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Polyurethane/Bentonite/Chitosan Blend for Improved Thermal and Protection Microorganisms for Paint Application

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Abstract. In this study polyurethane synthesis was carried out using the pre-polymer method using the reaction of *Toulana Diisocyanate* (TDI) with oleic acid-based palm oil polyols. To provide heat resistance properties for coating paint material, add bentonite (B) and chitosan (K) to polyurethane samples. The concentrations of bentonite and chitosan used were 1% b / b, 2% b / b and 3% b / b, respectively. Palm oil-based oleic acid polyol samples were analyzed for chemical compound structure using Fourier Transform Infrared (FTIR) obtained by O-H group at a wavelength of 3437.15 cm⁻¹. Preparation of bentonite and chitosan purification was done by adding cetyltrimethyl ammonium bromide solution to bentonite solution and CH₃ 3 COOH 2% solution and NaOH into chitosan solution, successfully increasing the d-spacing layer with the acquisition of 1.144 nm to 1.513 nm in bentonite and 1.117 nm to 1.475 nm in chitosan and an increase in the value of heat resistance is evidenced by the results of observations using XRD and Thermogravimetric Analysis (TGA).

1. Introduction

Progress in the field of material science is increasing, in the last few decades research on coating paints that are environmentally friendly continues to be pursued. Polyurethane is a material commonly used by the automotive industry as a coating material, because polyurethane has a large range of mechanical strength, excellent abrasion resistance, hardness and flexibility at low temperatures, and is resistant to corrosion and chemicals [2].

Polyurethane is a thermoplastic polymer that results from the reaction between polyols and isocyanates [3]. At present, polyols in polyurethane are generally synthesized from petroleum so that they are not environmentally friendly. In addition, with the limited availability of petroleum and fluctuating prices, the search for alternative petroleum substitutes as raw materials for making polyols must be carried out.

An alternative that can be used to minimize the use of petroleum is to use vegetable oil. Vegetable oil is an ingredient available in nature, easily available at affordable costs. Vegetable oil from natural sources is biodegradable and has the potential as a renewable natural resource for environmentally friendly materials. Some researchers have succeeded in synthesizing vegetable oil-based



polyurethanes. Polyurethane synthesis from various vegetable oils such as palm oil, sunflower oil, camelina oil, lanola oil and nulin oil has been successfully carried out [5]. While [7] has successfully synthesized polyurethane from neem oil. With the availability of vegetable oil abundant in nature, it is cheap and safe for the environment, so it is very suitable to be used [4].

In addition to improving the quality of paints and coatings produced and handling the thermoplastic properties of polyurethane, the addition of bentonite-chitosan polymer as a filler can be considered. Addition of bentonite into the polymer matrix shows an increase in thermal stability, fire resistance and corrosion resistance for surface coating applications [1]. In addition, according to the results of the study [10] shows that the intercalation of chitosan through the cation exchange process can improve the thermal stability and antimicrobial activity of nanocomposites.

In this study, the manufacture of vegetable oil-based polyurethane will be carried out. In order to be applied as a polyurethane coating, modification is carried out by adding bentonite to improve the physical and mechanical properties of polyurethane. The resulting polyurethane coating is further modified by the addition of chitosan to provide anti-bacterial properties, so that the paint obtained will not only have strength, stiffness, resistance to heat, corrosion resistance and chemicals.

2. Method

2.1. Material

The materials used in this research are polyol based on palm oil (with material such as: oleic acid based on palm oil, glycerol), Toluene diisocyanate (TDI), clay from North Aceh (Na^+ type), cetyltrimethylammonium bromide (CTAB) supplied from Fluka, octadodecylamine (ODA, Merck) and dimethylformamide (DMF, 4-molecular sulfuric acid, 99%, Fisher), Metallic sodium, n-hexane, sodium hydroxide, diethylether, xylene, polyethylene glycol and lead mono oxide, Dibutyl tin dilaurate (DBTDL), and ingredients commonly used for the manufacture of paints such as: titanium dioxide, MF resin, epoxy resin, n-butanol, barytes, silica, solvent CIX (nine carbon containing hydrocarbon) and Urea Formaldehyde (UF) Sodium Chloride (NaCl, Merck) resin, Ethyl Alcohol ($\text{C}_2\text{H}_5\text{OH}$, 95%, System) and Dioxane (Mallinckrodt). The epoxy resin used has a viscosity of 450 to 650 mPa at 25°C, epoxy equivalent of 182 to 192 g/equiv and a density of 1.15 g/cc at 25°C and a melamine resin.

2.2. Method

To produce this polyurethane through several stages of workmanship, here are the steps in general: 1) synthesis of palm oil-based polyols with epoxidation and hydroxylation steps and their characterization, 2) polyurethane preparation by polymerization of polyols with toluenediisocyanate and their characterization; 3) preparation of Clay and characterization, 4) preparation of nanocomposite chitosan and its characterization, 5) making polyurethane/clay/chitosan nanocomposite and its characterization.

2.2.1. Synthetic polyol of palm oil

A stirred reactor with three necked flasks of 250 ml, accompanied by a mechanical stirrer and a cooling system using a water batch. The optimum reaction is to mix 0.2 mol oleic acid (OA), 0.4 mol glycerol (gly), 0.025 moldodecylbenzene sulfonic acid (DBSA), and 30 grams of 3A molecular sieve. After filtration to release molecular sieve, the reactants are then washed with NaCl solution to remove residual unreacted glycerol.

2.2.2. Synthesis of Polyurethane

Polyol (12 grams) in a DMF solution is placed in a 3-liter neck flask of 0.5 liters. This equipment is equipped with mechanical stirrer, thermometer, heating mantle and input and gas output for continuous treatment. When the isoclinic synthesis temperature is reached (70°C), TDI (6 grams) is

added and stirred with a stirrer. The reaction temperature is continuously allowed to take place under conditions 70°C to 80°C and the sample is taken periodically to test the isocyanate content. After theoretically, the percentage value of NCO% of the reaction was stopped and cooling and the polyurethane was stored in a bottle under the condition of room temperature.

2.2.3. Preparation of clay

As much as 18.2 grams of cetyltrimethyl ammonium bromide (CTAB) was dissolved with 250 ml of distilled water in 500 ml of beaker glass, this solution was then heated at 80°C for 1 hour. Separated 20 grams of bentonite dissolved with 250 ml of distilled water on a 1000 ml glass beaker. Furthermore, dispersion of bentonite solution was put into CTAB solution and stirred for 1 hour. Strain, bentonite continues to be washed with distilled water several times until there is no more chloride or bromide. The filtrate was tested by dripping AgNO₃ 1M until no white precipitate was formed. Bentonite is put in an oven at a temperature of 60 °C, then filtered using a 100 µm sieve tray.

2.2.4. Preparation of nanocomposite chitosan

A number of Tripoli phosphate solutions were added to the chitosan solution. Distirer at 1200 rpm to obtain chitosan emulsion. Added acetic acid to make chitosan emulsion pH 3.5 with the result will be chitosan suspension. Furthermore, bentonite was analyzed to find out the structure of chitosan crystals.

2.2.5. Manufacture of Polyurethanes/Clay/Chitosan Nanocomposites

Polyurethane/Bentonite/Chitosan Nanocomposite mixed in a beaker glass using a stirrer. In this procedure, a certain amount of bentonite and chitosan is used by mixing in the polyurethane each of 1, 2, 3wt% (wt%). The total volume used in each mixing is 40 grams. Furthermore, chemical structure analyzed by using FTIR. Analysis of crystal structure of bentonite and chitosan nanocomposite.

2.3. Characterization Techniques

2.3.1. FTIR Spectroscopy Analysis

FTIR is a very common tool used to identify chemical solutions of both organic and inorganic materials. This tool can also be applied to analyze solids, solutions and also gases. FTIR generates data that can be analyzed in the form of interfaces and also in the form of spectrum.

2.3.2. X-Ray Diffraction (XRD)

XRD is used to test the expansion of the bentonite layer used as a filler for the polymer. The XRD graph is Obtained through a detector called Scintag Pad V theta-2 theta goniometer and Si (Li) Peltier detector, and by using CuK α radiation at wavelength $\lambda = 1.540562$ angstroms.

2.3.3. Thermogravimetric Analysis (TGA)

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

3. Result and Discussion

3.1. FTIR Spectroscopy Analysis

In this study, the use of palm oil oleic acid was used as a vegetable oil-based polyurethane constituent. The selection of palm oil as a raw material for making polyols is based on abundant availability, natural sources are renewable and have unsaturated fatty acid content greater than saturated fatty acids.

Epoxidation oil from palm oil is obtained from the reaction between paracetate acid and oleic acid. The epoxide oil formed is an intermediate compound that can react further to form diol compounds, because it has two reactive sites, namely carbonyl groups that can connect glycerides with fatty acids and also epoxide groups. So that the process of forming polyols will occur if the epoxide group reacts with alcohol.

The polyol products that have been produced are tested qualitatively using Fourier Transform Infra-Red (FTIR). The results of FT-IR spectroscopic analysis of polyol compounds were carried out to detect or shift the peaks which can be related to the reaction process that is shown in Figure 1.

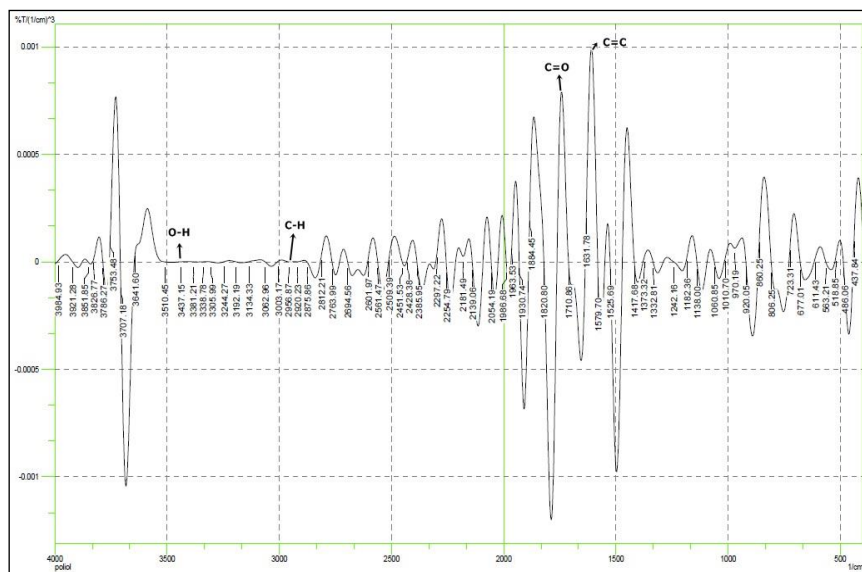


Figure 1. FTIR Spectra of Polyol Synthesis Based on Palm Oil

The spectrum of group C = O (carbonyl) at transmission 1680-1750 cm^{-1} shows that the palm oil oleic acid polyol is 1710.86 cm^{-1} . The presence of group C = C is shown in the transmission of wave numbers 1550-1670 cm^{-1} . In the polyol raw material, the wave number obtained is 1631.78 cm^{-1} . The polyol compound from palm oil oleic acid which has occurred at the initial stage is the formation of intermediates between epoxide compounds through the reaction between hydrocarbons not saturated with palm oil and formic acid. The results of FT-IR analysis have shown the formation of hydroxyl groups on the epoxide compound of palm oil, the reaction lasts for 2 hours at a temperature of 60°C as evidenced by the absorption of OH wave numbers widened at 3305.99 cm^{-1} , 3338.78 cm^{-1} , 3381.21 cm^{-1} and 3437.15 cm^{-1} . The hydroxy group formed is the hydroxy group in the secondary C atom. The results of measurements of the hydroxyl group wavelength in the previous study were 3475 cm^{-1} [9], 3396 [11], 3384.90 cm^{-1} [8], 3412.38 cm^{-1} [6].

The presence of hydroxyl groups is determined by absorption of wavelengths between 3000-3600 cm^{-1} . This states that the reacted compounds have formed the desired polyol product from the formation of the hydroxyl group.

3.2. X-Ray Diffraction (XRD)

Addition of bentonite and chitosan as function fillers to improve the physical properties of the resulting polyurethane coating paint. Purification stages of filler materials are bentonite and chitosan are the first part that must be passed before the two materials are reacted together with polyurethane. This purification step is intended to remove impurities contained in bentonite and chitosan. While the opening stage of d-spacing with surfactant aims to increase the distance between layers formed in bentonite and chitosan, so as to maximize filler interaction [11].

Bentonite and chitosan from purification could experience swelling (the power expands) so that the polymer can be intercalated into the mineral gallery and form nanocomposites. This swelling will affect the quality of the bentonite produced during mixing.

X-ray diffraction (X-RD) analysis is an effective method for measuring crystal structures. If a beam of X-rays is dropped on a crystal sample, the crystal field will refract the X-rays which have a wavelength equal to the distance between the sides of the crystal. X-rays are refracted and captured by the detector then translated as a diffraction peak. This analysis aims to determine the components and amount of minerals contained and the large opening of the interlayer layer (d-spacing). Changes in diffracted intensity are measured and plotted against the diffraction angle (2θ). Figure 2 below shows the results of the large test opening of the d-spacing layer of bentonite and chitosan layers.

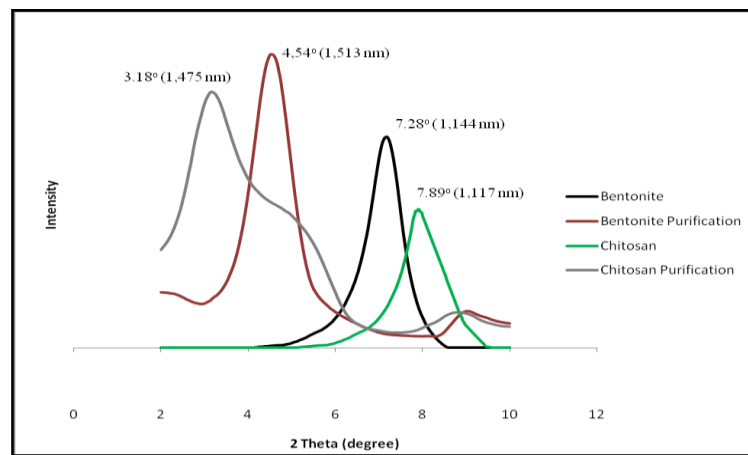


Figure 2. Graph of XRD Analysis Result

Based on Figure 2, the d-spacing layer of the two types of filler namely bentonite and chitosan before and after opening results in values that are not significantly different. By using a peak setting of 2θ which produces data at a reflection angle of 2° to 10° , it shows that, bentonite before purification has a peak maximum reflection angle at 7.28° with a d-spacing value of 1.144 nm, and the d-spacing size increases to 1.513 nm at the peak of the maximum reflection angle 4.54° . While the chitosan before purification has a d-spacing size of 1.117 nm at the peak of the maximum reflection angle of 7.89° and has increased at 3.18° with a d-spacing value of 1.475 nm after purification. This proves that by opening the layer distance (d-spacing layer) on bentonite and chitosan it can improve physical properties.

3.3. Thermogravimetric Analysis (TGA)

The study of thermal stability determined by thermogravimetric analysis (TGA) was carried out for the degradation of the characteristics of specimens using TGA. All measurements are carried out under nitrogen flow (20 ml / min), maintaining a constant heating rate of $10^\circ\text{C} / \text{min}$ and using an alumina container. Thermal stability is a very important parameter for the processing and use of materials. The manufacture of these composites requires mixing of fillers and matrices at high temperatures, so that the effect of degradation on the properties of ingredients containing fillers can be calculated. Several research reports have been investigated on the study of thermal stability of Polyurethane / Bentonite / Chitosan through TGA. The following is a graph of the TGA test results on ten polyurethane samples that have been added with bentonite fillers and chitosan and pure polyurethane without mixing with filler [12].

Thermogravimetric analysis (TGA) of pure PU and PU/B/K (Polyurethane/Bentonite/Chitosan) nanocomposites shown in Figure 3 TGA can be used to characterize any material that shows changes in material weight during heating, and to detect phase changes due to the process decomposition. Reduction of the initial weight of PU puree samples at $50\text{--}250^\circ\text{C}$ by 5%, decomposition of PU puree at

500°C. For PU / B / K 1: 1% b/b nanocomposite weight reduction at the beginning of 50-300 °C by 5% and decomposition at 510°C, PU/B/K 1: 2% b/b decomposition at 512°C, and PU/B/K 1: 3% b/b decomposition at 514°C without residue. In PU/B/K 2: 1% b/b initial weight reduction of 50-300°C by 5% and for decomposition at 518°C, PU/B/K 2: 2% b/b decomposition at 520°C, and PU / B / K 2: 3% b/b decomposition at 531°C. Whereas PU/B/K 3: 1% b/b nanocomposite weight reduction at the beginning was also 50-300°C by 5% and decomposition at 553°C, PU/B/K 3: 2% b/b decomposition at 560°C, and PU/B/K 3: 3% b/b decomposition at 580°C, this proves that the PU / B / K nanocomposite has experienced an increase in thermal stability [13].

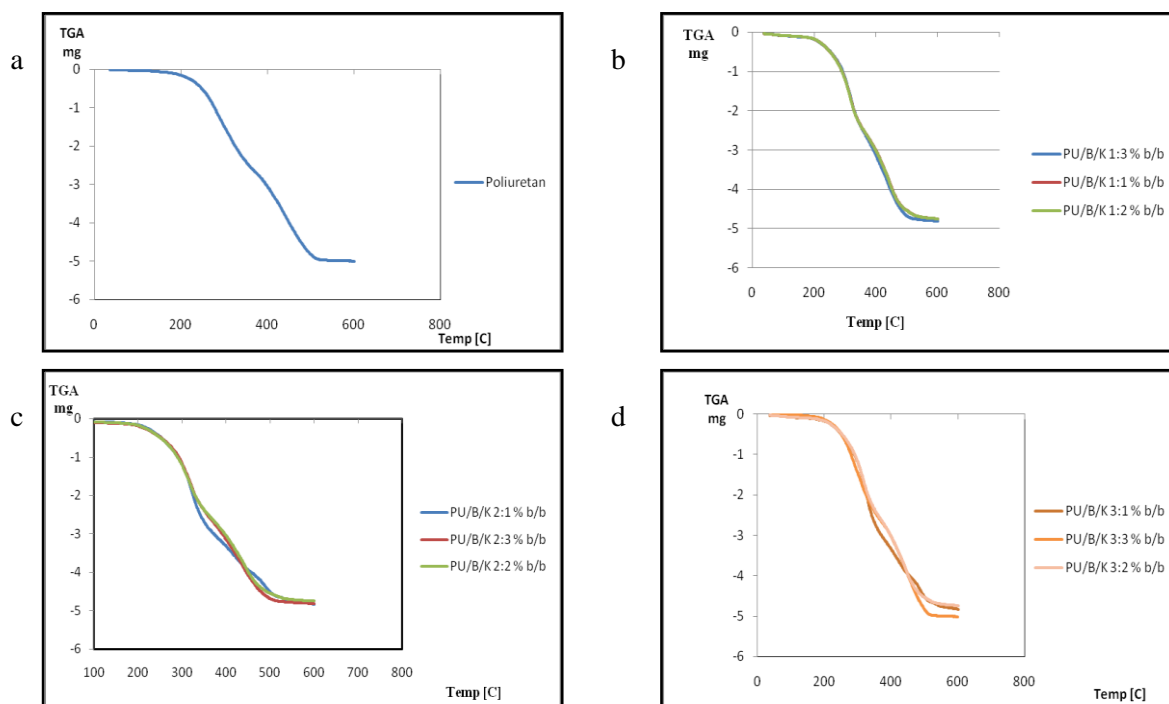


Figure 3. Thermogram of nanocomposite polyurethane, pure PU, b PU/B/K 1: 1% b/b, PU/B/K 1: 2% b/b, PU/B/K 1: 3% b/b, c PU/B/K 2: 1% b/b, PU/B/K 2: 2% b/b, PU/B/K 2: 3% b/b, d PU/B/K 3: 1% b/b, PU/B/K 3: 2% b/b, PU/B/K 3: 3% b/b.

4. Conclusion

The manufacture of polyols based on oleic acid in palm oil through the process of epoxidation and hydrolysis reaction, with the addition of toluenediisocyanate and bentonite-chitosan fillers has been produced to produce polyurethane / bentonite / chitosan nanocomposite paints. From the results obtained in FT-IR analysis the absorption of -OH groups widened at a wavelength of 3305.99 cm^{-1} , 3338.78 cm^{-1} , 3381.21 cm^{-1} and 3437.15 cm^{-1} . Based on the XRD curve, purification stages for bentonite and chitosan can increase the d-spacing layer in the filler with the acquisition of 1.144 nm to 1.513 nm in bentonite and 1.117 nm to 1.475 nm in chitosan. As well as based on the thermal test, it was found that the polyurethane coating added with the filler material had increased heat compared to polyurethane without the filler material.

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