Moisture Content and Glass Transition Temperature of the Spray Dried Natural Dye: Talisay (*Terminalia Catappa)* leaves and Mahogany (*Swietenia macrophylla*) Bark.

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***Abstract*—Natural dyes are potential colorants for textile and gained economic advantage over synthetic dyes, due to its non-toxic, non-carcinogenic and nature friendly feature. However, in spite of these advantages, natural dyes have poor storage stability. One way to address such problem is through spray drying; wherein the crude extracts are converted into powder form by atomization process. Currently, there are only limited studies about the shelf-life of the powdered natural dyes. In the presented research, the author evaluated the storage properties of the selected powdered natural dye: Talisay (*Terminalia Catappa)* Leaves and Mahogany *(Swietenia Macrophylla)* Bark by determining their glass transition temperature (T_g) and moisture content using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), respectively. The effects of varying air relative humidity to the equilibrium moisture content (EMC) of the colorant were also investigated in this study. Results showed that the selected dye powders have different degradation temperature and glass transition temperature. With this, it is recommended to dry the selected dye at different operating parameters. In addition, results from EMC curve, indicates that the Mahogany bark resembles the most stable powdered product due to its low EMC value even at varying relative humidity.**

***Keywords*—Equilibrium Moisture Content, Glass Transition Temperature, Natural Dye, Spray Drying**

I. Introduction

Textile dyeing plays a significant role in clothing industry. It adds market value and increase the desire of the customer to buy certain product. Anciently, textile dyeing was practiced using natural colorant, until synthetic dyes were invented and commercialized [1]. Synthetic dyes are synthesized from petrochemical sources through hazardous chemical process which, in effect, may cause problems with the environment as well as the human health. Due to these, interest with the production and commercialization of dye stuff from natural resources were rekindled.

Philippines has vast amount of natural resources that are potential source of natural dye. Among these are: Talisay Leaves, and Mahogany Barks. Crude extract from these sources were converted into powdered form using Spray Dryer. Powdered dyes are preferred over liquid dyes because they are easier to transport and provides longer shelf-life.

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However, studies indicates that parameter optimization of spray drying process mainly depends on the storage characteristic of the powdered dye [2]. But due to lack in information and literatures about these dye sources, optimization process becomes difficult. Hence, establishment of storage characteristics of each dye source is essential in spray drying optimization.

One of the minor constituents of the atmosphere is water vapor and it can be significant for the storage of materials. Excess moisture can make the product sticky and can cause clumping once the dried product is exposed to the environment [3]. It can also hasten the degradation of the powder. With this, it is necessary to identify the moisture content at which a solid material generates water vapor pressure equal to the surrounding environment to prevent dilapidation of the powder [4]; the moisture content related to these phenomena is known as the Equilibrium Moisture Content (EMC).

Aside from water content, the stability of the dried powder also decreases dramatically when the product undergoes transition from the glassy to rubbery stage, which led to the paramount importance of the Glass Transition Temperature (T_g). This temperature is considered as a function of a storage condition as water and moisture activity [5]. Thus, by controlling environmental conditions of the powdered products, their stability is increased.

To understand the storage characteristics of the spray dried Talisay Leaves and Mahogany Bark, the author evaluated and identified the Moisture Content and Glass Transition Temperature (T_g) using the Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) techniques, respectively. The author also provided an equilibrium moisture content curve to investigate the effect of varying relative humidity with the storage capability of the powdered dye. These datum are important because these can be used as basis in optimizing the spray dryer design and operation.

II. Materials and Method

A. Spray Dying Process

The basic idea of spray drying is the production of highly dispersed powders from a fluid feed by evaporating the solvent [6]. This is achieved by mixing a heated gas with an atomized fluid of high surface-to-mass ratio droplets, within

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the drying chamber, causing the solvent to evaporate uniformly and quickly through direct contact.

In the study, extracts (Talisay leaves and Mahogany bark) were placed inside the feed tank of the DOST developed spray dryer and were dried and powdered for at least 6 hours.

B. Moisture Content (MC)

Moisture content is often the only parameter used to define moisture conditions in hygroscopic products. It is important to consider because it influences the chemical and mechanical aspect of the dried powder. Accurate determination of the product's water content and mechanism of water-solid interaction is required to define suitable processing, packaging, storage condition and shelf-life [7]. One common technique used to determine this variable is through thermogravimetric analysis (TGA). TGA provides comprehensive information on mass change and characteristic temperature ranges for moisture release [8]. During TGA analysis, the release of water appears as a weight-loss step at a certain temperature that is easily evaluated and ideally quantifies the amount of water present in the sample.

In this research, moisture analysis for the dye powders of Talisay Leaves and Mahogany Bark were analyse using TGA Q-50. Wherein, samples of 5-10 mg were placed inside a platinum cell and heated at the rate of 10 ºC min^{-1} up to 110 ºC. The evaluated results are then used for Equilibrium Moisture Content (EMC) calculations.

TGA analysis is also significant because it can be used to understand the degradation temperature of the powdered sample. This temperature set the limit for the heating rate used during Differential Scanning Calorimeter (DSC) testing. To determine such parameter, the selected natural dye powder was heated in TGA Q-50 at the rate of 10 ºC min^{-1} up to 800ºC.

C. Equilibrium Moisture Content (EMC)

Equilibrium Moisture Content (EMC) is the moisture content at which a solid material generate water vapor pressure equal to its environment [9]. Under at constant temperature and relative humidity, the moisture content of the spray dried sample will become constant at sufficient time, implying that the net moisture exchange with the atmosphere is zero. EMC is vital in understanding the shelf-life of the spray dried powder because it rates the mechanical and chemical degradation of the product.

To determine the EMC of the dried natural dyes, three (3) weighing bottles holding one (1) gram (±0.01 g) of powders from Talisay leaves and Mahogany bark were placed inside the desiccators that contains sulphuric acid solutions with concentrations of 50%,70% & 90% (by weight) to maintain the relative humidity of the system. Temperature in this part was held constant; using room temperature as the basis. To prevent the formation of moulds in the sample, cottons containing 2-3 drops of formic acid were placed at the top of each weighing bottles. Samples are taken out of the desiccators every 48 hours to measure the change in their weight. This is done until it reached a constant weight. Then EMC is calculated using the equation below:

$$EMC = \frac{(w_f - w_i) + (M_i . w_i)}{w_i .(1 - M_i)} \tag{1}$$

Where w_i is the initial weight of the samples, w_f is the final weight of the sample after equilibrium and M_i is the initial moisture content fraction that were determined in TGA Q-50.

The value of EMC depends on the material, temperature and the relative humidity of the surrounding air at which it is in contact. At equilibrium, the relationship between EMC and Relative Humidity (RH) of the powdered dye can be graphically represented [9]. In this paper, the EMC obtained after the experiment were graphed with respect to RH.

D. Glass Transition Temperature (T_g)

The deteriorative phenomenon that occurs most frequently in the powdered products has been associated with the transition from glossy to rubbery state. In powdered products, when a critical temperature, related to glass transition temperature (T_g), is reached, a sequence of deleterious events occur such as stickiness and caking [10]. To prevent these undesirable phenomena, it is important to identify the glass transition temperature.

There are several techniques that can be used to measure the glass transition temperature of the powdered product; one technique is using Differential Scanning Calorimetry (DSC). It utilizes heat flow and compares the amount of heat supplied to the test sample and a similarly heated reference to determine transition point. T_g is typically calculated by using a half-height technique in transition region.

For the selected powdered dye (Talisay Leaves and Mahogany Barks), the glass transition temperature were identified using DSC Q200-TA. Wherein, each dye samples with recorded different weight were placed in a T-zero aluminum pan and crimped with a T-zero aluminum lid. The operating parameters used in DSC operation are summarized in Table 1. Meanwhile, an empty T-zero aluminum pan and lid are used for reference cell. Glass transition temperature is evaluated in the DSC thermograph, which is obtained after each run.

TABLE 1: DSC PARAMETER

Test Sample	Trial Number	Weight	Ramp and Equilibrium Temperature
Talisay Leaves	1	10.8 mg	5-300^{0}C/min Equilibrate @ 30 ^{0}C
	2	16.4 mg	5-190^{0}C/min Equilibrate @ 45^{0}C
Mahogany Bark	1	7.8 mg	5-180 ^{0}C/min Equilibrate @ 45 ^{0}C
	2	7.5 mg	5-180^{0}C/min Equilibrate @ 45^{0}C

III. Results and Discussion

Presented in figures 1 and 2 are the TGA thermograph for the moisture analysis of the Talisay Leaves and Mahogany Bark, respectively. It can be noted from these figures that the initial weight of the sample decreases as the temperature increases, indicating that moisture is evaporated during the test.

For powdered Talisay leaves, as represented in figure 2, the initial decomposition temperature (IDT) begins at 172.87°C losing 10.73% moisture. This temperature only signifies that the powder starts to disintegrate and should not be operated nor stored at the said temperature. In addition, this parameter also served as basis for the limitation of the DSC heating rate to avoid full decomposition of the sample. Meanwhile, the maximum rate of decomposition temperature (MRDT) for powdered Talisay leaves is observed to be at 279.03°C, losing 54.11% moisture content; and the material eventually degrade as the temperature increases. This rate is displayed by the diagonal slope that can be observed after the radius of curvature in figure 2. Lastly, based on the same figure, the final moisture loss at 800°C is 80.47%, this value denotes that the powder collapsed at this condition due to loss of water. Therefore, to prevent degradation of the product, it is advisable to operate such materials at the temperature range below IDT, which is represented by the plateau part of the thermograph.

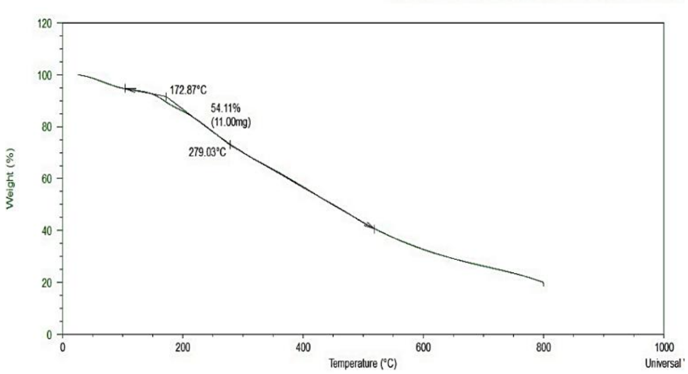

Fig. 1. Powdered Talisay Leaves TGA Thermograph

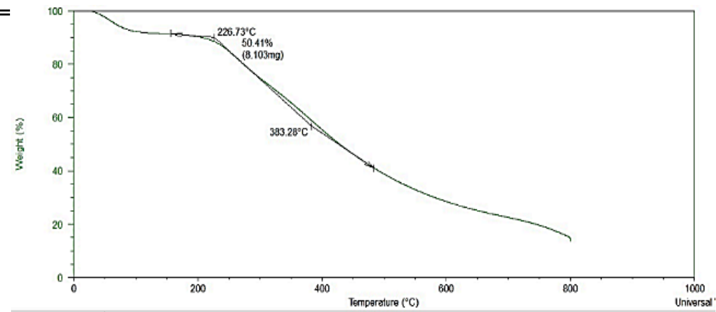

Fig. 2. Powdered Mahogany Bark TGA Thermograph

The same explanation goes with the loss of moisture in Mahogany bark. Wherein, it's IDT and MRDT, as graphed in figure 2, are: 226.73°C, 383.28°C, respectively. While the percentage moisture loss at the said temperature is: 50.41.

Glass transition temperature of the powdered Talisay leaves and Mahogany bark were summarized in Figures 3 and 4, respectively. Figure 4 shows the thermograph for the powdered Talisay leaves which is operated at the heating rate of 5°C/min to 190°C/min. Based from this figure, it can be noted that the glass temperature is very close to the observed endothermic peak. By getting the midpoint temperature between the observed changes in heat flow, the recorded glass temperature for Talisay leaves is 155°C. This temperature is significant because it influences the process ability and storage stability of the powder. Storing dried powder and operating spray dryer above the glass transition temperature may cause stickiness and caking of the product. Meanwhile, the observed endothermic peak shows that the sample will begin to melt at 160°C. This temperature is very close with the previous recorded IDT of 172.87°C. In addition, careful analysis of DSC result is needed, since some of the data from the graph may cause confusion during interpretation. As observed, a small endothermic peak at temperature of 145°C is noted in Figure 4. This peak is caused by impurities present in the sample and should not be mistaken to glass temperature. Meanwhile, the interpretation for figures 5 is the same with case of the Talisay leaves. Wherein, the recorded glass transition temperature is 125°C.

Comparison of TGA and DSC thermograph were also presented in figures 5 and 6. These figures were shown to validate the results of the two test. Based from these, it can be noted that initial degradation temperature of the sample is very near the melting temperature. Confirming that the powdered sample will degrade between this temperature range.

Literatures indicate that EMC is a function of the temperature, relative humidity and the nature of the product. In this study the EMC is determined using equation 1 and were graphed against the varying relative humidties (see

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figure 7). However, prior to equation 1, the initial moisture content were identified using TGA Q-50 and based from the result the initial moisture content of the powdered Talisay leaves and Mahogany bark are as follows: 0.05769 and 0.06125.

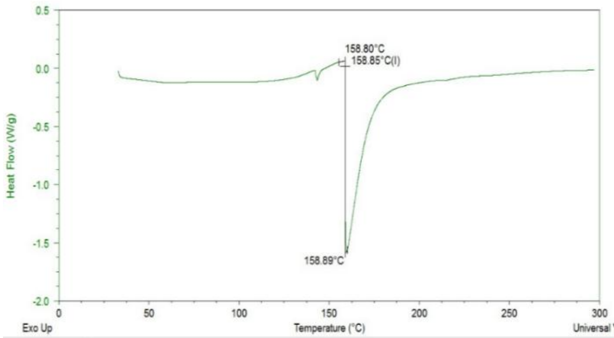

Fig. 3. Talisay Leaves DSC Thermograph

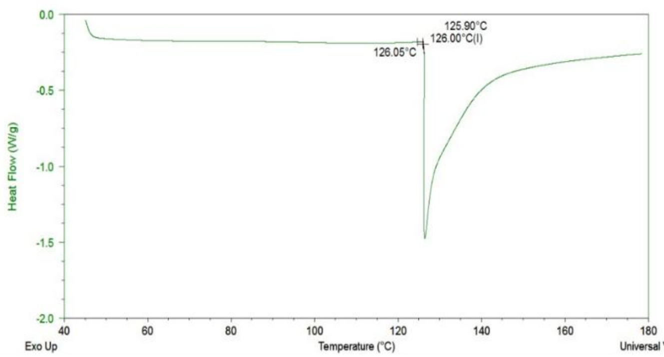

Fig. 4. Mahogany Bark DSC Thermograph

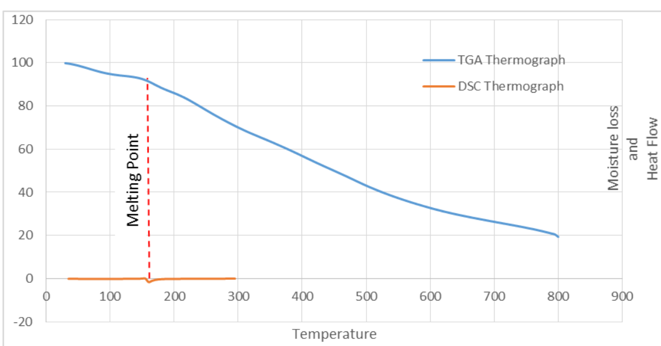

Fig. 5. TGA and DSC Thermograph of Powdered Talisay Leaves

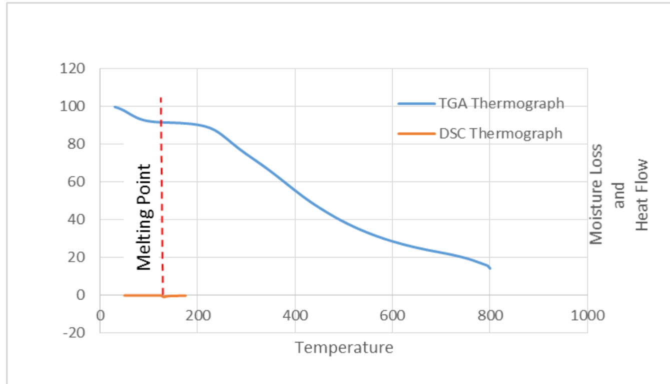

Fig. 6. TGA and DSC Thermograph of Mahogany Bark

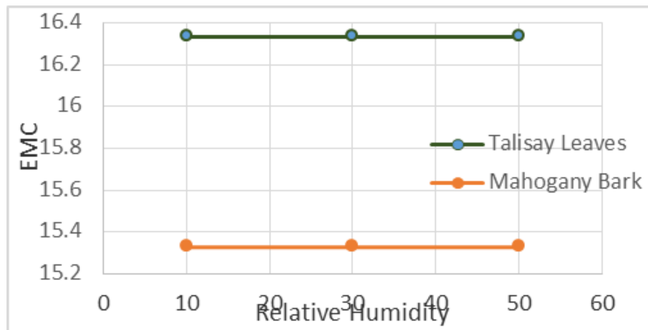

Fig. 7. EMC Curve

Comparison of the EMC curves among the samples shows that the spray dried Mahogany barks has the lowest EMC, which means this sample is easier to store and operate in varying humidity inside the dryer. The results also show that at higher relative humidity, the spray dried samples absorbs more moisture from the environment. Meaning, the moisture content of air is proportion to the moisture content of the samples. However, the graph also indicates that increased in relative humidity results to a minimal effect on the EMC which indicate that spray dried powders can be stored at room temperature even at high humidity.

IV. CONCLUSION

Thermogravimetric analysis (TGA) and differential scanning (DSC) are two techniques used to understand and identify the moisture content and the glass transition temperature of the spray dried natural dye. It was noted, that at the same operating drying parameters, all of the samples have different storage characteristics. Wherein, the Talisay leaves show the lowest glass transition temperature, melting temperature and degradation temperature. Indicating that Talisay leaves should be operated and stored in lower temperature than the Mahogany bark. Meanwhile, curves from EMC stipulates that Mahogany bark is the most stable powdered dye among the samples since it reflects the lowest EMC at varying relative humidity.

V. Reference

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