The effect solvent type on natural fiber immersion process on tensile strength of cellulose-based bioplastic

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Abstract. Environmental pollution caused by the use of conventional plastics is increasing. This is due to the high use of conventional plastics and the difficulty of being degraded in nature. Several studies continue to be developed to make plastics that are easily degraded in nature, namely bioplastics. Bioplastic is a type of plastic made from renewable materials and can be decomposed in nature with the help of microorganisms. The manufacture of bioplastics is done by dissolving raw materials such as rice straw, sugarcane bagasse, cocoa husks, and tea waste into various solvents, namely trifluoroacetic acid (TFA), N, N-dimethylformamide (DMF), trifluoroacetic acid anhydride (TFAn), and citric acid. The resulting bioplastics were analyzed for tensile strength and elongation at break. The results showed that the use of rice straw as a raw material in the manufacture of bioplastics showed good results where the composition of the high cellulose content of rice straw was 61.8% and the tensile strength that had met SNI was 43 MPa using trifluoroacetic acid (TFA) as a solvent. However, a good elongation at break was produced by cocoa husks with a value of 28% using trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAn) as solvents.

1. Introduction
Plastics produced from petrochemicals have been widely used in everyday life. However, this type of plastic has a negative impact on the environment because it is difficult to decompose and is toxic [1]. With increasing concern about the environmental damage caused by non-biodegradable materials, the development of biodegradable materials can be applied to overcome this obstacle [2]. One of them is a bioplastic which has attracted a lot of attention as a potential product as a substitute for conventional plastic products [3].

Bioplastic is the latest generation of plastic which is almost entirely made of renewable materials and can be decomposed by microorganisms to reduce the negative impact on the environment and energy consumption [4,5]. Bioplastics are generally made from renewable materials such as polysaccharides (cellulose, starch, pectin, chitin), proteins (gluten, casein, gelatin), lipids (animal and vegetable oils), or from certain substances produced by some micro-organisms (microalgae) [6]. Generally, bioplastics made from cellulose are due to the abundance of cellulose which is renewable and suitable to be used to replace synthetic polymers in the production of plastics [7].

Cellulose is one of the most abundant polymers in nature, and is found as a structural component in the cell walls of plants and algae, and is available in several forms of biomass. Cellulose is a nontoxic, biodegradable, solid homobiopolymer, white in its pure state, with a molecular mass of around 1.44 x 10^6 to 1.8 x 10^6 g. It has high tensile strength and Young's modulus, high crystallinity (89%), a high degree of polymerization, and high specific surface area [8,9].
Cellulose is the main ingredient used in the manufacture of bioplastics because cellulose can be found in agricultural, food, and other wastes. The composition of cellulose content in rice straw is 61.8% [10], sugarcane bagasse is 40% [11], cocoa husk is 40% [12], and tea waste is 17.5% [13]. The potential cellulose content contained in these various wastes can be used for the manufacture of bioplastics. So that it can be a solution in overcoming environmental problems caused by the waste and can increase the use value. The purpose of this study was to analyze the type of solvent used in the process of making cellulose-based bioplastics. The types of solvents analyzed were trifluoroacetic acid (TFA), N, N-dimethylformamide (DMF), trifluoroacetic acid anhydride (TFAn), and citric acid.

2. Methods

Bioplastics are produced directly from several wastes using a variety of different solvents. The rice straw is dissolved in trifluoroacetic acid (TFA). It was maintained under magnetic stirring (about 800 rpm) at room temperature and then poured into a crystal container for printing. After that, the container is maintained under a laminar hood and closed [5]. The sugarcane bagasse phthalate is dissolved in N, N-dimethylformamide (DMF) and then molded into a polytetrafluoroethene mold and dried a cabinet oven with air circulation at 50 °C for 12 h [14]. Cocoa husk are mixed into a solvent mixture consisting of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAn) and poured into molds made of non-adhesive plastic materials, or molds made of glass or ceramic materials, in order to obtain bioplastic films and sheets [15]. The tea waste is made by mixing it into citric acid. The sample was stirred magnetically in an oil bath at 60 °C for 12 hours, then poured into a polystyrene petri dish 100 x 15 mm. Then, the bioplastic is dried at room temperature or in an oven (70 °C) for 3 hours [16]. Furthermore, the tensile strength and elongation at break were analyzed by tensile testing machine.

3. Result and Discussion

3.1. Tensile Strength

Mechanical properties such as tensile strength and elongation at break are important parameters in packaged products. Generally, biodegradable packaging has poor mechanical properties, so efforts need to be made to improve these mechanical properties. Some materials such as rice straw [5], sugarcane bagasse [14], cocoa husk [15], and tea waste [16] research has been carried out on tensile strength and elongation at break.

![Figure 1. Tensile Strength of Cellulose Based-Bioplastics](image-url)
From Figure 1, the best tensile strength in rice straw with a yield of 43 MPa followed by sugarcane bagasse, cocoa husks and tea waste with a successive value of 30.6, 20 and 6.1 MPa. Rice straw has a high cellulose content of 61.8%. Where the tensile strength will increase with the addition of increasing cellulose content [17]. In addition, the extraction of cellulose in rice straw using trifluoroacetic acid (TFA) provides a bioplastic tensile strength comparable to polystyrene and similar properties to polyvinyl chloride (PVC) [10]. It exhibits the high mechanical properties of bioplastics produced using trifluoroacetic acid (TFA) [5]. The use of DMF solvent on sugarcane bagasse has good solubility due to the destruction of hydrogen bonds in polysaccharides. As well as showing good chemical modification efficiency which produces bioplastic films that are not cracked and have a tensile strength of up to 30.6 MPa [14]. The cocoa husk produced a tensile strength of 20 MPa using a mixture of TFA and TFAn solvents. TFAn is a compound that does not contain water. As a result, the cocoa husk are partially dehydrated due to insufficient water content to hydrolyze cellulose [15]. The lowest tensile strength in tea waste using citric acid is 6.1 MPa. Because the use of citric acid cannot react thoroughly with the matrix components contained in the tea waste [16]. In addition, citric acid acts as a plasticizer and reduces intermolecular interactions so that it will reduce its tensile strength [18].

3.2. Elongation at Break

Elongation at the break as shown in Figure 2, the best results were obtained on cocoa husks with a yield of 28%, followed by tea waste, rice straw, and sugarcane bagasse with consecutive values 13, 6.1 and 2.35%. In cocoa husks, bioplastics produced by mixing TFA and TFAn solvents provide the advantage of a much faster spread. In addition, the mixing will be reactive, resulting in the acylation of cellulose and cellulose derivatives with the resulting carboxylic acid. As well as obtaining bioplastics that have greater elasticity properties [15]. In addition, TFAn which is anhydrous or a compound that does not contain water will affect the elongation at the time of breaking the bioplastic. Moisture in bioplastics will affect multiple mechanical behaviors which can be exploited to obtain shrink films and sheets [5]. In tea waste using citric acid, the elongation at break is quite high, namely 13%. This is because citric acid is hygroscopic so that the bioplastic film can absorb and retain moisture which causes elongation at break to increase proportionally [16]. Citric acid acts as a plasticizer which makes the cellulose ring more flexible so that the elongation at break is relatively increased [18], [20]. In rice straw, elongation at break was produced by 6.1% using TFA. Generally, TFA will provide elongation at this high break time because TFA can be a natural plasticizer so that it can reduce polymer stiffness [12]. However, in rice straw, this is not the case. Elongation at break is quite low due to the high content of cellulose contained in rice straw, which is 61.8%. An increase in cellulose content will cause a decrease in elongation at break [17]. The lowest elongation at break was produced by bagasse using DMF solvent, which was 2.35%. This is due to the degradation of the bagasse fraction during chemical modification and the low level of substitution of the -hydroxyl group [14].
Different types of raw materials will also display various mechanical properties such as stiffness, elasticity, tensile strength, thermal stability, brittleness, yield strength, and permeability [1], [5]. For elongation at break, all materials do not meet where the elongation at break according to SNI 7818: 2014 is 400 – 1120% [19].

4. Conclusion
Cellulose is a natural polymer that has the potential to be used in the manufacture of bioplastics. In addition, presence of cellulose is abundant in plants and waste. The use of rice straw as a raw material in the manufacture of bioplastics showed good results where the high cellulose composition of rice straw was 61.8% and the tensile strength that had met SNI 7818: 2014 was 43 MPa using TFA solvent while the best elongation at break was produced at cocoa husk is 28% using TFA and TFAn solvents but does not meet SNI 7818: 2014. So it is necessary to make efforts to increase elongation at break. The development of bioplastics derived from cellulose from waste will provide great benefits in addition to increasing the use value as well as reducing waste that can pollute the environment and encourage industrial growth.

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