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Application of modified corn starch in stabilization of ultrasonic-assisted pickering oil in water emulsion

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Abstract

Starch is a sustainable and cheap raw material claimed as a good emulsion stabilizer for edible products either in food or pharmaceutical industry. To produce an emulsion stabilized by food based edible stabilizer, this study focused on the non-chemical starch modification for oil in water (O/W) emulsion stabilization produced by ultrasonic emulsification. The results showed that the finest emulsion was obtained at power rate of 500 W for 7 mins of sonication. The stability of the emulsion was investigated by turbidity, centrifugal stability values and droplet size. Pre-gelatinized corn starch (PCS) stabilizer showed better emulsion stability compared to gelatinized corn starch (GCS) due to the different polysaccharide components of the two modified cornstarch. GCS mainly contained amylose while the PCS contained both amylose and amylopectin. The emulsion, stabilized by 6 wt.% of PCS and addition of 3 wt.% of tween-80 exhibited excellent storage stability, along the 30 days storage. The results showed the lowest turbidity of 1.01 cm^{-1}, centrifugal stability value of 36.85% and average droplet diameter of 14.27 µm.

1. Introduction

Emulsion system known as one of the commonly used structures to carry bioactive compound in protected manner against adverse environmental condition (Niu *et al.*, 2020). In pharmaceutical, cosmetic and food industries, oil in water (O/W) emulsion is used to protect some notable liphophilic compounds such as carotene, curcumin, oleoresin and various oils containing bioactivity properties. Oil in water emulsion consists of the oil phase dispersed on the water continuous phase, generally stabilized by emulsifying agents (Hai *et al.*, 2020). The common way to stabilize emulsion is by adding chemically synthesized surfactant. Even though synthetic surfactants can efficiently stabilized emulsion with relatively small droplet size, the use of these compounds raising some controversies in the food and pharmaceutical industries due to the reported side effects to human health (Csáki, 2011). For that reason, the use of food derived particles to stabilized emulsion is proposed as an innovative alternative to the synthetic surfactant. Previous research present quite satisfying result in the employment of soy soluble polysaccharide (Chivero *et al.*, 2016), gum arabic (Ferraz *et al.*, 2021), octenyl succinate starch (Song *et al.*, 2015), soy protein isolates (Zhang *et al.*, 2021) and various modified starch (Gao *et al.*, 2021) in stabilizing emulsion.

Driven by the high demand of a food grade, low cost, and easily produced natural sourced emulsion stabilizer, starch attracts the attention of many researchers and the producer of emulsion-based product. Starch is sustainable, inexpensive, biodegradable, and commonly tagged as a food-grade material. However, it was found that the stability of an emulsion is determined by the size of starch particles and the characteristics of the starch, such as water affinity (Song *et al.*, 2015). The purpose of adding an emulsifier is to reduce the surface tension between the two phases to make it easier to form the desired emulsion. Accordingly, the high hydrophilicity of the starch materials may result in a less stable emulsion. In that manner, modification of the raw starch materials is mandatory. Modification of starch aims to improve starch performance and control the hydrophobicity exhibiting interfacial activity (Apostolidis *et al*., 2023). Several methods have been carried out to modify the nature of starch, such as octenyl succinic anhydride (OSA) modification (Agama-Acevedo and Bello-Perez, 2017), heat treatment (Zhao *et al.*, 2020), acid hydrolysis (Li *et al.*, 2012) and gelatinization (Garcia *et al.*, 2020). Among the modifications applied on the starch materials, non-chemical modification provides.

Gelatinization is carried out by heating starch with

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excess water causing the starch granules to swell and crystallites melting (Xu *et al.*, 2020). The modification procedures change the rheological characteristics of the starch granules depends on the process condition and the molecular structures. A previous study explored the stability of O/W emulsion stabilized by gelatinized various starch (Guedes Silva *et al.*, 2021). The results postulated that the emulsion stability depends on the type of the starch lipid complexes attached on the interfacial surface of the oil and water. While other studies explained that a fully pre-gelatinized waxy rice starch can produced a stable oil in water emulsion (Yulianingsih and Gohtani, 2019). Gelatinized starch dispersion can be seen as a combination of amylopectin-rich fractions dispersed in an amylose-rich continuous. Several methods can be used to separate fractions of amylose and amylopectin-rich gelatinized starch dispersion. Separation of gelatinized starch dispersion can be easily carried out by centrifugation method to obtain precipitate and supernatant fractions from starch dispersion (Vernon-Carter *et al.*, 2015). Another method of starch modification is the starch pregelatination process. Starch pregelatination is starch which is gelatinized and then dried which causes the starch granules to swell and increase instability on the granule's integrity. Restrictions on the movement of oil droplets due to hydrocolloids and the increase of the hydrocolloid concentration can increase the stability of the emulsion (Kaltsa *et al*., 2013). Moreover, starch chains released during gelatinization are able to migrate to the oil-water interface to form complexes with lipids, causing a relatively fast decrease in interfacial tension (Guedes Silva *et al.*, 2021).

The addition of stabilizer is not the only option to stabilize emulsion. Emulsion is a thermodynamically unstable system due to the continuous natural interaction between each droplet. The addition of stabilizer prevents the interaction of each droplet by steric repulsion or modifying the solution rheology. However, the high stability of an emulsion can also be achieved by physically modifying the droplet size in such a way that the interfacial film tension cannot drives the droplets coalescence. The assistance of ultrasonic waves for emulsification process has proven to be able to produce such droplets that are small enough to resist the interfacial tension of the oil and water (Modarres-Gheisari *et al.*, 2019). Ultrasonic emulsification involves mixing or homogenization in low temperature and relatively short time so that the active component tends to be stable (Zhang *et al.*, 2020). The ultrasound process produces a smooth and stable emulsion with high-speed homogenization (Zhou *et al.*, 2011). Ultrasonic treatment in fairly high intensity (more than 25 Hz) is able to improve the emulsification properties and surface hydrophobicity which also induced smaller droplets (Kaltsa *et al.*, 2013).

There is a dearth of information on the eminence of the ultrasonic emulsification process and the prospect of the modified starch complexes to stabilize pickering emulsion. Therefore, the present works focused on the investigation of the modified (gelatinized and pre-gelatinized) corn-starch in stabilizing oil in water emulsion. This study also focuses on the interaction between the modified starch conjugated with synthetic surfactant under the process of ultrasonication, which was rarely discussed on the previous study. Considering that the starch modification methods were resulting on the different kind of polysaccharides (amylose and amylopectin), a novel study is expected. The characteristics of the modified starch was analyzed and the emulsion stability was examined based on the droplet size, turbidity and centrifugation value.

2. Materials and methods

2.1 Materials

A local brand corn starch used as a stabilizer without any pretreatment. Tween 80 as conjugated synthetic surfactant purchased from a local chemical distributor. Extra virgin food grade olive oil (Bertolli ©, Mizkan America Inc., United States) used as the oil phase in preparation of oil in water emulsions. Distilled water was used in any procedure requiring water as the materials.

2.2 Starch modification

To prepare the gelatinized corn starch, the method was adapted from a previous study (Gómez-Luría *et al.*, 2019) with some necessary adjustment (Nafiunisa *et al.*, 2022). The procedure started by hydration of corn starch in aqueous dispersion, gelatinization induced by heat and finished by amylose-amylopectin separation. The GCS was then used directly without drying for stabilizing the O/W emulsion.

Meanwhile, modification of corn starch by pregelatinization methods was adapted from the previously studied methods with some appropriate modification (Yulianingsih and Gohtani, 2020). A dispersion of 5% w/w corn starch on an aqueous solution was heated at 85°C for 10 mins under continuous agitation at 200 rpm. After the completion of gelatinization process, the solution was brought in to room temperature and poured into a clean stainless steel tray (200 mm × 250 mm). The height of the solution inside the tray was kept under 10 mm height to provide good surface area. The PCS dried inside a low temperature air dryer for 24 hrs at 45°C. Thereafter the dry solid flat sheet PCS was ground using ball mill for 3

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hrs and sieved to obtain 100 mesh powder. The PCS powder is made in bulk prior to the preparation of the emulsion and safely stored inside a double vacuum box filled with silica gels.

2.3 Characterization of the modified corn starch

FTIR (frontier spectrometer; Perkin-Elmer Inc., USA) analysis was used to observed the functional groups of the raw corn starch and the modified GCS and PCS. The SEM (JSM-6510; Jeol. Ltd, Japan) morphology analysis of the starch was only conducted for the solid-state starch (raw starch and PCS). The solid-state starch was also observed for the water wettability analysis using optical static contact angle (OCA 25, DataPhysics Instruments GmbH, Germany). To calculate the average particle size and the homogeneity of the modified starch, PCS and GCS were analyzed by Laser Particle Size Analyzer (LLPA – C10, Labtron Equipment Ltd., United Kingdom).

2.4 Emulsion preparation

Coarse emulsion was prepared by dissolving the modified starch (PCS and GCS) at various concentrations of 4%, 5% and 6% (% w/w basis) with and without surfactant. The concentration of Tween 80 as the surfactant varied at 1%, 2% and 3% (% w/w basis). The ratio of oil:water was fixed at 2:8 (weight ratio). Afterwards the solution was mixed and homogenized using a rotor stator homogenizer (IKA Disperser, T 10 basic ULTRA-TURRAX®) at 11000 rpm for 5 mins. To obtained fine emulsion, homogenization was continued using ultrasonic processor (Biosafer Cell Disruptor, Bio900-92, China) at various sonication power rate (300, 400 and 500 W), 4 second pulse on and 2 second pulse off. Emulsification assisted with ultrasonic waves was conducted at various time processes of 7, 8 and 9 mins.

2.5 Investigation on emulsion stability

The stability of the emulsion investigated was based on the turbidity changes of the solution, the centrifugation stability and the microscopic visualization of the oil droplets.

2.5.1 Physical stability of emulsion

One ml of the upper layer of the fine emulsion was diluted 300 times in distilled water. Afterward, the absorbance was analyzed using an ultraviolet-visible (UV-Vis) spectrophotometer at wavelength of 600 nm. Then the turbidity value is calculated based on the spectrophotometric absorbance using the following equation (Teng *et al.*, 2020):

$$T = 2.302 \frac{A \times V}{0.01} \quad (1)$$

Where A is the absorbance measured by UV-Vis spectrophotometer and V is the dilution factor.

2.5.2 Centrifugal stability of emulsion

The physical stability of the fine emulsion was characterized based on the separation of the cream layer and the water layer after accelerated separation by centrifugation force. Prior to the centrifugation, a sample of emulsion was diluted 300 times using distilled water and centrifuged at 4000 rpm for 30 mins. After that, the bottom layer of the emulsion was taken carefully using syringe needle and the absorbance value was calculated on ultraviolet-visible (UV-Vis) spectrophotometer at wavelength of 600 nm. The centrifugation value (Ke) is calculated using the equation (Shi *et al.*, 2022):

$$K_e = \frac{A - A_0}{A} \times 100\% \quad (2)$$

Where A is the absorbance before centrifugation and A_0 is absorbance after centrifugation.

2.5.3 Microscopic visualization

The microstructural aspects of the O/W emulsion were assessed qualitatively and quantitatively using an optical microscope (SINHER XSZ-107). Each emulsion with a magnification of 400 times. One ml upper layer of each emulsion sample was diluted in distilled water until the droplets are presentable. The droplet sizes were determined by means of an optical microscope figure. The microscope sample was collected freshly from the emulsion tube and directly analyzed after the dilution process. For each sample, around 200-300 droplets were counted for the population of the average droplet size. The droplets diameters were individually measured and classified by the help of software, Image-J. A data spreadsheet classification was interpreted to get the average droplets size and the plot of droplets size distribution.

3. Results and discussion

3.1 Characterization of corn starch modification

3.1.1 FTIR analysis

Figure 1 shows the FTIR analysis of the pure cornstarch, Tween-80, the modified corn starch (PCS and GCS) and the complex of modified starch-surfactant. The spectrum of the raw corn starch, GCS and PCS shows a broad peak at 3255 cm^{-1}, 3266 cm^{-1} and 3266 cm^{-1} originating from the aromatic hydroxyl groups of the amylose and amylopectin on the starch (Gómez-Luría *et al.*, 2019). However, the addition of tween-80 into the solution slightly shifts the peaks to 3495 cm^{-1}

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and 3426 cm^{-1}, for GCS-Tween and PCS-Tween respectively. The Tween-80 shows a broad peak on 3489 cm^{-1}, indicating the RCH2-OH groups of the Tween 80 (Bide *et al.*, 2021). Following that, it also implies that the addition of Tween-80 on to the modified starch complex would affect the functional groups of the stabilizer.

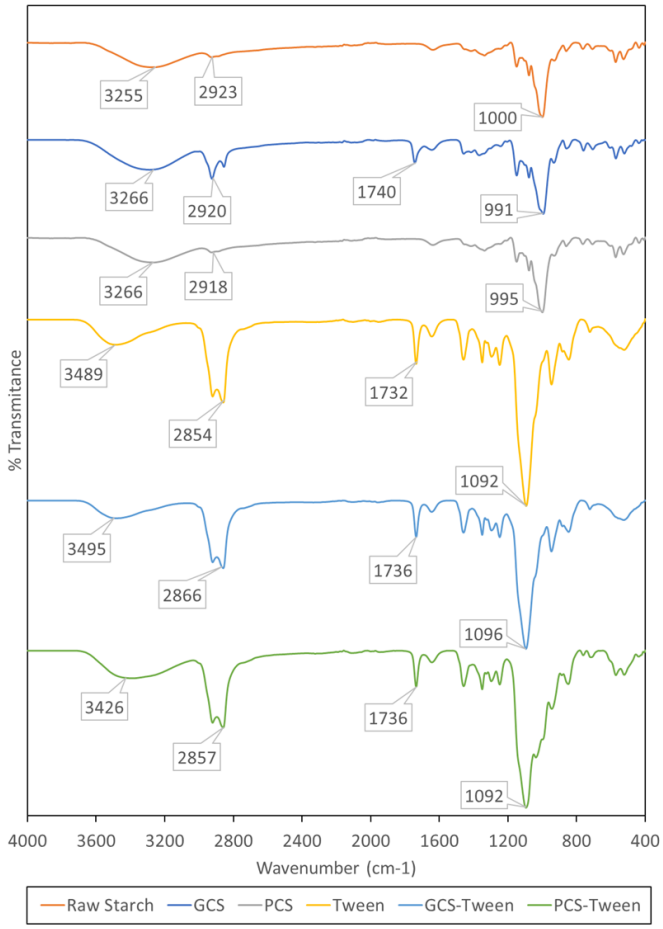

Figure 1. FTIR spectrum of the raw cornstarch, tween-80, and the modified stabilizer (PCS, GCS, PCS-Tween, GCS-Tween).

The raw starch, GCS and PCS shows a low intensity peak at 2923 cm^{-1}, 2920 cm^{-1} and 2918 cm^{-1}, indicates the $–CH_2$ stretch bands of the starch. On the other hand, a more pronounced peak at 2854, 2866 and 2857 cm^{-1} present after the addition of Tween-80, assigned to the long alkanes chain of the surfactant. Strain vibrations of C=O groups were found in all of the sample at a wavenumber range from 1732 – 1740 cm^{-1}. As for the peak around 991 – 1096 cm^{-1}, found in all starch FTIR sample, is the typical C–O stretching within the glucose-based ring of the starch (Willfahrt *et al.*, 2019).

3.1.2 Morphology of the pregelatinzed corn starch

The analysis of scanning electron microscope (SEM) and water affinity test only conducted on the PCS due to the phase difference of the two-kind modified starch. PCS was in solid powder form while the GCS was a viscous aqueous solution.

As shown in Figure 2 the surface of the PCS powders was compared to the surface of an original corn -starch. From the analysis, a visible difference between the PCS particles and the neat starch particles can clearly be observed. The neat cornstarch showed a typical smooth surface of a raw starch, while the PCS gives of a formation of flakes like structure. A closer examination to the starch morphological structure shows that the PCS had a gritty, rough and uneven texture. The morphology might be the result of a strong molecular interaction between the starch constituents, which forms a continuous phase of a polymer matrix. The uneven texture of PCS shows the potential of a better emulsion stabilizer, due to the larger surface contact area of the starch particles with the oil droplets and the surrounding water (Wigati *et al.*, 2023). The morphological difference between the neat corn starch and the modified PCS shows that the modification was successfully conducted. In general, starch molecules undergo a starch nanostructure dissociation along the pre-gelatinization process, which results a rougher surface structure (Zhu *et al.*, 2022). Compared to other granular starches such as potato or rice starch, corn-starch granules show an irregular surface shape with some channels or cavities (Guo *et al.*, 2021). Those surface structures allowed more binding-effect due to the surface open structure. A similar result where the pregelatinized starch shows more texture than the raw one was also presented on the previous study of a pregelatinized rice starch (Liu *et al.*, 2017). The formation of an amorphous structure in pregelatinization corn starch can also improve the performance of the interface oil – water through amorphous starch bonds (Xu *et al.*, 2020).

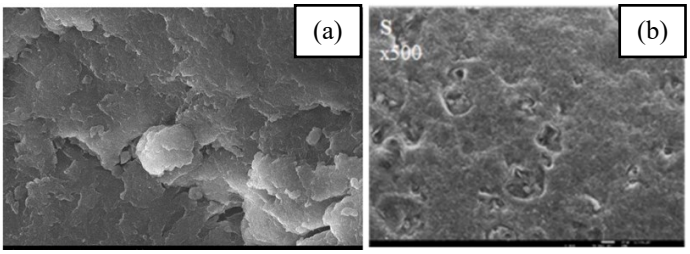

Figure 2. SEM of (a) pregelatinization corn starch (b) pure corn starch.

3.1.3 Water affinity analysis

As mentioned in the methodology section, the characterization of the water affinity of the modified starch was only conducted for the PCS due to the difference phase of the two modified starch. Prior to the analysis, the grounded powder of PCS and raw corn starch powder are packed using pellet powder presser. Figure 3 shows a droplet of the water stays on the surface of the pressed powder; the contact angle of PCS was determined at 28°. While the contact angle of the raw corn-starch was not able to be determined due to the fast permeation of the water to the surface of the powder.

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The water affinity analysis is measured by determining the contact angle which can indicate the hydrophilic or hydrophobic nature of the solid particles. A solid particle having a contact angle of less than 90° is considered more suitable for stabilizing O/W emulsions, while a contact angle of more than 90° is used to stabilize W/O emulsions (Cui *et al.*, 2020). Higher water contact angle value shows that the surface was more hydrophobic, and vice versa. From the analysis, both PCS and raw corn starch are still considered to have hydrophilic properties, which are suitable to stabilize an O/W emulsion. While the GCS that definitely soluble on water solution can also considered to be better suited as O/W emulsion stabilizer than the W/O emulsion. The previous study report that the stabilization of O/W emulsion using modified hydroxyapatite (HAp) particle were successfully carried if the particles were in the range of water contact angle of 20.33°-56.34° (Ribeiro *et al.*, 2022).

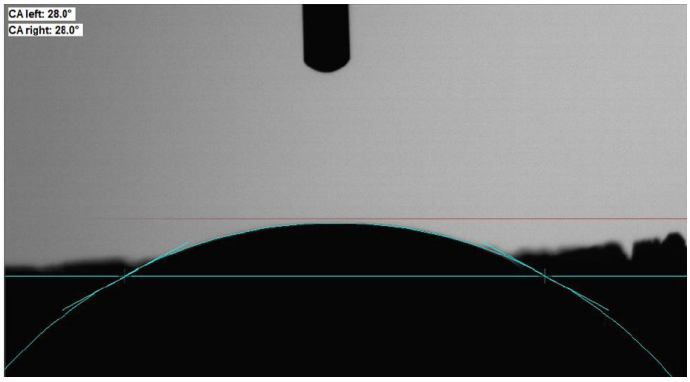

Figure 3. Water contact angle (WCA) of the PCS.

However, the analysis also reveals that the PCS shows a higher water contact angle compared to the raw corn starch, indicating that the PCS has more hydrophobic properties than the untreated corn starch. The slight increase of the hydrophobic properties was preferable in modifying an emulsion stabilizer. A particle with amphiphilic properties has a high interfacial activity which better in stabilizing the O/W emulsion (Gómez-Luría *et al.*, 2019).

3.1.4 Particle size analysis of the modified starch

Figure 4 shows that the average diameter of the GCS particles was 27.14 µm and the PGS was 62.21 µm. The PGS particles are a larger size due to the heating process in the pregelatinization process to become powder. While the GCS stabilizer remains in a liquid phase during the analysis. The previous study presented that a stabilizer particle within the size range of 10 nm to 100 µm can be irreversibly adsorbed on the oil-water interface, resulting in emulsions with droplet sizes ranging from 10 to 100 µm (Zhao *et al.*, 2020).

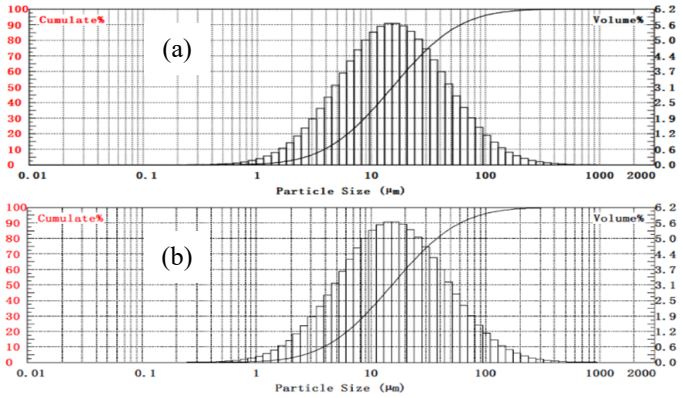

Figure 4. Particle size analysis of (a) GCS (b) PCS.

3.2 Stabilization of oil in water emulsion

3.2.1 Optimization of power rate and time in ultrasonic emulsification process

It is known that frequency, ultrasonication time and power of irradiation are the most important parameters for the ultrasonic emulsification (Modarres-Gheisari *et al.*, 2019). To determine the optimum conditions in the emulsions production, the effect of the ultrasonic power rate irradiation and processing time on the stability of the emulsion was investigated. The process was carried under various power rates (300 W, 400 W, 500 W) and various ultrasonication time of 7 – 9 mins, while the proportion of PCS and GCS stabilizer were kept the same at 5% weight.

Table 1 shows that as the power rate increases, the turbidity and the centrifugation stability values decrease for both stabilizer (PCS and GCS). At the highest power rate of 500 W, the turbidity value of gelatinized corn starch was 1.02 cm^{-1} and the centrifugation value was 74.16%, while the turbidity value of gelatinized corn starch was 2.27 cm^{-1} and the centrifugation value was 76.28%. The decrease in the turbidity value is caused by the strong ultrasonic waves which can destroy the oil droplet into smaller and scattered particles. Ultrasonic works by generating cavitation bubbles which are generated under the strong physical action of cavitation. Cavitation bubbles have strong kinetic energy and can break large granules and the emulsion system becomes more uniform and stable. Increasing the ultrasonic power rate results in an increase in cavitation, adding bubbles with a smaller size, thereby reducing particle size, increasing droplet scattered, uniform droplet size, and lowering the turbidity value so that the emulsion becomes more stable (Wang *et al.*, 2022). A higher turbidity value indicates that the emulsion has a larger particle size and a tendency for a turbid emulsion color.

The optimum conditions for the ultrasonic process are also influenced by the ultrasonic processing time. The ultrasonication was carried out to determine the optimum process time at 7 to 9 mins, at steady power rate of 500 W and 5% weight of stabilizer. The effect of

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Table 1. Effect of ultrasonic power rate to the stability of O/W emulsion.

Power Rate (W)	Pregelatinization		Gelatinization	
	Turbidity (cm^{-1})	Centrifugation (%)	Turbidity (cm^{-1})	Centrifugation (%)
300	2.05	89.01	2.91	88.35
400	1.57	84.48	2.75	86.53
500	1.02	74.16	2.27	76.28

ultrasonication processing time is shown in Table 2. The turbidity and emulsion stability towards centrifugation was increased along the processing time. The lowest turbidity and centrifugation stability values were obtained at 7 mins ultrasonication time. The phenomenon was observed for both stabilizer, PCS and GCS. A similar result was also found on the previous research, where a nanoemulsion produced using ultrasonication and soy protein isolate-phosphatidylcholine stabilizer shows an increase of turbidity values at 10 mins of ultrasonic induction (Teng *et al.*, 2020). An over longer induction of ultrasonic waves can produce too much turbulence on the emulsion solution, which lead to the emulsion instability. The increase of collisions frequency between each oil droplet inside the continuous phase of the emulsion resulted to the droplets aggregation (Shi *et al.*, 2022). The turbidity and centrifugation stability values are inversely proportional to the stability of the emulsion, the smaller the turbidity value and the centrifugation value, the more stable the emulsion (Li *et al.*, 2014).

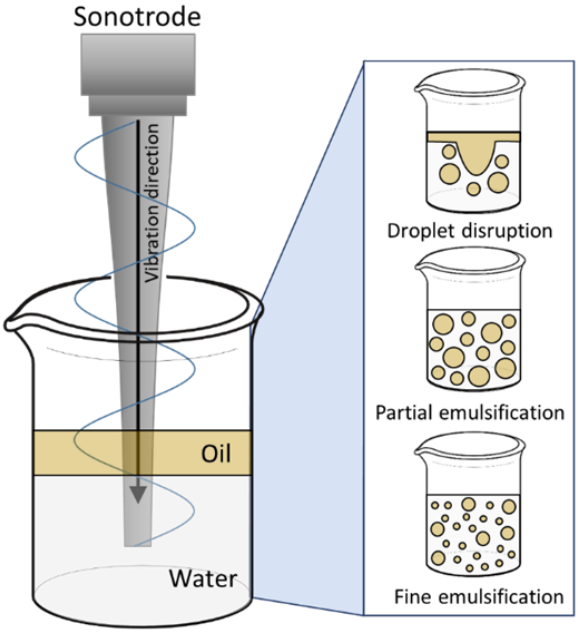

Figure 5. Schematic of droplet breakout during ultrasonic emulsification.

From the investigation, the most stable O/W emulsion stabilized using modified corn starch produced at the operation condition of 500W ultrasonic power rate and 7 mins of sonication. The schematic of ultrasonic emulsification presented on Figure 5.

3.2.2 Stabilization of oil in water emulsion using modified corn starch (pregelatinzed corn starch and gelatinized corn starch)

From the thermodynamics point of view, the emulsion is an unstable system. During storage and transportation, time have a significant effect on its physical and chemical properties (McClements and Gumus, 2016). Along the storage time, the droplet particles absorb energy in the nanoemulsion system, enhancing brownian motion, resulting in deemulsification, flocculation, coalescence, ostwald ripening and gravity separation (Sarheed *et al.*, 2020). Therefore, the storage properties of O/W emulsions stabilized by modified corn starch were investigated during the 30 days of storage (room condition), using centrifugal stability index (Ke) and turbidity as indicators. The Ke value indicates the stability of emulsion induced by centrifugal force along the time (Hien and Dao, 2021; Shi *et al.*, 2022). Turbidity analysis indicates the degree of turbidity of the emulsion, which is also related to the distribution of droplets in an emulsion. The increase of turbidity during the storage period indicates an aggregation of oil droplets in the emulsion due to the dominant attraction in one phase (Sharma *et al.*, 2021). The trend of turbidity test and centrifugal stability analysis results has an inverse relationship with the emulsion stability (Wang *et al.*, 2022).

Figure 6 shows the stability characteristic of the O/W emulsions with the addition of PCS and GCS. Each analysis shows the same trend where the emulsion shows instability, indicated by the increase of turbidity of the emulsion upper layer solution and the centrifugal stability values along the time. The results also show that

Table 2. Effect of ultrasonication time to the stability of O/W emulsion.

Time (mins)	Pregelatinization		Gelatinization	
	Turbidity (cm^{-1})	Centrifugation (%)	Turbidity (cm^{-1})	Centrifugation (%)
7	1.02	74.16	2.27	76.28
8	1.34	82.13	2.44	84.18
9	1.81	88.45	3.03	87.21

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the addition of 6% weight of modified corn starch (PCS and GCS) gives the lowest turbidity among 30 days of storage. Moreover, increasing the stabilizer concentration from 4 to 6% weight gives better emulsion stability. In which proves that PCS and GCS modified corn starches were suitable to stabilize the O/W emulsion. The viscosity of the aqueous phase increased along with the increased of starch particle concentration, leading to the increase of attractive forces between starch particle and oil droplet. Additionally, the adsorption of particle at the emulsion droplet surface increased the effective density of the droplets, thus minimizing the density difference between the droplets and continuous phase (Song *et al.*, 2020; Shen *et al.*, 2022)

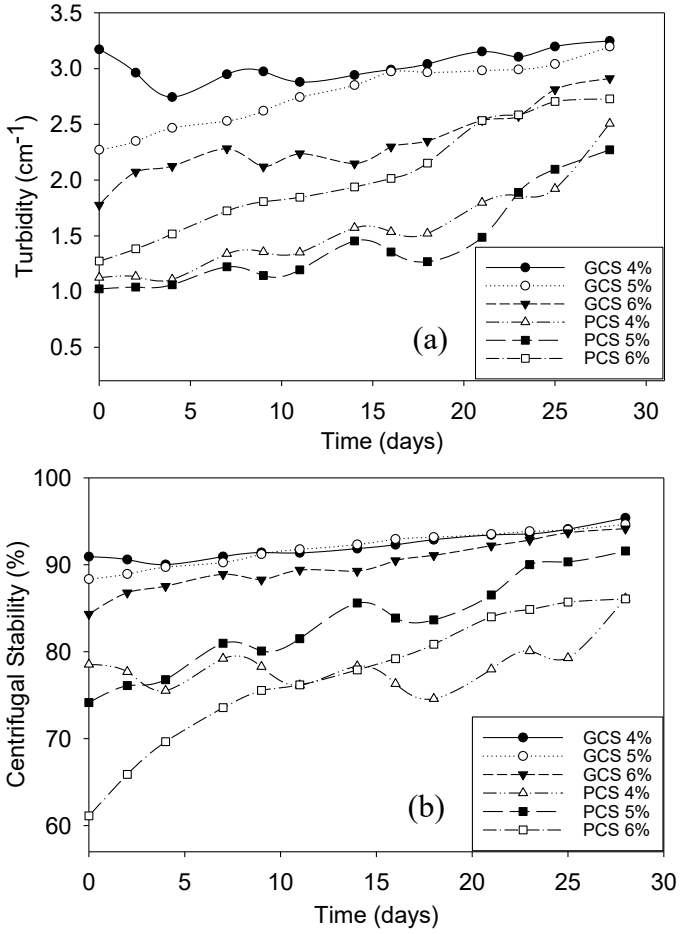

Figure 6. Stability of O/W emulsion stabilized by modified corn starch (PCS and GCS), characterized by the, (a) Turbidity, (b) Centrifugal stability.

In addition, the turbidity and centrifugal stability test also reveals that the PCS stabilizer shows more stable emulsion compared to the emulsion stabilized by GCS. The emulsion stabilized by PCS shows lower turbidity and centrifugal stability values than GCS stabilized emulsion for all concentration. The lowest turbidity of 1.78 cm^{-1}, for the GCS stabilized emulsion, obtained with the addition of 6% wt. stabilizer. While the PCS stabilized emulsion achieved the lowest turbidity of 1.02 cm^{-1}, by the addition of 5% wt. stabilizer. Similar results present on the centrifugal stability analysis where the lowest Ke value of 84.33% and 61.12% reach by the addition of 6% wt. PCS and GCS stabilizer, respectively. It may be due to the different starch molecule composite on the GCS and PCS modified starch. Along the modification process, GCS and PCS contain different kinds of starch composite. In which the GCS stabilizer mainly contains amylose, while the PCS contain amylose and amylopectin (Gómez-Luría *et al.*, 2019; Yulianingsih and Gohtani, 2020). The aqueous aggregation of amylose is linked to the interchained of the double helix crystalline structure (Vernon-Carter *et al.*, 2015; Zhu *et al.*, 2022). Meanwhile, amylopectin is responsible as the starch amorphous component. The amorphous fractions are more susceptible to hydrolysis and water swelling compared to the crystalline fraction (Apostolidis *et al.*, 2023). Those, the PCS stabilizer with more amorphous component of starch had a better ability to stabilize the O/W emulsion. This was due to the rheological characteristic of the amorphous hydrocolloid of amylopectin which able to restrict the oil droplet movement (Chivero *et al.*, 2016).

3.2.3 Stabilization of oil in water emulsion using complexed of starch-surfactant

The addition of Tween 80 combined with modified corn starch has been shown to reduce the droplet size on the O/W emulsion. Figure 7 shows the turbidity and centrifugal stability values of the emulsion stabilized by the complex of starch-surfactant at various surfactant concentrations. The pickering emulsion stabilized by the addition surfactant shows a similar trend with the one without addition of surfactant. Where, the PCS stabilizer resulted on more stable emulsion compared to the GCS stabilizer. The values of turbidity and centrifugal stability show a slight increase over time, indicating that the emulsion is still going through a phase separation along the storage. However, the emulsion is quite stable compared to the emulsion without addition of surfactant. The emulsion stabilized by modified corn starch has an average of 77.6% increase on turbidity values after 28 days. On the other hand, the emulsion stabilized by complexed of starch-surfactant shows an average increase of 9.4% of turbidity values under the same storage time. Moreover, the addition of surfactant also decreases the overall value of the stability parameter (turbidity and centrifugal stability) compared to the emulsion stabilized by only modified starch. A similar result found on the previous research where a more stable emulsion was produced by addition of anionic rice bran cellulose and lauric arginate (Angkuratipakorn *et al.*, 2020). The co-stabilization of emulsions, by either electrostatic or steric stabilized nanoparticles with anionic, cationic or non-ionic surfactants had also been studied (Yuan and Williams, 2016). When the surfactant molecule reacts with the particle surface, the resultant

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surface modification appears to generate faster wetting kinetics for particles at the oil/water interface and yields enhanced stabilization.

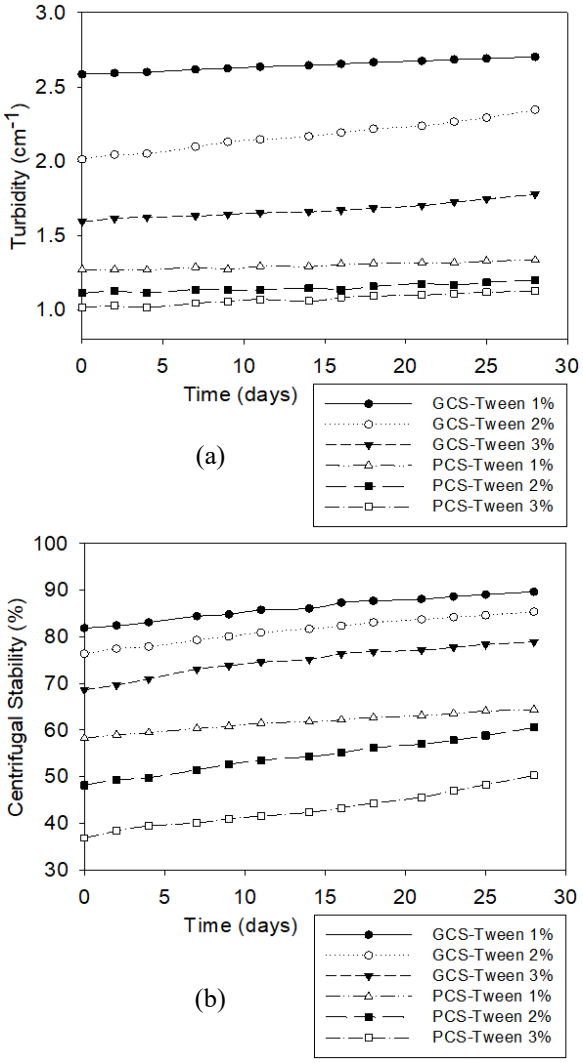

Figure 7. Stability of O/W emulsion stabilized by complexes of starch – surfactant, characterized by the, (a) Turbidity, (b) Centrifugal stability.

3.2.4 Microscopic visualization

The addition of gelatinization corn starch and pregelatinization corn starch was carried out with variations of 4%, 5% and 6% (%w/w water-based). While the emulsion stabilized by the complex of starch-surfactant was investigated at various surfactant concentration (1%, 2%, 3% w/w water-based). Stability of the emulsion was then tested for droplet size, then stored for 30 days. Figure 9 shows the droplets of the O/W emulsion on day 0 (freshly made emulsion) and day 30. Furthermore, the detailed average droplets size was presented in Table 3.

The addition of GCS and PCS as the emulsion stabilizer increases the stability of the emulsion droplets, reduces the occurrence of coalescence and slows down the separation of the emulsion phase. From the microcosmic point of view, droplet size represents the key indicators for testing the stability of emulsion systems (Zhang *et al.*, 2020). Emulsion storage for 30 days showed an increase in the size of the emulsion droplets, which indicated the instability of the emulsion during storage time. The phenomena were in coherence to the stability analysis based on turbidity and centrifugal stability. The addition of more stabilizer particles increases the stability of the emulsion. Showing that the oil droplets was able to stick on the surface of solid particles of the excipients, resulting in a droplet size reduction of the oil (Niczinger *et al.*, 2017). However, along time, coalescence in unavoidable where two or more droplets' aggregates to form larger droplets. The droplets aggregation causing the formation of creaming which easily reflects the light resulted to a turbid layer at the top of the emulsion (Piorkowski and McClements, 2014). The amylose part on GCS is flexible at the interface which can surround the curve of oil droplets, whilst the amorphous structure of PCS holds up more water and swelled up hider the droplets movement (Xu *et al.*, 2020). Figure 8 shows the visual of the GCS and PCS emulsion creaming after 30 days of storage.

The droplet size in an emulsion is affected by the concentration and type of emulsion used (Gorjian *et al.*,

Table 3. The average diameter of the oil droplets from emulsion stabilized with various stabilizer.

Stabilizer	Starch Conc.	Surfactant Conc.	Average Diameter of Droplets (µm)	
			Day-0	Day-30
GCS	4 wt.%	-	26.18	32.01
	5 wt.%	-	20.13	25.46
	6 wt.%	-	19.97	22.82
PCS	4 wt.%	-	26.14	32.76
	5 wt.%	-	23.73	29.93
	6 wt.%	-	22.17	27.01
GCS-Tween	5 wt.%	1 wt.%	20.67	28.71
	5 wt.%	2 wt.%	19.44	23.97
	5 wt.%	3 wt.%	16.89	25.08
PCS-Tween	5 wt.%	1 wt.%	19.88	32.44
	5 wt.%	2 wt.%	18.31	28.97
	5 wt.%	3 wt.%	14.27	20.64

https://doi.org/10.26656/fr.2017.8(S1).12

2022). The lipophilic, hydrophilic and low molecular weight groups on the Tween 80 tend to absorb more quickly on the droplet surface. Reducing the interfacial tension between oil and water phase during the ultrasonic emulsification process, producing a smaller droplet size (Taha *et al.*, 2020). This is in accordance with the previous study, which showed that smaller droplet sizes could be produced adding more surfactant and stabilizer concentrations. The droplet microscopic visualization of the O/W emulsion stabilized by the complex of starch-surfactant also showed on Figure 9.

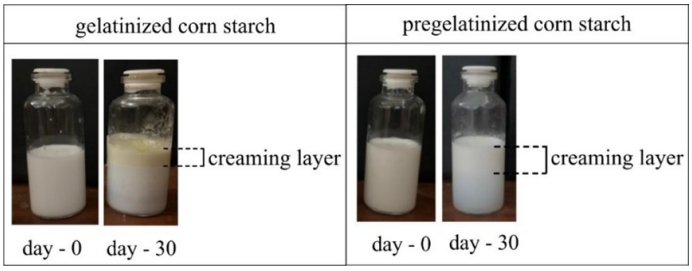

Figure 8. The visualization of the CGS and PCS creaming layer.

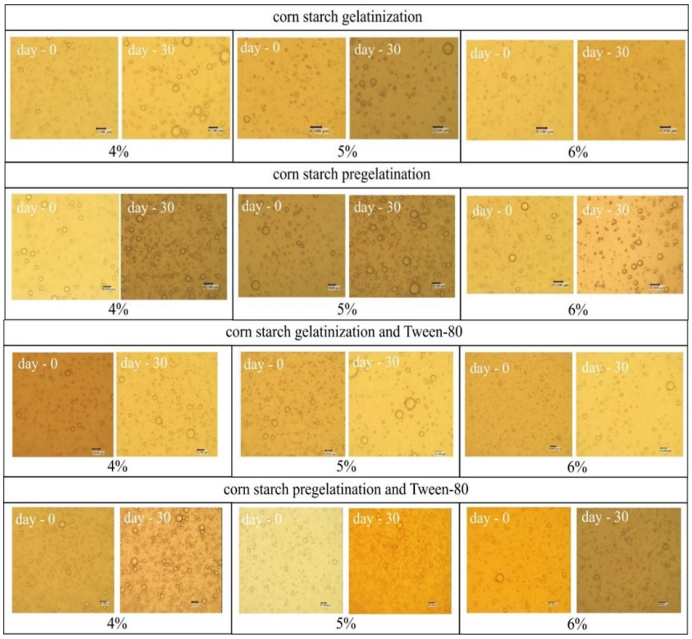

Figure 9. Microscopic morphology of the oil droplets of the emulsion.

4. Conclusion

The modified cornstarch (PCS and GCS) is successfully used to stabilize oil-water emulsions produced by ultrasonic emulsification. The ultrasonic emulsification produced the most stable emulsion by the increase of power rate to 500 W and the maximum sonication time of 7 mins. PCS and GCS showed good performance in stabilizing olive oil droplets in water. A stable emulsion with low turbidity and centrifugal stability values obtained at the addition of 6% weight of PCS and GCS. The combination of Tween 80 and modified cornstarch can further reduce the turbidity, centrifugal stability values and droplet size of the emulsion. Furthermore, it was found that PCS stabilizer produced a more stable emulsion compared to GCS, with and without the complexation of Tween-80. The most stable emulsion is obtained by the addition of 5% weight PCS along with 3% weight addition of tween-80. The emulsion characterized with turbidity of 1.01 cm^{-1}, centrifugal stability value of 36.85%, and average droplet diameter of 14.27 µm. The complex of pregelatinized cornstarch and tween-80, can be used as an emulsion stabilizer, however, the actual stabilizing mechanism still requires further studies.

Conflict of interest

The authors declare no conflict of interest.

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