PRELIMINARY STUDY IN FINDING BIOELASTOMER BASED ON VEGETABLE OIL: DIMER ACID PREPARATION

KAJIAN AWAL PEMBUATAN BIOELASTOMER BERBASIS MINYAK NABATI : PREPARASI ASAM DIMER

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Abstract

Dimer acid is the main material in the synthesis of bioelastomer. The preparation of dimer acid from vegetable oil such as crude palm oil and jatropha seed oil via Diels-Alder reaction were investigated. The dimer acid based vegetable oil was obtained by reacting vegetable oil with 12% by weight of acrylic acid and 0.05 – 0.15% by weight of iodine catalyst at temperature 191.25 – 247.5 ^{o}C for 1 – 2 hours. Dimer acids were analyzed using Fourier transform infrared spectroscopy, degree of acidity and acid value determination. The results show that the degree acidity (pH) of dimer acid from crude palm oil and jatropha seed oil were 2.18 – 2.35 and 2.46 – 2.56, respectively. The acid value of dimer acid from palm oil is 89.07 – 90.07 mg KOH/g sample and acid value of dimer acid from the jatropha seed oil is 63.80 – 80.43 mg KOH/g sample. Although the acid value is still lower than the commercial dimer acid (Empol 1016), the FTIR results showed that both dimer acids had some dicarboxylic acid functional groups as appeared in Empol 1016. So both vegetable oils have potential as a raw material for bioelastomer synthesis.

Keywords : acid value, crude palm oil, dimer acid, FTIR, jatropha seed oil

Abstrak

Asam dimer merupahan bahan utama dalam sintesis bioelastomer. Pembuatan asam dimer yang bersumber dari minyak nabati seperti minyak kelapa sawit dan minyak biji jarak melalui reaksi Diels-Alder sedang diselidiki. Asam dimer dari minyak nabati diperoleh dengan mereaksikan minyak nabati dengan 12% berat asam akrilat dan 0,05 – 0,15% berat katalis yodium pada suhu 191,25 – 247,5 ^{o}C selama 1 – 2 jam. Asam dimer yang diperoleh kemudian dianalisa dengan menggunakan Spektroskopi Inframerah Transformasi Fourier, derajat keasaman dan perhitungan kadar asam. Hasil penelitian menunjukkan bahwa derajat keasaman (pH) asam dimer dari minyak kelapa sawit dan minyak biji jarak masing-masing adalah 2,18 – 2,35 dan 2,46 – 2,56. Kadar asam dari asam dimer minyak kelapa sawit adalah 89,07 – 90,07 mg KOH/g sampel dan kadar asam dari minyak biji jarak adalah 63,80 – 80,43 mg KOH/g sampel. Walaupun kadar asam ini masih lebih rendah dari kadar asam asam dimer komersial (Empol 1016), hasil analisis FTIR menunjukkan bahwa kedua asam dimer memiliki beberapa kelompok fungsional asam karboksilat seperti yang ada pada Empol 1016. Sehingga kedua minyak nabati ini memiliki potensi sebagai bahan baku untuk sintesis bioelastomer.

Kata kunci : *kadar asam, minyak kelapa sawit, asam dimer, FTIR, minyak biji jarak*

INTRODUCTION

The preparation of bioelastomer based on vegetable oils had been pretty much done (Lubguban *et al.*, 2011; Wang *et al.*, 2012; and Purbaya, 2013). However, only Purbaya's research which tried to find a material that had a self-healing ability. Although the results showed that the material had only a little a self-healing ability, sunflower oil can be a source of bioleastomer which has self-healing properties.

The development of bioelastomer product based on sunflower oil in Indonesia will face some problems because sunflower oil is difficult to obtain. Therefore, it is necessary to find alternative vegetable oils other than sunflower oil, which can be a source of bioelastomer.

Indonesian local resources such as palm oil and jatropha seed oil have the potential to be processed into bioelastomer, because both oils contain a high percentage of unsaturated fatty acid, 37 – 56% in palm oil (Ketaren, 1986) and

97% in jatropha seed oil (Setyadi *et al*., 2003). The high unsaturated fatty acid contained in palm oil and jatropha seed oil allow both oils can be a raw material for producing bioelastomer, but it must be converted first into dimer acid. Because, dimer acid is a raw material for producing bioelastomer such as self-healing rubber (Cordier *et al*., 2008 and Montarnal *et al*., 2008).

Bioelastomer based on palm oil and jatropha seed oil are expected to be an alternative new rubbery material other than natural rubber and synthetic rubber. In addition, dimer acid-based bioelastomer has the potential to have a healing ability property if the obtained bioelastomer has a hydrogen bond (Cordier *et al*., 2008; Montarnal *et al.,* 2008-2010; and Tournilhac *et al*., 2010).

Bioelastomer synthesis will be carried out in three stages, 1) preparation of dimer acid, 2) preparation of oligoamide, and 3) synthesis of bioelastomer. For the current study, the research that has been done was the preparation of dimer acid.

Dimer acid usually was prepared from tall oil (a by-product of the kraft process of wood pulp manufacture), which was reacted with acrylic acid, wherein the reaction took place with or without catalyst (Ward, 1973; Cosgrove, 1991, Jevne and Schwebke, 1979; Tramount and Charleston, 1992). In contrast to the previous studies, dimer acid in this study was prepared from palm oil and jathropha seed oil.

The aim of this research is to obtain dimer acid by reacting palm oil or jatropha seed oil with acrylic acid in iodine catalyst. The obtained product was then characterized by using infrared spectroscopy, degree of acidity (pH) and acid value determination.

MATERIAL AND METHODS

This research was conducted in October to December 2014 in The Technology Laboratory of Balai Penelitian Sembawa.

A. Materials and Apparatus

The materials were palm oil, jatropha seed oil, acrylic acid (Merck), iodine (Comax), and Empol 1016 (BASF). The apparatus consists of a reaction flask, a stirrer, a dropping funnel and a heating mantle.

B. Research Methods

Dimer Acid Preparation

The dimer acids were prepared by reacting palm oil or jatropha seed oil with acrylic acid and catalyst iodine. Vegetable oil (palm oil or jatropha seed oil) was mixed with 12% by weight of acrylic acid and 0.05 to 0.15% of iodine catalyst at room temperature. The mixtures were heated at 191.25 – 247.5 ^oC for 1 to 2 hours (the modified method of Ward *et a*l., 1973).

Acid Value Determination

The acid value of dimer acid was determined by using ISO 1242: 1999. Two grams sample was added 5 ml of ethanol, which had been neutralized and five drops of phenolphthalein indicator (2 g/l solution in ethanol). The titration was conducted by adding KOH (0,1 mol/l), where KOH solution should be standardized before the test was performed. The titration was continued until the color changed.

Degree of acidity (pH)

The degree of acidity (pH) was deterimed by using a Mettler Toledo 320 pHmeter.

FTIR Analysis

The analysis of FTIR (Fourier transform infrared) was used to determine the functional groups contained in the sample. FTIR data were obtained using a Perkin Elmer 2000 spectrum at room temperature. Spectra obtained after the sample was scanned 16 times. The samples were prepared by dripping a drop of sample between two KBr discs.

RESULTS AND DISCUSSION

The result of the reaction between palm oil and jatropha seed oil can be seen in Table 1. The degree of acidity (pH) dimer acid from palm oil was not too much different from dimer acid based on jatropha seed oil. In the other hand, the acid value of dimer acid based on palm oil tended to be larger than dimer acid from the jatropha seed oil. If both dimer acids compared to commercial dimer acid (Empol 1016), the acid value of both dimer acid were lower than empol 1016, where the acid value of Empol 1016 dimer acid is 199.02 mg KOH/g.

Table 1. The dimer acid from palm oil and jatropha seed oil.

Parameters	Palm oil-based dimer acid		Jatropha seed oil-based dimer acid	
	DA_1	DA_2	DA_3	DA_4
pH	2.18	2.35	2.46	2.56
Acid value, mg KOH/g sample	89.07	90.07	80.43	63.80

Linoleic acid is the main compound for the formation of dimer acid. The low of acid value for both of dimer acid might be caused by a low content of linoleic acid in both vegetable oil, 11 % and 4,2 %, respectively. In the other hand, tall oil contained 40% linoleic acid, so dimer acid derived from tall oil has a higher acid value.

The results were also supported by infrared results. Figure 1 shows FTIR spectra of the commercial dimer acid (Empol 1016) as compared. Figure 2 and 3 show the FTIR spectra of palm oil, jatropha seed oil and the product (Dimer acids). The assignment and identification of each spectrum based on infrared analysis that has been done on palm oil, jatropha seed oil and dimer acid (Atiku *et al.*, 2014; Man *et al.*, 1999; Guillen *et al.*, 1997; and Socrates, 1994).

The infrared curve of Empol 1016 dimer acid has some infrared absorption peaks (Fig. 1), the peaks are : 1) 1706 cm^{-1} represents the C=O stretching from dimer acid, 2) 1411 cm^{-1} represents a combination of C-O stretching and O=H deformation , 3) 1283 cm^{-1} represents C-O stretching from dimer acid, 4) 934 cm^{-1} represent O-H···O from out-of-plane deformation of dimer acid, 5) a very broad peak in the range of 3500 s/d 2500 cm^{-1} represents the peak of OH stretching hydrogen bonding of carboxylic acid dimer.

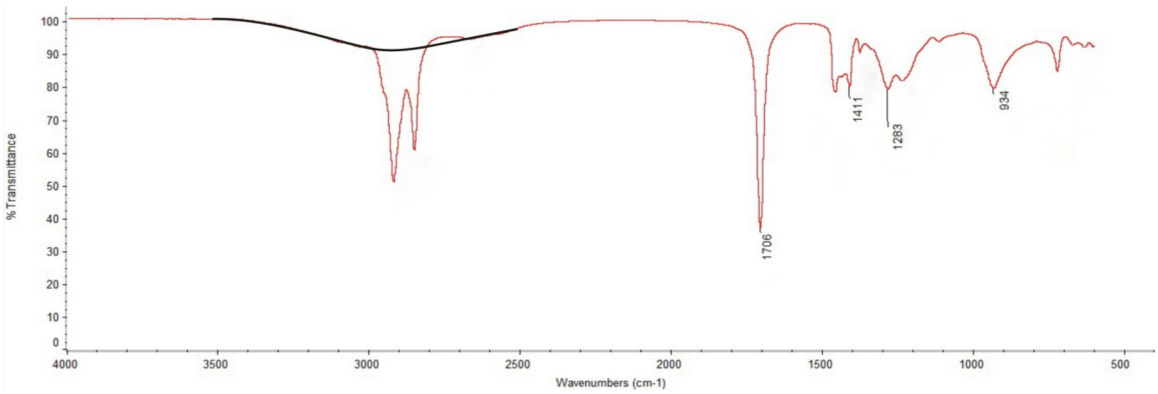

Figure 1. FTIR spectra of Empol 1016-based dimer acid

The infrared curve of Empol 1016-based dimer acid also has some absorption peaks that also owned by palm oil and jatropha seed oil, such as 2921, 2852, 1458, 1376, 1236, 1116, and 722 cm^{-1} (Atiku *et al.*, 2014; Man *et al.*, 1999; Guillen *et al.*, 1997; and Socrates, 1994). It showed that the Empol 1016 dimer acid still contained the functional groups of vegetable oil as a raw material in the dimer acid preparation.

Figure 2 shows the FTIR spectra of dimer acid that were prepared from palm oil. The dimer acid absorption peaks were appeared in both samples, DA_1 and DA_2. The dimer acid DA_1 only had one absorption peak of dimer acid, 1708 cm^{-1} which represented C=O stretching of dimer acid. Meanwhile, the dimer acid DA_2 had two peaks that indicate the appearance dimer acid absorption peak, at 1704 and 1295 cm^{-1}. These peaks represent the C=O stretching and C-O stretching of dimer acid, respectively. These results indirectly supported the previous results, which the dimer acid DA_2 had a higher acid value compared to dimer acid DA_1.

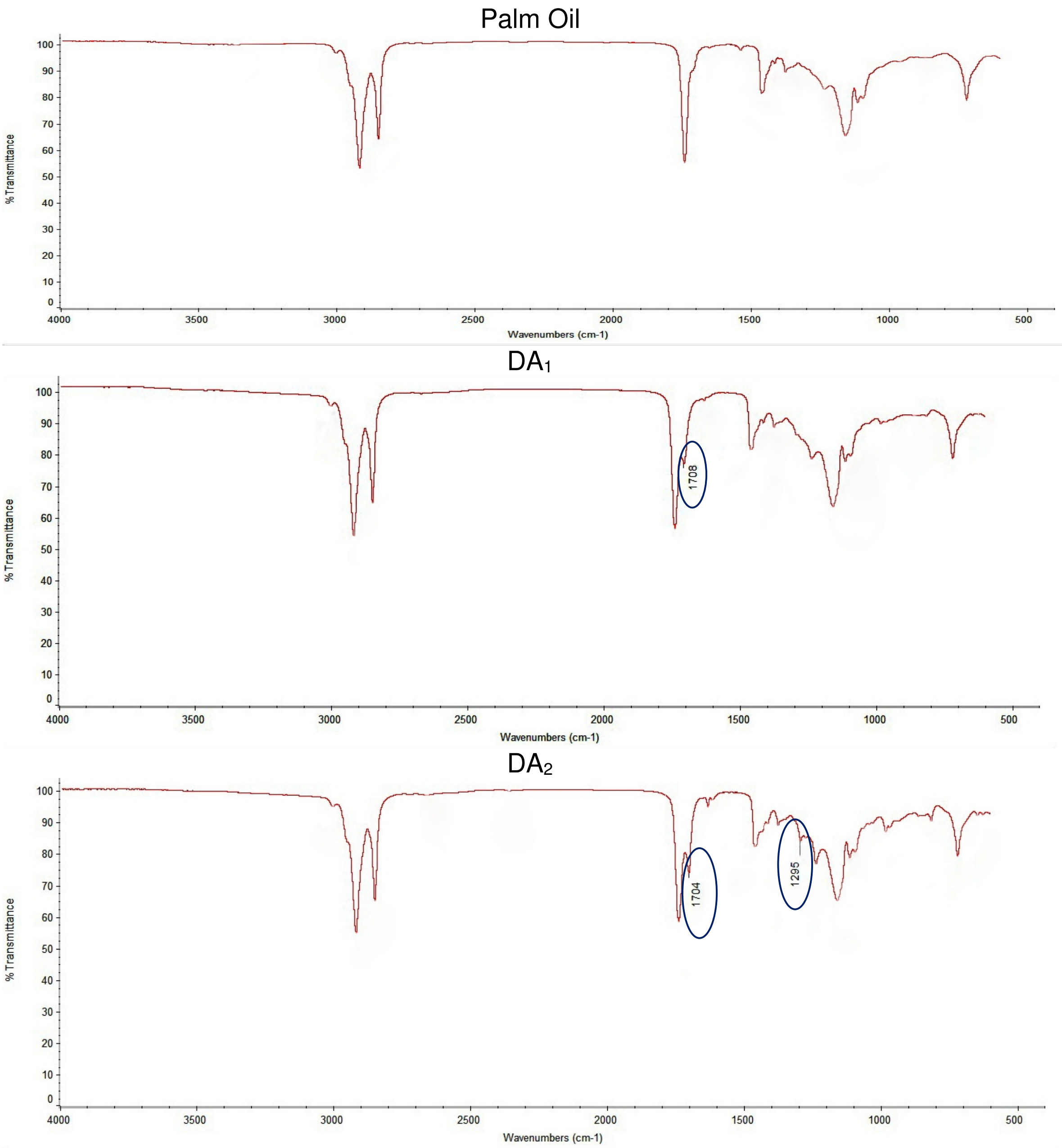

Figure 2. FTIR spectra of palm oil (raw material), dimer acid DA_1 and DA_2 (product)

Figure 3 shows the FTIR spectra of jatropha seed oil, dimer acid DA_3 and DA_4. Both acids show the appearance of dimer acid functional groups. Dimer acid DA_3 had five peaks of dimer acid functional groups, these are : 1) at 1704 cm^{-1} represented C=O stretching of dimer acid, 2) at 1295 and 1277 cm^{-1} represented C-O stretching of dimer acid), 3) at 909 and 863 cm^{-1} represented O-H···O out of plane deformation of dimer acid. While, dimer acid DA_4 only had three dimer acid absorption peaks, 1) 1708 represented C=O stretching of dimer acid, and 2) 915 and 844 cm^{-1} represented O-H···O out of plane deformation of dimer acid. These results also supported the acid value analysis.

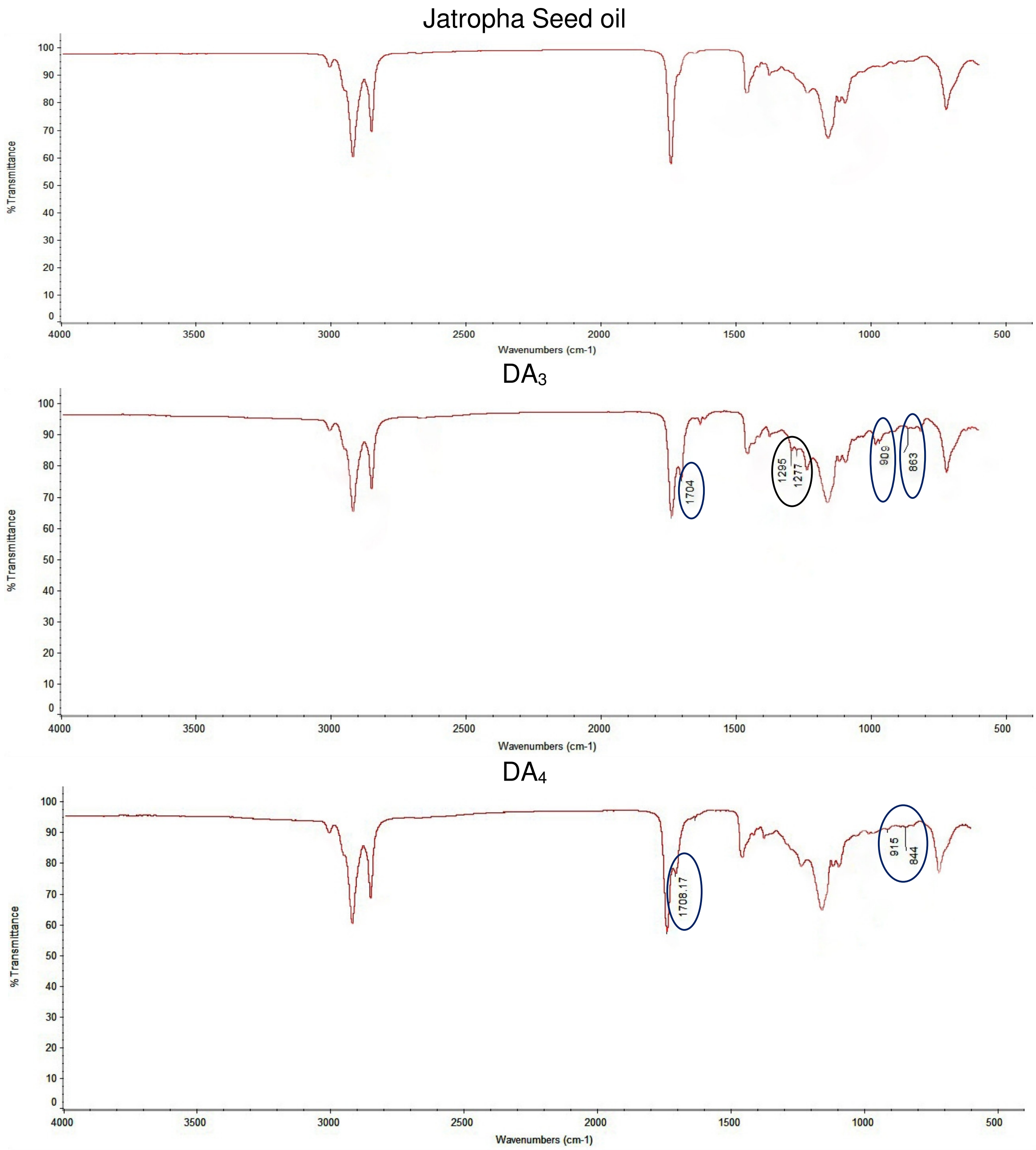

Figure 3. FTIR spectra of jatropha seed oil (raw material), dimer acid DA_3 and DA_4 (product)

According to the infrared results, dimer acid based on jatropha seed oil had a more functional group of dimer acid peaks than palm oil-based dimer acid. But, if we compared to sunflower oil-based dimer acid (Purbaya, 2013), both dimer acid had less dimer acid functional groups, nevertheless, the synthesis for both dimer acid should be continued until the third stage of the bioelastomer synthesis, in order to determine the effectiveness of these vegetable oils.

CONCLUSION

The preparation of dimer acids from vegetable oil were synthesized by reacting crude palm oil or jatropha seed oil with acrylic acid in iodine catalyst. The acid value and the FTIR results confirmed that dimer acids from palm oil or jatropha seed oil have some functional groups of dimer acid, hence both vegetable oils have potential as a raw material for bioelastomer synthesis.

SUGGESTION

For future study, it is suggested to increase the amount of dicarboxylic acid functional groups in dimer acid and the process of dimer acid purification.

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