Microwave-Assisted-Cationic Polymerization of Different Type Palm Oils with Boron Trifluoride Etherate Catalyst

Muhamad Farid[1], Bambang Soegijono[1,*], and Zainal Alim Mas'ud[2]

[1]*Department of Physics, Universitas Indonesia, Kampus Baru UI, Depok 16424, Indonesia*

[2]*Department of Chemistry, Bogor Agricultural University,*
Jl. Tanjung Kampus IPB Darmaga, Bogor 16680, West Java, Indonesia

Abstract: *Indonesia is a major producer of palm oils. However, more than 76% of the production is exported as crude palm oil (CPO) with low economic values. Chemical conversion is necessary to produce more valuable derivatives of renewable biobased material including a thermoplastic polymer. In this study, crude palm oils (CPO), refined-bleached deodorized palm oil (RBDPO) and refined bleached deodorized palm oil olein (RBDPOO) were converted under microwave-assisted cationic polymerization with the boron trifluoride etherate catalyst. The precursors were irradiated using the commercial microwave with various reaction conditions. The raw material compositions, iodine values, and functional groups of the raw material and polymers were analyzed by gas chromatography, titrimetry, and Fourier Transform infrared spectrophotometry, respectively. The differential scanning calorimetric (DSC) was used to observe the thermal characteristics of the polymers. The iodine value of the resulting polymer products was lower than the raw materials which indicated the decrease of the C=C bonds due to the polymerization. This result is supported by the decreased intensity of alkene bands in the infrared spectra of the product. The DSC thermogram curve proved that the product is a thermoplastic polymer with a melting point ranged from 40.3 to 45.2 °C; and the freezing point of 22.5 to 28.1 °C. In conclusion, palm oil-based thermoplastic polymer was successfully synthesized and characterized, and the best result was achieved when using RBDPOO as starting material.*

Keywords: *palm oil; cationic polymerization; microwave; biobased materials*

■ INTRODUCTION

Indonesia and Malaysia are the main producers of palm oils with the production continue to increase annually [1]. The area of oil palm plantations in Indonesia in 2014 reached 6.4 million ha with a production of 22.9 million tons, and 17.46 million tons were exported with a value of US $ 17.46 million [2]. The economic value of palm oils can be enhanced by the production of the more valuable derivative product, the oleochemical compounds before being exported [3].

Based on their functional groups, the oleochemical preparation of biobased oils comes from the reaction to carboxy groups or fatty acid chains. The oleochemical products of the carboxy group reaction of the biobased oils are soap, fatty acids, fatty amine, fatty alcohols, glycerol [4], fatty amide amides, quaternary ammonium compounds, amine oxides, fatty alcohol ethoxylate and so on [5-6]. The oleochemical products derived from the unsaturated fatty acid chain, such as oleic acid and linoleic acid, are obtained by epoxidation, the opening of the epoxidized fatty acid ring, hydroformylation, dimerization, oxidative termination, ozonolysis, and metathesis reaction [4,7]. Polymerization through epoxides produces polymers of different hardness [7]. The other reaction of the unsaturated fatty acid chain was the cationic polymerization conducted in the presence of acid. Cationic polymerization and cationic copolymerization process of various oil have been done

[8-13] which unfortunately has not involved palm oil yet. Microwaves have been widely used in facilitating the synthesis process, including polymer synthesis [14-16] and have never been also used for palm oil polymerization.

In this paper, different condition of microwave-assisted-cationic polymerization of CPO, RBDPO, and RBDPOO with the boron trifluoride etherate catalyst of were studied, The obtained polymers were analyzed by titrimetry and Fourier Transformed infrared spectrophotometry and were then compared to the raw material. The differential scanning calorimetric (DSC) was used to observe the thermal characteristics of the polymers.

■ EXPERIMENTAL SECTION

Materials

Crude palm oil (CPO) was obtained from Sei Mangkei Palm Oil Innovation Center, Kab. Simalungun, North Sumatra; refined-bleached deodorized palm oil (RBDPO) was received from PT Bina Karya Prima, Medan Satria, Kota Bekasi; and refined bleached deodorized palm oil olein (RBDPOO) was purchased from the market in Bogor. All raw materials were directly used without any purification. Chemicals for analysis with analytical grade were obtained from Merck: $K_2Cr_2O_7$, HCl 32%, KI, $Na_2S_2O_3.5 H_2O$, soluble starch, cyclohexane, CH_3CO_2H, Wijs solution, NaOH, CH_3OH, boron trifluoride-methanol-complex 20%, NaCl, hexane, anhydrous Na_2SO_4, and fatty acid methyl ester (Supelco). Chemical for polymerization using boron trifluoride diethyl ether complex ($BF_3.C_4H_{10}O$) was acquired from TCI.

Instrumentation

The fatty acid composition was analyzed using Shimadzu GC-2010 Plus gas chromatography, with stationary phase of Cyanopropyl methyl sil capillary column l = 60 m, $\varnothing_{in}$ = 0.25 mm, film thickness 0.25 μm. Infrared spectra were taken using Shimadzu Prestige-21 FTIR spectrophotometer with DRIFTS module. The Reactions were carried out in glass vials ($\varnothing_{in}$ = 20 mm, h = 50 mm) inserted in threaded PTFE reactors (workshop made, $\varnothing_{in}$ = 60 mm, $\varnothing_{out}$ = 100 mm, h = 85 mm) and the microwave oven used was Sharp R 222 Y (S) (220 V, 50 Hz, 2450 MHz; input 0.7 kW output 399 W; Thermoanalysis was observed using DSC Instruments Netzsch DSC 200 F3 Maia under nitrogen atmosphere.

Procedure

Characterization of raw materials

Iodine values (titrimetric methods) [17], and fatty acid composition [18-19], of all oil raw materials (CPO, RBDPO, and RBDPOO) were analyzed. All oil raw materials (CPO, RBDPO, and RBDPOO) were also characterized by FTIR [20].

Micro-wave assisted cationic polymerization

The irradiation on raw materials was carried out by the threaded PTFE reactors in 3 vial glass bearing, each containing 3 g of material under microwaves irradiation with 399 W power for 10 min.

Determination of minimum time of irradiation with 399 W power. Into an Erlenmeyer flask, 18 g of raw material and 0.9 g of catalyst were added, then it was stirred using magnetic stirrer for 1 h. Two vials each containing 3 g of raw material and 3 g of raw material that has been mixed with the catalyst were put into threaded PTFE reactor. The reactor was closed; then it was irradiated with 399 W power for 1 min. The vials were removed from the reactor and allowed to stand for 24 h. The experiment was repeated under irradiation time of 2, 3, 4 and 5 min.

Determination of the effect of power and irradiation time. Into an Erlenmeyer, 30 g of raw materials and 1.5 g of catalyst were added, then stirred using a magnetic stirrer for 1 h. Into a threaded PTFE reactor, 2 vials were inserted, each containing 3 g of raw material and 3 g of raw material that has been mixed with the catalyst. The reactor was closed, then irradiated under 399 W power for 5 min. The vials were removed from the reactor and allowed to stand for 24 h. The irradiation was repeated under 399 W power and for 10 min. The irradiation was repeated under different power: 279.3; 199.5 and 119.7 W.
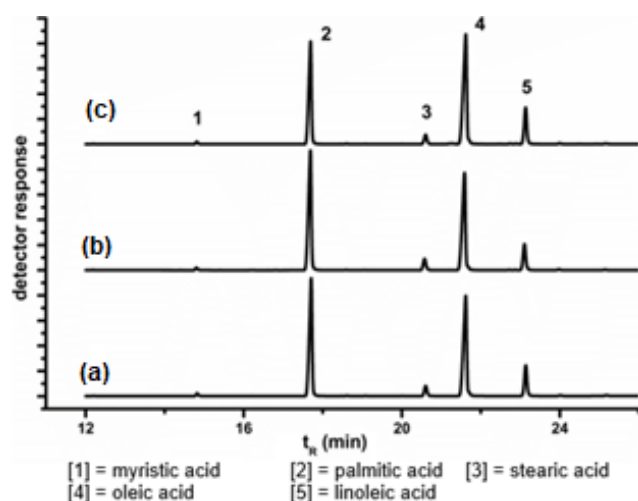
Fig 1. GC chromatogram of (a) CPO, (b) RBDPO and (c) RBDPOO methyl ester fatty acid

[1] = myristic acid   [2] = palmitic acid   [3] = stearic acid
[4] = oleic acid   [5] = linoleic acid

Characterization of polymerization products

Solid polymerization products were analyzed for their solubility in cyclohexane, iodine value, FTIR spectra and DSC thermogram for studying time and microwave irradiation power impact.

■ RESULTS AND DISCUSSION

Iodine Values, Fatty Acid Composition of the Raw Materials and FTIR Spectra

The three raw materials (CPO, RBDPO, and RBDPOO) used in this study came from different sources and were not from a series of CPO-RBDPO-RBDPOO processing processes. Thus, the iodine values found were irregular. Basically, in a series of processing from CPO-RBDPO-RBDPOO, iodine value would increase. The iodine value and infrared spectrum of this raw material were used to follow the cationic polymerization process. The iodine value of the raw material was 56.62 for the CPO which was higher than that in the literature [21-22]. This phenomenon is probably due to the presence of another nonglyceride unsaturated material which gives a positive contribution to iodine value. The iodine value of the RBDPO was 52.04 (according to the vendor was 52.41), this value was close to the literature value [21]. The iodine value of the RBDPOO was 50, lower than the literature value of 56 [23-24]. The lowest value for RBDPOO is due to the low unsaturated fatty acid content of the CPO raw material.
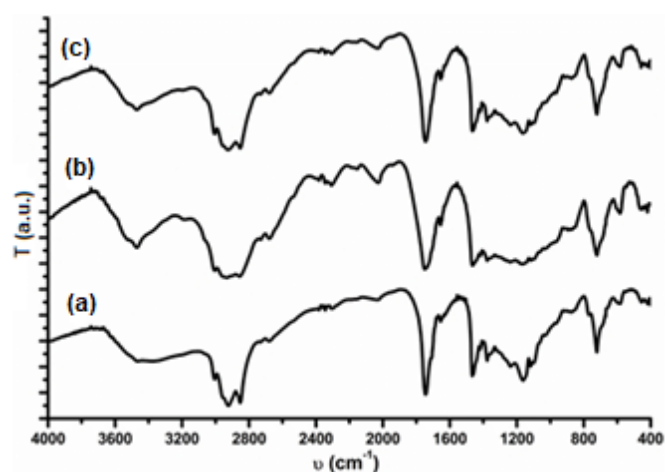

Fig 2. FTIR spectra of (a) CPO, (b) RBDPO, and (c) RBDPOO

Table 1. The fatty acid composition of palm oil (% w/w)

Fatty acid	CPO	RBDPO	RBDPOO
C12:0 (Lauric Acid)	0.07	0.09	0.10
C14:0 (Myristic acid)	0.68	0.67	0.62
C16:0 (Palmitic acid)	33.76	35.00	27.61
C16:1 (Palmitoleic acid)	0.11	0.10	0.12
C18:0 (Stearic acid)	2.85	3.26	2.66
C18:1 (Oleic acid)	32.66	31.38	36.81
C18:2 (Linoleic acid)	8.91	7.83	10.51
C18:3 (γ–linolenic acid)	0.00	0.03	0.03
C20:0 (Arachidic acid)	0.24	0.26	0.23

The GC chromatogram of the fatty acid composition is shown in Fig. 1. All of the raw materials of oil (CPO, RBDPO, and RBDPOO) show the five main components of fatty acids, namely myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid (Table 1). The palm oil processing increased the unsaturated component (C18:1 and C18:2) and lowered the saturated component (C16:0 and C18:0) which was in line with the iodine value.

The FTIR spectra of the raw material are shown in Fig. 2. The three raw materials exhibit similar patterns because they contain the same groups. All raw materials have signals at wave number of 2922 (–C–H (CH$_2$) stretching asymmetric), 2852 (–C–H (CH$_2$) stretching symmetric), 1745 (C=O ester stretching), 1465 cm^{-1} (–C–H (CH$_2$, CH$_3$) bending/scissoring), 1377 (–C–H (CH$_3$) bending symmetric), 1238 (–C–O or –CH$_2$– stretching, bending), 1163 (–C–O or –CH$_2$– stretching,

bending), and 721 cm^{-1} (–(CH$_2$)$_n$–, or –HC=CH– (cis-) bending/rocking) that were similar to literature [25-28].

Microwave-Assisted Cationic Polymerization

The effect of microwave irradiation on raw material

In the absence of a catalyst, the CPO, the RBDPO and the RBDPOO subjected to microwave irradiation treatment at 2450 MHz frequency, 399 W power for 10 min did not give the visually changes. Previous research on the effects of microwave irradiation on various oils/fats have been widely practiced [29-31]. All of them showed changes in chemical and physical parameters that are directly proportional to the power and time of irradiation. However, they did not produce solid and color changes, indicating that there was no polymerization and formation of double bonds conjugated reaction occur due to microwave irradiation treatment.

The effect of catalyst

The three raw materials (CPO, RBDPO, and RBDPOO) which were added with catalyst, and stirred for 1 h underwent the reaction indicated from the visual change from pale yellow to red to dark brown viscous liquid. This phenomenon was similar to other research [32-34]. This occurs due to the formation of conjugated dienes and triene. The conjugated polyene molecule requires only a small amount of energy for electronic excitation (the radiative energy of the visible beam area is sufficient), giving rise to dark appearance [35].
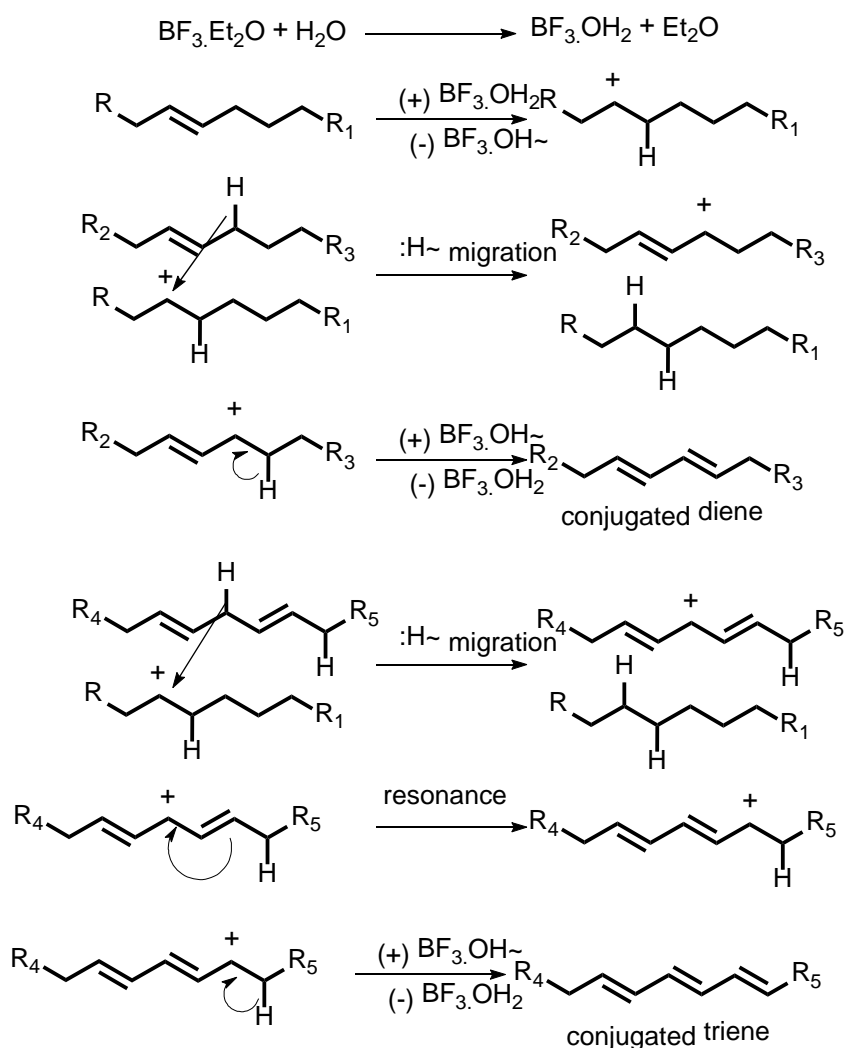

Fig 3. Conjugated alkene formation mechanism

The mechanism can be explained as follows: Catalyst $BF_3.Et_2O$ reacts with water to form $BF_3\bullet OH_2$. Species $BF_3\bullet OH_2$ reacts with the –CH=CH– alkene group (oleate) to form saturated carbocation ($-CH_2-HC^{\oplus}-$) [8, 36-39]. The Saturated carbocation can react through 2 pathways. In the first pathways, it reacts with the –CH_2–CH=CH– alkene group (oleate) which forms the allyl cation ($-CH^{\oplus}-CH=CH-$). This allyl cation protons into the conjugate base of $[BF_3.OH]^-$ forms a conjugated diene. In the second pathways, the carbocation reacts with the bis-allylic group –CH=CH–CH_2–CH=CH– alkene (linoleate) which initially forms –CH=CH–$CH^{\oplus}$–CH=CH– cations, and subsequently undergoes rearrangement into –CH=CH–CH=CH–$CH^{\oplus}$– cation. This bisallylic cation proton release into the conjugate base of $[BF_3.OH]^-$ to generate a conjugated triene (Fig. 3) [12].

The effect of power and time of microwave irradiation

The microwave irradiation treatment with 399 W power in less than 5 min did not produce any solid polymer after sitting for 24 h. The microwave irradiation with 399 W power for 5 and 10 min resulted in brown solids. The minimum time of microwave irradiation with 279.3 W power to produce brown solids was 10 min. As the control, the raw material without catalyst addition was treated in the same reactor. This study showed that there was no cross contamination characterized by the absence of changes/reactions to the control, indicating the absence of a $BF_3.Et_2O$ (volatile) catalyst that escapes from the first vial (contains a mixture of raw material and catalyst) to the second vial (containing only raw material) even in a closed PTFE reactor. The slow reaction of the cationic polymerization was characterized by the only formation of the light brown liquid mixture which was not solidified even though the reaction mixture is allowed for 1 month at room temperature.

The reaction of conjugated alkene formation was characterized by the appearance of dark brown color. there was also an additional reaction of polymerization and Diels-Alder addition which was indicated by the formation of solids. The polymerization reaction occurs because of the carbocation formed by the reaction of the
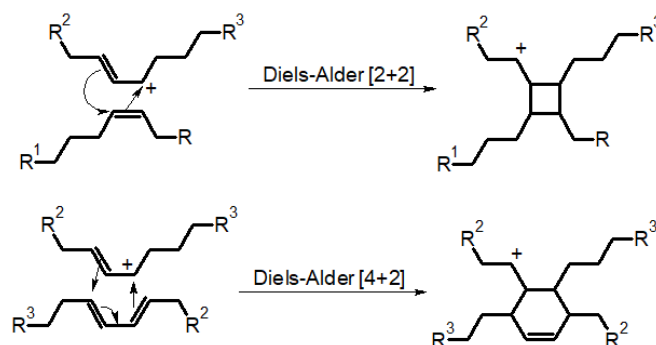

Fig 4. Diels–Alder reaction mechanism

–CH=CH– alkene group (oleate) with the $BF_3.Et_2O$ catalyst reacts with the alkene group (oleate) to another glyceride molecule through a cationic addition mechanism to form a polymer [8,36-39]. The Diels-Alder reactions that cross the hydrocarbon chain can occur in either a glyceride molecule or among molecules of glyceride (polymerization) (Fig. 4) [7,9-13].

Characterization of cationic polymerization products

The cationic polymerization products from CPO, RBDPO, and RBDPOO were characterized in the form of solubility in cyclohexane, iodine value, infrared spectra, and its DSC thermogram. Study on the effects of time and power of microwave irradiation that produce solids after 24 h allowed to be performed on RBDPOO.

Changes in iodine value and infrared spectrum of raw materials and their polymer

The iodine value of the raw materials and their cationic polymerization products are shown in Table 2. The cationic polymerization process converts the bond of C=C to C–C. The decrease of the C=C bonding content was indicated by the decrease of the iodine value of polymerization products when compared to the raw materials [9-13,31,40]. As can be seen in Table 2 (entry 1 vs. 3), the irradiation of CPO, RBDPO, and RBDPOO with the energy of 399 W for 5 min reduced the iodine value, where RBDPOO showed the highest reduction of iodine value. Therefore, RBDPOO had the largest degree of polymerization conversion.

In this study, the effect of the power on the reduction of iodine value was also evaluated. While the power of 279 W may reduce the iodine value of

RBDPOO from 52.28 to 43.42 (Table 2, entry 1 vs. 2), the application of 399 W irradiation gave a higher reduction from 52.28 to 41.99 (Table 2, entry 1 vs. 3). We also found that the longer irradiation time, the lower the iodine value will be. Treatment of RBDPO under 399 W for 10 min allowed us to have lower iodine value comparing to 5 min of irradiation (Table 2, entry 3 vs. 4).

In general, the longer the irradiation time and the stronger the irradiation power will decline the iodine value of the product. All cationic polymerization product was soluble in cyclohexane due to the absence of crosslink. Additional experiments were carried out by performing copolymerization of divinyl benzene, yielding the product which was insoluble in cyclohexane and has the iodine value of 39.49 (smaller than the RBDPOO cationic polymerization product). Similar results were obtained when soybean oil was used as raw material [36-39]. It indicated that the increasing number of double bonds in RBDPOO which underwent the copolymerization reactions and the inclusion of the aromatic structure of the DVB into the copolymer.

The results of FTIR scanning of raw materials and their polymers are shown in Fig. 5 to 7. The cationic polymerization process converted the C=C bond to C–C, as indicated by reduction peak intensity in all spectra at wave numbers 3006 (=C–H cis stretching), 1654 and 1648 (C=C stretching), and 723 cm^{-1} (=C–H cis stretching) [25-28]. Besides, the peak intensity in wave number 968 cm^{-1}, proved that the rearrangement of some initial cis-double bonds of RBDPOO to trans-double bonds occurs in the presence of catalyst [12]. The splitting of the 1740 cm^{-1} wave number spectral peak presumably due to oxidation of C=C group from conjugated triene (–C=C–C=C–C=C–) by oxygen from atmosphere to form conjugated diene with C=O group (–C=C–C=C–(C=O)–) during the microwave irradiation in the cationic polymerization process.

DSC thermogram curve of cationic polymerization products

The DSC thermogram curve of the polymer resulted from the 399 W power microwave irradiation

Table 2. The iodine value of raw materials and their cationic polymerization products (g I$_2$/100 g sample)

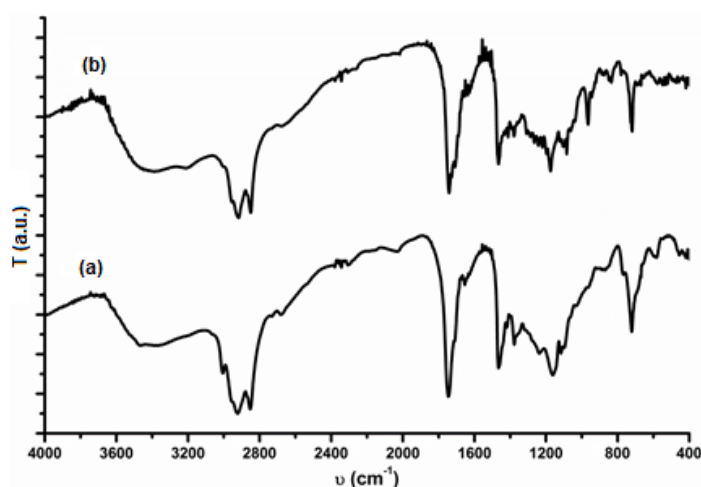|	Raw material		
	CPO	RBDPO	RBDPOO
Blank	56.62	52.04	50.28
Irradiation 279.3 W, 5 min			43.42
Irradiation 399 W, 5 min	49.98	44.99	41.99
Irradiation 399 W, 10 min			40.32

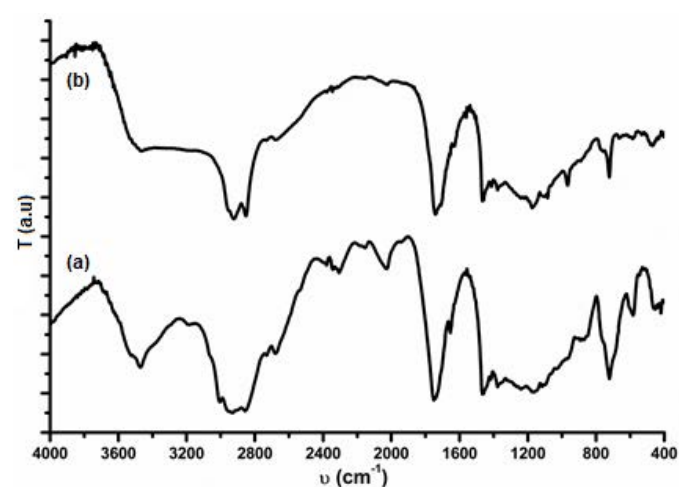**Fig 5.** FTIR spectrum of (a) CPO and (b) it's cationic polymerization product

Fig 6. FTIR spectrum of (a) RBDPO and (b) it's cationic polymerization product

treatment of CPO, RBDPO, and RBDPOO which is shown in Fig. 8. The thermogram curve is analogous to the general thermogram curve of the oil, i.e., the heating curve is endothermic, and the cooling curve is exothermic [41-44].

The heating curve of the CPO cationic polymerization product (CPO-a) and RBDPOO (RBDPOO-a) gave nearly similar curves having two endothermic transitions. Higher thermal transitions for CPO cationic polymerization products occurred when the temperature was 40.3 °C, while the RBDPOO cationic polymerization product occurred at 45.2 °C. A higher thermal transition was thought to be a melting point. The heating curve of the RBDPO cationic polymerization product (RBDPO-a) had three different thermal transitions, i.e., the lower first thermal transition was the shoulder of the second higher thermal transition (44.2 °C), and both were endothermic, while the third thermal transition (47.1 °C) was exothermic.

The cooling curve of CPO cationic polymerization product (CPO-b), RBDPO (RBDPO-b) and RBDPOO (RBDPOO-b) had the similar curve that has an exothermic
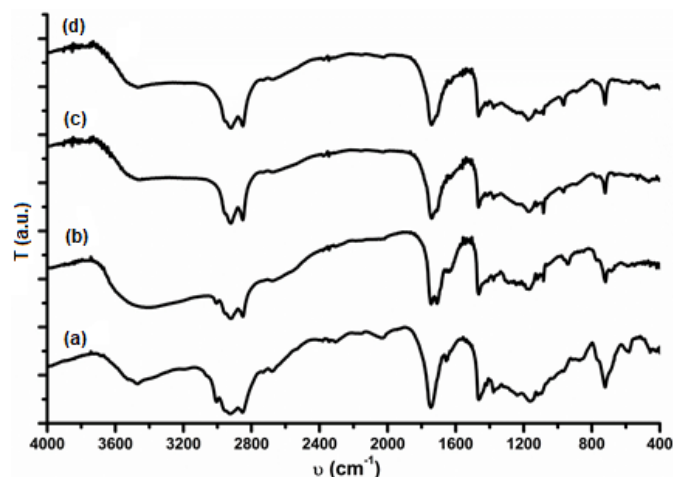

Fig 7. FTIR spectrum of (a) RBDPOO, and it's cationic polymerization product irradiated with (b) 279.3 W, 5 min.; (c) 399 W, 5 min.; and (d) 399 W, 10 min
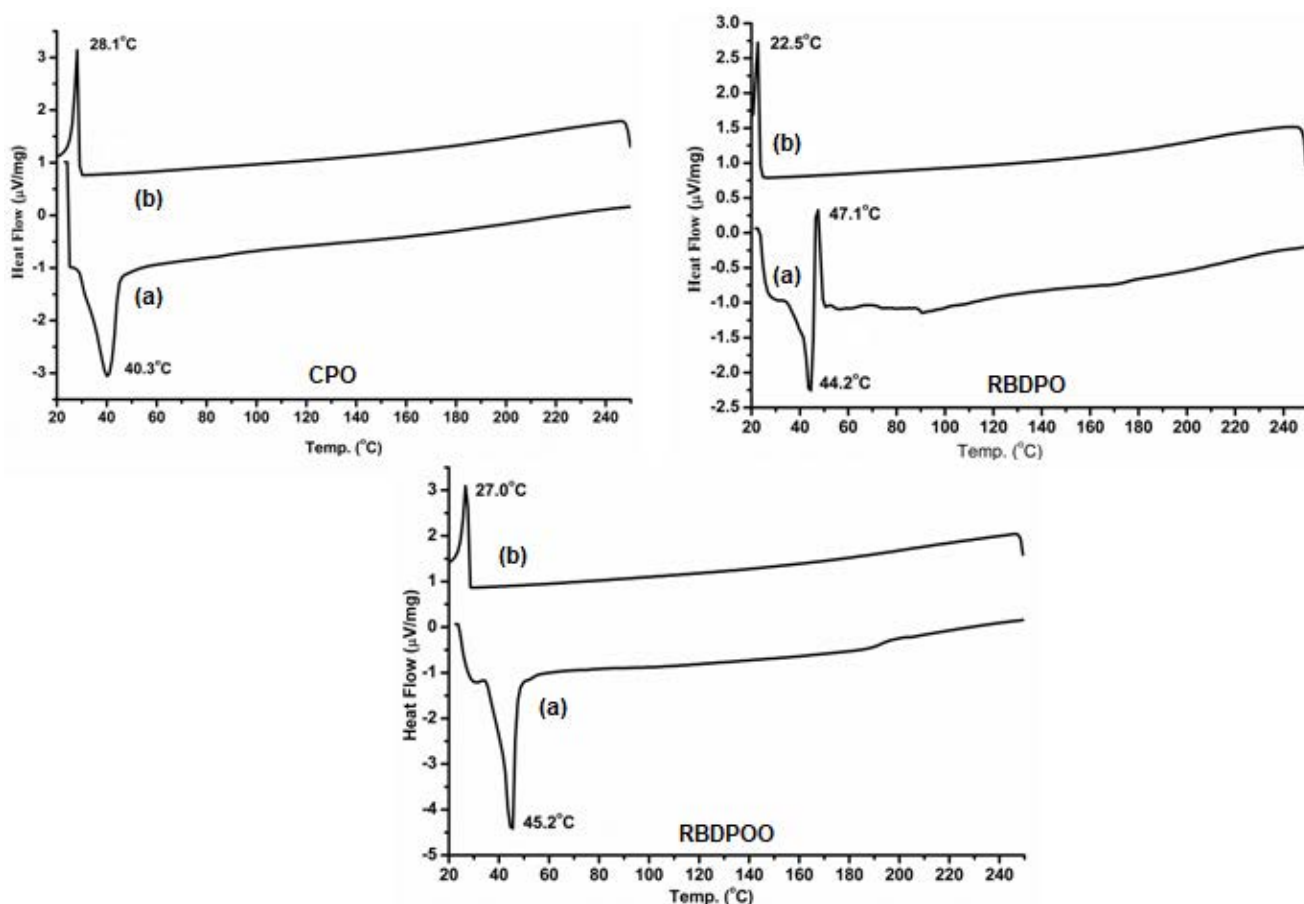

Fig 8. DSC thermogram cationic polymerization product of Palm oil a) heating curve, b) cooling curve
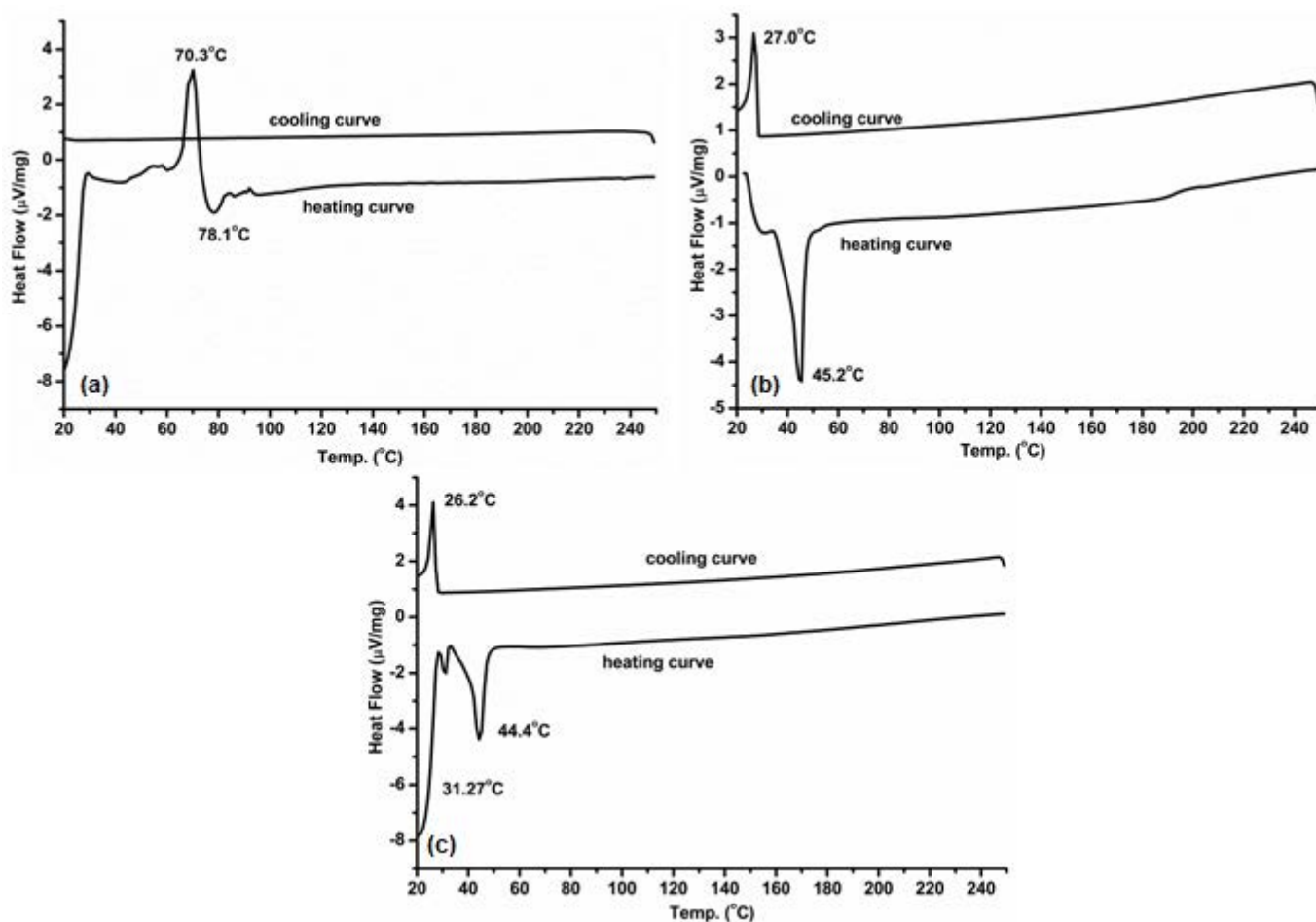
Fig 9. DSC thermogram cationic polymerization of RBDPOO at a different time and power irradiation. (a) 279.3 W, 5 min, (b) 399 W, 5 min, and (c) 399 W, 10 min

transition and was thought to be the crystallization temperature, of different value. The crystallization temperature for CPO, RBDPO, and RBDPOO cationic polymerization products were 28.1, 22.5, and 27 °C, respectively.

The different irradiation power and different irradiation times for RBDPOO raw material resulted in diverse DSC thermogram curves (Fig. 9). The RBDPOO–irradiated heating thermogram curve which was 279.3 W power irradiated (RBDPOO-a) shows an exothermic transition at 70.3 °C and the forming of thermoset polymers were characterized by the absence of thermal transition on the cooling curve (RBDPOO-b). While the irradiation treatment product was 399 W power for 5 min (RBDPOO-a) and 10 min (RBDPOO-a) shows an endothermic heating thermogram curve that occurred at

45.2 and 44.4 °C. The cooling thermogram curve shows an exothermic transition of product crystallization which was resulted from 399 W power irradiation treatment for 5 min (RBDPOO-b) at 27.0 °C and for 10 min (RBDPOO-b) at 26.2 °C.

To prove that the polymer of RBDPOO irradiated under 399 W power for 5 min was a thermoplastic polymer, a scanning process was performed by heating and cooling for 4 cycles in the temperature range 20 to 80 °C (Fig. 10). Due to the heating and cooling treatment, transition temperature shifted to a certain temperature. The shift in the temperature of the endothermic transition due to the heating treatment of the polymer was exhibited successively at 39.6, 32.9, 34.1, and 34.1 °C. On the other hand, the shift of the exothermic transition temperature due to the cooling treatment was observed successively at
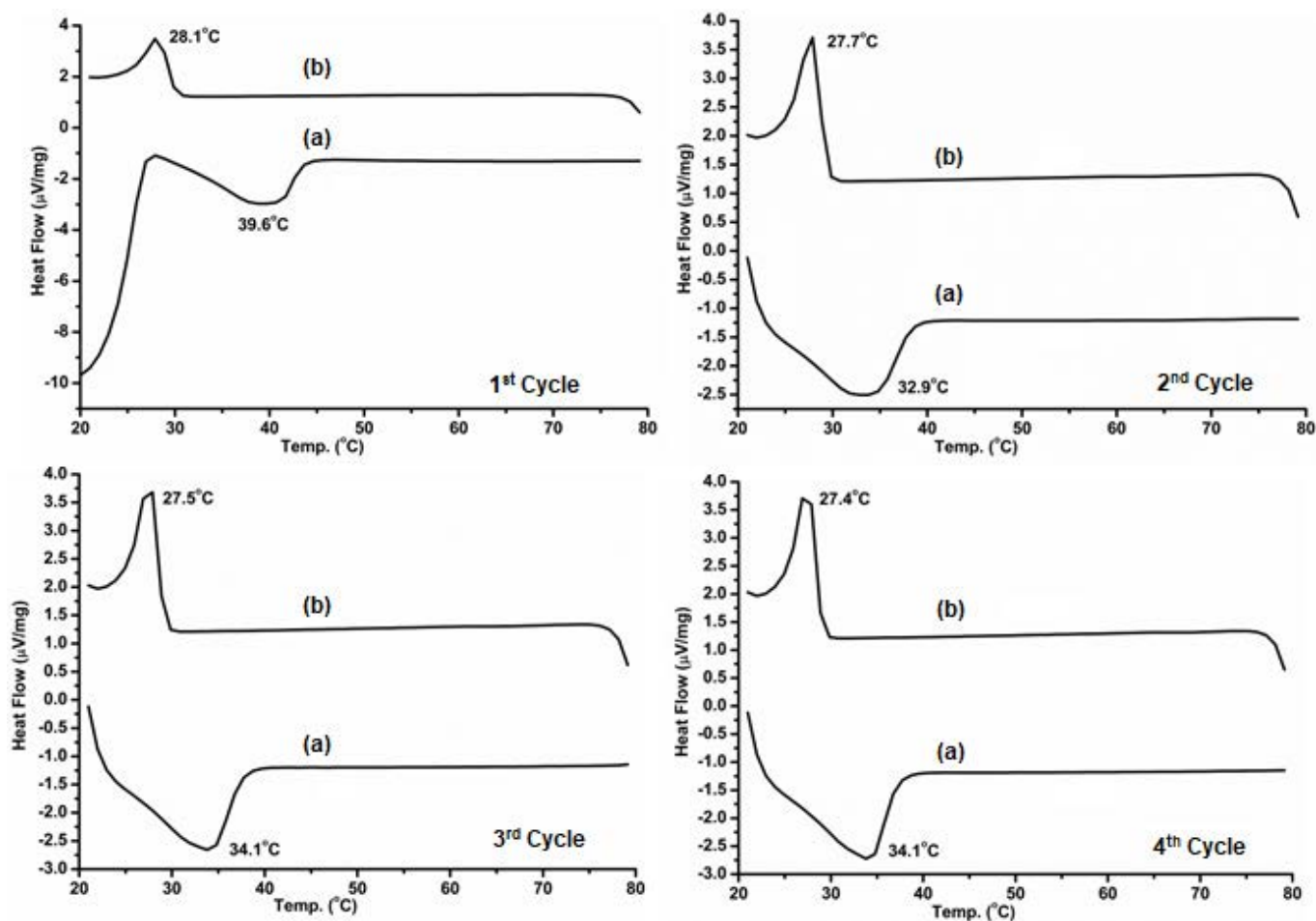
Fig 10. DSC (a) heating and (b) cooling thermogram cationic polymerization product of RBDPOO (399 W, 5 min) (cycle curve)

a temperature of 28.1, 27.7, 27.5, and 27.4 °C. This shows that after the polymerization process, the polymer formed must undergo curing treatment in order to obtain a thermally stable final form.

■ CONCLUSION

Palm oil in the form CPO, RBDPO and RBDPOO can be microwave assisted cationic polymerized using 5% $BF_3.Et_2O$ catalyst with a minimum time of 5 min irradiation and 399 W irradiation power. The product was solidified after allowed to stand for 24 h. The characteristic of products was depended on the time and power of microwave irradiation where 10 min irradiation and 399 W irradiation power gave the best product seen from its lowest iodine value. The product had a lower iodine value compared to the raw material due to the

conversion of some C=C double bond to become a C–C single bond that supported by infrared spectra. The polymers formed were thermoplastic and soluble in cyclohexane, and had different infrared spectra from their original raw materials. This polymer must undergo curing to become thermally stable.

■ ACKNOWLEDGMENTS

■ **REFERENCES**

[1] FAO, 2016, *FAOSTAT*, http://faostat3.fao.org/download/Q/QC/E, accessed on May 7, 2016.

[2] BPS, 2016, *Luas Areal Tanaman Perkebunan Besar Menurut Jenis Tanaman (000 Ha, 1995-2014*)*, https://www.bps.go.id/linkTabelStatis/view/id/1665, accessed on May 7, 2016.

[3] Sulistyanto, A.I., and Akyuwen, R., 2011, Factors affecting the performance of Indonesian's crude palm oil export, *International Conference on Economics and Finance Research, IPEDR*, 4, 281–289.

[4] Corma, A., Iborra, S., and Velty, A., 2007, Chemical routes for the transformation of biomass into chemicals, *Chem. Rev.*, 107 (6), 2411–2502.

[5] Appalasami, S., and de Vries, R.J., 1990, The future of palm oil in oleochemicals, *Palm Oil Dev.*, 14 (3), 18–29.

[6] Rupilius, W., and Ahmad, S., 2006, The changing world of oleochemicals, *Palm Oil Dev.*, 44 (15), 21–28.

[7] Petrović, Z.S., 2010, Polymers from biological oils, *Contemp. Mater.*, I (1), 39–50.

[8] Larock, R.C., Hanson, M., and Li, F., 2002, Lewis acid-catalyzed polymerization of biological oils and resulting polymeric materials, *U.S. Patent 2002/0095007 A1*, July 18, 2002.

[9] Ionescu, M., and Petrović, Z.S., 2008, Cationic polymerization of biological oils, *U.S. Patent 2008/0281071 A1*, November 13, 2008.

[10] Ionescu, M., and Petrović, Z.S., 2009, Cationic polymerization of biological oils with superacid catalysts, *U.S. Patent 7501479 B2*, March 10, 2009.

[11] Ionescu, M., and Petrović, Z.S., 2009, Cationic polymerization of biological oils, *U.S. Patent 2009/0309064 A1*, December 17, 2009.

[12] Ionescu, M., and Petrović, Z.S., 2011, "Polymerization of Soybean Oil with Superacids" in *Soybean-Applications and Technology*, Eds. Tzi, B.N., InTech, Rijeka, Croatia, 365–386.

[13] Ionescu, M., and Petrović, Z.S., 2011, Cationic polymerization of biological oils, *U.S. Patent 8013088 B2*, September 6, 2011.

[14] Zong, L., Zhou, S., Sgriccia, N., Hawley, M.C., and Kempel, L.C., 2003, A review of microwave-assisted polymer chemistry (MAPC), *J. Microwave Power Electromagn. Energy*, 38 (1), 49–74.

[15] Sinnwell, S., and Ritter, H., 2007, Recent advances in microwave-assisted polymer synthesis, *Aust. J. Chem.*, 60 (10), 729–743.

[16] Sosnik, A., Gotelli, G., and Abraham, G.A., 2011, Microwave-assisted polymer synthesis (MAPS) as a tool in biomaterials science: How new and how powerful, *Prog. Polym. Sci.*, 36 (8), 1050–1078.

[17] AOAC, 2012, AOAC official method 993.20, *Iodine value of fats and oils wijs (cyclohexane–acetic acid solvent) method*, 19th ed., Official methods of analysis of AOAC international, AOAC, Arlington, Virginia.

[18] AOAC, 2012, AOAC official method 969.33, *Fatty acids in oils and fats preparation of methyl esters boron trifluoride method*, 19th ed., Official methods of analysis of AOAC international, AOAC, Arlington, Virginia.

[19] AOAC, 2012, AOAC official method 963.22, *Methyl esters of fatty acids in oils and fats gas chromatographic method*, 19th ed., Official methods of analysis of AOAC international, AOAC, Arlington, Virginia.

[20] Shimadzu Corporation, 2002, *Instruction Manual IRPrestige-21*, Shimadzu Corporation, Kyoto, 78.

[21] Firestone, D., 1994, Determination of the iodine value of oils and fats: summary of collaborative study, *J. AOAC Int.*, 77 (3), 674–676.

[22] Balai Besar Industri Agro, 2013, *Laporan uji profisiensi Balai Besar Industri Agro Tahun 2013 komoditas: crude palm oil (CPO)*, Balai Besar Industri Agro, Bogor.

[23] Siew, W.L, 2011, "Palm Oil" in *Vegetable Oils in Food Technology Composition, Properties and Uses*, 2nd ed., Eds., Gunstone, F.D., Blackwell Publishing Ltd., Oxford, 25–58.

[24] Komite Akreditasi Nasional, 2008, *Program Uji Profisiensi KAN XI/2008: Minyak Goreng*, Jakarta.

[25] Chapman, D., 1965, Infrared spectroscopy of lipids, *J. Am. Oil Chem. Soc.*, 42 (5), 353–371.

[26] Freeman, N.K., 1968, Applications of infrared absorption spectroscopy in the analysis of lipids, *J. Am. Oil Chem. Soc.*, 45 (11), 798–809.

[27] Guillén, M.D., and Cabo, N., 1997, Infrared spectroscopy in the study of edible oils and fats, *J. Sci. Food Agric.*, 75 (1), 1–11.

[28] Guillén, M.D., and Cabo, N., 1997, Characterization of edible oils and lard by fourier transform infrared spectroscopy. Relationships between composition and frequency of concrete bands in the fingerprint region, *J. Am. Oil Chem. Soc.*, 74 (10), 1281–1286.

[29] Farag, R.S., Hewedi, F.M., Abo-Raya, S.H., and El-baroty, G.S.A., 1991, A comparative study on the deterioration of oils by microwave and conventional heating, *Grasas y Aceites*, 42 (3), 187–193.

[30] Kreps, F., Vrbiková, L., Schmidt, S., Sekretár, S., and Híreš, O., 2014, Chemical changes in microwave heated vegetable oils, *Eur. J. Lipid Sci. Technol.*, 116 (12), 1685–1693.

[31] Abbas Ali, M., Bin Mesran, M.H., Abd Latip, R., Othman, N.H., and Nik Mahmood, N.A., 2016, Effect of microwave heating with different exposure times on the degradation of corn oil, *IFRJ*, 23 (2), 842–848.

[32] Whiteley, J.M., Elizabeth and Turner, L.B., 1941. Treating fatty oils and the like, *U. S. Patent 2260417*, October 28, 1941.

[33] Cowan, J.C., Wheeler, D.H., Teeter, H.M., Paschke, R.E., Scholfield, C.R., Schwab, A.A., Jackson, J.E., Bull, W.C., Earle, F.R., Foster, R.J., Bond, W.C., Beal, R.E., Skell, P.S., Wolff, I.A., and Mehltretter, C., 1949, Polymerization of drying oils, *Ind. Eng. Chem.*, 41 (8), 1647–1653.

[34] Croston, C.B., Tubb, I.L., Cowan, J.C., and Teeter, H.M., 1952, Polymerization of drying oils. VI. Catalytic polymerization of fatty acids and esters

with boron trifluoride and hydrogen fluoride, *J. Am. Oil Chem. Soc.*, 29 (8), 331–333.

[35] Pavia, D.L., Lampman, G.M., Kriz, G.S., and Vyvyan, J.R., 2009, *Introduction to Spectroscopy*, 4th ed., Brooks/Cole, Cengage Learning, Belmont, 15–104.

[36] Li, F.K., and Larock, R.C., 2002, Novel polymeric materials from biological oils, *J. Polym. Environ.*, 10 (1-2), 59–67.

[37] Lu, Y.S., and Larock, R.C., 2009, Novel polymeric materials from vegetable oils and vinyl monomers: Preparation, properties, and applications, *ChemSusChem*, 2 (2), 136–147.

[38] Xia Y., and Larock, R.C., 2010, Vegetable oil-based polymeric materials: synthesis, properties, and applications, *Green Chem.*, 12 (11), 1893–1909.

[39] Xia, Y., Quirino, R.L., and Larock, R.C., 2013, Bio-based thermosetting polymers from vegetable oils, *J. Renewable Mater.*, 1 (1), 3–27.

[40] Llevot, A., 2017, Sustainable synthetic approaches for the preparation of plant oil-based thermosets, *J. Am. Oil Chem. Soc.*, 94 (2), 169–186.

[41] Kawamura, K., 1979, The DSC thermal analysis of crystallization behavior in palm oil, *J. Am. Oil Chem. Soc.*, 56 (8), 753–758.

[42] Kawamura, K., 1980, The DSC thermal analysis of crystallization behavior in palm oil, II, *J. Am. Oil Chem. Soc.*, 57 (1), 48–52.

[43] Man, Y.B.C., Haryati, T., Ghazali, H.M., and Asbi, B.A., 1999, Composition and thermal profile of crude palm oil and its products, *J. Am. Oil Chem. Soc.*, 76 (2), 237–242.

[44] Zhang, X., Li, L., Xie, H., Liang, Z., Su, J., Liu, G., and Li, B., 2013, Comparative analysis of thermal behavior, isothermal crystallization kinetics and polymorphism of palm oil fractions, *Molecules*, 18 (1), 1036–1052