

# REVISTA

DE PIELĂRIE ÎNCĂLȚĂMINTE  
Leather and Footwear Journal

March / Martie 2023  
Volume / Volumul 23  
No / Numărul 1

INCDTP - SUCURSALA INSTITUTUL DE CERCETĂRI PIELĂRIE ÎNCĂLȚĂMINTE  
INCDTP - DIVISION: LEATHER AND FOOTWEAR RESEARCH INSTITUTE



PIELĂRIE/LEATHER   ÎNCĂLȚĂMINTE/FOOTWEAR   BUNURI DE CONSUM DIN CAUCIUC/RUBBER GOODS



#### AIMS AND SCOPE

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* (Print ISSN 1583-4433) is published 4 times a year, by Leather and Footwear Research Institute (ICPI) Bucharest, Romania, Division of The National Research and Development Institute for Textiles and Leather (INCDTP), CERTEX Press.

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* aims to present current science and technology developments as well as initiatives in Romania and South Eastern Europe region. The Journal publishes original research papers of experimental and theoretical nature, followed by scientific, technical, economic and statistic information, reviews of local and foreign conferences, congresses, symposia, with the purpose of stimulating the dissemination of research results.

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* focuses particular attention on the key areas of new systems and technologies applied in leather, footwear and rubber goods sectors; biomaterials, collagen-based medical devices, biochemistry of collagen; environment; innovation; leather and parchment cultural heritage; management and marketing, quality control; applications of IT field in these sectors, and other related fields.

#### OPEN ACCESS STATEMENT

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* is a peer reviewed, open access journal. All articles published open access will be immediately and permanently free for everyone to read, download, copy and distribute, under the provisions of a Creative Commons Attribution (CC BY) which lets others distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), include in a collective work (such as an anthology), text or data mine the article, even for commercial purposes, as long as they credit the author(s), do not represent the author as endorsing their adaptation of the article, and do not modify the article in such a way as to damage the author's honor or reputation.

#### PEER-REVIEW PROCEDURE

Submission of a manuscript to *Revista de Pielărie Încălțăminte* implies that the work described has not been published before (except in the form of an abstract or as part of a published lecture, review, or thesis); that it is not under consideration for publication elsewhere; that its publication has been approved by all coauthors, if any.

Submitted manuscripts are double-blind peer-reviewed by two qualified reviewers selected by the Editorial Board. The manuscript will be accepted for publication provided reviews are favorable. In case of diversified opinions of the reviewers, the Editorial board will make the final decision. If the paper is not accepted for publication, the manuscripts and the figures will not normally be returned. The authors will be notified as soon as possible of the result of the paper evaluation (to be published, to be modified, rejected).

#### JOURNAL SPONSORSHIP

Edited with the sponsorship from the Ministry of Education, Research and Innovation of Romania, National Authority for Scientific Research. We are pleased to acknowledge support from the following: The Confederation of National Associations of Tanners and Dressers of the European Community – COTANCE, Belgium; Romanian Leather and Fur Producers Association, APPBR, Romania; SFERA FACTOR, Romania.

#### COPYRIGHT

The copyright for all articles published in *Revista de Pielărie Încălțăminte / Leather and Footwear Journal* shall remain the property of the author(s). The copyright on the layout and final design of the articles published in *Revista de Pielărie Încălțăminte / Leather and Footwear Journal* belongs to

INCDTP – Division: Leather and Footwear Research Institute and cannot be used in other publications.

#### ABSTRACTING AND INDEXING

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* is acknowledged in Romania by the National University Research Council (CNCSIS) in B+ Category (code 565), and is indexed in Chemical Abstracts Service (CAS) Database, USA, CAB Database (CAB International, UK), Elsevier's Compendex and SCOPUS, CrossRef, EBSCO, CiteFactor, Research Bible, and listed in AcademicKeys, Environmental XPRT, MIAR, Electronic Journals Library, Cosmos Impact Factor, Science Library Index, Scilit, CNKI Scholar, DRJI, Journal TOCs, Root Indexing and SCIOPIO.

INCDTP-ICPI is a member of The Publishers International Linking Association, Inc. (PILA), a nonprofit corporation doing business as Crossref. As a PILA member, we have the right to assign Digital Object Identifiers (DOIs) to journal content. DOIs are persistent links to an object/entity and can be used to cite and link to any article existing online, even if full citation information is not yet available. We strongly recommend that authors cite references using DOIs where possible. For details regarding citation format and examples, please visit the Instructions for Authors section on *Revista de Pielărie Încălțăminte / Leather and Footwear Journal's* website, <http://www.revistapielarieincaltaminte.ro>

#### FEES AND SUBSCRIPTIONS

*Revista de Pielărie Încălțăminte / Leather and Footwear Journal* requires article processing charges of 200 EURO per article, for accepted manuscripts, payable by the author to cover the costs associated with publication. There are no submission charges.

Hard copies of journal issues are available for purchase at subscription rates of 160 EURO for companies and 100 EURO for individual subscribers, while the rate for a single issue is 40 EURO. Subscriptions (include mailing costs) can be made at the editorial office, to the following address:

INCDTP – DIVISION: LEATHER AND FOOTWEAR RESEARCH INSTITUTE, 93 Ion Minulescu Street, postal code 031215, sector 3, Bucharest, Romania, Europe.

Both article processing charges and subscription fees are to be paid in the following account:

Account holder: INCDTP – Division: Leather and Footwear Research Institute; Address of the account holder: 93 Ion Minulescu Street, postal code 031215, sector 3, Bucharest, Romania, Europe

IBAN Code: RO25 RNCB 0074029208380005

Bank code: 300413024

Swift bank address: RNCBROBU; Bank: BCR sector 3 (ROMANIAN COMMERCIAL BANK – SECTOR 3); Bank address: 11 Decebal Blvd., Bl. S14, sector 3, Bucharest, Romania.

#### CORRESPONDENCE

Editor-in-Chief – Dana Gurău

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

CERTEX Publishing House – Bucharest, 16 Lucrețiu Pătrășcanu St., sector 3; Tel./ Fax: (0040) 21 340.55.15; [certext@ns.certext.ro](mailto:certext@ns.certext.ro)

Website: <http://www.revistapielarieincaltaminte.ro>

Facebook: <http://www.facebook.com/LeatherFootwearJournal>

Title DOI: <https://doi.org/10.24264/lfj>

## EDITOR IN CHIEF

Dana GURĂU

## EDITOR

Dr. Gheorghe COARĂ

## EDITOR

Dr. Laurenția ALEXANDRESCU  
Director

## EDITOR

Dr. Carmen GAIDĂU  
Head of Leather  
Research Department

## EDITOR

Dr. Mihaela NIȚIUȚĂ

INCDTP - Division: Leather and Footwear Research Institute, Bucharest

## EDITORIAL ADVISORY BOARD

**Prof. Dr. Aurel ARDELEAN**

Western University "Vasile Goldis" Arad  
94-96 Revoluției Blvd., 310025, Arad, Romania  
Member of the Romanian Academy of Medical Sciences,  
Member of Academy of Science, New York  
Tel./Fax: +40 257 28 03 55  
e-mail: [rectorat@uvvg.ro](mailto:rectorat@uvvg.ro)

**Emeritus Prof. Dr. Aurelia MEGHEA**

Head of Projects and Grants Department, Romanian Academy  
General Director of Research Centre for Environmental  
Protection and Eco-Friendly Technologies, UPB  
University "Politehnica" of Bucharest  
1-7 Polizu, sector 1, 011061, Bucharest, Romania  
Tel.: +4021 3154193  
e-mail: [a\\_meghea@gmail.com](mailto:a_meghea@gmail.com), [aurelia@acad.ro](mailto:aurelia@acad.ro)

**Prof. Dr. Anton FICAI**

University "Politehnica" of Bucharest  
Faculty of Applied Chemistry and Materials Science  
1-7 Polizu, sector 1, 011061, Bucharest, Romania 35100,  
Phone/Fax: 004021 402 3852  
e-mail: [anton.ficai@upb.ro](mailto:anton.ficai@upb.ro)

**Prof. Dr. Behzat Oral BITLISLI**

Ege University Faculty of Engineering  
Head of Leather Engineering Department  
35100, Bornova, Izmir, Turkey  
Tel: + 90 232-311 26 44; Fax: +90 232 342 53 76  
e-mail: [oral.bitlisli@ege.edu.tr](mailto:oral.bitlisli@ege.edu.tr)

**Prof. Dr. Viaceslav BARSUKOV**

National University of Technology & Design  
2, Nemyrovych-Danchenko Str., Kiev, Ukraine  
Tel./Fax: +380 (44) 290-05-12  
e-mail: [keeh@knutd.com.ua](mailto:keeh@knutd.com.ua)

**Prof. Dr. Mehmet Mete MUTLU**

Ege University, Faculty of Engineering  
Leather Engineering Department,  
35100 Bornova, Izmir, Turkey  
Tel.: +90 232 3880110 – 2644; Fax: + 90 232 342 53 76  
e-mail: [mete.mutlu@ege.edu.tr](mailto:mete.mutlu@ege.edu.tr)

**Prof. Dr. Todorka Gancheva VLADKOVA**

University of Chemical Technology and Metallurgy,  
Bld. Kliment Ohridsky 8, Sofia, 1756, Bulgaria  
e-mail: [tg@uctm.edu](mailto:tg@uctm.edu)

**Prof. Dr. Margareta FLORESCU**

The Bucharest Academy of Economic Studies  
6 Piata Romana, 010374, Bucharest, Romania  
Tel.: +40 21 319 1900; +40 21 319 1901; Fax: +40 21 319 1899  
e-mail: [icefaceus@yahoo.com](mailto:icefaceus@yahoo.com)

**Prof. Dr. Hüseyin Ata KARAVANA**

Ege University, Faculty of Engineering  
Leather Engineering Department,  
35100 Bornova, Izmir, Turkey  
Tel.: +90 232 3880110 – 2644; Fax: + 90 232 342 53 76  
e-mail: [huseyin.ata.karavana@ege.edu.tr](mailto:huseyin.ata.karavana@ege.edu.tr)

**Prof. Dr. Wuyong CHEN**

National Engineering Laboratory for Clean Technology of Leather  
Manufacture, Sichuan University,  
Chengdu 610065, Sichuan, P. R. China  
Tel: +86-(0)28-85404462; +86-28-85405840  
Fax: +86-28-85405237  
e-mail: [wuyong.chen@163.com](mailto:wuyong.chen@163.com)

**Dr. Ding ZHIWEN**

China Leather & Footwear Industry Research Institute  
18 Jiangtaixi Road, Chaoyang District,  
Beijing, P. R. China, 100015  
Tel: +86-10-13701315570  
e-mail: [ding-zhiwen@263.net](mailto:ding-zhiwen@263.net)

**Assoc. Prof. Dr. Alina IOVAN-DRAGOMIR**

"Gh. Asachi" Technical University of Iasi  
28 Dimitrie Mangeron Blvd., Iași, Romania  
Tel.: +40 232 21 23 22; Fax: +40 232-21 16 67  
e-mail: [adragomir@tex.tuiasi.ro](mailto:adragomir@tex.tuiasi.ro)

**Assoc. Prof. Dr. Sergiu Stelian MAIER**

"Gh. Asachi" Technical University of Iasi  
28 Dimitrie Mangeron Blvd., Iași, Romania  
Tel.: +40 232 21 23 22; Fax: +40 232-21 16 67  
e-mail: [smaier@ch.tuiasi.ro](mailto:smaier@ch.tuiasi.ro)

**Assoc. Prof. Dr. Zenovia MOLDOVAN**

University of Bucharest  
90-92 Șos. Panduri, 050663, sector 5, Bucharest, Romania  
Tel.: +40 21 4103178/125  
e-mail: [z\\_moldovan@yahoo.com](mailto:z_moldovan@yahoo.com)

**Prof. Dr. Aura MIHAI**

"Gh. Asachi" Technical University of Iasi  
28 Dimitrie Mangeron Blvd., Iași, Romania  
Tel.: +40 232 21 23 22; Fax: +40 232-21 16 67  
e-mail: [amihai@tex.tuiasi.ro](mailto:amihai@tex.tuiasi.ro)

**Assoc. Prof. Dr. Dana Corina DESELNICU**

University "Politehnica" of Bucharest  
1-7 Polizu, sector 1, 011061, Bucharest, Romania  
Tel.: +40 021 212 99 52  
e-mail: [dana.deselnicu@upb.ro](mailto:dana.deselnicu@upb.ro)

ISSN: 1583-4433

Volume 23, No. 1, March 2023

<https://doi.org/10.24264/lfj.23.1>

	<b>CONTENTS</b>	<b>CUPRINS</b>	<b>SOMMAIRE</b>	
<b>Heru Budi SUSANTO</b> <b>Swatika JUHANA</b>	Reduction of Pollutants in the Tanning Industry Using the Reverse Tanning Method against the Physical Properties of Leather	Reducerea poluanților din industria de pielărie utilizând metoda tăbăcirii inverse și influența acesteia asupra proprietăților fizice ale pielii	Réduction des polluants dans l'industrie du cuir en utilisant la méthode de tannage inverse et son influence sur les propriétés physiques du cuir	3
<b>Prasetyo HERMAWAN</b> <b>Sekar Nirwana SARI</b> <b>Wahyu Fajar WINATA</b> <b>Elis NURBALIA</b>	Effect of Isocyanate as Cross-linker to Reduce Delamination of Finished Leather for Automotive Seat Cover	Influența izocianatului ca reticulant în vederea reducerii exfolierii pieilor finisate destinate tapițerii auto	L'effet de l'isocyanate comme réticulant pour réduire le délaminage du cuir fini destiné au garnissage automobile	11
<b>Gresy GRIYANITASARI</b> <b>Ambar PERTIWININGRUM</b> <b>Nanung Agus FITRIYANTO</b> <b>Yuny ERWANTO</b>	The Effect of Heating Time on the Thermal Stability of Chrome-Tanned Leather	Influența timpului de încălzire asupra stabilității termice a pielii tăbăcite în crom	L'effet du temps de chauffage sur la stabilité thermique du cuir tanné au chrome	19
<b>Darina ZHELEVA</b> <b>Rashko DIMITROV†</b>	Study of Adhesion-Cohesion Interactions between Polymers in Adhesive Compositions	Studiul interacțiunilor de aderență-coeziune dintre polimeri în compozițiile adezive	Étude des interactions d'adhésion et d'cohésion entre les polymères dans les compositions adhésives	31
<b>Berihun NEGASH</b>	An Application of Pareto Analysis and Cause-and-Effect Diagram in Raw Hide and Skin Defects Minimization in Ethiopia: Selected Case Dire Dawa City Slaughterhouse (Ethiopia)	O aplicație a analizei Pareto și a diagramei cauză-efect în minimizarea defectelor pielii brute în Etiopia: Studiu de caz – Abatorul din Dire Dawa (Etiopia)	Une application de l'analyse de Pareto et du diagramme de causes et effets dans la minimisation des défauts de la peau en Ethiopie : Cas sélectionné de l'abattoir de la ville de Dire Dawa (Ethiopie)	43
<b>Laurenția ALEXANDRESCU</b> <b>Mihai GEORGESCU</b> <b>Maria SÖNMEZ</b> <b>Mihaela NIȚUICĂ</b> <b>Maria-Daniela STELESCU</b> <b>Dana GURĂU</b>	Biodegradable Polymer Composite Based on Polyvinyl Chloride and Poly (Ethylene-Vinyl Acetate) Waste	Compozit polimeric biodegradabil pe bază de policlorură de vinil și deșeuri de poli(etilenvinil acetat)	Composite polymère biodégradable à base de chlorure de polyvinyle et de déchets de poly(éthylène-acétate de vinyle)	55
	European Research Area	Spațiul european al cercetării	Espace Européen de la Recherche	63
	National and International Events	Evenimente naționale și internaționale	Événements nationaux et internationaux	69



# REDUCTION OF POLLUTANTS IN THE TANNING INDUSTRY USING THE REVERSE TANNING METHOD AGAINST THE PHYSICAL PROPERTIES OF LEATHER

Heru Budi SUSANTO, Swatika JUHANA\*

Department of Leather Processing Technology, Politeknik ATK Yogyakarta, Sewon, Bantul, 55281, Yogyakarta, Indonesia,  
swatika.rustiawan@gmail.com

Received: 11.08.2022

Accepted: 16.01.2023

<https://doi.org/10.24264/lfj.23.1.1>

## REDUCTION OF POLLUTANTS IN THE TANNING INDUSTRY USING THE REVERSE TANNING METHOD AGAINST THE PHYSICAL PROPERTIES OF LEATHER

**ABSTRACT.** This study aims to tan the skin with reverse tanning based on the order of pH, thereby reducing the use of chemicals and water due to the pH regulation process. The reverse tanning method will result in a faster tanning process and reduce the use of many chemicals, so that the pollutant load released from the tanning process will be much reduced. Conventional leather tanning is carried out through many processes starting from the BHO (Beam House Operation) process, tanning, post-tanning, and finishing; this process is carried out through a 14-15 step process that produces a large number of pollutants. This is because in conventional leather processing a lot of pH adjustment processes are carried out that go back and forth. In this study the leather processing steps were ordered based on the pH of the tanning process, the chemicals and the pH of the process were regulated by the sequence of the process steps to avoid some repeated acidification and basification/neutralization as in conventional leather processing. The process begins with soaking, liming, fleshing, deliming, tanning, dyeing, fatliquoring, and chrome tanning. This process begins with an alkaline pH of 11 and ends with an acidic pH of 3.8. Chrome tanning is done with variations in the amount of chrome of 2%, 3%, 4%. The results showed that leather with 4% chromium produced the highest  $T_s$  of 103 °C, tensile strength of 39.86 N, tearing strength of 13.19 N/mm, seam strength of 12.8 N/mm, elongation of 46.87%, Cr content (VI) 1.68 ppm. These results have met the standard ISO/TR 20879:2007 Footwear. The reverse tanning process with a process from high to low pH without adjusting the pH back and forth by adding solutions and salts means reducing liquid waste in the leather tanning process. So, this process can reduce the amount of liquid waste or pollutants.

**KEY WORDS:** reverse tanning, leather processing, chrome tanning, shrinkage temperature

## REDUCEREA POLUANȚILOR DIN INDUSTRIA DE PIELĂRIE UTILIZÂND METODA TĂBĂCIRII INVERSE ȘI INFLUENȚA ACESTEIA ASUPRA PROPRIETĂȚILOR FIZICE ALE PIELII

**REZUMAT.** Acest studiu își propune tăbăcirea pielii prin procesul de tăbăcire inversă în funcție de ordinea pH-ului, reducând astfel utilizarea substanțelor chimice și a apei datorită procesului de reglare a pH-ului. Metoda de tăbăcire inversă va avea ca rezultat un proces de tăbăcire mai rapid și va reduce utilizarea multor substanțe chimice, astfel încât încărcătura poluantă eliberată din procesul de tăbăcire va fi mult redusă. Tăbăcirea convențională a pielii se realizează prin multe operațiuni pornind de la cele umede, tăbăcire, post-tăbăcire și finisare, acest proces fiind realizat în 14-15 etape care produc o cantitate mare de poluanți. Acest lucru se datorează faptului că în prelucrarea convențională a pielii sunt efectuate o mulțime de procese de ajustare a pH-ului în ambele sensuri. În acest studiu, etapele de prelucrare a pielii au fost ordonate în funcție de pH-ul procesului de tăbăcire, substanțele chimice și pH-ul procesului a fost reglate de succesiunea etapelor pentru a evita unele acidificări și alcalinizări/neutralizări repetate, așa cum se întâmplă la prelucrarea convențională a pielii. Procesul implică înmuierea, cenușărirea, șeruirea, decalcifierea, tăbăcirea, vopsirea, ungerea și tăbăcirea în crom. Acest proces începe cu un pH alcalin de 11 și se termină cu un pH acid de 3,8. Tăbăcirea în crom se face cu variații ale cantității de crom de 2%, 3%, 4%. Rezultatele au arătat că pielea cu 4% crom a generat cea mai mare valoare a  $T_s$  de 103 °C, rezistență la rupere de 39,86 N, rezistență la sfășiere de 13,19 N/mm, rezistența cusăturii de 12,8 N/mm, alungire de 46,87%, conținut de Cr (VI) 1,68 ppm. Aceste rezultate au îndeplinit standardul ISO/TR 20879:2007 Încălțăminte. Procesul de tăbăcire inversă începând de la un pH ridicat până la un pH scăzut fără ajustarea pH-ului prin adăugarea de soluții și săruri înseamnă reducerea deșeurilor lichide în procesul de tăbăcire a pielii. Deci, acest proces poate reduce cantitatea de deșeuri lichide sau poluanți.

**CUVINTE CHEIE:** tăbăcire inversă, prelucrarea pielii, tăbăcire în crom, temperatură de contracție

## REDUCTION DES POLLUANTS DANS L'INDUSTRIE DU CUIR EN UTILISANT LA MÉTHODE DE TANNAGE INVERSE ET SON INFLUENCE SUR LES PROPRIÉTÉS PHYSIQUES DU CUIR

**RÉSUMÉ.** Cette étude vise à tanner la peau en utilisant un tannage inverse basé sur l'ordre du pH, réduisant ainsi l'utilisation de produits chimiques et d'eau en raison du processus de régulation du pH. La méthode de tannage inverse entraînera un processus de tannage plus rapide et réduira l'utilisation de nombreux produits chimiques, de sorte que la charge polluante libérée par le processus de tannage sera considérablement réduite. Le tannage conventionnel du cuir est réalisé à travers de nombreux processus à partir des opérations de rivière, tannage, post-tannage et finition, ce processus est réalisé en 14-15 étapes qui produisent une grande quantité de polluants. En effet, dans le traitement conventionnel du cuir, de nombreux processus d'ajustement du pH sont effectués dans les deux sens. Dans cette étude, les étapes de traitement du cuir ont été ordonnées en fonction du pH du processus de tannage, les produits chimiques et le pH du processus ont été régulés par la séquence des étapes pour éviter une acidification et une basification/neutralisation répétées comme dans le traitement conventionnel du cuir. Le processus commence par le trempage, le pelanage, l'écharnage, le déchaulage, le tannage, la teinture, la nourriture et le tannage au chrome. Ce processus commence avec un pH alcalin de 11 et se termine avec un pH acide de 3,8. Le tannage au chrome se fait avec des variations dans la quantité de chrome de 2%, 3%, 4%. Les résultats ont montré que le cuir avec 4 % de chrome

\* Correspondence to: Swatika JUHANA, Politeknik ATK Yogyakarta, Sewon, 55281, Bantul, Yogyakarta, Indonesia, swatika.rustiawan@gmail.com

produisait la Ts la plus élevée de 103 °C, une résistance à la traction de 39,86 N, une résistance à la déchirure de 13,19 N/mm, une résistance des coutures de 12,8 N/mm, un allongement de 46,87 %, une teneur en Cr (VI) de 1,68 ppm. Ces résultats sont conformes à la norme ISO/TR 20879:2007 Chaussures. Le processus de tannage inverse avec un pH élevé à faible sans ajuster le pH dans les deux sens en ajoutant des solutions et des sels signifie la réduction des déchets liquides dans le processus de tannage du cuir. Ainsi, ce processus peut réduire la quantité de déchets liquides ou de polluants.

MOTS CLÉS : tannage inverse, traitement du cuir, tannage au chrome, température de retrait

## INTRODUCTION

Leather is a waste from the meat industry which will be damaged by the autolysis process if it is not immediately preserved [1]. Raw hide in order to be used must be processed through a tanning process. Tanning is a chemical process that reacts skin collagen with chemicals so that cross-linking occurs, resulting in a tanned leather that is stable and resistant to external influences [2].

Chrome tanning is the most widely used tanning in the leather industry, as it can provide leather with a comfortable feel and high hydrothermal stability. In addition, compared to chrome-free tanning, chrome tanning is more suitable for the production of various types of leather. Crust skin from chromium tanning has better compatibility/compatibility with chemical retanning and fatliquoring, in other words, it is easy to retan and fatliquor without causing negative effects [3]. Conventional chrome tanning has the characteristics of releasing excessive chromium into the waste and abundant chromium shavings. The release of chromium into the waste is caused by imperfect absorption of chromium powder, namely 40%-70% absorbed and the release of free/unbound and unstable chromium from the skin during post tanning processes such as rewetting, retanning, neutralizing, dyeing and fatliquoring processes done after chrome tanning to improve leather grip and feel, as well as leather coloring. It is expected that the addition of chromium at the end of the process can reduce the release of chromium to waste.

Conventional leather processing is usually carried out through many processes to remove various biological, inorganic, and organic materials. The process starts from BHO, tanning, post-tanning, and finishing, this leather processing is carried out up to 4-15 steps of the process which produces a large

amount of water pollutants and chemicals. This is because conventional leather processing is mostly done by adjusting the pH that goes back and forth. In this study the leather processing steps were sequenced to overcome the problems associated with the conventional method, wherein the skin charge, chemical and process pH were set for reversal of the process steps to avoid some repeated acidification and basification/neutralization as in conventional leather processing. In this study, it is expected that there will be savings in chemicals, water and time so that the tanning process is more efficient.

The conventional method of making leather goes through 14-15 steps consisting of soaking, liming, reliming, deliming, removing fat, protein scraping, acidification, tanning, basification, rechroming, neutralization, washing, retanning, dyeing, fatliquoring, and fixation. This conventional tanning produces a large amount of liquid waste, about 30-40 m<sup>3</sup> per 1 ton of raw hide raw material, in which the wastewater contains pollutants such as BOD, COD, TDS, sulfides, chlorides, sulfates, chromium, total ammonia, total nitrogen [4].

The increase in pollutants in conventional processes is mainly due to the fact that the leather processing technique uses a "do-undo" process scheme such as swell-deswell (liming-deliming), pickle-depickle (pickling-basification), rechroming-basification (acidification-basification), and neutralization-fixation (basification-acidification) [5]. In other words, conventional methods in skin processing cause the pH range of the process from start to finish to be wide and varied [6]. Such changes in pH require the repeated use of large amounts of acids and bases, resulting in the production of salts of calcium, sodium, and chromium ions, as well as increasing COD, TDS, chlorides, sulfates, and other minerals in tannery wastewater [1].



The post tanning process goes through 7-8 main steps consisting of rechroming, basification, neutralization, washing, retanning, basic coloring, oiling, and fixation. This post-tanning process is in the pH range of 4.0-6.5 and contains many chemicals, thus contributing significantly to TDS, COD, and heavy metal pollution [3]. Several attempts have been made to fabricate leather processing steps with clean technology [7, 8]. However, these efforts are specific to each operating unit. Therefore, the application of all advanced technologies and eco-friendly chemicals and machine modifications should be carried out for the development of integrated leather processing methods and revamping of the process sequence. Very little effort has been made to change the whole or part of the leather processing step. Thanikaivelan *et al.* tried to process skin in a narrow pH range of 4 to 8.0 [1, 9]. Later, a three-step tanning process was developed which involves enzymatic dehairing, fiber opening using enzymes or alkali, and chrome tanning without acidification at pH 8.0 [10, 11]. An integrated one-step wet finishing process has been developed [12, 13]. Furthermore, process integration has been attempted by combining tanning and post-tanning in one process [14].

This research as a novelty step will be made an effort to reverse the steps of the conventional tanning process, by treating the leather for the post tanning process (retanning, dyeing and fatliquoring) carried out in the pre tanning process (beam house)

with no neutralization process, followed by chrome tanning at pH 3.5 – 4.0 without pickle process [9].

## EXPERIMENTAL

### Materials and Method

#### Instruments

Drum process, pH paper, glass tools. The resulting leather is tested according to ISO/TR 20879:2007 footwear standards, covering tensile strength, tear strength, seam strength, elongation, remaining Cr (VI), and shrinkage temperature (Ts).

#### Materials

The materials used in this research are salt-resistant leather, water, surfactant, Na<sub>2</sub>S, lime, NH<sub>4</sub>Cl, bating agent, degreasing agent, glutaraldehyde, syntan, dyestuff, fatliquour oil, synthetic oil, HCOOH, chrome sulfate powder.

#### Method

Salt-preserved goat skin is processed conventionally by soaking, liming, fleshing, deliming and then processed by retanning, dyeing, and fatliquoring. Finally it is tanned using chrome tanning agent. Tests were carried out for physical and chemical test parameters. The reverse tanning process in this study can be seen in Table 1.

Table 1: Reverse tanning process

No.	Process	Chemicals	%	Time	Process control
1	Salt-preserved goat skin Weighing				
2	Washing and Soaking	Water Wetting agent	500 0.5	60'	Drain, wash 2-4 rpm pH 7
3	Liming	Water Na <sub>2</sub> S Water Lime Water Water	150 2.5 50 6 50 50	30' 30' 30' 30'	2-4 rpm pH 11-12
				30' run 15' res	

No.	Process	Chemicals	%	Time	Process control
4	Fleshing				
5	Delimiting	Water	200		6-8 rpm
		NH <sub>4</sub> Cl	2		
		Bating agent	1		
		Degreasing agent	1	90'	Check pH
		HCOOH	0.5	30'	pH 6,7,8
		Washing			
6	Retanning, dyeing, and fatliquoring	Water	100		10-12 rpm
		Syntan	5	30	
		Glutaraldehyde	4	30	
		Dyestuff	2	60	
		Sulfited oil	5	15	
		Synthetic oil	3	60	
7	Fixation	HCOOH	0.5 – 1	30'	10-12 rpm pH 3.5-4
8	Tanning	Chrome sulphate	Variation 2, 3, 4	90'	10-12 rpm
				180'	Drain, hanging, drying

## RESULTS AND DISCUSSIONS

This research of reverse tanning by treating the leather from washing after delimiting, retanning, dyeing, fatliquoring, fixation, and tanning. In the reverse tanning process, it only goes through 8 stages from high pH 11-13 to pH 3.5-4 at the end of the

process. The resulting leather is tested according to ISO/TR 20879:2007 footwear standards. Variations in the amount of chromium in reverse tanning include the amount of chromium 2%, 3%, 4% of the weight of the skin. Variations in the amount of chromium can be seen in Table 2.

Table 2: Variations in the amount of chromium, pH of delimiting and product code

Variations of chromium (%)	pH of delimiting		
	6	7	8
2	A	D	G
3	B	E	H
4	C	F	I

The test results of leather from process reverse tanning with several treatments are

carried out were physical and chemical tests according to ISO/TR 20879:2007 for Footwear.

Table 3: Results of leather physical and chemical test results of reverse tanning

No.	Various Test	Test Results									
		A	B	C	D	E	F	G	H	I	Remark
1	Tear Strength (N) (ISO 17696:20011)	51.74	37.80	25.97	44.77	41.90	45.54	48.06	32.27	39.86	Min. 30
2	Colour Fastness (ISO 17700:2011)										
	Wet (20 cycles) Greyscale	4	4	4	4	4	4	4	4	4	Min. 2
	Dry (100 cycles)	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	Min. 2
3	Lastability (mm) (ISO 17693:2011)	23.50	13.26	17.07	19.80	15.0	13.18	21.18	17.70	12.28	Min. 6
4	Seam Strength (N/mm) (ISO 17697:2011)	5.55	1.77	4.90	5.67	4.29	4.26	5.14	2.55	4.34	Min. 3
5	Breaking strength (N/mm) (ISO 17706:2011)	11.18	14.17	12.13	13.30	13.02	17.40	12.82	8.99	13.19	Min. 10
6	Elongation (along) (%) (ISO 17706:2011)	18.72	46.82	44.50	23.05	53.36	51.10	48.10	19.10	46.87	Min. 7



7	Chromium (6) content (mg/kg) (ISO 17075:2007)	0.34	0.34	0.42	0.25	1.57	1.71	1.74	2.13	1.68	Max. 3
8	Shrinkage Temperature (Ts) (°C) SNI 06-7127-2005	86.9	92.5	98.8	87.7	95.3	100.1	90.7	96.9	103.3	Min 100°C

The thickness, direction of the collagen fibers, and the angle of the collagen fibers to the grain layer affect the tear strength of tanned leather, the higher the tear strength, the better the resulting quality [15]. The tear strength can be increased by controlling the percentage (amount) of the bating material used and the time of the protein scraping process (bating). The use of too much bating material and too long bating processing time will result in low tear strength.

On leather code B and H the sewing strength test does not meet the requirements of ISO/TR 20879:2007 Footwear – Performance requirements for components footwear – Uppers. The strength of the suture is influenced by the thickness of the skin, the content and density of the collagen protein, the angle of the interwoven collagen fibers and the thickness of the corium. So that the protein erosion process will greatly affect the sewing strength of the leather, the greater the percentage of enzymes used and the longer the protein erosion process will reduce the sewing strength of the tanned leather.

Tensile strength is the maximum force required to pull the skin to break, expressed in kg/cm<sup>2</sup> or N/mm<sup>2</sup>. Tensile strength is one of the important parameters that becomes a benchmark for the quality of tanned leather because it can describe the strength of the bond between the collagen fibers that make up the skin and the tanning agent. A good tanning process will produce leather with high tensile strength. Tensile strength in its application is very important, especially in the leather product/goods industry. The tensile strength of the leather that is less than the requirement will cause the leather to break or

crack easily. Tensile strength testing is generally carried out to determine the mechanical properties of a material. For treatment with variation code H, the tensile strength test does not meet the requirements of ISO/TR 20879:2007 Footwear – Performance requirements for components footwear – Uppers. Factors that can affect the tensile strength are the quality of raw leather, leather preservation methods, and processes during tanning, such as liming, bating, oiling, and stretching [16]. Mann (1981) said that the physical properties of the skin are influenced by the structure of the skin tissue, namely the collagen bundles that make up the skin that are irregularly woven with each other, branching in all directions [17]. The angle formed by the webbing of the beam determines the high and low tensile strength, at a webbing angle of less than 450, the leather will have a high tensile strength and vice versa if the angle formed by the collagen fibers is more than 450 then the resulting tensile strength will be higher. A small collagen bundle angle will produce a leather that is strong and less elastic, but softer than leather with a larger collagen bundle angle. The results of the shrinkage temperature test showed that the lowest shrinkage temperature was in variation A, which was 86°C and the highest was in variation I, which was 103.3°C, this indicates that the higher the addition of chromium, the more cross-linking occurs so that the chemical stability of the collagen structure increases. The increase in shrinkage temperature was caused by the stabilization of the chemical reaction of the collagen structure with the equalizer [18].

Leather elongation is an increase in the length of the leather at the time it is stretched to break divided by its original length, expressed in percent. Elongation shows the elongation of the leather, the longer the size of the leather at the time of breaking, the greater the value of the elongation strength, which indicates that the quality of the elongation strength is good. However, the stretch is limited to a certain value because if it is too stretchy the leather will not be able to maintain its shape when leather products are made. Of all the variations in the research, it meets the requirements of ISO/TR 20879:2007 for Footwear, namely a minimum of 7% for length and 15% for across. In order to maintain the elongation value at a certain value, the inner coating material is usually added according to the desired elongation.

The skin shrinkage temperature is the temperature reached when the skin shrinks to a maximum of 0.3% of the initial length, if the skin is heated slowly in a heating medium, (SNI 06-7127-2005: Test Method for Tanned Skin Shrinkage Temperature). One of the parameters that determine skin maturity is to know the shrinkage temperature. The shrinkage temperature is the temperature at which the skin shrinks due to the breaking of the cross-links between the leather and the tanning agent due to the influence of heating. Ripe skin will have a higher number of cross-links than unripe skin, so it is more capable and resistant to physical forces that attack it, including boiling water [19]. Each type of tannery produces leather with different heat resistance, this is due to the different types of chemical bonds formed between the tanning agent and the leather.

The higher the percentage of addition of tanning material, the higher the shrinkage temperature, this indicates that the tanning material that enters and binds to the skin

forms more compact fiber bonds, so that the resistance to heat increases, the shrinkage temperature is the temperature at which the collagen structure shrinks. Shrinkage occurs due to folding of the polypeptide chain due to the breaking of the strength of the woven fibers by extreme conditions (e.g. heating) [20]. Shrinkage temperature is a temperature that can cause damage and tends to cause a decrease in the binding capacity of substances contained in proteins [21]. The shrinkage temperature is closely related to the maturity of the skin, the more skin fibers that bind to the tanning agent, the higher the maturity of the resulting skin so that the shrinkage temperature is higher. The higher the shrinkage temperature, the better the quality of the product because the skin's resistance to heat (hydrothermal) is higher.

The reverse tanning process with a process from high to low pH without adjusting the pH back and forth by adding solutions and salts means reducing liquid waste in the leather tanning process. So, this process can reduce the amount of liquid waste.

## CONCLUSIONS

The results of the study concluded that the highest shrinkage temperature was code I (reverse tanning with 4% chromium of the skin weight). Reverse tanning code I with 4% chromium of the skin weight, by process with weighing, soaking, liming, fleshing, deliming, retanning, dyeing, fatliquoring, fixation, and chrome tanning with 4% chromium. The results showed that leather with 4% chromium produced the highest Ts of 103°C, tensile strength of 39.86 N, tearing strength of 13.19 N/mm, seam strength of 12.8 N/mm, elongation of 46.87%, Cr content (VI) 1.68 ppm. These results have met the standard ISO/TR 20879:2007 Footwear.



## REFERENCES

1. Triatmojo, S., Zainal Abidin, M., Penyamakan Kulit Ramah Lingkungan, Gadjah Mada University Press, Yogyakarta, **2014**.
2. Ali, A.A., Gasmelseed, G.A., Ahmed, A.E., Innovation an Eco Friendly Technology: Tanning System Using Semi Chrome and Improved Indigenous Tannins (*Acacia nilotica* Pods), *J Biotechnol Biomed*, **2019**, 2, 15-23, <https://doi.org/10.26502/jbb.2642-9128006>.
3. Thanikaivelan, P., Rao, J.R., Nair, B.U., Development of a Leather Processing Method in Narrow pH Profile. Part 1. Standardisation of Unhairing Process, *J Soc Leather Technol Chem*, **2000**, 84, 276-284.
4. Aloy, M., Folachier, A., Vulliermet, B., Tannery and Pollution, Centre Technique Du Cuir: Lyon, France, **1976**.
5. Bienkiewicz, K., Physical Chemistry of Leather Making, Krieger Publishing, Malabar, FL, **1983**.
6. Heidemann, E., Fundamentals of Leather Manufacture, Eduard Roether KG, Darmstadt, **1993**.
7. Simoncini, A., Sammarco, U., The Possibility of Reducing the CODs Deriving from the Fatliquoring of the Softy Leathers in Residual Baths, Proceedings of the XXIII IULTCS Congress, Germany, **1995**.
8. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., Progress and Recent Trends in Biotechnological Methods for Leather Processing, *Trends Biotechnol*, **2004**, 22, 181-188, <https://doi.org/10.1016/j.tibtech.2004.02.008>.
9. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., Recent Trends in Leather Making: Processes, Problems, and Pathways, *Crit Rev Environ Sci Technol*, **2005**, 35, 37-79, <https://doi.org/10.1080/10643380590521436>.
10. Thanikaivelan, P., Rao, J.R., Nair, B.U., Development of a Leather Processing Method in Narrow pH Profile. Part 2. Standardisation of Tanning Process, *J Soc Leather Technol Chem*, **2001**, 85, 106-115.
11. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., Stepping into Third Millennium: Third Generation Leather Processing - A Three Step Tanning Technique, *J Am Leather Chem Assoc*, **2003**, 98, 173-184.
12. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., Biointervention Makes Leather Processing Greener, An Integrated Cleansing and Tanning System, *Environ Sci Technol*, **2003**, 37, 2609-2617, <https://doi.org/10.1021/es026474a>.
13. Ayyasamy, T., Thanikaivelan, P., Chandrasekaran, B., Rao, J.R., Nair, B.U., Development of an Integrated Wet Finishing Process: Manufacture of Garment Leathers, *J Am Leather Chem Assoc*, **2004**, 99, 367-375.
14. Ayyasamy, T., Thanikaivelan, P., Rao, J.R., Nair, B.U., The Development of an Integrated Rechroming-Neutralization-Post Tanning Process: Manufacture of Upper Leathers from Goatskins, *J Soc Leather Technol Chem*, **2005**, 89, 71-79.
15. Suparno, O., Wahyudi, E., Pengaruh konsentrasi natrium perkarbonat dan jumlah air pada penyamakan kulit samoa terhadap mutu kulit samoa, *Jurnal Teknologi Industri Pertanian*, **2012**, 22, 1, 1-9.
16. Pahlawan, I.F., Kasmudjiastuti, E., Pengaruh Jumlah Minyak terhadap Sifat Fisis Kulit Ikan Nila (*Oreochromis niloticus*) untuk Bagian Atas sepatu, **2012**, available at

- <https://majalahkkponline.files.wordpress.com/2013/05/artikel-6-nila.pdf>.
17. Mann, I., Teknik Penyamakan Kulit Untuk Pedesaan (terjemahan), Angkasa, Bandung, **1981**.
18. Covington, A.D., Tanning Chemistry, The Science of Leather, The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK, **2009**.
19. Purnomo, E., Pengetahuan Dasar Teknologi Penyamakan Kulit, Akademi Teknologi Kulit, Departemen Perindustrian, Yogyakarta, **1985**.
20. Sarkar, K.T., Theory and Practice of Leather Manufacture, Publ. The Author 4 Second Avenue, Mahatma Gandhi Food, Madrat, **1985**.
21. Ayufita, D.P., Pengaruh Lama Perendaman Dalam Garam Jenuh Terhadap Kualitas Fisik Kulit Pari Tersamak, Fakultas Pertanian, Universitas Gadjah Mada, Yogyakarta, **2007**.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).



## EFFECT OF ISOCYANATE AS CROSS-LINKER TO REDUCE DELAMINATION OF FINISHED LEATHER FOR AUTOMOTIVE SEAT COVER

Prasetyo HERMAWAN, Sekar Nirwana SARI, Wahyu Fajar WINATA\*, Elis NURBALIA

Program Studi Teknologi Pengolahan Kulit, Politeknik ATK Yogyakarta, Indonesia, wahyufajarwinata88@gmail.com

Received: 30.11.2022

Accepted: 03.02.2023

<https://doi.org/10.24264/lfj.23.1.2>

### EFFECT OF ISOCYANATE AS CROSS-LINKER TO REDUCE DELAMINATION OF FINISHED LEATHER FOR AUTOMOTIVE SEAT COVER

**ABSTRACT.** This study aims to improve the quality of finished leather for seat covers by knowing the effect of isocyanate as a cross-linker to reduce delamination on the finished leather. Delamination is a condition where the three layers of finish (base coat, medium coat, and top coat) do not stick together, resulting in the lifting of the top coat during the adhesion test. The raw material used in the trial is C60 quality crust dyed cowhide, 1.1 mm to 1.4 mm thick with an area of  $\pm 3$  sqft. The stages of the finishing process include semi-finished selection, stacking, spraying (base coat), rest, stacking, roller embossing, rest, milling, stacking, spraying (medium coat, top coat), rest, stacking, laboratory, and measuring. The formulation of the improved seat cover article was carried out by increasing the percentage of cross-linker in the base coat mixture. The production formulation used 2% cross-linker, trial 1 used 3% cross-linker, and trial 2 used 4% cross-linker. The best results are with the addition of 4% cross-linker to reduce delamination and have an adhesion resistance value of 24.5 N. The conclusion is that the greater the addition of cross-linker as much as 4% in the base coat of the article seat cover will reduce delamination, increase thickness from 1.1 mm to 1.2 mm, improve color fastness resistance to a value of 4, and reduce softness value from 3.92 mm to 3.42 mm.

**KEY WORDS:** leather, cross-linker, delamination, adhesion

### INFLUENȚA IZOCIANATULUI CA RETICULANT ÎN VEDEREA REDUCERII EXFOLIERII PIEILOR FINISATE DESTINATE TAPIȚERIEI AUTO

**REZUMAT.** Acest studiu își propune să îmbunătățească calitatea finisajului pieilor pentru tapițerie auto prin determinarea efectului izocianatului ca agent de reticulare în vederea reducerii exfolierii pielii finisate. Exfolierea este un fenomen în care cele trei straturi de finisaj (strat de bază, strat intermediar și strat superior) nu rămân lipite, ceea ce duce la desprinderea stratului superior în timpul testului de aderență. În studiu s-a folosit ca materie primă pielea bovină crust vopsită de calitate C60, cu o grosime de 1,1 mm până la 1,4 mm, cu o suprafață de  $\pm 3$  m<sup>2</sup>. Etapele procesului de finisare includ selecția semifabricatelor, stivuire, pulverizare (strat de bază), repaus, stivuire, imprimare model, repaus, vâlcuire, stivuire, pulverizare (strat intermediar, strat superior), repaus, stivuire, testare de laborator și măsurare. Formula pentru produsul îmbunătățit de finisare a pielii pentru tapițerie auto a fost realizată prin creșterea procentului de agent de reticulare din amestecul pentru stratul de bază. Pentru formula de bază s-a folosit 2% agent de reticulare, pentru varianta 1 s-a folosit 3% agent de reticulare, iar pentru varianta 2 s-a folosit 4% agent de reticulare. Cele mai bune rezultate au fost obținute la adăugarea de 4% reticulant pentru a reduce exfolierea, variantă pentru care s-a determinat o valoare a rezistenței aderenței de 24,5 N. În concluzie, cantitatea de reticulant mai mare, de 4%, în stratul de bază al produsului pentru finisarea pielii destinate tapițeriei auto reduce exfolierea pielii, crește grosimea de la 1,1 mm la 1,2 mm, îmbunătățește rezistența culorii la o valoare de 4 și reduce valoarea moliciunii de la 3,92 mm la 3,42 mm.

**CUVINTE CHEIE:** piele, reticulant, exfoliere, aderență

### L'EFFET DE L'ISOCYANATE COMME RÉTICULANT POUR RÉDUIRE LE DÉLAMINAGE DU CUIR FINI DESTINÉ AU GARNISSAGE AUTOMOBILE

**RÉSUMÉ.** Cette étude vise à améliorer la qualité de finition des cuirs pour le garnissage automobile en déterminant l'effet de l'isocyanate en tant qu'agent de réticulation afin de réduire le délaminage du cuir fini. Le délaminage est un phénomène où les trois couches de la finition (couche de base, couche intermédiaire et couche de finition) ne restent pas collées, ce qui entraîne le décollement de la couche de finition lors du test d'adhérence. Une peau bovine en croûte teinte de qualité C60, de 1,1 mm à 1,4 mm d'épaisseur, d'une surface de  $\pm 3$  m<sup>2</sup> a été utilisée comme matière première dans l'étude. Les étapes du processus de finition comprennent la sélection des semi-fabriqués, l'empilement, la pulvérisation (couche de base), le repos, l'empilement, l'impression du motif, le repos, le foulage, l'empilement, la pulvérisation (couche intermédiaire, couche de finition), le repos, l'empilement, les tests et mesures en laboratoire. La formule de la finition améliorée du cuir pour le garnissage automobile a été réalisée en augmentant le pourcentage d'agent de réticulation dans le mélange de la couche de base. Pour la formule de base, 2 % d'agent de réticulation ont été utilisés, pour la variante 1, 3 % d'agent de réticulation ont été utilisés et pour la variante 2, 4 % d'agent de réticulation ont été utilisés. Les meilleurs résultats ont été obtenus avec l'ajout de 4 % d'agent de réticulation pour réduire le délaminage, pour lequel une valeur de force d'adhérence a été déterminée de 24,5 N. En conclusion, la plus grande quantité d'agent de réticulation, 4 %, dans la couche de base du produit de finition du cuir pour le garnissage automobile réduit le délaminage du cuir, augmente l'épaisseur de 1,1 mm à 1,2 mm, améliore la solidité des couleurs à une valeur de 4 et réduit la valeur d'assouplissement de 3,92 mm à 3,42 mm.

**MOTS CLÉS :** cuir, agent de réticulation, délaminage, adhérence

\* Correspondence to: Wahyu Fajar WINATA, Program Studi Teknologi Pengolahan Kulit, Politeknik ATK Yogyakarta, Indonesia, wahyufajarwinata88@gmail.com

## INTRODUCTION

The quality testing of finished leather is important because consumer judgment heavily depends on it. Therefore, several things need to be considered in developing finished leather, namely the need to understand the skin's structure, the selection of raw materials and chemicals, and process control. The product development aims to improve quality so that consumers can accept it. According to Wiyodiningrat *et al.* (2012), the skin must have good quality, no defects due to insect/parasite bites, imperfections due to wounds/scratches, and others. The selling price has a high added value [1]. In the development of the leather processing industry, it is necessary to improve the basis of processing and testing technology to produce higher quality leather, and to be able to follow the development of fashion (fashionable), so that both local and international markets can accept it. One type of leather that can penetrate the global market is upholstery leather.

Upholstery leather is tanned using chrome tanning material, vegetable tanning material, or a combination of both with synthetic tanning materials (syntan) [1, 2]. They are made from whole cow and buffalo leather (whole hide).

Making quality upholstery leather requires a layer of granules [1]. Upholstery leather is usually used to make car seats and furniture-making materials, each of which has technical requirements according to its needs [1, 3]. Upholstery leather is very different from upper shoes regarding chemical properties and use. Upholstery leather is resistant to various temperatures, so it will not stick when hot or crack when the temperature is low. Currently, nitrocellulose has been replaced with a dispersed resin, which can be used as a binder in the finishing process [4].

Purnomo (2011) says that leather generally undergoes a stage called finishing, even though it is done very simply [5]. Efforts to improve the appearance of finished leather aim to increase its attractiveness and selling power. The repair process includes repairing

existing defects caused by natural defects, storage (wounds, disease marks, and insects), and those that occur during the process. These defects include uneven and faded colors and do not match color standards. This needs to be repaired and perfected, even if only to adjust the hue, shading, and color tone. Finishing is also done for specific purposes, such as giving a different look, pattern, touch/feel/handle, softer, smoother, rougher, oily, waxy, silky, contrasting color, brilliant, pull-up, antique, two-tone, and others. The object of finishing is to give specific properties to the surface/grain and simultaneously highlight and maintain the natural properties of the leather. In general, there are three layers in the leather finishing stage: the base coat layer, the color coat layer, and the top coat layer.

The excellent adhesion of the initial and base coats greatly influences the following process. Therefore, the use of quality materials needs attention [6]. The ingredients' composition affects the leather surface's absorption properties and the finished leather's degree of penetration. Adhesion is also influenced by the mechanical application type, which is the drying method. The adhesion of the finished leather is tested by a quick reference test in which an adhesive tape is applied to the leather specimen. Quantitative measurement of adhesion is carried out in a tensile strength tester. The leather specimen is attached to a strong support surface using a two-component adhesive for a specified time.

Delamination is a type of layer deformation in a laminated material caused by stress and pressure on the material [7, 8]. Based on ISO 11644:2009, delamination is obtained by testing the grain of the leather strip that has been glued to the adhesive plate using an adhesive film. Delamination occurs if, during the test, the top layer or individual layers stick to the adhesive plate. One way to minimize the occurrence of delamination on the skin is usually done by cross-linking. Cross-linking is joining two polymer molecular chains by bridging between elements, groups, or compounds that are joined by carbon atoms in the main chain of chemical bonds [9].

Cross-linkers are chemical substances that react with various functional groups to make polymer binders through cross-linking. Binder polymers are polymers that are capable of forming upon drying the surface of the film layer. There are three types of polymer binders in leather finishing: acrylic, butadiene, and polyurethane [10]. Each binder polymer has its properties and characteristics depending on the cross-linker used to form the cross-linking. The bond structure of the polyurethane binder has high strength and cohesion energy and produces more strong bond strength [11]. The formation of cross-linking will also result in the finished leather becoming more resistant to friction, to water and solvents, to adhesion, and to abrasion [12-14]. Therefore, the formation of cross-linking in polyurethane binders is very important [15]. Polyurethane binders are formed due to the reaction between isocyanate groups (R - N = C = O) with hydroxyl groups (OH). This study will use isocyanate compounds in the form of polyurethane binders as cross-linkers. Isocyanate compounds have an -NCO functional group that will interact with the hydroxyl group (-OH) of the binder, which occurs at low temperatures (< 150 °C) [16, 17]. Variations in the use of isocyanate as a cross-linker are expected to provide optimum

conditions in producing finished leather for automotive seat cover.

## EXPERIMENTAL

### Materials and Methods

#### Materials

The materials that have been used in the research are crust-dyed leather with quality: C60, thickness 1.1-1.4 mm, 3 sqft, isocyanate (cross-linker), Compound Manama DLH, polyurethane, silicon, wax, pasta color, H<sub>2</sub>O. All materials are of technical grade.

#### Methods

The crust-dyed leather that has been used previously has gone through a conventional process consisting of soaking, liming, deliming, bating, pickling, tanning, retanning, dyeing, fat liquoring, fixing, and so on. At the finishing stage, the variation has been done by using isocyanate as a cross-linker on the base coat, medium coat, and top coat, according to Table 1. The finished leather is then analyzed for adhesion resistance, thickness, color-fastness, and softness. Analysis refers to ISO 11644:2009(E) IULTCS/IUF 470:2009(E).

Table 1: Formulation of Base, Medium, and Top Coat Finished Leather for Automotive Seat Cover

Parameters	Formulation		
	A1 (2%)	A2 (3%)	A3 (4%)
1. Base coat			
Compound Manama DLH	1000	1000	1000
Pasta color	100	100	100
Isocyanate	22	33	44
2. Medium coat			
Water		240	
Silicone		30	
Polyurethane		760	
Pasta color		100	
Isocyanate		79.03	
3. Top coat			
Water		235	
Silicone		102	
Wax		40	
Polyurethane		676	
Isocyanate		147.44	

## RESULTS AND DISCUSSIONS

The process of forming cross-linking between the hydroxyl group (-OH) on the binder and the -NCO group on the isocyanate will result in strong cross-linking as shown in Figure 1. This interaction occurs after the C=N double bond is broken to form a carbonyl

(positive charge). The hydroxyl group will be free to attack the carbonyl by releasing hydrogen. So that cross-linking will be formed between isocyanate and hydroxyl groups to form polyurethane binders. The cross-linking is expected to reduce the delamination on finished leather for automotive seat cover so that high-quality products are produced.

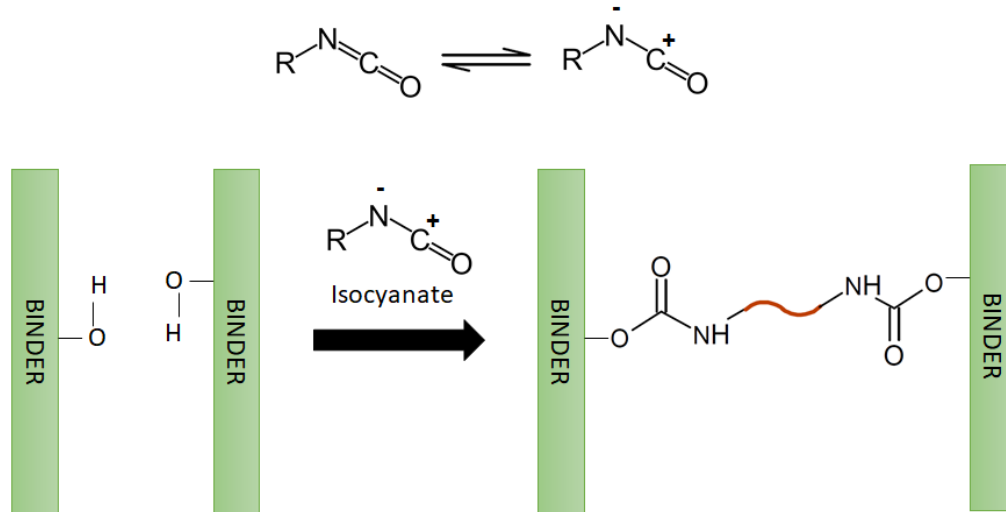


Figure 1. Interaction of hydroxyl group from the binder and isocyanate group as cross-linker

The adhesion resistance test is a test to measure the resistance of the finishing layer to be separated from the substrate (leather). The finishing formulation for finished leather for automotive seat cover uses 2% cross-linker isocyanates (A1) with an adhesion resistance value of 12.4 N. However, the A1 formulation has a delamination result that is not following the standard (ISO 11644:2009(E) IULTCS/IUF 470:2009(E)), namely peeling off the top coat without being followed by a base coat layer (Figure 2a). The adhesion resistance test for finished leather for automotive seat cover, which uses 3% cross-linker isocyanates (A2), has decreased by 11.9 N. This result still follows the standard, which is more than 3 N (Figure 2b). The results of the adhesion resistance test from finished leather for automotive seat cover with 4% cross-linker

isocyanates (A3) also showed good delamination; namely, the three finishing layers (base coat, medium coat, and top coat) appeared to stick together and peel off so that the leather on the crust was visible at 24.5 N (Figure 2c).

The addition of a cross-linker in the base coat indicates an increase in the force required to separate the finishing layer from the leather. The results of the adhesion resistance test of the A3 formulation were more excellent than the A1 and A2 formulations of the adhesion resistance test. This indicates that the delamination process decreases in the A3 formulation. This shows that more use of cross-linker in the base coat can improve the inter-coat adhesion on the automotive seat cover finishing layer.



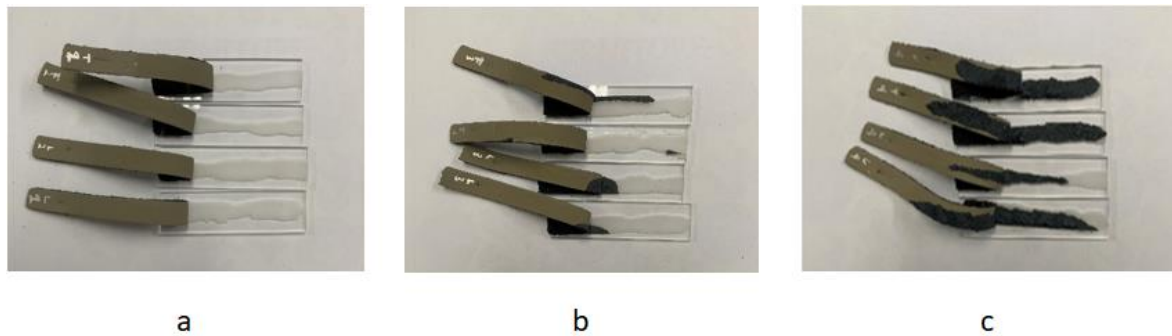


Figure 2. Adhesion test on Finished Leather for Automotive Seat Cover Using Isocyanate (a) 2%, 12.4 N adhesion resistance (b) 3%, 11.9 N adhesion resistance; and (c) 4%, 24.5 N adhesion resistance

One of the parameters to determine the quality of finished leather for automotive seat cover is the thickness test. The thickness test on the finished leather for automotive seat cover is a combination of the thickness of the crust leather and the finishing layer or the total of the finished leather. The higher the ratio between (NCO):(OH), the faster the finishing layer will dry [18-20]. The faster the

finishing layer dries, the less absorption it will have on the leather, so it will cause the finishing layer on the leather surface to be thicker. The standard thickness of finished leather for automotive seat cover is usually in the range of 1.0-1.4 mm. The thickness of the finished leather for the sample formulations A1, A2, and A3 was 1.1; 1.2; and 1.2 mm (Table 2).

Table 2: Test result for Finished Leather for Automotive Seat Cover

Parameters	Cross-linker variation formulation		
	A1 (2%)	A2 (3%)	A3 (4%)
Adhesion Resistance (N)	12.4	11.9	24.5
Thickness (mm)	1.1	1.2	1.2
Color-fastness to Dry Rubbing	-	-	4
Color-fastness to Wet Rubbing	-	-	4
Color-fastness to Rubbing with Benzine	-	-	4
Softness (mm)	3.92	3.60	3.42

The color fastness test for finished leather for automotive seat cover was carried out with 3 types of tests using dry felt, wet felt with water, and wet felt with petrol/benzine. The color fastness test on dry felt was carried out for 2000 cycles with a minimum value of 4 (good). The color fastness test standard for wet felt with water is carried out for 1000 cycles per minute with a minimum value of 4 (good). The standard for color fastness testing for wet felt with petrol/benzine is carried out for 10 cycles per minute with a minimum value of 4 (good). The higher the color fastness value, the better the color fastness test of finished leather [7]. This can also

indicate that the more cross-linkers are added, the more cross-linking is formed. This can increase the bond strength between layers (base, medium, and top coat) on the finished leather. The more cross-linking that is formed will increase the value of the color fastness of a material [21].

The color fastness test was only carried out on automotive seat covers using the A3 formulation because only the A3 formulation had results without delamination. The color fastness test results of A3 were obtained with a value of 4 (following the standard). The results of the color fastness test can be seen in Figure 3.

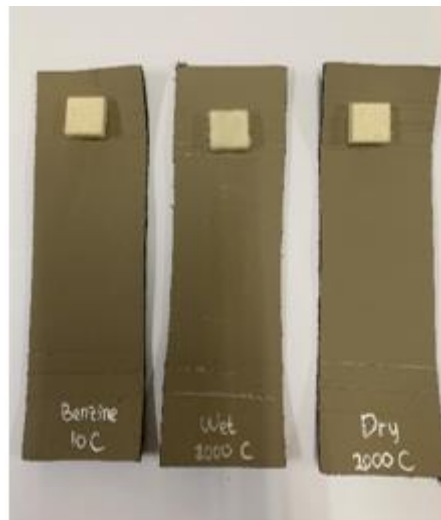


Figure 3. Test Results for Color fastness Formulation A2 with 4% cross-linker

Softness testing of finished leather for automotive seat cover has a standard of 3-4 mm. The results of testing the sample formulations A1, A2, and A3 obtained 3.92, 3.60, and 3.42 mm, respectively. Then the addition of a cross-linker results in a reduction in the softness of the finished leather. This could be due to the cross-linker isocyanates being very easily dispersed into a dilute mixture. These materials have high reactivity and can be used on the base and top coats. Polyisocyanates are used to harden polyurethanes through crosslinking reactions (Fig. 1) and are related to previous research [22, 23]. Softness testing of finished leather for automotive seat cover has a standard of 3-4 mm. If the thickness of the finished leather for automotive Seat cover is <3 mm, it will increase the air permeability but can also decrease the dimensional stability of the leather, so it is not suitable for finished leather for automotive seat cover [24].

## CONCLUSIONS

The addition of isocyanate as a cross-linker by 4% in the automotive seat cover base coat can reduce delamination, increase the thickness from 1.1 mm to 1.2 mm, improve the color fastness resistance to a value of 4, and reduce the softness value from 3.92 mm to 3.42 mm. The greater the addition of isocyanate as a cross-linker can improve the

quality of finished leather for automotive seat cover.

## REFERENCES

1. Wiyodiningrat, S., Setyamurti, R., Pahlawan, I.F., Research on Making Environmentally Friendly Upholstery Leather / Carseat for Automotive, *Majalah Kulit, Karet Dan Plastik*, **2012**, 28, 1, 09-17, <https://doi.org/10.20543/mkkp.v28i1.200>.
2. Gaoming, C., Bingzhang, L., Bo, L., *A Study of Cattle Hide Automobile Upholstery*, Beijing: China Leather Industry Research Institute, **2011**.
3. Cech, P. and Stadnik, J., VOC Emissions from Natural Upholstery Leathers, *Polish Journal of Environmental Studies*, **2021**, 30, 6, 4945-4955, <https://doi.org/10.15244/pjoes/134851>.
4. Thorstensen, T., *Practical Leather Tehnology*, 4th edition. Florida. New York: Robert E. Keiger Publishing Company Malabar, **1993**.
5. Purnomo, E., *Softy Leather*. Yogyakarta: Politeknik ATK Yogyakarta, **2011**.
6. John, G., *Possible Defects in Leather Production*. Hemsbach: Lampertheim, **1997**.
7. Suriani, M.J., Rapi, H.Z., Ilyas, R.A., Petru, M., Sapuan, S.M., Delamination and Manufacturing Defects in Natural Fiber-Reinforced Hybrid Composite: A Review,

- Polymers*, **2021**, 13, 1323, <https://doi.org/10.3390/polym13081323>.
8. Patten, E.W., Atwood, S.A., Van Citters, D.W., Jewett, B.A., Pruitt, L.A., Ries, M.D., Delamination of a Highly Cross-Linked Polyethylene Liner Associated with Titanium Deposits on the Cobalt-Chromium Modular Femoral Head Following Dislocation, *J Bone Jt Surg (Br)*, **2010**, 92-B, 9, 1306-1311, <https://doi.org/10.1302/0301-620X.92B9.24290>.
  9. Musa, B.H., Hameed, N.J., Effect of Crosslinking Agent (Glutaraldehyde) on the Mechanical Properties of (PVA/Starch) Blend and (PVA/PEG) Binary Blend Films, *J Phys Conf Ser*, **2021**, 1795, 1, 012064, <https://doi.org/10.1088/1742-6596/1795/1/012064>.
  10. Olle, L., Bacardit, A., Morera, J.M., Bartoli, E., Argelich, J., Cross-linked Polymers for Aqueous Finishing. Binders Crosslinked with Polyaziridine. Part I: Behaviour of Polyurethane, *J Soc Leather Technol Chem*, **2008**, 92, 3, 96-102.
  11. Sun, M., Bi, Y., Zhuang, W., Chen, S., Zhao, P., Pang, D., Zhang, W., Mechanism of Polyurethane Binder Curing Reaction and Evaluation of Polyurethane Mixture Properties, *Coatings*, **2021**, 11, 1454, <https://doi.org/10.3390/coatings11121454>.
  12. Sarkar, K., *Theory and Practice of Leather Manufacture*, Mahatma Gandhi road. Madras: Second Avenue, **1995**.
  13. Bacardit, A., Shendrik, A., Combalia, F., Jorge, J., Olle, L., Study of Cross-Linking Reactions on Butadiene Binders in Aqueous Finishing, *J Soc Leather Technol Chem*, **2010**, 94, 248-253.
  14. Cheaburu-Yilmaz, C.N., Ozkan, C.K., Yilmaz, O., Synthesis and Application of Reactive Acrylic Latexes: Effect of Particle Morphology, *Polymers (Basel)*, **2022**, 14, 11, 2187, <https://doi.org/10.3390/polym14112187>.
  15. Olle, L., Frias, A., Sorolla, S., Cuadros, R., Bacardit, A., Study of the Impact on Occupational Health of the Use of Polyaziridine in Leather Finishing Compared with a New Epoxy Acrylic Self-Crosslinking Polymer, *Prog Org Coat*, **2021**, 105, 106162, <https://doi.org/10.1016/j.porgcoat.2021.106162>.
  16. June, Y.-G., Jung, K.I., Choi, M., Lee, T.H., Noh, S.M., Jung, H.W., Effect of Urethane Crosslinking by Blocked Isocyanates with Pyrazole-Based Blocking Agents on Rheological and Mechanical Performance of Clearcoats, *Coatings*, **2020**, 10, 961, <https://doi.org/10.3390/coatings10100961>.
  17. Panwiriyarat, W., Tanrattanakul, V., Pillard, J.-F., Pasetto, P., Khaokong, C., Effect of the Diisocyanate Structure and the Molecular Weight of Diols on Bio-Based Polyurethanes, *J Appl Polym Sci*, **2013**, 130, 1, 453-462, <https://doi.org/10.1002/app.39170>.
  18. Liow, K.S., Sipaut, C.S., Mansa, R.F., Ung, M.C., Ebrahimi, S., Effect of PEG Molecular Weight on the Polyurethane-Based Quasi-Solid-State Electrolyte for Dye-Sensitized Solar Cells, *Polymers*, **2022**, 14, 3603, <https://doi.org/10.3390/polym14173603>.
  19. Gogoi, R., Alam, M., Khandal, R., Effect of Increasing NCO/OH Molar Ratio on the Physicomechanical and Thermal Properties of Isocyanate Terminated Polyurethane Prepolymer, *Int J Basic Appl Sci*, **2014**, 3, 2, 118-123, <https://doi.org/10.14419/ijbas.v3i2.2416>.
  20. Sebenik, U., Krajnc, M., Influence of the Soft Segment Length and Content on the Synthesis and Properties of Isocyanate-Terminated Urethane Prepolymers, *Int J Adhes Adhes*, **2006**, 27, 7, 527-535, <https://doi.org/10.1016/j.ijadhadh.2006.10.001>.
  21. Lv, Z., Tan, T., Hussain, M., Zhou, W., Ma, M., Effects of Crosslinking Sericin on the Color Fastness and Antioxidant Activity of Naturally Colored Silk, *Fibers Polym*, **2022**, 23, 658-665, <https://doi.org/10.1007/s12221-022-3082-y>.
  22. Ahmed, S., Zohra, F.-T., Ecological Aspects of Cross Linking Agents and Their Role in Leather Finishing for the Production of Finished Leather, *LeatherAge*, **2011**, XXXIII, 2, 67-71.
  23. Rosita, G., Changes in the Formation Characteristics of Polyurethane Based on HTPB and TDI Reaction Composition, *Jurnal Teknologi Dirgantara*, **2016**, 14, 2, 159-170, <https://doi.org/10.30536/j.jtd.2016.v14.a2420>.

24. Roh, E.K., Effect of Punching on Physical and Mechanical Properties of Leathers: Focus on Car Seat Covers, *Journal of Engineered Fibers and Fabrics*, **2019**, 14, <https://doi.org/10.1177/1558925019890569>.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).



# THE EFFECT OF HEATING TIME ON THE THERMAL STABILITY OF CHROME-TANNED LEATHER

Gresy GRIYANITASARI<sup>1,2</sup>, Ambar PERTIWININGRUM<sup>2</sup>, Nanung Agus FITRIYANTO<sup>2</sup>, Yuny ERWANTO<sup>2\*</sup>

<sup>1</sup>Center of Standardization and Services for Leather, Rubber, and Plastics Industry, Ministry of Industry, Jl. Sokonandi No. 9  
Yogyakarta, Indonesia 55166

<sup>2</sup>Division of Animal Products Technology, Faculty of Animal Science, Universitas Gadjah Mada, Jl. Fauna No. 03, Bulak  
Sumur, Yogyakarta, Indonesia 55281

Received: 30.11.2022

Accepted: 13.02.2023

<https://doi.org/10.24264/lfj.23.1.3>

## THE EFFECT OF HEATING TIME ON THE THERMAL STABILITY OF CHROME-TANNED LEATHER

**ABSTRACT.** Chrome tanning is an essential process to convert raw animal skin into leather, in which collagen, as the main structure of leather, is stabilized against degradation through cross-linking using chromium, consisting of two steps: penetration and basicity. However, the uptake of chrome in leather still needs to be improved. The purpose of this study was to find the best heating time in the chrome tanning process by thermal analysis. Pickled sheepskin was used as raw material for the chromium tanning process. The samples were varied into four categories: heated at the penetration stage of the tanning process (Initial Heating), heated at the basification stage of the tanning process (Final Heating), and heated both at the penetration and basification stage (Continuous Heating). In this study, the thermal stability of wet blue leather was evaluated by shrinkage temperature behavior (Ts), thermogravimetry analysis (TGA/DTG), and differential scanning calorimetry (DSC). The tanning efficiency was measured by Cr<sub>2</sub>O<sub>3</sub> content. The results demonstrated that wet blue samples heated continuously shows better thermal characteristics. In conclusion, the results can be used for finding the best possible technique for the leather tanning process using chrome salts to gain thermal stability.

**KEY WORDS:** chrome tanning, leather, thermal stability

## INFLUENȚA TIMPULUI DE ÎNCĂLZIRE ASUPRA STABILITĂȚII TERMICE A PIELII TĂBĂCITE ÎN CROM

**REZUMAT.** Tăbăcirea în crom este un proces esențial pentru transformarea pielii brute în piele finită, în care colagenul, ca structură principală a pielii, este stabilizat împotriva degradării prin reticulare folosind crom, constând în două etape: pătrunderea tanantului și bazificare. Cu toate acestea, absorbția cromului în piele are nevoie de îmbunătățire. Scopul acestui studiu a fost de a găsi cel mai bun timp de încălzire în procesul de tăbăcire în crom prin analiza termică. S-a folosit piele de oaie piclată ca materie primă pentru procesul de tăbăcire în crom. Probele au fost împărțite în patru categorii: încălzite în stadiul de pătrundere a tanantului (încălzire inițială), încălzite în stadiul de bazificare al procesului de tăbăcire (încălzire finală) și încălzite atât în stadiul de pătrundere a tanantului, cât și în cel de bazificare (încălzire continuă). În acest studiu, stabilitatea termică a pielii wet blue a fost evaluată prin temperatura de contracție (Ts), analiza termogravimetrică (TGA/DTG) și calorimetria de scanare diferențială (DSC). Eficiența tăbăcirii a fost măsurată prin conținutul de Cr<sub>2</sub>O<sub>3</sub>. Rezultatele au demonstrat că probele de piele wet blue încălzite continuu prezintă caracteristici termice mai bune. În concluzie, rezultatele pot fi folosite pentru găsirea celei mai bune tehnici posibile pentru procesul de tăbăcire a pielii folosind săruri de crom pentru o stabilitate termică mai mare.

**CUVINTE CHEIE:** tăbăcire în crom, piele, stabilitate termică

## L'EFFET DU TEMPS DE CHAUFFAGE SUR LA STABILITÉ THERMIQUE DU CUIR TANNÉ AU CHROME

**RÉSUMÉ.** Le tannage au chrome est un processus essentiel pour convertir la peau animale brute en cuir, dans lequel le collagène, en tant que structure principale du cuir, est stabilisé contre la dégradation par réticulation à l'aide de chrome, composé de deux étapes : pénétration et basicité. Cependant, l'absorption du chrome dans le cuir doit encore être améliorée. Le but de cette étude a été de trouver le meilleur temps de chauffage dans le procédé de tannage au chrome par l'analyse thermique. La peau de mouton picklée a été utilisée comme matière première pour le processus de tannage au chrome. Les échantillons ont été répartis en quatre catégories : chauffés à l'étape de pénétration du processus de tannage (chauffage initial), chauffés à l'étape de basification du processus de tannage (chauffage final) et chauffés à la fois à l'étape de pénétration et de basification (chauffage continu). Dans cette étude, la stabilité thermique du cuir wet blue a été évaluée par la température de rétrait (Ts), l'analyse thermogravimétrique (TGA/DTG) et la calorimétrie différentielle à balayage (DSC). L'efficacité du tannage a été mesurée par la teneur en Cr<sub>2</sub>O<sub>3</sub>. Les résultats ont démontré que les échantillons de cuir wet blue chauffés en continu présentent de meilleures caractéristiques thermiques. En conclusion, les résultats peuvent être utilisés pour trouver la meilleure technique possible pour le processus de tannage du cuir en utilisant des sels de chrome pour une plus grande stabilité thermique.

**MOTS CLÉS :** tannage au chrome, cuir, stabilité thermique

## INTRODUCTION

Leather is the first biomaterial humans ever made and has continuously been produced until now. The characteristic of

leather as the raw material used for a wide variety of products is still irreplaceable. Nowadays, 80-90% of leather is produced by the chrome tanning process using trivalent chromium (Cr<sup>3+</sup>) salt as the tanning agent [1, 2].

\* Correspondence to: Yuny ERWANTO, Division of Animal Products Technology, Faculty of Animal Science, Universitas Gadjah Mada, Jl. Fauna No. 03, Bulak Sumur, Yogyakarta, Indonesia 55281, [yunyer@ugm.ac.id](mailto:yunyer@ugm.ac.id)

The chrome-tanned leather has excellent organoleptic properties, versatile applicability, and hydrothermal stability compared with other-tanned leather [3]. Thus, the chrome tanning process is still the most popular and widely preferred system in leather tanning industries.

Chrome tanning is an essential process to convert raw animal skin into leather, in which collagen, as the main structure of leather, is stabilized against degradation through cross-linking using chromium consists of two steps: penetration and basicity. In the first step, basic chrome sulfate will penetrate the collagen matrix. Then, the chromium and the carboxyl collagen will form inter and intra-molecular cross-links through the basicity step [1]. However, the uptake of chrome in leather is only 40-70% [2, 4], and as a consequence, 30% of chrome is discharged into tannery effluent resulting in environmental stress and severe health effects on humans because chromium ( $\text{Cr}^{3+}$ ) might potentially transform into hexavalent chromium ( $\text{Cr}^{6+}$ ).

Poor chromium uptake can cause parallel problems: low quality of tanned leather produced, high level of toxicity in the environment, and resulted in increased amount of production costs [5]. Thus, research in the area of chromium tanning still focuses on a cleaner tanning process by increasing chrome uptake [1, 5]. However, a more efficient tanning process needs to be achieved to increase chromium uptake without adding more chromium which might harm the environment and cause higher costs. Temperature is an additional driving force in the tanning process that can affect the diffusion rate [6] and the reaction rate of basification [6]. However, the appropriate heating time still needs to be explored to achieve better chromium uptake.

One of the most significant changes caused by the tanning process is the increase in thermal stability using various methods [7]. Thermal analysis is a helpful group of analytical techniques to measure the property of leather as a function of temperature. Remembering that collagen is the primary structural element in the extracellular matrix of animal skin, one of the methods to measure the quality of tanned leather is its thermal resistance against shrinkage, which indicates the amount of chromium reacted with the collagen carboxyl leather [1]. The more chromium can be fixed to the collagen carboxyl group, the higher the thermal stability. Unfortunately, such an indicator still lacks the molecular level observation of collagen in the tanning process [4]. Thermogravimetry Analysis (TG/DTG) and Differential Scanning Calorimetry (DSC) are the most used methods to characterize collagen-based material. Therefore, investigation of the thermal behavior of wet blue leather with different heating stages using TG/DTG and DSC will drive a new strategy in the tanning process.

## MATERIAL AND METHODS

### Samples Preparation

Pickled sheepskins have been selected for this experiment since it is the raw material in the worldwide garment industry, and there is still severe research about sheep leather's thermal properties. Pickled sheepskins were obtained from skin suppliers in Yogyakarta, Indonesia. Then, the skin was cut approximately into 10 x 10 cm samples from the same lateral positions of the sheepskin following the line of the backbone of the sheep, assuming that the samples have similar thicknesses and properties. Meanwhile, chemical stores in the same region acquired NaCl, H<sub>2</sub>O, basic chromium sulfate (BCS), HCOONa, and NaHCO<sub>3</sub>. BCS used in this study was Chromosal® chrome tanning salt from

Lanxess contained approximately 26% of Cr<sub>2</sub>O<sub>3</sub> content and 33% basicity [8].

### Chromium Tanning Procedure

The chrome tanning was conducted in a 1000 mL glass beaker covered with aluminum foil to prevent loss of liquid caused by heating. It was kept in the water bath to maintain the temperature. The samples were varied into four categories: heated at the penetration

stage of the tanning process (Initial Heating), heated at the basification stage of the tanning process (Final Heating), and heated both at the penetration and basification stage (Continuous Heating). The control experiment was performed by tanning the sheepskin at room temperature (Without Heating). The temperature was heated as soon as the beaker was placed in the water bath until the targeted temperature was achieved at 40 ± 2 °C.

Table 1: Chrome tanning recipes

Stage	Chemicals	Quantity (%)	Duration (min)	Remarks
Penetration	BCS	3	30	Penetration was checked
	BCS	3	30	
	HCOONa	1	30	
Basification	NaHCO <sub>3</sub>	0.375	15	pH = 4
		0.375	15	
		0.375	15	
		0.375	15	
Horse up	-	-	90	Stirred and then drained Overnight
	-	-		

The percentage of chemicals and water in this experiment was calculated based on the weight of the pickled sheepskin. Before tanning, the samples were stirred with 100% of water and 8% of NaCl for 10 minutes (pH = 3). This step was conducted in the beaker glass at room temperature. Then, the samples were added with chemicals based on the tanning recipes from Schroepfer & Meyer [9] and Mengistie *et al.* [1] with slight modifications, as seen in Table 1. Before the addition, HCOONa and NaHCO<sub>3</sub> were diluted 1:10 with water. After horsing up, each wet blue leather sample was stored in a plastic bag for analysis.

### Tanning Efficiency

The tanning efficiency in this study will be measured by the content of Cr<sub>2</sub>O<sub>3</sub> in the wet blue leather. The samples were analyzed for the Cr<sub>2</sub>O<sub>3</sub> content using titration [10]. Samples were ground and weighed into a conical flask. 10 mL of nitric acid was added and let stand for 2 minutes. Then, 15 mL of sulfuric/perchloric acid mixture and a few antibumping grains

were added. A funnel was placed in the flask's neck and brought to a boil on a wire gauze over a moderate flame. When the reaction mixture began to become orange, the flame was reduced. After the color has completely changed, it was heated for at least 2 minutes. Then, it was left for 5 minutes until cool and diluted to 200 ml. It was boiled for 10 minutes to remove chlorine and let it cool. Next, 5 mL of orthophosphoric acid was added to cover up any iron.

The obtained solution was added to the potassium iodide solution and left in the dark. After that, 0,1 mol/L sodium thiosulfate solution was titrated until the solution was either light green or blue using 5 mL of starch indicator solution that was added at the end of the process. The amount of chrome oxide can be calculated by equation (1).

$$w_{Cr} = \frac{V1 \times 0.00253 \times 100 \times F}{m_0} \quad (1)$$

where  $w_{Cr}$  is the percentage by mass on dry matter of Cr<sub>2</sub>O<sub>3</sub>,  $V1$  is the volume of 0.1 mol/L of thiosulfate solution (mL),  $m_0$  means the

weight of the samples (g), and F is the correct factor to 0% volatile matter that was calculated by equation (2).  $w_w$  is the content of volatile matter (%).

$$F = \frac{100}{100 - w_w} \quad (2)$$

### Shrinkage Temperature

Each sample was cut into three rectangular shapes with a size of  $(50 \pm 2) \times (3 \pm 2)$  mm. The shrinkage temperature test was conducted using a digital shrinkage temperature tester with the ISO 3380 [11] method. One end of the sample was attached to a fixed holder and the other was attached to a movable hook. Next, the threads, pulleys, and mass were adjusted so that the sample was attached to the load pressure. Water : glycerine (75:25) was placed in a beaker glass and heated at the rate of temperature  $2 \text{ }^\circ\text{C}/\text{minute} \pm 0,2 \text{ }^\circ\text{C}/\text{minute}$ . The digital panel will show the temperature when the sample shrinkage at  $150 \text{ } \mu\text{m}$ . The average of three pieces of samples is the shrinkage temperature.

### Thermogravimetry (TG) and Derivative Thermogravimetry (DTG)

TG/DTG curves were obtained in a temperature range of  $30\text{-}550 \text{ }^\circ\text{C}$ , utilizing STA 200 RV Thermal Analyzer under a nitrogen atmosphere ( $100 \text{ mL}/\text{min}$ ) with a heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$ . An Aluminum sample pan containing a mass of around  $7\text{-}9 \text{ mg}$  was used in the analysis. Data were analyzed by Origin software.

### Differential Scanning Calorimetry (DSC)

DSC curves were obtained at the temperature range of  $30\text{-}550 \text{ }^\circ\text{C}$ , utilizing the software STA 200 RV Thermal Analyzer under nitrogen atmosphere ( $5 \text{ }^\circ\text{C}/\text{min}$  heating rate)

with an aluminum pan containing sample mass around  $7\text{-}9 \text{ mg}$  as a reference. Also for DSC, data were analyzed by Origin Software.

## RESULTS AND DISCUSSION

### Tanning Efficiency

The efficiency of chromium tanning in this study is depicted with the  $\text{Cr}_2\text{O}_3$  content of wet blue leather. The effect of heating on  $\text{Cr}_2\text{O}_3$  uptake is shown in Fig. 1. Leather that is tanned without heating neither at the penetration nor the basification stage shows the lowest content of  $\text{Cr}_2\text{O}_3$ . Meanwhile, leather with continuous heating has uptake more  $\text{Cr}_2\text{O}_3$  than others. The reaction between chrome and collagen increases when the temperature rises [6]. The optimal uptake of  $\text{Cr}_2\text{O}_3$  appears at the longest heating time, starting from the beginning of the penetration stage until the end of the basification stage.

Temperature is one of the factors that affect the reaction between chromium and collagen because it can influence viscosity, equilibrium composition, and chromium polymerization. Then, heating can increase acid-base dissociation in the chromium complexes aqua ligands [12]. However, a study by Bickley *et al.* [13] found that the diffusion of chromium in the collagen matrix will only increase when the temperature is lower than  $50 \text{ }^\circ\text{C}$ . When chrome was fixed at a temperature of more than  $60 \text{ }^\circ\text{C}$  chrome content will be high but the chrome precipitation on the surface of the leather will be uneven. The results are in accordance with this study since the leather tanning process was heated at the temperature of  $40 \text{ }^\circ\text{C}$ . The chrome uptake of heated samples shows higher  $\text{Cr}_2\text{O}_3$  content than those without heated samples.



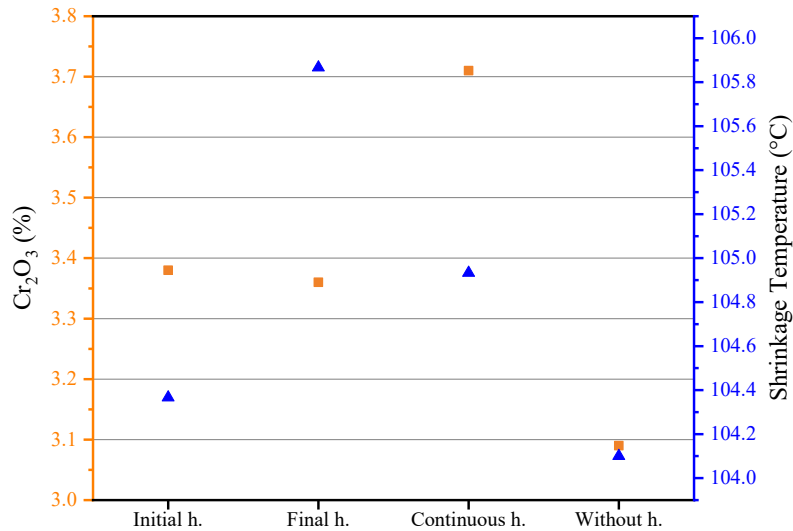


Figure 1. Cr<sub>2</sub>O<sub>3</sub> content and shrinkage temperature of different heating times

### Shrinkage Temperature Behaviour

The success of a leather tanning process is generally indicated by the shrinkage temperature (Ts), the temperature at which a sudden and irreversible shrinkage occurs when it is heated gradually in the aqueous solution [14]. The result of this study is expressed in Fig. 1 that the unheated sample shows the lowest Ts as the Cr<sub>2</sub>O<sub>3</sub> content. However, Final heating samples show the highest Ts with lower Cr<sub>2</sub>O<sub>3</sub> uptake and Continuous heating samples show the highest content of Cr<sub>2</sub>O<sub>3</sub> with lower Ts. Those results are consistent with the study conducted by Mengistie *et al.* [1] that compared with lower temperature, heating at 40 °C in the tanning process could result in higher Ts but the chrome uptake was lower. In contrast, higher Ts normally means higher Cr<sub>2</sub>O<sub>3</sub> content because chrome fixation on collagen is increased [6].

It might be caused by the nature of collagen changing early in the process as a result of increased temperatures [1]. Shrinking is the process to break and unravel the hydrogen bonding in the triple helices besides entailing the chrome-collagen bonds [6]. Thus, the higher temperature might shrink the collagen before it fully tanned which allows the

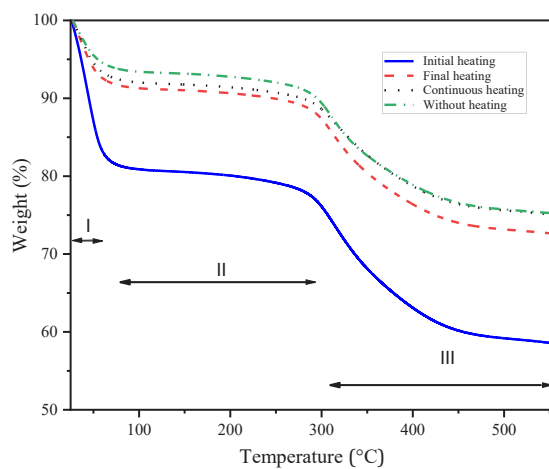
pores less open for chrome to get to the reaction site [1]. According to Esteban *et al.* [14], determining shrinkage temperature involves a series of processes starting with the first shrinkage when the individual fiber is noticed, other fibers follow the shrinking fiber to shrink, and most fibers shrink at the same time. The initial temperature when most fibers simultaneously shrink is the Ts. This process is still followed by the fibers experiencing concurrent shrinking, the last individual fibers shrinking, and finally, the fibers ultimately shrinking.

### TG and DTG Analysis

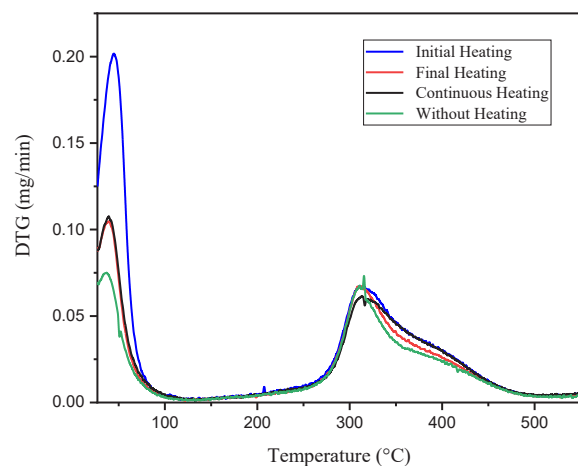
Thermogravimetry analysis is a widely used method for analyzing material decomposition and thermal stability by measuring mass change as a function of temperature in scanning mode or time in isothermal mode [15]. Fig 2a and b present the TG and DTG curves of the wet blue samples with different heating times. The thermogravimetric curve shows that all samples have three decomposition stages. The first stages happened at a temperature of about 26.744-60.03 °C (Table 1) which mainly indicates the loss of water, volatile compounds

with low molecular weight [16], and trapped gasses [17].

At the first stage of decomposition, the Initial Heating sample lost a higher percentage of mass (18.85%) than those of other samples. As explained by Gil *et al.* [18] that at the temperature up to 100 °C, leather focused on the loss of water presented in minor weight loss in the TGA curve, it is expected that the Initial Heating sample has a higher amount of water than the other samples. The initial heating sample only heated at the penetration stage and then decreased temperature at the beginning of the basification stage. When it is heated, more water-containing chromium diffuses in the collagen fiber. Then the temperature at the basicity is decreased which might cause less chrome to react with collagen carboxyl and result in a higher weight loss percentage at the third stage.



(a)



(b)

Figure 2. TG (a) and DTG (b) curves of wet blue samples

From Fig. 2a, it is found that the last stage goes from 284.029-549.913 °C. This stage is characterized by the most significant amount of weight loss and detected as peak and shoulder at the DTG curves (Fig. 2b). Most total volatiles are decomposed in this stage, including collagenous materials as the main component of leather. Moreover, the shoulder at a temperature of 330-440 °C appears more

At the same stage, the Without Heating samples lost a lower percentage of mass (6.252%), as described in Table 2. Meanwhile, The Final Heating and Continuous Heating show similar weight loss results at the first stage of decomposition, and both are higher than those Without Heating. It can be assumed that heating can increase the water penetration into the collagen matrix. The second stage occurred between 56.873-291.361 °C (Fig. 2b). In this stage, the chemisorbed water and low molecular weight molecules are responsible for mass loss [17]. As described in Table 2, the loss of weight for all samples shows a similar percentage and they show relatively small degradation at this stage. This might be due to the adsorbed or unstructured water being evaporated at about 100 °C and the collagen has just started to decompose at about 200 °C [19].

separated which might be due to collagen's varying degree of crosslinks. Mostly, at this range of temperatures, the carbonaceous components are decomposed [16]. Moreover, the scission of the hydroxyl groups happened at a temperature of around 300 °C [19]. From Table 1, the onset temperature of Continuous Heating is higher followed by a lower percentage of weight loss than those of others.

This result is consistent with the results of the Cr<sub>2</sub>O<sub>3</sub> content explained in Fig. 1. This result is also found in stages one and two. It shows that penetrating and basifying at a higher

temperature in the chrome tanning process can delay the leather fibers' decomposition and improve thermal stability [20].

Table 2: TG data of the wet blue leather at the different decomposition stages

Parameter	Initial Heating	Final Heating	Continuous Heating	Without Heating
Stage 1				
Onset Temperature (°C)	26.744	27.303	27.413	27.594
End temperature (°C)	58.635	58.496	60.03	56.873
Weight loss (%)	18.854	8.297	7.84	6.252
Stage 2				
Onset temperature (°C)	58.635	58.496	60.03	56.873
End temperature	281.276	288.119	291.361	286.686
Weight loss (%)	2.065	2.207	2.045	2.199
Stage 3				
Onset Temperature (°C)	284.029	288.119	291.361	286.686
End temperature (°C)	549.760	549.913	549.879	549.878
Weight loss (%)	20.482	16.829	15.015	16.285

The DTG peaks can be attributed to the thermal degradation of collagen leather (Fig. 2b). The peaks start at about 100 °C and end at about 550 °C for all wet blue samples with different heating times. The DTG curves show that the thermal decomposition of all the samples starts at the same temperature. However, the shoulder at about 380 °C appears

more separated from the peak at 330 °C. The heating treatment seems to have the most influence on the fractions of leather disintegrating at the temperature of 330-440 °C. Many polymer decompositions took place at this range of temperature [19], and most organic components are decomposed.

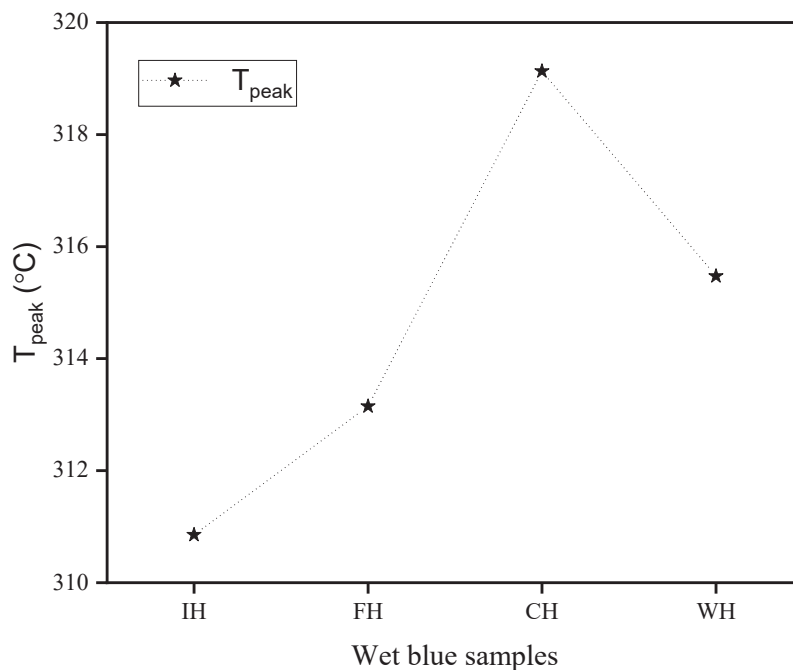


Figure 3. The temperature of the maximum decomposition rate (T<sub>peak</sub>)

The thermal stability of the samples in this study can be characterized by the temperature of the maximum rate of mass loss ( $T_{peak}$ ). As shown in Fig. 3, all of the samples show  $T_{peak}$  at the range of temperature 310-320 °C. The peak of the Continuous Heating sample is significantly lower than that of other heating treatment samples but shows a higher  $T_{peak}$  in the DTG curve (Fig. 3). This result is consistent with the previous analysis that heating continuously from the beginning until the end of the chrome tanning process increases the chrome – collagen coordinate covalent bonds. At the diffusion stage, heating could help the chromium to penetrate into the collagen matrix and at the basification stage, heating could accelerate the reaction rate of collagen carboxyl and chromium. Amino acid carboxyl groups might dissociate during molecular

thermal motion and release  $H^+$  because heating could decrease the pH of the amino acid chromium complex solution. By increasing the temperature, the dissociated carboxyl group of the amino acid may penetrate the inner part of the complex and coordinate with the chromium ion, resulting in a smaller amount of dissociated amino acid and a larger number of dissociated amino acid carboxyl groups in the solution [21].

### DSC Evidence of The Thermal Denaturation in Leather

The broader the peak of DSC thermogram indicates that the diffusion of the tanning agent across the thickness of the sheepskin is caused by the uneven crosslinking [22].

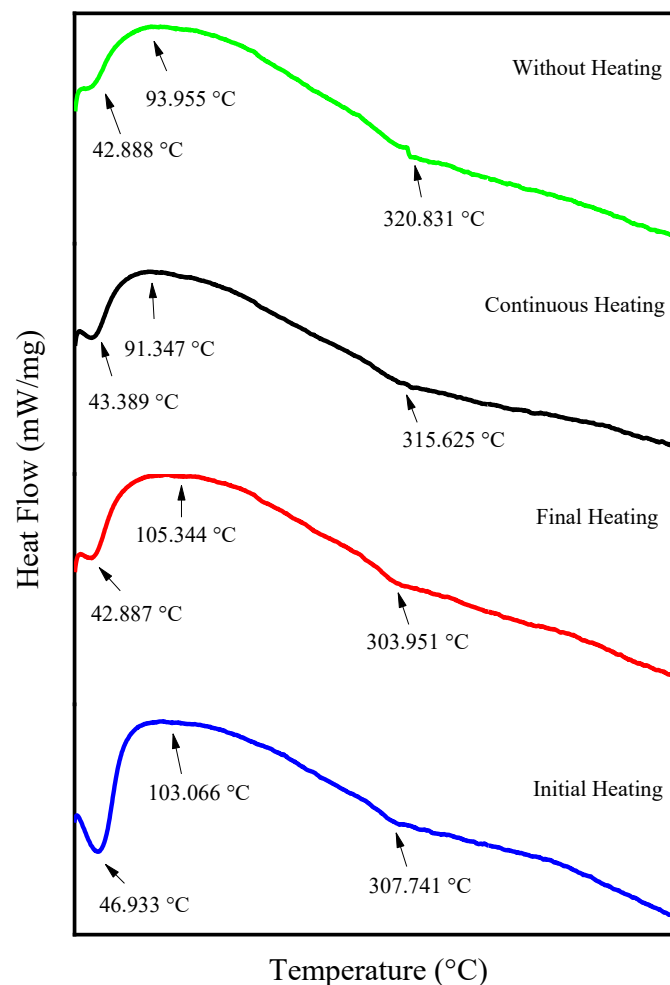


Figure 4. DSC Thermogram of wet blue samples



The overlay DSC thermogram of the wet blue samples is presented in Fig. 4. It can be seen that the samples show similar trends indicating that the collagen leather used has the same characteristic. There are three peaks observed from the thermograms as presented in Fig. 4. The first peaks are endothermic peaks in the range of temperature of 42.887-46.993 °C, the second peaks were at 91.347-105.344 °C, and the last peaks at 303.951-320.831 °C. The first ones indicate loose water and pore water evaporation of wet blue leathers [23]. It can be observed as the glass transition (T<sub>g</sub>) temperature which manifests as a subtle shift in the slope of the thermogram [24]. From Fig. 4 all of the samples in the experiment show a similar T<sub>g</sub> unless the Initial Heating (46.933 °C). According to Jeyapalina *et al.* [25] tanning agents are a plasticizer in the leather tanning process. It is possible that chrome salts will work by inserting themselves between the chains of the polymer and therefore changing the forces that are keeping the chains together. As a result, T<sub>g</sub>, as a viscoelastic transition is depressed. Thus, T<sub>g</sub> of more stable leather is lower than that of unstable leather.

At a higher temperature, the collagen gains enough energy to rearrange its microstructure as presented in the second peaks of DSC thermograms. These peaks can be observed as crystallization temperature (T<sub>c</sub>). Quite unexpectedly that the T<sub>c</sub> of Continuous Heating show is lower than those of other samples. This might be due to the effect of moisture content to support collagen–chrome crosslinking [9, 25]. This result is consistent with the TG results (Fig. 2a) that at the second stage of the decomposition, the excess water is still degraded. Besides, the curves are broader than other curves as an indication of how abrupt the temperature transition was and the uneven distributions of the collagen population with different thermal stability [22].

When the temperature is higher than 200 °C (third peaks) the collagen might be concluded as melting temperature (T<sub>m</sub>) [26]. T<sub>m</sub> is the temperature where the crystalline zone in the amorphous matrix is melted. Compared with others, T<sub>m</sub> Without Heating presents multiple peaks in accordance with the DTG analysis (Fig. 2b) that at the temperature of about 300 °C samples experienced a major weight loss. Meanwhile, Continuous Heating exhibits a smaller melting peak than other samples. This might be due to a higher degree of crosslinking that affect the T<sub>m</sub> of wet blue leather.

## CONCLUSIONS

In this study, an experimental investigation was carried out to predict the thermal behavior of wet blue leather tanned with different heating times, namely Initial Heating, Final Heating, Continuous Heating, and Without Heating. Differential Scanning Calorimetry and Thermogravimetry analysis combined with Shrinkage Temperature and Cr<sub>2</sub>O<sub>3</sub> content was used in this study to observe the effect of heating time on the thermal stability of leather. The obtained results can be used for finding the best possible technique for the leather tanning process using chrome salts to gain thermal stability.

## Acknowledgements

We are grateful to the Doctoral Dissertation Research Program of the Ministry of Research, Technology, and Higher Education for the financial support with contract number 089/E5/PG.02.00.PT/2022; 1924/UN1/DITLIT/Dit-Lit/PT.01.03/2022 and to the Center of Standardization and Services for Leather, Rubber, and Plastics Industry. Ministry of Industry for the laboratory facilities.

## REFERENCES

1. Mengistie, E., Smets, I., van Gerven, T., Ultrasound Assisted Chrome Tanning: Towards a Clean Leather Production Technology, *Ultrason Sonochem*, **2016**, 32, 204–212, <https://doi.org/10.1016/j.ultsonch.2016.03.002>.
2. Sathish, M., Dhathathreyan, A., Rao, J.R., Ultraefficient Tanning Process: Role of Mass Transfer Efficiency and Sorption Kinetics of Cr (III) in Leather Processing, *ACS Sustain Chem Eng*, **2019**, 7, 3875–3882, <https://doi.org/10.1021/acssuschemeng.8b04876>.
3. Wang, L., Han, W., Yu, Y., Zhou, J., Zhang, W., Shi, B., Thermodynamic Investigation on Chrome and Aluminum Tanning, *J Am Leather Chem Assoc*, **2017**, 112, 360–366.
4. Zhang, Y., Mansel, B.W., Naffa, R., Cheong, S., Yao, Y., Holmes, G., Chen, H.L., Prabakar, S., Revealing Molecular Level Indicators of Collagen Stability: Minimizing Chrome Usage in Leather Processing, *ACS Sustain Chem Eng*, **2018**, 6, 7096–7104, <https://doi.org/10.1021/acssuschemeng.8b00954>.
5. Zhu, R., Yang, C., Li, K., Yu, R., Liu, G., Peng, B., A Smart High Chrome Exhaustion and Chrome-Less Tanning System Based on Chromium (III)-Loaded Nanoparticles for Cleaner Leather Processing, *J Clean Prod*, **2020**, 277, 123278, <https://doi.org/10.1016/j.jclepro.2020.123278>.
6. Covington, A.D., *Tanning Chemistry: The Science of Leather*, Royal Society of Chemistry: Cambridge, **2009**.
7. Carşote, C., Badea, E., Miu, L., della Gatta, G., Study of the Effect of Tannins and Animal Species on the Thermal Stability of Vegetable Leather by Differential Scanning Calorimetry, *J Therm Anal Calorim*, **2016**, 124, 1255–1266, <https://doi.org/10.1007/s10973-016-5344-7>.
8. Lanxess, Chromosal B.
9. Schroepfer, M., Meyer, M., DSC Investigation of Bovine Hide Collagen at Varying Degrees of Crosslinking and Humidities, *Int J Biol Macromol*, **2017**, 103, 120–128, <https://doi.org/10.1016/j.ijbiomac.2017.04.124>.
10. BSN SNI ISO 5398-1: 2013: Kulit - Penentuan Kimiawi Kadar Krom Oksida - Bagian 1 : Kuantifikasi Dengan Cara Titrasi; Jakarta, **2013** (in Indonesia).
11. ISO 3380:2015 - Leather - Physical and Mechanical Tests - Determination of Shrinkage Temperature up to 100 °C (IULTCS/IUP 16); 3rd edition, International Organization for Standardization: Switzerland, **2015**.
12. Sreeram, K.J., Ramasami, T., Sustaining Tanning Process through Conservation, Recovery and Better Utilization of Chromium Related Papers Sustaining Tanning Process through Conservation, Recovery and Better Utilization of Chromium, *Resour Conserv Recycl*, **2002**, 38, 185–212, [https://doi.org/10.1016/S0921-3449\(02\)00151-9](https://doi.org/10.1016/S0921-3449(02)00151-9).
13. Bickley, J.C., Lee, H., Whitton, J.B., Comparison between Conventional Chrome Tannage and Heated Low Float Tannage, *J Soc Leather Technol Chem*, **1967**, 51, 385–397.

14. Esteban, B., Baquero, G., Cuadros, R., Morera, J.M., Proposal and Application of a New Method to Determine Leather Shrinkage Temperature, *Thermochim Acta*, **2021**, 698, <https://doi.org/10.1016/j.tca.2021.178880>.
15. Bañón, E., García, A.N., Marcilla, A., Thermogravimetric Analysis and Py-GC/MS for Discrimination of Leather from Different Animal Species and Tanning Processes, *J Anal Appl Pyrolysis*, **2021**, 159, <https://doi.org/10.1016/j.jaap.2021.105244>.
16. Liu, J., Luo, L., Zhang, Z., Hu, Y., Wang, F., Li, X., Tang, K., A Combined Kinetic Study on the Pyrolysis of Chrome Shavings by Thermogravimetry, *Carbon Resour Convers*, **2020**, 3, 156–163, <https://doi.org/10.1016/j.crcon.2020.11.003>.
17. Saadatkah, N., Carillo Garcia, A., Ackermann, S., Leclerc, P., Latifi, M., Samih, S., Patience, G.S., Chaouki, J., Experimental Methods in Chemical Engineering: Thermogravimetric Analysis—TGA, *Can J Chem Eng*, **2020**, 98, 34–43, <https://doi.org/10.1002/cjce.23673>.
18. Gil, R.R., Girón, R.P., Lozano, M.S., Ruiz, B., Fuente, E., Pyrolysis of Biocollagenic Wastes of Vegetable Tanning. Optimization and Kinetic Study, *J Anal Appl Pyrolysis*, **2012**, 98, 129–136, <https://doi.org/10.1016/j.jaap.2012.08.010>.
19. Sebestyén, Z., Czégény, Z., Badea, E., Carsote, C., Şendrea, C., Barta-Rajnai, E., Bozi, J., Miu, L., Jakab, E., Thermal Characterization of New, Artificially Aged and Historical Leather and Parchment, *J Anal Appl Pyrolysis*, **2015**, 115, 419–427, <https://doi.org/10.1016/j.jaap.2015.08.022>.
20. Yang, L., Liu, Y., Wu, Y., Deng, L., Liu, W., Ma, C., Li, L., Thermal Degradation Kinetics of Leather Fibers Treated with Fire-Retardant Melamine Resin, *J Therm Anal Calorim*, **2016**, 123, 413–420, <https://doi.org/10.1007/s10973-015-4873-9>.
21. Wang, S., Chen, W., Yang, L., Zhang, J., Effect of Microwave Irradiation on the Solution of Amino Acid Chromium Complexes, *Leather and Footwear Journal*, **2020**, 20, 43–50, <https://doi.org/10.24264/lfj.20.1.5>.
22. Tang, H.R., Covington, A.D., Hancock, R.A., Use of DSC to Detect the Heterogeneity of Hydrothermal Stability in the Polyphenol-Treated Collagen Matrix, *J Agric Food Chem*, **2003**, 51, 6652–6656, <https://doi.org/10.1021/jf034380u>.
23. Balasubramanian, V., Velappan, B., Vijayan, S.K., Jabamani, H., Nagarajan, V., Victor, J.S., Ranganath, S.P., Badiger, M. V. Chinnaraj, V.K., Chellappa, M., Studies on the Use of Sodium Polyacrylate (SPA) for Low-Salt Animal Skin Preservation, *Environ Sci Pollut Res*, **2019**, 27100, <https://doi.org/10.1007/s11356-019-05871-y>.
24. Leyva-Porras, C., Cruz-Alcantar, P., Espinosa-Solís, V., Martínez-Guerra, E., Piñón-Balderrama, C.I., Martínez, I.C., Saavedra-Leos, M.Z., Application of Differential Scanning Calorimetry (DSC) and Modulated Differential Scanning Calorimetry (MDSC) in Food and Drug Industries, *Polymers (Basel)*, **2020**, 12, <https://doi.org/10.3390/polym12010005>.
25. Jeyapalina, S., Attenburrow, G.E., Covington, A.D., Dynamic Mechanical

Thermal Analysis (DMTA) of Leather Part 1: Effect of Tanning Agent on the Glass Transition Temperature of Collagen, *J Soc Leather Technol Chem*, **2007**, 91, 236–242.

26. Cucos, A., Budrugaec, P., Mitrea, S., Hajdu, C., The Influence of Sodium Chloride on the Melting Temperature of Collagen Crystalline Region in Parchments, *J Therm Anal Calorim*, **2013**, 111, 467–473, <https://doi.org/10.1007/s10973-012-2453-9>.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).

## STUDY OF ADHESION-COHESION INTERACTIONS BETWEEN POLYMERS IN ADHESIVE COMPOSITIONS

Darina ZHELEVA\*, Rashko DIMITROV†

University of Chemical Technology and Metallurgy, Sofia, Bulgaria, Kl. Ohridski blvd., 8, e-mail: darinajeleva@abv.bg

Received: 12.12.2022

Accepted: 23.02.2023

<https://doi.org/10.24264/lfj.23.1.4>

### STUDY OF ADHESION-COHESION INTERACTIONS BETWEEN POLYMERS IN ADHESIVE COMPOSITIONS

**ABSTRACT.** The results of the research prove that adhesives based on chloroprene rubber can be obtained not only in combination with phenol-formaldehyde resins, but also with other polymers. Selected chlorobutyl rubber (CIIR) and high styrene rubber (KER) proved to be substitutes for phenolic resins, which were used to obtain adhesive compositions with good properties. Despite the existing opinion on the same polarity of the components of the adhesive composition, guaranteeing the most favorable properties, it was shown that compositions with different polarity have all the parameters of quality adhesives. Components with different polarity also show the effect of mutual reinforcement, which determines the alignment, orientation ability of macromolecular chains and occurrence of cohesion and adhesion interactions. The observed textures obtained after mechanical impact proved this claim. Adhesives with more developed textures have better adhesive properties. The selected research methods successfully predict the properties of the components and facilitate their selection and amount.

**KEY WORDS:** adhesives, rubbers, mutual reinforcement, morphology

### STUDIUL INTERACȚIUNILOR DE ADERENȚĂ-COEZIUNE DINTRE POLIMERI ÎN COMPOZIȚIILE ADEZIVE

**REZUMAT.** Rezultatele cercetării demonstrează că adezivii pe bază de cauciuc cloroprenic pot fi obținuți nu numai în combinație cu rășini fenol-formaldehidice, ci și cu alți polimeri. Cauciucul clorobutil (CIIR) și cauciucul cu conținut ridicat de stiren (KER) selectate s-au dovedit a fi înlocuitori pentru rășinile fenolice, care au fost folosite pentru a obține compoziții adezive cu proprietăți bune. În ciuda opiniei existente cu privire la aceeași polaritate a componentelor compoziției adezive, garantând cele mai favorabile proprietăți, s-a demonstrat că și compozițiile cu polaritate diferită au toți parametrii adezivilor de calitate. Componentele cu polaritate diferită arată, de asemenea, efectul de întărire reciprocă, care determină alinierea, capacitatea de orientare a lanțurilor macromoleculare și apariția interacțiunilor de coeziune și aderență. Texturile observate obținute în urma impactului mecanic au dovedit această afirmație. Adezivii cu texturi mai dezvoltate au proprietăți adezive mai bune. Metodele de cercetare selectate pot prevedea cu succes proprietățile componentelor și facilitează selecția și cantitatea acestora.

**CUVINTE CHEIE:** adezivi, cauciucuri, întărire reciprocă, morfologie

### ÉTUDE DES INTERACTIONS D'ADHÉSION ET D'COHÉSION ENTRE LES POLYMÈRES DANS LES COMPOSITIONS ADHÉSIVES

**RÉSUMÉ.** Les résultats de la recherche démontrent que les adhésifs à base de caoutchouc chloroprène peuvent être obtenus non seulement en combinaison avec des résines phénol-formaldéhyde, mais également avec d'autres polymères. Le caoutchouc chlorobutyle (CIIR) et le caoutchouc à haute teneur en styrène (KER) sélectionnés se sont avérés être des substituts aux résines phénoliques, qui ont été utilisées pour obtenir des compositions adhésives avec de bonnes propriétés. Malgré l'opinion existante sur la même polarité des composants de la composition adhésive, garantissant les propriétés les plus favorables, il a été démontré que les compositions de polarité différente possèdent également tous les paramètres des adhésifs de qualité. Les composants de polarité différente montrent également l'effet de renforcement mutuel, qui détermine l'alignement, la capacité à orienter les chaînes macromoléculaires et l'apparition d'interactions de cohésion et d'adhésion. Les textures observées obtenues à partir de l'impact mécanique ont prouvé cette affirmation. Les adhésifs avec des textures plus développées ont de meilleures propriétés adhésives. Des méthodes de recherche sélectionnées peuvent prédire avec succès les propriétés des composants et faciliter leur sélection et leur quantité.

**MOTS CLÉS :** adhésifs, caoutchoucs, renforcement mutuel, morphologie

\* Correspondence to: Darina ZHELEVA, University of Chemical Technology and Metallurgy, Sofia, Bulgaria, Kl. Ohridski blvd., 8, e-mail: darinajeleva@abv.bg



## INTRODUCTION

In modern technologies adhesives are used for bonding different materials. The mechanical strength of the adhesive joint is different and depends on the adhesive composition and the type of bonding substrates. There are many combinations of components and modifiers used to improve a number of properties, namely: adhesion, cohesion, heat resistance, cold resistance and others [1-21]. The most widely used compositions are adhesives based on chloroprene rubber (CR). The most commonly used modifiers for this elastomer are phenol-formaldehyde and coumarone-indene resins [10, 11, 21]. Compositions have also been developed involving thermoplastic polymers and elastomers. For example, the adding of a high molecular weight chlorine-containing polymer in CR significantly improves its properties, especially the adhesion of materials based on PVC (polyvinyl chloride), genuine leather, PVA (polyvinyl acetate). Other polymers used are PAM (polyacrylamide), thermoplastic elastomers (styrene-isoprene-styrene). Applications have rubber flour; 1,5-diaminocaproic acid to increase bond strength; nitrooligomers containing a number of polar groups [13, 14]. Different monomers have been grafted onto the CR macromolecules, namely: MMA (metamethylacrylate), SBS (styrene-butadiene-styrene), PVC, PSC (piperylene-styrene copolymer), etc. [8, 15]. Grafting of CR has successfully been processed to enhance the bond strength by using methyl methacrylate monomer [16-18]. The optimal amount of PSC was found to increase the compatibility between the adhesive and the substrate [15]. Despite the rich set of published compositions, there are no sufficiently well-developed theoretical conclusions to predict the probable properties

of the compositions in a given selection of components.

The selection of components, their amount and technological regime is very important for obtaining of adhesives with valuable qualities, as well as the interactions between them. Many polymers are incompatible with each other, but in some cases, this leads to an improvement in a number of properties and mutual reinforcement.

With the present research an attempt has been made to achieve theoretically substantiated results, with which to predict the selection of the components by type and amount and the effect when applying the prepared adhesive composition. Also, to study the orientation effects and interactions between the selected components of the adhesive compositions: chloroprene rubber and chlorobutyl rubber; chloroprene rubber and high styrene resin, to achieve good adhesion properties.

Five types of adhesives-solutions based on chloroprene rubber were used by adding the following polymers (chlorobutyl rubber and high styrene resin, respectively) in different percentage ratios.

## EXPERIMENTAL

### Objects of Investigation

Polychloroprene adhesive solutions are prepared in laboratory conditions, respectively: PCL0; PCL1; PCL2; PCL3; and PCL4 with varying amounts of chlorobutyl rubber (CIIR) and high styrene polymer (KER). The bonding substrates used are samples of vulcanised butadiene styrene rubber with trade name "Duropor".

### Ingredients

The quantities of the used ingredients for rubber compounds are presented in Table 1.

Table 1: Ingredients for rubber compounds

Ingredients, phr	Adhesives code				
	PCL0	PCL1	PCL2	PCL3	PCL4
Chloroprene rubber <b>CR</b> (Baypren 210)	100	100	30	100	100
ZnO	5	5	5	5	5
MgO	4	4	4	4	4
Chlorobutyl rubber <b>CIIR</b> (Lanxness Clorbutyl 1240)		30	100		
High Styrene Rubber (KER 1904)				30	40

*Chloroprene Rubber (CR)*, grade Baypren 210 (LANXESS) [22]: poly(2-chloro-1,3-butadiene), mercaptan modified; of medium crystallization rate;  $\rho=1.23 \text{ g/cm}^3$ ; melting point  $\sim 86 \text{ }^\circ\text{C}$ ;  $T_g \sim -40 \text{ }^\circ\text{C}$ ;  $M_m = 120000$ ; Mooney viscosity UHL(1+4)100 $^\circ\text{C} = 43\pm 4$ .

*Zinc oxide (ZnO)* (Brüggemann): used as a vulcanizing agent for CR [22]. White, solid, powder with particles size  $0.8\div 2.0 \text{ }\mu\text{m}$ , moisture content  $< 0.2 \%$ ;  $\rho=4.9 \text{ g/cm}^3$ .

*Magnesium oxide (MgO)* grade Elastomag 100 (Morton) [22] used as a scorch retarder for adhesives. White, crystalline powder with particles size  $>150 \text{ }\mu\text{m}$ ;  $\rho = 3.2 \text{ g/cm}^3$ ; pH 10.3; BET surface area  $104\text{-}141 \text{ m}^2/\text{g}$ .

*Chlorobutyl Rubber (CIIR)*, grade Clorbutyl 1240 (Lanxness) [22]: colorless, chlorinated isobutylene-isoprene copolymer with low Mooney viscosity UHL(1+4)100 $^\circ\text{C}=38 \pm 4$ ;  $\rho = 0.92 \text{ g/cm}^3$ ; chlorine content 1.25% vol.%.

*High-Styrene Rubber*, grade KER 1904 [22]: high content of 83% bonded styrene in the polymer. It plays an important role as reinforcing agent for rubber. White granulate, non-toxic, odorless; Mooney viscosity ML(1+4)100 $^\circ\text{C}=45\text{-}60$ , Shore hardness  $> 93$ .

Solvents: *Acetone* (Sigma-Aldrich): CAS No 67-64-1, 97%, mol. weight  $58.08 \text{ g/mol}$ ; *Toluene* (Sigma-Aldrich): CAS No 108-88-3, 99.8% anhydrous, mol. weight  $92.14 \text{ g/mol}$ ; *Petroleum benzine* (Merck KGaA): CAS No 64742-49-0, boiling range  $40\text{-}60 \text{ }^\circ\text{C}$ .

## Methods for Preparation of Polychloroprene Adhesives in Laboratory Conditions

### Obtaining the Rubber Compounds on the Mixing Roller

The compounding of rubber components is performed by open laboratory mixing roller with sizes: L/D  $320\times 360$ , revolutions of the slower roll  $25 \text{ min}^{-1}$  and friction 1.27 [23].

About adhesive **PCL0**: first, the chloroprene rubber is plasticized on cold roll for 10 min, then the MgO is added, and finally the ZnO. For the adhesive **PCL1**: chlorobutyl rubber (CIIR) is added after CR and before the metal oxides. About **PCL2**: due to the high content of CIIR, it is first plasticized on the rolls, and then CR, MgO and finally the ZnO are added. About **PCL3** and **PCL4**: due to difficulties in processing the components, a change in the sequence of the ingredients was necessary, i.e., first, the KER is plasticized, the adding of the CR and finally the metal oxides.

### Obtaining Adhesive Solutions

Using direct dissolving methods, the prepared rubber compound is dissolved in the selected solvents. The compound left for swelling in the solution during 24 h. Then the solution is left for stirring in glass flask at 250 rpm for 4 h at room temperature until homogeization was finished [1, 23].

**Adhesive PCL0:** A rubber compound containing: only CR, ZnO and MgO (see Table 1) was used, dissolved in the following solvents in the ratio of acetone: toluene: petroleum benzene = 1:1.1:1.3 with a concentration of 25% [1, 23]. Complete homogenization of the mixture was observed after 4 h.

**Adhesive PCL1:** A rubber compound containing: CR, ZnO, MgO and CIIR (30 phr) was used (Table 1), dissolved in the following solvents in the ratio of acetone: toluene: petrol = 1:1.1:1.3 with concentration of 25%. Complete homogenization of the mixture was also observed after 4 h.

**Adhesive PCL2:** To prepare **PCL2** the same procedure was used as for **PCL1**, the amount of CIIR is 100 phr. The rubber compound was dissolved in toluene at a concentration of 25%. Using the same solvents (acetone, toluene and petroleum benzene), homogenization was very difficult and after 2 h a separation of two phases was observed. The solvent mixture used proved to be unsuitable for the chlorobutyl rubber, and that acetone was a poor solvent for this rubber. The use of toluene alone resulted in complete dissolution of the rubber mixture. No such phenomenon was reported for adhesive PCL1. Probably the CIIR in an amount of 30 phr does not affect the dissolution process in this solvent system.

**Adhesive PCL3:** A rubber compound containing: CR, ZnO and MgO and KER (30 phr) (Table 1) was used, dissolved in the following solvents in the ratio of toluene: petroleum benzene = 3:1 with a concentration of 25%. Without the presence of acetone in the solvent mixture resulted in complete dissolution and homogenization of the adhesive composition after 4 h.

**Adhesive PCL4:** The same procedure was used for the preparation of **PCL4** as for **PCL3**, but the amount of KER is 40 phr. The same solvents were used as for **PCL3**.

After preparation, the adhesives were analyzed [1, 23].

## Methods for Investigation

### *Determination of the Viscosity by Höppler Viscometer*

A Höppler rheoviscometer is used to determine the dynamic viscosity. The viscosity is calculated using the following formula [23]:

$$\eta = k \cdot p \cdot t$$

(1)

$\eta$  – viscosity [cP];  $\kappa$  – constant of relatively tube;

$p$  – shear stress [g/cm<sup>2</sup>];  $t$  – time for passage of the ball [s].

Measurements are made according to standard BDS EN 12092:2003.

### *Optical Microscopy*

A polarization microscope is used for morphological studies [24].

The samples are subjected to mechanical impact by metal blade. In the resulting texture are made repeated measurements with graticule in different areas of its deformation band width ( $d$ ) and total width of the texture ( $L$ ). The ratio between the total width of the deformation texture and the deformation band width is represented by coefficient of mechanical crystallization (CMC) of the adhesive.



The samples are subjected to mechanical impact by metal blade. In the resulting texture are made repeated measurements with graticule in different areas of its deformation band width ( $d$ ) and total width of the texture ( $L$ ). The ratio between the total width of the deformation texture and the deformation band width is represented by coefficient of mechanical crystallization (CMC) of the adhesive.

### *Determination of Peel Resistance*

To determine the strength of adhesive joint by peel resistance tests are prepared samples by the same standard material with thickness 2 mm. The adhesive bond strength was measured according to EN 1392:2006 standard. The samples are joined and are pressed and subjected to separation. The disbonding is done on dynamometer at a speed of 100 mm/min. The load (power) is

recorded, causing breaking of the adhesive bond in each of the zones. Then the peel strength [N/mm] of the investigated samples is calculated [23]. Measurements are made according to standard ISO 17708:2018.

## RESULTS AND DISCUSSION

### Determination of the Viscosity of Investigated Adhesives

The data for the rheological measurements of the investigated adhesive compositions are presented in Table 2.

Table 2: Viscosity of investigated adhesives in dependence of the shear stress

Shear stress, [g/cm <sup>2</sup> ]	10	20	30
Viscosity of PCL0, [cP]	2234	2095	1912
Viscosity of PCL1, [cP]	704	667	543
Viscosity of PCL2, [cP]	566	400	314
Viscosity of PCL3, [cP]	465	362	286
Viscosity of PCL4, [cP]	625	495	477

The Table 2 shows that **PCL0** adhesive has the highest viscosity, while the adding of other polymers that are amorphous and lower molecular weight reduces the percentage of crystalline phase in the studied composites. They have a certain plasticizing effect, which reduces the viscosity.

An interesting phenomenon is observed with the adhesives **PCL3** and **PCL4**, in which the high-styrene resin KER participates. When increasing the amount of KER from 30 to 40 phr an increase in viscosity is observed. Not only the viscosity increases, but also the other studied indicators, which are described below in the text. Changes in the properties of the composition are predicted by the theory of reinforcement of polymers [24-26]. According to one of its postulates, when the polymers are incompatible and with excited adhesion, commensurate with the cohesion of the reinforced polymer, come into contact, it

follows the improvement of the properties. In this case, high-styrene rubber (KER), placing its macromolecules in the mass of chloroprene rubber, rearranges its spherulitic structure into a new one with linearly oriented macromolecules, which is composed of associates of the two polymers (KER and CR). In this arrangement, the cohesion and adhesion interaction is improved with an easier orientation option and increased strength under mechanical impacts. This can be seen from the texture of Fig. 8. Increasing the amount of KER increases the total adhesion, which adhesion by 30 phr of KER resin it is still minimal.

### Morphology of the Studied Adhesive Films

The results obtained from the measurement of the coefficient of mechanical crystallization (CMC) are presented in Fig. 1:

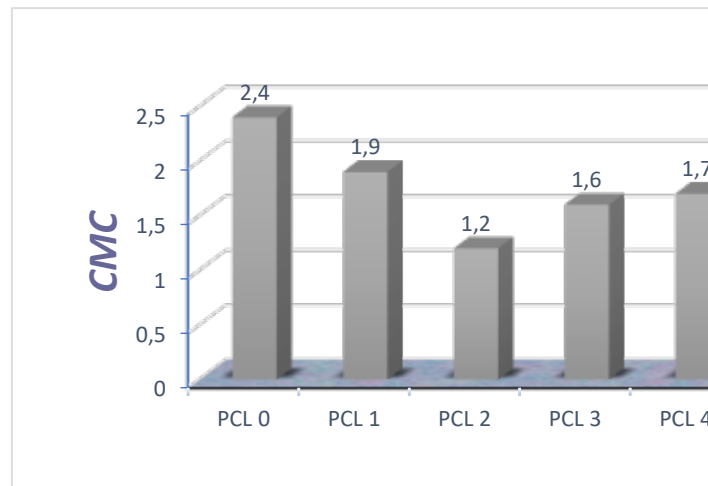


Figure 1. Coefficient of mechanical crystallization (CMC)

From the data it can be concluded that the value of CMC is the highest at **PCL0**, i.e., the adhesive composition is only with chloroprene rubber. When another polymer is introduced into the adhesive composition, which is amorphous, the crystallization of the chloroprene rubber deteriorates and therefore the CMC values are lower (for **PCL1**, **PCL2**, **PCL3** and **PCL4**). The lowest value is for **PCL2**, which is logical, since the participating amorphous polymer (CIIR) is 100 phr and CR is only 30 phr. At the **PCL4** adhesive opposite effect is observed, i.e., the crystallization of the adhesive improves with increasing KER content.

To observe the morphological structure of the polymers individually and in combination in the adhesive compositions, microscopic photographs were taken at 70 and 315 times magnification.

#### *Micrography of Chloroprene Rubber Film /CR/*

Figures 2a and b show optical microscopy images of film from chloroprene rubber (CR) in polarized light, in the undeformed and deformed states, respectively. Under mechanical influence, spherulites turn into fibrils and a very good orientation and crystallization ability of CR is observed. Its macromolecules show a pronounced orientation ability in the direction of impact.

The adding of other polymers impairs the crystallization ability of the rubber. The physicomechanical parameters of **PCL0** show high values of bond strength, but differing in each zone of the bonded samples (non-uniform bonding along the sample length) [27].

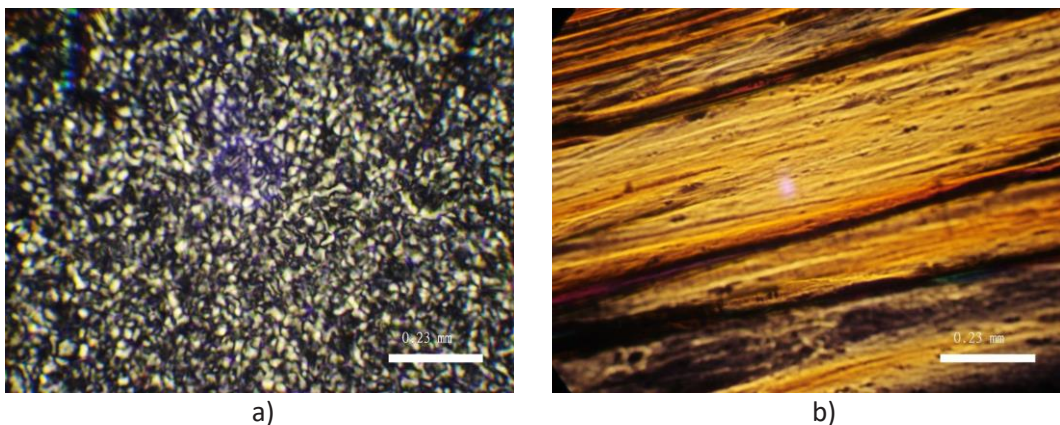


Figure 2. Micrography of adhesive film based on CR (a) in polarized light in undeformed; and (b) deformed state



*Micrography of Chlorobutyl Rubber /CIIR/*

The observed structure of chlorobutyl rubber at room temperature is typically amorphous (Fig. 3). For this reason, the adhesive **PCL2** almost masks the effect of CR crystallization (Fig. 6), as a result of the deteriorating homogeneity of the composition.

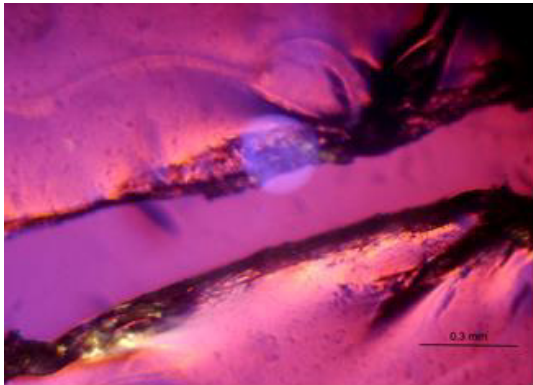


Figure 3. Micrography of Chlorobutyl rubber (CIIR) film in polarized light, after mechanical impact

styrene rubber) and the other phase is styrene.

After mechanical impact the structure is torn, no orientation effects are observed. Cohesion forces are weak, which is the reason for the mechanical impact of the two phases to separate and to obtain unordered zones with undefined composition.

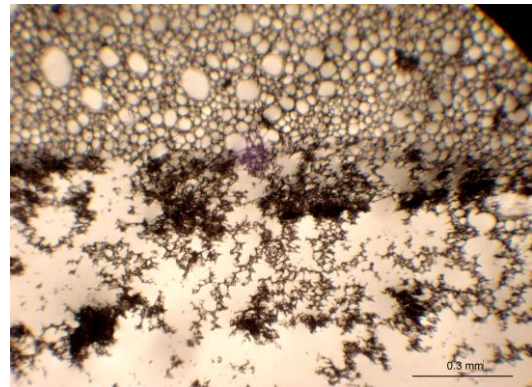


Figure 4. Micrography of High-Styrene Rubber (KER) film in polarized light in deformed and undeformed state

*Micrography of High-Styrene Rubber /KER/*

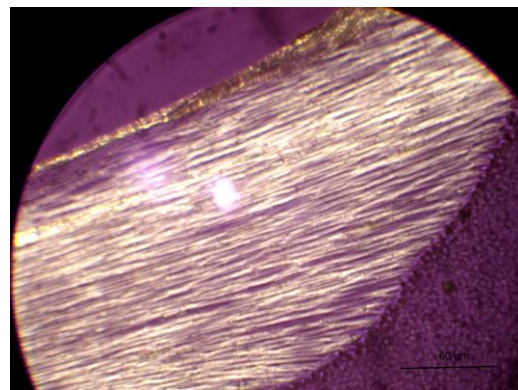
Fig. 4 shows the cellular structure of KER, each cell being composed of two layers: one is a continuous phase of SBR (butadiene

*Polychloroprene Adhesives in the Presence of CIIR and KER Polymers*

The morphological observations of **PCL1** are shown in Fig. 5 a,b.



a)



b)

Figure 5. Micrographs of PCL1 adhesive (100 CR: 30 CIIR) in: a) unpolarized light, b) polarized light, after standing of the film for 72 h

This structure consists of cells composed of the macromolecules of the chloroprene rubber, in which the amorphous

coacervates of the chlorobutyl rubber visible as dark spots are located [24].

Spontaneous crystallization was observed after standing the film during 72 h. Under mechanical impact (Fig. 5b) the texture has pronounced orientation effects and the observed structure is fibrillar. This texture consists of the macromolecules of chloroprene rubber (CR) in result of the recrystallization of spherulites into fibrils. The observed dark elongated zones between the fibrils are the amorphous coacervates of chlorobutyl rubber (CIIR), which are oriented under the influence of chloroprene rubber. The fibrils of CR have a higher density around them (higher percentage of crystallinity). The measured coefficient of mechanical crystallization is 1.9.

Mixing the two incompatible rubbers disrupts the forces of interaction between the macromolecules of each [24, 25]. This happens on the contact surface, where surface stresses occur. Under their influence, amorphous coacervates of CIIR are formed, which are covered by a network of CR. The macromolecules of network formations are in an ordered state. With their presence, these CIIR coacervates stimulate the formation of contact macromolecular formations that are absent in the pure CR (Fig. 2).

In deformation, the pre-arranged structure with increased intermolecular interaction facilitates orientation in fibrils. In this case, it is very likely that CIIR will also show some plasticizing effect to aid orientation. A mutual reinforcement effect is observed, although the two polymers are incompatible [24, 26].

Fig. 6 shows the overmolecular structure of the adhesive film of **PCL2** with composition: chloroprene rubber /CR/- 30 phr and chlorobutyl rubber /CIIR/- 100 phr. It can be seen that CIIR is formed as separate coacervates. Most likely, CIIR coacervates are infiltrated by the CR spherulitic aggregates [24], unlike **PCL1**. Here the continuous phase is CR and the interrupted phase is CIIR, which has crystallized.

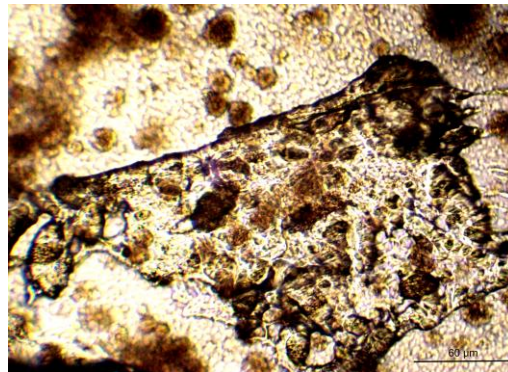


Figure 6. Micrograph of PCL2 (30 CR: 100 CIIR)

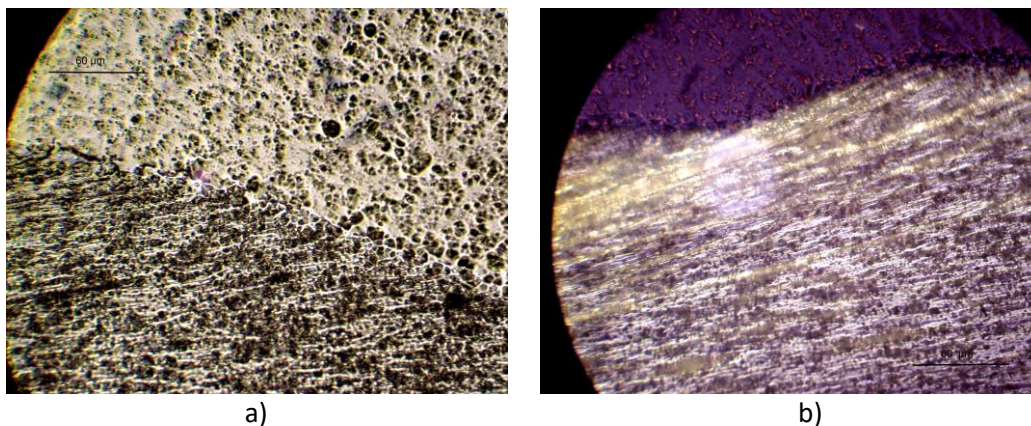
In this adhesive composition, after a film stay of 72h a weak, impaired orientation ability, lack of fibrils was observed. The structure breaks down very easily under mechanical impact. Exceptional amorphization, with insignificant crystalline phase, which decreases during prolonged stay. The coefficient of mechanical crystallization (CMC) is 1.2. The results show that the cohesion forces of the two elastomers exceed the adhesion between them. This composition of the adhesive does not satisfy the requirement of the 6<sup>th</sup> postulate of the reinforcement theory, namely that the adhesion between elastomer and reinforcing agent is commensurate with the cohesion of the reinforced elastomer [25, 26]. Therefore, the obtained values of the adhesive are reduced.

Fig. 7a,b shows the overmolecular structure of adhesive **PCL3** with composition: chloroprene rubber /CR/- 100 phr and high-styrene rubber /KER/- 30 phr. In Fig. 7a, filamentous structures obtained from the orientation effect of CR are observed. Under their influence, the fields of KER have also been oriented. After standing of the film 72h (Fig. 7b), no spontaneous crystallization was observed. But under mechanical impact, the structure passes into a well-defined fibrillar phase. Under the influence of CR, KER polymer also undergoes some orientation. The resulting fibrillar structure shows that CR in combination with KER can induce good mechanical properties of the adhesive



composition. The coefficient of mechanical crystallization is 1.6. This phenomenon proves the mutually reinforcement between

incompatible polymers, where one of them can acquire properties significantly better than those when used as a pure product.



a) b)  
Figure 7. Micrographs of PCL3 (100 CR: 30 KER) in:  
a) unpolarized light and b) polarized light, after a stay of the film 72 h

During the studies, it was found that the amount of KER is a significant factor influencing the properties of the composition. In the amount of 40 phr in **PCL4** the orientation ability of the composition is significantly increased compared to **PCL3**. The effect can be seen in Fig. 8, in which the texture is represented by a compact mass with well-formed fibrils.

crystallization of CR is much more efficient. The coefficient of mechanical crystallization (CMC) is 1.7. As the amount of KER increases to 40 phr, the orientation and crystallization ability increase, and the indicators for bond strength also increase. There is a mutual reinforcement of the two polymers involved in the adhesive mixture, which fully correlates with the strength and rheological data. Therefore, in a certain, optimal amount of KER in such an adhesive composition, the adhesion properties of KER are increased, as opposed to its use alone.

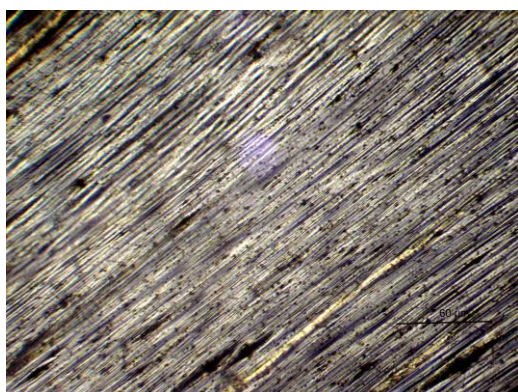


Figure 8. Micrograph of PCL4 (100 CR: 40 KER) in polarized light, stay of the film 72 h

In this adhesive composition, after a stay of the film for 72 hours, completely different structures are observed. CR has crystallized, KER is in the form of amorphous zones. Around the amorphous associates there is a string of crystals, i.e., there the

In conclusion, it can be said that the adhesion properties of materials that do not have good adhesive properties on their own can be used as adhesion activators in combination with other appropriately selected materials. In the resulting compositions, the components mutually reinforce each other under the influence of surface stresses occurring at the interface between the phases. Under their influence, the macromolecular chains change into a linear arrangement with enhanced cohesion and adhesion interactions.

## Results of Determination of Adhesive Bond Strength

To clarify the correlation between rheological tests and microscopic observations, physico-mechanical tests of the five model adhesive compositions studied were performed.

Adhesives were applied with brush as two layers. The open time are 10 min for the first layer and 25 min for second layer. After drying, the samples were activated at 70-80 °C for 10 s. Then samples were pressed at 4 atm for 30 s. The peeling test was done using Dynamometer after 168 h.

The reported results for the bond strength are presented in Fig. 9.

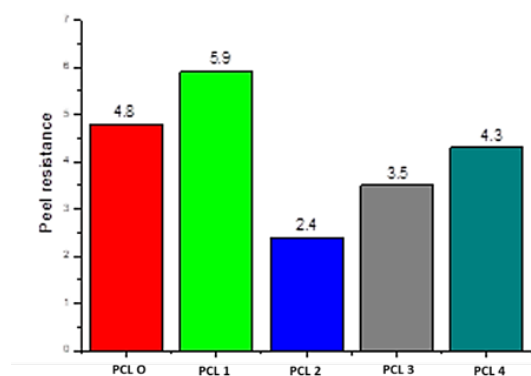


Figure 9. Peel resistance after 168 h

For **PCL1** adhesive, the strength values increase when amount of CIIR is 30 phr. Therefore, this polymer in such a concentration can completely replace the widely used phenol-formaldehyde resin.

The adhesive properties of **PCL2** deteriorate sharply compared to **PCL1**. The CIIR polymer is in a too large amount (100 phr) and reduces adhesion. This adhesive differs from the others by its low initial adhesion, which property is suitable for its use for auxiliary bonding of internal shoe details (linings, soles, insoles, etc).

When using KER in an amount of 30 phr (at **PCL3**) in an adhesive composition deteriorates the physico-mechanical properties of the bond strength compared to

**PCL0**. Increasing the amount of KER (**PCL4**) improves the strength values, which fully correlates with the microscopic observations of the mutual reinforcement of the two polymers.

## CONCLUSIONS

The possibility of obtaining adhesive compositions based on chloroprene rubber (CR) in combination with polymers that have not been used for this purpose, namely chlorobutyl rubber (CIIR) and high styrene polymer (KER), has been proven.

It was found that the properties of the studied model adhesives depend on the amount of components in the adhesive, influencing their cohesion and adhesion interactions in the adhesive composition.

It has been proven that adhesive compositions can have good properties in combination of polar (CR) and non-polar (KER) components.

The use of the method of optical microscopy for determining the mechanical crystallization facilitates the selection of components for adhesive compositions and can be used to predict the properties of adhesives.

It has been confirmed that the compatibility of the polymers used in the model adhesive compositions is not a decisive factor in obtaining good adhesion properties of the bonded compounds. The improvement is due to the reinforcing effect of one polymer relative to the other.

## Acknowledgment

The author expresses her gratitude and her thanks to the teacher and researcher – Rashko Dimitrov† from the University of Chemical Technology and Metallurgy for the invaluable help in conducting the microscopy analysis and discussion of the observed effects.

## REFERENCES

1. Kardashov, D., *Synthetic Adhesives*, 3rd ed. (Revis. Extend.), Khimiya, Moscow, **1976** (in Russian).
2. Zakharov, N., *Chloroprenovye kauchuki i rezina na ih osnove*, Kimiya ed., **1978** (in Russian).
3. Shvarz, A., Dinzbarg, B., *Sovmeshtenie kauchukov s plastikami i sinteticheskimi smolami*, Kimiya ed., Moscow, **1972** (in Russian).
4. Keybal, N., Bondarenko, S., Kablov, V., Sergeev, G., Polichloroprenovye klei s povishennoy adgezionnoy sposobnostyu k vulkanizatam na osnove chloroprenogo kauchuka, *Kauchuk i Rezina*, **2005**, 2, 49 (in Russian).
5. Bondarenko, S., Keybal, N., Kablov, V., Sposob krepleniya rezin drug k drugu, Patent 2004114395/04, SSSR, 11.05.**2004**.
6. Nikulcheva, N., Prohorov, V., Razrabotka receptury modificirovannogo kleya na osnove PCP kauchuka tipa NAIRIT-NT, *Nauka-Proizvodstvu* **2000**, Soob.2 (in Russian).
7. Evtimova, R., Dimitrov, R., Tzekov, V., Izsledvane varhu formiraneto na lepeni shevove s lepila na baza elastomeri, *Koji i Obuvki J*, **2004**, 3, 19 (in Bulgarian).
8. Chen, J., Yang, F., Progress in the Development of CR Adhesive, *Journal of China Chemistry and Adhesion*, **2000**, 2, 79-82.
9. Robbins, J., Water-based Systems Make Inroads into Traditional Solvent Borne Technology, *Adhesives and Sealants Industry*, March **2003**, <https://www.adhesivesmag.com/articles/85273-polychloroprene-contact-adhesives>.
10. Martinez, J., Garcia, T., Effects of Hydrocarbon Tackifiers on the Adhesive Properties of Contact Adhesives Based on Polychloroprene, *J Adhes Sci Technol*, **1996**, 10, 12, 1383-1399, <https://doi.org/10.1163/156856196X00319>.
11. Pilato, L., *Phenolic Resins: A Century of Progress*, Springer Heidelberg Dordrecht London New York, **2010**, p. 439, <https://doi.org/10.1007/978-3-642-04714-5>.
12. Martinez, J.M., *Adhesion Science and Engineering-2: Surface, Chemistry and Application*, Chapter 13: Rubber base Adhesives, **2002**, p. 577, <https://documents.in/document/adhesion-science-and-engineering-rubber-base-adhesives.html>
13. Prohorov, V., Maltsev, I., Kovalenko, E., *Sovershenstvovanie tehnologii skleivaniya izdelii iz koji*, Monography, **2002**, p. 21 (in Russian), <http://window.edu.ru/catalog/pdf2txt/417/76417/57651>.
14. Keibal, N., Bondarenko, S., Kablov, V., Modification of Adhesive Compositions Based on Polychloroprene with Element-Containing Adhesion Promoters, *Polymer Science, Series D. Glues and Sealing Materials*, **2011**, 2, 267, <https://doi.org/10.1134/S199542121104006X>.
15. Jankauskaite, V., Zuknene, K., Mickus, K.V., AFM Surface Studies of Polychloroprene /Piperylene-Styrene Copolymer Blends, *Mater Sci*, **2005**, 11, 3.
16. Anneq, F., Shahid, M., Saleem, M., Awais, M., Shoaib, B., Adel Umer, M., Enhacement in Bonding Strength and Ageing Resistance of Polychloprene Solvent Base Adhesives through Graft Copolymerization, *J Adhes Sci Technol*, **2020**, <https://doi.org/10.1080/01694243.2020.1857581>.
17. Alexandrescu, L., Ficai, M., Albu, L., Leca, M., Mihut, M., Influence of Montmorillonite Nanoparticles on Polychloroprene Adhesive Properties, *Leather and Footwear Journal*, **2013**, 13, 61-80, <https://doi.org/10.24264/lfj.13.1.5>.
18. Alexandrescu, L., Sonmez, M., Georgescu, M., Nituica, M., Gurau, D., Moldovan, Z., Influence of Particle Size and Phase Distribution on Adhesion of Adhesive Dispersions Based on Polychloroprene Grafted with MMA, *Proceedings of the 5th International Conference on Advanced Materials and Systems – ICAMS 2014*, 23-25 October **2014**, Bucharest, Romania, 21-26.
19. Barkauskas, R., Fataraitė, E., Batisaitė, A., The Modification of Rheological Behavior



- of Solvent– Based Adhesive by Disperse Filling, *Mater Sci*, **2003**, 9, 3.
20. Kotova, S., Lyusova, L., Glagolev, V., Smirnova, M., Promotory adgezii dlya elastomernykh kleevykh kompozicii holodnogo otvergdenia, in: Prom. proizvodstvo I izpolzovanie elastomerov, **2009**, №2-3.C.9-11 (in Russian).
21. Zheleva, D., Untersuchung der Wechselwirkung Zwischen Kautschuk und Harz in Polychloroprenklebstoffen, *Gummi Fasern Kunststoffe Magazin (GAK)*, **2013**, 9, 614.
22. Dishovsky, N., Tsenkov, G., *Spravochnik po kauchuk*, 1st Ed., Sofia, **2006**, p. 246 (in Bulgarian).
23. Evtimova, R., Grozdanova, V., *Rakovodstvo za uprajnenia po tehnologia na izdelia ot koji*, UCTM Ed., Sofia, **2006** (in Bulgarian).
24. Dimitrov, R., Orientierungseffekte in zweiphasigen, *Kautschuk, Gummi Kunststoffe*, **1982**, 35, 11/82, 934-938.
25. Dimitrov, R., Eine nene Hypothese für die Verstärkung von Polymeren, in: *18 Fachtagung über Verarbeitung und Anwendung von Polymeren*, **2003**, ISBN: 3-00-012510-8.
26. Dishovsky, N., Radulov, I., Dimitrov, R., *Usilvane na elastomerite*, 1st Ed., Sofia, **2005**, p. 66 (in Bulgarian).
27. Zheleva, D., Ruskova, K., Metal Oxides Influence on the Morphology and Structure of the Polychloroprene Adhesive Composition, in: *2019 IEEE II International Conference of High Technology for Sustainable Development (HiTech)*, **2020**, 1-5, <https://doi.org/10.1109/HiTech48507.2019.9128251>.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).

# AN APPLICATION OF PARETO ANALYSIS AND CAUSE-AND-EFFECT DIAGRAM IN RAW HIDE AND SKIN DEFECTS MINIMIZATION IN ETHIOPIA: SELECTED CASE DIRE DAWA CITY SLAUGHTERHOUSE (ETHIOPIA)

Berihun NEGASH\*

Dire Dawa University, Institute of Technology, Postal Address: 1362, Postal Code: 3000, Dire Dawa, Ethiopia, email: negashber2005@gmail.com

Received: 25.09.2022

Accepted: 27.02.2023

<https://doi.org/10.24264/lfj.23.1.5>

## AN APPLICATION OF PARETO ANALYSIS AND CAUSE-AND-EFFECT DIAGRAM IN RAW HIDE AND SKIN DEFECTS MINIMIZATION IN ETHIOPIA: SELECTED CASE DIRE DAWA CITY SLAUGHTERHOUSE (ETHIOPIA)

**ABSTRACT.** According to the reports of CSA (Central Statistics Agency) 2020 Ethiopia is the 10<sup>th</sup> in the world and 1<sup>st</sup> in Africa by cattle production. Furthermore, the leather sector is the priority sector in Ethiopia. Leather industries are facing challenges in improving productivity and quality in the competitive market nowadays. The input materials for leather industries are goat and sheep skin, and cattle hide in Ethiopia. However, there are raw hide and skin defects due to preslaughter, during slaughter and post-slaughter process. This study focuses on the minimization of the major defects in preslaughter and during the slaughter of raw hide and skin process by application of Pareto analysis and fishbone diagram in Ethiopia in the case of Dire Dawa city. The Pareto analysis reveals that priority should be given to solving the problems of pre-slaughter and during-slaughter defects of raw hide and skin. Based on cause-and-effect diagram analysis, the main causes are: machine, material, environment, man, measures and management, root causes, heated metal shape for brand mark, during diseases different action is taken, hit animal using different steel, grass used for food, animals home making material, drinking water, stick, topography, hot area, old area, lack of awareness about hide and skin outputs, traditional methods of water in forage for the animals during farming, traditional methods used for medications for raw hide and defects identified. Finally, a few recommendations are made to reduce raw hide and skin defects.

**KEY WORDS:** raw hide and skin quality management in preslaughter and during slaughter, leather, Pareto and fishbone diagram

## O APLICAȚIE A ANALIZEI PARETO ȘI A DIAGRAMEI CAUZĂ-EFECT ÎN MINIMIZAREA DEFECTELOR PIELII BRUTE ÎN ETIOPIA: STUDIU DE CAZ – ABATORUL DIN DIRE DAWA (ETIOPIA)

**REZUMAT.** Potrivit rapoartelor CSA (Agenția Centrală de Statistică) din 2020, Etiopia este pe locul 10 în lume și pe primul loc în Africa la producția de vite. În plus, sectorul de pielărie este sectorul prioritar în Etiopia. Industria de pielărie se confruntă în prezent cu provocări în ceea ce privește îmbunătățirea productivității și calității pe piața competitivă. Materiile prime pentru industria de pielărie din Etiopia sunt pieile de capră, de oaie și de bovine. Cu toate acestea, există defecte ale pielii brute apărute în urma prelucrării înaintea, în timpul și după sacrificare. Acest studiu se concentrează pe minimizarea defectelor majore ale pieilor brute în etapa de dinaintea sacrificării și în timpul sacrificării prin aplicarea analizei Pareto și a diagramei cauză-efect în cazul orașului Dire Dawa din Etiopia. Analiza Pareto dezvăluie că trebuie să se acorde prioritate soluționării problemelor defectelor pielii brute înaintea și în timpul sacrificării. Conform analizei diagramei cauză-efect, s-au identificat cauze-rădăcină ale defectelor pielii, împărțite în patru mari categorii, și anume defecte cauzate de utilaje, mediu, om, de natură materială, care includ: forma metalului cu care se marchează animalul, diferite acțiuni întreprinse în timpul îmbolnăvirii, scarificarea animalului folosind tipuri diferite de oțel, iarba folosită pentru hrană, materialele din care sunt făcute adăposturile animalelor, apa potabilă, ustensilele folosite, topografia, zona fierbinte, zona veche, lipsa de conștientizare privind destinația pielii, metode tradiționale de a hrăni și adăpa animalele, metode tradiționale de a trata animalele cu medicamente. În cele din urmă, se fac câteva recomandări pentru a reduce defectele pielii brute.

**CUVINTE CHEIE:** gestionarea calității pielii brute înaintea și în timpul sacrificării, piele, analiza Pareto și diagrama cauză-efect

## UNE APPLICATION DE L'ANALYSE DE PARETO ET DU DIAGRAMME DE CAUSES ET EFFETS DANS LA MINIMISATION DES DÉFAUTS DE LA PEAU EN ÉTHIOPIE : CAS SÉLECTIONNÉ DE L'ABATTOIR DE LA VILLE DE DIRE DAWA (ÉTHIOPIE)

**RÉSUMÉ.** Selon les rapports du CSA (Agence Centrale des Statistiques) de 2020, l'Éthiopie se classe au 10<sup>e</sup> rang mondial et au 1<sup>er</sup> en Afrique pour la production bovine. Par ailleurs, le secteur du cuir est le secteur prioritaire en Éthiopie. L'industrie du cuir est actuellement confrontée à des défis pour améliorer la productivité et la qualité sur un marché concurrentiel. Les matières premières pour les industries du cuir en Éthiopie sont la peau de chèvre, de mouton et de bovin. Cependant, il y a des défauts dans le cuir brut résultant de la transformation avant, pendant et après l'abattage. Cette étude se concentre sur la minimisation des défauts majeurs des peaux brutes au stade de pré-abattage et pendant l'abattage en appliquant l'analyse de Pareto et le diagramme de causes et effets au cas de Dire Dawa, en Éthiopie. L'analyse de Pareto révèle que la priorité devrait être accordée au traitement des défauts de la peau brute avant et pendant l'abattage. Selon l'analyse du diagramme cause-effet, les causes profondes des défauts cutanés ont été identifiées, réparties en quatre grandes catégories, à savoir les défauts causés par les machines, l'environnement, l'homme, la nature matérielle, qui comprennent : la forme du métal avec lequel l'animal est marqué, les différentes actions menées pendant la maladie, la scarification de l'animal à l'aide de différents types d'acier, l'herbe utilisée pour l'alimentation, les matériaux dont sont faits les abris pour animaux, l'eau potable, les ustensiles utilisés, la topographie, la zone chaude, la zone ancienne, la méconnaissance de la destination de la production de cuir, les méthodes traditionnelles d'alimentation et d'abreuvement des animaux, les méthodes traditionnelles de traitement des animaux avec des médicaments. Enfin, quelques recommandations sont faites pour réduire les défauts de la peau brute.

**MOTS CLÉS :** gestion de la qualité des peaux brutes avant et pendant l'abattage, cuir, analyse de Pareto et diagramme de causes et effets

\* Correspondence to: Berihun NEGASH, Dire Dawa University, Institute of Technology, Postal Address: 1362, Postal Code: 3000, Dire Dawa, Ethiopia, email: negashber2005@gmail.com

## INTRODUCTION

The words “hides and skins” are often used interchangeably; however, according to the British standard definitions, hide is the raw skin of mature animals of larger kinds, such as cattle, horses, and other large animals [1]. Raw hide and skin, the main byproducts of the meat industry are the basic raw materials for the leather industry [2]. Raw hides and skins, the most valuable byproduct of the meat industry, are normally converted into leather [3].

The bovine animal hide and ovine animal skin have different steps to convert them into different leather products. Generally, leather is the output of hide and skin. According to the reports of CSA (Central Statistics Agency) 2020, Ethiopia is the 10<sup>th</sup> in the world and 1<sup>st</sup> in Africa by cattle production. However, in Ethiopia, there is a high incidence of raw hide and skin defects caused by different mechanisms or sources. Generally, the defects happen during pre-slaughter, during slaughter, and post-slaughter process. The leather industry is one of the fastest-growing economic sectors in Ethiopia [4]. The 26 operational tanneries in the country have a soaking capacity for 15,650 sheep and goat skins and 9,725 cattle hides per day [5].

The leather sector in Ethiopia faces several challenges. Large numbers of hides and skins are discarded or their quality is substantially reduced by factors that can be avoided. Some of these factors are inherent to the production structure and animal husbandry practices, whereas others arise from the dispersal of the slaughter facilities, unfavorable marketing structures, poor handling (e.g., presentation and transportation) of the raw stock, and insufficient collection and preparation for

further processing and export [6]. In pre-slaughter stage or cattle cultivation, breeding and different traditional cattle handling systems affect the raw hide and skin during the growth of the animal. During the slaughter of animals a lot of defects can occur due to the lack of awareness of the abattoirs or butchers, due to using traditional facility, lack of awareness about stunning animals before slaughtering, and position during slaughtering, affecting the quality of raw hides and skins in Ethiopia. This study focuses on analysis of raw hide and skin defects in pre slaughter stage and during slaughter using Pareto analysis and cause and effect diagram to recommend the solutions.

Hides and skins are important economic products contributing to the largest share of the total and agricultural export commodities followed by live animals in Ethiopia [7]. The ones who bear the greatest responsibility in delivering high-quality raw hides and skins to the tanneries are the traders, thus playing a key role in the tanneries' economic viability [8].

Skins and hides defects are classified into two main groups. The first group is those created or acquired during the life of the animal (pre-mortem defects) and the second group is those that occur during and after the slaughtering of animals (post-mortem defects) [9]. This study focuses on pre-slaughter and during slaughter stages to minimize raw hide and skin defects because for post-slaughter stage there is no tannery or other industry in Dire Dawa.

### Pre-Slaughter Defects

The pre-slaughter defects include cockle, which is due to an allergic skin hypersensitivity reaction to parasitic infestation, grain scratches, pox lesions, warts, tick damage,

branding, age (shrinkage) and poor substance (thickness of the skin or hide, toughness of the fibres and the closeness of the texture of the fibres). The following defects are the same defects happening in Ethiopian cattle cultivation (Figures 1-3, source:

<https://www.iowabeefcenter.org/bch/CongenitalDefectsCattle.pdf>; Figure 4, source: <https://encrypted-tbn0.gstatic.com/images>, and Figure 5, source: <https://www.mdpi.com/2076-2615/8/8/13>).



Figure 1. Hairlessness (hypotrichosis) in a calf



Figure 2. Extra toes (polydactyly)



Figure 3. Weaver calf



Figure 4. Brand mark



Figure 5. Fire-heated irons used for branding on farm

### During Slaughter Defects

The major slaughter defects are fly cuts (scores), holes (a complete perforation of the skin or hide resulting from a knife or flaying

appliance), poor pattern (an asymmetric skin or hide due to bad opening cuts or distortion during drying because of uneven tension), and vein marks (traces of blood vessels in the skin where the blood was not completely drained).



Figure 6. Lack of skill in the slaughtering house  
Source: Addis Ababa Abattoirs enterprise



Figure 7. Lack of skills in traditional slaughtering  
Source: Photo taken in Raya region in 2018

To the best of my knowledge, there is no study that focuses on raw hide and skin defect minimization in pre-slaughter and during slaughter stages or Pareto diagram and fishbone diagram implementation in literature concerning raw hide and skin defects. Importantly, motivation from a real-life leather industry problem in the context of Ethiopia drives me to conduct this study. The researcher thus believes this study has practical managerial application in a slaughterhouse to minimize the defects of raw hide and skin in Ethiopia, Dire Dawa city.

## EXPERIMENTAL

### Material and Methods

Cattle hide, goat and sheep skins were used for this study to minimize the defects in preslaughter, during slaughter and post slaughtering process in Dire Dawa city. To minimize the defects in each process, a checklist was used for gathering and organizing the frequency or defect data, a Pareto chart was used to prioritize the defect to solve the problem based on the 80/20 rule, and a cause-and-effect diagram to identify the root causes, main cause and to overcome the problems at each stage.

### An Overview of the Pareto Chart and Cause-and-Effect Diagrams

The Pareto chart is useful for non-numeric data, such as 'cause', 'type' or 'classification', and is useful to prioritize where action and process changes should be focused and are commonly used for identifying the downtime and other wastages. It uses bar diagrams to sort problems based on frequency, severity, nature, or source and displays the size of which problems are vital ones [10]. Pareto analysis helps to identify different defects and classify them according to their significance. These defects often lead to the rejection of raw materials [11]. Pareto chart is important to give priority based on frequency, time, and costs and to solve it by the 80/20 rule.

To determine possible root causes of rejection, the Cause-and-Effect Diagram (CED) is also a very useful tool. It helps to identify, sort, and display the causes of a specific problem or quality characteristic. It graphically illustrates the relationship between a given outcome and all the factors that influence the outcome and hence identifies the possible root causes i.e., basic reasons for a specific effect, problem, or condition [11]. Fish bone diagram was used to show the relationship among all possible grouped causes and main cause [12]. Therefore, in this study cause and effect



diagram helps to identify the root cause of defects in preslaughter and during the

slaughter of bovine and ovine animals in Ethiopia (Dire Dawa slaughterhouse).

### An Overview of Leather Processing in Ethiopia

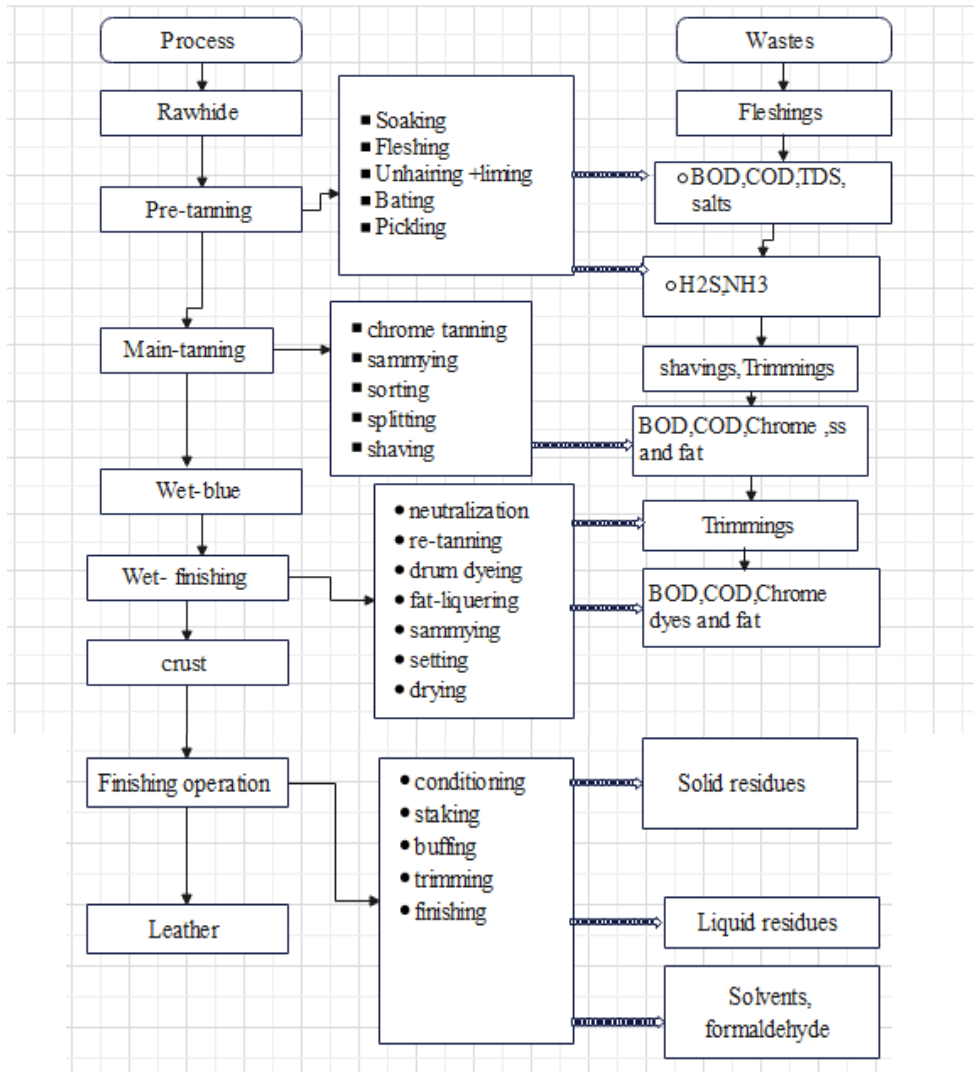


Figure 8. Leather processing in Ethiopia

Leather processing involves converting raw hides and skins into finished leather, by carrying out processes such as soaking, fleshing, unhairing, bating and pickling in the first stage. The above figure shows different processes for converting raw hide and skin into leather by using different mechanisms, process parameters and technical parameters.

Figure 1 illustrates the process flow chart of leather manufacturing. Raw hides and skins are collected from different parts/areas of Ethiopia and preserved in raw hide and skin

storehouse. Using a soaking drum, the soaking operation is carried out to remove blood, salts and other external materials. Then, liming process is carried out on the flesh side to remove the hair from the skin or hide. Deliming process is done with different chemicals to open up the fiber of skin or hides and make them suitable for bating, pickling and tanning process. As shown in the above figure the raw hide chrome tanning is applied in Ethiopia and the wet blue leather is passed through

different mechanisms and processes to produce finished leather outputs.

**Methodology**

The study was conducted on slaughter house in Dire Dawa where cattle were flayed for meat production. Data were collected from

the slaughter house where fresh raw hide and skin were collected. The raw hides and skins have defects due to different root causes. A Pareto chart was constructed to analyze the defects and to identify significant rejections of raw hide and skin.

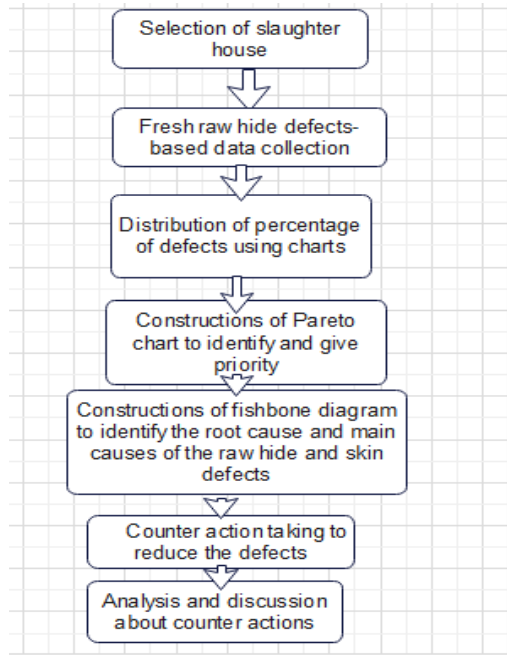


Figure 9. Research design framework

**Data Collection and Analysis**

Table 1: Raw hide and skin defects analysis using Pareto chart at preslaughter stages

Types of defects observed at slaughter	Number of defects happening during growth	0.0%
Cockle	1500	22.8%
Shrinkage	1000	38.1%
Scratch	950	52.5%
Brand marks	870	65.8%
Pox lesions	800	77.9%
Pox lesions	720	88.9%
Scar from wounds	400	95.0%
Tick mark	250	98.8%
Poor substance	80	100.0%

From Table 1 the data showed the frequency of different defects occurring in different stages but not ordered based on Pareto analysis principles. The defects occurring with a higher frequency at slaughter

stage are cockle (1500), shrinkage (1000) and others listed above, due to different reasons. Therefore, in the pre-slaughter stage, raw hide and skin defects affect the leather quality. Proper handling system, creating awareness

for cattle cultivators (husbandry stages), solving genetics problems, and their feeding system are very important to minimize pre-slaughter raw hide and skin defects.

Furthermore, prioritizing has been done to use for Pareto chart analysis.

### Number of defects happening during growth or frequency

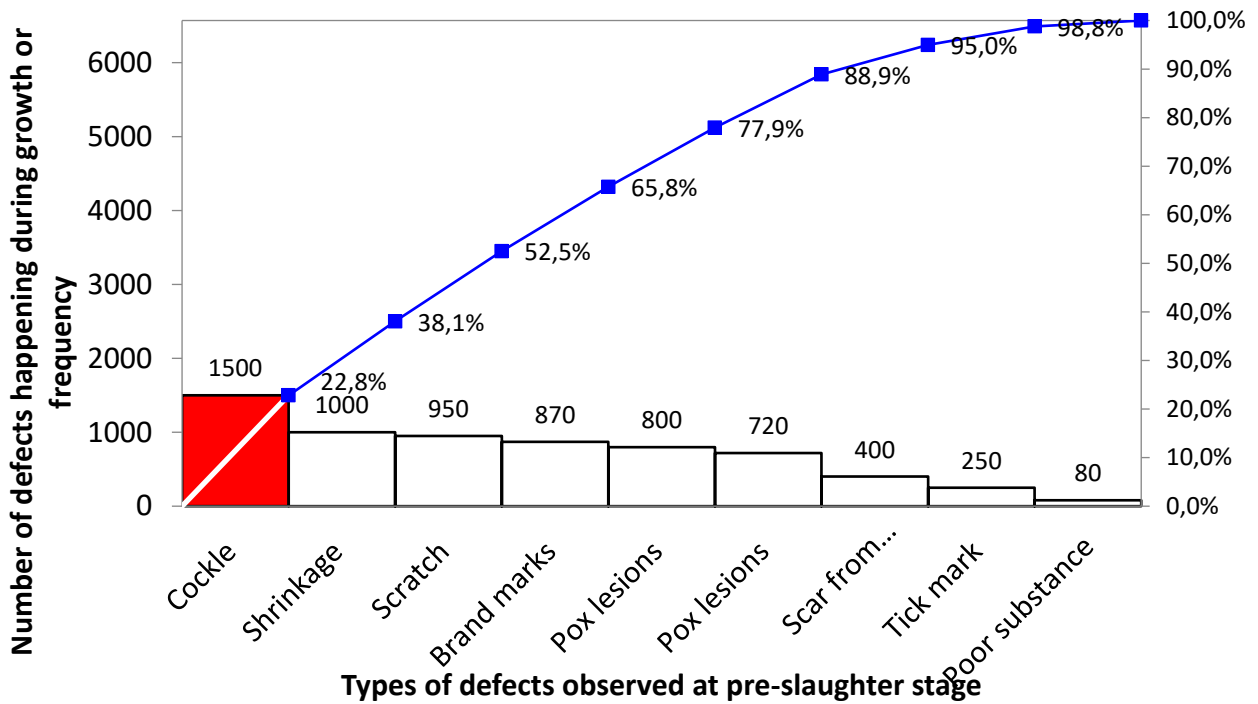


Figure 10. Pareto chart analysis in pre-slaughter stage

From the Pareto analysis (Figure 10), it is seen that the most significant source of defects of raw hide and skin in the preslaughter stages is cockles (22.8) and the second is shrinkage

(38.1). Here, the cockle and shrinkage are the few factors causing 60.9% of raw hide and skin defects.

### Number of defects happening during growth or frequency

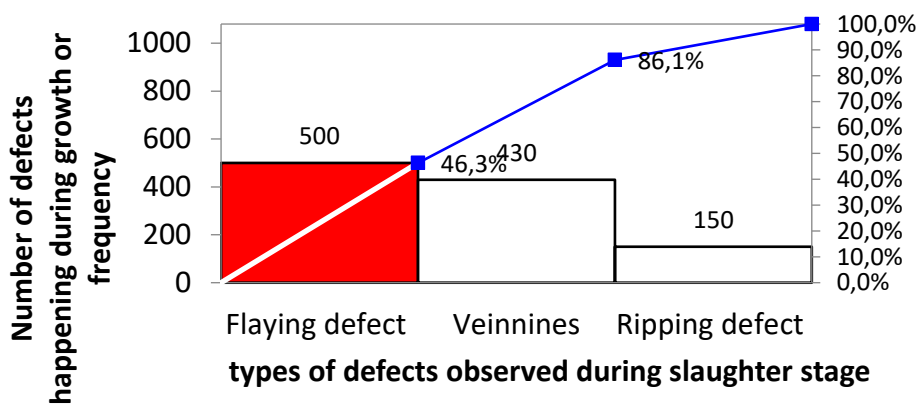


Figure 11. Pareto chart analysis in slaughtering stage

From the Pareto analysis (Figure 11), it is seen that the most significant source of defects of raw hide and skin during the slaughtering stage is flaying (46.3), followed by veininess (86.1). Here, the flaying and veininess are the few factors causing 132.4% of raw hide and skin defects.

In both cases, Pareto chart principle or 80/20 rule can be applied in this process and by removing 20% of the major defects we can improve 80% of the leather product and satisfy our customers' needs.

**Cause-and-Effect Diagram Application in Raw Hide and Skin Defect in Preslaughter of Cattle**

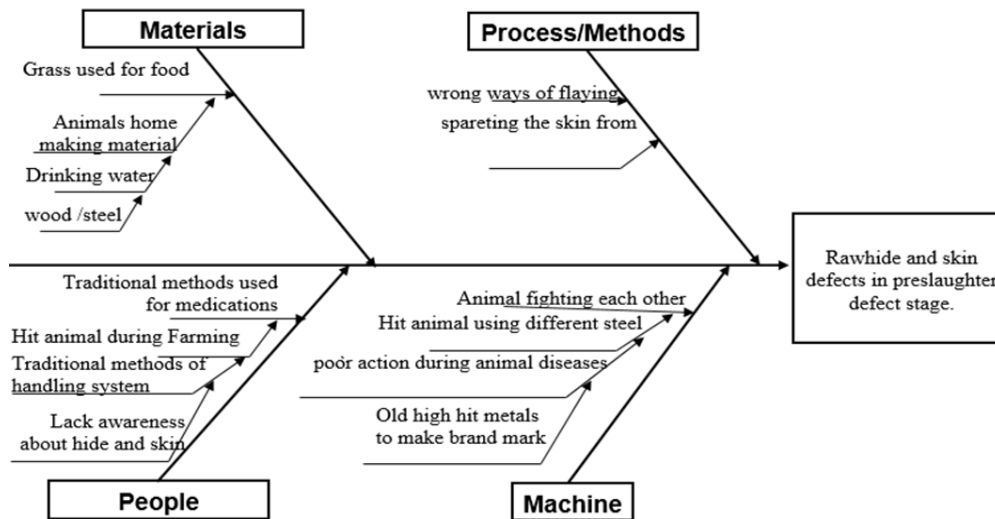


Figure 12. Cause and effect diagram application in preslaughter stages

The cause-and-effect diagram for raw hide and skin defects is illustrated in Figure 12, the main causes for raw hide and skin defects in the preslaughter stages are categorized on the basis of the influence of peoples, machines, materials, and processes/ methods. Due to a lack of skills/awareness of husbandry, traditional methods of handling animals during farming and traditional methods used for medications. For machine-related causes,

heated metal shape for brand mark, poor action during animals' diseases, hit animals using different steel and animals fighting each other and the root cause of materials, grass used for food, animal home making material, drinking water and wood/steel for animals' houses. Furthermore, in the process of flaying, the root causes of raw hide and skin defects are the wrong ways of separating skin or hide from the corpse.

Cause-and-Effect Diagram Application in Raw Hide and Skin Defects During Slaughtering Process

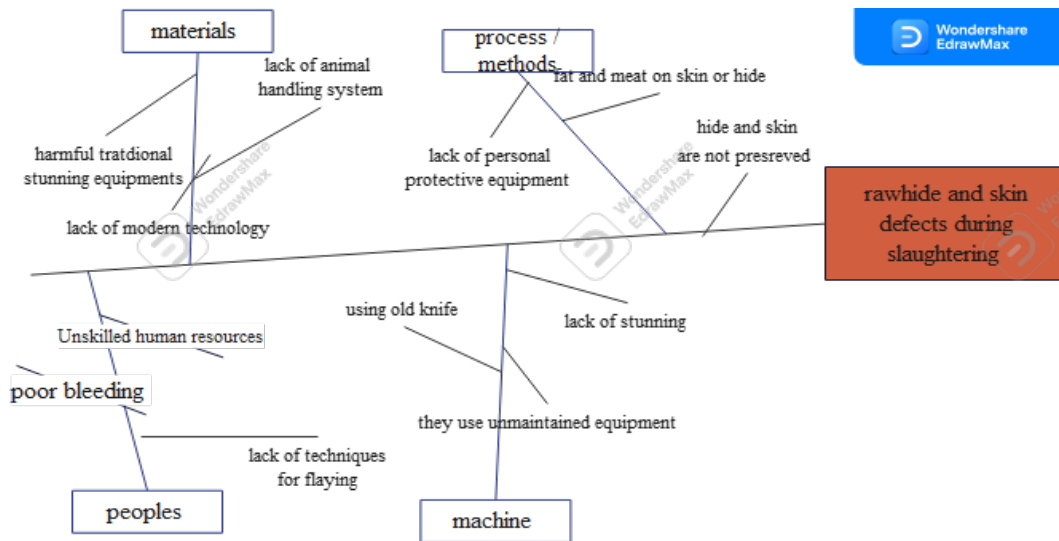


Figure 13. Fishbone diagram analysis during slaughtering process

The cause-and-effect diagram for raw hide and skin defects is illustrated in Figure 13, showing the main causes for raw hide and skin defects during slaughtering stages are categorized on the basis of the influence of people, machine, materials, and processes/methods. A lack of skills/awareness of butchers, poor bleeding, and inappropriate methods of flaying, are affecting the quality of raw hide and skin during slaughtering. Machine-related causes include old or unsuitable knives, no use of stunning/electronic or mechanical equipment, poor quality steel. High skin or hide-defected animals, traditional stock used to fall down the animals, poor quality gloves, poor quality footwear, and poor protective clothes are the

root causes of raw hide and skin defects in terms of materials and processes.

RESULTS AND DISCUSSIONS

Table 2 shows that the main causes (machine, processes/ methods, people and materials) have their own root causes that affect the quality of raw cattle hide and goat (sheep) skins. Therefore Table 2 showed that main causes and root causes of raw hide and skin were identified and corrective actions were recommended for minimizing the defects of raw hides and skins. Hence, by implementing the corrective actions, the defects of the raw hide and skins were minimized in the pre-slaughter stage.

Table 2: Recommended actions for pre-slaughter hide and skin defects

S. No.	Main causes	Root causes	Recommended corrective actions to minimize the raw hide and skin defects
1	Machine	<ul style="list-style-type: none"> <li>• Old high-hit metals to make brand marks</li> <li>• Poor action during animal disease</li> <li>• Hit animals using different steel</li> <li>• Animals fighting each other</li> </ul>	<ul style="list-style-type: none"> <li>✓ Equipment used for stunning and correct stunning position</li> <li>✓ Stunner in the correct position</li> <li>✓ Using scientific medications for animal health</li> <li>✓ Prepare handling in the husbandry stage</li> </ul>
2	Process/methods	<ul style="list-style-type: none"> <li>• Wrong ways of flaying</li> <li>• Separating the skin from meat</li> </ul>	<ul style="list-style-type: none"> <li>✓ Sterilize the cutting knife in water at 82°C</li> <li>✓ Remove head after skinning</li> </ul>



S. No.	Main causes	Root causes	Recommended corrective actions to minimize the raw hide and skin defects
3	People	<ul style="list-style-type: none"> <li>• Lack of awareness about hide and skin</li> <li>• Traditional methods of handling system</li> <li>• Hit animals during farming</li> <li>• Traditional methods used for medications</li> </ul>	<ul style="list-style-type: none"> <li>✓ Do not leave any hair or skin pieces on the skin or hide</li> <li>✓ Do not leave the carcass to bleed while flaying</li> <li>✓ Create awareness about the advantages of raw hide and skin</li> <li>✓ Acquiring knowledge for husbandry about handling of their cattle, goat and sheep.</li> <li>✓ Using systems and technologies for farmers</li> </ul>
4	Materials	<ul style="list-style-type: none"> <li>• Grass used for animal food</li> <li>• Animal home making materials</li> <li>• Drinking water, wood/steel</li> </ul>	<ul style="list-style-type: none"> <li>✓ Animals presented for slaughter should be sufficiently clean</li> <li>✓ Animals be allowed enough rest (24 hours) before slaughter to improve quality of meat and hides and skins</li> <li>✓ The animals should be given a good drink of water for cooling them down and facilitating the loosening of the attachment between the hide/skin and the flesh for ease of flaying</li> <li>✓ Good animal rest pre-slaughter</li> </ul>

As shown in Table 3, the main causes (machine, process/method, people, and materials) and root causes that affect the raw hide and skin quality during the slaughtering process in Dire Dawa city. As a result, the

recommended actions were important to minimize the defects of cattle hide and sheep/goat skin during the slaughtering process in the Dire Dawa slaughterhouse (Dire Dawa administration city).

Table 3: Recommended corrective action during the slaughtering stage

S. No.	Main causes	Root causes	Recommended corrective actions
1	Machine	<ul style="list-style-type: none"> <li>• Unsuitable knife</li> <li>• Poor quality steel</li> <li>• Using old facility</li> <li>• Not using electronic or mechanical stunning methods</li> </ul>	<ul style="list-style-type: none"> <li>✓ Flay cuts, scores and gouges</li> <li>✓ Use clean hooks, knives and protective clothes</li> <li>✓ Good quality and modern knives</li> <li>✓ Using electronic and mechanical stunning methods</li> </ul>
2	Process/Methods	<ul style="list-style-type: none"> <li>• Leaving meat/fats in the skin or hide</li> <li>• Not removing heads after skinning</li> <li>• Unpreserved raw hide and skin</li> <li>• Poor quality of protective apron, cloth and gloves</li> </ul>	<ul style="list-style-type: none"> <li>✓ Using proper methods to remove fats to get high-quality skin and hide</li> <li>✓ Fresh raw hide should be properly preserved</li> </ul>
3	People	<ul style="list-style-type: none"> <li>• Unskilled human power</li> <li>• Wrong methods of flaying</li> <li>• Poor bleeding</li> </ul>	<ul style="list-style-type: none"> <li>✓ Best bleeding practice</li> <li>✓ Used flaying sequence operations</li> <li>✓ Using the best evisceration technique</li> </ul>

S. No.	Main causes	Root causes	Recommended corrective actions
4	Materials	<ul style="list-style-type: none"> <li>• High skin or hide defective animals</li> <li>• Traditional rope to fall down the animals for slaughtering</li> <li>• Poor quality glove</li> <li>• Poor quality footwear</li> <li>• Poor protective apron</li> </ul>	<ul style="list-style-type: none"> <li>✓ Checking the skin of animals during slaughtering to prevent defects</li> <li>✓ Instead of using traditional methods of rope to fall down the animals better to use electronic or mechanical stunning methods</li> <li>✓ Good quality glove</li> <li>✓ Good quality footwear</li> <li>✓ Good protective apron</li> </ul>

## CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Raw hide and skins are one of the most common problems in the leather manufacturing industry in Ethiopia. It should be minimized to ensure the highest quality level of the raw hide and skin at pre-slaughter and during slaughter stages. In this work, Pareto analysis and cause-and-effect diagram are used to identify and evaluate different types of defects that occurred in the Dire Dawa slaughterhouse. After Pareto analysis, it is found that cockle and shrinkage constitute above 80% of total defects at pre-slaughter stage. Furthermore, the raw hide and skin defects during the slaughter process are analyzed using a Pareto chart that shows 86.1% of defects of raw hide and skin can be minimized by using 80/20 rules. Then root causes of the raw hide and skin defects at pre-slaughter stages are analyzed using a cause-and-effect diagram. Four different main cause areas and different types of root causes that are responsible for raw hide and skin defects at pre-slaughter and during slaughter stages are found. Finally, a few corrective actions are taken and some suggestions are recommended for minimizing raw hide and skin defects to increase the quality and productivity of Ethiopian leather industry.

## REFERENCES

1. Adem, M., Production of Hide and Skin in Ethiopia; Marketing Opportunities and Constraints: A Review Paper, *Cogent Food Agric*, **2019**, *5*, 1, <https://doi.org/10.1080/23311932.2019.1565078>.
2. Sarker, M.I., Long, W., Liu, C.K., Preservation of Bovine Hide using Less Salt with Low Concentration of Antiseptic, Part I: Effectiveness of Developed Formulations, *J Am Leather Chem Assoc*, **2017**, *113*, 1, 12-18.
3. Wu, J., Zhao, L., Liu, X., Chen, W., Gu, H., Recent Progress in Cleaner Preservation of Raw Hides and Skins, *J Clean Prod*, **2017**, *148*, 158-173, <https://doi.org/10.1016/j.jclepro.2017.01.113>.
4. Abadi, Y., Current Problems of the Leather Industry, in: R.C. Merkel, G. Abebe and A.L. Goetsch (eds.), *The Opportunities and Challenges of Enhancing Goat Production in East Africa*, Proceedings of a conference held at Debu University, Awassa, Ethiopia from November 10 to 12, **2000**, pp. 139-143.
5. United Nations Industrial Development Organization, Annual Report 2008, Industrial Development Board, Vienna, **2009**.
6. Kahsay, T., Negash, G., Hagos, Y., Hadush, B., Pre-slaughter, Slaughter and Post-slaughter Defects of Skins and Hides at the Sheba Tannery and Leather Industry, Tigray Region, Northern Ethiopia, *Onderstepoort J Vet Res*, **2015**, *82*, 1, <https://doi.org/10.4102/ojvr.v82i1.931>.
7. Alemnesh, B., Getachew, T., Tariku, J., Assessment of Quality and Marketing of Hide and Skin in Adamitulu Jidokombolcha and Bora Woreda in East Shewa Zone of

- Oromia Regional State, Ethiopia, *Int J Livest Prod*, **2018**, 9, 10, 269-279, <https://doi.org/10.5897/IJLP2017.0372>.
8. Jabbar, M.A., Kiruthu, S., Gebremedhin, B., Ehui, S., Essential Actions to Meet Quality Requirements of Hides, Skins and Semi-Processed Leather from Africa, A Report Prepared for The Common Fund for Commodities, Amsterdam, The Netherlands, **2002**.
9. Tolossa, Y.H., Skin Defects in Small Ruminates and Their Nature and Economic Importance: The Case of Ethiopia, *Glob Vet*, **2013**, 11, 5, 552-559, <https://doi.org/10.5829/idosi.gv.2013.11.5.76200>.
- 10 Benjamin, S.J., Marathamuthu, M.S., Murugaiah, U., The Use of 5-WHYs Technique to Eliminate OEE's Speed Loss in a Manufacturing Firm, *J Qual Maint Eng*, **2015**, 21, 4, 419-435, <https://doi.org/10.1108/JQME-09-2013-0062>.
- 11 Ahmed, M., Ahmad, N., An Application of Pareto Analysis and Cause-and-Effect Diagram (CED) for Minimizing Rejection of Raw Materials in Lamp Production Process, *Management Science and Engineering*, **2011**, 5, 3, 87-95, <https://doi.org/10.3968/j.mse.1913035X20110503.320>.
- 12 Hailu, H., Tabuchi, H., Ezawa, H., Jilcha, K., Reduction of Excessive Trimming and Reject Leather by Integration of 7 QC Tools and QC Story Formula: The Case Report of Sheba Leather PLC, *Ind Eng Manage*, **2017**, 6, 3, <https://doi.org/10.4172/2169-0316.1000223>.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).

# BIODEGRADABLE POLYMER COMPOSITE BASED ON POLYVINYL CHLORIDE AND POLY (ETHYLENE-VINYL ACETATE) WASTE

Laurenția ALEXANDRESCU\*, Mihai GEORGESCU, Maria SÖNMEZ, Mihaela NIȚUICĂ, Maria-Daniela STELESCU, Dana GURĂU

INCDTP - Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., sector 3, Bucharest, Romania,

laurentia.alexandrescu@icpi.ro

Received: 31.10.2022

Accepted: 28.02.2023

<https://doi.org/10.24264/lfj.23.1.6>

## BIODEGRADABLE POLYMER COMPOSITE BASED ON POLYVINYL CHLORIDE AND POLY (ETHYLENE-VINYL ACETATE) WASTE

**ABSTRACT.** This paper presents experiments on developing and characterizing biodegradable polymer composites based on polyvinyl chloride and expanded poly(ethylene vinyl acetate) (EVA) post-consumer waste. This type of waste is a thermoplastic material collected from the footwear industry, residues from the production of outer and intermediate soles and used footwear. It is used due to its shock absorption properties and low density (0.6-0.8 g/cm<sup>3</sup>). To make these products, EVA is injected into molds, a process that generates waste that cannot be reused. In this paper, a method of EVA waste recovery is presented and the possibility of developing a recycled product is investigated. Expanded EVA waste is cryogenically ground to sizes of min. 500 nm, functionalized by a mechanical process at temperature with polydimethylsiloxane (PDMS) and mixed in the composite in various proportions (10, 20, 50%). This composite will be made into a low-density product, with low cost, recovery and reuse of waste, and last but not least, biodegradable. The methodology for making the new materials involves the following steps: sorting waste, grinding, functionalization and compounding. These operations are easy to manage and do not involve new equipment. Compounding, the most important operation, will be performed on an extruder-granulator. The experimented biodegradable composites were physico-mechanically characterized. Waste transformation (ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and the sustainable use of this waste, contributing to sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of waste on the environment.

**KEY WORDS:** expanded EVA waste, polymer composite, biodegradability

## COMPOZIT POLIMERIC BIODEGRADABIL PE BAZĂ DE POLICLORURĂ DE VINIL ȘI DEȘEURI DE POLI(ETILENVINIL ACETAT)

**REZUMAT.** Prezentă lucrare experimentează realizare și caracterizare de compozite polimerice biodegradabile pe bază de policlorură de vinil și deșeuri post-consum de poli(etilenvinil acetat) (EVA) expandat. Acest tip de deșeu este un material termoplastic colectat din industria de încălțăminte, din resturi din producția de tălpi exterioare și intermediare și încălțăminte utilizată. El este utilizat datorită proprietăților de absorbție a șocurilor și densitate mică (0,6-0,8 g/cm<sup>3</sup>). Pentru realizarea acestor produse, EVA este injectat în matrițe, proces care generează deșeuri ce nu pot fi reutilizate. În această lucrare se prezintă o metodă de recuperare a deșeurilor EVA și se investighează posibilitatea dezvoltării unui produs reciclat. Deșeurile de EVA expandate sunt măcinate criogenic la dimensiuni de min. 500 nm, funcționalitate prin procedeu mecanic la temperatură cu polidimetilsiloxan (PDMS) și amestecate în compozit în proporții variate (10, 20, 50%). Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, valorificare și reutilizare a deșeurilor și, nu în ultimul rând, biodegradabil. Metodologia de realizare a noilor materiale implică următoarele etape: sortarea deșeurilor, măcinarea, funcționalizarea și amestecarea. Aceste operațiuni sunt ușor de gestionat și nu implică echipamente noi. Compundarea, cea mai importantă operațiune, se realizează pe un extruder-granulator. Compozitele biodegradabile experimentate au fost caracterizate fizico-mecanic. Transformarea deșeurilor (măcinate și funcționalizate) în noi produse cu valoare adăugată va duce la îmbunătățiri remarcabile ale ciclului de viață al materiilor prime și la utilizarea durabilă a acestor deșeuri, contribuind la sustenabilitate, îmbunătățirea eco-eficienței și a eficienței economice, precum și la reducerea „presiunii” deșeurilor asupra mediului.

**CUVINTE CHEIE:** deșeu de EVA expandat, compozit polimeric, biodegradabilitate

## COMPOSITE POLYMÈRE BIODÉGRADABLE À BASE DE CHLORURE DE POLYVINYLE ET DE DÉCHETS DE POLY(ÉTHYLÈNE-ACÉTATE DE VINYLE)

**RÉSUMÉ.** Le présent article expérimente la création et la caractérisation de composites polymères biodégradables à base de chlorure de polyvinyle et de déchets post-consommation de poly(éthylène-acétate de vinyle) (EVA) expansé. Ce type de déchet est un matériau thermoplastique collecté dans l'industrie de la chaussure, à partir de résidus de production de semelles extérieures et intermédiaires et de chaussures usées. Il est utilisé en raison de ses propriétés d'absorption des chocs et de sa faible densité (0.6-0.8 g/cm<sup>3</sup>). Pour fabriquer ces produits, l'EVA est injecté dans des moules, un processus qui génère des déchets non réutilisables. Dans cet article, une méthode de valorisation des déchets EVA est présentée et la possibilité de développer un produit recyclé est étudiée. Les déchets EVA expansés sont broyés cryogéniquement jusqu'à des tailles de min. 500 nm, fonctionnalisés par un procédé mécanique en température avec du polydiméthylsiloxane (PDMS) et mélangé au composite dans diverses proportions (10, 20, 50%). Ce composite sera transformé en un produit à faible densité, à faible coût, en récupérant et en réutilisant des déchets et, enfin et surtout, biodégradable. La méthodologie de fabrication de nouveaux matériaux comprend les étapes suivantes : tri des déchets, broyage, fonctionnalisation et mélange. Ces opérations sont faciles à gérer et ne nécessitent pas de nouveaux équipements. Le mélange, l'opération la plus importante, est réalisé sur une extrudeuse-granulatrice. Les composites biodégradables testés ont été caractérisés physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée entraînera des améliorations remarquables dans le cycle de vie

\* Correspondence to: Laurenția ALEXANDRESCU, INCDTP - Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., sector 3, Bucharest, Romania, [laurentia.alexandrescu@icpi.ro](mailto:laurentia.alexandrescu@icpi.ro), [laura\\_alexandrescu@yahoo.com](mailto:laura_alexandrescu@yahoo.com)

des matières premières et l'utilisation durable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique, ainsi que réduire la « pression » des déchets sur l'environnement.

MOTS CLÉS : déchet EVA expansé, composite polymère, biodégradabilité

## INTRODUCTION

Methods of eliminating waste that pollute the environment have been approached through several technologies: depollution (deposition on the ground, burial, composting, burning), valorization through reuse and/or energetic recycling (incineration) and/or mechanical and/or chemical (pyrolysis, gasification, hydrolysis, etc.). In the integrated concept of polymer waste management, along with these methods, the possibilities of reducing quantities by reusing them into new biodegradable polymer composites are also included. If the re-introduction of these materials into the production circuit is carried out without taking into account the influences of the content of non-polymeric impurities and those resulting from specific destruction processes, then the materials resulting from simple mechanical recycling have mechanical properties that are all the lower the more the content of non-polymeric impurities is higher. For this reason, these polymers can be used for peripheral, low-performing applications [1-2]. It has been demonstrated that the residual properties can be brought to useful values by modification with a primary polymer and necessarily by subsequent homogenization from the melt, i.e., by mechanical recycling, the method of diluting defects.

Composites represent a versatile and very valuable family of materials, which can solve a series of existing problems in various applications/industries, because they facilitate the introduction of new properties in materials. The development of environmentally friendly "green" materials is due to the biodegradability of these polymeric materials (from various sources), low weight, low cost, high availability, high specific resistance, as well as due to the possibility of adapting existing equipment to processors in the field, to mass production [2-4].

Ethylene vinyl acetate (EVA) is a thermoplastic elastomer widely used in the production of footwear. Due to its outstanding flexibility, abrasion resistance and

low density (below  $1\text{g/cm}^3$ ), EVA is used to make outsoles and midsoles for sneakers and other types of shoes. Unlike other materials, such as thermoplastic polyurethane (TPU) and polyvinyl chloride (PVC), EVA is easier to process and allows the production of higher performing running shoes with greater shock absorption capabilities [5]. EVA midsoles and outsoles are usually made by injection molding at temperature; EVA expands into a foam [6]. This process is automated and allows for high production due to the short processing time (usually in minutes) [7]. Currently, a real recycling process for EVA has not yet been validated industrially and the residues generated in the injection process are used as fillers [8, 9] or thrown in the landfill [10]. With an estimated annual production of 24 billion shoes [11] (most of which contain EVA soles), it is easy to understand the importance of reuse [12]. Lopes *et al.* [13] used EVA waste as a filler for natural rubber, styrene-butadiene rubber, and acrylonitrile-butadiene rubber in vulcanization/pressing sole manufacturing processes. Two percentages of waste were tested (10 phr and 20 phr) and the produced shoe soles showed good mechanical properties. Pavia Junior *et al.* [10] evaluated the recovery of EVA waste in micronized form and added to virgin material. These studies confirmed the possibility of successfully using these wastes for the production of footwear components with mechanical performance comparable to virgin ones.

Most synthetic polymers made from petroleum and its allied components are not degradable after they are transformed into wastes. Today, more and more scientists shifted their attention to the eco-friendly polymeric materials [14]. The polymers used are mainly polyethylene, polypropylene, polyvinyl chloride, polyester or polycarbonate, which share the fact that most surface and/or volume modifications are necessary to achieve outstanding properties [15]. Being one of the largest polymers, polyvinyl chloride (PVC) is widely used and essential in almost all



fields. The optimal ratio of properties and costs makes PVC a material capable of competing with both natural materials and other polymers in many areas of science and engineering.

Polyvinyl chloride (PVC) is one of the most used types of polymers (40% of dedicated polymeric materials) for biomedical and food applications. Although much has been done to replace PVC in medical applications, it remains the most used polymer in medical device manufacturing. PVC applications include blood bags and tubes, intravenous containers and components, dialysis equipment, inhalation masks, examination gloves, etc. [16]. PVC-based polymeric materials are subject to continuous research for new modifications and improvements [17, 18]. Polymer based composites modified with EVA waste (WEVA/PVC) are increasingly popular since it is a feasible solution not only to the growing environmental issue, but also to the expensive cost of certain polymer-based materials [19, 20].

Properties such as hardness, density, tensile strength, elongation, flow index and tear strength of polymer composites compounded with waste polyvinyl chloride (WPVC) and 10, 20 and 50% waste EVA (WEVA) were evaluated, compared with the blank sample composed of WPVC. The influence of conventional polymer processing techniques, such as twin-screw extrusion, addition of compatibilizer and functionalization of the fiber using a functionalization agent, on the performance of the physico-mechanical properties of the experimental composites was investigated. The addition of 10 g (%) polyethylene-graft-maleic anhydride (PE-g-MA) as a compatibility agent between EVA waste and PVC improved the mechanical performance of the composite, while processing in a corotating double screw extruder favored the distribution of the cryogenically ground EVA waste powder in the WPVC matrix.

## EXPERIMENTAL

### Materials and Methods

#### Materials

Polyvinyl chloride waste (WPVC) obtained from post-consumer shoe soles and expanded poly(ethylene vinyl acetate) waste (WEVA) obtained from manufacturing soles for footwear by cutting out from expanded EVA plates, ground in a polymer-specific mill with knives and sieves, with 2-3 mm granulation, also ground and sieved, with a grain size smaller than 500 nm, polyethylene-graft-maleic anhydride (PE-g-MA) in the form of yellow granules, viscosity of 240000 cps and an acidity index of 43.1 mg KOH/g and polydimethylsiloxane (PDMS), clear, colourless liquid, viscosity of  $1.00 \cdot 10^{-4} \text{ m}^2\text{s}^{-1}$  at 25°C and density of 0.977g/cm<sup>3</sup>, the last two manufactured by Sigma Aldrich.

Functionalization of ethylene vinyl acetate waste particles was achieved by mixing with a stirrer with helical paddles, for 2h at a temperature of 80°C with slow dripping of polydimethylsiloxane (PDMS) and a speed of 40 rpm. Different percentages of functionalizing agent relative to the amount of waste were experimented, but the percentage of 5% was selected, being considered optimal due to the degree of absorption, the elimination of expanded particles agglomeration, work method and the favorable influence on the physical-mechanical characteristics of the composite.

#### Preparation of Various Types of Biodegradable Polymer Composite

Recycled polyvinyl chloride, polyethylene-graft-maleic anhydride and waste WEVA particles were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 3 min. at 155°C to melt the plastomer, mixed for 5 min. at 165°C and 2 min. at 160°C for homogenisation. The total time was 10 minutes. Table 1 shows tested formulations.

Table 1: Control – A0 and WPVC/PE-g-MA/WEVA polymer composite formulations with varying WEVA amounts (A1-10%; A2-20%; A3-50%)

Compound	A0	A1	A2	A3
	WPVC	10%WEVA	20%WEVA	30%WEVA
Recycled polyvinyl chloride	270	285	270	225
Waste EVA functionalized with PDMS	-	15	30	75
PE-g-MA	30	30	30	30
Total	300	330	330	330



Figure 1. Brabender Plasti-Corder Mixer 350

The Brabender mixing diagrams, Figure 2, show the following: chamber temperature increases from 155 to 160°C for the control sample – PVC waste and A0, with a maximum mixing force of 182 N/mm in 48s. When adding particles, the mixing force decreases (158 N/mm for 10-20% mixture of WEVA (samples A1 and A2) and 145 N/mm for 50%

WEVA – A3 mixture). The time needed to reach maximum force, increases proportionally to the amount of WEVA mixture, from 40s – control sample to 45s – A1, 48s – A2, and 53s – A3. The temperature in the chamber decreases, at the maximum force, from 180°C – A0 control sample to 195°C – A1, 205°C – A2 and 211°C – A3.

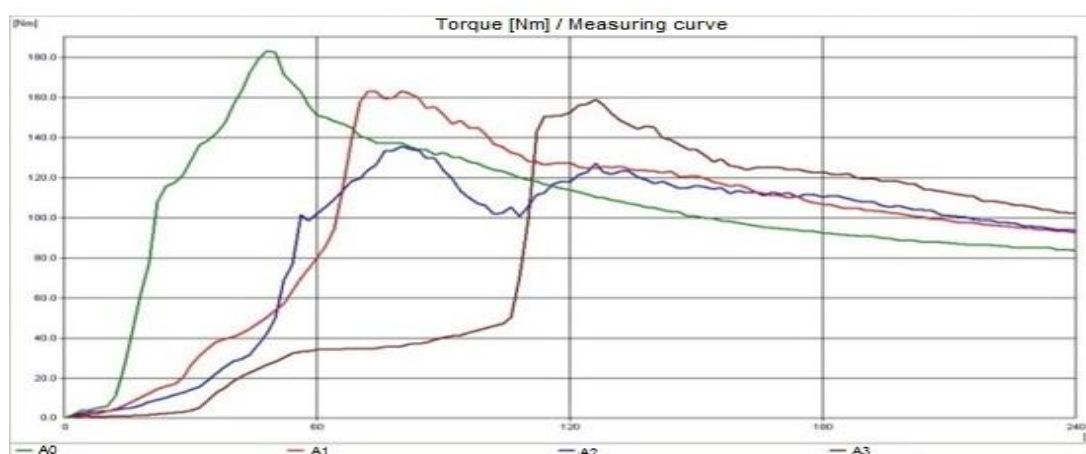


Figure 2. The overlapping Brabender mixing diagrams of control sample and PVC/PE-g-MA/WEVA polymer composite formulations with varying WEVA amounts (A1-10%; A2-20%; A3-30%)

According to the diagrams (Fig. 2-3), the following can be observed: in the first portion (A-B), the elastomer is introduced into the mixer and the torque increases. The first loading peak, A, corresponds to the

plasticization of PVC waste, PE-g-MA and EVA waste. As the torque increases, so does the temperature due to friction. The torque starts to decrease until it reaches B, mainly due to the homogenization and plasticization of the

ingredients, as well as due to the increase in temperature as a result of the shear forces, which indicates the homogenization of the mixture. As a result, a maximum torque value is obtained due to the compaction and homogenization of plastic waste. This is

generally followed by a decrease in the value of the torque, which indicates both the homogenization of the mixture and the increase in the temperature of the mixture due to friction at a higher rotational speed (60 rpm) with the mixer closed.

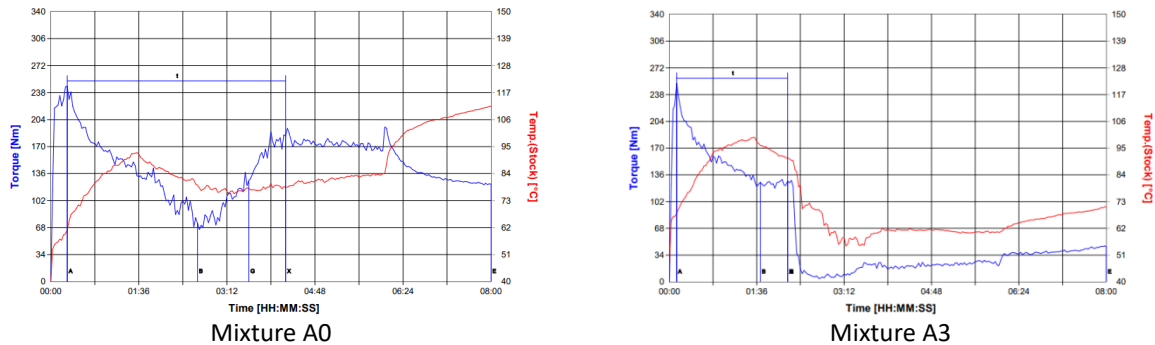


Figure 3. Torque and temperature variation depending on time, recorded using the Brabender Plasticorder while obtaining samples N0 and NP4

From the diagrams shown in Figure 3, it can be seen that the temperature in the mixing chamber increases, depending on the percentage of protein waste introduced into the polymer composite (starting from 90-96°C, it decreases to 80°C – in the control sample, then it increases to 110°C – at the end of mixing. In the case of biocomposites, the temperature in the mixing chamber increases, depending on the percentage of protein waste introduced into the polymer composite

(starting from 90-96°C, it decreases to approximately 55°C – in the sample with the highest EVA concentration – A3, then increases to 72°C – at the end of mixing. This decrease is due to the elastic behavior of the composite. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite. Industrially, the composites are made on an extruder-granulator with a capacity of 50Kg/h.

Table 2: Characteristics presented in Brabender processing diagrams for polymer biocomposites with EVA waste

Characteristics	Sample code			
	A0	A1	A2	A3
Temperature at loading peak, °C	94	94	96	97
Temperature at the inflection point, °C	78	70	67	61
Maximum temperature, °C	110	99	82	73
Energy at loading peak, Nm	246.0	255.9	230.0	243.6
Maximum energy, Nm	183.5	171.4	169.6	159.1
Energy in gelation zone, kNm	10.3	33.7	33.1	94.7
Specific energy, kNm/g	0.7	0.8	0.6	0.6
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3



Figure 3. Double screw granulator extruder with corotation TSE 35 type

The working method on the extruder-granulator is presented in Table 3. In order to process composites in good conditions, the

initial working temperature was established at 165°C.

Table 3: The working method on the extruder-granulator

Order of introducing ingredients	Time (minutes)	Speed	Temperature, °C
Plasticization of plastomer	1' 30"	40 rpm	160°C
+ EVA waste	4' 30"	20 rpm	165°C
Homogenization	2'	80 rpm	160-145°C
TOTAL	8'	20-60 rpm	45°C-145°C

The obtained product is in the form of cylindrical granules with a height and diameter of 2 mm, it contains nanometric substances in its composition, and the

physical-mechanical and chemical characteristics fall within the requirements set by the standards in force.

Table 4: Technological parameters for the extruder-granulator

No.	Name of the technological parameters	U/M	Composite type	
			A0	A1-A3
1.	Temperatures in:	°C		
	-area I		110±2	120±2
	-area II		100±2	110±2
	-area III		90±2	100±2
2.	Blade-knife speed	rpm	600-800	700-900
3.	Pellet cutter amperage	A	1-2	1.5-2.5

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

### Testing Methods

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

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

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A

wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Repeated flexing – Ross Flex – SR ISO 132/2018 is the test that determines the resistance of the specimens to the appearance and propagation of cracks when they are subjected to repeated flexing at an angle of 90 degrees, on a mandrel with a diameter of 10

mm, up to 150,000 cycles or until the crack appears or the material breaks.

## RESULTS AND DISCUSSIONS

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP – Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state. (See Table 5).

Table 5: Physical-mechanical characteristics of mixtures – NC series

Physical-mechanical characteristics	Sample code			
	A0	A1	A2	A3
Hardness, °Sh A	44	65	68	72
Elasticity, %	32	20	21	22
100% modulus, N/mm <sup>2</sup>	1.0	1.96	1.65	1.70
300% modulus, N/mm <sup>2</sup>	2.0	-	0.84	-
Tensile strength, N/mm <sup>2</sup>	14.23	3.75	3.05	2.14
Elongation at break, %	740	300	280	220
Residual elongation, %	28	28	26	26
Tear strength, N/mm	24.39	21.42	16.9	17.29
Specific gravity, g/cm <sup>3</sup>	1.2	1.15	1.11	1.12
Resistance to abrasion, mm <sup>3</sup>	123.45	203.79	224.26	246.46
Rosflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			90.000 cycles crack appear, resist up to 109.000 cycles

- The hardness increases proportionally with the amount of EVA waste used in compounding, from 44°Sh A for the control sample A0 to 72 °Sh A for the composite with a percentage of 30% functionalized EVA waste;
- The elasticity decreases, it also decreases compared to the control (this is due to the fact that the polymer chain is interrupted by the waste during compounding), but it increases insignificantly in proportion to the amount of waste due to the plasticity of the waste;
- Tensile strength and Elongation at break values decrease proportionally with the percentage of waste used;
- Tear strength and Residual elongation decrease proportionally with the percentage of waste
- Density decreases from 1.16 g/cm<sup>3</sup> in the control sample W) to 1.05 g/cm<sup>3</sup>

- in the sample with 50% percentage of functionalized wood waste;
- Abrasion increases proportionally with the amount of functionalized waste, but falls within the standardized value for PVC shoe soles, namely 250 mm<sup>3</sup>.
- Repeated flexions – Ross Flex – The footwear standards in force specify values of 150,000 cycles when determining repeated flexions for PVC shoe soles. From the values presented in Table 5, it appears that only composites A1 and A2 with EVA waste content of 10-20% fall within the limits imposed by the standard, and 50% do not fall within this value (at 90,000 cycles cracks appear, resist up to 109,000 cycles). The others have values higher than 150,000 cycles, higher than the values imposed by the standard.

The composite granules were processed into finished products, plates, soles and seals,



by injection into molds. Injection molding is a cyclical, intermittent process, in which the composite granules are heated to melting temperatures, and the melt is forced to pass through a narrowed hole, into a molding chamber, the mold. The form (mold) into which the molten material is injected, is cooled with water in the case of thermoplastic materials, until the material solidifies. The advantage of this technology is represented by the processing speed of an injected part, the period of a production cycle being 3-5 minutes, depending on the weight of the material filling the mold. The technology is clean, it does not result in waste or burrs due to the fact that the filling material of the mold is dosed automatically, and the composite

materials can be recirculated in the production process at least 5 times without changing their properties.

The optimal working parameters to make prototype products are:

- working temperature of 170°C;
- injection with the pressure of 300 KN;
- injection time (depending on the size of the mold) – 32 min;
- cooling time – 4 min.

Below are the finished products made, the ones most frequently requested by beneficiaries and processed in the microproduction section.



Plate from PVC mixed with 10% ground EVA of 0.35 mm granulation



Soles from PVC mixed with 10% ground EVA of 0.35 mm granulation



Plate and soles from PVC mixed with 10% ground EVA of 0.35 mm granulation

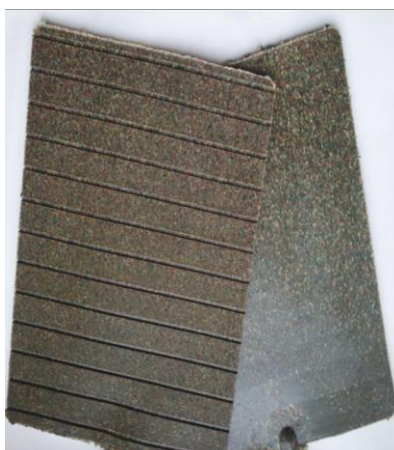


Plate from PVC mixed with 10% ground EVA of 0.5 mm granulation



Soles from PVC mixed with 10% ground EVA of 0.5 mm granulation



Plate and soles from PVC mixed with 10% ground EVA of 0.5 mm granulation

Figure 4. Finished products processed in the microproduction section

## CONCLUSIONS

The composites experimented in this work based on post-consumer PVC waste (transparent PVC medical products) and EVA waste functionalized with PDMS compounded with a compatibilizing agent – PE-g-MA processed on a twin-screw granulator extruder have values of physical-mechanical properties that fall within the product standards specific to PVC-based shoe soles. The materials experimented respect the principles of the circular economy, by using recycled materials in the composition, PVC and EVA waste, and they can be reused up to five times without their properties changing.

Thus, the WPVC/WEVA biocomposite has a great potential for use in the shoe industry as shoe soles, boots and sandal strips. Production of new recycled footwear components (e.g., soles) based on medical wastes PVC and EVA wastes will definitely contribute to lower environmental footprint and sustainable development in this industrial sector.

## Acknowledgements

This paper is funded by the PN 19 17 01 03/2019 project: “Biodegradable composites from technological and post-consumption polymeric wastes by designing and applying 4R eco-innovative technologies (4R-ECO-MAT)”.

## REFERENCES

1. Staicu Dimonie, D., Science of Organic and Composite Materials, Chapter 2.2 Recycling Polymer Materials (in Romanian), Technical Press, **1989**, 34-52.
2. de Almeida Lucas, A., Ambrósio, J.D., Bonse, B.C., Prado Bettini, S.H., Natural Fiber Polymer Composites Technology Applied to the Recovery and Protection of Tropical Forests Allied to the Recycling of Industrial and Urban Residues, in: P. Tesinova (ed.), Advances in Composite Materials – Analysis of Natural and Man-Made Materials, **2011**, 163-194, <https://doi.org/10.5772/19141>.
3. Pickering, K.L., Efendy, M.G.A., Le, T.M., A Review of Recent Developments in Natural Fibre Composites and Their Mechanical Performance, *Compos Part A Appl Sci Manuf*, **2016**, 83, 98-112, <https://doi.org/10.1016/j.compositesa.2015.08.038>.
4. Muthuraj, R., Misra, M., Defersha, F., Mohanty, A.K., Influence of Processing Parameters on the Impact Strength of Biocomposites: A Statistical Approach, *Compos Part A Appl Sci Manuf*, **2016**, 83, 120-129, <https://doi.org/10.1016/j.compositesa.2015.09.003>.
5. Shimazaki, Y., Nozu, S., Inoue, T., Shock-absorption Properties of Functionally Graded EVA Laminates for Footwear Design, *Polym Test*, **2016**, 54, 98–103, <https://doi.org/10.1016/j.polymertesting.2016.04.024>.
6. Nautiyal, O.H., Molding of EVA Soles Using Expanding and Reducing Agents, *Int J Eng Sci Technol*, **2012**, 4, 7, 3050–3058.
7. Groover, M.P., Fundamentals of Modern Manufacturing, Part II Engineering Materials, 4th ed., John Wiley & Sons Inc., **2010**.
8. Garcia-Morales, M., Partal, P., Navarro, F.J., Martinez-Boza, F., Gallegos, C., Gonzalez, N., Gonzalez, O., Munoz, M.E., Viscous Properties and Microstructure of Recycled EVA Modified Bitumen, *Fuel*, **2004**, 83, 31–38, [https://doi.org/10.1016/S0016-2361\(03\)00217-5](https://doi.org/10.1016/S0016-2361(03)00217-5).
9. Santos, J., Cerezo, V., Soudani, K., Bressi, S., A Comparative Life Cycle Assessment of Hot Mixes Asphalt Containing Bituminous Binder Modified with waste and Virgin Polymers, *Procedia CIRP*, **2018**, 69, 194–199, <https://doi.org/10.1016/j.procir.2017.11.046>.
10. Paiva Junior, C.Z., Peruchi, R.S., de Carvalho Fim, F., de Oliveira Silva Soares, W., da Silva, L.B., Performance of Ethylene Vinyl Acetate Waste (EVA-w) when Incorporated into Expanded EVA Foam for Footwear, *J Clean Prod*, **2021**, 317, 128352, <https://doi.org/10.1016/j.jclepro.2021.128352>.

11. The World Footwear **2021** Yearbook, available at <https://www.worldfootwear.com/yearbook/the-world-footwear-2021-Yearbook/226.html>, accessed 5 Jul 2022.
12. Muthu, S.S., Li, Y., Chapter 12 – The Environmental Impact of Footwear and Footwear Materials, in *Handbook of Footwear Design and Manufacture*, 2nd edition, **2021**, 305, <https://doi.org/10.1016/B978-0-12-821606-4.00015-6>.
13. Lopes, D., Ferreira, M.J., Russo, R., Dias, J.M., Natural and Synthetic Rubber/Waste - Ethylene-Vinyl Acetate Composites for Sustainable Application in the Footwear Industry, *J Clean Prod*, **2015**, 92, 230–236, <https://doi.org/10.1016/j.jclepro.2014.12.063>.
14. Queiroz, A.U.B., Collares-Queiroz, F.P., Innovation and Industrial Trends in Bioplastics, *Polym Rev*, **2009**, 49, 65, <https://doi.org/10.1080/15583720902834759>.
15. Xu, Y., Wu, Q., Lei, Y., Yao, F., Zhang, Q., Natural Fiber Reinforced Poly(Vinyl Chloride) Composites: Effect of Fiber Type and Impact Modifier, *J Polym Environ*, 2008, 16, 250–7, <https://doi.org/10.1007/s10924-008-0113-8>.
16. Abdellah-Ali, S.F., Mervette, E.B., Abdelhamed, M., El-Rafey, E., Formulation and Characterization of New Ternary Stable Composites: Polyvinyl Chloride-Wood Flour-Calcium Carbonate of Promising Physicochemical Properties, *J Mater Res Technol*, **2020**, 9, 12840–12854, <https://doi.org/10.1016/j.jmrt.2020.08.113>.
17. Titow, M.V., *PVC Technology*, Springer Science & Business Media, **2012**.
18. Ali, S.F.A., Althobaiti, I.O., El-Rafey, E., Gad, E.S., Wooden Polymer Composites of Poly(vinyl chloride), Olive Pits Flour, and Precipitated Bio-Calcium Carbonate, *ACS Omega*, **2021**, 6, 23924–23933, <https://doi.org/10.1021/acsomega.1c02932>.
19. Jariwala, H., Jain, P., A Review on Mechanical Behavior of Natural Fiber Reinforced Polymer Composites and its Applications, *J Reinf Plast Compos*, **2019**, 38, 441–53, <https://doi.org/10.1177/0731684419828524>.
20. Joshi, P.S., Marathe, D.S., Mechanical Properties of Highly Filled PVC/Wood-Flour Composites, *J Reinf Plast Compos*, **2010**, 29, 2522–33, <https://doi.org/10.1177/0731684409353815>.

© 2023 by the author(s). Published by INCDTP-ICPI, Bucharest, RO. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).

## EUROPEAN RESEARCH AREA

### COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council will issue a monthly **COTANCE Newsletter** with the purpose of **promoting an improved image of leather** to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at <https://www.euroleather.com/index.php/newsletter>, and were also published in the 2019-2022 issues of *Leather and Footwear Journal*. Newsletter 1 of 2023 is given below.



NEWS 1/2023

### *Leather and Alternatives*

Our German member Verband der Deutschen Lederindustrie e.V. (VDL) has been added to the list of qualified trade associations under the German Unfair Competition Act (Gesetz gegen den unlauteren Wettbewerb) and is now authorised to issue legal warnings to companies using the word leather in a misleading way in their advertising. In COTANCE, we care about transparency, and we fight against unfair claims. We are not doing this to make money or gain notoriety, but simply because our affiliated companies are harmed when others misuse the term leather. Let us be clear, we are not against leather alternatives – but **we are against consumer deception**. That is why it is sometimes worthwhile for us to take note of what others are doing.



A former Adidas marketing executive, Eric Liedtke gives us food for thought in "Microplastics are becoming an omnipresent killing machine", an interview published in "Brand Eins" (issue 2/23).



For starters, he doesn't like the term **sustainability**, arguing that it needs to be explained and only makes sense if companies outline exactly which measures they are taking and which they are not. We can only agree.



Liedtke describes **PET (polyethylene terephthalate)** as an eternal material that never completely disappears. It eventually decomposes into microplastics and enters our food chain, our bloodstream and our lungs via soil, air and water. He therefore calls microplastics *an omnipresent killing machine* and can imagine that in the future recycled plastic will no longer be considered sustainable. Here, too, we can only agree.

Therefore he advises a shift to **plant and mineral materials**, which at the end of their use do not turn into waste, but return to the earth. Here, we would like to add **animal-based materials**.



Liedtke also estimates that as a consumer you need a doctorate if you want to find your way through **sustainability smokescreens** such as *compostable, regenerative or recycled*. Many buyers of jerseys made from recycled PET would be surprised to learn that they pump more microplastics into the environment with the recycled jersey than with a jersey made from new PET fibres. Also, here we can only agree. Advertising is advertising and rarely serious science.

While Liedtke attests that customers are interested in environmentally friendly products, he notes that **recycled plastic is still plastic**. Indeed, there are no simple solutions.

His brief description of **marketing** is also interesting: "How do you make an object of desire out of a random product that ultimately nobody needs? Through good storytelling". Often, leather is misrepresented to tell stories about other materials and it is here that COTANCE and its members step in to make sure that truth about leather is understood.

An insightful article that evidences that there are **many ways to make the world a better place**. None is easy or perfect, but some are deceptive and using incorrect means. And even though Liedtke did not mention leather in the interview, **leather, as a natural material, used since the eve of time, is one of these ways!**





edited by



in collaboration with



### News Release from the IULTCS

28 February 2023

### Winners of three 2023 IULTCS Young Leather Scientist Grants for research announced

The Executive Committee of the IULTCS is pleased to announce the winners of the 2023 IULTCS Research Commission (IUR) Young Leather Scientist Grants. The research grants are awarded to three young scientists, under the age of 35. The monetary awards help support the work of young talent in the leather sector.

This is the ninth year of the grants which have been generously supported by industry. The Selection Committee of IUR, chaired by Professor Dr Michael Meyer, is pleased to announce the following recipients:

#### Tyson Foods: Young Leather Scientist Grant 2023 Basic Research

Tyson Foods has provided the sponsorship of a €1,500 grant for Basic Research to Dr Ilaria Quaratesi from the Leather and Footwear Research Institute (ICPI), Bucharest, Romania. The title of the project is 'Non-toxic and biodegradable supramolecular additive with flame retardant and antimicrobial properties for the tanning industry'.

The project's main objective is to develop an antimicrobial flame retardant, which can as well be used in the leather industry basing on hydroxyl apatite and cyclodextrines using an ultrasound assisted continuous flow process. Flame retardancy and antimicrobial activity will be tested according to standardised procedures.



Dr Ilaria Quaratesi

### **Erretre: Young Leather Scientist Grant 2023 Machinery / Equipment**

Erretre has provided the sponsorship of a €1,000 grant for Machinery / Equipment research to PhD candidate Vasanth Swaminathan from SRM Institute of Science and Technology, Chennai, India. The title of the project is 'Reduction of carbonization and gas emissions using mechanotronics based intelligent laser beam machining, with machine learning, for cutting leather with better environmental measures for operator health'.

The project's main objective is to optimise leather cutting by variation of the distance and pulse width of a laser diode assisted machining. Effects on different parameters as carbonization, rate of material removal, kerf width and emission rate will be investigated, and carbonization will be followed by using image processing.

### **Dr Mike Redwood: Young Leather Scientist Grant 2023 Sustainability / Environmental Award**

Leather Naturally has provided the sponsorship of a €1,000 grant for Sustainability / Environment research to Dr Yue Yu from Sichuan University, Chengdu, China. The title of the project is 'Controllable oxidation and degradation of lignin via H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> from biomass into a retanning agent for sustainable leather manufacturing'.

The project's main objective is to develop a light-coloured, lignin-based retanning agent which can be used as a green substitute for aromatic syntans using H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> synergistic oxidation technology. The oxidation mechanism has to be investigated, followed by research about the interaction mechanism between oxidized lignin and Cr-tanned leather. Finally a new retanning process is to be developed and its environmental impact will be evaluated.

The grants have been very successful and well received by industry. Referring to the awardees of the 2023 grants Dr Meyer said "All three project proposals show technological knowledge at a very high level and demonstrate the competitiveness of the leather industry with other industries worldwide. We are very happy that the profile of the Young Leather Scientist Grants continues to grow and thank our sponsors for the support that they continue to give. It will enable our young scientists to contribute their scientific knowledge, to the benefit of the leather community. We look forward to seeing the research outcomes of the projects we are supporting and wish them every success as they contribute to expanding our industry knowledge."

## NATIONAL AND INTERNATIONAL EVENTS

### 11<sup>th</sup> FREIBERG LEATHER DAYS 28-29 JUNE 2023, FREIBERG, GERMANY

On **28 and 29 June 2023**, the **11<sup>th</sup> Freiberg Leather Days** will take place finally back in **Freiberg/Germany**. We welcome you to the conference hall “Nikolaikirche”. Look forward to the keynote speech by Professor Wilhelm Windisch from the Technical University of Munich on the topic: “Can we still afford livestock?”

This year, after the first day's lecture programme, you will have the opportunity to take part in an iPad rally (also formerly also called a scavenger hunt) of the CityHunters® through Freiberg. Here you will form a team with other participants and try to solve the quests. Afterwards, the VGCT invites you to the common dinner at the Freiberg Brauhof.

First speakers from various fields have already committed to submit their presentation. If you would like to present **new ideas, findings or applications in the field of tanning and leather technology** or in related industries, we look forward to receiving your submission **by March 28<sup>th</sup>, 2023**.

More information: <https://www.freibergleatherdays.com/>

### 12<sup>th</sup> EDITION OF THE INTERNATIONAL CONFERENCE “AGRICULTURE FOR LIFE, LIFE FOR AGRICULTURE” 8-10 JUNE 2023, BUCHAREST, ROMANIA



#### The Rector's Foreword

Welcome to the Twelfth Edition of the International Conference “Agriculture for Life, Life for Agriculture”, organized by the University of Agronomic Sciences and Veterinary Medicine of Bucharest between **8th and 10th June 2023**.

As the first agricultural school established in 1852, our university has responded to the exigencies of professional training for the development of Romanian agriculture, despite times of hardship. Last year's conference stands proof that our university remains a standard of certainty in a world full of unknown. Unlike most events from the previous year, that have been either postponed or canceled altogether, “Agriculture for Life, Life for Agriculture” was moved into the online environment. With a one of kind platform and discussion space, authors have been given the possibility to present their articles and also network during the two conference days. Moreover, both the articles and plenary sessions are still accessible to everyone with a registered account, free of charge on the 2023 A4LIFE Conference Website. The articles published after the conference are also available, free of charge, here: <https://agricultureforlife.usamv.ro/index.php/publications>.

Facing the current challenges of society and primarily dedicated to the life sciences, University of Agronomic Sciences and Veterinary Medicine of Bucharest is oriented towards the integrated approach to the economic, social and environmental realities. True to its mission, our university aims to gather together researchers, students and professionals from agriculture and industry every year, in order to share the results of their scientific research, innovative ideas and practical experience related to agriculture, life and the environment. The 2023 Edition of our Conference shows the level of innovation embedded in our approach towards education and research.

We believe that agriculture is life, science and art and hope that the international community of researchers concerned with life sciences will find in our conference the opportunity to identify solutions that can contribute to the sustainable development of our planet. Furthermore, we hope you award us your confidence once again and trust that we can deliver an unforgettable academic event.

We invite you to celebrate together the joy of this event!

On behalf of the organizing committee,  
Sorin-Mihai CÎMPEANU  
Rector of USAMV of Bucharest

More information: <https://agricultureforlife.usamv.ro/index.php>

**18<sup>th</sup> INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT  
TOWARDS A POLLUTION FREE SOCIETY  
11-15 JUNE 2023, VENICE, ITALY**



The Environmental Chemistry Division of the Società Chimica Italiana and the University Ca' Foscari of Venice will organize the 18th ICCE Conference 2023 in Venice (Italy), a biennial conference under the auspice of the Division of Chemistry and the Environment (DCE) of the European Chemical Society (EuChemS).

ICCE 2023 will address scientists in academia, industry, consultancies, and in governmental institutions alike, providing a unique and inspiring information and communication platform for environmental scientists and a forum of professional exchange with collaborators and colleagues.

Conference topics will include *analysis and modelling of environmental contaminants*, impacts of *climate change* on local to global circulation of chemicals, *nano-size* particulate materials and *microplastics* in the environment, *atmospheric pollution*, *environmental risk and impact assessment*, role of chemistry in the *circular economy*, *emerging contaminants*, *water pollution*, innovations in *water and wastewater treatment*, *biotransformation* of organic pollutants, *green chemistry*, *ecotoxicology*, *LCA*, *environmental sustainability*, environmental impacts on *cultural heritage*, *university education* in environmental chemistry, and many other important topics.

More information: <https://icce2023.com/>

**10<sup>th</sup> INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT - CHANIA 2023  
21-24 JUNE 2023, CHANIA, GREECE**

The Conference aims to address the significant issue of sustainable solid waste management through the promotion of safe practices & effective technologies. The Conference focuses mainly on modern solid waste technologies. It aims to stimulate the interest of scientists and citizens and inform them about the latest developments in the field of municipal solid waste management. Separation at source, Biological Treatment, the treatment at central facilities, waste prevention, biowaste utilization, recycling promotion, Waste-to-energy technologies & energy recovery, smart technologies for waste management, sludge management, agricultural and livestock waste, management of specific waste streams (construction & demolition waste, waste from electrical and electronic equipment, etc.), biotechnology, Best Available techniques, symbiosis networks, energy consumption and saving, carbon footprint and water footprint, zero-waste initiatives, plastics and bioplastics, marine litter constitute main conference subjects. Special attention will be drawn to the valorization prospects & the products from solid waste, such as: biofuels, compost, materials, etc.

It is also our ambition to strengthen the link of the applied research with industry. Hazardous waste & Household hazardous waste also constitute target area of the conference. Emphasis will be placed on circular economy in all key action areas (production, consumption, waste management, secondary raw materials, innovation, investment & monitoring) and all priority sectors (food waste, plastics, biomass and bio-based-products, construction & demolition waste, critical raw materials), as well as waste management issues and resource efficiency in islands and generally isolated and remote areas.

The Conference will provide an opportunity to bring together scientists & professionals from government departments, industries, Municipalities, private institutions, research & education institutions, being a forum for the exchange of the most recent ideas, techniques & experiences in all areas of solid waste management. A special full one-day workshop will also focus on representatives of local authorities and municipalities in order to promote integrated solid waste management schemes.

**Call for Papers**

Authors are invited to submit an extended abstract of maximum 2 pages in English, including figures and tables (as MS Word file). The abstracts can be submitted electronically via the specific form no later than **28th February 2023**.

Abstracts will be accepted based on quality, originality and relevance to the conference themes. All accepted papers will be published as the conference proceedings (in electronic form), while the high quality papers after evaluation will be published in collaborating scientific journals. We look forward to receiving your paper and we hope to see you actively taking part in the CHANIA 2023 Conference.

**Paper Submissions**

After the end of the review process of the abstracts, the authors of the papers accepted for oral and poster presentation are asked to submit a full paper with maximum length of 12 pages. Please send the full paper by email to [konmoust@central.ntua.gr](mailto:konmoust@central.ntua.gr) until **30th April 2023** at the latest.

*More information: <https://chania2023.uest.gr/>*





## INSTRUCTIONS FOR AUTHORS

### Publication Ethics and Malpractice Statement

*Revista de Pielărie Încălțăminte* publishes peer-reviewed articles. It is necessary to agree upon. The Publication Ethics and Malpractice Statement for *Revista de Pielărie Încălțăminte*, based on COPE's Best Practice Guidelines for Journal Editors, clearly outlines standards of expected ethical behavior for all parties involved in the act of publishing (the author, the journal editor(s), the peer reviewer and the publisher) and is available on the journal's website, <http://www.revistapielarieincaltaminte.ro>.

### Open Access Statement

*Revista de Pielărie Încălțăminte* is a peer reviewed, open access journal. All articles published open access will be immediately and permanently free for everyone to read, download, copy and distribute, under the provisions of a Creative Commons Attribution (CC BY) which lets others distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), include in a collective work (such as an anthology), text or data mine the article, even for commercial purposes, as long as they credit the author(s), do not represent the author as endorsing their adaptation of the article, and do not modify the article in such a way as to damage the author's honor or reputation.

### Open Access Publication Fee

*Revista de Pielărie Încălțăminte* requires article processing charges of 200 EURO per article, for accepted manuscripts, payable by the author to cover the costs associated with publication. There are no submission charges.

### Author Rights

The copyright for all articles published in *Revista de Pielărie Încălțăminte* shall remain the property of the author(s). The copyright on the layout and final design of the articles published in *Revista de Pielărie Încălțăminte* belongs to INCDTP – Division: Leather and Footwear Research Institute and cannot be used in other publications.

### Presentation of Papers

The scientific papers should be presented for publishing in English only. The text of the article should be clear and precise, as short as possible to make it understandable. As a rule, the paper should not exceed fifteen pages, including figures, drawings and tables. The paper should be divided into heads and chapters in a logical sequence. Manuscripts must meet high scientific and technical standards. All manuscripts must be typewritten using MS Office facilities, single spaced on white A4 standard paper (210 x 297 mm) in 11-point Times New Roman (TNR) font.

### Paper Format

**Title.** Title (Centered, 12 pt. TNR font) should be short and informative. It should describe the contents fully but concisely without the use of abbreviations.

**Authors.** The complete, unabbreviated names should be given (Centered, 10 pt. TNR font), along with the affiliation (institution), city, country and email address (Centered, 9 pt. TNR font). The author to whom the correspondence should be addressed should be indicated, as well as email and full postal address.

**Abstract:** A short abstract in a single paragraph of no more than 200-250 words must accompany each manuscript (8 pt. TNR font). The abstract should briefly describe the content and results of the paper and should not contain any references.

**Keywords.** Authors should give 3-5 keywords.

### Text

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

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

**Results and Discussions.** This section may be separated into two parts. Unnecessary repetition should be avoided.

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

**Acknowledgements.** Should be as short as possible.

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

**Diagrams, Figures and Photographs** should be constructed so as to be easy to understand and should be named "Figures"; their titles should be given below the Figure itself. The figures should be placed immediately near (after or before) the reference that is being made to them in the text. Figures should be referred to by numbers, and not by the expressions "below" or "above". The number of figures should be kept to minimum (maximum 10 figures per paper).

**Tables.** Should be numbered consecutively throughout the paper. Their titles must be centered at the top of the tables (12 pt. TNR font). The tables text should be 9 pt. TNR font. Their dimensions should correspond to the format of the Journal page. Tables will hold only the horizontal lines defining the row heading and the final table line. The tables should be placed immediately near (after or before) the reference that is being made to them in the text. Tables should be referred to by numbers, and not by the expressions "below" or "above". The measure units (expressed in International Measuring Systems) must be explicitly presented.

**Formulas, Equations and Chemical Reactions** should be numbered by Arabic numbers in round brackets, in order of appearance, and should be centered. The literal part of formulas should be in Italics. Formulas should be referred to by Arabic numbers in round brackets.

**Nomenclature.** Should be adequate and consistent throughout the paper, should conform as much as possible to the rules for Chemistry nomenclature. It is preferable to use the name of the substances instead of the chemical formulas in the text.

**References** should be numbered consecutively throughout the paper in order of citation in square brackets; the references should list recent literature also. Footnotes are not allowed. If the cited literature is in other language than English, the English translation of the title should be provided, followed by the original language in round brackets. Example: Handbook of Chemical Engineer (in Romanian), vol. 2, Technical Press, Bucharest, 1951, 87.

We strongly recommend that authors cite references using DOIs where possible. DOIs are persistent links to an object/entity and can be used to cite and link to any article existing online, even if full citation information is not yet available. DOIs should always be displayed as full links. Example: Onem, E., Cin, G., Alankus, A., Pehlivan, H., Mutlu, M.M., Utilization of Chestnut Shell Wastes as a Dyeing Agent for Leather Industry, *Revista de Pielărie Încălțăminte (Leather and Footwear Journal)*, **2016**, 16, 4, 257-264, <https://doi.org/10.24264/lfj.16.4.1>.

**Citation of Journal Articles:** all authors' names (surname, name initials), abbreviated journal title, year, volume number, issue number, full page reference, e.g.: Helissey, P., Giorgi-Renault, S., Renault, J., *Chem Pharm Bull*, **1989**, 37, 9, 2413-2425.

In case the reference is not cited in original, the author(s) should also list the original paper that has been consulted.

**Citation of Books:** authors' full name and name (initials), title of the book, issue number in Arabic numbers, publishing house, editors' names (if present), city where the book has been published, year of publication, the page(s) containing the text that has been cited.

**Citation of Patents:** all authors' names (surname, name initials), or company's name, country and patent number, date of issuance.

Paper template is available for download on the journal's website, <http://www.revistapielarieincaltaminte.ro>.

### Manuscript Submission

By submitting your manuscript to be considered for publishing in *Revista de Pielărie Încălțăminte* you are giving consent to processing personal data for administration and publication purposes. Our Privacy Policy is available on the journal's website.

Manuscripts should be submitted in electronic format by email to the following address:

Dana Gurău, Editor-in-chief  
INCDTP - Leather and Footwear Research Institute (ICPI)  
93 Ion Minulescu St., code 030215, Bucharest, Romania  
Phone: +4021-323.50.60; Fax: +4021-323.52.80.  
E-mail: [jlfjournal@gmail.com](mailto:jlfjournal@gmail.com)



# INCDTP - SUCURSALA INSTITUTUL DE CERCETĂRI PIELĂRIE ÎNCĂLȚĂMINTE

