Thermal Analysis of Chitin in different aging of *Leucaena leucocephala* pods

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***Abstract*—In this work, the thermal analysis of chitin with different aging of *Leucaena leucocephala* pod were investigated by means of thermogravimetry analyses and differential scanning calorimetry under dynamic nitrogen atmosphere in the range of 25^{0}C-500^{0}C. The samples also have been test with chromameter to find the colour characteristic. The results obtained were compared with literature to find the similarities of the chitin characteristic. From results, the different aging of samples gives a slightly different curve for TGA and DSC. The first stage of mass loss was at temperature between 50 to 100^{o}C while the second stage mass loss is between 150 to 450^{o}C. The maximum degradation temperature (DTG_{max}) was observed at between 300 to 350^{o}C for all the samples. Subsantially, the two phase mass loss and temperature at DTG_{max} in thermogravimetry analysis showed a similar characteristic of chitin reported from several previous studies. In Differential scanning calorimetry, the samples melting temperature (T_m) was recorded as close to each other which are 90 ^{o}C. However, melting enthalpy (ΔH_m) showed a value that is distinct for each sample. This may due to the different chemical composition from each sample. Therefore, further study can be made to know better the chitin characteristic from this sample with different type of analysis.**

Keywords— Chitin; characterize; thermal degradation; thermogravimetry.

I. Introduction

Chitin ($(C_8H_{13}O_5N)n$) is the second most abundant biopolymer after cellulose found in arthropods such as insects, crustaceans, arachnids and myriapods (Liu et al., 2012). It is also an essential component of the cell walls and septa of all pathogenic fungi, and occurs in the cyst walls of pathogenic amoebae, the egg-shells and gut lining of parasitic nematodes and the exoskeletons of invertebrate vectors of human disease including mosquitoes, sand flies, ticks and snails (Lenardon et al., 2010). It is naturally white, hard and inelastic nitrogenous polysaccharide (Dutta, Dutta, & Tripathi, 2004). Traditionally, the source of chitin is shellfish waste from shrimp, crab and lobster processing (Synowiecki, Ali, & Quawi, 1997). This is due to the large amount of this waste is generated for seafood industry annually.

Leucaena leucocephala is a well known tree since 1970s and early 1980s. Because of its worldwide success as a long lived tree which is highly in nutrition forage tree, it was known as miracle tree. Not only limited to that, Leucaena has its great variety of uses such as provide firewood, timber, human food, green manure, shade and erosion control (Brewbaker and Sorensson, 1990).

The conventional extraction process from animal source requires a lot of chemical due to the chitin chemical bond with protein. Moreover, the chemical chitin purification is extremely hazardous, energy consuming and threatening the environment. The use of animal sources also require additional steps such as mechanical grinding, demineralization with acid and deproteination with alkali which can cause depolymerization that can affects the properties such as molecular weight, viscosity, and degree of acetylation of chitin.

In regards to the large fields of applications of chitin biopolymers, the accurate knowledge of their thermal degradation appears to be of great importance in order to define the applications of such materials. Thermal behavior can be achieved by using some physical chemistry techniques, especially thermal analysis methods DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis).

In the TGA curves of the chitin sample reported by Moussout et al. (2016), there were three characteristic temperature intervals of weight loss. The first one (44^{0}C -102^{0}C) with 10-15% weight loss, corresponds to the evaporation of physically adsorbed and strongly hydrogen bonded water to chitin. The second weight losses, occurring in the range 250^{0}C - 400^{0}C, were 65 %, and were caused by depolymerisation or decomposition of polymer chains through deacetylation and cleavage of glycosidic linkages.

Wang et al. (2013) obtained a sharp but wide endothermic peak from DSC at the temperature range from 52.30 to 112.38 °C from Antarctic krill chitin. This could be due to the loss of absorbed water and hydrogen-bonded water to the polysaccharide structure. In the second heating program, the glass transition (Tg) in the thermogram can be shown by the stepwise increase from 164.96 °C. The endothermic peak centered at 378.68 °C could be related to the decomposition of acetyl-glucosamine units.(Wang et al., 2013).

The objective of this study is to characterize chitin in with different aging of *Leucaena leucocephala* skin by using Chromameter and also to study the thermal properties of sample by Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC).

II. METHODOLOGY

A. Materials

Seven different ages of *Leucaena Leucocephala* were collected from the tree in local area in Shah Alam. The pods were then dried and ground in dry mill. Table 1 shows the age of each sample.

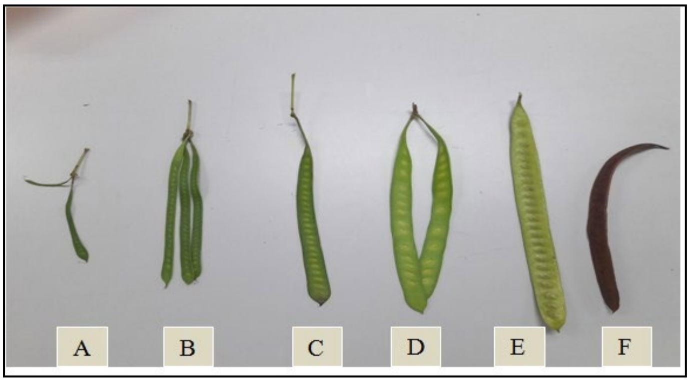

Fig 1: Six different ages of *Leucaena Leucochephala* pods

Table 1: The different aging of the samples

Sample	Age	Size	Colour
A	7 days	Length:10 cm Width:0.5 cm	Dark green
B	15 days	Length:17 cm Width:1.0 cm	Light green
C	25 days	Length:21 cm Width:1.7 cm	Light green
D	28 days	Length:22 cm Width:1.8 cm	Yellowish green with yellow pods
E	42 days	Length:26 cm Width:2.3 cm	Yellowish green with brownish pods
F	56 days	Length:26 cm Width:2.3 cm	Brownish with black pods

III. RESULTS AND DISCUSSION

A. Thermogravimetry analysis

The first stage of mass loss at temperature between 50 to 100°C contributes to the loss of water (Anthony et al., 2016;Kumari et al., 2015). Previous literature which report a close value to this result is between 30 to 180^{0}C (Kaya et al., 2016) and 50 to 150^{0}C (Kumari et al., 2015).This can be explained from the sample aging where water contents increase as the aging increase and it will later decrease when the sample is begun to old and wilt.

The second mass loss is between 150 to 450°C which reflects the compound thermal decomposition (Kumari et al., 2015; Sagheer, Al-sughayer, Muslim, & Elsabee, 2009). This decomposition occurs slightly in different temperature range between the samples. This might result from the degradation of different molecular structure that constitute in the samples. This result agreed with the previous study by Kumari et al. (2015) and Moussout et al. (2016). The second stage of mass loss in the extracted chitin reported by Wang et al. (2013) between 260 to 400 °C was contributed by the dehydration of polysaccharide rings and polymerization and decomposition of acetylated and de-acetylated units of chitin.

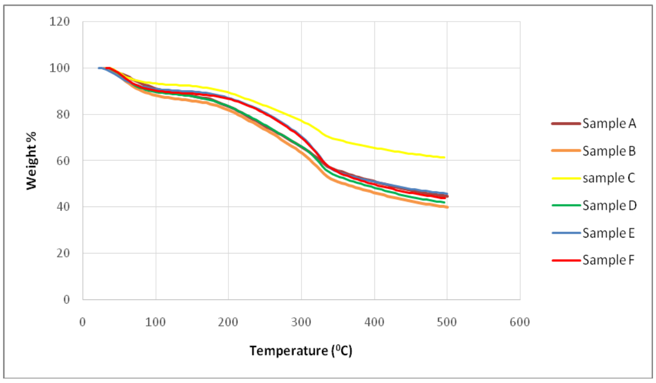

Fig 2: The TG curve for different aging of samples under TGA analysis

B. Differential Scanning calorimetry

The DSC curve of samples in figure 2 showed a sharp endothermic peak in the temperature range from 80 to 100°C. This could be due to the loss of absorbed water and hydrogen bonded water to the polysaccharide structure as suggested in previous study by Wang et al. (2013). A broad endothermic peak in contrast is reported by another study in between temperature of 35 to 150^{0}C for chitin extracted from shrimp shells (Praveen & Yijayalakshmi, 2014).

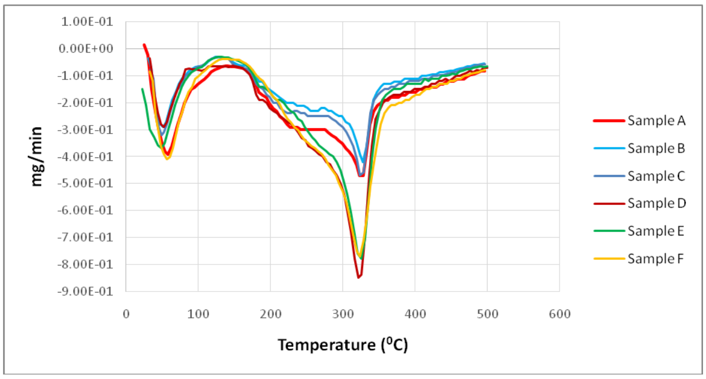

Fig 3: DSC curve for different aging of samples.

Two thermal factors, melting temperature (T_m) and melting enthalpy (ΔH_m) were identified according to maximum endothermic peaks of diagrams and compared for different samples. The samples melting temperature show a value that is close to each other which is around 90^{0}C. The melting enthalpy, ΔH_m in the other hand shows a distinct value. These values are tabulated in the table 2 below. The higher the melting point and melting enthalpy, the more stable and good thermal properties of the sample composition (Sahraee, Milani, Ghanbarzadeh, & Hamishehkar, 2017). This results show that sample A has the most stable chemical composition and good thermal properties. The older the sample, the seeds become more prominent. Some of plant seeds have surface cells containing gums, mucilage, fiber and protein (Mirhosseini & Amid, 2012). Sample which more seeds have poor thermal stability because of the present of this compound such as in sample D and E. Previous study mostly does not mention these thermal properties on extracted chitin. However, the good thermal property is one of criteria that is important to be considered.

Table 2: The thermal properties of samples

Sample	T_m (^{0}C)	ΔH_m (Jg^{-1})
A	85	380.99
B	78	186.22
C	80	172.50
D	75	181.20
E	70	174.17
F	80	248.59

C. Chromameter Test

Table 4.2 shows the coordinates of the sample obtained from chromameter test. From the coordinates obtained, it can be concluded that the different aging of the sample gives distinct colour characteristic. As the age is increase, the lightness of the sample will decrease because aging cause the surface of the samples become darker in colour. Red/ green coordinates, a* shows a descending value due to the green colour of samples decrease respect to aging. As for the yellow/blue colour, the coordinates show an increasing value due to the samples become more yellowish colour as the sample aging.

Table 3: Coordinates of the samples in Chromameter test.

Sample	L*(lightness)	a*(red/green)	b*(yellow/ blue)
A	L*=60.23	a*=-4.71	b*=7.16
B	L*=52.47	a*=-11.49	b*=17.59
C	L*=51.39	a*=-16.83	b*=32.59
D	L*=55.21	a*=-19.61	b*=36.01
E	L*=52.77	a*=-13.28	b*=30.39
F	L*=35.53	a*=11.87	b*=11.52

IV. CONCLUSION

This study revealed the thermal properties of Leucaena Leucocephala skin pods with respect to aging. From the results, it can be concluded that the different aging of samples give different thermal properties. The TGA and DSC analysis was convincingly signifies the present of chitin from the samples by showing a result that is identical to the previous study. However, not all the sample aging showed a good result. The thermal characteristic of sample A, which is the youngest one of the sample showed a good similarities to chitin from previous report. In addition, sample A showed a most stable thermal property. Further study is required to determine the chemical composition of this sample. Therefore, sample A aging is a good sample if further study is to be done. For future research, the sample could be analyzed with other techniques to determine its chemical composition such as elemental analysis or Fourier Transform infra red. It is recommended that the seeds of the Leucaena for sample D, E and F are removed before the extraction is made because the result of analysis showed a poor thermal characteristic with this sample.

ACKNOWLEDGMENT

Thank you to my supervisor Puan Noorharliza Abd Razak and Universiti Teknologi Mara.

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