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Preparation of Composite Reinforced Agent Based on Sweet Sorghum Stalk Fiber through Alkali Pressure Steam Treated Method

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Abstract

Increasing global concern to environmental issues and sustainability related to preservation of non-renewable natural resources has encouraged research to develop new environmental friendly materials and products based on renewable natural resources. Sweet sorghum stalk fiber has a potency to become composite reinforcement because it has a good mechanical properties, environmental friendly and inexpensive. The preparation process of sweet sorghum stalk fiber is needed to improve its compatibility with polypropylene. Alkali pressure steam is the method used in conducting fiber preparation. In this study, alkali pressure steam treatment with 0%, 5% and 10% NaOH and pressurized steam for 1 and 3 minutes was carried out to change the hydrophobicity of sweet sorghum stalk fiber. The most optimum result was obtained at 5% NaOH concentration with 3 minutes pressure steam soaking, showing cleaner and fibrillated morphology based on FESEM testing. It was less lignin and hemicellulose content as indicated by FTIR testing result, better hydrophobicity as indicated through Sessil Drop testing result that showed contact angle of 120.9◦, as well as significant increase in crystallinity index of 6.3% as indicated through XRD test result. The increase in the hydrophobicity of the modified sorghum fiber indicated the increase of the natural fiber compatibility with polymer matrix.

INTRODUCTION

Since years ago, plant fibers have been used especially for energy, building materials, paper, textile and clothing. In recent years, biological resources as a renewable material, one of which is biomass, have emerged as potential sources of new material to improve polymer properties, for example physical, mechanical properties, and degradability. So, new technology applications of natural fiber as reinforcement in polymer composite materials are highlighted. Cellulose as composite reinforcement have attracted significant attention because of their properties, such as low cost, nonabrasive, renewable and biodegradable. Cellulose can be extracted from agricultural waste such as stalk, husk, bagasse, bunch, etc. Based on the type of feedstock, the first generation was natural carbohydrate biomass and protein, the second one were agro industrial residues, and finally, the last generation referred to algal. Residues from agricultural crops can be reused and become lignocellulose resources. Lignocellulose is the most plentiful and renewable bio resources. One important renewable natural fiber resources, that has not been well investigated is sweet sorghum (SS). It is cultivated in hot and warm countries due to its drought resistance (Pires et al., 2019; Tan et al., 2022; Vázquez-Núñez et al., 2021).

Recently, SS has been quite widely admitted for its potential as a lignocellulose resources. It was domesticated in Africa, becomes

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an important food crop and ranked after wheat, rice, corn and barley. It has been developed in Indonesia and its stalk has similar component compare to wood. It makes a potential fiber source for composite reinforcement. Sweet sorghum stalk (SSS) extract can be easily fermented as ethanol because of high concentration of sugar. The main problem is the large scale of waste after the extraction process. Starting of this problem, SSS has become a novel and potential raw material for composite reinforcement. Moreover, it has higher cellulose content than bagasse and rice straw (Handayani et al., 2019; Ismojo et al., 2018; Pires et al., 2019; Qi et al., 2015; Yuanita et al., 2019).

In general, natural fibers are hydrophilic, where the most polymer matrix are hydrophobic. Non polar polymer matrix will have low compatibility with polar natural fibers. The other problem is lignin and hemicellulose content of the fiber can absorb moisture easily. This phenomenon created the intermolecular hydrogen bonding in fiber. The condition will give result in the lack of interface between them and leads failure during the stress transfer from one phase to another (Jaafar et al., 2019; Olonisakin et al., 2021; Qi et al., 2015; Yuanita et al., 2019). Therefore, it is very important to modify the fibers with a treatment. Certain treatment on the natural fibers are required to improve compatibility between hydrophilic natural fiber and hydrophobic polymer matrix. Compatibility which is related to wetting characteristic is needed when foreign surface is put in the molten polymer as matrix material (Yuanita et al., 2017).

Sodium hydroxide (NaOH) is usually used for fiber alkali treatment, with concentration and temperature process variation. The alkalization treatment was done by soaking SSS fiber in 4% (w/w) NaOH in agitated condition for 3 hours at temperature 70-90 ◦C in repeated 3 cycles prior to bleaching treatment (Ismojo et al., 2018). While Handayani used NaOH 15% solution for 1 hour at 70 ◦C, Husnil, Ismojo and Yuanita used NaOH 10% solution for 2 hours at 70 ◦C when treated the SSS fiber before bleaching treatment (Handayani et al., 2019; Husnil et al., 2019; Ismojo et al., 2019; Yuanita et al., 2019). Pressurized cooker treatment for SSS fiber has been done by Ismojo with the variation of heating time and the result showed that there was an increasing in crystallinity index compared to pristine fiber (Ismojo et al., 2020). To the best of our knowledge, the treatment of SSS using combination of alkali and pressure steam is limited, a study to prove the effect of Alkali Pressure Steam (APS) treatment for SSS waste is an interesting research. Pressure cooker treatment which combine with alkali will give better result in crystallinity index and hydrophobicity properties of the SSS fiber, in comparison only with alkaline treatment or only with a pressure cooker.

Thus, the objective of this study is to investigate the effect of different NaOH concentration and pressure steam soaking time on change in the crystallinity index and hydrophobicity properties of the SSS fiber.

MATERIALS AND METHODS

Materials

The SSS were collected from local farmer in Bogor. Leaves and nodes were removed and stalks were further wash in tap water. Sodium hydroxide (NaOH) in pellet form was purchased from Merck.

Method

Fiber preparation

The SSS was cut, crushed and then sieved until passing 100 mesh size screen. And then, 6 grams of the fiber was placed and proceed in to pressure cooker with 0%, 5% and 10% NaOH solution for 1 and 3 minutes. After APS process, the fiber was dried for 2 days under sunlight and followed by oven drying at 50◦C for 120 minutes.

Characterization

Fourier Transform Infrared (FTIR) spectra were recorded using Perkin-Elmer UATR Two FTIR spectrometer (Waltham, MA, USA). Each sample recording consisted of 30 scans recorded from 800 to 4000 cm^{-1}. Pristine, hydrothermal, and APS treated of SSS fiber samples were analyzed.

X-Ray diffraction (XRD) was used to determine the crystallinity of the SSS fiber after different treatment. Each material in the form of milled powder was placed on the sample holder and levelled to obtain total and uniform X-ray exposure. XRD was performed on an X-Ray Diffractometer Philips PW 1710 (EA Almelo, The Netherlands) using monocromatic Cu K-α radiation of $\lambda = 15.418$ nm at a voltage of 40 kV and a current of 30 mA with step 0.02◦ and time/step around 20 s from $2\Theta = 5$ to 50, 30 min per sample. The crystallinity index CrI, was determined based on reflected intensity

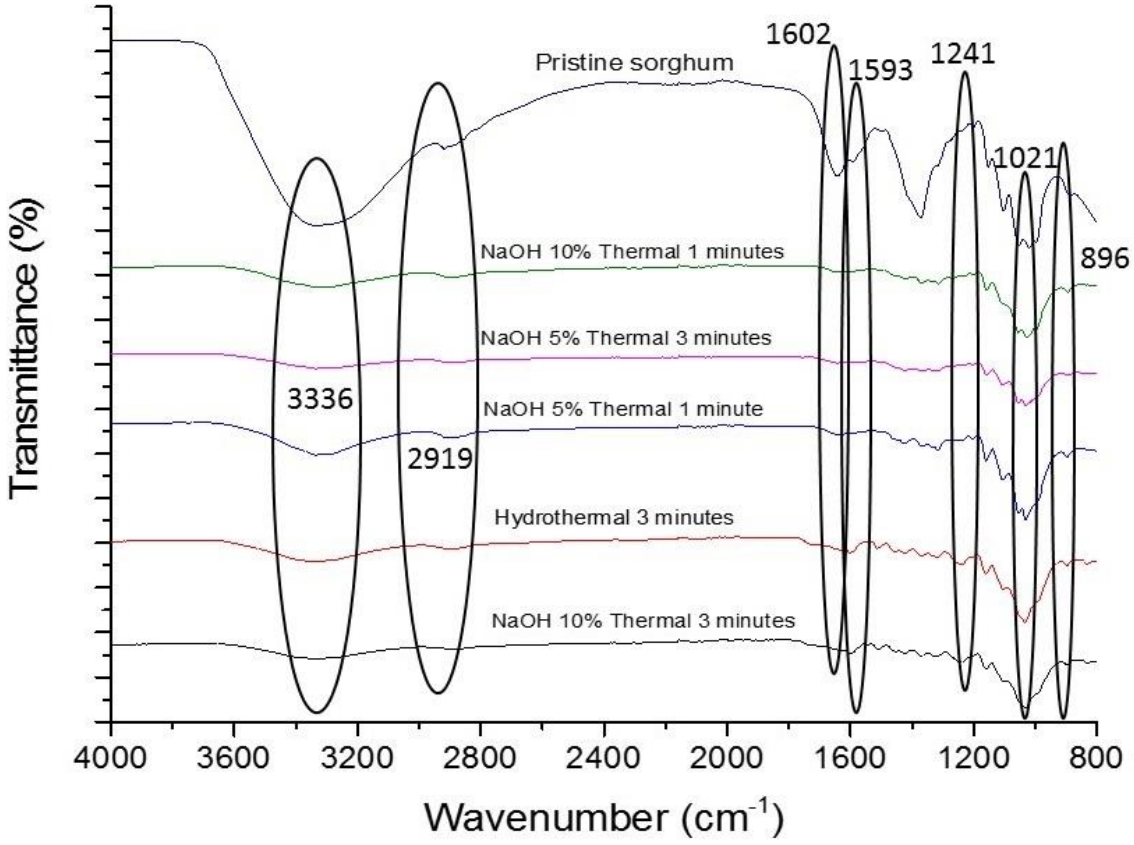

Figure 1. FTIR analysis of pristine sorghum and treated sorghum

data following the method of Segal equation (Nam et al., 2016).

$$CrI\ (\%) = \frac{I_{002} - I_{amp}}{I_{002}}\ x\ 100\% \qquad (1)$$

where CrI is crystallinity index, I_{002} is the maximum intensity of the (002) and I_{amp} is the intensity of the (100) lattice diffraction peak of the sample. The diffraction peak of the plane (002) is located at the diffraction angle around 2Θ = 22◦ and the intensity scattered by the amorphous part is measured as the lowest intensity at the diffraction angle around 2Θ = 16◦.

Field Emission Scanning Electron Microscopy (FESEM) FEI INSPECT F50 (Hillsboro, OR, USA) was used to observe the morphology of the SSS fiber. The effect of the treatment was assessed using a comparison of the pristine and treated SSS. Image was taken at an accelerated voltage of 20 kV.

The contact angle measurement technique is used to find out the wettability of the fiber surface to the matrix. It is used to find the hydrophobicity of the fiber. In this method, a water droplet is placed to the fiber surface with the help of the glass pipet. The volume of the water droplet kept constant for all the samples. The experimental setup used for contact angle measurement consist of camera holder, camera, test sample holder and fiber placed on a holder rest. The image result was analyzed with Image J software.

RESULTS AND DISCUSSION

Functional group analysis

The FTIR spectra of pristine and treated SSS were illustrated in Figure 1. It showed a comparison of transmission of FTIR spectra in SSS fiber, among pristine and treated fibers. FTIR spectra analysis determine that broad band at 3336 cm^{-1} indicated OH bond of lignin, hemicellulose and cellulose and 2919 cm^{-1} indicated C-H bond of sorghum (Handayani et al., 2019). The figure showed that there was significant increase in the % transmittance which indicated that the O-H groups were degraded during treatment. The peaks between 3000 and 2800 cm^{-1} can be attributed to C-H aliphatic stretching in methoxyl, in methyl, and methylene groups of propyl side chain present in

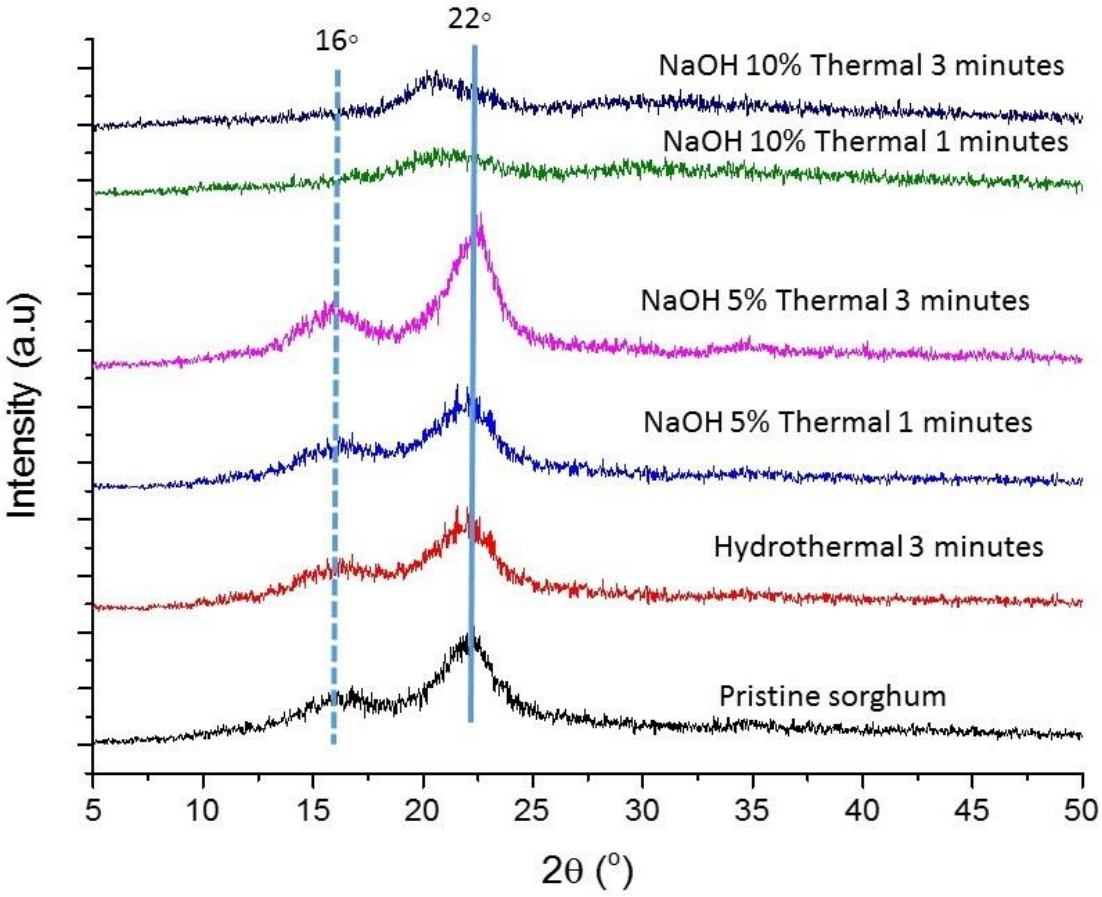

Figure 2. XRD analysis

lignin. The peaks between 1635-1595 cm^{-1} were assigned to C=C stretching in aromatic rings of S and G units in lignin. The treated fiber showed higher % transmittance at that particular peak compared to the pristine fiber. It indicated that the treatment eroded lignin so that decreasing the concentration of aromatic ring. The peak of 1241 cm^{-1} indicated aromatic bond, C-C asymmetric of lignin, C-O and C-C bond of lignin. While 1021 and 896 cm^{-1} showed C-O-C bond of hemicellulose monomer and C-O and C-O-C stretching of lignin (Iskandar et al., 2022; Yuanita et al., 2020; Zevallos Torres et al., 2021). There was a shift in spectra of lignin and hemicellulose to the treated fibers, both with hydrothermal and APS treatment. This showed that the amount of lignin and hemicellulose in the treated sorghum fiber has decreased.

Fiber crystallinity analysis

XRD diffractograms for pristine and treated SSS fibers are shown in Figure 2. The figure showed almost the same shape with two peaks, located at 2θ, 16◦ and 22◦, are according to crystallography plane (10-1) and (002), respectively.

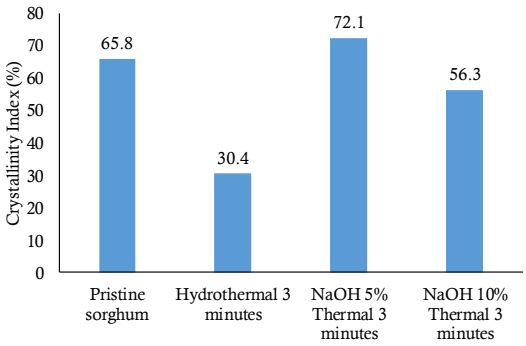

Figure 3. Crystallinity index.

XRD result are also ensured with the FTIR spectra and it can be showed that the removal of amorphous part, lignin and hemicellulose, has occurred during the treatment. Observation of XRD testing which was calculated by Segal equation (1) could be seen in Figure 3. Upon removal the amorphous materials by APS treatment, the crystallinity index increased from 65.8% for pristine to 72.1% for 5% NaOH and thermal 3 minutes (Figure 3). While the combination of higher NaOH concentration (10%) and thermal in 3 minutes has possibly resulting in a relatively harsh condition

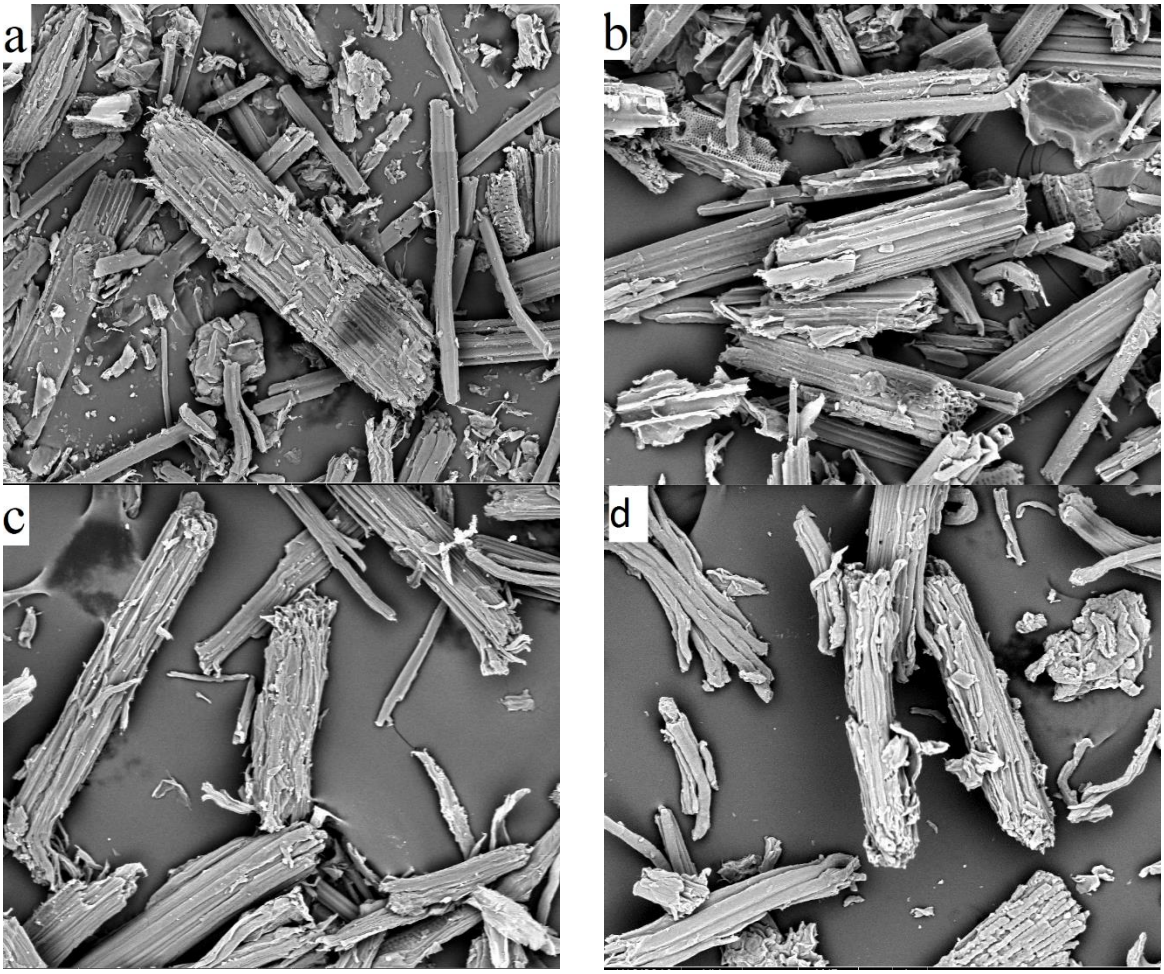

Figure 4. Morphology of sorghum (a) pristine, (b) hydrothermal, (c) NaOH 5% thermal 3 minutes, (d) NaOH 10% thermal 3 minutes.

where not only lignin and hemicellulose that are eroded but also the cellulose are degraded. The crystallinity index was decrease for treatment with 10% NaOH thermal 3 minutes. However as can be seen in Figure 3, the hydrothermal treatment gives the lowest crystallinity index. One possible explanation is probably because the hydrothermal treatment with 3 minutes process could not remove and degrade the amorphous part, lignin and hemicellulose. Hydrothermal treatment without alkalization requires a longer processing time like previous research (Ismojo et al., 2020). The hydrothermal treatment only made the fiber swollen and the water was absorbed by the fiber, caused the crystallinity index decreased.

Fiber morphology analysis

Morphology identification of the fiber has been done by FESEM analysis. Figure 4 is the image of FESEM result of the pristine and treated sorghum fiber. Pristine sorghum fiber is shown in Figure 4a, the fiber is still in bundles, together binding with lignin and hemicellulose. The treatment, both hydrothermal and alkali thermal, promoted the defibrillation phenomena (Figure 4b, 4c and 4d). The surface of treated fiber became cleaner and smoother than pristine fiber. However, fiber with hydrothermal treatment (Figure 4b) has not been appeared significantly different with pristine fiber. The fiber has not fibrillated compared to alkali thermal treated (Figure 4 c and 4d). Figure 4c and 4d shows the fibrillated fiber which indicated APS treatment method succeed to scrape lignin and hemicellulose. The fibrillation is attributed to the separation of the fiber due to the removal of the lignin and hemicellulose which bind cellulose. This result was in line with FTIR and XRD result which analyzed the reduction of lignin and hemicellulose content as amorphous part of the fiber.

Sessil drop analysis

The contact angle of the fibers was measured and in each value presented in Figure 5. If the contact angle is less than 90◦, then the fiber

has a hydrophilic nature. If the contact angle is more than 90◦, then the fiber has become hydrophobic (Atmakuri et al., 2020). It was found that the fiber which is treated with NaOH 5% thermal 3 minutes has contact angle 120.9◦, more than 90◦, which mean this treatment has successfully made the fiber become hydrophobic. Thermal energy of APS treatment broke hydrogen bond of the OH group and then Na^+ ion of the NaOH solution substituted the hydrogen so the OH become O-Na group which has more hydrophobic. The following reaction take place during alkali thermal treatment of natural fiber (Yuanita et al., 2020).

$$\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O-Na} + H_2O \quad (2)$$

However, there is a decrease in the value of the contact angle on the fiber with NaOH 10% thermal 3 minutes. As previously mention, treatment with 10% NaOH gave relatively harsh condition to the fiber. More Na+ ion during the reaction and that ion is able to widen and penetrate the small pores between the lattice planes of cellulose. This phenomena could make the fiber-O-Na structure with relative bigger dimension and larger distance between molecules (Yuanita et al., 2020). As a result, this gave bigger rooms for H_2O molecules and made the fiber become more hydrophilic compared to the pristine and other treated fiber.

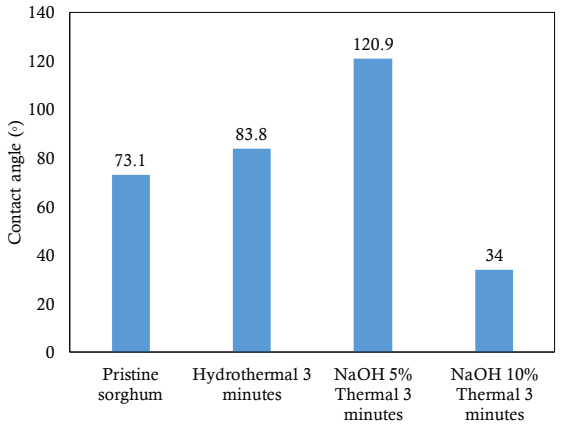

Figure 5. Contact angle of pristine and treated SSS.

CONCLUSION

The research revealed that fiber modification of SSS was treated with APS. The morphology, crystallinity and hydrophobicity of the fiber were examined. The APS treatment could decrease the content of lignin and hemicellulose. In addition, this treatment method can enhance hydrophobicity of the fiber based on Sessil drop testing analysis. The optimum result was obtain with method of 5% NaOH concentration and 3 minutes pressure-soaking. In the future studies, we will investigate the effect of SSS with APS treated as reinforcement with high crystallinity and better hydrophobicity to the PP matrix.

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