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#### ASSESSMENT OF SHOE UPPER LEATHER PRODUCED FROM ENVIRONMENTALLY FRIENDLY TANNIN MATERIALS FOR THE MANUFACTURE OF THERAPEUTIC FOOTWEAR

Akawu I, Tagang J.I., Yakubu M.K., Akawu P.I. and Oparah E.N.

Nigerian Institute of Leather and Science Technology (NILEST), Zaria, Nigeria Correspondence: jerryakawu@gmail.com

### ABSTRACT

Researchers have pointed out that the upper part of therapeutic footwear should be made from leather or a combination of materials with a smooth inner lining. This study aims to evaluate the quality of shoe upper leather made based on environmental considerations for therapeutic footwear manufacture, specifically for individuals with diabetes. The leather utilised in this research is vegetable-tanned, a more sustainable and environmentally conscious alternative to conventional chrome tanning methods. Sixteen (16) different tannin ratios of Divi-Divi (DD), Acacia nilotica (AN) and Pakia clappertoniana (PC) were explored to enhance the resultant leather. The tanning trials were conducted with a 30% blend for shoe upper leather. Important physical properties determined following the official methods of the International Union of Leather Technologists and Chemist Society (IULTCS) include tensile strength, elongation at break, Lastometer, Apparent density, Indentation index, resistance to compression, water vapour permeability, water vapour adsorption and shrinkage temperature. The findings revealed that tannin ratio B4 (PC:DD (3:1)) produced the highest shrinkage temperature at 85°C, while tannin ratio B2 (PC:DD (1:1)) exhibited the highest resistance to compression at 6.65 N/mm<sup>2</sup>, a low water vapour permeability of 0.12%, and an elongation of 52%. Tannin ratio B3 (PC:DD (1:3)) displayed water vapour adsorption of 13.5%, an apparent density of 5.63 kg/m<sup>3</sup>, and tannin ratio A1(DD) demonstrated an indentation index of 37, and a tensile strength of 33.2  $N/mm^2$ . The results of the Lastometer test exceeded the standard value of 7 mm distension. The outcomes suggest that the vegetable-tanned leather utilised in eco-friendly therapeutic footwear exhibits comparable physical properties to traditional chrome-tanned leather commonly used in the footwear industry. In conclusion, this study posits that vegetable-tanned leather can serve as a viable, eco-friendly alternative to traditional chrome-tanned leather in producing therapeutic footwear for individuals with diabetes while maintaining quality standards.

#### **KEYWORDS**

Therapeutic footwear, manufactured, environmentally-friendly vegetable tannins, and diabetes

#### **ARTICLE HISTORY:**

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### **INTRODUCTION**

A shoe is not merely a covering for the foot, as Boulton *et al.* (2005) emphasised. It serves a multifaceted purpose encompassing protection, comfort, style, athletic performance, and foot health promotion, as underscored in the Global Report on Diabetes (2016). Footwear design should

prioritise alleviating pressure points, reducing shock and shear forces, and accommodating deformities by providing support and stability, as Jerry *et al.* (2016) advocated. Interestingly, many individuals suffering from foot issues may not readily attribute them to their choice of footwear, often disassociating their foot health from their shoe selection (Mauch *et al.*, 2009; Pavlackova *et al.*, 2015). They might even fail to connect the discomfort experienced by wearing shoes themselves. In conditions such as diabetes or arthritis, where the feet are particularly vulnerable or display clear signs of damage, footwear becomes paramount in creating a conducive environment for foot health (Luo *et al.*, 2022). Extensive documentation suggests that employing appropriate footwear, including vegetable-tanned leathers, among other materials, can significantly contribute to preventing and treating foot-related issues in individuals with diabetes mellitus and diabetic foot problems. Surprisingly, there remains a scarcity of literature addressing the role of clinicians in ensuring suitable footwear for patients with diabetes mellitus (Jerry *et al.*, 2014).

Even in the face of unfavourable underfoot conditions, early humans sought ways to enhance comfort and protect their feet from external harm (Williams, 2015). It is speculated that primitive footwear might have been crafted from vegetable fibres, although archaeological records offer no definitive traces of such materials (Pavlackova *et al.*, 2015). Many of the foot ailments patients present have their roots in footwear-related issues. When pressure from footwear intermittently affects areas of the foot with limited soft tissue covering over superficial bone, it can develop painful corns or even ulcers. Likewise, friction between the foot and the shoe can result in blisters or calluses (Abdissa *et al.*, 2020). The choice of material for crafting footwear carries substantial significance, tracing back to the origins of footwear history as a functional and aesthetically pleasing article. Primarily, two fundamental attributes, comfort and appearance, have always characterised footwear. These attributes are defined in the materials employed, the tools, machinery, and devices utilised during production, and the processes of manufacture. Equally vital are the design and shape of the footwear, offering a globally and individually traceable evolution and analysis (Kutnjak-Mravlinčić *et al.*, 2019).

In the leather industry, production involves three fundamental operations: beam house, tanning yard, and finishing yard. The tanning process is pivotal as it chemically stabilises hides and skins against chemical and bacterial threats, transforming raw materials into leather. Notably,

two primary tanning methods exist: chrome tanning and vegetable tanning. Chrome tanning, though effective, presents concerns due to toxicity at high concentrations, posing risks of mutagenicity and teratogenicity. In contrast, vegetable tanning stands out as environmentally friendly, often heralded as the "green tanning agent" due to its biodegradable nature (Koloka & Moreki, 2011; Spier *et al.*, 2015). Vegetable tanning has historically been a prominent alternative to chrome tanning, aligning with environmentally conscious practices. Notably, vegetable-tanned leather boasts exceptional qualities such as fullness, moldability, wear resistance, air permeability, and solidity (Kutnjak-Mravlinčić *et al.*, 2019).

Leather is an exceptionally suitable choice among the myriad options for upper materials. Leather offers dual plasticity characteristics, allowing it to retain its shape and elasticity, stretch, and revert to its original form (Luo *et al.*, 2022). In therapeutic footwear, an essential intervention to prevent ulcer recurrence, leather's advantage is its ability to maintain water vapour permanently. However, a drawback arises when leather shoes become wet, necessitating careful drying away from direct heat sources to prevent distortion. This stems from leather's plastic nature, as it readily conforms to any shape when exposed to moisture and heat. In this context, this study endeavours to assess the quality of therapeutic leather footwear constructed using eco-friendly vegetable tannins, particularly tailored for individuals with diabetes.

### MATERIALS AND METHODS

### **Collection and Preparation of Raw Materials:**

The pods of *C. coriaria* and the husks of *P. clappertoniana* were gathered from NILEST, Samaru-Zaria, located in Kaduna State. These raw materials were subsequently processed into a fine powder within the quality control laboratory at NILEST, employing a crusher with a 0.44 mm mesh sieve. This preparation was a crucial prerequisite for the ensuing tanning trials.

## **Tanning Trials:**

For the tanning experiments, goat skins were selected as the primary material. These skins were systematically bifurcated along the backbone during the pickling phase. This deliberate division minimises potential disparities from stratigraphical and topographical variations within the skins.

The tanning processes for both *C. coriaria and P. clappertoniana* were conducted following a recipe conforming to the standards of a full vegetable tannage. The tannage offers amounted to 30 % of the pelt's total weight in both cases.

# Physical Analysis of the Leather:

The sampling and subsequent sample preparation, necessary for chemical and physical assessments, were executed strictly with the guidelines delineated in IUC2 and IUP2 of the IULTCS official analysis method, precisely as prescribed. Furthermore, all pertinent physical parameters, including shrinkage temperature (Ts, °C), apparent density (g/cm<sup>3</sup>), tensile strength/elongation (N/mm<sup>2</sup>), resistance to compression (Kgf/cm<sup>2</sup>), indentation index (1/100mm), and lastometer measurements (mm), were conducted in strict adherence to the revised IULTCS official methods of analysis, as officially documented in March 2001.

# **RESULTS AND DISCUSSION**

To assess the impact of light exposure on vegetable-tanned leathers, a series of dyes with varying degrees of lightfastness were subjected to fading tests using a specialised textile known as "blue wool references." The outcomes of these tests are categorised on the blue scale, where Class 1 represents the most significant change (indicating very low light fastness), and Class 8 signifies the most negligible change, exemplifying excellent light fastness. The criteria for a footwear material's light fastness depend on its intended usage. In principle, all materials employed for the outer layers of shoe uppers or those exposed to light within footwear design should achieve a minimum of Class 3 light fastness, as stipulated by SLTC (1996, as referenced by Haron *et al.*, 2012).

The extent of fading, as related to the grey scale used to evaluate colour changes, is a fundamental parameter for estimating the rate of tannin oxidation. Notably, leather samples tanned with DD ratios A1 and D1 exhibited superior light fastness (3-4) compared to PC ratio B1 (2-3). However, PC ratio C1 met the required standard of Class 3 (as shown in Table 1). Consequently, when combining DD with PC and AN in various ratios, there was a decline in light fastness. It is worth noting that this decrease in light fastness could be mitigated through the dyeing process. The behaviour of DD-tanned leather suggests it serves as a better base colour for leathers intended to be dyed with a wide range of light colours.

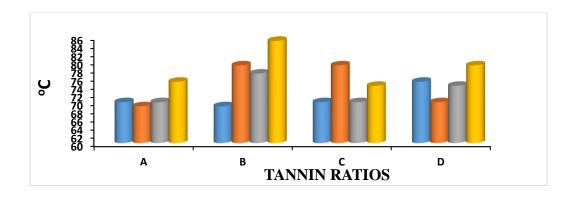


Figure 1: Shrinkage Temperature of the leathers tanned with different tannin ratios

Key: Preparations of different ratios of *Caesalpinia coriaria* (DD), *Parkia clappertoniana* (PC) and *Acacia nilotica* (AN) as a control

	1	2	3	4
Α	DD	DD:AN(3:1)	DD:AN(1:1)	DD:AN(1:3)
В	PC	PC:DD(1:1)	PC:DD(1:3)	PC:DD(3:1)
С	PC	PC:DD(1:1)	DD:AN(1:1)	DD:AN(1:3)
D	DD	DD:AN(1:1)	MDD:AN(1:1)	PC:DD(1:1)

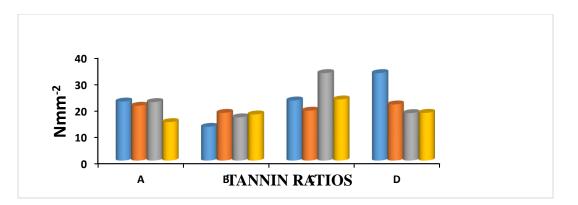
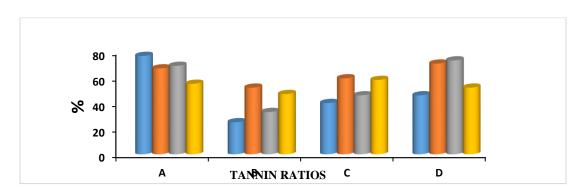


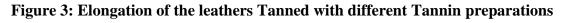
Figure 2: Tensile Strength of the leathers tanned with different Tannin ratios

The tannin ratio B4, with a blend of PC and DD in a 3:1 ratio, demonstrated the highest shrinkage temperature, reaching 85°C. This outcome underscores the synergistic effect of combining PC and DD in a 3:1 ratio, effectively enhancing the shrinkage temperature from 80°C (as seen with B1, PC alone) to 85°C. Conversely, tannin ratios B2 (PC: DD, 1:1) and B3 (PC: DD, 1:3) slightly reduced shrinkage temperature by 1°C and 2°C, respectively. This trend indicates that a higher proportion of DD in the mixture correlates with a lower shrinkage temperature. The results from tannin ratio B4 suggest that the (PC: DD) 3:1 ratio could be judiciously employed when prioritising end-user hydrothermal stability (refer to Figure 1). It is worth noting that the observed range of shrinkage temperature values aligns with findings reported by Mahdi in 2012.

In summary, all four tannin ratios enhance the overall quality of the resulting leather. Figure 2 displays the effects of different PC and DD ratios on tensile strength, showcasing a substantial increase. Tensile strength values for leathers produced from these ratios ranged between 15 N/mm<sup>2</sup> and 35 N/mm<sup>2</sup>. Notably, the combination of DD and AN in a 1:1 ratio denoted as C3, and DD alone with ratio D1 yielded notably high tensile strength values, reaching 35 N/mm<sup>2</sup>. Conversely, introducing sodium bisulfite in the modified tannins mixture M (DD:AN, 1:1) reduced tensile strength to 19 N/mm<sup>2</sup>. This suggests that the addition of sodium bisulfite had an adverse impact on the leather's tensile strength.

In alignment with UNIDO standards, the suggested minimum tensile strength value for leathers tanned with Chromium salts is 10 N/mm<sup>2</sup>. Similarly, Sharphouse (1983, reaffirmed in 2000) noted that a tensile strength value of 10 N/mm<sup>2</sup> is favourable for vegetable-tanned leathers. Significantly, all tensile strength values of leather samples tanned with PC, DD, and the modified mixture exceeded the recommended standards for shoe-upper leather. A higher tensile strength value is desirable for all vegetable-tanned leathers, serving as a critical indicator of leather quality. Tensile strength, one of the fundamental parameters characterising the mechanical properties of materials, holds significance in routine quality control tests within the leather industry, helping ascertain maximum stress and breaking elongation for leathers.





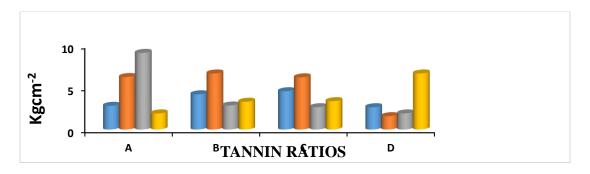
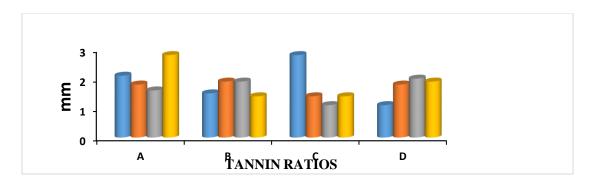


Figure 4: Resistance to compression of the leathers tanned with different Tannin Ratios

Regarding elongation, the leathers tanned solely with PC, as evident in Figure 3 (B1 and C1), exhibited elongation values of 23% and 30%, respectively. These values fall below the recommended standards, typically 40% to 70%. In contrast, the combinations of PC: DD and PC: AN in varying tannin ratios yielded elongation percentages within the recommended standard. When DD was used in isolation, such as in A1 and D1 from Figure 3, elongation values reached 78% and 42%, respectively. These divergent values for PC and DD may be attributed to the distinct classes of tannins present in these two plant sources. Modifying the tannins, DD and PC increased the elongation percentage.

Figure 4 illustrates how changes in the DD:PC combination correlate with variations in resistance to compression. Among these combinations, A3 (DD:AN, 1:1) demonstrated the highest resistance to compression at 9.093. In B2 (PC:DD, 1:1), the highest resistance to compression was measured at 6.657. C2 (PC/DD, 1:1) yielded a peak value of 6.190, while D4 (PC:DD, 1:1) achieved the highest resistance to compression at 6.651. These results suggest that the 1:1 ratios of DD:PC and DD:AN yield the highest resistance to compression. Consequently, all leathers tanned with PC and DD exhibit notable shape retention properties and solidity. Moreover, these findings imply that the shape retention properties and solidity of such leathers surpass those tanned with chrome.



**Figure 5: Thickness of leathers Tanned with different Tannin Preparations** 

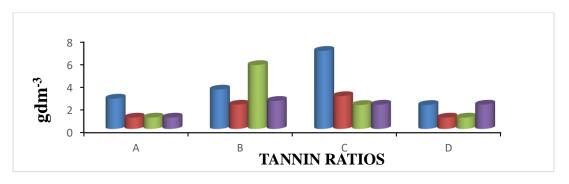


Figure 6: Apparent Density of the leathers Tanned with different Preparations

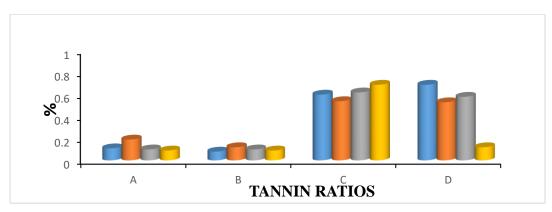
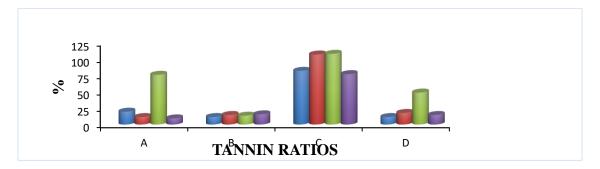


Figure 7: Water Vapour Permeability of the leathers tanned with different Preparations

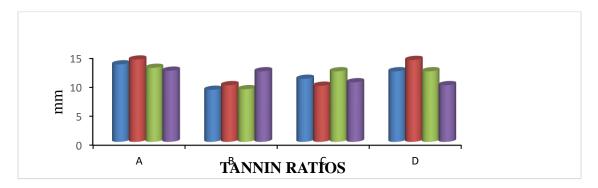
All leathers produced using various tannin ratios exhibited thicknesses within the recommended standards, typically ranging from 0.8 mm to 2.6 mm (as depicted in Figure 5). However, tannin ratios A4 (DD:AN, 1:1) and C1 (PC) yielded a thickness of 3 mm, surpassing the recommended standard. This slight deviation may be attributed to the inherent nature of the animal source used. Notably, no significant variations in thickness were observed when employing the different tannin

ratios derived from DD, PC, and their modified form M(DD:AN, 1:1, C3). The results suggest that these types of leather are well-suited for producing shoes and leather goods across a broad spectrum. They possess the requisite suppleness to bend freely and repeatedly without risk of breaking, and they exhibit impressive shape retention properties.

Regarding the indentation index results, leathers tanned with different ratios, such as A3 (DD:AN, 1:1), C3 (DD:AN, 1:1), and D1 (DD) returned values of 8 mm, 7 mm, and 6 mm, respectively. These values correlate with the thickness measurements seen in Figure 5. It is not surprising that these values are relatively low because the same tannin ratios resulted in thinner leathers, as evident in Figure 5. The indentation index assesses a leather's compressibility under demanding conditions. Consequently, except for ratios A3, C3, and D1, all leathers are expected to exhibit favourable compressibility characteristics.



**Figure 8: Water Vapour Absorption of the leathers Tanned with different Preparations** 



**Figure 9: Distention of Leathers Tanned with Different Preparations** 

One of the critical indicators for assessing leather's thermal insulation and durability is its apparent density, as depicted in Figure 7. Lower density is associated with greater comfort and reduced weight. Among the results obtained, tannin ratios B1 (PC), B3 (PC:DD, 1:3), and C1 (PC) yielded higher apparent density values of 4 g/dm<sup>3</sup>, 64 g/dm<sup>3</sup>, and 74 g/dm<sup>3</sup>, respectively. In contrast, leathers from other tannin ratios exhibited lower apparent density values, generally falling below 3. It is worth noting that the apparent density requirements can vary depending on the intended use of the leather.

The permeability of water vapour through surface materials and its interaction with water are pivotal factors influencing the comfortable use of footwear. Figure 8 illustrates the behaviour of water vapour permeability and water vapour absorption for different tannin ratios. These results suggest that leathers tanned with ratios A and B exhibit a minimal capacity for water vapour and limited vapour permeability, often referred to as "breathability." In contrast, leathers tanned using ratios C and D displayed the highest capacity for removing foot sweat, ranging from 0.6% to 0.8%. These variations in water vapour behaviour in tannin ratios A and B versus C and D may be attributed to the specific tannin ratios employed and the inherent characteristics of the raw hides and skins. These results point to a discernible impact on hygiene and comfort during wear.

Figure 9 portrays the distention of leathers tanned with various tannin ratios. Distention, which measures burst strength, reveals how leathers deform under the impact of force. The standard requirement for the burst strength test is typically specified as 7.0 mm distention at grain crack under a load of 20 kg. The burst strength values from the samples suggest that all meet the required standards, indicating a favourable response of the leather in toe-lasting conditions.

# CONCLUSION

This study evaluated the quality of therapeutic leather footwear tailored for individuals with diabetes, manufactured from eco-friendly vegetable tannins. It encompassed the utilisation of 16 distinct formulations. The findings of this investigation offer compelling evidence that these formulations yield high-quality leather footwear, meeting the requisite standards for therapeutic use among diabetic patients. The amalgamation of two to three eco-friendly, indigenous tanning materials exhibits a notable advantage in formulating an effective production recipe. This research further underscores the latent potential for Nigeria to achieve self-sustainability in tanning materials for the leather industry, thereby reducing reliance on chrome-tanned leathers, which can pose risks to individuals with diabetes. This research underscores the importance of incorporating eco-friendly materials into producing therapeutic leather footwear. It underscores the necessity for ongoing production process optimisation to enhance product quality continually. Importantly, it advocates avoiding chrome-tanned leather to avert potential adverse effects on diabetes individuals.

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