Sudan [5]. Foot ulcers can affect as many as 44.5% of diabetic individuals in Bangladesh. Men are more at risk (45.6%) than women are, and those who live in rural regions are more at risk (45.5%) than those who live in cities [6]. In Nigeria, according to Tagang [7], the feet of female patients were more damaged than those of male patients. With a percentage of up to 36% for women and 27% for men, lesions on the plantar of the feet are most common in the area between the second and fifth toes. The rate of damage to the entire metatarsophalangeal joint is up to 35% for women and 27% for men. At the heel position, this rate is 32% for female patients,

and 16% for male patients. Gopi Chellan and colleagues' research [8] indicates that the following rates of foot injuries occur in India: 11.9% in the big toe, 7.5% in the mid-foot, 15.5% in the forefoot and remaining toes, 4.2% in toe deformities, 37.4% in muscle, and 6.4% in bone.

By 2012, Cynthia Formosa et al. [9] determined that the highest rate of lesions on diabetic feet in Malta was in the big toe joints, accounting for 49.4%. Next is the hallux, accounting for 39%, and the metatarsal head, accounting for 24%. Research by S.O. Oyibo et al. [10] in Manchester states that 86.7% of patients had foot ulcers. Forefoot ulcers make up 76.7% of them. 2.1% comes from Charcot feet. 11.2% of patients needed specific foot care and amputation surgery. The majority of patients only have one foot ulcer, while 16% of patients have more than one. As to the 2011 National Institutes of Health data from the United States [11], approximately thirty percent of individuals with diabetes who are 40 years of age or older experience decreased sensation in their feet. Big toe joint ulcers account for 27% of all ulcers, according to research by Waaijman et al. [12]. A study conducted in Vietnam in 2002 by Bui, M.D. [13] revealed the prevalence of foot ulcers among people with diabetes. In particular, the toe tips account for 31.5 percent, while the instep, heel, and space between the toes each have a 9.3 percent share. The percentage of common foot ulcers in diabetes patients was found by Dang, T.M.T. [14] in 2011 to be as follows: 15.6% in the heel, 17.7% in the plantar, and 28.9% in the toes. In order to investigate the external sources of foot ulcers, Le, B.N. [15] studied 58 male and 36 female diabetes patients in Vietnam in 2018. These studies have only focused on: 1) determining the rate and causes of foot ulcers for treatment, not evaluating other types of foot damage; 2) carry out a survey in a single place; 3) a small-scale survey of diabetic foot patients; 4) not paying attention to foot measurements for the purpose of designing shoes and insoles.

Research on anthropometry and foot damage to design and produce shoes for diabetic patients is still relatively new in Vietnam. There are no diabetic-specific or therapeutic shoes available in Vietnam. Numerous anthropometric investigations on diabetic patients' feet have been conducted recently [16–19], as has the design of shoe lasts for male diabetic patients [20]. However, comprehensive research on evaluating foot damage is lacking, particularly in the case of female diabetic feet. Therefore, in this study, we concentrated on measuring the feet and evaluating the pathology or damage of the feet in female diabetic patients in different locations in Vietnam to serve as a basis for designing shoes and insoles for patients.

EXPERIMENTAL

Subjects and Methods

Subjects

We concentrate on diabetic patients over 40 in this study. To be able to measure the feet of diabetic patients with different levels of complications, we selected two medical locations as follows:

1) Khoai Chau district medical central, Hung Yen province. At this Center, diabetic patients, usually patients with mild disease, periodically come for examination and get medicine and referred to as patients' group 1.

2) Department of Endocrinology – National Hospital of Endocrinology. This is a leading hospital specializing in diabetes treatment. At this hospital, there are not only patients living in Hanoi but also patients living in the Northern provinces of Vietnam, who come for examination and treatment. Patients here suffered from various foot complications, with a higher risk of ulceration compared to group 1 and referred to as patients' group 2.

In total, 295 female diabetic patients' feet were examined at these 2 locations; group 1 consisted of 116 individuals, and group 2 consisted of 179 individuals.

Measurement Method

In this study, we used the same foot measurement method as demonstrated in the previously published foot study of male diabetic patients [19]. We directly measured both bare feet in an upright position. The foot measuring device includes a soft narrow tape measure, a caliper with a 1 mm scale, and a footprint device. Measurement time is from 9 am to 11 am on weekdays. Foot measurements are as follows [19]:

Lf – Foot length; Lmb – Length to medial ball; Llb – Length to lateral ball; L5toe – Length to the end of 5th toe; Lh – Length to the widest point of the heel Rmb – Width of medial ball; Rlb – Width of lateral ball; Rb – Width of ball; Rh – Width of heel; Vmb – Medial ball girth; Vlb – Lateral ball girth; Vb – Ball girth; Vw – Waist girth; Vins – Instep girth; Vh – Heel (cross) girth; Va – Ankle girth; C1toe – Height at 1st toe; Cmb – Medial ball height; Cmd – Height at midfoot point; Cins – Instep height; Cla - Height at lateral ankle center; α – Angle of the big toe.

H - Longitudinal arch factor. This is one of several indexes to help classify feet into 3 groups, as follows: subjects with normal, *pes cavus* (high arched), *pes planus* (flat) [21], or into 4 groups, i.e. one more group of *halluxvalgus* foot [22, 23].

Assessing Foot Damage Method

Along with measuring the feet, the patient's foot damage/pathology is recorded according to symptoms [24]:

- Normal feet without complications and losing protective sensation;
- Foot pain and swollen metatarsophalangeal joints;
- Skin changes (dry, cracked skin);
- Corns;
- Deformity of the foot, big toe bending outward/twisting;
- Foot ulcers;
- Loss/ impairment of protective sensation;
- Amputation.

The patient's foot lesions were recorded by observing them, interviewing the patient, reviewing medical examination results, and taking photos of the damaged feet with a digital camera.

Analyzing Measurement Data

The maximum, minimum, mean and standard deviation values of the left and right foot measurements are determined and compared. A Student Samples T-Test was conducted in order to find statistical significance of left and right foot measurements. The difference between the average values of foot measurements of the two groups of patients were calculated. We compared the average values of foot measurements according to age groups with each other, specifically age groups: 41-50, 51-60, 61-70 and 71-80 years old. The statistical significance of these comparisons was also found using the Student Samples T-Test [23].

Statistics on Foot Injuries/Pathologies

The actual condition of the feet of women with diabetes according to each type of injury is statistically and evaluated. From there, it is possible to initially determine the number/proportion of feet that need to use different types of therapeutic shoes [22]:

1) "Extra Depth Diabetic Shoes" and "Diabetic Inlays" (A5500) are for patients whose feet do not have loss of sensation, deformity, or a history of foot ulcers.

2) "Extra Depth Diabetic Shoes" and "Custom Molded Inlays" (A5512) are for patients who have lost protective sensation in the foot, have no deformity/mild deformity in the foot, or have a history of plantar ulceration.

3) "Custom Molded Diabetic Shoes" and "Custom Molded Inlays" (A5513) are for patients with loss of protective sensation in the foot with deformity or a history of sole ulceration or amputation.

To be able to design custom molded insoles for patients, in addition to assessing foot damage, it is necessary to determine the pressure distribution on its plantar [22].

RESULTS AND DISCUSSIONS

Female Diabetes Patients' General Information

Table	1: Female diabetes patients' information

Information		Patients	group 1		Patients group 2			
Information	Min	Max	Average	Min	Max	Average		
Height, cm	140	171	156.2 ± 4.6	138	170	154.1± 5.1		
Weight, kg	35	81	53.7 ± 8.2	35	78	54.7± 7.3		
Age, year	37	75	58.9 ± 6.9	39	91	65.8±8.4		
Year of diabetes, year	1	18	4.5 ± 3.2	1	41	10.6±8.1		

The average height of studied female patients is 154.1 - 156.2 cm, which is the average height of Vietnamese women, the average of weight is 53.7 - 54.7 kg, BMI about 22.6 indicates the normal body. According to age and number of years of diabetes, patients in group 1 have less age (58.9 years) and number of years of diabetes (4.5 years) than patients in group 2 (65.8 years) and 10.6 years.

Table 2 presents statistical results about the age distribution of patients at two medical locations. It shows that, in patients' group 1, the age group of 51 to 60 years old accounts for a large portion (up to 50.9%); the age group of 50 years accounts for 19%, while the age group of 71 to 80 years contributes a small proportion (about 2.6%). Group 1 has no patients over 80 years old. Meanwhile 43.6% of patients in group 2 are aged from 61 to 70 years old; patients aged from 51 to 60 and from 71 to 80 also account for a large proportion, 22.9% and 25.7%, respectively. The number of patients up to 50 years and over 80 years accounts for a small proportion of about 3.9%. This is reasonable because patients' group 2 is from central hospital, which frequently examines and treats critical cases sent from medical station in addition to treating patients in Hanoi. Meanwhile,

diabetes often tends to get worse over with duration or patient's age.

			Patient	s group 1			
Group of age year	<50	51÷60	61÷70	71÷80	>80	Total	
Quantity, people	22	59	32	3	0	116	
Rate, %	19.0	19.0 50.9 27.6		2.6	0	100	
			Patients	s group 2			
Quantity, people	7	41	78	46	7	179	
Rate, %	3.9	22.9	43.6	25.7	3.9	100	

Table 2: Number of patients according to age group

Table 3: Female diabetes patients job	Table 3:	Female	diabetes	patients'	job
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Job	Officers	Officers Workers		Others	Total		
	Patients group 1						
Quantity	11	19	60	26	116		
Rate (%)	ate (%) 9.5 16.4		51.7	22.4	100		
		Pati	ents group 2				
Quantity	36	49	65	28	179		
Rate (%) 20.2 2		27.6	36.4	15.8	100		

The highest number of patients' group 1 patients are farmers (51.7%), workers (16.4%), officials (9.5%) and others (22.4%). The number of patients in group 2 who are

officials and workers is higher, reaching 20.2% and 27.6%, respectively, while the number of patients who are farmers decreased significantly to 36.4% (Table 3).

Female Diabetes Patients' Foot Measurement

Table 4: The difference between the average of left and right foot measurements in 2 group patients

	Patients group 1							Patients group 2								
ц	Foo	t measu	rement	values,	mm	Dev	iation,	mm	Foot	t measu	rement v	alues, r	nm	Dev	viation, r	nm
Foot measureme	Left	Right	Difference	Difference Max	p(two-tailed)	Left	Right	Difference	Left	Right	Difference	Difference Max	p(two-tailed)	Left	Right	Difference
Lf	230.8	230.4	0.4	5.0	0.556	8.6	8.7	-0.1	227.5	228.4	-0.9	9.0	0.315	9.6	9.6	-0.1
Lmb	168.5	168.6	-0.1	5.0	0.409	6.9	6.9	-0.1	163.2	163.1	0.1	11.0	0.860	8.4	8.2	0.2
Llb	150.0	149.9	0.1	5.0	0.271	6.2	6.2	0.0	145.0	146.6	-1.6	11.0	0.015	8.0	7.8	0.2
L5toe	193.8	193.5	0.3	9.0	0.618	7.6	7.8	-0.2	188.2	189.6	-1.4	7.0	0.091	8.3	8.4	-0.2
Lh	39.3	40.0	-0.7	8.0	0.548	7.8	7.8	0.0	38.5	38.8	-0.3	7.0	0.312	8.8	8.3	-0.5
Rmb	93.6	93.3	0.3	7.0	0.095	5.2	5.2	0.0	88.6	89.4	-0.8	13.0	0.170	5.8	5.6	0.2
Rlb	89.1	89.0	0.1	9.0	0.146	5.2	4.9	0.3	84.9	86.3	-1.5	10.0	0.007	5.9	6.4	-0.5
Rb	101.7	102.5	0.4	9.0	0.547	5.5	5.2	0.4	92.7	92.2	0.5	10.0	0.415	6.1	5.9	0.2
Rh	61.0	60.7	0.3	5.0	0.378	3.8	3.9	-0.1	58.6	59.0	-0.4	9.0	0.274	4.8	4.9	0.0
C1toe	19.7	20.1	-0.4	2.0	0.096	1.7	1.8	-0.1	18.3	18.9	-0.5	4.0	0.005	1.9	2.1	-0.2
Cmb	31.1	30.8	0.3	3.0	0.129	2.9	3.1	-0.2	29.8	30.7	-0.9	8.0	0.007	3.2	3.2	0.0
Cmd	44.1	43.7	0.4	3.0	0.167	4.7	4.5	0.2	52.1	52.8	-0.7	10.0	0.153	4.3	4.3	0.0
Cins	60.0	59.8	0.2	3.0	0.333	5.0	4.9	0.0	63.2	63.3	-0.1	10.0	0.847	4.5	4.4	0.1
Cla	59.4	59.4	0.0	3.0	0.726	3.3	3.1	0.1	56.3	57.6	-1.3	9.0	0.000	4.4	4.6	-0.2
Vmb	210.2	210.1	0.1	3.0	0.678	10.1	10.8	-0.7	206.5	207.6	-1.1	19.0	0.333	13.1	13.1	0.1
Vlb	212.4	212.3	0.1	10.0	0.618	9.9	10.2	-0.3	210.6	210.3	0.3	13.0	0.787	13.2	13.1	0.1
Vb	223.7	223.7	0.0	5.0	0.582	11.5	11.9	-0.5	219.0	219.3	-0.3	20.0	0.793	11.9	12.0	0.0

Revista de Pielărie Încălțăminte 24 (2024) 2

161

	Patients group 1								Patients group 2							
Ħ	Foot measurement values, mm					Dev	Deviation, mm		Foot	Foot measurement values, mm			Deviation, mm			
Foot measuremen	Left	Right	Difference	Difference Max	p(two-tailed)	Left	Right	Difference	Left	Right	Difference	Difference Max	p(two-tailed)	Left	Right	Difference
Vw	217.5	217.5	0.0	5.0	0.682	13.6	13.7	-0.1	215.2	215.1	0.2	24.0	0.907	12.9	12.9	0.0
Vins	242.0	242.6	-0.6	5.0	0.572	13.0	13.0	0.0	238.7	240.5	-1.8	20.0	0.189	14.4	14.0	0.4
Vh	292.9	292.8	0.1	5.0	0.733	13.1	13.5	-0.5	289.1	289.5	-0.4	20.0	0.784	19.2	19.2	0.0
Va	190.1	190.2	0.0	3.0	0.742	17.0	16.7	0.3	192.7	192.9	-0.3	19.0	0.875	15.5	15.5	0.0
α	4.9	9.9	5.0	18.0	0.058	8.3	8.2	0.0	7.8	9.8	-1.8	25.0	0.029	5.3	5.5	-0.2
Н	0.7	0.7	0.0	0.6	0.058	0.2	0.1	0.1	0.8	0.8	0.0	0.6	0.033	0.2	0.2	0.0

The two patient groups' average values for the length, width, and height of their right and left feet (Table 4) differ by no more than 1.3 mm, whereas the group's circumference measures show a maximum variation of 2 mm. The results of Levene's Test and T test for left and right foot both found p-value and p(two-tailed) value greater than 0.05. This confirms that there is no difference in the left and right foot of group 1.

There are differences in some measurements for patients in group 2, including thumb height C1toe, medial ball height Cmb, height at lateral ankle center Cla, angle of the big toe α , and longitudinal arch factor H (p<0.05 and p(two-tailed) <0.05). When experiencing varying levels of foot damage, this also indicates larger variability in the diabetic foot measurement values. This is also consistent with the maximum difference of the left and right feet of group 2. This difference value is often larger than the corresponding values of group 1 (Table 4).

The left and right foot measurements of the two patient groups have standard deviations that are similar to the foot value, typically being less than 1 mm. The feet of individuals without the disease resemble this [25].

There is a maximum 5 mm difference in the average value of the foot measures between patients in groups 1 and 2. Patients in group 1 were 2.6 mm longer in the foot than patients in group 2 (Table 5). This is reasonable because group 1 patients are on average 2.1 cm taller than group 2 patients. Similarly, the ball girth Vb and the ball width Rb are bigger by 4.5 mm and 2.7 mm, respectively.

Patients in group 2 have smaller big toe angles in their feet than patients in group 1, which can be attributed to the patients' tendency to push their big toes outward as a result of their diabetes. The same goes for the foot arch coefficient. This value (0.8) in group 2 patients' feet is larger than that of group 1 patients' feet (0.7), indicating that diabetic patients' foot arches tend to lower with the course of their condition. This demonstrates how beneficial it is for diabetes people to use diabetic or customized molded insoles.

The results of the T Test in Table 5 confirm that there is no difference between the foot length measurements Lf of the two groups of patients (p>0.05, p(twotailed)=0.0860>0.05). Meanwhile, there were differences in all remaining foot measurements between patients in groups 1 and 2 (p<0.05, p(two-tailed) < 0.05). The standard deviation value of foot measurements at two medical facilities also clearly shows this. Compared with the corresponding standard deviation of foot measurements in group 1 patients, the majority of foot measurements in group 2 patients have higher standard deviations. The significant variation in parameter values in the feet of group 2 patients is also indicated by high standard deviation values.

	Foo	t measurement	values, mm	Deviation, mm			
Foot measurement	Group 1	Group 2	Difference	p(two-tailed)	Group 1	Group 2	Difference
Lf	230.6	228.0	2.6	0.0860	9.6	8.7	0.9
Lmb	168.6	164.2	4.4	0.0000	8.3	6.9	1.4
Llb	150	145.8	4.2	0.0000	7.9	6.2	1.7
L5toe	193.7	188.9	4.7	0.0000	8.3	7.7	0.6
Lh	39.5	38.6	0.9	0.0000	8.5	7.8	0.7
Rmb	93.5	89.0	4.4	0.0000	5.7	5.2	0.5
Rlb	89.1	85.6	3.5	0.0000	6.2	5.1	1.1
Rb	95.1	92.4	2.7	0.0000	6.0	5.4	0.6
Rh	60.9	58.8	2.1	0.0000	4.9	3.8	1.1
C1toe	19.9	18.6	1.3	0.0020	2.0	1.7	0.3
Cmb	31	30.3	0.7	0.0041	3.2	3.0	0.2
Cmd	53.9	52.5	1.4	0.0096	4.3	4.6	-0.3
Cins	59.9	62.2	-2.7	0.0100	4.4	5.0	-0.6
Cla	59.4	57.0	2.4	0.0005	4.5	3.2	1.3
Vmb	210.2	207.0	3.1	0.0000	13.1	10.5	2.6
Vlb	212.4	210.5	1.9	0.0001	13.2	10.0	3.2
Vb	223.7	219.2	4.5	0.0001	12.0	11.7	0.3
Vw	217.5	215.1	2.4	0.0493	12.9	13.7	-0.8
Vins	242.3	239.6	2.7	0.0478	14.4	13.0	1.4
Vh	292.9	289.3	3.5	0.0046	16.2	13.3	2.9
Va	190.2	192.8	-2.7	0.6560	15.5	16.8	-1.3
α	7.4	8.8	-1.4	0.0023	7.2	5.4	1.8
Н	0.7	0.8	-0.1	0.1700	0.2	0.2	0.0

Table 5. The difference between the average	a of foot measurements of group 1 and group 2
Table 5. The difference between the average	e of foot measurements of group I and group Z

In order to assess how age affects foot parameter values, we examined the average foot measurement values across three age groups, which together account for a large proportion of the patients in each group (Tables 6 and 7).

Table 6: The average of the feet of patients in group 1 according to three age groups

		Foot measurement values by age group							
Foot	Average, mm	41-50 (n	=20)	51-60 (ı	า=59)	61-70 (n=35)			
measurement		Value, mm	Difference	Value, mm	Difference	Value, mm	Difference		
Lf	230.6	232.1	-1.5	230.1	-0.5	230.0	-0.60		
Lmb	168.6	171.3	-2.7	167.7	-0.9	168.1	-0.60		
Llb	150.0	152.8	-2.8	149.4	-0.4	148.9	-1.00		
L5toe	193.7	194.1	-0.4	191.3	-0.7	191.9	-0.10		
Lh	39.5	40.0	-0.5	39.1	-0.4	39.0	-0.50		
Rmb	93.5	92.9	0.6	93.0	0.2	92.2	-0.50		
Rlb	89.1	90.5	-1.4	89.3	0.2	87.9	-1.20		
Rb	95.1	96.4	-1.3	94.8	-0.3	95.0	-0.10		
Rh	60.9	61.0	-0.1	60.9	0.4	59.6	-0.90		
C1toe	19.9	19.1	0.8	19.0	-0.1	19.2	-0.10		
Cmb	31.0	31.6	-0.6	30.9	-0.1	31.0	0.00		
Cmd	53.9	52.0	1.9	44.5	-0.6	45.0	-0.10		
Cins	58.9	60.9	-2	60.1	-0.3	60.5	0.10		
Cla	59.4	57.2	2.2	58.5	0.2	58.5	0.20		

Revista de Pielărie Încălțăminte 24 (2024) 2

		Foot measurement values by age group							
Foot	Average. mm	41-50 (n:	=20)	51-60 (r	า=59)	61-70 (n=35)			
measurement	0 - ,	Value, mm	Difference	Value, mm	Difference	Value, mm	Difference		
Vmb	210.2	212.2	-2	211.7	-0.8	209.5	2.90		
Vlb	212.4	216.1	-3.7	214.2	-0.7	211.7	2.80		
Vb	223.7	226.3	-2.6	223.1	-0.2	221.0	1.80		
Vw	217.5	220.2	-2.7	215.3	-0.7	213.6	1.50		
Vins	242.3	244.8	-2.5	241.9	-0.4	240.4	0.10		
Vh	292.9	295.8	-2.9	293.7	-0.1	289.8	4.00		
Va	190.2	192.4	-2.2	191.4	-0.8	189.6	1.40		
α	7.4	6.2	1.2	7.8	0.4	8.5	1.10		
Н	0.7	0.6	0.1	0.7	0.0	0.8	0.10		

Table 7: The average of the feet of patients in group 2 according to three age groups

		Foot measurement values by age group							
FOOT	Average, mm	51-60 (n=41)	61-70 (n=78)	71-80 (n=46)		
measurement		Value, mm	Difference	Value, mm	Difference	Value, mm	Difference		
Lf	228.0	228.4	-0.4	228.8	-0.8	226.3	1.6		
Lmb	163.2	162.5	0.6	163.8	-0.6	162.5	0.7		
Llb	145.8	145.7	0.0	146.1	-0.4	145.1	0.7		
L5toe	188.9	188.4	0.5	189.4	-0.5	188.6	0.3		
Lh	38.6	38.0	0.7	39.0	-0.4	38.4	0.2		
Rmb	89.0	88.8	0.2	89.1	-0.1	88.7	0.3		
Rlb	85.6	85.6	0.0	85.7	-0.1	85.3	0.3		
Rb	92.4	92.1	0.3	92.5	-0.1	92.3	0.2		
Rh	58.8	58.4	0.4	58.9	-0.1	58.4	0.4		
C1toe	18.6	18.5	0.2	18.7	-0.1	18.5	0.1		
Cmb	30.3	30.2	0.0	30.4	-0.2	30.1	0.2		
Cmd	52.5	52.8	-0.3	52.4	0.1	53.0	-0.5		
Cins	63.2	63.4	-0.2	63.0	0.2	64.0	-0.8		
Cla	57.0	57.4	-0.5	57.4	-0.4	56.0	1.0		
Vmb	207.0	206.1	0.9	208.1	1.0	206.0	1.0		
Vlb	210.5	210.4	0.0	211.2	-0.7	209.5	1.0		
Vb	219.2	218.6	0.5	219.8	-0.6	218.2	1.0		
Vw	215.1	215.6	-0.5	214.8	0.4	215.1	0.1		
Vins	239.6	239.8	-0.2	240.0	-0.4	239.2	0.4		
Vh	289.3	287.7	1.6	290.1	-0.8	288.6	0.7		
Va	192.8	191.1	1.7	192.5	0.3	192.1	0.7		
α	8.8	7.5	1.3	8.6	0.2	9.1	-0.3		
н	0.8	0.8	0.0	0.7	0.0	0.8	0.0		

The results shown in Tables 6 and 7 indicate that there is no large difference between the foot measurement average value of the group and the foot measurement values for each age group. In particular, based on three primary measures, the ball girth Vb is not greater than 2.6 mm, the ball width Rb is not greater than 1.3 mm, and the foot length Lf difference is 1.5 mm (group 1) and 1.6 mm (group 2).

We conducted Independent Samples Ttests to find the statistical significance of the results comparing feet between groups by age; the feet of each age group were compared with the average value of each group (Table 8). For the feet of group 1, all pvalues of Levene's Test and p(two-tailed) values of T test have values greater than 0.05. This confirms that there is no difference in main foot measurements according to age group of group 1.
Group 2 had similar results to group 1, except the p(two-tailed)-value for groups 51– 60-year-old and 71–80-year-old reached lower than 0.05, showing that the initial hypothesis is no longer valid.

Table 8: p(2-tailed)-value of the independent Samples T-test for the main measurements of the foot, comparing age groups

Comparing groups		p(two-tailed)-value			
		Rb	Vb		
Group 1					
Groups of 41-50 and 51-60 years old	0.056	0.053	0.061		
Groups of 41-50 and 61-70 years old	0.058	0.062	0.071		
Groups of 51-60 and 61-70 years old	0.984	0.055	0.132		
41–50-year-old group and average value of group 1	0.060	0.161	0.057		
51–60-year-old group and average value of group 1	0.992	0.887	0.908		
61–70-year-old group and average value of group 1	0.989	0.351	0.076		
Group 2					
Groups of 51-60 and 61-70 years old	0.800	0.149	0.592		
Groups of 51-60 and 71-80 years old	0.227	0.029	0.844		
Groups of 61-70 and 71-80 years old	0.142	0.421	0.466		
51–60-year-old group and average value of group 2	0.778	0.135	0.834		
61–70-year-old group and average value of group 2	0.514	0.830	0.693		
71–80-year-old group and average value of group 2	0.241	0.269	0.648		
2 age groups of 2 groups of patients					
2 groups 51-60 years old	0.192	0.000	0.014		
2 groups 61-70 years old	0.334	0.000	0.046		

We continue to compare the values of foot measurements of two groups of patients aged 51-60 years and 61-70 years old (Table 9). Independent Samples T-tests were performed for these comparisons (Table 8). The results showed that there was no difference in foot length Lf (p values>0.05), but there were differences in width Rb and toe joint circumference Vb according to age groups of the 2 groups of patients (p values < 0.05).

Table 5. Comparison of foot measurements by two age groups of two patient groups	Table 9: Con	nparison of fo	oot measurements b	by two age	e groups of two	patient gro	oups
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	Foot measurement values by a				ge group, mm	
	51-60			61-70		
Foot measurements	Group 1	Group 2	Difference	Group 1	Group 2	Difference
Lf	230.1	228.4	1.7	230.0	228.8	1.2
Lmb	167.7	162.5	5.2	168.1	163.8	4.3
Llb	149.4	145.7	3.7	148.9	146.1	2.8
L5toe	191.3	188.4	2.9	191.9	189.4	2.5
Lh	39.1	38.0	1.1	39.0	39.0	0.0
Rmb	93.0	88.8	4.2	92.2	89.1	3.1
Rlb	89.3	85.6	3.7	87.9	85.7	2.2
Rb	94.8	92.1	2.7	95	92.5	2.5
Rh	60.9	58.4	2.5	59.6	58.9	0.7
C1toe	19.0	18.5	0.5	19.2	18.7	0.5
Cmb	30.9	30.2	0.7	31	30.4	0.6
Cmd	44.5	50.8	-6.3	45	50.4	-5.4
Cins	60.1	63.4	-3.3	60.5	63.0	-2.5
Cla	58.5	57.4	1.1	58.5	57.4	1.1
Vmb	211.7	206.1	5.6	209.5	208.1	1.4
Vlb	214.2	210.4	3.8	211.7	211.2	0.5
Vb	223.1	218.6	4.5	223.0	219.8	3.2
Vw	215.3	215.6	-0.3	213.6	214.8	-1.2

	Foot measurement values by age group, 51-60 61-70				, mm	
Foot measurements	Group 1	Group 2	Difference	Group 1	Group 2	Difference
Vins	241.9	239.8	2.1	240.4	240	0.4
Vh	293.7	287.7	6.0	289.8	290.1	-0.3
Н	0.7	0.8	-0.1	0.6	0.7	-0.1

Consequently, it is evident that the level of foot damage mostly determines the variation in the average measurements of a patient's foot rather than age. It is obvious from this that determining the level of damage to the feet is essential in order to identify which feet require the use of specific shoe types [24].

Diabetic Women's Feet Damaged Condition

In addition to fitting properly, diabetes patients' shoes and insoles must also lower body pressure on the foot plantar and lower peak pressure, which can lead to foot ulcers. As a result, while designing and producing shoes or shoe insoles for diabetes patients, consideration must be given to both foot measurements and the many forms of foot injury. Diabetes patients who are female generally have large calluses on their ankles and metatarsophalangeal joints; the big toe joint is frequently enlarged and slightly deformed; some have a history of ulcers on the plantar of their feet; and there are minor ulcers on their ankle flexors. Numerous patients' feet have two or more different kinds of injury. Table 10 lists the percentage of patients' feet with various injuries.

The diabetes status of patients' group 1 is basically still mild, as shown by the number of patients with undamaged feet accounting for 50.9%. The number of female patients with pain and swollen metatarsophalangeal joints is relatively large, accounting for 26.7%. The number of patients with dry foot skin, cracked skin and calluses is almost equal proportions, roughly 18.1%. The number of patients with foot ulcers accounted for 4.3% and no patients had to have a foot amputated. Patients in group 2 have more serious diabetes than those in group 1. The percentage of patients with normal feet dropped to 32.3%, indicating this, whereas the percentage of feet with damage of all kinds sharply climbed. Eight percent of feet have ulcers or a history of ulcers, and two individuals had a portion of one foot amputated. More than 62.1% of patients had two different forms of foot injuries, which is a rather high percentage.

	Group 1		Group 2			
Foot conditions	Rate, %	Duration of diabetes, year	Rate, %	Duration of diabetes, year	Type of shoes [24]	
Normal feet without complications and losing protective sensation	50.9	3.8 ± 2,8	32.3	4.68 ± 2.5	A5500	
Foot pain and swollen metatarsophalangeal joints	26.7	4.16 ± 2,1	33.5	5.90 ± 2.7	A5500; A5512*	
Skin changes (dry, cracked skin)	18.1	4.39 ± 2,8	29.6	6.80 ± 3.9	A5500; A5512*	
Corns	15.5	5.23 ± 3,8	27.9	6.50 ± 4.4	A5500; A5512*	
Deformity of the foot, big toe bending outward/twisting	13.8	5.46 ± 4,1	22.4	8.80 ± 5.9	A5512; A5513*	
Foot ulcers	4.3	5.82 ± 4,3	8.4	8.58 ± 5.1	A5512; A5513**	
Loss/ impairment of protective sensation	4.6	6.97 ± 5,5	7.9	7.91 ± 6.8	A5512; A5513**	
Amputation	0	0	0.1	15 ± 9.8	A5513	
Total	133.9		162.1			

Table 10: Damaged feet conditions of female diabetes patients

Note: * cases of ulcers on the soles of the feet and impaired/loss of sensation.

** cases where the foot is deformed and loses protective sensation

The percentage of shoe types required for each female patients has been preliminary determined based on the US Medicare Program's guidelines for utilizing therapeutic shoes/shoe insoles in doctor's prescriptions [24]. The results are displayed in Table 11.

Type of shoes	Patients group 1	Patients group 2	Both groups
A5500, %	87.4	70.5	79.0
A5512,%	11.5	24.4	17.9
A5513 <i>,</i> %	1.1	5.1	3.1
Total, %	100	100	100

Table 11: Preliminary statistical results of research on shoe types for women with diabetes

Consequently, up to 96.9% of female patients with diabetes require "Extra Depth Diabetic Shoes"; of these, 79.0% utilize "Diabetic Inlays", 17.9% require "Custom Molded Inlays", "Custom Molded Diabetic Shoes" and "Custom Molded Inlays".

CONCLUSIONS

Women with diabetes who experience foot issues typically get worse over time. Variations in foot measurements of height, width, and circumference depend on damage or pathology and are independent of age. As a result, it is not possible to create and produce one type of shoes for feet with the wide range of difficulties associated with diabetic feet. In order to design and manufacture shoes for individuals with diabetes, it is necessary to examine the foot dimensions and shape as well as gauge the extent of the patient's foot damage.

According to the research on foot damage in women with diabetes, up to 96.9% of female patients need to use "Extra Depth Diabetic Shoes"; 17.9% of patients needed "Custom Molded Inlays"; 3.1% of patients need to use "Custom Molded Diabetic Shoes" and "Custom Molded Inlays". Therefore, it is essential to create and produce customized shoes and shoe insoles for diabetes patients in addition to conducting "Extra Depth Shoes" research on the mass production of shoes for these individuals. Conclusions of this study serve as the foundation for developing and producing shoes and insoles for diabetic Vietnamese women based on their anthropometric characteristics and foot issues.

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EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

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NEWS 4/2024



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as leather articles can be easily repaired, reused, and repurposed, making it the best choice for sustainable practices.



Because Leather champions durability, it is natural that we keep REUSING it.

- **Choosing leather** allows you to **REUSE** it, meaning re-wearing your leather footwear naturally season after season. And if issues like worn heels or soles arise, you can have them repaired quickly and affordably in just one day at your local shoe repair workshop.

- **Choosing leather** allows you to **REUSE** it by passing your cherished leather item over from generation to generation. Think of your father's leather briefcase, a symbol of his hard work and dedication, or the leather couch you took from home when moving into your first apartment. Quality vintage items like this never go out of fashion.

- and of course, **choosing leather** brings economic advantages. Extending the life of leather items means we shop less and save money (just shared one of the secrets of wealth - no need to thank us :))

For more inspiration on leather's longevity and versatility visit the world's first-ever digital exhibition "<u>It's a Long Story</u>" by **Leather Naturally**.



Because Leather is ageing gracefully, it's remarkably simple to REPAIR it.

When you repair your leather goods, you breathe new life into your favourite items, deepening the connection between you and the goods that are part of your personal story. Just as

we strive to repair relationships rather than end them, fixing leather enhances its longevity and value.

Watch the <u>Alliance France Cuir</u> demonstration on how nice and beneficial it is to repair your leather items. Well, if a leather bag survived a 476 kg metal band saw cutting at 100 metres per minute, imagine how well it can withstand everyday wear and tear!



Or explore the 120-year-old craftsmanship of the <u>BootRepair Company</u> and be amazed by the heritage behind each repair. So then next time, instead of buying a new pair of shoes, consider repairing them or treating them to a leather spa experience.

Remember, by repairing your leather items, you not only reduce waste and save money but also strengthen the bond with your personal belongings.

Because leather is a very supple material, it is extremely easy to REPURPOSE it.

Leather belts can be creatively repurposed into carry bags, camera straps, stylish dog collars, or personalised bracelets. Leather wallets can be transformed into durable ties for gardening or workshops, chic pulls for DIY furniture, or elegant bookmarks.

And it's not just individuals who are doing this; brands like Hermès are championing the reinvention of everyday objects using leather leftovers and other materials, in their <u>Petit h atelier</u>. They forge surprising connections between artists and craftsmen, creating new alliances between expertise and natural materials. Why not join the movement?

To start with, get inspired with <u>Nquart</u>'s step-by-step leather crafting guides and create your own exclusive, personalised leather items. Enjoy each stage of this creative process - give it a try and have fun!



Alternatively, discover how to upcycle your old leather jacket with just a few simple steps by watching a <u>short video from craftsman Yusuf Osman</u>.

The leather has so much to offer! Beyond being beautiful, natural, and durable, leather articles can be easily repaired, reused, and repurposed, making it the best choice for sustainable practices. By extending the life of leather goods, we minimise waste, reduce landfill use, and lessen environmental impact.

If leather isn't one of the best sustainable investment decisions, we don't know what is!

Agree? Help us spread the word to have more people celebrate the versatility and sustainability of leather!



If you want to go further: Green Deal Leather - Final Conference | <u>Website</u> Alliance France Cuir | <u>Website</u> Leather Naturally | <u>Website</u>



On May 16, in Brussels, the European Tanning and Leather social partners, COTANCE and industriAll Europe held the Green Deal Leather Final Conference, concluding a two-year, EU-funded Social Dialogue project <u>'Towards Zero Adverse Impact of the European Leather Industry – GREEN DEAL LEATHER</u>'.



The event attracted around 100 on-site attendees and marked the end of a successful, EUfunded social dialogue project between the European social partners as well as national representatives from Spain (ACEXPIEL), Portugal (APIC), France (FFTM), Hungary (MKZS), Italy (UNIC), Germany (VDL), and Austria (FVTBSL).



The two-year EU-funded Green Deal Leather (GDL) project has, for the first time, provided comprehensive data on workplace safety within EU tanneries, detailed in the "Injuries/Incidents at the Workplace" study released in Lineapelle/Milan on 19 September 2023.



Additionally, the project unveiled findings on the carbon footprint of leather in the "Carbon Footprint of European Bovine Leather" study, presented at the Final Conference in Brussels on 16 May. Both studies highlighted the industry's environmental and social credentials, providing tanneries with guidance to enhance their sustainability.

The main insights on occupational health and safety include:

- Tannery-related accidents in EU countries surveyed (Italy, Spain, France, Germany, Portugal, Hungary, and Austria) declined by 16%, from 1,317 in 2019 to 1,102 in 2021.
- However, with an incidence rate of 3.2% in 2021, 15% on the way to/from work, and over 90% of recorded accidents being qualified as of "minor" severity, there is still room for improvement.

Safety at the Workplace Study

Judith Kirton-Darling, General Secretary of industriAll European Trade Union said at the Green Deal Leather Final Conference:

"Good occupational health and safety practices in the workplace, with ongoing training and checks, are essential to keep tannery workers safe. Social dialogue is key, and trade unions and workers' representatives must be able to highlight any issues to management and know that they will be acted on swiftly. These preliminary results are a baseline and now we must work together to achieve zero accidents."





European Tannery: Safety First!

The main insights into the environmental impact include:

- Calculating leather's carbon footprint is a complex exercise that requires a thorough understanding of the tanning industry, its processes and products.
- The result obtained with the ECO2L method indicates an average of 8kg of CO2 per m2 of bovine leather in EU tannery processes.
- This figure can vary based on specific characteristics of the leather, such as thickness and performance requirements. Therefore, since each batch of leather is made to order, customers have the opportunity to influence the eco-design of their leather products.
- Excluding the impact of livestock breeding reveals the actual footprint of leather tanning and the importance of chemicals used during the tanning process, but also that replacing one chemical with another that has a lower carbon footprint does not always result in overall improvement.

Carbon Footprint Study

Mr Manuel Rios, President of COTANCE: "Through the Green Deal Leather project, COTANCE continues to equip European tanners with the tools and intelligence needed to progress towards a more sustainable future. We believe that transparency is key to advancing our social and environmental credentials and dispelling common misconceptions about leather. We are proud to undertake this journey hand in hand with our social partners."





European Tannery: Environment Matters!

The Final Conference of the <u>GDL project</u> showcased the work and achievements of the social partners, who, in these last two years, have gathered and produced data that will greatly benefit the tanning and leather sector globally. By working together in social dialogue, the European leather industry produces tools and intelligence which contribute to worker safety, protect the environment, and promote sustainable, highquality leather, supporting millions of jobs worldwide.

So, next time you're deciding between leather and another material, remember that choosing European leather not only offers a high-quality experience that you can enjoy for a long time but also delivers a product crafted with the utmost care for both employees and the environment.





European Leather is your smart choice!



If you want to go further: Green Deal Leather - Final Conference | <u>Press Release</u> EURACTIV about us | <u>Website</u> Brussels Times about us | <u>Website</u>

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References. Must be numbered in the paper, and listed in the order in which they appear.

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