Scientific Research Publishing

Journal of Materials Science and Chemical Engineering, 2024, 12, 1-9
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Physical and Chemical Properties of Horns Sheaths Particles for the Manufacture of Composite Materials

Tawe Laynde[1], Zakari Yaou[2], Karga Tapsia Lionel[3], Konai Noel[2], Danwe Raidandi[2]

[1]Department of Wood Construction, University Institute for Wood Technology, University of Yaounde 1, Yaounde, Cameroon
[2]Department of Industrial and Mechanical Engineering, National Advance School of Engineering, University of Yaounde 1, Yaounde, Cameroon
[3]Department of Mechanical Petroleum and Gas Engineering, National Advance School of Mines and Petroleum Industries, University of Maroua, Maroua, Cameroon
Email: tawecm5@yahoo.fr

How to cite this paper: Laynde, T., Yaou, Z., Lionel, K.T., Noel, K. and Raidandi, D. (2024) Physical and Chemical Properties of Horns Sheaths Particles for the Manufacture of Composite Materials. *Journal of Materials Science and Chemical Engineering*, **12**, 1-9.
https://doi.org/10.4236/msce.2024.125001

Received: February 29, 2024
Accepted: May 7, 2024
Published: May 10, 2024

Abstract

Salvaged cow horns from slaughterhouses have been transformed into fine particles for a physical characterization that has led us to determine the humidity rate (2.34% ± 0.054%), the actual density situated between 0.586 g/cm^3 and 0.732 g/cm^3, the swelling rate (12%), and one chemical characterization that permitted us to determine the rate of dry matters (97.05%), of mineral matters (2.5%), of protein matters (94.52%). From these weak values, it can easily be seen that cow horn case doesn't absorb much water and improve the mechanical characteristics of the composite; the high rate of protein shows that keratin which is the structural molecule favors its gripping as reinforcing element in the manufacturing of composite materials.

Keywords

Horns, Fibers, Polymer Loads, Physical Properties, Chemical Composition

1. Introduction

For many years, laboratories and technical centers spread around the world have focused their research on how to insert vegetal and animal fibers into materials. These research works tend to preserve the environment and reduce the exploitation of non-renewable materials. The idea of using horns keratin from hoof in industry is not new; in fact, materials containing keratin such as wool, hairs, bird feathers…now constitute a real field of interest for scientists. They are being used in many fields such as medicine for treatment, in electronics for optoelec-

tronics, bio drawers or even in our everyday life for housing and clothes, since they are light, cheap, have interesting mechanic properties, di-electric, chemical, thermal and optical and upon all, they are abundant in nature. Instead of considering these materials as a waste without any added value, valorizing them through the exploitation of their properties and their salvaging in other industrial sectors constitute nowadays a real challenge for scientists. For example, physic-mechanical properties of bio-based bricks [1], mechanic and physical properties of particle board panels produced with horns sheaths [2], and African tree bark exudate extracts as bio hardeners of fully bio sourced thermoset tannin adhesives for wood panels [3] was studied. Our present study aims at taking both scientific and environmental steps into the said field. Some research works have been realized on the characterization of keratin as biomedical material [4] and others were based on the mechanical characterization of cow horns case through digital correlation [5] and, according to the water absorption rate and the stand of horns fibers [6]. Further research works have been carried out later on, based on this fiber as load with epoxide matrix [7]. The use of this fiber as load has led us to find out the physical and chemical properties that make its qualities or peculiarities as load in the manufacturing of composite materials.

2. Materials and Methods

2.1. Preparation of Raw Material

The horn processing process is shown in **Figure 1**. The beef horns in **Figure 2(a)** are collected from the Maroua slaughterhouse and washed with water and caustic soda to clean the fat. Then, they are dried at room temperature for 48 hours before being crushed into fine particles (**Figure 2(b)**) then packaged.

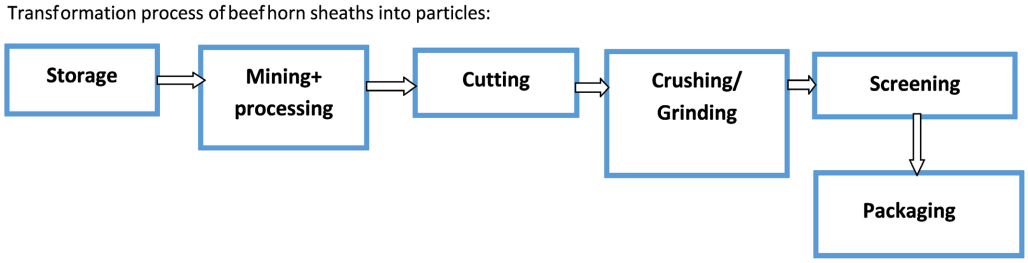

Figure 1. Synoptic diagram of the transformation of beef horn sheaths into particles.

(a) (b)

Figure 2. (a) Beef horn sheaths; (b) fine sheath particles almost ready to be used.

2.2. Physical Properties of Bovine Horn Powder

2.2.1. Moisture Content of Horn Powder

We use 10 ceramic crucibles in which we pour the micronized powder after recording the mass m_{ih} of each. We place the test pieces in the oven and set the temperature at 103˚C. We dry it for 72 hours. We record the set masses which are the dry masses of the test pieces [8]. We calculate the moisture content T_{ih} of each test piece.

The moisture content is obtained by averaging the records of the moisture content of the specimens obtained from the following relationship:

$$T_{ih} = \frac{m_{ih} - m_{is}}{m_{is}} \times 100 \tag{1}$$

where

m_{ih} = wet mass of the powder;

m_{is} = dry mass of the powder;

T_{ih} = Wetness rate of the powder.

2.2.2. Density of Bovine Horn Powder

The determination of the density of a powder is determined by the way it is used. The powders are poured into a container placed on a tared scale to measure the mass. The entire device is placed in a blender. During extrusion, cohesiveness is obtained by melting the resin. The horn sheath powder behaves as if it were wet. We then perform two types of density measurements:

The poured density;

The wet density.

Apparent density or poured density: It consists of placing a volume with a capacity of 1 m^3 empty on the SEDITECH scale, precision to 1/1000e and taring. Fill it with horn sheath powder, for a volume υ_i of the powder, we find a mass mi. The experiment is repeated 10 times, the density value is determined by the formula bellow:

$$\rho_{\upsilon_i} = \frac{m_i}{\upsilon_i} \tag{2}$$

Wet density: it consists in pouring distilled water of a mass m1 into a balloon of volume V_0 of mass m_0. Then add a mass m_2 of powder in the balloon and allow the entire device to rest. Use the formation of air bubbles and measure the mass m_3. The wet density is calculated by the relationship (3). The experiment is repeated 10 times and the average of the records is determined, which is the wet density of the powder.

$$\rho_m = \frac{\rho_{water}\left(m_2 - m_0\right)}{\left(m_2 - m_0\right) - \left(m_3 - m_1\right)} \tag{3}$$

with m_0: mass of the balloon;

m_1: water mass;

m_2: mass of the powder;

m_3: water mass + powder + balloon, ρ_{water} = 1 g/cm^3.

2.2.3. Swelling Rate

The principle consists of relating the volume of the substrate sample after immersion to the volume occupied by this dry substrate sample. For example, a 25 g sample of ground beef horn sheath was hydrated at room temperature (25˚C) with 250 ml of demineralized water in a 1000 ml graduated burette. After adding demineralized water, the mixture was slightly shaken, covered and left for 18 hours for complete hydration. Excess water is removed by filtration. The volumes occupied by the sample before and after immersion were read directly into the burette after impact settlement (250 strokes.min^{-1} for 3 minutes) at Densitap ETD-20. The swelling was calculated according to the formula (4):

$$TG = \frac{V_I - V_S}{V_S} \times 100 \tag{4}$$

where

V_I: volume occupied by a given sample mass after immersion;

V_S: volume occupied by this very sample, dried before immersion.

2.3. Chemical Composition of Bovine Horn Granules

2.3.1. Water and Volatile Matter Content

Water and volatile matter content is determined in accordance with French standard NF V 03-903. It is equivalent to the mass loss experienced by the sample after being dried in an oven at 103˚C ± 2˚C until it reaches constant weight. Rated H, the water and volatile matter content is expressed as a percentage by mass and is equal to:

$$H = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{5}$$

where

m_0: is the crucible tare (in g);

m_1: is the mass of the crucible and the test sample before heating (in g);

m_2: is the mass of the crucible and the residue after heating, up to weight constant (in g).

Also expressed as a percentage by mass, the dry matter content of the sample is rated MS and is deduced from the value of H:

$$\mathrm{MS} = 100 - H = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \tag{6}$$

2.3.2. Mineral and Organic Matter Content

Mineral content (or mineral ash) is determined according to the standard French NF V 03-322. The dry sample is calcined in a furnace at 550˚C until it reaches constant weight. Being weighed, the calcined residue obtained is a clear and slight grey powder. Rated MM, the mineral content is expressed as a mass percentage. MM which is equal to:

$$\mathrm{MM} = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \tag{7}$$

where

m_0: is the crucible tare (in g);

m_1: is the mass of the crucible and the test sample before heating (in g);

m_2 is the mass of the crucible and the residue after calcination up to constant weight (in g).

The weight difference between the mass of dry matter and the mass of mineral matter is equivalent to the mass of organic matter. Rated MO and also expressed in mass percentage, the organic matter content of the sample can therefore be given by the difference:

$$\mathrm{MO} = \mathrm{MS} - \mathrm{MM} \tag{8}$$

2.3.3. Protein Content

The protein content is determined by the Kjeldhal method according to the French standard NF V 18-100. This method consists of transforming the organic nitrogen contained in the treated sample into mineral nitrogen (ammonia) by mineralization and then in the acid-base determination of this ammonia. Mineralization of the test sample (from 0.5 to 1.5 grams of sample depending on the estimated protein content) is carried out with concentrated sulphuric acid (12.5 mL at 95%) in the presence of two catalyst pellets ($CuSO_4$). Conducted at 400˚C using a Tecator Digestor 2020 device, it lasts about two hours. The reaction products are then alkalinized with a 40% soda solution.

After cooling, the ammonia produced is automatically entrained by steam distillation using a Tecator Kjeltec 2200 apparatus. In order to determine the total nitrogen content of the organic matter, the ammonia is then titrated with a 0.1 N hydrochloric acid solution by turning a mixture of coloured indicators in a boric acid solution of 4%, bromocresol green and methyl red. By convention, the protein content of the sample is then obtained by multiplying the total nitrogen content by an empirical conversion factor. This coefficient takes into account the average molecular weight of the amino acids composing the proteins to be quantified. It is fixed at 6.25 on the basis of an average nitrogen content in proteins of 16%. Noted P, the protein content is expressed as a percentage by mass and is equal to:

$$P = 6.25 \times \frac{M_N \times C \times \left(V_1 - V_0\right)}{m} \times 100 \tag{9}$$

where

M_N: is the molecular weight of nitrogen (M_N = 14.007 g·mol^{-1});

C: It is the concentration of the hydrochloric acid solution (in mol·L^{-1});

V_0: is the volume used of the hydrochloric acid solution on a blank sample (in mL);

V_1 is the volume of hydrochloric acid solution used (in mL);

M: is the mass of the test sample (in mg).

2.3.4. NMR Spectroscopy of Keratin

Nuclear magnetic resonance is a method for determining the structure of com-

pounds. This method makes it possible to specify the structural formula, the stereoche*mis*try and in certain cases, the conformity of the material studied [9].

The NMR spectrum of horn keratin was studied on an advanced 400 mhz BRUKER spectrometer, the spectrum was recorded at a rotation speed of 12 khz. The spectrum is measured in CPMAS with a contact time of 1 ms. Each spectrum was recorded for approximately 10 hours with a relaxation time of 5 s.

3. Results and Discussions

3.1. Physical Properties

3.1.1. Moisture Content of the Powder

The records obtained during the tests for the determination of the moisture content of the horn powder, give us the average value of the moisture content which is equal to 2.34% ± 0.054%. The moisture content of the horn powder being low, this is an advantage during the shaping of the composite because the thermo pressing temperature can reach 200˚C depending on the operating conditions which will reduce the pressing time which will be very economical for the production of the composites. The low moisture content of the fibers improves the mechanical characteristics of the composite material [10]. Dehydration is necessary before the composite is developed [11]. This result is similar to the work on the characterization of palm kernel shell powder [8].

3.1.2. Density of Bovine Horn Powder

From the records obtained from the tests, the average bulk density of the resulting cow horn powder is:

ρ_a = 0.586 ± 0.025 g/cm^3 and ρ_m = 0.732 ± 0.014 g/cm^3 The actual density of the powder is between ρ_a and ρ_m, *i.e.*:

0.586 ± 0.025 g/cm^3 ≤ ρ_r ≤ 0.732 ± 0.014 g/cm^3 these values are relatively low, this powder is hydrophilic, this is particularity a remarkable advantage for its use as a filler for polymers. More to that, this low value offers an advantage in transport sectors such as automotive and aeronautics.

3.1.3. Swelling Rate

The average of the records (**Figure 3**) gives us the swelling rate equal to 12% which means that the material made from horn fibers is moisture resistant like the one made with the 0.96% epoxy matrix [7].

3.2. Chemical Properties

The chemical composition of bovine horn particles is given in **Table 1** below.

The values of the chemical composition above, allowed us to generate the diagram in **Figure 4** below. We note that horn powder contains a large quantity of protein 94.52% and less water 2.21% and mineral 2.5%.

3.2.1. Dry Matter and Water Content

The dry matter content of horn particles varies from 96.5% to 97.6%. However, as with all vegetable matter, the dry matter content varies with humidity. The

Table 1. Chemical composition of bovine horn particles.

Chemical Composition	Content (%)
Dry matter content	97.05
Water content	2.21
Mineral content	2.5
Protein content	94.52

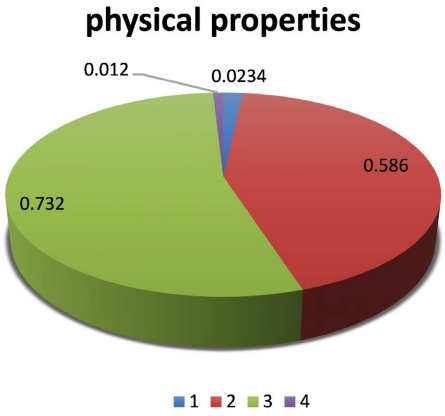

Figure 3. Physical properties.

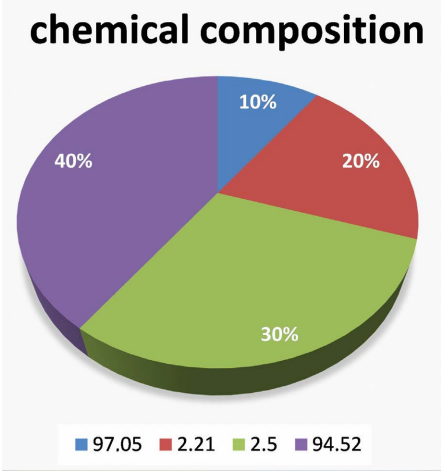

Figure 4. Chemical properties.

average water content is 2.12% ± 0.072% which is very economical in terms of time for the implementation of the composite.

3.2.2. Mineral Content

The mineral content is low, this observation was also made on the mineral content obtained on a whole kenaf stem (3.9%) [12].

3.2.3. Protein Content

The protein content of horns is 94.52%; the protein content of horn particles is very sensitive to its state of maturity as that of vegetable matter [13]. This value

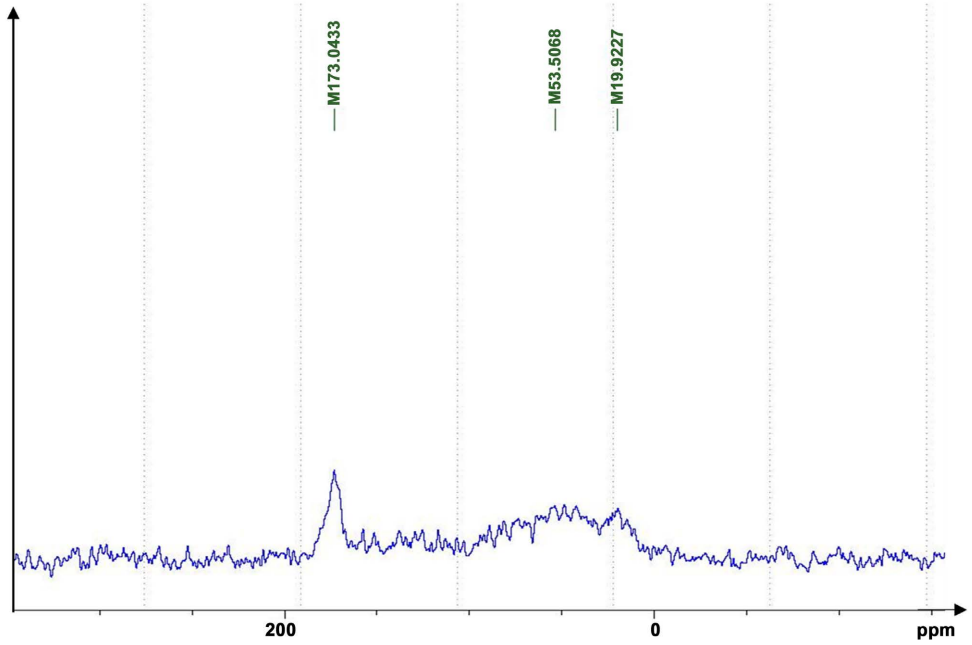

Figure 5. 13C NMR spectrum of bovid horn keratin.

is similar to collagen-based products such as bone glue, which has a protein content of 95% compared to dry matter [14].

3.2.4. NMR Spectroscopy of Keratin

The peaks of the spectrum in the **Figure 5** reflect the chemical shifts of the components or functional groups of the monomers present keratin. Each peak is associated with either a functional group or a monomer. The 173.04 ppm peak correspond to the presence of crystalline helical structures and the 53.2 ppm, and 19.92 ppm peaks correspond to the amide bonds of proteins.

4. Conclusion

The work we have just carried out on the transformation of beef horn cases into particles by studying the physical and chemical properties is satisfactory because these properties confirm the use of beef horn particles as reinforcement in the manufacture of polymers. The high level of keratin, which is a structural molecule, promotes cohesion between the particles and the matrix.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Makomra, V., Tapsia, L.K., Ndiwe, B., Kaoutoing, M.D., Konai, N., Njom, A., Laynde, T. and Raidandi, D. (2022) Physico-Mechanical Properties of Bio-Based Bricks. *Journal of Materials Science and Chemical Engineering*, **10**, 16-29. https://doi.org/10.4236/msce.2022.104002

[2] Laynde, T., Raidandia, D., Yona, C., Konai, N., Lionel, K.T. and Yannick, N.E. (2019) Mechanic and Physical Properties of Particle Boardpanels Produced With Horns Sheaths. *European Journal of Engineering and Technology*, **7**, 9-17.

[3] Ndiwe, B., Pizzi, A., Tibi, B., Danwe, R., Konai, N. and Amirou, S. (2019) African Tree Bark Exudate Extracts as Biohardeners of Fully Biosourced Thermoset Tannin Adhesives for Wood Panels. *Crops and Products*, **132**, 253-268. https://doi.org/10.1016/j.indcrop.2019.02.023

[4] Kakkar, P., Balaraman, M. and Ganesh, S. (2014) Extraction and characterization of keratin from bovine hoof: A potential material for biomedical applications. *Springer Plus*, **3**, Article No. 596. https://doi.org/10.1186/2193-1801-3-596

[5] Zhang, D.-S., Arola, D. and Luo, M. (2006) Analysis of the Mechanical Behavior of Bovine Hoof Horn Using Digital Image Correlation. *Chinese Journal of Biomedical Engineering* (*English Edition*), **15**, 103-112.

[6] Li, B.W., Zhao, H.P., Feng, X.Q., Guo, W.W. and Shan, S.C. (2010) Experimental Study on the Mechanical Properties of the Horn Sheaths from Cattle. *Journal of Experimental Biology*, **213**, 479-486. https://doi.org/10.1242/jeb.035428

[7] Kumar, D., Rajendra Boopathy, S. and Sangeetha, D. (2016) Investigation on Tribological Properties of Horn Fibre Reinforced Epoxy Composites. *Journal of Mechanical Engineering*, **2**, 138-147.

[8] Djomi, R., Meva'a, L.J.R., Nganhou, J., Mbobda, G., Njom, A.E., Bampel, Y.D.M. and Tchinda, J.B.S. (2018) Physicochemical and Thermal Characterization of Dura Palm Kernel Powder as a Load for Polymers: Case of Polyvinyl Chloride. *Journal of Materials Science and Chemical Engineering*, **6**, 1-18. https://doi.org/10.4236/msce.2018.66001

[9] Mansouri, H.R. and Pizzi, A. (2007) Recyclet Polyurethane Nanopowders as Active Extenders of UF and PF Wood Panels Adhesives. *Holz als Roh- und Werkstoff*, **65**, 293-299. https://doi.org/10.1007/s00107-006-0168-y

[10] Augier, L.M. (2007) Étude de l'élaboration des matériaux composites PVC/bois à partir des déchets de menuiserie: Formulation, caractérisation, durabilité et recyclable. Thèse de doctorat, Institut national polytechnique de Toulouse, France.

[11] Čuk, N., Kunaver, M. and Medved, S. (2011) Properties of Particleboards Made by Using an Adhesive with Added Liquefied Wood. *Materials and Technology*, **45**, 241-245.

[12] Ververis, C., Georghiou, K., Christodoulakis N. and Santas, P. (2004) Fiber Dimensions, Lignin and Cellulose Content of Various Plant Materials and Their Suitabilityfor Paper Production. *Industrial Crops and Products*, **19**, 245-254. https://doi.org/10.1016/j.indcrop.2003.10.006

[13] Webber, C.L., Bledsoe, V.K. and Bledsoe, R.E. (2002) Kenaf Harvesting and Processing. In: Janick, J. and Whipkey, A. (Eds.), *Trends in New Crops and New Uses*, ASHS Press, Alexandria, VA.

[14] Nenonene, A. (2009) Elaboration et caractérisation mécanique de panneaux de particules de tige de kénaf et de bioadhésifs à base de colle d'os, de tannin ou de mucilage. These de Doctorat de l' Universite de Toulouse, 217.