

Synthesis of a Carbon-activated Microfiber from Spider Webs Silk

E Taer¹, W S Mustika¹ and R Taslim²

¹ Authors' Department of Physics, Faculty of Mathematics and Natural Sciences, University of Riau, INDONESIA.

² Authors' Department of Industrial Engineering, Faculty of Science and Technology, State Islamic University of Sultan Syarif Kasim, INDONESIA.

Email: erman.taer@yahoo.co.id, widyasintamustika@ymail.com

Abstract. Carbon fiber of spider web silk has been produced through the simple carbonization process. Cobwebs are a source of strong natural fiber, flexible and micrometer in size. Preparation of micro carbon fiber from spider webs that consist of carbonization and activation processes. Carbonization was performed in N₂ gas environment by multi step heating profile up to temperature of 400 °C, while the activation process was done by using chemical activation with KOH activating agent assistance. Measurement of physical properties was conducted on the surface morphology, element content and the degree of crystallinity. The measurement results found that micro carbon fiber from spider webs has a diameter in the range of 0.5 -25 micrometers. It is found that the carbon-activated microfiber takes the amorphous form with the carbon content of 84 % .

1. Introduction

Carbon material is one of the functional materials that are intensive studied in the recent decades [1]. Various aspects of life can be attributed to the use of carbon such as, health, beauty, water purification and gas, as well as the supply of energy storage device [2,3]. The wide range of carbon application because its excellent properties such as high surface area and good electrical conductivity. The availability of carbon in various forms such as: particle, fiber and granules as well as various sizes in the nanometer, micrometer and millimeter into its own advantages in the preparation for the use of a unique carbon. Carbon fiber itself can still be categorized further into carbon fiber hollow and solid [4]. Besides, the source of carbon material origin becomes a major factor in the production of carbon. One step to produce carbon fiber is to perform the carbonization process to transform it into carbon fiber material. Preparation the fiber material is a research process that requires a lot of development.

The supply process of original carbon fiber material is relatively expensive that can become a problem in the development of carbon fiber on a large scale [5]. The availability of fiber in nature may be one of the choices in the development of carbon fiber. Some natural fiber material which had been made into a carbon fiber including cottons and cocoons [6,7,8]. Spider web silk is one of the fiber materials that are naturally available in a microsize. The spider web properties were strong and relatively flexible that was certainly a special consideration in the selection of this material as a carbon source of natural fiber. In this study will be focused on the production process of carbon fiber from spider web silk that be emphasized at adjustment of pyrolysis condition. This study was concentrate on



observation of the morphological structure to see the size of the carbon fibers, the supporting element content and the degree of crystallinity of the carbon fiber of cobwebs.

2. Experiment

A Common houses spider web (CHSW) (*Parasteatoda tepidariorum*) was selected as a raw materials for production of carbon activated microfiber. The preparation of the carbon activated microfiber materials consist of some stages i.e collecting, washing, drying, molding pellets, carbonization and activation as shown in Figure 2. Sample CHSW weighing ± 0.13 g was immersed in distilled water for 48 hours and continued with the process washing at 80°C with rotation speed of 300 rpm for 15 minutes using a hot plate stirrer and then dried for 36 hours using an oven. The CHSW sample is formed into the pellets using a Hydraulic Press at a pressure of 6 tons. Pellet CHSW carbonized up to a temperature of 400°C in an environment of nitrogen gas (N_2). The process was performed by multistep heating profile with N_2 gas flow rate of 1.5 L/min that had been reported previously [9,10]. CHSW carbonization profile shown in Figure 1. The heating process begun at room temperature 30°C up to soaking temperatures of 280°C for 4 hours 17 minutes with a temperature increase rate of 1°C/min . Next, the sample was heated at a temperature of 280°C for 1 hour, then heating is continued up to a temperature of 400°C at a rate of temperature rise of 3°C/min for 40 minutes. This process had been successfully transformed into activated carbon CHSW. After the carbonization process, carbon CHSW was activated by using 0.7 M KOH .

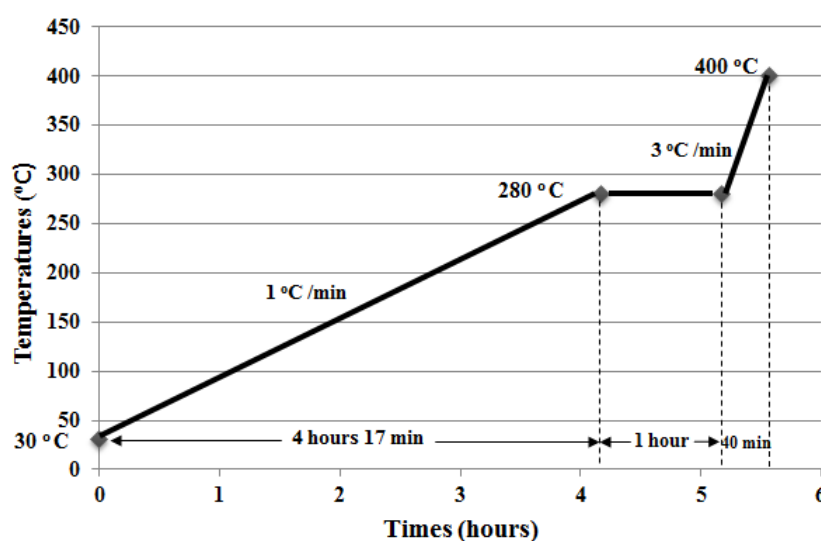


Figure 1. Carbonization process of CHSW.

Structure CHSW samples were analyzed using X-Ray Diffraction instrument. This analysis used the instrument X 'Pert Pro in diffractometer cubic system, using a light source and wavelength anode $\text{Cu K}\alpha$ was to 15.406 nm in the range of diffraction angle (2θ) is 10 - 100° . The surface morphology and chemical composition of the samples was measured using a Hitachi S-3400N. SEM measurements was performed at a potential of $10,000\text{ V}$ used a detector of back scatter electron (BSE).

3. Result and Discussion

CHSW main stages to transform into carbon microfiber (CMF) were the washing process, carbonization and activation. Overall treatment have a purpose to remove other materials than carbon, so these processes lead to loss of mass in the sample. The sample mass shrinkage data are presented following in Table 1.



Figure 2. The sample for each step in preparation process: a) a spider web once collected, (b) after washing, (c) after drying, (d) after compression, (e) after carbonization.

Table1. Mass shrinkage of the sample.

Process	Initial mass (g)	Final mass (g)	Mass lost (%)
Washing	1.298	0.356	72.57
Carbonization	0.334	0.157	52.99
Activation	0.157	0.154	1.91

The mass loss occurred when washing the sample were equal to 72.57%, this process removed dust and dirt on CHSW. Carbonization process caused mass loss of 52.99%. This carbonization process caused evaporation elements other than carbon, which can evaporate at a temperature ≤ 400 °C. The activation process caused a small mass loss of 1.91%. This mass loss was caused by breaking the carbon chains and carbon material that binded to the elements or compounds in addition to carbon.

CHSW sample XRD pattern shown in Figure 3. The peak of carbon for dhkl field (002) and (100) appeared at a diffraction angle 2θ in the range of 15 to 35°. Sharp peaks that appearing are impurities other than carbon, namely SiO_2 , the same result had also been reported in a previous article [11]. Characterization of samples CHSW before carbonization indicated that CHSW was carbon in the form of compounds. CHSW sample peak was detected at diffraction angles 2θ of 22.728° and 42.799°. Carbonization process caused the peak shift at diffraction angles 2θ of 26.399° and 43.637°, while the activation process brought out carbon peaks at diffraction angles 2θ of 26.065° and 43.976°.

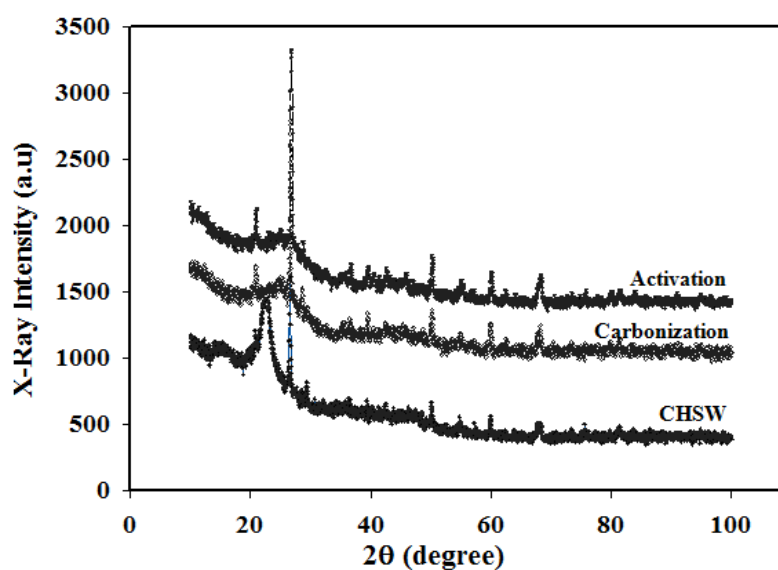


Figure 3. XRD pattern of CHSW sample.

SEM micrographs after washing, carbonization and activation are shown in Figure 4. This figure showed that the morphology CHSW was a form of fiber. After carbonization the carbon morphology CHSW like fine long fibers. Diameter of carbon fiber were in the range 0.5 to 25 μm . The activation process showed a clearer shape fiber with an average size of 8.72 μm .

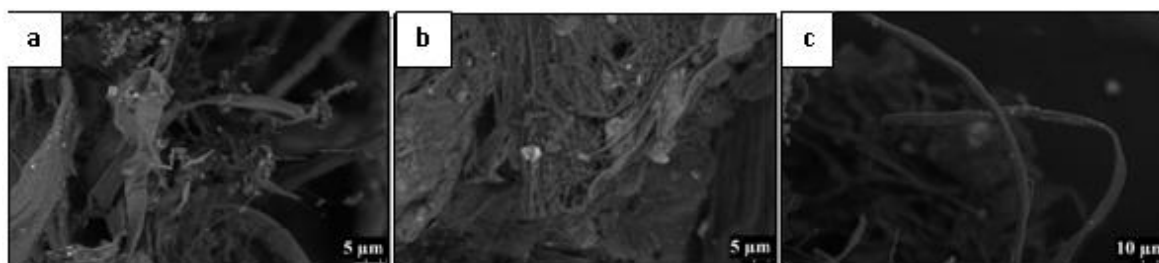


Figure 4. Figure of sipeder web fiber: (a) raw materials as prepared, b) after carbonization, c) after activation process.

Figure 5 and Table 2 respectively presents a test EDX spectrum and composition of constituent elements of CHSW and activation CHSW. Raw material showed carbon element content of 50.68%. Carbonization process that had been carried out successfully increases the carbon content in CHSW which amounted to 77.34%. In addition to the element carbon in the samples indicated the presence of other elements such as Al, Si and Ca. The EDX test results correlated with the XRD data. XRD data also indicate the presence of materials Si, Al and Ca are characterized by the presence of a sharp peak at two-theta angle 28.78° , 21.065° and 50.302° , 60.152° , respectively [12-13]. Chemical activation process managed to reduce impurities in this reality was supported by data that the percentage of materials non-carbon apparent decrease as the data shown in Table 4. On the other hand, KOH activators increase the oxygen content (O) on carbon CHSW so that the composition of C was reduced quantitatively. The activation process caused KOH bound with sample group of oxygen. Washing step can eliminate K bond, but cannot sever the bond of O.

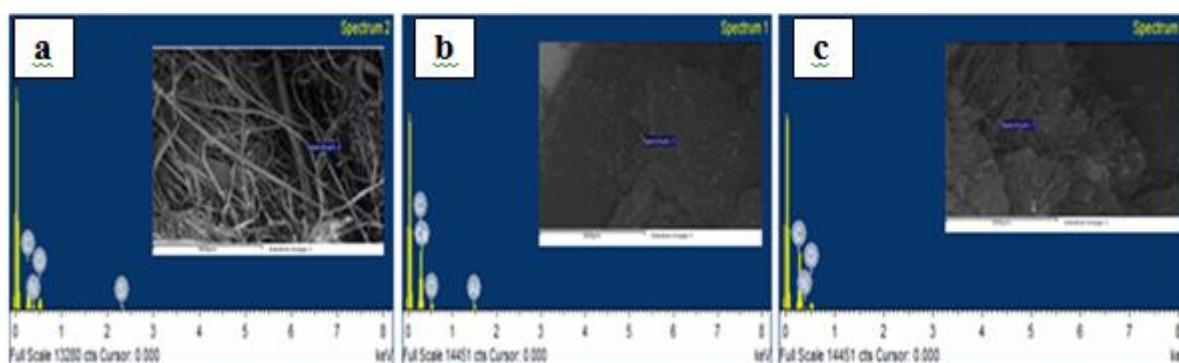


Figure 5. The EDX spectrum of CHSW sample, a) after washing process, b) after carbonization process and c) after activation process.

Table 2. EDX data of CHSW.

Unsure	Percentage of mass (%)			Percentage of atomic weight (%)		
	CHSW	Carbonization	activation	CHSW	carbonization	activation
C	50.68	77.34	72.49	57.95	83.47	77.51
N	11.70	17.63	4.12	11.48	14.28	3.77
O	33.60	-	23.25	28.85	-	18.66
S	4.02	-	0.15	1.72	-	0.06
Al	-	3.43	-	-	1.65	-
Si	-	0.62	-	-	0.28	-
Ca	-	0.99	-	-	0.32	-
Total	100.00	100.00	100.00	100.00	100.00	100.00

Some literature had been describing the micro carbon fiber synthesis of various types of raw materials. The following comparison of micro carbon fiber and research conducted are summarized in Table 3. Based on the data shown in Table 3 is clearly indicated that CHSW is an acceptable range for a micro carbon fiber. The other side of excellence CHSW is available in lengths of more than the other micro carbon. This fact is supported by the data that the natural fiber silk spider webs have a regular shape in the form of a network arrangement. Shape structures are at the network will also produce carbon micro-fiber with the same structure. Another advantage that can be written in this paper is certainly the cost of providing relatively low, so the micro carbon fiber of spider silk network's potential to be developed in a number of applications in the future [1].

Table 3. Micro carbon fibers from several precursors.

Precursor	Fiber size	Reference
Phenol-formaldehyde and tetraethyl orthosilicate	1 μm	[14]
Polyacrylonitrile (China Fabric)	12.7 μm	[15]
spider silk scaffold and CNT	1 μm	[16]
Carbon Microfiber Fabric ACC-5092-20	10 μm	[17]
Silk Cocoon	10-40 nm	[6]
Banana Peel	26 nm	[18]
CHSW	0.5-25 μm	Recent study

4. Conclusions

Based on all the data and analysis that has been done can be concluded that the carbon activated microfiber made from the spider web shows potential to be developed as a functional carbon material. The size of the diameter and length were very supportive and a high purity level cause the carbon fiber of spider webs easy to be activated, and was developed as a raw material for a variety of applications.

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