FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 7 No. 3, June (Special Issue), 2023, pp 193 - 197
DOI: https://doi.org/10.33003/fjs-2023-0703-1744

A COMPARATIVE STUDY ON PRESERVATION OF ANIMAL SKIN USING GAMMA IRRADIATION AS AN ALTERNATIVE TO SALT CURING TECHNIQUE

[*1]Akawu, P. I., [2]Onoja, M. A., [3]Musa, Y., [1]Akawu, I., [1]Akintade, S. A., [1]Jakheng, W. E., [3]Aliyu, U. S.

[1]Nigerian Institute of Leather and Science Technology, Zaria
[2]Department of Physics, Ahmadu Bello University, Zaria
[3]Centre for Energy Research and Training, Ahmadu Bello University, Zaria

*Corresponding authors' email: patienceakawu35@gmail.com

ABSTRACT

The study on investigation of the physico-mechanical properties of hide/skin (Sokoto red goat) using gamma ray irradiation as alternatives to salt curing preservation technique aims at converting flayed skin into the state of being resistant to putrefaction and it is accomplished by destroying active bacteria. The leather industry being one of the largest contributors to Nigeria's economy requires more attention to be given to it. Despite its contribution to the economy of the nation, the methods of processing leather poses serious threat to the environment. The Salt preservation, the conventional method of preserving skin is practiced by most tanners and it employs approximately 40-50% sodium chloride which is subsequently removed into the environment during soaking operation and this pollutes the environment. To overcome the limitation of such method, an eco-friendly method was introduced, which is the irradiation (Gamma ray) method which serves as a safer and ecofriendly alternative technique of preservation. The type of tanning method applied after preservation is the vegetable tanning method using the Divi-divi(Caesalpinia coriaria) pods which is also eco-friendly. From the research carried out, the leather preserved using gamma had 21.878 N/mm^2 at 300Gy, 3.27 Kg/cm^2 at 300Gy, 0.33mm at 350Gy, 75^oC at 200Gy, and 0.537g/cm^3 at 150Gy which are the highest values for tensile strength, resistance to compression, indentation index, shrinkage temperature, and apparent density respectively as compared to the salt cured samples which had 23.963 N/mm^2, 4.50 Kg/cm^2, 0.23 mm 72^oC, and 0.515 g/cm^3 values for tensile strength, resistance to compression, indentation index, shrinkage temperature, and apparent density respectively. The results obtained from gamma irradiation were within the range of recommended standards, hence could be looked into as an alternative for a hazard-free and ecofriendly method of animal skin preservation in the leather industry.

Keywords: Preservation, Animal Skin, Irradiation Technique, Leather

INTRODUCTION

The leather industry is counted among the oldest industries in the world, which nowadays plays a large role in the economic system globally. Looking through the ages, we can state that leather is a sustainable material, because while people eat meat, they will have this raw material available (Gudro *et al*., 2014).The modern commercial leather-making process involves three basic phases: preparation for tanning, tanning, and processing tanned leather. As a preliminary step, a hide must be carefully skinned and protected both in storage and transportation before reaching the tannery. A hide will begin to decompose within hours of an animal's death; to prevent this from happening, the hide is cured by a dehydrating process that involves either air-drying, wet or dry salting, or pickling with acids and salts before being shipped to a tannery. The leather industry is a high pollutant (polluting) industry. Deterioration of the skin starts within 5–6 hours after flaying; hence, there is a requirement for an effective preservative. Thus, it is essential to preserve the protein matrix and to arrest temporarily microbial attacks as well. Preservation is accomplished either by destroying active bacteria, by preventing bacterial activity or by preventing bacterial contamination (Valeika *et al*., 2017). Skins which are the byproducts of meat industry are the actual raw materials of the leather industry. Few hours after animal is flayed, skin falls vulnerable due to bacteria assault in case it is not well cured. Proteins of the skin are the main inviter of bacteria and it is only through curing that the raw stock can resist disintegration and reserve leather quality (Unango *et al*., 2019). Worldwide, skin is mostly preserved using Sodium Chloride ($NaCl_2$) which is polluting the environment by increasing soil salinity, affecting water body, releasing of more than 40 % Total Dissolved Solids (TDS) and 55 % Chloride ion (Cl^-). Previous study has revealed that the main components of fresh skin are moisture (60-70 %), proteins (25-30 %), fats (2 %), carbohydrates and mineral ingredients constitute 1 %. This huge amount of moisture lets bacteria to double in their numbers in less than 4 hours at 25 ^0C whereby the bacteria may have serious grain peeling and voids in the skin from 15-24 hours. The standard salt curing method for skins allows 40–50 % sodium chloride to be used in preservation based on its dehydrating power and bacteriostatic property that can reduce moisture content from 70 % to 30 % making the condition of the skin non- conducive for bacterial growth. Though the method is cost effective and easy to practice; it was evaluated that nearly 3 million tons (annually) of untreated salt are being discharged during first unit processing of leather and this leads to significant contribution of salinity to the soil, affecting water body, facilitate soil erosions and release of more than 40 % of TDS and about 55 % of chlorides in soaking liquors (Unango *et al*., 2019), 90% of the used water as effluent. The most common preservation systems act by reducing the bacterial activity by means of drying, salting or refrigerating the substrate as soon as possible since flaying. Among these methods, salting techniques are the most viable and, therefore, industrially widespread, although a high load of chloride ion is inevitably released into the waste water (Beghetto *et al*., 2013).There are developed methods of short-term preservation, which can be divided into physical and chemical (Valeika *et al*., 2017). Physical methods include: cooling with addition of ice; cooling in vacuum; irradiation or electron beam processing.

Chemical methods of short-term preservation are more welcome due to simplicity of use and needless of special equipment. Such materials as neem oil, potassium chloride, polyethylene glycol silica gel, sodium sulphite with acetic acid, and acetic acid with benzoic acid are investigated as possible preservatives for short-term preservation of skins/hides. The main problem of the use of these suggested methods is that preservation materials act on collagen, they cause undesirable changes in dermal structure and these factors require changes in leather processing technology seeking to produce high quality leather (Valeika *et al.*, 2017). Application of Salt for preservation on wet skin, is the conventional method of curing which is followed by most of the tanners because of its practical advantages; employs approximately 40-50% sodium chloride on raw material and is subsequently removed during the soaking operation. The use of salt increases the pollution load of tannery effluents, however, which becomes highly contaminated with increased total dissolved solids (TDS) and chlorides (Cl^-). It is therefore noteworthy that all chlorides, which fall into wastewater of tanneries are not eliminated from it and passed into environment (Kanagaraj & Chandra, 2002). The problem of salinity is especially pronounced in arid areas. It affects the quality of water used for irrigation. It was reported that there is no available technology for the treatment of effluent containing sodium chloride due to its high stability and solubility. The TDS load in effluent causes change in osmotic conditions for many organisms living in the water. High salinity results in loss of biodiversity of the river by changing the ionic composition. It has also been suggested that the high saltwater used for irrigation purposes may increase surface salinity through evaporation resulting in lesser crop yield. Also, the chlorides may be flushed from the soil by rain and re- enter the eco-system, which may ultimately end up in the groundwater, causing adverse effects on ecosystems like water, soils and plants (Uddin *et al.*, 2019). Moreover, tanning industry involves chemical reactions and mechanical changes which use a lot of water. It could have adverse effect on the environment and human health if it is not properly managed. The residents around the river and /or the tannery reported the death of their cattle, drying up of green plants, waterborne diseases and bad smell that resulted due to the pollution. Uncontrolled release of tannery effluents to natural water bodies causes environmental degradation and increases health risks to human beings. The environmental degradation caused is depletion of dissolved oxygen in streams/rivers, eutrophication of water bodies, toxicity to fishes and other aquatic flora and fauna. Moreover, local inhabitants are suffering from water borne diseases associated with water pollution, e.g., gastroenteritis, hyperchloremic acidosis, hypertension, arteriosclerosis, cardiac arrest, retinal toxicity, hepatic fibrosis, hepatocellular cancer, diabetes, sperm damage, feto-maternal death, and impaired neurobehavioral functions (Pc, 2016).

The aim of this research is to investigate the physico-mechanical properties of hide/skin (Sokoto red goat) preserved using Gamma photons irradiation as an alternative to salt curing technique for Leather production. This will be achieved through preserving skin using the salt curing and Gamma photons irradiation. Also the preserved skins will be tanned using vegetable tannins and then some of the physico-mechanical properties of the tanned leathers will be determined, such as: Shrinkage Temperature, Tensile strength,Resistance to compression, indentation index, and Apparent density.

MATERIALS AND METHODS

Materials and Equipment

The materials and equipment used in this study include: Fresh goat skins (Sokoto red goat), Co-60 Gamma radiation source, Tensile strength machine (INSTRON 1026), Cutting machine (Fortuna Model 5003, FON 602-M87x20), Lastometer (STD 104), Shrinkage temperature apparatus (SATRA TM 17:1997), Vernier Caliper, Micrometer screw gauge, and Divi divi (*Caesalpinia coriaria*) pods.

Sample Collection

Five (5) fresh hides of goat skins (taken not later than 2 hours after flaying) were used. The skins were gotten from the abattoir at Dogarawa, Sabon Gari, Zaria.

Sample preparation

The fresh goat skins obtained were cut along the butt (backbone portion of the skin) into circular pieces of diameter 10cm each and formed into experimental series resulting to a total of fifteen (15) skin samples. Ten samples for gamma irradiation process were used, and five (5) remaining pieces of the goat skin samples were used for salt curing.

Gamma Irradiation of the Sample

The skin samples were irradiated at Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria. The Gamma (Co-60) source is in a cylindrical lead shield. It has an activity of 123MBq and was adjusted to a source-to skin distance (SSD) of 0.5cm. Each sample piece was placed in the compartment such that the non-hairy part of the skin was facing the source. After irradiation at a given time, the sample was removed. The doses were rationalized for each piece of skin sample as 50Gy, 100Gy, 150Gy, 200Gy, 250Gy, 300Gy, 350Gy, 400Gy, 450Gy and 500Gy respectively. The time required for the application of each dose will be calculated:

$$\text{Time}=\frac{Dose}{Dose\ rate} \quad (1)$$

Salt preservation technique

Five (5) goat skin samples were used for this technique. The method of salting was carried out very conscientiously in order to avoid putrefaction of the skin. Sufficient salt was required to completely saturate the skin so as to stop any bacterial growth. For this reason, raw hide was salted with 40-50% salt in relation to the skin weight. This equates to more than one centimeter layer of salt on the flesh side of the skin. After the treatment (preservation) each experimental series would be stored in polyethylene bags. The commercial chemical materials conventionally used for leather processing was then employed.

Tanning Process

The stages and procedures for tanning according to (Covington, 1997):

Beam House Operation includes the following procedures:

i. *Soaking*: - One (1) part of the skin will be pre-soaked in five (5) part of water at room temperature plus 0.04 part of detergent for 2 hours to remove dirts.
ii. One (1) part of the main skin will be soaked with ten (10) of water at room temperature plus 0.03 part of detergent for 24 hours and drained on beam.
iii. *Unhairing*: - one (1) part of water will be added to the skin at room temperature, followed by 0.03 part sodium sulphide and pulped for 60 minutes.

iv. *Liming*: - 0.03 part of Calcium hydroxide will be added to the pelt for 2 hours, followed by ten (10) part of water to cover and left for 24 hours.
v. *Deliming*: - The limed pelt will be delimed in 0.7 part of water and 0.03 part of ammonium sulphate salt for 60 minutes and will be checked for deliming using phenolphthalein (pH 8 to 9).
vi. *Bating*: -This will be carried out with 0.008 part of bate powder for 25 minutes, then drained and washed twice.
vii. *Pickling*: -The pelt will be acidified in one part of water, 0.1 part of Sodium chloride and 0.01 part of formic acid respectively at room temperature and it will be run for 20 minutes and then run for 1 hour after which it will be left stationary overnight. pH will be checked (4.0 to 5.5).

Tanning Yard Operation includes the following:

i. *Tanning:* -This will be carried out using the same pickle liquor in short float tannage. For Divi divi tannage, one part of the pickled pelt will be tanned with crushed Bagaruwa in 3 lots (0.1 part each) at intervals of 30 minutes.
ii. *Fat liquoring*: -This will be carried out for both tannages in one part of leather plus 0.6 part of water at 50 ^{o}C with 0.04 part of fat liquor for 45 minutes, then 0.01 part of formic acid will be added and run for another 15 minutes.
iii. Finally, the tanned leather will be drained, washed, tested for shrinkage temperature and hung to dry; furthermore, it will be conditioned, staked, toggled, trimmed, buffed and de-dusted and then taken for physical and mechanical tests.

Finishing Yard Operation.
This involves dyeing and pigmenting.

Determination of hide and leather properties
Shrinkage Temperature Determination
The shrinkage temperature of the tanned skin will be measured using SATRA TM 17:1997 Shrinkage Temperature apparatus (Allen, 2015). Each sample of leather fibre will be cut and immersed in a closed convection circuit comprising the transparent sample chamber (sight glass) connected to a pipe with a small water reservoir which will be heated with a Bunsen burner. The temperature of the water in contact with the leather strip will be monitored with the thermometer immersed alongside the leather strip in the transparent sample chamber. A safety valve will be fitted to the apparatus which limits the pressure corresponding to a temperature of 120 ^{o} C. The temperature at which the leather shrinks to one–third of its length will be taken as the shrinkage temperature.

Measurement of Thickness
Each of the samples of leather will be cut in a circular shape. A standard dial micrometer gauge will be loaded with a mass of 500 gcm^{-2} at the presser foot. The gauge will be set to zero and then used to measure the thickness of the leather in four (4) positions at 1 cm from the edge. The central position will be marked and then the other three to form an equilateral triangle. Each reading will be taken in 5 s of dwell and on the grain side.

Measurement of the Apparent Density of Leather
Here, the diameter of the leather will be measured at two positions at right angles using Vernier Callipers. The diameter readings will be taken both on the flesh and the grain sides. The weight of the leather sample will be taken three (3) times using a weighing balance. The mean diameter will be determined and the thickness will be used as the height to calculate the volume. The apparent density will be calculated thus;

$$\text{Apparent density} = \frac{\text{mass}}{\text{Volume}} \qquad (2)$$

Measurement of the Resistance to Compression
The thickness of the leather will be measured in four positions under a pressure of approximately 20 g cm^{-2} (no added weight). The mean thickness will be determined and then thickness will be measured again in the same positions using a 200 g load. The measurement will be repeated for both the flesh and grain sides.

Measurement of Indentation Index
The thickness of the leather will be measured in four positions with a load of approximately 20 g. The mean thickness (t_o) will be determined and then the thickness will be measured again in the same positions with a load increase of 1000 g. The mean thickness (t_1) will also be determined. The measurement was repeated for both the flesh and grain sides. Indentation index is the difference between the two means ($t_o - t_1$) for either surface (grain or flesh) expressed in 1/100 mm.

Measurement of Tensile Strength
The samples will be cut parallel and perpendicular to the back bone in a dumbbell shape – the thickness and width of the specimen will be measured in the same position using a standard micrometre screw gauge and Vernier Caliper, one at the midpoint and the other two midway. The width will be measured on the flesh and grain side, and then the mean thickness (mm) and width (cm) will be determined. The area of cross section of each specimen will be calculated by multiplying its width by its thickness (SLTC, 1996). The jaws of the tensile machine (Instron 1026) will be set 50 mm apart, and then the sample clamped between the jaws, so that the edges of the jaws lay along the mid line. The machine will run until the specimen was broken and the highest load reached be taken as the breaking load. Tensile strength load is expressed in Newton (SLTC, 1996) as calculated using equation.

$$\text{Tensile strength} = \frac{\text{maximum breaking load}}{\text{initial free length}} \times 100 \qquad (3)$$

Percentage Elongation at Break
The initial free length between the clamps before and after final free length will be set at 5 cm and the elongation calculated from a graphical read out (SLTC, 1996), while the percentage elongation at break will be evaluated thus:

$$\text{Elongation (\%)} = \frac{\text{final free length} - \text{initial free length}}{\text{initial free length}} \times 100 \qquad (4)$$

RESULTS AND DISCUSSION
Preservation by Irradiation
The ten skin samples were preserved using the Cobalt 60 gamma source according to the doses and time calculated using the relationship in equation (1).
()The skins exposed to 50, 100, 150, 200, 250, 300,and 350 Grays were all successfully preserved except those irradiated at 400, 450 and 500 Gray which got damaged, they were found to produce very foul odour and a great degree of hair slip was also observed. As soon as they got dipped into water during the soaking stage, they were no longer held together, that is, they were found to be scattered in pieces.

Tanning

The preserved goat skins were tanned using the vegetable tanning method. Chrome tanning method was not employed because it would have been a deviation from the aim of the research, which is to achieve an eco- friendly process of preservation and Chrome has also been discovered to be a toxic chemical to the environment. The plant used was the Divi divi (*Caesalpinia coriaria*) pods. Tanning is the final process of skin preservation.

Measurement ofPhysicomechanical Properties

The results for the different physico-mechanical properties of the tanned leathers after being passed through different preservation techniques are displayed in Tables accordingly. The properties of the irradiated samples include Tensile strength, resistance to compression, shrinkage temperature, indentation index and apparent density.

Gamma Irradiated Samples

Table 1. shows the various properties of the gamma irradiated samples. Tensile strength is used to determine the maximum load a leather can withstand without being fractured when stretched.(Dennis *et al.,* 2020) reported that the value of 12N/mm^2 tensile strength was also good value for the vegetable tanned leathers. In this work, it was found to be between the range of 3.00 N/mm^2 and 21.878 N/mm^2 at doses of 50Gy and 300Gy respectively. The resistance to compression was within the range of 2.10 Kgcm^{-2} and3.27 Kgcm^{-2} at doses of 50Gy and 300Gy respectively. Shrinkage temperature of leather is the temperature at which a leather shrinks when heated in water at 2 °C min^{-1} and it is commonly related to degree of tannage. In other words, it is the effect of wet heat on the integrity of the material usually at the denaturation transition. The discerned initiation of the transition is referred to as the shrinkage temperature reflecting the observation that collagenic materials respond to wet heat by shrinkage (SLTC, 1999, Covington, 2009). It was found to be highest at 75 ºC and lowest at 70 ºC at doses of 300Gy and 150 Gy respectively which still falls within the recommended minimum value of 60ºC according to (Dennis *et al*., 2020) . The indentation index is a property which measures the compressibility of leather under severe circumstances. It was found to be highest at 0.33mm and lowest at 0.19mm at doses of 350Gy and 200Gy respectively. The apparent density is defined as the bulk density of the leather. It provides the mass per unit volume of loose packed powders. One of the useful signs for thermal insulation and durability of leather is the apparent density. To obtain a greater comfort, a lower density is related to lower weight. However the apparent density depends on what the leather would be used for (Britlisli *et al*., 2004). It was found to be within the range of 0.377 g/cm^3 and 0.537 g/cm^3 at doses of 100Gy and 150Gy respectively which fall within the acceptable value of 0.49 g/cm^3 according to (Series & Science, 2018). There were no values for the properties of leathers preserved with radiation doses of 400, 450 and 500Grays. This was because they got damaged during the stage of beam house operation before reaching the tanning stage. Repeated exposure was done using different skins at those same doses and the same outcome was seen. This could be due to the high doses at which the skin samples were exposed.

Table 1: Gamma Irradiated Samples

Dose (Gy)	Tensile Strength (N/mm^2)	Resistance to compression Kgfcm^{-2}	Indentation index (mm)	Shrinkage Temperature (ºC)	Apparent Density (g/cm^3)
50	3.000	2.10	0.29	73	0.526
100	2.183	2.76	0.25	72	0.377
150	18.028	3.05	0.30	70	0.537
200	11.256	3.11	0.19	70	0.402
250	15.498	2.74	0.25	72	0.440
300	21.878	3.27	0.22	75	0.483
350	16.128	2.29	0.33	73	0.412

Salt Irradiated Samples

Table 2. shows the salt cured leathers were found to have an average tensile strength of 23.96N/mm^2, resistance to compression of 4.50kgcm^{-2}, shrinkage temperature of 72ºC, apparent density of 0.472g/cm^3 and indentation index of 0.23mm.

Table 2: Salt cured samples

Tensile Strength (N/mm^2)	Resistanceto Compression (Kg/cm^{-2})	Indentation index(mm)	Shrinkage Temperature (ºC)	Apparent Density (g/cm^3)
23.963	**4.50**	**0.23**	**72**	**0.515**

CONCLUSION

The use of irradiation as a preservation technique for skin/hide presents a promising alternative to the traditional salt-curing method, which has been known to contribute significantly to environmental pollution. The application of irradiation technique to leather production has been shown to produce leathers with good physicomechanical properties, making it a viable solution to the environmental and health concerns associated with the salt-curing technique. Therefore, based on the positive results obtained from the irradiated samples, the application of irradiation in skin/hide preservation is highly recommended as a viable eco-benign technique for leather production. This could help to reduce the environmental impact of the leather industry while still producing high-quality leathers that meet the necessary standards. For future work in research and leather producing industries, an industrial irradiator (automated) should be used instead of a source where dose depends on length of time of irradiation. This would help in shortening the time taken in preservation and also aid in exposing larger sizes of hides and skins at a time. Adequate personal protection equipment should also be made available for the operators and safety measures should also be enforced.

REFERENCES

Beghetto, V., Zancanaro, A., Scrivanti, A., Matteoli, U., & Pozza, G. (2013). The Leather Industry : A Chemistry Insight Part I : an Overview of the Industrial Process. *Sciences At Ca' Foscari*, *1*(June 2013), 12–22. https://doi.org/10.7361/SciCF-448

Dennis, K. O., Jackson, N. O., Arthur, S. O., & Alvin, A. S. (2020). Evaluation of the physical properties of leathers tanned with Plectranthus barbatus Andrews extracts. *African Journal of Biotechnology*, *19*(3), 137–141. https://doi.org/10.5897/ajb2016.15406

Gudro, I., Valeika, V., & Sirvaityte, J. (2014). Short term preservation of hide using vacuum: Influence on properties of hide and of processed leather. *PLoS ONE*, *9*(11). https://doi.org/10.1371/journal.pone.0112783

Kanagaraj, J., & Chandra Babu, N. K. (2002). Alternatives to salt curing techniques - A review. *Journal of Scientific and Industrial Research*, *61*(5), 339–348.

Pc, S. (2016). Advances in Recycling & Waste Management : Open Access. *Advances in Recycling & Waste Management*, *1*(1), 1–10. https://doi.org/10.4172/2475-7675.1000104

Uddin, M., Uddin, N., Acter, T., Ahmed, S., Hasan, J., Mim, S., Hossain, M., Mukta, N. A., & Bari, L. (2019). *Eco-Friendly Goat Skin Preservation : An Approach for TDS , Salinity Reduction in Tannery Waste Water*. 1–13. https://doi.org/10.23880/jenr-16000182

Unango, F. J., Duraisamy, R., & Ramasamy, K. M. (2019). Preparation and characterization of eco-friendly ash salts for Goat skins preservation. *International Journal of Innovative Technology and Exploring Engineering*, *8*(11 Special Issue), 184–190. https://doi.org/10.35940/ijitee.K1039.09811S19

Valeika, V., Beleska, K., Mikulyte, S., & Valeikiene, V. (2017). Short-term preservation of hide/ skins as an approach to greener approach. *Proceedings of ISER International Conference*, *September*, 10–13.