Effect of Concentration of Catalyst (BF$_3$-Diethyl Etherate) on Synthesis of Polyester from Palm Fatty Acid Distillate (PFAD)

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Abstract - Palm Fatty Acid Distillate (PFAD) can be used as raw material for synthesis polyester. The aim of this research is to synthesis of polyester and to determine the effect of concentration of catalyst on polymerization methyl ester PFAD. The esterification stage was done at temperature 70 °C, reaction time 120 minute, reactant ratio 1:8 (PFAD: methanol), concentration of catalyst (H$_2$SO$_4$) 1% (w/w) PFAD; polymerization stage was done at temperature 126-132°C, polymerization reaction time 4 hours; variation of concentration of catalyst (BF$_3$-diethyl etherate) 0%, 6.9%, 9.2%, 11.5% (w/w) methyl ester; and polymerization stage was done at temperature 175-200 °C, reactant ratios (w/w) 1:1 (polymerized ME : ethylene glycol), reaction time 4 hours and all of stage was stirred at 150 rpm. The results showed, in the esterification stage was obtained methyl ester with iodine value 77.29 g I$_2$/100 g, viscosity 6.90 cP, density 0.89 1kg/m$^3$ and analysis by using GC-MS showed that the purity of methyl ester was 82.23% and molecular weight 267.97 g/mol. Decreasing in iodine value from 77.29 lI$_2$/100 g to 74.97-59.99 g lI$_2$/100 g indicated that the polymerization process had taken place. In polymerization stage was obtained light brown colored liquid for concentration of catalyst 0%; viscous, light brown colored liquid for concentration of catalyst 6.9%; and gel polyester, viscous, dark brown colored solid at room temperature for concentration of catalyst 9.2% and 11.5% with acid value from 8.19 to 26.14 mg KOH/g, viscosity from 0.07 to 15.2 P, and molecular weight 288.81 to 1522.07 g/mol which is more suitable for applications of modified polyester. Analysis by using GC showed that the purity of polyester is equal to 65.49%.

Keywords — polyester, palm fatty acid distillate, polymerization concentration of catalyst, biodegradable polymer

I. INTRODUCTION

Indonesia is one of the largest palm oil producer in the world [1]. In the processing of palm oil is obtained some derivatives such as Palm Fatty Acid Distillate (PFAD) [2]. PFAD has a potential use as a raw material in the synthesis of polyester. Polyester has many uses such as for making bottles, films, tarpaulin, canoes, liquid crystal displays, holograms, filters, fiber and etc [3]. Polyester has many advantages, resistant to humidity and UV when left in the open air. Polyester fiber have high strength and low water absorption when it is compared with other industrial fibres [4].

Polymer is the most important chemical industrial products that are used in many applications. Almost the most current polymer is produced from petrochemical substance that cannot be renewed. Therefore, the alternative material needs to be known [5]. Currently, vegetable oils are excellent source of renewable materials an alternative material for oil-based polymers because of ecological and economical concern.

Polyesterification is a process of condensation or step-growth polymerization where in the process will be produced polyester and water or alcohol as by product. Direct reaction of diacids or anhydrides with diols are often avoided because of the high temperatures required to completely eliminate water. However, this reaction used to produce low molecular weight. Using dimethyl ester has been used to advantage instead of direct esterification with diacid or dianhydride because reaction is fast and dimethyl ester is often more easily purified and has better solubility characteristics. The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an external acid [6]. In this paper,
polymerization will be catalyzed by boron trifluoride diethyl etherate as strong acid. Catalyst of polymerization has a function to accelerate the reaction by produce an active group to extend the polymer chains [7]. Therefore, it is important to determinethe effect of concentration of catalyson polymerization methyl ester PFAD.

II. MATERIALS AND METHODS

Main materials that are used in this research as PFAD, BF$_3$-diethyl etherate, methanol, sulfuric acid and ethylene glycol. The main equipments are a glass batch reactor, a hotplate with magnetic stirrer, reflux condenser and thermometer.

Esterification stage [8], that is reaction between PFAD and methanol was held in a glass batch reactor on the top of a stirring hotplate for 120 minutes with mole ratio 1:8 at 70°C by using 1% sulfuric acid (w/w) and 150 rpm stirring. Density (piconometer), viscosity (viscosimeter Ostwald), iodine value (AOAC 920.158) and composition (GC-MS) of product methyl ester was analyzed. Polymerization stage [9], that is reaction methyl ester by using catalyst BF$_3$-diethyl etherate with concentration was varied from 0%, 6.9%, 9.2% and 11.5% (w/w) at 126-132°C for 4 hours and 150 rpm stirring. Iodine value of polymerized methyl ester was analyzed.

Polyesterification stage [9], that is reaction between polymerized methyl ester and ethylene glycol in the same reactor for 4 hours with mass ratio 1:1 at 175-200°C, 150 rpm stirring and sampling was performed every 1 hours for analysis of acid value (ASTM D4662-03). Viscosity (viscotester VT-04F), molecular weight (the end group method), structure (FT-IR) and composition (GC) of polyester was analyzed.

III. RESULTS AND DISCUSSION

The initial material that was used for the synthesis of polyester was methyl ester by esterification of methanol and PFAD by using sulfuric acid as catalyst. The result of analysis composition PFAD by using GC-MS was shown in Figure 1.

![Figure 1. GC-MS Chromatogram of PFAD](image1)

GC-MS showed that the average molecular weight of PFAD was 270,84 g/mole with 53.27% unsaturated fatty acids. PFAD would be reacted to produce methyl ester by the following reaction (equation 1):

$$\text{R-COOH} + \text{H}^+ \rightarrow \text{R-COOH}^+ + \text{H}_2\text{O}$$

The result of analysis composition methyl ester by using GC-MS was shown in Figure 2.

![Figure 2. GC-MS Chromatogram of Methyl Ester](image2)

GC-MS showed that the average molecular weight of PFAD was 267.97 g/mole with the purity 82.23%. Methyl ester would be used as a raw material for polyester. Analysis of the characteristics of methyl ester PFAD were shown in table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Iodine Value</td>
<td>77.29 g l/100 g</td>
</tr>
<tr>
<td>Viscosity (30 °C)</td>
<td>6,90 cP</td>
</tr>
<tr>
<td>Density (30 °C)</td>
<td>859.91 kg/m$^3$</td>
</tr>
</tbody>
</table>

Polymerization reaction stage of methyl ester PFAD was performed by using catalyst boron trifluoride diethyl etherate and then polyesterification stage of polymerized methyl ester and ethylene glycol to produce polyester following the reaction as shown in equation (2). For concentration of catalyst 0% were obtained light brown colored liquid polyester. For concentration of catalyst 6.9% were obtained viscous, light brown colored liquid polyester; and for concentration of catalyst 9.2% and 11.5% were obtained gelpolyester, viscous, dark brown colored solid at room temperature. Polyester that synthesized has a group of molecules that can be identified by using FT-IR.

The result of analysis spectrum of polyester was shown in Figure 3.

An ester compound was characterized by the presence of stretching band C=O, C-O and O-H [10]. The formation of polyester was shown by vibration peak at wave number 1751,36 cm$^{-1}$ that indicated a stretching band C=O ester for all run. The difference between the C=O group of acid and ester was at wave number 1730-1700 cm$^{-1}$ for acid where as at wave number 1760-1793 cm$^{-1}$ for ester [11]. On the other hand, the weakening of the stretching band O-H hydrogen bond at wave number 3500 cm$^{-1}$ - 3400 cm$^{-1}$ supported the formation of polyester. Polymerization was characterized by the

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absence of vinyl group (-C = CH₂) at wave number 990 cm⁻¹-910 cm⁻¹ that indicated decreasing of unsaturated bond. This means that polymerization reactions occur on termination of a double bond. The peak vibration that has formed is the presence of C-H group absorption at wave numbers 732.95 cm⁻¹, 871.82 cm⁻¹, 972.12 cm⁻¹, and 2792.93 cm⁻¹. 2939.52 cm⁻¹ and C-H alkyl group at wave numbers 1465.90 cm⁻¹. The result of analysis qualitative for composition polyester by using GC was shown in Figure 4.

Analysis of polyester by using GC shown the purity of polyester was 65.49%. Effect of concentration of catalyst on iodine value of polymerized methyl ester was shown in Figure 5. Figure 5 showed that iodine value tends to decrease with increasing in concentration of catalyst. The most important parameter in the synthesis of a polymer was the number of double bonds that exist in a sample which can be shown by iodine value.

**Table 2. The Characteristic of Polyester**

<table>
<thead>
<tr>
<th>Concentration of Catalyst</th>
<th>Appearance</th>
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<tbody>
<tr>
<td>0%</td>
<td>light brown colored liquid</td>
</tr>
<tr>
<td>6.9%</td>
<td>viscous, light brown colored liquid polyester</td>
</tr>
<tr>
<td>9.2 and 11.5%</td>
<td>gelpolyester, viscous, dark brown colored solid at room temperature</td>
</tr>
</tbody>
</table>
Molecular weight of polymer was the main attention in practice of synthesis polymer. Polyester had the carboxyl end group and hydroxyl group at the other end [16]. Zhang, et. al. (1994) used end group methods to determine molecular weight in the synthesis of polycaprolactone [17]. Molecular weight of polyester in this research was also determined by end group methods. Polyester with linear high molecular weight polymer, was generally thermoplastic with a molecular weight about 10,000 – 30,000 g/mole. High molecular weight of polyester could be used for the application of powder coating and drying binder. Polyester with low molecular weight that is between 500-7,000 g/mole. Polyester with low molecular weight may be linear or branched with carboxyl and hydroxyl end group. For special purposes, polyester with low molecular weight 1,000-5,000 g/mole was modified due to functional group being more reactive than polyester with high molecular weight [18].

Polyesterification was reversible polycondensation reaction [3]. The results showed that increasing in concentration of catalyst would increase molecular weight. But at concentration of catalyst 11.5%, decreasing in molecular weight had occurred. This condition happened because of increasing in concentration of polymer that had formed caused equilibrium conditions had turning to form reactants back.

The results showed that product of polyester had a range of 1,352.26 – 1,522.07 g/mole. Therefore, this polyester could be counted polyester with relatively low molecular weight that was more suitable for the application of the modified polyester. The low molecular weight polyester was formed due to the raw material which was used was a methyl ester of PFAD which had all little double bonds. Effect of concentration of catalyst on viscosity of polyester was shown in Figure 8.
which led to the appointment of the larger viscotester value [19]. This result was suitable for this research.

IV. Conclusions

The conclusion that can be drawn from this research is the product of polyester from PFAD has physical properties that close to the commercial polyester has a good quality of acid value and can be classified in low molecular weight of polyester which is more suitable for the application of modified polyester. The synthesis of polyester reaction is a reversible reaction in which the acquisition of the product depends on the concentration of catalyst.

REFERENCES


