Properties of polyvinyl alcohol composite filled Ampel bamboo (Bambusa vulgaris) microfibrils fibrillated by mechanical treatment

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Abstract. Composite for food packaging is mostly made from petroleum-based synthetic polymers that require a long period to be degraded naturally. This condition encourages the study of the use of cellulose microfibrils or organic materials as fillers and reinforcement for food packaging composites to reduce the dominance of synthetic polymers. The purpose of this study was to determine the characteristics of polyvinyl alcohol composites with fibrillated cellulose microfibrils from Ampel bamboo pulp (Bambusa vulgaris), both bleached and un-bleached. Pulp from Ampel bamboo produced by the soda process was fibrillated using a disc refiner in 10, 20, and 30 times repetition variations. Microfibril concentration of 0.1 wt% dry based on the weight of the polyvinyl alcohol (PVA) matrix. Composite preparation was carried out by dissolving polyvinyl alcohol using a hot plate stirrer at 80 °C, 300 rpm for 30 minutes. The composite solution is poured in a mold measuring 20 x 16 x 0.1 cm. Morphology characteristics from microfibrils were evaluated by scanning electron microscopy (SEM). The mechanical characteristics tested with UTM Shimadzu 1 kN in accordance to ASTM D 882-75b standard. PVA composites filled with cellulose microfibrils from bleached Ampel bamboo pulp have better mechanical characteristics than composites with unbleached pulp. Mechanical treatment in various replications in the disc refiner machine can increase tensile strength, tensile modulus, and composite elongation.

1. Introduction

Packaging technology is developing rapidly in line with the development of science and human civilization. The industrial revolution has changed the order of human life toward modern life, followed by changes in packaging technology. This technology includes aspects of food protection such as nutritional quality, taste, contamination and causes of food damage. It also related to marketing aspects such as maintaining quality, improving appearance, product identification, composition information, and promotion. Among these packaging materials, plastic is the most popular packaging material and widely used. This packaging material has various advantages i.e. flexible, transparent, strong, and can be combined with other packaging materials. It also less corrosive and the price is affordable.
This condition encourages many studies on the possibility of using natural fibers as filler in place of synthetic fibers to reduce the dominance of synthetic polymers. The use of lightweight, renewable natural materials instead of heavy metal or mineral-based materials is important to generate lighter materials. The natural material has been used as a filler or reinforces materials in thermoplastic composites. However, the main disadvantage in natural fibers-synthetic polymer composites is the poor compatibility between the hydrophobic properties from the polymer matrix and the hydrophilic properties of natural fibers [1].

The level of plastic product consumption in Indonesia is around 10 kg/capita/year. The needs of national plastic products reach 4.6 million tons per year with an average growth of 5% per year where the biggest portion (40%) is for packaging plastics. Consumption of plastic packaging in Indonesia in 2011 was around 1.8 million tons. In 2017, it was estimated to reach 1.8 million tons, up from 2016 of 1.6 million tons. While domestic production estimated at 2.3 million tons or down from last year's 2.4 million tons [2]. On the other hand, plastic packaging also has weaknesses such as not heat resistant and has a potency to contaminate the product so that it risks the safety and health of consumers. Plastics are included in non-biodegradable materials. In addition, the basic ingredients cannot be since it made of petroleum-based materials.

The development of environmentally friendly packaging materials technology that can be naturally degraded is directed by making biodegradable polymer-based packaging with similar properties to commercial plastics and also fill for another requirement especially for maintain food durability and harmless to the environment. Among the type of polymers, polyvinyl alcohol (PVA) is known as a synthetic polymer that is easy to degrade and suitable to be mixed with natural polymers such as cellulose, starch and chitosan. On the other words, PVA has promising potential for applications in various industrial fields such as biomedicine and packaging because it is supported by biodegradable, biocompatible properties, chemical resistance and other good properties [3, 4]. PVA is a water-soluble polymer with a dominant hydroxyl group [5]. PVA polymers have been widely used as active oxygen barrier packaging materials that are good, mechanical properties, chemical resistance, good film-forming ability, water solubility, and others. This good water solubility causes this type of film to be susceptible to moisture, thus, for packaging purpose of foods which require low humidity other components need to be added [6].

Several studies have been carried out to improve the properties of plastic packaging composites, for example adding natural microfibrils fiber as fillers or reinforcement. Research on PVA composites with reinforced cellulose fibrils matrix obtained from sulfite pulp, and mechanically fibrillated using ultraturrax or chemically using 10% sulfuric acid for 16 hours at 60 °C has been carried out by Zimmermann et al. in 2004, Sedlarik et al. [7] produced PVA composites with high stiffness properties by utilizing fibers from kraft pulp, rutabaga, flax and hemp which were processed by ultrasonicators. Composite research based on natural fiber-pulp PVA was also carried out by Syamani et al. [8] and Kusumaningrum et al. [9]. There are also composite PVA-microfibrils of palm frond pulp filled with chitosan [10].

In this study, PVA polymers function as composite matrices and treated Ampel bamboo pulp microfibrils as fillers. Mechanical treatment, including refining process in some circulation is expected to defibrillated the fibers in radial direction which could enhance aspect ratio and further affect on mechanical properties improvement of composites. The purpose of this study was to determine the characteristics of the composite from PVA mixed microfibrils of Ampel bamboo pulp was bleached and unbleached after fibrillation process by a disc refiner of 10, 20, and 30 times repetitions.

2. Materials and Methods
The materials used in this research are technical grade of polyvinyl alcohol (PVA) polymer as matrix and Ampel bamboo pulp as fillers. Sodium hydroxide for pulping process was in technical grade, while hydrogen peroxide and acetic acid for bleaching process were in pure analysis grade which purchased from MERCK, Indonesia. All chemicals were used as received without purification.
Ampel bamboo chips were alkali treated with 2.5% of Sodium hydroxide at 170 °C for 2 hours using digester to produce unbleached pulp. As much as 10 g of unbleached pulp were added 40 mL of hydrogen peroxide than processed at 100 °C for 3 hours to produce bleached pulp. Subsequently, were added by 100 mL of acetic acid than washed until neutral.

Ampel bamboo pulp that has been bleached and unbleached was fibrillated by a disc refiner in three repetitions, i.e. 10, 20 and 30 times. PVA polymer dissolved in 100 ml of distilled water at temperature 80 °C using a hot plate stirrer for 30 minutes. The microfibril concentration was 0.1 wt% dry based on the weight of the PVA matrix. The composites based on the PVA polymer matrix were prepared by the wet method which was started by mixing PVA solution and microfibril of Ampel bamboo pulp in an erlenmeyer. The process of mixing composite material was carried out on a hot plate stirrer at a temperature of 80 °C, 300 rpm for 30 minutes until evenly mixed. After all the ingredients are thoroughly mixed, it is continued to be made as composite sheets by casting molding method. The mix solution of the composite materials poured into mold with size 20 x 16 cm. The solution in the mold left to stand for 24 hours at room temperature to remove gases due to stirring. Then, the PVA composite was dried in an oven at 40 °C for 24 hours. The target density of composite is 1 g/cm³.

Morphological characteristics of microfibrils were observed by scanning electron microscopy (SEM). Mechanical characteristics of composite was tested with Universal Testing Machine (UTM) Shimadzu LoadCell 1 kN according to ASTM D 882-75b standard for the Standard Method of Tensile Properties of Thin Plastic Sheeting test [11] with a tensile speed of 50 mm/min.

3. Results and Discussion

3.1. Morphology characteristics

According to Fakhrzzy et al. [12] reported that the chemical composition of Ampel bamboo particles is 44.0% of cellulose, 30.5% of hemicellulose and 22.3% of lignin. In this research, the chemical composition from unbleached Ampel bamboo pulp after alkali process is composed by cellulose in 65.2%, hemicellulose in 21.7% and lignin in 9.8%, while bleached pulp is composed by cellulose in 85.6%, hemicellulose in 13.1% and lignin in 0.2%. Ampel bamboo pulp is mechanically fibrillated using a disc refiner to reduce fiber bundles. The fibrillation process with a disc refiner was carried out in 10, 20 and 30 replications. Figure 1 shows the Ampel bamboo pulp that has been bleached and unbleached after going through the fibrillation process 10, 20 and 30 replications with a disc refiner. The microfibrils have better performance and morphology becomes a colloid form in line with the increase of fibrillation repetition process. The size of the fibers after the fibrillation process is smaller (5.1 µm-500 nm) due to the increase of repetition in the refining process as a mechanical treatment by disc refiner. According to Spence et al. [13] refining process is a treatment mechanically which can be used after a chemical process, to reduce consumption energy during the formation of fiber size by homogenization.

Figure 1. Samples of Ampel bamboo pulp bleached (A, B and C) and Ampel bamboo pulp unbleached (D, E and F)
Figure 2. SEM images of unbleached Ampel bamboo pulp without fibrillation (A), fibrillation with disc refiner in 10 repetitions (B), 20 repetitions (C), and 30 repetitions (D)

Figure 2 and Figure 3 show the changes of Ampel bamboo microfibrils after the process by disc refiner that image with scanning electron microscopy (SEM) for unbleached and bleached respectively. In the SEM image, there is a morphological change in the unbleached after undergoing the fibrillation process with a disc refiner where more repetitions of fibrillation make the fiber bundle more defibrillated as shown in Figure 2 (B,C,D). The fibrillation of the pulp fibers can be seen from the smaller diameter of the fibers due to the increase of fibrillation repetition by disc refiner.

The fibrillation process using a disc refiner presses the slurry pulp to pass through the gap between the rotor and stator disk. The surface of the disk is above bars and grooves so that the slurry pulp will experience repetitive pressure. These mechanical treatments cause changes in the morphology of the pulp and multiply reactive groups due to changes in the surface area [14]. According to Syamani et al. [8], the refining process with a disc refiner needs to be done before further fibrillation process. This because the refining process causes fibrillation or fiber bundle decomposition on the outer surface of the pulp fiber by stripping the external layer of cell wall gradually (layers P and S1) and causing the S2 layer to be exposed.
3.2. Mechanical characteristics

The tensile modulus (TM) parameter describes the stiffness properties of the composite. The magnitude of TM value from PVA composite with Ampel bamboo microfibrils presented in Figure 4. In general, TM values of PVA composite with microfibril of Ampel bamboo unbleached pulp are higher in the range of 0.15-0.19 GPa compared to composites with unbleached pulp (0.11-0.16 GPa) and pure PVA (0.07 GPa).

Mechanical treatment by disc refiner able to improve TM value that more repetition of the fibrillation process increased TM value from composite. The stiffness properties of composites higher due to exposed secondary wall of fibers improve surface roughness that could facilitate PVA molecules penetration to the fibers surface. Exposed fiber surface in line with refining repetition. As reported by Syamani et al. [8] where the refining process for Acacia pulp was able to increase the tensile modulus of PVA- Acacia pulp composite. The combination of the fibrillation process by disc refiner and ultrasonication has proven to increase the tensile modulus value of composite from PVA with oil palm empty fruit bunches [15].

Figure 3. SEM images of bleached Ampel bamboo pulp without fibrillation (D), fibrillation with disc refiner in 10 times (E), 20 times (F), and 30 times (G) repetition.
The tensile strength (TS) value of composite shows in Figure 5. The TS value of the PVA composite with microfibril bleached pulp higher than with unbleached pulp were ranged from 11.63-14.28 MPa. These result might be caused by lignin cover the cell wall which inhibit fibrillation, which suggest for higher refining repetition for unbleached pulp. In general, increasing the repetition of the pulp fibrillation process by disc refiner increased the TS value of PVA composite. The TS value of PVA composite made of pulp with 30 repetitions of fibrillation was higher compare to composites from PVA with microfibrils that fibrillated 10 and 20 repetitions and pure PVA. The increasing of TS value from composite prove that there is an internal interaction between the microfibrils and the PVA matrix. It can be said that the presence of Ampel bamboo microfibrils in PVA composite proven to functions as composite reinforcement material and not as a filler. However, it should be noted that the optimum limit of the addition of fillers and reinforcement to polymer matrix based on composites with microfibrils from natural fibers so that later it does not reduce the tensile strength of the composites. Slightly different of TS between pure PVA and PVA reinforced with treated Ampel bamboo pulp could be aglomeration among fibers which interfere interaction between PVA molecules and fibers.

Figure 4. Tensile modulus value of composite

![Tensile modulus graph](image1)

Figure 5. The tensile strength value of composite

![Tensile strength graph](image2)

The enhancement of tensile strength also influenced by fiber defibrillation which improved hydrogen bonding between fibers and polymer matrix. A more open from fiber surface will increase
The strength of the composite. Different results reported that fibers which are not bleached with integrated treatment had reduced tensile strength values. This is caused by the degradation of the fiber length which decreases the aspect ratio value. The fiber aspect ratio affects the mechanical properties of cellulose derivatives and microcrystalline cellulose due to decreased bonding ability [16].

![Figure 6. Elongation value from composite](image)

The bleaching process of Ampel bamboo pulp has a significant influence on the elongation value of the PVA-microfibril of the Ampel bamboo pulp composite was shown in Figure 6. There is an increase in elongation value of about 10-15 times in PVA composites with bleached pulp compared to PVA-microfibril unbleached pulp composites. The number of fibrillation repetitions can also increase the value of composite elongation. The range elongation value of composite from PVA-microfibrils of Ampel bamboo unbleached pulp was 17.86-20.75% and 248.16-286.04% for PVA composite with Ampel bamboo bleached pulp which is still below the elongation value from pure PVA (351.12%).

The increase from mechanical treatment influence the occurrence of fiber fibrillation, shorten the length of the fiber and break down hydrogen bonds in the cellulose structure [17] so that the amorphous part of the cellulose reduced and leaves a rigid crystalline part. This is in line with the increase of fibrillation repetition in this study which results are quite influential in increasing the stiffness and elongation of PVA-based composites. The bleaching process on Ampel bamboo pulp microfibrils also able to shed parts of microfibrils which can interfere compatibility with the polymer matrix. Eventually, it can increase the ductility of the composite which can be seen from the tensile strength and elongation values.

4. Conclusion
The bleaching process on Ampel bamboo pulp able to reduce the amorphous parts and components of fiber which can interfere with the compatibility of microfibrils with the PVA matrix polymer into a composite. Repetition in the process of Ampel bamboo pulp fibrillation by disc refiner proven to break down the fiber bundle from the pulp into a single fiber that more compact to bind with PVA matrix into a composite. The increase of fibrillation repetitions able to enhance mechanical properties especially for bleached pulp rather than unbleached pulp. The composite was manufactured from PVA-bleached pulp with 30 times of repetitions have higher value in tensile modulus in 0.2 GPa, tensile strength in 15 Mpa, and elongation 280% than other compositions. Mechanical treatment by disc refiner proven to improve the composite properties based on PVA polymer.
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