



Study of Crystallinity Index and Thermal Properties of Sweet Sorghum Fiber after Pressurized-Cooker Treatment

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The main purpose of the research is to investigate the effect of thermal treatment through commercial pressure cooker (5, 25, and 60 min) on thermal and crystallinity properties of stalk sweet sorghum fibres. Crystallinity index and thermal stability of the fibers have been studied by using X-ray diffraction (XRD) and simultaneous thermal analysis (STA) characterization, respectively, compared to untreated fibers. The result of this study shows that this treatment increased crystallinity index and thermal stability properties of the fibers. This result also shows that sorghum fiber can be used for a reinforcement candidate in thermoplastic matrix.

alkalinization, acetylation, and bleaching treatments can reduce their hydrophilic properties, as a result the compatibility between natural fibers and hydrophobic polymers increased. On the other hand, these methods are not environmentally friendly. In this context, the motivation of this research is to study the effect of thermal treatment through commercial pressure cooker, as the simplest and greenest process,^[12] on changes in crystallinity index and thermal properties of stalk sweet sorghum fibers.

1. Introduction

The strict regulations on the environment, and the limited resources that come from nature, encourage researchers to look for environmentally friendly and renewable materials. Natural fiber emerged as an alternative material that is sustainable and widely available in nature.

At present, natural fibers are widely applied as fillers and reinforcement materials in polymer composites for various applications, at least in part, to replace glass fibers.^[1-6] This is due to some interesting properties, such as renewability, sustainability, no impact on global warming, low cost, biodegradability, nonabrasive properties during processing, and well mechanical properties comparable to glass fibers.^[2] On the other hand, natural fibers have major weaknesses that are naturally hydrophilic so that the bonding interface between natural fibers with a hydrophobic matrix is weak, low maximum working temperature processing, and seasonal.^[7]

Several experiments have been carried out to correct these deficiencies, including modifying natural fibers through chemical methods. Based on reports from literature,^[8-11]

2. Experimental Section

2.1. Materials

The fiber used in this research was the stalk sweet sorghum fiber grounds. They were obtained from Southeast Asian Ministers of Education Organization—Tropical Biology (SEAMEO-BIOTROP) Bogor in West Java Indonesia.

2.2. Preparation of Sorghum Fibers

Sweet sorghum fiber ground was cut using a crusher and filtered using a 100 mesh filter. The fibers that passed from the filter were soaked in a pressure cooker (Oxone Ox-1060F with dimension 50 × 30 × 29 cm), variation in soaking time (5, 25, and 60 min). After that, the fiber sample was filtered and dried in a vacuum furnace at a temperature of 50 °C for 120 min.

2.3. Characterization

2.3.1. X-ray Diffraction (XRD)

XRD was carried out using the Shimadzu XRD-7000 X-ray diffractometer with a voltage of 40 kV and current of 20 mA using Cu-K α radiation, and the intensities were measured in the range of 5° < 2 θ < 40°. The resulting diffractogram was used to calculate the crystallinity index of untreated and treated sorghum fibers, Equation (1) was initially proposed by Segal et al in 1959,^[13] which is:

$$CrI = (I_{002} - I_{am}) / I_{002} \times 100\% \quad (1)$$

where *CrI* is the crystallinity index, *I*₀₀₂ is the maximum intensity of the (002) lattice diffraction, and *I*_{am} is the intensity diffraction of the amorphous band.

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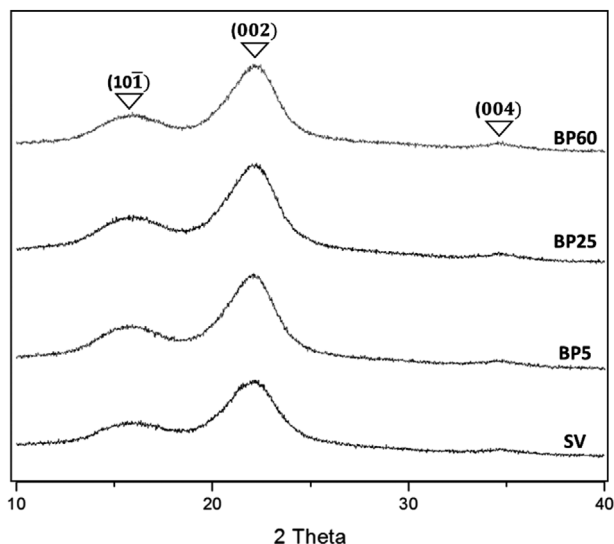


Figure 1. XRD diffractograms for the untreated and treated sorghum (SV: sorghum virgin/untreated sorghum; BP: pressurized-cooker; 5, 25, and 60 minute).

2.3.2. Thermogravimetric Analysis (TGA)

The thermal stability of untreated and treated sorghum was performed using simultaneous thermal analysis (STA) 6000/8000, Perkin Elmer instrument. All samples were heated from 40 °C to 500 °C at a heating rate of 10 °C min⁻¹. Then, the experiment was continued from 500 °C to 800 °C, at heating rate of 60 °C min⁻¹, to burn the remains of organic material during the heating process.

2.4. Results and Discussion

X-ray diffractograms for untreated and treated sorghum fibers are shown in **Figure 1**. The figure shows almost the same shape with three peaks of the crystalline plane. The peaks 1, 2, and 3, located at 2 thetas 16.1°, 22.1°, and 34°, are according to crystallography plane of (10-1), (002), and (004), respectively.^[14,15] In the literature,^[16] the peak contribution to the field (004) is almost irrelevant with the other two peaks. Therefore, based on his research, the first and second intensity peaks can be analyzed and considered as an indication of cellulose content.

Cellulose consists of crystalline and amorphous structures. The strength of cellulose fibers increases with increasing crystalline content in cellulose, but on the other side their flexibility decreases. The crystallinity index is an important parameter in determining the crystalline structure portion in cellulose. **Table 1** shows the value of the untreated and treated crystallinity index of sorghum fibers which were calculated using the Segal equation. Table 1 shows an increase in the value of the crystallinity index of fibers from the pressurized-cooker treatment, compared to those untreated fibers. Increasing the crystallinity index value of the fiber indicates that the structure of cellulose is more ordered or crystalline increases and the amorphous region decreases. While the effect of the length of treatment time on changes in the crystallinity index was not significant, even

Table 1. Comparison of crystallinity index between untreated and treated sorghum fibers.

	SV	BP5	BP25	BP60
I_{am}	2620	2811	3023	2678
I_{002}	5107	6205	6351	5839
CrI	48.7	54.7	52.4	54.1

appeared to be almost similar, and the presto-boiled treatment at 5 min showed the highest value when compared with the time of 25 and 60 min. The duration of the treatment causes the destruction of hydrogen bonds in cellulose due to the hydrolysis of excess water molecules, and this causes the crystalline portion in cellulose to decrease.

The increase in the crystallinity index of fibers subjected to pressurized-cooker treatment shows that the crystalline portion of the fiber increases, and on the other hand, the amorphous decreases. **Figure 2** shows the FE-SEM morphology of untreated and treated sorghum fibers. Images show that the pressurized-cooker treatment dissolves some of the amorphous content in fibers, such as wax, lignin, and hemicellulose. It is marked by partition pattern along the fiber bundle surfaces. During this treatment process, water will evaporate and be absorbed by sorghum fibers and cause the fibers to become swollen and fibrillated.

The thermal properties of natural fibers are one of the important parameters to be studied, especially their use as reinforcement in polymer composite materials.^[17] The process of making polymer composites involves the mixing process, natural fibers as a reinforcement, and polymers as a matrix, at high temperatures with a specific time. In thermoplastic polymer materials, the mixing process is usually carried out at a temperature of around 200 °C.^[15] Therefore, a good thermal stability is needed to prevent the degradation process of the fiber, and the result will impact the mechanical properties of composite materials.^[15,17]

Figure 3 shows the degradation behavior of untreated and treated sorghum fibers. As shown in **Figure 3a**, thermal degradation occurs in three main stages, for both untreated and treated sorghum fibers. This phenomenon is found and explained in detail in refs.^[18-20] In the first stage, this occurs under a temperature of 100 °C. Loss of weight is caused by the dispersion of water content in the fiber. The water contained in the fiber can be in the form of free water or linked water.^[6] Free water is water that sticks to the surface of natural fibers and will evaporate at lower temperatures (25–150 °C), and linked water is water that forms bonds with hydroxyl groups on lignin, hemicellulose, and cellulose, and evaporates at higher temperatures. After free water evaporates, degradation in range of 150–500 °C occurs in linked water at lignin, hemicellulose, and cellulose. The next stage is related to the thermal degradation of hemicellulose and some portions of lignin. It occurs at a range of 150–350 °C. Finally, at high-temperature range 310–400 °C, it shows the process of thermal degradation for cellulose and lignin, and almost cellulose component decomposed.^[18-20] Lignin, because it consists of phenyl groups, has a wide temperature degradation range of 250–600 °C^[18] or 200–700 °C,^[20] when compared with hemicellulose and cellulose.

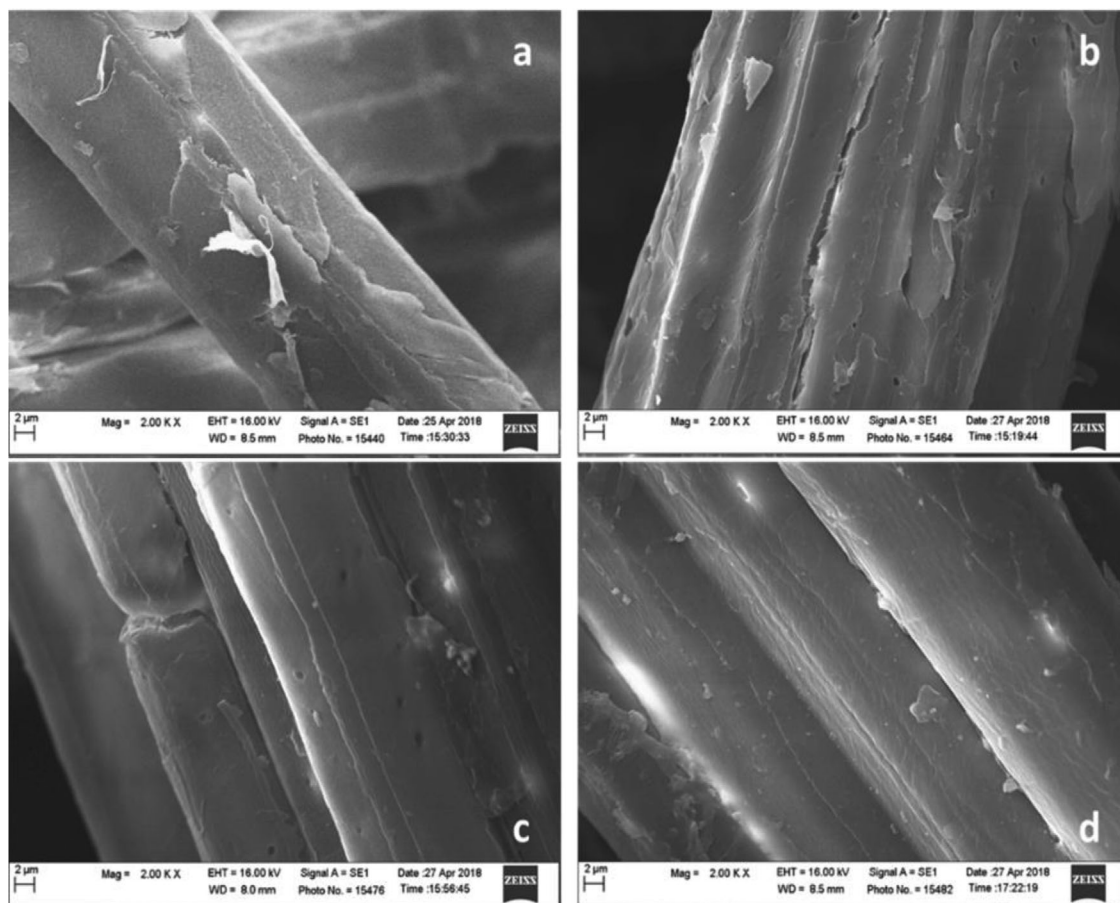


Figure 2. FE-SEM sorghum fiber: a) SV, b) BP5, c) BP25, and d) BP60.

Related to the results of this study, as shown in Figure 3b, it shows in detail the thermal degradation of sorghum fibers in the temperature range of 100–300 °C. The figure shows the stability of sorghum fibers under pressurized-cooker treatment was better when compared to untreated fibers. The initial temperature degraded fiber (T_i), a sample loses 3% of its weight,^[18] BP5 sorghum fiber has the best thermal stability when compared with BP25, BP60, and untreated fibers. The highest values of T_i for fibers are BP 5, BP25, SV, and 60, of which the highest are 251, 64, 60, and 59 °C, respectively. The high value of T_i in BP5 fibers may be associated with low volatility and hemicellulose. Figure 3a shows the next thermal degradation at a range of 240–390 °C. These results clearly show that the thermal stability of sorghum fibers under pressurized-cooker treatment is higher than untreated sorghum fibers. Higher crystallinity index value indicates the portion and the regularity of cellulose structure increases and becomes denser, which makes the heat transfer difficult. The difficulty of heat transfer in the fiber causes higher thermal stability.^[17,20]

3. Conclusion

The effect of thermal treatment of sorghum fiber through pressurized-cooker treatment, variations of heating time, changes in fiber structure was carried out in this study. The

observations of XRD showed that sorghum fibers, which were modified by pressurized-cooker treatment, contained more regular cellulose content (crystalline) compared to untreated sorghum fibers. This is proven with increasing in the crystallinity index of the sorghum fiber after treatment. The increased in the crystallinity index of the fiber, slows down the degradation process, and increases the thermal stability of sorghum fibers.

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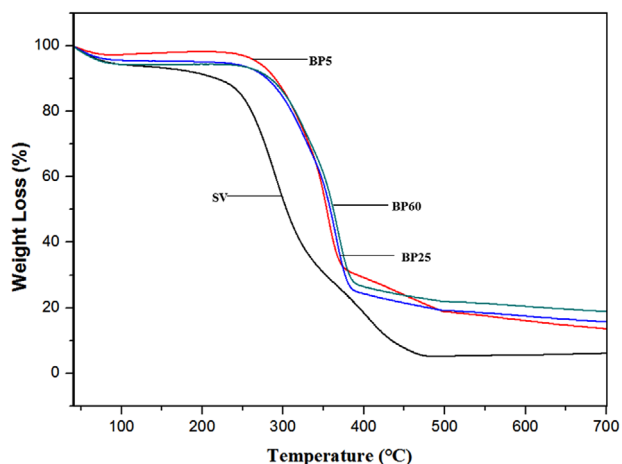
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Conflict of Interest

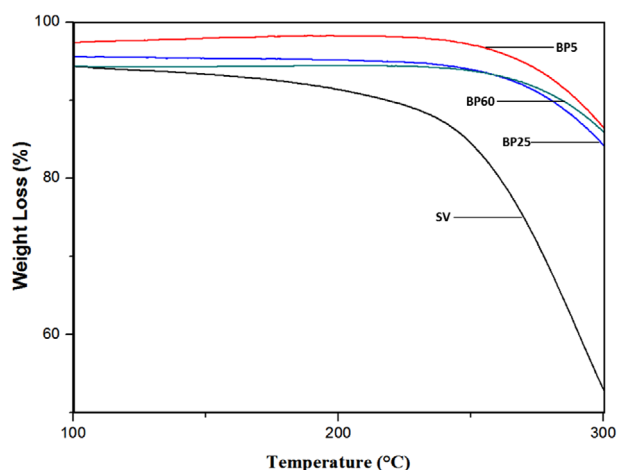
The authors declare no conflict of interest.

Keywords

crystallinity, pressure cooker, sorghum fiber, thermal properties



(a)



(b)

Figure 3. TGA curves of untreated and treated sorghum in the temperature range of, a) 40–700 °C, b) 100–300 °C.

- [1] C. Borsoi, L. C. Scienza, A. J. Zattera, *J. Appl. Polym. Sci.* **2013**, *128*, 653.
- [2] H. L. Ornaghi Jr., A. S. Bolner, R. Fiorio, A. J. Zattera, S. C. Amico, *J. Appl. Polym. Sci.* **2010**, *118*, 887.
- [3] D. Romanzini, H. L. Ornaghi Jr., S. C. Amico, *Mater. Res.* **2012**, *15*, 415.
- [4] C. Alves, P. M. C. Ferrão, A. J. Silva, L. G. Reis, M. Freitas, L. B. Rodrigues, D. E. Alves, *J. Cleaner Prod.* **2010**, *18*, 313.
- [5] N. Sgriccia, M. C. Hawley, M. Misra, *Composites, Part A* **2008**, *39*, 1632.
- [6] J. H. S. Almeida Jr., H.L. Ornaghi Jr., S. C. Amico, F. D. R. A. Amado, *Mater. Des.* **2012**, *42*, 111.
- [7] R. S. Santos, A. A. Souza, M. A. De Paoli, C. M. L. Souza, *Composites, Part A* **2010**, *41*, 1123.
- [8] M. Chalid, I. Prabowo, *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* **2015**, *9*, 342.
- [9] E. Yuanita, J. N. Pratama, J. H. Mustafa, M. Chalid, *Procedia Chem.* **2015**, *16*, 608.
- [10] Y. A. Husnil, Ismojo, A. S. Handayani, D. A. Setiaji, M. Chalid, *IOP Conf. Ser.: Mater. Sci. Eng.* **2019**, *509*, 012016.
- [11] Ismojo, R. Pratama, G. Ramahdita, A. Zulfa, M. Chalid, *Mater. Sci. Forum* **2018**, *929*, 70.
- [12] S. Komarneni, Y. D. Noh, J. Y. Kim, S. H. Kim, H. Katsuki, *Z. Naturforsch. B* **2010**, *65*, 1033.
- [13] L. Segal, J. J. Creely, A. E. Martin, C. M. Conrad, *Text. Res. J.* **1959**, *29*, 786.
- [14] P. Sunkyu, O. B. John, E. H. Michael, A. P. Philip, K. J. David, *Biotechnol. Biofuels* **2010**, *3*, 10.
- [15] V. Tserki, N. E. Zafeiropoulos, F. Simon, C. Panayiotou, *Composites, Part A* **2005**, *36*, 1110.
- [16] D. F. Alfred, *Cellulose* **2014**, *21*, 885.
- [17] P. Matheus, L. Heitor, J. Ornaghi, J. Z. Ademir, *Materials* **2014**, *7*, 6105.
- [18] C. U. Maheswari, K. Obi Reddy, E. Muzenda, B. R. Guduri, A. Varada Rajulu, *Biomass Bioenergy* **2012**, *46*, 555.
- [19] M. M. Kabira, H. Wanga, K. T. Laua, F. Cardona, *Appl. Surf. Sci.* **2013**, *276*, 13.
- [20] H. S. Kim, S. Kim, H. J. Kim, H. S. Yang, *Thermochim. Acta* **2006**, *451*, 181.