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Thermogravimetric Analysis of the Thermal Degradation of an Animal Biomass used as Load to Improve the Characteristics of Polymers

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Abstract **- The environmental constraint forces material science to move towards a sustainable approach, which promotes recycling, to reduce the environmental impact of materials and manufacturing processes. The main objective of the present work is to study the temporal degradation that a bio-composite material integrating a bio load from ox horns can undergo, and this, under the effect of the temperature which is considered here variable in the interval included between 0 and 1000°C. This new material is developed by using a biomass made from ox horns as a biological load to improve the characteristics of existing polymers, while exploiting animal dries. The purpose of the analysis is to evaluate the degradation behavior of the biomass under the effect of a variable temperature. The review confirmed that the wastes studied can improve the thermal properties of existing polymers simply and cost-effectively, with potentially significant environmental and economic benefits.**

Keywords: **Natural resources, Biodiversity, Biomaterials, Innovative composites, Bio load, Thermogravimetric analysis.**

INTRODUCTION

The material science, especially polymers is less and less focused on the synthesis of new polymers developed from scratch. This is one of the reasons that explain the growing focus on blends based on the combination of existing polymers, which has created a very attractive area of material sciences. From another point of view, developing a composite material from existing polymers is considerably cheaper than developing a new molecule. Because the implementation of the improvement of the performances of the existing materials is rather easier from the applicative point of view (internal mixer, extruder, injection press, etc...) if compared to the expensive elaboration of a chemical synthesis, with less flexibility and is also not accessible for all. From another perspective, materials composed of existing polymers are easily and quickly accepted by users than new polymers, this is due to the fact that their behavior outside the laboratory is unknown [1]. The realization of new composite materials also gives us the possibility to exploit and valorize waste [2], in our case we are going to concentrate on the horns of the oxen that we plan to exploit as bio-charges to produce a new bio-composite material.

The realization of such a mixture between an existing polymer and a bio-load derived directly from nature will allow us to improve the properties of the base product or even add further properties such as: reinforcement to shocks, chemical resistance, thermal stability, ... etc. [3]–[5].

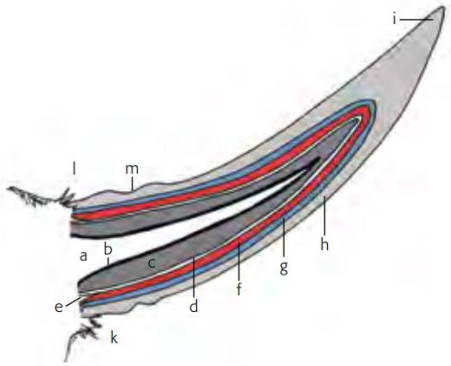
Recently, Jammoukh et al. [6] have developed a new material by exploiting animal waste. Mechanical properties (through tensile tests) of a bio-sourced material (ox horn) were studied to evaluate its performances. This study showed the great mechanical potential of this material also the and the possibility of its use as a biological origin load to reinforce and improve the mechanical characteristics of existing polymers. From the same perspective, Jammoukh et al.[7] have also numerically studied the elastic characteristics of this bio load, this work has also highlighted the mechanical performance of this biomass. Moumen et al. [8] joins this study by investigating, via numerical modeling, the mechanical characteristics of the same bio-load, this converges with the previous study but using numerical simulation of the behavior of polymers reinforced by bio mass from ox horn.

The previous investigations have mainly analyzed the mechanical characteristics of this bio-mass, but to determine the use cases of the matter as a bio load, it is also necessary to evaluate the thermal properties [9]. For this reason, samples designed for Thermogravimetric Analysis' method was used to determine the thermal behavior as a function of the variation of the mass of the bio load. Subsequently we will consider the possibilities of compatibility between the bio load under examination and the PVC, in order to obtain better thermomechanical properties [10].

This paper will be divided into two main sections: the first one concerns the experimental procedure, where an introduction of the bio-load will be presented, followed by the preparation of the samples then the preparation of the experiment and the experimental device (the thermogravimetric analyzer). The 2nd section will be devoted to the presentation and discussion of the experimental results.

GENERALITIES ON OX HORN

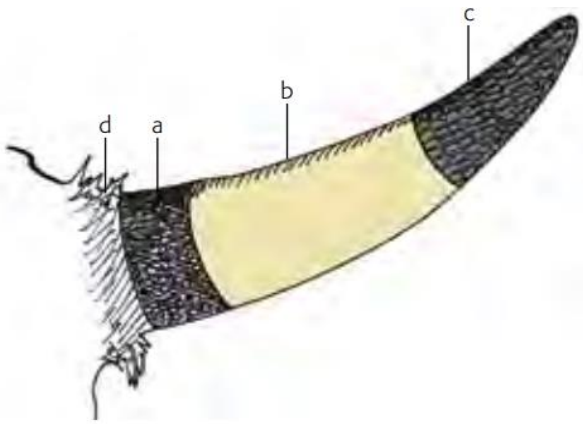
The structure of the horn is different from the other parts of organisms that contain keratin. The epidermis does not form desquamated keratinocytes, but secretes a keratinous substance in the form of small cylinders, which are maintained by a horny mastic that fills the gaps. [4], [6], [11].



a Sinus frontal
b Muqueuse du sinus frontal
c Cornillon : prolongement dans la corne de l'os frontal
d Périoste
e Hypoderme
f Derme
g Couche germinative de l'épiderme
h Gaine (en corne)
i Extrémité
k Peau pileuse
l Poils
m Anneaux

Figure 1 : Structure of the horn (section) [9].

The dermis nourishes the epidermis by giving it blood and lymphatic vessels. The hypodermis (e) (Fig.1) disappears at the level of the horn until it forms only a few fibers of connective tissue. It adheres to the periosteum of the cornucopia (c) (Fig.1) whereas it is loose and elastic on the rest of the animal's body to allow movement of the muscles [4], [6], [11]. The sheath is the external layer of the horn, it is adjusted to the horn and its point exceeds it of 5cm to 15cm.



a Zone basale, étroite, fines villosités
b Zone intermédiaire, quasiment aucune villosité
c Extrémité, villosités marquées
d Peau pileuse

Figure 2: Areas of the dermis of the horn after removal of the sheath [9]

The extremity (zone c) (Fig.2) of the sheath is thick and compact, its tip constitutes the oldest part of the horn. The intermediate part of the sheath is of regular thickness with a surface that is generally smooth. [4], [6], [11].

The horn is a "dead" skin formation. This tissue, which is produced by the living, is composed of various keratins (sulfur-rich protein forming fibers). Due to its nitrogen content of 12-15% and its high concentration of keratin, horn is a valuable material for many fields, especially material science. This material is very easy to work with once it is heated and softened. [4], [6], [11]. In this study, this material is used as a load in a polymer to improve its thermal properties.

EXPERIMENTAL PROCEDURE

1. Preparation of the sample:

In order to transform the horn into a biological load, a process of separation of the sheath and the horn was anticipated.

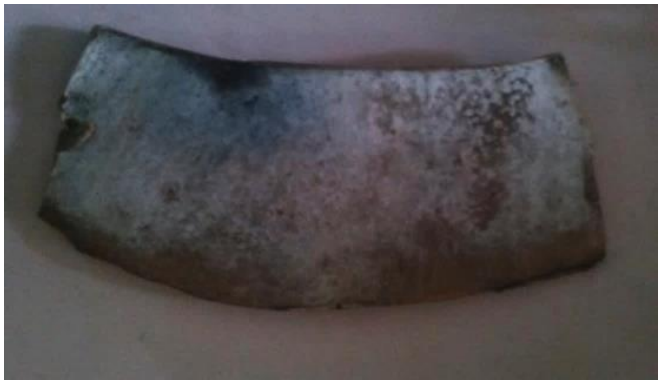


Figure 3: Sheath of the horn in a compressed state [10]

A reheating and softening of the sheath was proceeded so that it becomes easy to manage At the end, samples of dimensions adapted to those of the crucible-sample holder of the thermogravimetric analyzer were cut.[12].

Figure 4 : Sheath of the horn in powder state

2. Equipment:

The Thermogravimetric Analyzer (TGA) measures the temporal evolution of the degradation (ready or set) of the mass of a sample placed in an oven with a temperature control system, and a weighing device called a 'microbalance'[5], [13].

The bio mass samples submitted to the test are placed in inert crucibles (in our case alumina for fire applications, or more rarely platinum or silica) and then positioned on a weighing arm equipped with thermocouples.

The oven is regulated by means of thermocouples, based on a prior calibration on reference materials. A classical ATG allows to expose samples up to temperatures of about 1000°C. Depending on the model of the ATG, the gas sweeping and the extraction of the decomposition effluents can be done either horizontally or vertically [13].

This device can be coupled with gas identification and quantification devices, such as Fourier Transform Infrared Spectrometers (FTIR) or Gas Chromatography-Mass Spectrometer (GC-MS) [5], [13].

Figure 5: The thermogravimetric analyzer from CTPC laboratory.

Table 1:
Specific parameters of the thermogravimetric analyzer:

Parameters	Specification
Maximum sample weight	1g
Weighing accuracy	+/- 0.01%
Sensitivity	0.1µg
Dynamic derivative of the baseline	<50µg
Temperature range	Ambient of 1000°C
Temperature calibration	Point du Curie
Oven cooling (forced air/N2)	1000 to 50°C < 12min
Accuracy of the isothermal temperature	+/- 1%
Controlled heating rate	0.1 to 100°C/min
Sample containers	Platinum 50, 100µL

3. Operating principle:

The operating principle of the ATG furnace is shown in Figure 6. The thermal stress on the material in the crucible is multiple:

- Radiation from the walls and the heating body of the furnace.
- A convective solicitation by movement of the carrier gas and emission of gas at the surface of the decomposing material.

- A stress by conduction through the walls of the crucible, of the weighing arm. [10][11].

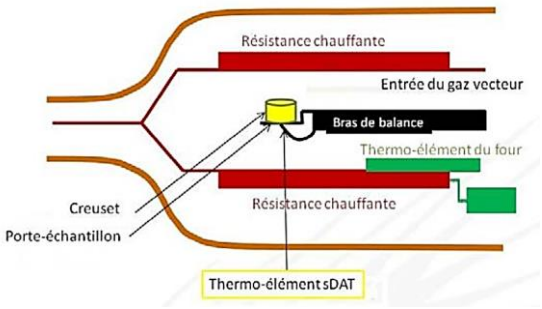


Figure 6: Principle of TGA.[11]

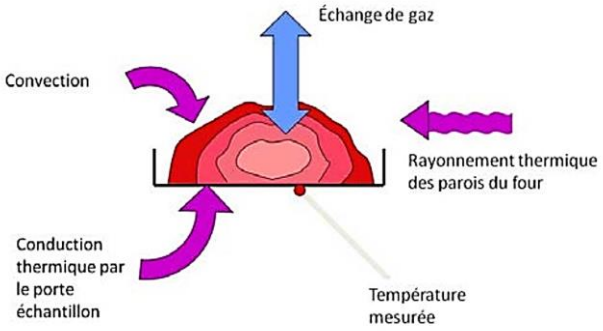


Figure 7: Thermal solicitation in TGA [13]

4. Measurements:

In terms of measurements, the device allows direct measurement of the mass of the sample as a function of time, which can also be associated with temperature measurements taken at several points under the weighing arm (between 3 and 5 points depending on the version) [9].

RESULTS AND DISCUSSIONS

H. Experimental results:

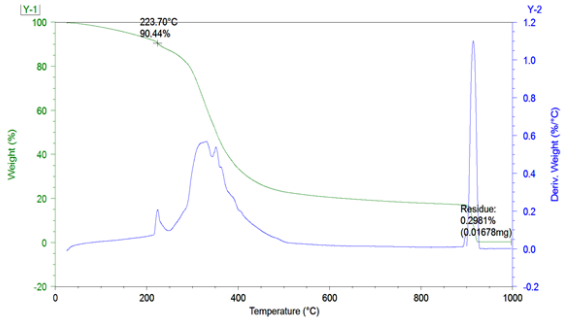


Figure 8: Thermogravimetric analysis of the horn from TGA analyzer.

1. Interpretation of thermogravimetric results:

In order to visualize the mass variations, a numerical simulation was used, resulting in the following graph:

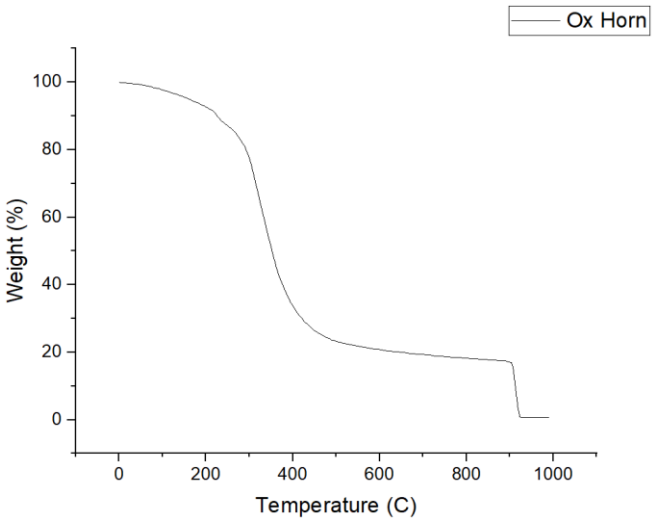


Figure 9: Digital TGA plot of a sample of the horn sheath.

Table 2:
Variation of the mass according to the thermogravimetric result.

Starting weight	Final weight	Lost weight
5,6592mg	0,0168mg	5,6422mg

Table 3:
Temperatures estimated from thermogravimetric analysis.

Critical temperature 1 (T_1)	Critical temperature 2 (T_2)	Critical temperature 3 (T_3)	Final Temperature (T_f)
50°C	250°C	910°C	1000°C

The thermogravimetric curve reveals three main phases of thermal transformation of the bio load:

- *Phase 1:*

A first transformation phase located in a temperature range between 50°C and 250°C, with a mass loss of about 13%. In this temperature range, we observe a first endothermic peak, well resolved, located at 223.70°C and for a mass loss of 9.56%. This peak is due to a dehydration reaction of the bio charge. This initial loss of mass observed mainly between T=100°C and T= 250°C corresponds to the elimination of water associated with keratin, the main component of bovine horn [15]. The presence of almost 15% of bio mass in the form of moisture shows that the purity of the Bio load sample could be higher than 90% keratin, depending on the nitrogen and water composition [5], [15].

- *Phase 2:*

A second phase located in a temperature range between 250°C and 900°C with a global mass loss of 70%. In this interval, a second broad and less resolved endothermic peak is observed which spreads out between 250°C and 510°C with a maximum located at approximately 335°C and a significant mass loss estimated at 24%.

This peak refers essentially to the process of denaturation of the helix of the keratin molecule and its degradation. However, the width of the peak and the possible overlap of two or more peaks in this temperature range suggests that we are in the presence of several reaction processes. Indeed, we are not dealing here with a pure keratin sample; the bio load analyzed contains several other organic elements besides keratin, such as polypeptides. Thus, the weight loss in this processing step can be related to the denaturation of the keratin helix structure, the degradation of the backbone and the destruction of chain linkage and peptide bridges [5], [16], [17].

There are several chemical reactions that break down horn, including keratin, into lighter products and volatile compounds such as Carbon Dioxide (CO2), Hydrogen Sulfide (H2S), Hydrogen Cyanide (HCN) and Water (H2O) [14]. Thermal degradation began at about 50°C and becomes more severe above 300°C [15]. In other terms, it is mainly a weight reduction appears random process of primary carbonization, forming rough molten benzene rings [18] [13], [16].

- *Phase 3:*

A third phase located between 900°C and 1000°C, in this temperature interval, a third endothermic peak, well resolved, is observed at 917°C. At this stage, the sample shows an important mass drop of almost 15%. This peak probably corresponds to the decomposition of the degradation residues formed at the end of the second phase. Nevertheless, this sudden weight loss just above 900°C may also be due to an instrumental artifact.

2. *Interpretation of the results of the Deriv.Weight trend:*

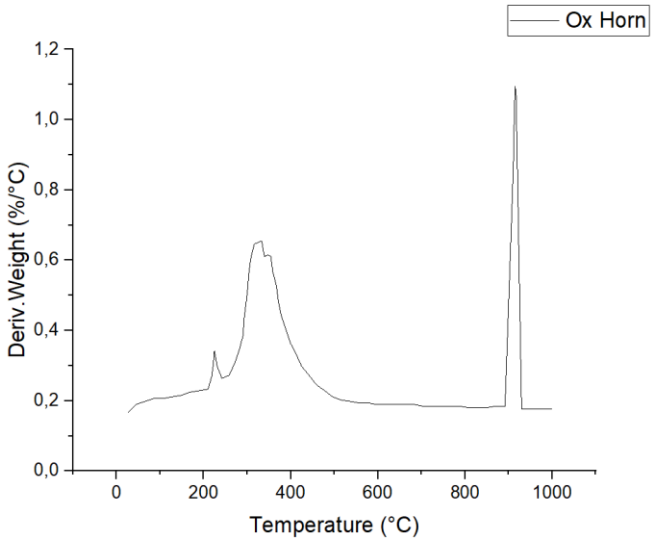


Figure 10: Digital Deriv.Weight plot of a sample of the horn sheath.

The Deriv.Weight trend shows three peaks, two of which are quite distinct from the third, suggesting that the thermal degradation of bio mass (horn) is a complex process, occurring through three different degradation steps.

In particular, the first peaks, at about 200 °C, are related to the removal of moisture and highly volatile components. According to the literature, biomass degrades during heat stress by three different steps [19], [20]. In agreement with the literature, the horn sheath shows that the degradation of, mainly keratin, occurs from 250 °C, while the dehydration of the structure and the departure of the particles from water take place before, between 100°C and 250°C, respectively. Based on the Deriv.Weight curve, the bio mass derived from the horn was pyrolyzed at three different operating temperatures, which are 225, 350 and 900 ° C [18], [21], [22].

CONCLUSION

The thermogravimetric analysis was used to study the thermal behavior of samples of ox horn, in the perspective of their use in the development of a new bio-composite material benefiting from the thermal qualities of this bio load. The experimental results obtained, showed the existence of three stages of transformation. The first stage between 50°C and 250°C, with a loss of mass of about 13%, the second located in a temperature range between 250°C and 900°C with a global loss of mass of 70% and the last stage is located between 900°C and 1000°.

It should be noted that the ox horn sheath has a relatively high thermal stability. Indeed, up to a temperature of 250°C, the loss of mass is minimal and of the order of 10%. In addition, in this temperature range there is no degradation of this bio load but only a departure of water molecules and a loss of moisture of this sheath.

This thermal stability of the ox-horn sheath is comparable, if not better than that of some commonly used polymers, such as PVC, for example. Therefore, this analysis allowed concluding that the qualitative behavior of this bio load is considered favorable to its development for the innovation of new bio-filled materials based on polymers.

As a perspective, it is planned to go further in this study and identify more precisely the chemical processes involved in the mass loss of the bioburden in the different transformation phases. For this purpose, the coupling of complementary techniques such as thermogravimetric analysis - mass spectrometry (TGA-MS) or thermogravimetric analysis - Fourier Transform Infrared Spectroscopy (TGA-FTIR) is necessary to be able to correlate the weight loss process with the chemical processes.

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