Microwave-assisted cationic polymerization of palm olein and their urea inclusion products

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Abstract. Cationic polymerization is affected by the relative amount of unsaturated bond (C=C) in the compound. The enrichment of an unsaturated triglyceride fraction from oils may be performed using urea inclusion techniques. In this study, palm olein was enriched-unsaturated fraction using urea-methanol system. The palm olein and its urea-inclusion products were cationic polymerized with ethereal boron trifluoride catalyst and followed by irradiation using a commercial microwave (microwave-assisted). The microwave irradiated products were cured at 110 °C for 24 hours. Fatty acid composition of the palm olein and its urea-inclusion products were analyzed by gas chromatography. Iodine numbers, functional groups, and ultraviolet absorption spectra of all palm olein origin, urea inclusion products and polymerization products were analyzed using titrimetric, ultraviolet spectrophotometric, and Fourier Transform infrared spectrophotometric methods. Differential scanning calorimetric (DSC) was used to observe the thermal characteristics of the polymer. Urea-inclusion process increased the unsaturated fatty acid components as indicated by the increased iodine number, intensity of alkene band absorptions in the infrared spectra, and the absorbance of the ultraviolet spectra. The polymer formation is converting the C=C group to C-C, which is indicated by the opposite of the urea inclusion process. The curing process results in reformation of new C=C bonds that were similar to that of the urea inclusion process. The DSC thermogram curve shows that the enrichment process improves the thermal stability of the polymer formed.

1. Introduction
Cationic polymerization and cationic copolymerization process of various oil (except palm oil) have been investigated [1-6]. Microwaves have been widely used in facilitating the synthesis process, including in polymer synthesis (except palm oil) [7-15]. Previous studies (2017) showed that palm oil in several forms, i.e., crude palm oil (CPO), refined bleached deodorized palm oil (RBDPO), and refined bleached deodorized palm oil-olein (RBDPOO) can also be polymerized through microwave-assisted cationic polymerization with boron trifluoride ethereal catalyst.

Cationic polymerization is affected by the relative amount of the unsaturated bond (C=C) in the materials. Therefore, the unsaturated components are required. The enrichment of an unsaturated triglyceride fraction from oils may be performed using urea inclusion techniques [16-22]. In this study, palm olein enriched the unsaturated fraction using urea-methanol system.
As physical process (urea inclusion) and chemistry process (cationic polymerization) were focused on the C=C bond, we observed the fatty acid composition (GC), the conversion of double bonds (iodine number, infrared and ultraviolet spectra) as well as the thermal properties (DSC thermogram) of the products.

2. Experiment
RBDPOO raw material was purchased from a market in Bogor, directly used without purification. Chemicals for analysis with analytical grade were obtained from Merck: K₂Cr₂O₇, HCl 32%, KI, Na₂S₂O₃.5 H₂O, soluble starch, cyclohexane, CH₃CO₂H, Wijs solution, NaOH, CH₃OH, boron trifluoride-methanol complex 20%, NaCl, hexane, and anhydrous Na₂SO₄. Fatty acid methyl ester standard for fatty acid analysis was acquired from Supelco. Boron trifluoride ethyl ether complex (BF₃.C₄H₁₀O) for polymerization was acquired from TCI.

The urea inclusion was a modified procedure [22]. There were five treatments on urea (weight) - methanol (volume), i.e. (70:50), (60:50), (50:50), (40:50) and (30:50).

The iodine numbers followed an AOAC method [23]. The fatty acid composition was analyzed according to AOAC methods [24 and 25] using Shimadzu GC-2010 Plus gas chromatography, with stationary phase of Cyanopropyl methyl sil capillary column l = 60 m, Øin = 0.25 mm, film thickness 0.25 μm. The ultraviolet spectra was taken using Shimadzu Pharmaspec UV-1700 spectrophotometer and the infrared spectra was taken using Shimadzu IRPrestige-21 FTIR spectrophotometer. Both spectra was taken following the manual instruction of the respective instrument. Thermal properties were analyzed using DSC Instruments Shimadzu DSC 60 under nitrogen atmosphere.

Polymerization reaction was carried out in 100 mL erlenmeyer. The irradiation processes were performed in glass vials (Øin = 20 mm, h = 50 mm) inserted in threaded PTFE reactors (workshop made, Øin = 60 mm, Øout = 100 mm, h = 85 mm) as shown in Figure 1. The microwave ovens used was Samsung MG23H3185PK (230 V, 50 Hz, 2450 MHz; input 1400 W output 800 W).

![Figure 1. The PTFE reactor](image)

3. Results and Discussion

3.1. Characteristics of the RBDPOO and its urea inclusion products
In accordance with previous result [17, 20, 22], the urea inclusion process increases the content of the unsaturated fatty acid fraction (Table 1, C18:1 and C18:2). Increasing the content of unsaturated fatty acids results in the increasing iodine number (Table 2), increased infrared absorption (Fig. 2) at ν 1580 cm⁻¹–1650 cm⁻¹ [26-29], and ultraviolet absorption at λ 220 nm–280 nm (Fig. 3) as well. It is presumably due to the increasing number of the unsaturated carbon-carbon bond. The more the urea used in the mixture, the higher the content of the unsaturated fatty acids.
Table 1. Fatty acid compositions

| Oil Type          | C14:0 | C16:0 | C18:0 | C18:1 | C18:2 |
|-------------------|-------|-------|-------|-------|-------|
| RBDPOO(60:50)-S   | 0.70  | 28.53 | 3.02  | 39.06 | 11.80 |
| RBDPOO(60:50)-U   | 0.83  | 33.16 | 3.47  | 44.70 | 13.41 |
| RBDPOO(50:50)-S   | 0.72  | 29.35 | 2.97  | 38.62 | 11.49 |
| RBDPOO(50:50)-U   | 0.71  | 29.76 | 3.05  | 40.17 | 12.13 |
| RBDPOO(40:50)-S   | 0.65  | 26.67 | 2.68  | 35.06 | 10.47 |
| RBDPOO(40:50)-U   | 0.64  | 26.74 | 2.70  | 35.80 | 10.93 |

Table 2. Iodine numbers of palm oil olein, the urea inclusion products, and the derived polymers

| Oil Type          | Oils form | Polymer without curing | Polymer with curing |
|-------------------|-----------|------------------------|---------------------|
| RBDPOO            | 54.47     | 29.07                  | 41.50               |
| RBDPOO(60:50)-U   | 60.80     | 18.39                  | 27.37               |
| RBDPOO(50:50)-U   | 57.48     | 23.70                  | 30.96               |
| RBDPOO(40:50)-U   | 56.20     | 26.92                  | 31.70               |

3.2. Characteristics of the RBDPOO polymers

The cationic polymerization process converts the C=C bonds to C-C bonds. The change is shown by decreasing the iodine number, the different infrared spectra (Fig. 4), and the shift in ultraviolet spectra (Fig. 5). There is a decreasing infrared absorption on wavenumbers C=C (1654 cm\(^{-1}\), 1648 cm\(^{-1}\)) and =C-H (3025 cm\(^{-1}\), 3006 cm\(^{-1}\), 1418 cm\(^{-1}\), 968 cm\(^{-1}\), 914 cm\(^{-1}\), and 723 cm\(^{-1}\)). In addition to the cationic polymerization, it is also suspected that the reaction of the formation of the double bond is conjugated resulting in an increase in the ultraviolet absorption.

The curing process resulted in the reaction of the reformation of double bonds again was marked by the increase of iodine number (Table 2: 29.07 to 41.50; 18.39 to 27.37; 23.70 to 30.96 and 26.92 to 31.70); and deformation the conjugated double bond so that the decrease of ultraviolet absorption because the conjugate bond increase the ultraviolet absorption. The curing also changes the thermal transition pattern (Fig. 6 and Fig. 7). Heating up to 150 °C deforms the resulted polymers.
3.3. Characteristics of polymers of the RBDPOO urea inclusion product

The polymerization of urea inclusion (60:50) of the RBDPOO shows some results similar to the original RBDPOO. The change is shown by the decreasing iodine number (60.80 to 18.39; Table 2); different infrared spectra (Fig. 8), and different ultraviolet spectra (Fig. 9). The curing also changes the thermal transition pattern (Fig. 10 and Fig. 11). Without curing, heating up to 150 °C supposedly forms a new polymer because showed the different DSC thermogram pattern.
The polymerization of the urea inclusion (50:50) RBDPOO again shows some results similar to the original RBDPOO. The variation is shown by the decreasing iodine number, the different infrared spectra (Fig. 12), and the different ultraviolet spectra (Fig. 13). The curing also produces a different thermogram (Fig. 14). These patterns are similar to that of the polymerized urea inclusion (60:50) of the RBDPOO.
The polymerization of urea inclusion (40:50) RBDPOO shows similar results with the starting RBDPOO. The change is shown by the decrease of iodine number, the change of the infrared spectra (Fig. 15), and the ultraviolet spectra (Fig. 16). The curing process also produces a thermogram (Fig. 17) with a completely different pattern with the previous thermograms.

4. Conclusions
The urea inclusion process increases the unsaturated fatty acid content of the RBDPOO as evidenced by chromatography, spectrometry, and titrimetry techniques. This process is limited by the ratio of urea-methanol (60:50) to (40:50). The post-polymerization thermal treatment is required to complete the reaction. Further studies are needed to determine this thermal treatment in terms of temperature and time of reaction. The proper enrichment process might improve the thermal stability of the polymer.

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