See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/350521863

A Review of Natural Plants as Sources of Substances for Cleaner Leather Tanning Technologies

Article *in* Textile & Leather Review · September 2021 DOI: 10.31881/TLR.2021.03

CITATION: 3	ŝ	READS	
4 authors, including:			
1	Kallen Mulilo Nalyanya Egerton University 13 PUBLICATIONS SEE PROFILE		Ronald Rop University of Kabianga 23 PUBLICATIONS 243 CITATIONS SEE PROFILE
	Zephania Birech University of Nairobi 36 PUBLICATIONS 171 CITATIONS SEE PROFILE		
Some of the authors of this publication are also working on these related projects:			

 Project
 Leather quality View project

 Project
 development of novel point of care diagnostics for T2DM and T1DM View project



Textile & Leather Review

ISSN: 2623-6257 (Print) 2623-6281 (Online) Journal homepage: <u>www.textile-leather.com</u> Journal doi: <u>10.31881/TLR</u>

A Review of Natural Plants as Sources of Substances for Cleaner Leather Tanning Technologies

Kallen Mulilo Nalyanya, Ronald K. Rop, Arthur S. Onyuka, Zephania Birech

How to cite: Nalyanya KM, Rop RK, Onyuka AS, Birech Z. A Review of Natural Plants as Sources of Substances for Cleaner Leather Tanning Technologies. Textile & Leather Review. 2021. <u>https://doi.org/10.31881/TLR.2021.03</u>

How to link: https://doi.org/10.31881/TLR.2021.03

Published: 31 March 2021

This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License



A Review of Natural Plants as Sources of Substances for Cleaner Leather Tanning Technologies

Kallen Mulilo NALYANYA^{1*}, Ronald K. ROP², Arthur S. ONYUKA³, Zephania BIRECH⁴

¹Department of Physics, Faculty of Science, Egerton University ²Department of Mathematics, Actuarial and Physical Science, School of science, University of Kabianga ³Kenya Industrial Research and Development Institute, Nairobi ⁴Department of Physics, College of Biological and Physical Sciences, University of Nairobi *kallenmulilo@ymail.com

Review

UDC 675.024.3 DOI: 10.31881/TLR.2021.03

Received 30 January 2021; Accepted 23 March 2021; Published Online 31 March 2021

ABSTRACT

The stringent environmental regulations and compliance regarding leather tanning has compelled leather industry to seek alternative cleaner ingredients that have the capacity to minimize or prevent pollution caused by hazardous chemicals. Practical measures have so far involved replacing the current use of synthetic chemicals such as chromium salts, dyes, fatliquors and surfactants or minimizing their usage by incorporating agro-based organic components. Numerous papers have documented the use of different plant extracts at different stages of leather processing such as tanning, retanning, dyeing and fatliquoring. This present article details the specific plants and the leather processing stage at which they are applied and eventually the quality of the resulting leather. This article attempts to compile a considerable number of investigations published on physical properties of leather that is processed using natural plants. It has been shown that there are striking similarities in leather properties of leather processed using natural plants, stages of application and the corresponding physical properties which could provide a crucial assistance to research focusing on environmental protection and physical properties of leather which would in turn improve the quality of the resulting leather.

KEYWORDS

Vegetable tanning, Leather, Hazardous, Environment

INTRODUCTION

Leather industry, which thrives on a by-product of the meat industry, plays a critical role in the global economy and especially in the developing countries, by contributing towards the Gross Domestic Product (GDP), as a source of livelihoods, offering employment opportunities and supporting other downstream industries [1,2]. The potential of this industry is immense, owing to the demand for meat and leather products by the increasing world population. However, environmental concerns and the inferior quality of leather threaten the industry's ability to penetrate the turbulent high market and comply with tough environmental regulations [2,3]. The last two decades have witnessed a growing consumer awareness leading towards the demand for quality leather products that meet the performance and durability criterion, in accordance with the occupational and safety footwear EC mark (Dir.89/686/EEC). Conversely, the growing aware-

ness among consumers towards human and environmental health crusaded by legislative policies such as UNEP and USEPA have compelled the industry to comply with the stringent environmental regulations [4]. Therefore, the appropriate strategy by the industry should be geared towards producing quality leather using environmental-friendly and cleaner manufacturing technologies to secure prospective markets for a viable and sustainable industry [5].

For leather products, the performance requirement is measured in terms of the functional property and the aesthetic values that the product should possess [6,7]. These include the physical (mechanical), hydrothermal and chemical stability, fastness, and organoleptic (tactile or sensorial character) properties of the resulting leather [7-9]. These properties are easily achievable by using the chromium tanning agent which, among the tanning technologies, is the most outstanding due to its superior performance characteristics it confers to leather [10,11]. Nevertheless, chromium is a limited natural resource, which when subjected to accelerated ageing conditions, oxidizes to form toxic and carcinogenic species that have an adverse impact on the environment and human health [12]. Consequently, much research has delved into cleaner tanning systems that are more eco-friendly and less hazardous to both the environment and human health [10, 12-14]. Many of the adopted technologies involve the use of eco-benign natural plant products either synergistically or using singular essence extracts [15-23]. Natural plant tannins contain polyphenols that can be categorized into hydrolysable or condensable tannins [13]. Hydrolysable phenols consist of glucose polyesters that have either gallic or ellagic tannins. On the other hand, condensable phenols consist of catechin monomers, also known as flavonoids [24]. The introduction of plant products into leather processing potentially contributes to the filling action of the leather structure, which alters the strength properties and uniformity of the properties. The interaction between the plant polyphenols and collagen molecules results with bond formation or crosslinking that resultantly modifies the quality of leather by affecting the physical and organoleptic properties of the final leather product [25,26]. The modification depends on the number of galloyl groups and the molecular size. The intergalloyl C-C bonds restrict the flexibility of the galloyl groups, thus hindering the collagen-polyphenol hydrophobic interactions hence affecting structural and physical properties [25]. Beside the phenolic antioxidants, which inhibit the oxidation of some tanning agents, the plant products have the potential to replace the synthetic tanning agents. In this present article, the authors have compiled research on some of the cleaner tanning systems that have used plant products and the corresponding quality impact on the final leather product. The aim is to further the previous work on the use of plant-based products to mitigate environmental challenges faced by the leather industry [12].

QUALITY PARAMETERS OF LEATHER

Strength properties

The strength properties of the manufactured leather determine the functionality of the final product, the routine quality and the serviceability assessment of the material [3,27,28]. Therefore, these properties form essential index of assessing the utility of the final leather product for various applications [29]. The strength properties include flex resistance, tear strength, elongation at break, tensile strength and colour fastness [27].

Tensile strength

This is the maximum tensile stress leather can withstand without plastic deformation or breaking/rupturing the leather [30]. It is given in terms of force per unit area of cross section while applying force in linear direction. It determines the structural resistance of leather, and beyond it the material goes from being elastic to

being plastically deformed [3]. Since the strength of the leather is determined by the fibrous structure and any modification of the structure, then any bond formation that occurs in the leather matrix affects these properties [10,11]. The acceptable standard minimum of tensile strength for upper leather, lining, furniture and goods is 15, 15, 10 and 10 N/mm², respectively [31].

Percentage elongation

Elongation refers to the ability of leather to lengthen/stretch under tensile force without breaking (elasticity) [3]. Leather considered for garment should possess appropriate elongation since low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even become unusable [7]. Upper leather and footwear upper should possess high flexibility to prevent the appearance of cracks and tears in the ball area [32,33]. High elasticity allows the material to withstand the elongation stresses to which it is subjected during footwear lasting, especially on the toe area [34]. The recommended minimum percentage of elongation for quality chrome-tanned leather is 40-80% [31,35,36].

Tear strength

Tear strength is the measure of the resistance of a material to tear forces, calculated by the maximum force or average of the peak forces in Newtons per unit of thickness of the material in mm [37]. Tear strength in bovine hide is dependent on the interweaving angle and crosslinking of the fibre bundles [28]. The recommended minimum value for tear strength of chrome-tanned shoe upper side leather is 40 N/mm.

Grain burst (mm)

This parameter verifies if the grain layer of the leather breaks upon being folded. It indicates a level of elasticity derived from the specific processing step and determines the durability of leathers for footwear uppers as per ISO 3379:2015. The minimum grain burst requirement for the manufacture of footwear is 7 mm.

Flexural resistance and endurance

Bally flex or pliability is an indication of the finishing resistance to crack and crease when repeatedly flexed, emulating the flexing of the actual use of the shoe. Flex is an inevitable encounter for majority of leather applications such as footwear at the vamp, toe and heel bends, hence a prerequisite property for any leather meant for footwear upper to endure a predetermined number of flexes to gain qualification. The flexing endurance of leather measures the ability of leather and leather-cloth to withstand repeated flexing without cracking. The ISO 5402:2003 test method embarked the performance requirement for the ball flex/linear flex to be no significant damage at 150K cycle at dry stage [35].

Ball burst (distension and load crack)

Shoe upper leather often shows slight crack in the toe area at the time of lasting operation despite the leather having good tensile and tear strength properties. The stipulated distension and the load at break/ burst are 7 mm and 20 N, respectively.

Shrinkage temperature

This is a parameter used to characterize the thermal stability of leather. It is the temperature at which the leather starts to shrink in water or over a heating media [29]. It determines the degree of crosslinking in leather by the tanning agents, since the higher the degree of crosslinking, the higher the shrinkage temperature. The threshold of the shrinkage for a quality leather is 75 °C. Due to this, the shrinkage temperature remains an important index, which reflects the quantity of new bonds formed in collagen and the quality of tanning and tanned leather. Usually, the users of leather, as raw material for shoes, garment or other, require the shrinkage temperature of leather to be not less than 100 °C [29,38].

Organoleptic properties

These properties are also known as tactile and visual evaluation properties or sensory properties or bulk properties [39,40]. These properties include surface colour, texture like softness and roughness, structure fullness or compactness, grain tightness, smoothness, dye uniformity and general appearance [39].

NATURAL PLANT PRODUCTS IN LEATHER TANNING TECHNOLOGIES

Tanning processes involving vegetable tannins, organic compounds and chromium salts

Sirvaityte et al. investigated the possibility of using essential oils from *Thymus vulgaris* (thyme) as a natural alternative preservative in leather tanning technology [41]. The essential oil of thyme was the more active component in the mixture of essential oil and the synthetic biocide used for the preservation of chromed leather. The shrinkage temperature of the leather treated with essential oils was 113 °C. The tensile strength and elongation at break were 16.7 N/mm² and 66.5 %, respectively.

Musa et al. investigated the possibility of using Lawsonia inermis (henna) leaves as a retanning agent for the wet blue leather and the physical properties of the resulting leather were compared with those of the leather retanned using wattle [42]. Henna-retanned leather recorded good tightness and their dyeing characteristics were better in comparison to the wattle-retanned leather. The shrinkage temperature of the wet blue leather was 109 °C while that of the henna-retanned and the wattle-retanned leather was 121 °ºC and 123 °^oC, respectively. The organoleptic properties of the henna crust leather, such as fullness, grain tightness, roundness, grain smoothness, softness and general appearance, were superior to those of the wattleretanned crusted leather. The tensile strength, elongation, tear strength, load at grain crack and distension at grain of the experimental leathers were 25.23 N/mm², 60.15 %, 39.93 N/mm, 24 kg and 10.64 mm, respectively, while those for control leathers were 25.09 N/mm², 64.58 %, 42.37 N/mm, 26 kg and 11.6 mm, respectively. In this case, the strength values of the leather retanned with henna met the standards stipulated by UNIDO [31]. The study also alluded to the possibility of using henna leaves as mordanting agents. Apart from the use of tannic acid as an explicit tanning agent, Colak et al. investigated the antioxidant effects of tannic acid on the formation of formaldehyde and Cr (VI) in leathers [43]. The wet blue sheepskins were treated with tannic acid of concentrations of 0.1, 0.5, 1, 2, and 3% during the retanning process. It was observed that increasing tannic acid concentration significantly improved the physical properties of the resulting leathers. The tensile strength, percentage elongation, tear load and shrinkage temperature at 3 wt. % tannic acids were 17.8 N/mm², 49.5%, 35.9 N/cm, and 130.8 °C, respectively.

Bitlisli et al. determined the physical properties of the split suede leather treated with *Aloe barbadensis miller L. (Aloe vera*) and chromium [44]. When compared with the physical properties of leather tanned

with chromium only, the tear strength of the leather treated with *Aloe vera* 6% wt. weas comparatively higher. The *Aloe vera* concentrations improved the moisture content and the softness of the final leather. Affiang et al. developed a fatliquoring system by using seed oil extracted from the *Aradirachta indica* (neem) [45]. They sulphated the extracts by using sulphuric acid followed by the addition of sodium hydroxide in order to maintain the pH at 5.0. The physical properties of the chromed goatskins processed by this fatliquoring system were compared with those processed by using the imported palm oil fatliquor. The tensile strength, elongation at break and tear resistance of experimental leathers were 14.15 N/mm², 49.0 % and 61.01 N, respectively, while those of the control leathers were 19.03 N/mm², 56% and 67 N, respectively. The organoleptic properties for the experimental leathers were comparable to the control leathers and the difference was insignificant.

Sivakumar et al. used castor oil as a vegetable-based fatliquor and fatliquored the chromed leather [46]. The results indicated that the strength properties of the leather fatliquored by these oils were comparable to those of the leather fatliquored by using other imported fatliquors. The strength properties of the leathers were above the quality standards for tensile strength as per UNIDO [31]. Quadery et al. extracted fatliquor oils from *Pongamia pinnata L.* (Karanja) seed oil by sulphation process followed by the addition of sodium hydroxide to maintain the pH at 5.0 with concentrated sulphuric acid [47]. The prepared fatliquor was applied for the processing of chrome-tanned goatskins. The physical properties of skins were compared with those of the skins fatliquored by fatliquor from castor oil. The tensile strength, elongation and tear resistance of the leather fatliquored with experimental oils were comparable with those fatliquored by using imported fatliquors.

Kusumawati et al. evaluated the effect of using different concentrations of *Indigofera tinctoria L*. (indigo), as a natural dye, to the quality of chrome-tanned milkfish skins [48]. The concentrations used were 20%, 25% and 30%. The results showed that different concentrations have significant effect (p < 0.05) on the rub resistance on wet and dry coating, fastness to perspiration, tensile strength and elongation at break of the resulting leather. The 25% concentration gave the best quality in terms of the physical properties and dyeing characteristics. The highest score for tensile strength was obtained when using 30% indigofera solution showing the score of 18.94 N/mm². This value was higher in comparison to the value of the synthetic dyeing system; a fact attributed to the significant content in indigofera.

Tanning processes involving vegetable tannins, organic compounds and other non-chromium inorganic materials

Haroun et al. investigated the interactions of *Acacia nilotica* spp. tomentosa pods (garad), used as a vegetable tanning agent, and aluminium sulphate, with collagens at pretannage and retannage stages [49]. In this tanning system, the authors evaluated two methodologies; the authors compared the vegetable pretannage followed by aluminium sulphate retannage with that of the reversed order, aluminium pretannage followed by vegetable retannage. Indeed, the former methodology resulted in superior leather with optimum results obtained when 10% and 2% of vegetable tannins and aluminium sulphate were used, respectively. The optimum concentrations of the garads improved the percentage elongation of the final leather to 60.5% and the shrinkage temperature, pretanned with different aluminium retanning, to 125 °C. This is probably due to the enhanced cross-links, stabilized complexes and new bond formation that eventually increased hydrothermal stability of the resulting leather. The tensile strength of leather using the former methodology similarly showed higher values compared to the latter methodology. This study unravels a chromefree tannage system that yields leathers of shrinkage temperature greater than 100 °C, elongation of 65.6 %, and tensile and tear strengths of 38 N/mm² and 98 N/cm, respectively. The study showed that a combination of vegetable tannage of garad followed by aluminium sulphate retannage effectively crosslinks collagens, resulting in good quality leather as evidenced by high strength properties and shrinkage temperatures. Musa and Gasmelseed developed a combination tanning system based on garad and aluminium [50]. Results showed that a combination system of 2% of Al_2O_3 followed by 20% of garad produces leathers of shrinkage temperature above 101 °C. Similarly, the physical properties were above the UNIDO-recommended minimum. The study attributed the excellent hydrothermal stability and physical properties to aluminium, which enhances amount of garad fixation as indicated by the increased garad exhaustion.

Musa et al. and Musa et al. extended the research area by evaluating the combination tanning process based on *Lawsonia inermis* (henna) leaf extract and tetrakis hydroxymethyl phosphonium sulphate (THPS) and aluminium sulphate, respectively, for production of upper leather [51,52]. In the evaluation of this regime, two methodologies involved varying the order in the combination; henna extracts (20%) followed by tetrakis hydroxymethyl phosphonium sulphate (1.5%) and tetrakis hydroxymethyl phosphonium sulphate followed by henna extracts. The second permutation resulted with superior leathers, both in strength and organoleptic properties and the shrinkage temperature of 96 °C. Also compared with the leathers tanned with henna alone (control), the shrinkage temperature dropped to 84 °C. From this study, generally leathers tanned with henna and THPS showed better fullness, dye uniformity, softness, smoothness and general appearance. Similarly, the strength properties of the experimental leathers were above the minimum required standards. More so, the use of THPS increased henna fixation and exhaustion, which may explain the increased shrinkage temperature observed.

Aravindhan et al. evaluated the Tara-THPS combination tannage system [53]. Pretannage with glutaraldehyde or THPS were employed in order to improve the tannin uptake/penetration. The resulting leathers recorded shrinkage temperature of 88 °C. The system was found versatile in tannage of both upper and garment leather since the strength and organoleptic properties were similar to those of the leather tanned with chromium. This combination is effective since it also has both scavenging effect of free formaldehyde and Cr (VI). The adjunct of THPS has additional importance. In the subsequent study by Plavan et al., the tanning process was based on using Tara and mimosa tannins with an aluminium adjunct as tanning agents [54]. Leathers tanned with Tara tannins have more stable properties than those not tanned with those tannins. The developed technology produced leathers with the shrinkage temperature of 98 °C, tensile strength of 18.2 N/mm², and elongation at break of 42%. The shrinkage temperature was enhanced up to 106 °C as a result of treating the pelt with THPS in the place of chromium before tanning with Tara-aluminium.

Tannic acid, as a precursor, has been used immensely in the leather tanning process as a green material. This is partly due to its low molecular weight compared to other vegetable tannins, which allows it to effectively penetrate the collagen fibres. Fathima et al. studied the tanning system combining tannic acid, aluminium and silica [55]. Apart from improving the hydrothermal stability, the presence of aluminium in the precursor of tannic forms an aluminium-tannic acid complex that gives the leather a pastel colour. The presence of silica in the system gives the leather softness and a fluffy feel. The shrinkage temperature was found to increase with sodium metasilicate and aluminium sulphate offers. It was shown that 5% of both sodium metasilicate and aluminium sulphate concentrations were optimum for better results. The strength and organoleptic properties were either comparable to or higher than those of the conventionally chrometanned leather. The optimum amount of tannic acid, aluminium sulfate and sodium metasilicate was found to be 10, 5, and 5 wt. %, respectively, which correspondingly yielded leathers with the shrinkage temperature of up to 95 °C. In a related study by Saravanabhavan et al., a combination tannage system based on tannic acid (10%), zinc (10%) and silica (5%) was used to tan garment leathers [13]. The physical strength and organoleptic properties of the leather from the experimental system were generally comparable to those of the leather tanned using chromium salts, while the shrinkage temperature was 85 °C. Later, Fathima et al. developed an organic tanning system using a vegetable tannin precursor of tannic acid and THPS as an alternative to the chrome tanning system [56]. There was no difference between the physical and organo-leptic properties of the experimental leather and the chrome-tanned leather. Furthermore, the shrinkage temperature of the experimental leather increased to as high as 88 °C.

Ding et al. used a combination of genipin and aluminium for the tanning process and evaluated the physical properties of the resulting leather against the aluminium-glutaraldehyde and mimosa-aluminium leathers prepared as controls [57]. In this system, bated pelts were pretanned with the 6%-aluminium and then tanned with the 6 wt. %-genipin. The shrinkage temperature of the leather produced by this technology was 89 °C (measured by DSC) and 92 °C when measured using traditional measurement. The physical-mechanical properties of the experimental leathers were similar to those of the leather used for the control in the experiment.

Ali et al. used extracts from *Faidherbia albida* (Haraz) combined with aluminium as an alternative tanning system for the production of upper leathers [29]. The system involved altering the order of application commutatively i.e., applying Haraz followed by aluminium and applying aluminium followed by Haraz with the concentrations of 20% of Haraz and 2% of Al_2O_3 by weight. The shrinkage temperature in the Haraz-Al methodology was 100 °C, and 98 °C in the Al-Haraz methodology. Similarly, Haraz-Al combination system resulted in leathers with better organoleptic and strength properties that satisfy the standard of quality leather.

Tanning processes that involved using vegetable tannins and other organic materials

Omur and Mutlu chemically modified the condensed tannins from mimosa and quebracho by applying sulphitation, sulpho methylation and novalac synthesis [58]. The aim was to enhance the colour fastness of mimosa- and quebracho-tanned leathers that usually change colour and darken upon exposure to light for a prolonged period. Leathers tanned with tannins from quebracho and sulpho-methylated mimosa exhibited improved colour fastness to light [10]. Incorporating UV stabilized groups into flavonoid structures of both quebracho and mimosa was done in order to inhibit bond rearrangements by oxidative free radical mechanism. The modification did not significantly alter the physical properties, which agreed closely with those tanned with standard tannins. The values of strength properties were within the recommended standard limits.

Tanning processes utilizing pure vegetable tannins

Later Musa and Gasmelseed studied the possibility of using the garad as a vegetable tanning agent for upper leather [59]. In the study, they compared the physical properties of the leathers tanned with garad with those tanned with chromium. The difference between the tensile strength, tear strength, elongation at break, load at grain and distension at grain crack were not significant (p<0.05). In the same study, the researchers extended the tanning system by combining garads and Oxazolidine tannage for production of garment leathers. Investigating different concentrations of garad powder and oxazolidine, a combination of 20% of garad powder and 4% of oxazolidine provided a shrinkage temperature of 102 °C. The system also produced leathers with good organoleptic properties and physical properties comparable to the chromium tanning system. Later, Ozkan and co-workers investigated the prowess of vegetable tannins of *Acacia nilotica L*. for tannage and determined a spectrum of the resulting physical characteristics [60]. The lasto-

meter tests were as follows: strength at grain crack - 30.5 N, grain distension at crack - 14.68 mm, strength at ball burst - 35.5 N, ball burst grain distension - 15.67 mm, tensile strength - 21.69 N/mm², percentage elongation - 86.66 %, and tear load - 70.06 N. In the subsequent study, Ali et al. combined 80% of Acacia nilotica pods (garads) and 20% of Azadirachta indica (neem) barks spray-dried powder mixture as a full vegetable tanning system to produce shoe upper leathers [61]. The parameters of the resulting leathers were as follows: tensile strength - 20 N/cm², tear strength - 4.4 N/cm, percentage elongation - 40.5%, grain distension - 8.9 mm and shrinkage temperature > 82 °C. The results showed that the garad-neem blend enhances the quality of the final leather to almost double the magnitude of the leather tanned by conventional pure Acacia nilotica pods (garads). The blend also improved the fullness and fellness, quality parameters recommended for good leather. The complementing effect arises from the fact that Acacia nilotica contains hydrolysable tannin while Azadirachta indica bark contains condensed tannin. A comparative study done by Kuria et al. assessed the physical properties of leathers tanned Acacia xanthophloea, Acacia nilotica, standard mimosa and Hagenia abyssinica plants [62]. Leathers tanned with Acacia xanthophloea recorded the highest shrinkage temperature of 85 °C, while that of the leathers tanned with commercial mimosa, Acacia nilotica and Hagenia abyssinica was 83 °C, 82.5 °C and 80 °C, respectively. However, the leather tanned with Acacia xanthophloea recorded the lowest tensile strength of 20 N/mm², while Hagenia abyssinica, commercial mimosa and Acacia nilotica had a tensile strength of 27.91 N/mm², 28.8 N/mm² and 29.22 N/mm², respectively. Hussein [63] extracted the tannins from Acacia seyal bark (Taleh), whose content was determined to be 28.9%, and used them for retanning the upper and garment materials. With this content of tannins, Taleh forms a potential source of tannins for both vegetable tanning and retanning. Furthermore, the resulting leather exhibited competitive quality in terms of strength properties. For instance, the range of tensile strength was 21.5-31 N/mm² and the percentage of elongation was 42-63.5%.

Nasr et al. investigated vegetable tanning systems that involved quebracho and mimosa plant extracts [64]. They then compared the physical properties of the resulting tanned leather with those of chrome-tanned leather. From the results, chrome-tanned leather had the highest tensile and tear strengths, elongation and water permeability followed by quebracho-tanned leathers and then mimosa-tanned leathers. The superiority of quebracho over mimosa could be explained by higher tannin content (35%) against 18% of tannin content in mimosa.

Huantian et al. used the 20%-quebracho solution as a vegetable tannin for the tanning process and leathers recorded a shrinkage temperature of 78.4 °C [65]. When the quebracho tanning was followed by post-treatment with transglutaminases (enzymes), the shrinkage temperature slightly improved by 2 °C. When quebracho was combined with transglutaminase and laccase (another enzyme) in a one-step treatment, the shrinkage temperature increased to 84 °C. Conclusively, enzymes assisted in the collagen crosslinking and the phenol oxidizing hinders the uptake or penetration of the tannins into the leather. The eucalyptus bark contains simple phenolics, such as gallic, ellagic and protocatechuic acid, as well as derivatives and flavonoids. It also contains complex polyphenolic compounds, such as ellagitannins (hydrolysable tannins) and proanthocyanidins (condensed tannins). Pinto et al. [66] characterized the eucalyptus globule bark as a source of tannin extracts and applied them for the retanning process. The results from the study showed that all the strength properties fulfilled the required minimum standards.

CONCLUSION

This review compiles the papers on the use of natural plants in the leather tanning process and the way their use impacts the quality of the resulting leather. This lays the foundation for the possibility of their adoption in the leather tanning industry due to the adherence to standards. The reviewed literature focused on studies that employed natural plants or extracts or combinations of natural plant extracts and showed the physical properties of the final leathers. The natural plants have been demonstrated to be effective in improving several physical and organoleptic properties of interest to the quality of leather, mainly the tensile strength, tear strength, elongation, distension at grain crack and grain burst. Although most studies were conducted with physical and organoleptic properties in mind, the overall concerns of the leather industry need to be addressed. As much research delves into plant products that replace synthetic agents and producing leathers with greater variety of property profiles which can compete favourably with synthetic leather, the actual leather must adhere to both human and environmental health. The safety of these leathers for a direct contact with the foot must be achieved. The overall and specific plant products must be tested thoroughly to demonstrate the novelty in their use and meet the stringent requirements. The application of some plants may be limited due to their insufficient quality, safety and lifespan of their usage. More research is needed to unravel suitable extraction methods, possible synergy of plants and plants that can possibly reduce the toxicity of chromium use.

Funding

This research was funded by the National Research Fund-Kenya (NRF-KE) of 2016/2017.

Conflicts of Interest

The authors declare no conflict of interest.

REFERENCES

- [1] Ozgunay H, Colak S, Mutlu MM, Akyuz F. Characterization of Leather Industry Wastes. Polish J of Environ Stud. 2007; 16: 867-873.
- [2] Habib AB, Noor IA, Musa AE. Effect of some Skin Defects on Physical Properties of the Leather. Journal of Applied and Industrial Sciences. 2015; 3: 112-119.
- [3] Nalyanya KM, Rop RK, Onyuka A, Kamau J. Tensile properties of Kenyan Indigenous Boran bovine Pickled and Tanned hide. Internat J of Sc and Res. 2015a; 4: 2149-2154.
- [4] Dixit S, Yadav A, Dwivedi PD, Das M. Toxic Hazards of Leather Industry and Technologies to Combat Threat: A Review. J Cleaner Prod. 2015; 87: 39-49.
- [5] Krishnamoorthy G, Sadulla S, Sehgal PK, Sehgal Mandal AB. Aldehyde Greener approach to leather tanning process: d-Lysine aldehyde as novel tanning agent for chrome-free tanning. Journal of cleaner production. 2013; 42: 277-286.
- [6] Urbanija V, Gersak J. Impact of the Mechanical Properties of Nappa Clothing Leather on the Characteristics of Its Use. Journal of the Society of Leather Technologists and Chemists. 2004; 88: 181-190.
- [7] Ork N, Ozgunay H, Mutlu MM, Ondogan Z. Comparative Determination of Physical and Fastness Properties of Garment Leathers Tanned with Various Tanning Materials for Leather Skirt Production. Tekstil ve Konfeksiyon. 2014; 24: 413-418.
- [8] Xiao-Lei Z, Qing-Lan L, Wei-Ping Z. Evaluation of Leather Handle Character by Discriminatory Two Class Analysis. Journal of the Society of Leather Technologists and Chemists. 2006; 91: 201-207.

- [9] Mutlu MM, Ork N, Yegin O, Bas S. Mapping the variations of tensile strength over the area of sheepskin leather. Annals of University of Oradea. 2014; 51: 57-162.
- [10] Covington D. Tanning Chemistry-The Science of Leather. The Royal Society of Chemistry, Cambridge. 2009.
- [11] Nalyanya KM, Rop RK, Onyuka A, et al. Influence of UV radiation on the viscoelastic properties and dynamic viscosity of bovine hide using dynamic mechanical analysis. J Therm Anal Calorim. 2015b; 123:363–370.
- [12] Nalyanya KM, Rop RK, Onyuka A, Birech Z. Recent use of selected phytochemistry to mitigate environmental challenges facing leather tanning industry: a review. Phytochem Rev. 2018a; 18:1361-1373. DOI 10.1007/s11101-019-09651-x.
- [13] Saravanabhavan S, Fathima NN, Rao JR, Nair BU. Combination of White Minerals with Natural Tannins Chrome-Free Tannage for Garment Leathers. Journal of the Society of Leather Technologists and Chemists. 2004; 88: 76-81.
- [14] Hui C, Jun G, Zhi-Hua S. A Cleaner Chrome-Free Tanning Regime: Sulfonated Urea-Phenol Formaldehyde Condensed Polymer and Ferrous Sulfate Tanning. JALCA. 2014; 105: 18-24.
- [15] Liu CK, Aldema- Ramos M, Latona NP, Latona RJ. Leather coated with mixture of humectant and antioxidants to improve ultraviolet and heat resistance. JALCA. 2009; 104: 161-168.
- [16] Metreveli N, Namicheishvili L, Jariashvili K, et al. Mechanisms of the Influence of UV Irradiation on Collagen and Collagen-Ascorbic Acid Solutions. International Journal of Photoenergy. 2006; 2006:1–4.
- [17] Pereira JA, Oliveira I, Sousa A, et al. Walnut (Juglans regia L.) leaves: Phenolic compounds, antibacterial activity and antioxidant potential of different cultivars. Food and Chemical Toxicology. 2007; 45: 2287-2295.
- [18] Bayramoglu EE, Korgan A, Kalender D, et al. Elimination of free formaldehyde in leather by Vinca rosea and Camellia sinensis extracts. JALCA. 2008; 103: 119-123.
- [19] Contini M, Baccelloni S, Massantini R, Anelli, G. Extraction of natural antioxidants from hazelnut (Corylus avellana L.) shell and skin wastes by long maceration at room temperature. Food Chemistry. 2008; 110: 659-669.
- [20] Owlad M, Aroua MK, Daud WAW, Baroutian S. Removal of hexavalent chromium-contaminated water and wastewater: A review. Water Air Soil Pollut. 2009; 200: 59-77.
- [21] Wang XS, Li ZZ, Tao SR. Removal of chromium (VI) from aqueous solution using walnut hull. Journal of Environmental Management. 2009; 90: 721-729.
- [22] Metreveli NO, Namicheishvili LO, Jariashvili K, et al. UV-Vis and FT-IR Spectra of Ultraviolet irradiated collagen in the presence of antioxidant ascorbic acid. J Ecotoxicol and Envir Saf. 2010; 73:448-455.
- [23] Bayramoglu EE, Onem E, Yorgancioglu A. Reduction of Hexavalent Chromium Formation in Leather with Various Natural Products (Coridothymus capitatus, Olea europaea, Corylus avellana, and Juglans regia), Ekoloji. 2012; 21: 114-120.
- [24] Falcao L, Araujo MEM. Vegetable tannins used in the manufacture of historic leathers. Molecules. 2018; 23:1081.
- [25] Nalyanya KM, Rop RK, Onyuka A, et al. Investigating mechanical properties of leather treated with Aloe barbadensis Miller and Carrageenan using existing theoretical models. Polym Bull. 2018b; DOI 10.1007/s00289-019-02706-1
- [26] Nalyanya KM, Rop RK, Onyuka A, et al. Effect of crusting operations on the physical properties of leather. Leather and footwear Journal. 2018c; 18: 283-294.

- [27] Valeika V, Sirvaityte J, Beleska K. Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather. Mater Sc (Medziagotyra). 2010; 16: 330-336.
- [28] Basil-Jones MM, Edmonds RL, Cooper SM, et al. Collagen Fibril orientation and tear strength across ovine skins. J Agr Food and Chem. 2013; 61: 1227-1233.
- [29] Ali SB, Haroun HE, Musa AE. Haraz Bark Powder extract for manufacture of Nappa upper leather as alternative retanning agent. J for prods and Industr. 2013; 2: 25-29.
- [30] Liu CK, Latona NP, Taylor M, et al. Characterization of mechanical properties of leather with airborne Ultrasonics. JALCA. 2015; 110: 88-93.
- [31] UNIDO. Acceptable quality standards in the leather and footwear industries, United Nations Industrial Development Organization, Vienna. 1996.
- [32] SATRA. Shoe and allied trade research association. Testing Equipment Catalogue. 2011.
- [33] ESA (Ethiopian Standards Agency). The quality standards for leather and leather products, Addis Ababa, Ethiopia. 2012.
- [34] INESCOP (Center for Technology and Innovation). http://www.manual for Oxazolidine Tanned Leather: Environmentally Friendly Oxazolidine-Tanned Leather (LIFE08 ENV/E/000140).com. Accessed on June 21, 2013.
- [35] Ashebre M. Performance of leather uppers of local footwear products and the determinants. Internat J Advancem & Technol. 2014; 3: 26-30.
- [36] Inanc L, Gulumser G. Determination of the Effects of Splitting and Shaving Operations before Tanning at Shoe Upper Leathers on the Quality of Leather. Tekstil ve Konfeksiyon. 2015; 25: 365-370.
- [37] Cloete SWP, van Schalkwyk SJ, Brand TS, et al. The effects of dietary energy and protein concentrations on ostrich skin quality. South African Journal of Animal Science. 2006; 36: 40-44.
- [38] Ibrahim AA, Youssef MSA, Nashy E-SHA, Eissa MM. Using of Hyperbranched Poly (amidoamine) as Pretanning Agent for Leather. Internat J Polym Sc. 2013; 2013: 1-8.
- [39] Musa AE, Aravindhan R, Madhan B, et al. Henna–aluminium Combination tannage: a greener alternative tanning system. JALCA. 2011; 106: 190-199.
- [40] Musa AE, Gasmelseed GA et al. Eco-friendly Vegetable Combination Tanning System for production of hair-on shoe upper leather. Journal of Forest Products & Industries. 2013b; 2: 5-12.
- [41] Sirvaityte J, Siugzdaite J, Valeika V, Dambrauskiene E. Application of essential oils of thyme as a natural preservative in leather tanning. Proceedings of the Estonian Academy of Sciences. 2012; 61: 220–227.
- [42] Musa AE, Madhan B, Madhulatha W, et al. Henna extract: Can it be an alternative retanning agent? JALCA. 2008; 103: 188-193.
- [43] Colak SM, Dandar U, Kilic E. Antioxidant Effect of Tannic Acid on Formation of Formaldehyde and Hexavalent Chromium Compounds in Leather. Tekstil ve Konfeksiyon. 2014; 24: 105-110.
- [44] Bitlisli BO, Yasa I, Aslan A, et al. Physical and antimicrobial characteristics of Aloe vera treated split suede leather. JALCA. 2010; 105: 34–40.
- [45] Affiang SD, Ggamde G, Okolo VN, et. Synthesis of Sulphated-Fatliquor from Neem (Azadirachta Indica) Seed Oil for Leather Tannage. American Journal of Engineering Research (AJER). 2018; 7: 215-221.
- [46] Sivakumar V, Prakash PR, Rao PG, et al. Power ultrasound in fatliquor preparation based on vegetable oil for leather application. Journal of Cleaner Production. 2008; 16: 549-553.
- [47] Quadery AH, Uddin MT, Azad MAK, et al. Fatliquor preparation from Karanja seed oil (Pongamia pinnata L.) and its application for leather processing. IOSR Journal of Applied Chemistry (IOSR-JAC). 2015; 8: 54-58.

- [48] Kusumawati F, Riyadi PH Rianingsih L. Applications Indigo (Indigofera tinctoria L.) as Natural Dyeing in Milkfish [Chanos chanos (Forsskal, 1775)] Skin Tanning Process. Aquatic Procedia. 2016; 7: 92 – 99.
- [49] Haroun M, Palmina K, Gurshi A, Covington D. Potential of Vegetable Tanning Materials and Basic Aluminium Sulphate in Sudanese Leather Industry. Journal of Engineering Science and Technology. 2009; 4: 20 - 31.
- [50] Musa AE, Gasmelseed GA. Development of Eco-friendly Combination Tanning System for the Manufacture of Upper Leathers. International journal of advance industrial engineering. 2013a; 1: 9-15.
- [51] Musa AE, Madhan W, Rao JR, et al. Colouring of leather using henna-natural alternative material for dyeing. Journal of American Leather Chemists Association. 2009; 104: 183-190.
- [52] Musa AE, Madhan B, Kanth SV, et al. Cleaner tanning process for the manufacture of upper leathers. Clean Techn Environ Policy. 2010; 12: 381–388. DOI 10.1007/s10098-009-0216-5.
- [53] Aravindhan R, Madhan B, Rao RJ. Studies on Tara-Phosphonium Combination Tannage: Approach towards a Metal Free Eco-Benign Tanning System. JALCA 2015; 110: 80-88.
- [54] Plavan V, Koliada M, Valeika V. Eco-benign semi-metal tanning system for cleaner leather production. Journal of society of leather technologists and chemists. 2017; 101: 260-265.
- [55] Fathima NN, Saravanabhavan S, Rao RJ, Nair BU. An Eco-Benign Tanning System Using Aluminium, Tannic Acid, and Silica Combination. JALCA. 2004; 99: 73-781.
- [56] Fathima NN, Aravindhan R, Rao JR, Nair BU. Tannic Acid-Phosphonium Combination: A Versatile Chrome-Free Organic Tanning. JALCA. 2006; 101: 161-168.
- [57] Ding K, Taylor MM, Brown EM. Tanning effects of aluminium- Genipin or vegetable tannin combinations. JALCA. 2008; 103: 377-382. Ali AEH, Gasmelseed GA, Ahmed AH. Utilization of Improved Indigenous Tannins of Grain Powder (Acacia Nilotica) in Eco Friendly Tannage. Int J of Multidisciplinary and Current research. 2016; 4: 14-20.
- [58] Omur S, Mutlu MM. Modification of Mimosa and quebracho tannins and the lightfastness properties of the processed leathers. Tekstil ve Konfeksiyon. 2016; 26: 230-235.
- [59] Musa AE, Gasmelseed GA. Eco-friendly Vegetable Combination Tanning System for production of hair-on shoe upper leather. Journal of Forest Products & Industries. 2013b; 2: 5-12.
- [60] Ozkan CK, Zengin ACA, Dandar U, et al. A new vegetable tanning material for leather industry: Acacia nilotica L. XXXIII IULTCS Congress November 24th – 27th, 2015 Novo Hamburgo/Brazil, 169-174.
- [61] Ali AEH, Gasmelseed GA, Ahmed AH. Utilization of Improved Indigenous Tannins of Grain Powder (Acacia Nilotica) in Eco Friendly Tannage. Int J of Multidisciplinary and Current research. 2016; 4: 14-20.
- [62] Kuria A, Ombui J, Onyuka A, et al. Quality Evaluation of Leathers Produced by Selected Vegetable Tanning Materials from Laikipia County, Kenya, IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS). 2015; 9: 13-17.
- [63] Hussein SA. Utilization of Tannins Extract of Acacia seval Bark (Taleh) in Tannages of Leather. Journal of Chemical Engineering & Process Technology. 2017; 8: 334. DOI: 10.4172/2157-7048.1000334.
- [64] Nasr AI, Abdelsalam MM, Azzam AH. Effect of tanning method and region on physical and chemical properties of Barki sheep leather. Egyptian journal of sheep and goat sciences. 2013; 8: 123-130.
- [65] Huantian C, Changqing W, Crescent S, Leslie S, Wenging X. Final report environmentally friendly leather tanning using enzymes. EPA Grant Number: SU835511. 2014.
- [66] Pinto PCR, Sousa G, Crispim F, et al. Eucalyptus globulus Bark as Source of Tannin Extracts for Application in Leather industry. ACS Sustainable Chemistry and Engineering. 2013; 1: 950-955.