Provision of micro-nano bacterial cellulose as bio plastic filler by sonication method

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Abstract. Research and development of bioplastic has increased recently as a solution for substitution of conventional plastic which have many negative impacts to environment. However, physical properties and mechanical properties of its still lower than conventional plastic. An alternative solution for that problem is by using fillers that can increase the strength. Bacterial cellulose is considered as potential source for filler, but still need to be explored more. The privileges of bacterial cellulose are easy to get and does not have lignin, pectin, and hemicelluloses which are impurities in other celluloses. This research focused on gaining bacterial cellulose in micro-nano particle form and its impact on increasing the strength of bio plastic. Ultrasonication has been used as method to form micro-nano particle from bacterial cellulose. The result showed this method may form the particle size of bacterial cellulose approximately ± 3μm. Next step, after getting ± 3μm particle of bacterial cellulose, is making bio plastic with casting method by adding 1% of bacterial cellulose, from the total material in making bio plastic. Physical characteristic of the bio plastic which are tensile strength 11.85 MPa, modulus young 3.13 MPa, elongation 4.11% and density 0.42 g/cm³. The numbers of physical properties show what, by adding 1% of bacterial cellulose, the strength of bio plastic was significantly increase, even value of tensile strength has complied the international standard for bio plastic.

1. Introduction

Research and development of bio plastic is increased recently, however in comparison bio plastic industry is stagnant. Bio plastic from starch takes about 50% of the market in bio plastic. Unfortunately, physical properties, mechanical properties and thermal properties of bio plastic from starch are lower than conventional plastic. Moreover, the strength, flexibility, and stability are considered as most important characteristic on producing bio plastic. Using filler which may increase those properties is an alternative solution for that problem [1].

Nanocellulocused particle is a new kind of cellulose form which is characterized by an increase in crystallinity, aspect ratio, surface area, and increase in the ability of dispersion and biodegradation. With those new characteristics, nanoselulosa particles can be used in a lot of fields, such as filler to reinforcing polymers, additives for biodegradable products, strengthening the membrane, thickener for dispersion, and media for carrying drug and implant [2]. Bacterial cellulose has several advantages as a source of cellulose compared to wood or non-wood resources, among others, it can be harvested in a shorter time, easily cultivated, and reduce the exploitation of forests to meet the needs of cellulose for
industry. Furthermore, not like other cellulose, bacterial cellulose has no lignin, pectin, and hemicelluloses which are impurities in cellulose which means fewer steps in production. More studies on bacterial cellulose need to be done inorder knowing the use of bacterial cellulose for various areas of application not only limited on food product as we know recently.

Nanomaterial is a very attractive material compare to its macroscopic form due to significantly different characteristic. There is quantum attractive phenomena which appear due to particle size reduction into nano form. With nanotechnology every material can be lighter, more stable and increase in functionality. Nanotechnology offers many advantages and opputunities in the field of product innovation and development of bio plastic.

Nano material can be made by top-down method such as ball milling and ultasonication. Ultrasonic is sound vibration with higher frequency than human, which are approximately more that 20 kHz [3]. Ultrasonication is the most effective technique in mixing, reaction process, and breaking materials that use high energy input [4]. Up level of ultrasonic range for gas is 5 MHz and 500 MHz for liquid and solid material [5]. The wide range used of ultrasonic can be break into two part. First part is sound with low amplitude (high frequency). Usually use for analyzing speed and absorption of wave in the range 2 to 10 MHz. Second is high energy wave that located in 20 to 100 kHz. This wave can be used as cleaner, in the area of plastic composting, and organic or non organic materials modification [5].

High intensity ultrasonication can induce physical and chemical properties of material. One of physical effects of high-intensity ultrasonication is emulsification. This effect can be used in Some applications such as dispersion of filler in the polymer base, emulsification of inorganic particles inpolymer base, as well as the formation and cutting of plastic [6]. Chemical effects of ultrasonication can causes increasing interaction between molecules in materials that lead into changing of chemical properties of materials. The change is caused by ultrasonic wavelength, which is higher than molecules wave length. The wave interaction occurs through a liquid medium. The wave produced by the electric power is transmitted by the liquid media to the intended field through acoustic cavitations phenomena. This phenomenon makes a local pressure in the fluid and rising the temperature [7]. Ultrasonication on liquids has various parameters such as frequency, pressure, temperature, viscosity, and concentration of sample. Ultrasonication affect the degradation of polymer [7].

2. Material and Method
2.1 Materials and Tools
Coconut water, urea, sugar, acetic acid, sodium hydroxide, sodium hypochlorite, sago starch, and glycerin were purchased from a local retailer. Distilled water was produced in own laboratorium.
Tools are hotplate stirrer, beaker glass, beaker, 41 Whatman filter papers, plastic mould, Elmasonic S 300 H ultrasonic batch and Buchi B 290 spray dryer.

2.2 Methodology
This research was conducted in three stages: first is production of bacterial cellulose, second is making of micro-nano from bacterial cellulose that is produced in first stage, and final stage is manufacturing bioplastics. The method of making micro-nano cellulose bacteria is ultrasonication. The layer of bacterial cellulose was dryed then tested tensile. Bacterial cellulose was heated in NaOH 5%, 100°C for 4 h. After that, washed and dryed and then grinding. Cellulose fiber, water content, water absorption in the raw materials are calculated. Next step is ultrasonication of bacterial cellulose at 55°C for 12 h. This process is done in two times. Producing nano bacterial cellulose was started by sieving it in 100 mesh sieve (±149 μm). Furthermore, this 100 mesh bacterial cellulose, is ultrasonicated with 20 kHz-10 MHz frequency. Ultrasonic wave would generate acoustic cavitations when put in liquid medium. In the process ultrasonic wave was beamed into liquid medium to produce cavitations bubble. During the cavitations process, bubble collapse would appear which the break of wave by sound is. This phenomenon made a high energy hotspot. This hotspot is local heat around 5000 K with 1000 ATM pressure and heating rate approximately 1010 K/s which could change the bacterial cellulose into nano form. The final step was producing nano bacterial cellulose into powder. This process was done by drying nano bacterial cellulose with spray dryer. Casting method was used to manufacture the bioplastics. 1% nanoselulosa added into 100 mL of distilled water plus 3 mL of glycerol and 10 g of sago starch and then stirred for 1 h at 80-85°C. After 1 h, the solution then printed in the mould. Analysis of the results was performed tensile test, SEM analysis, FTIR and density.

Scanning Electron Microscope Analysis
Determination of particle size and morphological surface with SEM Analysis. The morphology of micro-nano bacterial cellulose was observed by using a field emission scanning electron microscope (FE-SEM, S-3400N, Hitachi, Japan) at an accelerating voltage of 10 kV. Powdered micro-nano bacterial cellulose were spread onto the copper grids coated with a carbon supported film and a thin Au–Pd conductive coating was then used to reduce the charge effect. Photos is taken with magnification desirable. SEM analyzes were performed on the raw materials and the results of micro-nano bacterial cellulose.
Fourier Transform Infra Red Analysis

FTIR Analysis is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties.

Tensile Testing of Thin Plastic Sheeting (Film) ASTM D882

Tensile tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. Specimens are placed in the grips of the Universal Tester and pulled until failure. For ASTM D882 the test speed and grip separation are based on the elongation to break of the material. Elongation and tensile modulus can be calculated from crosshead displacement, or with an extensometer. Tensile testing is performed on the raw material (bacterial cellulose) and bioplastics.

3. Result and Discussion

3.1 Bacterial Cellulose

Cellulose, which is produced with fermentation, is kind of microbial polysaccharide that formed by cellulose fibres from Acetobacter xylinum. This cellulose is famous as bacterial cellulose (BC). One of the food products made from coconut water are classified as food dessert that can be used as raw material for bioplastics is bacterial cellulose (bioselulosa) because base on the chemically classified cellulose. BC is a very unique material for cellulose is produced lignin free, has high mechanical properties and does not damage the environment (biodegradable) that can replace synthetic polymer that is currently widely used, both in the food industry and non-food. Bacterial cellulose is a polymer that has supramolecular and higher in crystallinity. Physical properties are yellowish white in colour, transparent, and formed in slippery and elastic layers.

Purification processes performed by heating in 5% NaOH. Purification is intended to eliminate the components of non-cellulose and residual bacteria that remain. The components of non-cellulose is expected to block the hydrogen bonding between cellulose molecular chains that lead to a lowering of the mechanical strength properties of cellulose.

Bacterial cellulose has 0.9-1.0% of cellulose fibers. Base on tensile testing analysis of bacterial cellulose has 380.56 Mpa in tensile strength test. The more layers formed the higher tensile strength number. Modulus young approximately 18 Gpa, elongation 11.3 % and density around 1.15 g/cm³. Bacterial cellulose has high porosity, hydrophilic and 700% water absorption.
Bacterial cellulose is raw material in this research can be seen in Figure 1. The high water content in the bacterial cellulose (wet form) to be a problem in the drying process so that the necessary reduced in size, and then dried (dry form). Bacterial cellulose is reduced in size aims to remove the water that is bound in the material so that it will speed up the drying process. Dried bacterial cellulose is milled with a mill grinding to be a powder. The test results SEM the layer of bacterial cellulose can be seen in Figure 2. SEM analysis showed that the morphology of the fiber of bacterial cellulose is still composed and bonded with regularly.

![Figure 1. Bacterial cellulose (BC)](image)

3.2 *Micro-nano Bacterial Cellulose*

Ultrasonication process has been successful in reducing the size of the bacterial cellulose particle to ± 3 μm. The test results SEM the particle of bacterial cellulose can be seen in Figure 3. SEM analysis results indicate that the particle size varies between 2.61 until 4.02 μm. It does not look homogenous. The overall condition of the particles seen from SEM images tend to clump together. Ultrasonication duration of the process may lead to particles that have been split to merge back so particles clump together from the SEM image. Clumps occur due to user does not use surfactants. Sonication treatment resulted in a decrease in the molecular weight of the bacterial cellulose which ultrasonic waves break the chemical bonds of bacterial cellulose. Because the bonds are broken, the size
becomes smaller. The longer the time giving ultrasonic waves to the solution of bacterial cellulose, cellulose chemical chain truncation process also continues to run. Jin Li et al., (2008) claimed the fastest ultrasonic degradation occurs in polymers with the largest molecules. In this study, the degradation process is slow due to the size of the bacterial cellulose molecules are very small \[8\]. Hydrolysis process using hydrochloric acid (HCl) with 3.5 M concentration conditions, 55°C temperature for 6 h. This process has been successful in reducing the size of the bacterial cellulose fibers to ± 7 μm. SEM testing results against bacterial cellulose can be seen in Figure 3b [9].

![Figure 3. SEM analysis results](image)

Preparations micro-nano bacterial cellulose stored in liquid form can be seen in Figure 4(a), dry (b) and in packaged form (c). It can be applied as reinforcement in the manufacture of bioplastics.

![Figure 4. Nano bacterial cellulose form liquid (a), dried (b), in package (c)](image)

### 3.3 Physical Characteristic of Bioplastics

The physical characteristics of bio plastics which produced by adding 1% of nano bacterial cellulose are tensile strength of 11.85 MPa, Young modulus of 3.13 MPa, elongation of 4.11% and density 0.42 g/cm³. The characteristic of tensile strength is lower than bioplastics from breadfruit starch-chitosan-sorbitol with a value of 16.34 MPa [10]. There is a possibility to increase the tensile strength by increasing the percentage of nanobacterial cellulose. Nevertheless, the elasticity is higher when compared to the starch bioplastics breadfruit-chitosan-sorbitol with a value of 2.72 MPa [10].
According to Bourtoom (2008) [11], to increase the elasticity of the bioplastic can be done by the addition of plasticizers. The tensile strength value fulfilled the standard for tensile strength values which is 10-100 MPa, but lower when compare to the polypropylene (conventional plastics) 24.7 MPa [12]. Test FTIR as an analysis conducted to determine the functional groups on the polymer. FTIR spectra generated from testing bioplastics are presented in Figure 5. Based on the image seen on the identification of functional groups in bioplastic films formed on IR absorption spectrum is a combination of the specific functional group contained in each of the constituent components of bioplastics. So it can be seen clearly that the bioplastics obtained a bioplastic produced through a process of mixing (blending), it can be seen because no new functional groups. In addition, it can be concluded also that the plastic is formed while still having hydrophilic properties such as its constituent components. The existence of functional groups such as CH (frequency 2900-3010 cm\(^{-1}\)), C-NO\(_2\) (frequency 1300-1500 cm\(^{-1}\)), -N = N (frequency from 1575 to 1650 cm\(^{-1}\)) and - (CH\(_2\))\(_n\) (frequency 750 cm\(^{-1}\)), shows the plastic film can be degraded by either ground. Because nanotechnology is still relatively expensive, the recommendations are using bioplastics for intelligent/smart packaging.

![Figure 5. FTIR results](image)

4. Conclusion
The particle size of micro-nano bacterial cellulose which was produced is ± 3 μm. The physical characteristics of bioplastics by adding 1% of micro-nano microbial cellulose which are tensile strength of 11.85 MPa, Young modulus of 3.13 MPa, elongation of 4.11% and density of 0.42 g / cm\(^3\).

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