

## **EFFECTS OF ULTRASOUND ON THE MORPHOLOGY, PARTICLE SIZE, CRYSTALLINITY, AND CRYSTALLITE SIZE OF CELLULOSE**

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**Abstract:** The aim of this study is to optimize ultrasound treatment to produce fragment of cellulose that is low in particles size, crystallite size, and crystallinity. Slurry of 1 % (w/v) the cellulose was sonicated at different time periods and temperatures. An ultrasonic reactor was operated at 300 Watts and 28 kHz to cut down the polymer into smaller particles. We proved that ultrasound damages and fragments the cellulose particles into shorter fibers. The fiber lengths were reduced from in the range of 80-120  $\mu\text{m}$  to 30-50  $\mu\text{m}$  due to an hour ultrasonication and became 20-30  $\mu\text{m}$  after 5 hours. It was also found some signs of erosion on the surface and stringy. The acoustic cavitation also generated a decrease in particle size, crystallinity, and crystallite size of the cellulose along with increasing sonication time but it did not change d-spacing. However, the highest reduction of particle size, crystallite size, and crystallinity of the cellulose occurred within the first hour of ultrasonication, after which the efficiency was decreased. The particle diameter, crystallite size, and crystallinity were decreased from 19.88  $\mu\text{m}$  to 15.96  $\mu\text{m}$ , 5.81  $\text{\AA}$  to 2.98  $\text{\AA}$ , and 77.7% to 73.9% respectively due to an hour ultrasound treatment at 40 °C. The treatment that was conducted at 40 °C or 60 °C did not give a different effect significantly. Cellulose with a smaller particle and crystallite size as well as a more amorphous shape is preferred for further study.

**Keywords:** *crystallite size, microcrystalline cellulose, particle size analyzer, SEM image, ultrasonication, X-Ray Diffraction*

## INTRODUCTION

Cellulose, the most abundant renewable biopolymer on earth, is produced by nature at annual rate of over 50 billion tons [1]. The utilization of cellulose becomes more important because it does not compete with staple food needs. Since a few decades ago depolymerisation of cellulose is a subject of interest. It can be depolymerized to oligomer and/or glucose [2-5]. However, the yield of the hydrolysis process is still low. Consequently it requires the development of preparing cellulose materials before converted into oligomeric and monomeric sugars.

Based on molecular structure cellulose is a polar molecule that makes it insoluble in nonpolar organic solvents. It contains some -OH groups and has intra and intermolecular hydrogen bonds. The ability to form these kinds of hydrogen bonding makes it relatively high in crystallinity and insoluble in aqueous solution [6]. Cellulose materials consist of crystalline and amorphous parts in varying proportions. It depends on the source of the biomass, such as cotton has 58 % and *Halocynthia* has 74 % crystalline portions [7]. Physical and chemical properties of cellulose are affected by the arrangement of cellulose molecules as well as of amorphous and crystalline portions. Amorphous cellulose has lower level of order compared to crystalline cellulose. Most of the reactants, therefore, easily penetrate only on the amorphous regions where the reaction usually takes place [8].

It is also reported that there is a significant difference in the hydrolysis behavior of the amorphous and crystalline portions within microcrystalline cellulose in hot compressed water. The amorphous portion is much more reactive than the crystalline portion. The minimal temperature to break the glycosidic bonds in the amorphous portion is around 150 °C. It is lower than that of the crystalline portion which starts at around 180 °C [1]. Based on this reason, changing the structure of the cellulose to become more amorphous is very important because the cellulose is more susceptible to reaction.

On the other hand, ultrasound begins to be widely used in polymer degradation. Ultrasonic degradation of polymers becomes an interesting process because it does not cause changes in chemical properties of polymers. Xiaodong studied the effects of ultrasound on a polysilane solution [9], Oustland and Striegel studied the effects of ultrasound on a solution of poly( $\gamma$ -benzyl-L-glutamate) [10], Mohod and Gogate studied the effects of ultrasound on carboxymethylcellulose (CMC) and polyvinyl alcohol (PVA) [11], Goodwin studied the effects of ultrasound on cellulose ethers solution [12]. All of their results commonly showed that ultrasound caused the decrease of the intrinsic viscosity or average molecular weight of the polymer samples. Furthermore, due to the driving force for the dissolution, low molecular weight of polymer is more soluble than higher molecular weights. The higher the molecular weight needs more entropic driving force for dissolution than that of the smaller ones. Therefore, the ultrasonic treatment on the cellulose can be assumed to increase the dissolution of the polymer via the molecular chain scission.

Cellulose is a high molecular weight of biopolymer composed of glucose monomers through  $\beta$ -1,4-glycosidic bonding as well as intra and intermolecular hydrogen bonding. It also has a high percentage of crystalline portions. These kinds of the structure make it very strong and difficult to dissolve or to hydrolyze. To obtain easier dissolution and hydrolysis, the structure should be changed. The objective of the study is to modify the cellulose structure so that particle size, crystallite size, and crystallinity decrease

through cutting glycosidic bonds. Attempt to achieve the goals was done by means of ultrasonication. Ultrasound can be assumed to break down the cellulose structure especially the crystalline regions. These fragmented polyglucose can be expected to be more efficiently converted to glucose and/or oligosaccharide by means of hydrolysis or further conversion into fuel (alcohol).

## MATERIALS AND METHODS

### Materials

Avicel microcrystalline cellulose (MCC) that has fiber length in the range of 60-80  $\mu\text{m}$ , average particle diameter of 19.88  $\mu\text{m}$ , and 77.70 % crystalline was used. This sample was produced by Asahi Kasei Chemicals Corp. Demineralised water was used as a solvent as well as a hydrolysis reagent.

### Methods

Slurry of 1 % (w/v) cellulose in water was ultrasonicated at 40 or 60 °C within 1, 2, 3, 4, and 5 hour periods. Ultrasonic bath SU-27TH which has an output power of 300 watts, frequency of 28 kHz, and 500 watts heater was used in this study. After ultrasonication, the colloid suspension was centrifuged at 5000 rpm for 30 minutes. The resulting supernatant was freeze dried and stored at 5 °C for further testing. Microstructural analysis was performed using a scanning electron microscope (FEI Inspect S-50 that using data analysis software server XT microscope). The sample surfaces were coated with a thin layer of gold using a Bal-Tec SCD 005 sputter coater to provide electrical conductivity. Particles size of samples was measured using particle size analyzer (Beckmann Coulter LS 200). X-ray diffraction measurements were performed on diffractometer (PanAnalytical Xpert Pro) using Cu K $\alpha$  radiation. The samples were scanned over a 2 $\theta$  range varying from 5° to 89°. Crystallinity of the sample was calculated using High ScorePlus software, the d-spacing was calculated using the Bragg's equation, and the crystallite size was calculated using the Scherrer equation (1):

$$L = \frac{0.9\lambda}{H \cos \theta} \quad (1)$$

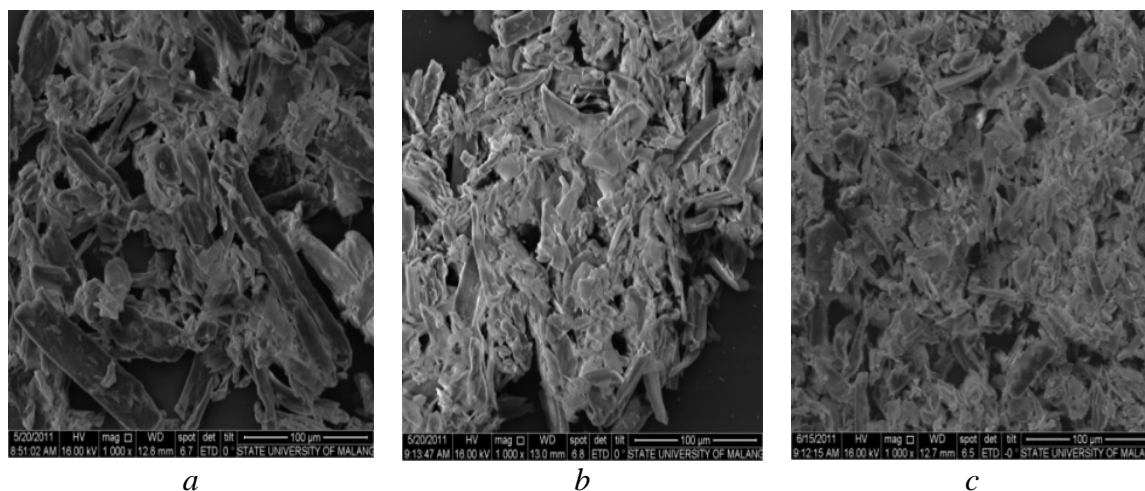
where  $L$  is the crystallite size perpendicular to the plane,  $\lambda$  is X-rays wavelength,  $H$  is the full width at half maximum in radians and  $\theta$  is the Bragg angle [7, 13].

## RESULTS AND DISCUSSION

### Morphology analysis

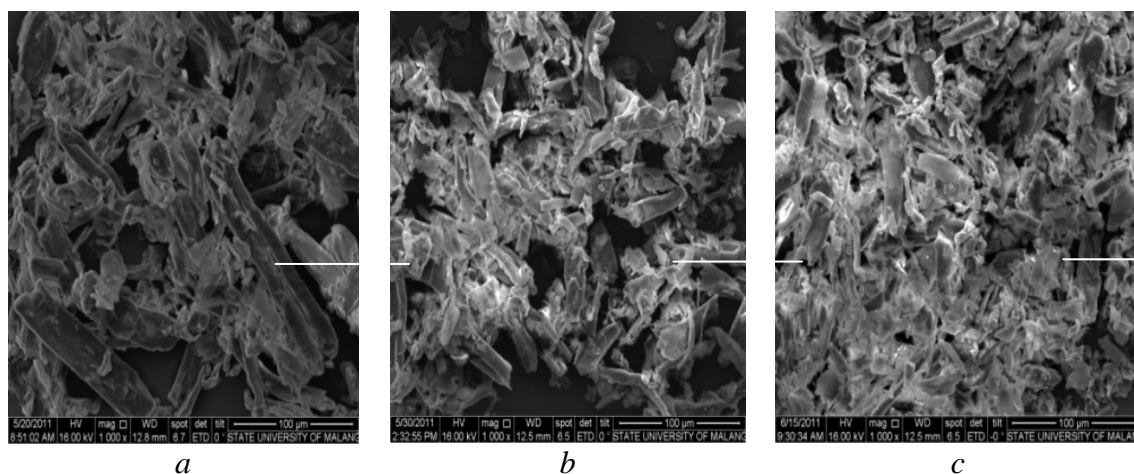
SEM images of the cellulose in different time periods at 40 °C ultrasonication are shown in Figure 1. It can be seen that the initial sample of cellulose particles had the form of long fibers (Figure 1a). After being treated by ultrasound for an hour, the cellulose was damaged and fragmented into shorter fibers and some signs of erosion

occurred on the surface (Figure 1b). After sonicated for 5 hours it was fragmented further and some cellulose particles began stringy (Figure 1c). The initial fiber lengths of cellulose were in the range of 80-120  $\mu\text{m}$ . Because of ultrasound, it was reduced to 30-50  $\mu\text{m}$  due to an hour treatment and fell down to 20-30  $\mu\text{m}$  after 5 hours.



**Figure 1.** SEM images of initial sample (a), after being treated at 40 °C for 1 hour (b) and for 5 hours (c)

A similar reduction occurred when it was sonicated at 60 °C. It was also damaged and fragmented into shorter fibers and erosion occurred on the surface due to ultrasound treatment. Furthermore, it was fragmented further and began stringy (Figure 2).



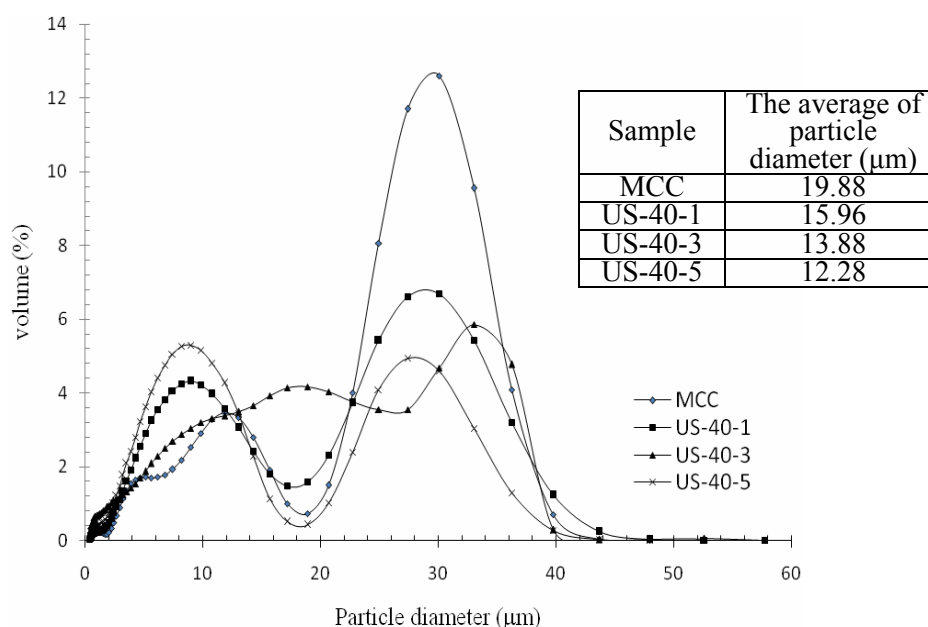
**Figure 2.** SEM images of initial sample (a), after being treated at 60 °C for 1 hour (b) and for 5 hours (c)

The occurrence can be explained by phenomena of acoustic cavitation. Ultrasound generated micro bubbles that collide with single fiber. The micro bubbles collapse and generate a large local energy due to the cavitation effects. The magnitude of local energy intensity is proportional to the number of bubbles collapse during cavitation that is equivalent to the duration of sonication. The emission of cavitation energy can loosen cellulose surface fibers and lead to bond breakages, especially in the damaged structure

[14]. Thereby, the ultrasonic impact will gradually degrade the cellulose fibers into smaller size. The longer time of ultrasonic treatment has possibility produce the greater destruction by local energy released in the cavitation. However, the effect of ultrasound on the morphology due to sonication temperature which was conducted at 40 and 60 °C could not be identified clearly despite water with higher temperature has greater kinetic energy [15].

### Particle size analysis

It was found that particle size cellulose was reduced proportionally to the duration of ultrasonication time (Figure 3). The average of particle diameter was decreased from 19.88  $\mu\text{m}$  to 15.96  $\mu\text{m}$  after being treated for an hour ultrasonication and became 12.28  $\mu\text{m}$  after 5 hours when it was treated at 40 °C (Figure 3). Similarly, there was particle diameter reduction when it was sonicated at 60 °C (Figure 4).

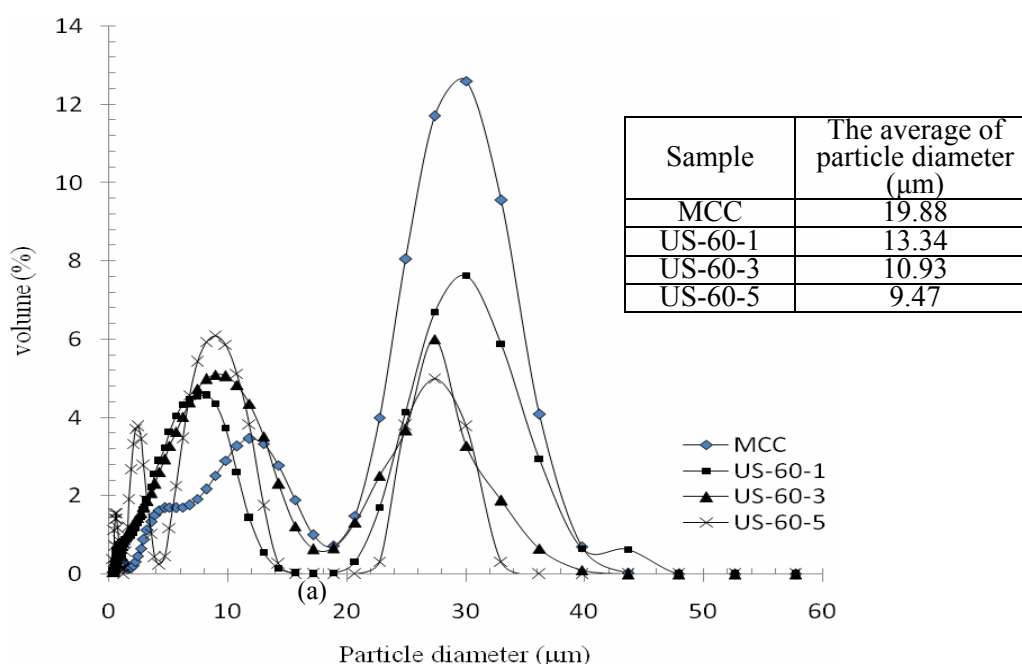


**Figure 3.** Particle sizes of cellulose as a function of ultrasonication time at temperatures of 40 °C

This reduction of particle diameter was resulted by cavitation energy generated by ultrasound. The cavitation energy produced shock waves that raised local pressure changed and shifted in liquid so that resulting in damaged on cellulose particle. Accordingly, it generated fragments of the cellulose as well as erosion on the surface so that resulted in particle diameter reduction. These data also support the morphology analysis in which destruction of particles increased when ultrasonication was performed at the longer time and leading to a smaller particle size. However, when it was treated at 60 °C the rate of particle size decrease was slightly greater than that of at 40 °C. The phenomena indicated that the difference of sonication temperature gives the different effect in size reduction. Considering that the higher temperature produced cavitation



energy which has a higher kinetic energy from the collapsing of bubbles, it confirmed that the greater destruction of the cellulose particles occurs under such situations.



**Figure 4.** Particle sizes of cellulose as a function of ultrasonication time at temperatures of 60 °C

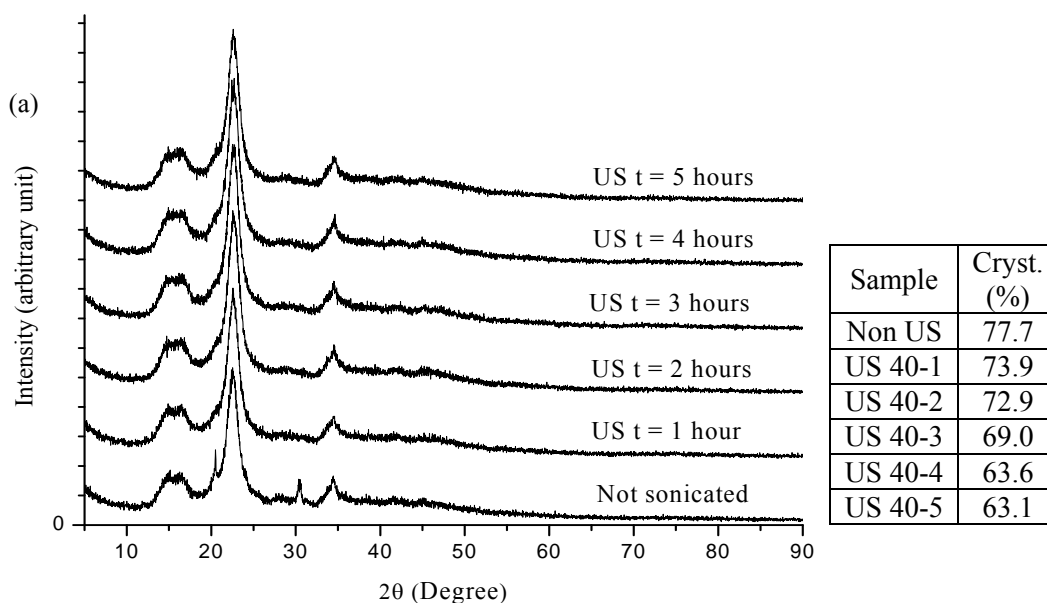
### X-ray diffraction analysis

Cellulose is composed of polyglucose chains with crystalline regions of a certain size and every crystallite polyglucose chain is separated by a distance of d-spacing [10]. The cellulose sonicated for different time periods and temperatures. The initial crystallinity of the cellulose was 77.70 % for this study. It was found that ultrasonic treatment caused a decrease in the crystallinity of samples (Figures 5 and 6).

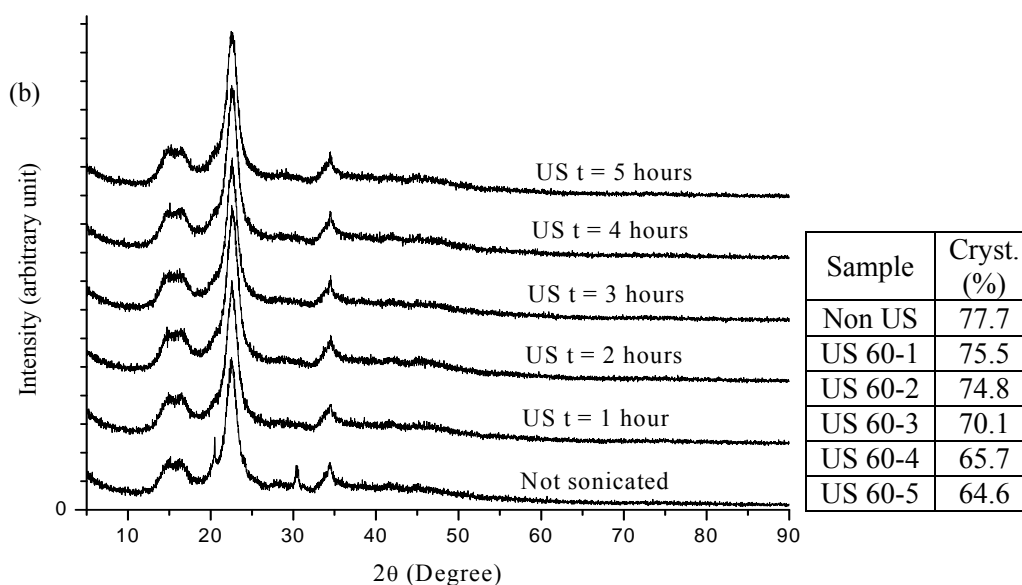
In addition, the crystallinity of the samples decreased with increasing ultrasonication time. For instance, at 40 °C ultrasound treatment, crystallinity of the cellulose was reduced to 69.0 % due to 3 hour ultrasonication and became 63.1 % after 5 hours (Figure 5). Similarly, the crystallinity of sample fell down to 70.1 % after being treated for 3 hours and became 64.6 % after 5 hours (Figure 6) when it was treated at 60 °C. It seemed that the different temperature treatment slightly led to different crystallinity of product.

It was also found that the crystallite size was decreased because of ultrasound (Figure 7), but there were no significant changes to the d-spacing (Table 1 and 2). The decrease in crystallinity and crystallite size of the cellulose occurred because of the impact of hot spots generated during the collapse of cavitation [15].

Water, a solvent as well as a hydrolysis reagent, which is irradiated using ultrasound, will produce bubbles. These bubbles oscillate, grow a little more during the expansion phase of the sound wave, then they shrink during the compression phase.

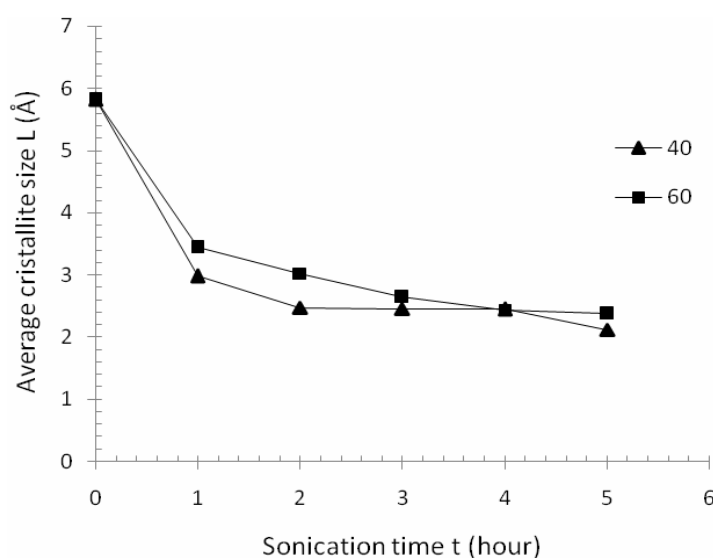


**Figure 5.** X-Ray diffraction patterns of cellulose sonicated for various time at 40 °C



**Figure 6.** X-Ray diffraction patterns of cellulose sonicated for various time at 60 °C

Under the proper conditions, these bubbles undergo a violent collapse which generates very high pressure and temperature on the surface of cellulose particles. Hoffmann suggested the existence of a layer in the bubble-solution interface where temperature and pressure may be beyond the critical conditions of water (647 K, 22.1 MPa) and have physical properties intermediate between those of a gas and a liquid. The supercritical water which was obtained during the collapse of cavitation bubbles generated sonolytic reactions [16].



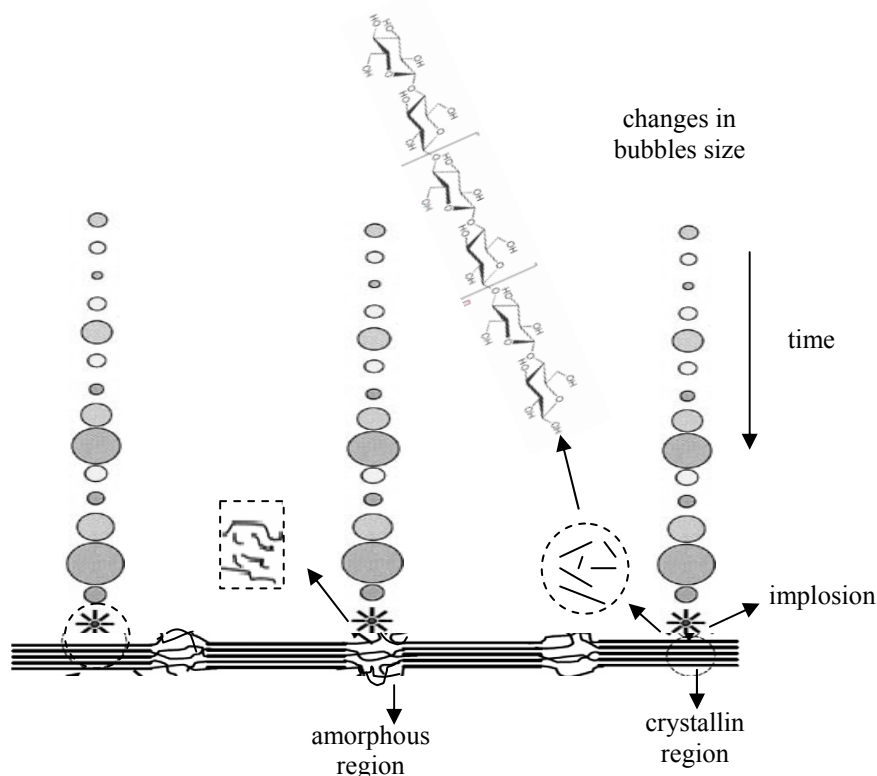
**Figure 7.** Crystallite size ( $L$ ) of cellulose as a function of ultrasonication time at temperature of 40 and 60 °C

On the cellulose surface, the intense physical stresses produced by acoustic cavitation resulted particle breakage and followed by fragmentation to smaller particles (Figure 8). Moreover, Sasaki [17] described that cellulose can be degraded in supercritical conditions. The degradation of cellulose in supercritical water conditions begins with the formation of swelling on the surface of cellulose. The water that diffuses to this surface can loosen polyglucose chains so that its particles become smaller and partially the constituent parts of crystalline will turn into amorphous parts [17]. The difference of cavitation temperature also influenced the crystallinity and crystallite size of fragmented cellulose as a product of ultrasonic treatment. The cellulose was fragmented into smaller particles and dispersed when ultrasound was being treated. After the treatment was completed, some crystalline particles aggregated again. At higher temperatures (60 °C), the fragmented particles aggregated to form more regular arrangement so that they had slightly greater crystallinity and crystallite size than that of at 40 °C.

**Table 1.** Effect of ultrasonic treatment that conducted at 40 °C for various time (hour)

2θ angle	d-spacing					
	Non US	US-40C-1	US-40C-2	US-40C-3	US-40C-4	US-40C-5
14.89	5.95	6.01	6.14	5.99	5.86	5.97
16.20	5.47	5.35	5.22	5.32	5.43	5.40
20.49	4.33	-	-	-	-	-
22.58	3.94	3.94	3.94	3.93	3.92	3.93
30.45	2.94	-	-	-	-	-
34.44	2.60	2.59	2.60	2.60	2.59	2.60





**Figure 8.** Schematic diagram of cellulose breakage generated by acoustic cavitation

**Table 2.** Effect of ultrasonic treatment that conducted at 60 °C for various time (hour)

2θ angle	d-spacing					
	Non US	US-60C-1	US-60C-2	US-60C-3	US-60C-4	US-60C-5
14.89	5.95	5.89	5.89	5.93	5.97	6.01
16.20	5.47	5.29	5.30	5.43	5.38	5.38
20.49	4.33	-	-	-	-	-
22.58	3.94	3.92	3.94	3.94	3.92	3.94
30.45	2.94	-	-	-	-	-
34.44	2.60	2.60	2.60	2.60	2.30	2.60

A crystalline solid is a type of matter that has atoms, ions, or molecules arranged in a regular, three-dimensional repeating pattern called a lattice that can be described by separate imaginary planes. The distance between these planes is called the d-spacing. The units of a crystalline solid lattice, whether they are atoms, ions, or molecules, are bonded to each other, giving the solid a strong structure. It had been found that there were no changes of d-spacing due to cavitation treatment at both temperatures in various time periods. When crystalline parts of cellulose treated with acoustic cavitation, they may be broken or crushed to smaller particles resulting decrease in crystallinity and crystallite size. However, after the treatment was completed the dispersed crystalline parts aggregated in the arrangement with the same d-spacing.

## CONCLUSIONS

Ultrasound damages and fragments the cellulose particles into shorter fibers. The fibers length were reduced from in the range of 80-120  $\mu\text{m}$  to 30-50  $\mu\text{m}$  due to an hour ultrasound treatment and fell down to 20-30  $\mu\text{m}$  after 5 hours. It was also found some signs of erosion on the surface and stringy. The acoustic cavitation also generated a decrease in particle size, crystallinity, and crystallite size of the cellulose along with increasing ultrasonication time but it did not change d-spacing. However, the highest reduction of particle size and crystallite size to the cellulose occurred within the first hour of ultrasonication, after which the efficiency of the ultrasonication decreased. The particle diameter, crystallite size, and crystallinity were decreased from 19.88  $\mu\text{m}$  to 15.96  $\mu\text{m}$ , 5.81  $\text{\AA}$  to 2.98  $\text{\AA}$ , and 77.7% to 73.9% respectively due to an hour ultrasound treatment at 40  $^{\circ}\text{C}$ . However, when the cellulose was being treated at 60  $^{\circ}\text{C}$  the particle diameter, crystallite size, and crystallinity became 13.34  $\mu\text{m}$ , 3.44  $\text{\AA}$ , 75.5% respectively. It means that the ultrasound treatment which was conducted at 40  $^{\circ}\text{C}$  or 60  $^{\circ}\text{C}$  did not give a different effect significantly.

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