# ON THE THERMAL BEHAVIOR OF DIFFERENT TANNED BOVINE LEATHERS

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***Abstract:*** *Leather is one of the most globally spread biomaterial which is obtained by the processing of different animal skins. It encompasses a wide palette of applications, from footwear and clothing to upholsteries and different types of furniture [1], [2], [3]. The main constituent of animal skins is collagen, a supramolecular fibrillar protein in the form of a triple helix. This form endows leather with elasticity, good mechanical properties and softness. A major disadvantage resides in the inapplicability of raw animal hides, due to their microbiological instability and decay through rotting. Microbiological stability is obtained through the tanning process, characterized by protein crosslinking and drying afterwards. After tanning the leather exhibits the required properties for the desired specific applications in terms of aspect, availability and sustainability [4], [5]. The study aims to elucidate the thermal decomposition process of chrome-free tanned bovine hide (wet-white) using a new product based on titanium and aluminium salts compared with the same hide tanned by chromium salts (wet-blue). The thermal behavior was studied by dynamic thermogravimetry in nitrogen atmosphere, up to 700 °C. A comparative thermal decomposition study between the different tanned bovine leathers was undertaken.*

***Keywords:*** *Bovine leather, Thermogravimetric analysis, Thermal decomposition*

## 1. INTRODUCTION

Leather is one of the most widely spread biomaterial from collagen protein, which is modified for avoiding its putrefaction. One such a way may be achieved through complete stabilization with Cr III salts. Through this procedure, some properties, such as water absorption resistance, increase, together with putrefaction resistence, drying or swelling [6]. Collagen may be extracted as hydrolyzate with the Sörensen method [7]. Other improved characteristics include mechanical properties and elasticity. The tanning process consists of protein crosslinking and drying. Afterwards the tanned leather exhibits the mentioned properties for sought applications [4]. Cr III salts are still widely used as tanning material among the tanning agents. Leather manufacturing is known as one of the most polluting industry, due to the inorganic waste generated during operations. The Cr salts are heavy environmental and health pollutants. It is therefore that research in obtaining Cr free leather has expanded [1], for instance, replacing Cr III salts with waste of ultrapure titanium [5].

This study compares the thermal behavior in inert atmosphere of a Cr free ‘wet–white’ tanned leather (with a new product containing titanium and aluminium salts) compared with the same leather Cr III tanned (‘wet–blue’), for gaining new insights and knowledge on this aspect.

## 2. EXPERIMENTAL

### 2.1. MATERIALS

The synthesis method of Ti–Al tanning agent and the obtaining of wet–white and wet–blue products were described in the literature [4], [5].

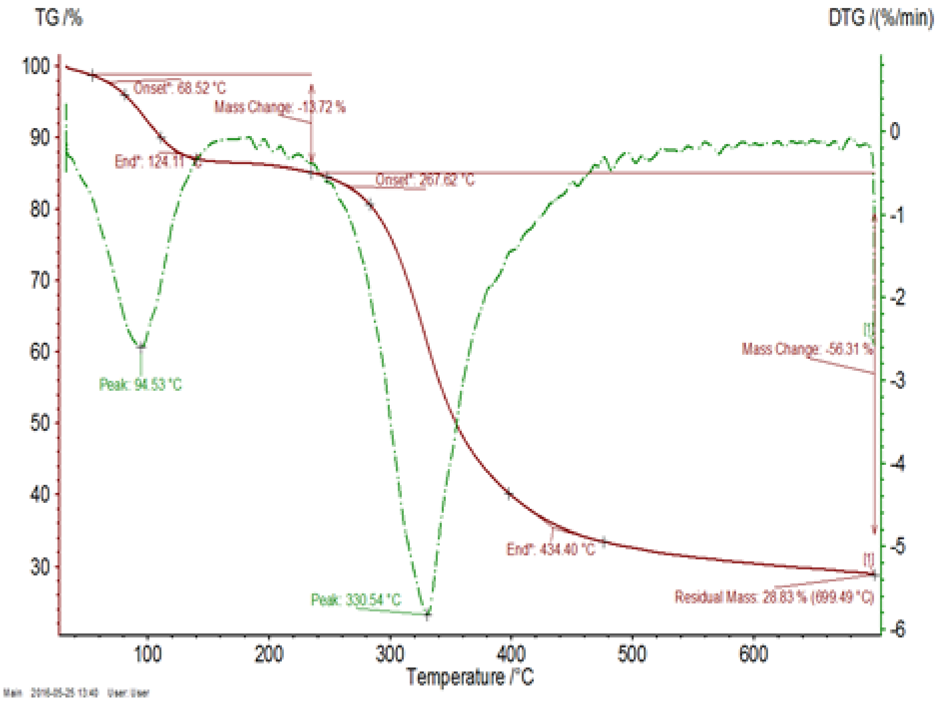
### 2.2. EQUIPMENT

The thermal degradation process was undertaken by means of a device of simultaneous TGA/DTG/DTA analyses STA 449F1 Jupiter model (Netzsch, Germany). 10 mg of sample was heated in the range 30–700 ºC under a nitrogen atmosphere (flow rate 50 mL $min^{-1}$), in an open $Al_2O_3$ crucible and a second identical empty one was used as reference material. A heating rate of 10 ºC $min^{-1}$ was applied. The glass transition temperature domain ($T_g$) was determined by using the Differential scanning calorimetry (DSC) technique. The thermograms were recorded on a DSC 200F3 Maia (Netzsch, Germany) calibrated with five metals (In, Sn, Bi, Hg, Co) according to standard procedures. Samples were heated in aluminium crucibles with pierced and pressed lids for removal of any volatiles released during heating. Sapphire is used for absolute heat capacity values determination. The used DSC device covers a temperature range of –150 to 500 ºC and cooling is made with liquid nitrogen. The experiments were conducted in nitrogen, as inert atmosphere, with a heating/cooling rate of 10 ºC/ –10 ºC and in the temperature range –50 to 300 ºC.

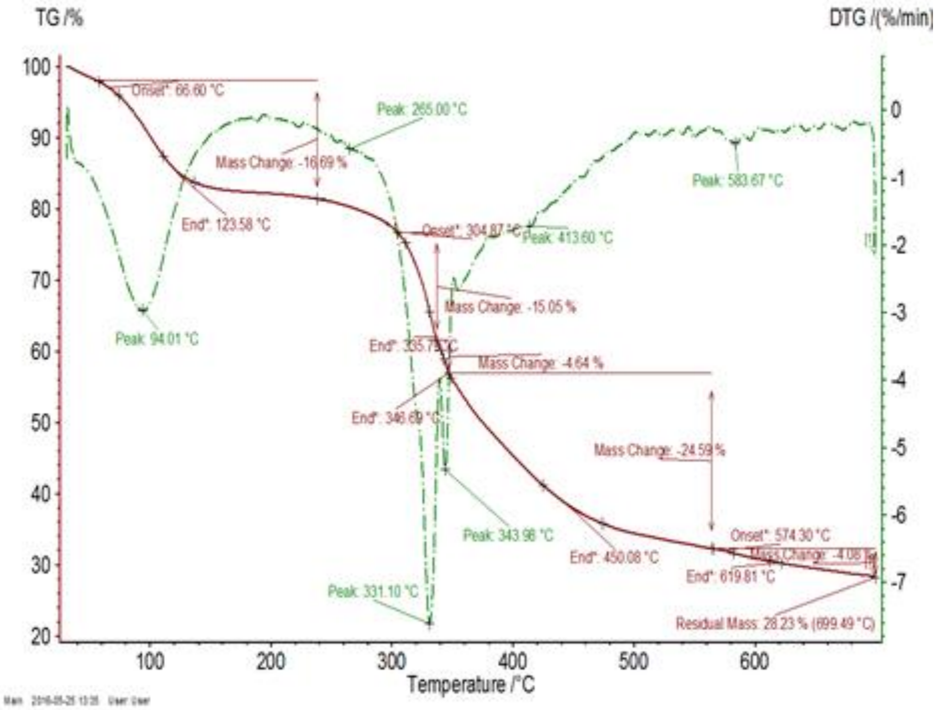
## 3. RESULTS AND DISCUSSIONS

In the case of both measurements, the first thermal decomposition stage is assigned to humidity loss, in the range 56–139 ºC with a mass loss of up to 17 % (Fig. 1). With the aid of the first derivative (DTG) curve, one may observe that, except the ‘wet-white’ sample, which decomposes in two stages, the ‘wet-blue’ sample degrades in at least three stages. The main thermal decomposition process occurs at the initial temperature of 268 ºC, for ‘wet-white’ leather, and 305 ºC for ‘wet-blue’ leather, hence the presence of Cr increases thermal stability and also, generates the lowest residual mass value (28.23 %), residual mass values varying in the range 28.23, for ‘wet-blue’ leather, to 36.87 % for ‘wet-white’ leather.

The thermal decomposition studies were in a good correlation with the DSC ones (Fig. 2). The first DSC heating curves exhibited a wide endotherm profile corresponding to fibrillar collagen denaturation and water loss. This denaturation is specific to biphasic amorphous-crystalline structure specific to collagen based materials, in which the triple helix crystalline collagen structure is incorporated into an amorphous matrix. Total heat value was measured by integrating the endothermic signal and was of 370.7 J $g^{-1}$ for ‘wet-white’ leather and 439.4 J $g^{-1}$ for ‘wet-blue’ leather, the latter value being the highest due to Cr hardening the denaturation process and thus increasing the enthalpy of the process.




***a)***




***b)***

***Fig. 1:*** *TG/DTG thermograms of the studied samples: (a) wet-white and (b) wet-blue leather*

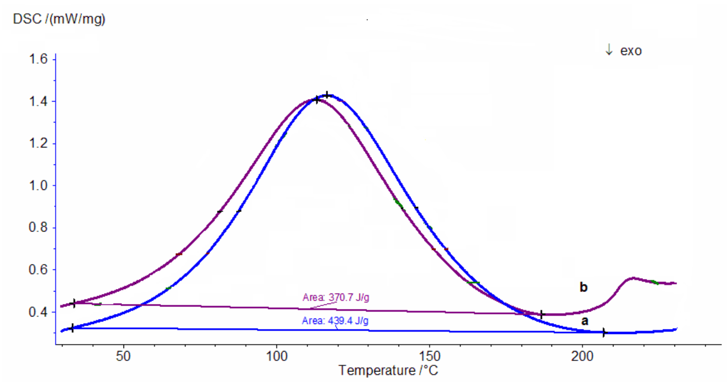



***Fig. 2:*** *DSC curves of the first heatings of: (a) wet-blu and (b) wet-white leather*

## 4. CONCLUSIONS

There were undertaken comparative thermal stability studies between wet–white and wet–blue processed bovine leathers. A similar thermal behavior was observed for both samples. In the case of the wet-blue tanned leather, the presence of Cr led to an increase in thermal stability. The first DSC heating curves exhibited a wide endotherm profile due to the overlapping of collagen denaturation with water loss. Total heat value was the highest for 'wet-blue' leather, due to Cr hardening the denaturation process.

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