Cationic polymerization of waste palm cooking oil under microwave irradiation

Zainal Alim Mas’ud1, Muhamad Farid1, Herlambang Surya1, Soegijono Bambang2,*

1 Department of Chemistry, Bogor Agriculture University, Kampus IPB Dramaga, Bogor, Indonesia
2 Department of Physics, University of Indonesia, Depok, Indonesia
* Corresponding author: bambangsg11@gmail.com

Abstract. Waste palm cooking oil is one of the largest waste types in Indonesia and it is potential as a source of renewable materials. Conversion of the material was carried out by the cationic polymerization of the double bond (C=C) in the triglyceride. The polymerization using boron trifluoride-etherate (BF3-etherate) as the catalyst was performed under microwave irradiation. The irradiation was varied in some power settings and reaction times. The fatty acid components after purification were analysed using gas chromatography (GC). The parameter analysed were iodine number (titrimetric), maximum wavelength absorption (UV-visible spectrometry), functional groups (Fourier transform infrared spectrometry, FTIR) and thermal properties (differential scanning calorimetry, DSC). The treatment using microwave irradiation produced solid polymer form with lower iodine number, meaning that the double bond in the fatty acid has reduced. The small amount of the double bond was also reflected by a hypochromic shift in the UV-vis spectra, as well as decreasing peak intensity at the C=C stretch in the FTIR spectra. The DSC thermogram of the product shows two endothermic transitions, indicating the melting point of the monomer and the polymer product.

Keywords: Cationic polymerization; Microwave; Renewable materials; Waste palm cooking oil

1. Introduction

Palm cooking oil consumption in Indonesia is very high, particularly for frying. The used cooking oil or wasted cooking oil (WCO) cannot be reused for health reasons [1, 2] and will risk to pollute the environment. The high amount of WCO in Indonesia is potential as a raw material for producing renewable material. In this study, the WCO was polymerized with boron trifluoride etherate (BF3-etherate) under microwave induction.

Cationic polymerization converts the double bonds in the triglycerides. The initiation step begins with reaction of the double bond with BF3-etherate to become carbocation; then in the propagation step the carbocations attack other double bonds to form polymers (Fig 1). To speed up the reaction, the polymerization can be inducted by microwave [3]. The polymerization will decrease the amount of the double bond in the triglycerides. The decreasing of double bond can be observed according to the iodine
number, infrared (FTIR) spectra, and ultraviolet (UV-Vis) spectra as well. The thermal properties of polymer can be observed using differential scanning calorimetry (DSC) instrument.

2. Experiment

WCO was collected from surrounding the IPB Campus, Dramaga, West Java, then purified with warm water and some activated carbon powder. The composition of fatty acid in purified WCO (p-WCO) was analysed using GC (Shimadzu GC-2010 Plus, employing stationary phase: cyanopropyl methyl sil capillary column). For the analysis of fatty acid in p-WCO, the triglyceride in p-WCO convert into fatty methyl ester to make it volatile. The functional groups were identified using FTIR-ATR (ALPHA BRUKER) and the absorption was determined using UV-Vis spectrophotometer (Shimadzu Pharmaspec UV-1700). All chemicals for determining saponification number, free fatty acid value, and iodine number were analytical grade, purchased from MERCK.

The P-WCO was reacted with BF₃-etherate (TCI) (5%/g WCO) and the mixture was stirred for 15 minutes. Afterward, the mixture was divided into some glass vial for microwave irradiation in a commercial microwave oven. The microwave irradiation was varied by the oven power (450, 600, 800 watt) and time length (3 and 5 minutes). The vial were labelled as WCO i;j (i for the oven power and j for time length of the irradiation). The vials were inserted into a PTFE reactor that was placed in the oven. The solid-form product was further analysed for the iodine number, functional groups, and maximum wavelength absorption. The product with the lowest iodine number was observed for the thermal properties using a differential scanning calorimeter (DSC).

3. Result and discussion

3.1. Characteristic of the WCO

There are four fatty acids in the WCO sample (Table 1). The fatty acid composition confirms that the fatty acids come from palm oil, since palmitic acid and oleic acid are the major constituents in WCO [4].

![Diagram of polymerization of triglycerides with linoleic acid as model.](image-url)
Table 1. The major fatty acid components of P-WCO before polymerization.

| Fatty Acid       | Composition (%) |
|------------------|-----------------|
| Palmitic acid    | 38.34           |
| Stearic acid     | 3.58            |
| Oleic acid       | 40.07           |
| Linoleic acid    | 11.01           |

The infrared spectrum (Fig 2) shows triglyceride functional groups in the WCO. The vibrations peak appear are C-H (sp$^2$) (2921 cm$^{-1}$), C-H (sp$^3$) (2851 cm$^{-1}$), C=O ester (1742 cm$^{-1}$), C-H (1460-1374 cm$^{-1}$), C-O (1158-1093 cm$^{-1}$), and C=C cis (720 cm$^{-1}$). This spectra is similar to Vlachos et al. [5] report.

Figure 2. Infrared spectrum of the P-WCO before polymerization.

Chemical properties of the oil (Table 2) show that iodine number and free fatty acid (FFA) constituent are off the Indonesia National Standard (SNI). It clearly indicates that the oil has been used. The FFA component is higher than the standard due to hydrolysis of the triglyceride; the low iodine number is also interpreted due to oxidation reaction of the double bonds present in the triglyceride. The reactions occur during frying activities [6].

Table 2. Chemical properties of the P-WCO.

| Parameter                  | WCO   | SNI Oil |
|----------------------------|-------|---------|
| Free fatty acid value (%)  | 0.84  | Max 0.3%|
| Saponification number (g KOH/g oil) | 123.50 | 196-206 |
| Iodine number (mg I$_2$/100 g oil) | 37.78  | 45-46   |
3.2. Reaction between WCO and BF$_3$-etherate

The reaction between the WCO and the BF$_3$-etherate changed the WCO colour from golden yellow to reddish brown. The colour change is a consequence of the transformation of the conjugate system from unpolymerized double bond in the triglyceride (Fig 2). The colour change occurred during stirring. The purpose of stirring is to homogenize the reaction of the WCO and the BF$_3$-etherate, to facilitate the initiation step. The initiation process begins with the reaction between the acid and the double bond in the triglycerides to form carbocation. In this step triglyceride not yet polymerized and some double bond some double bonds form the conjugate system. The propagation process is accelerated by the microwave irradiation. In propagation process double bond start to attack carbocation to start polymerized, because of this process amount of double bond in triglyceride is decrease.

There are five type of solid products obtained from the irradiation (Table 3). The solid form is suspected as polymer products. The minimum oven power that produce solid form product is 450 watts and 5 minutes' irradiation (WCO 450;5). However, that reaction condition gives viscous liquid. The higher power than 450 watts with the same irradiation time gives solid products without any viscous liquid. The sample with no irradiation (WCO 0;0) does not show significant change as compared to the raw material (WCO) except the colour. high power produces products with solid products because the higher the radiation energy the higher the energy that allows the polymerization reaction to pass through the activation energy.

![Reaction mechanism on conjugation system.](image)

**Figure 3.** Reaction mechanism on conjugation system.

| Sample     | State          | Colour          |
|------------|----------------|-----------------|
| WCO        | Liquid         | Golden yellow   |
| WCO 0:0    | Liquid         | Reddish brown   |
| WCO 450;3  | Viscous liquid | Reddish brown   |
| WCO 450;5  | Solid with viscous liquid | Reddish brown |
| WCO 600;3  | Solid with viscous liquid | Brown       |
| WCO 600;5  | Solid          | Brown           |
| WCO 800;3  | Solid          | Brown           |
| WCO 800;5  | Solid          | Brown           |
3.3. Iodine Number and Spectral Properties of the Polymerization Product

The polymerization products exhibit lower iodine number compared to the raw material (Table 4), indicating lower extent of the double bond due the polymerization reaction. This is in contrary to the product with no microwave-induced irradiation (WCO 0;0). Similarly, the products with viscous liquid forms (WCO 450;5 and WCO 600;3) do not show significant decrease in the iodine number parameter. The irradiation times do not give significant change in iodine number for the same irradiation power of the microwave oven.

Table 4. Iodine number of products and the raw material.

| Sample   | Iodine number |
|----------|---------------|
| WCO      | 37.78         |
| WCO 0;0  | 36.71         |
| WCO 450;5| 27.22         |
| WCO 600;3| 13.48         |
| WCO 600;5| 6.88          |
| WCO 800;3| 10.15         |
| WCO 800;5| 8.18          |

Spectral analysis is used to support the decrease in iodine number qualitatively. FTIR spectra of the products show similar functional groups with the raw material, but the intensity of C=C (720 cm\(^{-1}\)) in the product weakens. The presence of BF\(_3\)-etherate in the WCO demonstrates trans C=C (970 cm\(^{-1}\)) (Fig 3). The C=C in trans conformation may be due to the rotation of cis C=C, which is the natural conformation in fatty acids. The intensity trans C=C weakens within 5 minutes’ irradiation time (Fig 4). UV-Vis spectra specifies a hypsochromic shift in the products (Fig 5). This shift occurs as a consequence of lessening amount of chromophore group (C=C) in the triglycerides [7].

Figure 4. FTIR spectrum of the polymerization products (WCO 450;5, WCO 600;3, WCO 600;5, WCO 800;3, WCO 800;5) and the raw material (WCO).
3.4. **Thermal Properties**

The DSC thermogram depicts two endothermic transitions. The first transition peak is at temperature 26.56°C and second peak is at 41.12°C (Fig 6). The first transition peak designates a melting point of the monomer [8] and the other is of the polymerization product. The DSC thermogram shows the polymerization process has not been completed because there are still monomers, the incomplete of the polymerization process visually can be seen that there is still a reddish-brown colour which prevents triglycerides that have not been polymerized. The process still needs to cure to complete the process.

![Figure 6. Thermogram of the polymer product.](image_url)

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4. **Conclusion**

Wasted cooking oil can be polymerized with BF3-etheral catalyst with microwave induction. The resulted product showed a decrease in the intensity of double bond as confirmed by a decrease in iodine number, a weakening intensity of the double bond stretch on the FTIR spectra and hypsochromic shift
in the UV-Vis spectrum. The DSC thermogram shows an endothermic transition, meaning that polymerization does occur. The polymerization process still needs to curing to complete the reaction.

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