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Analysis on Thermal Degradation and Chemical Contents of Bamboo *Gigantochloa brang.*

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ABSTRACT

The degradation and chemical contents of a tropical bamboo *Gigantochloa brang* were studied and analyzed. The fourier transform infrared (FTIR) spectroscopy and thermal gravimetric analysis (TGA) equipment were used in the analyzing. The studies revealed the presence of basic functional groups p in the bamboo consisting mainly of ester, carbonyl and hydroxyl. The chemicals present vary in compositions depending on the location and position on bamboo samples taken. The same set of activation energies (105, 127, 100, 236, and 46 kJ/mol, respectively) were applied to all of the bamboo samples. Low reactivity of lignin components and hemicellulose occurred due to the peculiarities in the bamboo chemical structure/composition. The extractive and the moisture content was not taken into consideration in the kinetic study since they consists of less than 10%. The mechanism of the decomposition reactions were taken as three-step reactions involving hemicellulose, cellulose, and lignin with activation energies and dynamics of the related volatile fractions. The activation energy carried out in this study provides better insight into the thermal decomposition process as it provide more information on critical energy needed to start a reaction. The decomposition activation energy range obtained in this study could help in understanding the thermal decomposition stability of bamboo fibers and its application in natural fiber reinforced polymer composite industry. The activation energy can be useful in evaluating other parameters of thermal kinetics.

Keywords: Tropical bamboo *Gigantochloa brang*, degradation, chemical composition, FTIR, TGA.

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INTRODUCTION

Due to their robust chemical and good physical properties the plant based materials have often being used as durable goods and parts of materials for construction. These materials are often referred to as lignocellulosic based on their main chemical components, cellulose and lignin. At high temperature, these lignocellulosic materials are subjected to thermal degradation. This process can occur in different forms depending on the temperature and environment where they are exposed to.

Fourier transform infrared spectroscopy (FTIR) was a useful technique for studying of the bamboo decay chemistry, as well as to characterize the chemistry of bamboo. It is also useful in analyzing the chemical and structural changes that occur in bamboo components due to different temperatures. Thermal gravimetric analysis (TGA) has been used to study the thermal stability of selected bamboo species. The measurements in TGA can be performed during a rising in temperature, at static rate (isotherm) or under a temperature program. TGA is one of the thermal analysis techniques used to quantify weight change and thermal decomposition of sample. It was reported that the chemical composition, heating rate, temperature, and inorganic substances are the major factors that affect the thermal behaviour of biomass.

In micro particular scale, the plant cell wall of bamboo is principally made of the polymer cellulose in the form of microfibrille, hemicellulose, and lignin. The composition of these four constituents of wall in bamboo tissue varies from one species to one another and presents the different physical structures. Like all the polymer composites, the variation in their rates within bamboo materials has an impact on the thermo-mechanical and thermo-dielectric properties. The information on the thermic stability of the material is required to determine the thermo mechanical or thermo dielectric properties. The bamboos species of Malaysia under genus *Gigantochloa*, the Buluh Brang (*Gigantochloa brang*) was analyzed for thermal degradation. The process of degradation of bamboo material through thermal analysis was studied and tested to determine the influence of the wall constituents. The thermal characterizations of selected bamboo species were performed using the FTIR and TGA techniques.

MATERIALS AND METHOD

Samples preparation

Three years old bamboo culms *Gigantochloa brang* were collected from the experimental fields of the Forest Research Institute Malaysia (FRIM), The selected bamboo culms were cut at 15 cm ground above level and diameter of the culms range between 11-17 cm. Ten (10) bamboo culms of this species were harvested and cut into internode and node strips. The epidermis of each strip was first slightly scraped off with a fine blade. The remaining material was divided evenly based on volume into inner, middle and outer layers along the radial direction. The 15 cm long fresh bamboo sections cut from each culm locations were oven dried at 50°C for 72 h. Some portion of the bamboo samples were reduced into chips using a commercial chipper, then screening to the size between 40 mesh (425µm) and 60 mesh (250 µm).

FTIR measurements

The Fourier transform infrared spectroscopy (FTIR) was performed by means of a Nicolet AVATAR 360 spectrometer, taking 32 scans for each sample with a resolution of 4 cm^{-1}. The bamboo samples were pounded in a mortar and ~1 mg of the obtained powder was dispersed in 100 mg of KBr. The bamboo samples were dried before dispersion in KBr, and the mixed powder was pressed into a disk that was immediately analyzed.

Thermal gravimetric analysis (TGA) measurements

Simultaneous thermogravimetric and differential thermogravimetric analyses were carried out using a Shimadzu (Model 30) thermal analyzer at heating rates of 20°C min^{-1} and the temperature ranged between 30 and 1000°C under nitrogen atmosphere. Each bamboo sample mass of about 5 mg and particle sizes below 0.18 mm were distributed evenly in an open platinum crucible used. These experimental conditions ensure a negligible spatial gradient of the temperature inside the samples with negligible effects on the thermal decomposition of *G. brang.* Duplicate samples of TGA were taken for each sample to cross check if the two curve overlap on each other.

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RESULT AND DISCUSSION

FTIR Analysis

The fibers from three (3) different positions of the internodes or the nodes show the same absorption bands with no significant differences in intensity. This suggests that irrespective of the location of the fiber, the chemical compositions of the bamboo fiber are similar in all respect. The absorbance at 3411, 2906, 1734, 1430, 1161, 1049, 897 cm^{-1} are associated with the typical absorption of lignocellulosic materials [1][2] [3]. These absorbance were present in all the FTIR of the bamboo studied irrespective of the location of the fiber. All FTIR spectra are dominated by the peaks at 3411 and 1048 cm^{-1} indicating the stretching vibrations of O–H and C–O, respectively, present in the bamboo constituents. Furthermore, chemical compositions of bamboo fiber have shown that it contain mainly of cellulose, hemicellulose, and lignin like other common lignocellulosic fiber such as wood, empty fruit bunch fiber, coir fiber etc [4]. Table 1 shows the IR absorptions of wavelength of peaks used for FTIR analysis and corresponding functional groups.

Table 1: Wavelength of peaks used for FTIR analysis and corresponding functional groups.

Wavenumber (cm^{-1})	Phenomenon	Functional Group
3600-3200	OH stretch	Alcohols, water
3550-3000	NH stretch	Primary amines
3000-2850	CH stretch	Alkyl groups
1475-1400	CH2	Methylene groups
1465-1440	CH3	Methyl groups
1800-1680	C=O stretch	Carbonyls groups
1670-1615	C=C stretch	Alkenes
1200-1070	C-O stretch	Ethers

Table 2: The main IR peaks and their corresponding functional groups for the internode and node of *G. brang*.

Frequency [cm^{-1}]			Frequency [cm^{-1}]			Assign-ment	Remark
Internode of *G. brang* species			Node of *G. brang* species				
Outer (A)	Middle (B)	Inner (C)	Outer (A)	Middle (B)	Inner (C)		
3412	3414	3413	3412	3411	3415	OH	stretching frequency of hydroxyl
2889	2903	2928	2889	2913	2933	C-H	stretching vibration
1736	1733	1732	1736	1735	1732	C=O	stretching frequency of carbonyl group
1513	1509	1501	1513	1513	1514	C=C	stretching frequency of aromatic group
1426	1428	1427	1426	1426	1426	O-H	plane bending vibration of hydroxyl
1050	1044	1046	1050	1054	1052	C-O-C	asymmetric stretching of ester group
834	830	828	834	833	832	C-H	stretching of β-glucosidic linkage

Figures 1, 2 and Table 2 showed the main IR peaks and their corresponding functional groups for the internode and node of *G. brang* species. It can be seen that all the spectra are typical style of lignocellulosic fiber as described below. The absorption at 3412 cm^{-1} and 2899 cm^{-1} are attributed to the stretching vibration of –OH groups and to C–H stretching, respectively, corresponding to the aliphatic moieties of hemicelluloses, cellulose and lignin. The band at 1733 cm^{-1} is ascribed to stretching vibration of the carbonyl group (C = O) [22] of the cellulose and hemicelluloses components in the bamboo fiber [5][2][22].

The small absorbance's at 1603, 1510, 1459 and 1335 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C–O stretching in aromatic ring of the lignins [3][6][7]. The bands in the 1640 and 1604 cm^{-1} region may be attributed to C-O stretching vibration of the alpha keto carbonyl in the cellulose component of bamboo [8]. The bands in the region 1248–1049 cm^{-1} have been assigned by previous workers and were attributed to C–O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose and lignin [7][9][10]. Although, the second most prominent and strong band at 1046 cm^{-1} was attributed to C–O stretching in cellulose, hemicelluloses, and lignin or C–O–C stretching in cellulose and hemicelluloses component [7][11]. The peak at 833 cm^{-1} is due to b-glucosidic linkage while the peaks at

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664 and 607 cm^{-1} are due to out-of-plane bending vibration of intermolecular H-bonded O–H group and out-of-plane O–H bending [9].

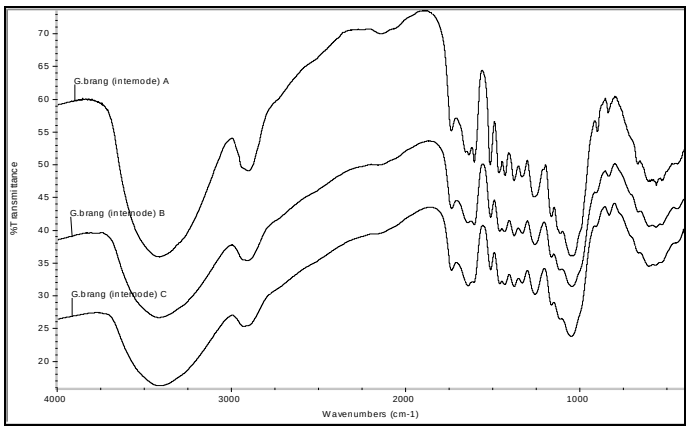

Figure 1: FTIR spectra of *Gigantochloa brang* at the internode

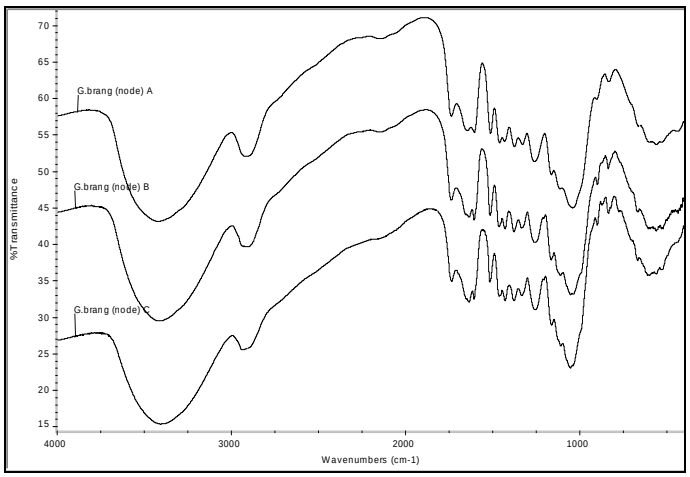

Figure 2: FTIR spectra of *Gigantochloa brang* at the node

Comparing all the spectra at different locations and positions, the peaks at the frequencies 3410 cm^{-1} and 1051 cm^{-1} are the dominant feature in the spectrum. The strong and broad band at 3410 cm^{-1} originates from OH stretching. On the other hand, the sharp and strong band at 1049 cm^{-1} is attributed to C-O stretching in cellulose, hemicelluloses, and lignin or C-O-C stretching in cellulose and hemicelluloses [12]. Also, the intensive band at 1643 cm^{-1} is assigned to H-O-H bending of absorbed water. The small absorbance at 1520, 1447, and 1335 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C-O stretching of the lignin components of various bamboo species [13].

The sharp band observed at 1733 cm^{-1} is due to the absorption of carbonyl stretching of ester and carboxyl groups, which are the most abundant in bamboo hemicelluloses [14]. The band in the region of 1248-1059 cm^{-1} involves the C-O stretching vibrations of the aliphatic primary and secondary alcohols in the cellulose, hemicellulose and lignin [9][15]. Previous studies have shown that lignocellulosic fibers can experience significant weight loss due to partial dissolution of hemicelluloses, lignin and pectin when treated with alkali [6][9][16]. The C=O absorption band of the carbonyl group at 1733 cm^{-1} disappears on alkali treatment of natural fibers which is an evidence that this band is due to hemicellulose component of natural fiber [2]. A small sharp band at 903 cm^{-1} arises from α-glucosidic linkages between the sugar units in hemicelluloses and celluloses [9][15].

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Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a useful method for the quantitative determination of the degradation behaviour and the composition of the natural fiber [17]. Table 3, Figures 3 and 4 showed the TGA curves of the outer, middle and inner layer of *G. brang* internodes. The samples were designated as GBIA (outer), GBIB (middle) and GBIC (inner) layer of *G. brang* internodes respectively. Likewise, GBNA (inner), GBNB (middle) and GBNC (outer) layer of *G. brang* nodes respectively. The TGA curves showed a slight weight loss before 100°C, which can be attributed to the evaporation of water. The slight weight loss ranged between 6.4 to 7.5% in which the middle position recorded the least value. The lower values of moisture content as shown in Table 3 might be due to reduction in hydrophilic tendency associated with the reduction of the free hydroxyl of the phenolic group present in the cellulosic and lignin component [7]. Similar observations were recorded with *G. brang* at the nodes where the weight loss ranged between 4.9 to 7.1% in which the middle position recorded the least value.

Table 3: Thermal degradation temperatures and residue weight of *G. brang*

Location / Position	Moisture	T_{10} (°C)	T_{30} (°C)	T_{50} (°C)	T_{70} (°C)	Residual weight % at 800°C
Inter node:						
GBIA (outer)	7.5	268	347	375	659	26.1
GBIB (middle)	6.4	216	327	365	387	7.6
GBIC (inner)	7.4	195	325	367	401	14.1
Node:						
GBNA (inner)	7.1	238	327	362	387	11.2
GBNB (middle)	4.9	241	330	363	390	13.5
GBNC (outer)	6.0	216	329	364	711	28.3

Note: The samples were designated as GBIA (outer), GBIB (middle) and GBIC (inner) layer of *G. brang* internodes respectively. Likewise, GBNA (inner), GBNB (middle) and GBNC (outer) layer of *G. brang* nodes respectively

The comparison of *G. brang* at the internode and node degradation under nitrogen atmosphere revealed striking similarities of the shape of the TGA curves. This behavior was in agreement with the results obtained by Xie *et al.* (2007) [18] and Mui *et al.* (2008) [14] during the investigation of the degradation of wood and their derivatives under nitrogen atmosphere. However, the temperature range, the weight losses and the rates of thermal at the different stages of the thermal degradation (de-volatilization and combustion steps) changed with each different fiber and at any specific location on the plant [19]. It was observed that the *G. brang* internode samples are stable up to 210°C and thereafter starts to decompose. Table 4 below shows decomposition temperatures, the outer, middle and inner location of the *G. brang* fiber at the node and internode decomposed in two stages which are mainly due to cellulose, lignin and hemicellulose. The degradation temperatures for the outer layers at different time intervals are higher than those for the middle and inner layer in both internode and node.

At 50% weight loss the decomposition temperature occurs at 375, 365 and 367°C for the GBIA (outer), GBIB (middle) and GBIC (inner) sample of *G. brang* internodes. Variation in decomposition temperature becomes more visible at 70% weight loss following the same pattern. This increasing trend of decomposition temperature indicated that the thermal stability of the inner layer at the internode of G. brang is higher than that of the outer layer while the thermal stability of the middle layer recorded the least stability. The weight loss at this temperature region (above 800°C) corresponded to the formation of volatile products which arose from random chain scission and intermolecular transfer involving tertiary hydrogen abstractions from the hemicellulose, cellulose and lignin [20][21]. The outer samples of *G. brang* nodes and internodes show the highest residual weight at the internode and node respectively. Table 3 and Figure 5 showed the decomposition temperatures for *G. brang* at the internode and node.

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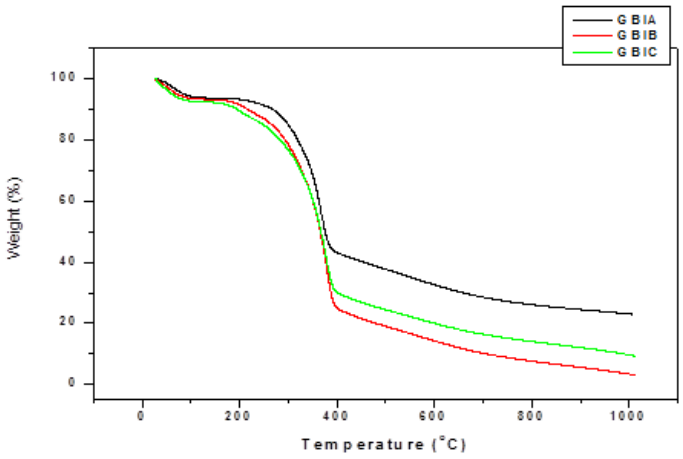

Figure 3: Thermogravimetric analysis of *G. brang* internode under nitrogen

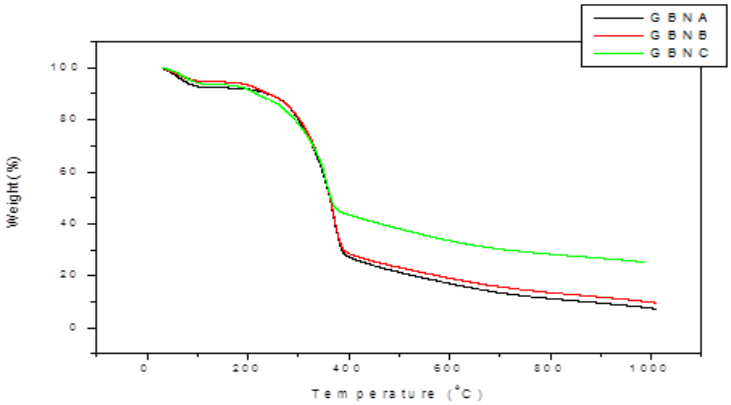

Figure 4: Thermogravimetric analysis of *G. brang* node under nitrogen.

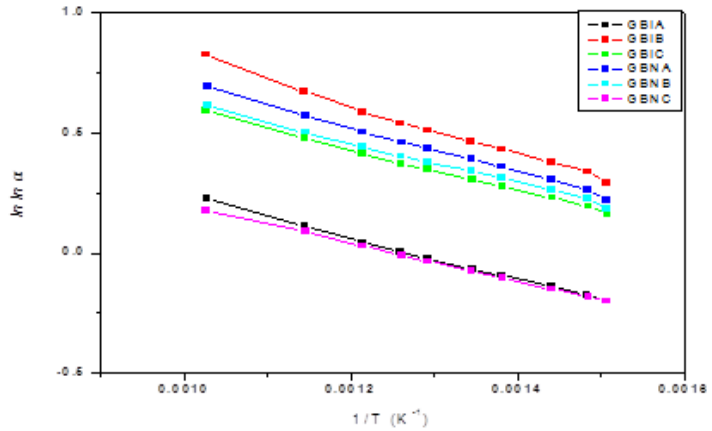

Figure 5: Plots of *ln (ln l/α)* versus *l/T* for the degradation of *Gigantochloa brang* (for selected values between 230 - 700°C).

Table 3: Decomposition temperatures for *G. brang* at the internode and node samples.

Samples	First decomposition	Second decomposition	Maximum temperature
The outer, middle and inner location *G. brang* fiber at node and internode.	Between 210°C and 390°C (mainly cellulose and hemicellulose)	Between 390°C and 800°C (decomposition of lignin)	800°C (residual weight loss)

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CONCLUSIONS

The basic functional groups present in *G. brang* are mainly ester, carbonyl and hydroxyl. These were confirmed by the FTIR analysis. The *G. brang* species present properties which vary depending on the location and position on bamboo culms due to variation in chemical compositions.

The FTIR and TGA curves appear qualitatively similar for both cases, apart from a higher overlap between the hemicellulose and cellulose zones for various bamboo culms. From the quantitative point of view, based on the definition of characteristic reaction temperatures, *G. brang* shows lowest reactivity of lignin components and hemicellulose probably because of peculiarities in their chemical structure/composition.

The decomposition reaction of *G. brang* used in the study can be described well by a simple mechanism. The mechanism of the decomposition reaction was taken as three-step reactions involving hemicellulose, cellulose, and lignin with activation energies and dynamics of the related volatile fractions are in good agreement with the previous studies.

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