

SYNTHESIS AND PROPERTIES OF ETHOXYLATED GLYCEROL MONOOLEATE AS PALM OIL BASED NONIONIC SURFACTANTS

SINTESIS DAN PROPERTI GLISEROL MONOOLEAT ETOKSILAT SEBAGAI SURFAKTAN NONIONIK BERBASIS MINYAK KELAPA SAWIT

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ABSTRACT

Palm oil based nonionic surfactants were synthesized by reacting glycerol monooleate with ethylene oxide at 80 °C in the prescence of an alkaline catalyst. Purification of the products was conducted by use of acetic acid and black carbon which gave ethoxylated products (EGMO) with a higher level of viscocity and greater solubility in water. Physical and chemical properties of the product such as surface activity, cloud point, acid value, ester value, hydroxyl value, and hydrophilic-lipophilic balance was also determined and results varied depending on the reagent molar ratio. The synthesized EGMO were soluble in water and therefore show potential use as surface active agents in personal care and cosmetic products.

Keywords: *nonionic surfactant, ethoxylation, glycerol monooleate, palm oilKata*

INTRODUCTION

Palm oil is one of the highly potential vegetable oils for the substitution of products derived from petroleum such as surfactants. With the advanced development of oleochemistry, surfactants from palm oil is becoming an interesting issue to be investigated. Many types of surfactants are found in the market, among them are ionic, nonionic, or zwitter ionic. These surface active agents are used in many personal care and cosmetic products as well as industrial processes. They can act as a detergent, emulsifier or dispersants in colloidal systems⁽¹⁾.

Development of bio-based surfactants has been performed by various chemical reactions, such as ethoxylation, esterification, sulfonation, or amidation. In the case of ethoxylation reaction, it generally occurs in the prescence of an alkaline catalyst, usually potassium hydroxide (KOH) or sodium hydroxide (NaOH), and a starter^(2,3). The starter in the synthesis of nonionic surfactant could be a fatty alcohol, an alkyl phenol, or a fatty acid, which are hydrophobic molecules containing a polar group with an active hydrogen. Fatty alcohols do not predominantly exist in nature and a reduction step from fatty esters is required to obtain the fatty alcohol as a starting material and therefore a more effective method is desirable.

Direct ethoxylation of fatty acid methyl esters such as glycerol monooleate (GMO) is a favorable method since it is able to reduce the production cycle of fatty alcohols thus significant cost reduction could be expected^(4,5). We have previously reported a direct ethoxylation of GMO from palm oil in the presence of an alkaline catalyst at temperatures of 120 to 180 °C⁽⁶⁾. The ethoxylation reaction proceeded and ethylene oxide (EO) was inserted between the carbonyl carbon and fatty acid group at the ester bond. The aim of this present study is to further investigate the preparation of ethoxylated glycerol monooleate (EGMO) at a lower

temperature of 80 °C in 1 atm and determine their properties after purification with acetic acid and black carbon.

MATERIAL AND METHODS

Materials

GMO was synthesized by a typical esterification reaction of glycerol and fatty acid of palm oil which was provided by PT. Sumiasih, Indonesia. Ethylene oxide (Sigma Aldrich) and KOH (Merck) were used for the ethoxylation process. Water was redistilled, acetic acid (Merck) and carbon black were used for purification.

A 2 L autoclave reactor was used for ethoxylation and gas chromatography (Shimadzu 14A, column DB5-MS 30 m x 0.25 mm x 0.25 µm, FID detector) was required for determination of components in the starting material GMO. Vapour Pressure Osmosis (VPO K700 KNAEOR with Euro Osmo K7000) and liquid chromatography-mass spectroscopy (Perkin Elmer Series 200) was applied for molecular weight determination. For surface tension analysis, a tensiometer (Torsion Balance Supplies) equipped with a Pt-Ir du Noüy ring was used. Viscosity was determined with an Ostwald viscometer, whereas density was revealed with a standard picnometer.

Methods

Synthesis of ethoxylated glycerol monooleate (EGMO)

GMO and 1 % KOH were introduced into the reactor and the mixture was stirred for 2 hours without heating until the mixture was neutral. EO was flowed into the reactor and the mixture was heated at 80 °C for 2 hours. At the end of the process, the reaction was stirred for 3 hours in room temperature of 29 °C. Ethoxylation was performed with variation of molar ratio of GMO and EO. The EGMO product was

purified by using acetic acid and adsorption with black carbon.

Determination of physical and chemical properties of EGMO

Acid, ester, and hydroxyl value were determined by standard titration analysis. An Ostwald viscometer and picnometer were used for determination of viscosity and density. The solubility in water was determined by observing the appearance of 0.01–1 % EGMO product in demineralized water. Surface tension analysis was conducted using a torsionmeter (Torsion Balance Supplies) for surface and interfacial tension of 0.05 % aqueous EGMO product at 25 °C equipped with a Pt-Ir du Noüy ring.

Cloud point was determined by freezing (± 4 °C) 1 % of aqueous solution of ethoxylation product and then heating it to 100 °C. The temperature when the clear solution suddenly becomes cloudy is recorded as the cloud point. Sodium chloride was used when the cloud point was not observed to the boiling point of water. Hydrophilic lipophylic balance (HLB) which is useful to identify surfactants for oil in water systems was determined by a calculation made by Sasol Olefin & Surfactants with the following equation⁽⁷⁾:

$$HLB = \frac{20 \times \text{MW Hydrophilic}}{\text{MW Total}} \quad (1)$$

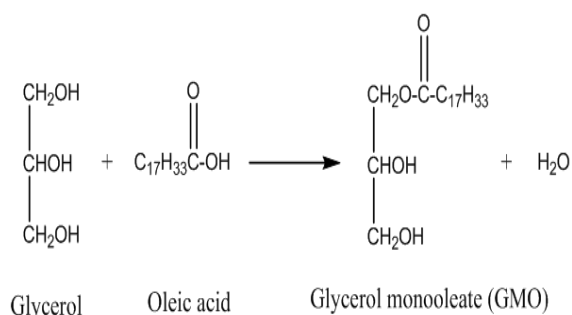
The molecular weight of the ethoxylation product was determined by vapor pressure osmosis whereas samples were injected to the sample valve and the molecular weight was recorded. Composition of the products was evaluated by LC-MS with positive ion mode. Methanol and water with ratio 80:20 was used as the mobile phase at a flow rate of 0.1 mL/min. Electrospray was carried out using column C18 (RP 18) Vydac with column length of 250 mm, ID: 2 mm, and particle size: 5µm.

RESULT AND DISCUSSION

Direct ethoxylation of GMO

GMO as the starting material was analyzed by gas chromatography. The GMO were synthesized by a typical fischer esterification of glycerol and a mixture of fatty acid from palm oil which mainly contained oleic acid, commercially available in the local market. The types of fatty acid in the esters in the synthesized GMO were determined as shown in Fig. 1. Results show that the GMO sample was dominated by esters of oleic acid (76.58 %) and linoleic acid (16.44 %). Other fatty acid esters with small concentration were also detected as stearic acid (2.41 %), palmitic acid (0.83 %), and linolenic acid (0.20 %).

Synthesis of the nonionic surfactant was performed by reacting GMO with EO at 80 °C in the prescence of an alkaline catalyst. Table 1 shows the parameters of reaction of the ethoxylation products. GMO as the starting material has one ester group in its molecule. As reported in other direct ethoxylation papers ⁽¹⁻⁵⁾, the ethylene oxide is selectively inserted between the carbonyl group and ester bond. The ethoxylation product consists of two parts; the hydrophobic portion from oleic acid and the hydrophilic portion from ethylene oxide insertion.



Scheme 1. Esterification of glycerol and oleic acid to glycerol monooleate (GMO)

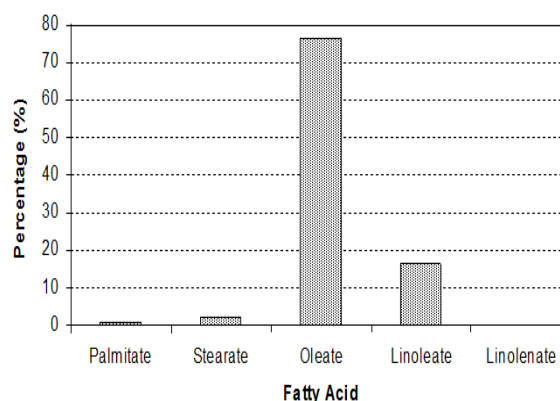
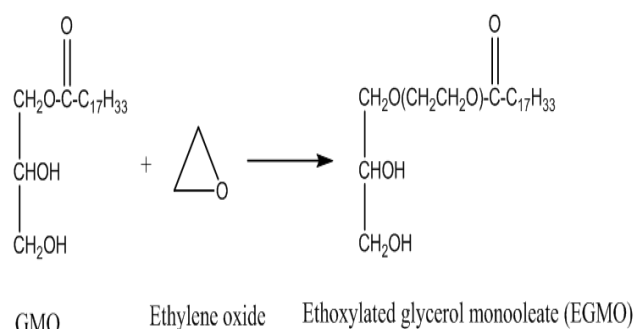


Fig. 1 Types and composition of fatty acids in the starting material

An amount of KOH was used as a catalyst in the ethoxylation reaction and therefore purification is needed to separate the catalyst from the product, whereas the unreacted EO which remained in the gas form after the reaction was purged out of the reactor. The process resulted in three EGMO products based on the variation of reagent molar ratio GMO : EO, labeled as A, B, and C. The three EGMO products



Scheme 2. Ethoxylation of GMO to ethoxylated glycerol monooleate (EGMO)

Table 1. Ethoxylation products and reaction parameters

GMO : EO (mol)	EGMO	KOH (% wt/wt)	Time (minute)	Temperature (°C)	Purification	pH
1:2	A	1	120	80	-	9.8
1:6	B	1	120	80	-	7.8
1:10	C	1	120	80	-	7.8
1:2	AP	1	120	80	Purified	5.0
1:6	BP	1	120	80	Purified	5.0
1:10	CP	1	120	80	Purified	3.8

EGMO = ethoxylated products; GMO:EO = molar ration of GMO and EO; A, B, C = ethoxylated products A, B, and C before purification; AP, BP, and CP = ethoxylated products A, B, and C after purification

Physical and chemical properties of EGMO product

The acid and ester values of EGMO products are illustrated in Fig. 2. It can be seen that an increase of acid value was detected after purification. Before the EGMO purification, the acid value of A was 0.41. An increase of more than 5 points was seen after purification where the acid value of AP elevated to 6.07. This was also observed for B and C with acid values of 0.50 and 0.37 which increased to 4.29 and 4.14 for BP and CP, respectively. This increasing of acid value was due to the addition of acetic acid which reacts with KOH, leaving free fatty acids in the mixture. An increase of ester value was also observed. Due to the greater amount of free fatty acid after purification, a higher saponification or ester value was obtained. Ester value of A, B, and C was 98.86, 79.44, and 61.83. Meanwhile after purification, the ester values increased to 101.27, 82.17, and 68.26 for AP, BP, and CP, respectively. The density and viscosity of the purified ethoxylation products can be seen in Table 2. Higher density was observed with increasing GMO : EO molar ratio. This indicated that the ethoxylation occurred and the molecular weight increased. The highest was recorded for product CP with density of 1.0368 g/cm³ and viscosity of 135.07 cp. The level of viscosity was also increased with the

increase of pressure and reagent molar ratio.

The amount of hydrophilic part in the molecule which is the amount of EO inserted into the structure was analyzed and calculated by LC-MS method as can be seen in Table 2. When a higher GMO : EO ratio was applied, a larger number of EO and average molecular weight (MW) was detected. The highest MW of 1198 with 17 molecules of EO inserted was observed for product CP. This MW value was much higher when compared to the parent GMO of 420.

Various procedures have been developed to determine the HLB of different surfactants. For example, a correlation between the HLB number and the cloud points of polyoxyethylene derivatives has been reported⁽⁵⁾. This illustrated the cloud point of a 5% aqueous solution plotted against the HLB number. A good linear correlation between the HLB number and the water titration value for polyhydric alcohol esters was also reported (6). But few have revealed the method for HLB determination from fatty esters.

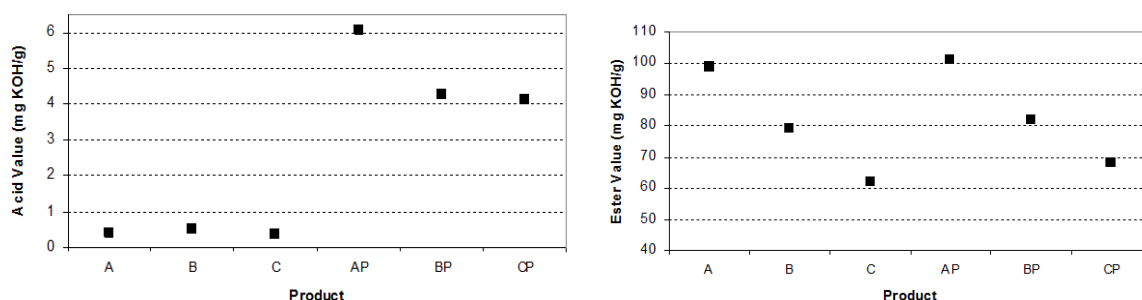


Fig. 2. Acid and ester values of the EGMO products before and after purification. A, B, C = ethoxylated products A, B, and C before purification; AP, BP, CP = ethoxylated products A, B, and C after purification.

Table 2. Physical and chemical properties of EGMO products

EGMO	GMO : EO (mol)	OH ⁻ (mg KOH/g)	MW (g/mol)	EO (molecule)	HLB	Cloud Point (°C)	ρ 40°C (g/cm ³)	η 40°C (cp)
AP	1:2	250	460	1	1.98	22	0.9855	-
BP	1:6	160	878	10	10.02	-	1.0244	112.81
CP	1:10	121	1198	17	12.49	-	1.0368	135.07
GMO	-	140	420	-	-	26.5	0.9392	67.04

EGMO = ethoxylated products; GMO:EO = molar ration of GMO and EO; A, B, C = ethoxylated products A, B, and C before purification; AP, BP, and CP = ethoxylated products A, B, and C after purification

Physical and chemical properties of EGMO product

Because of the variety of product composition in the EGMO products, the main component in each product was used for the HLB calculation. This method should at least give a rough estimate of the HLB number. The HLB value was higher with the increase of MW and number of EO inserted in the structure.

The EGMO products have different appearance when added to water at room temperature. In three different aqueous concentrations, they are all soluble in the aqueous form at concentration of 0.01 (%wt/v), although among them form cloudy solutions at a higher concentration. Meanwhile, the parent GMO showed poor solubility in water giving a cloudy and non-homogeneous mixture. The difference in appearance can be seen in Table 3 below.

The efficiency of a surfactant is generally evaluated by its ability to reduce surface tension in a solution. The surface

tension in an aqueous solution of EGMO product as surfactant was performed by measuring the surface tension of different concentrations of the surfactant in water.

Table 3. Appearance of aqueous EGMO products at room temperature

EGMO	0.01 (%wt/v)	0.1 (%wt/v)	1 (%wt/v)
A	□	■	■
B	□	□	■
C	□	□	□
AP	□	■	●
BP	□	■	●
CP	□	□	■
GMO	●	●	●

□ = clear, dissolve; ■ = cloudy, homogenous; ● = cloudy, non-homogenous; A, B, C = ethoxylated products A, B, and C before purification; AP, BP, and CP = ethoxylated products A, B, and C after purification

The result is presented in Fig. 3. At surfactant concentration of zero, the surface tension was measured as 63 mN/m. After the addition of surfactant, the surface tension decreased to 27-36 mN/m. This indicated that the surfactant had the ability

to lower the surface tension of water. EGMO products of A, B, and C before purification gave lower surface tension than that of the ones purified. At a concentration of 0.05%, it was observed that EGMO product A, B, and C reduced the surface tension of water from 63 mN/m to 33 mN/m, 32.5 mN/m, and 31.5 mN/m. While for those products after purification, the surface tension of EGMO product AP, BP, and CP slightly increased to 32.8 mN/m, 36.5 mN/m, and 36.5 mN/m, respectively. These results show that the surface tension of water could be reduced to the 32-36 mN/m using ethoxylated products with different MW of 460 (AP), 878 (BP), and 1198 (CP), however, the solubility of these products in water gave different trends as previously summarized in Table 3. The EGMO product CP having higher MW showed the best performance demonstrating ability to form a homogeneous aqueous EGMO solution up to concentration of 1(% wt/v).

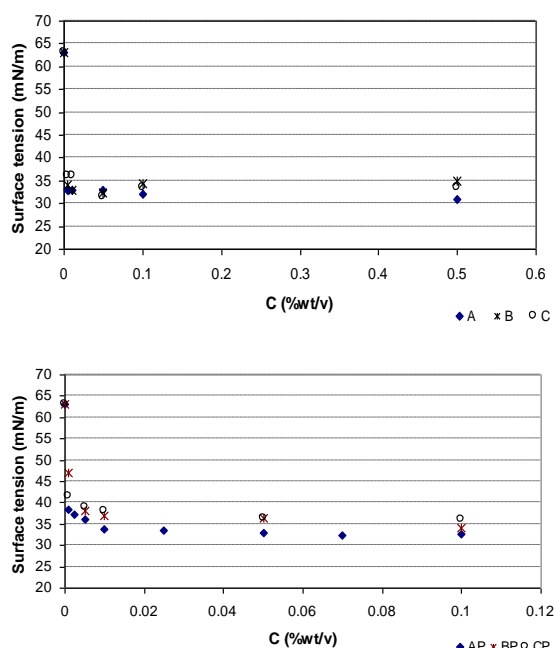


Fig. 3 Surface tension measurement of aqueous EGMO products as surfactants. A, B, C = ethoxylated products A, B, and C before purification; AP, BP, and CP = ethoxylated products A, B, and C after purification

The palm oil based nonionic surfactant, EGMO product AP, BP, and CP synthesized from GMO and EO and further purified with acetic acid and black carbon exhibited good performance as surface active agents of oil-in-water (o/w) emulsion systems of white oil and 10 ml aqueous EGMO⁽⁸⁾. These emulsions did not observe separation of oil and water phase even after centrifugation at 3000 rpm for 10 minutes and therefore are potentially used the formulation of natural cosmetics.

CONCLUSION

Direct ethoxylation of GMO proceeded at a mild temperature of 80 °C in the presence of 1 % KOH as catalyst. The molecular weight of the EGMO product depended on the GMO : EO molar ratio and showed different physical and chemical properties. Purification of the EGMO products A, B, and C by addition of acetic acid and black carbon yielded products AP, BP, and CP with a greater acid value, ester value, density and viscosity, and was able to decrease the surface tension of water from 63 mN/m to 32-36 mN/m in a 0.05 % aqueous EGMO surfactant. The CP product showed the best performance with ability to form a homogeneous aqueous EGMO solution up to concentration of 1(% wt/v). The EGMO were stable in room temperature and therefore have potential use as palm oil based nonionic surfactants for many personal care and cosmetic products.

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