Physical changes and FTIR analysis of kenaf core fiber heat treated in air

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Abstract. In this paper physical changes (hygroscopic and color properties) and FTIR analyses of kenaf core fiber heat treated in air were studied. The fibers were heated in air at temperature of 103, 165, 175, 185, 195 and 205 °C for 15 minutes. For physical changes hygroscopic and color analysis were carried out where moisture absorption and kenaf core color lightness were measured. FTIR of treated and untreated fibers were analyses to find possible changes in the spectrum and also relation between moisture absorption and OH groups of the fibers. Ratio between OH band height (3332 - 3346 cm^{-1}) and absorbed moisture band height (1630 - 1640 cm^{-1}) was used to find relation between absorbed moisture and OH groups. The results showed moisture absorption decreased as treatment temperature increased. However for fiber treated at 165 and 175 °C, moisture absorption was not significantly different. Fiber darkness only increased for fibers treated above 175 °C. FTIR results showed no substantial chemical changes between treatments; however, through deduction, heat treatment cause degradation of OH groups. As a conclusion, chemical modification that changes hygroscopic and color properties of fiber only minimum and possibly occurred at surface of fiber, thus cannot be detected directly by FTIR analysis.

1. Introduction

Heat treatment has been known to improve dimensional stability and durability of wood. Commercially, heat treated wood has been introduced as early as 1930's with process call Lignostone and Staybwood. In more recent times, several heat treatment processes for wood emerges in Europe such as Thermowood, Plato Wood, OHT-Oil Heat Treatment, Bois Perdure, Rectification, WTT and Huber Holz. These process treats wood at temperatures between 160 °C and 260 °C with different process conditions and duration. Normally, duration of treatment would involves hours of exposure to heat [1]. At around 250 °C, even minimum exposure of heat flux can cause wood ignition [2]. Apart from temperature, duration of exposure at particular heat flux can also lead to wood ignition[3]. Therefore, to prevent wood ignition, heat treatment with high temperature and/or long duration require

deprived of oxygen condition.

Dimensional stability that achieved through thermal treatments on wood relates to reduction of available hydroxyl site in wood cell wall to form hydrogen bond water [4]. The other physical change experienced by wood is color changes where longer duration and higher treatment temperature produce darker color wood [5-6]. Degradation of lignin and non-cellulosic polysaccharides (hemicellulose, pectin, gum, etc.) cause changes in wood color. Heated acetylated hemicelluloses produce acetic acid which catalyzed hydrolysis of hemicellulose into soluble sugars. Heat caused sugars to caramelized into brown color which affect the wood color [7].

Fourier-transform infrared spectroscopy (FTIR) has been used in many study to qualitatively confirm chemical changes caused by chemical reactions, heating or decaying wood [8-10]. Other researchers use FTIR as quantitative tools to measure the ratio of lignocellulose components and composites material [11-12]. FTIR analysis was used in this study to detect changes on chemical groups through qualitative and quantitative analysis.

Although woods and kenaf core material are both lignocelluloses materials, smaller size of kenaf core fiber would influence drying, heating and reaction of heat treatment process [13]. As this study was carried out in air with the presence of oxygen, fiber degradation is expected to be accelerated. To prevent kenaf core fiber ignition, treatment parameter in this study was limited to 205 °C and 15 minutes of exposure.

Few studies were carried out on kenaf bast fiber. Heat treatment of kenaf bast shows an improvement on tensile strength for fiber treated at 140 °C for 2.5 to 10 hours[14-15]. While kenaf bast fiber heated for 1 hour at 160 °C produce higher tensile modulus compare to fiber heated at 140°C for same duration [16]. Due to the morphological difference between kenaf bast and core and short duration of heating (15 minutes), this study chose 165 °C to 205 °C as parameter of studies. Treatment temperature of 165 °C is within range where of extractives and hemicellulose begin to degrade [17].

The objectives of this paper are to study the effect heat treatment on moisture absorption and color of kenaf core fiber. Furthermore, because moisture absorption relates to formation of hydrogen bond between hydroxyl groups of fiber and water molecules from environment, FTIR is used to detect changes of -OH composition. Reduction in -OH composition can reduce the hydrophilicity of kenaf core fibre thus increase the compatibility between kenaf core fiber and hydrophobic polymer matrix in natural fiber composite.

2. Materials and Methods

Kenaf core fiber size 40 µm was supplied by LKTN (Kota Bharu, Malaysia). Fiber was heated in gravimetric oven for 15 minutes at 103 °C (drying temperature), 165, 175, 185, 195 and 205 °C.

For moisture absorption, heat treated fiber were directly stored in desiccator for 10 days and then weighted. Then samples were heated for 3 days at 103 °C to achieve bone dry condition. Then the fiber weighted again. Moisture content was determined using equation 1.

$$Moisture\ content\ (\%) = \frac{Weight_{after\ dessicator} - Weight_{Bone\ dry}}{Weight_{Bone\ dry}}\ x\ 100\% \qquad (1)$$

For color changes, samples were arranged and a photo was taken in a single shot as shown in **Figure 1**. The colors from each specimen were cropped and analyzed using open source software, GIMP (GNU image manipulating program). The peak for each color histogram (Top menu: Colors > Curve) were acquired and compared between the treatments.
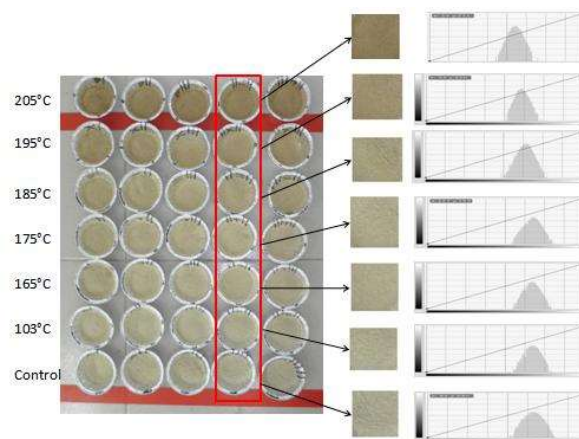
Figure 1 Color analysis of heat treated kenaf core fiber.

In this study, color changes were analyzed using lightness data (also referred as intensity or value) which were transformed RGB (red, green and blue) system to HSL (hue, saturation and lightness) based on equation 2.

$$L = \frac{\max(r, g, b) + \min(r, g, b)}{2} \qquad (2)$$

Where L is lightness (in GIMP color histogram; lightness referred as Value channel), max and min is maximum and minimum value among red, green and blue channel respectively [18].

FTIR analysis was carried out using Nicolat Spectroscopy machine. The samples were scanned (4 replications for each treatment) from wavelength of 650 to 4000 cm^{-1}. For qualitative analysis, bands between treatments were compared. While for qualitative analysis, the ratio of bands within the treatments was determined and then the ratio is compared between the treatments. The results for both qualitative and quantitative analysis were modified from transmittance to absorbance throughout the study for determination of area under and band height using equation 3.

$$A = 2 - \text{Log}_{10} (T \%) \qquad (3)$$

Where A is absorbance and T % is transmission in percentage [19]. The absorbance results, as shown in Figure 2, were analyzed using OriginPro 8 SR4 v8.0951 (B951) for baseline correction, band height, area and position.

Samples thickness of powdery samples like kenaf core fiber cannot be precisely controlled. Even for same samples, amount and size of sample will produce variation in band because height of band is related to amount of sample thickness or cencentration as mention in Lambert-Beer law [20]. Therefore this study use bands ratio to empirically analyze the changes caused by heat treatment.

The ratio of Band A and B was introduced in this study to show changes in C-OH in plane stretching based on OH stretching of absorbed water (refer to Figure 2). Band labelled A (3332 - 3346 cm^{-1}) were identified as hydrogen bonded OH group [21-24]. While band labelled B (1630 - 1640 cm^{-1}) represents OH stretching from absorbed water [8], [12], [24-27].
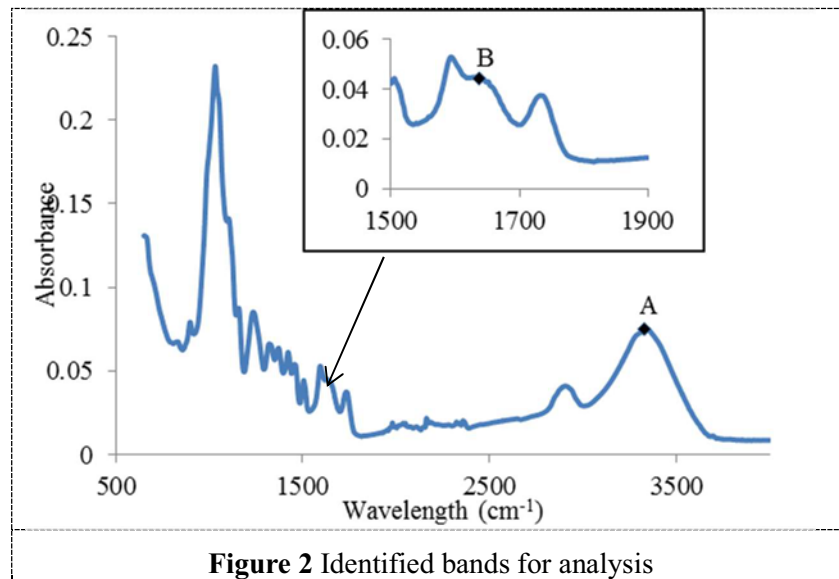
Figure 2 Identified bands for analysis

Two approaches were used to acquire the data for ratio; ratio based on band height and ratio based area under graph.

3. Results and discussions

3.1 Moisture absorption and color changes

Figure 3 shows the ability to absorb water from environment decrease as treatment temperature increase. Even drying process (treatment at 103 °C) has reduce the ability of fiber to absorbed moisture, while fiber treated at 165 and 175 °C does not significantly differ in amount of moisture absorbed. After treatment temperature increased more than 175 °C, the ability to absorb moisture gradually reduced as the temperature increase. Similar trend is also reported for heat treated bamboo scrimber [28]. There is a possibility that the reduction of moisture absorption relates to increase in crystallinity of cellulose and loss of -OH groups due to degradation of hemicellulose.

Figure 3 also shows the similarities between moisture content and color changes for heat treated kenaf core fiber. Compare to untreated fiber; the ability to absorb moisture decrease by 0.4 % for fiber treated at 103 °C (dried fiber), 1.0 % for 165 and 175 °C, 1.5 % for 185 °C, 2.0 % for 195 °C and 2.6 % for 205 °C. However, lightness value when compare to untreated fiber, the value increase by 4.4 for dried fiber (103 °C), 2.4 for fiber treated at 165 °C and 0.4 for fiber treated at 175 °C. Then , compared to untreated fiber, the value decrease by 6.6 for fiber treated at 185 °C, significantly reduce further by 13.2 and 28.6 for fiber treated at 195 and 205 °C respectively.

Both properties show that at temperature of 185 °C and above, ability to absorb moisture and maintain color lightness decrease. The darker color indicates changes in extractives and structural component such as lignin and/or hemicellulose. The other possibility is reaction between sugars and sugar/protein in presence of heat, such as caramelization and Maillard reaction, may produce colored compound of kenaf core fiber [7], [29]. Therefore the chemical changes that affect the color changes begin at 175 °C. This is also in agreement with bamboo scimber heated at 170 °C where the L value begin to drop significantly [28]. This is an indicator that heat treatment begin to significantly alter the composition of the fiber.
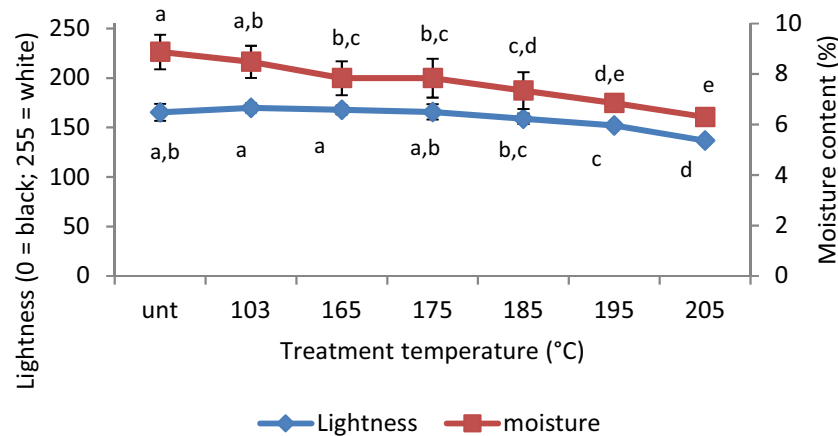
Figure 3 Color and moisture content of heat treated fiber.

3.2 FTIR analysis

Figure 4 shows the bands for qualitative analysis using FTIR. It is worth to mention that the presented figures are carefully selected among treatment replication so that the bands do not overlapped with each other. The bands position and shapes is almost similar among all treatments. This results is in agreement with untreated kenaf fibre analyzed using FTIR reported by other researcher [30-31]. This indicates the treatment does not cause major chemical changes to kenaf core fiber.
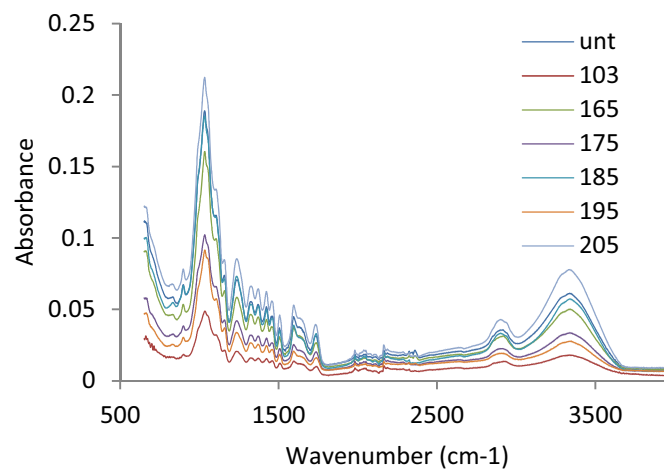
Figure 4 FTIR spectroscopy of untreated and heat treated fiber.

For qualitative analysis, Table 1 shows the A:B ratio of FTIR bands. Using band height ratio produce significant reduction trend for fiber heated at 103 until 185 °C. On contrary, ratio based on band area show insignificant reduction between fibers treated at 103 and 175 °C; significant reduction only begin at 185 °C. After 185 °C, both ratios either calculated by height or area show a significant increase for fiber treated at 195 and 205 °C. Based on dispersion of data, as shown by coefficient of variance (CoV) also known as relative standard deviation (RSD), the dispersion for ratio based on band height is smaller compare to ratio based on integrated area thus produce more significant results for ratio based on height. Therefore ratios based on band height were selected in further analysis. Other researchers also use band height due to better value provided RSD [32].

Table 1 Ratio of band A:B

Treatment	Ratio A:B (band height)		Ratio A:B (band area)	
(°C)	Average	CoV (%)	Average	CoV(%)
untreated	0.488 [B,A]	9.2	0.0912 [A]	7.5
103	0.499 [A]	12.4	0.0817 [B,A]	12.6
165	0.477 [B,A,C]	4.3	0.0824 [B,A]	13.6
175	0.451 [B,A,C]	3.5	0.0826 [B,A]	7.2
185	0.431 [C]	9.8	0.0735 [B]	16.0
195	0.438 [B,C]	1.5	0.0778 [B,A]	11.9
205	0.444 [B,C]	7.3	0.0786 [B,A]	17.2

Ratio A:B represents the intensity of infrared band absorbed by bonded OH group (band A) compare to 1 unit of infrared band absorbed to OH molecules of water (band B). Generally band height and/or integrated areas are proportional to the quantity of a specific component present in a sample [33]. Therefore, actual unit of OH group affected by the treatment did not presented by Table 1 because the amount of water within the fiber affected by the treatment temperature is lower as shown by Figure 3. Because of bands are directly proportion quantity and ratio between bands must be same; mass and band height of band A equal to mass and height of band B. Therefore equation 4 can be applied.

$$\text{Band }_{(A)} \text{ x Mass }_{(A)} = \text{Band }_{(B)} \text{ x Mass }_{(B)} \tag{4}$$

$$\text{Mass }_{(A)} \text{ x } [\text{Band }_{(A)} / \text{Band}_{(B)}] = \text{Mass }_{(B)} \tag{5}$$

Therefore,

$$\text{Mass }_{(A)} \text{ x (ratio A:B)} = \text{Mass }_{(B)} /\text{(ratio A:B)} \tag{6}$$

$$\text{Mass }_{(A)} = \text{Mass }_{(B)} /\text{(ratio A:B)} \tag{7}$$

By applying Equation 7, the actual unit of -OH group affected by the treatment were deducted and presented in Figure 5 Amount of -OH group (by deduction). The results shows that although drying process (treatment at 103 °C) cause the ability to absorbed moisture from the environment decrease, it does not cause the degradation OH in the hemicellulose within fiber because hemicellulose only starts to degrade at 160 °C [17]. The treatment at 165 °C and 175 °C cause a significant decrease of OH compared to untreated and dried fiber. Generally the -OH degradation is gradual as the treatment temperature increase but the degradation is insignificant to modify FTIR bands as inspected by qualitative analysis in Figure 4. Therefore, it is expected that the -OH group modification only occurred at the surface level of the fiber as treatment duration is short.
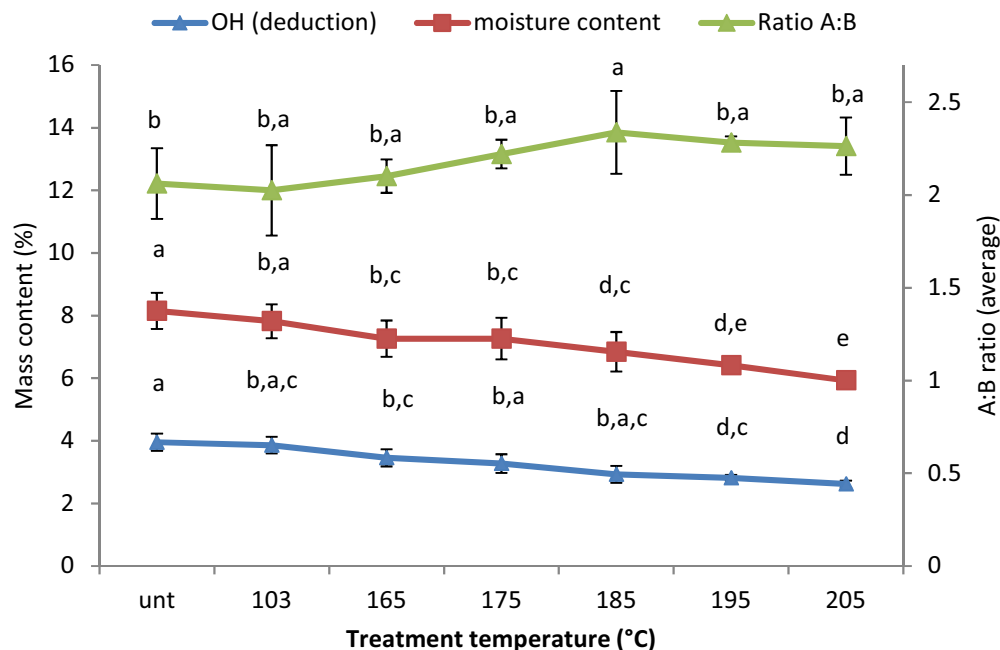
Figure 5 Amount of -OH group (by deduction)

4. Conclusion

This study concludes that heat treatment on kenaf core fiber causes physical modification in term of moisture absorption and color of kenaf core fiber. Chemical modification is not observable in qualitative FTIR band analysis but can be quantitatively deduced using band of absorbed water in FTIR and actual moisture absorption. The results show the reduction of OH group within kenaf core fiber due to heat treatment only begins after 175 °C.

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