Production and Characterization of Glue from Tannery Hide Trimming Waste

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Abstract. Animal glue is the most important protein adhesive obtained from animal hides, skins, and bones through hydrolysis of the collagen. The main raw material used for the study is hide trimming waste from Bahir Dar tannery plc. In this research parameter that were studied are pretreatment and conditioning techniques during animal glue production. The hide trimming waste after pretreatment were soaked for 4 h in lime solution and washed with water and followed by neutralized by hydrochloric acid. The extraction processes were taken place at temperature of 60, 65 & 70 °C and the time of 2.5, 3 & 3.5 h in water bath. After extraction the solution was filtered with nylon cloth to separate the non collageneous materials. The filtered glue solution was concentrated in rotary vacuum evaporator. Then the glue was cooled and characterized and best results were obtained at a temperature of 6 °C and at time of 3 h. The best results or quality indicators at the optimum temperature (6 °C) and time (3 h) were viscosity (90 cp), moisture content (14.6%), ash content (2.23%), density (1259 kg/m^3), yield (32 g glue/100 g of hide), PH (5.98), water solubility by color (black), and shear strength (260 MN).

Keywords: Hide · Soaking · Collagen · Hydrolysis · And glue

1 Introduction

The leather industry generally uses hides and skins as raw materials, which are the by-products of meat and meat products industry. A recent report revealed that leather and leather products are one of the major external trade sectors which contribute up to 1.39% share of the total export earnings. However, these industries are 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%. Solid wastes in leather processing constitute beam house, 80; tanning, 19; finishing, 1% [1].

An adhesive is a material that is applied to the surfaces of articles to join them permanently by an adhesive bonding process. Adhesives, also known as glue, cement,

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mucilage, or paste, is any substance applied to one surface, or both surfaces, of two separate items that binds them together and resists their separation [2]. The use of adhesives offers many advantages over binding techniques such as sewing, mechanical fastening, thermal bonding, etc. These include the ability to bind different materials together, to distribute stress more efficiently across the joint, the cost-effective of an easily mechanized process, an improvement in aesthetic design, and increased design flexibility [3]. One of Natural adhesives (glues) is Hide glue which is used in woodworking. It may be supplied as granules, flakes, or flat sheets, which have an indefinite shelf life if kept dry. Hide glue is a protein derived from the simple hydrolysis of collagen which is a principal protein constituent of animal hides. Collagen, hide glue and gelatin are very closely related with respect to protein and chemical composition. An approximate chemical composition is Carbon (51–52%), Hydrogen (6–7%), Oxygen (24–25%) and Nitrogen (18–19%) [4].

The first stage in glue or gelatin production is the pretreatment and curing process. Pretreatment is the process by which tissue is soaked in either acid or alkali in order to increase the availability of collagen to the hydrolytic environment. The pretreatment procedure used depends upon the facilities and the nature of the stock. In its natural state, collagen is water-insoluble and must be conditioned to solubilize the protein. Collagen molecules are triple helices of amino acid sequence and contain both non-polar and charged acidic and basic side chains. The conversion of collagen to soluble protein of animal glue involves the breaking of the intra- and intermolecular polypeptide bonds through the use of acid or alkali pretreatment before the extraction takes place. There are acidic, alkaline and enzymatic pretreatment methods.

Ethiopia has more than forty tannery industries that process leather for production of bags, gloves, shoes, clothes, etc. in the country. In addition to this, the country is exporting leather to abroad countries to support its economy. Even though the country has many numbers of tanneries and the tanneries support the country's economy, the wastes generated by those industries are harmful to the environment. The waste types generated in these tannery industries are hide trimming, fleshing, chrome shaving dust, glue blue, etc., In Bahir Dar tannery plc, these waste are discharged around Abbay River and some of them are simply landfilled. Hide trimming waste and other tannery wastes are dangerous for humans, animals as a whole to the environment.

Now a day's Ethiopia is importing glue from abroad countries with high currency for different purposes [5]. But many researches indicate that glue can be produced from hide trimming waste. During production, there is a step that yields a glue called an extraction. So, in the extraction process the treated/conditioned 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. Cooking at the correct temperature and for the right length of time breaks down the collagen and converts it into glue. If the temperature or timing is off, the quality of the glue will be poor and/or ruined. Therefore, the temperature and timing of extraction need to be studied carefully. So, this research focuses on the production and characterization of glue from hide trimming waste to protect environmental pollution and to save foreign currency and to determine the effect of temperature and time on the yield of glue during the extraction process.

2 Methodology

The extraction of hide glue carried out by alkaline and thermal method. The Alkaline method used for soaking in order to weaken the peptide bond which holds protein molecule together and the thermal method was used to break down the peptide bond completely.

2.1 Glue Production

Raw Material Preparation: 10 kg of samples were brought from Bahir Dar Tannery plc. The sample was cleaned with tap water. Large size of hide was cut with uniform size (2 cm × 2 cm) by using sharp knife. 1% sodium hydroxide solution was prepared (8 g of sodium hydroxide pellet was dissolved in 200 ml of water). 100 g of cutted hide trimming waste sample was weighed by beam balance and dropped in to the plastic jar which contains the NaOH solution. The plastic jar which contains the sample was shaken for 4 h at 120 rpm.

Glue Extraction: The collagen solution which was obtained from the soaked hide was transferred to the extraction vessel by water bath. The extraction was taken place at various time (2.5, 3 & 3.5 h), and temperatures (60, 65 and 70 °C). After extraction process completed, none collagen part from the extraction vessel was separated from the liquor solution. The liquor solution was filtered by using nylon cloth and concentrated using vacuum evaporator. The concentrated glue was cut by knife in to flake forms. The flake glue was characterized and finally packed.

2.2 Physicochemical Analysis

Moisture Content: The ash and moisture content of glue was determined by using Association of Official Analytical Chemists (AOAC International) method [6]. The 10 g sample was measured and transfer to Petri-dish with a temperature of 103–105 °C for 1 h. After 1 h, the moisture content was determined by the equation of above literature. 2 g mass of sample was weighed before drying (m_1) and Mass of sample was weighed after drying (m_2). The moisture of the sample was obtained by subtracting m_2 from m_1. Then the moisture content of the sample was determined by the following formula.

$$\text{Moisture content}\,(\%) = \frac{\text{Weight of moisture in glue} \times 100\%}{\text{Weight of glue before drying}} = \frac{(\text{m1} - \text{m2})}{\text{m1}} \times 100\% \tag{1}$$

Ash Content: The ash content of glue was determined by taking 2 g of sample in the furnace at 950 °C for 12 h. 2 g mass of sample was weighed before burn (m_1) and Mass of sample was weighed after burn (m_2). Ash content of the glue was determined by the following formula:

$$\text{Ash content }(\%) = \frac{\text{Mass of dry glue sample } \times \text{ } 100\%}{\text{Mass of original glue sample}} = \frac{\text{m2}}{\text{m1}} \times 100\% \quad (2)$$

Viscosity Determination: The Viscosity profile of the glue was obtained using a viscometer (LvDv I+, Brookfield, USA) with the spindle set at 200 rpm and at a temperature of 60 °C following the technique proposed by Association of Official Analytical Chemists (AOAC International) [3].

Water Solubility of Adhesive Resin: Water solubility of the cured resin was tested depends on the conations of water (hot or cold). One gram of cured resin was finely grounded and soaked in 5 ml of water for five days. The water solubility was soak solution. Any discoloration in the soak solution is an indication that the resin has not been fully cured and the adhesive is dissolving in water the darker the color of the soak solution, the greater the solubility of the resin [3].

Determination of Density: The densities of the glue were determined by taking the weight of a known volume of the glue in a density bottle (pycnometer) using an analytical balance.

$$\text{Density of glue} = \frac{\text{Mass of glue obtained}}{\text{Volume of solution taken}} \quad (3)$$

Shear Strength: The test consists essentially of two rectangular sections, typically 25 mm wide, 100 mm long and 1.6 mm thick, bonded together, with an overlap length of 25 mm ASTM (American Society for Testing of Materials). The single-lap specimen is easy to prepare and test. A fixture is used to ensure correct overlap and accurate alignment of the adherend. This may include control of the fillet. Testing can be conducted using standard tension/compression mechanical test equipment. The lap-shear strength (t) is given by: [7].

$$\text{t (shear strength)} = \frac{\text{pressure}}{\text{area}} = \frac{\text{P}}{\text{bL}} \quad (4)$$

3 Results and Discussion

The laboratory test results of some quality indicators performed on the produced glue are shown in Table 1.

Table 1. Laboratory test result of quality indicator for produced glue at optimum conditions.

Parameter	Produced glue	Standard glue	Deviation
PH	5.89	6.06	0.17
Density (g/cm^3)	1.259	1.270	0.11
Viscosity (cp)	90	80.0	10
Moisture content (%)	14.6	15.0	0.4
Ash content (%)	2.23	2.00	0.23
Solubility (color)	Black	Black	0
shear strength (MN)	260	$>$200	60

Table 1 shows that the quality indicator ash content had the maximum deviation while PH had the minimum deviation density between the values of the quality indicators for standard glue compared with values obtained for the produced glue.

The hide extracted glue was solubilized completely in hot water 50–55 °C, but the solubility was decreased in cold water. The colors of all the dissolved glue are black shows that the glue is best soluble in water.

Density is the mass per unit volume of a substance; increase in water quantity in produced glue increases the volume of the glue thus reduces its density. Increase in water content of the glue makes the glue less dense, hence reduces its ash content.

PH is a measure of acidity or basicity of glue. The standard PH value of glue is 6.06. The most equivalent PH value of the produced to the standard glue (6.06) is 5.89 with deviation of 0.17.

The viscosity of the produced glue was higher when compared with standard glue, this might be due to the temperature of glue was lower.

The moisture content of the glue was small to compare with standard glue this due to the length of time was higher in the vacuum evaporator. So that most of water removed.

The higher ash content shows that the glue contains inorganic substance. This is because of salt and other substance which retards the rate of burning.

The shear strength of the produced glue was higher than the standard glue. This might be the extraction process was takes place at optimum parameter.

3.1 Effect of Temperature on Physiochemical Property of Glue

Effect of Temperature on Yield: Temperature is one of the basic important factors for the production of hide glue, because hide glue is protein in nature and proteins denature at high temperature. So, determining the optimum temperature is one of the major tasks during glue production. As shown in Fig. 1 below the yield is highest (32 g glue/100 g hide) at 65 °C. But above and below 65 °C the yield is lower. This due to denaturation of the glue (above 65 °C) and there is still some unextracted glue with the hide (below 65 °C).

It is also because elevated temperature (i.e., 65 °C) breaks high amount of collagen in the pelt, which in turn facilitates the conversion of collagen in to glue than low temperature [8].

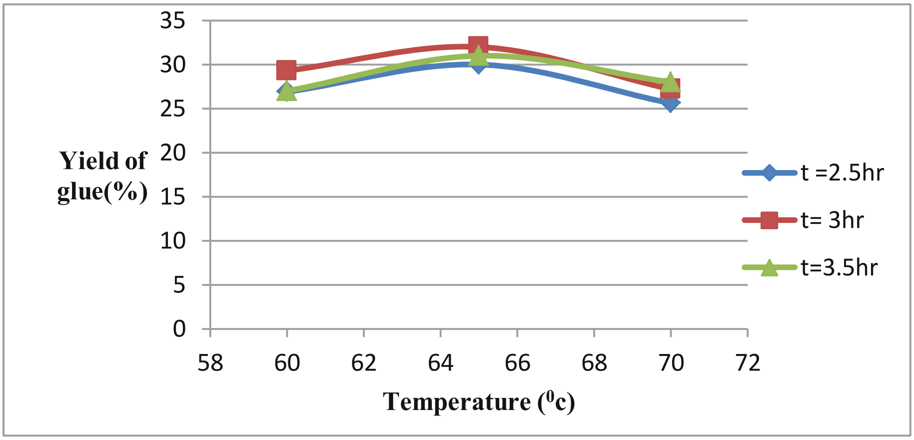

Fig. 1. Effect of temperature on yield

Effect of Temperature on Viscosity: Viscosity is the resistance to flow. The more water added to the glue, the lighter and less sticky it becomes, it flows faster (its resistance to flow reduces). Hence, the viscosity reduces. As shown in Fig. 2, the maximum viscosity is occurred at a temperature of 65 °C. But after this temperature the viscosity is gradually decreased. Therefore, the best temperature that gives the maximum viscosity (90 cp) is 65 °C. The viscosity increment at this temperature, i.e. 65 °C, is probably due to linking of glue molecule to form aggregate. In other word, at high temperature the protein molecule may denature [9].

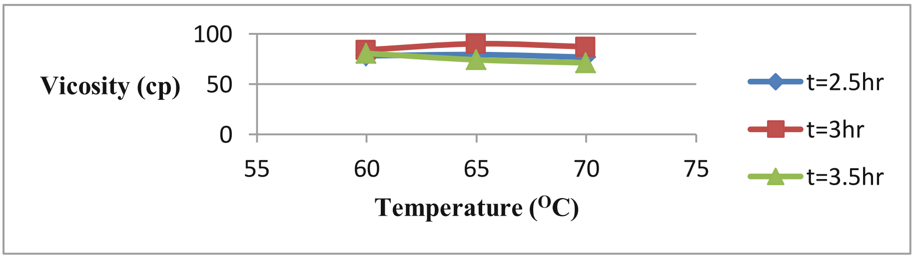

Fig. 2. Effect of temperature on viscosity

Effect of Temperature on Moisture Content: At temperatures of 60, 65 and 70 °C, the corresponding minimum moisture contents are 15.04, 14.6 and 15% respectively. Generally, the moisture content of the glue increases, as the temperature increases except for the time of three hours (Fig. 3). The lower the moisture content is the better the glue.

So, the optimum temperature is 65 °C which gives 14.6% moisture content that is less than the standard value (which is 8%–16%). 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% [10].

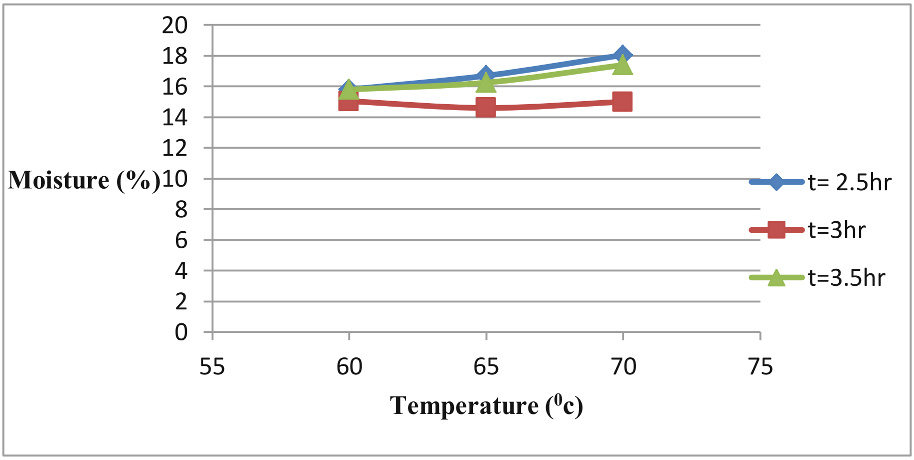

Fig. 3. Effect of temperature on moisture content

Effect of Temperature on Ash Content: Ash content is the amount of residue obtained when a sample is burnt under controlled condition so that all ignitable mass is removed. The denser the glue, the more the ash obtained [11]. Increase in water content of the glue increases the volume of the glue and reduces its density. Therefore, increase in water content of the glue makes the glue less dense, hence reduces its ash content. The lower the ash content is the better the glue. As shown from Fig. 4, the minimum ash content (2.33%) is occurred at a temperature of 60 °C. The ash content also increased with temperature. So, the optimum temperature for the case of ash content is 60 °C. The ash content of the glue is affected by the curing method used. The standard value for ash content is 2%–5% [10, 12].

Effect of Temperature on Shear Strength: The higher the shear strength is the better the glue. From Fig. 5 shown below the maximum shear strength (260 MN) occurs at 65 °C. So, the optimum temperature that gives the maximum shear strength of the glue is 65 °C. This is the most important of all the test factors and, unless considered in conjunction with this, the others are of only limited value. The stronger a glue, the greater the resistance offered by its jelly to outside pressure [12].

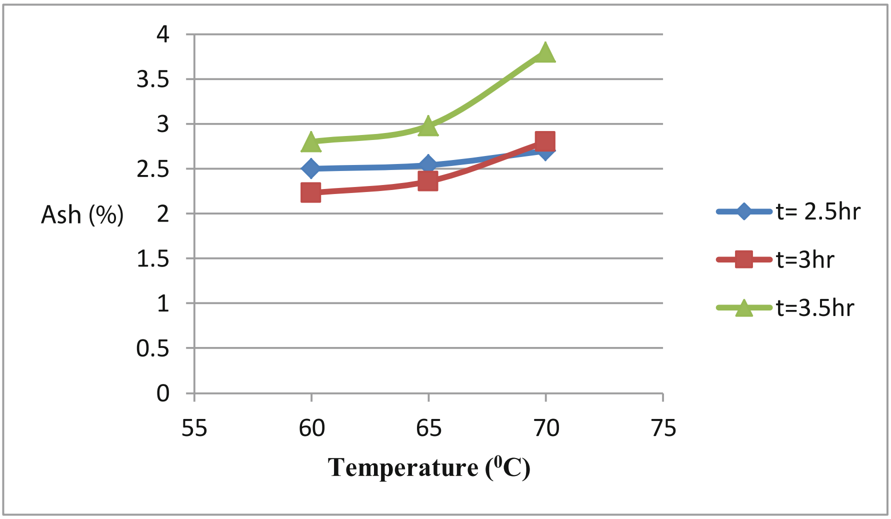

Fig. 4. Effect of temperature on ash content

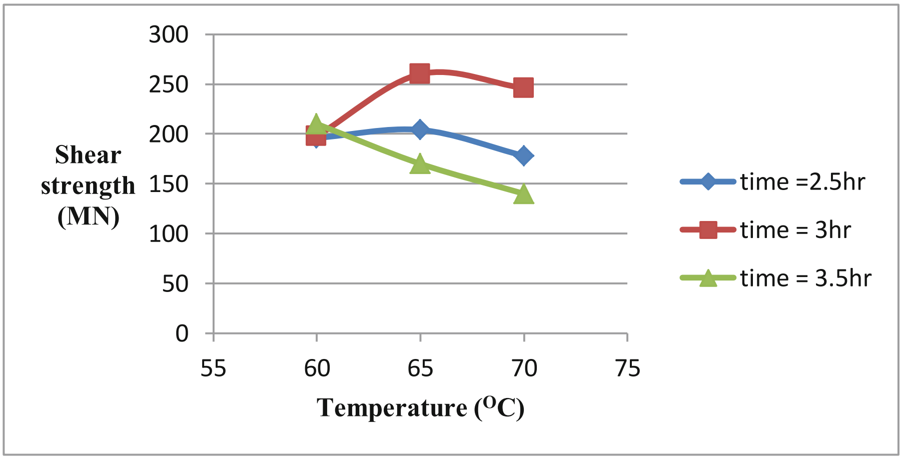

Fig. 5. Effect of temperature on shear strength

3.2 Effect of Time on Physio-Chemical Property of Glue

Effect of Time on Yield: Not only temperature affects the yield of glue, but time also affects its amount in the extraction process. So, determining the optimum time requirement is important for glue production. From Fig. 6 below the highest yield is obtained at 3 h. But before and after 3 h duration of extraction time the yield is lower. This is due to before 3 h there is still some unextracted glue with the hide and after 3 h there is some denaturation of the glue. Generally, the yield is maximum at 65 °C and 3 h [8].

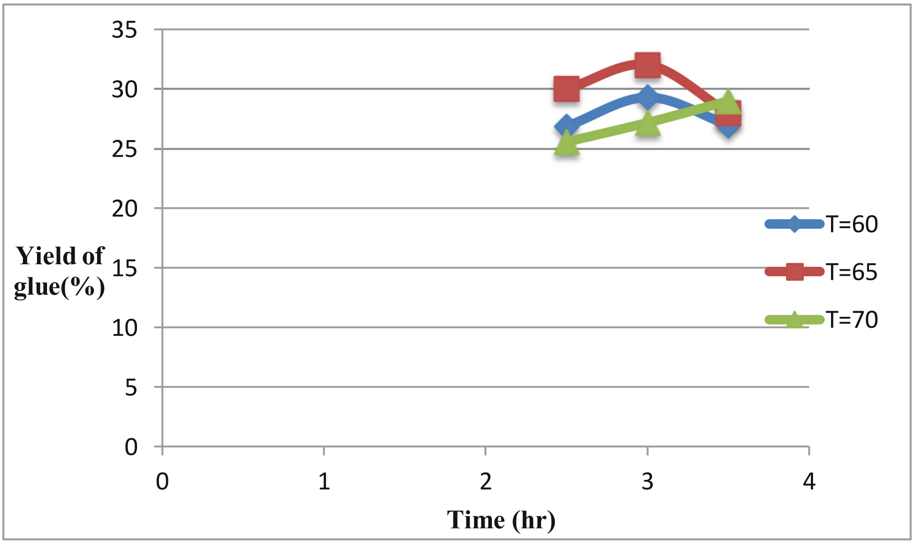

Fig. 6. Effect of time on yield

Effect of Time on Viscosity: As shown in Fig. 7 for the case of time effect, the maximum viscosity is occurred at a time of 3 h. So as shown from Figs. 2 and 7, the maximum viscosity is obtained at a temperature of 65 °C and a time of three hours, this is probably due to the time needed for linking of glue molecule to form aggregate [9]. Therefore, the optimum time and temperature are 3 h and 65 °C.

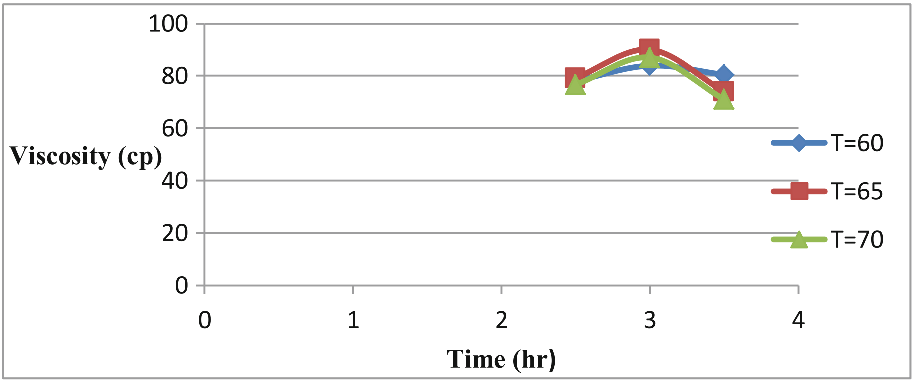

Fig. 7. Effect of time on viscosity

Effect of Time on Moisture Content: Time has an equivalent effect on the moisture content of the glue as temperature. As shown from Fig. 8, the minimum moisture content is 14.6% at a time of 3 h. So, the optimum time that gives the minimum moisture content (14.6%) is 3 h. Generally, as shown from Figs. 3 and 8 the optimum time and temperature are 3 h and 65 °C respectively [10].

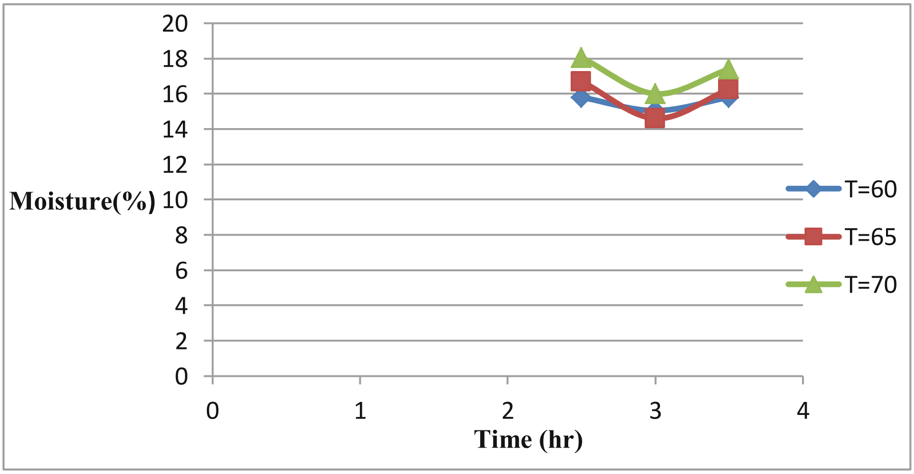

Fig. 8. Effect of time on moisture content

Effect of Time on Ash Content: As shown from Fig. 9, the ash content is minimum at a time of 3 h. So, the optimum time and temperature that gives the minimum ash content (2.23%) are 3 h and 60 °C. This value (2.23%) is almost equivalent to the standard value (2.0%) [10, 12].

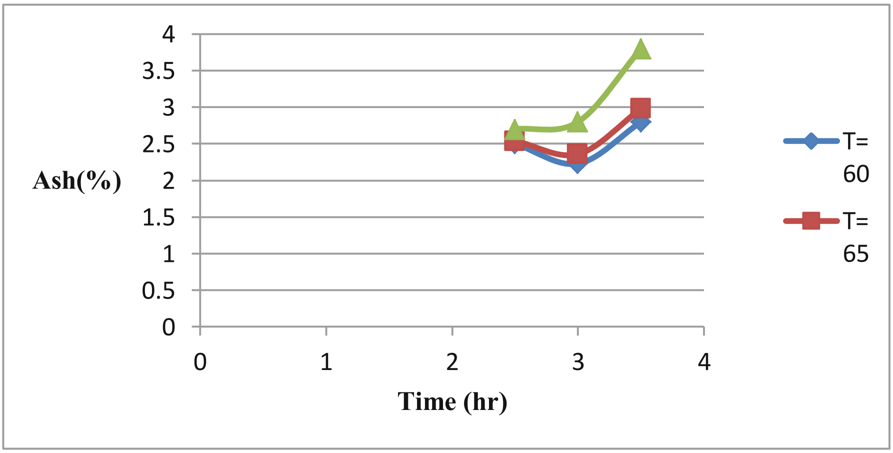

Fig. 9. Effect of time on ash content

Effect of Time on Shear Strength: The maximum shear strength (260 MN) occurs at a time of 3 h. Above three hours of extraction time the shear strength of the produced glue declines very quickly as shown in Fig. 10 which is due to the presence of non-collagen materials in the glue and resulted in denaturation of glue. Generally, the optimum time and temperature that gives the maximum shear strength are 3 h and 65 °C respectively [12].

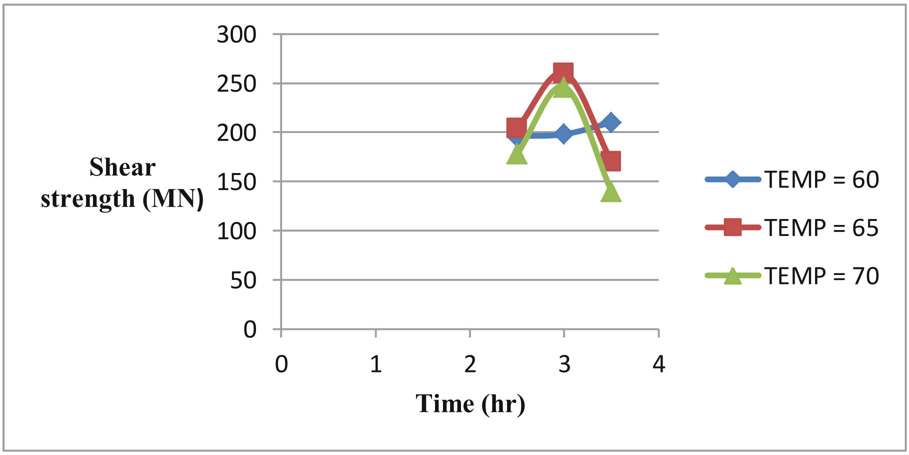

Fig. 10. Effect of time on shear strength

4 Conclusion

One of the well-known types of glue is animal glue. Animal glue could be bone glue, hide glue, fish glue, flesh glue, etc. Hide glue is the most important type of animal glue. It can be produced by the methods that were developed by the above work. The ph, density, viscosity, moisture content, ash content, solubility (color) and shear strength with the value of 5.89, 1.259 g/cm^3, 90 cp, 14.6%, 2.23%, black color and 260 MN were obtained are within the standard range. The effect of temperature and time during extraction of glue also investigated and showed that the optimum value were 65 °C and 3 h for temperature and time respectively. So producing hide glue by the method that was formulated in the above is acceptable.

Even though Ethiopia has plenty of raw materials from its tannery industries for the production of animal glue; it is still importing glue from abroad countries with high currency. Therefore, producing glue by studying its feasibility to replace the imported glue and saves foreign currency is not questionable.

References

1. Aftab, Md., et al.: Resource addition to leather industry: adhesive from chrome shaving dust. J. Sci. Innov. Res. **6**(4), 138–141 (2017)
2. Adhesive – Wikipedia. https://en.wikipedia.org/wiki/Adhesive. Accessed 24 Mar 2019
3. ASTM D2559-04: Standard Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions, ASTM International, West Conshohocken, PA (2004)
4. Hide Glue Info | Bjorn Hide Glue. https://bjornhideglue.com/hide-glue-info/. Accessed 24 Mar 2019
5. The data source for import statistics i.e. Ethiopian Revenue and Customs Authority and Central Statistic Agency of Ethiopia. http://www.csa.gov.et

6. Horwitz, W. (ed.): Official Methods of Analysis AOAC International, 17th edn. Association of Official Analytical Chemists, Gaithersburg (2000)
7. Broughton, W.R., Mera, R.D.: Review of durability test methods and standards for assessing long term performance of adhesive joints. National Physical Laboratory Teddington, Middlesex, UK (1997). ISSN 1361-4061
8. Pizzi, A., Mittal, K.L. (eds.): Handbook of Adhesive Technology, 2nd edn. Taylor & Francis Group, LLC, New York (2003)
9. Thomas, R.K.: Encyclopedia of Chemical Technology, vol. 12, pp. 436–440. Wiley. http://www.scribd.com/doc/30116669
10. Hand World lingo, Animal glue. http://www.worldingo.com/ma/enwiki/en/animalglueanf.htm. Accessed 27 Nov 2010
11. Milligan, M., Higgins, B.: Hide Glues. Bone Glues and Industrial Gelatins, Johnstown, New York, USA (2009)
12. Testing of glue. http://www.oldandsold.com/articles30/glue-2,shtml. Accessed 27 Apr 2018
13. Taylor, M.M., et al.: Chemical modification of protein products isolated from chromium-containing solid tannery waste and resultant influence on physical and functional properties. JALCA **94**, 171–181 (1999)
14. Khatoon, M., Kashif, S., Saad, S., Umer, Z., Rasheed, A.: Extracton of amino acids and proteins from chrome leather waste. J Waste Recycl. **2**(2), 6 (2017)
15. Islam, R.M.S.: Physical, chemical and environmental parameter of glue manufacture in Bangladesh. IOSR J. Appl. Chem. (IOSR-JAC) **11**(2), 1–7 (2018)
16. Hadush, A., Hagos, Z., Gebrehawaria, G., Brhane, Y., Gopalakrishnan, V.K., Krishna Chaithanya, K.: Production and characterization of animal glue from solid skin waste of Axum town, Ethiopia. J. Pharm. Res. **12**(2), 174–177 (2018)
17. Gunorubon, A.J., Misel, U.: Production of glues from animal bones. ARPN J. Eng. Appl. Sci. **9**(9), 1592–1597 (2014)
18. Milligan, M., Higgins, B.: Hide Glues. Bone Glues and Industrial Gelatins. Johnstown, New York (2009)
19. Animal glues: a review of their key properties relevant to conservation. https://www.researchgate.net/publication/272311539
20. Omm-e-Hany, Syed, S.S., Beena, Z., Aamir, A., Asia, N.: Wood adhesives derivation from tannery waste protein: a comparison with some commercial wood adhesives. Bull. Env. Pharmacol. Life Sci. **4**(7), 172–178 (2015)
21. Sunder, V.J., Gnanamani, A., Muralidharan, C., Chandrbabu, N.K., Mandal, A.B.: Recovery and utilization of proteinous wastes of leather making: a review. Rev. Environ. Sci. Biotechnol. **10**, 151–163 (2011)
22. Frihart, C.R., Hunt, C.G.: Adhesives with wood materials, bond formation and performance, chapt. 10, pp. 10–24 (2010)
23. da Silva, L.F.M., Öchsner, A., Adams, R.D. (eds.): Handbook of Adhesion Technology. Springer, Heidelberg (2011). https://doi.org/10.1007/978-3-642-01169-6