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The effect of processing conditions on the physiochemical properties of tannery waste based adhesive target for wood binding application

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Abstract

Glue produced from tannery waste (pelt) have long history with respect to its applications. It used in structural adhesives, sizes and consolidates not only in furniture making but also in the preparation and conservation of the most varied materials such as those found in natural history collections. Ethiopia has one of the largest livestock populations in the world providing a strong raw material base for the leather industry. Due to improper disposal of the solid wastes from different production of leather processing, there is loss of byproducts which resulted environmental pollution. Therefore, this research aimed at characterizing the lime pelt, optimizing the process parameter for glue production and quality characterization of the glue. Standard methods such as ASTM was used. The samples were processed/soaked with lime (2-10%) for several weeks (2-5 weeks) and boiled for about 4 hrs. at 60 ^{o}C to 90 ^{o}C for glue extraction. Further, the extract was analyzed for its pH, viscosity, ash content, and moisture content. The pelt characterization showed higher mineral contents which ranges (5.9- 4285 mg/kg). Soaking of the pelt, in 10% lime solution, for 2 weeks and boiling at 90^{o}C were found to be the optimum conditions for glue extraction. At this optimum process parameters, the viscosity, yield, moisture content and Ash content were 201 mP, 0.17g / g of pelt, 14.2% and 6.54% respectively. From the mechanical test results, it can be concluded as the glue produced at the optimum conditions can be used as a wood adhesive.

Key words: Glue, Mechanical test, Protein, Pelt, Tannery solid waste, Viscosity, Yield

1. Introduction

1.1 Background

Adhesion is the state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both while an adherent is a substrate held to another substrate by an adhesive [47]. Adhesive is any non-metallic material that is capable of joining bodies together by surface adhesion and internal strength without the structure of the bodies undergoing significant changes [48]**.** Adhesives are gluing materials which are directly extracted either from natural sources such as bone, gums and starches or synthetically derived from chemicals like urea formaldehyde [49]**.**

Proteins have been used since many years as wood adhesives, mainly bio-based protein [50]. Protein wood adhesive can be divided into plant protein adhesive and animal protein adhesive [51]. In this research the animal protein adhesive from leather waste (lime pelt) had been studied for the application of wood binding. Different researchers reported the potential of animal-based glue in the adhesion industry. J. S. Siak et al., 2000 prepared the animal-based glue, which was successfully applied in the production of wood composite materials [52]. Jing-yu Shi et al., 2012 used an animal glue as a core sand binder, and made a systematic study on the application of different wood products [53].

Leather industry is among the largest industries in the world producing a wide range of products. The industry recycles an organic waste originated from the meat industry into leather. Raw hide/skin is transformed into leather by means of a series of chemical and mechanical operations. The series of operation involved in leather making generates substantial quantities of solid, liquid, and gaseous wastes [1]**.** Tannery solid wastes have different characteristics. Some tannery solid wastes made of organic collagen protein will rot away after being placed for a period of time in nature environment. These tannery solid wastes contain collagen protein, which is a valuable resource. Collagen proteins have application for making gelatin, additive component for cosmetics, biomaterial for medical products, for animal feed staff, nutrition component for health care products, and as raw material for protein based industrial products [2]**.**

However, insufficient management of these solid waste creates a variety of problems that endanger public health and the environment in general. These wastes are disposed in ways that have been reported to cause the pollution of surface and underground waters and air quality [53]; affect the health of residents living within the vicinity of the abattoirs, destroy affected water bodies, [54]; discharge of these solid waste to environment causes outbreak of water borne diseases and other respiratory and chest diseases [55].

Therefore, it is important to reuse the byproduct of tanneries obtained so as to reduce the pollution and to have better value addition to these wastes. Effective reutilization of this resource is crucial to prevent economic losses and environmental pollution. This study aimed at determining the optimum conditions for the production of wood adhesives from tannery waste protein (i.e. trimmed and flesh hide/skin) and characterization of the animal glue obtained at optimized processing conditions.

1.2 Statement of the problem

Ethiopia has one of the largest livestock populations in the world providing a strong raw material base for the leather industry. Currently, Ethiopian leather industry is in the forefront of the leather sector development within the Eastern and Southern Africa region. However, the series of operation involved in leather making discharging and dumping their wastes and effluents without treatment into nearby water bodies. Out of 1000 kg of rawhide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather. Tannery generates a huge amount of solid waste as follows: fleshing, 50–60; chrome shaving, chrome splits and buffing dust 35–40%; skin trimmings, 5–7; and hair, 2–5% [6]. Due to improper disposal of the solid wastes from different production of leather processing, there is environmental pollution. This research tried to alleviate challenges regarding the proper utilization of the byproducts.

Furthermore, most wood processing industries in Ethiopia uses synthetic wood adhesive imported from abroad, this costs a lot of hard currency for the country. This research is intended to maximize import substitute of wood adhesive which has wide applications in different areas.

Numerous researches have been conducted to produce wood adhesives from tannery wastes. However, some challenges still exist because protein wastes from tanneries are potentially difficult from other categories of solid wastes due to the presence of different chemicals and variety of hides which are generally used in leather manufacturing. Besides, due to poor production process under extreme conditions, adhesives typically lack durability. Therefore, process parameters to produce wood adhesive form tannery waste protein should be optimized. In this research, we have attempted to study and optimize various parameters for the production of wood adhesive form tannery waste protein.

1.3 Objective of the study

1.3.1 General objective

The general objective of this research was to determine the optimum condition for the production of wood adhesives from tannery waste protein (i.e. trimmed and flesh hide/skin).

1.3.2 Specific objectives

The specific objectives of this study were to: -

- Characterize tannery solid waste (i.e. trimmed and flesh hide/skin) from leather factory.
- Extract protein from tannery solid waste (i.e. trimmed and flesh hide/skin).
- Convert protein into wood adhesive.
- Optimize the effect of boiling temperature, concentration of the reagent and soaking time.
- Analyze the quality of the wood adhesive.

2. Literature review

2.1 Wood adhesive

According to Adhesive Sealant Council in America, adhesive is a material used for bonding that exhibits flow at the time of application. There is no simple theory of adhesion, and the truth for any one system is probably a combination of adsorption, electrostatic attraction and diffusion. Adhesives are substances that are able to make things adhere or stick together without deformation or failure through a process called adhesion [7]. Wood adhesives are polymeric materials that are capable of interacting physically or chemically, or both, with the surface of wood in such a manner that stresses are transferred between bonded members. Adhesives and the physicochemical phenomenon of adhesion play an important role in more than 70% of all wood-based materials in use today. This includes not only bonded wood products but paper products, paints, and finishes. By far, the largest amount of adhesive is used to manufacture building materials such as plywood and other laminated veneer products, particleboard, oriented strand board, fiberboard, laminated beams and timbers, edge- and end jointed products, windows and frames, architectural doors, and fiberglass insulation. Adhesives are used in lesser amounts to assemble building materials in residential and industrial construction, particularly in panelized floor and wall systems. Significant amounts are also used in nonstructural applications such as furniture, overlays, floor coverings, countertops, ceiling and wall tiles, trim, and accessories [8].

2.2 Classification of wood adhesives

Wood adhesives are categorized as either natural or synthetic. Synthetic adhesives consist of either prepolymers (oligomers) or polymers that are synthesized from petrochemically derived raw materials. Adhesives must be applied in liquid form to disperse over and wet the surface of wood. Adhesive prepolymers can be applied directly if they are liquids or can be applied as solutions, usually water solutions. Adhesive prepolymers cure by further reaction of the oligomers to form polymers in situ. Often the curing reactions are facilitated by the addition of a crosslinking agent or catalyst and by the application of heat. Synthetic polymers, when used as adhesives, are melted, dissolved in a solvent, or emulsified in a solvent prior to application. The solvent is usually water. After application, polymer-based adhesives set by solidification of the melted polymer by cooling or by removal of the solvent via either evaporation or adsorption or both [9].

Natural adhesives that have been used by the forest products industry include adhesives derived from starch, soybeans, animal waste and by-products of the meat processing adhesives derived from starch, soybeans, animal waste and by-products of the meat processing and tanning industries, and casein from skim milk. Of these, protein-based adhesives (soy, blood, and casein) were most commonly used. However, adhesives derived from natural sources were limited to dry interior applications. Natural adhesives are generally dispersed in water prior to application and cure primarily by solvent removal, although some are formulated with the addition of cross-linking agents. The early wood composite products industry was founded on the use of this type of adhesive for plywood production [9].

2.3 Sustainable resources for wood adhesives production

2.3.1 Lignin

Lignin is composed of cross-linked phenolic C6C3 units. The major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl and carboxyl groups. Most of the available lignin comes as a by-product of the pulping process. These lignin derived fragments have low value and usually serve as fuel for the recovery boiler of pulp and paper mills. They are very heterogeneous in their structure with structural units that range from almost native to highly degraded. The structure of lignin plays a key role in the required modifications and crosslinking to allow for better adhesive properties of the derived adhesive. Commercial lignin types from different processes are divided into two main categories. Sulfur containing lignin (mainly kraft lignin found in the black liquor of kraft pulping process and lignosulfonate lignin in the sulphite liquor of sulfate pulping process) and non-sulfur biorefinery lignin (soda, organ solve, steam explosion, hydrolysis, diluted acid, pyrolytic, high-pressure refining, ammonia-fiber-expansion lignin, etc.) [10].

Lignin-based adhesive systems have been the subject of several researcher. Self-bonding properties of wood particles and improvement of those by enzyme treatment has been well researched. Lignin has been primarily used as partial replacement of phenol in phenol-formaldehyde (PF) resins for plywood production. The chemical structure of lignin lowers the reactivity of the resin, which is a disadvantage in applications where fast curing times are desired. Danielson and Simonson reported that although 50% of kraft lignin as a replacement for PF resin could give good results regarding resin viscosity, storage stability and bonding ability, the pressing time had to be raised by 30%. Although no difference in plywood bonding is detected between commercially mixed lignin from black liquor and lignin from other wood species (bamboo, eucalyptus), only 15% phenol can be replaced by lignin without affecting bond properties [11].

2.3.2 Tannins

Tannins occur naturally in bark, wood, leaves and fruits of plants. Tannins are used in various industrial applications, mainly in the manufacturing of inks, textile dyes and as a corrosion inhibitor. Although tannin occurs in many plant species, only a few have high enough concentration to make its extraction worthwhile. Tannin can, for example, be extracted from pine, quebracho, oak, chestnut, wattle, eucalyptus, myrtle, maple, birch and willow. Different extraction methods are used, the most common ones being maceration, Soxhlet extraction supercritical CO_2 and percolation. Other rare techniques such as microwave and ultrasound assisted extraction has also been studied to increase tannin yield. The extraction method affects adhesive properties of tannin extracts [12].

Commercial tannin-formaldehyde applications already exist and several reviews on the use of tannin as a wood adhesive can be found in literature. Currently, tannins are not available in large enough quantities to compete with synthetic adhesives in most parts of the world. It should be noted that tannin-based adhesives typically give particleboards with better water and moisture tolerance compared to those given by UF resins. Although most commercial applications and studies focus on condensed tannins due to their higher reactivity, some studies have been done on the use of hydrolysable tannins as wood adhesives. They react through their low reactivity meta-sites, but it is still possible to substitute a large amount of phenol in PF resins by hydrolysable tannins. Tannin adhesives due to their phenolic nature have very low formaldehyde emissions. The emissions have been even further reduced by using non-emitting hardeners or by using tannins that are cured by auto condensation in the absence of aldehydes. The autocatalytic hardening can occur in highly reactive tannins, such as in procyanidins, without the need of an external catalyst [13].

2.3.3 Starch

Starch is a polysaccharide derived from the seeds, roots and leaves of plants. It acts mainly as the energy storage unit of plants and can be found in large quantities in corn, wheat, potato, rice, tapioca and sago. In pure form, it is insoluble in cold water. Starches can be dry roasted in the presence of an acid catalyst to form dextrins. Depending on roasting time, dextrins can be divided into white dextrins, canary (yellow) dextrins and British gums. Unlike starches, dextrins are soluble in water, and the viscosity of dextrin solution is easier to adjust than that of starches [14].

The adhesive bonding strength of natural starch is not strong enough to glue wood, and the amount of research done is not as great as for some of the other bio-based adhesives. Most recent starch adhesive research focuses on replacement or extender for solid wood dispersion adhesives to reduce material cost and increase viscosity. The studies on the use of starch as a wood adhesive have focused on corn starch in starch/polyvinyl alcohol, starch/isocyanates and starch/tannin adhesives. Also, rice, rye, wheat and potato starch have been evaluated for use in particleboards. The adhesive properties of starch vary greatly depending on where it is derived from. Starch adhesives rely on hydrogen bonding forces, which are much weaker than chemical bonds. They also easily form hydrogen bonds with water molecules, leading to poor water resistance. Higher bonding strength and better water resistance can be achieved by crosslinking starch using crosslinking agents such as sodium borate, epoxy chloropropane, hexamethoxymethylmelamine, formaldehyde, and isocyanates [15].

2.3.4 Protein

Proteins are complex macromolecules consisting of amino acid monomers, which are chemically linked together to form polypeptide chains. The chemical links are mainly amide bonds that are stable but can be degraded using strong acids. The most common source of proteins is the mechanical or solvent extraction of oils, soy, palm, canola, cottonseed and sunflower oils making up the biggest markets. Soy flour is the cheapest option but also the one with the lowest protein content. The most commonly produced isolates have a protein content of 80–90%. Protein content greatly affects the properties of the final adhesive. The adhesive performance of soybean proteins is also affected by particle size, nature of the surface, structure of the protein, viscosity and pH [16].

A detailed review on the use of soy protein as wood adhesive can be found in literature. Soy protein adhesives were used for wood and paper and as binders in coatings and paints. The soy proteins used as plywood adhesives were typically denaturized by caustic treatment. The products had typically short pot lives, poor biological stability, low solid content, slow pressing times and very poor water resistance, which limited them to mainly interior applications. As a wood adhesive, soy protein is inexpensive, easy to handle, has low pressing temperatures and can bond wood with relatively high moisture content. However, soy protein adhesives have high viscosities and short pot lives and the wood composites bound with them have relatively low strength, low water tolerance, and are sensitive to biological degradation. Protein adhesives are also quite sensitive to changes in temperature, pH, ionic strength and pressing conditions. The adhesive properties highly depend on protein content. The high viscosity of soy adhesives can be lowered by using low solids' content or by hydrolysis of the protein. Hydrolysis breaks the protein macromolecules into small fragments, which also leads to inferior bond strengths [17].

2.4 Production of wood adhesive from tannery waste protein

2.4.1 Tannery waste protein

Protein-based adhesives can be derived from animal and agricultural sources. These were widely used in the past as wood adhesives. Animal gelatin is obtained from waste and by-products of the meat-processing and tanning industries. The most common starting materials are hides, trimmings from the leather industry, sinews, and bones of cattle and other animals [3].

Leather industry has been categorized as one of the highly polluting industries and there are concerns that leather-making activity can have adverse impact on the environment. The global production of about 24 billion m^2 of leather by 2005 presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing. The tannery effluents are characterized by high contents of dissolved, suspended organic and inorganic solids giving rise to high oxygen demand and potentially toxic metal salts and chromium metal ion. The disagreeable odor emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia and other volatile organic compounds are also associated with tanning activities. Solid wastes generated in leather industries contribute mainly skin trimmings, keratin wastes, fleshing wastes, chrome shaving wastes and buffing wastes. It constitutes protein as the main component. If these protein and other chemicals, which are present in the chemical treated protein, are not utilized properly it will pose hazardous pollution problem to the environment [2].

From the wet salted hide purchased by the tannery only 30-35% is theoretically convertible in to leather and of this amount, only some 30% is eventually converted in to high quality leather with further 10% yielding lower grade material. The remaining part of the hide with excess processing chemicals and large volumes of water employed from the solid and liquid residues. A variety of chemicals are used in the tanning industry, including lime, sodium chloride, sodium carbonate, ammonium chloride, sulfuric acid, tannins and dyes. All tanneries need large amount of water for processing leather. High amount of reusable wastes is generated in the leather industry. Leather industries emit all the three type of waste in the form of waste water, solid waste and air emission [19].

The major solid wastes in tannery consist of dusted curing salt, wet trimmings, dry trimmings, wet shaving, buffing, non proteinous waste; non collagenous protein wastes, untanned collagen and tanned collagen. These wastes are generally separated at the source. During handling of raw skins, adhered dusted salt, which is contaminated with blood, hair, dirt and certain type of bacteria is removed and dumped. Trimmings are cuttings of edges of raw skins. Fleshing is the flesh material of the limed skins generated during fleshing operation. Chrome wet shaving is produced when skins are shaved for proper thickness after chrome tanning [20].

Except dusted salt, most of the solid wastes have a potential to generate valuable product due to its protein content. The main problem with these wastes is their high chromium content. The chrome tanned waste contains chromium in trivalent form but it was found that when the solid wastes are used in making poultry feed the chromium is converted to hexavalent form which is carcinogenic. The mixing of this metal in poultry feed could produce serious human health problems. It is estimated that for a tannery producing on an average 10,000 kilograms of skins per day, a total of about 5,500 kilograms of solid waste would be produced per day. Some of this solid waste or by-product is used in gelatin, glue, textile and artificial leather industries. It is estimated that 33% of the original protein material leaves the tannery in the form of effluent sludge, fleshing, trimmings, shavings etc., of which the greater part would appear as solid wastes [20].

About 35% of all tannery solid waste is trimming and shaving of various types. 2% of tannery solid waste account for finished waste. Waste water screenings and sludge account for about 60% of tannery solid waste. 3% of tannery solid waste is floor sweeping. Historically, shavings, trimmings and splits from the chromium tanning of hides and skins have been disposed off in landfills. However, increasing local restrictions on land disposal and the high cost of incineration have stimulated the search for alternative treatments [21].

2.4.2 Wood adhesive production process from tannery waste protein

Wood adhesives are derived by the hydrolysis of the protein constituent collagen of animal hides. Collagen in its natural state is water insoluble and must be conditioned to solubilize the protein. Collagen molecules are triple helices of amino acid sequences and contain both nonpolar and charged acidic and basic side chains.

The conversion of collagen to the soluble protein of animal glue (gelatin) involves breaking the intra- and intermolecular polypeptide bonds through the use of acid or alkali and heat.

Basic production process for wood adhesive generally involve alkaline pretreatment. The raw materials for hide glues include salted, limed, or pickled hide trimmings or splits, and chrome-tanned leather scrap. Tanned leather scrap requires special processing because of the chrome tannage. Hide glues from hide trim and splits are prepared by initial washing with water. The stock is then soaked in lime (calcium hydroxide) and water for a period of weeks, which dissolves and removes extraneous protein-related materials, as well as conditioning the collagen for subsequent glue extraction by hydrolysis. The conditioned collagen is then washed with water, followed by acidulation with dilute acid such as sulfuric, hydrochloric, or sulfurous, for pH adjustment, followed by a final water rinse.

Chrome-tanned leather scrap for hide glues may be treated initially with lime or caustic, followed by a strong acid bath to remove the tannage. The stock is then soaked in magnesium hydroxide and rinsed prior to extraction. Alternatively, the chrome stock may be treated with a magnesium hydroxide soak only, prior to extraction, in which case the chromium tanning salts remain in the residue after extraction. The treated collagen is transferred to extraction kettles or tanks, where it is heated with water to convert the collagen and extract the glue. Several hot water extractions at progressively higher temperatures are made under carefully controlled conditions. Separate, successive dilute glue solutions are removed from the stock until the glue is completely extracted, usually in four extractions.

The dilute glue extractions, ranging from 2 to 9% glue solids, are filtered and concentrated by vacuum evaporation to 20 to 50% concentration prior to drying. In some plants the glue is chilled until it will gel, then dried in tunnel dryers which circulate heated air over gelled sheets stacked on wire nets with air space between, taking up to 48 h to dry. In newer installations, the concentrated glue solutions are cooled to the gelling point and are extruded in noodle form into a continuous dryer which completes the drying in 2 to 2 and 1/2 h by circulating conditioned, filtered, heated air. The dried product, at 10 to 15% moisture content, is then ground to the desired particle size [21].

2.5 Factors influencing the quality of wood adhesive

2.5.1 Effects of humidity and water

Frank S. et al, 2013 [23] have been calculated percentage reduction of elastic properties from dry to wet to compare the results from various experiments. Form the result, the humidity is not only significantly affecting the performance of the adherent wood, but also of adhesives typically used in wood bonding themselves. Most wood adhesives are significantly softened by water contact or elevated humidity. Probably significantly influenced by the amount of humidity, results show increased variability. A very distinct softening effect was observed for phenol-based adhesives with a reduction of modulus between 20% and 100% compared to the dry state. Modulus reduction of 75% for a structural UF adhesive, other UFs, which were designed for particle board or MDF production, showed only moderate modulus reduction in the range of 10–30% in wet state compared to the dry condition. After re-drying most of the adhesives regained their original performance [24].

2.5.2 Effects of temperature

The percentage reduction of elastic properties of cured adhesives is based on a temperature increase from room temperature (around 20 ^{0}C) up to 70 ^{0}C, which reasonably corresponds to temperature conditions potentially occurring in bond service, e.g. in sun-heated roof constructions. The storage modulus (DMA), the reduction of indentation modulus (NI), and the reduction of tensile modulus of adhesive films were taken into consideration. The formaldehyde-based adhesives UF and PRF/PF, which are highly cross linked thermosets, showed only minor changes of mechanical performance at elevated temperature. UF and amine modified UF remained relatively stable with a low reduction of modulus in the range of only 10%. The same stands for PRF with a reduction of app. 25%. In case of PRF one study showed even slightly increased modulus (but also hardness) values in the temperature range up to 70 ^{0}C. A similar effect of increased modulus was observed under isothermal conditions at elevated temperature (90 ^{0}C and 150 ^{0}C, respectively) where an increase in storage modulus for PRF up to 27% was recorded. This effect is most likely due to post curing of unreacted domains within the adhesive [25].

2.5.3 Effects of post curing, ageing and creep

During their service life, adhesives in wood products undergo some alterations in properties depending on ambient mostly climatic conditions. Such changes may result in improved bond performance due to adhesive post-cure or relaxation of bond line regions or in a degradation of bond performance due to chemical deterioration of the adhesive but also the wood phase, local crack initiation or delamination and extended creep. Post curing leading to improved mechanical properties was reported for different adhesive types. Under favorable conditions a range of reaction-curing adhesives showed a further increase of e.g. storage modulus indicating a higher cross link density. Also, reorganization processes within cross-linked polymers such as the re-arrangement of methylene-ether-bridges towards more stable methylene-bridges in amino resin adhesives potentially take place. Improved bonding performance after controlled post curing was observed by a number of studies. In particle board or fiber board production it is common sense to not completely cool down panels after hot-pressing, but to stack them at elevated temperatures, which results in a significant increase in internal bond strength and decreased thickness swelling. Especially for phenolic adhesives this mechanism is extremely important for bond quality. In contrast, UF bonded panels need to be cooled down to temperatures less than 70 ^{0}C to avoid possible hydrolysis of the adhesive [26].

3. Material and Methods

3.1 Sample collection

The lime pelt was collected from Batu Tannery Sh. Co. The collected sample was stored at 4^0c until the analysis.

3.2 Raw material characterization

3.2.1 Sulphate content

Sulfide is produced by decomposition of organic matter and bacterial reduction of sulfate. It is sometimes found in industrial or municipal wastewater. The sulfide content was analyzed using APHA 4500-S method.

3.2.2 Chloride

The sodium chloride content was analyzed using Argentometry method.

3.2.3 Total nitrogen

The Kjeldahl method of nitrogen analysis is the worldwide standard for calculating the protein content in a wide variety of materials. The total nitrogen content was determined according to Kjeldahl distillation method (27).

3.2.4 Crude fiber

Crude fiber is loss on ignition of dried residue remaining after digestion of sample with 1.25% HCL and 1.25% NaOH solutions under specific conditions. Method is applicable from which fat can be extracted to leave workable residue. The crude fiber content was analyzed according to AOAC official method 962.09 (28).

3.2.5 pH value

pH is a measure of the acidity or alkalinity of a solution or material. The pH scale measures this value on a logarithmic scale from 0-14, with 0 being the most acidic and 14 the most alkaline. The test method used to analyze the pH was Modified SLTC/IULTCS1996 method (29).

3.2.6 Water soluble matter

The water soluble matter was determined using the IUC; BS1309:5 test methods. The level of water soluble present was determined by shaking the degreased leather in water. This resulting solution was filtered and a portion was evaporated, thus allowing the soluble to be quantified. The ratio of organic to inorganic substances can also be calculated by adding sulphuric acid to the dried extract (thereby converting any inorganic salts to the stable sulphate form and then ashing to remove the organic portion.

3.2.7 Calcium content

The calcium content was analyzed using APHA 3111C method (30).

3.3 Glue preparation

The sample, which has been taken from Batu tannery, was prepared for extraction by washing and soaking it with different concentration of lime (2-10%). The amount of sample was 500 g and the amount of water used for washing and soaking and neutralization was 1.5 L and 1 L respectively. The time taken for soaking was different for each reagent concentration because of their effect on the pelt. The pelt was soaked for 2 to 5 weeks in lime solution. During soaking the amount of pelt was increased from the original weight. Then boiling of the pelt in pure water was followed after washing it with several rounds of tap water and neutralization. Nevertheless, it was necessary to boil the pelt in order to achieve the entire extraction of the glue. The extraction was by using 1:2 ratio of tap water. RSM was applied to the experimental data using a commercial statistical package: Design-Expert version 7.0 (Stat-Ease Inc., Minneapolis, U.S.A). Finally, the product was dried in tray dryer prior to collection of the final product.

3.4 Analysis of Physico-chemical properties

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR analysis was according to Park et al., 2015 [56]. Room temperature single-photon emission from individual perovskite quantum dots. Acs Nano, 9(10): 10386-10393). A Perkin Elmer IR SUBTECH Spectrum ASCII PEDS spectrophotometer from 4000 to 400 cm^{-1} range, by Fourier Transformed and KBr pellets was used to obtain the absorption spectra in infrared region for the glue.

3.4.2 pH

pH of the glue solution was determined according to Modified SLTC/IULTCS1996 method (31). The sample dissolved in distilled water. After being dissolved, pH of the glue solution was determined using digital pH meter (Jenwey, model 3510).

Figure 1. pH measurement. (Arrow points to the sample)

3.4.3 Viscosity

Viscosity is defined as the resistance of a liquid material to flow. It is usually measured in fundamental units of poise or centipoise. The measurement of viscosity of glue is important to determine the quality of the product.

Procedure

First, 50 ml of 12.5% glue solution was prepared. The solution was heated to a temperature of 60°C. Finally, the sample was measured using viscometer (VK 2000, Spain) for subsequent measurement following the manufacturer user guide manual.

Figure 2. Sample in the viscometer for viscosity measurement (Arrow points to the sample).

3.4.4 Moisture content

Moisture content value is the amount of total water found in the sample. In this study, a standard method AOAC (32) was used in the determination of moisture content. In short, it was estimated from the weight loss of the glue upon evaporation at 110°C for 16 hr in an oven.

% moisture content = Original weight - Dry weight / Original weight * 100

3.4.5 Ash content

Ash refers to any inorganic material, such as minerals, present in a sample. It's called ash because it's residue that remains after heating which removes water and organic materials.

Procedure

Ash content was estimated from weight loss upon ignition at 600°C for 2 h in a muffle furnace according to AOAC (2000) method. The 10 g sample was weighed in aluminum foil. The sample was dried in an oven at 110°C for 16 h in order to evaporate the moisture. The remaining sample weight was measured. After that, the dry sample was added to the crucible and then ignited in the furnace for 2 h at 600°C. Finally, the ash was placed in a dissector for dry cooling and the amount of ash was measured.

3.5 Mechanical strength test

3.5.1 Tensile strength test

Wood was prepared according to ASTM D 903-49 method for mechanical tests. Wood specimens with dimensions of 25mm (Width), 100mm (Length) and 4mm (thickness) were cut and then coated with aluminum foil to prevent them from dust. These wood pieces were polished using sand paper, and then a constant amount of the prepared glue (30 mg/cm^2) was applied on to 3 cm by 2.5 cm area of one end of the wood pieces using brush. Then, two brushed wood pieces were left at room conditions for 5 min then assembled and pressed in a hydraulic press (Model No- 3890 Auto M; Carver, Inc., Wabash, IN, USA) at 2 MPa for 10 min. The tensile strength test was done according to ASTM D 903-49 method. Before testing, the wood specimens were conditioned for 3 days at room temperature to attain its strength. Finally, tensile strength (N) of the assembly was measured by a shear strength test using universal tester machine (model no-DIN 50106) at crosshead speed of 1 mm/min for each joint. Then, readings were taken from computer display.

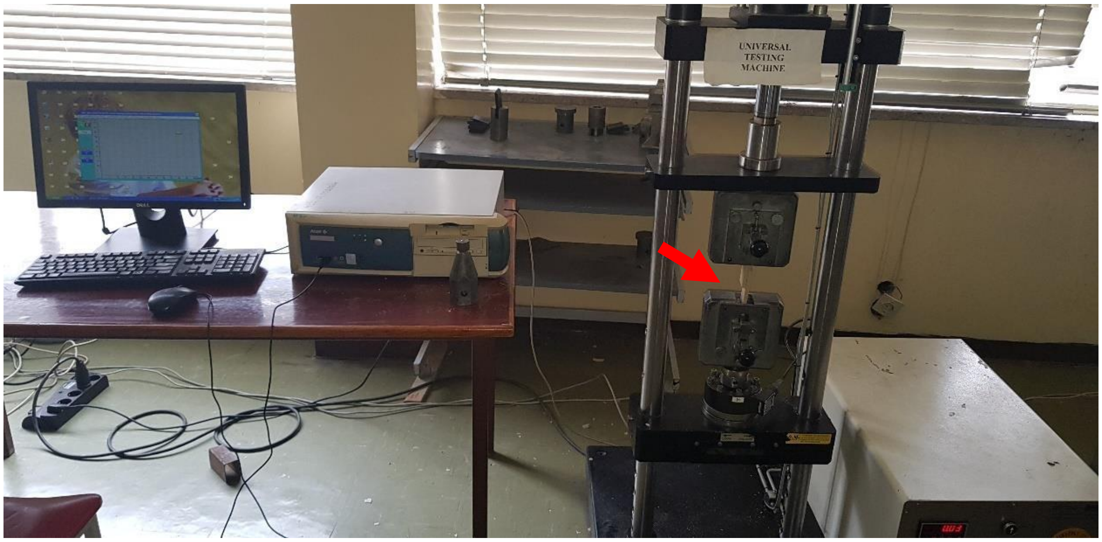


Figure 3. Universal testing machine (Arrow points to the wood sample).

3.5.2 Water Resistance

Water resistance of the wood assemblies was measured following ASTM Standard Methods D1183-96 and D1151 00 (33). The preconditioned specimens were soaked in tap water at 23 ^{0}C for 48 h, and wet strength was tested immediately after soaking.

3.6 Experimental design and Data analysis

A statistical software package (Design- Expert ®, version 7.0, Stat-Ease, Inc., Minneapolis, MN) was used for the glue extraction experiment. Response Surface Method (RSM) was used to optimize the conditions for the extraction of glue. Three factors were considered in this study. These were boiling temperature, soaking time and concentration of lime. Each factors were evaluated with two levels. Response variable of glue were assessed in terms of yield, moisture content, ash content, pH and viscosity to sort out optimum soaking time, boiling time and concentration of lime for the production of quality glue. The statistical analyses were done using analysis of variance (ANOVA), Duncan’s post-hoc test with a significant level of $p \leq 0.05$.

4. Results and Discussions

4.1 Raw material characterization results

The raw material for the production of wood adhesive, which is trimmed and flesh hide/skin, is characterized for the following parameters.

Table 1: Raw material characterization results

pH	Sulphate (mg/kg)	Calcium (mg/kg)	Chloride (mg/kg)	Total nitrogen (mg/kg)	Crude fiber (mg/kg)	Water soluble matter (mg/kg)
10.34±0.8	2134 ±9	4285±11	2342±13	25.83±2.3	8.6±1.5	5.9±1.2

Values were means ± standard deviation for three samples (n= 3)

4.1.1 pH

The result obtained from pH measurement for the lime pelt was 10.34 ±0.8. The reason for high value of P^H was excessive use of lime and sodium sulphide in the production of lime pelt. The P^H of this pelt was far above the standard limits (ISI 2000) (34) which is set to be 7.8. A large fluctuation in P^H value exerts stress on aquatic environment and may adversely affect some sensitive species of aquatic flora and fauna. The analysis made by Chowdhury et al., (35) also showed higher value of P^H which was 12.5±0.5.

4.1.2. Sulphate content

The mean sulphate concentrations in the lime pelt was 2134 ±9 mg/kg. The result revealed that the effluents of liming and unhairing stage contained very high concentration of sulphate. This was due to the use of significant amount of sodium sulphide salts. The high concentrations of sulphate in the tannery effluent may also result from many auxiliary chemicals used in the industries. This result was in agreement with the result reported by Chowdhury et al., (35).

4.1.3. Chloride content

The chloride content of the lime pelt was 2342±13 mg/kg. The mean chloride value of the pelt was much higher than the ISW-BDS-ECR (36) standard (600 mg/L) for tannery effluents into rivers and surroundings areas. The high values of chloride in the pelt might be due to the chloride salts used in hide and skin preservation, and also in the pickling process. Thus, it remains as a burden in the environment. The value was very high compared to the standard limits, indicating chloride pollution. Chloride is essential for cell functions in plant and animal life, but high level of chloride (>1000 mg/L) in water can cause human illness and can affect plant growth.

4.1.4. Calcium content

The calcium content in the lime pelt was 4285±11 mg/L. This result was significantly higher than the analysis made by S. Sivasubramanian et al, 2007(37). The higher value of calcium content indicated that the use of high amount of calcium salt usage during lime processing. Since surplus calcium salt content in lime pelt has negative effect on leather quality such as uneven reaction with dyes and fat liquor in tanned hides, it will be necessary to use the lime pelt split with other products such as glue processing.

4.1.5. Nitrogen Compounds

The concentration of total nitrogen was 25.83±2.3 which highly deviates from the standard limit (36). Significant nitrogen loads and resulting discharge of ammonia nitrogen are typically associated with tanning processes. The use of ammonium salts in the process is a main source of ammonia nitrogen in tannery effluents (up to 40 percent). Other sources of ammonia nitrogen are dyeing and animal proteins generated from beam house operations. The majority of total nitrogen matter (measured as Total Kjeldahl Nitrogen, TKN) is discharged from the liming process in the beam house operations, which, as a whole, account for approximately 85 percent of TKN load from a tanning facility. About 75% of the organic waste from a tannery was from pre-tanning processes and 70% of this waste was from hair rich in nitrogen Kamini et al., (38).

4.1.6. Water soluble matter

The water soluble matter of lime pelt was 5.9±1.2%. The level of water-soluble matter present in leather can indicate the degree of unbound tans and non-tans, salts and other substances present. The tanning process and chemicals/substances used resulted in a proportion of the tannins being bound to the skin collagen structure via hydrogen bonding. This quantification revealed that there was a proportion that will remain unbound and these, along with water soluble salts and unfixed dyes. The result obtained in this research had some variation with the report made by S. Sivasubramanian et al, (37).

4.1.7. Crude fiber

In the conventional fiber opening process, lime increases the pH from 7-8 to 12-13 and causes osmotic swelling due to ionic imbalances built up in the matrix. The hydrostatic pressure built up would enhance the splitting up of fiber bundles, separation of unwanted interfibrillary materials such as proteoglycans, globular proteins, reticulin, etc., and easy removal of flesh. However, in the case of R-amylase-based fiber opening, at least two different mechanisms can be proposed. Allen TH et al., (39) suggested that the R- amylase breaks the O-linkage between the protein and carbohydrate moiety. The conventional liming method removes all the inter fibrous materials, especially proteoglycans, and produces a system of fibers and fibrils of collagen that are clean.

4.2 Optimization of glue Production

Optimization is the act of obtaining the best result under given circumstances. In design, construction, and maintenance of any engineering system, engineers have to take many technological and managerial decisions at several stages. The ultimate goal of all such decisions is either to minimize the effort required or to maximize the desired benefit. Since the effort required or the benefit desired in any practical situation can be expressed as a function of certain decision variables, optimization can be defined as the process of finding the conditions that give the maximum or minimum value of a function.

Glues with different parameters that affect its quality were produced. The parameters were screened based on their high impact on glue quality and yield.

Table 2: Optimization of glue processing

Run	Factor 1 Boiling Temperature (°C)	Factor 2 Soaking time (week)	Factor 3 Conc. of reagent (%)	Response 1 Yield (g)	Response 2 Moisture content (%)	Response 3 Ash content (%)	Response 4 pH	Response 4 Viscosity (mP)
1	60.00	2.00	10.00	54	**13.4**	**7.21**	**8.21**	**209**
2	60.00	5.00	10.00	72	**11.6**	**3.12**	**7.1**	**190**
3	100.23	3.50	6.00	65	**13.0**	**3.21**	**5.5**	**183**
4	60.00	5.00	2.00	58	**13.6**	**4.56**	**4.0**	**153**
5	75.00	6.02	6.00	53	**11.5**	**3.10**	**6.9**	**215**
6	75.00	3.50	6.00	67	**13.9**	**2.14**	**7.2**	**195**
7	90.00	5.00	2.00	61	**16.4**	**6.21**	**6.6**	**243**
8	75.00	3.50	6.00	68	**10.1**	**1.24**	**9.2**	**154**
9	49.77	3.50	6.00	56	**12.0**	**2.10**	**6.2**	**147**
10	75.00	3.50	6.00	73	**19.7**	**1.43**	**7.5**	**250**
11	90.00	2.00	2.00	65	**14.1**	**3.14**	**8.1**	**201**
12	75.00	3.50	6.00	62	**13.2**	**3.12**	**9.0**	**229**
13	75.00	0.98	6.00	54	**14.5**	**5.21**	**6.7**	**193**
14	60.00	2.00	2.00	48.9	**16.1**	**3.21**	**7.2**	**175**
15	90.00	2.00	10.00	88.4	**14.2**	**6.54**	**8.2**	**201**
16	75.00	3.50	12.73	74	**15.2**	**3.47**	**9.5**	**234**
17	75.00	3.50	-0.73	65	**14.0**	**3.19**	**6.2**	**191**
18	75.00	3.50	6.00	68	**12.9**	**2.45**	**7.3**	**176**
19	90.00	5.00	10.00	78	**12.5**	**1.58**	**8.2**	**217**
20	75.00	3.50	6.00	73	**13.5**	**3.47**	**9.8**	**167**

4.2.1 Yield

Final Equation in Terms of Actual Factors:

Yield =
-73.22499

+2.09559 * Boiling temp.
+30.77254 * soaking time
-3.19126 * conc. of reagent
-0.23056 * Boiling temp. * soaking time
+0.044375 * Boiling temp. * conc. of reagent
+0.052083 * soaking time * conc. of reagent
-7.93700E-003 * Boiling temp. 2
-1.89364 * soaking time2
+0.087260 * conc. of reagent2

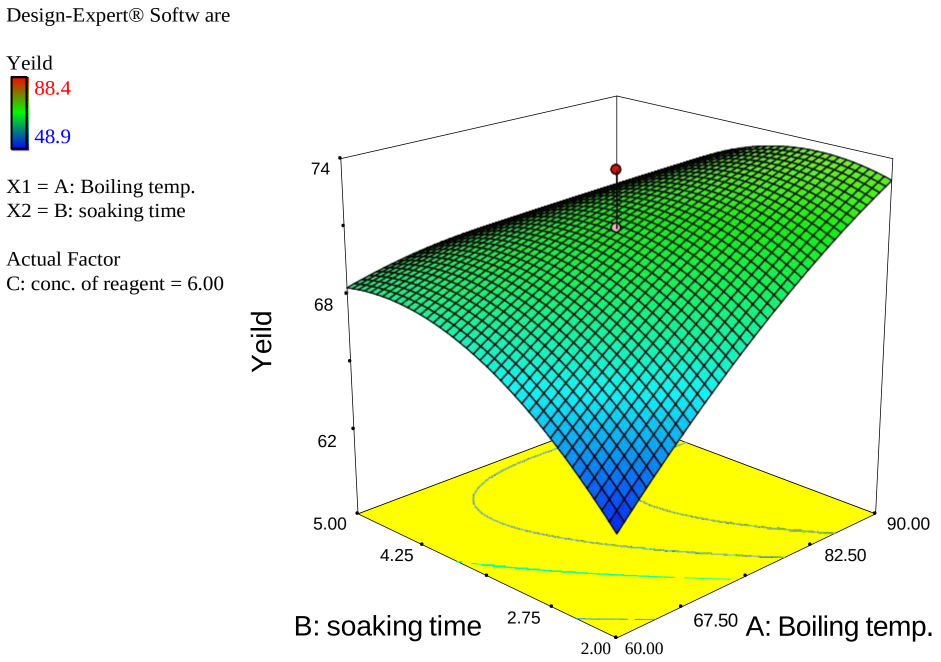


Figure 4. Effect of soaking time and boiling temperature

As it can be seen from the graph, when the soaking time and boiling temperature increases the yield shows increment up to some level. The interaction effect from the result showed that the boiling temperature has more effect on the yield than the soaking time. The highest yield approximately 69% was obtained at the boiling temperature of 75^0c and concentration of reagent at approximately 3.5.

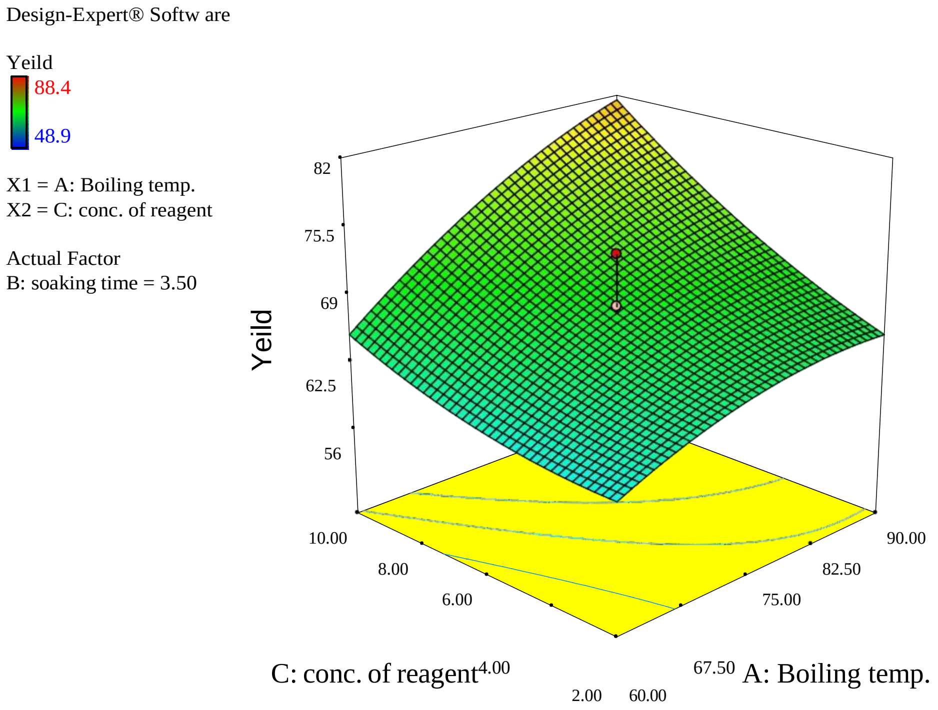
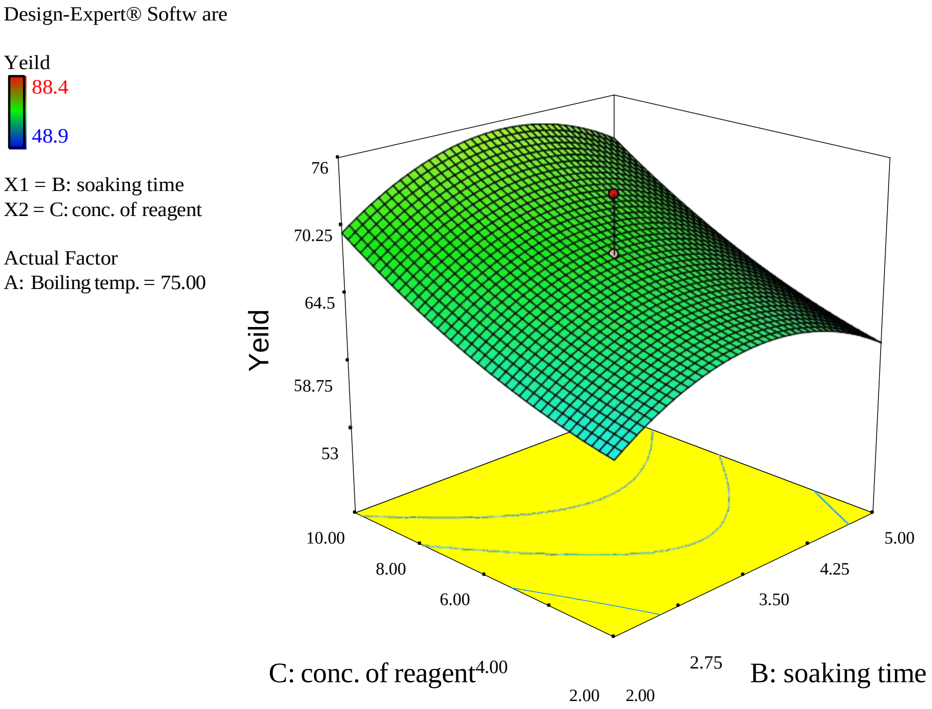


Figure 5. Effect of concentration of reagent and boiling temperature

From the above figure, it can be observed that as the concentration of reagent increases the yield increases too. As the boiling temperature increases the yield increased slightly. The interaction effect of both boiling temperature and concentration of reagent showed significant influence on the yield.


Design-Expert® Softw are
Yeild
88.4
48.9
X1 = B: soaking time
X2 = C: conc. of reagent
Actual Factor
A: Boiling temp. = 75.00
Yeild
76
70.25
64.5
58.75
53
10.00
8.00
6.00
4.00
2.00
C: conc. of reagent
2.00
2.75
3.50
4.25
5.00
B: soaking time

The above figure shows the interaction effect of soaking time and concentration of reagents on yield. It can be observed from the graph that as the concentration of reagent increase the yield increases too. And as soaking time increased up to some level the yield increases. But after the soaking time of 3.5 week the yield decreased significantly. From the interaction effect, the maximum yield was obtained at higher concentration of reagents and lower soaking time.

4.2.2 Viscosity

Higher value of viscosity was shown in the glue which was soaked in 6% lime for 3.5 week then boiled at a temperature of 75 ^{0}C. The value was 250 ±13 mP. Glue which was soaked in 6% lime and then boiled at 77 ^{0}C was shown lower viscosity. The value was 147± 2.15 mP. Akpa Jackson Gunorubon and Uku Misel [40] reported lower values of viscosity of glue from waste cattle bone which was 83.25 cp.

The viscosity increment at low temperature is probably due to linking of glue molecule to form aggregate. In other word, at high temperature denatures the protein molecule resulted in decreasing the viscosity [57].

4.2.3 pH

Higher value of pH was shown in the glue which was soaked in 3.5% lime for 3.5 week then boiled at a temperature of 75^{0}C. The value was 9.8. Glue which was soaked in 2% lime and then boiled at 60^{0}C showed lower pH value which was 4.

4.2.4 Ash content

Higher value of Ash content was shown in the glue which was soaked in 10% lime for 2 week then boiled at a temperature of 60 ^{0}C. The value was 7.21 ±13. Glue which was soaked in 3.50% lime and then boiled at 75 ^{0}C was shown lower ash content. The value was 1.24 ±23. The standard value for ash content is 2% - 5% [36]. However, Abuarra A et al., [41] reported higher values of ash content for animal-based wood bio-adhesive.

4.2.5 Moisture content

Higher value of moisture content was shown in the glue which was soaked in 6% lime for 3.5 week then boiled at a temperature of 75^{o}C. The value was 15.7. Glue which was soaked in 6 % lime and then boiled at 75^{0}C was shown lower moisture content. The value was 10.1 ±2.3.

Moisture content is the amount of water in the glue. The high amount of water in the glue makes the glue easily putrefied. The glue will be brittle in little amount of moisture. The standard value for moisture content of the glue is 8% - 16% [35]. Abuarra A [41] reported the moisture content for animal-based wood bio-adhesive to be 8.72 %.

4.3 FTIR analysis

The absorption band of the wavelength represents the functional group. The interpretation of marked FTIR spectrum used to determine the chemical bond in a molecule [58]**.** The Fourier transform infrared (FTIR) spectrum of the animal glue is shown in figure 6. The FTIR spectrum is used to identify the component responsible for sticky nature of the glue. The absorption band at 2957 cm^{-1} wave number represents CH_2 asymmetrical stretch bond [59]. The absorption peaks in the range of 2838- 2590 revealed the presence of carboxyl group [59]. The wavelength at 1923 cm^{-1} is mainly associated with the C=O stretching vibration and is directly related to the backbone conformation which is used to verify the secondary structure of protein [58]**.** Besides, it is the proof of the existence of carboxylic acid ester, indicating that an esterification reaction happens between the -COOH of the animal glue. The alkali-based hydrolysis of amide produces primary amine which is supported by the N-H bending vibration combined with C-N stretching vibration in the presences of small amount percent of C-C stretching vibrations and normally occurs in between 1550 – 1600cm^{-1} [59]. Functional groups of amine group confirmed that the existences of proteins in the latex. This proteins contribute for sticky nature of the animal glue.

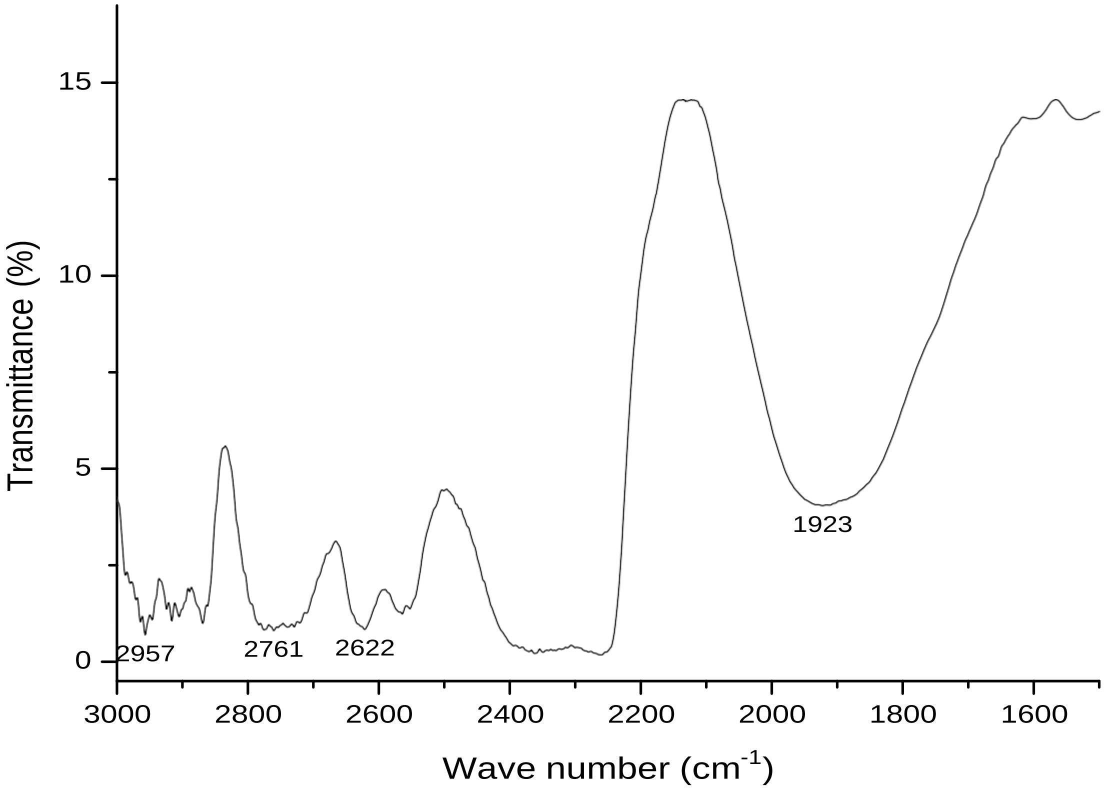


Figure 6. FTIR spectrum of the animal glue

4.4 Mechanical strength test

4.4.1 Tensile strength Strength

The Mechanical strength tests were performed for the glue produced at optimum condition from the design experiment which is Run 15 (10 % lime concentration, 2 weeks of soaking time and 90 ^{O}C Boiling point) and other two samples (Run 19 and Run 16).The three samples are selected based on the results of responses as per the experimental design.

Tensile strength at rupture is calculated by the following equation:

R_m = max. tensile force /stress area [N/mm^2]

Table 3. Tensile Strength Rm for the prepared glue

Run	**Conc. Of reagent (%)**	**Soaking time (weeks)**	**Boiling temperature (^0C)**	**Tensile Strength Rm (N/mm^2)**
15	10	2	90	15.98
19	10	5	90	13.21
16	12.73	3.5	75	5.65

Bonding shear strength of the protein glue depends on its ability to disperse in water and on the interaction between a polar and polar groups of the protein with those of the substrate. In the native protein, most of the polar and a polar groups are unavailable due to internal bonds resulting from van der Waals forces, hydrogen bonds, and hydrophobic interactions. These interactions can lead to increased adhesive strength of modified blood protein with wood. H. Lin, S. Gunasekaran, (43) reported lower values of shear strength for cow blood adhesive.

The Force-elongation-diagram (stress–strain curve) for a material gives the relationship between stress and strain. It is obtained by gradually applying load to a test coupon and measuring the deformation, from which the stress and strain can be determined. The Force-elongation-diagram for tensile test specimen for the three samples is shown in the figure below.

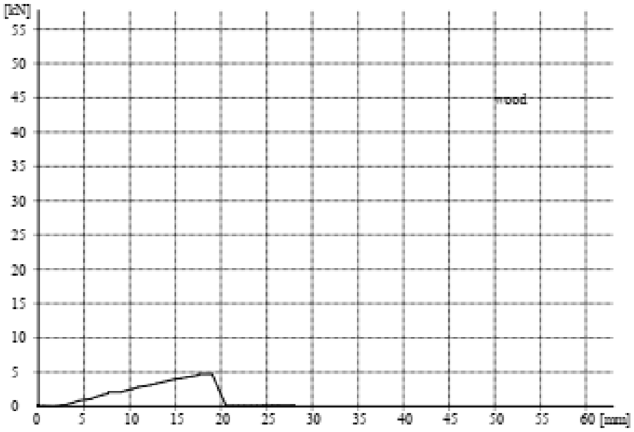


Figure 7. Force-elongation-diagram for tensile test specimen for the glue at optimized condition

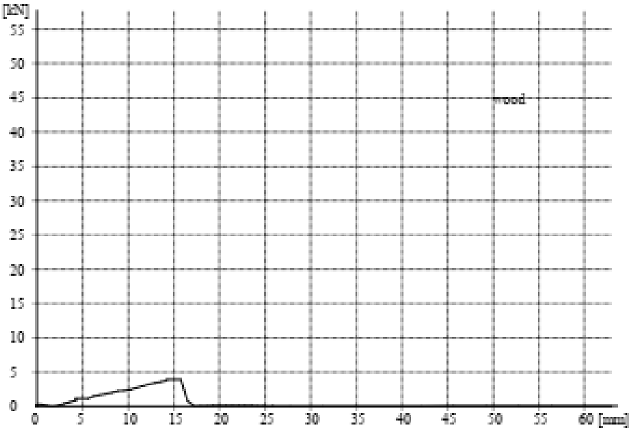


Figure 8. Force-elongation-diagram for tensile test specimen for the glue at run 19

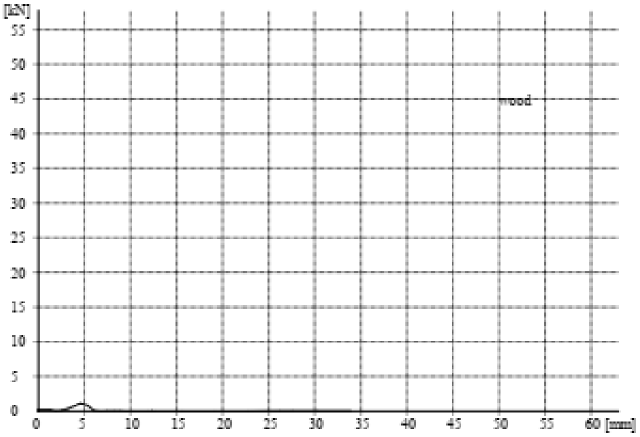


Figure 9. Force-elongation-diagram for tensile test specimen for the glue at run 16

The stress-elongation diagram for the three tensile specimen which shows the relationship between the stress applied and the percentage elongation for the glue at optimized condition is shown in the figure below.

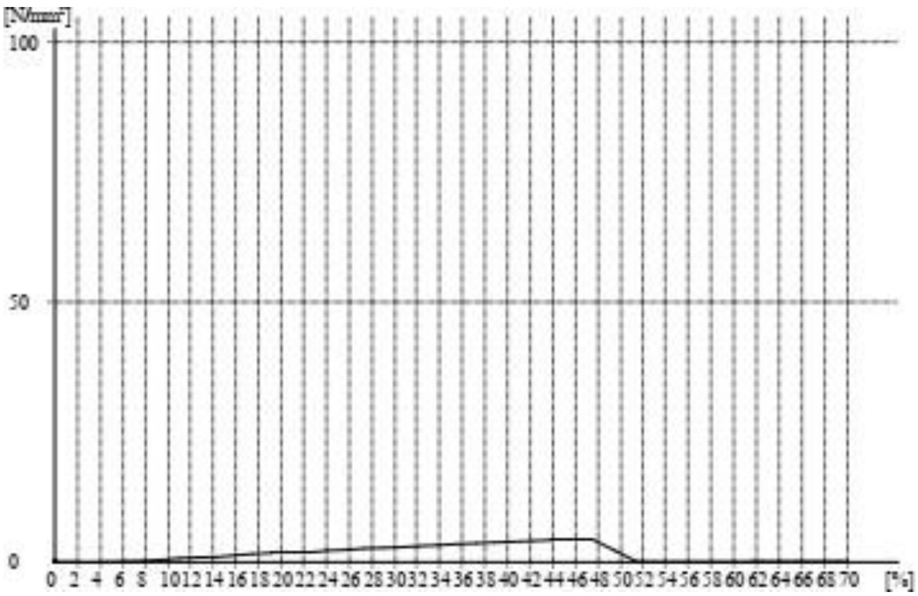


Figure 10. Stress-elongation-diagram for tensile specimen for the glue at optimized condition

From the mechanical test results, it can be concluded as the glue produced at the optimum conditions can be used as a wood adhesive.

4.4.3 Water resistance

Table 4. Water resistance of prepared glue (PG) and commercial glue (WF)

Adhesives	**Water resistance (MPa)**
Prepared glue	0.73 ± 0.08
Commercial glue	1.29 ± 0.45

The water resistance for the prepared glue was 0.73 Mpa. This value was lower as compared to the test result for commercial glue which was 1.29 MPa. The lower value of water resistance for prepared glue might be due to the inferior ability of bio based adhesives as compared to the petroleum based adhesives. Guangyan

Qi and Xiuzhi Susan Sun (44) reported higher values for water resistance value of synthetic as well as bio based adhesives.

Considering that gelatinous glues are a chemical derivative of collagen, they can generally be considered a suitable type of adhesive for skins and other collagen-based products, as they are able to develop good chemical adhesion to the substrate. Gelatin-based glues containing long protein chains (i.e. having high gel strength such as hide glue) also show very strong cohesion and would thus be an appropriate choice (Nanke Schellmann, (45). Thus, animal based glue can be considered good quality in terms of bonding strength for dry (indoor) applications but somewhat inferior for wet (outdoor) uses.

5. Conclusions and Recommendations

5.1 Conclusions

Results of optimization by response surface method (RSM) showed that extraction conditions significantly changed the extraction yield and viscosity of the extract. Numerical optimization determined the optimum extraction conditions to be soaking of the pelt in 10% lime solution, for 2 weeks and boiling at temperature of 90^{o}C. The glue characterization results indicated as the glue can be a good alternative for commercialization. Besides, the mechanical property tests confirmed the comparative shear strength with the commercial one.

5.2 Recommendations

From the aforementioned outputs obtained from the study on the optimization of glue production, the following points are recommended:

- The present study only utilizes fleshing wastes and trimmings to recycle and produce glue. However, in this study, it is highly recommended that studies in the future should consider all other leather wastes in the reutilization process.
- Other chemicals need to be considered for soaking purpose of the glue.
- It is recommended to test enzymatic hydrolysis and compare with the hydrolysis method.
- Further characterization of the glue using UV spectrum, TGA, DSC, and SEM

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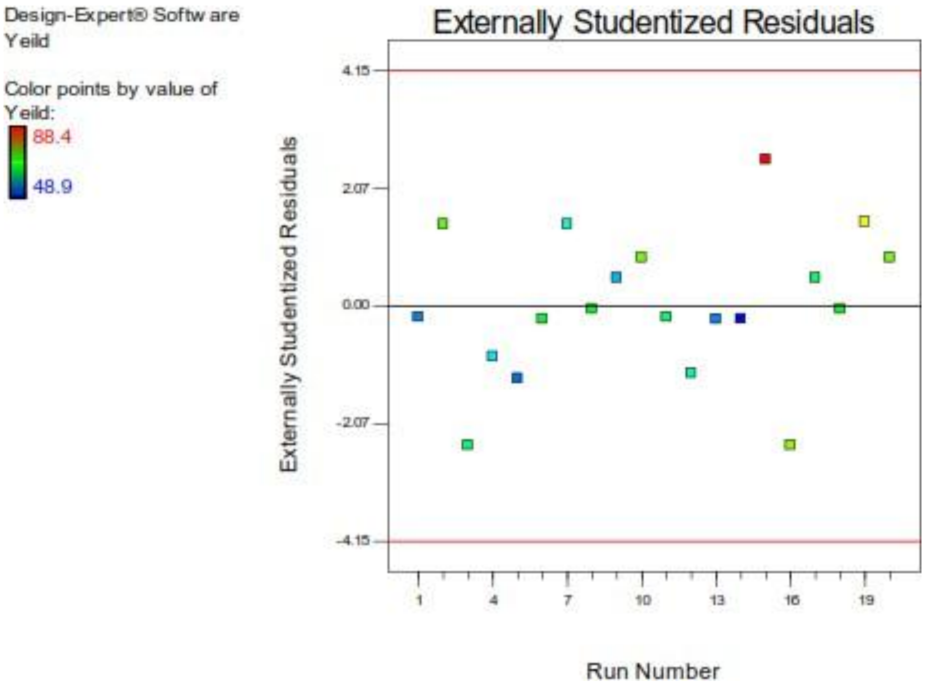
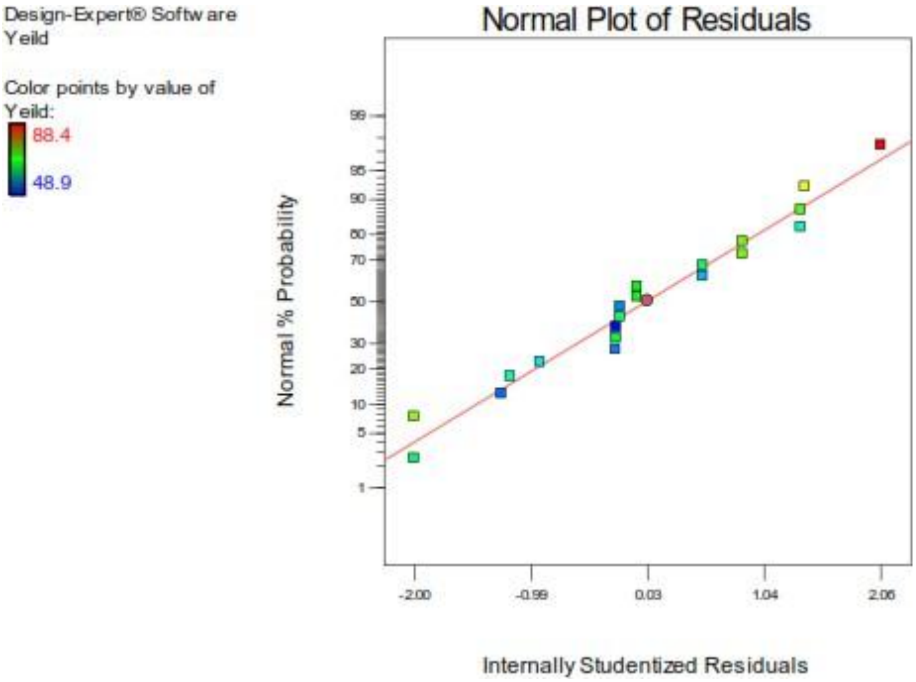
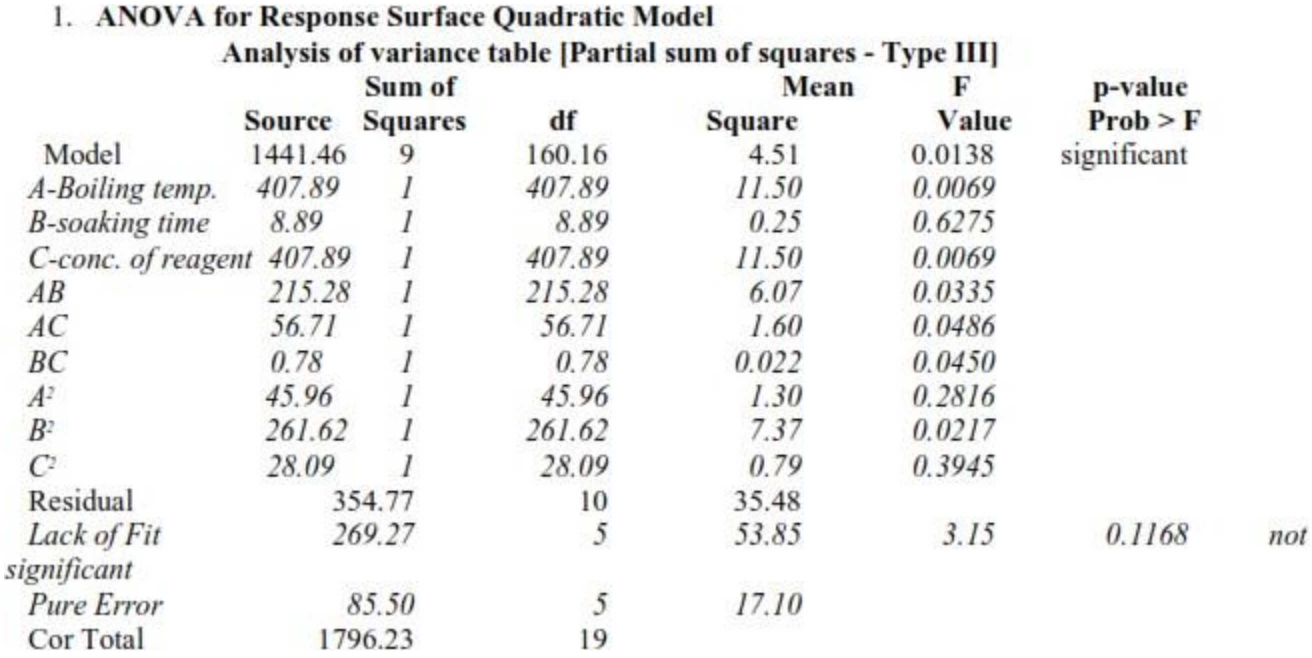
Annex

Appendix 1- Supplementary data of Experimental design







1. **ANOVA for Response Surface Quadratic Model**

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1441.46	9	160.16	4.51	0.0138	significant
A-Boiling temp.	*407.89*	*1*	*407.89*	*11.50*	*0.0069*	
B-soaking time	*8.89*	*1*	*8.89*	*0.25*	*0.6275*	
C-conc. of reagent	*407.89*	*1*	*407.89*	*11.50*	*0.0069*	
AB	*215.28*	*1*	*215.28*	*6.07*	*0.0335*	
AC	*56.71*	*1*	*56.71*	*1.60*	*0.0486*	
BC	*0.78*	*1*	*0.78*	*0.022*	*0.0450*	
A^2	*45.96*	*1*	*45.96*	*1.30*	*0.2816*	
B^2	*261.62*	*1*	*261.62*	*7.37*	*0.0217*	
C^2	*28.09*	*1*	*28.09*	*0.79*	*0.3945*	
Residual	354.77	10	35.48			
Lack of Fit	*269.27*	*5*	*53.85*	*3.15*	*0.1168*	*not significant*
Pure Error	*85.50*	*5*	*17.10*			
Cor Total	1796.23	19				

Appendix 2- Photos during laboratory activities.