Synthesis of Castor Oil-Based Polyols Reinforced with Organoclay-Chitosan as Nanocomposite Polyurethane Coatings in The Application of Environmentally Friendly Medical Equipment

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Abstract. In this research, castor oil is used as raw material for making polyols. This review provides an overview of polyurethane coatings for the application of anti-bacterial medical devices. The anti-bacterial properties used in this review are chitosan. Chitosan is an amino polysaccharide that has a great structural tendency to produce bioactive materials with innovative properties and a variety of applications, especially in the biomedical field. To improve the physical and mechanical properties of polyurethane such as heat resistance, modifications were made with the addition of bentonite. This study with a variation of polyurethane/bentonite/ chitosan ratio of 2, 3 and 4 (% w / v), as well as tests conducted in the form of FTIR, TGA, and anti-bacterial tests. The results obtained for the best level of thermal stability in polyurethane / bentonite / chitosan 4%: 4% with a temperature of 600.94 °C and remaining weight 7.5 mg, while the anti-bacterial test obtained the largest inhibitory zone in polyurethane/bentonite/ chitosan 4%: 4% for Staphylococcus Aureus bacteria at 7.66 mm and Escherichia Coli bacteria at 5.8 mm.

1. Introduction

The consumption of polyurethane polymer materials has increased every year. Specifically in the medical field, polyurethanes are used as face shields, blood bags, infusion tubes. The main medical instrument used in medicine is a stethoscope. However, in this case, several problems arise that become obstacles to health, namely the use of a stethoscope not only for one patient but many patients who use it so that the resulting transmission of bacteria is increasingly easy.

Therefore, it is necessary to modify polyurethanes on antibacterial medical devices. Polyurethanes are produced from the reaction between polyols and isocyanates. Generally, polyurethanes are made from petroleum-based polyols. However, the current condition of petroleum is running low. Environmental problems and risks are a major concern as a reduction in conventional petroleum reserves. Therefore, it is necessary to divert raw material for making polyols, such as vegetable oils such as soybean oil, sunflower oil, canola oil, flaxseed oil, and castor oil. Utilization of vegetable oils is currently in the spotlight of the chemical industry because they are one of the most important renewable chemical platforms because of their universal availability, biodegradability, low prices, and exceptional environmental credentials (ie, low levels of environmental toxins and low toxicity to humans). Now natural ingredients are taking advantage of in research and development, with vegetable
oils derived from polymers/composites used in various applications including coatings, adhesives, and biomedicine [1].

R Sudrajat said in his research using Jatropha curcas oil has a hydroxyl number of polyols obtained at 3461 cm⁻¹. The length of time the reaction has an effect on increasing the hydroxyl number, i.e. the longer the reaction time, the hydroxyl number obtained will be even greater. In this study using castor oil-based polyols with ricinoleic acid content which represents 90% of the total fatty acid content [2] with a methylation method and a longer reaction time.

To improve the mechanical properties of polyurethane products as a coating on medical devices used fillers such as bentonite and chitosan. Chitosan has various applications in the biomedical field such as wound healing, antibacterial coatings, tissue engineering scaffolding, membrane separation, stent coatings, sensors, and drug delivery systems [3]. Chitosan has the potential for a wide variety of applications in biocompatibility (non-toxic), biodegradability, antimicrobial properties, and friendly natural environment so as to provide a good opportunity for future progress. One of the main disadvantages of coating vegetable oil-based polymers is not being able to withstand high temperatures [4]. Therefore, the current development of science about nanotechnology not only produces materials that are anti-bacterial but also able to withstand heat. So, in this study utilizing the use of nanocomposite bentonite as a filler material in a polyurethane matrix as a heat-resistant reinforcement and an increase in the mechanical properties of the coating material.

This research will make castor oil-based polyurethane as a paint and coating material. To improve the physical and mechanical properties of polyurethane such as having strength, heat resistance, corrosion resistance, and chemicals as well as having resistance to bacteria, modifications were made by adding bentonite and chitosan with various concentrations.

1.1. Vegetable Oil-Based Castor Oil Polyols

Vegetable oil is an ingredient available in nature, easily available at affordable costs. Vegetable oil sourced from nature is biodegradable and has potential as a renewable natural resource for environmentally friendly materials. Vegetable oil has been applied as an ingredient for making biodiesel, lubricants, cutting fluid (liquid cutting) (liquid for cutting and forming metal materials), paints and coatings [5]. The use of vegetable oil in this study is due to seeing that oil is running low and is expected to be a new alternative to produce polyurethane. One of the natural ingredients that have the potential to be used as polyols is castor oil or so-called castor oil which in its molecular structure contains three hydroxyl groups. Jatropha oil is widely used in the chemical industry because of the hydroxyl group in the middle of the carbon chain at C12 and the existence of double bonds which allows it to produce chemical derivative products from the oil. Castor oil can be considered a polyol because there are several hydroxyl groups.

Polyols are organic compounds which have more than one hydroxyl group and, in the material industry is widely used both as reagents and additives. Polyol compounds can be obtained directly in nature such as starch, cellulose, sucrose, and lignin or even industrial chemicals. Polyols from vegetable oils have been widely developed to be able to replace petroleum-based polyols in the manufacture of polyurethanes and polyesters, and have also been widely used as plasticizers in the polymer matrix to produce a material, as well as softeners and stabilizers with the aim of obtaining certain hardness and softness so that the material it is easily formed into various types of goods as needed [6].

There are two methods of making polyols from vegetable oils such as castor oil through the method of epoxidation and hydroxylation. Epoxidation reaction is the reaction of converting unsaturated bonds of a compound into a saturated bond in the form of an oxidant group by oxidizing the compound. The hydroxylation reaction is the reaction of opening the oxidant group to the hydroxyl group which is carried out on an epoxy compound. Hydroxylation is a reaction that adds a hydroxyl group to an organic compound. In this reaction, it can also be called the opening reaction of the oxygen ring on the epoxide compound. The process of hydroxylation of epoxy oil is carried out by reacting epoxy and methanol compounds. The results of the hydroxylation process are organic compounds in the form of hydroxyl compounds or also called polyol compounds.
1.2. Polyurethane Paint and Coating

Polyurethane is a polymeric material that has the characteristic presence of urethane (-NHC=O-) functional groups in the main polymer chain. The urethane function group is produced from the reaction between compounds containing hydroxyl groups (OH) commonly called polyols and compounds containing isocyanate groups (-NCO-). Polyurethanes are generally synthesized from vegetable oils that are converted into derivatives, for example, alkyd resins and alkyd based polyols. The polyols are then reacted with different diisocyanates to obtain polyurethane coatings [7]. Polyurethanes (PU) are block copolymers containing hard and soft segments in which hard semicrystalline segments are formed by the reaction of polyisocyanates and extender chains (diol/diisocyanate) and amorphous soft segments consisting of long polyol chains [8].

Polyurethanes are block copolymers formed from the reaction of polyamide between (or poly-) isocyanate (toluene 2,4-diisocyanate [TDI], diphenylmethane diisocyanate, naphthalene 1,5-diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate) and (di-poly or alcoholic acid) or other compounds containing active hydrogen atoms, as raw material for polyurethanes. Isocyanates can react with hydroxyl groups such as alcohol to form urethane, the reaction mechanism of isocyanates with hydroxyl groups of alcohol compounds is determined by the reactivity of various types of hydroxyl groups. Diol amides and polyols from vegetable oils have been used as the main ingredients to synthesize polyurethanes with aliphatic and aromatic isocyanates [9]. The longer the reaction time for making polyurethane, the more bonds are formed, so the higher the temperature needed to break the bonds, in other words, the mechanical properties are also increasing [10].

Polyurethane (PU) coatings have excellent resistance in terms of toughness, low temperature, flexibility, corrosion resistance, and chemical resistance, so it is used in various applications such as the maintenance industry for chemical resistance [7] and biomedical devices.

2. Research Methods

2.1. Materials

Polyols based on castor oil, acetic acid 2% and glacial 100%, Aquadest, Chitosan, Bentonite 100 mesh, Diisocyanate toluene (TDI), Cetyl trimethyl ammonium bromide (CTAB), Formic acid, H$_2$SO$_4$ 96%, NaOH 0.1 N, Methanol 98%, Molecular sieve, Nutrient agar, Steel plate. A set of polyurethane synthesis tools, Magnetic stirrer, Penangas, Centrifuge, 50 ml Beaker glass, 100 ml, 500 ml, and 1000 ml, 5 ml and 25 ml volume pipettes, Petri dishes, Filter paper, Analytical scales, Analytical Fourier Transform Spectrophotometer Equipment FTIR), Thermal Gravimetry Analysis (TGA) Equipment.

2.2. Synthesis of polyols

2.2.1. Epoxidation

30 ml of 30% H$_2$O% is inserted into the reactor then added CH$_3$COOH 100% as much as 50 ml and H$_2$SO$_4$ 96% as much as 2 ml. Stirred at a speed of 200 rpm and a temperature of 40 ºC for 1 hour. Then 100 ml of castor oil were added and stirred at a speed of 200 rpm at 40 ºC for 3 hours. and cooled to room temperature and separation of the oil phase as the oxidized oil for use in the hydroxylation process.

2.2.2. Hydroxylation

Entered 100 ml of methanol, 50 ml of glycerin, H$_2$SO$_4$ 96% 2 ml catalyst and 5 ml of water into a 350 ml three-neck flask heated to 40 ºC, then added the solution of the oxidized oil and stirred for 2.5 hours at 50 ºC, and cooled to temperature room, then transferred to a separate flask and separated polyols, analyze with FTIR to find out the OH group in the polyol.

2.3. Processing of Bentonite

Dissolved 18.2 grams of cetyl trimethyl ammonium bromide (CTAB) with 250 ml of distilled water into 500 ml of beaker glass, then heated at 80 ºC for 1 hour. Dissolved 20 grams of bentonite with 250 ml of distilled water into 1000 ml glass beaker, Dispersion of bentonite solution is put into a temperature of 80ºC for 1 hour in CTAB solution and stirred for 1 hour, filtered, and bentonite washed with distilled water and dried at 60 ºC.

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2.4. Making Polyurethane / Bentonite / Chitosan Coatings

Montmorillonite and chitosan were mixed 2, 3, 4 (% w / v) into 16 ml of castor oil polyols on beaker glass using 600 rpm magnetic stirred for 1 hour, then added 4 ml of toluene and stirred for 5 minutes, the resulting polyurea applied to metal specimens, chemical structure analysis of polyurethane coatings, bentonite, chitosan by using FTIR, heat resistance analysis of coatings by using TGA, Bacterial susceptibility testing by disk diffusion method.

3. Results

Table 1. Design data for analysis of polyurethane by weight percent of bentonite and chitosan on the inhibition zone area of Escherichia Coli and Staphylococcus Aureus bacteria.

| Bentonite: Chitosan (% b/v) | Inhibition zone area (mm) |
|-----------------------------|---------------------------|
|                            | Bacteria                  | Bacteria                  |
|                            | Escherichia Coli          | Staphylococcus Aureus     |
| -                          | Identified                | Identified                |
| 2 : 2                      | 0                         | 1.3                       |
| 2 : 3                      | 2                         | 2                         |
| 2 : 4                      | 3.2                       | 5.3                       |
| 3 : 2                      | 0                         | 1.6                       |
| 3 : 3                      | 2                         | 2                         |
| 3 : 4                      | 5.3                       | 6.73                      |
| 4 : 2                      | 1.3                       | 1.6                       |
| 4 : 3                      | 4.5                       | 5.3                       |
| 4 : 4                      | 5.8                       | 7.66                      |

Based on table 1 shows the sample that has the most powerful anti-bacterial activity, namely in S. aureus with inhibition zone area of 7.66 mm while the strongest antibacterial activity on E. coli with inhibition zone area of 5.8 mm. The data in table 1 shows that the inhibition produced by E. coli bacteria is smaller than that of S. aureus, this is because E. coli is a gram-negative bacteria that have thinner and more complex cell walls with high lipid content, so it is difficult to penetrate. While S. aureus is a gram-positive bacterium that has a simple and thick cell wall, single layer, low lipid content, layers of a cytoplasmic membrane composed of peptidoglycan and teichoic acid in the form of water-soluble polymers so that gram-positive bacteria are more easily penetrated by substances that come from preparations. Overall, the results of antibacterial polyurethane research that provided the strongest activity were polyurethane research results with S.aureus bacteria, with an area of inhibition zone of 7.66 mm.

Epoxide oil from castor oil is obtained from the reaction between parasitic acid (C₃H₆O₃) and castor oil, while parasitic acid is produced from the reaction between hydrogen peroxide (H₂O₂) and glacial acetic acid (CH₃COOH) with the help of a concentrated sulfuric acid catalyst (H₂SO₄). Hydrogen peroxide is used to oxidize double bonds into epoxide groups during the epoxidation process. The castor oil epoxy results obtained have a brighter color compared to the color of castor oil ricinoleic acid [11]. The formed epoxide oil is an intermediate compound which can react further to form diol compounds because it has two reactive sites, the carbonyl group which can connect glycerides with fatty acids and also epoxide groups. So the process of forming polyols will occur if the epoxide group reacts with alcohol. The reaction of the formation of epoxide compounds in vegetable oils has been carried out by [4],[5],[10].
Table 2. FTIR spectrum results data

| Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|------|-----------|-----------------|----------|----------|------|------------|
| 1    | 686.66    | 0               | 548      | 690.52   | 771  | 774        |
| 2    | 709.8     | 0               | 2980     | 717.52   | 705.95 | 766       | 779       |
| 3    | 1458.18   | 0               | 2525     | 1477.47  | 1454.33 | 769       | 790       |
| 4    | 3421.72   | 41              | 80       | 3660.89  | 3101.54 | 124       | 172       |

Based on table 2 shows FTIR analysis results have shown the formation of N-H urethane groups in castor oil polyurethane compounds, the reaction lasts for 1 hour at room temperature as evidenced by the absorption of the NH wave number that widens at 3402.43 cm\(^{-1}\) and 3483.44 cm\(^{-1}\) measurement results NH group wavelengths in previous studies were 3300 cm\(^{-1}\) [12], 3311 cm\(^{-1}\), 3315 cm\(^{-1}\) and 3316 cm\(^{-1}\) [9]. While uptake of wave number C=O urethane widened at 1681.93 cm\(^{-1}\) and 1728.22 cm\(^{-1}\), in the previous study of 1720 cm\(^{-1}\) [12], while the CH group at absorption was 2854.65 cm\(^{-1}\), 2908.65 cm\(^{-1}\) and 2947.23 cm\(^{-1}\) in the previous study of 2924.10 cm\(^{-1}\) [9]. The analysis shows that the formation of polyurethanes is seen from the absorption of wavelengths in the functional groups N-H, C=O urethane, and C-H. Detected functional groups represent polyurethane functional groups (-NHCOO-) in the form of wavelengths absorbing the bonds of separate functional groups.

Based on the analysis results it can be seen that the functional groups of pure PU and PU / Bent / Ch did not experience changes in functional groups. Mixing PU with bentonite and chitosan materials did not affect the wavelength absorption of the polyurethane functional group itself, the same as the results of previous studies on FTIR analysis of commercial polyurethanes (PUK), palm oil polyurethanes (PU-MKS) and palm oil + polyurethane (PU polyurethanes -MKS- Clay) [8]. This is due to the process of mixing bentonite and chitosan with polyurethane which occurs only in physical bonds rather than chemical bonds. Thus, no chemical bond changes occur so that the wavelength absorption of the PU / Bent / Ch functional groups detected remains the same.

Figure 1. Results of FTIR Commercial Polyurethanes (PUK), Polyurethane Palm Oil (PU-MKS) and Polyurethane Palm Oil + Clay (PU-MKS-Clay)

Sources of bacterial contamination in the hospital area can come from patients, the environment (air, space, and facilities available for operations), surgery materials and equipment, and members of the surgery team. To protect and prevent bacteria from being contaminated, efforts required include coating medical devices with anti-bacterial polyurethane paint. Surgical wound infections can also be caused by bacteria such as Staphylococcus aureus, and Escherichia coli [11]. The types of bacteria used in this study are Staphylococcus aureus and Escherichia coli. These bacteria are pathogenic and can cause diarrheal diseases, meningitis, skin infections and cause sores such as ulcers presented in Figure 1.
Bacteria representing Gram negative categories or groups in this study were E. coli while those representing Gram positive bacteria were Staphylococcus aureus. Bacteria E. coli and Staphylococcus aureus are often found in medical devices, for which both bacteria were tested in this study. The method used in this antibacterial test is the halo zone. To find out whether this polyurethane has antibacterial properties, the inhibition zone observation was continued for 24 hours. After being observed at 24 hours the bacteria experienced inhibitory regions. In figure a planted PU / B / K in S. Aureus bacteria has a wider inhibition zone compared to the media in picture b which is planted PU / B / K in E. coli bacteria. Whereas in pictures c and d planted with pure PU and empty plate samples do not have inhibitory zones but bacteria grow in the surrounding area. That is because there is no chitosan content in the sample presented in Figure 2.

4. Conclusion
From the anti-bacterial test results, the largest inhibitory zone area was polyurethane / bentonite / chitosan 4%: 4% with area for Staphylococcus Aureus bacteria of 7.66 mm while for Escherichia Coli bacteria it had inhibition zone area of 5.8 mm. From the results of the analysis of thermal stability using TGA. The best thermal resistance in 4%: 4% polyurethane / bentonite / chitosan is at a temperature of 600.94 °C with a remaining weight of 7.5 mg. From the results of the analysis of functional group characteristics using FTIR, there is no change in chemical bonds that occur between pure polyurethanes and polyurethanes / bentonite / chitosan so that the absorption wavelengths of the detected functional groups remain the same.

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