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Thermal analysis of a model bio-membrane

Human and snake skins

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Abstract Thermal properties of some shedded snake skins in comparison with human skins are represented by thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) to predict process condition as dermal pathway for administration of drugs or it be used as model membranes for permeation studies. Thermal behavior by TG/DTG and DTA curves for four kinds of shedded snake skins as Boelens Python (BP), Eastern Indigo Snake (EIS), Emerald Tree Boa (ETB), and Cascavel (CBR) were similar in relation to their decomposition temperatures at 100 °C and 230–400 °C of its constituents, however, their properties were different in the residue content (inorganic or carbonaceous substances). Similar thermal properties were also exhibited by human skins' samples, however, they presented different residue and constituents' content.

Keywords Thermal analysis · Human skin · Snake skin · Model membranes

Introduction

Shedded snake skins are natural biological macromolecules. The use of these skins precludes the use of live animals and skin from deceased animals. Shed snake skin was shown to be similar to human stratum corneum in terms of thickness, composition of constituents, and structure, but more closely resemble the human cuticle and anatomically they are different from human skin for they have the heterogeneous reptilian integument [1]. Some thermoanalytical studies about drug permeation on snake skin and skin disease have been done on the last years [2, 3]. Human skin consists of two distinct layers, a stratified vascular epidermis and an underlying dermis of connective tissue. The stratum corneum, which is the outermost layer of mammalian epidermis and consists of corneocytes embedded in a lipid matrix, typically provides the major barrier to most transdermal drug absorption [4]. The impedance of the human skin is dominated by the stratum corneum at low frequencies. It has generally been stated that skin impedance is determined mainly by the stratum corneum at frequencies below 10 kHz and by the viable skin at higher frequencies, the measured volume or skin layer is highly dependent on frequency. This will of course be dependent on factors such as skin hydration, electrode size, and geometry, but may nevertheless serve as a rough guideline. The stratum corneum (SC) may have a thickness of from about 10 µm (0,01 mm) to as much as 1 mm or more. It is a solid-state substance, not necessarily containing liquid water, but with a moisture content dependent on the surrounding air humidity. SC is not soluble in water, but the surface will be charged and a double layer will be formed in the water side of the interphase. Stratum Corneum can absorb large amounts of water, it may be considered as a solid-state electrolyte, perhaps with few ions free to move and contribute to dc conductance. The SC contains such organic substances as keratinized proteins and lipids, which may be highly charged but bound, and therefore, contribute only to ac admittance. Skin admittance varies greatly both between

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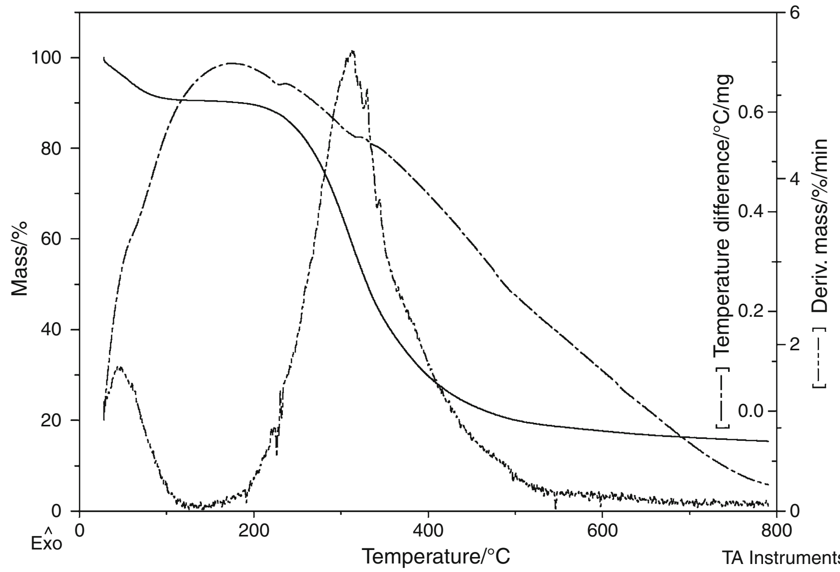

Fig. 1 TG/DTG/DTA analysis of BP snake skin (Boelens Python)

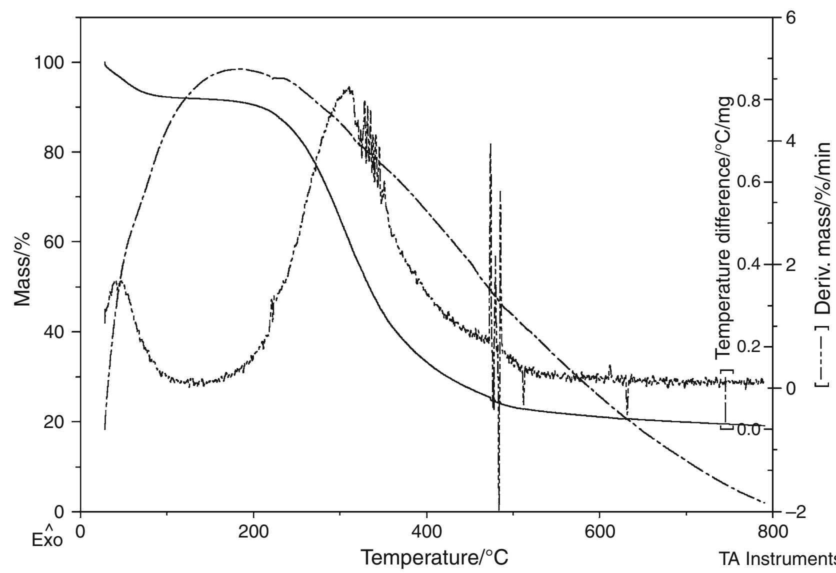

Fig. 2 TG/DTG and DTA profiles of EIS snake skin (Eastern Indigo Snake)

persons and between different skin sites on the same person. Changes in sweat gland activity and ambient relative humidity during the day or year or season are also reflected in large variations in skin admittance, mainly because of changes in skin hydration [5].

In recent years, there is a growing interest in employing the transdermal pathway for administration of drugs. Shedded snake skins can assist the understanding of transdermal patches. The snake skins can also be used as model membranes for permeation studies [1, 3]. The word "model" is ambiguous, a model can be a three dimensional representation of an object, but it can also be a person presenting fashion, an object used to produce casting molds, an instrument for physical model experiments, a substitute for something, and an illustration of a mathematical expression, etc. The word "model" has essentially two different interpretations: prototype/picture and equivalent/substitute. Mathematical models should also be mentioned, which are a sort of predictive substitute for reality. A characteristic of models is that they represent selected properties of the reality they reflect. Then predictive function is of great interest, because they are often used to investigate a specific side of the functionality or structure of the original. Tregear in 1966 presents a model of the skin comprising 12 resistors and 12 capacitors in his book [5]. Shedded snake skin, rabbit skin, and human skin were compared directly by measuring their transition temperatures by differential scanning calorimetry. There were strong similarities in the curves for the three kinds of skins [6]. If one can continue the correlation of thermal

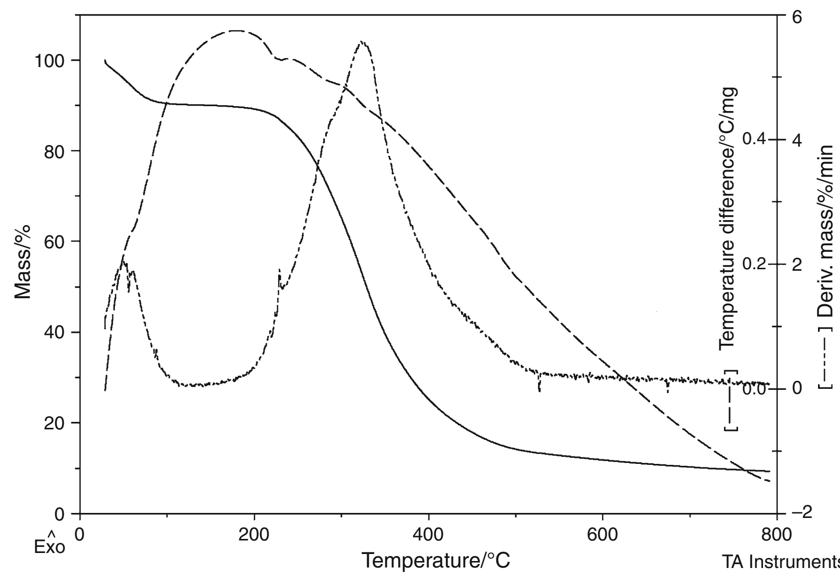

Fig. 3 TG/DTG/DTA curves of ETB snake skin (Emerald Tree Boa)

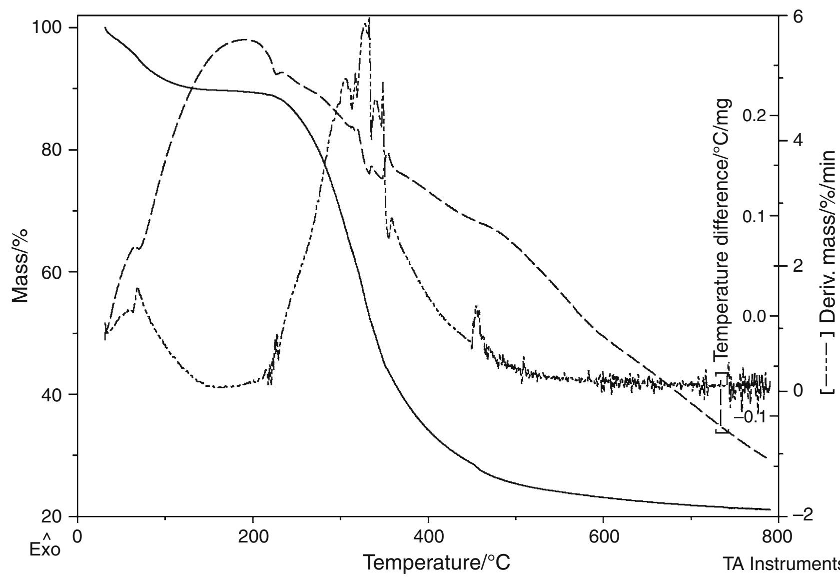

Fig. 4 TG/DTG and DTA analysis of CBR snake skin (Cascavel)

properties by TG, DTG, and DTA between the various sources of skins, then one can study the effects of chemicals and radiation on shedded snake skins as a predictive model for human skin behavior. The present study focuses on evaluation of the attributes of some shedded snake skins in comparison with human skin by thermal analysis.

Experimental

Samples

Shedded snake skins

Boelens Python (BP), *Morelia boeleni*; Eastern Indigo Snake (EIS), *Drymarchon Corais*; Emerald Tree Boa (ETB), *Corallus Caninus* from Toledo Zoo, USA; and Cascavel (CBR), *Crotalus Durissus Collineatus* from Minas Gerais, Brazil. These skins are composed of a border area 100–120 μm in thickness and a core area of 20–50 μm in thickness.

Human skins

The samples of human light skins were in a physiologic serum. The first from a male, a part from the head scalp with few hairs and exposed to sun. The second sample from a female, a part from the middle of her back, not exposed to sun. The samples presented layers of the epidermis and dermis and both were from Rio de Janeiro, Brazil.

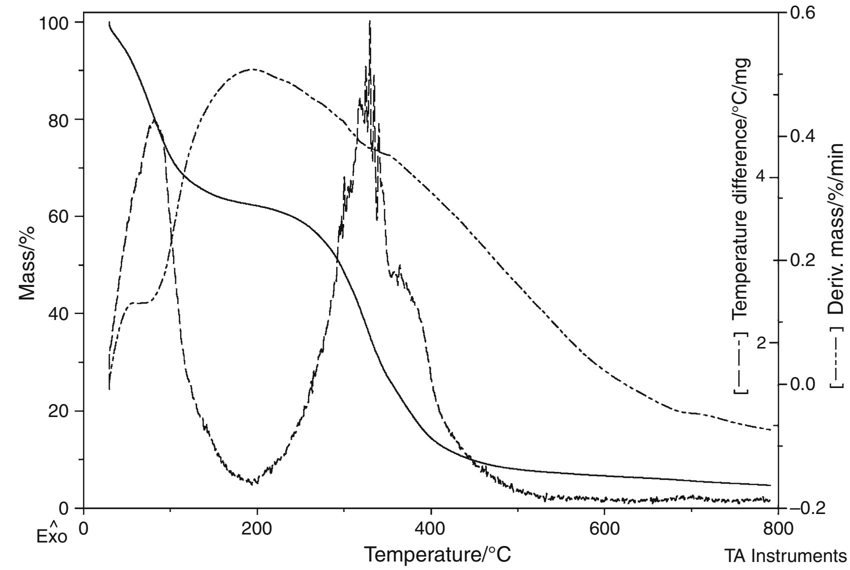

Fig. 5 TG/DTG/DTA profiles of male human skin (Pele 1)

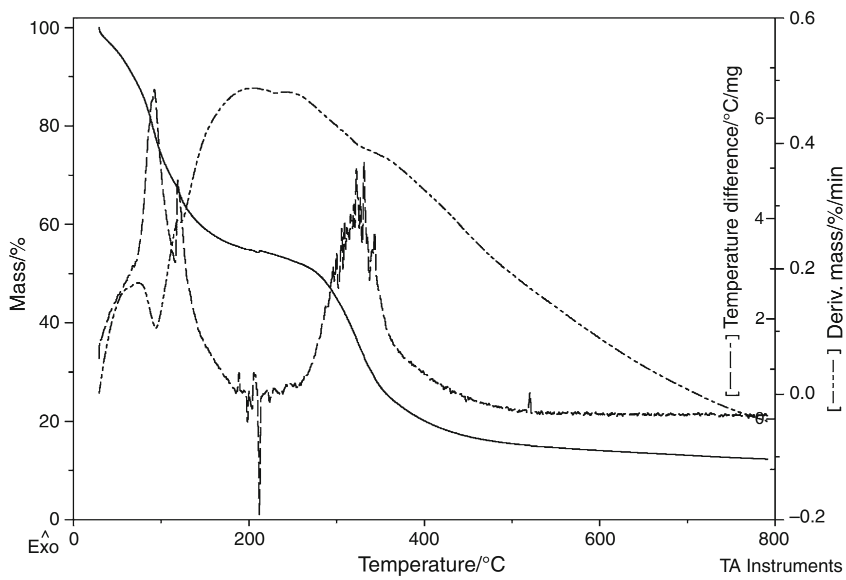

Fig. 6 TG/DTG and DTA curves of female human skin (Pele 2p)

TG/DTG/DTA analysis

Thermal behavior of samples was analyzed on a TA Instruments SDT 2960, at heating rate of 10 °C/min in nitrogen atmosphere. Samples sizes were 3–5 mg and a flow rate of 120 mL/min and over a temperature range of room temperature to 800 °C.

Results and discussion

Thermal properties of some shedded snake skins in comparison with human skins are represented by thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) to predict process condition, such as transdermal pathway for administration of drugs or it be used as model membranes for permeation studies. Figure 1 presents TG/DTG/DTA curves for Boelens Python (BP) snake skin. TG curve shows two decomposition stages, first a weight loss of moisture or a lubricant (10%) at 100 °C and a principal degradation at around 60% at 230–400 °C and is related to the proteins and lipids from skins and an amount of residue (15%) at 800 °C, suggesting inorganic substances or carbonaceous material. DTG curve shows some degradation stages at 300–400 °C and DTA thermogram shows two endothermic events close to 230 and 310 °C.

The thermogravimetry (TG/DTG) and DTA of Eastern Indigo Snake (EIS) skin as shown in Fig. 2 revealed TG curve a weight loss of moisture or a lubricant (8%) at

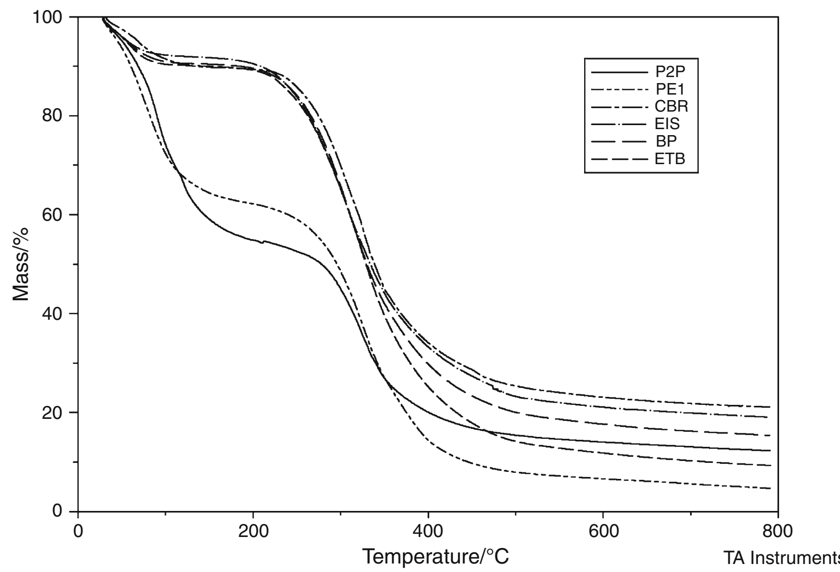

Fig. 7 Comparison of TG analysis for different human and snake skins

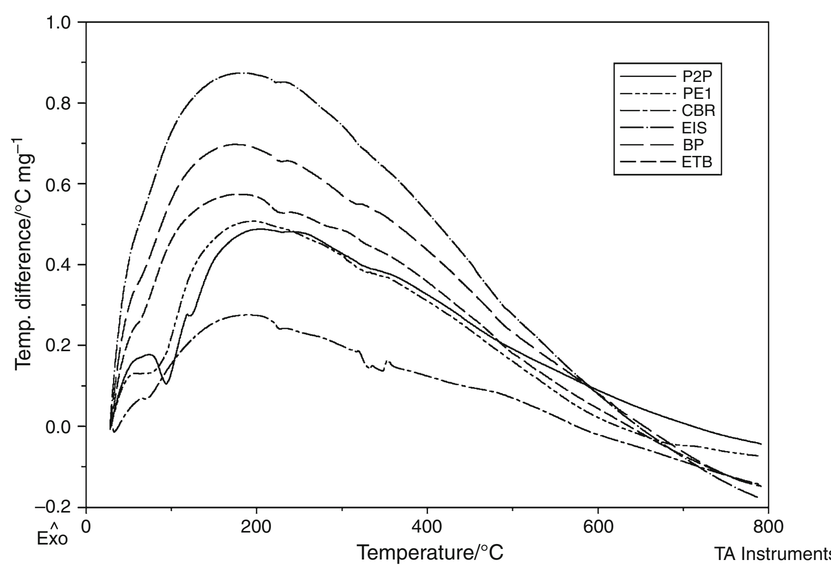

Fig. 8 Diagram of DTA profiles for different human and snake skins

100 °C and a weight loss of 60% at 230–400 °C, referent the decomposition of proteins and lipids from the skin at higher temperatures and 19% of residue at 800 °C, probably due to inorganic substances or carbonaceous material. DTG curve revealed various degradation stages above of 300 °C and DTA curve presents two endothermic events at 230 and 310 °C.

Figure 3 exhibits TG/DTG/DTA profiles for Emerald Tree Boa (ETB) snake skin samples. The TG showed two decomposition stages, a first weight loss due to moisture or a lubricant (10%) at 100 °C and a second weight loss of 65% at 230 to 400 °C, due to proteins and lipids degradation and with 9% of residue at 800 °C. DTG curve presents a maximum rate of decomposition at 325 °C and DTA curve showed two endothermic events at 230 and 325 °C, relative to decomposition.

Figure 4 presents the TG/DTG and DTA thermogram for CBR snake skin. The TG showed two degradation profiles, the first one a weight loss of 10% at 100 °C is the percentage weight loss that is again due to moisture or lubricant and the second degradation stage of 60% at 230–400 °C, possibly due to the loss of proteins and lipids and a residue of 20% at 800 °C. DTG curves showed various degradation stages at 300–400 °C and DTA curve demonstrated four endothermic events at 800 °C.

TG/DTG/DTA curves for the male human skin sample are presented in Fig. 5. TG curve showed two decomposition stages, first a weight loss of 30% at 100 °C that can be related to the serum and moisture from the skin and second a weight loss of 55% at 250–400 °C due to proteins and lipids and a residue of 5% at 800 °C probably due to the inorganic substances, such as Ca, K, and Na. DTG profiles exhibited various degradation stages at 300–400 °C, suggesting degradation of cellular proteins (albumin, enzymes, and globulins) and lipids. DTA thermogram showed two endothermic events at around 100 and 300 °C.

Figure 6 shows TG/DTG/DTA curves for a female human skin sample, where the TG curve presented two decompositions, first weight loss of 40% at 100 °C suggests the serum and moisture and second weight loss of 40% at 280–400 °C due to proteins and lipids and a residue of 12% at 800 °C, probably due to the inorganic substances (Ca, K, and Na). DTG profiles exhibited two stages at around 100 °C and various degradation stages at 300–400 °C. DTA curve showed three endothermic events at approximately 100, 230, and 310 °C.

A comparison of TG thermal profiles for four kinds of shedded snake and two human skins are given in Fig. 7. All samples presented two decomposition stages, but all exhibited different amounts of residues. The CBR sample had a maximum residue of 20% and a minimum value was observed for a male human skin with 5% at 800 °C.

Figure 8 presents a diagram where DTA curves overlap for four kinds of shedded snake and two human skins. All samples showed similar thermal transitions in the temperature range of 100–400 °C, but some presented two endothermic events and others three events, all due to the decomposition of organic substances.

Conclusions

Thermal behavior of TG/DTG and DTA profiles for four kinds of shedded snake skins such as BP, EIS, ETB, and CBR was similar in relation to the decomposition temperatures of its constituents or substances, but their properties were different in the residue content (inorganic or carbonaceous substances). Similar thermal properties were also exhibited by human skin samples; however, they presented different residue and constituent content. Therefore, this study indicated that shedded snake skins can be used as model membranes for permeation of drugs or application of sunscreen lotion based on their thermal properties.

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