Synthesis and characterization of chitosan-bentonite modified polyurethane with biomedical potential

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Abstract. Research on the manufacture of polyurethane with chitosan and bentonite fillers modified with CTAB into montmorillonite (MMT) which will be applied to medical devices. The raw polyurethane from castor oil and diisocyanate is in the form of Toluene Diisocyanate (TDI). The addition of chitosan to castor oil polyurethane functions as an anti-bacterial agent. Pure polyurethane still has a deficiency of high temperatures and therefore added MMT which functions as a heat-retaining agent. The bacteria used are E. coli bacteria and Staphylococcus Aureus bacteria. The results showed a polyurethane that can withstand high temperatures is PU-MMT-CS 6%. The best anti-bacterial properties were obtained in polyurethane containing chitosan with higher concentrations (PU-MMT-CS 6%)

1. Introduction
Polyurethane is a polymeric material that has a characteristic feature of the urethane (-NCOO-) functional group in the polymer main chain. The urethane function group is produced from a reaction between a compound containing a hydroxyl (-OH) group commonly called a polyol with a compound containing an isocyanate group (-NCO-). Polyurethane is generally synthesized from vegetable oils which are converted into derivatives, for example, alkyd resins and based on alkyd polyols. The polyol is then reacted with a different diisocyanate to obtain a polyurethane coating [1]. Depending on types of raw materials, their composition and processing conditions, the properties can be tailored to produce a broad range of PU, widely used as coatings, films, adhesives, sealants, foams and fibers [2-4].

Polyurethane is produced from the reaction between polyols and isocyanates. In general, polyurethane made from petroleum-based polyols. However, the current oil condition is running low. Environmental problems and risks are a major concern as a reduction in conventional petroleum reserves. Therefore, it is necessary to transfer the raw materials for making polyols, namely vegetable oils such as soybean oil, sunflower oil, canola oil, flaxseed oil and castor oil. Castor oil is a triglyceride oil from various fatty acids which can be obtained from the seeds of the kepyar plant (RicinusCommunis L). Castor oil can be considered a polyol because there are several hydroxyl groups.

Nowadays, clay minerals or layered-silicates are extensively used as reinforcing materials for improving many properties of polymers such as mechanical, gas barrier, heat resistance, flame retardancy, dyeability and many others. The main benefits of clay minerals as reinforcing materials are
their low density, abundant availability, low cost, high aspect ratio and large specific surface area, which causes great enhancement in the properties of polymers [4-7].

Chitosan is a derivative compound from the results of the chitin deacetylation process. Chitin is found in various living organisms such as shrimp, crabs, insects and turtles. Chitin and chitosan have the potential for a wide variety of applications ranging from Biocompatibility (non-toxic and low immunogenicity), biodegradability, antimicrobial properties, and a friendly natural environment so as to provide good opportunities for future progress [8].

2. Method

2.1. Material and research tools

The materials used in this study is a castor oil-based polyols, Toluene Diisocyanates (TDI), Cetyltrimethylbromontid ammonium (CTAB), Bentonite, AgNO30.1N, acetic acid, distilled water, H2O2 30%, sulfuric acid, and chitosan.

The stages of this study include four stages, namely epoxidation of castor oil followed by hydroxylation to obtain castor oil polyol compounds, preparation of bentonite into montmorillonite, preparation of chitosan and the manufacture of polyurethane coating paint through polymerization of polyols with toluene diisocyanate bentonite their characteristics Bacteria of Staphylococcus aureus and e. Coli, and Nutrient Broth.

2.2. Polyol synthesis

In the epoxidation stage, the polyol synthesis process is carried out in a 350 mL 3 flask equipped with a mechanical stirrer and cooling system. In the reactor, 60 mL of 100% CH3COOH is added and 30 mL of 30% H2O2 is slowly stirred. Through the dropper funnel, 2 mL of concentrated H2SO4were added and stirred slowly at 30°C for 1 hour. Then through the dropper funnel, oleic acid is added slowly as much as 100 mL. The temperature is maintained at 30°C and continues to be stirred for 3 hours. The reaction results are oleic acid epoxidation compounds, which are desired at room temperature and oil phase separation as oxidized oil which will then be used in the hydroxylation process.

At the stage of hydroxylation as much as 100 mL of methanol 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 a temperature of 40°C. The mixture was added with an oxidized oil solution to the three neck squash, stirred at 50°C for 2 hours. Then it is cooled at room temperature and transferred to a separate flask to separate the polyol formed and then stored in a glass bottle. Then analysed by FTIR to find out OH groups in polyols.

2.3. Bentonite purification

A total of 18.2 grams of cetyltrimethyl ammonium bromide (CTAB) were dissolved with 250 mL of distilled water in a 500 mL beaker glass, this solution was heated at 80°C for 1 hour. In a separate place 20 grams of bentonite is dissolved with 250 mL of aquades in a glass beaker of 1000 mL. Forward, dispersion of bentonite solution was put into CTAB solution and stirred for 1 hour. Bentonite is filtered and then washed with distilled water several times until there is no more bromide. The filtrate was tested by dripping AgNO3 1 M until a white precipitate was formed. Bentonite is put into an oven at 60°C, then filtered using a 100 µm sieve tray.

2.4. Preparation citosan

A total of 4.25 grams of chitosan was dissolved in a 2% glacial acetic acid solution of 100 mL while in a stirrer with a speed of 500 rpm for 2 hours with a pH of 4.0 until chitosan suspensions were obtained. Then 50 mL of 0.1 N NaOH was dripped slowly into the chitosan suspension. Then in chitosan suspension rinsed using 150 mL distilled water or until neutral pH and dried in an oven at 60°C then chitosan is analysed.
2.5. Manufacture of polyurethane coating
A number of castor oil polyols are mixed with organoclay in mixing containers and at room temperature for 55 minutes and with 200 rpm stirrer rotation to obtain a homogeneous mixture, then add diisocyanate (TDI) and stir it again for 5 minutes until the mixture is homogeneous. Then applied to the specimen prepared metal material, the results of the test panel are left at room temperature to vaporize the solvent. Polyurethane film coating on metal specimens was tested thermographimetry, FTIR, and SEM.

2.6. Material characterization and testing

2.6.1. Fourier Transform Infra-Red (FTIR) spectrometer. An FTIR spectrometer (Nicolet iS50ATR-ThermoFisher Scientific) was used to record the FTIR spectra of neat PU and CPN films, in a scan range from 4000cm\(^{-1}\) to 400cm\(^{-1}\) and with a resolution of 4cm\(^{-1}\). For each specimen, an average of 32 scans was recorded.

2.6.2. Thermo Gravimetric Analyzer (TGA). TGA analysis is carried out using the Shimadzu DTG-60 instrument. Samples were weighed with mg mass and heated at room temperature to 800°C with a heating rate of 20°C/minute. Analysis is carried out by gradually increasing the temperature of the sample and determining the heavy loss of temperature changes. All specimens were tested under the flow of nitrogen gas.

2.6.3. Bacterial vulnerability test. Antimicrobial effectiveness of PU-MMT-CS fibers against E. coli and S. aureus can be determined [9]. An electrospun mat (10 mm × 20 mm) was immersed in a test tube containing 4 mL of isotonic solution where 0.5 mL of E. coli and S. aureus inoculum, adjusted for 10\(^7\) CFU/mL cell concentration, were given. The test tube was stirred at 200 rpm at 37°C and the sample suspension solution from the test tube in each analysis and serially diluted with water pepton buffer. A sample of 100 μL of this suspension then spread to the LB plate using a spread plate method. These plates were incubated for 24 hours at 37°C and colony forming units (CFU) were calculated. Reducing the percentage of bacteria is calculated according to:

\[
\text{Bacterial reduction (\%) = } \frac{(B - A)}{B} \times 100
\]

Where log means 10 bacterial densities for the treated substrate and B is an untreated substrate. There were no pure pu and modified pu used as control samples.

3. Result and discussion
The manufacture of castor oil based polyurethane coatings is to react the synthesized polyols with isocyanates. Isocyanates used toluene disocyanate (TDI). The castor oil polyol produced is slightly yellowish in colour, after being reacted with TDI and applied to the specimen the material remains a yellowish colour. Application of castor oil polyurethane coatings on material specimens with MMT fillers: CS 4%, 5% and 6%.orphological Analysis Using SEM.
3.1. FTIR analysis

![Figure 1](image1.png)

**Figure 1.** FTIR polyurethane castor oil (pure PU) spectrum, PU-MMT-CS 4%, PU-MMT-CS 5%, PU-MMT 6%.

The FTIR spectrum of polyurethane coating is shown in Fig. 1. The results of FTIR analysis have shown the formation of urethane groups N-H, C-H and C = O which indicate the formation of a polyurethane functional group (-NHCOO-) in the form of wavelength absorption of separate functional group bonds. The absorption of the N-H wave number widened at 3310 cm⁻¹, while the absorption of the wave C = O urethane group widened at 1724 cm⁻¹, and while the C-H group at 2918 cm⁻¹ absorption, whereas for the absorption of O-H wave numbers that widen at 3598 cm⁻¹.

3.2. Antibacterial test

![Figure 2](image2.png)

**Figure 2.** Thermogravimetric (TGA) characterization of pure PU (A), PUMJ-MMT-CS 4% (B), PUMJ-MMT-CS 5% (C), PUMJ-MMT-CS 6% (D).

Thermogravimetric (TGA) characterization of 4% (A) PU-MMT-CS Polyurethane, 5% (B) PU-MMT-CS, and 6% (C) PU-MMT-CS are shown in Figure 2. TGA analysis can be used to characterize any material that shows changes in material weight during heating, and to detect phase changes due to the decomposition process. At temperatures of 50°C-200°C indicate heavy losses due to evaporation of water and volatile compounds. At 345 °C there is a thermal increase. For polymer it was degraded -6.73 mg and the remaining 3.27 mg, for B polymer degraded -6.73 mg and remaining 3.27 mg, for C...
polymer degraded -5.84 mg and remaining 4.16 mg, for D polymers degraded -3.1 mg and remaining 6.9. From the results obtained, it can be concluded that the 6% PUMJ-MMT has the best thermal resistance.

3.3. Bacterial analysis

As shown in Figure 3, pure PU showed no antibacterial activity, whereas PU-MMT-CS 4% showed antimicrobial activity against S. aureus for a period of 120 hours (5 days), where antibacterial activity increased with increasing PU concentration. Although PU-MMT-CS 4% and PU-MMT-CS 5% showed several barriers to E. coli, antimicrobial activity was dependent on MMT concentration, and time. However, in this study there were also obstacles of PU-MMT-CS 4% and PU-MMT-CS 5% gradually decreased after 70 hours of treatment? After 70 hours, PU-MMT-CS 4% and PU-MMT-CS 5% released almost all MMT to the medium. Therefore, the final amount of MMT released into the medium slows down over time.

4. Conclusion
From the results of this research it can be concluded that the synthesis of castor oil polyol can be used as a raw material for polyurethane which is reacted with isocyanate in the form of TDI. The highest temperature polyurethane in the sample containing the highest MMT is PU-MMT-CS 6%. The higher the level of chitosan in polyurethane samples, the better the anti-bacterial properties.
Acknowledgements
The Author would like gratefully and acknowledgement thanks to Directorate of student Affairs and Education Ministry of Research Technology and Higher Education of Indonesia and Lhokseumawe Politecnic State.

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