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The Effect of pH and High-Pressure Homogenization on Droplet Size

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ABSTRACT
This study aims to revisit the effect of high pressure on homogenization and the influence of pH on the emulsion droplet sizes. The high-pressure homogenization (HPH) involves two stages of processing, where the first stage involves in blending the coarse emulsion by a blender, and the second stage requires disruption of the coarse emulsion into smaller droplets by a high-pressure homogenizer. The pressure range in this review is in between 10-500 MPa. The homogenised droplet sizes can be reduced by increasing the homogenization recirculation, and there is a threshold point beyond that by applying pressure only, the size cannot be further reduced. Normally, homogenised emulsions are classified by their degree of kinetic stability. Dispersed phase present in the form of droplets while continuous phase also known as suspended droplets. With a proper homogenization recirculation and pressure, a more kinetically stable emulsion can be produced. The side effects of increasing homogenization pressure are that it can cause overprocessing of the emulsion droplets where the droplet sizes become larger rather than the expected smaller size. This can cause kinetic instability in the emulsion. The droplet size is usually measured by dynamic light scattering or by laser light scattering technique. The type of samples used in this reviews are such as chocolate and vanilla based powders; mean droplet sizes samples; basil oil; tomato; lupin protein; oil; skim milk, soymilk; coconut milk; tomato homogenate; corn; egg-yolk, rapeseed and sunflower; Poly(4-vinylpyridine)/silica; and Complex 1 until complex 4 approaches from author case study. A relationship is developed between emulsion size and pH. Results clearly show that lower pH offers smaller droplet of emulsion and the opposite occurs when the pH is increased.

Keywords: High-pressure homogenization, the effect of pH, stable emulsion.

1 INTRODUCTION

Homogenizer has been used in the industry such as for pharmaceuticals, food and dairy industry, petroleum and chemical [1, 2]. One of the reasons why a homogenizer has become very popular is due to its recent improvements in the design of using high pressure to improve the emulsion characteristics such as improved stability and smaller droplet sizes. A piston pump in HPH can create pressure up to 500 MPa, and the emulsion from HPH is usually allowed to accelerate to high velocities through a narrow-gap valve which then can help to increases velocity of the fluid and may result in depressurization with consequent high shear stress and cavitation [3-5]. In other words, the emulsions that are passing through HPH are going to become twisted and deformed due to high mechanical stress exposure [6-8]. In comparison with conventional homogenization (pressure: 20 to 50 MPa), HPH allows room for improvement where HPH helps to improve the quality aspects, such as improved the stability of the emulsion and microbial and enzymatic inactivation [5, 9, 10]. The increased pressure level can help to improve the products by reducing creaming rate and become more stable [11]. Also, Peng, Dong [12] stated that either surfactant or high energy are needed for the emulsion to have a narrow size distribution and very small droplet sizes. Usually, HPH can reduce the size of globules to less than 1 μm and recently, HPH can achieve pressures that exceeding more than 200 MPa [2]. For example, as the study made by Park, Min [5], the author is using a laboratory-scale HPH (M-110Y,

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Microfluidics, USA) on the chocolate and vanilla powder emulsions with processing pressure ranging from 20 to 150 MPa. The average droplet sizes for the chocolate and vanilla-powder emulsions at a low homogenising pressure of 20 MPa are 5.91 and 2.44 μm, respectively [5]. The average droplet sizes for the chocolate and vanilla-powder emulsions at a medium homogenising pressure of 60 MPa are 5.52 and 2.38 μm, respectively [5]. The average droplet sizes for the chocolate and vanilla-powder emulsions at a high homogenising pressure of 100 MPa are 5.11 and 2.48 μm, respectively [5]. Another example which is made by Kubo, Augusto [4] where the author is using HPH (Panda Plus, GEA Niro Soavi, Italy) on tomato juice emulsions at pressures ranging from 0 to 100 MPa. The average droplet sizes for the tomato juice emulsion at a low homogenizing pressure of 25 MPa is 74.1 μm, while at a medium homogenizing pressure of 50 MPa is 41.1 μm, and lastly, at the high homogenizing pressure of 100 MPa, the average droplet sizes for tomato juice emulsion is 41.1 μm [4]. From both of the examples describes above which uses different homogenizer types shows that at different homogenising pressure, the average droplet sizes for different emulsion are different but still the droplet sizes did reduce much further when very high homogenising pressure is applied. However, for the tomato juice emulsion at medium (50 MPa) and high (100 MPa), homogenising pressure show that the average droplet sizes are the same which is probably due to overpressure (overprocessing) applied on the tomato juice. This effects still need to be considered in the study. In an emulsion, the size of the droplet and the size distribution of the droplet must be improved by reducing its size and distribution where this can enhance stability, solubility, reaction intensity and mouthfeel [1, 5]. The emulsions that have smaller particles with higher protein solubility in dairy products can efficiently be created by using HPH [1, 5]. HPH also offers a smaller size of emulsions when the homogenizing time is increased. Using the homogenising pressure of 100 MPa for 90 minutes can provide nano-sized emulsions [13]. HPH mechanically reduces the size of globules to less than 1 μm and is used to produce an emulsion of uniform composition and higher stability [2].

For processing using HPH, as stated it usually involves two stages. The first stage is by using a blender such as rotor-stator blender to blend the coarse emulsions and then the second stage is to disrupt the coarse emulsions into smaller droplet sizes. To reduce the droplet size much further, the homogenization process or recirculation can be increased. Thus it depends on the characteristics of the materials and machines used. Usually, the samples which are homogenised will be passed through a coil that is cooled by an ice mixture, and this can help it to cool down [5]. The droplet sizes of the emulsion can be measured by using the dynamic light scattering (DLS) or by laser-light scattering technique [14, 15]. Other techniques that can be used to measure the droplet sizes are such as optical microscopy [1], photon correlation spectroscopy [2] and direct video imaging [16].

The droplet size of the emulsion also can be stated as the volume-weighted diameter by eq (1) and as droplet size distribution, where n_i is the number of particles of diameter d_i [5]. The Sauter mean diameter also can be used to calculate the droplet size [17]. It can be defined as eq (2), where n is the number of droplets between two consecutive diameters and d_i is the droplet diameter.

The polydispersity index (PI) as defined as the ratio of weight average molecular weight to number average molecular weight (eq (3)). The state of emulsion size distribution can be indicated by using PI, and usually a particle size distribution of the emulsion which is more concentrated can be indicated from smaller PI [12]. Both the average droplet sizes and PI are required to reflect the average emulsion particle size [12]. PI also can be expressed as eq (3), where PI is defined as the ratio of M_w/M_n [18]. M_w is the molecular weight distribution that places a greater emphasis on larger molecules than that of smaller molecules in the distribution. M_n refers to the average molecular weight of the molecules in the polymer.

With the addition of pH and emulsifiers in the emulsions can help to affect the droplet sizes of the emulsions too. Based on the study made by Yin, Zhang [19] by using four complex approaches used indicating a change in pH affects the droplet sizes. The four complex approaches will be explained later in the discussion. At lower pH (acidic), the four complex approaches for the emulsion have longer stability against the changes of different NaCl concentration and pH due to smaller droplet sizes [19]. The equipment involves the homogenization process are such as Ultra Turraxx model [20], laboratory-scale HPH (Microfluidics) [5], Niro-Soavi Panda two-stage homogenizer [21] and some others. In this study, the model used to measure the droplet sizes are such as Mastersizer instrument [22] and Zetasizer Nano-ZS90 [19]. The materials covered are soybean oil, medium chain triglyceride (MCT) [12]; chocolate and vanilla-based products [5]; basil oil [23]; coconut milk [24]; soy milk [9]; lupin protein [1]; tomato [6]; and skim milk [25]. To control the pH, the materials used are pea protein isolate (PPI), soybean soluble polysaccharide (SSPS) [19]; poly(4-vinylpyridine)/silica (P4VP/ SiO_2) nanocomposite microgel [20]; sunflower, rapeseed and egg-yolk lecithin [26]; corn O/W emulsion stabilized with silk fibroin [27]; and whey protein microgels (WPM) [28]. Generally, the samples used in this reviews are such as chocolate and vanilla based powders; mean droplet sizes samples; basil oil; tomato; lupin protein; oil; skim milk, soymilk; coconut milk; tomato homogenate; corn; egg-yolk, rapeseed and sunflower; Poly(4-vinylpyridine)/silica; and Complex 1 until complex 4 approaches from author case study.

This review is carried out to understand the effect of the different pressure of HPH on droplet sizes on different materials and the influence of different pH value on the droplet sizes which can affect its sizes. Some related issue like the stability of emulsions and temperature effect on emulsion will not be covered here. The storage time which can affect the droplet size is mentioned here in brief. Also, the relationship between viscosity and shear rate will be discussed here in relation with the HPH on droplet sizes. This outcome can be used for the industries for references.

2 MODELS

$$d_{43} = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \quad (1)$$

$$d_{32} = \frac{\sum_i n d_i^3}{\sum_i n d_i^2} \quad (2)$$

$$\mathrm{PI} = \frac{M_W}{M_N} \quad (3)$$

$$E(Wm^{-3}) = \frac{P(\mathrm{Pa})}{10^{-4}(\mathrm{s})} \quad (4)$$

$$E > 10^{12}\ \mathrm{Wm^{-3}} \quad (5)$$

$$\tau = K\gamma^n \quad (6)$$

$$\mu = e^{(A\log(\gamma)+B)} \quad (7)$$

$$d_i = a + b\left(p^H\right) + c\left(p^H\right)^2 + d\left(p^H\right)^3 \quad (8)$$

3 RESULTS AND DISCUSSIONS

Figure 1 shows emulsion droplet size with pressure for four emulsions, namely, chocolate, vanilla, MDS and Basil oil studied by [5, 12, 23]. As can be seen from the Figure 1, the particle size in chocolate-based emulsion decreases as the pressure increases. At 100 MPa, the chocolate-based emulsion has 5.12 μm mean particle size, which decreases from 29.01 μm [5]. Majzoobi et al. (2013) stated that HPH creates a high turbulence and shear, united with compression, acceleration, pressure drop and impact, broke down the particles and dispersed them all over the product [5]. It is efficient for the droplet sizes to be reduced at an elevated pressure of HPH [5, 29-31].

The vanilla-based emulsion droplet size also decreased by HPH from 4.18 µm (control) to 2.44 µm (20 MPa) as shown in Figure 1. Increasing the pressure higher is unable to decrease the particle size due to its tiny initial particle which is smaller than chocolate-based emulsion (Figure 1). While for the MDS, the initial data already has the smallest particle size compare to chocolate- and vanilla-based. The MDS has shown that as the HPH increased from 40 to 130 MPa, the particle size remains smaller without a noticeable change in size. For the basil oil (Figure 1), it shows that increasing the HPH up to 50 MPa will decrease the emulsion droplet size.

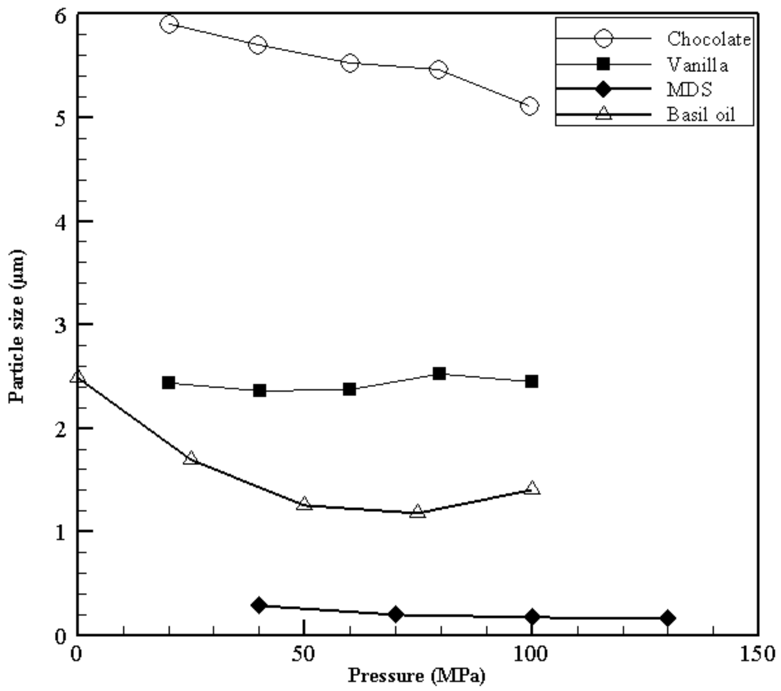

Figure 1: Mean particle size of chocolate- and vanilla-based products subjected to high-pressure homogenization (20–100 MPa), MDS value subjected to 40-130 MPa HPH and basil oil subjected to 0-100 MPa HPH [5, 12, 23].

This is probably due to the amount of energy used is quite high which then helps to break the emulsion droplets. However, as the use of pressure increased above 85 MPa, it causes the droplets formations with the larger size. This phenomenon is the same as previous study before for MDS where it is because of over processing. Figure 2 shows the particle size distribution of the control products which is before the HPH treatment applied. Based on the volume distribution shown (Figure 2), the tomato has the highest peak of the volume distribution followed by lupin protein, chocolate, and vanilla-based products. For tomato, the highest volume distribution is between 10^2 and 10^3 μm. Lupin protein has the highest distribution between 10^1 and 10^2 μm. In the chocolate and vanilla-based emulsion, the control products have from small to large size distribution. For the lupin protein, it has a unimodal distribution of the unprocessed solution with aggregates of proteins bigger than 1 μm.

After HPH treatment had applied (Figure 3) at the smaller droplet sizes with a bimodal distribution of chocolate and vanilla-based products, peaks were observed. This means that HPH causes a smaller particle sizes distribution. Overall, at the different pressure, the particle size distributions were not significantly different. For the tomato-based products, as 25 MPa HPH applied, there is an increasing particle size distribution between 750 to 900 μm (Figure 3). This means that for tomato-based products, as the pressure increases, the droplet sizes also reduced. For lupin protein (Figure 3), an increase up to 50 MPa homogenization pressure causing the movement in the size distribution on the way to smaller groups of 0.1 to 10 μm.

At 100 MPa, for lupin protein (Figure 4) the particle size distribution was similar to that at 50 MPa (Figure 3). At 150 MPa, the combinations of bigger formations with sizes of up to 100 μm was stimulated. Figure 5 shows that emulsions that have a high percentage of oil will have larger mean droplet sizes for the same homogenising conditions. This occurrence may be due to the limitations of the surface-active agents in the oil concentrated emulsions. The proteins decrease when the oil content increases, causing in reducing stability in the proteins, which can cause coalescence in the oil droplets and larger droplet sizes [11]. Figure 5 shows the particle size distribution of skim milk measured using integrated light scattering [25]. It shows that raw skim milk that is not homogenised shows a monomodal distribution of sizes around 0.120 μm of the average diameter. This is likely as casein micelles are present in skim milk [25]. For the homogenised skim milk and homogenised skim milk with added Tween samples show a bimodal distribution curve, with fat globules sizes of about 1.2 μm of diameter [25]. In the presence of Tween, the sizes of the particles reduced. For the skim milk, after homogenization pressure is applied, it shows a reduction in droplet sizes. Figure 6 shows the mean droplet diameter measured as d_{32} against oil mass fraction or concentration for the emulsion containing whey protein concentrates and sunflower oil. From Figure 6, oil concentrations increase, a greater mean droplet diameter found for similar homogenising conditions. Figure 6 also shows the changes in mean droplet size d_{32} and d_{43} of emulsions as a function of supercritical fluid extracts (SFE) concentrations. The line for each data was drawn based on the power fit curved line [11, 33]. As the oil concentration increases (Figure 6), a high pressure is needed to reduce the droplet size. In this study, 300 MPa is an ideal pressure for higher oil concentration of 50 %.

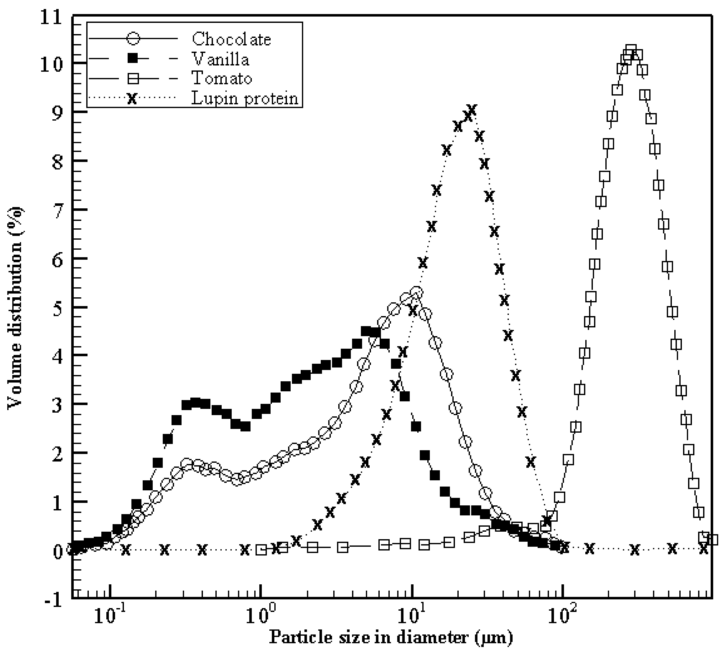

Figure 2: Particle size distribution of the control (0 MPa) based products of chocolate- and vanilla-based products, tomato and lupin protein [1, 5, 6].

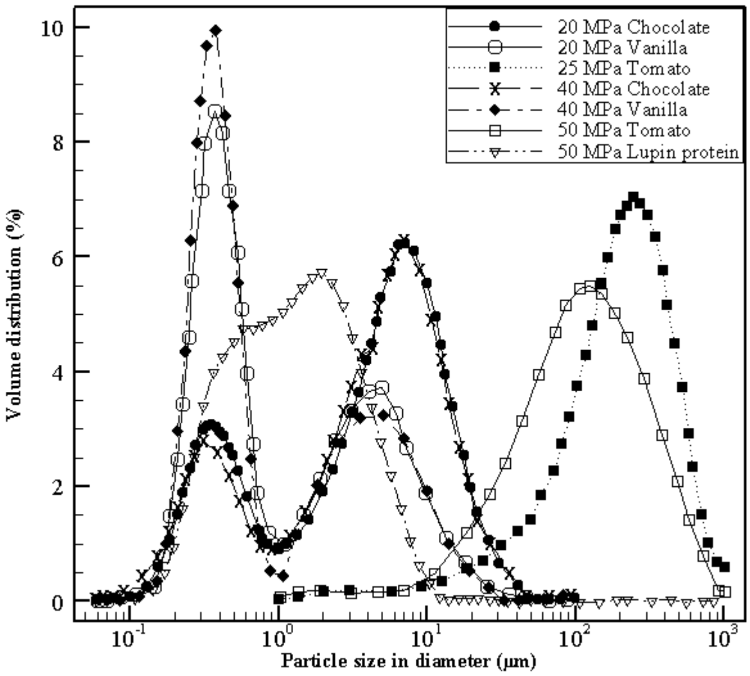

Figure 3: Particle size distribution of chocolate- and vanilla-based products, tomato and lupin protein subjected to 20-50 MPa [1, 5, 6].

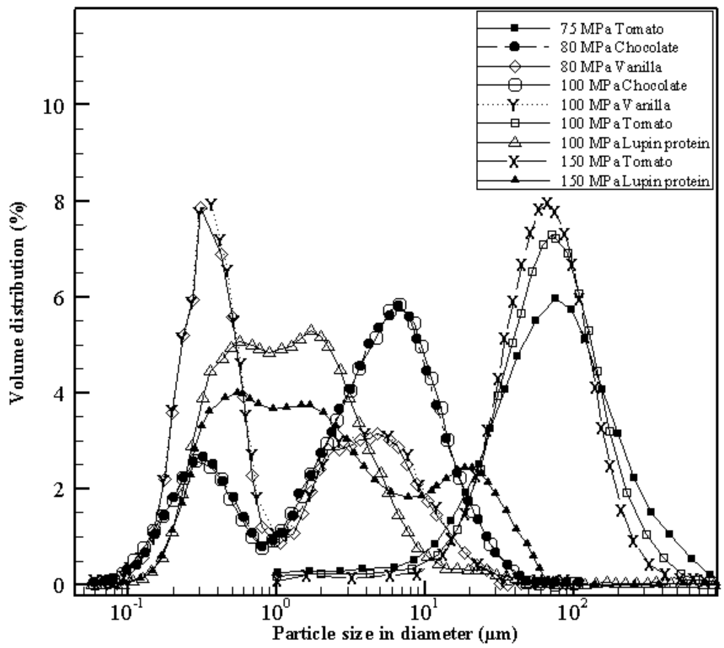

Figure 4: Particle size distribution of chocolate- and vanilla-based products, tomato and lupin protein subjected to 70-150 MPa [1, 5, 6].

In Figure 6, it also shows the changes in mean droplet size (d_{32}, d_{43}) of emulsions containing 0.1 to 0.9 weight % of SFE extracts, 10 weight % of oil and 20 mM bis-tris with pH =7.0 against SFE concentration. [33]. For this emulsion, it was homogenised at 20.7 MPa, and then the final emulsion was homogenised at 3.4 MPa. The droplet particle size for d_{32} and d_{43} also can be expressed as eq (1) and eq (2). According to Figure 6, the d_{32} mean droplet sizes were reduced from 0.90 μm (0.1 weight %) to 0.47 μm (0.9 weight %) as the SFE concentrations increase. When adding more than 0.5 weight % emulsion (d_{43}), the size of the fat globules did not show significant changes compare with d_{32} except that their droplet size becomes a bit larger.

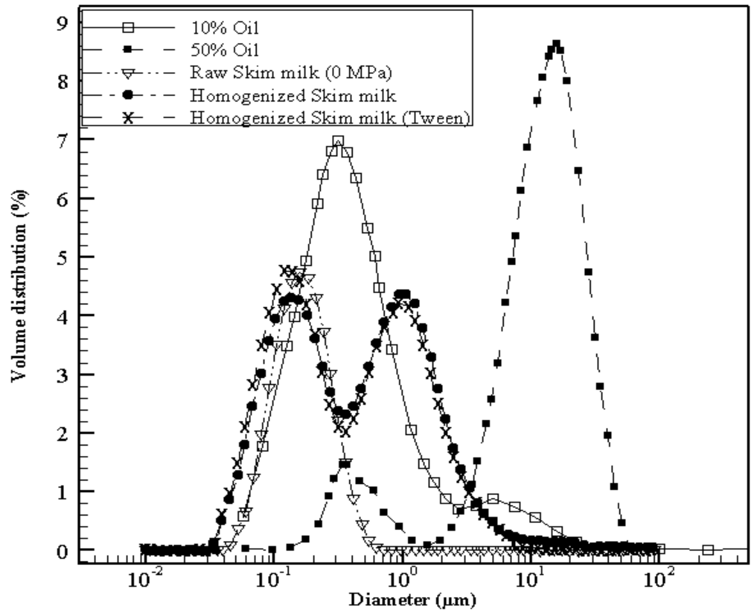

Figure 5: Effect of oil concentration (10% and 50%) on O/W emulsion homogenized at 150 MPa and skim milk (raw, homogenized and homogenized with Tween at 34.5 MPa) on their droplet size distribution [11, 25].

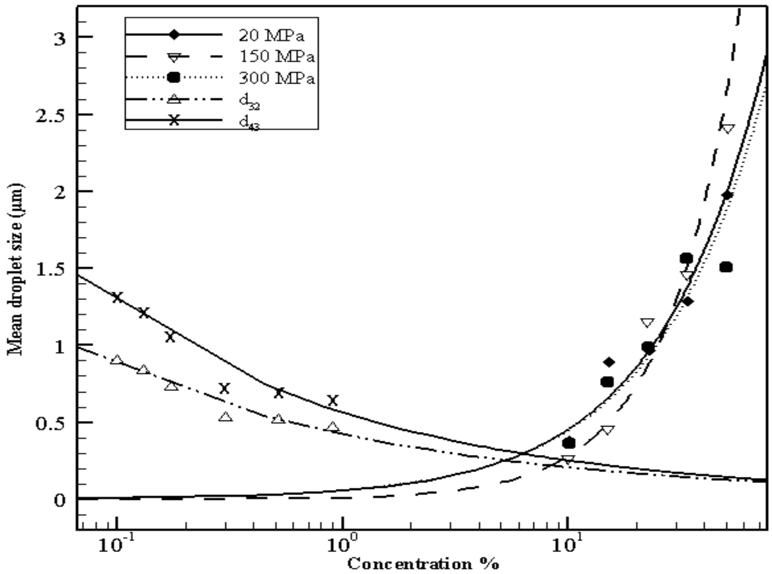

Figure 6: Mean droplet size in emulsions homogenized at 20, 150 and 300 MPa against oil concentration in percentage (%) [11, 33].

However as the concentration of SFE increased, the droplet sizes for d_{43} is also reduced. For this study, as the emulsion concentration increases, the droplet sizes reduce even though the emulsion is homogenised at 20.7 MPa. For the study of an emulsion containing whey protein concentrates and sunflower oil, as the oil concentrations increase, the droplet sizes are larger with lower homogenising pressure (20 MPa). However, if the 300 MPa homogenising pressure was used, the emulsion droplet size containing more than 50 % oil concentrations can be reduced. Figure 7 shows the volume % of the various size of droplets vs. droplet size for few emulsions namely, Chocolate, Vanila, Oil, and Tomato. As can be seen in Figure 7, the mean droplet diameters and the droplet size distributions are different for all the emulsions considered. The peak volume percentage for oil decreases as the oil % drops from 50 to 10 and same goes for peak particle diameter. Compared to different materials from tomato, chocolate and vanilla based products subjected to 25 and 20 MPa respectively, oil with 50 % concentration has the highest volume distribution peak. This is followed by vanilla based with its peak at the smallest diameter range in between 20 and 80 μm and tomato with its peak distribution at 800 μm . Figure 8 shows the particle size distribution of oil with 10 and 50 % concentration subjected to 150 and 300 MPa compared with other materials, namely, lupin protein, tomato and soymilk subjected to 150, 200 and 300 MPa respectively. At 300 MPa homogenization pressure, a broad tail appears in the particle size distribution. This is probably due to the emulsion created has very small droplet sizes, and then recoalescence may occur in the homogenization chamber. Since 300 MPa is a very high pressure, it may cause a very great impact on the rheology of the emulsions. At 300 MPa HPH for oil with a concentration of 10 and 50% (Figure 8), the emulsion usually gets exposed to shear stress which is high and temperature in the homogenizing valve, where this can cause the emulsified proteins become too denatured to play their stabilizing role, [11].

While for the soymilk products homogenized at 200 and 300 MPa (Figure 8) shows that the samples homogenized at 300 MPa showed a larger mean diameter compared to 200 MPa, which indicates that there is a presence of droplets aggregates. In general, a 200 MPa treatment for soymilk samples gave the narrower range in the size distribution of particles compared with a 300 MPa treatment of oil concentration and soymilk samples. Viscosities vs. shear rate for various materials are shown in Figure 9 on a log-log scale. Also, the investigation has confirmed that at HPH at very high pressure can help to reduce the viscosity of the solutions (Figure 9). In Figure 9 data is mostly fitted to power fit curve and it can be defined by eq (7), with the value of A and B coefficients are different with different homogenizing pressure and materials (Table 1). This relationship would offer a thumb rule for industrial application. In the rheometer, at high shear rates, the apparent viscosity can reach a constant value either because only single droplets persist or the number of flocculated droplets remains constant since the rate of floc formation is equal to that of floc disruption as mentioned by [34] stated in [11].

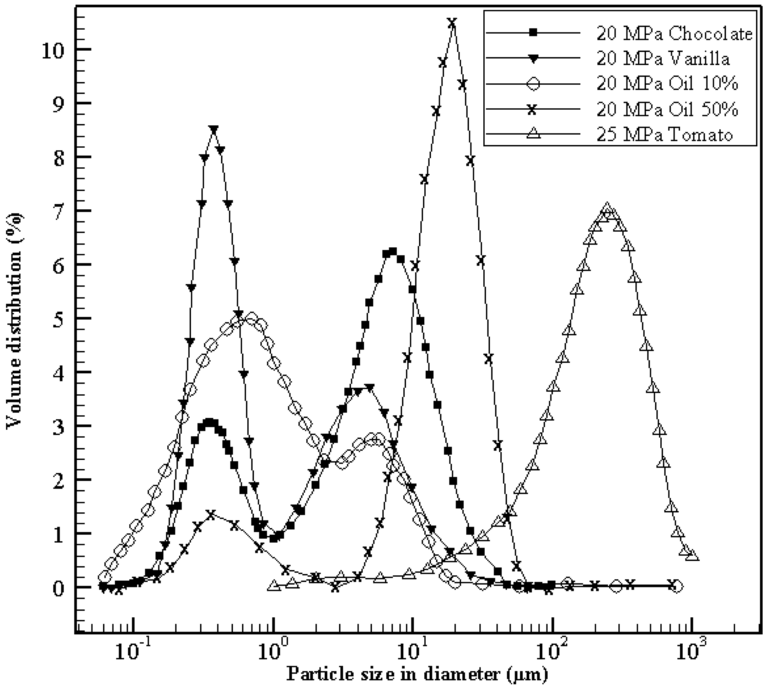

Figure 7: Effect of homogenizing pressure conditions of 20 MPa on droplet size distributions of 10% and 50% oil concentration of O/W emulsions, tomato based at 25 MPa, chocolate and vanilla based products at 20 MPa [5, 6, 11].

Table 1: Sample of coconut milk, oil with 50% mass fraction and tomato homogenate with different pressure and A and B coefficients obtained from equation (7) and data obtained from [11, 24, 36].

Sample name	MPa	A coefficient	B coefficient
Tomato homogenate	0.1	-9.0630E-001	1.8094E+000
Coconut milk	15	-1.3839E-001	-2.8813E+000
Oil (50% concentration)	20	-6.2336E-001	1.3023+000
Coconut milk	21	-2.0559E-001	-2.3158E+000
Coconut milk	27	-1.8732E-001	-1.9518E+000
Tomato homogenate	100	-8.2382E-001	1.5560E+000
Oil (50% concentration)	150	-6.0674E-001	9.1073E-001
Oil (50% concentration)	300	-1.3103E-001	-3.2675E+000
Tomato homogenate	300	-8.2851E-001	1.3619E+000
Tomato homogenate	500	-8.9900E-001	2.2522E+000

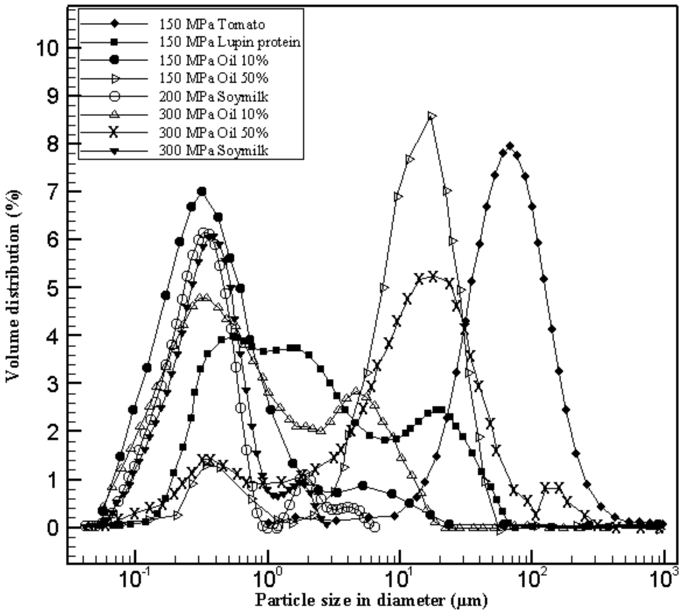

Figure 8: Effect of homogenizing pressure conditions of 50-300 MPa on droplet size distributions of 10% and 50% oil concentration of O/W emulsions, tomato based, lupin protein and soymilk products *[1, 6, 9, 11]*.

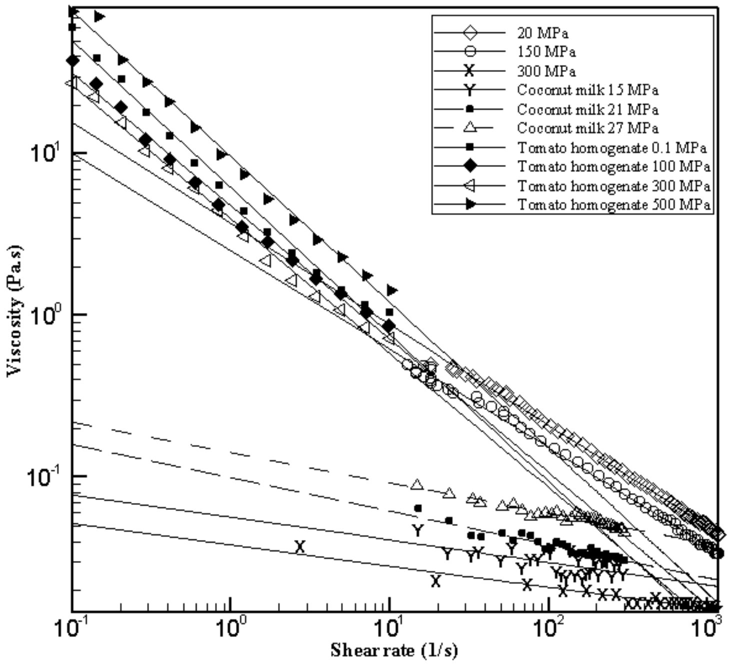

Figure 9: Effect of homogenizing pressure on rheological properties of emulsions: viscosity vs. shear rate of 50% mass fraction of O/W emulsions homogenized at three different pressures: 20, 150 and 300 MPa, the coconut milk at three different pressures: 15, 21 and 27 MPa and tomato homogenate after treatment for 15 min at 30 ºC combined with four different pressures: 0.1, 100, 300 and 500 MPa [11, 24, 36].

With high pressure, lowest viscosity can be achieved. This is due to in the homogenising valve, it has high shear stress and energy density, where at high pressure, the flocculation droplet will not be able to occur at the homogenizer exit, so a smaller and fine droplet size can be produced. The energy can be expressed as eq (4) and eq (5). As can be seen from Figure 9, with high pressure, lowest viscosity can be achieved. Figure 9 shows the plot of homogenised coconut milk which contains apparent viscosity against shear rate at five levels pressure different [24]. Power law model was used on the samples to define the rheological behaviour [24]. The model was defined in the eq (6) where τ is the shear stress, γ is the shear rate, K is the consistency index (Pa s^n) and n is the flow behaviour index. The apparent viscosity decreases with increasing shear rate for the homogenised coconut milk during the early stage. The apparent viscosity changed slightly after a sharp reduction to become steady at rates of higher shear.

As the pressure level increased, it allows the droplets size reduction (Figure 9). This means that in the colloidal system, there are large numbers of droplet presented and blocked the flow. The increase of apparent viscosity is due to high pressure. After passing thru higher pressure, the emulsion becomes more viscous. At all homogenising pressures, coconut milk which is characterised by n values less than 1 showed power-law pseudoplastic behaviour. There is no communication between particles as the emulsions display low viscosity with Newtonian flow behaviour at low homogenising pressure [24]. Torres et al., (2007) stated that the K values are related to the viscosity, and the flow behaviour index (n) provided information about the effects of shear on the system [35].

Also, the effects of applying different homogenising pressures obtained with rheometer after treatment on the tomato homogenate for 15 min at 30 ºC are also shown in Figure 9. The curves for tomato homogenate at atmospheric pressure (0.1 MPa) shows that the value of viscosity decreased with shear rate getting higher which indicate that tomato homogenate displays pseudoplastic flow behaviour [36]. This result is the same with all other given pressures (100, 300 and 500 MPa) of tomato homogenate. For the tomato homogenate treated at 500 MPa showed the highest viscosity and the sample treated at 300 MPa have the lowest viscosity. The pH can have a significant effect on the size of the emulsion droplets. Table 2 shows the pea protein isolate (PPI) in preparation condition which is utilised to build complexes of soluble soybean polysaccharide (SSPS) [19]. The homogenization pressure used for PPI study is 85 MPa.

As can be seen from Table 2, in the PPI study, there are four complex approaches that were used. The Complex 1 is the mixture of PPI and SSPS at pH 3.25 [19]. Complex 2 is by mixing centrifuged PPI at 6800 g with SSPS at pH 3.25 [19]. Complex 3 is the mixture of centrifuged PPI at 2790 g and SSPS at neutral pH and then adjusting to pH 3.75 [19]. Lastly for Complex 4 is the mixture of PPI and SSPS at neutral pH and then modifying to pH 3.75 [19]. For the PPI and SSPS study, there are four complex approaches that were used; they are Complex1 until Complex4 [19]. The preparation condition can be seen in Table 2. For the study based on $P4VP/SiO_2$, out of three protocol in the study, only one is used that is Protocol 1. Equivalent quantities of oil and an aqueous dispersion of different pH values are found in a batch of an emulsion of Protocol 1, which are place at room temperature [20]. In a thermostat bath of 20 °C, the two phases were kept to be homogenised at 13000 rpm with Ultra Turrax T25 homogenizer for two minutes at 20 °C [20].

In Table 3, after homogenization treatment, the four complex approaches in this study display similar particle size of about 200 nm (measured as D_h , hydrodynamic diameter), which size is much smaller compared to the particles prior homogenization. The diameter for the mixed PPI at pH 3.25 (Complex 1) shows the largest droplet sizes before homogenization treatment was applied with the PI also highest among the other three complexes. After homogenization treatment was applied, roughly the droplet sizes are almost the same as about 200 nm, but the PI values are different. Based on the result in Table 3 above, it might indicate that with HPH applied within the range of pH in between 3.0 and 4.0, it can cause the droplet sizes to be reduced. For the egg-yolk lecithin, rapeseed, and sunflower, the pH value for each substance was adjusted to pH =8.0 [26] (Table 3). As demonstrated in Table 3, HPH reduced the droplet sizes in nanoemulsions comprising rapeseed (296 ± 18 nm), sunflower lecithin (417 ± 25 nm) and the control egg-yolk lecithin emulsions (243 ± 12 nm). These emulsions were visually pH stable for at least one months [26].

Table 2: Preparation conditions of materials used [19, 20, 26, 27].

Sample	Preparation Condition
SSPS	pH 7.0 or pH 3.25
PPI	pH 6.8
PPI1	Adjusting PPI to pH 3.25
PPI2	Centrifuging PPI1 at 6800 g
PPI3	Centrifuging PPI at 2790 g and then adjusting pH to 7.0
PPI4	Adjusting PPI to pH 7.0
Complex1	Mixing PPI1 with SSPS at pH 3.25
Complex2	Mixing PPI2 with SSPS at pH 3.25
Complex3	Mixing PPI3 with SSPS at pH 7.0 and then adjusting Ph to 3.5
Complex4	Mixing PPI4 with SSPS at pH 7.0 and then adjusting pH to 3.5
Corn	Silk fibroin was used to prepare 10 % (by mass) corn O/W emulsions at ambient temperature by adjusting the pH to 7.0 using 1 M HCL or 1 M NaOH
$P4VP/SiO_2$	Prepared by using batch emulsion containing equal volumes (5.0 mL) of oil and aqueous dispersion at different pH values or salt concentrations
Egg-yolk lecithin, rapeseed, sunflower	The samples prepared by HPH and the pH value of all formulations was adjusted to pH 8.0 with 0.01 $mol L^{-1}$ NaOH solution.

In Table 3 also shows the results of corn O/W emulsions droplet sizes decreased about 470 nm as the mass fraction of silk fibroin increased up to 1 % (by mass). The corn oil emulsion was acclimatised to pH 7.0 [27]. Figure 10 can be obtained by using eq (8). The data in Figure 10 was fitted to polynomial curve fitting with third order. The a, b, c, and d are constant, and the value is different from each material (Table 4). Homogenised egg-yolk lecithin, rapeseed, and sunflower with the added of 1 M NaCl solution at various pH values are shown. It is shown that silk fibroin (1% by mass) stabilized with corn O/W emulsion of mean particle size.

Figure 10 shows the average drop diameters arithmetic mean and median diameter for O/W emulsion of P4VP/SiO_2 particles (freshly set emulsion) as a function of pH using batch emulsion where sizes are determined using light diffraction. In the ranges of 3-5 μm is the mean standard deviation. At around pH 5-6, a different narrow minimum happens. At around pH 5-6, the droplet sizes are smaller compared to the others. The apparently measured diameter is greater than the individual drops if in dilution the flow is stable. For the corn O/W emulsions, the mean particle diameter (d_{32}) continued moderately small (<1 mm) from pH = 2.0 to 8.0 except at pH =4.0, representing that tiny aggregation of droplet happened during packing. Silk fibroin-stabilized emulsions suggested being remained stable to droplet aggregation [27].

In Figure 10, the study of egg-yolk lecithin, rapeseed, and sunflower by [26] are also shown. Figure 10 shows that among the three samples, egg-yolk lecithin has the smallest sizes. In general, the samples for egg-yolk lecithin does not have any significant changes in droplet sizes as the pH value moves from pH 2.0 to pH 8.0. For the rapeseed samples, it shows droplet sizes change from about 300 nm or 0.300 μm to about 400 nm or 0.400 μm from pH 2.0 to pH 8.0 respectively. For the rapeseed, samples homogenised with pH above 7.0 show larger droplet sizes. While for the sunflower samples, the smallest droplet sizes about 500 nm or 0.500 μm were observed at pH 2.0 and 5. At pH 4.0, it shows the largest droplet sizes for sunflower samples about 620 nm or 0.620 μm . In general, different pH media will give different droplet sizes, and it also depends on the materials of the homogenised samples. Freshly prepared Complex 1 (mixed PPI at pH 3.25) and Complex 2 (mixed centrifuged PPI at pH 3.25) emulsions, which have 285 and 269 nm of droplet sizes(Figure 10), correspondingly, were accustomed to pH 5 and 6, and to 0.2 M NaCl concentration was added, and to investigate the long-term stability the emulsions were stored at 4 °C [19]. After 85 days of storage (Figure 10), at pH 3.25, in emulsions kept at pH 5 and 6, an increase of droplet sizes and a whey layer were discovered. Meanwhile, emulsions reserved at pH 5 and six which contains 0.2 M NaCl shows creaming. Complex 2 emulsions (Figure 10) stay homogeneous with or without the involvement of 0.2 M NaCl after 87 days of storage suggests that compared to Complex 1 emulsions, Complex 2 emulsions are more stabilised. Based on this result, it can be assumed that the change of pH value can affect the droplet size, but it also depends on the characteristics of the materials.

Table 3: Droplet sizes after homogenization of different samples [19, 26, 37].

Sample	Without homogenization		After homogenization	
	Droplet size (nm)	PI	Droplet size (nm)	PI
Complex 1	1555 ± 455	1.0	213 ± 9	0.65 ± 0.04
Complex 2	412 ± 18	0.48 ± 0.04	192 ± 4	0.44 ± 0.03
Complex 3	580 ± 42	0.36 ± 0.03	195 ± 8	0.49 ± 0.03
Complex 4	744 ± 88	0.57 ± 0.03	218 ± 9	0.72 ± 0.02
Egg-yolk lecithin	-	-	243 ± 12	0.08 ± 0.04
Rapeseed	-	-	296 ± 8	0.28 ± 0.08
Sunflower	-	-	417 ± 25	0.44 ± 0.14
Corn	-	-	470 ± 50	-

Table 4: List of various a, b, c and d coefficients for eq (8) and the data obtained from [20, 26, 27].

Samples	a-coeffiecient	b-coefficient	c-coefficient	d-coefficient
P4VP/SiO_2 (median diameter)	1.08E+002	-9.01E+000	1.51E-001	8.37E-002
P4VP/SiO_2 (arithmetic mean diameter)	1.06E+002	-3.99E+000	-9.58E-001	1.57E-001
Corn	-5.17E+000	4.2775E+000	-8.45E-001	4.97E-002
Egg-yolk	3.02E-002	-2.58E-003	5.93E-004	-3.81E-005
Rapeseed	8.73E-003	4.77E-003	-6.0E-004	-5.17E-011
Sunflower	1.01E-002	-5.22E-003	1.0E-003	-6.53E-005
Fresh prepared complex 1	2.31E-001	3.77E-002	-9.16E-003	8.91E-004
Fresh prepared complex 2	3.58E-001	-3.57E-002	3.43E-003	1.63E-004

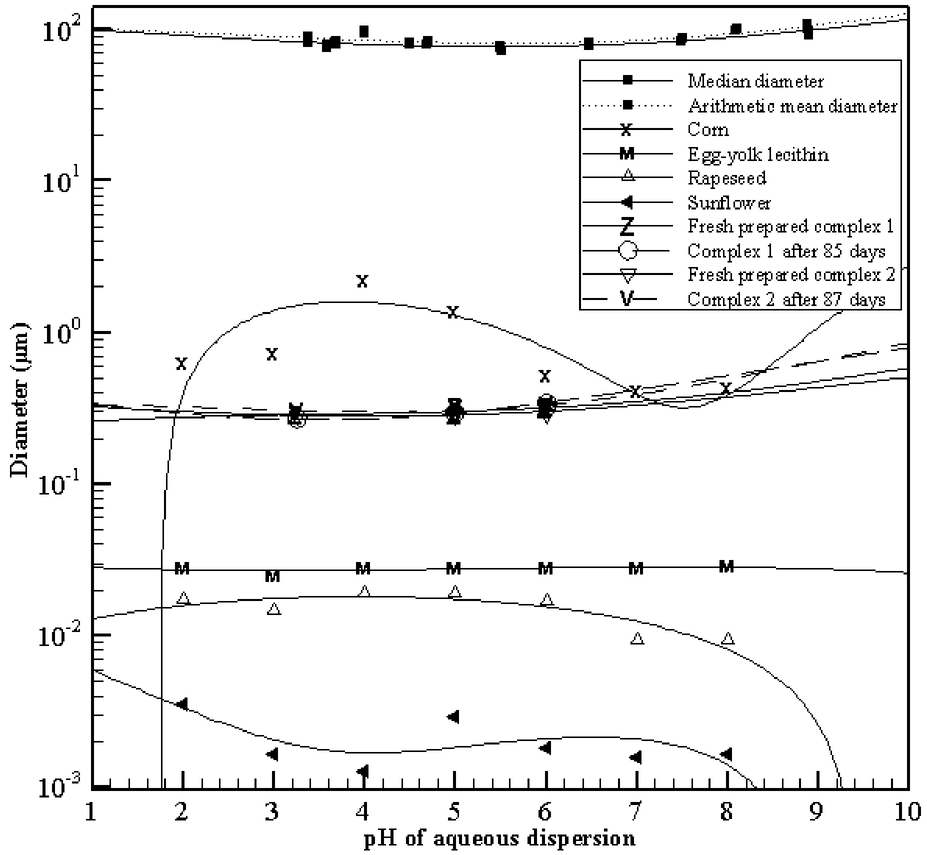

Figure 10: Average drop diameters of the arithmetic mean and median diameter for O/W emulsions as a function of pH for freshly prepared emulsions using batch emulsion [20, 26, 27].

4 CONCLUSIONS

1. Based on the reviewed study, a high-pressure homogenization can effectively reduce the droplet sizes of the emulsions from coarse emulsion into smaller droplets. This indicates that with proper homogenization recirculation and pressure, a stable emulsion with reduced droplet size can be produced. However, at some point this depends on the emulsion characteristics, with increased high pressure too, some emulsion will not be able to be reduced any further sizes. The side effects of increasing homogenization pressure are that it can cause overprocessing of the emulsion droplets where the droplets size become larger rather than the smaller expected size. This can cause instability in the emulsion.
2. There are few solid contributions to this investigation:
3. The diameter of emulsions can be expressed as a fourth order polynomial of p^H ($d_i = a + b\left(p^H\right) + c\left(p^H\right)^2 + d\left(p^H\right)^3$) the coefficients of seven emulsions are derived from the experimental data.
4. Viscosity can be expressed as a logarithmic function of shear rate ($\mu = e^{(A\log(\gamma)+B)}$) and shear rate is dependent on the shear stress. The coefficients for few emulsions are calculated from the experimental results.

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LIST OF SYMBOLS

Symbols	Meaning
n_i	Number of particles of diameter
d_i	Diameter (μm)
d_{32}	Sauter mean diameter (μm)
d_{43}	Volume weighted diameter (μm)
D_h	Hydrodynamic diameter (nm)
DLS	Dynamic light scattering
E	Energy (Wm^{-3})
HPH	High-pressure homogenization
K	Consistency index $(Pa.s^n)$
MCT	Medium chain triglyceride
MDS	Mean droplet size
n	Flow behaviour index
O/W	Oil in water
P	Pressure (Pa)
P4VP/SiO_2	Poly(4-vinylpyridine)/silica
PI	Polydispersity index
PPI	Pea protein isolate
SFE	Supercritical fluid extracts
SSPS	Soybean soluble polysaccharide
τ	Shear stress (N/m^2)
TEM	Transmission electron microscopy
TW-20	Tween 20
γ	Shear rate (1/s)
μ	Viscosity (kg/m/s)

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