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Investigation into the Bating Potential of *Musa Accuminata* (Banana) Peel in the Production of Leather

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Abstract
Increasing environmental pressures are forcing tanneries to reduce the level of nitrogenous compounds in generated effluents, due to strict regulations on effluent quality from various unit processes which bating plays a vital role. Bating imparts smoothness and stretchy effect to the resultant leather with the addition of proteolytic enzymes which are expensive, hence the need for alternative sources. This research investigated the bating potential of dried Musa *acuminata* peel in the production of leather. The functional groups present in both conventional bate and dried sieved *M acuminata* peels were analyzed using Fourier Transform Infrared instrument. Bating trials were varied based on the weight of the three goat skins with reference to the percentages offered as: 1%, 2 % and 3 % of *M. acuminata* at 310 K for 30, 45, 50, 60 and 120 min respectively. Absorptive frequencies of the powdered bate, M. *acuminata* and raw pelt (treated raw skins) shows that there were –C=O functional groups in M. *acuminata* and raw pelt but absent in the conventional bate before applications on the pelts. Absorptive frequencies for conventional bate and M. *acuminata* on Pelts after application on the pelts shows that carbonyl group were absent in Conventional bate; 2 % M. *acuminata* and 3 % M. *acuminata* on the pelt which shows that carboxylic acid ionizes to effect bating of the collagen but was not observed in sample 2 % M. *acuminata* (1543.1 cm^{-1}). Temperature of 310 K at which bating was carried out with respect to the time taken (35, 80, 60 and 50 was used for comparison between Sample of 3 % M. *acuminata* (50 min of mechanical agitation, at 310 K activity environment) when compared with the conventional bate of 1 % offered (35 min of mechanical agitation, at 310 K activity environment) accounts for 15 min difference for the M. *acuminata* peel to achieve the needed porosity via the ionization of the carboxylic group before and after bating. Shrinkage temperature for samples of Conventional bate (1 %) M. *acuminata* (1 %) M. *acuminata* (2 %) and M. *acuminata* (3 %) range from 369 – 371 K with respect to chrome tanning. Ball burst analysis for samples. M. *acuminata (1 %)*, M. *acuminata (2 %)* and M. *acuminata* (3 %) indicated that the force at load crack (N) for the control sample was higher than those of samples M. *acuminata* (2 %) and M. *acuminata* (3 %). The retention at burst in maximum value for all the other samples was higher than that of the control while in displacement the control sample (Conventional bate) gave the highest value on Load at crack.

Keywords*:* Musa *acuminata*, bate, porosity, shrinkage temperature, ball burst

1. INTRODUCTION

The leather tanning and products industries play prominent roles in the world's economy, particularly for developing countries. The industry sustainably recycles skins which are by-products of the meat industry and prevents their disposal on to the environment (Ashton *et al.,* 2021). The scarcity of natural resources and the accumulation of pollution caused by human activity brought about the development of production technology that is less harmful to the environment (Rajamani *et al.,* 1995). Leather manufacture is divided into three processes namely: (i). Beam house (ii). Tanning yard and (iii) Finishing operation (Peter *et al.,* 2019). Bating is one of the processes in the manufacture of leather (beamhouse) where chemical method cannot be substituted for bacterial or enzymatic action (Reed, 2005; Covington, 2009).

Enzymes are gaining more recognition because of advancements made in purification, development and improvement, and they are also considered environmentally friendly. The use of enzymes for leather processing has become a very efficient tool in achieving these goals. Another benefit is the replacement of harmful substances by enzymes for better quality. For an enzymatic preparation to be effective the degreasing agent with triple actions are considered, namely: proteolysis, lipolysis and emulsification (Renata *et al.,* 2021). Bating process makes use of enzymes (usually proteases) to catalyse hydrolysis of non-structured proteins such as hair roots and pigments (Mwinyihija, 2010) and optimized at 310 K. Enzymes have huge potential in the leather industry to digesting or modifying very specific organic components

with minimum environmental impact (Richard and Walter, 2013). Consequently, fowl droppings and dog dung are used to give the leather the required degree of softness flaccidness, pliability and elasticity by opening up the corium fibre (Casano *et al.,* 2001; Thorstenson, 1978; 1993).

The main enzymes that are of interest to the leather industry are as follows:

Protease hydrolyses the protein fraction of dermatan sulfate, making the collagen more accessible to water and reducing the attachment of the basal layer. In addition, they act in the removal of globular proteins and improves the quality of the leather

Lipases hydrolyses/degrades fats, oils and greases present in the hypoderm

Keratinase hydrolyses the keratin of hair and epidermis and break down the disulfide bonds of this molecule (Jatavathu, 2011; De Souza and Gutterres, 2012). These enzymes are further modified as pancreatic or bacterial bates (Sharphouse, 1983).

The use of enzymes directly in leather dyeing has led to better exhaustion of dye as collagenase-assisted process allows for 99 % uptake of dye (Kanth, 2006). The emergence of commercial proteases that are active in acidic media has made it possible to be used directly in the skin/hide pickling process which might have an additional effect on the collagen chemistry.

There are more than thirty different types of collagen which all contain three-stranded helical segments of similar structure (Richard and Walter, 2013), collagen like many other proteins, loses its flexibility upon drying. If dehydration proceeds below a threshold value it may result in irreversible conformation or breakdown because water serves as a plasticiser. The shrinkage temperature values of collagen are influenced by pH values, addition of solvents and detergents, cross linking and water content (Bienkiewicz, 1983). Thermal transitions are commonly investigated using differential scanning calorimetry, thermogravimetry and dynamic mechanical thermal analysis (Richard and Walter, 2013). Collagen is relatively inert to chemical and biological attack, but to increase both mechanical strength and ability to resist deterioration, hides and skins are stabilised by tanning agents such as mineral (371 K) or vegetable (355 K) hydrothermal stability (Bailey, 1992).

Ball burst test is another physical property for testing quality of leathers. It is intended to indicate the grain resistance to cracking during top lasting of shoe uppers. Various studies have found different value for grain crack and grain burst tests for sheep and goats tanned leathers. Grain crack have been reported to range from 6.74 – 10 mm and 9 – 10 mm respectively (Alex *et al.,* 2016).

2. EXPERIMENTAL

2.0 Materials and Method

Ripened species of *M. acuminata* were collected from Sabon Gari Market in Zaria, Kaduna State and the banana peels cut into small pieces, dried under shade for 10 days before they were grounded into powdery form using Procter milling machine and sieved through 0.2 – 0.5 mm mesh and kept in a polythene bag (Gary, 2004). Three raw goat skins (medium) were purchased from Samaru market in Zaria, Kaduna State. One was divided into two equal parts (skins), A_1 for control and A_2 experimental because of their similarities in collagen composition, two full goat skins were used as B_1 and C_1 for experimental. A_1, A_2, B_1 and C_1 were done in duplicates respectively.

Fourier Transform Infrared (FTIR) Analysis for Conventional bate and *M. acuminata* Samples

The FTIR spectra for conventional bate (proteolytic enzymes) and *M. acuminata* samples were performed at the Department of Chemistry, Ahmadu Bello University Multi-User Laboratory in Zaria). Conventional bate (proteolytic enzymes) and *M. acuminata* samples (5.0 mg) were allowed the passage of light using Cary 630 Agilent Technology FTIR spectrometer in the range of 4000-650 cm^{-1} , resolution (8), sample scans (16), background scans (16), 25x, 081 numerical aperture (NA), customized to deliver spatial resolution of 1-2 microns, equipped with standard software with controlled magnification switching (3.3 micron and 0.66 micron pixel) eliminating sample preparation, time consumption with real time visual feedback.

2.1 Bating Trials and Tanning

The conventional method of tanning by Wang and Attenburrow, (1993) was adopted with modification on the bating process. The pelts were removed from the delimed liquor, rinsed and separated into four bowls, as A_1, A_2, B_1 and C_1 respectively. One percent (1 %) of the conventional bate on A_1, 1 % of M. *acuminata* on A_2; 2 and 3 % of M. *acuminata* on B_1 and C_1 (duplicates) respectively based on pelt weight were applied at 310 K for 30, 45, 50, 60 and 120 min to avoid acid swelling prior to thumbs /porosity integrity tests. Wet (wet-blue leathers for shrinkage temperature test) and dry finishing (crust leathers for measurement of distension and strength of grain by ball burst analysis) were carried out to ascertain some of the physical / mechanical properties of the resultant leathers.

2.2. Shrinkage Temperature

This was carried out on the wet blue leather sample. About 5.5 ± 0.5 ml of distilled water was transferred

into a glass tube and the test piece (A rectangular test piece of 50 mm ± 2 mm x 3.0 mm ± 0.2 parallel to the back bone of the skin) immersed using a glass rod. The test piece end was attached to the test piece holder and the other end to a movable holder. A thread was attached to balance the pulley and the mass. Sufficient warm water was used to give a depth of 30 mm. Water was further heated to (373 K) maintain the rate of the temperature rise at 2± 0.2 ° C/min. After 30 seconds intervals the temperature and the corresponding position of the pointer were monitored for the reduction in size of the leather test sample and the final temperature recorded. This test is achieved using Figure I set-up (Journal Society of Leather Technologists Chemists, 2000).

2.3 Measurement of Distension and Strength of Grain by Ball Burst Analysis

Three (3) pieces of leather discs were cut based on official sampling positions. The thickness was measured, grained up in three positions under a load of 500 gcm^2 using a standard gauge. This method determines the force required in breaking the strength of the grain during lasting operation of shoe uppers (Journal Society of Leather Technologists Chemists, 2000). Muver electronic lastometer model number 5077.ET attached with Epson (EPL-6200) printer was used for this analysis.

3. RESULTS AND DISCUSSION

Table 1 shows the absorptive frequencies of the powdered bate, M.*acuminata* and raw pelt (treated raw skins) indicating that there were –C=O functional groups in M .*acuminata* and raw pelt but absent in the conventional bate before applications on the pelts. Table 2 shows the adsorptive frequencies for conventional bate and M. *acuminata* on Pelts after application on the pelts. Carbonyl group were absent in sample A_1, B_1 and C_1 which shows that carboxylic acid ionizes to effect bating of the collagen but was not observed in sample A_2 (1543.1 cm^{-1}). The bating performance of M. *acuminata* in digesting the inter-fibrillary protein of the collagen could be attributed to its large surface area and discrete pore sizes of the collagen for penetration and adsorption of subsequent chemicals. Some enzymes such as protease, amylase xylanase, cellulose and pectinase (Mahwish *et al.,* 2020) present in M. *acuminata* could also be responsible for the degrada-

Table 1: Adsorptive Frequency (FTIR) Results for Materials before Application

M. accuminata		*Conventional Bate*		*Raw Pelt*	
Freq	**Assignment**	**Freq.**	**Assignment**	**Freq.**	**Assignment**
3283.8	N-H	3746.0	O-H(phenol)	3693.8	O-H(phenol)
2922.2	C-H	3690.1	O-H(phenol)	3652.8	N-H
1733.2	C=O	3649.1	N-H	3280.1	NH_2
1599.0	N-H	3098.7	NH_2	2922.2	CH_2
1375.4	CH_2	2922.2	CH_2	1744.4	C-H
1319.5	CH_2	1002.7	C-O	1744.4	C=O

Table 2: Adsorptive Frequency (FTIR) Results for Conventional bate / M. acuminata on Pelts after Application

Sample A_1		Sample A_2		Sample B_1		Sample C_1	
Freq	Assignment	Freq	Assignment	Freq	Assignment	Freq	Assignment
3697.5	*O-H*	3619.2	*O-H*	3652.9	*O-H*	3753.4	*O-H*
3652.8	*N-H*	2855.1	*C=C*	3697.5	*N-H*	3697.6	*N-H*
3283.8	*NH_2*	1543.1	*C=O*	3280.1	*NH_2*	3285.1	*NH_2*
2922.2	*CH_2*	1457.4	*C-H*	2922.2	*CH_2*	2922.2	*CH_2*
1338.1	*C-H*	1028.7	*C-O*	1028.7	*C-O-C*	1028.7	*C-O*

A_1 = 1 % Conventional bate; A_2 = 1 % M. *acuminata*; B_1 = 2 % M. *acuminata*; C_1 = 3 % M. *acuminata* (Pelt = Treated raw skins)

tion of the hair tuft (root) with some degree of flaccidity (Renata et al., 2021).

Functional groups at 1733.2 cm^{-1} in banana and 1744.4 cm^{-1} in raw pelt which accounts for -C=O as

–COOH, or –$COOCH_3$
Carboxylic esters

Bating was achieved through the ionization of the carboxylic acid to carboxylate as follows:

$$-COOH \rightleftharpoons -COO^- + H^+ \quad (1)$$

The H^+ accounts for the acidity of the solution with the capacity for removing lime from the collagen matrix making available the $-COO^-$ for cross linkages with tanning agents. The pH for dried crude M. *acuminata* peel extract 7.8 – 7.9 which is close to conventional bate of 8.0 – 8.2 (United Nations Industrial Development Organization, 1996). A cross sectional area of the pelts were cut and tested using phenolphthalein indicator from pink to colourless as an indication of complete bating from pH 12 to 7.8 using M. *acuminata* peel extract.

Table 3 shows the temperature (310 K) at which bating was carried out with respect to the time taken (35, 80, 60 and 50). Comparison between Sample C_1 (50 min of mechanical agitation, at 310 K activity environment) when compared with the conventional bate A_1 (35 min of mechanical agitation, at 310 K activity environment) this accounts for 15 min difference for the M. *accuminata* plant to achieve the needed porosity via the ionization of the carboxylic group before and after bating (opening up of the fibre matrix). Higher percentage of M. *accuminata* is needed for 2/3 cross sectional area penetration this was observed in B_1 and C_1 while A_2 was insignificantly digested. Conventional processes such as pickling and chrome tanning were carefully carried out to avoid acid swelling and precipitation of the basic chromium sulphate employed in tanning to achieve hydrothermal stability of the collagen matrix as a priority. The shrinkage temperature values obtained were the same (371 K) with the standard for chrome tanned leathers, which reflects the unit bound chrome per collagen matrix (chrome uptake by the leather fibres) for strength, structural and hydrothermal stability (Rashid *et al.,* 2014; Yang *et al.,* 2014). Table 4 presents the Ball burst analysis for all the samples. A_1, A_2, B_1 and C_1 indicated that the force at load crack (N) for the control sample was higher than those of samples B_1 and C_1 *M. acuminata*. The retention at burst in maximum value for all the other samples was higher than that of the control. The significance of lastometer test is to determine the strength of the resultant leather with respect to shape retention and the force required in breaking the strength of the grain without premature (grain) failure. The maximum required standard is 7 mm (Luijten, 1998), but in this work the values were above 10 mm. While in displacement the control sample (A_1) gave the highest value on Load at crack. This suggests that the grain could withstand stretch during the process of making shoes bags, belts etc.

Table 3: Porosity / Shrinkage Temperature Test

Samples	Temperature (K)	Porosity Time (min)	Shrinkage Test (Ts, K)
A_1	310	35	371
A_2	310	80	370
B_1	310	60	369
C_1	310	50	371

Ts = shrinkage temperature

4. CONCLUSION

The use of M. *acuminata* has proven to be effective in the bating of leather because of the enzymes activity on the peel of M. *acuminata* via higher percentage offer. Consequently, the FTIR results shows the carboxylic group present ionized to give a hydrogen proton which is acidic with the capacity for removing lime from the collagen matrix making available the COO^- for cross linking with tanning agents. The resultant leather produced has good grain properties and can withstand stretch during the process of shoe making.

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Table 4: Ball Burst Analysis

S/N	Thickness (mm)	Distention at burst (mm)	Distention at break (mm)	Force at break (N)	Force at burst (N/mm)
A_1	1.53	10.55	11.34	40.55	28.11
A_2	1.52	10.57	11.33	40.58	28.17
B_1	1.64	11.04	11.08	35.78	20.64
C_1	1.63	10.22	10.65	38.06	24.51

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