

## Synthesis of Alkyd Resin Modified with Waste Palm Cooking Oil as Precursor Using Pretreatment with Zeolite Adsorbent

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### Abstract

Research on synthesis of alkyd resin (AR) modified with waste palm cooking oil (WPCO) as precursor using alcoholys-polyesterification method was successfully conducted. The modified alkyd resin was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetry-Differential Thermal Analysis (TG-DTA). The pretreatment was carried out for WPCO by applying adsorption technique using zeolites to remove free fatty acid (FFA). Modified alkyd resin was synthesized with the main ingredients composition consisting of WPCO, glycerol, anhydrous phthalate with the oil length of 40% at the total weight of 27.54 grams, and a small amount of CaO as catalyst. The characterization result using FTIR showed the presence of typical alkyd resin compound group at the absorption peaks 1597.06 and 1651.07 consecutively as the vibration of benzene ring from the phthalate and C=C stretching of unsaturated fatty acids. The thermal characterization was performed by using TG-DTA analysis showing that the transition glass and recrystallization at the temperature 390.25 °C and 482.46 °C respectively.

### Keywords

Modified alkyd resin, waste palm oil, zeolites, adsorption

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## 1. INTRODUCTION

Alkyd resin is an additive that serves as a binder in the paint industry, coating, plastic industry, adhesives, etc. Alkyd resin is widely used in anti-corrosion coating industry, such as in automotives and shipbuilding industry. Alkyd-based coating are well-known for good corrosion protection, high gloss, and the ease of application even over poorly teated surface (Gan and Tan, 2001). They are used for protecting surfaces against various environmental effects like UV-radiation, chemical invasion and mechanical stresses (Oladipo et al., 2013). Alkyd resin specifically can be called as a plasticizer in the manufacture of plastics. The use of alkyd resin is important in manufacturing industry to provide additional strength, flexibility, endurance, and other positive properties (Momodu et al., 2011; Atta et al., 2013; Haryono et al., 2005). Alkyd resins are unsaturated hydroxylated polyesters resins modified with vegetables/marine oils or their fatty acid. Therefore alkyd resins are main product of poly condensation reactions between poly carboxylic acids and poly alcohol in presence of fatty acids or vegetable oils (Ibrahim et al., 2014). Oil modified alkyd resins are usually prepared via alcoholysis and polyesterification of polyhydric alcohols and dibasic acids together with the modifying oils.

The basic reaction of alkyd resin is esterification, which shown below:



Alkyd resins used in industry are still dominated by derivative products from petroleum, especially the phthalate group. In fact, phthalates can be degraded into digestion, such as Di-2-ethylhexyl phthalate (DEHP) because alkyd resins from petroleum are less heat-resistant (Haryono et al., 2005; Waskitoaji et al., 2012). The petroleum based products are expected to decline in future years because their unrenewable properties. Nowadays, some research are conducted to try finding the substitute of petroleum with renewable natural resources, such as plants and animals oils. Several research studies have begun to switch to vegetable oil as a modified alkyd resin substituent because it is considered safer, non-toxic, and biodegradable by having properties as alkyd resins similar to petroleum derivatives (Haryono et al., 2005; Waskitoaji et al., 2012; Vaidya et al., 2012; Galli et al., 2014). Therefore, it is also important for companies to develop alternative sources which is decrease their production cost.

Alkyd resins modified with vegetable oils have been produced in industries such as soybean oil, sunflower seed oil, and

castor oil (Haryono et al., 2005). Alkyd resin contains agro (50-70%) and petroleum (25%) base raw materials as compared to commercial resin contain 50-70% petroleum based products is highly hydrophilic, hence it can be used in emulsion polymer synthesis (Uzoh et al., 2013). The development of modified alkyd resin using vegetable oil began to be expanded because of its good result compared to alkyd resin of petroleum oil, in addition to its better price and productivity.

Some research on the synthesis of alkyd resin using various vegetable oil precursors has shown the good results based on the parameters of alkyd resin properties. Menkiti and Onukwuli (2011) studied the relation between oil length variation and the properties of rubber-seed oil based alkyd resin products. In addition, Igbo et al. (2014) examined the modification of sesame oil-based alkyd resin. Shaker et al. (2012) also did the research on jojoba oil-modified alkyd resins according to the standard parameters of alkyd resin. Meanwhile, Isaac and Nsi (2013) successfully synthesized cotton-based oil-based alkyd resins with polybasic acid variables. Based on those studies on the precursor of alkyd resin, it can be concluded that alkyd resin can be produced using vegetable oil. Vegetable oil industry, especially palm oil is a large industry in line with its use. A number of food industries consume a lot of cooking oil, such as crackers industry and restaurants potentially provide waste cooking oil. The post-processing of frying makes the cooking oil become harmful waste because it could cause damage to the liver, heart, and blood vessels as what was tested on Wistar rats (Rukmini, 2007). On the other hands, if WPCO is disposed to the environment may cause large contamination. One of the way to utilize this waste palm cooking oil is to make it as a precursor for alkyd resin synthesis.

In the synthesis process of alkyd resin, vegetable oil is often supplemented with a polyol compound, such as glycerol or pentaerythritol for the occurrence of an alkylolysis process that produces monoglycerides, before the alkyd resin esterification process is carried out (Menkiti and Onukwuli, 2011; Igbo et al., 2014). It is interesting that the heating process of cooking oil will trigger a hydrolysis process that produces glycerol and free fatty acids (Aziz et al., 2013). Therefore, glycerol from the used cooking oil will become polyols in the synthesis of alkyd resin by removing the product-free fatty acids from the hydrolysis of cooking oil first. However, the comparison of the results using additional glycerol in the alcoholysis process is still required. The previous research, based on patent EP 1 984 420 B1, has successfully synthesized a fat-based polymer using a glycerin-based alcoholic process.

The process of removing free fatty acids from used cooking oil is done by adsorption technique using zeolite. Based on US patent 6 229 032 B1 (P.A et al., 2001) and the previous research by Taylor et al. (1984), the removal of free fatty acids using zeolites has already been conducted. In general, zeolites are crystalline aluminosilicates in which the three components, namely aluminium, silicon, and oxygen, are arranged in a fixed, dimensional framework with cavities and pores of uniform size and shape. The Zeolite network is composed of  $\text{SiO}_4$  and

$\text{AlO}_4$  tetrahedra in which the negative charge on the latter is neutralised by cations like metal ions, ammonium ions, or alkali metal ions.

## 2. EXPERIMENTAL SECTION

### 2.1 Time and Place of Research

This research was conducted from October 2016 until November 2016 at the Laboratory of Waste Treatment Politeknik ATK Yogyakarta. Characterization of materials was conducted in the Laboratory of Instrumentation and Polymer Technology Politeknik ATK Yogyakarta and Laboratory of Organic Chemistry Universitas Gadjah Mada.

### 2.2 Materials and Instrumentations

Materials used in this study were waste palm cooking oil taken from crackers home industry at Bantul Yogyakarta and zeolites adsorbent industrial grade. The chemicals were pure products of analytical quality, i.e. glycerol, anhydrous phthalate, CaO, KOH, ethanol 95%, Xylene, phenolphthalein. The characterizations were done by FTIR (Shimadzu 8201PC) and TG-DTA (Perkin Elmer Diamond) under air atmosphere from 30 to 1000°C at a heating rate of 10°C.min<sup>-1</sup>. The equipments were used such as glassware, batch system equipment (three neck boiling flask, glass condenser), magnetic stirrer, thermometer and shaker.

### 2.3 Methods

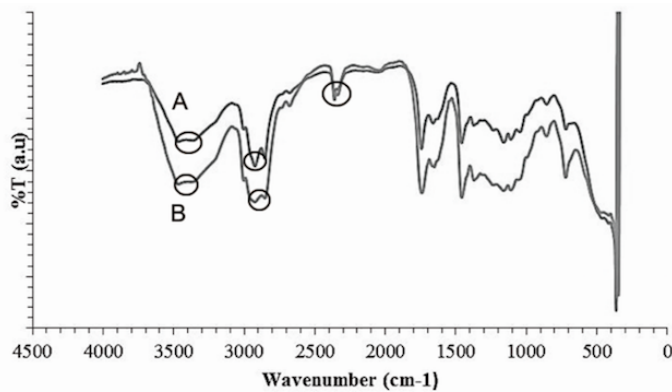
#### 2.3.1 Pretreatment of WPCO

Pretreatment of the waste palm cooking oil was conducted by applying adsorption method using 0.3 g zeolite in 150 mL cooking oil which was heated around 100 °C for 2 hours. The percentage of FFA was determined using AOCS method with few modification. Fifty mL of ethanol were used to dissolve 2 g of sample and titrated against 0.1 N sodium hydroxide solution. FFA was expressed as palmitic acid

#### 2.3.2 Synthesis of alkyd resin

The synthesis of alkyd resin was carried out with the main ingredients composition of cooking oil, glycerol, and anhydrous phthalate with an oil length of 40% and a total weight of 27.54 grams. In the synthesis process, the oil was mixed with glycerol and a small quantity of CaO as a catalyst. This mixture was heated in a heating mantle at the temperature of 230-250 °C for 2 hours. To indicate the reaction, after two hours a little amount of aliquot was taken to check the solubility in Methanol as a sign of the formation of monoglyceride. Then, at the onset of the second phase, the temperature of reaction was lowered to 180 °C.

Anhydrous phthalate was added as dissolved in Xylene by 10% of total weight charged of the mixture. Aliquots were taken every 30 minutes to check the decrease in the number of acid. The reaction was stopped when the number of acid reached 10 mg KOH g<sup>-1</sup>. The determination of acid amount used the procedure of AOCS method. Then, alkyd resin as the result was cooled and characterized with FTIR.



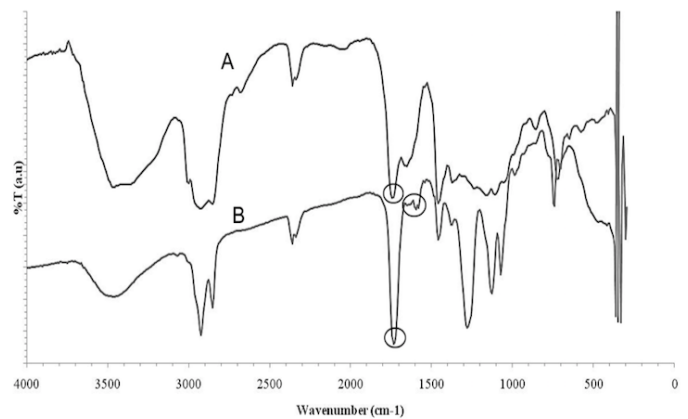
**Figure 1.** FTIR Spectra of WPCO (A) Before Adsorption; (B) After Adsorption

### 3. RESULTS AND DISCUSSION

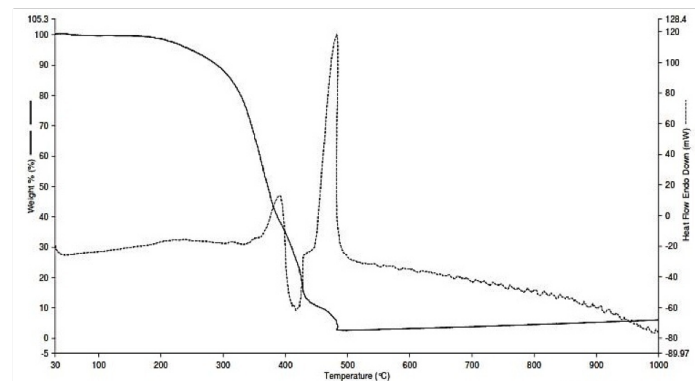
The pretreatment of WPCO was done before the synthesis which used adsorption method with zeolite as the adsorbent to remove the free fatty acid. The adsorption was done in 150 mL WPCO compounded with 0.3 g zeolite which was heated around 100 °C for 2 hours. After the adsorption, the % FFA was checked using AOCS method, and the value was 0.003%.

The characterization of WPCO before and after the adsorption were analyzed using FTIR. The FTIR spectra shown in Figure 1 illustrates the functional group of oil in general. It shows the peak of -OH at 3464.15  $\text{cm}^{-1}$ , C=O at 1743.65  $\text{cm}^{-1}$ , and -CH at 2924.09  $\text{cm}^{-1}$ . The FFA property is related to a large part of spectrum, such as the bands due to bonded O-H, C=O stretching in ester, C-H and the fingerprint region of oil at 1500 – 1000  $\text{cm}^{-1}$  (Man, 1999). The qualitative result which was based on the FTIR data demonstrated that the FFA in WPCO after the adsorption was reduced compared to that in WPCO before the adsorption. The intensity number of -OH, -C=O, and -CH bands before adsorption was higher compared to that after adsorption. Besides, some of the bands in the fingerprint of oil region were shifted.

The characterization of alkyd resin and FTIR in comparison to WPCO after the adsorption is presented in Figure 2. The FTIR spectra showed the presence of a typical alkyd resin compound group at the absorption peak of 1597.06  $\text{cm}^{-1}$  due to the vibration of benzene ring from the phthalate. It also occurred in the absorption at 1651.07  $\text{cm}^{-1}$  because of the C=C stretching of the unsaturated fatty acids, as well as a characteristic of chain ester band at 1735.93  $\text{cm}^{-1}$ . The presence of O=C-O-C also exhibits the characteristic of ester bands at 1126.43  $\text{cm}^{-1}$  (Uzoh et al., 2013). The absorption of C-O alicyclic also appeared at 1072.42  $\text{cm}^{-1}$ . FTIR spectra of WPCO showed the vibration peak of stretching C=O from ester triglyceride group at 1743.65, while in alkyd resins spectra appeared in 1735.93. The absorption peak vibration of stretching OH, aliphatic C-H stretching and C-H bending appeared in both WPCO and alkyd resin spectra at 3464.15  $\text{cm}^{-1}$ , 2924.09  $\text{cm}^{-1}$ , and 1458.18  $\text{cm}^{-1}$ .



**Figure 2.** FTIR Spectra of (A) WPCO after adsorption; (B) Alkyd Resin Modified WPCO



**Figure 3.** TG-DTA Thermogram of Alkyd Resin Modified WPCO

The thermal properties of AR was studied using TG-DTA. About 9.981 mg of the sample was heated under the air atmosphere from 30 to 1000 °C at a heating rate of 10 °C.  $\text{min}^{-1}$ . The TG-DTA thermogram shown in Figure 3 showed melting, recrystallisation and further melting. The transition glass and recrystallization occurred at 390.25 °C and 482.46 °C respectively. Thermogram TG-DTA of AR showed the degradation at four stages.

The first stage was at temperature 180 to 332.62 °C with the weight reduction of 22.368%. The second stage is endothermic reaction starting at 332.62 °C to 387.88 °C with the weight reduction of 60.669%. The third stage occurred at temperature 387.88 °C to 429.27 °C and exothermic reaction with the weight reduction of 85.308%. The fourth stage was endothermic reaction which occurred at temperature 429.27 to 498.53 °C with the weight loss 97.712%. The TGA curve showed better degradation behavior of alkyd resin compared to alkyd resin based on PET waste and camelina sativa oil. Alkyd resin based on PET waste has 75% weight loss at 375 °C (Güçlü, 2009) and 70% weight loss at 388 °C (Acar et.al, 2012). Additionally, alkyd resin based on camelina sativa oil has 60% weight loss at

398 °C (Nosal et al., 2015).

#### 4. CONCLUSIONS

The result has revealed that alkyd resin modified with waste palm cooking oil precursor which was pretreated with zeolites adsorption technique could be synthesized by alcoholysis-polyesterification method. In general, the result of characterization showed the presence of a typical alkyd resin compound group at the absorption peak 1597.06 and 1651.07 as the vibration of benzene ring from the phthalate and C=C stretching of unsaturated fatty acids.

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