Mechanical and thermal properties of biobased polyurethane / bentonit / chitosan nanocomposites for antibacterial coating

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Abstract

Polyurethanes (PU) is one of the most widespread material in the world. Polyurethanes is an important division of a synthetic polymer that has been used widely included in biomedical applications. Utilization of chitosan for anti-microbial properties of the material are also performed in this study, including testing to comprehend the development of harmful bacteria such as *Staphylococcus aureus*. Furthermore, the current development of the science of nanotechnology is not only to produce the anti-bacterial material, but also able to resist the thermal resistant. Therefore in this study, dispersion of bentonite nanocomposite as a filler material in the matrix as a reinforcement polyurethane to thermal insulation and improved mechanical properties of the coating materials. The results of the analysis of Fourier transform infrared (FTIR) have demonstrated the formation of clusters urethane N-H in the compound polyurethane palm oil, the reaction takes for 6 hours at a temperature of 80°C as evidenced by absorption wave number N-H widening out at 3320 cm⁻¹ and 3480 cm⁻¹. Analysis of x-ray diffraction (X-RD) is an effective method for measuring the crystal structure of pure bentonite and bentonite nanocomposite shows the result of d-spacing pure bentonite was 1,798 nm, pure chitosan was 1,142 nm, bentonite nanoparticles was 2,055 nm, chitosan nanoparticles was 1,571 nm respectively and polyurethane / bentonite / chitosan (PU/B/CH) nanocomposites were 3,386 nm. This d-spacing larger than that of the pure bentonite and chitosan.

Keynotes : polyurethanes, chitosan, bentonite, thermal, antibacterial

Introduction

Vegetable oil is the material available in nature, easily obtainable at reasonable 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 a material for making biodiesel, lubricants, cutting fluids (liquid cutting) (fluids for cutting and shaping metal material), paints and coatings, etc. [1].

In this decade, Polyurethanes (PU) is one of the most popular material in the world. Polyurethanes is an important division of a synthetic polymer that has been used widely in biomedical applications and a wide range of industries, especially the automobile industry. Products containing polyurethane coatings including furniture, synthetic resins, construction material, fiber, paint, elastomers, and synthetic leather materials [2].

In 2010, the global polyurethane market consumption reached 13.65 million tons, worth US$ 33 billion. The market research firm in the US named Market and Market (M&M) predicts
that global demand for polyurethane will grow by 4.76%/year until 2016. About 73% of polyurethane was consumed by the four segments of industry (28% furniture, 25% construction, 12% electronics, and 8% automotive industries). Demand for 2011-2016 is estimated to grow by about 7.3%/year. In 2010, about 13% or 1.77 million tonnes of the total consumption of polyurethane applied to the paint and coatings industry. Companies M & M predicts that this figure will rise by 4.9%/year to reach 2.36 million tons in 2016 [3]. When this has been a lot of use of bentonite nanocomposite as a filler material in a polyurethane matrix that is as reinforcement for retaining heat and increase the mechanical properties of the coating material [4].

Various research and development for the synthesis of polyurethanes has been done by several researchers with a variety of raw materials used to obtain polyurethane include, metilendifenildiisocyanate and polyl [5, 6, 7, 8], toluene diisocyanate and polyl [9], hexamethylenediisocyanate and polyl [10]. Meanwhile, to provide heat-resistant properties of the polyurethane material has been used bentonite [5, 7, 8].

From the results of research conducted by previous researchers to improve the heat resistance of the polyurethane material, the addition of bentonite in the polyurethane coating [5, 7, 8]. While the percent increase in the temperature of material obtained after being nanocomposite of 62% on 330°C [5], 490°C [7, 8].

In addition, the current development of the science of nanotechnology not only produce material that can withstand the heat but also anti-microbial. So in this study make use of chitosan nanoparticles as a filler material in the matrix polyurethane as an anti-microbial and an increase in heat-resistant properties of the coating material [9, 10].

**Experimental**

**Material**

Palm oil oleic acid, 100% and 2% acetic acid glacial, formic Acid, distillate water, aquadest, 200 mesh North Acehinese Bentonite, Cetyltrimethyl Ammonium Bromontide (CTAB), Glycerin, 50% H₂O₂, concentrated H₂SO₄, NaOH 0.1 N, Methanol, Metilendifenil 4,4-diisocyanate (MDI), molecule sieve. In outline the stages of this study include: 1) epoxidation palm oil followed by hydroxylation to produce polyol palm oil and its characterization, 2) the manufacture of polyurethane by polymerizing polyol with methylene diisocyanate and its characterization, 3) the preparation of bentonite nanoparticles and their characterizations, 4) preparation of chitosan nanoparticles and its characterization, 5) the manufacture of polyurethane paint/bentonite/chitosan nanocomposite and its characterization.

**Synthesis of Polyol**

1. **Epoxidation process**

30 mL 30% H₂O₂ was added 50 mL 100% CH₃COOH and 2 mL concentrated H₂SO₄ in 350 mL three neck flask equipped with a thermometer and a 200 rpm stirring speed condenser in 40-45°C for 1 hour to make paraatat acid. Furthermore, 100 mL oleic acid entering into a three-neck flask containing a mixture of acid paraatat. Heat, stir, and keep the mixture at 45-60°C for 5 hours. The product is cooled in room temperature and separation of the oil phase as epoxidised oil which is further used in the hydroxylation process [8, 13, 15, 16].

2. **The process of hydroxylation**
100 mL methanol was added 50 mL glycerin, 2 mL concentrated H₂SO₄, and 5 mL water in a 350 mL three neck flask, heat to 40°C. Mix plus epoxidized oil solution into a 350 mL three neck flask was stirred at 50°C for 2 hours. Furthermore, cooled to room temperature. Then transferred to a separating flask and the bottom layer disposed while polyol (top layer) is stored in a glass bottle. Subsequently analyzed by FTIR to determine the OH groups in the polyol [8, 13, 15, 16].

**Synthesis of Polyurethanes**

The synthesis of polyurethane using prepolymer methods that using the reaction of MDI with polyols based palm oil without adding other materials (solvent, catalyst or activator) following these procedures: Some polyol heated at 60°C for 1 hour in a 350 ml three-neck flask equipped thermometer and condenser. Put MDI (Metilendifenil Diisosianat) little by little, the solution was stirred for 6 hours with 200 rpm. The reaction was stopped after a point is reached and carried -NCO polyurethane refrigeration and stored in glass bottles under room temperature conditions. Then analyzed using FTIR to determine the polyurethane functional groups [7, 8, 10].

**Preparation of Bentonite Nanoparticles**

0.05 mole (18.2 grams) cetyl ammonium trimethylbromtontide (CTAB) and 250 mL distilled water is placed in a 500 ml beaker glass. The solution is heated at 80°C for 1 hour. Furthermore, 20 grams bentonite and 500 mL distilled water is stirred at separate place in 1000 ml beaker glass. Furthermore emperat bentonite is added to a solution of CTAB and stirred for 1 hour. Furthermore bentonite continuously washed with distilled water. Bentonite then placed for drying in an oven at 60°C. Bentonite filtered by a sieve tray with 100 μm size to produce bentonite nanoparticles. Furthermore bentonite analyzed using X-RD to determine the crystal structure of bentonite [5, 6, 7, 8].

**Preparation of Chitosan Nanoparticles**

4.25 grams chitosan was dissolved in 100 mL 2% glacial acetic acid solution while 500 rpm stirred for 2 hours at pH 4.0 to obtain a suspension of chitosan. Furthermore, the chitosan solution was dripped slowly into 50 mL 0.1 N NaOH chitosan nanoparticle suspension while washed using distilled water until neutral and dried in an oven at a temperature 60°C. Furthermore, chitosan nanoparticles were analyzed using X-RD to determine the crystal structure of chitosan nanoparticles [11, 12].

**Making Polyurethane/Bentonite/chitosan nanocomposite Coating**

Polyurethanes/Bentonite/chitosan nanocomposite mixed in glass beaker used a 600 rpm magnetic stirrer for 1 hour. In this procedure a number of bentonite and chitosan is used by mixing in polyurethane respectively of 0.5, 1.5, 2.5 weight percent (wt%). Total weight used in any mixing is 40 grams. Then analyzed the chemical structure of the polyurethane paint/bentonite nanocomposite using FTIR. Analysis of the crystal structure of bentonite nanocomposite used X-RD. Furthermore, the heat resistance of paint coatings were analyzed using TGA.

**Characterization Results**
1. **FT-IR Analysis**

Infrared spectroscopy of nanocomposite obtained with KBr pellet using a Shimadzu FTIR spectrophotometer. The spectra obtained in the mid-infrared region (4000-400 cm\(^{-1}\)) at room temperature.

2. **X-ray diffraction analysis**

X-ray diffraction (XRD) analysis in the samples was performed with a Shimadzu XRD-7000 X-Ray diffractometer Maxima with Cu anode tube. XRD analysis aims to determine the material's crystal form. Changes in the intensity of the diffracted measured, recorded and plotted against the diffraction angle (2). Analysis using XRD allows to determine the crystal structure, phase of quantitative and qualitative analysis, crystal size, as well as the calculation of lattice of a material.

3. **Thermogravimetric analysis**

TGA analysis used Shimadzu DTG-60. The sample is weighed with the mass mg and heated at room temperature up to 800°C with a heating rate of 20°C/min. The analysis was performed by raising the temperature of the sample gradually and determining the weight loss to changes of temperature. All specimens were tested under the flow of nitrogen gas.

**Results and Discussion**

**Results of Polyols from Palm Oil**

Epoxide palm oil is obtained from the reaction between paracetic acid and oleic acid. While parasetic acid produced from the reaction between hydrogen peroxide and glacial acetic acid with the aid of concentrated sulfuric acid catalyst. Hydrogen peroxide is used to oxidize the double bond into epoxide cluster in epoxidation process. Results epoxide palm oil obtained had a similar color to oleic acid in palm oil. Oil epoxide formed an intermediate compound that can react further to form a diol compound, because it has two places, namely reactive carbonyl groups can connect with fatty acid glycerides and epoxide groups. So that the process of formation of the polyol will happen when the epoxide groups react with alcohol. Reaction formation of epoxide compounds in vegetable oils have been done by the Gala (2011), Odetoye (2012), Harjono (2012), Hazmi (2013), Zaimahwati (2015).

![Epoxidation process of palm oil oleic acid](image)

**Figure 1.** Epoxidation process of palm oil oleic acid [8].

Polyol produced from oil hydroxylation epoxide derived from palm oil oleic acid epoxidation process. Polyol formation occurs when alcohol reacts with epoxide groups. In this hydroxylation process to use a mixture of methanol and glycerin, where the use of methanol in excess amounts can reduce the occurrence of cross linkage to the polyol obtained. The results of the analysis of FT-IR has demonstrated the formation of hydroxyl groups on the compound epoxide palm oil, the reaction lasted for 2 hours at 60°C as evidenced by absorption wave numbers OH flaring out at 3305.17 cm\(^{-1}\), 3391 cm\(^{-1}\) and 3433.44 cm\(^{-1}\), the formed hydroxy group is a hydroxy group at the secondary C atom. The results of the measurement of the hydroxyl
Results Characterization of polyurethane (PU)

Manufacture of polyurethane coating materials based on palm oil, which is reacting polyol with an isocyanate synthesis results. Isocyanate used methylene 4,4 diphenyldiisocyanate (MDI) is one of the isocyanate compound that highly reactive and has two isocyanate groups. In the manufacture of polyurethane prepolymer method used, that is a method in which the polyol component is reacted with a diisocyanate to form a prepolymer with isocyanate end groups, and there are still isocyanate excess.

In the experimental synthesis of polyurethane polyols are used 100 mL and 10 mL MDI, polyol was heated at 60°C for 1 hour and then dropped MDI slowly and the temperature is set at 80°C for 6 hours. When added to the isocyanate solution is brownish yellow and after the time of...
synthesis is achieved obtained polyurethane dark yellow. Subsequently analyzed by FTIR to determine the functional groups shown in Figure 3.

The results of the analysis of FT-IR has demonstrated the formation of clusters urethane N-H in the compound polyurethane palm oil, the reaction lasts for 6 hours at 80°C as evidenced by absorption wave number N-H flaring out at 3320 cm\(^{-1}\) and 3480 cm\(^{-1}\). The results of the measurement wavelength N-H group in a previous study that is 3300 cm\(^{-1}\) [9], 3311 cm\(^{-1}\), 3315 cm\(^{-1}\), 3316 cm\(^{-1}\) [8], 3345 cm\(^{-1}\) [10]. While absorption wave numbers -HNCOO- group widened at 1731-1734 cm\(^{-1}\), in a previous study in 1530 cm\(^{-1}\) [10].

Figure 3. FT-IR spectra of palm oil Polyurethanes (PU), Polyurethane/bentonite nanocomposite (PU/B), Polyurethanes/chitosan nanocomposite (PU/CH), and polyurethane/bentonite/chitosan (PU/B/CH).
Figure 4. Results of FTIR and films Pre-PUh, and PUh [10].

Based on the results of the analysis showed that the functional group from pure PU, PU/Bentonite, PU/Chitosan, and PU/B/CH nanocomposite unchanged functional groups. Mixing PU material bentonite and chitosan does not affect the absorption wavelength of functional groups polyurethane itself, just as the results of previous research on the analysis of FTIR PU, PU-plasma, PU-AAM, PU-CH-0.5, and PU-CH-2.0 [9], and Pre-PUh and PUh [10].

Characterization of Bentonite into montmorillonite

Bentonite taken in Teupi Reusep Muara Batu village, North Aceh, bentonite brownish gray (Figure 6.a), and montmorillonite (Figure 6.b). Based on the results of chemical analysis, bentonite from north Aceh containing 51.6% [17].
Organoclay is the result of modified bentonite with trimethyl surfactant cetyl ammonium bromide (CTAB), which with the addition of the surfactant can widen the area d-spacing bentonite layer itself. D-spacing layer is an area where polyurethane can enter into it when composited.

**Characterization of Bentonite and Chitosan Using X-RD**

Analysis of x-ray diffraction (X-RD) is an effective method for measuring crystal structure (d-spacing layer) of pure bentonite and bentonite nanocomposite. If the X-ray beam at the sample drop on the crystal, then the crystal will refract the field of X-ray that has a wavelength equal to the distance between the lattice in the crystal. X-rays refracted and captured by the detector is then translated as a diffraction peak.

The analysis shows the figure 4.4 d-spacing layer of pure bentonite 2° (d-spacing = 1,798 nm), 2.42° pure chitosan (1,142 nm), bentonite nanoparticles 3.06° (2055 nm), chitosan nanoparticles 7.08° (1,571 nm), and PU/B/CH nanocomposite that is 4.46° (3,386 nm). From the results it can be concluded that the d-spacing layer regions most wide PU/B/CH nanocomposite.

**Figure 6.** a. Bentonit, b MMT synthesis results
**Figure 7.** Results of X-RD analysis of pure bentonite, pure chitosan, bentonite nanoparticles, chitosan nanoparticles, and PU/B/CH nanocomposite.

*Characterization Using Thermogravimetric Analysis (TGA)*

Thermogravimetric analysis (TGA) of pure PU and PU/B/CH (Polyurethane/Bentonite/Chitosan) nanocomposite is shown in Figure 8. TGA images can be used to characterize any material that shows the weight change material upon heating, and to detect the phase change because of the decomposition process. Reduction of initial weight at 50-200°C PU pure sample as much as 5%, the decomposition of pure PU at a temperature 500°C. For PU/B/CH 0.5:0.5 wt% nanocomposite weight reduction at the start of 200-300°C at 5% and decomposition at 510°C, PU/B/CH 0.5:1.5% wt 512°C decomposition temperature, and PU/B/CH 0.5:2.5% wt decomposition at 514°C without remainder. At PU/B/CH 1.5:0.5 wt% reduction in baseline weight of 200-300°C at 5% and for the decomposition at a temperature of 518°C, PU/B/CH 1.5:1.5 wt% decomposition at a temperature of 520°C, and PU/B/CH 1.5:2.5 wt% decomposition at a temperature of 531°C. While PU/B/CH 2.5:0.5 wt% weight reduction in early nanocomposite also 200-300°C decomposition of 5% and at a temperature of 553°C, PU/B/CH 2.5:1.5 wt% decomposition at a temperature of 560°C, and PU/B/CH 2.5:2.5 wt% decomposition at 580°C, this proves that the PU/B/CH nanocomposite has increased thermal stability.
**Figure 8.** thermogram of the polyurethane nanocomposite, (a) PU:B:CH 0.5:0.5 wt%, (b) PU:B:CH 0.5:1.5 wt%, (c) PU:B:CH 0.5:2.5 wt%, (d) PU:B:CH 1.5:0.5 wt%, (e) PU:B:CH 1.5:1.5 wt%, (f) PU:B:CH 1.5:2.5 wt%, (g) PU:B:CH 2.5:0.5 wt%, (h) PU:B:CH 2.5:1.5 wt%, (i) PU:B:CH 2.5:2.5 wt%, (j) pure PU.

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<tr>
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<th>PU (%wt)</th>
<th>B : CH (%wt)</th>
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<tr>
<td>Sampel 1</td>
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<td>Sampel 2</td>
<td>38</td>
<td>0.5:1.5</td>
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<td>Sampel 3</td>
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<td>Sampel 4</td>
<td>38</td>
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<td>Sampel 5</td>
<td>37</td>
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<td>Sampel 6</td>
<td>36</td>
<td>1.5:2.5</td>
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From Table 2 it can be seen that increasing concentrations of bentonite and chitosan is added, the higher the thermal polyurethane nanocomposite itself, where the percent of increase in temperature obtained from this study is 86%. In previous studies of polyurethane nanocomposite thermal analysis has also been done by some researchers, such as the polyurethane/clay nanocomposite [5, 7, 8]. With the temperature attained percent increase above 62% [5]. The results of thermogravimetric analysis (TGA) 9. images in an earlier study POB-PU/MMT (PU MKS-Clay) weight reduction at the start of 150-200°C at 5% and decomposition at 490°C [8], whereas in this study PU/B/CH 2.5:2.5 wt% weight reduction was obtained at the beginning 200-300°C by 5% decomposition at 580°C.

![Figure 9. Commercial thermogram of PU, PU MKS, MKS PU-Clay [8].](image)

**Conclusion**

Oleic acid based on the principle of palm oil by epoxidation and hydroxylation reactions, with the addition of 4,4-methylene diphenyldiisocyanate and with the addition of bentonite / chitosan (B/CH), has successfully synthesized to produce polyurethane paint/nanocomposite. In this study, the decomposition of PU obtained at temperatures 500°C while the addition of B:CH 2.5:2.5 wt% is obtained at 580°C. It can be concluded that with the addition of bentonite and chitosan can improve the heat resistance of polyurethane which will be applied as paint coatings. The results showed that the bentonite after organophilic treated with surfactant be applied as the polymer matrix can improve optimal thermal stability.

**Literatures**


