



Modification of polyurethane coating based on palm oil with filler bentonite to improve heat resistant properties

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Abstract

This work aims to prepare and characterize polyurethane nanocomposite sequences modified with bentonite as fillers and palm oil as a soft segment component while Toluene Diisocyanate (TDI) was chosen as a hard segment component. Bentonite fillers are needed to provide heat resistance to the polyurethane coating. Morphological, structural and thermal polyurethane nanocomposites are characterized by SEM, FTIR, and TGA. FTIR analysis is the NH urethane group in palm oil polyurethane compounds while the absorption of C=O urethane group widens at 1735 cm⁻¹. While the CH group occurs at absorption wavelengths of 2120-2180 cm⁻¹, adding bentonite (7% by weight) is completely laminated and well dispersed in the form of a mixture of peeling / intercalating layers in the polymer matrix. Polyurethane nanocomposites have a morphology separated by clearer microphase. The resulting thermal stability is higher compared to the addition of bentonite 3 and 5% by weight. Because of its enhanced features, the polymer developed can be considered a material with heat resistance as a coating.

Keywords: Polyurethane, Bentonite, Polyol, Palm Oil and TDI (*Toluene Diisocyanate*).

1 Introduction

The fact that technology development has been in quick progress is nowadays a benchmark for developing anti-bacterial coatings that can be used on medical devices. The method that can be done by engineering material, or often referred to as modification. One of them is the manufacture of polyurethane. Environment friendly research on paints and coatings continues to be carried out to date. Polyurethane as a coating material has been widely employed as a coating material, hardness and flexibility at low temperatures, and has resistance to corrosion and chemicals [1].

Polyurethane (PU) is a copolymer block containing hard and soft segments in which the semicrystalline hard segment is formed by the reaction of the polyisocyanate and extender chain (diol/diisocyanate). And the soft segment consists of a polyol chain [2]. At present, polyols in polyurethane are synthesized from petroleum. The availability of petroleum which is running low now encourages others to look for new alternatives as substitutes for petroleum. One alternative that can be used is vegetable oil. The synthesis has been carried out with various vegetable oils such as canola oil, camelina oil, lanola oil, sunflower oil, nulin oil [3], and neem oil. Then the synthesis of polyurethane from vegetable oil obtained from various types of plants such as jatropha, oil palm, soybeans, and cotton [1]. In other words, vegetable oil can replace petroleum (petrochemical) as a raw material for making polyols. Besides, the use of polyols from

vegetable oils is superior because of their abundant availability in nature and easily biodegradable.

In this study, palm oil was used for polyol synthesis. The current information about polyols originating from palm oil is still limited. The main components which are triglycerides are the glycerol triester and unsaturated fatty acids. Because of the unsaturated fatty acid content, palm oil can carry out epoxidation and hydroxylation reactions to form polyols which will be used for the manufacture of polyurethanes.

Polyol is an organic compound that has more than one hydroxyl group in the material industry is used very widely in both reagents and additives. The characteristics of polyurethane produced are very dependent on the amount of crosslinking that occurs in the hydroxyl group because it determines the molecular weight obtained. The lower the molecular weight, the more the molecular weight of the polyol chain, and the more polyurethane produced is more flexible [4]. Polyols can be made by opening epoxy rings of oil using sulfuric acid catalysts, phosphoric acid, hydrochloric acid, and organic acids such as sulfonic acid [5]. The double bond part which is the unsaturated part can be opened through the epoxidation process and the next process will produce a hydroxyl group through the hydroxylation process. This compound contains the hydroxyl group that is called the polyol.

Polyurethane has properties that are very easily modified with other materials. In addition to improving the quality of the paint and coating

materials and handling thermoplastic properties in polyurethane, the material is chosen to improve the mechanical properties of the polyurethane. Bentonite obtained from the purification of clay can be used as a filler (filler) in polyurethane. Bentonite contains 50 – 80 % montmorillonite and the rest are impurities. Therefore, to improve the physical properties of bentonite such as mechanical properties and thermal resistance, bentonite purification must be done first with sedimentation before the surface treatment step is carried out [6]. In addition, bentonite was carried out into the polymer matrix by showing an increase in thermal stability, fire and corrosion resistance for coating applications.

Polyurethane is basically a copolymer block formed by a polyaddition reaction of three main components including diol or polyol, diisocyanate or polyisocyanate, and extender chain. In practice, only a few isocyanates are commonly used to prepare PU and most of them are aromatic compounds such as 4,4'-methylenebis (phenyl isocyanate) (MDI), toluene diisocyanate (TDI), and some aliphatic compounds such as hexamethylene diisocyanate (HDI), or cycloaliphatic compounds such as 4,4'-diisocyanate dicyclohexylmethane (H_{12} MDI) or hydrogenated MDI [7].

The advantage of polyurethane coatings is that polyurethane generally shows fumigation or drying at room temperature. In some cases where the coating material shows a high fogging or drying temperature ($> 100^{\circ}C$), it is reacted with isocyanates to reduce the fumigation temperature from high to ambient temperature [5]. In the coating industry, that polymer is widely used because of its scratch resistance, stiffness, hardness, flexibility and resistance to abrasion can be applied in various fields [8].

Although there are many advantages possessed by polyurethane, there are disadvantages that have become natural, namely lower heat resistance more than other polymers. Therefore, to cover these deficiencies, modifications will be made through the addition of montmorillonite (MMT) or commonly known as bentonite mixed into a polyurethane matrix.

The use of bentonite in engineering materials (composites) that is one of them the application of bentonite as a nano-sized filler (filler) and better known as nanofiller. The compatibility of a filler material with a polymer matrix is influenced by particle size whose a small filler can increase the degree of polymer reinforcement by a larger size, as well as the smaller particle size the higher the bond between the filler and the polymer matrix.

Modification of clay surface is important to be able to form the interlayer and dispersion of clay in order that the desired properties will be obtained. Modifications can be made by adding surfactants in which the bentonite which was originally hydrophilic is fruitful to become organophilic. The modified bentonite is called organoclay. Changes in bentonite

properties are the result of replacing inorganic cations in bentonites with diffraction organic cations. With the entry of surfactants into bentonite, d-spacing in bentonite will become larger (intercalated).

Isocyanate is the main monomer in polyurethane formation. The Isocyanates have very high reactivity, especially with nucleophilic reactants. The reactivity of the cyanate group ($-N = C = O$) is determined by the positive properties of the natural carbon cumulative double bond consisting of N, C, and O. Commonly used as diisocyanates is 2,4-toluene diisocyanate (TDI), 4,4'-methylene-bis phenylisocyanate (MDI), 1,6-hexamethyl diisocyanate (HDI), 2,2,4-trimethyl-1,6-hexamethyl diisocyanate (TMDI), and 1,5-naphthacene diisocyanate (NDI). The selection of isocyanates to be used to make polyurethane is largely determined by the properties and characteristics of the desired polyurethane end product. For example, to obtain rigid and hard polyurethanes, aromatic isocyanates are used although the resulting polyurethane compounds are less stable against ultraviolet oxidation and sinat [4].

This study generally aims to make polyurethane coatings modified by adding fillers such as the bentonite. Also, the effect of the addition of bentonite on the coating polyurethane produced.

2 Methodology

This research is divided into five sub-sections, namely: 2.1) Stage of raw material preparation, 2.2) Stage of making polyol, 2.3) Stage of purification of bentonite, 2.4) Stage of making polyurethane, and 2.5) Stage of analysis.

2.1 Stage of Raw Material Preparation

Vegetable oil used in this study is palm oil from the Cot Girek, in North Aceh. The palm oil used that has been through FTIR analysis to see the presence of hydroxyl groups from oil while the isocyanate used is Toluene Diisocyanate (TDI) supplier from Chemical Reagent Co., Ltd. Then in the preparation phase of bentonite from North Aceh, purification needs to be done first to remove impurities.

2.2 Stage of Making Polyols

The stage of making this polyol consists of two stages, namely the epoxidation reaction and the hydroxylation reaction. These reactions should be carried out in successive times and do not provide a long time interval to proceed to the next reaction which will cause a decrease in the hydroxyl number. In the epoxidation stage, the palm oil used is reacted with CH_3COOH and H_2O_2 and using an H_2SO_4 catalyst to form an epoxide compound. Then, Palm Oil proceed with the hydroxylation reaction which reacts with oil that has been oxidized with alcohol, then the catalyst and water to produce hydroxyl groups from opening the epoxide ring.

2.3 The Stage of Purification of Bentonite

In the purification stage, bentonite is carried out by adding surfactants to the bentonite which has undergone a reduction in size up to 100 meshes. The surfactant used is Cetyl Trimethyl Ammonium Bromide which functions to enlarge d-spacing in bentonite. Then, the filtrate is washed with AgNO_3 solution until a white precipitate is formed and followed by drying bentonite in the oven.

2.4 Stage of Making Polyurethane

In the process of making polyurethane, isocyanate and palm oil are reacted. However, to increase the heat resistance properties of the resulting polyurethane, purified bentonite is added. Bentonite was added with each weight to see how the influence of the increased use of bentonite on polyurethane on the properties of heat resistance.

3 Research Procedure

3.1 Making Polyol

The process of polyol synthesis passes through two stages, namely the epoxidation and hydroxylation. In the epoxidation stage, the polyol synthesis process is carried out in The 350 mL- three-neck rounded flask equipped with a mechanical stirrer and cooling system. In the reactor, 60 mL of 100% CH_3COOH was added and 30 mL of 30% H_2O_2 was slowly stirred. Through the dropper funnel, 2 mL of concentrated H_2SO_4 were added and stirred slowly at 30°C for one hour. Then, through the dropper funnel, it is added slowly as much as 100 mL of palm oil oleic acid. The temperature is maintained at 30°C and continued to be stirred about three 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, there were as much as 100 mL of methanol and 50 mL of glycerin, a concentrated H_2SO_4 catalyst of 2 mL and 5 mL of water into a 350 mL three neck flask were added and 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 in two hours. After that, it is cooled at room temperature and transferred to a separate flask to isolated the polyol formed and stored it in a glass bottle. Furthermore, it was analyzed by FTIR to determine OH groups in polyols.

3.2 Bentonite Purification

A total of 18.2 grams of Cetyl Trimethyl Ammonium Bromide (CTAB) were dissolved with 250 mL of aquadest in a 500 mL beaker glass. his solution was heated at 80°C for 1 hour. In a separate place, 20 grams of bentonite are dissolved with 250 mL of aquadest in a glass beaker of 1000 mL. Furthermore, dispersion of bentonite solution was put into CTAB solution and stirred for one hour.

Bentonite is filtered and then washed with distilled water several times until there is no more bromide. The filtrate was tested by dripping AgNO_3 1M until a white precipitate was formed. Bentonite is put into an oven at 60°C , then filtered by using a $100\ \mu\text{m}$ sieve tray.

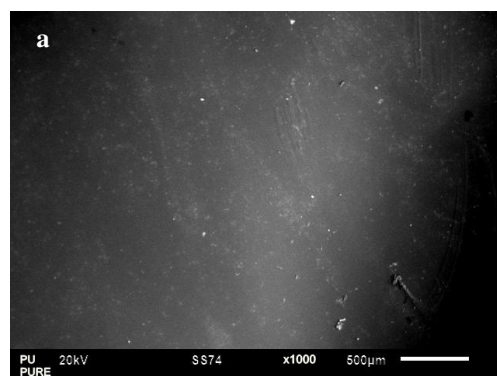
3.3 Polyurethane coating Manufacturing

Palm oil mixed with polyol, bentonite, and then the TDI into the beaker glass stirred with a magnetic stirrer at a speed of 600 rpm for 1 hour. In this procedure, a number of bentonites were used 3, 5 and 7 weight percent (wt%) respectively. The resulting polyurethane is then cooled at room temperature. Furthermore, the chemical structure of polyurethane and bentonite paints were analysed by using FTIR. Analysis of coating heat resistance was analyzed by using TGA and surface shape analysis by SEM.

4 Results and Discussion

4.1 Characterization Morphology of Polyurethane Nanocomposite Using SEM

In order to determine the morphology of polyurethane composites, SEM analysis was carried out. SEM micrographs for polyurethane nanocomposites at 500x and 1000x magnification are presented in the figure 1 (a-d) on SEM micrographs distributed homogeneously in a lighter polymer matrix representing individual layers of bentonite nanoparticles. Homogeneous dispersion of the bentonite layer appears more clearly at 7% by weight (figure 1 (d) seen as the darker domain of polyurethane and the lighter (white) domain of bentonite particles that spread randomly in the polymer matrix. In addition, bentonite nanoparticles are dominated by morphologically exfoliated with a small amount that has intercalation morphology of polyurethane nanocomposites [11]. Mixed structures obtained from the structure of bentonite in polyurethane nanocomposites may be caused by the reaction between the hydroxyl group $-\text{CH}_2\text{CH}_2\text{OH}$ in bentonite with TDI isocyanate groups and prepolymers. Therefore, the bentonite layer can become peeled and well dispersed in the polymer matrix. Similar morphological results were obtained by other authors [12-14].



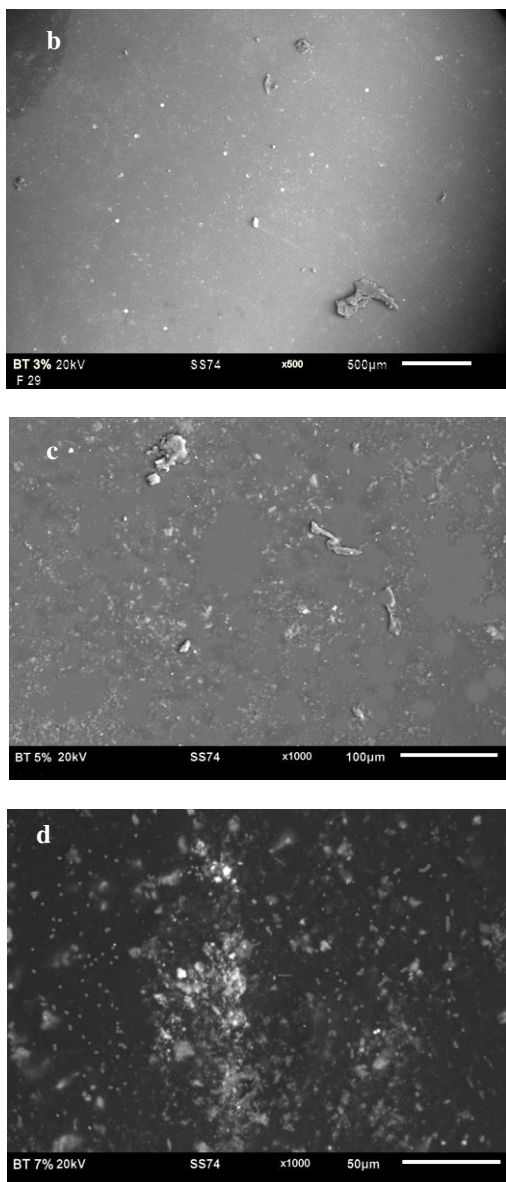


Figure 1. SEM micrographs of the selected nanocomposites polyurethane with (a) polyurethane pure (b) 3 wt% (c) 5 wt% (d) 7 wt%

4.2 Characterization Structural of Polyurethane Nanocomposite Using FTIR

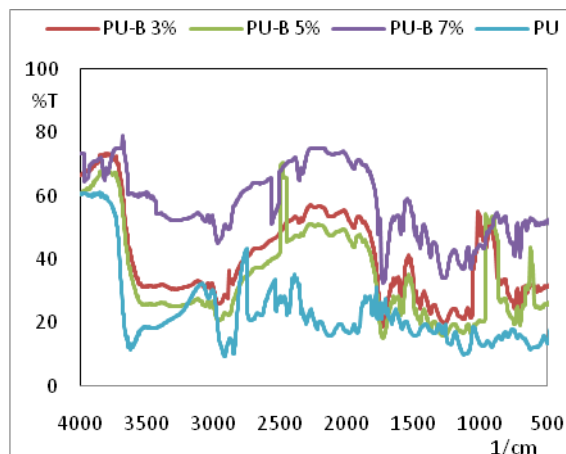


Figure 2. FTIR characterization of pure polyurethane samples and with the addition of bentonite fillers

The results of FTIR characterization have shown the formation of the N-H urethane group in palm oil polyurethane compounds. The reaction which lasted for 2 hours with a temperature of 60°C was proven by wave number absorption of 3374 cm^{-1} . While the absorption of C=O urethane groups widened at 1735 cm^{-1} and the C-H group occurred at wavelength absorption of 2120-2180 cm^{-1} . From the results of the analysis obtained, shows that the formation of polyurethane is found from the presence of wavelength uptake in the functional groups N-H, C=O urethane and C-H. Likewise, the polyurethane functional group in the formula -NHCOO- which has been recorded.

4.3 Thermal characterization of Polyurethane Nanocomposite Using TGA

Thermogravimetric (TGA) characterization is used to determine the change in weight of each material that occurs due to heating. Thermogravimetric also detect changes due to decomposition. In pure polyurethane (PU) samples, the initial weight reduction occurs at 50-600°C, decomposition of pure PU at a temperature of 200°C of - 8.07 mg and remaining 1.93 mg.

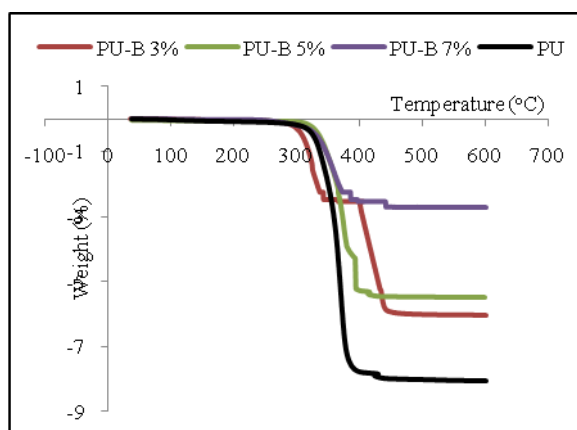


Figure 1. TGA characterization of pure polyurethane samples and with the addition of bentonite fillers

As polyurethane with the addition of bentonite (PU-B) 3%, there was an initial weight reduction at a temperature of 470°C of -6.06 mg and remaining 3.94 mg. At 5% PU-B and it occurred at 510°C of -5.5 mg and the remaining 4.5 mg. At 7% PU-B, there was an initial weight reduction at 570°C of -2.73 mg and the remaining 7.27 mg. From the resulting data, it can be understood that polyurethane with the addition of bentonite fillers can experience increased thermal stability. And the best stability is at U-B at 7%.

5. Conclusion

Polyurethane nanocomposites based on a combination of soft (palm oil) and hard (TDI) segments with the addition of bentonite fillers (3%, 5% and 7% by weight). According to the results obtained, bentonite is oriented towards hard and soft segments. SEM analysis revealed homogeneous dispersion and the presence of dispersed bentonite morphology in the Polyurethane matrix. FTIR analysis shows the C = O group at a wavelength of 1735 cm⁻¹ and the C-H group at a wavelength of 2120-2180 cm⁻¹. According to the TGA analysis, the addition of bentonite by 7% by weight causes an increase in the thermal stability of polyurethane nanocomposites. It is said that the higher the percent of bentonite added to PU, the better the heat-resistant properties.

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