

Cellulose Palmitate Biopolymer for Composite: Preparation and Application

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Abstract. Organic polymer or biopolymer is polymer that processed using natural material. The advantages of biopolymer are environmental friendly, take less energy for production and reduce dependence on fossil raw materials. Composite is material that produced by mixing two or more substances so it will has best properties from the elements. One of the applications of composite material is on the body of patrol boat. The main objective of the present study was developing composite based biopolymer fiber with similar properties comparable to synthetic polymer fiber using waste materials of plant origin, especially by the utilization of palmitoyl chloride as palm waste. Cellulose palmitate was prepared from cellulose and palmitoyl chloride. It was compared with the commercial one, cellulose acetate. The composite was made with many variable of resin. They are unsaturated polyester and epoxy resin. Parameter observed were tensile strength, charpy impact strength and morphology analysis. From the experiment found that cellulose palmitate gave higher performance when it was mixed with epoxy resin. It reached 32.99 MPa of tensile strength and 32.48 J/m² of charpy impact strength. But when composite was made from unsaturated polyester, cellulose acetate gave better performance. The development of biopolymer must be done continuously to get better result to substitute metal as body of patrol boat.

Keywords: Biopolymer; cellulose palmitate; cellulose acetate; composite; resin

Introduction

Cellulose, the main component of the stems of cereal grains (such as straw), grasses and wood, is a non-edible plant resource that is being regarded as a promising material for biopolymer production. Cellulose is used often in our daily lives, from the pulp found in paper to the fiber in our clothing. The amount of cellulose produced in one year is nearly 130 billion tons.

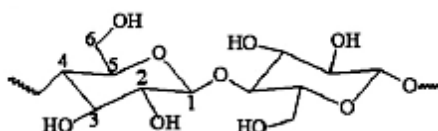


Figure 1. Cellulose structure.

Cellulose is composed of units of β -D- glucopyranose that bound one to another by glycoside bonds. Cellulose molecules are shaped entirely linear and has a strong tendency to form hydrogen bonds intra and intermolecular. Cellulose molecules together form aggregates in the form of microfibrils, in which places very regular (crystalline) interspersed with areas that are less organized (amorphous). Microfibrils are to form fibrils and finally cellulose fibers. As a result of the fibrous structure and hydrogen bonds are strong cellulose has a high tensile strength and insoluble in most solvents.

Cellulose has a molecular structure that is strong, but stiff and brittle, absorb large amounts of water, and do not melt when heated. In order to use cellulose as an ingredient in a polymer, a large number of additives needed to improve the strength. Development of biopolymers that use non-food materials such as cellulose, has a practical characteristics such as high-level resistance strength, heat and water resistant, good moldability including fluidity, and achieve a certain composition ratios.

In previous research has been carried out the manufacture of cellulose cardanol from cashew nuts. Cashew nuts are widely cultivated in India, Vietnam, and other countries, and approximately 1.4 million tons of cashew nut shells are produced each year. Cashew nut shells contain an oily substance called cardanol's unique molecular structure that is flexible and water-repellant (hydrophobic) and contains a reactive site. If cardanol was bound to cellulose, it can be made the new resin of superior durability. Approximately 0.4 million tons of cardanol can be extracted from the 1.4 million tonnes of cashew shells. Most of the shells have not been used productively, but have been burned or thrown away. Every year, 0.4 million tons of this "unique natural oil", oil that has so much added value that can reduce people's dependence on oil and holds the key to minimizing the impact on the environment, are not used effectively.

Composite materials are formed from two or more base material with different material properties and it has better properties than the former material. Fiber composites (fibricus composite), is a composite consisting of fibers and matrix (base material) produced in the fabrication, such as fiber plus resin adhesive. For example the fiber reinforce plastic (FRP), pulp cement board (STD).

Environmental friendly, composites materials fabricated using plant based biopolymer offer an attractive alternative to conventional petroleum based materials. Indeed during the last few years, biopolymer composites have received much more attention than ever before from the research community all over the world. The 'green' composites prepared

using these natural fibers demonstrate good mechanical properties such as tensile, compressive and flexural strength and may be used for various applications.

Experimental

Preparation of Cellulose Palmitate

Cellulose palmitate synthesis was initiated by mixing Pyridine as solvent with activated cellulose in a three-neck flask. Before refluxing, Nitrogen gas was blown to the flask to remove gas that can interfere with the reaction. Then the reaction mixture was added with palmitoyl chloride to produced yellow mixture. After 3 h reaction at temperature of 70°C, the reaction mixture became brown and viscous. Then methanol was added until white solid particle was obtained. The synthesized product was then washed repeatedly with methanol until the odor of pyridine was lost and resulting white precipitate cellulose (yield: 85.84%).

Characterization of Cellulose Palmitate (Degree of Substitution Determination)

Samples were crushed into powder, then each sample was weighed with the weight of 0.5 grams. Each sample was added 50 mL of water and NaOH solution standardized in advance as much as 25 mL, then the sample is heated. After cooling, samples were filtered and the filtrate was put in a measuring cup. The filtrate samples were taken every 5 mL, and then titrated with standardized HCl solution using Phenolphthalein indicator. Titration of a solution made up of pink right turn into a clear solution. Duplo titration was performed.

Cellulose Palmitate Fiber and Cellulose Acetate Fiber Preparation

Cellulose palmitate and cellulose acetate were dissolved with stirring into technical dichloromethane (DCM) and acetone, respectively. Furthermore, soluble cellulose palmitate and soluble cellulose acetate that have been cast on the glass and allowed to dry (solvent evaporates). These cellulose palmitate and cellulose acetate were cut lengthwise to form fibers.

Composite Preparation

Composite material was made using two variables, unsaturated polyester resins and epoxy resin. The hand lay-up methodology involved applying catalyzed resin to the tooling surface, placing an individual layer of fabric to the mold, permeating the resin through the fabric thickness with hand rollers and brushes, and then repeating this procedure for the build-up of the remaining laminate. Comparison of Epoxy resin and hardener was 1:1.

While for unsaturated polyester and methyl ethyl keton (MEK) the composition must be 200 gr and 2 mL.

Tensile Strength

Samples were prepared conditioned at temperatures of 23°C and 50% relative humidity for 48 h prior to testing. Tests conducted in accordance with ASTM D3039 with a withdrawal speed of 2 mm/min at temperatures of 24.1°C and relative humidity 50% to 5 specimens.

Charpy impact strength

Samples were prepared conditioned at temperatures of 23°C and 50% relative humidity for 48 h prior to testing. Tests carried out in accordance with ISO 179 with a speed of 2.9 m/s and a load of 4 and 2 Joules at temperatures of 23.2°C and 50% relative humidity. Tests were carried out on specimens' unnoticed with edgewise position.

Results and Discussion

The method of characterization of cellulose palmitate that used to measure the degree of esterification can be done in many ways, the principle is to know the number of moles of ester substituted into cellulose managed quantitatively.

Table 1. Result of degree of substitution.

Sample	Degree of Substitution (DS)
Cellulose Palmitate 1 gr	1.2847
Cellulose Palmitate 2 gr	0.1339
Cellulose Palmitate 5 gr	0.6308

The degree of substitution shows the average rate of substitution per glucose unit in the cellulose. If each unit of glucose is esterified by a substituent, then the DS is 1. If the entire hydroxy group is esterified in each glucose unit, the DS is 3. DS can also be defined as the number of moles of substituent per mole of glucose units bound (or glucose esters). Commercially, cellulose is esterified produced by DS levels above 0.1. The higher the rate of DS, the higher the plasticity of cellulose esters. The cellulose palmitate that are produced fulfill the requirement for commercial level, which is above 0.1.

The mechanical properties are usually studied by observing the nature of tensile strength (σ) using a dynamometer measurement tensometer or, if the material given voltage. Practically tensile strength is defined as the magnitude of the maximum load (F_{maks})

required to break the specimen material, divided by the cross sectional area of the material. Because while under the influence of stress, the specimen deformation (deformation) the definition of tensile strength expressed by the original cross-sectional area (A_0).

$$\sigma_t = F_{maks} / A_0 \quad (1)$$

During deformation, it can be assumed that the volume of the specimen does not change, so the comparison with the cross section of the original cross-sectional area at any time, $A_0 / A = l / l_0$, with L and l_0 is the length of each specimen at all times and before. When a defined amount of elongation (ϵ) as the ratio of the length to the original length of the specimen ($\epsilon = \Delta l / l_0$) of the obtained equation,

$$A = A_0 / (1 + \epsilon) \quad (2)$$

The results of tensile strength properties are expressed in terms of the tensile curve, ie the ratio of the load to the area of cross-section, the extension of (stretching), referred to the tension-stretch curve. Tension-stretch curve shape is characteristic that shows indications of mechanical properties of soft, hard, strong, weak, brittle or hard.

From the Table 2 below it can be seen that for composites with epoxy resin showed that the commercial use of fiber composites provides higher mechanical strength compared to fiber biopolymer. As for composites with unsaturated polyester resin showed no significant differences for the mechanical strength of various fiber use, both commercial fiber and biopolymer fibers.

Table 2. Result of tensile strength test.

Resin	Fiber	Tensile Strength (MPa)
Epoxy Resin	Cellulose Palmitate	32.99 ± 1.99
	Cellulose Acetate	24.86 ± 3.41
	Carbon Fiber	116.8 ± 28.8
	Glass Fiber	113.0 ± 10.3
Unsaturated Polyester	Cellulose Palmitate	14.79 ± 2.04
	Cellulose Acetate	24.43 ± 5.34
	Carbon Fiber	30.47 ± 5.02
	Glass Fiber	49.84 ± 5.66

For the tensile strength of the glass fiber and epoxy resin composite is 113.0 ± 10.03 MPa. The glass fiber has the highest strength. This is due glass fiber has been fabricated with

special treatment that has a high plasticity, easily attached, sizes, thickness of fibers which are small and have a high enough strength.

For cellulose palmitate, obtained tensile strength of 14.79 MPa or smaller than the sample strength glass, carbon, and cellulose acetate.

For the tensile strength of the glass sample $89.23 \pm 32.40 \text{ kJ/m}^2$. The glass sample, has the highest strength it possessed impact while cellulose palmitate $1.89 \pm 0.63 \text{ kJ/m}^2$ smallest.

Elongation is one type of deformation. The elongation-to-break is the strain on a sample when it breaks. This usually is expressed as a percent. The elongation at break sometimes is called the ultimate elongation. Fibers have a low elongation at break and elastomers have a high elongation at break.

Table 3. Result for elongation at break.

Resin	Fiber	Elongation at Break (%)
Epoxy Resin	Cellulose Palmitate	3.80 ± 0.37
	Cellulose Acetate	2.40 ± 0.29
	Carbon Fiber	3.66 ± 0.65
	Glass Fiber	3.42 ± 0.25
Unsaturated Polyester	Cellulose Palmitate	0.575 ± 0.049
	Cellulose Acetate	0.941 ± 0.076
	Carbon Fiber	0.944 ± 0.271
	Glass Fiber	1.364 ± 0.133

In Table 3, shows that unsaturated polyester composite, the strongest elongation was on glass fiber and the lowest was on cellulose palmitate. While, for epoxy resin composite, the elongation at break has no significant differences for all fibers that used.

Table 4. Result of charpy impact strength.

Resin	Fiber	Charpy Impact Strength
Epoxy Resin	Cellulose Palmitate	32.48 ± 8.50
	Cellulose Acetate	15.90 ± 8.75
	Carbon Fiber	77.64 ± 9.19
	Glass Fiber	62.55 ± 10.77
Unsaturated Polyester	Cellulose Palmitate	1.89 ± 0.63
	Cellulose Acetate	3.04 ± 0.63
	Carbon Fiber	19.91 ± 5.7

The above test is performed according to ISO 179. Charpy Impact test results above show that strongest is glass fiber and the lowest was on cellulose palmitate.

These are the result of morphology test that used digital microscope. From the figure below, void was still found in the sample. It happened on preparation process and the void influenced the strength of composite.

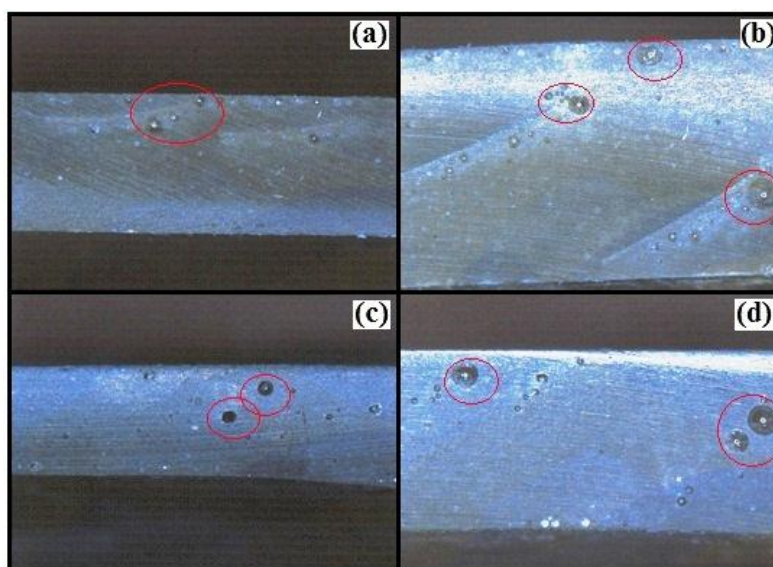


Figure. 2. Morphology of samples (a) Cellulose Palmitate (b) Cellulose Acetate (c) Carbon Fiber (d) Glass Fiber.

In order to achieve effective fiber reinforcement, interfacial strength between fiber and polymer matrix is the most essential factor. For a composite to be an effective load bearing system, the fibers and matrix must cooperate. This cooperation between the fibers and matrix will not exist without the presence of interface. The interfacial strength depends on the surface topology of the fiber. The interface acts as a ‘binder’ and transfers load between the matrix and the reinforcing fibers. The interfacial area plays a major role in determining the strength of composite material because each fiber forms an individual interface with the matrix.

For future applications, cellulose palmitate used as additional processes need to be made with the addition of additives or modifiers structure in order to increase the strength of cellulose palmitate.

Conclusion

In the results of this study can be ascertained that glass fiber is stronger than carbon fiber, acetate and palmitate. This is possible because strength or tensile strength increased and have an influence on unsaturated polyester. While the use of epoxy resins, commercial fiber gives better results biopolymer fibers. It can be caused by biopolymer fibers have not experienced such preliminary treatment on commercial fibers, and the fiber -making process has not performed optimal.

Basically this study is based on laboratory testing or research conducted by the author. Therefore, it is necessary to improve the sustainability of research on fiber composites. Because environmental issues are important in keeping the earth from damage and will require replacement alternative.

Reinforcement of the natural fiber is something that is quite difficult. Sometimes, the contour of the fiber is not in accordance with the wishes of the expected, in contrast to the treatment of synthetic fibers. Special treatment design composite sheet, the dough fiber, and the need to design the appropriate dose, in order to obtain optimum strength. The study should be repeated or that all forms, sustainable design better so that it can go beyond strander synthetic composite. Finally, it can be concluded that by utilizing cellulose palmitate with such additive and certain treatment, we can prepare user-friendly and cost-effective composite materials possessing suitable mechanical properties.

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