Synthesis of Cassava Bagasse Starch-Based Biocomposite Reinforced Woven Bamboo Fibre with Lime Juice as Crosslinker and Epoxidized Waste Cooking Oil (EWCO) as Bioplasticizer

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Abstract. An alternative available huge source of biocomposite matrix can be found in cassava bagasse regard with high amount of starch content and low protein. It can be reinforced by bamboo fiber. The objectives of this paper are to observe the optimum condition of woven bamboo fibre pattern confirmed by mechanical assessment. The research was conducted by bamboo fiber treatment, epoxidized waste cooking oil and cassava bagasse starch preparation as plasticizer and crosslinker respectively, and biocomposite preparation by different woven pattern, i.e. plain, twill, and random. The results showed that optimum condition of biocomposite could be achieved at plain woven bamboo fibre, 0.25 %v/v of lime juice, and 0.75 %v/v of EWCO with tensile strength of 38.49 MPa. It was considered that random pattern had lowest mechanical property. The effect of lime juice denoted increase tensile strength significantly at beginning. However, plasticizer resulted maximum tensile strength at 0.75 %v/v.

1. Introduction
Cassava starch industry releases by-product i.e cassava bagasse. It consists of a huge of residual starch [1]. Due to low ash and protein content, there is no allocation for ruminant source [2]. Reducing cassava waste production have transformed the bagasse into promising bioplastic source by using thermoplastic behaviour of residual starch. For example, raw material of biocomposite consisted of cassava peel and bagasse [3], thermoplastic starch from cassava bagasse and cassava starch and their blends with poly(lactic acid) [4], and cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch [5].

Thermoplasticized starch can be carried out by plasticizer addition. The additional of plasticizer can increase flexibility while decrease glass transition temperature (Tg) [6]. Currently, it has been promoted epoxidized palm kernel oil [7], Jatropha curcas oil [8], soybean oil [9] and epoxidized waste cooking oil (EWCO) [10]. EWCO can increase tensile strength and thermostability of sago starch-based composite reinforced by microfibrillated cellulose of bamboo [10]. Furthermore, disadvantages of starch-based biocomposites are low in tensile strength and water resistance. However, tensile strength of starch-based biocomposites can be increased by such additional protein [6]. An abundant amount of gelatin, i.e. 33% can be found in chicken feet [11]. Chicken feet were chosen as additional material as result of relatively inexpensive and easy to be isolated. As well as the addition of plasticizers and gelatin, the matrix can also be reinforced with the presence of citric acid as a crosslinker. Lime juice can be used as a crosslinker.
on the sago starch-based biocomposites preparation to improve its mechanical strength and water stability [12].

Bamboo fibers can be made from parts of the leaves and stems by chemical and mechanical processes [13]. Bamboo fiber is one of natural fibers widely used as a reinforcing agent in the preparation of biocomposite in accordance with its high fiber strength with excellent sophisticated properties, ecological benefits, the fastest growing grass plant in the world [14-15]. No more studies investigated woven fiber reinforced (bio)composites using fibers embedded in biodegradable matrices considering increase load carrying capacity of long fiber to prepare (bio)composite. Previously, Porras and Maranon [16] have observed compatibility of poly lactic acid matric reinforced woven bamboo fabric with increasing of tensile strength up to 77.58 MPa. Banana/kenaf fiber-reinforced hybrid polyester composites released improvement of tensile strength with plain woven type [17].

Therefore, in this paper the woven bamboo fiber reinforced cassava bagasse starch-based biocomposite crosslinked by lime juice, gelatin from chicken feet, and EWCO as plasticizer is observed. The purpose of this research is to study the effects of the woven bamboo fibre pattern on the performance of the cassava bagasse starch-based biocomposite and to investigate the effect of the addition of lime and EWCO in the biocomposite.

2. Research Methodology

2.1. Materials

The biocomposite was prepared in laboratory scale. Petung bamboo (Dendrocalamus asper) was obtained from Sragen. N-hexane ($\rho = 0.67$-$0.68$ gr/mL), $\text{H}_2\text{O}_2$ (50%), and alcohol (96%) of PT. Bratachem, HCl 37% from Mallinckrodt, NaOH (99%), 98% of $\text{H}_2\text{SO}_4$, $\text{H}_3\text{PO}_4$, and 100% of acetic acid from Merck were used. The cassava bagasses were obtained from tapioca industry in Pati. Waste cooking oil, lime, and chicken feet were obtained from traditional markets in Semarang.

2.2. Methods

2.2.1. Bamboo Pretreatment. Bamboo was cut into 30 cm x 3 cm then soaked in NaOH 1 M for 3 hours [18]. The obtained bamboo fiber was then washed with water to remove the NaOH content. Dewaxing was then performed by extraction using a mixture of n-hexane: alcohol (2:1) with a base volume of 300 mL in soxhlet for 6 hours for ± 20 g of bamboo fiber. The bamboo fiber was then delignified to remove the lignin content with NaOH 2 M solution at 78 ºC for 4 hours with two repetitions for ± 20 grams of bamboo fiber with a 1000 mL basis [19]. The delignified product was then washed using aquadest to achieve a neutral pH. It was then bleached using 4% of $\text{H}_2\text{O}_2$ solution at 80 ºC for 3 hours with 2 repetitions for ± 20 g of bamboo fiber on a 500 mL basis [19]. The bleaching result was next washed using aquadest to neutralize the pH. The neutralised product was then dried in the sun. Dry bamboo fibers were then woven with plain, twill, and random patterns [17].

2.2.2. Bagasse/Tapioca Starch Preparation. The process of making bagasse or tapioca starch conducted in this study refers to previous research [11]. The cassava starch was sorted and washed thoroughly. It was then added with water the squeezed and filtered using a filter cloth. The supernatant was collected and left to precipitate. The water at the top phase was discarded, while the precipitate was taken. Obtained starch was dried in the sun until the water content evaporated. After drying, the starch was then reduced in size by high energy milling ellips 3D until a mesh size of 100 mesh (149 $\mu$m).

2.2.3. Gelatine Preparation. The preparation of gelatin conducted in this study referred to the previous method [11]. Chicken feet were skinned, dried in the sun and was reduced in size using a crusher. The chicken feet were soaked in water at temperature 35 ºC and were constantly stirred to remove fat as it later was washed with running water. The product was then demineralized by soaking it in 3% HCl solution for 24 hours at 10 ºC and then washed with running water to remove acid excess and obtain pH
above 4. Subsequently, the chicken feet product was soaked in NaOH solution (4 g/100 mL) for 72 hours at room temperature. The product was washed under running water to remove excess base. Furthermore, the extraction process was done by soaking the chicken feet in aquadest with pH 4 (prepared by using H3PO4) and was kept constantly stirred. After the extraction process, the product was centrifuged for 30 minutes then filtered using Whatman paper. The filtrate was concentrated using rotary evaporator and freeze dried to form into powder.

2.2.4. *Epoxidized Waste Cooking Oil Preparation*. EWCO preparation method used in this study refers to the previous method [10]. As much as 150 mL used cooking oil was mixed with acetic acid 100% of 8.8 mL and sulfuric acid 98% of 0.34 mL in a three-neck flask at 50 °C while stirred for 30 min with stirring speed of 30 rpm. Hydrogen peroxide 50% was added as much as 37.7 mL slowly for 30 minutes and allowed to stand for 4.5 hours at 50 °C to produce an epoxidized waste cooking oil. The resulting exposed epoxidized waste cooking oil was extracted with diethyl ether until it formed two distinct layers to obtain pure epoxidized waste cooking oil. The product was then washed with 70 °C hot water to dissolve free fatty acids.

2.2.5. *Biocomposite Production*. The preparation of the matrix solution referred to the existing method [12]. As much as 4% w/v starch with 40 mL basis or 1.6 gram of starch were dissolved in aquadest. It was then added with gelatin as much as 20% w/w or 0.32 gram and epoxidized waste cooking oil (EWCO) according to variables 0.5 %v/v, 0.75 %v/v, and 1 %v/v. The mixture was homogenized with ultrasonic homogenizer for 4 x 15 minutes. The result of this process was a stable suspension/paste. The solution was heated to a gelatinization temperature of 90 °C with constant stirring of 6 rpm. The temperature was then decreased to 60 °C and lime juice was added according to the predetermined variables of 0.25 %v/v, 0.375 %v/v, and 0.5 %v/v. The mixture was again stirred with constant stirring of 6 rpm for 15 minutes. Afterwards, the solution was poured onto acrylic casting. This casting was then allowed to be dry at room temperature for 3 days.

2.3. *Characteristic Analysis*

2.3.1. *Mechanical Analysis*. The Tensile Strength test was performed using CT3 Texture Analyzer (AMATEK Brookfield, USA) at Diponegoro University Integrated Laboratory. The Tensile Strength (TS) test was as follows: the film sample to be tested was cut to size (5 x 0.5 cm), then attached vertically to the hook in the Texture Analyzer tool with normal stretching. After the film was mounted on each of the hooks, the tensile strength test was performed. The test was performed three times.

3. *Results and Discussion*

3.1. *Effects of Woven Patterns on Tensile Strength*

At times the interfacial bonds of different materials, i.e. matrix and filler, create new problems such as adhesion or inter-molecular attractiveness and poor water uptake [20]. Therefore, this study observed mechanical property effect of bamboo fiber woven pattern which plasticized by EWCO (Epoxidized waste cooking oil) and crosslinked by lime juice.
Table 1. Woven bamboo fiber pattern with tensile strength at varying compositions.

| No | Composition (%v/v) | No Woven | Plain | Twill | Random |
|----|-------------------|----------|-------|-------|--------|
| 1  | 0.25 0.5          | 7.3 ± 5.3 | 7.4 ± 1.2 | 3.9 ± 0.7 | 3.5 ± 0.9 |
| 2  | 0.25 0.75         | 3.3 ± 1.4 | 38.5 ± 35.3 | 20.8 ± 10.7 | 3.8 ± 1.4 |
| 3  | 0.25 1            | 13.6 ± 7.1 | 9.0 ± 26 | 3.0 ± 1.5 | 4.6 ± 2.1 |
| 4  | 0.375 0.5         | 19.8 ± 3  | 18.1 ± 1.2 | 19.6 ± 1.8 | 3.6 ± 1.0 |
| 5  | 0.375 0.75        | 21.6 ± 4.8 | 26.5 ± 0.5 | 10.5 ± 8.6 | 3.1 ± 1.2 |
| 6  | 0.375 1           | 11.1 ± 3.8 | 21.6 ± 4.8 | 15.4 ± 0.3 | 9.7 ± 3.5 |
| 7  | 0.5 0.5           | 11.7 ± 3.7 | 8.0 ± 2  | 11.4 ± 15.7 | 8.1 ± 2.4 |
| 8  | 0.5 0.75          | 28.5 ± 2.7 | 15.4 ± 5.5 | 24.5 ± 10.8 | 8.1 ± 2.1 |
| 9  | 0.5 1             | 11.8 ± 7  | 16.7 ± 6.9 | 8.1 ± 5.3 | 2.5 ± 1.7 |

Based on Table 1, it can be seen that the film with plain woven pattern tend to have higher tensile strength than that of with twill and random woven patterns at increase of cross linker and plasticizer concentration. The plain-woven type has better uniform distribution of pressure in both longitudinal and transverse directions [17]. Higher tensile strength is obtained when the fiber has a longitudinal orientation so that the load pulls in the direction of its orientation. Generally in plain woven type, the fibers are connected to one another, causing the fibers not to easily shift in addition to having a large number of crosslinkings making it more robust [17]. Additional of crosslinker can be resulted increasing tensile strength up to 0.375 %v/v, while more crosslinker can give insignificant increase of tensile strength. It might be resulted no more bonding between OH group from cassava starch with crosslinker. The lowest tensile strength of random pattern can be caused by any void in biocomposite resulting decrease tensile strength, while at void given lowest strength to accept the load during mechanical assessment [21]. When the biocomposite receives the pull load, the area of tension will move to the areas that are void so that the stress concentration occurs in that particular area. Furthermore, the matrix of the biocomposite can not be well distributed on random fibers resulting in a biocomposite that is easily broken with low tensile strength [21].

3.2. Effects of Epoxidized Waste Cooking Oil on Tensile Strength

This effects analysis was performed on biocomposites with the same composition of lime juice and woven fiber patterns on various EWCO compositions. The results of the analysis can be seen in figure 1 below.
Figure 1. Tensile strength of biocomposite at various EWCO (%v/v) and lime juice (%v/v) compositions.

Based on the results of the above analysis, the composition of biocomposites with 0.25% v/v lime juice has the greatest tensile strength of 19.84 MPa with addition of 1 %v/v EWCO, while the biocomposite with 0.375% v/v lime juice has the highest tensile strength obtained of 21.62 MPa with the addition 0.75 %v/v EWCO. In the composition of 0.5 %v/v lime juice, the highest tensile strength comes with the addition of EWCO 0.75 %v/v with value of 28.52 MPa. From these results it can be seen that the magnitude of tensile strength tend to increase with the addition of EWCO. It was obtained in previous research that EWCO can diffuse into the matrix of cassava starch and interact with matrix molecules through covalent bonds, hydrogen bonds, and van der Waals [22]. Hydrogen bonds between the molecules causes the starch chains to congregate together in groups and intertwined to form a larger fiber [23] as well as forming a very neat network of fibres [24]. This then causes distribution of external pressure or load transfer that causes the biocomposite film to become more stable and robust [23; 24; and 25]. Furthermore, due to opening reaction of EWCO by -COOH group of citric acid (from lime juice) (26) the plausible crosslinked structure within EWCO plasticized matrix form by bagasse starch. This reaction was adopted from previous research (27). The fully reaction can be seen in Figure 2.
Figure 2. The opening ring of EWCO by citric acid from lime juice crosslinking within bagasse starch matrix

From the results of the tensile strength analysis, on average the optimum result can be obtained in biocomposite containing 0.75 %v/v of EWCO. If compared to using glycerol as a plasticizer, EWCO has a higher tensile strength. Furthermore, when EWCO is added further, the tensile strength test results show a decrease. It is resulted from the great interaction between EWCO and starch molecules that allow damage to the matrix molecule and reduce the density of the matrix molecule [Belhassen 2014]. Thus, the increased bond between molecular matrices and EWCO actually further reduces the amount of tensile strength obtained [22].

3.3. Effects of Lime Juice on Tensile Strength
Crosslinking is commonly used to improve starch performance in various applications. The starch may be crosslinked with crosslinking agents such as phosphorus oxychloride, 1,2,3,4-diepoxyc-butane, and others to improve its mechanical characteristics [27]. Lime Juice contains citric acid that can be used as crosslinking agent. Citric acid was chosen as a crosslinker because it is water soluble and is an organic acid [28]. This analysis was performed on biocomposites with the same EWCO compositions and woven fiber patterns for various compositions of lime juice. The results of the analysis can be seen in figure 2 below.
Based on the analysis result in figure 3 above, it can be seen that tensile strength tends to increase in the composition of 0.375 %v/v lime juice reaching 21.62 MPa. With the addition of lime juice the tensile strength increases. However at some point when the concentration gets too high the tensile strength decreases. Lime Juice contains citric acid which can be used as a crosslinker in the manufacture of biocomposites to increase its mechanical strength and water stability [10]. According to Awadhiya [28], citric acid as a crosslinker serves to bind molecules chemically. Crosslinking occurs in hydroxyl groups and starch contains a large amount of hydroxyl groups making crosslinking effortless [27].

The tensile strength analysis conducted was obtained optimum result in the addition of 0.375 %v/v lime juice with value of 18.06 MPa. When lime juice is added further, the tensile strength test results show a decrease. Citric acid has the ability to form crosslinking with starch molecules by forming hydrogen bonds. Crosslinking combines the starch molecules so that the molecular weight of the starch increases and provides better bonding between the molecules, thereby increasing the tensile strength. At low concentrations, citric acid is not strong enough to form crosslinking with molecules so that the resulting tensile strength is low. Conversely, if the concentration citric acid is too high it will cause excessive crosslinking and limit the mobility of starch molecules that cause the resulting tensile strength to be low [27].

4. Conclusion
The optimum biocomposite performance was obtained in biocomposite composed of 0.75% v/v EWCO; 0.25%v/v lime juice and bamboo fiber with plain woven pattern with tensile strength of 38.49 MPa. The addition of EWCO that can diffuse into the matrix of bagasse/tapioca starch and interact with the matrix molecules through various bonds that cause the biocomposite to become stronger. The optimum EWCO composition used was 0.75% v/v. Lime Juice contains citric acid which can be used as a crosslinker in the manufacture of biocomposites to increase its mechanical strength and water stability. The optimum lime juice addition composition is 0.375% v/v.
For further research, it is necessary to examine the type of woven pattern, plasticizer, and crosslinker that greatly match the biocomposite so as to increase the maximum biocomposite performance by taking advantage of underutilized materials. Matrix that can fully distribute over fibers in the drying process needs to also be further investigated.

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