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REVISTA DE PIELĂRIE ÎNCĂLŢĂMINTE LEATHER AND FOOTWEAR JOURNAL

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IDENTIFYING BARRIERS FOR IMPLEMENTING GREEN SUPPLY CHAIN MANAGEMENT (GSCM) IN FOOTWEAR INDUSTRY OF BANGLADESH: A DELPHI STUDY APPROACH

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IDENTIFYING BARRIERS FOR IMPLEMENTING GREEN SUPPLY CHAIN MANAGEMENT (GSCM) IN FOOTWEAR INDUSTRY OF BANGLADESH: A DELPHI STUDY APPROACH

ABSTRACT. The footwear industry is the second largest export earning sector of Bangladesh, contributing to earning $1.234 billion in 2016-17. Despite its ample opportunity to value addition to national economy, the sector faces enormous image crisis at home and abroad because of non-existent green practices in the supply chain. The tenet of Green Supply Chain Management (GSCM) practices is to diminish or obviate wastages, greenhouse gas emission, and energy consumption and promotes reuse, recycle, remanufacture and reverse logistics. The study was designed to identify the barriers for implementing Green Supply Chain Management (GSCM) practices in Footwear Industry of Bangladesh. A two round Delphi study approach was conducted from five industrial experts and five academic experts to identify the common barriers. The study identified twenty two barriers whereas the lack of commitment of management is the paramount. Financial constraint, lack of energy management & wastage management as well as lack of source of eco-friendly materials are the second most important barriers. The internal barriers and regulations & awareness barriers were classified as the top source and features barriers respectively. The study result may provide insight to the management in formulating strategies and tactics to implement green practices in footwear industry for sustainability.
KEY WORDS: barrier, GSCM, footwear industry, Bangladesh, Delphi

IDENTIFICAREA BARIERELOR PENTRU PUNEREA ÎN APLICARE A GESTIONĂRII LANŢULUI DE APROVIZIONARE ECOLOGICĂ (GSCM) ÎN INDUSTRIA DE ÎNCĂLŢĂMINTE DIN BANGLADESH: ABORDARE UTILIZÂND METODA DELPHI

REZUMAT. Industria de încălţăminte este cel de-al doilea sector ca mărime la nivelul veniturilor din exporturi din Bangladesh, contribuind la venituri de 1,234 miliarde de dolari în perioada 2016-2017. În ciuda oportunităţilor sale ample de a aduce valoare adăugată economiei naţionale, sectorul se confruntă cu o criză imensă a imaginii în ţară şi în străinătate din cauza lipsei de practici ecologice în lanţul de aprovizionare. Principiul practicilor de gestionare a lanţului de aprovizionare ecologică (GSCM) este de a diminua sau de a evita pierderile, emisiile de gaze cu efect de seră şi consumul de energie, promovând reutilizarea, reciclarea, recondiţionarea şi logistica inversă. Studiul a fost conceput pentru a identifica barierele în calea implementării practicilor de gestionare a lanţului de aprovizionare ecologică (GSCM) în industria de încălţăminte din Bangladesh. S-a realizat un studiu pe baza metodei Delphi în două etape, condus de cinci specialişti din industrie şi cinci specialişti academici pentru a identifica barierele comune. Studiul a identificat douăzeci şi două de bariere, dintre care lipsa angajamentului conducerii este cea mai importantă. Constrângerile financiare, lipsa gestionării energiei şi gestionarea deşeurilor, precum şi lipsa sursei de materiale ecologice sunt barierele de pe locul doi ca importanţă. Barierele interne şi cele privind reglementările şi conştientizarea au fost clasificate drept sursa principală a acestora. Rezultatul studiului poate oferi managerilor o perspectivă referitoare la formularea de strategii şi tactici pentru punerea în aplicare a practicilor ecologice în industria de încălţăminte pentru dezvoltarea sustenabilităţii.
CUVINTE CHEIE: barieră, GSCM, industria de încălţăminte, Bangladesh, Delphi

IDENTIFICATION DES OBSTACLES À LA MISE EN ŒUVRE DE LA GESTION DE LA CHAÎNE D'APPROVISIONNEMENT ÉCOLOGIQUE (GSCM) DANS L'INDUSTRIE DE LA CHAUSSURE AU BANGLADESH: UNE APPROCHE DE LA MÉTHODE DELPHI

RÉSUMÉ. L'industrie de la chaussure au Bangladesh est le deuxième secteur en ce qui concerne les gains à l'exportation, ayant une contribution de 1.234 milliards de dollars pendant 2016-2017. En dépit de ses nombreuses possibilités d'apporter une valeur ajoutée à l'économie nationale, le secteur fait face à une énorme crise d'image dans le pays et à l'étranger en raison du manque de pratiques environnementales dans la chaîne d'approvisionnement. Le principe des pratiques chaîne d'approvisionnement gestion écologique (GSCM) est de réduire ou d'éviter les pertes, les émissions de gaz à effet de serre et la consommation d'énergie, et de promouvoir la réutilisation, le recyclage, la rénovation et la logistique inverse. L'étude a été conçue pour identifier les obstacles à la mise en œuvre des pratiques de gestion de la chaîne d'approvisionnement écologique (GSCM) dans l'industrie de la chaussure au Bangladesh. On a approché la méthode Delphi en deux étapes, conduite par cinq experts de l'industrie et cinq experts universitaires pour identifier les obstacles communs. L'étude a identifié vingt-deux obstacles, notamment le manque d'engagement de la direction est le plus important. Les contraintes financières, le manque de la gestion d'énergie et la gestion des déchets, le manque de la source de matières écologiques sont les obstacles seconde en importance. Les obstacles internes et les obstacles concernant les règlements et la sensibilisation ont été considérés comme leur principale source. La conclusion de l'étude peut donner aux directeurs un aperçu quant à la formulation des stratégies et des tactiques pour mettre en œuvre des pratiques respectueuses de l'environnement dans l'industrie de la chaussure pour le développement durable.
MOTS CLÉS: obstacle, GSCM, industrie de la chaussure, Bangladesh, Delphi

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INTRODUCTION

The leather and footwear industries are playing a pivotal role in Bangladesh export earnings where each of these industries are largely interrelated with each other. The leather industry is the second largest export earning sector of Bangladesh. According to Export promotion Bureau (EPB) in 2017-18 it has reached 709.51 million USD, which is 34.26 million USD less from the previous year, with a negative growth rate of 4.61%. The overall leather industry is classified into three broad categories such as finished leather, leather products, and footwear. In these three categories, only footwear industry is showing a positive growth rate with export earnings of 357.98 million USD, which is 22.12 million USD higher than the same period of the previous year. The non-leather footwear industry is also showing an upward trend with export earnings of 150.14 million USD and growth rate 7.26% accordingly. Experts are claiming that due to lack of environmental sustainable practices, the industry is facing problems to export market. Bangladesh has a great opportunity to grasp the international leather-footwear market where it is contributing less than 1% at present. So, sustainable manufacturing practice and green supply chain management are gaining crucial factors for this industry's survival and uplifting.

Rapid industrialization with the help of high technology influenced the higher energy consumption and more utilization of resources in order to satisfy human needs that are increasing total supply chain activities. These activities are major significant factors in the depletion of natural resources, arousing climatic problems, more waste generation, emission of harmful gases, and breaking down the ecosystem. GSCM is the sustainable environmental practice whose mantra is to overcome environmental disruption, it corroborates environmental management principles with supply chain activities in order to either improve the environmental performance or to preserve the natural ecosystem with efficient use of natural resources. Therefore, GSCM is an important and emerging 21st century trend among all industrial activities; competitive regulatory and community pressures address these serious environmental issues by greening their supply chains, controlling waste in all forms comprising energy emissions, chemical, hazardous substances, and solid waste in the supply chain [1].

Green Supply Chain Management (GSCM)
= Green Purchasing + Green Manufacturing/Materials Management
+ Green Distribution/Marketing + Reverse Logistics [1] (1)

Equation 1 shows this GSCM equation graphically, where reverse logistics "closes the loop" of a generic forward supply chain and comprises reuse, remanufacturing, and/or recycling of materials into new materials or other products creating value to the market. The main aim is to eliminate or optimize waste (energy, resources, emissions of chemicals and hazardous substances and solid wastes).

GSCM is a structured closed loop approach to upgrade performance of the products and operations/processes paying special attention to the requirements of the environmental regulations predefined by legislation and focuses at limiting the wastes within the industrial system so that energy resources are optimally preserved and hinder the dissemination of detrimental materials into the environment, comprising all aspects of product's life cycle which covers the design phase, manufacturing phase and the distribution phase to the end users of the product including reuse, recycle, recovery and also its final disposal. The focal point of GSCM tends to be integrated and ecologically optimized, while traditional SCM that focuses more on the final product without considering human toxicological effect and environmental disruptions [2]. As day proceeds global manufacturing systems are upgrading, rapidly changing and environment and social issues are becoming more important as well as compulsory in managing any business [3]. That is why, nowadays it is very important to implement green supply chain practices for any kind of industry. At present, Bangladeshi government is paying more focus on successful tannery relocation with Effluent treatment plant

(ETP) and providing cash incentive for leather & footwear export in order to uplift this industry. So it is the right time to implement green supply chain practices to attract international buyers and preserve the ecosystem. The main aim of this research work was to identify the common barriers for implementing GSCM practices in footwear industry of Bangladesh through two round Delphi study with the help of industrial and academic experts.

LITERATURE REVIEW: BARRIERS OF GSCM

Green supply chain management is a paradigm to new industrial sustainability both in terms of environment related problems and efficiency. The aim of GSCM is to consume the energy and resources effectively for making environment friendly supply chain while reducing the impact at each stage with a strategy for meeting the challenge to minimize carbon emission and enhance sustainability followed by green purchasing, green manufacturing, green packing, green distribution and marketing [2]. GSCM is duly defined as "integrating environmental thinking into supply chain management, includes product design, material sourcing and selection, manufacturing process, delivery of the final product to the consumers as well as end-of-life management of the product after its useful life" [4].

There are many barriers that are responsible for implementing GSCM in different industries. Many articles were observed in order to get a comprehensive idea about the considered most frequent barriers. The identified barriers are listed such as commitment from top management, lack of govt. rules & regulations, lack of knowledge on sustainability, society's awareness on Environment, nature of raw materials, buyers outsourcing strategy, market competition & uncertainty, lack of training on GSCM, financial constraint, interest in investment, lack of acceptance of new technology, lack of energy management & waste management, lack of integration of IT system, customer unawareness towards GSCM, lack of availability of skilled human resource, poor supplier commitment, lack of experience, poor organizational culture in implementing GSCM and lack of poor transport & logistics system. On the other hand, there are several factors which are involved during footwear purchasing such as style, comfort, price, colour, upper materials, outsole materials that may have also a significant effect on GSCM practice [5].

Table 1: Enlistment of barriers of GSCM observed from different articles

S. No.	Listing of barriers	Resources
1	Lack of commitment from top management	[6,7,8,9,10,11,12,13]
2	Lack of govt. rules and regulations	[4,7,10,11,15,16]
3	Lack of knowledge and experience	[4,7,10,11,13,17]
4	Market competition and uncertainty	[11,18,19,20,21]
5	Lack of training on GSCM	[7,17,22,23]
6	Financial constraint	[3,7,11,15,17,24,25,26]
7	Lack of acceptance of new technology	[6,7,9,15,17,27,28,29,30]
8	Lack of energy management and waste management	[9,12,31]
9	Lack of integration of IT system	[6,7,9,17,32]
10	Customer interest towards GSCM	[7,11,13,22,32]
11	Lack of availability of skilled human resource	[7,8,10,17]
12	Poor supplier commitment	[4,7,8,11,22]
13	Poor organizational culture in implementing GSCM	[18,19,33,34]
14	Lack of management initiatives for transport and logistics	[9,12]

Recently a research study revealed the most critical success factors in implementing GSCM practices in footwear industry which are support & commitment of top management, customer awareness, long-term economic benefit, govt. legislation towards GSCM implementation, SC members' awareness and literacy, involvement of suppliers in green practice, global competitiveness, pressure from NGOs and society, encouragement to technology advancement, organizational policy supporting GSCM [34]; support and commitment of top management was identified as the most important driver in greening the SC of leather footwear industry [34]. To the best of our knowledge there was no Delphi study approach to identify the barriers of GSCM in Bangladeshi footwear study. Moreover, since experts' opinion may differ from one to another, this study will surely contribute a lot to identifying the probable barriers which will contribute to controlling the barriers.

COMPONENTS OF GREEN SUPPLY CHAIN MANAGEMENT

Green procurement, Green design and Manufacturing and Green Distribution and Reverse Logistics are the generic components of GSCM as mentioned Figure 1 [35]. This figure represents a single organization's internal supply chain, its major operational elements and the relation to external organizations.

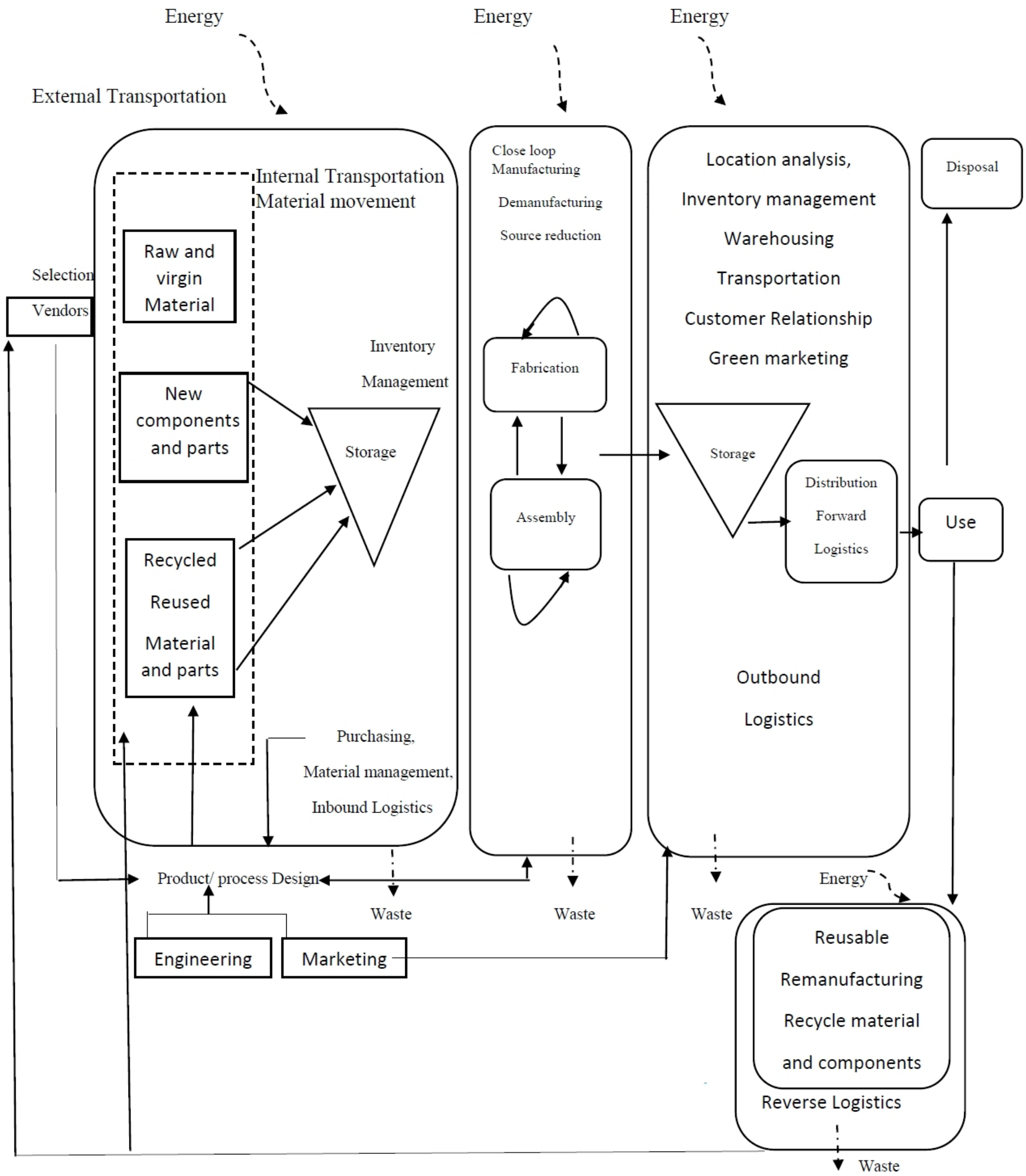

Figure 1. Processes involved in green supply chain management [35]

Green Procurement

Green procurement can be termed as a set of approaches followed by an organization to select suppliers who are maintaining eco-friendly methods and environmental legislations when manufacturing practices. The focus of it is to reduce the source of wastage, expedite recycling, reuse and reduce the uses of resources, and searching alternative eco-materials [36].

Design for Environment (DFE) – Green Design

DFE is a systematic and structured approach where environmental impact of a product is considered through its entire life cycle at the time of designing a product. Green designing is a very important factor in GSCM which intends to develop more environmentally amiable products and processes. The ultimate goal of green design is to diminish the damage in the whole designing process [7].

Green Manufacturing

Green manufacturing is an integration of multidisciplinary approach which focuses on reducing energy consumption and material used by using green energy, developing and selling green products and incorporating green processes in the business operations [37]. Remanufacturing is a vital element of GSCM practices which comprises three phases: collection, remanufacturing and redistribution processes of returning a used product to like-new condition with a warranty to match [36].

Green Marketing

Nowadays green marketing has gained a paramount importance to the consumers as a part of environmental awareness. The green consumers are those who avoid any product which may harm any living organism, cause disruption to the natural eco-system at any phases of the product. Green product can be used for several reasons, comprising manufactured through a green way or products when consumed for a greener way of life.

Green Distribution and Reverse logistics

Green distribution system consists of green packaging and green logistics. Packaging features have an impact on distribution; better packages help to rearrange the loading patterns can minimize the material usage and increase the warehouse space efficiency and minimize the double handling [38]. The reverse supply chain demonstrates the activities of recycling, remanufacturing, reclamation and reverse logistics which are inter-related to the closed supply chain loop as depicted in Figure 1.

RESEARCH METHODOLOGY

'Delphi may be characterized as a method for structuring a group communication process so that the process is effective in allowing a group of individuals, as a whole, to deal with a complex problem. To accomplish this "structured communication" the following is provided: some feedback of individual contributions of information and knowledge; some assessment of the group judgment or view; some opportunity for individuals to revise views; and some degree of anonymity for the individual responses' [39]. In this method, a group of experts exchange views and each independently provides their feedbacks and assumptions to a facilitator who reviews the data and issues a summary report. The group members discuss and review the summary report, and give updated forecasts to the facilitator, who again reviews the material and issues a second report. This process continues until all participants reach a consensus. The experts at each round have a full record of what forecasts other experts have made, but anonymity does not permit to know who made which forecast. This method allows the experts to express their opinions freely.

Table 2: Composition of Delphi panels

Round	Respondents	
	Academicians	Industrial
1	5	5
2	5	5
Total	10	10

In this research work five academic and five industrial experts were selected for the survey round. There were some minimum requirements to select the expert panels. The academic experts were selected who have had a teaching career on footwear supply chain management more than 5 years and industrial experts were also chosen who have more than 5 years experience in supply chain and logistics management at reputed footwear companies. The survey was carried out in two phases whereas some frequently identified barriers of GSCM for any industry from thorough literature review; data were supplied to the expert panel in order to provide a score according to Likert scale rating system with an additional scope to introduce new barrier.

Table 3: Likert scale ranking system

Strongly disagree	1
Disagree	2
Neither agree or disagree (Neutral)	3
Agree	4
Strongly agree	5

A total of fourteen barriers were identified from literature review that were enlisted in the survey format and another option was there to add extra barriers conceived by the experts. In the second phase all barriers were subdivided into different categories such as internal and external barriers based on their sources. Again all identified twenty two barriers were fragmented into regulations & awareness barriers, financial barriers, technology & expertise barriers, product barriers and others based on features of barriers in order to know the most probable sources of barriers which will aid to identify and control the barriers with the help of pie chart, bar chart, Pareto diagram along with statistical analysis.

RESULTS AND DISCUSSION

At the first phase of the survey total 14 barriers were supplied to the expert panels, identified from literature review to make a score as per Likert scale ranking system with an additional option to add new barriers whereas additional 8 barriers were found from the experts. From Table 4, it is seen that lack of commitment from top management was identified as the most important barrier. But there is a significant difference of mean value between academic and industrial experts in case of B1 and B13 barriers whereas industrial experts are giving them comparatively less importance than academic experts. We have found extra eight barriers from this study such as Lack of source of eco-friendly materials (B4), Nature of raw materials (B8), Society's awareness on Environment (B12), Interest in investment (B13), Type of footwear manufactured in Bangladesh (B16), Lack of global value chain integration (B17), Buyers outsourcing strategy (B20) and Sea port congestion (B22) as mentioned in Table 4. The industrial experts are demanding sea port congestion (B22) as a barrier to GSCM whereas academic experts are giving it less importance comparatively.

Table 4: Enlisted total 22 barriers with Likert scale scoring from the final round of the study

ID. NO.	Barriers list	Academic Panel Mean (M1)	Industrial panel Mean (M2)	Combined mean	ǀM1-M2ǀ	Grand total score
B1	Lack of commitment from top management	5	4.4	4.7	0.6	47
B2	Financial constraint	4.4	4.6	4.5	0.2	45
B3	Lack of energy management and waste management	4.6	4.4	4.5	0.2	45
B4	Lack of source of eco-friendly materials	4.6	4.4	4.5	0.2	45
B5	Customer interest to buy GSCM sourced goods	4.4	4.2	4.3	0.2	43
B6	Lack of govt. rules and regulations	4.4	4	4.2	0.4	42
B7	Lack of training on GSCM	4.2	4.2	4.2	0	42

B8	Nature of raw materials	4.2	4	4.1	0.2	41
B9	Poor supplier commitment	3.8	4.2	4	0.4	40
B10	Poor organizational culture in implementing GSCM	4.2	3.8	4	0.4	40
B11	Lack of management initiatives for transport and logistics	3.8	4	3.9	0.2	39
B12	Society's awareness on Environment	3.8	4	3.9	0.2	39
B13	Interest in investment	4.2	3.6	3.9	0.6	39
B14	Market competition and uncertainty	3.6	4	3.8	0.4	38
B15	Lack of acceptance of new technology	3.8	3.8	3.8	0	38
B16	Type of footwear manufactured in Bangladesh	3.8	3.8	3.8	0	38
B17	Lack of global value chain integration	3.8	3.6	3.7	0.2	37
B18	Lack of knowledge and experience	3.6	3.6	3.6	0	36
B19	Lack of integration of IT system	3.8	3.4	3.6	0.4	36
B20	Buyers outsourcing strategy	3.6	3.6	3.6	0	36
B21	Lack of availability of skilled human resource	3.4	3.2	3.3	0.2	33
B22	Sea port congestion	2.8	3.8	3.3	1	33

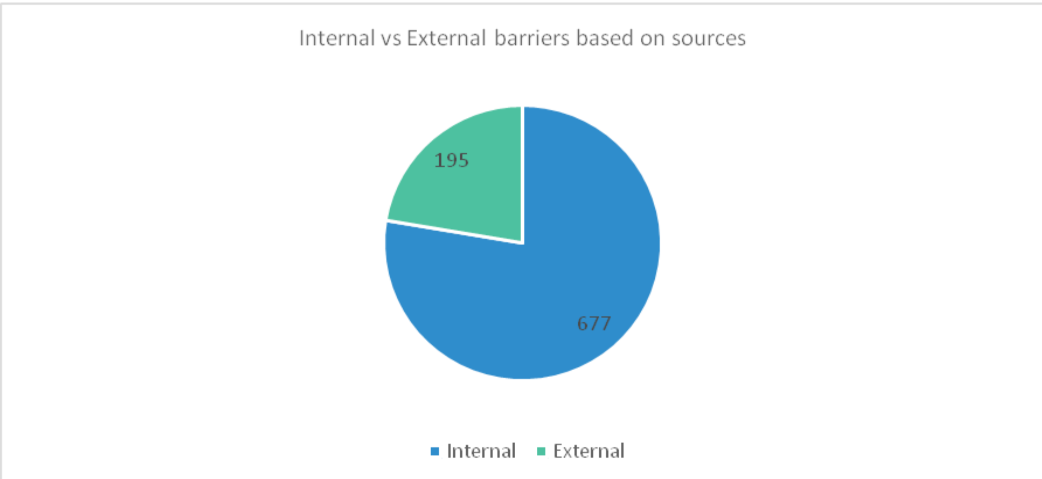

Figure 2. Internal & External barriers score comparison obtained from Likert scale

All barriers were classified as internal and external based on their sources from the supply chain. The barriers which are related directly with the manufacturer and supplier end, were termed as internal barriers and the barriers which are out of control of manufacturer and supplier were termed as external barriers. Total seventeen internal barriers were identified as B1, B2, B3, B4, B7, B8, B9, B10, B11, B13, B15, B16, B17, B18, B19 and B20. On the other hand, B5, B6, B12, B14, B22 were identified as external barriers. So it can be concluded that manufacturer and supplier are mostly responsible for maximum barriers of GSCM.

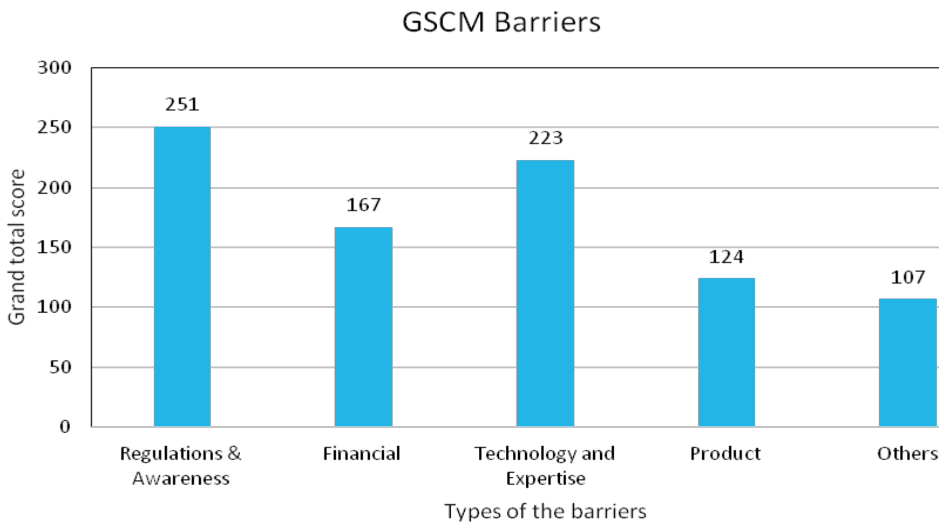

Figure 3. Score of five classified barriers of GSCM based on features

Then total barriers were also classified into five categories based on their features. These are Regulations & Awareness barriers (B1, B5, B6, B9, B10, B12), Financial barriers (B2, B3, B13, B15), Technology and Expertise barriers (B7, B11, B17, B18, B19, B21), Product barriers (B4, B8, B16) and Others (B14, B20, B22). From the Figure 3, it is observed that Regulations and Awareness barriers are the first hindrance to implement GSCM, then Technology and Expertise Barrier, Financial barriers, Product barriers and others respectively. In this research product barrier came to light as a new barrier as it was not found in any previous literature. Footwear is mainly produced from leather and synthetic materials and various chemicals are also involved in manufacturing a pair of footwear. Since these components and chemicals are mostly have a significant environmental impact, it is very necessary to find eco-friendly materials and chemicals.

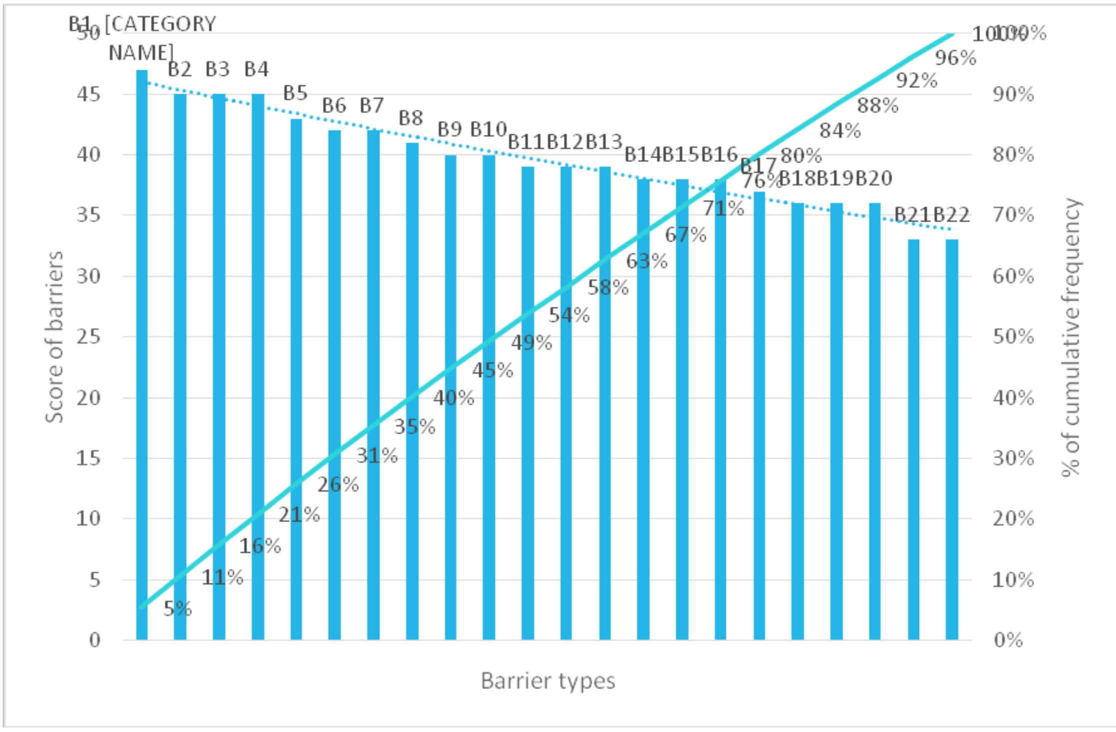

Figure 4. Pareto diagram for barrier (B1 to B22) analysis

In order to find the barriers' contribution to the total impact, Pareto analysis was carried out which is generally known as the 80/20 principle. It is observed from the Figure 4 that there is a straight linear relationship between the cumulative score and first 18 barriers (B1 to B18) were responsible for 80% impact. So it can be summarized that all of the individual barriers have a significant impact towards GSCM.

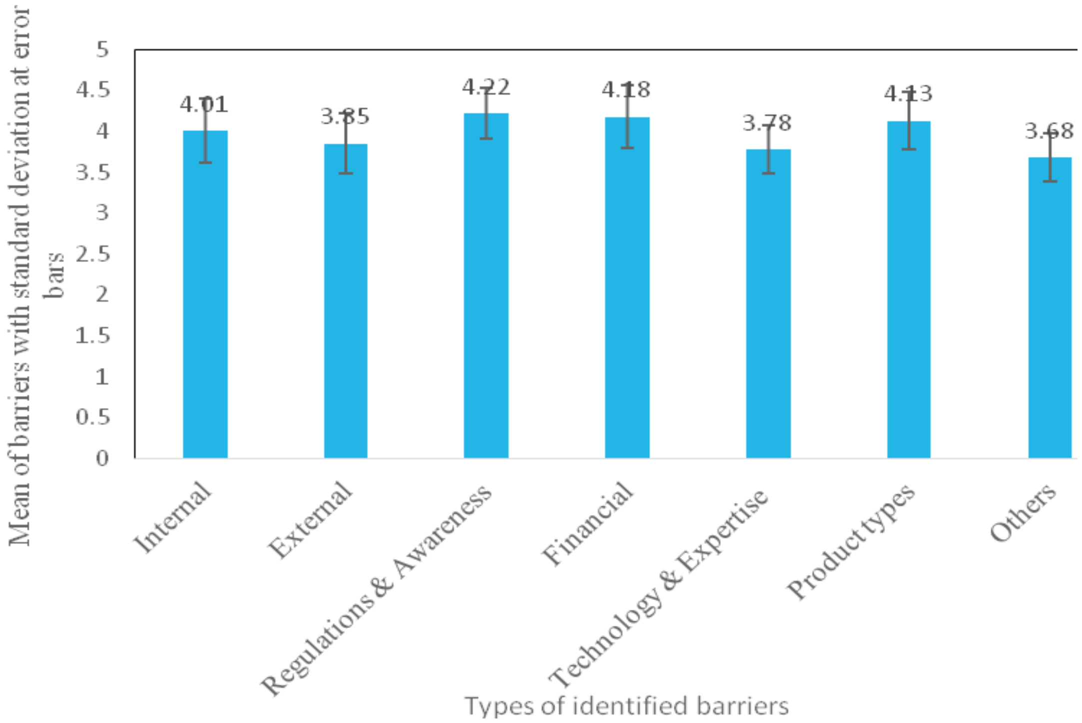

Figure 5. Mean and standard deviation of total classified barriers

Regulations and awareness barriers such as Lack of commitment from top management (B1), Customer interest to buy GSCM sourced goods (B5), Lack of govt. rules and regulations (B6), Poor supplier commitment (B9), Poor organizational culture in implementing GSCM (B10) and Society's awareness on Environment (B12) were identified as the most crucial factors for implementing green supply chain management.

CONCLUSION

It has gained a burning issue to implement GSCM practices to get competitive advantages in export market as well as domestic market for Bangladeshi footwear industry. Top management, monitoring of govt. rules & regulations, raising awareness through green marketing may play a pivotal role in case of GSCM implementation. All of these identified twenty two barriers are not the impediments for all factories. The top management of factories should investigate their present conditions and find out their probable barriers and its effect and relationship towards other barriers. Then applying a PDCA (Plan, Do, Check and Act) cycle, the barriers may be controlled. The relationship among the barriers were not identified in this study which may be investigated in a future study. Since the Delphi study is highly based on the experts' decisions, the results may vary from one to other industrial experts. It would be more effective, if we could manage more experts' opinions. GSCM tools identification and its performance measurement system may be investigated in the future research.

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AN EMPIRICAL ANALYSIS ON EXPORT STATUS QUO AND INTERNATIONAL COMPETITIVENESS OF CHINESE FOOTWEAR PRODUCTS

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AN EMPIRICAL ANALYSIS ON EXPORT STATUS QUO AND INTERNATIONAL COMPETITIVENESS OF CHINESE FOOTWEAR PRODUCTS

ABSTRACT. This paper firstly studies the current status quo from the points of view, such as the export scale, export quantity and trade partners, and then compares and measures the export competitiveness of footwear between China and other major exporting countries by using international market share, trade competitiveness index, revealed comparative & competitive advantage index and product export unit price. The results show that the international market share of China's footwear industry has an absolute advantage, but the growth rate of the international competitiveness index has a sliding trend. The international competitiveness of China's footwear industry faces a certain challenge. The key to improve the international competitiveness of China's footwear industry lies in optimizing the export structure of products, developing diversified markets, paying attention to quality certification and export environmental protection requirements, etc.
KEY WORDS: China's footwear industry, working shoes, international market share, international trade competitiveness, competitive advantage

O ANALIZĂ EMPIRICĂ PRIVIND STATU-QUOUL EXPORTULUI ŞI COMPETITIVITATEA INTERNAŢIONALĂ A ÎNCĂLŢĂMINTEI DIN CHINA

REZUMAT.Acest articol studiază în primul rând statu-quoul actual al exportului, cantitatea de export şi partenerii comerciali, apoi compară şi măsoară competitivitatea exporturilor de încălţăminte din China şi din alte ţări exportatoare majore, utilizând cota de piaţă internaţională, indicele de competitivitate, indicele avantajului competitiv şi comparativ şi un preţ unitar de export al produsului. Rezultatele arată că cota de piaţă internaţională a industriei de încălţăminte din China are un avantaj absolut, însă rata de creştere a indicelui de competitivitate internaţională are o tendinţă de scădere. Competitivitatea internaţională a industriei de încălţăminte din China se confruntă cu o anumită provocare. Cheia pentru îmbunătăţirea competitivităţii internaţionale a industriei de încălţăminte din China constă în optimizarea structurii exportului produselor, dezvoltarea pieţelor diversificate, acordarea atenţiei cerinţelor de calitate şi cerinţelor de protecţie a mediului etc.
CUVINTE CHEIE: industria încălţămintei din China, încălţăminte de lucru, cota de piaţă internaţională, competitivitatea comerţului internaţional, avantaj competitiv

UNE ANALYSE EMPIRIQUE DU STATU QUO D'EXPORTATION ET DE LA COMPÉTITIVITÉ INTERNATIONALE DES CHAUSSURES CHINOISES

RÉSUMÉ. Cet article étudie tout d'abord le statu quo actuel du point de vue des exportations, des quantités exportées et des partenaires commerciaux, puis compare et mesure la compétitivité à l'exportation des chaussures entre la Chine et les autres grands pays exportateurs en utilisant la part du marché international, l'indice de compétitivité, l'indice de l'avantage comparatif et concurrentiel et le prix unitaire à l'exportation des produits. Les résultats montrent que la part du marché international de l'industrie chinoise de la chaussure présente un avantage absolu, mais le taux de croissance de l'indice de compétitivité internationale a tendance à baisser. La compétitivité internationale de l'industrie chinoise de la chaussure est confrontée à un certain défi. La clé de l'amélioration de la compétitivité internationale de l'industrie chinoise de la chaussure réside dans l'optimisation de la structure d'exportation des produits, le développement de marchés diversifiés, l'attention accordée à la certification de qualité et aux exigences de protection environnementale, etc.
MOTS CLÉS : industrie chinoise de la chaussure, chaussures de travail, part du marché international, compétitivité du commerce international, avantage compétitif

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INTRODUCTION

In view of the increasingly fierce competition in global footwear industry, this paper explores the current status of China's footwear products and compares the export competitiveness of these products against those manufactured by other countries. Besides, the author discussed how should China improve the international competitiveness of its footwear products and expand the share in the global market. The research findings will help China maintain its dominance in the footwear industry.

STATUS QUO OF EXPORT OF WORKING SHOES IN CHINA

Scale of the Exports

In 2008, the financial crisis swept the world, China's footwear exports have been deeply affected with the two consecutive years of small decline in exports. The government maintained growth, increased export support and boosted the confidence of export enterprises. Then from 2010 to 2014, the export of footwear increased year by year. China's exports of working shoes rose to $1002 million in 2014 from $428 million in 2009, increased by 1.34.

Table 1: 2008-2016 Export Amount of Footwear in China, US$ million

Year	2008	2009	2010	2011	2012	2013	2014	2015	2016
Exports Value	561.6	428.2	611.1	771.2	784.8	896.2	1002.9	898.3	821.4

From 2015 to 2016, under the influence of weak global economic recovery and lower market demand, there was a consistent negative growth in shoe exports in the world's major footwear exporting countries and China. China's export amount fell to 898 million dollars, and further declined to 821 million dollar in 2016.

Export Quantity

Table 2: 2008-2016 Export Quantity of Footwear in China, Million Pairs

Year	2008	2009	2010	2011	2012	2013	2014	2015	2016
Exports Amount	52.5	18.5	57.1	64.9	63.7	72.1	43.2	34.2	53.6

From 2008 to 2016, the export quantity of Chinese working shoes is huge. There was an uneven trend of first increasing, then declining and then rising again. In 2013, the export quantity of shoes reached the highest of 72.1 million pairs in the history. As can be seen from Table 2, the export of Chinese working shoes experienced two difficult periods. In 2009, the export of footwear products fell to 18.5 million pairs, down by 65% over the same period of 2008. Exports fell to 34.2 million pairs in 2015, down by 21% from the same period in 2014.

Export Partner

The USA, EU, Japan and Russia are the main target markets of China's footwear products. In recent years, in order to maintain the market competitiveness of footwear products, China continuously adjusts its market structure, from European and American countries to emerging ones, like South America and Middle East countries.

Table 3: 2016 Major Export Countries of Chinese Footwear

Export Countries	USA	UK	Chile	Germany	The United Arab Emirates	Italy
Exports (USD million)	175.2	115.8	40.3	32.9	31.3	28.6
Proportion (%)	21	14	5	3.8	3.8	3.5

As can be seen from Table 3, the main countries of China's footwear exports in 2016 were the United States, the UK, Chile, Germany, the United Arab Emirates and Italy, which accounted for 51.7% of China's total footwear exports. The United States, as one of the world's leading consumer goods markets, still has a clear import dependency on China's clothing and footwear, with imports of working shoes reaching US $1.75 million, or 21%, in 2016. EU countries are still the main export countries of China's working shoes. The shares of South America and Middle East countries rose slightly.

RESEARCH METHODS AND SOURCES OF DATA

The data of this paper mainly comes from the United Nations Commodity Trade Statistics Database, the official website of WTO, China Statistics Yearbook and the websites of the Ministry of Commerce and National Bureau of Statistics of the People's Republic of China. Considering the continuity and availability of statistical data and the need of research, this study defines the statistical range of footwear products as "cowhide working shoes" (Commodity specification includes mid-back, cowhide upper, PU sole, without brand and others), HS code is 6403400.90, mainly including mid-back safety shoes, metal head boots, labor protection shoes, cold boots, etc.

ANALYSIS OF INTERNATIONAL COMPETITIVENESS OF CHINA'S WORKING SHOES

According to the data of the United Nations Trade Statistics Database, in recent years, China, India, and Indonesia in Asia, Italy, Germany and France are the main export countries of the world working shoes. This study sorts out the opinions on international competitiveness, collects relevant data, and uses international market share, trade competitiveness index, revealed comparative & competitive advantage index and product export unit price to compare and measure the export competitiveness of footwear products between China and several other major exporting countries. Then, the relevant measures and suggestions to improve the international competitiveness of China's footwear exports are explored.

International Market Share

The international market share is the proportion of an industry or a product's total export to the world's total export. The greater the proportion is, the stronger the international competitiveness of the industry or the product of the country, and vice versa.

Table 4: 2008-2016 International Market Share of Working Shoes Exported from Major Countries in the World, %

Year	China	Italy	Germany	France	Indonesia	India
2008	31.98	19.02	6.95	7.17	3.23	1.29
2009	30.17	22.83	7.08	6.01	2.83	0.61
2010	34.05	19.98	6.38	5.11	3.95	1.65
2011	35.82	18.26	6.10	4.53	3.91	1.39
2012	38.59	17.12	5.74	3.58	4.07	0.89
2013	38.58	15.41	5.24	3.02	3.91	1.74
2014	39.11	14.46	5.14	2.66	3.67	2.52
2015	39.97	14.34	5.28	2.23	3.63	2.36
2016	37.76	15.86	5.48	2.12	4.85	3.64

According to the calculation, the total market share of China, Italy, Germany, France, Indonesia and India reached 69.71% in 2016, which was 2/3 of the global export of working shoes. From 2010 to 2016, China's international market share of working shoes has always been ranked first in the world with its annual average share of 38.70%, and international competitiveness is the strongest. This is mainly due to the fact that as a large producer of light industrial products, China has formed a complete industrial chain in the fields of R&D and design, material development, technical application, and production and processing. Each link has reached a relatively high level of proficiency, and formed relatively high overall production efficiency. With a large export scale, it far exceeds other countries. In the next few years, China's export of working shoes will continue to maintain its large market share.

At the same time, the market share of footwear design and production in the older countries such as Italy, Germany and France tends to decline, and France had the largest decline and plummeted from 7.17% in 2010 to 2.12% in 2016. The Southeast Asian countries (Indonesia and India) benefit from the global shoe-making pattern shift, the shoe-making industry has obtained the unprecedented development and grabbed the low-grade market that originally belongs to China, and their market share presents the obvious rising trend, reducing the gap with China and becoming China's potential competitors.

Trade Competitiveness Index

The trade competitiveness index (TC index) is the ratio of the difference between the import and export trade of an industry or a product in a country to its total import and export trade, which reflects the competitive advantage and disadvantage of a certain kind of product or industry in a country relative to the same product in other countries on the world market.

Table 5: 2008-2016 Export Competitiveness Index of Working Shoes in Major Countries of the World

Year	China	Italy	Germany	France	Indonesia	India
2008	1	0.19	-0.26	-0.16	0.92	0.95
2009	1	0.20	-0.23	-0.23	0.89	0.91
2010	1	0.14	-0.28	-0.28	0.72	0.97
2011	1	0.13	-0.26	-0.27	0.65	0.96
2012	1	0.18	-0.23	-0.26	0.58	0.94
2013	1	0.20	-0.23	-0.30	0.61	0.96
2014	1	0.18	-0.19	-0.37	0.64	0.98
2015	0.99	0.26	-0.19	-0.38	0.58	0.98
2016	0.99	0.27	-0.17	-0.44	0.69	0.98

The policies of encouraging exports and restricting imports are prevalent in the non-developed countries, so that the trade competitiveness index cannot accurately reflect the international competitiveness of products. It can be seen from Table 5 that Asian countries (China, Indonesia and India) are all performing well, China and India have stable export scale, their trade competitiveness indexes approached or maintained at 1 over the years, and their export of footwear products has a pattern of output-type vertical division of labor, with very small import proportion, the strongest international export competitiveness, and very obvious competitive advantage. The trade competitiveness indexes of the two countries are similar, with a strong competitive relationship. The value of Indonesia's trade competitiveness index of working shoes, shows that Indonesia's export of working shoe has been recognized by the global market and has a strong international competitiveness.

In European countries, Italy's trade competitiveness index hovers between 0.13 and 0.27, which rises slowly, and its shoe production efficiency is higher than the international level, indicating a competitive advantage in the world. The TC index of Germany and France is negative, indicating that the production efficiency of this kind of shoes in two countries is lower than the international level, and the import of working shoes is higher than the export, showing a pattern of input vertical division of labor.

Revealed Comparative Advantage

The Revealed Comparative Advantage Index (RCA), proposed by Balassa (1965), refers to the export-relative performance index, which excludes the influence of the fluctuation of national total export and the fluctuation of global total export, and can better reflect the relative advantages of a country's export of an industry compared with the world's average export level.

Table 6: 2008-2016 Revealed comparative advantage index of export of working shoes from major countries in the world

Year	China	Italy	Germany	France	Indonesia	India
2008	3.50	5.49	0.74	1.89	3.69	1.14
2009	3.07	6.87	0.77	1.58	2.97	0.41
2010	3.24	6.51	0.75	1.50	3.76	1.13
2011	3.89	7.19	0.74	1.39	3.45	0.83
2012	3.38	6.13	0.73	1.15	3.85	0.55
2013	3.25	5.53	0.68	0.99	3.99	0.96
2014	3.09	5.05	0.63	0.87	3.86	1.47
2015	2.84	5.06	0.64	0.73	3.89	1.44
2016	2.77	5.29	0.63	0.67	5.17	2.15

Italy is a tradidional shoe making country with a high level of exports. With its superb leather-making technology, improved design, perfect hand-making skills and the combination of comfort and beauty, Italian shoes have always been popular among consumers, and thus Italy firmly controls the high-grade market of the global footwear industry. As can be seen from Table 6, Italy's revealed comparative advantage has been maintained above 5, and its overall position of superiority is unshakable. Indonesia, in second place, showed a steady and upward trend, with a leap-forward growth to 5.17 in 2016, and only 0.08 points lower than Italy. In contrast, China's revealed comparative advantage index as a whole shows a slow downward trend, in 2011 and with fluctuations, falling to 2.77 in 2016, which shows that China's comparative advantage was obvious and competitive in the early stage, but not optimistic in the next few years.

Comparative Advantage Index

The CA index evolved from the RCA index. Taking into account the import factors, it subtracts the import comparative advantage from the export comparative advantage of the industry, and to some extent, makes up for the deficiency of the trade competitiveness index and the revealed comparative advantage index, making the measurement of international competitiveness more realistic. When the CA index ≥ 0, the product has the revealed competitive advantage, the larger the value is, the more obvious the advantage is. If the CA index < 0, the product does not have the revealed competitive advantage, the smaller the value is, the more obvious the competitive disadvantage is.

Table 7: 2008-2016 Revealed competitive advantage index of export of working shoes from major countries in the world

Year	China	Italy	Germany	France	Indonesia	India
2008	3.49	2.38	-0.57	-0.01	3.54	1.13
2009	3.07	2.85	-0.53	-0.35	2.79	0.4
2010	3.24	4.31	0.01	0.43	3.43	1.12
2011	3.39	2.96	-0.64	-0.46	2.68	0.82
2012	3.38	2.26	-0.55	-0.32	1.95	0.54
2013	3.24	1.79	-0.55	-0.46	3.09	0.95
2014	3.08	1.46	-0.55	-0.59	3.09	1.46
2015	2.82	2.09	-0.43	-0.56	2.90	1.43
2016	2.75	2.09	-0.41	-0.93	4.23	2.14

As can be seen from the table, Germany and France's CA index is less than 0, which indicates a weak competitive advantage. France's CA index fell to -0.93 in 2016, the lowest in years. The revealed competitive advantage indexes of the other four countries are positive, indicating that the footwear exports of China, Italy, Indonesia, India and other countries have significant competitiveness and competitive advantages, but there are great differences in the values, with fluctuations. China's CA index is basically the same as the RCA index, indicating that the import of working shoes is basically negligible and has little impact on exports.

From the development trend of the revealed comparative advantage, Italy and China as a whole show a declining trend, and its revealed competitive advantage weakens and international competitiveness declined. Indonesia and India, on the other hand, show a marked upward trend after the fall, and Indonesia is the most prominent, with the fall ending abruptly in 2015 and rising suddenly to 4.23 in 2016, showing a strong competitive momentum.

Comparison of Unit Price of Working Shoes for the Export

Price is one of the important factors reflecting the international competitiveness of products.

Table 8: 2008-2016 Unit price of working shoes for the export from major countries of the world

Year	China	Italy	Germany	France	Indonesia	India
2008	10.70	25.00	22.76	30.12	22.76	13.13
2009	23.15	24.93	23.15	30.28	23.15	13.34
2010	10.70	24.70	26.82	28.68	26.82	26.82
2011	11.88	27.53	26.79	26.79	26.79	14.52
2012	12.33	26.11	23.93	30.24	23.93	13.48
2013	12.43	28.04	23.93	30.66	23.93	14.95
2014	23.21	29.17	23.21	26.86	23.21	16.24
2015	26.24	25.27	26.24	16.13	42.67	14.16
2016	15.32	25.89	15.31	17.01	15.33	15.21
Unit Price	15.32	26.29	23.57	26.31	25.40	15.78

In 2016, under the recession of international demand market, the export quantity of working shoes in several major export countries has been increased against the falling trend, which shows that the global demand for working shoes still has a certain space; but with the exception of Italy, the unit price of shoes consistently and dramatically fell.

Through calculation and comparison, it is known that the average price of China's working shoes for export has been at a low level for a long time, and the average export unit price ($15.32) over the years has not only been lower than the world average level, but also lower than that of Indonesia ($25.40), and only slightly higher than that of India ($15.78). On the one hand, it shows that China's shoe-making export enterprises continue to enjoy the traditional industrial advantages and labor advantages, and greatly increased the comparative advantages of the middle- and low-grade products of working shoes through large-scale production, cost reduction and other ways; on the other hand, it also shows that China's footwear products are low in added value and still rely on "low grade, low quality, and low price" to penetrate the international market.

CONCLUSION AND SUGGESTIONS

After more than 20 years of developments, China's footwear exports have reached about 65% the world's total shoe exports, and thus China has become the world's largest producer and exporter, mainly targeting markets such as the United States, the European Union, Russia and Japan. However, in recent years, with the appreciation of exchange rate and the rigid increase of essential productive factors (like labor & material cost) as well as the unshakable dominance of Italy and other exporters, Southeast Asian competitors are gradually rising, the international competitiveness of China's footwear industry has been challenged, so that China maintains its competitive advantage.

Optimize the Product Structure, and Increase the Added Value of Products

In the course of many years' development, China's shoe-making industry has formed a perfect industrial chain. In the international market, China obtained more than 1/3 share of the international market share by the way of "low price". Its export quantity accounts for 65% of the world, and the space for the promotion of its share is limited. The export footwear products are mainly middle- and low-grade products, with low price and low profits. In the development process of Chinese shoe-making and export enterprises, under the premise of keeping the steady quantity and amount of exports, we should vigorously carry out technological innovation, pay attention to the inherent quality of the products and the fashion, function and environmental protection of the products, optimize the product structure, and improve the added value of products. Towards quality orientation instead of quantity orientation, the proportion of middle- and low-grade products should be reduced to improve the comprehensive international competitiveness of products.

Actively Adjust the Market Structure and Open up Diversified Markets

With lower prices and good quality, China's footwear products are mainly exported to the United States, the European Union, Russia and other export destination countries, and have a steadily rising market share. China has a deep market overlapping with several other major export countries, which intensifies the competition.

Therefore, while consolidating the original markets, it is imperative to seek and exploit the emerging markets and further promote the diversified market share. The Belt & Road spans 65 countries and regions on the three continents of Asia, Europe and Africa, forming a closed onshore and offshore economic loop. The countries along the line have a large population, totally about 4.5 billion, and their total economic output accounts for over 50% of global economic output. They have a broad market prospect and strong demands for China's light industrial products. With the help of the strategic opportunity of the Belt & Road, the Chinese shoe-making and shoe exporting enterprises study the demands for shoe products along this line, divide the key markets, base themselves on the advantages of overseas regions, expand the radiation circle, form a market development pattern with multi-support, and get rid of the difficulties of being restrained by the European and American markets.

Pay Attention to Quality Certification and Export Environmental Protection Requirements

In recent years, trade protectionism prevails in European and American countries, which construct technical barriers to strictly control and test raw materials and possible harmful substances produced in the production process. China's footwear exports have become a high-risk area of trade friction, and exports are seriously hindered. Following the EU countries, China's other main export markets, such as Saudi Arabia in the Middle East, implement market access system for China's imported footwear products without certificates, which makes the goods refused to enter after being shipped to the port of entry. Chinese shoe-making and shoe export enterprises must actively understand and study the environmental standards, certification standards, and project testing of importing countries, increase investment in environmental protection, standardize their own business behavior, comply with industry rules, and apply to authorities for certification of various environmental protection labels to obtain market passes, so as to have a foothold in the international market.

Implement the "Brand-oriented" Strategy

After the transfer of the early world shoe-making center to Korea, Japan and Taiwan, Italy carried out the strategy of "quality orientation instead of quantity orientation" for product upgrading and brand building. Italian shoes become the symbol of high-grade which dominate the world market. It is difficult to take a long way by copying others' design and having low-price competition. Chinese enterprises must fully realize that establishing the brand recognized by the international market is the only way for the long-term development of the enterprises and the only way to maintain and improve the international competitiveness of Chinese footwear products. Implementing "brand-oriented", that enterprise studies the main market of product sales pertinently, accurately defines the attributes, culture, consumers and other factors of the brand to be promoted, and makes good design and manufacture of the products, so as to be approved by the consumers.

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PRACTICES ON ECOLOGICAL CHROMIUM TANNING SYSTEM

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PRACTICES ON ECOLOGICAL CHROMIUM TANNING SYSTEM

ABSTRACT. Chromium tanning using less chromium salts at higher initial pH values is one of the approaches offered in recent years in order to overcome environmental problems caused by conventional chromium tanning. However this system couldn't be directly switched to application due to its potential risks. In the present study this ecological approach was investigated at industrial scale. The variables used in the research were: pre-tanning agents, initial pH of tanning and tanning agents. Various wet-end and finishing processes depending on three different types of products were applied according to the company's production line. Chromium contents of the leathers and remaining amounts in effluents were determined for each trial. Also, the physical properties of the leathers were investigated. Along with maintaining similar properties and quality from the produced leathers, chromium remaining in residual baths could be reduced up to 92 and 76% by alternative formulations respectively in 500 kg and 6000 kg batches.
KEY WORDS: leather, chromium tannage, high exhaustion

PRACTICI PRIVIND SISTEMUL DE TĂBĂCIRE ECOLOGICĂ ÎN CROM

REZUMAT. Tăbăcirea în crom care utilizează mai puţine săruri de crom la valori iniţiale mai ridicate ale pH-ului este una din abordările apărute în ultimii ani pentru a rezolva problemele de mediu cauzate de tăbăcirea convenţională în crom. Cu toate acestea, acest sistem nu a putut fi pus în aplicare în mod direct din cauza potenţialelor riscuri. În studiul de faţă această abordare ecologică a fost investigată la scară industrială. Variabilele utilizate în cercetare au fost: agenţi de pre-tăbăcire, pH iniţial al tăbăcirii şi agenţilor de tăbăcire. Au fost aplicate diferite procedee umede şi finisaje în funcţie de trei tipuri diferite de produse, conform liniei de producţie a companiei. Conţinutul de crom din piele şi cantităţile rămase în efluenţi au fost determinate pentru fiecare încercare. De asemenea, au fost investigate proprietăţile fizice ale pielii. Pe lângă menţinerea unor proprietăţi şi a calităţii pielii fabricate, cromul rămas în flotele reziduale ar putea fi redus până la 92 şi 76% prin recepturi alternative, în loturi de 500 kg, respectiv de 6000 kg.
CUVINTE CHEIE: piele, tăbăcire în crom, epuizare mare

PRATIQUES SUR LE SYSTÈME DE TANNAGE ÉCOLOGIQUE AU CHROME

RÉSUMÉ. Le tannage au chrome utilisant moins de sels de chrome à des pH initiaux plus élevés, est l'une des approches proposées ces dernières années pour surmonter les problèmes environnementaux causés par le tannage au chrome conventionnel. Cependant, ce système ne pouvait pas être directement transféré à l'application en raison de ses risques potentiels. Dans la présente étude, cette approche écologique a été étudiée à l'échelle industrielle. Les variables utilisées dans la recherche étaient: agents de prétannage, pH initial du tannage et des agents de tannage. Différents procédés par voie humide et de finition ont été appliqués avec trois types de produits différents, en fonction de la chaîne de production de l'entreprise. Les teneurs en chrome des cuirs et les quantités restantes dans les effluents ont été déterminées pour chaque essai. De plus, les propriétés physiques des cuirs ont été étudiées. En plus de maintenir les propriétés et une qualité similaires des cuirs produits, le chrome restant dans les bains résiduels pourrait être réduit jusqu'à 92 et 76% par des formulations alternatives en lots de 500 kg et respectivement 6 000 kg.
MOTS CLÉS : cuir, tannage au chrome, épuisement de bain élevé

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INTRODUCTION

As the hides/skins are protein based, they are putrescible by bacterial activity in wet-form until tanning process. The tanning process is the stabilization of the collagen matrix to retain a separated fiber structure and to increase the hydrothermal stability. This is the stage at which the pelt becomes "leather" and is then resistant to putrefaction or rotting. Organic or inorganic based materials which are able to crosslink with reactive groups of the collagen are used in the tanning process [1].

Modern tanning chemistry can be classified by mineral tanning, vegetable tanning, oil tanning, aldehyde tanning, syntans, and organic tanning. Chrome, among mineral tanning materials is the most widely used tanning material in leather production due to its unique features that it gives to the leather. Chrome tanning provides better leather characteristics than other tanning materials such as high thermal stability, light weight and high strength properties [2].

Conventional chromium tanning process which is used for approx. 80% of produced leathers consists of three main steps namely pickling, tanning, and basification. Pickling is being performed along with brine solutions and acids and tanning is being carried out by using 8-10% of basic chromium sulphate over pelt weight. Then, in basification step reactivity of chromium is increased and fixation is achieved by introduction of alkali salts. Since whole of the chromium used in process cannot be exhausted, approx. 1/3-1/4 of it (1500–5500 mg/L) remains in bath at the end of the process [3-5]. So, the conventional chrome tanning method is associated with large release of chromium content in the effluent [6].

Although the methods of recycling chrome are well known and applied, pollution related to chrome continues to be one of the most important problems in leather industry [7, 8].

Chromium compounds are among dangerous wastes, and they have several harmful impacts on soil, water and living beings due to their toxic effects. For example, Cr(III) content between 10-100 ppm in soil affects the microorganism population and reduces CO_2 formation, therefore it affects the biological reactions in soil in the negative way. Wastewaters that include chrome reduce the efficiency of the soil when discharged to agricultural land, and prevent the growth of the plants in these lands [9].

Treatment, storage and disposal of this chromium containing effluents and sludge pose a major challenge. There are various approaches i.e. ameliorating the parameters of chrome tanning, modifying chrome tanning agents or the collagen and using auxiliary agents and/or combination tanning agents towards preventing these technical and environmental problems caused by conventional chromium tanning [10-14]. Among these alternatives, higher exhausting chromium tanning technology applied at higher initial pH values without pickling by lower chromium offer has been a promising one in recent years.

However this technology is not directly switched to application in the industry due to potential risks like incomplete penetration and precipitation of chromium on the leather surface due to high initial pH values and possible quality variations in the final products. In the present research adopting of higher exhausting ecological chromium technology instead of existing conventional chromium tanning is investigated in laboratory, pilot and industrial scales at a leading company in Turkish leather industry by designing various experiments to optimize the process and to maintain similar properties and quality from the produced leathers.

EXPERIMENTAL

Materials and Methods

Lime split domestic (bovine hides from Ankara region) pelts (to be approx. 50 kg per each trial) which were conventionally processed were used as material. They were delimed and bated according to company's production route. As blank, the first trial was performed according to company's conventional chromium tanning system with pickling. Other trials were performed without pickling and the necessary pH values depending on the pre-tanning agents were adjusted by using non-swelling acids. An aldehyde, a sulphonylchloride and a highly reactive syntan which are available in the market were selected to be used as pre-tanning agents. After pre-tanning stage, the pH of the pelts were adjusted to 5-5.5 and 6-6.5 respectively and for each pH value chromium tanning was performed independently by using 5% standard basic chromium sulphate and 6% of a commercial chromium tanning agent having lower basicity and Cr_2O_3. The trial scheme is given in Fig. 1.

In residual tanning baths total chromium and COD values were determined according to SM 3120 B and SM 5220 standard methods [15, 16]. After tanning, wet-end processes were carried out in one batch according to company's standard upper leather production route.

Cr_2O_3 contents [17], shrinkage temperatures [18], tensile strengths and percentage extensions [19], resistance to grain cracking and grain crack indexes [20] and tear loads [21] of the produced leathers were determined according to related standards.

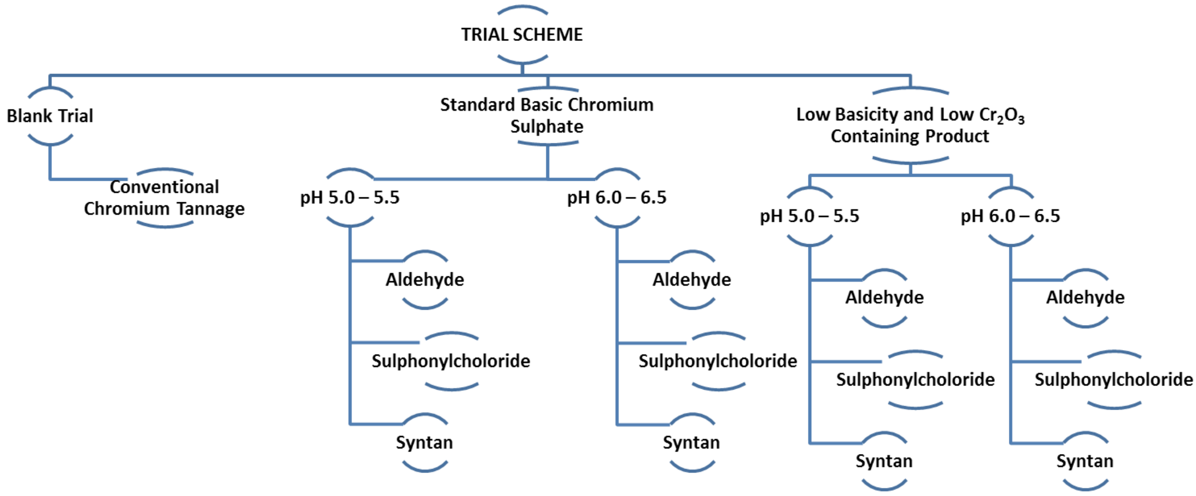

Figure 1. Trial scheme

RESULTS AND DISCUSSIONS

Cr_2O_3 contents of the leathers and COD values and amount of chromium remaining in residual baths are given in Table 1.

Considering the values given in the table it is seen that 4142 mg/L chromium remains in residual bath in conventional chromium tanning system which dramatically decreases to varying values between 16.9-1347 mg/L in chromium tanning trials at high initial pH values without pickling. In this new ecological tanning system amount of chromium remaining in residual baths can be reduced up to 67.5 % to 99.5% comparing to conventional tanning while 3.12-4.83% of Cr_2O_3 bound to the leathers depending on the type of system used in trials as presented in Fig. 2.

The key to this system lies in the reaction with the collagen polypeptide chain. By introducing additional anionic groups, the iso-electric point (IEP) is effectively shifted from conventional IEP of collagen. This shift in IEP of the polypeptide chain enables faster chromium penetration during tannage at pH 4.5-6.0 than conventional tanning at a pH of 3.0. The chrome fixation is also improved due to the increased number of non-ionised carboxyl groups in collagen [3].

From the evaluation and comparison of the physical test results of the leather samples produced higher exhausting technologies with conventional produced leather samples it was seen that most of the physical properties were found comparable with a few exceptions (Table 2).

Table 1: Residual bath and leather parameters of tanning trials

pH	Trials	Leather Parameters			Residual Bath	
		Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Cr (mg/L)	COD (mg/L)
-	Conventional Cr tanning	Homogenous	1.34	3.97	4142	7440
6.0-6.5	LowBasicity&Cr_2O_3 (LBCr)	Not Homogenous	1.54	3.28	125	4480
6.0-6.5	Cr_ Aldehyde	Not Homogenous	1.41	4.65	16.9	11400
6.0-6.5	Cr_ Sulphonylchloryde	Not Homogenous	1.55	4.09	64.3	7840
6.0-6.5	Cr_ Syntan-1(F90)	Homogenous	1.66	3.18	536	7800
6.0-6.5	LBCr_ Aldehyde	Not Homogenous	1.46	4.17	88.9	8800
6.0-6.5	LBCr_Sulphonylchloryde	Homogenous	1.41	4.02	219.2	51200
6.0-6.5	LBCr_Syntan-1(F90)	Homogenous	1.51	3.38	81.3	4000
5.0-5.5	Cr_ Aldehyde	Not Homogenous	1.56	4.37	217.8	760
5.0-5.5	Cr_ Sulphonylchloryde	Not Homogenous	1.56	4.83	109.7	3200
5.0-5.5	Cr_ Syntan-1(F90)	Not Homogenous	1.51	3.98	661.2	280
5.0-5.5	LBCr_Aldehyde	Homogenous	1.51	3.96	629	6560
5.0-5.5	LBCr_Sulphonylchloryde	Not Homogenous	1.43	3.16	340.5	760
5.0-5.5	LBCr_Syntan-1(F90)	Homogenous	1.65	3.12	1347	8320

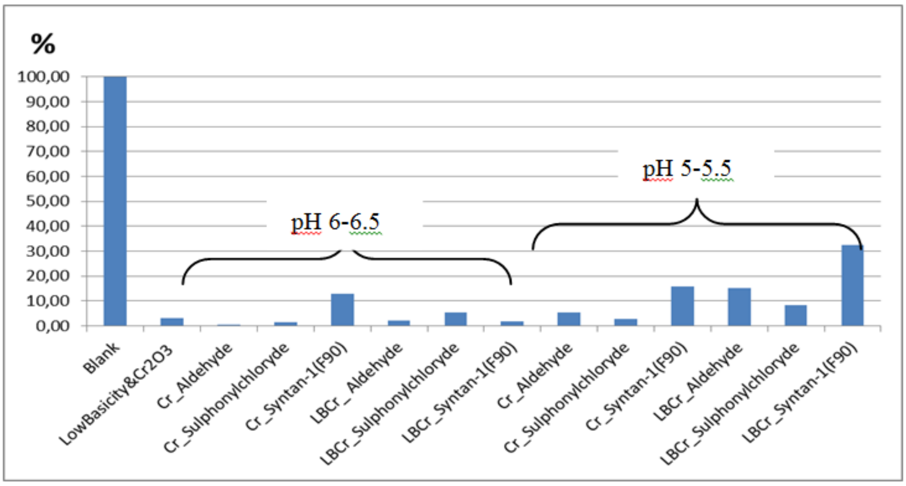

Figure 2. Comparison of mg/L chromium in residual baths

Table 2: Physical properties of the final leather products

pH	Trials	Leather Parameters					
		Ts (°C)	Tensile Strength (N/mm^2)	Elongation (%)	Lastometer (kg)	Lastometer mm	Double Edge Tear (N/mm)
-	Conventional Cr tanning	119	18.4	46.1	18.6	7.37	74.18
6.0-6.5	LowBasicity&Cr_2O_3 (LBCr)	112	20.1	60.1	16.4	6.65	113.85
6.0-6.5	Cr_Aldehyde	118	12.9	40.8	19.7	7.42	65.21
6.0-6.5	Cr_Sulphonylchloryde	120	16.7	63.9	15.0	6.51	105.70
6.0-6.5	Cr_Syntan-1(F90)	115	14.4	46.0	21.9	7.61	91.43
6.0-6.5	LBCr_ Aldehyde	115	17.7	59.2	20.4	6.68	95.40
6.0-6.5	LBCr_Sulphonylchloryde	119	15.2	53.2	20.2	7.94	79.99
6.0-6.5	LBCr_Syntan-1(F90)	119	17.4	50.5	21.5	7.27	108.56
5.0-5.5	Cr_Aldehyde	119	10.1	46.6	15.8	7.10	70.45

5.0-5.5	Cr_Sulphonylchloryde	115	17.6	56.3	25.8	9.08	111.15
5.0-5.5	Cr_Syntan-1(F90)	121	16.2	56.2	20.8	7.10	113.55
5.0-5.5	LBCr_Aldehyde	118	15.4	57.9	21.4	7.54	80.72
5.0-5.5	LBCr_Sulphonylchloryde	119	12.7	68.7	25.8	8.37	64.92
5.0-5.5	LBCr_Syntan-1(F90)	119	13.5	61.1	23.1	7.52	84.77

Besides consideration and evaluation of chemical and physical data obtained from the analysis and tests, a committee comprising members from production supervisors, quality control and marketing departments of the company, made evaluations considering their existing product properties in terms of handle, touch and physical appearance and costumer demands. From the final evaluations considering both physical and chemical data and committee's remarks it was concluded that best results were obtained from Cr_Aldehyde, Cr_Sulphonylchloryde, Cr_Syntan-1(F90), LBCr_Syntan-1(F90) trials conducted at pH 5-5.5 and decided to make further studies to improve and verify these process designs in higher batches at pH 5.5-6.0. Additionally the committee offered to include two more synthetic tannins ((Syntan-2(HS) and Syntan-3(CAT)) to the trials considering the promising results of Syntan-1(F90).

The verification trials were conducted with 500kg of batches of pelts to simulate industrial scale production.

Table 3. Residual bath and leather parameters of verification trials

pH	Trials	Leather Parameters Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Residual Bath Cr (mg/L)	COD (mg/L)
-	Conventional Cr tanning	Homogenous	1.25	4.07	4142	15000
5.5-6.0	Cr_ Aldehyde	Homogenous	1.65	4.50	325	4800
5.5-6.0	Cr_ Sulphonylchloryde	Homogenous	1.61	4.70	383	5200
5.5-6.0	Cr_ Syntan-1(F90)	Homogenous	1.62	4.10	520	6880
5.5-6.0	Cr_ Syntan-2(HS)	Homogenous	1.53	3.40	875	11500
5.5-6.0	Cr_ Syntan-3(CAT)	Homogenous	1.57	4.10	400	8400
5.5-6.0	LBCr_Syntan-1(F90)	Homogenous	1.53	2.90	405	8006

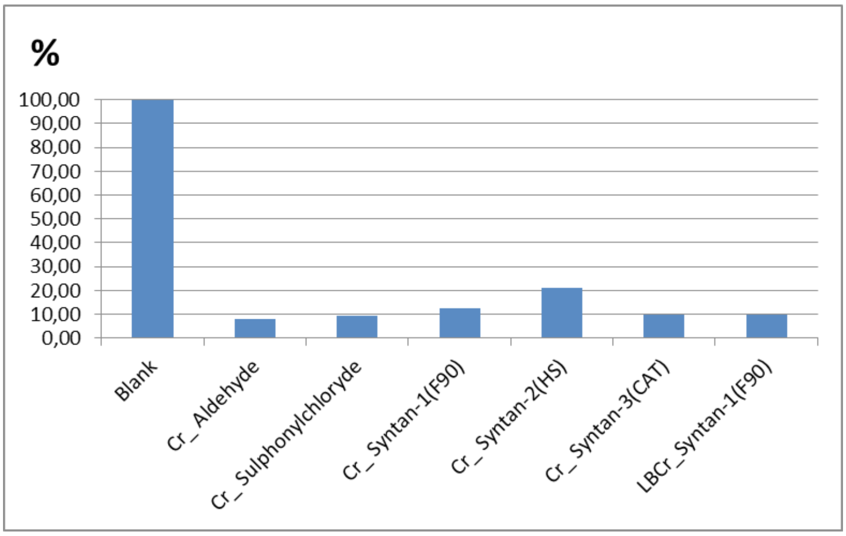

Figure 3. Comparison of mg/L chromium in residual baths of verification trials

In verification trials it was seen that chromium remaining baths were varying between 325-875 mg/L (Table 3), which means the amount of chromium remaining in residual baths could be reduced up to 78.87% to 92.15% comparing to conventional tanning while 2.9-4.7% of Cr_2O_3 bound to the leathers depending on the type of system used in verification trials as presented in Fig. 3.

Table 4: Physical properties of the final leather products of verification trials

pH	Trials	Leather Parameters Ts (°C)	Tensile Strength (N/mm²)	Elongation (%)	Double Edge Tear (N/mm)
-	Conventional Cr tanning	110	11.9	51.6	46.0
5.5-6.0	Cr_Aldehyde	124	13.9	50.3	108.4
5.5-6.0	Cr_Sulphonylchloryde	118	15.2	45.8	95.9
5.5-6.0	Cr_ Syntan-1(F90)	121	18.4	50.2	111.5
5.5-6.0	Cr_ Syntan-2(HS)	108	12.3	45.2	77.3
5.5-6.0	Cr_ Syntan-3(CAT)	101	15.5	45.3	100.0
5.5-6.0	LBCr_Syntan-1(F90)	109	20.5	50.9	119.4

From the evaluation and comparison of the physical test results of the verification trials' leather samples with conventional produced leather samples it was seen that most of the physical properties were found better or comparable but a few exceptions in shrinkage temperature (Table 4).

Besides consideration and evaluation of chemical and physical data obtained from the analysis and tests, the evaluation committee of the company, re-made evaluations and concluded to make industrial scale (6 tons of hide) trials with Cr_ Syntan-1(F90) and Cr_ Syntan-2(HS).

Table 5: Residual bath and leather parameters of industrial trials

pH	Trials	Leather Parameters Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Residual Bath Cr (mg/L)	COD (mg/L)
5.5-6.0	Cr_ Syntan-1(F90)	Homogenous	1.01	4.65	1750	7400
5.5-6.0	Cr_ Syntan-2(HS)	Homogenous	1.11	3.60	1000	8500

In industrial trials chromium remaining baths were found to be 1750 and 1000 mg/L (Table 5) for Cr_ Syntan-1(F90) and Cr_ Syntan-2(HS) respectively. Which means amount of chromium remaining in residual baths could be reduced 57.75 and 75.86% comparing to conventional tanning and 4.65 and 3.60% of Cr_2O_3 were bound to the leathers.

Table 6: Physical properties of the final leather products of industrial trials

pH	Trials	Leather Parameters Ts (°C)	Tensile Strength (N/mm²)	Elongation (%)	Double Edge Tear (N/mm)
5.5-6.0	Cr_ Syntan-1(F90)	110	10.3	37.6	38.2
5.5-6.0	Cr_ Syntan-2(HS)	103	9.6	30.1	27.8

The physical test results of the verification trials' leather samples are given in Table 6. Although some of the physical test results of the leathers seem to be slightly lower comparing with conventional produced leather samples, taking in consideration the product type chosen to be produced, organoleptic controls and fulfillment of customer desires, the committee concluded that the results were satisfactory.

CONCLUSIONS

In leather production the chrome tanning method is the most widely used tanning system all over the world despite the storage and disposal of solid wastes and sludge containing high amounts of chromium poses a major challenge. For this reason many researches based on higher exhausting and lower chromium used technologies have emerged in the recent past. However, these technologies are not directly accepted by the industry due to risks and some possible changes in quality issues. Accordingly, in the present project one of these approaches: chromium tanning without pickling process, using less chromium salts at higher initial pH is tried in industrial scale at a leading company in Turkish leather industry.

The theory was applied at laboratory, pilot and finally industrial scale with various tanning parameters like different initial pH values and pre-tanning materials. Chromium content of the leathers and the Cr_2O_3 remaining in effluents were determined for each tanning application. Also, the physical properties of the leathers were investigated. The amount of chromium remaining in residual baths could be reduced up to 99.5%, 92.15% and 75.86% in laboratory, pilot and industrial scale productions, respectively comparing to conventional tanning with satisfactory chromium contents and leather properties.

Along with decreasing the amount of residual chromium, this approach also offers the benefits of considerable decrease in load of treatment plant associated with noticeable decreases in chromium and salt in effluents, reducing treatment costs and potential utilization of sludge i.e. as compost.

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BIOCOMPOSITES FROM TANNED LEATHER FIBRES WITH APPLICATIONS IN CONSTRUCTIONS

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BIOCOMPOSITES FROM TANNED LEATHER FIBRES WITH APPLICATIONS IN CONSTRUCTIONS

ABSTRACT. In tanneries, only approx. one-third of the total mass of raw hides and skins is converted to finished leather, while two-thirds become either dissolved or solid waste. As part of the natural materials category, usually considered waste, leather fibers introduced into cement mortar panels play a fundamental role in construction due to both insulation properties and mechanical strength. Waste is introduced as a powder or filler or as aggregates in the concrete mix, with energy, economic and environmental benefits. The originality and innovative contribution of the scientific paper consists in re-evaluation of tanned leather waste from the leather sector by turning them into raw materials with added value and using them in construction materials industry, by developing new production concepts for new biocomposite materials.
KEY WORDS: tanned leather fibres, biocomposites, Portland cement

BIOCOMPOZITE DIN FIBRE DE PIELE TĂBĂCITĂ CU APLICAŢII ÎN CONSTRUCŢII

REZUMAT. În tăbăcării, doar cca. o treime din masa totală a pieilor brute de animale mari şi mici este transformată în piele finită, în timp ce două treimi devin fie deşeuri dizolvate, fie solide. Făcând parte din categoria materialelor naturale, considerate de obicei deşeuri, fibrele de piei introduse în panouri din mortar de ciment, joacă un rol fundamental în construcţii datorită atât proprietăţilor de izolare, cât şi de rezistenţă mecanică. Deşeurile sunt introduse ca pulbere sau umplutură sau ca agregate în amestecul de beton, avand avantaje din punct de vedere energetic, economic şi de protecţie a mediului. Originalitatea şi contribuţia inovatoare a lucrării ştiinţifice constă în reevaluarea deşeurilor din piele tăbăcită din sectorul de pielărie prin transformarea acestora în materii prime cu valoare adăugată şi prin utilizarea în industria materialelor de construcţie prin dezvoltarea unor noi concepte de producţie pentru materiale biocompozite noi.
CUVINTE CHEIE: fibre de piele tăbăcită, biocompozite, ciment Portland

BIOCOMPOSITES DE FIBRES DE CUIR AVEC APPLICATIONS DANS L'INDUSTRIE DE LA CONSTRUCTION

RÉSUMÉ. Dans les tanneries, seulement env. un tiers de la masse totale des peaux bruts est converti en cuir fini, tandis que deux tiers deviennent des déchets solides ou dissous. Faisant partie de la catégorie des matériaux naturels, généralement considérés comme des déchets, les fibres de cuir introduites dans les panneaux de mortier de ciment jouent un rôle fondamental dans la construction en raison à la fois des propriétés d'isolation et de la résistance mécanique. Les déchets sont introduits sous forme de poudre ou de charge ou sous forme d'agrégats dans le mélange de béton, avec des avantages énergétiques, économiques et environnementaux. L'originalité et la contribution innovante de l'article scientifique consistent à réévaluer les déchets de cuir tannés du secteur du cuir en les transformant en matières premières à valeur ajoutée et en les utilisant dans l'industrie des matériaux de construction pour développer de nouveaux concepts de production pour de nouveaux matériaux biocomposites.
MOTS CLÉS : fibres de cuir, biocomposites, ciment Portland

INTRODUCTION

The leather processing industry has made significant efforts in recent years on the improved efficiency in using energy and materials, as well as in discarding the use of hazardous materials in production phases [1]. Solid waste (from raw hide and tanned leather, residual wool and sludge from wastewater treatment) is a significant issue of the leather sector [2-3].

Nowadays, the cement industry is responsible for 5-7% of global CO_2 emissions. To reduce them, new technological solutions and new building materials have recently been developed to protect natural resources. Thus, the concept of "green" materials involved both natural fibers and a large amount of waste. Natural fibers are used to improve the mechanical performance of cement-based composites instead of synthetic ones (e.g.

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PVA or polypropylene) as they provide greater tensile strength, ductility and post-cracking behavior and, at the same time, are increasingly appreciated due to their specific properties, low prices, health benefits and recyclability.

A ton of wet salted hide produces over 100 kg of waste of tanned leather waste [4]. The leather shaving process is done in tanneries in order to obtain a uniform leather thickness, but due to its low specific weight, a large amount of waste is accumulated in tanneries.

The paper presents the obtaining of biocomposites using leather shavings, with application in constructions. Three types of biocomposites were obtained by mixing 1% of 3 types of leather fibers: leather fibers treated with concentrated sulfuric acid (FPA); leather fibers neutralized with calcium hydroxide (FPN) and leather fibers immersed in a polymer binder (FP) with common Portland cement commercially known as Structo Plus®.

EXPERIMENTAL PART

Materials and Methods

Leather shavings used in this work comes from the shaving process of 35 kg of hides from the SC PIELOREX SA tannery in Jilava, Ilfov County.

Leather shavings were chemically treated to immobilize the chromium ion in the common Portland cement matrix.

Obtaining of Leather Fibers

Tanned leather waste (shaving and small pieces) was defibrated with a knife mill used in the rubber industry, resulting in about 100 kg of tanned leather fibers. 600 g of leather fibers were hydrolyzed with 2% concentrated sulfuric acid solution at 80°C for 60 minutes resulting in FPA fibers. Then some of these fibers were neutralized with a 10% sodium hydroxide solution, so the pH increased from 1.78 to 6.12 (FPN fibers). Also, 330 g of leather fibers were immersed in a 3.5% polymer binder solution used in the pulp and paper industry (FP fibers).

Table 1 shows the physicochemical analyses of leather fibers treated with concentrated sulfuric acid and neutralized with calcium hydroxide (FPA and FPN).

Table 1: Physicochemical characterisation of tanned leather fibres

No.	Characteristics	UM	Sample code/ determined values		Method standard
			FPA	FPN	
1	Dry substance	%	8.53	12.12	SR EN ISO 4684 : 2006
2	Ash	%	18.29	21.70	SR EN ISO 4047 : 2002
3	Total nitrogen	%	12.66	12.71	SR ISO 5397 : 1996
4	Dermal substance	%	71.15	71.43	SR ISO 5397 : 1996
5	Chromium oxide	%	5.16	4.37	SR EN ISO 5398/1 :2008
6	pH	pH unit	1.78	6.12	STAS 8619/3 :1990
7	Calcium oxide	%	0.23	0.25	

Values of ash, total nitrogen and dermal substance are reported free of volatile matter.

Obtaining of Biocomposites

In the laboratory phase, cement composites reinforced with tanned leather fibers were obtained at a content of 1% by weight (replacing cement with leather fibers) which have been studied physically and mechanically.

The biocomposites were made by mixing 1% leather fibres with composite additivated Portland cement (Structo Plus®). This cement is made in Romania for residential and commercial buildings, interior and exterior elements (paving blocks) and contains a component (Duraditiv®) whose action improves the properties of concrete ensuring durability of the final product.

Physicomechanical Characterisation of Biocomposites with Leather Fibres and Portland Cement

Characterisation of biocomposites was conducted at the Technical University of Civil Engineering of Bucharest (UTCB).

Determination of mechanical strengths (compressive and flexural strength) was conducted according to the following standards: STAS 4606-1980 «Natural heavy weight aggregates for mortars and concrete with mineral binding material. Testing methods», and EN 196-1:2016 «Methods of testing cement. Determination of strength».

The samples were made in metal moulds of 40x40x160 mm on solid brick, according to STAS 2634-80. The samples were evaluated after 7 and 28 days in terms of physicomechanical properties (compressive and flexural strength).

Compressive strength of biocomposites was determined after 7 and 28 days and results were compared with the control containing only cement. Charts are the average of 3 determinations of compressive strength.

RESULTS AND DISCUSSIONS

The analysis of experimental data showed that the values of compressive strength of FPA, FPN and FP biocomposites are higher compared to the control sample (without leather fibers), after 7 days, by 36÷48,7%, and after 28 days, they are 11,6÷13,2% higher. (Fig. 1 and 2)

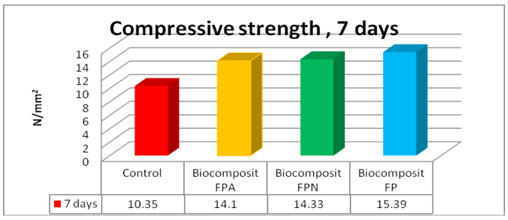

Figure 1. Compressive strength of biocomposites after 7 days

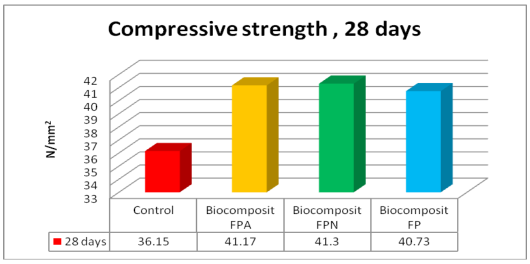

Figure 2. Compressive strength of biocomposites after 28 days

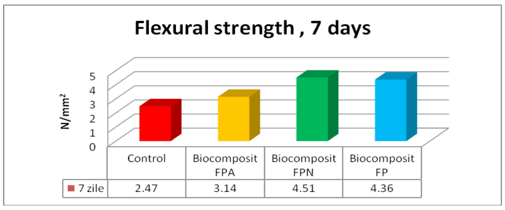

Figure 3. Flexural strength of biocomposites after 7 days

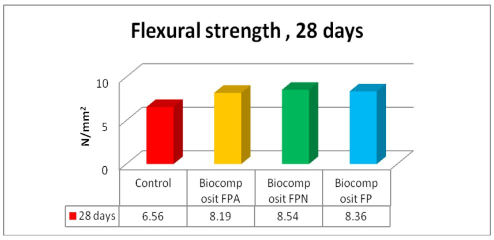

Figure 4. Flexural strength of biocomposites after 28 days

Flexural strength of biocomposites was determined after 7 and 28 days and results are presented in comparison with the control containing only cement (Fig. 3 and 4).

Analysis of charts 3 and 4 shows that flexural strength of FPA, FPN and FP biocomposites are higher compared to the control (without leather fibers), after 7 days by 27,1÷82,6%, and 28 days, values are 24,8÷30,2% higher.

Technology of Obtaining Biocomposites - Conceptual Model

In order to make an accurate conceptual model a series of tools are used for modelling, among which the most frequently used is the entity-relationship diagram.

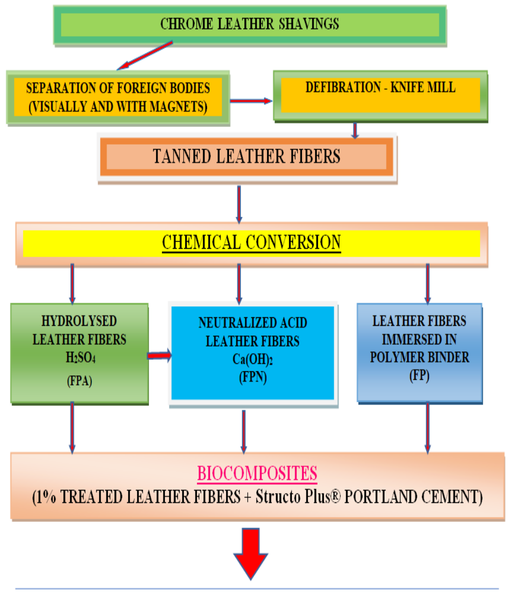

Figure 5. Technology for obtaining biocomposites with leather fibers – conceptual model

CONCLUSIONS

Experiments were carried out to obtain biocomposites from leather waste with applications in the building materials industry. Three kinds of fibres were obtained, namely acid-treated leather fibres (FPA), calcium hydroxide-neutralized leather fibers (FPN) and leather fibres immersed in a polymer binder (FP). Biocomposites were made by blending 1% of treated leather fibers and conventional Portland cement with the trade name Structo Plus®.

The effect of adding chemically treated leather shavings on the characteristics and microstructure of biocomposites has been studied. The addition of low-pH treated leather waste (sulfuric acid) minimizes Portlandite formation and favours the formation of calcium sulphate.

The results obtained for mechanical strength (compressive and flexural strength) of FPA, FPN and FP leather fibers biocomposites both after 7 days and 28 days are higher than the control (no fibre).

In conclusion, the shavings waste resulting from leather processing can be used to obtain biocomposites with applications in the construction industry.

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THE SHOCK ABSORPTION FUNCTIONALITY OF NANOMATERIALS BASED SHOES DURING BODY MOTION

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THE SHOCK ABSORPTION FUNCTIONALITY OF NANOMATERIALS BASED SHOES DURING BODY MOTION

ABSTRACT. The violent movement of human body will bring great impact to feet; therefore the shock absorption function of sports shoes is very important. The main factors affecting the shock absorption function is the material and structure of sole. In order to investigate the effect of nanomaterials on the shock absorption function of sports shoes, the impact tests were carried out on the thermoplastic elastomer (TPE) soles which were added or not added with nano-carbon black and the ordinary rubber soles. The impact energy was set as 6 J and 10 J, and the shock absorption performance was determined according to the test results. Thirty volunteers attended comfort tests which were designed to test the comfortability of the three kinds of sports shoes. The results demonstrated that the sport shoes which were added with the nano-carbon black had the best shock absorption performance. The impact peak value and G value of the sports shoes which were added with nano-carbon black were 13.57% and 17.86% lower than the shoes with the ordinary rubber soles when the impact energy was 6 J; the impact peak value and G value of the shoes with the ordinary TPE soles were 1.54% and 10.71% lower. When the impact energy was 10 J, the peak value and G value of the shoes which were added with nano-carbon black were 8.96% and 13.51% lower, while the impact peak value and G value of the shoes which were equipped with the ordinary TPE soles were 4.32% and 8.11% lower. The findings suggested that nanomaterials was effective in enhancing the shock absorption performance of sports shoes and that the shock absorption performance of sports shoes which were produced using nanomaterials was better than that of ordinary sports shoes. Moreover the results demonstrated that the shock absorption effect of sports shoes was limited, excessively large impact might weaken shock absorption effect.
KEY WORDS: nanomaterial, human motion, shock absorption, cavity structure, ventilation technology, comfortability

FUNCȚIONALITATEA DE ABSORBȚIE A ȘOCURILOR A ÎNCĂLȚĂMINTEI DIN NANOMATERIALE ÎN TIMPUL MIȘCĂRII

REZUMAT. Mișcarea violentă a corpului uman are un impact puternic asupra picioarelor; prin urmare, funcția de absorbție a șocurilor a încălțămintei sportive este foarte importantă. Principalii factori care afectează funcția de absorbție a șocurilor sunt materialul și structura tălpii. Pentru a investiga efectul nanomaterialelor asupra funcției de absorbție a șocurilor la încălțămintea sportivă, s-au efectuat teste de impact cu tălpi din elastomer termoplastic (TPE) la care s-a adăugat sau nu negru de fum nano și cu tălpi de cauciuc obișnuite. Energia de impact a fost stabilită la 6 J și 10 J, iar performanța de absorbție a șocului a fost determinată în funcție de rezultatele testelor. Treizeci de voluntari au participat la testele de confort care au fost concepute pentru a testa confortul celor trei tipuri de pantofi sport. Rezultatele au demonstrat că pantofii sport cu talpă la care s-a adăugat negru de fum au avut cea mai bună performanță de absorbție a șocurilor. Valoarea maximă a impactului și valoarea G a încălțămintei sportive cu talpă la care s-a adăugat negru de fum au fost cu 13,57% și 17,86% mai mici decât în cazul încălțămintei cu tălpi obișnuite din cauciuc atunci când energia de impact a fost de 6 J; valoarea maximă a impactului și valoarea G a încălțămintei cu tălpi obișnuite TPE au fost de 1,54% și 10,71% mai mici. Când energia de impact a fost de 10 J, valoarea maximă și valoarea G a încălțămintei cu talpă la care s-a adăugat negru de fum au fost cu 8,96% și 13,51% mai mici, în timp ce valoarea maximă a impactului și valoarea G a încălțămintei cu tălpi obișnuite din TPE au fost cu 4,32% și 8,11% mai mici. Constatările au sugerat că nanomaterialele au avut eficiență în creșterea performanțelor de absorbție a șocurilor și că performanța de absorbție a șocurilor a pantofilor sport fabricați folosind nanomateriale a fost mai bună decât cea a pantofilor sport obișnuiți. Mai mult, rezultatele au demonstrat că efectul de absorbție a șocurilor al pantofilor sport a fost limitat, iar impactul excesiv de mare ar putea slăbi efectul de absorbție a șocurilor.
CUVINTE CHEIE: nanomaterial, mișcare umană, absorbția șocului, structura cavității, tehnologie de ventilație, confort

LA FONCTIONNALITÉ D'ABSORPTION DE CHOCS DES CHAUSSURES À BASE DE NANOMATÉRIAUX AU COURS DU MOUVEMENT DU CORPS

RÉSUMÉ. Le mouvement violent du corps humain a un impact important sur les pieds ; par conséquent, la fonction d'absorption des chocs des chaussures de sport est très importante. Les principaux facteurs affectant la fonction d'absorption des chocs sont le matériau et la structure de la semelle. Afin d'étudier l'effet des nanomatériaux sur la fonction d'absorption des chocs des chaussures de sport, les essais d'impact ont été effectués sur les semelles en élastomère thermoplastique (TPE) ajoutées ou non avec du noir de carbone nano et des semelles en caoutchouc ordinaires. L'énergie d'impact a été fixée à 6 J et 10 J et la performance d'absorption des chocs a été déterminée en fonction des résultats du test. Trente volontaires ont participé à des tests de confort conçus pour tester le confort des trois types de chaussures de sport. Les résultats ont montré que les chaussures de sport aux semelles qui ont été ajoutées avec le nano-carbone noir ont eu la meilleure performance d'absorption des chocs. La valeur maximale de l'impact et la valeur G des chaussures de sport aux semelles ajoutées avec du nano-carbone noir étaient 13,57% et 17,86% inférieures à celles des semelles en caoutchouc ordinaires lorsque l'énergie d'impact était de 6 J ; la valeur maximale de l'impact et la valeur G des chaussures aux semelles TPE ordinaires étaient 1,54% et 10,71% inférieures. Lorsque l'énergie d'impact était de 10 J ; la valeur maximale et la valeur de G des chaussures aux semelles ajoutées avec du nano-carbone noir étaient 8,96% et 13,51% inférieures, tandis que la valeur maximale d'impact et la valeur G des chaussures aux semelles ordinaires en TPE étaient 4,32% et 8,11% inférieures. Les résultats ont montré que les nanomatériaux étaient efficaces pour améliorer les performances d'absorption des chocs des chaussures de sport et que la performance d'absorption des chocs des chaussures de sport fabriquées à l'aide de nanomatériaux était meilleure que celle des chaussures de sport ordinaires. En outre, les résultats ont montré que l'effet d'absorption des chocs des chaussures de sport était limité, un impact excessivement grand pouvant affaiblir l'effet d'absorption des chocs.
MOTS CLÉS : nanomatériau, mouvement humain, absorption des chocs, structure de la cavité, technologie de ventilation, confort

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INTRODUCTION

The foot of human body is a natural shock absorption structure. The arch of the foot plays a key role in the shock absorption of feet. During motion, feet will suffer impact when touching the ground, and may have different injuries in different parts, such as ankle sprain and tendon injury. Feet will bear multiple impacts when walking, let alone strenuous exercise [1]. According to the relevant statistics [2], the impact of feet during long-distance running was about three times that of jogging. Such a frequent and huge impact is difficult to offset by the structure of the foot itself, which will make the feet exhausted. The protection of sports shoes for feet reflects on its shock absorption property. The shock absorption of shoe sole materials has a direct impact on the shock absorption of sports shoes. In recent years, nanocomposites have been widely used in shoemaking.

Nanotechnology combines modern science and technology and has gradually developed in recent years. Nanomaterial features are low weight, strong hardness and long service life [3]. With the maturity of technology, nanotechnology can be used in daily life such as manufacture of running shoes besides aerospace, microelectronics & computer, and environment and energy. Some experts have made relevant studies. Song *et al*. [4] proposed that nanotechnology had deep influence on sports engineering field and has been extensively applied in sportswear and equipment. Considering the popularization and risks of running, Bassiri *et al*. [5] applied nanotechnology in the manufacture of shoe sole to prevent different injuries. Lutpi *et al*. [6] proposed that the application of nanocomposite in the sole of running shoes had been a new development direction. Ramsay *et al*. [7] considered that the application of nanotechnology could enhance the exercise capacity and technical level of athletes. Therefore nanomaterial has been extensively recognized and applied in shoemaking. In this study, the sports shoes whose soles were made of three different materials were tested using a shock absorption testing machine, and the vibration reduction performance of the materials was determined based on the testing results.

Nanomaterials and their Application in Shoemaking

Nanomaterial is a kind of particulate solid material whose diameter is less than 100 nm. It contains a variety of solid components, which can be crushed such as metals, nonmetals, simple substances and compounds [8]. Nanomaterials are often not directly used as raw materials for industrial production, but are used for modifying the target materials as a kind of filler material similar to “additives” to enhance the mechanical properties and save cost. Nanomaterial particles are unable to be observed by optical microscopy, but they are also not microscopic. Therefore, nanomaterials are also called mesoscopic materials; but nanomaterials have the performance which the same materials do not have in macroscopic state such as small-size effect, interfacial effect and macroscopic quantum tunneling effect [9]. The non-nanomaterials which are added with nanomaterials are called nanocomposites. Nanocomposites have been extensively applied in different fields, such as the building industry and textile industry.

Nanomaterial has an extensive application in shoemaking. Carbon black and white carbon black have been extensively applied for decades. Its compensation function can strengthen the colloid part of shoes, for example, the mechanical performance of shoe sole and heel. Nano-zinc oxide has more functions. It can have the effect achieved by ordinary zinc oxide, at a lower dosage, which can save cost and zinc resource. Therefore it can replace traditional zinc oxide in shoe colloid. Moreover the three nanomaterials shown in Table 1 all have bactericidal effect. Hence shoes which are made of one of the three nanomaterials and fibre materials also have bactericidal effect.

Table 1: Some common nanomaterials used in shoemaking

Name	Application in shoemkaing industry	Technical status
Carbon black	Mostly used in the black rubber of rubber shoes and the black heel of leather shoes and sports shoes.	The technology has been matured and extensively applied.
White carbon black	Has the same application range with carbon black, but in white or color shoes.	The technology has been matured and extensively applied.
Nano-zinc oxide	It can be used in the manufacturing of shoe heel at a dose which is half that of traditional zinc oxide, which can save cost.	Mass use in some shoe factories
	Replacing ordinary zinc oxide with less amount in the manufacturing of shoe glue	Needs to be promoted
	Being added to fibre materials, and can resist bacteria	Needs to be promoted

Shock Absorption Function of Sports Shoes

When sportsmen do exercise especially fast running, the legs will receive an impact force generated by the ground and will be injured if motion posture fails [10]. At that moment the shock absorption function of sports shoes will take effect. Sports shoes protects sportsmen by generating resistance to impact force via the changes of internal structure of shock-absorbing materials or the deformation of the special structure of sole. In simple words, function of shock absorption is the ability of absorbing or weakening shock wave.

The shock absorbability of sports shoes will be affected by the surface environment of sport field, motion posture, exercise intensity, and the hardness, thickness, materials and structure of the sole of sports shoes [11]. After excluding the human factors, i.e. motion posture and exercise intensity, the materials and structure of sports shoes is the factor which has the largest influence on shock absorbability and is controllable. A qualified sportsman will select shoes which are made of different materials and structures according to different situations. Indexes for evaluating the shock absorbability of sports shoes include impulse; plantar pressure associated indexes including distribution of plantar pressure, average pressure and changes of buffer pressure value during landing and ground reaction force associated indexes including impact force peak value, G value and maximum load rate [12].

The Shock Absorbing Materials of Sports Shoes

Material of sole is an important controlling factor which affects the shock absorption performance of sports shoes. Many materials can be used for manufacturing soles. For example, polyvinyl chloride (PVC) which is featured by the excellent thermal stability, low price and strong abrasive resistance and has defects of poor sliding and folding resistance is not suitable for sports shoes, and moreover the production and using process of PVC may produce toxic substances [13]. Shoes whose soles are made of polyurethane (PU) are characterized by excellent durability, exercise support capacity, sliding resistance, elasticity and shock absorption performance, but the shortcomings of high risks of fracture, poor ductility and strong water absorptivity are not beneficial in the process of running [14]. Thermoplastic elastomer (TPE) has been extensively applied in the shoemaking industry because of its advantages of strong tensile and tearing strength, low-temperature resistance, air permeability and sliding resistance, but is difficult to be further promoted for its high production cost [15]. In such a case, nano-inorganic filler is needed. It can improve the mechanical performance, reduce production cost, kill bacteria and strengthen flame resistance. The objective of the paper is to test the shock absorptivity of the sports shoes which was equipped with soles that were made of nano-carbon black added TPE.

MATERIALS AND METHODS

Preparation of the Nanocarbon Black Added TPE

As the soles of running shoes available on the market do not meet experimental results, the experimental sole material was manufactured by the authors. The preparation process of the nano-carbon black added TPE [10] is shown below. The synthesized TPE glue liquor was added with anti-aging agent with a mass fraction of 1%. After even mixing, it was added with deionized water whose volume was 1/3 that of the container loaded withe the glue liquor. Next the mixture was heated in water bath at a temperature of 105°C. Then the glue was cut into pieces and dried to the constant weight in a vacuum environment at a temperature of 50°C. Then it was milled several times using a double-roll mill and added with nano-carbon black in a ratio of 1:25. After even mixing, stearic acid, zinc oxide, remaining carbon black, accelerator DM, accelerator D and antioxidant RD and sulphur. The formula used in the milling is shown in Table 2.

Table 2: The milling formula of carbon black

Ingredient	TPE	Sulphur	Antioxidant RD	Accelerator D	Accelerator DM	Zinc oxide	Stearic acid	Carbon black
Ratio/copy	100	1.9	1.1	0.5	1.3	3.9	1.5	50

The physical indexes of the nano-carbon black added TPE are shown in Table 3.

Table 3: Various physical indexes of TPE added with nano-carbon black

Item	Air permeability (mm/S)	Water absorption degree (%)	Tensile strength (MPa)	Density (mg/m^3)	Hardness (ShawW)	Compression Set (%)
Index	256	320	0.42	0.23	26	8.5
Remark			No patch			

EXPERIMENTAL

Test on the Shock Absorption Performance of Shoe Soles

Materials and Instruments

The materials were three kinds of sports shoes which were equipped with nano-carbon black added TPE sole, ordinary TPE sole and ordinary rubber sole. The sports shoes were the same in the style and size, all of them were new products.

A shock absorption test machine was used. The impactor weighed 9 kg, the diameter of the cylindrical object was 5 cm, and the head of the impactor was a hemisphere with a radius of 4 cm. The parameters were detected using the accelerometer fixed on a lead ball in the process of impact.

Test Methods

The heel part of the sole was impacted by the shock absorption test machine. The height when the impactor impacting at the sole in a static state was set as 0, and the impact energy was controlled by adjusting the height of the impactor, and the heel of the shoe sole was hit by the energy of 6 J and 10 J respectively. The impact energy was first low and then high, and 3 groups of effective impact data were collected under each impact energy, the average values were taken as the final results. The interval between the impacts was 2 min. After the impacts at two different energies completed, another pair of shoes was tested. Proper indexes were selected according to the data collected. The sports shoes showing the poorest shock absorption performance was taken as the criterion in the determination of the shock absorption performance of the soles.

RESULTS AND DISCUSSION

Analysis on the Difference of Shock Absorption Performance

The shock absorption performance of the sports shoes was measured using impact peak value and G value (the ratio of the maximum accelerated speed produced during impact to the gravitational acceleration). According to relevant regulations, the main objective of shock absorption was to reduce impact peak value and G value. Therefore smaller impact peak value and G value indicated better shock absorption performance under the same impact. Table 4 shows that the impact peak value and G value of every shoe increased with the increase of impact energy, suggesting the shock absorption of any pair of shoes was limited. The horizontal comparison of the data demonstrated that the shock absorption performance of the no. 1 shoes was the best, and that of no. 3 shoes was the poorest no matter under 6 J or 10 J, i.e. the shock absorption performance of the sports shoes which were equipped with the nano-carbon black added TPE sole was the best.

Table 4: Comparison of impact pack value and G value between different shoes under different impact energies

	Impact energy	No. 1 shoes	No. 2 shoes	No. 3 shoes
Impact peak value	6J	1872.85 N	2133.55N	2166.98N
	10J	2622.89N	2756.57N	2880.98N
G value	6J	23	25	28
	10J	32	34	37

Analysis on the Attenuation Rate of Shock Absorption Performance

It was found that the shock absorption performance of no. 3 shoes was the poorest; therefore the impact peak value of G value of no. 3 shoes were taken as the criteria. As shown in Table 5, the impact peak value and G value of no. 1 shoes were 13.57% and 17.86% lower than that of no. 3 shoes when the impact energy was 6 J; the impact peak value and G value of no. 2 shoes were 1.54% and 10.71% lower than that of no. 3 shoes. Thus it could be concluded that the shock absorption performance of no. 1 and no. 2 shoes was better than that of no. 3 shoes. The difference between no. 1 shoes and no. 3 shoes was larger. When the impact energy was 10 J, the difference changed, but the tendency was the same. Moreover the difference between no. 1 shoes and no. 2 shoes was the addition of nano-carbon black. Therefore it was concluded that the addition of nanomaterials could enhance the shock absorption performance of shoes. The vertical comparison of the differences suggested that the attenuation rate of no. 1 shoes and no. 2 shoes both decreased, indicating the shock absorption effect weakened with the increase of the impact energy.

Table 5: The comparison of no. 3 shoes with no. 1 and no. 2 shoes in the impact peak value and G value

	Impact energy	No.1 shoes	No. 2 shoes
Impact peak value	6J	-13.57%	-1.54%
	10J	-8.96%	-4.32%
G value	6J	-17.86%	-10.71%
	10J	-13.51%	-8.11%

CONCLUSION

It could be concluded that nanomaterials could improve the shock absorption performance of sports shoes. Moreover the vertical comparison of the shock absorption performance under two different impact energies suggested that the shock absorption of the soles was limited, and the shock absorption effect decreased with the increase of impact strength. In conclusion, sports shoes which are made of nanomaterials are more excellent in shock absorption compared to sports shoes which are made of ordinary materials.

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STUDY OF VEGETABLE EXTRACTS EFFECT ON WET-WHITE LEATHER

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STUDY OF VEGETABLE EXTRACTS EFFECT ON WET-WHITE LEATHER

ABSTRACT. Although the worldwide leather production is based on chromium tannage, there is an increasing share of chrome and metal free tannages. This is mainly due to the growing demand for chrome free leathers in the automotive industry. The aim of this work was the study of vegetable extracts effect on the retannage of wet-white leather, produced by the glutaraldehyde and syntan pre-tannage process, evaluating the bath exhaustion and physical-mechanical leather properties. For that, the leather thickness was adjusted to 1.4 mm and a retanning process was applied to small leather pieces by neutralization, retanning with vegetable extracts, dyeing and fat-liquoring. It was shown that the absorption of vegetable extracts by the leather was greater and faster for the hydrolysable tannins (natural chestnut vegetable extract) than for condensed tannins (mimosa vegetable extract). Different vegetable extracts: natural chestnut, sweetened chestnut, quebracho, gambier, mimosa, tara and cashew, were applied in order to evaluate their effects on leather properties. Properties, as physical-mechanical tests for tear strength, and for ball burst test (to evaluate the grain cracking), and leather behavior regarding softness and grain firmness, were evaluated for the different leather pieces.
KEY WORDS: glutaraldehyde, leather, vegetable extracts, wet-white

STUDIUL INFLUENŢEI EXTRACTELOR VEGETALE ASUPRA PIELII WET-WHITE

REZUMAT. Deși producția de piele la nivel mondial se bazează pe tăbăcirea în crom, există o cotă tot mai mare de procese de tăbăcire fără crom și fără metale. Acest lucru se datorează în principal cererii din ce în ce mai mare de piele fără crom în industria automobilelor. Scopul acestei lucrări a fost studierea influenței extractelor vegetale asupra revitalizării pieilor wet-white, obținute prin procedeul de pre-tăbăcire cu glutaraldehidă și sintani, evaluând gradul de epuizare a flotei și proprietățile fizico-mecanice ale pielii. Pentru aceasta, grosimea pielii a fost ajustată la 1,4 mm și s-a efectuat un proces de retăbăcire a bucăților mici de piele prin neutralizare, retăbăcire cu extracte vegetale, vopsire și ungere. S-a demonstrat că absorbția extractelor vegetale în piele a fost mai mare și mai rapidă în cazul taninurilor hidrolizabile (extract vegetal natural de castan) decât în cazul taninurilor condensate (extract vegetal de mimosa). Au fost folosite diferite extracte vegetale: castan natural, castan îndulcit, quebracho, gambir, mimosa, tara și caju, pentru a evalua efectele acestora asupra proprietăților pielii. S-au evaluat proprietățile diferitelor bucăți de piele prin teste fizico-mecanice pentru a determina rezistența la rupere și rezistența la crăparea feței, precum și comportamentul pielii în ceea ce privește moliciunea și fermitatea feței.
CUVINTE CHEIE: glutaraldehidă, piele, extracte vegetale, wet-white

ÉTUDE DES EFFETS DES EXTRAITS VÉGÉTAUX SUR LE CUIR WET-WHITE

RÉSUMÉ. Bien que la production mondiale de cuir soit basée sur le tannage au chrome, il y a une part croissante de tannages sans chrome et sans métal. Ceci est principalement dû à la demande croissante de cuirs sans chrome dans l'industrie automobile. Le but de cet article était d'étudier l'effet des extraits végétaux sur le retannage du cuir wet-white, produit par le procédé de pré-tannage au glutaraldéhyde et au syntan, en évaluant l'épuisement du bain et les propriétés physico-mécaniques du cuir. Pour cela, l'épaisseur du cuir a été ajustée à 1,4 mm et un procédé de retannage a été appliqué aux petites pièces de cuir par neutralisation, retannage avec des extraits végétaux, teinture et graissage. Il a été montré que l'absorption des extraits végétaux par le cuir était plus grand et plus rapide pour les tannins hydrolysables (extrait végétal naturel de châtaigne) que pour les tanins condensés (extrait végétal de mimosa). Différents extraits végétaux: châtaigne naturelle, châtaigne adouci, quebracho, gambier, mimosa, tara et noix de cajou, ont été appliqués afin d'évaluer leurs effets sur les propriétés du cuir. On a évalué les propriétés du cuir par les tests physico-mécaniques pour la résistance au déchirement, et pour l'essai d'éclatement de balle (afin d'évaluer le gerçure de la fleur), et le comportement du cuir en matière de douceur et de fermeté de la fleur.

MOTS CLÉS : glutaraldéhyde, cuir, extraits végétaux, cuir wet-white.

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INTRODUCTION

The research centers throughout the world have undertaken a lot of work on new tanning process in order to replace the chromium tanning process. Conventional chromium tanning is the most widely process used in the world and generates a significant pollutant load with a reasonable chromium content in the waste water and in the solid wastes. Nevertheless, the process has significant advantages as its high thermal stability [1] and its versatility of end products obtained, very important characteristics for shoe upper leather.

The last few years, wet-white tanning appeared as an alternative to chromium tanning process, mainly for automotive leather, furniture and children's shoes. This process is mainly based on glutaraldehide and a syntan pre-tannage [2]–[4]. After this pre-tannage, the process is followed by thickness adjustment, retanning using polyphenols (vegetable and syntan tanning agents) and other organic-synthetic agents, dyeing and fat-liquoring.

The use of vegetable extracts for wet-blue retannage is a normal way to obtain certain characteristics of the final leather product. Vegetable tannage and vegetable combination tannages have been always used in leather production [5], [6].

In this work, it is studied the effect of vegetable extracts when applied as retanning agents for wet-white leather. For that, a wet-white based process developed by INDINOR, a Portuguese chemical company, was used.

EXPERIMENTAL

Materials and Methods

The raw material used in this work was wet-white leather prepared by INDINOR, a chemical company located at Portugal, using the process showed in the Table 1.

The process was made on bovine pickled pelt (lime spiltted) and chemicals quantity was calculated as % based on pickled pelt weight.

Table 1: Wet-white pre-tannage process

Chemical	Chemical Quantity (%)	Time (min)	Temp.(ºC)	Control
Water	50	15	25	ºBe = 6.5
NaCl	6			
Add pelts				
		10		pH = 2.8
Fortan GL	2.5	60		
Fortan GL	2.5	120		
Inditan FC Liq.	2.0	60	35	pH = 4.2
Sodium Formiate	0.5			
Sodium Bicarbonate	0.25			
Inditan Voc Liq.	6	120		
Run 5 min each 2 hours, overnight				
		30		pH= 4.4
Drain				
Wash with Water	100	10	25	
Drain, squeeze and shave				

Wet-white leather, thus prepared, was shaved to a thickness of 1.4 mm in a shaving machine and submitted to the respective process depending on the study in question.

For all the trials, small pieces of wet-white were used, always from the same zone near the back-bone. The chemicals used were all obtained from INDINOR: Fortan GL (gluteraldehyde based); Inditan FC Liq. (masking phtalic salt); Inditan VOC Liq. (synthetic tannin); Indinol BE (natural oil); Indinol HS (emulsion of synthetic fats); Indinol EAF (sulphited fish oil); Indinol LOX (lanolin based oil)

The trials were carried out using laboratory drums (LFA-9293, Mathis), with temperature and speed control and product quantities were based on the weight of wet-white hide pieces used.

Vegetable Extracts Absorption

The up-take of the vegetable extracts by the leather was studied for hydrolysable tannins (natural chestnut vegetable extract) and condensed tannins (mimosa vegetable extract).

In each trial, wet-white shaved pieces weighing approximately 100 g were washed with 300% w/w of water at 35ºC during 10 min, neutralized with 1.5% w/w of sodium formiate and 0.5 % w/w of sodium bicarbonate to a pH of 6 in 200% w/w of water at 35ºC and during 30 min, washed again with 300% w/w at 40ºC during 10 min, and treated with 12% w/w of vegetable extract, natural chestnut in one case and mimosa in the other, in 200% w/w of water at 40ºC. Samples from the vegetable retanning bath were taken at 1 min, 15 min, 30 min, 60 min and 120 min of running time, and evaluated to read the absorbance in a spectrophotometer UV-VIS according the method cited in [7].

Vegetable Effect on Leather: Physical and Mechanical Properties

The effect of vegetable extracts on leather physical mechanical properties was studied for eight vegetable extracts: natural chestnut, sweetened chestnut, mimosa, tara, cashew, gambier and quebracho. For each trial, samples from shaved wet-white pelt, weighting approximately 100 g, were submitted to retanning, dyeing and fat-liquoring process showed in the Table 2.

Table 2: Wet-white retanning, dyeing and fat-liquoring process

Process	Chemical	Chemical Quantity (%)	Time (min)	T (ºC)
Washing	Water	300	10	35
		Drain		
Neutralization	Water Sodium Formiate Sodium Bicarbonate	200 1.5 0.5	30	35
		pH Control (6) and drain		
Washing	Water	300	10	40
		Drain		
Retanning	Water Vegetable Extract	200 12	120	40
		add		
Dyeing	Water Dyestuff	50 2	30	50
		add		
Fat-liquoring	Indinol BE Indinol HS Indinol EAF Indinol LOX	2 3 3 4	60	50
		add		
Fixation	Formic Acid	1	30	50
		pH Control (4.2) and drain		
Washing	Water	300	10	25
		Squeeze, Dry and Stacked		

After this process the hide pieces were squeezed, dried and stacked. Properties, as physical-mechanical tests according to ISO 3377:2002 for tear strength, and ISO 3379:1976 for ball burst test (to evaluate the grain cracking), and leather behavior regarding softness and grain firmness, were evaluated for the different leather pieces.

RESULTS AND DISCUSSIONS

Vegetable Extracts Absorption

Wet-white shaved pieces were treated with 12% w/w of vegetable extract according the process described above. Two replicas were done with natural chestnut in one case and two replicas with mimosa in the other case. Samples of the vegetable retanning bath were taken at 1 min, 15 min, 30 min, 60 min and 120 min of running time for reading the absorbance. Results for vegetable extract exhaustion in bath are shown in Figures 1 and 2.

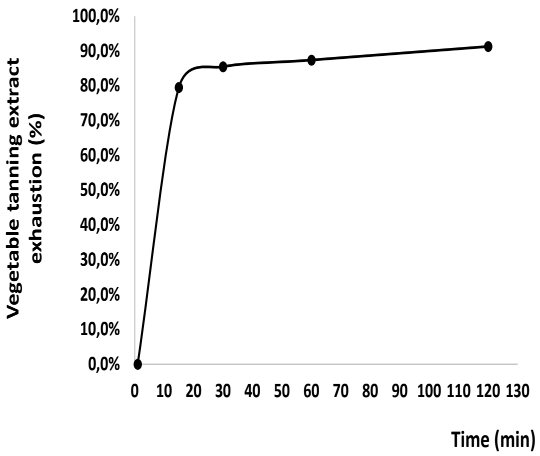

Figure 1. Wet-white absorption of natural chestnut extract

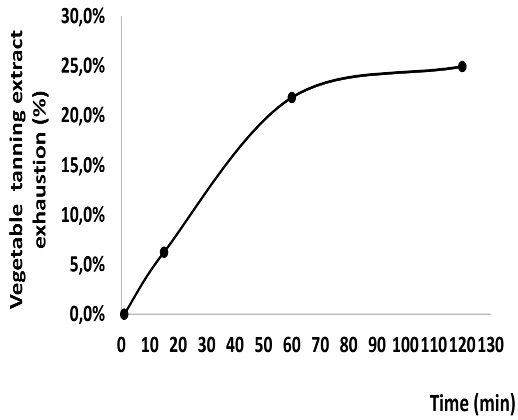

Figure 2. Wet-white absorption of Mimosa extract

From the figures it can be seen that the up-take is greater and faster in the case of natural chestnut. This indicates a better reactivity of natural chestnut extract comparing with mimosa extract. For a better up-take of mimosa extract it would be necessary more time.

Vegetable Effect on Leather: Physical and Mechanical Properties

A complete wet-end process was applied to wet-white shaved pieces in order to evaluate leather properties, as physical-mechanical tests according to ISO 3377:2002 for tear strength, and ISO 3379:1976 for ball burst test (to evaluate the grain cracking), and leather behavior regarding softness and grain firmness. Results for physical-mechanical tests are shown in Table 3.

Table 3: Physical and Mechanical Tests

Vegetable Extract	Tear Strength (N)	Ball burst test	
		Load (N)	Distension (mm)
Tara	325	579.3	9.2
Cashew	261	498.0	8.7
Natural Chestnut	270	510.9	8.2
Mimosa	202	247.0	7.8
Sweetened Chestnut	112	262.1	7.7
Gambier	179	200.8	7.1
Quebracho	121	282.0	8.0

The results obtained, when compared with the reference values generally accepted for footwear application: 200 N for load and 7 mm for distension in ball burst test and 120 N for tear strength, are very good with evidence for tara extract.

The evaluation of the leather pieces obtained showed a good softness and grain firmness, in general, with a tendence for less softness in the case of tara, cashew and natural chestnut.

CONCLUSIONS

The aim of this work was the study of vegetable extracts effect on the retannage of wet-white leather, produced by the glutaraldehide and syntan pre-tannage process, evaluating the bath exhaustion and physico-mechanical leather properties.

It was shown that the absorption of vegetable extracts by the leather was greater and faster for the hydrolysable tannins (natural chestnut vegetable extract) than for condensed tannins (mimosa vegetable extract). Hydrolysable tannins have a natural acidity that result in a high degree of tannin fixation comparing to condensed tannins and for this reason a better absorption was achieved.

Physical mechanical properties of leather were good satisfying the minimum required for footwear and characteristics as leather firmness and softness were good although tara, cashew and natural chestnut have generated some hardness. All the vegetable extracts can be used as retanning agents and the choice depends on the desired leather final product.

Nevertheless, a validation of these results at a larger scale will be important.

Acknowledgements

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PRODUCTIVITY IMPROVEMENT OF LEATHER PRODUCTS INDUSTRY IN BANGLADESH USING LEAN TOOLS: A CASE STUDY

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PRODUCTIVITY IMPROVEMENT OF LEATHER PRODUCTS INDUSTRY IN BANGLADESH USING LEAN TOOLS: A CASE STUDY

ABSTRACT. There is great potential for the leather industry in Bangladesh to become one of the country's major foreign exchange earners, experts say. After readymade garments (RMG), productivity improvement can help to enrich profit of a leather products industry by minimizing excess work and developing a new method for particular operation. Nowadays, productivity improvement is a popular topic for any kinds of industry. Therefore, improving productivity is one of the main concerns of leather products industries. Lean manufacturing tools are most important tools that can help to increase productivity in leather products industry. In Bangladesh, few industries use these lean tools which can be proved as a real beneficial one. Hence, this study addresses the implementation of lean principles in a leather goods manufacturing industry in order to evaluate present process cycle efficiency (PCE), lead time and productivity prior to developing an improved strategy to bring the improved PCE, productivity and to reduce the lead time. By applying lean tools in the industry at the production line for bi-fold wallet, productivity has been improved by 85.42%. At the beginning state, the PCE was found 38.19% and after the implementation of lean tools, it would be 77.51% and lead time would also be reduced by 46.68% evaluated by takt time, bottleneck analysis, cause-effect analysis and Pareto analysis. The production flow was optimized by minimizing several non-value-added (NVD) activities such as bottlenecking, machine breakdown, queue time, waiting time, material handling time, etc.

KEY WORDS: productivity, lean tools, PCE, lead time, Pareto chart, wallet production line

ÎMBUNĂTĂȚIREA PRODUCTIVITĂȚII INDUSTRIEI PRODUSELOR DIN PIELE DIN BANGLADESH UTILIZÂND INSTRUMENTE SUPLE: UN STUDIU DE CAZ

REZUMAT. Industria de pielărie din Bangladesh are un mare potențial de a deveni unul dintre sectoarele cele mai profitabile din țară, conform experților. După îmbrăcămintea de masă, îmbunătățirea productivității poate contribui la creșterea profitului industriei produselor din piele prin reducerea la minimum a excesului de muncă și prin dezvoltarea unei noi metode pentru o anumită operațiune. În prezent, îmbunătățirea productivității este un subiect popular pentru orice tip de industrie. Prin urmare, îmbunătățirea productivității este una dintre principalele preocupări ale industriei produselor din piele. Instrumentele suple de producție sunt cele mai importante instrumente care pot contribui la creșterea productivității industriei produselor din piele. În Bangladesh, puține industrii folosesc aceste instrumente suple, care pot fi de real folos. Prin urmare, acest studiu abordează implementarea unor principiilor suple în industria de fabricare a articolelor din piele pentru a evalua eficiența ciclului de proces (PCE), timpul de producție și productivitatea înainte de a dezvolta o strategie pentru a îmbunătăți PCE și productivitatea și pentru a reduce timpul de producție. Prin aplicarea instrumentelor suple în industrie în linia de producție a portofelului cu îndoitură, productivitatea a fost îmbunătățită cu 85,42%. La început, PCE a fost de 38,19%, iar după implementarea instrumentelor suple, ajunge la 77,51%, iar timpul de execuție se reduce cu 46,68%, evaluat în funcție de timp, analiza blocajelor, analiza cauză-efect și analiza Pareto. Fluxul de producție a fost optimizat prin reducerea la minimum a câtorva activități care nu adaugă valoare (NVD), cum ar fi blocajele, defectarea mașinilor, timpul de așteptare, timpul de manipulare a materialelor etc.

CUVINTE CHEIE: productivitate, instrumente suple, PCE, timp de execuție, diagramă Pareto, linie de producție a portofelelor

AMÉLIORATION DE LA PRODUCTIVITÉ DE L'INDUSTRIE DES PRODUITS EN CUIR AU BANGLADESH À L'AIDE D'OUTILS DE GESTION ALLÉGÉE: UNE ÉTUDE DE CAS

RÉSUMÉ. L'industrie du cuir au Bangladesh a un grand potentiel pour devenir l'un des secteurs les plus rentables du pays, selon les experts. Après les vêtements de masse, l'amélioration de la productivité peut contribuer à la croissance des bénéfices de l'industrie des produits en cuir en minimisant l'excès de travail et par l'élaboration d'une nouvelle méthode pour une opération. À l'heure actuelle, l'amélioration de la productivité est un sujet populaire pour tous les secteurs. L'amélioration de la productivité est donc l'une des principales préoccupations de l'industrie des produits en cuir. Les outils de gestion allégée sont les outils les plus importants qui peuvent aider à accroître la productivité de l'industrie des produits en cuir. Au Bangladesh, peu d'industries utilisent ces outils qui peuvent s'avérer utiles. Par conséquent, cette étude porte sur la mise en œuvre des principes de la gestion allégée dans la fabrication des produits en cuir pour évaluer l'efficacité du cycle de processus existant (PCE), le temps de la production et la productivité avant d'élaborer une stratégie pour améliorer le PCE et la productivité et pour réduire le temps de production. En appliquant les outils de gestion allégée à la ligne de production de portefeuilles, la productivité a été améliorée de 85,42%. Au début, le PCE était 38,19%, et après la mise en œuvre des outils de gestion allégée, il atteint 77,51% et le temps d'exécution est réduit de 46,68%, évalué par temps de prise, analyse des goulots d'étranglement, l'analyse cause-effet et l'analyse de Pareto. Le flux de production a été optimisé en minimisant les multiples activités et les temps sans valeur ajoutée tels que les goulots d'étranglement, les pannes de machines, les temps d'attente, les temps de traitement des matériaux, etc.

MOTS CLÉS : productivité, outils de gestion allégée, PCE, temps d'exécution, diagramme de Pareto, ligne de production de portefeuille

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INTRODUCTION

Manufacturing is a vital sector in society, irrespective of being a high or low-income economy [1]. The leather sector is playing a vital role in our national economy, earning us huge amounts of export earnings. Most leather goods and footwear manufactured here are export-oriented. According to the Export Promotion Bureau (EPB), leather exports totaled USD 116.73 million in the last fiscal year 2016-2017; the amount was USD 92.50 million the previous year [2]. In the world, it is one of the leading manufacturing industries based on raw material, geographical condition, and workforce and is highly favorable for the growth of leather products industry. The demand for processed leather products is rapidly increasing in the busy world and consequently, it seems a rapid expansion of leather products industry in Bangladesh as well as in other countries. It needs several production steps to produce the finished goods from raw materials. Today higher productivity achievement is a very important factor for the production field. With the higher productivity, other various factors must be taken into consideration in manufacturing industries such as global competition, lead time and customer need in terms of quality and quantity [3, 4]. Continuous improvement with or without capital infusion necessitates competitive manufacturing [5]. Lean manufacturing is based on the Toyota Production System developed by Toyota which focuses on eliminating waste, reducing inventory, improving throughput, and encouraging employees to bring attention to problems and suggest improvements to fix those [6]. Lean manufacturing has been increasingly applied by leading manufacturing companies throughout the world. A core concept of lean manufacturing is pulling production in which the flow on the factory floor is driven by demand from downstream pulling production upstream. Some of the changes required by lean manufacturing can be disruptive if not implemented correctly and some aspects of it are not appropriate for all companies [7, 8]. A lean manufacturing facility is capable of producing the product in only the sum of its value-added work content time [9]. The main scope of lean manufacturing is to eliminate waste and reduce the cycle time to increase the profit and competitiveness by increasing the production and decreasing the cost of product [10]. On the other hand, applications of lean manufacturing in the continuous process sector have been far fewer [11-13]. To sustain the positive growth, it is necessary to ensure the proper utilization of resources. Financial growth of any industry largely depends on minimizing excess work and productivity improvement. This study was masterful with some specific objectives which were to identify, quantify and to reduce the NVD activities and time towards the exalted PCE and therefore to reduce the lead time.

METHODOLOGY

The primary data was collected from personal observations of researchers of bi-fold wallet production lines at different production stages from a leading export-oriented leather products industry in Bangladesh. The secondary data was taken through the internet, books, journals, related studies and other sources of information. The methodology of carrying out this project work is divided into the following steps. In each of the steps, lean tools have been used which have been discussed in each section further [14].

Process mapping ⟶ Takt time calculating ⟶ Lead time counting ⟶ Bottleneck Analysis ⟶ Cause-effect analysis ⟶ Introducing time reducing technique ⟶ Results

Process Mapping

A process map is a planning and management tool that visually describes the flow of work [15]. Process maps show a series of events that produce an end result. It shows who and what is involved in a process and can be used in any business or organization and can reveal areas where a process should be improved [16]. There are many research articles that have discussed about the process mapping techniques used in various small and medium scale manufacturing industries [17]. The present & proposed process mapping of bi-fold wallet production line are shown in the following Figures 1 & 2.

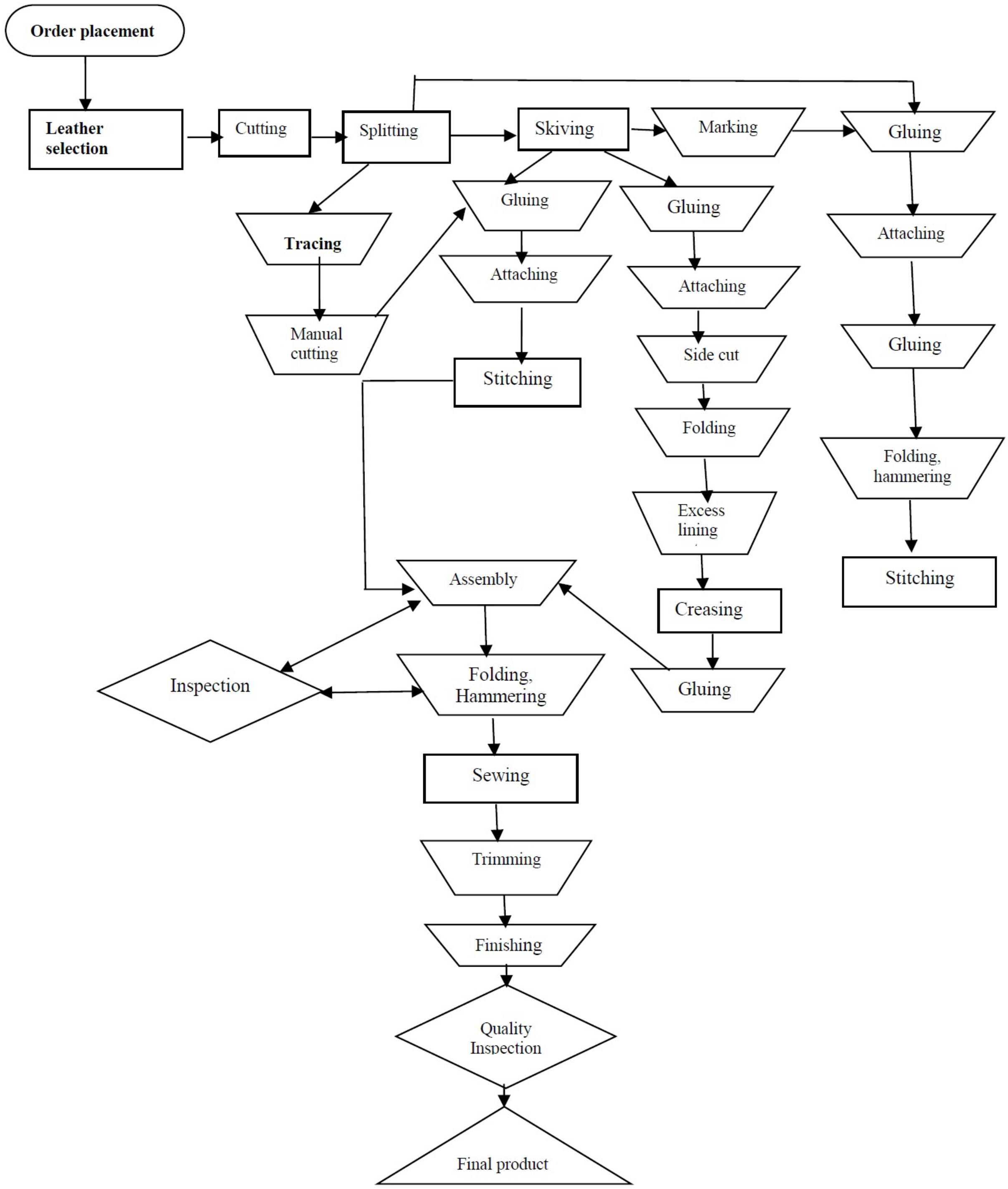

Figure 1. Present process mapping of bi-fold wallet production line

Proposed Process Mapping

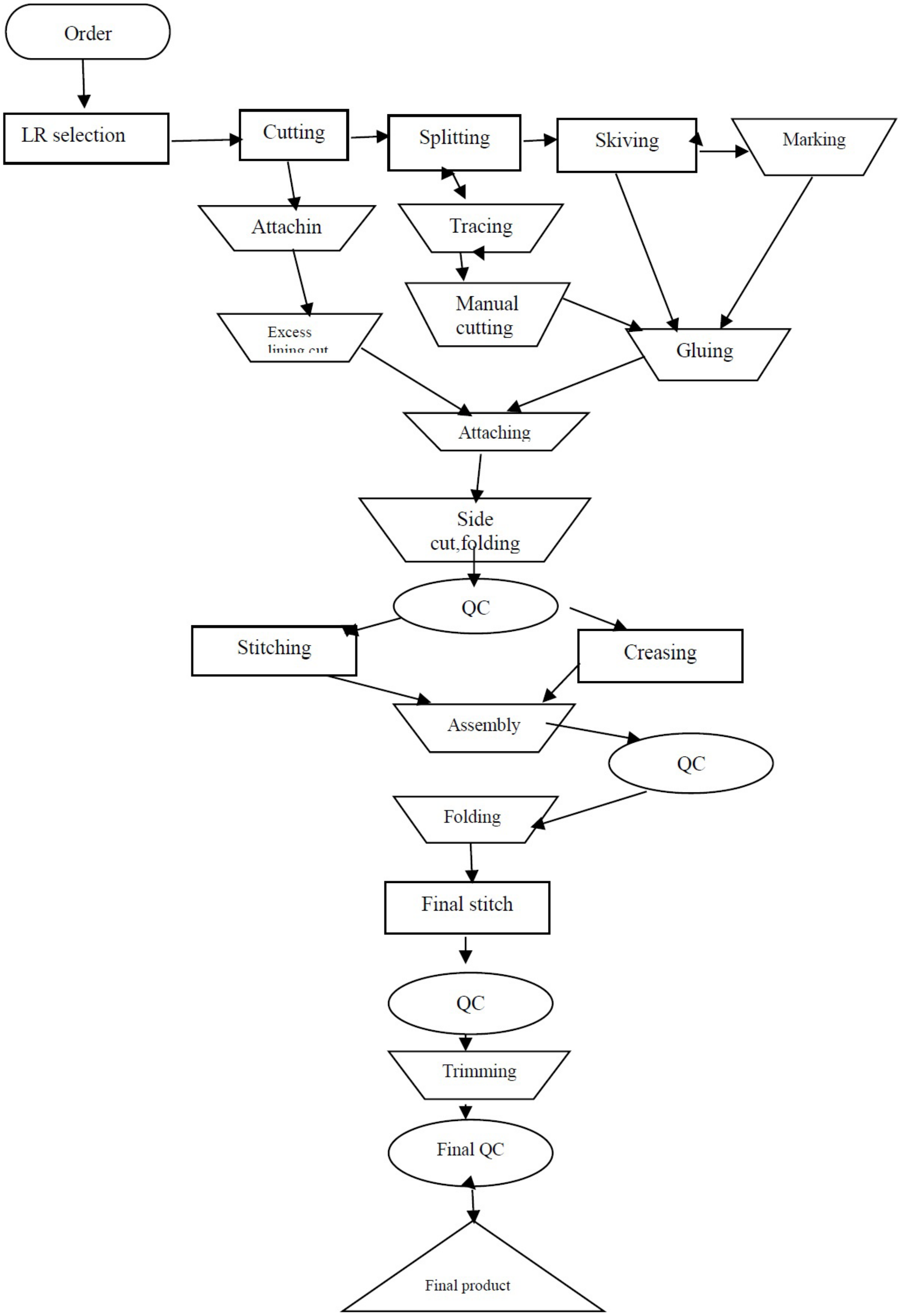

Figure 2. Proposed process mapping of bi-fold wallet production line

Takt Time Analysis

Takt-time is the unit of time in which a product must be produced (supply rate) in order to match the rate at which that product is needed (demand rate) [18]. It is calculated by dividing the total available time per day by the daily customer demand:

Takt time = Available work time/ Customer's demand

Available production time = (7 hours 45 minutes) ×8

= 465 × 8 minutes

= 3720 minutes

Customer's demand is 50 pcs of Double wallet.

Takt Time Formula = 3720/50 = 74.4 minutes/wallet

In this research, after receiving order, the production process started and the final product (Double wallet) was delivered to the customer. The factory had 8 days to deliver 50 pcs of wallet, of which 1 day was off-day. The factory has a 9-hour workday for its workers and staffs, of which 1 hour is allocated lunch break, 15 minutes is wasted in the startup process in the morning.

Data Analysis

Information related to assembly line [19-21] such as production time, inventory storages, inspections, rework loops, number of workers and operational hours per day were collected and documented in Tables 1 & 2.

Table 1: Existing cycle time analysis of bi-fold wallet production line

No	Operation name	Average cycle time (sec)	No. of workers	Waiting time in seconds	Total waiting time	Process gap time (sec)	No. of pcs of work	Total time (sec)
1	Cutting leather, lining, net	6	4				1800	10800
2	Splitting leather	4	1				750	2823
3	Skiving	12	1			86400	250	3000
3	Marking outer top	50	1				50	2500
4	Foam attaching on lining	56	2				50	2800
5	Excess lining cutting	20	1	16	800		50	1000
6	Gluing outer top	25	1	25	1250		50	1250
7	Lining with foam attaching on outer top	9	1	19	950		50	450
8	Adhesive applying on top side	10	1	18	900		50	500
9	Folding, hammering	45	1				50	2250
10	Stitching	10	1			293	50	500
11	Gluing center piece	20	1			293	100	2000
12	Center piece attaching on lining	18	1	2	200		100	1800
13	Stitching	10	1	40	4000		100	1000
14	Gluing on step pocket	10	1			293	360	3600
15	Lining attaching	6	1	4	1440		360	2160
16	Top side folding, hammering	40	2				360	7200
17	Gluing on stamp pocket	12	1	16	2400		150	1800
18	Lining attaching	6	1	22	3300		150	900
19	Side cut for folding	5	1	23	3450		150	750
20	Folding, hammering excess lining cutting	45	1				150	6750
21	Inspection	10	1	35	5250		150	1500

No	Operation name	Average cycle time (sec)	No. of workers	Waiting time in seconds	Total waiting time	Process gap time (sec)	No. of pcs of work	Total time (sec)
22	Creasing	20	1			3750	150	3000
23	Window pocket tracing	18	1				50	900
24	Manual cutting	88	1				50	4400
25	Gluing on window pocket	15	1	73	3650		50	750
26	Net attaching on window pocket	10	1	78	3900		50	500
27	Side cut for folding	5	1	85	4250		50	250
28	Top side folding, hammering	23	1	67	3350		50	1150
29	Inspection	18	1	72	3600		50	900
30	Creasing	20	1			350	50	1000
31	Gluing on both sides of step pocket	5	1				360	1800
32	Assembling 3 step pockets	25	1				120	3000
33	Stamp pocket placing	12	1	17	850		120	1440
34	Excess lining cutting	20	1	11	550		50	1000
35	Stitching	10	1			4050	50	500
36	Assembling 2 step pockets	15	1				50	750
37	Window pocket placing	20	1				50	1000
38	Excess lining cutting	22	1				50	1100
39	Stitching	5	1			2850	50	250
40	1 step pocket, 1 cut pocket attaching	40	2			405	100	4000
41	Joining window and 1 cut pocket by stitching	10	1	17	850		50	500
42	Assembling asther-1	50	1			285	50	2500
43	Assembling asther-2	50	1			300	50	2500
44	Joining by stitching	10	1			2350	50	500
45	Attaching Asther on outer top	55	1				50	2750
46	Gluing three sides of outer	20	1	35	1750		50	1000
47	Folding, hammering	62	1				50	3100
48	Final stitching	12	1	50	2500		50	600
49	Trimming, thread cutting	25	1	37	1850		50	1250
50	Final checking	50	1	12	600		50	2500
51	Packaging	30	1	32	1600		50	1500
	Total	1244			53240	101619		102373

Present Process Cycle Efficiency

Process Cycle Efficiency (PCE) is measured as the percentage of ration of VD time and lead time, where lead time is the summation of value-added time (VD) and non-value-added time (NVD) [22]. PCE is a measure of the relative efficiency in a process - it represents the percentage of value-add time (changing form, fit, function) of a product down the critical path.

Value added time = 102373 seconds = 28.44 hrs

Non-value-added time = Set-up time + Total waiting time + Total process gap time

= (10800+53240+101619) seconds = 165659 seconds = 46.02 hrs

Lead time = Value added time + Non-value-added time

= (102373+165659) seconds = 268032 seconds = 74.45 hrs

No. of worker = 14

Productivity = 0.048

PCE = (Customer Value Added Time ÷ Process Lead Time) ×100%

= (102373 ÷ 268032) ×100% = 38.19%

Bottleneck Analysis

The bottleneck of a production system is recognized as the machine that has the strongest impact on the overall system performance [23]. By definition, a bottleneck is a phenomenon where the competency of a complete system or line is restricted or limited by a single or limited number of components or resources and analysis of such event is called bottleneck analysis. Hence, bottleneck analysis is nothing but identifying which part/machine of the manufacturing process/line limits the overall output and focuses on improvement the performance of that part/machine of the process/line [24]. Bottleneck analysis is usually done along with the Time Study Method. From the process map and cycle time analysis table, we can calculate the time required in each path.

Path-1: Splitting-Skiving-Making-Gluing-Attaching-Gluing-Folding-Stitching = 297 seconds

Path-2: Splitting-Gluing-Attaching-Stitching =106 seconds

Path-3: Splitting-Skiving-Gluing-Attaching-Side Cut-Folding-Excess lining cut-Creasing =270 seconds

Path-4: Splitting-Skiving-Gluing-Attaching-Side Cut-Folding-Excess lining cut-Creasing =270 seconds

Path-5: Splitting-Tracing-Manual Cutting-Gluing-Attaching-Side Cut-Folding-Creasing =576 seconds

Path-6: Creasing-Gluing-Assembly-Folding-Final Stitch-Trimming-Finishing-Inspection-Final product= 736 seconds

Here, Path-6 takes the longest period of time to complete one cycle. So, the Bottleneck is Path-6.

Cause-Effect Analysis

As the Ishikawa diagram is prior to any data analysis, every possible cause is taken into consideration. It is a visualization tool for categorizing the potential causes of a problem in order to identify its root causes [25]. Although it was originally developed as a quality control tool, it can be used just as well in other ways [26]. For instance, it can be used to discover the root cause of a problem, uncover bottlenecks in your processes, identify where and why a process is not working etc. Since we found that lead time is 88.8 minutes/wallet, whereas, takt time is 93 minutes/wallet; this is a serious problem that may cause huge delay in delivery. Therefore, we used Fishbone Diagram to find out possible cause behind this which is shown in the following Figure 3.

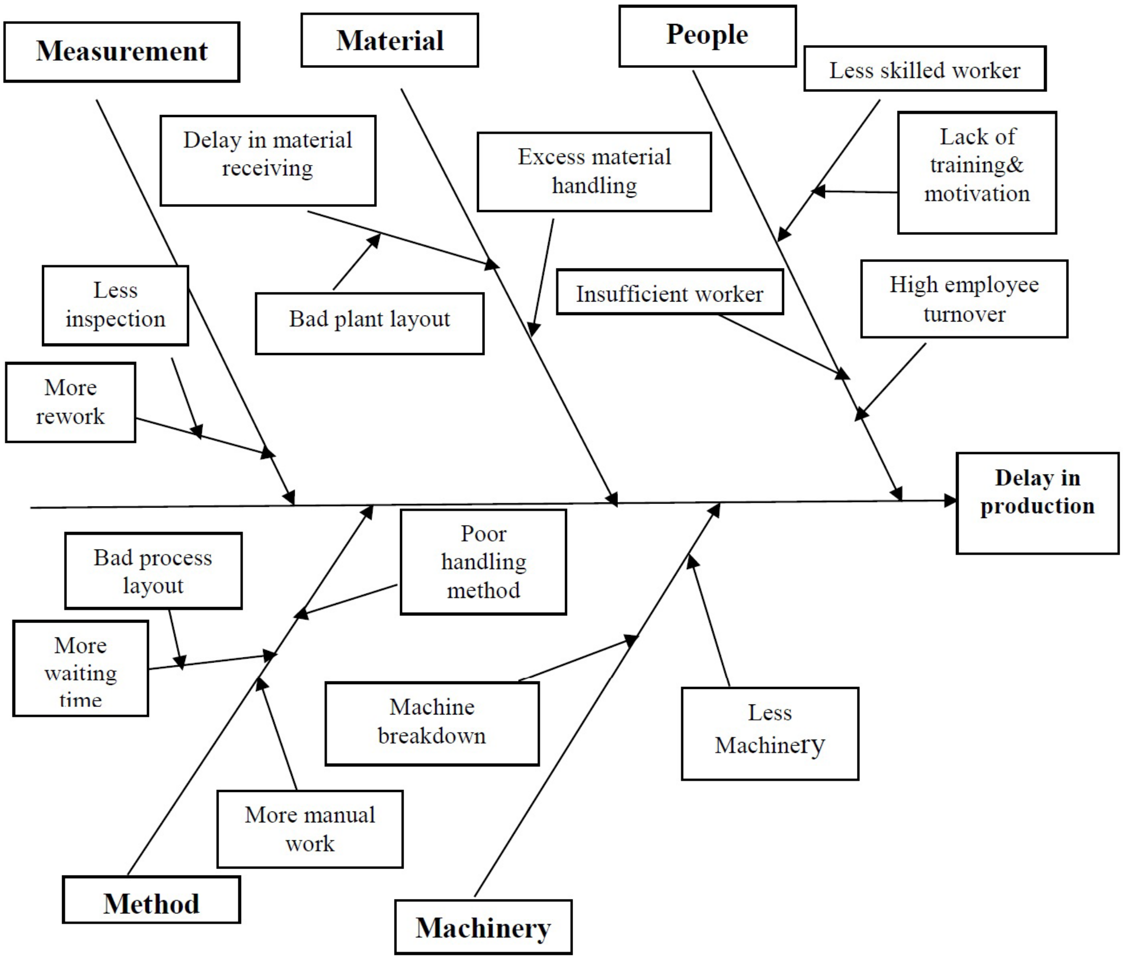

Figure 3. Cause-effect analysis of bi-fold wallet production line

Pareto Analysis

It is a statistical technique in decision making that is used for selection of a limited number of tasks that produce significant overall effect. It uses the Pareto principle – the idea that by doing 20% of work, 80% of the advantage of doing the entire job can be generated [27]. The Pareto Principle also known as the "80/20 Rule" which is the idea that 20% of causes generate 80% of results [28-30]. In this study, by using this tool it was tried to find out the 20% of causes that is generating 80% NVD activities. This tool focuses on the most damaging causes on a project.

In this essence, the application of the Pareto chart consisting of causes for downtime or NVD activities along the X axis while the Y axis represents the cumulative percentage of downtime. Most of the NVD activities were documented on sewing, pre-lasting, post-lasting and finishing steps where these were frequently observed due to different causes. The highest frequency of NVD activities that derived the down time were found for mainly needle & threads breakage while the lowest frequency was varied shown in the following Figure 4.

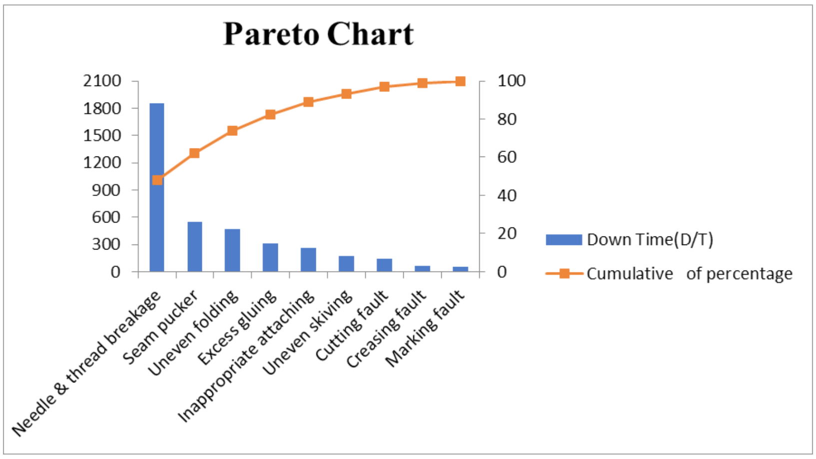

Figure 4. Pareto chart of bi-fold wallet production line

Table 2: Cycle time analysis for proposed way of bi-fold wallet production line

No	Operation name	Average cycle time (sec)	No. of workers	Waiting time (sec)	Total waiting time	Process gap time (sec)	No. of pcs of work	Total time (sec)
1	Cutting leather, lining, net	6	4				1800	10800
2	Splitting leather	4	1				750	2823
3	Skiving	12	1				250	3000
4	Marking outer top	50	2				50	2500
5	Foam attaching on lining	56	2				50	2800
6	Excess lining cutting	20	1	16	800		50	1000
7	Gluing on outer top	25	1				50	1250
8	Lining & foam attaching on outer top & gluing on top side	19	1	6	300		50	950
9	Folding, hammering	45	1				50	2250
10	Stitching	10	1			237	50	500
11	Gluing center piece	20	1			237	100	2000
12	Center piece attaching on lining	18	1	2	200		100	1800
13	Stitching	10	1	10	1000		100	1000
14	Gluing on step pocket	10	1			237	360	3600
15	Lining attaching	6	1	4	1440		360	2160
16	Top side folding, hammering	40	1				360	14400
17	Gluing on stamp pocket	12	1			237	150	1800
18	Lining attaching & side cut	11	1				150	1650
19	Folding, hammering excess lining cutting	45	1				150	6750
20	Inspection	10	1	19.36	2905		150	1500
21	Creasing	20	1				150	3000
22	Window pocket tracing	18	1				50	900
23	Manual cutting	88	2				50	4400
24	Gluing on window pocket, net attaching & side cut	30	1	14	700		50	1500

No	Operation name	Average cycle time (sec)	No. of workers	Waiting time (sec)	Total waiting time	Process gap time (sec)	No. of pcs of work	Total time (sec)
25	Top side folding, hammering & inspection	41	1	3	150		50	2050
26	Creasing	20	1	24	1200		50	1000
27	Gluing on both sides of step pocket & assembling 3 step pockets	40	1				120	4800
28	Stamp pocket placing & excess lining cutting	33	1	7	840		120	3960
29	Stitching	10	1	30	3600		120	1200
30	Assembling 2 step pockets	15	1				50	750
31	Window pocket placing	20	1				50	1000
32	Excess lining cutting	22	1				50	1100
33	Stitching	10	1	12	600		50	500
34	1 step pocket, 1 cut pocket attaching	40	2				100	4000
35	Joining window and 1 cut pocket by stitching	10	1	17	850		50	500
36	Assembling asther-1	50	1				50	2500
37	Assembling asther-2	50	1				50	2500
38	Joining by stitching	10	1	40	2000		50	500
39	Attaching asther on outer top	55	2				50	1375
40	Gluing three sides of outer	20	1	15	750		50	1000
41	Folding, hammering	62	1				50	3100
42	Final stitching, thread cutting	45	1	17	850		50	600
43	Final checking	50	1	12	600		50	2500
44	Packaging	30	1	32	1600		50	1500
		Total =1218			Total =20385	Total =948		Total =110768

Process Cycle Efficiency after using Lean Tools:

Value added time = 110768 seconds= 30.8 hrs

Non-value-added time = Set-up time + Total waiting time + Total process gap time

= (10800+20385+948) seconds= 32133 seconds=8.93 hrs

So, Lead time = Value added time + Non-value-added time

= (110768+32133) seconds = 142901 seconds=39.69 hrs

No. of workers = 14

Productivity = 0.089

Productivity improvement = (0.089-.048)/0.048 ×100%=85.4%

PCE = (Customer Value Added Time ÷ Process Lead Time) ×100%

= (110768 ÷ 142901) ×100%= 77.51 %

Existing Productivity:

Value added time = 102373 seconds or, 28.43 hrs

Non-value-added time = 165659 seconds or 46.02 hrs

Lead time = 268032 seconds or 74.45 hrs
Productivity = 0.048
Process cycle efficiency =38.19%

Productivity after using Lean Tools:
Value added time = 110768 seconds or 30.77 hrs
Non-value-added time = 32133 seconds or 8.92 hrs
Lead time = 142901 seconds or 39.69 hrs
Productivity = .089
Process cycle efficiency = 77.51%

Results:
Productivity improvement = (.089-.048)/.048 ×100%= 85.42%
Lead time reduction = (74.45-39.69)/74.45×100% =46.69%
Value added time increased = (30.77-28.43)/28.43×100%= 8.23%
Non- value-added time reduction = (46.02-8.93)/46.02×100% = 80.59%
PCE improvement = (77.51-38.19) %= 39.35%

CONCLUSION

The leather products industry is one of the key export-earning sectors in Bangladesh. Productivity improvement is a crucial matter in this industry. The profit earning of this industry totally rely on productivity improvement. The implementation of the lean concept in the leather products industry is primarily focused in order to reduce lead time and improve PCE. This model paves the way to ease implementation of lean concepts in leather products industry not only in Bangladesh but around the globe.

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POLYAMIDE/POLYETHYLENE/GRAPHITE NANOCOMPOSITES: DEVELOPMENT AND MORPHO-STRUCTURAL AND PHYSICAL-MECHANICAL CHARACTERISATION

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POLYAMIDE/POLYETHYLENE/GRAPHITE NANOCOMPOSITES: DEVELOPMENT AND MORPHO-STRUCTURAL AND PHYSICAL-MECHANICAL CHARACTERISATION

ABSTRACT. This paper presents the development of bipolymer nanopolymers - polyamide and polyethylene - compatibilised with polyethylene-graft-maleic anhydride and graphite nanoparticles. Polyamide/polyethylene (PA/PE) composites are studied because both components are relatively inexpensive, advantageous and are processed by injection. Compatibilisation of binary polymer compounds can be accomplished by adding a grafted copolymer, the segments of which have physical or chemical affinity with the two immiscible homopolymers. In this case, polyethylene-graft-maleic anhydride (PE-g-MA) was used. Graphite-containing polymer composites are considered a new generation of materials with predefined properties, in this case, resistance to impact. The combined effects of graphite and compatibilizing polymer (PE-g-MA) were studied on the structure and properties of the new materials. The tested nanocomposites were characterized morpho-structurally (SEM, FT-IR spectrometry) and physico-mechanically.

KEY WORDS: nanocomposites, compatibiliser, graphite, morpho-strucutral characterisation, bipolymer

NANOCOMPOZITE POLIAMIDĂ/POLIETILENĂ/GRAFIT: REALIZARE ȘI CARACTERIZARE MORFO-STRUCTURALĂ ȘI FIZICO-MECANICĂ

REZUMAT. În această lucrare se prezintă realizarea unor nanocompozite bipolimerice – poliamidă și polietilenă – compatibilizate cu polietilenă grefată cu anhidridă maleică și nanoparticule de grafit. Compozitele din poliamidă/polietilenă (PA/PE) sunt studiate deoarece ambele componente sunt relativ ieftine, cu proprietăți avantajoase și sunt prelucrate prin injecție. Compatibilizarea compușilor polimeri binari poate fi realizată prin adăugarea unui copolimer grefat, ale cărui segmente au afinitate fizică sau chimică cu cei doi homopolimeri imiscibili. În acest caz, s-a utilizat polietilenă grefată cu anhidridă maleică (PE-g-MA). Compozitele polimere conținând grafit sunt considerate o nouă generație de materiale cu proprietăți prestabilite, în acest caz de rezistență la impact. Au fost studiate efectele combinate ale grafitului și polimerul compatibilizator (PE-g-MA) asupra structurii și proprietăților materialelor noi experimentate. Nanocompozitele experimentate au fost caracterizate morfo-structural (SEM, spectrometrie FT-IR) și fizico-mecanic.

CUVINTE CHEIE: nanocompozite, compatibilizator, grafit, caracterizare morfo-structurală, bipolimer

NANOCOMPOSITES POLYAMIDE/POLYÉTHYLÈNE/GRAPHITE: RÉALISATION ET CARACTÉRISATION MORPHO-STRUCTURELLE ET PHYSICO-MECANIQUE

RÉSUMÉ. Dans cet article on présente la réalisation des nanopcomposites bipolymères - polyamide et polyéthylène - compatibilisés avec le polyéthylène greffé avec de l'anhydride maléique et des nanoparticules de graphite. Les composites polyamide/polyéthylène (PA/PE) sont étudiés car les deux composants sont relativement peu coûteux, avantageux et sont traités par injection. La compatibilité des composés polymères binaires peut être réalisée en ajoutant un copolymère greffé dont les segments ont une affinité physique ou chimique avec les deux homopolymères non miscibles. Dans ce cas, du polyéthylène greffé de l'anhydride maléique (PE-g-MA) a été utilisé. Les composites contenant des graphites contenant des polymères sont considérés comme une nouvelle génération de matériaux aux propriétés prédéfinies, dans ce cas la résistance aux chocs. Les effets combinés du graphite et du polymère compatibilisant (PE-g-MA) ont été étudiés sur la structure et les propriétés des nouveaux matériaux expérimentaux. Les nanocomposites expérimentaux ont été caractérisés du point de vue morpho-structurel (MEB, spectrométrie FT-IR) et physico-mécanique.

MOTS CLÉS : nanocomposites, compatibilisant, graphite, caractérisation morpho-structurelle, bipolymère

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INTRODUCTION

Compound polymers are widely used to prepare new materials. The disadvantage of this study is that polymers are not usually compatible, and preparation of compounds with suitable properties (mainly processing and physical-mechanical) is not high performance. During the last few decades, polymer-matrix composites have been of interest to industry and academia, especially in the areas of automotive, aerospace, electronic systems, medical products, civil construction, chemical industries and other consumer applications [1]. Polyamide/polyethylene (PA/PE) composites are interesting, because both components are relatively low cost, with advantageous properties and are processed by melt-injection [2]. Some researchers worked on blending PA6/HDPE (polyamide 6/high density polyethylene) with varying compositions. They reported that the composition PA6/HDPE (2%) had increased modulus, hardness and strength [3]. Zhou *et al*. [4] studied the PA6/PPS-CF (carbon fiber) composites and reported that increase in addition of carbon fiber (CF) content in PA6/PPS composite decreases the impact strength. Li *et al*. [5] investigated the mechanical properties of PA6-polyurethane (PU) block copolymer reinforced short glass fibers (SGF) and concluded that impact strength decreased with addition of SGF. Compatibilisation of binary polymer compounds can be accomplished by adding a grafted copolymer, the segments of which have physical or chemical affinity with the two immiscible homopolymers [3]. In this case, polyethylene-graft-maleic anhydride (PE-g-MA) was used. Polymer nanocomposites containing graphite were considered a new generation of composite materials due to their unique properties, attributed to the high aspect ratio of inorganic granules [4, 5]. Graphite nanoparticles are used as reinforcement in fabrication of polymer composites to enhance mechanical, electrical and thermal properties [6-10]. Some researchers tested the mechanical properties of high density polyethylene nanocomposites reinforced with graphite [11-14] or oxidized graphite [15]. The combined effects of graphite and compatibilising polymer (PE-g-MA) treatment on the structure and properties of graphite PA/PE/g-MA composites were studied. The optimal formulation was used to prepare a series of nanocomposites in various technological conditions. The correlation among their physical-mechanical and morpho-structural properties was also studied.

EXPERIMENTAL

Materials and Methods

Materials

Composites contain the same two polymer components in variable proportions: the polyamide (PA) elastomer PA6 (POLIMID B AV NATURALE – Poliblend Engineering Polymers, Italy), with the following characteristics: specific weight, 1.40g/cm^3; impact resistance, 1.4 KJ/m^2; melt flow index (230°C/2.16 kg), 14g/10 min; melt temperature, 215-230°C; and high density polyethylene (HDPE -TIPELIN 1108J - for impact and injection molding - MOL Petrochemicals Group) with the following characteristics: impact resistance, 3 KJ/m^2; flex module, 1.5 Mpa; M.F.I. (190°C/2.16 kg), 8g/10 min; specific weight, 0.96 g/cm^3; and melting point 170-180°C. Other components: compatibilizers - polyethylene grafted with maleic anhydride PE-g-MA from Sigma Aldrich and graphite nanoparticles (G), black pellets with dimensions 3-4 nm and 99,5% concentration from Skyspring Nanomaterials USA. As graphite is a material with high chemical inertia, to increase its reactivity, it was compounded with molybdenum bisulfite, in proportion of 0.2% compared to the polymer, purchased from Sigma Aldrich.

Preparation of Polymer Nanocomposites Polyamide/Polyethylene/Carbon Fibres

Polyamide (PA), polyethylene (HDPE), PE-g-MA, graphite nanoparticles (G) and molybdenum bisulfite were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 2 min. at 230°C to melt the plastomer, mixed for 3 min. at 240°C, and 2 min. at 200°C for homogenisation. The total time was 7 minutes. Table 1 shows tested formulations.

Table 1: Control and PA/PE-gMA/HDPE/G polymer nanocomposite formulations with varying G amounts (GPE1-0,1%; GPE2-0,5%; GPE3-1%; GPE4-2%; GPE5-3%)

Compound	GPE1	GPE2	GPE3	GPE4	GPE5
Polyamide - sebamid	270	270	270	270	270
Polyethylene	30	30	30	30	30
Graphite	0.3	1.5	3	6	9
PE-g-MA	9	9	9	9	9
Molybdenum bisulphite	0.6	0.6	0.6	0.6	0.6
Total	309.9	311.1	312.6	315.6	318.6

The Brabender mixing diagrams, figures 1 and 2, show that the temperature in the chamber drops from 220 to 213°C for higher percentages of graphite (starts at 213°C, decreases to about 140°C with a peak of 150°C at the end, in the case of the 0.1 g percentage, and a lower peak at 175°C in the case of 3% G percentage), and there are minor time variations in achieving maximum mixing forces. The maximum force is achieved at 90 s in the case of 0.1% G percentage and 80 s. in the case of maximum percentage of 3% and its value exceeds 400 Nm.

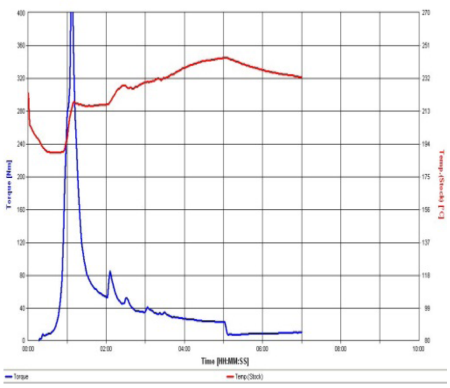

Figure 1. Brabender mixing diagram for PA

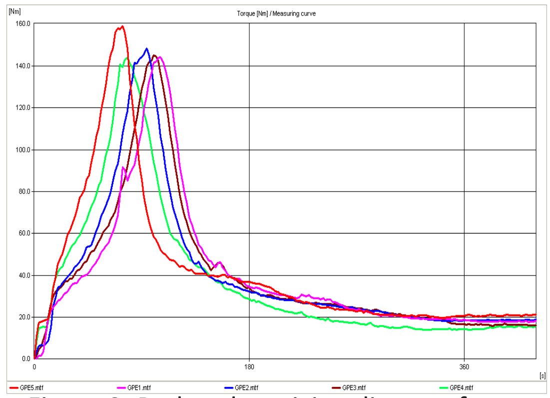

Figure 2. Brabender mixing diagram for composite GPE 1-5

The compounds were then compression-molded (using an electrically heated laboratory press) to achieve a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN.; temperature 230°C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Testing Methods

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

Hardness of the samples was measured by Shore “D” Durometer according to SR ISO 7619-1:2011.

Melt flow index. Samples were tested using a Haake Melt Flow Index device that displays values for the melt volume rate (MVR – cm^3/10min) as well as melt flow rate (MFR – g/10min). Working temperature (chamber temperature up to 350°C), 2 heating areas, operating according to ISO 1133 standard.

Shock resistance tests were conducted using an INSTRON equipment with pendulum hammer, which can carry out Izod or Charpy tests with a wide range of testing capacity (0.7-27.847 J), according to STAS 7310-87.

SEM. Films obtained by evaporating the disperse medium at 105°C from the dispersions GPE1-GPE5 were cryogenically fractured and their cross sections were analyzed by SEM, using an ESEM QUANTA 200 instrument operating in low vacuum, equipped with LFD detector.

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

RESULTS AND DISCUSSIONS

The polymer structures obtained, in initial state and after accelerated ageing were characterized in terms of their physical-mechanical properties, and results are presented in table 2. Analyzing the values of physical-mechanical tests reveals the following:

- Hardness of PA/PE-g-MA/G polymer nanocomposites increases by two percents, proportionally with the amount of oxidized graphite compared to that of polyamide (sample PA - 78°Sh). The higher value is given by the composite with 5% oxidized graphite – GPE5-80°Sh.

Table 2: Physical-mechanical characteristics of studied PA/GO polymer composites

Mixtures	PA	GPE1	GPE2	GPE3	GPE4	GPE5
NORMAL STATE						
Hardness °Sh D SR ISO 7619-1:2011	78	78	79	79	79	80
Tensile strength, N/mm^2 SR ISO 37:2012	30.5	21.0	24.4	25.5	26.5	36.4
Density, g/cmm^3 SR ISO 2781:2010	1.14	1.14	1.14	1.14	1.14	1.15
Izod shock resistance, $[KJ/m^2]$ STAS 7310-87	2.5	6.12	7.23	7.81	7.26	6.84
Melt flow index - 230°C pressure of 5 Kg, g/10min	160	169	180	199	174	139
ACCELERATED AGEING 2000 X 168 h SR ISO 188 : 2007						
Hardness °Sh D SR ISO 7619-1:2011	77	77	77	77	78	79
Tensile strength, N/mm^2 SR ISO 37:2012	26.8	28.5	30	37.7	49.2	51.6

- Similar to hardness, the value of tensile strength of nanocomposites increases compared to the value specific to polyamide (sample PA – 30.5 N/mm^2), the higher value is that of sample GPE5-36.4 N/mm^2 (3% G).
- Density increases proportionally with the amount of graphite added to the mixture.
- In order to test resistance to high temperature, accelerated ageing tests were conducted on the samples conditioned at 200°C for 168h. The analysis of obtained values shows they have changed very little, the samples were not damaged and did not change their shape.
- In order to estimate the resistance of brittleness of polymer nanocomposites, they were tested by Izod shock resistance method (STAS 7310-87). This determination is the most important one due to the fact that one of the requirements of polymer nanocomposites is optimized shock resistance, for use in heavy blow conditions. PA value is 2.5 KJ/m^2. All tested nanocomposites have increased values compared to the control sample (PA), ranging between 6.12 and 7.81 KJ/m^2. Increased values were obtained for samples GPE3 (PA/PE-g-MA/PE/G-1% G) – 7.81 KJ/m^2 and GPE4 (PA/PE-gMA/PE/G-2% G) – 7.26. Graphene concentrations higher than 1% lead to decreases in shock resistance values similarly to tensile strength values. This leads to the conclusion that percentages in the 0.1-1% range lead to maximum values of Izod shock resistance

parameters, higher percentages result in lowering this parameter's values.

- In order to establish the technological parameters for processing GPE1-GPE5 polymeric architectures in finished products, tests were carried out to determine the melt flow index at a temperature of 230°C and a pressure of 5 kg. The analysis of the obtained values (Table 2) shows an increased flow compared to PA (160 g/10 min) for the samples: GPE1 (0.1% G) - 169 g/10 min, GPE2 (0.5% 180 g/10 min, GPE3 (1% G) 199 g/10 min, GPE4 (2% G) 174 g/10 min and GPE5 (3% G) 139 g/10 min. Graphite concentrations higher than 1% lead to lower melt flow index values, but higher than the sample PA.
- SEM image of the cross section of the fracture obtained from polyamide elastomer (PA), presented in Figure 3, emphasizes a lamellar structure. On the other hand, the SEM images of cross sections of the fracture obtained from the other three samples (PA, GPE1, GPE3 and GPE5), shown in the Figures 3-6, in which the nanocomposites with rates differ from G, have completely different aspects: they show a biphasic type morphology consisting in spheroid particles distributed within a matrix with less evident lamellar morphology. The number of particles increases directly with the amount of G of the nanocompound.

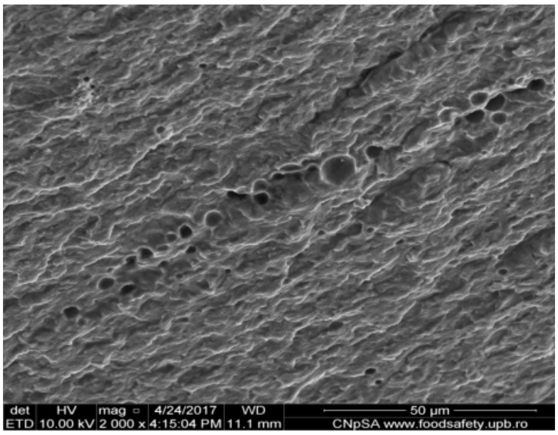

Figure 3. SEM image for PA sample

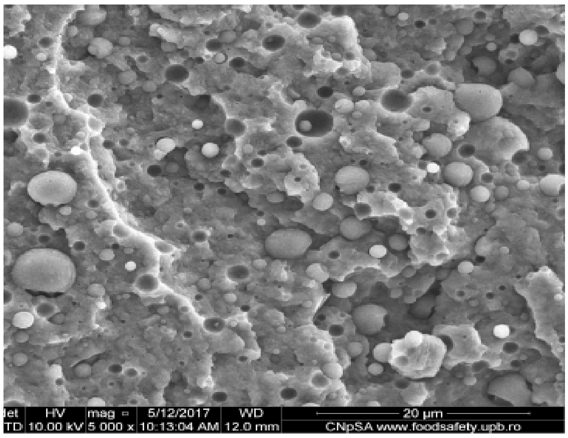

Figure 4. SEM image for GPE1 sample

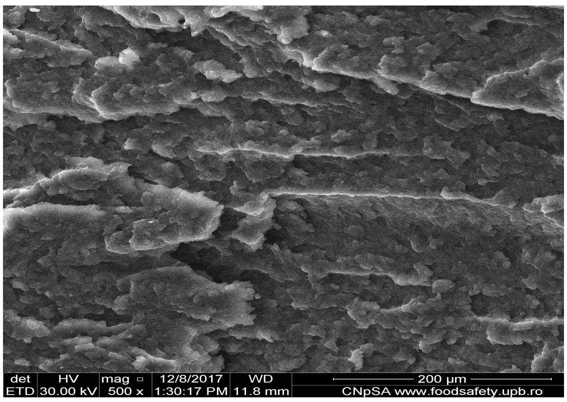

Figure 5. SEM image for GPE3 sample

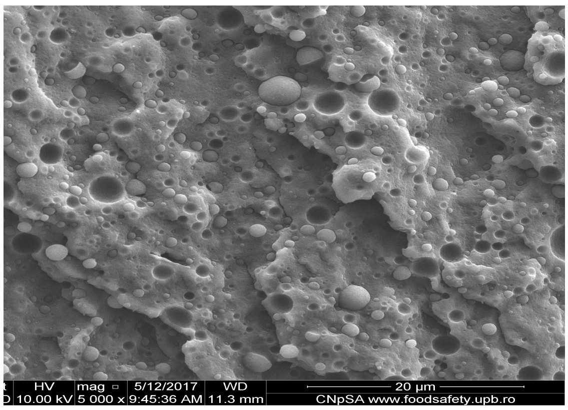

Figure 6. SEM image for GPE5 sample

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

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

1. The IR spectrum recorded for polyamide (figure 7) shows absorption at the following wavelengths: 1190 cm^{-1} specific to CO-CH_2 bonds, 1275 cm^{-1} absorption specific to C-O (carboxy), 1567 cm^{-1} absorption specific to the NH group, 1633 cm^{-1} absorption specific to the C=C bond, and the absorption band at 3300 cm^{-1} is specific to C-N bonds.
2. The overlapping spectra (figures 8, 9) show the presence of PA and very weakly G in compounds. The basic structural element of polyamide is the amide group (-CO-NH-), while graphite, C-O, C=C and C=O, and absorptions for the two materials overlap in the spectra. The major presence of PA is seen from the intensity of characteristic peaks.

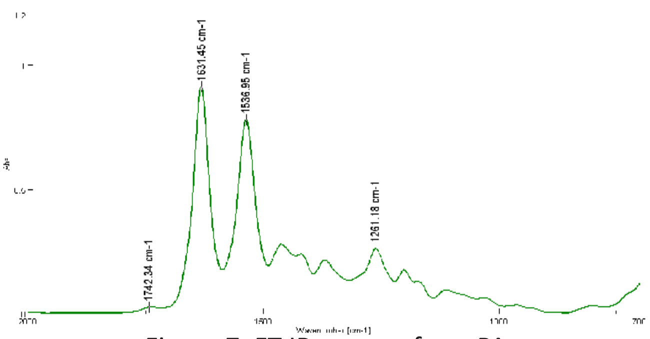

Figure 7. FT-IR spectra from PA

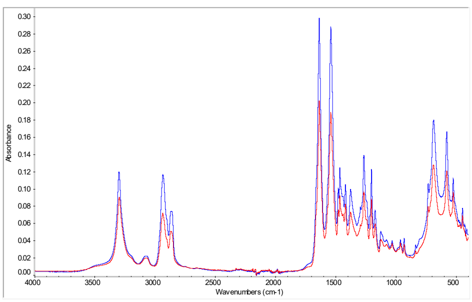

Figure 8. FT-IR spectra from PA/-GPE3

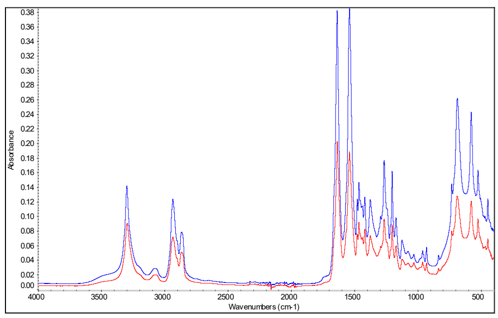

Figure 9. FT-IR spectra from PA/-GPE5

CONCLUSIONS

The paper presents the study of the new nanostructured polymer composites from polyamide/oxidized graphite nanoparticles-PA/G to manufacture, by injection, bearing seals, contact plates, and other components for the railway industry, with shock resistance higher than 5-8 kJ/m², wear resistance below 100 mm^3, resistance to temperatures of -40 - 240°C, resistance to impact and to outdoor applications, with temperatures ranging from -40 to +60°C, in rain, snow or sunshine.

Polyamide and oxidized graphite were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 2 min. at 230°C to melt the plastomer, mixed for 3 min. at 240°C and 2 min. at 200°C for homogenisation.

The polyamide/oxidized graphite nanocomposites were characterized by scanning electron microscopy (SEM) and Fourier transformation infrared spectroscopy (FT-IR) and physico-mechanically.

Graphene oxide concentrations higher than 1% lead to decreases in shock resistance values and tensile strength values. This leads to the conclusion that percentages in the 0.1-1% range lead to maximum values of physical-mechanical parameters.

Acknowledgements

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SYNERGIC EFFECT OF BOVINE HAIR HYDROLYSATE AND SULFITED LIGNINS ON LEATHER RETANNING

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SYNERGIC EFFECT OF BOVINE HAIR HYDROLYSATE AND SULFITED LIGNINS ON LEATHER RETANNING

ABSTRACT. The aim of this work was the study of bovine hair hydrolysate and sulfited lignins effect in leather retanning process. Bovine hair from hair-saving process was thermally digested in alkaline conditions and after pH adjustment and concentration, was tested as retanning agent. Physical-mechanical tests were applied to evaluate the tear strength and lastometer test (in order to evaluate the grain cracking), and leather behavior regarding softness, grain firmness, and color. The experiments showed that hair hydrolysate, sulfited lignins and its mixtures can be used as retanning agents with good results when compared with a dispersing agent and a synthetic tannin. The keratin hydrolysate was also tested as finishing agent against casein and showed that it is not a good alternative.
KEY WORDS: hair-saving, keratin, leather retanning, sulfited lignin

EFECTUL SINERGIC AL HIDROLIZATULUI DIN PĂR DE BOVINE ȘI AL LIGNINEI SULFITATE LA RETĂBĂCIREA PIELII

REZUMAT. Scopul acestei lucrări a fost studierea efectului hidrolizatului din păr de bovine și al ligninei sulfitate în procesul de retăbăcire a pielii. Părul de bovine din procesul de depărare a fost digerat termic în condiții alcaline și, după ajustarea pH-ului și concentrare, a fost testat ca agent de retăbăcire. S-au efectuat teste fizico-mecanice pentru a evalua rezistența la rupere și la crăparea feței și comportamentul pielii în ceea ce privește moliciunea, fermitatea și culoarea. Experimentele au arătat că părul hidrolizat, lignina sulfitată și amestecurile acestora pot fi utilizate ca agenți de retăbăcire cu rezultate bune în comparație cu un agent de dispersie și un tanin sintetic. Hidrolizatul de cheratină a fost, de asemenea, testat ca agent de finisare comparativ cu cazeina și s-a demonstrat că nu este o alternativă bună.
CUVINTE CHEIE: valorificarea părului, cheratină, retăbăcirea pieilor, lignină sulfitată

L'EFFET SYNERGIQUE DE L'HYDROLYSAT DE POILS DE BOVINS ET DE LA LIGNINE SULFITÉE SUR LE RETANNAGE DU CUIR

RÉSUMÉ. Le but de cet article a été d'étudier l'effet de l'hydrolysat de poils de bovins et de la lignine sulfitée dans le processus de retannage du cuir. On a digéré thermiquement les poils de bovins provenant du procédé d'épilage des poils dans des conditions alcalines et, après ajustement du pH et concentration, on a testé l'agent de retannage. Des tests physico-mécaniques ont été appliqués pour évaluer la résistance à la déchirure et l'essai du lastomètre (afin d'évaluer le gerçure de la fleur), et le comportement du cuir en ce qui concerne la douceur, la fermeté et la couleur de la fleur. Les expériences ont montré que l'hydrolysat de poils, la lignine sulfitée et leurs mélanges peuvent être utilisés comme agents de retannage avec de bons résultats en comparaison avec un agent dispersant et un tanin synthétique. L'hydrolysat de kératine a également été testé comme agent de finition contre la caséine et on a montré que ce n'est pas une bonne alternative.
MOTS CLÉS : récupération de poils, kératine, retannage du cuir, lignine sulfitée

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INTRODUCTION

Tanning process transforms animal hide into leather through a sequence of chemical, physical and mechanical operations including liming process. Liming process involves the removal of hair from epidermis of animal hide promoting swelling and preparing collagen and elastic fibers to be tanned.

This process, at industrial scale, is done with the application of alkali compounds such as calcium and sodium hydroxide, a reducing agent such as sodium sulfide or sodium sulfydrate, and some auxiliary chemicals [1]. Liming is normally done through the destruction of the hair fiber structure dissolving it in the bath. Another liming way is done with hair recovery preserving the hair fiber structure, usually known as the hair-saving liming process. Hair is mainly constituted by 95% keratin, being the other 5% non-keratin proteins [2]. Treatment and valorization of leather industry solid wastes is constantly developing, and the study of hair recovered in the hair-saving process is not an exception [3-5].

The pulp and paper industry produces sulfited lignins, which show a large field of applications. In the leather industry, this kind of substances could be used as dispersing and retanning agents. There are several types of sulfited lignins, depending on the raw material and type of process used in the pulp and paper production unity. One type of sulfited lignin particularly interesting to the tanning industry is the eucalypt origin, produced with magnesium sulfite [6].

Leather treatment comprises, among several processes and mechanical operations, the retannage process. This process is used to improve roundness, grain firmness and leather filling using vegetable tannins, syntans and various types of resins.

Research work has been published on the use of collagen hydrolysates obtained from chrome shavings and fleshings to develop products for leather retannage. Acrylic resins are used to prepare copolymers with collagen hydrolysates for leather retanning. Gluteraldehyde is also used to prepare copolymers with collagen hydrolysates for leather retanning [7-9].

In this work, the synergic effect of bovine hair hydrolysate and sulfited lignins is studied in the leather retanning process; hair hydrolysate was also tested as finishing agent against casein.

EXPERIMENTAL

Materials and Methods

Hair Hydrolysate and Retanning Agents Preparation

The hair used in this work was obtained from a hair-saving liming process described in Table 1. This process was developed by *CIETI* and *Curtumes Aveneda*, a Portuguese tannery.

The process was made on small pieces of bovine salted hide, after a normal soak. The quantity of chemicals was calculated as the % based on salted hide weight.

Table 1: Hair-saving Liming Process

Chemical	Chemical Quantity (%)	Time (min)	Temperature (ºC)	Control
Water	50			
Mazyme SDL (Amylase)	0.3	30	28	
Borron DL (Lipase)	0.15			
		Add		
Indical MS	1	90	28	
Erhavit DMC (Protease)	0.3			
add				
Calcium Hydroxide	1	45	28	
		Add		
Sodium Sulfide	0.75	60	28	Hair Removal
Sodium Sulfydrate	0.50			
	Remove the hair by filtration and add			

Water	100		
Calcium Hydroxide	1	30	28
Sodium Sulfide	0.5		
Run 10 min each hour overnight until 16 hours and drain			
Wash with Water	150	15	25
Drain and Flesh			

The hair obtained from this process was firstly characterized for moisture, mineral and organic matter content, and protein content [10]. Then, hair was hydrolyzed according a process developed by ISEP: 100 g of hair were mixed with 500 mL of water and 10 g of sodium hydroxide and shaken in a thermostatic water bath at 85ºC for 24 hours. After hydrolysis, the mixture was filtered and the liquid phase, the hair hydrolysate, was adjusted to pH 6 with hydrochloric acid and then concentrated by evaporation to about 35% of solids content. The final hydrolysate was designated as HK and characterized for moisture, mineral and organic matter content.

Then, different retanning agents were prepared by mixing hair hydrolysate and a sulfited lignin solution (50% conc.) for 30 minutes at room temperature, according to Table 2.

Table 2: Retanning agents preparation

Retanning Agent	Hair Hydrolysate Quantity (%)	Sulfited Lignin Quantity (%)
HK	100	0
HM	0	100
HMK20	20	80
HMK40	40	60
HMK50	50	50
HMK60	60	40
HMK80	80	20

Leather Retanning Trials

The ability of the retanning agents prepared was evaluated by the retannage of small pieces of wet-blue from the backbone hide zone, previously shaved to a thickness of 1.6 mm. The wet-blue shaved pieces, weighing approximately 100 g, were submitted to a retanning, dyeing and fat-liquoring standard process varying only the retanning agent as shown in Table 3 for each trial done.

Table 3: Summary of retanning trials

Retanning trial	Retanning Agent	Quantity used (%)
1	standard	4
2	HK	6
3	HM	6
4	HMK20	6
5	HMK40	6
6	HMK50	6
7	HMK60	6
8	HMK80	6

Chemicals used were all obtained from INDINOR, and the standard retanning agent was a mixture of 1% of Inditan RS (dispersing agent) and 3% of Inditan VOC (synthetic tannin). The trials were carried out using laboratory drums (LFA-9293, Mathis), with temperature and speed control, and chemicals quantities were based on the weight of wet-blue hide pieces used. The standard process used is shown in Table 4.

Table 4: Wet-blue Retanning, Dyeing and Fat-liquoring process

Process	Chemical	Chemical Quantity (%)	Time (min)	T (ºC)
Washing	Water	300	10	35
	Drain			
Neutralization	Water Sodium Formiate Sodium Bicarbonate	200 1.5 0.5	30	35
	pH control (≈ 6) and drain			
Washing	Water	300	10	35
	Drain			
Retanning	Water Fortan A40 (acrylic resin) Indinol EAF (sulfited oil)	50 3 2	15	30
	Add			
Retanning	**Retanning Agent** Mimosa Vegetable Extract Dyestuff	**x** 3 3	60	30
	Add			
Fixation	Water Formic Acid	100 1	45	50
	pH control (≈ 4) and drain			
Dyeing	Water Dyestuff	150 0.5	15	50
	Add			
Fat-liquoring	Indinol BE (natural oil) Indinol HS (synthetic oil) Indinol EAF (sulfited oil) Indinol LOX (lanolin based oil)	2 3 3 4	60	50
	Add			
Fixation	Formic Acid	0.5	30	50
	pH control (≈ 3.8) and add			
Washing	Water	300	10	25
	Squeeze, Dry and Stacked			

After this process the hide pieces were squeezed, dried and stacked. Properties, as physical-mechanical tests according to ISO 3377:2002 for tear strength, and ISO 3379:1976 for ball burst test (to evaluate the grain cracking), and leather behavior regarding softness and grain firmness, were evaluated for the different crust leather pieces obtained.

Leather Finishing Trials

Calf leather in crust stage was subjected to a finishing process. Four samples of A5 size were cut and named as I, II, III and IV.

Then, a Base Coat was applied with the components listed in Table 5. The dosage of this coat was 6 g/ft^2.

Table 5: Base Coat Components

Component	Quantity (g)
Water	620
Polax S80 (Wax)	100
Telaflex A23 (Acrylic resin for impregnation coats)	100
Telaflex U410 (Polyurethane emulsion)	100
Telafin Black (pigment)	80

After the application of this base coat and the respective drying, all the four samples were pressed at 100ºC, 1 second and 100 kgf/cm^2. The next step of the finishing process was to apply a Top Coat layer to each sample. The components of Top Coat are listed in Table 6. This composition was applied at 4 g/ft^2.

Table 6: Top Coat Components

Component	Sample I (g)	Sample II (g)	Sample III (g)	Sample IV (g)
Water	540	540	600	600
Glanz F (Mixture of Casein and Albumin)	400	---	400	---
Keratin Hydrolysate (Acrylic resin for impregnation coats)	---	400	---	400
GW 63 (Silicone emulsion)	30	30	---	---
Harter U (Polyaziridine crosslinker)	30	30	---	---

After the application of these top coats and the respective drying, all the four samples were pressed at 110ºC, 2 second and 100 kgf/cm^2, and the colour fastness to rubbing (50 cycles) was tested according to ISO 11640.

RESULTS AND DISCUSSIONS

Hair Hydrolysate and Retanning Agents Preparation

The hair quantity obtained from the hair-saving liming process was 8.4 g from 100 g of salted hide, and its characterization is shown in Table 7.

Table 7: Bovine hair characterization

Parameter	Result
Moisture, (%)	67%
Organic Matter, (% dry based)	92%
Mineral Matter, (% dry based)	8%
N Kjeldahl (g N/100g sample)	14.95g N/g sample

The final hair hydrolysate, obtained from the alkaline and thermal digestion, was characterized after pH adjustment and concentration. The results obtained are shown in Table 8.

Table 8: Hair hydrolysate (final) characterization

Parameter	Result
Total solids, (%)	37%
Organic Matter, (% dry based)	58%
Mineral Matter, (% dry based)	42%

Leather Retanning Trials

The dried and stacked crust leather pieces obtained from each trial were evaluated for physical-mechanical tests according to ISO 3377:2002 for tear strength, and ISO 3379:1976 for ball burst test (to evaluate the grain cracking) whose results are shown in Table 9.

Table 9: Physical and mechanical tests

Retanning Trial	Tear Strength (N)	Lastometer test Load (N)	Lastometer test Distension (mm)
1	169	406.7	7.8
2	176	371.9	7.3
3	176	430.0	7.0
4	209	328.7	7.0
5	211	392.6	7.0
6	212	415.3	7.3
7	151	291.0	7.1
8	146	260.4	6.8

The results obtained, when compared with reference values generally accepted for footwear application: 200 N for load and 7 mm for distension in lastometer test and 120 N for tear strength, are good except for trial 8 where the distension is closed to 7 but slightly less.

The evaluation of the crust leather pieces obtained for softness and grain firmness are shown in Table 10.

Table 10: Summary of retanning trials

Retanning trial	Softness*	Grain firmness**
1	3	3
2	4	4
3	4	4
4	3	4
5	3	4
6	3	4
7	3	4
8	3	4

* 1 = very hard; 5 = very soft
** 1 = grain very loose; 5 = grain very firm

Table 10 shows that the leather behavior is similar to the standard regarding softness and better than standard regarding firmness.

Leather Finishing Trials

Analyzing the four finished samples, it can be concluded that the leather finished with hair hydrolysate becomes too sticky.

The results of the colour fastness to rubbing (50 cycles) test, performed in dry conditions, done accordingly to the ISO 11640, are displayed in Table 11.

Table 11: Colour Fastness to Rubbing

Sample	Grey Scale
I	5
II	3
III	5
IV	4/5

The results of colour fastness to rubbing show that the samples with the casein/albumin finishing have better performance.

CONCLUSIONS

The aim of this work was the study of bovine hair hydrolysate and sulfited lignins effect in leather retanning process.

Hair from bovine hide can be obtained from a hair-saving liming process and, after alkaline and thermal digestion, gives rise to a hydrolysate that can be used as a retanning agent for wet-blue leather. The synergic effect of sulfited lignins and hair hydrolysate on leather retanning was studied. It was shown that hair hydrolysate, sulfited lignins and its mixtures can be used as retanning agents with good results when compared with a dispersing agent and a synthetic tannin. Physical mechanical properties of leather were good, satisfying the minimum normally accepted for footwear, also leather characteristics as firmness and softness presented very good results.

The hair hydrolysate was further tested as finishing agent against casein. The results obtained showed that it is not a good alternative as finishing agent.

A validation of these results at a pilot scale with different kind of hides will be important.

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