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DIFFERENTIATION OF THERMAL PROPERTIES OF POLLENS ON GENUS LEVEL

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ABSTRACT. This study was carried out to explain the thermal properties of pollen grains for three different genera. It was also aimed to determine how thermal properties are differed in pollen grains belong to different genera. The pollen genera *Salix*, *Betula* and *Fraxinus* were chosen. The observed results showed that pollen grains of different genus exhibits an important difference in their thermal stabilities. The thermograms of species belonging to *Fraxinus* genus revealed a five-staged thermal degradations while species from *Salix* and *Betula* genus revealed a four-staged thermal degradations. As is know very well, pollen grains are diamond of plant word and they have many applications in cosmetic, pharmacy, food and medical industry. The findings of the current study will be helpful for the future applications of pollen as a material in different fields.

1. INTRODUCTION

The genetic material needed for breeding and reproduction of plant species are carried by pollen grains [1]. The structural organization of pollen grains varies among different plant species [2-3]. This variation in the structure of plant pollens across species can also be seen in the physicochemical properties of the pollen grains belonging to that specific species. Looking at the structure of the pollen grain it can be divided into two main shells stick together protecting the internal genetic material very efficiently. Pollen grains are comprised of two shells, an inner layer, known as intine, is a cellulosic structure, and an external layer known as exine. The structural makeup of the external layer is composed of a polymer called sporopollenin [4]. These layers enable the pollen to protect the genetic material in an efficient way [5].

Researchers from divergent fields of science are focusing on the application of waste pollen grains which shed on the ground at different intervals throughout the year. Sporopollenin, extracted after acid, base and bleaching (by using hydrogen peroxide,

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alcohol or sodium hypochlorite) treatment can be used for a variety of applications including, drug delivery and adsorption studies [6-8]. As is known that physicochemical properties play a decisive role in determining the type of application for which a specific material will be used. These physicochemical properties show variation depending upon the type and source of a material. Among these characteristics, thermal stability is the most important property defining key features of a material. Like all other polymeric materials, it is thought that the physicochemical properties of all pollen grains might not be the same and they could vary from plant to plant and genus to genus.

Thermogravimetric (TG) thermal analysis examine the change in mass due to desorption, absorption, vaporization, oxidation, reduction, and decomposition of a sample as a function of temperature [9-10]. TGA is an analytical tool used for analyzing the thermal behavior of thermoplastics, thermosets, composites, films, fibers etc., [7, 11-13]. There are three main types of TGA; 1) Isothermal or Static TGA, in which change in overall weight of the sample is recorded keeping the temperature. 2) Quasi-static TGA where sample with constant weight is heated and changes at a temperature at different intervals are recorded. 3) Dynamic TGA is a type of thermal analysis the sample is heated at a constant temperature range increasing at a gradual rate, usually in relation with time. This technique is also known as to as thermodilatometry (TD) if the dimensions of analyte are recorded under trivial load [9-10, 14]. In the current study, in order to analyze the pollen grains diversity on the family level, we used dynamic thermogravimetric analysis (TGA).

This study was conducted to explain thermal properties of the pollen grains on a genus level by selecting three different genera. It was also aimed to reveal thermal properties for determining their correct application area in the industry in further studies.

2. Material And Methods

2.1 Sample collection

Three species of *Salix* i.e., *Salix babylonica*, *Salix caprea*, and *Salix fragilis*; one species of *Betula*, *Betula pendula* and one species of *Fraxinus* i.e., *Fraxinus excelsior* were used in the current research. Pollen samples of all the species were collected from Kastamonu province, Turkey. All the collected species were used for determining the thermal properties.

2.2 Dynamic thermogravimetric analysis (dTGA)

Dynamic thermal gravimetric analysis (dTGA) was used to examine the thermal degradation properties of studied species belong to three different genera. Almost 5 mg pollen grain from each species was transferred in a porcelain cup by using very tiny spoon and heated from room temperature to 650 °C using EXSTAR S11 7300 at a heating rate of 10 °C min^{-1}. The thermograms were taken at the end of the analysis and used for results interpretations.

3. Results And Discussions

The inspiration for the current research was taken from a very basic but answer requiring question i.e., whether the pollen grains from species of different genus exhibits any variation in their thermal stabilities. For this purpose, species were subjected to dTGA test selected from three different genus. The pollen grains collected from selected species of four different genus that are three species of *Salix*, one species of *Betula* and species of *Fraxinus* were subjected to TGA analysis. Thermograms of all the tested species from three genera a very different pattern of weight loss and degradation curves on genus level (Fig. 1). First, the thermograms of species belonging to *Fraxinus* genus revealed a five-staged thermal degradation while on the other hand species from *Salix* and *Betula* genus revealed a four-staged thermal degradation. Second, a significant difference was observed among the dTGmax value of different species from different genus (Table 1).

In all the thermograms, the first mass loss could be attributed to the evaporation of adsorbed water from the pollen grains structure [6, 15]. The second and third mass losses can be ascribed to the degradation of intine material (cellulosic structure, genetic material etc.) [15]. The last mass losses (fourth and fifth mass losses) around 410-650 °C is thought to be because of the degradation of exine material (sporopollenin). As it known, the sporopollenin is a tough polymeric structure due to which it is also known as the diamond of the plant world thanks to its awesome thermal properties. In a previous study conducted on pollen weight loss in relation to temperature revealed that the pollen of *Pinus thunbergii* is composed of 9.12% moisture, 4.46– 4.91% crude ash, 17.01–18.72% crude protein, 2.50–2.75% crude fat, 2.46–2.71% crude starch, 4.72–5.19% invert sugar and 1.91–2.10% reduced sugar [16]. In another report the increasing temperature results in the step by step degradation of different components at different temperature range. Carbohydrates were the first component to be modified (starting from 45 °C and culminating at 183 °C) followed by proteins (up to 183 °C), in agreement with the Maillard reaction and Strecker degradation mechanisms. On the other hand, it was reported that lipid degradation could be occurred until 300 °C which is very high thermal rate [17]. These results revealed that the thermal stabilities of pollen grains vary from genus to genus.

TABLE 1. Thermogravimetric analysis of selected species from three genus; *Salix, Betula* and *Fraxinus*. Also the recorded results were categorized according to weight loss in different stages.

	1st weight loss (%)		**2nd weight loss (%)**		**3rd weight loss (%)**		**4th weight loss (%)**		**5th weight loss (%)**	
Species	**25-100**	**DT$_{max}$ (°C)**	**100-250**	**DTG$_{max}$ (°C)**	**250-300**	**DTG$_{max}$ (°C)**	**300-400**	**DTG$_{max}$ (°C)**	**400-650**	**DTG$_{max}$ (°C)**
S. babylonica	6.1	57.9	8.4	210.2	43.4	317.6	16.8	432.5	-	-
S. caprea	3.5	64.3	6.2	211.8	27.5	320.1	9.9	432.1	-	-
S. fragilis	6.2	59.7	15.3	220.0	42.9	306.0	16.3	428.0	-	-
B. pendula	6.2	59.7	15.3	220.0	42.9	306.0	16.3	428.0	-	-
Fraxinus excelsior.	7.0	55.5	13.9	212.1	9.2	324.5	22.0	392.4	22.8	392.4

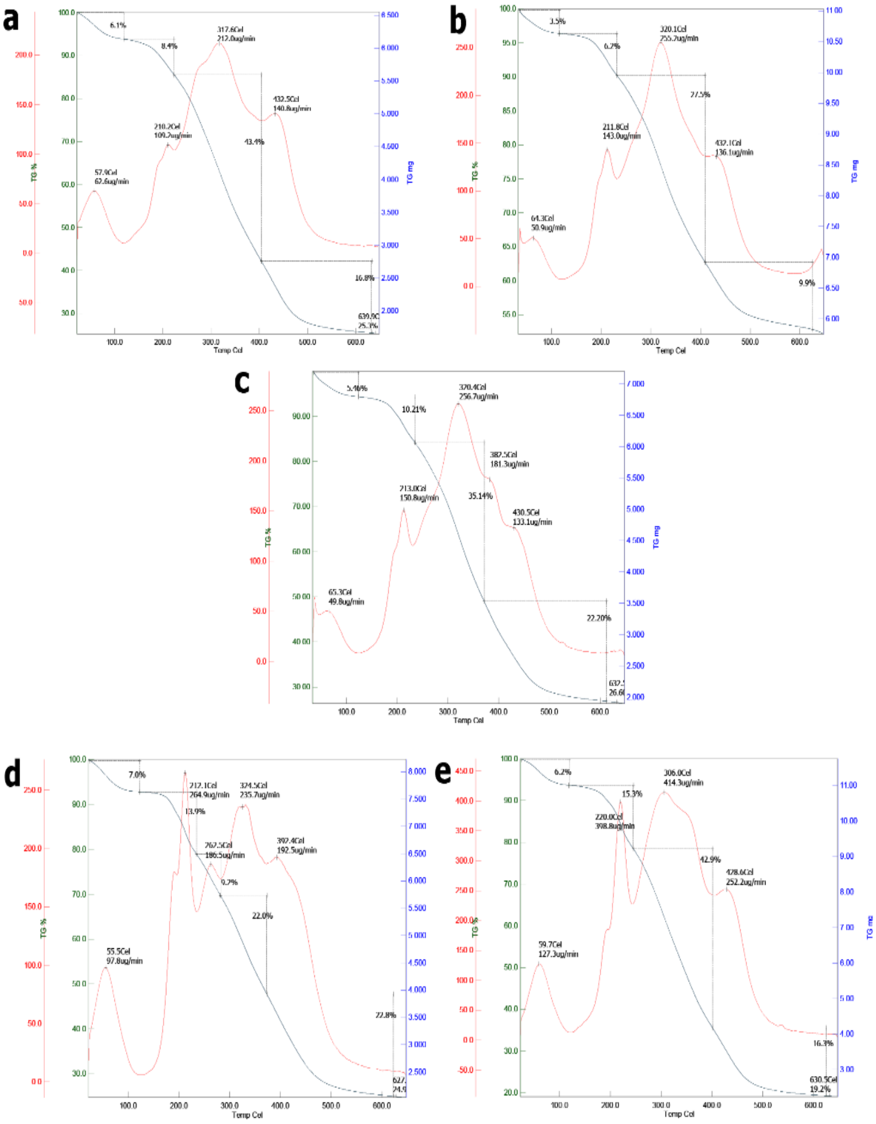

FIGURE 1. dTGA thermograms of; a) *Salix babylonica,* b) *S. caprea,* c) *S. fragilis*, d) *Fraxinus* excelsior and e) *Betula pendula*. In the figures, it is clearly shown that maximum degradations temperatures are visible in every steps.

4. Conclusion

Pollen grains have great potential to be used in cosmetic industry. Pharmacy, food and medical sciences thanks to their already known high thermal properties, homogeneity in size but it was not known how thermal properties of pollen grains are changed according to genus level. Here in the present study, it was clearly determined that there is a notable difference in thermal properties of pollen grains on genus level. Therefore, this study suggests that the chosen genus for pollen grain studies has an important role for determining their application areas.

Sporopollenins are scaffold materials produced by after harsh acid and base treatment to plant pollens. And these scaffolds have great interest by scientist especially their homogeneity in size, shape and its high thermal stability. But there are thousands of pollens belong to different taxa so here we recorded that it is very important to choose the sporopollenin in genus level before starting the study.

On the other hand, we tried to give an opinion to material scientist to choose the correct pollen genus for their study. For example, if they need high thermal properties, they can choose the pollen from the genus *Salix* or *Betula*. However, if they need a lower thermal stability, they can select pollen grains from *Fraxinus*.

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