Preparation, Characterization of Palm Oil Based Polyols Reinforced with Bentonite-Chitosan as A Sustainable Raw Material for Anti-Bacterial Polyurethane Coatings in Medical Devices

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Abstract. In this study, polyurethane synthesis was carried out using the prepolymer method using the reaction of toluene diisocyanate (TDI) with palm oil-based polyols. To provide heat and anti-bacterial properties in polyurethane coatings, the addition of bentonite (B) and chitosan (K) into polyurethane samples was carried out. The concentration of bentonite and chitosan used were 1.5%, 3.5%, and 5.5%, respectively. Polyurethane-bentonite-chitosan (PU-B-K) samples were analyzed using FTIR to analyze the structure of chemical compounds. Preparation of bentonite purification was carried out by adding cetyltrimethylammonium bromide solution to the bentonite solution. The expected results in this study are the nature of the bacterial resistance produced, while to see the characteristics FTIR tests were performed. Meanwhile, to see the heat resistance TGA test will be performed.

1. Introduction
Polyurethanes are thermoplastic polymers produced from the reaction between polyols and isocyanates [1]. Currently, polyols in polyurethanes are synthesized from petroleum. The availability of petroleum which is increasingly narrow now encourages other parties to look for new alternatives as a substitute for petroleum. One alternative that can be used is vegetable oil. Synthesis that has been carried out with various vegetable oils such as canola oil, camelina oil, lanola oil, sunflower oil, nulin oil [2], neem oil [3]. Then the synthesis of polyurethanes from vegetable oils obtained from various plants such as jatropha, palm oil, soybeans, and cotton [4]. In other words, vegetable oil can replace petrochemicals as the raw material for making polyols, besides that the use of polyols from vegetable oils is superior because of their abundant availability in nature and easily decomposed.

In this study, oil palm is used for the synthesis of polyols. At this time information on polyols derived from palm oil is still limited. The main components of palm oil are triglycerides or triglycerols which are triesters of glycerol and unsaturated fatty acids. Because the content of fatty acids is not saturated, palm oil can carry out epoxidation and hydroxylation reactions to form polyols which will be used for the manufacture of polyurethanes.

The advantage of polyurethane is that it is safe to use in the medical world. Polyurethanes are usually applied to paints and coatings, the automotive industry, fibers, construction materials, and synthetic
leather. With the addition of chitosan which is an alloy in modifying polyurethane, it can become antibacterial in polyurethane. According to the results of research showing that the intercalation of chitosan through the cation exchange process can increase thermal stability and antimicrobial activity of nanocomposites. Chitosan properties such as biodegradability, biocompatibility, non-toxic and antibacterial have become an attraction for the industry.

In this research, palm oil-based polyurethane will be made as a raw material for polyols modified with the addition of bentonite to improve the physical and mechanical properties of polyurethane. The resulting polyurethane coating was further modified with the addition of chitosan to provide antibacterial properties, so that the coatings obtained would not only have strength, stiffness, heat resistance, corrosion resistance, and chemicals, but also have resistance to bacteria.

1.1. Polyurethane

Polyurethanes are copolymer blocks that contain low molecular weight polyester or polyester segments associated with urethane groups (-NHCO-O-). This polymer is formed from the reaction between the polyisocyanate with a polymer that contains a hydroxyl group (polyester or polyether polyols) and chain elongation such as glycol and diamin [4].

Polyurethane is one of the classes with high deformation presentation, where polyurethane has a good degree of flexibility, requires a low degree of interaction between molecules and almost perfect crosslinking. Good crosslinking is caused by hydrogen double bonds. Chemically, crosslinking bonds are actually caused by three or more compounds involved in it. Once formed, this crosslinking bond is very unlikely to be moved by the act of heating even, except in some instances where the chemicals used are very unstable so they can act irreversibly. Therefore, polymers that have the ability to be separated from crosslinking by heat treatment become a polymer that is widely used and polyurethane is one of them [5].

1.2. Isocyanate

In the formation of polyurethanes it is very important to choose the right isocyanate to react with polyols because it will be able to determine the final results such as biuret, urea and urethane. Isocyanates can react with alcohol to form carbamate, with water to form urea and CO₂ gas, with amines to form urea, with urea to form urethane and isocyanate. Isocyanate is the main material for making polyurethanes. Commonly used as diisocyanate are 2,4-toluene diisocyanate (TDI), 4,4-methylene-bis phenylisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), 2,2,4-trimethyl-1,6- hexamethyl diisocyanate (TMDI), 1,5-naphtacene diisocyanate (NDI), as shown in Figure 1 [5].
2. **Research Methods**

2.1. **Materials**

A set of polyurethane synthesis tools, Magnetic stirrers, Penangas, Centrifuges, Petri dishes, Filter paper, Analytical scales, Fourier Transform Infra-Red spectrophotometers (FTIR), Thermal Gravimetry Analysis (TGA). Oleic acid based on palm oil, Galetic acetic acid, Aquadest, Bentonite, Commercial chitosan, Diisocyanate toluene (TDI), Cetyl trimethyl ammonium bromide (CTAB), 30% H₂O₂, concentrated H₂SO₄, Methanol, Nutrient agar, Steel plate.

2.2. **Synthesis of polyols**

2.2.1. **Epoxidation**

Polyol synthesis is carried out in a 350 mL size 3 neck flask equipped with a mechanical stirrer and cooling system. Then put into the reactor as much as 60 mL glacial CH₃COOH and 30 mL 30% H₂O₂ slowly while stirring. Through the dropper funnel, add 2 mL of concentrated H₂SO₄ and stir slowly to 30ºC for 1 hour. Furthermore, through the dropper funnel slowly added 100 ml of palm oil oleic acid. The temperature is maintained at 30ºC and continues to stir for 3 hours. The reaction product is an oleic acid epoxidation compound, which is cooled to room temperature and the separation of the oil phase as an oxidized oil which will then be used in the hydroxylation process.

2.2.2. **Hydroxylation**

100 mL of methanol were added 50 mL of glycerin, a concentrated H₂SO₄ catalyst of 2 mL and 5 mL of water into a 350 mL three neck flask, heated to 40ºC. The mixture was added to an oxidized oil solution into a three neck flask, stirring at 50ºC for 2 hours. Then it is cooled to room temperature and transferred to a separate flask to separate the formed polyols and then stored in a glass bottle. Furthermore, it was analyzed by FTIR to find out the OH group in polyols.

2.3. **Processing of Bentonite**

18.2 grams of cetyl trimetyl ammonium bromide (CTAB) dissolved with 250 mL aquades in 500 mL beaker glass, this solution is heated at 80ºC for 1 hour. Separately 20 grams of bentonite were dissolved with 250 mL of distilled water in a 1000 mL beaker glass. Subsequently the dispersion of bentonite solution was put into CTAB solution and stirred for 1 hour. Filtered bentonite then washed with distilled water several times until there are no more bromides. The filtrate was tested by dropping 1 M AgNO₃ until a white precipitate formed. Bentonite is put into the oven at 60ºC, then filtered using a sieve tray with a size of 100 μm.

2.4. **Making Polyurethane / Bentonite / Chitosan Coatings**

The polyol, bentonite, chitosan and TDI mixed into the beaker glass were mixed with a magnetic stirrer at 200 rpm for 1 hour. In this procedure, a number of bentonite and chitosan are used, each 1.5, 3.5 and 5.5 weight percent (wt%). The resulting polyurethane is then cooled to room temperature. Then the chemical structure of polyurethane, bentonite and chitosan were analyzed using FTIR.

3. **Results**

| Table 1. Experimental design of polyurethane-bentonite-chitosan synthesis on inhibition of the bacteria Staphylococcus Aureus (a) and Escherichia Coli (b). |
|---------------------------------------------------|
| **Inhibition zone area (mm)**                      |

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**Figure 1.** Examples of Some Isocyanate Compounds [3].
Table 2. Results of the characterization of palm oil polyols by FTIR

| Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area  | Corr. Area |
|------|-----------|----------------|----------|----------|-------|------------|
| 1    | 1651.07   | 0.053          | 0.043    | 1654.92  | 1562.34| 209.487    | 0          |
| 2    | 1762.94   | 0              | -0.006   | 1766.08  | 1759.08| 1.543.053  | 379.485    |
| 3    | 3336.85   | 0.006          | 0.001    | 3348.42  | 3302.13| 195.01.00  | 1.769      |
| 4    | 3383.14   | 0.006          | 0        | 3387.71  | 3367.71| 81.39.00   | 0.058      |
| 5    | 3406.29   | 0.005          | 0.001    | 3417.86  | 3390.86| 114.971    | 0.3951     |

Polyol formation process will occur if the alcohol reacts with the epoxide group. Therefore, a mixture of methanol and glycerin is used, where the methanol used also aims to avoid cross linkage in polyol products. In this hydroxylation process, the results obtained visually observed are products that consist of two layers, namely the upper layer which is turbid yellow, and the lower layer is turbid white. The obtained polyol product is expected to meet the standard characteristics of the polyol as the raw material for making polyurethane where the analysis shows that the number of hydroxyl numbers is determined because the polyol product of its hydroxyl group will react with isocyanate to form polyurethane as in Table 1.
The presence of a hydroxyl group is demonstrated by transmission in the wave number 3300-3600 cm\(^{-1}\). FTIR analysis results which have shown at figure 2 and table 2 that hydroxyl groups have formed on palm oil epoxide compounds as evidenced by the absorption of OH wave numbers that widen at 3336.85 cm\(^{-1}\), 3383.14 cm\(^{-1}\), and 3406.29 cm\(^{-1}\), it has been stated that the reaction of the compound the compound has formed the desired polyol product. The results of the wavelength measurement of hydroxyl groups in previous studies were 3384.90 cm\(^{-1}\) [2], 3412.38 cm\(^{-1}\) [6], 3445 cm\(^{-1}\) [7].

3.1. Results of Polyurethane Characterization with Bentonite and Chitosan Fillers

Polyurethanes are generally polymer compounds whose main chain constituents are urethane groups (-NHCOO-). This polymer has been widely used in the paint industry, printers, foams, elastomers and others. In the polyurethane coating industry is widely used because it has good scratch resistance, stiffness, hardness, good flexibility, resistant to abrasion, resistant to chemicals and corrosion, and has mechanical characteristics that can be applied in various fields.

Polyurethanes are made by the addition reaction between polyols and isocyanates. Initially the main raw material for the manufacture of paint came from petroleum-based materials. However, because the solvents used pose risks to human health, environmental pollution and cause global warming if they evaporate into the environment, other alternatives are used to prevent this by replacing petroleum into vegetable oils. Vegetable oil can be used because it is renewable and environmentally friendly.

Vegetable oil used in this study is palm oil. Which is used as a material for making polyols is oleic acid contained in the palm oil. To form polyurethane one more important component is isocyanate. Where the reaction of polyols and isocyanates will produce urethane groups. So that the polyurethane produced has better physical properties, it is added with additional fillers in the form of bentonite and chitosan.

Bentonite provides high thermal resistance properties, because bentonite has its constituent material called montmorillonite. Cethyl Trimethyl Ammonium Bromide (CTAB) is used as a surfactant to modify bentonite to form organobentonite by changing its nature from hydrophilic to more hydrophobic. With the insertion of the surfactant into the bentonite, d-spacing in the bentonite will become larger (intercalated). The use of chitosan as a filler in polyurethanes aims to provide anti-bacterial properties. Chitosan contains a functional group of positively charged amines which can inhibit bacterial growth and are non-toxic, because microbial membranes have a negative charge.

Palm oil based polyurethane coatings are made by reacting two main components namely polyols and isocyanates. The isocyanate used is toluene diisocyanate (TDI). Polyols will first be mixed with fillers in the form of bentonite and chitosan which will be stirred until all the homogeneous mixture is stirred for 60 minutes and then added toluene diisocyanate (TDI) in a ratio of 1:9 between the addition of TDI and polyols. Stirring is carried out to obtain a thick and homogeneous result. The resulting polyurethane product is then applied to the surface of the stainless steel plate provided, dried at room temperature for ± 2 days until it dries. Then the product is tested for characteristics with TGA and FTIR instruments. Meanwhile, to see the anti-bacterial activity test in quantity on the product is tested by weight loss techniques.

4. Conclusion

The addition of bentonite to polyurethanes to improve the resulting resistance properties depends on the weight percent of the bentonite added, the more bentonite added to the polyurethane, the higher the thermal resistance properties produced. The more weight percent chitosan added to polyurethane, the greater the bacterial resistance properties produced by the polyurethane.

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