
Long-term Stability of Orange Oil Emulsions Prepared by Spontaneous Emulsification Using Polyglycerol Esters Mixed with Sucrose Esters

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Abstract

Orange oil-in-water emulsions were spontaneously produced by adding an organic mixture consisting of orange oil and mixed surfactants between polyglycerol esters (PGE) and sucrose esters (SE) into a stirred aqueous phase. Emulsions were prepared either by using a magnetic stir plate or using an overhead stirrer. Mean oil droplet sizes of the produced emulsions were dependent on the types of surfactants, while the emulsion production capacity (500 -1,500 g emulsion), the stirring time (5-120 min), and the stirrer types (propeller stirrer - dissolver stirrer) did not have significant effects on mean oil droplet sizes ($p < 0.05$). The mean oil droplet sizes of orange oil emulsion produced by decaglycerol monolaurate (PGE-L) mixed with sucrose monomyristate (SE-M) at a ratio of 1:1 (prepared using a magnetic stir plate) were smaller than one micron and the mean droplet sizes did not significantly change over one-year storage ($p < 0.05$). Such long-term stability of orange oil emulsions suggested that Ostwald ripening were retarded in the prepared emulsions.

ความคงสภาพระยะยาวของอิมัลชันน้ำมันส้มที่เตรียมด้วยวิธีการเกิดอิมัลชันตัวเอง โดยใช้พอลิกลีเซอรอลเอสเทอร์ผสมกับซูโครสเอสเทอร์

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งานวิจัยนี้เตรียมอิมัลชันน้ำมันส้มในน้ำโดยวิธีการเกิดอิมัลชันตัวเอง โดยการเติมส่วนผสมระหว่างน้ำมันส้มและสารลดแรงตึงผิวชนิดผสมระหว่างพอลิกลีเซอรอลเอสเทอร์และซูโครสเอสเทอร์ลงในวัฏภาคน้ำระหว่างการกวนผสม อิมัลชันเตรียมได้โดยใช้แผ่นรองกวนแม่เหล็กหรือใช้เครื่องกวนแบบใบกวน ขนาดอนุภาคน้ำมันเฉลี่ยของอิมัลชันที่เตรียมได้ขึ้นอยู่กับชนิดของสารลดแรงตึงผิว ในขณะที่กำลังการผลิตอิมัลชัน (ตั้งแต่ 500 ถึง 1,500 กรัม) ระยะเวลาการกวน (ตั้งแต่ 5 ถึง 120 นาที) และชนิดใบกวน (ใบกวนชนิดใบพัด - ใบกวนชนิดทำละลาย) ไม่มีผลต่อขนาดอนุภาคน้ำมันเฉลี่ยอย่างมีนัยสำคัญ ($p < 0.05$) อิมัลชันน้ำมันส้มที่เตรียมโดยใช้เคซอิลิเซอรอลโมโนลอเรตผสมกับซูโครสโมริสเทตที่อัตราส่วน 1:1 (เตรียมโดยวิธีใช้แผ่นรองกวนแม่เหล็ก) มีขนาดอนุภาคน้ำมันเฉลี่ยต่ำกว่าหนึ่งไมครอน และขนาดอนุภาคน้ำมันเฉลี่ยไม่เปลี่ยนแปลงอย่างมีนัยสำคัญ ($p < 0.05$) ตลอดระยะเวลาการเก็บหนึ่งปี การคงสภาพระยะยาวของอิมัลชันน้ำมันส้มคาดว่าเกิดจากการลดอัตราการเกิดออสวอลล์ไรเฟนนิ่งในอิมัลชันที่เตรียมได้

1. Introduction

Orange oils extracted from orange fruit peels have been commonly used as flavor oils to enhance natural taste and aroma of orange fruits in food and beverage emulsion products. The initially prepared emulsions usually contain a high concentration of orange oil of 10-30 wt% and the finished products are diluted emulsions such as with an oil concentration of lower than 0.1 wt%. Orange oil emulsions are relatively unstable and prone to destabilization over storage time by Ostwald ripening. Several studies had shown that storage stability of orange oil emulsions could be improved by interfacial engineering [1-6], by incorporating triglyceride oil or ester gum in the oil phase [7-9], and by adding biopolymer thickening agents [10-12]. However, preparing orange oil-in-water emulsions with long-term stability is still considered a challenge.

Spontaneous emulsification is one of the emulsification methods that have potential application in flavor oil emulsions production. The advantage of spontaneous emulsification is low energy requirement and low investment cost compared to high pressure homogenization. This method applies additional hydrophilic surfactants. By adding hydrophilic surfactants into flavor oil phase and then adding flavor oil-surfactant mixtures into a stirred aqueous phase, flavor oil emulsions are spontaneously formed. Rapid diffusion of hydrophilic surfactants from oil phase to more-soluble aqueous phase would drag the oils across the oil-water interface to form oil droplets [13-16]. Types of surfactants play a key role in controlling sizes of emulsions produced by spontaneous emulsification. In most of previous studies, Tweens were the surfactants that had been used and different types of Tweens had been explored [15,17-18]. The mean droplet sizes of emulsions prepared by using Tween

80 were lesser than 100 nm, smaller than by using other Tween types. Some other surfactants such as sunflower phospholipids and mixed surfactants between Kolliphor HS15 and Span 80 also had been applied, but the mean droplet sizes of spontaneously formed emulsions were still larger than 20 μm [19-20]. The investigation on the use of other food surfactants would be worthwhile for more applications of this low energy emulsification method in food and beverage emulsion production.

Polyglycerol esters and sucrose esters are both food surfactants that produced from natural raw materials. Polyglycerol esters are synthesized from vegetable oil and glycerol, which glycerol could be obtained from biodiesel production [21-22]. Currently, there are not many studies on properties of polyglycerol esters, and the study on spontaneous emulsification by using this type of surfactant has not been reported yet. Sucrose esters are synthesized from vegetable oil and sucrose and their properties have been more widely studied. It had been shown that sucrose esters with mainly sucrose monostearate and sucrose esters with mainly sucrose monopalmitate could be employed to spontaneously form orange oil emulsions [23].

The objective of this study was to prepare orange oil emulsions by spontaneous emulsification using polyglycerol esters (PGE) and mixed surfactants between PGE and sucrose esters (SE). The effects of PGE types on oil droplet sizes were examined. The emulsification was conducted in both small and larger scale vessels. The effects of different process parameters such as stirring time, stirrer type, and emulsion scale-up size on mean oil droplet sizes were examined. The discussion on factors that possibly affected mean oil droplet sizes had been provided. Moreover, the storage stability of emulsions prepared by using PGE mixed with SE were investigated in comparison with

emulsions prepared by using only PGE.

2. Material and methods

2.1 Materials

Different types of polyglycerol esters (PGE) were supplied by Taiyo Kagaku Co., Ltd. (Mie, Japan). Decaglycerol monolaurate (PGE-L) or Sunsoft Q12S (commercial name) with a HLB value of 15.5, decaglycerol monomyristate (PGE-M) or Sunsoft Q14S (commercial name) with a HLB value of 14.5, decaglycerol monooleate (PGE-O) or Sunsoft Q17S (commercial name) with a HLB value of 12.0, and decaglycerol monostearate (PGE-S) or Sunsoft Q18S (commercial name) with a HLB value of 12.0 were used. SE-M or M1695 (commercial name) with a HLB value of 16.0 contains mainly of 70-74% sucrose monomyristate with 17-21% sucrose dimyristate. Note that all sucrose esters also contain some ash and moisture.

Orange oils were supplied by Thai-China Flavours and Fragrances Industry Co., Ltd. (Phra Nakhon Si Ayutthaya, Thailand). According to gas chromatographic analysis, orange oil is composed of 93% limonene, 2% β -myrcene, 1% decanal, and some small amounts of other compounds. Ethanol was supplied by RCI Labscan Limited (Bangkok, Thailand). Distilled water was used for emulsion preparation.

2.2 Spontaneous emulsification using a magnetic stir plate

Organic mixtures consisted of 10 g orange oil (10 wt% of total emulsions) and 2.5 g to 7.5 g surfactants (2.5 wt% to 7.5 wt% of total emulsions) were prepared. The mixtures of different types of PGE (liquid) and orange oil were prepared and mixed by using a stir rod. The mixtures of PGE-L (liquid phase), SE-M (solid powders), orange oil, and ethanol were prepared by addition of PGE-L to the initially prepared orange

oil-SE-M-ethanol mixtures and mixed by using a stir rod. The small amount of ethanol (~ 0.1 g ethanol/g SE-M) was added to increase solubility of SE-M in the oil phase and its effect on emulsion formation was considered minor [23].

The total amount of emulsion of 100 g was prepared in a glass bottle. The prepared orange oil-surfactant mixtures were added drop-wisely into distilled water during stirring by using a magnetic stir plate. The stirring speed of $\sim 1,100$ rpm was applied. After addition of orange oil-surfactant mixtures, the emulsion sample continued being stirred in the same bottle closed with a cap for 120 min.

2.3 Spontaneous emulsification in a stirred vessel

The total amounts of emulsions of 500 g and 1,500 g were prepared in standard glass beakers. The orange oil-surfactant mixtures were prepared according to section 2.2. The oil concentration of 10 wt% and the surfactant concentration of 7.5 wt% were used according to section 3. The prepared orange oil-surfactant mixture was poured directly into distilled water (at an approximate addition rate of 60 g/min) during stirring by using an overhead stirrer (IKA, RW20 digital, Germany). The stirring speed of $\sim 1,100$ rpm was applied. After addition of orange oil-surfactant mixture, the emulsion sample continued being stirred in the same beaker covered by aluminum foil for 5 to 120 min.

2.4 Measurement of oil droplet size distributions of emulsions

The droplet size distributions of emulsions were measured by using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). The refractive indices for water and orange oil are 1.333 and

1.472, respectively. The droplet sizes were reported as surface mean particle diameters, $d_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$, where d_i is the midpoint of the size interval i and n_i is the number of particles in that interval. The droplet size distribution width was reported as Span, $\text{Span} = (d_{90} - d_{10}) / d_{50}$, where d_{90} , d_{50} and d_{10} are the size which 90%, 50% and 10% of particle populations are below that size. The stability of emulsions was determined by measuring oil droplet size distributions of emulsions on the first day and after storage at room temperature of 30 ± 2 °C for 120 days and for one year.

2.5 Statistical analysis

All the experiments were conducted at least three replicates. The reported data were the mean \pm standard deviation. Means were compared by using ANOVA procedure and using Tukey Test ($p < 0.05$). Statistical analysis was performed by using SAS Enterprise Guide 7.1 software (SAS Institute Inc., Cary, NC, USA).

3. Results and discussion

3.1 Effect of PGE types and concentrations

Fig 1a and fig 1b show mean droplet sizes and droplet size distributions of orange oil emulsions prepared in an amount of 100 g. Different types of PGE were employed at a surfactant concentration of 7.5 wt%. Large white particles suspended in the aqueous phase were observed when using PGE-S. The mean particle size was $71.350 \pm 5.827 \mu\text{m}$ (Span = 1.12) as PGE-S self-aggregated as semi-solid gel. White emulsions were observed when PGE-O, PGE-M, and PGE-L were used. The mean droplet size was $9.150 \pm 3.083 \mu\text{m}$ (Span = 4.60) when using PGE-O and its broad droplet size distribution contained multiple peaks. The mean droplet sizes became narrower and much smaller of $0.534 \pm 0.059 \mu\text{m}$ (Span = 0.98) and $0.405 \pm 0.035 \mu\text{m}$ (Span = 0.78) when using PGE-M and

PGE-L, respectively.

Surfactant properties such as surfactant affinity in oils and surfactant aqueous solubility possibly had influence on oil droplet formation since these properties affected surfactant diffusion during spontaneous emulsification. PGE-M (HLB= 14.5, Molecular weight = 968 g/gmol) and PGE-L (HLB=15.5, Molecular weight = 940 g/gmol) having short hydrophobic tails and small molecular sizes diffused into aqueous phase rapidly. Small mean droplet sizes were obtained when orange oil emulsions were prepared by these two types of PGE. When PGE-O (HLB=12.0, Molecular weight = 1,023 g/gmol) and PGE-S (HLB=12.0, Molecular weight = 1,025 g/gmol) with longer hydrophobic tails and higher affinity in oil and lower aqueous solubility were used, emulsions with small mean droplet sizes could be not be obtained. PGE-S and PGE-O seemed to have a relatively similar HLB value, only PGE-S with a long saturated hydrocarbon tail (C18:0) became self-aggregated in organic phase, supposed by strong hydrophobic interaction. PGE-O with a monounsaturated tail (C18:1) showed some difficulty in emulsion formation as multiple peaks were observed. In this study, PGE-L had been chosen as the main studied surfactant since orange oil emulsions with a small mean droplet size and a unimodal droplet size distribution could be obtained.

Fig 1c and fig 1d show that concentrations of PGE-L influenced oil droplet sizes and droplet size distributions of produced emulsions. Orange oil emulsions prepared by using 2.5 wt% PGE-L had a mean droplet size of $2.190 \pm 1.089 \mu\text{m}$ and a broad droplet size distribution (Span = 4.68). As increasing PGE-L concentrations, the mean droplet sizes reduced and the oil droplet size distributions became narrow and unimodal. The mean droplet sizes were $0.489 \pm 0.059 \mu\text{m}$ (Span = 0.67), $0.405 \pm 0.035 \mu\text{m}$ (Span =

0.78), and $0.533 \pm 0.179 \mu\text{m}$ (Span = 0.65) as PGE-L concentrations increased to 5.0 wt%, 7.5 wt%, and 10.0 wt%, respectively. The mean droplet sizes were not significantly different after PGE-L concentrations became higher than 5 wt%. At low concentrations of PGE-L, the amounts of surfactants would not be sufficient to create small oil droplets which having large surface areas. In this study, surfactant concentration of 7.5 wt% had been chosen and used in emulsion preparation in all further experiments. This concentration also had been used in the previous work that using only sucrose esters [23], thus, the results from this study could be later used for comparison.

3.2 Effects of sucrose ester

Fig 2a and fig 2b show the mean droplet sizes and

the droplet size distributions of orange oil emulsions prepared by using mixed surfactants between PGE-L and SE-M at a 1:1 ratio (a total surfactant concentration of 7.5 wt%), in comparison with emulsions prepared by only PGE-L. Emulsions prepared by PGE-L mixed with SE-M had a unimodal size distribution and the mean droplet size was $0.745 \pm 0.118 \mu\text{m}$ (Span = 3.57). These emulsions had a larger mean droplet size and boarder droplet size distribution ($p < 0.05$) than orange oil emulsion prepared by using only PGE-L. The use of SE-M as a mixed surfactant possibly modified curvature of oil droplets as other studies also observed that mean droplet sizes of emulsions became altered after applying another mixed surfactant [24- 25].

3.3 Scale-up study in stirred vessels

Orange oil emulsions with an increased amount of

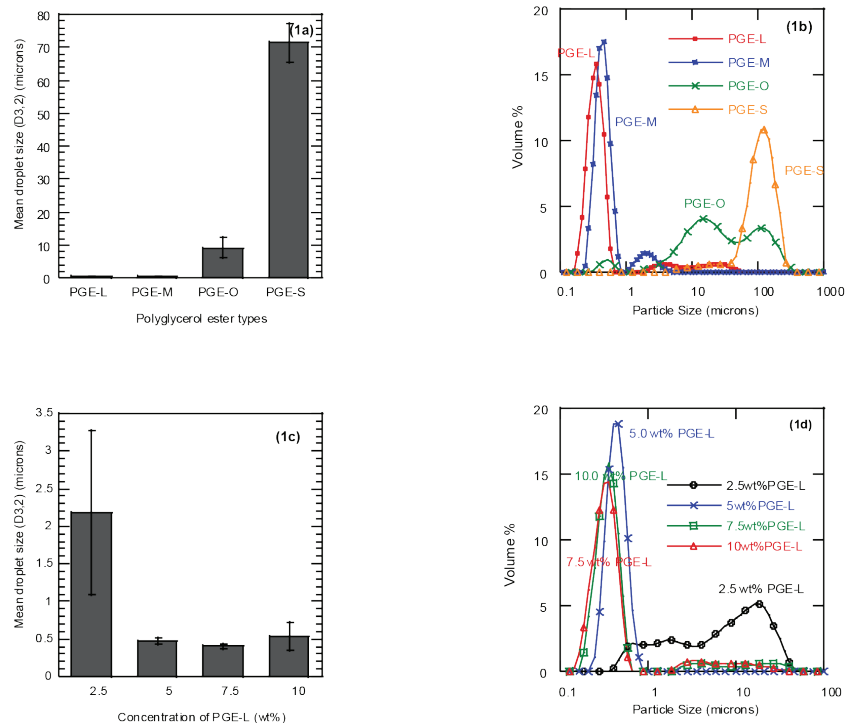


Figure 1 (1a) Mean droplet sizes and (1b) corresponding droplet size distributions of orange oil emulsions prepared on a magnetic stir plate by using 10 wt% oil and 7.5 wt% PGE. Different types of PGE were used. (1c) Mean droplet sizes and (1d) corresponding droplet size distributions of orange oil emulsions prepared by using different concentrations of PGE-L. [7]

500 g were prepared in a scale-up stirred vessel by using an overhead stirrer and a propeller stirrer, at a stirring speed of 1,100 rpm. Fig. 3a shows that the mean droplet sizes of emulsions were not significantly different when stirring for more than 5 min. The obtained mean droplet sizes were $0.363 \pm 0.010 \mu\text{m}$ (Span = 0.68) and $0.619 \pm 0.088 \mu\text{m}$ (Span = 1.06) when using

PGE-L and PGE-L mixed with SE-M, respectively. These sizes were slightly smaller ($p < 0.05$) than emulsions previously produced in an amount of 100 g by using a magnetic stir plate (fig 2).

Fig. 3b shows that the mean droplet sizes of orange oil emulsions prepared by using two types of stirrers,

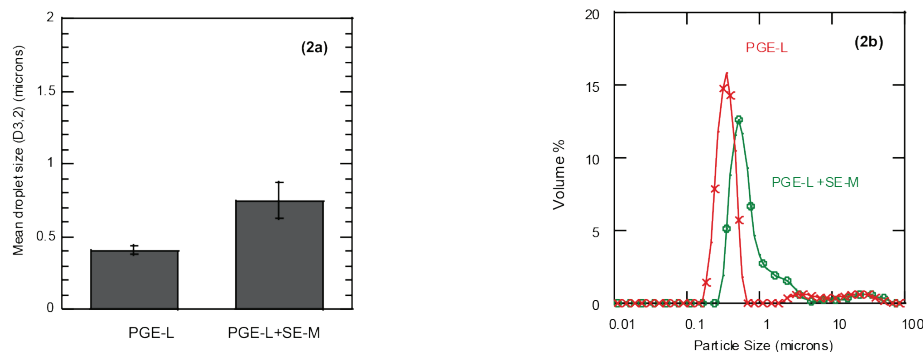


Figure 2 (2a) Mean droplet sizes and (2b) corresponding droplet size distributions of orange oil emulsions prepared on a magnetic stir plate by using 10 wt% oil and 7.5 wt% total surfactant consisted of only PGE-L and PGE-L and SE-M (mixed at a ratio of 1:1).

propeller stirrer (IKA Model R1342) and dissolver stirrer (IKA Model R1303). The mean droplet sizes were not significantly different when the same stirring speed was applied. The propeller stirrer of 50 mm diameter with 4 blades created an axial flow, while the dissolver stirrer of 42 mm diameter created a radial flow with a higher shear. The different flow patterns from the two types of stirrers seemed not differently affect mean oil droplets sizes. Here, organic mixtures were added into stirred aqueous phase. Borrin et al. [26] had found that types of stirrer had effects on oil droplet sizes of emulsions. Oppositely, in their study, water was added into viscous organic mixtures consisted of oil and surfactants, according to the procedure of phase inversion composition method. The type of stirrer should be suitable for highly viscous mixtures.

Fig.3c shows that the increase in emulsion sample

sizes from 500 g to 1,500 g did not significantly influence the mean droplet sizes of produced emulsions. The 500 g and 1,500 g of emulsions were prepared in a 1,000 mL (11 cm diameter) and 2,000 mL (13 cm diameter) standard beakers, respectively. Solè et al. [27] had prepared emulsions in 100 mL and 600 mL vessels by using a helix mixer. In their study of phase inversion composition method, high viscosity of stirred organic phase caused difficulty in mixing in a larger vessel. The adequate mixing was required to produce small sized oil droplets in the scale-up vessels by both mixing rates and water addition rates had to be adjusted. Here, the stirred samples were not highly viscous and emulsion sample sizes did not show effects on mean oil droplet sizes.

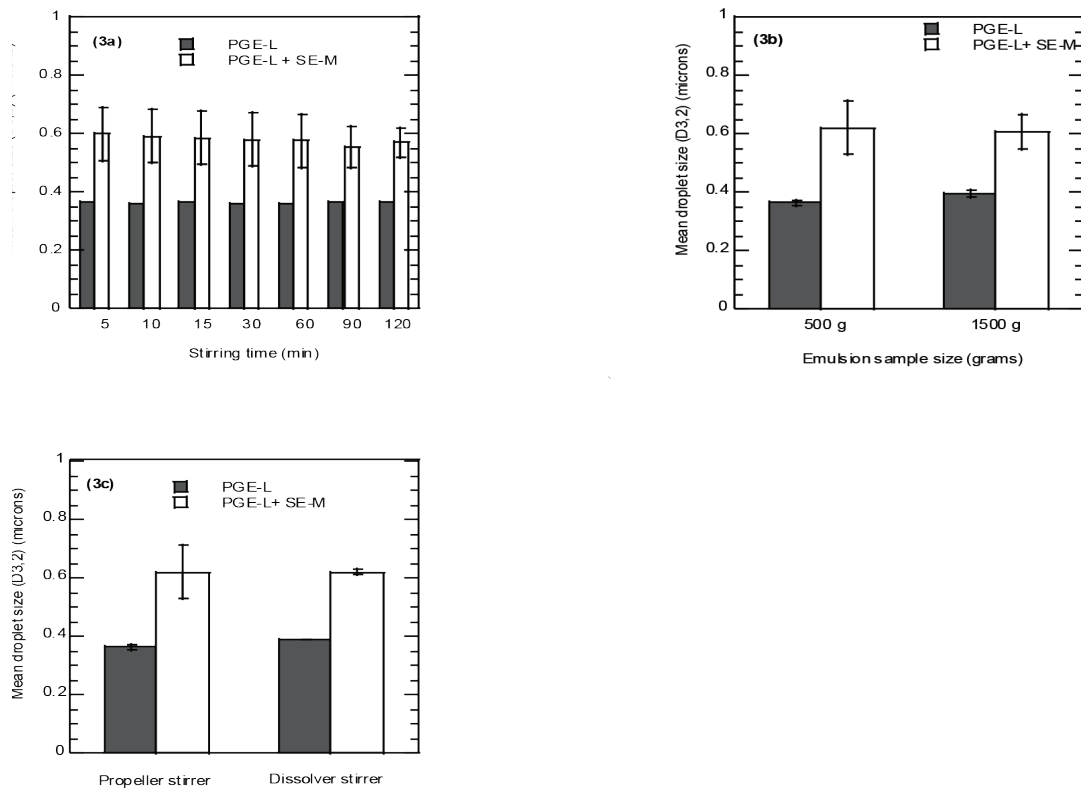


Figure 3 Mean droplet sizes of orange oil emulsion prepared in a stirred vessel by using 10 wt% oil and 7.5 wt% PGE-L or PGE-L mixed with SE-M. (3b) By applying two types of stirrer. (3c) By preparing two emulsion sample sizes. For (3a), (3b), and (3c), the stirring speed of 1,100 rpm was applied

3.4 Storage stability study

Fig 4a shows that the mean droplet sizes of emulsions stabilized by PGE-L (preparation by a magnetic stir plate) on Day 1 and after one year were $0.408 \pm 0.036 \mu\text{m}$ (Span = 0.82) and $1.030 \pm 0.272 \mu\text{m}$ (Span = 3.57), respectively. Fig 4b shows that the droplet size distributions of orange emulsions stabilized by PGE-L increased after 120 days storage and significantly increased after one-year storage. In contrast, fig 4c shows that the droplet size distributions of orange oil emulsions stabilized by PGE-L mixed with SE-M did not show an increasing trend over one-year storage, which the mean droplet sizes on Day 1 and after one year (fig 4a) were $0.720 \pm 0.084 \mu\text{m}$ (Span = 2.41) and $0.779 \pm 0.012 \mu\text{m}$ (Span = 1.66), respectively (not

significantly difference).

Orange oil emulsions are prone to destabilization by Ostwald ripening, indicating by oil droplet size distributions of orange oil emulsions usually increasing gradually over storage time [23]. Here, orange oil emulsions stabilized by PGE-L mixed with SE-M showed a high stability against Ostwald ripening, since oil droplet size distributions did not shift to beyond a micron size range after a year. It had been evidenced that the use of mixed surfactants improved Ostwald ripening stability of emulsions as compared to the use of single-type surfactant [28-32]. The mixed surfactants modified interfacial membrane thickness and surface elasticity [33, 34], which possibly created a mass transfer resistance that prevent transferring of oil molecules

between different sizes oil droplets. The combination of PGE-L and SE-M consisted of decaglycerol and sucrose headgroups possibly provided an interfacial membrane that resisted the transferring of orange oil molecules. The uses of mixed stabilizers between

PGE and SE had been mentioned by [35], and the long-term stability of orange oil-in-water emulsions stabilized by these two types of surfactants had been showing in this study.

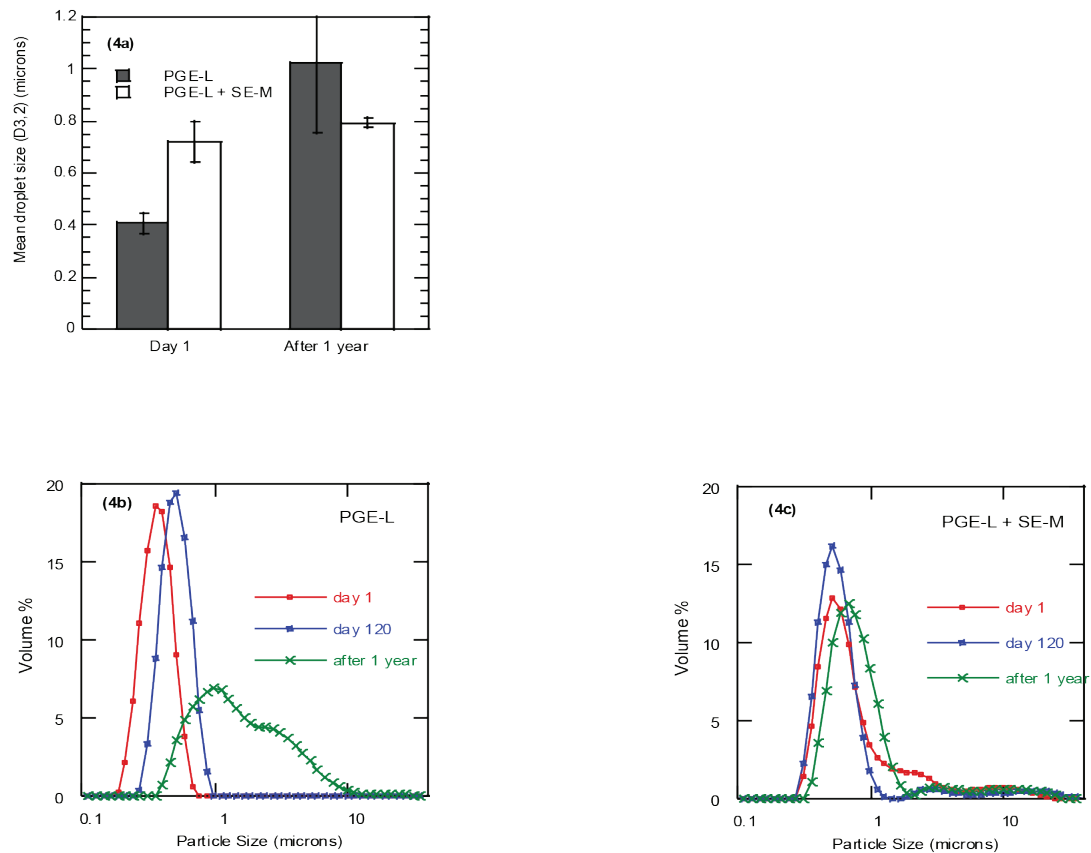


Figure 4 (4a) Mean droplet sizes of orange oil emulsion prepared on a magnetic stir plate by using 10.0 wt% oil and 7.5 wt% surfactant, measured on day 1 and after 1 year. (4b-4c) Corresponding droplet size distributions of emulsions measured on day 1, day 120, and after 1 year. (4b) Using only PGE-L (4c) Using PGE-L mixed with SE-M.

4. Conclusions

In the present study, orange oil emulsions were spontaneously produced by using mixed surfactants between PGE and SE. Mean oil droplet sizes of spontaneously formed orange oil emulsions were dependent

on PGE types. The mean droplet size of orange oil emulsions prepared by PGE-L mixed with SE-M was lesser than a micron and emulsions were able to produce in a small container by using a magnetic stir plate and in a scale-up vessel by using an overhead stirrer.

This study revealed that orange oil emulsions stabilized by PGE-L mixed with SE-M (prepared by using a magnetic stir plate) had a higher stability than orange oil emulsions stabilized by only PGE-L. The uses of mixed surfactants between PGE-L and SE-M improved orange oil emulsion stability, suggested by limiting Ostwald ripening destabilization. Decaglycerol monolaurate and sucrose monomyristate are suggested food surfactants for using in spontaneously food and beverage emulsion production and stabilizing orange oil emulsion products.

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