Synthesis and Characterization Thermal of Polyurethane/MMT from Castor Oil Polyols for Coating

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Abstract. The purpose of this research overall is the manufacture of polyurethane nanocomposite from castor oil with the addition of montmorillonite nanoparticles as coating material. This study consists of several stages, the manufacture of montmorillonite nanoparticles (MMT), the process of forming polyols from castor oil by epoxidation and hydroxylation reactions with catalysts. The manufacture of polyurethanes (PU) by reacting polyols from castor oil and organic montmorillonite nanoparticles was then characterized and applied to polyurethane nanocomposites as coating materials. Organic montmorillonite nanoparticles are made by an intercalation process with cetyl trimethyl ammonium bromide (CTAB). Polyurethane nanocomposite was prepared by adding organic montmorillonite nanoparticles in polyols before being mixed with toluene diisocyanate. The effectiveness of polyurethane nanocomposites as heat-resistant coatings was determined by thermal properties with thermo gravimetric analysis (TGA) equipment, then the adhesive strength was tested and the morphological properties of the material coating. The manufacture of polyurethane nanocomposite from castor oil as a film coating is applied to material and characterization.

1. Introduction

Jatropha oil (Jatropha curcas Linn) is a source of vegetable oil and is a triglyceride that can be distinguished from other triglycerides from its fatty acid composition. The fatty acids that make up the Jatropha oil include oleic acid (35-64%), linolenic acid (19-24%), palmitic acid (12-17%) [1]. Jatropha oil has its main constituent component is 77.3% unsaturated fatty acids. The existence of double bonds on organic compounds of unsaturated fatty acids through the epoxidation reaction followed by
hydroxylation will produce polyol compounds, as well as epoxidation of alkene compounds in the formation of diol compounds. Previously, epoxide was carried out on candlenut oil which was used as a softener in polyurethane foam [2]. Jatropha oil is an alternative raw material that can be used to produce polyol compounds [3]. Polyol made from vegetable oil have advantages, compared to Polyol made from petroleum (petrochemical), because in addition to the source they can be renewed and are easy to obtain and are more environmentally friendly [4]. A polyol is one of the polymer products used in the polyurethane type coatings and adhesives industry, where polyurethane requirements including polyol compounds are still fulfilled through imports from abroad.

A polyol is an organic compound that has more than one hydroxyl group and in the material, the industry is widely used both as a reagent and additive. Polyol compounds can be obtained directly in nature such as starch, cellulose, sucrose, and lignin or processed chemical industry. Industrial processing of these compounds is still widely carried out by relying on the processing of petro chemical industries where raw materials are derived from natural gas and petroleum is limited and cannot be renewed in addition to processing requires large amounts of energy, so it needs to be developed to be examined as an alternative material. Polyol from vegetable oils have been widely developed to replace petroleum-based Polyol in the manufacture of polyurethane and polyester, and have also been widely used as plasticizers in polymer matrices to produce a material, as well as softeners and stabilizers that aim to obtain certain hardness and softness so that the material It is easy to form various types of goods as needed [5] Polyol are part of polyurethane technology which is important after the isocyanate group, the hydroxyl functional is the polyol commonly used to form polyurethane derived from polyester or polyether or materials from nature, such as oil palm [6]. This polyol can crystallize, and this is an important aspect in several applications such as an adhesive [7]. Polyol developed specifically from vegetable oils for coating applications are reported by [8] also coatings from Jatropha oil [9]. The use of vegetable oil as a raw material for Polyol has several advantages, including; suitable for various types of surfaces, has a reactive functional group for drying with cross linkers, it is possible to be modified, cheaper, renewable and commercially available and Polyol derived from vegetable oils can be applied. The hydroxyl group in polyol resin has several important functions in coating materials in polyurethane systems. Its functions and uses include hydroxyl groups that play a role in cross linking with other groups, affecting the adhesion to metal substrates and improving compatibility with various types of resins and solvents.

Polyurethane is a polymeric material containing a urethane functional group (-NHC=O-) in its main chain, a urethane group formed from the reaction between an isocyanate group and a hydroxyl group. Polyurethane is a polymer material that is very easily formed for a variety of applications, including produced as foam, elastomers, plastics, material and adhesive surface coatings. Polyurethane in addition to its many advantages also has shortcomings that have become its natural characteristics, namely the ability that is very low to heat when compared with other polymers [10]. With the method commonly used to improve the mechanical properties of polyurethane involves various fillers to strengthen it. Some literature reports as fillers in polyurethane namely, lime, aluminum hydroxide, starch, silica and kaolin, graphite, the natural zeolite can increase heat from polyurethane foam [11].

Montmorillonite is one of the applications that is currently being studied because of its use as a nanosized filler known as nanofiller, which can be applied to polymeric materials to produce nanocomposite materials with only small quantities, increasing the basic properties of polymers, such as heat resistance, mechanical properties. The nanoparticle layer which can be intercalated and exfoliated makes it widely used as a nanocomposite filler to improve the physical properties of the nanocomposite [12]. In this study the development of Jatropha oil-based polyurethane nanocomposite material with the addition of montmorillonite nanoparticles. The purpose of adding a montmorillonite to increase the coating of heat-resistant material.
2. Experimental

2.1 Material
Castor oil, Glycerol 85% (Merck), dietyl metana diisocyanate (Merck), Peroxide 35% (Merck), glacial acetic acid (Merck), H$_2$SO$_4$ 96% (Merck), dibutyltin dilaurat (Merck), cetyl trimethyl ammonium bromide (Merck), Toluen diisosinat (TDI) Aldrich, Etanol 97% (Merck).

2.2 Epoxidation and Hydroxylation of Castrol Oil
Firstly, 60 ml of glacial acetic acid was put into reactor while 30 ml of 35 percent H$_2$O$_2$ added gradually while being stirred. Using funnel dropper, 2 ml of concentrated H$_2$SO$_4$ was added and stirred in the temperature of 40-45°C for 1 hour. Then, 100 ml of castor oil was added using funnel dropper at the same temperature while being stirred for 2 hours. The reaction result is an epoxy compound of oleic acid which later being separated from water phase. Then, waterbath was connected to the reactor, 50 ml of glycerol added while stirring at room temperature and 2 ml of concentrated H$_2$SO$_4$ added. To this mixture, 50 ml of ethanol p.a was added gradually and epoxy compound of oleic acid was put using funnel dropper. The mixture was being refluxed for 5 hours, and the reaction result was being evaporated. Filter result was being evaporated to obtain polyol and being tested using FTIR Shimadzu to prove hydroxyl group and to determine hydroxyl value using Wijs, AOAC 1995 method.

2.3 The Manufacture of Polyurethane Paint Coating
The manufacture of polyurethane film followed the procedure modification of polyurethane manufacture 16]. Castor oil-based polyol was mixed with arganoclay at room temperature for 10 minutes. Then, isocyanate (TDI) was added and was stirred again for 5 minutes to obtain homogeneous mixture. Then, it was applied to material specimen which had been prepared. Result specimen was being settled at room temperature in order to evaporate the solvent.

Gloss index and adhesivibility of polyurethane film layers on specimen were then tested. Table 1 shows the preparation of polyurethane-based paint coating. The preparation of polyurethane-based paint coating which would be made on Polyol: TDI ratio followed [4] and MMT usage ratio followed [16] and can be seen from Table 1.

3. Result and Discussion
Preparation of polyurethane coating film material is reacting castor polyol with isocyanate (TDI) plus Montmorillonite (MMT), and applied to iron specimens. The specimens are coated with polyurethane / MMT in the following comparisons.

| Polyol | TDI | MMT | Sample |
|--------|-----|-----|--------|
| 7%     | 3%  | 1%  | A      |
| 7%     | 3%  | 2%  | B      |
| 7%     | 3%  | 3%  | C      |
| 7%     | 3%  | 4%  | D      |
| 7%     | 3%  | 5%  | E      |

3.1 FTIR Characterization of Epoxidation and Hydroxylation of Castor Oil
The results of FT-IR spectroscopic analysis of epoxide compounds were carried out to detect or see the peak shift which could be related to the reaction process. The spectrum in the 1055.25 cm$^{-1}$ and 1013 cm$^{-1}$ shows the presence of C-O bonds in the epoxy ring of epoxide compounds of castor oil that occur in the reaction process.
Polyol compounds from castor oil that occur at the initial stage are the formation of intermediate compounds of epoxide, through the reaction between hydrocarbons not saturated with castor oil with acetate acid in equation (1) Odetoye, 2012. The results of FT-IR analysis showed the formation of hydroxyl groups on epoxide compounds of castor oil, the reaction lasted for 5 hours at a temperature of 60 °C as evidenced by the absorption of wave numbers that widened at 3394.25 cm⁻¹, and hydroxyl number of 132 KOH / g, hydroxy groups which formed due to the epoxide ring opening reaction. Uptake at wave number of 1372.6 cm⁻¹ indicates the presence of hydroxyl groups on secondary C atoms.

3.2 Characterization of Polyurethane as Material Coating Material

The manufacture of polyurethane composite coating materials is reacting castor oil polyols with isocyanates (TDI) plus montmorillonite resulting from the isolation of bentonite, and applied to metal specimens.

In Figure 1, the specimens of material are coated with polyurethane / MMT in the ratio of Polyol: TDI: MMT is 5: 3: 5% the results are better, on a flat and smooth surface. Figure 2 and Figure 3 specimen material with castor oil polyurethane coating, polyurethane coating with addition of montmorillonite.
In Figure 3 application of castor oil polyurethane coatings on material specimens with MMT fillers 1%, 2%, 3%, 4% and 5%.

3.3 Characterization of Bonding Powder Classification

In Table 2 shows that commercial PU and PUMJ-MMT 2% are classified into classification 1, this states that the material specimen applied with commercial PU has a damage level of around 5%.

| No | Specimen          | Classification |
|----|-------------------|----------------|
| 1  | PUMJ-MMT 1% (A)   | 4              |
| 2  | PUMJ-MMT 2% (B)   | 4              |
| 3  | PUMJ-MMT 3% (C)   | 1              |
| 4  | PUMJ-MMT 4% (D)   | 1              |
| 5  | PUMJ-MMT 5% (E)   | 0              |
| 6  | PU-Commercial     | 1              |

Commercial polyurethane (PU) reaction of butanediol as a source of polyols with isocyanates was applied to the material after being characterized by a detached area of 5% included in the classification. Specimens material were applied with 1% PUMJ-MMT and 2% PUMJ-MMT included in classification 4 meaning that the film layer regardless of the specimen area 35-65%. For 3% of PUMJ-MMT and 4% of PUMJ-MMT included in classification 1, it means that the film layer which is separated from the specimen area is 5%, this indicates the level of PUMJ-MMT damage is around 5%, while the addition of PUMJ-MMT 5% is not visible in the area apart (ISO 2409). The addition of MMT to castor oil polyols can increase the adhesive strength (adhesion). The adhesion between the coating film and the media can be caused by bonding forces, hydrogen bonding forces, dispersion forces, and mechanical bonding (pores) or combinations thereof. Adhesive strength is very dependent on the nature of the media surface with the resin. To get a bond that both media and polymers must be compatible and can build several types of bonding forces. Based on this, the good adhesion strength of natural polyurethane film material specimen media is caused by the formation of bonding forces between the material specimens and polyurethane films.

Montmorillonite (MMT) is adhesive or gluing, this occurs in the application of the bonding is the bond between the materials in a mixture. The strength of polyamide coating adhesives with the addition of 3% clay increases with the adhesive coating of polyimide without clay [15].

3.4 Gloss Characterization

In Figure 4 Commercial PU film coating power on plastic applications is statistically better than the synthesis power of PUMJ-MMT, and PUMJ / MMT gloss ability is better than Commercial PU gloss. The luster of the film layer depends on the smoothness of the film layer formed. The addition of montmorillonite (MMT) to castor oil polyols produces a layer of high glossy polyurethane film because of the nano size of MMT, the overall surface area of the particles will be greater, so increasing the amount of dye absorbed and will increase the amount of absorbed light will increase, with the addition of MMT [14] luster will increase.

| Specimen Code | 1  | 2  | 3  | Average |
|---------------|----|----|----|---------|
| A (1% MMT)    | 23.4| 24.6| 26.1| 24.7    |
Glossy power can be defined as the ability of the surface of the film to reflect back light. The smooth surface of the film can produce high gloss, whereas the rough surface of the film produces low gloss. Luster power increases with the addition of 5% MMT in polyurethane E can be seen in table 3.

3.5 Thermal Characterization

Thermogravimetric characterization (TGA) of PUMJ-MMT Polyurethane 1% (A), PUMJ-MMT 2% (B), PUMJ-MMT 3%, PUMJ-MMT 4% and PUMJ-MMT 5% are shown in Figure 5. Thermogravimetric can be used to characterize each material that shows changes in the weight of the material during heating, and to detect changes due to the decomposition process. The TGA curve is shown in Figure 5. The whole sample undergoes two stages in thermal degradation. The first stage, around 50-150 °C, indicates the loss of weight derived from evaporation of water and volatile compounds, for polyurethane compounds A, B, C, D and E each reduction - 0.23 mg, -0.19 mg, -0.08 mg, - 0.12 mg and - 0.15 mg lost an average weight of 15%.

In the second stage, around 300-450 °C, degradation comes from montmorillonite. At a temperature of 200 °C the polyurethane polymer began to degradation and followed by montmorillonite which was degraded to a temperature of 450 °C, for samples A - 5.24 mg, B - 5.07 mg, C - 5.04 mg, D - 4.89 mg and E - 4.91 mg. For Polymers A, B, C, D and E at a temperature of 450 °C experienced an increase in

| Temperature (°C) | A (mg) | B (mg) | C (mg) | D (mg) | E (mg) |
|------------------|-------|-------|-------|-------|-------|
| 0-150            | -0.23 | -0.19 | -0.08 | -0.12 | -0.19 |
| 150-300          | -0.59 | -0.63 | -0.52 | -0.56 | -0.71 |
| 300-450          | -5.24 | -5.07 | -5.04 | -4.89 | -4.91 |
| 450-600          | -8.04 | -8.38 | -8.45 | -8.12 | -7.98 |
thermal stability. It can be concluded that polymer A is degraded -8.04 and there is still a residue of 1.96 mg, polymer B is degraded -8.38 there is still a residue of 1.62 mg, polymer C is degraded -8.45 there is a residue of 1.55 mg, polymer D is degraded -8.12 mg there is still 1.88 mg remaining and the E polymer is degraded -7.98 mg remaining 2.02 mg. This data shows E polymer is more heat resistant than A polymer, B polymer, C polymer and D polymer.

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 toluene diisocyanate and bentonite-chitosan fillers has been conducted. Thus, from this research it can be concluded that the addition of montmorillonite can: i) increases the adhesive strength of the material coating applied to the surface of the material; ii) increases heat resistance in the film surface layer of material and iii) and montmorillonite isolated from bentonite can be applied as a filler in polyurethane castor oil composites.

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