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STRUCTURE CRYSTALLIZATION OF CELLULOSE KING PINEAPPLE LEAFS FIBER (AGAVE CANTALA ROXB) DUE TO SMOKE FUMIGATION

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ABSTRACT

The objective of this study is to determine the crystallization structure of cellulose fibers pineapple leaf king (Agave Cantala Roxb) as a result of fumigation treatment with variations fumigation time. The king pineapple leaf fiber (KPLF) chemical compounds EDAX analysis without and with fumigation treatment is done by using the Energy Dipersive Spectroscopy (EDS) worked as an integrated feature with the Scanning Electron Microscopy (SEM) Tescan Vega3SB. The crystallization structure analysis done with MiniFlexII Rigaku X-Ray diffraction (XRD) and the chemical elements quantitative analysis (% Wt) was tested with the RIR (Reference Intensity Ratio) method. The XRD diffraction with the X-Ray analysis showed that the KPLF cellulose crystallization structure be altered by the fumigation treatment. It was found that the KPLF degree of crystallinity and KPLF cristallinity index without fumigation are 70.73% and 58.62% respectively, while the KPLF degree of crystallinity and KPLF cristallinity index with 15 hours fumigation the are 72.32% and 61.72% respectively.

Keywords: king pineapple leaf fiber, fumigation, crystallinity degree, crystallinity index.

1. INTRODUCTION

Natural fibers have many advantages in the past few years. The advantage of natural fibers as reinforcement of composite materials when compared to synthetic fiber amplifier is that natural fiber has a low cost, low density, easily separated, widely available and renewable, biodegradable and environmental friendly [1, 2]. As a result, there is a motivation increased to explore new natural fiber that can be applied in the fields of automotive and structural that could accept loads, to replace synthetic fibers.

Natural fiber was formed from three main components which are highly complex structures, namely: hemicellulose, cellulose and lignin or called lignocellulose. Cellulose is a polymer containing a crystalline structure due to hydrogen bonding interactions between adjacent molecules. Cellulose molecules linked laterally by hydrogen bonds to form linear bundle, causing the crystal structure [3]. The crystalline cellulose level is one of the most important parameter because the cellulose crystal structure would affect the cellulose fiber physical and mechanical properties. Increasing the ratio of crystalline to the amorphous regions in the cellulose structure can affect the accessibility of the cellulose molecules and increase the stiffness, dimensional stability and the cellulose density on the chemical reactivity [4, 5].
In Indonesia, especially in Tana Toraja, South Sulawesi Propensi, where KPLF traditionally has long been used by the community, usually KPLF fumigated, which is strong and durable, were used for rigging and woven for dead body wrapping, [6]. Given the enormous potential of the KPLF as a fiber source then it is necessary to increase its role, not only as a traditional product, but also improve the function into a natural fiber composite reinforcing materials [7].

Before KPLF used as a composite reinforcement it needs to be fumigated with the aim to change the nature of the KPLF surface energy by eliminating the element of hemicellulose and lignin so that the KPLF surface roughness increased and become more compatible with the matrix. This process is signing that there is an interaction with the chemical elements contained in the smoke resulting a crystallization dimensional structure, morphology and KPLF mechanical properties [6, 7, 8]. The purpose of this study was to reveal the KPLF crystallization structure due to the fumigation treatment. The crystallization structure identification was using an X-Ray diffraction.

2. MATERIALS AND METHODS

2.1. Materials

The research materials in this study is the king pineapple leaf fibers obtained from Tana Toraja in South Sulawesi, Indonesia. The eleven month age KPLF was chosen for the fiber samples. Fibers are removed from the meat leafs mechanically with a leaf long range of 0.9 to 1 m, after immersion in fresh water for three weeks. Furthermore the KPLF was cleaned from dirt with aguades water. It was then dried up at a room temperature and was grouped for fumigation treatment.

2.2. Methods

2.2.1. Fumigation treatment

Furthermore KPLF was placed inside a fumigation box and the smoke was produced by burning coconut shells in a container which is connected by a pipe to drain the smoke continuously into the fumigation box. The KPLF fumigation time process are variated from 5,

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10, 15, and 20 hours and during the fumigation process takes place, the smoke temperature in the KPLF fumigation box are about 45° C [7]. Each KPLF sample that is untreated and treated was notated ie without fumigation is WF, five hours fumigation is F5H, ten hours fumigation is F10H, fifteen hours fumigation is F15H and twenty hours fumigation is noted as F20H.

2.2.2. Testing x-ray diffraction XRD

The KPLF testing without and with fumigation was separately pulverized into a fine powder. After that it was tested with the Mini FlexII Rigaku X-Ray Diffraction (XRD). Diffractogram pattern is recorded over a range of angles from 5° to 70° 2θ with a scan speed of 0.2°/s at a voltage of 30 kV and a current of 15 mA. The diffractogram sample analysis was done by using software built form PDXL2 machines equipped with ICDD card (International Centre for Diffraction Data) ver. 2011. The crystallinity index percentage and the degree of crystallinity were evaluated by the Segal method respectively using equations 1 and 2 as follows:

$$CI = \frac{I_{(0,02)} - I_{(am)}}{I_{(0,02)}} \times 100\ \% \quad (1)$$

$$\%\ Cr = \frac{I_{(0,02)}}{I_{(am)} + I_{(0,02)}} \times 100\ \% \quad (2)$$

With

CI : Crystallinity Index (%)

% Cr : Crystallinity degree (%)

$I_{(am)}$: Amorf diffraction intensity, taken the lowest value on an angle of 2θ about 18°

$I_{(0,02)}$: Maximum intensity peak associated with the crystal planes (0 0 2) are in the angle range between 22° - 23°, which represents the fiber crystallinity.

3. RESULTS AND DISCUSSIONS

The result of the chemical element quantitative measurements (% Wt) tested on the KPLF before and after fumigation treatment with RIR method (Reference Intensity Ratio), based on each sample diffractogram data is seen in Figure-1, wherein the chemical composition (Wt%) can be detected in the KPLF such as the Polyoxymethylene (H2CO), Andalusite Al 2 (Si O_4) O and Carbon (C_6O).

Figure-1 shows that KPLF without fumigation does not contain carbon and were dominated by Polyoxymethylene that has a wealness which is the high water absorption properties. There are another property which is the Andalusite Al_2 (SiO_4)O which is a crystal structure. Furthermore, after KPLF undergone with fumigation would resulted an increasing of carbon content until the F20H and Polyoxymethylene level dropped dramatically due to the KPLF humidity reduced [6], while the Andalusite (crystalline structure) increased in P15J, then declined in P20J due to the carbon level risein KPLF.

The carbon increased in fumigated KPLF is due to fiber cellulose that has a high absorption characteristic. Carbon is absorbed primarily from carbon dioxide (CO_2) molecules contained in the smoke through a diffusion process which is the molecules nature [13, 16].

This phenomenon occurs because each molecule has a kinetic energy to continue moving freely, quickly and randomly through a membrane or pores so that the atoms or molecules will collide until evenly distributed [14, 15, 17]. These points are occupied by atoms or molecules according to the crystal composition, in which each of the points in the lattice composition, sequence and a same orientation.

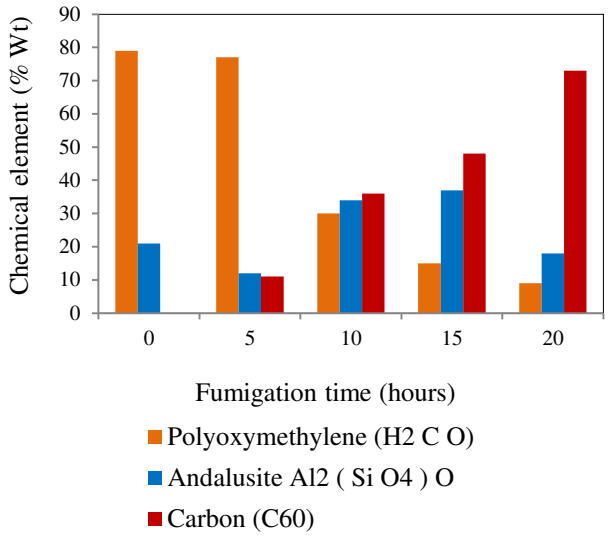
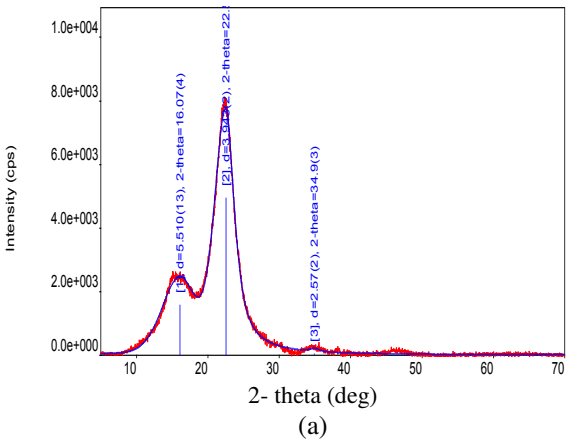


Figure-1. KPLF chemical element x-ray result (RIR) vs. fumigation time.

The crystallization structure analysis result from the Rigaku MiniFlexII X-Ray diffraction (XRD), obtained a diffractogram X-Rays pattern generally contain three peak diffraction which are at a 2θ angle of 16°, 22°, 35° where the peaks is related to the crystal planes (0 1 1), (0 0 2) and (4 0 0), [11, 12] and the pattern of X-Ray diffraction pattern, for the KPLF fiber without and with fumigation treatment as shown in Figure-2 (a, b , c, d and e), as follows:



(a)

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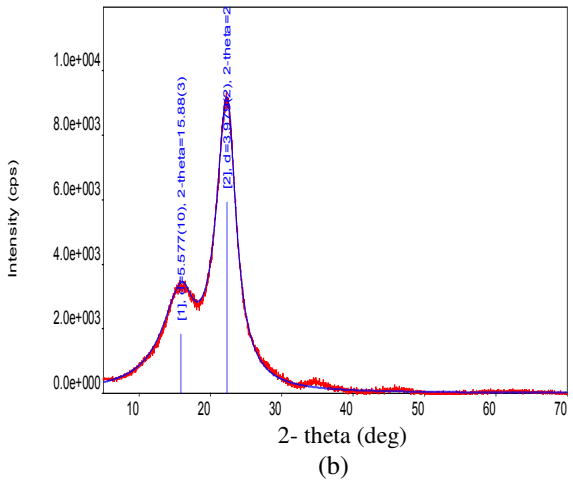
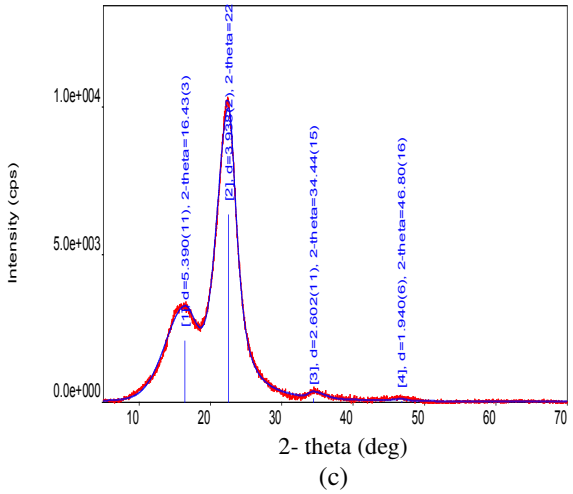
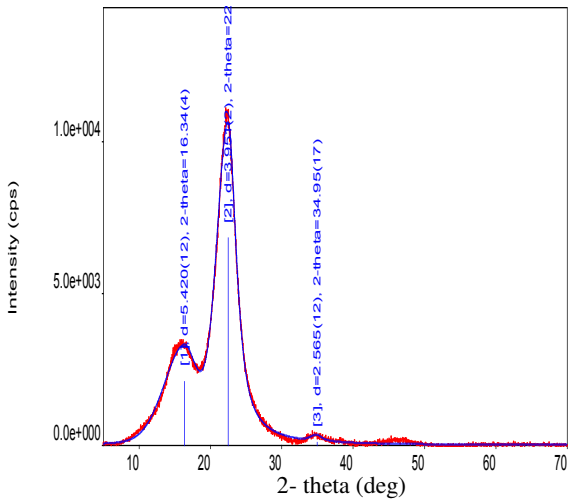


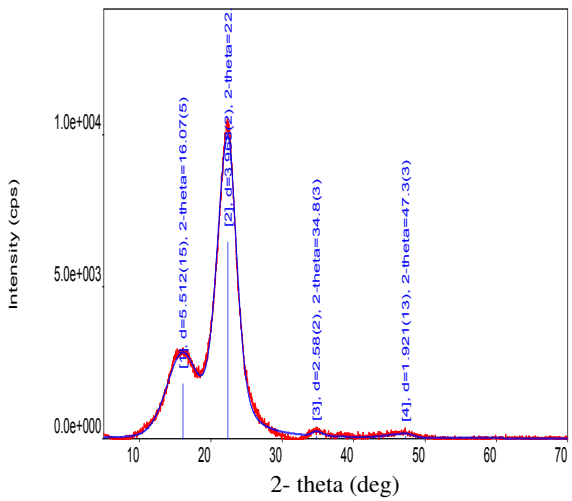
(b)



(c)



(d)



(e)

Figure-2. KPLF x-ray test results: (a). WF, (b). F5H, (c). F10H, (d). F15H, (e). F20H.

Based on the the crystallinity degree results calculation and KPLF crystallinity index using equations 1 and 2, the value of the crystallinity degree and KPLF crystallinity index with and without fumigation treatment, is shown in Figure-3 as follows:

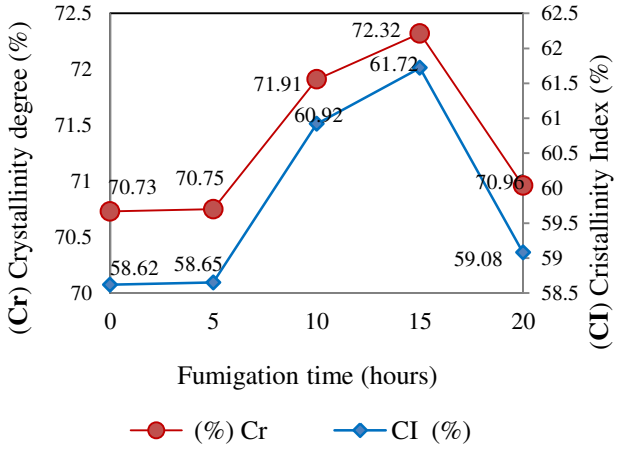


Figure-3. The crystallinity degree and crystallinity index KPLF vs. fumigation time.

The results obtained reveal that the effect of fumigating the king pineapple leaf fibers can have a good crystal domains, the KPLF degree of crystallinity and KPLF crystallinity index increased until the fumigation treatment 15 hours as seen in Figure-3, after that, the degree of crystallinity decreases. Total content of cellulose and non-cellulose fiber crystallinity influence the fiber nature and structure [9, 10]. Various models of the cellulose crystalline structure caused by hydrogen bonds intra and inter molecule that occurs through the hydroxyl group [11]. The diffraction peak around 22.5°, which is sharper, occurs in the 15 hours fumigation time (Figure-2)

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with the value of the degree of crystallinity and optimum crystallinity index (Figure-3). The degree of crystallinity and crystallinity index increase is due to the loss of amorphous components such as hemicellulose and lignin [6, 8, 12]. The degree of crystallinity is a material structure order [12]. The unit cell dimension is determined by the intersection of a, b, and c axes, while α, β, and γ is the angle between the axes of the crystal reference. Crystal geometry in a three-dimensional space which is the crystal characteristic has a different pattern.

The crystallisation structural analysis, performed by X-Ray diffraction (XRD), resulted a KPLF cellulose crystal size value without and with a fumigation treatment which has a tetragonal structure which has a that lattice parameter value a = b ≠ c and α = β = γ = 90°. Tetragonal are the crystal axes which are perpendicular one to the other, lattice intervals along two axis direction is the same, but a recurrence interval on all three axis directions are different. From the KPLF withour fumigation crystal size analysis are (7.81, 7.81, 5.55) Å, P5J (7.90, 7.90, 5.56) Å, P10J (9.09, 9.09, 14.61) Å, P15J (10.5, 10.5, 16.80) Å and P20J (9.01, 9.01, 14.01) Å. The KPLF cellulose crystal size values corresponding to the peak diffraction at 22.5°which is sharper as happened in P15J.

To determine the content of chemical compounds contained in KPLF without and with fumigation treatment it is carried out a test in which the sample is placed on a prepared then observed by means of Energy Dispersive Spectroscop 20 kV. From the SEM (EDS) observation obtained chemical compounds contained in KPLF without and with fumigation treatment as seen in Figure-4 as follows:

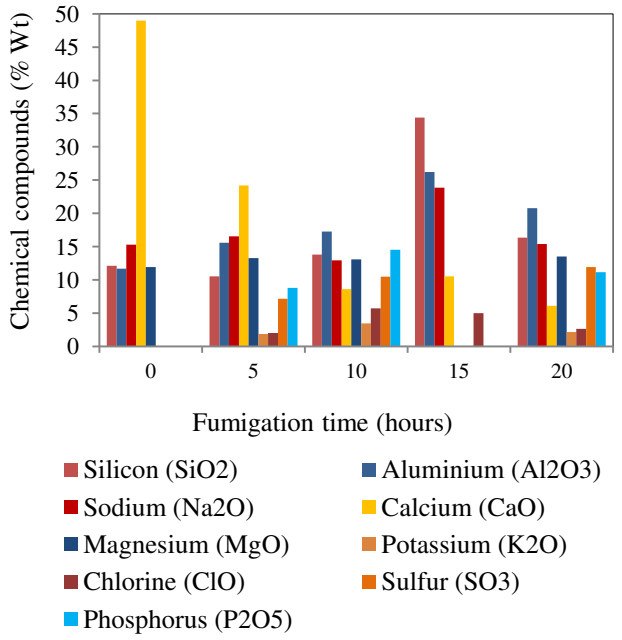

Figure-4. SEM image results (EDS), KPLF chemical compound vs. fumigation time.

In Figure-4, the apparent variety of chemical compounds contained in KPLF without fumigation and fumigation. KPLF chemical compounds without fumigation are dominated by CaO then this Ca O decreases until the P20J, SiO_2, Na_2O, Al_2O_3 compounds increased until P15J and each also decreased in P20J, while chemical compounds CIO, MgO, SO_3, K_2O and $P2O_5$, which is fluctuating appear on P5J and P10J then does not appear on P15J except CIO and reappeared on P20J. With the reduction of the compound and the increase of SiO_2 CaO, Na_2O, Al_2O_3 compounds, the mechanical properties of KPLF on P15J increased so that a KPLF single fiber optimal tensile strength is reach and declined again in P20J [6].

Based on the KPLF surface SEM images without and with fumigation treatment, the result could be seen in Figure-5 as follows:

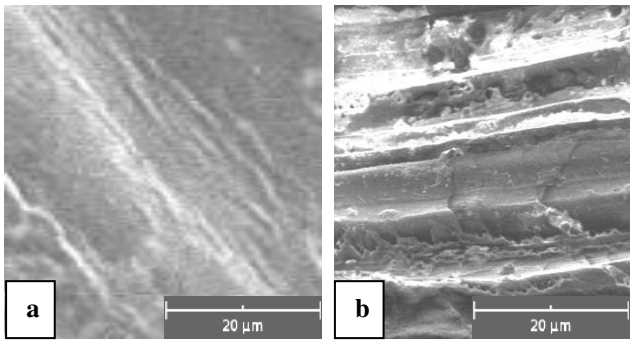

Figure-5. KPLF surface SEM test results: (a). WF, (b). F15H.

Figure-5 (a) is a KPLF cross section without fumigation which is still seems to be smooth as it is still covered by the lignin element and Figure 5 (b) is the KPLF surface fumigated for 15 hours where the apparent pattern or grooves were rough and very different from the KPLF without fumigation cross-section. This condition occurs due to the reaction of the chemical components which is the degradation of lignin and hemicellulose elements [6, 7], which would affects the KPLF surface become rough and grooved to facilitate the matrix wetting the KPLF so that an interface bonding occurs between KPLF and the compatible matrix.

4. CONCLUSIONS

Based on research results with the KPLF fumigation done, it can be concluded that the KPLF analysis with X-Ray diffraction method, resulted a cellulose crystallinity and crystallinity index increased until the 15 hours fumigation treatment, after which it decreased due to the amorphous structure of the fibers are degraded. With the KPLF crystallinity and KPLF crystallinity index increase it can improve the fiber mechanical strength, as the reinforcement of composite materials.

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