

Research Article

**Formation and stability study of flavor oil emulsions
stabilized by polyglycerol esters and by sucrose esters**

by

Asst. Prof. Dr. Suwimon Ariyaparakai

**Department of Food Biotechnology
Faculty of Biotechnology
Assumption University**

May, 2016

This research is supported by Assumption University Research grant (P57-0178)

Research Article

Formation and stability study of flavor oil emulsions stabilized by polyglycerol esters and by sucrose esters

by

Asst. Prof. Dr. Suwimon Ariyaprakai

**Department of Food Biotechnology
Faculty of Biotechnology
Assumption University**

May, 2016

This research is supported by Assumption University Research grant (P57-0178)

Formation and stability study of flavor oil emulsions stabilized by polyglycerol esters and by sucrose esters

Suwimon Ariyaprakai^{1}, Le Thi Ngoc Nhuong², and Huynh Tran Tran Tran³*

^{1*}Department of Food Biotechnology, Faculty of Biotechnology, Assumption University,
Hua Mak, Bangkok, 10240, Thailand

^{2,3}Faculty of Food Technology, Saigon Technology University, Ho Chi Minh City, Vietnam

^{1*}Corresponding author. Tel.: +662 300-4553 ext 3796; Fax: +662 300-4553 ext 3792; E-mail address:
suwimona@yahoo.com.

Abstract

In this work, flavor oil emulsions contained 5 wt% oil and 0.75 wt% emulsifier were formulated by using different combinations between flavor oils and food emulsifiers. Orange oil (*OO*), peppermint oil (*PO*), polyglycerol monostearate (*PGE*), and sucrose monostearate (*SE*) were employed to form emulsions by ultrasonic homogenization. Heat stability (storage at 100°C for 30 min) and freeze-thaw stability (storage at -20°C for 22 h. and at 30°C for 2 h.) of emulsions were investigated by observing droplets under a microscope, determining mean droplet sizes, and measuring amounts of destabilized oil. Ostwald ripening stability of emulsions was determined by measuring the droplet size distribution changes over 48 days of storage. The results showed that flavor oil emulsions stabilized by *PGE* and by *SE* were heat stable. Interestingly, flavor oil emulsions stabilized by *PGE* had better freeze- thaw stability compared to emulsions stabilized by *SE*. This property of *PGE* was suggested from polyglycerol interfacial layers reduced ice crystallization and reduced coalescence. The flavor oil emulsions stabilized by either *PGE* or *SE* underwent through Ostwald ripening destabilization and the ripening stability was improved by using mixed emulsifiers between *PGE* and *SE*. The information from this study could be useful for creating formulations of flavor oil emulsions that suitable for future applications in foods and beverages.

Keywords: Polyglycerol esters, Sucrose esters, Flavor oils, Emulsion stability, Freeze-thaw stability, Ostwald ripening

1. Introduction

Flavor oils are essential oils extracted from plants that have been used to enhance taste and aroma of foods and beverages. When flavor oils are applied in aqueous based products, normally flavor oils are incorporated as small oil droplets in the form of oil-in-water emulsions. Since flavorants must be homogeneously mixed throughout the products, dispersibility of oil droplets or emulsion stability is one of important factors to be considered. Particularly for beverages, destabilization of flavor oil emulsions leads to visual oil phase separation (or rining) that not appealing to consumers [1-3].

Physical stability of emulsions can be enhanced by reducing the sizes of oil droplets since smaller oil droplets cream slower and have lesser tendency to coalesce [4, 5]. The sizes of emulsions could be reduced to nanometer range [6, 7]. However, nanoemulsions contained flavor oils still undergo through Ostwald ripening destabilization because flavor oils have certain solubility in the aqueous phase. Flavor oils have tendency to diffuse and transfer between oil droplets and the coarsening of emulsions over time is unavoidable. This increases rates of oil phase separation and limited the applications of flavor oil nanoemulsions. The stability of flavor oil nanoemulsions against Ostwald ripening still requires improvement.

Recently, researchers are investigating on possibility to use emulsifiers produced from natural raw materials according to current industrial trends toward more natural and healthier food and beverage products. Polyglycerol esters of fatty acids and sucrose esters of fatty acids are some examples of those emulsifiers. Polyglycerol esters are produced from vegetable oils and sucrose esters are from sucrose and vegetable oils. Several studies had been shown the applicability of sucrose esters in many types of food emulsions. There were fewer research results related to applications of polyglycerol esters. Note that polyglycerol esters have been increasingly manufactured since a lot of excess glycerol from biodiesel production [8, 9]

The objectives of this study are to study the emulsifying properties of polyglycerol esters (*PGE*) and sucrose esters (*SE*) in formations of flavor oil emulsions and to investigate the stability of the formed emulsions. Orange oils (*OO*) and peppermint oils (*PO*) were employed because *OO* and *PO* are able to apply in various types of foods and beverages. *OO* is commonly used to provide tangy/orangey flavor and *PO* gives mint flavor. The Ostwald ripening stability was determined during forty eight days of storage. The emulsion stability after heating and freeze thawing were also examined. During food and beverage productions, thermal treatments at high temperatures are usually required and sometimes cold storage in a freezer is necessary.

2. Material and methods

2.1 Materials

Ryoto sucrose esters (*S1670*) and Ryoto polyglycerol esters (*S-10D*) were supplied by Mitsubishi-Kagaku Foods Corporation (Tokyo, Japan). *S1670* contained mainly of 50-53% sucrose monostearate (Mwt= 608.76) with 18-20% sucrose monopalmitate, 12-14 % sucrose distearate, 5-6% sucrose dipalmitate, and 5-10% sucrose alkylate. Note that sucrose esters also contained some ash and moisture. *S-10D* contained of decaglycerol monostearate (Mwt= 1025.26). Oil Red O was supplied by Sigma Chemical Company (St. Louis, MO, USA). Orange oil (*OO*) and peppermint oil (*PO*) were supplied by Thai-China Flavours and Fragrances Industry Co., Ltd. (Phra Nakhon Si Ayutthaya, Thailand). Corn oil (*CnO*) was supplied by Mazola Refined Corn Oil, Lam Soon Public Co., Ltd. (Samutprakarn, Thailand).

According to gas chromatographic analysis, *OO* was composed mostly of limonene (93%) and some small proportions of β -myrcene (2%), decanal (1%), and other compounds. *PO* consisted of menthol (38%), isomenthone (13%), *p*-menthone (12%), limonene (8%), 4 methyl-1-(1-methylethyl)-cyclohexene (5%), pulegone (4%), α -pinene (4%), β -pinene (4%), piperitone (1%), *trans*-caryophyllene (1%), α -terpineol (1%), and other compounds. *CnO* consisted of long chain fatty acids of C18:2 (53%), C18:1 (30%), C16:0 (12%) and C18:0 (3%).

Viscosity of *OO* and *PO* at $30 \pm 2^\circ\text{C}$ were 0.890 mPa.s and 3.367 mPa.s, respectively (measured by a capillary viscometer). Density of *OO* and *PO* at $30 \pm 2^\circ\text{C}$ were 848.1 kg/m³ and 895.0 kg/m³, respectively (measured by a pycnometer).

2.2 High intensity ultrasound homogenization

The stock emulsifier solutions (1.2 wt% emulsifier) were initially prepared in 20 mM phosphate buffer solutions at pH 7. The emulsifier stock solutions had to be heated at ~ 70 -80 $^\circ\text{C}$ for 1-2 h. until all emulsifier fully dissolved. The mixture (60 g) contained 5 wt% oil, 0.75 wt% emulsifier, and 94.25 wt% buffer solution (pH 7) were prepared by adding oil to the diluted stock emulsifier solution. The mixtures were homogenized by using an ultrasonic processor (UP400S, H7 sonotrode, Hielscher, Germany) at the amplitude of 122.5 μm for 5 min in continuous mode. All the prepared emulsion samples were kept in bottles (60 g) sealed with caps.

2.3 Emulsion storage

The emulsion bottles were kept at room temperature ($30 \pm 2^\circ\text{C}$) for 48 days during Ostwald ripening study. For heating stability study, the emulsion bottles were put in boiling water at 100 $^\circ\text{C}$ for 30 min. For freeze-thaw

stability study, the emulsion bottles were stored in a freezer at -20 ± 2 °C for 22 h and thawed at room temperature of 30 ± 2 °C for at least 2 h.

2.4 Measurement of emulsion properties

2.4.1 Droplet size measurement

The particle size distributions of emulsions were measured by using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). The refractive indices for water, *OO*, *PO*, and *CnO* are 1.333, 1.461, 1.461, and 1.470, respectively. The particle sizes were reported as surface-volume mean particle diameters, $d_{32} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$, and volume-weighted mean diameters, $d_{43} = \Sigma n_i d_i^4 / \Sigma n_i d_i^3$, where d_i is the midpoint of the size interval i and n_i is the number of particles in that interval. The reported particle size was the mean \pm standard deviation from at least two replicates.

2.4.2 Optical microscopy

The emulsion microstructure was examined by using a standard optical microscope (Alphaphot-2, YS2-H, Nikon Corporation, Japan) at a total magnification of 1000 \times . A few drops of emulsion sample were put on a glass slide and covered with a cover slid. The micrographs of magnified emulsion droplets were acquired using a microscope eyepiece camera (AM423 Dino-Eye USB, AnMo Electronics Corporation, Taipei, Taiwan) with software (DinoCapture Software) installed on a computer.

2.4.3 Measurement of amounts of free oil (destabilized oil)

The amounts of free oil (destabilized oil) in emulsion samples were measured using the principle of dye dilution method [10-13]. A stock solution of 0.0015 wt% Oil-Red O in *OO* or *PO* was initially prepared. Two grams (2 g) of stock Oil-Red O solution was added to the freeze thawed emulsion samples (60 g). The mixtures were vortexed for 30 s and centrifuged at the speed of 5,500 rpm for 5-10 min (Universal centrifuge, Model PLC-012, Gemmy Industrial Corporation, Taipei, Taiwan) to separate the colored oil upper layers from the lower layers of white emulsions. Some centrifuged samples might have to leave for many days until all left particles in the colored oil upper layers were settled down and became clear and non-turbid. The transparent colored oil was transferred by a micropipette into a plastic cuvette and measured its absorbance at a wavelength of 517 nm by using an ultraviolet-visible spectrophotometer (Spectronic Genesys 5, Milton Roy Company, Rochester, NY, USA). The measured absorbance was converted to weight percent of free oil by using prepared standard curves. Each reported amount of free oil was the mean \pm standard deviation from at least two replicates.

2.5 Interfacial tension measurement

The interfacial tensions between oil and water or between oil and emulsifier solutions were measured by using a spinning-drop video tensiometer (STV20, Data Physics, Germany) at $30 \pm 2^\circ\text{C}$. The rotational speeds were adjusted and the interfacial tension data were recorded after waiting until approaching equilibration. The reported interfacial tension value was the mean \pm standard deviation from at least two replicates.

3. Results and discussion

3.1 Effects of oil and emulsifier types on formation of emulsions

Figure 1 displays the mean droplet sizes of initial emulsions formed by ultrasonic homogenization and the first row of figure 2 showed their optical micrograph. The size distributions were also shown as data on day 1 in figures 3a, b, d, and e. The *PO* emulsions stabilized by *SE* had a smallest mean droplet size of 0.2 microns and the *OO* emulsions stabilized by *SE* had a larger droplet size by ~ 8 times. The mean droplet sizes of *PO* emulsions stabilized by *PGE* and *OO* emulsions stabilized by *PGE* were comparable and larger than *PO* emulsions stabilized by *SE* by ~ 2 -3 times.

Table 1 showed the measured interfacial tensions at *OO* – water and *PO*-water interfaces and the saturated interfacial tensions with *SE* and with *PGE*. (The emulsifier concentration required to saturate the interface were assumed to be reached at 1.2 wt% [14].) The interfacial tensions between *OO*- water interfaces were lower than between *PO*-water interfaces and *SE* could reduce the interfacial tensions better than *PGE*. Sucrose monostearate (*SE*) was a smaller surfactant with an unbranched sucrose headgroup while decaglycerol monostearate (*PGE*) had a long chained polyglycerol headgroup. These two emulsifiers possibly packed and behaved differently at the interface. From section 2.1, the molecular components in *OO* and *PO* were quite different and this also affected the interfacial tension. It was found here that the droplet size results in table 1 did not quite correlate with the measured saturated interfacial tensions (table 1). Despite the interfacial tension was lowest at *OO*-water interface when saturated with *SE*, the sizes of *OO* emulsions stabilized by *SE* were larger than other emulsions. Probably the sizes of emulsions prepared from 0.75 wt% emulsifier (figure 1) did not reach the limited droplet size yet. The sizes of emulsions could be smaller if increasing the concentrations of emulsifiers. Moreover, the size of emulsions could also be limited by the homogenization conditions such as by the volume of the mixing samples and the size of the ultrasonic probes. Physical properties of oils and emulsifier solutions such as viscosity might also have some effects.

Figure 1. Mean droplet sizes of initial emulsions and emulsions after heating (100°C/30 min) and after freeze thawing (-20°C/22 h and 30°C/2 h). The emulsions were prepared from 5 wt% orange oil (*OO*) and 5 wt% peppermint oil (*PO*) with addition of 0.75 wt% of sucrose esters (*SE*) and 0.75 wt% polyglycerol esters (*PGE*).

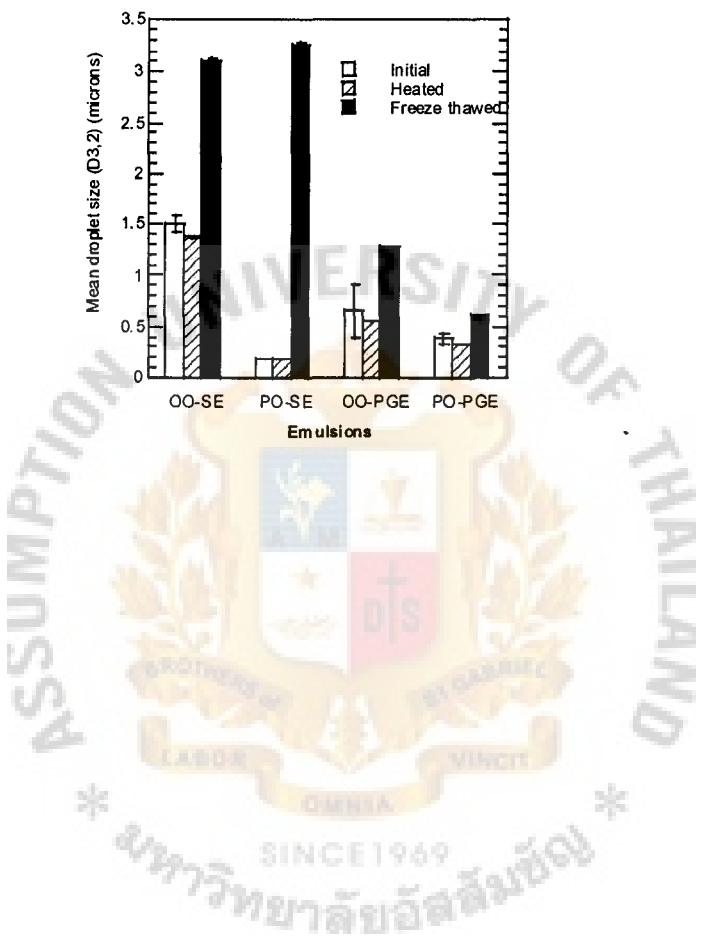


Figure 2. Optical micrographs of emulsions prepared from 5 wt% orange oil (*OO*) and from 5 wt% peppermint oil (*PO*) stabilized by 0.75 wt% of *SE* and by 0.75 wt% of *PGE*. Initial emulsions, emulsions after heating (100°C/ 30 min), and emulsions after freeze thawing (-20 °C/ 22 h and 30°C/ 2 h).

	OO-SE	PO-SE	OO-PGE	PO-PGE
Initial emulsions				
Heated emulsions				
Freeze thawed emulsions				

Figure 2. Optical micrographs of emulsions prepared from 5 wt% orange oil (*OO*) and from 5 wt% peppermint oil (*PO*) stabilized by 0.75 wt% of *SE* and by 0.75 wt% of *PGE*. Initial emulsions, emulsions after heating (100°C/ 30 min), and emulsions after freeze thawing (-20 °C/ 22 h and 30°C/ 2 h).

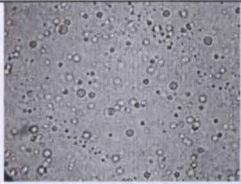
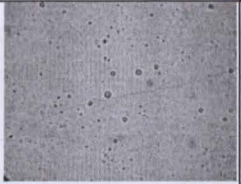
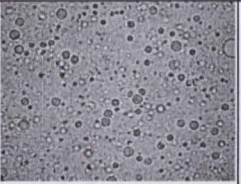

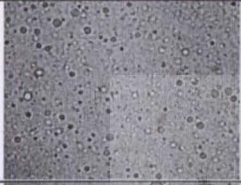

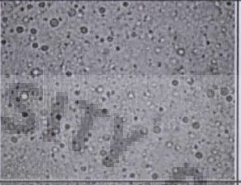
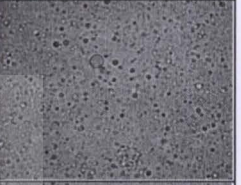
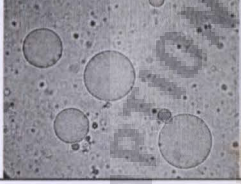


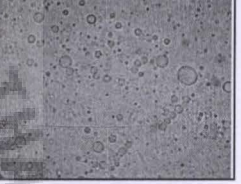
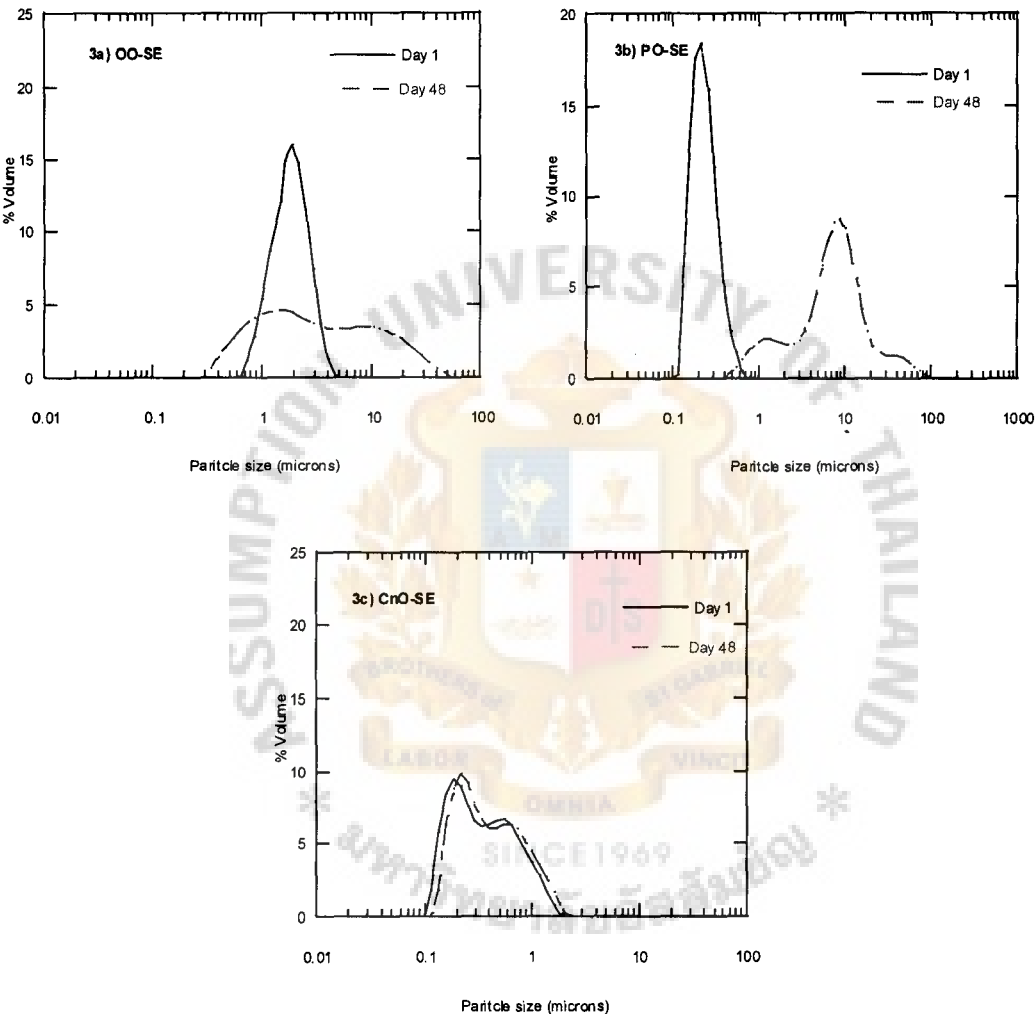
	OO-SE	PO-SE	OO-PGE	PO-PGE
Initial emulsions				
Heated emulsions				
Freeze thawed emulsions				

Figure 3. Droplet size distributions of emulsions prepared from 5 wt% oil and 0.75 wt% emulsions measured at day 1 and day 48. (a) Orange oil (*OO*) emulsions stabilized by *SE*. (b) Peppermint oil (*PO*) emulsions stabilized by *SE*. (c) Corn oil (*CnO*) emulsions stabilized by *SE*. (d) *OO* emulsions stabilized by *PGE*. (e) *PO* emulsions stabilized by *PGE*. (f) *CnO* emulsions stabilized by *PGE*.



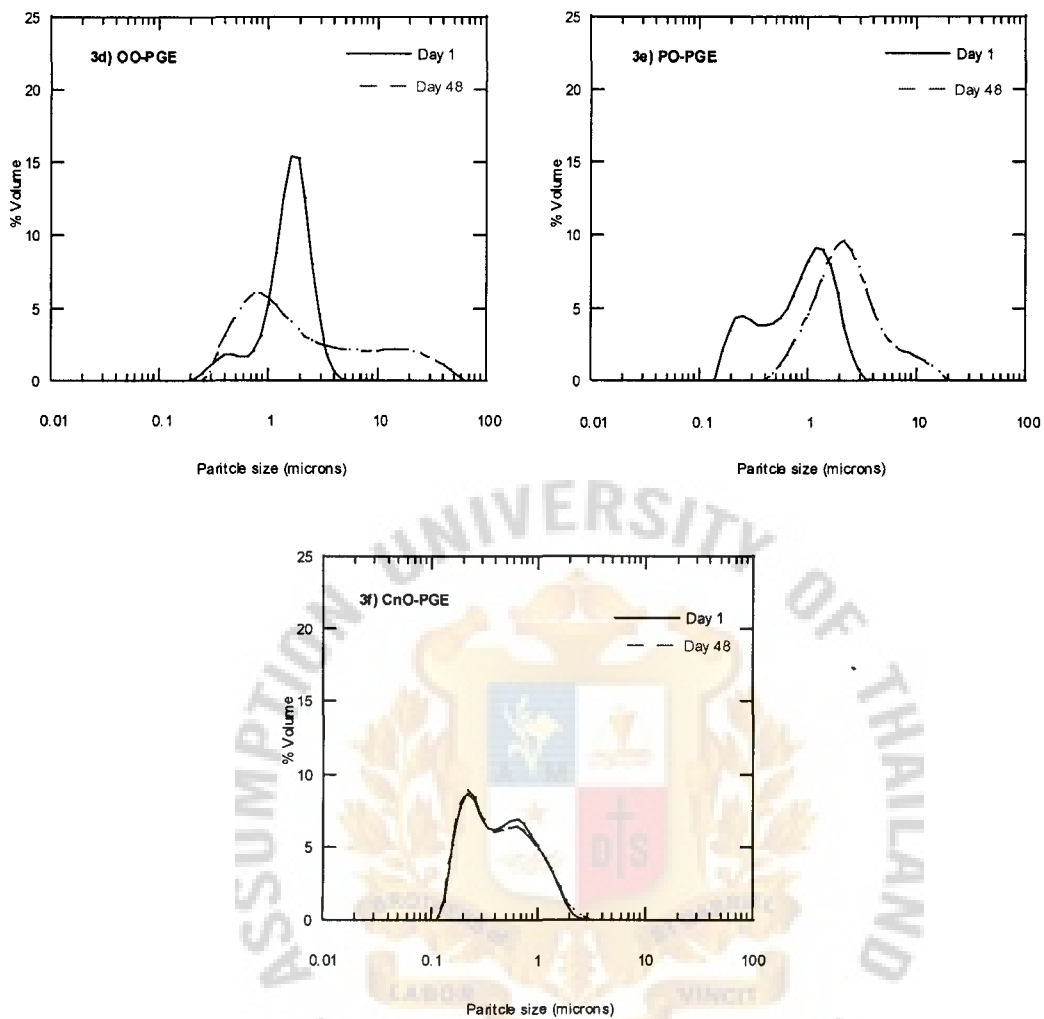


Table 1. The interfacial tensions at orange oil (*OO*) – water and peppermint oil (*PO*) -water interfaces (no emulsifier) and the saturated interfacial tensions with sucrose esters (*SE*) and polyglycerol esters (*PGE*) (with 1.2 wt% emulsifier aqueous solution).

	Interfacial tensions (mN/m)	Saturated interfacial tensions with <i>SE</i> (mN/m)	Saturated interfacial tensions with <i>PGE</i> (mN/m)
<i>OO</i> -water interface	28.5±0.7	1.6±0.1	11.3±0.6
<i>PO</i> -water interface	57.8±2.9	9.3±0.4	36.3±1.1

Data are provided as means ± standard deviation from at least two replicates.

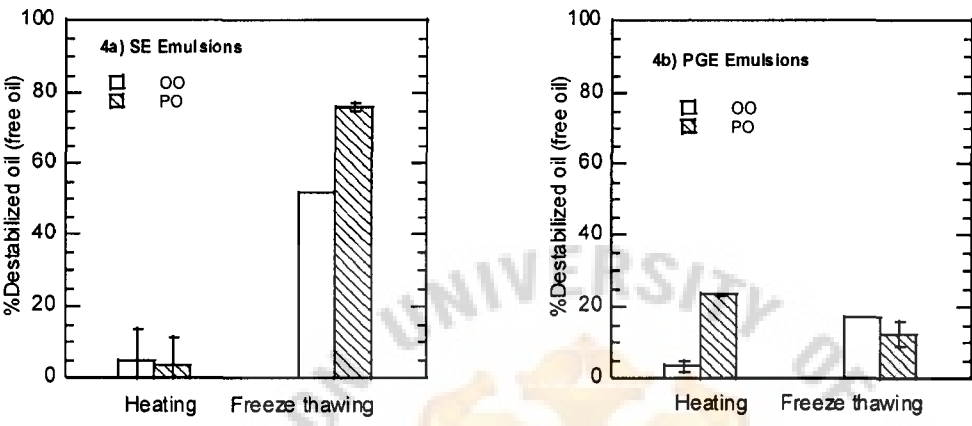
3.2 Study of heat stability and freeze-thaw stability

The second row of figure 2 displayed the micrograph of oil droplets in different emulsions after being heated at 100 °C for 30 min and the measured mean droplet sizes were shown in figure 1. No coalescence or flocculation were observed in emulsions (both *OO* and *PO*) stabilized by *PGE* and by *SE*. Their mean droplet sizes hardly changed from the initial emulsions. These indicated that emulsions having good heating stability. Figure 4 showed the measured amounts of destabilized oil after emulsions being heated and small amounts of destabilized oils were detected in all heated emulsions (figures 4a and b). This indicated quite stable emulsions and the results reasonably agreed with the size results.

Some emulsion samples had gone through freeze-thaw process (frozen at -20°C for 22 h and thawed at 30°C for 2 h). The micrograph of freeze thawed emulsions (both *OO* and *PO*) stabilized by *PGE* displayed comparable sizes and appearance to the initial emulsions (figure 2). The measured mean droplet sizes of before and after freeze thawing only slightly changed (figure 1). Differently, the mean droplet sizes of emulsions (both *OO* and *PO*) stabilized by *SE* significantly increased (figure 1) and very large coalesced oil droplets were observed (figure 2). Significantly amounts of destabilized oils (50-80%) were detected in emulsions (both *OO* and *PO*) stabilized by *SE* after freeze thawing (figure 4a). Much smaller amounts of destabilized oils were detected in emulsions (both *OO* and *PO*) stabilized by *PGE* (figure 4b). The emulsions stabilized by *PGE* exhibited better freeze-thaw stability than emulsions stabilized by *SE*.

It is interesting to observe here that emulsions stabilized by *PGE* were quite freeze-thaw stable as since several research groups are still trying to improve freeze-thaw stability of emulsions [11, 13, 15-20]. Probably the presence of interfacial layers of decaglycerol limited the ice crystallization and reduced coalescence between liquid oil droplets. Coalescence was prone to occur by growing ice crystals protruded into oil droplets that remained uncrystallize. This reason would be evident by another study finding that walnut oil emulsions stabilized by glycerol monostearate mixed with decaglycerol monolaurate also had good freeze-thaw properties [21]. Here, freeze-thaw destabilization was observed in emulsions (both *OO* and *PO*) stabilized by *SE* as we had observed before in our previous study using corn oil emulsions stabilized by *SE* [13].

Figure 4. Percentage of destabilized oil (free oil) of emulsions prepared from 5 wt% orange oil (*OO*) and from 5 wt% peppermint oil (*PO*) after heating (100°C/ 30 min) and after freeze thawing (-20 °C/ 22 h and 30°C/ 2 h). (a) Emulsions stabilized by 0.75 wt% of *SE* . (b) Emulsions stabilized by 0.75 wt% of *PGE*.



3.3 Ostwald ripening study

Figures 5a,b showed the measured mean droplet sizes of *OO*, *PO*, and *CnO* emulsions every 12 days during the storage. The measured mean droplets sizes of *PO* emulsions stabilized by *SE* and by *PGE* showed obviously increasing trends over time. The sizes of *PO* emulsions stabilized by *SE* and by *PGE* lesser increased when compared to *OO* emulsions. The sizes of *CnO* emulsions stabilized by *SE* and by *PGE* remained unchanged throughout the storage time. Accordingly, figures 3a-f showed the measured size distributions of *OO*, *PO*, and *CnO* emulsions on day 1 and day 48 of storage. After 48 days, the size distributions of *OO* emulsions stabilized by *SE* (Figure 3a), *PO* emulsion stabilized by *SE* (Figure 3b), *OO* emulsions stabilized by *PGE* (Figure 3d), and *PO* emulsion stabilized by *PGE* (Figure 3e) significantly deviated or became broader from the initial emulsions. The size distributions of *CnO* emulsions stabilized by *SE* (figure 3c) and by *PGE* (figures 3f) remained hardly change from the initial emulsions.

Here, *CnO* emulsions were used as control triglyceride emulsions to compare its stability with the flavor oil emulsions. *CnO* was composed of long chain fatty acids (section 2.1) that insoluble in water, and thus, no Ostwald ripening occurred in *CnO* emulsions. The observation of high stability of *CnO* emulsions over 48 days also indicated that *CnO* emulsions stabilized by these two types of emulsifiers were also stable from other destabilization mechanisms, especially, coalescence. Coalescence mostly occurs when amounts of emulsifiers are enough to fully coat around oil droplets to prevent close contact between oil droplets [22]. It would be reasonable to assume that no coalescence in flavor oil (both *OO* and *PO*) emulsions stabilized by *PGE* and by *SE* as well, since they were coated with the same types and same amounts of emulsifiers as the control *CnO* emulsions. The progressive changes in sizes of *OO* and *PO* (figures 3a, b, d, and e and figures 5a and b) should primarily come from the Ostwald ripening process. A similar way to differentiate between Ostwald ripening and coalescence had been reported before [23].

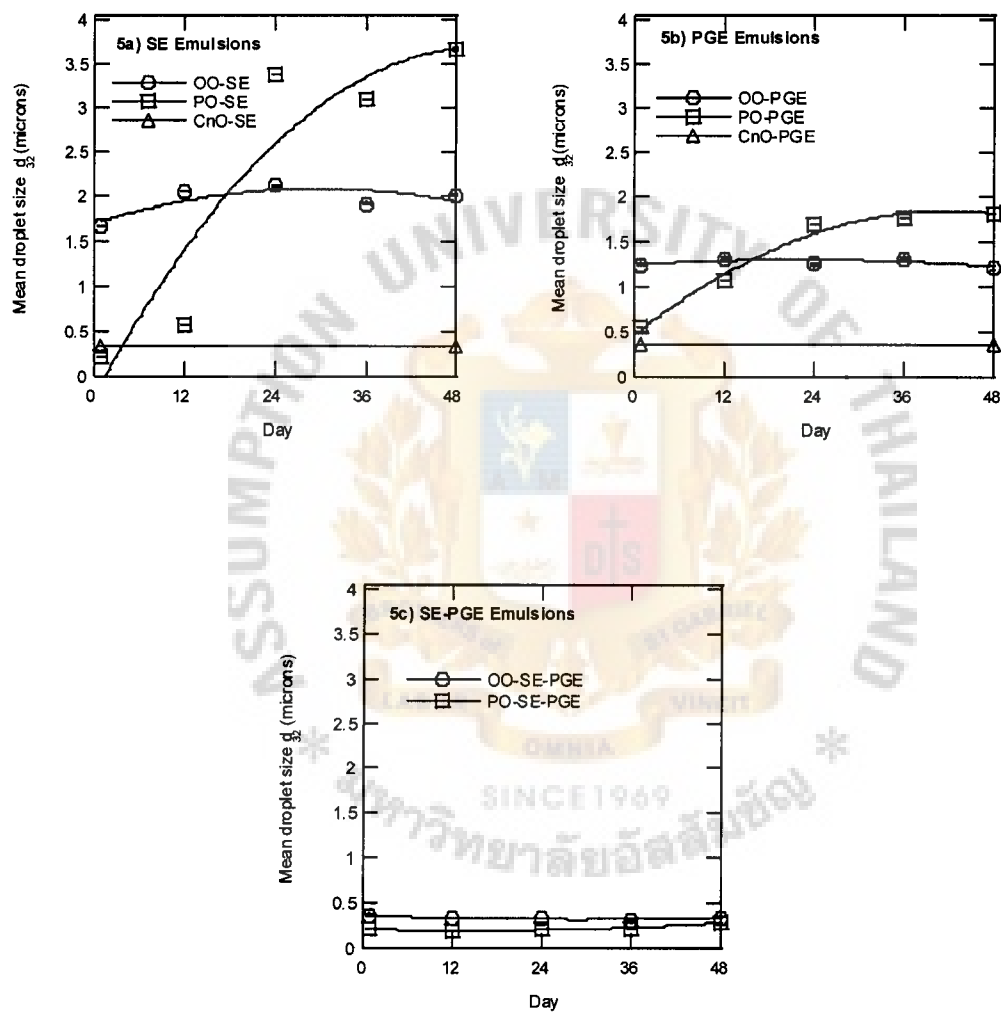
Ostwald ripening occurred in flavor oil emulsions contained polydisperse oil droplets. Because of the difference in Laplace pressures, the local aqueous oil solubility near small oil droplets were higher than at near larger oil droplets, creating the oil transfer driving force. The various small molecular components in flavor oils with different aqueous solubility were able to diffuse and possibly more than one components diffused at the same time. Therefore, the development of droplet size distributions (figures 3a, b, d, and e) of such complex mixtures over time were complicated. Limonene ($M_{wt} = 136.24$) was the main component in *OO* (93%) (section 2.1) which had a low molar volume of $0.162 \text{ m}^3/\text{kgmol}$. *PO* was composed mainly of menthol ($M_{wt} = 156.27$) (38%) and menthone

(Mwt= 154.2) (25%) (section 2.1) and their molar volumes were comparable of 0.176 m³/kgmol and 0.172 m³/kgmol, respectively. The diffusivity of limonene, menthol, and menthone in aqueous phase calculated from Wilke-Chang equation at 30°C were 8.47×10⁻¹⁰ m²/s, 8.06×10⁻¹⁰ m²/s, and 8.17×10⁻¹⁰ m²/s, respectively. Limonene had an order of magnitude lower in aqueous solubility (1×10⁻⁴ mol/l) compared to menthol (2.88×10⁻³ mol/l) and menthone (4.46×10⁻³ mol/l) [24]. Among those parameters, the oil aqueous solubility would largely dictate the effects of oil types on the oil transfer rates. By comparison the rates of droplet size increasing over storage time, the ripening rates in *PO* emulsions seemed to be faster than in *OO* emulsions (figures 5a,b)

In order to improve the stability of flavor oil emulsions, the mixture of *SE-PGE* (at 1 : 1 ratio) had been used as coated emulsifiers. Figures 5c showed that no increase in the mean droplet sizes in *OO* and *PO* emulsions stabilized by mixed *SE-PGE*. The mixed interfacial layer of *SE-PGE* better protected the molecular diffusion between oil droplets and improved Ostwald ripening stability of emulsions. The use of mixtures between sucrose esters and polyglycerol esters to stabilize flavor oil emulsions had been mentioned before in some other studies [1]. In general, emulsions stabilized by mixed interfacial stabilizers or multilayered membranes had better Ostwald ripening stability than using single emulsifier [25-28]. The properties of interfacial layers such as interfacial rheology, surface elasticity, and membrane thickness can influence the ripening rates [29, 30]. The interfacial controlled mechanisms played a role when these interfacial layers creating enough mass transfer resistance to resist diffusion of oil molecules between oil droplets. The magnitudes of resistance would also depend on molecular structures and compositions of the transferring oils.

There were several studies on effects of micelles on Ostwald ripening and they found that the presence of micelles could enhance the ripening rates [31-33]. In this study, the emulsifiers at the total concentration of 0.75wt% was used (because oil layers were observed after ultrasonication if using the lower concentrations) and it was possible to have some excess surfactants from coating droplet surface to form some small amounts of surfactant aggregates. We noted that the presence of those self-assembled aggregates might have some influences on the ripening rates.

Figure 5. Mean droplet size of emulsions prepared from 5 wt% orange oil (*OO*), from 5 wt% peppermint oil (*PO*), and from 5 wt% corn oil (*CnO*) measured periodically over 48 days of storage. (a) Emulsions stabilized by 0.75 wt% of *SE*. (b) Emulsions stabilized by 0.75 wt% of *PGE*. (c) Emulsions stabilized by 0.375 wt% of *SE* mixed with 0.357 wt% *PGE*.



4. Conclusions

In this study, emulsions contained orange oil (*OO*) and emulsions contained peppermint oil (*PO*) were formed by ultrasonication using sucrose monostearate (*SE*) and polyglycerol monostearate (*PGE*) as emulsifiers. It was found that heating did not have much influence on stability of emulsions stabilized by these two types of small molecular emulsifiers. The emulsions stabilized by *SE* were quite unstable if being frozen and thawed. Instead, emulsions stabilized by *PGE* had better freeze-thaw properties of lesser amounts of destabilized oils after thawing. It was suggested that the branched *PGE* containing ten terminal hydroxyl groups might affect and limit ice crystallization near oil droplet surfaces which reducing coalescence during freezing. After certain time of storage, the emulsions stabilized either by *SE* or by *PGE* gradually destabilized due to Ostwald ripening. The ripening rates could be retarded by creating higher interfacial oil transfer resistance using mixed emulsifiers between *SE* and *PGE*.

Acknowledgement

This research project was supported by Assumption University research grant (P57-0178). The emulsifiers used in this study were kindly donated by Caltech Corp., Ltd.

References

1. P.S. Given, *Current Opinion in Colloid & Interface Science*. **14**, 43-47 (2009)
2. D.T. Piorkowski and D.J. McClements, *Food Hydrocolloids*. **42, Part 1**, 5-41 (2014)
3. M. Shachman, in *The Soft Drinks Companion: A Technical Handbook for the Beverage Industry*. (CRC Press LLC, Boca Raton, London, New York, Washington, D.C., 2005)
4. T. Tadros, P. Izquierdo, J. Esquena, and C. Solans, *Advances in Colloid and Interface Science*. **108–109**, 303-318 (2004)
5. D.J. McClements and J. Rao, *Critical Reviews in Food Science and Nutrition*. **51** (4), 285-330 (2011)
6. J.M. Gutiérrez, C. González, A. Maestro, I. Solè, C.M. Pey, and J. Nolla, *Current Opinion in Colloid & Interface Science*. **13** (4), 245-251 (2008)
7. C. Solans, P. Izquierdo, J. Nolla, N. Azemar, and M.J. Garcia-Celma, *Current Opinion in Colloid & Interface Science*. **10** (3–4), 102-110 (2005)
8. R. Ciriminna, B. Katryniok, S. Paul, F. Dumeignil, and M. Pagliaro, *Organic Process Research & Development*. (2014)

9. Z. Gholami, A.Z. Abdullah, and K.-T. Lee, *Renewable and Sustainable Energy Reviews*. **39** 327-341 (2014)
10. J. Palanuwech, R. Potineni, R.F. Roberts, and J.N. Coupland, *Food Hydrocolloids*. **17** (1), 55-62 (2003)
11. P. Thanasukarn, R. Pongsawatmanit, and D.J. McClements, *Food Hydrocolloids*. **18** (6), 1033-1043 (2004)
12. S. Ariyaprakai, L. Tanachote, and P. Pradipasena, *Food Hydrocolloids*. **30**, 358-367 (2013)
13. S. Ariyaprakai and K. Tananuwig, *Journal of Food Engineering*. **152**, 57-64 (2015)
14. Y.K. Li, S.F. Zhang, J.Z. Yang, and Q.H. Wang, *Colloids and Surfaces A-Physicochemical and Engineering Aspects*. **248** (1-3), 127-133 (2004)
15. G.L. Cramp, A.M. Docking, S. Ghosh, and J.N. Coupland, *Food Hydrocolloids*. **18** (6), 899-905 (2004)
16. S.A. Vanapalli, J. Palanuwech, and J.N. Coupland, *Colloids and Surfaces A-Physicochemical and Engineering Aspects*. **204** (1-3), 227-237 (2002)
17. E. Magnusson, C. Rosen, and L. Nilsson, *Food Hydrocolloids*. **25** (4), 707-715 (2011)
18. L. Cornacchia and Y.H. Roos, *Food Hydrocolloids*. **25** (7), 1726-1736 (2011)
19. J. Palanuwech and J.N. Coupland, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*. **223** (1-3), 251-262 (2003)
20. G.G. Palazolo, P.A. Sobral, and J.R. Wagner, *Food Hydrocolloids*. **25** (3), 398-409 (2011)
21. S. Liu, C. Sun, Y. Xue, and Y. Gao, *Food Chemistry*. **196**, 475-485 (2016)
22. E. Nazarzadeh, T. Anthonypillai, and S. Sajjadi, *Journal of Colloid and Interface Science*. **397**, 154-162 (2013)
23. T.K.N. Hoang, V.B. La, L. Deriemaeker, and R. Finsy, *Langmuir*. **17** (17), 5166-5168 (2001)
24. Y. Ran, Y. He, G. Yang, J.L.H. Johnson, and S.H. Yalkowsky, *Chemosphere*. **48** (5), 487-509 (2002)
25. A. Chebil, J. Desbrières, C. Nouvel, J.-L. Six, and A. Durand, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **425** 24-30 (2013)
26. S. Mun and D.J. McClements, *Langmuir*. **22** (4), 1551-1554 (2006)
27. B. Zeeb, M. Gibis, L. Fischer, and J. Weiss, *Journal of Colloid and Interface Science*. **387** (1), 65-73 (2012)
28. J. Galindo-Alvarez, K.-A. Le, V. Sadtler, P. Marchal, P. Perrin, C. Tribet, E. Marie, and A. Durand, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **389** (1-3), 237-245 (2011)
29. M.B.J. Meinders and T. van Vliet, *Advances in Colloid and Interface Science*. **108-109**, 119-126 (2004)
30. M.B.J. Meinders, W. Kloek, and T. van Vliet, *Langmuir*. **17** (13), 3923-3929 (2001)

31. S. Ariyaprakai and S.R. Dungan, Journal of Colloid and Interface Science. **343** (1), 102-108 (2010)
32. A.M. Djerdjev and J.K. Beattie, Langmuir. **24** (15), 7711-7717 (2008)
33. J.V.L. Henry, P.J. Fryer, W.J. Frith, and I.T. Norton, Journal of Colloid and Interface Science. **338** (1), 201-206 (2009)

