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The Influence of Oil Concentration on the Rheological Properties of Flaxseed Oil Emulsion Stabilized by Pregelatinized Waxy Rice Starch

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Abstract The rheological properties of an emulsion are associated with the characteristics and stability of the emulsion. The research aimed to study the influence of oil concentration on the stability and rheological properties of flaxseed oil emulsion stabilized with pregelatinized waxy rice starch (0% amylose). Emulsion with 2.5, 5, 10, and 17.5% oil content contained 5 wt% pregelatinized waxy rice starch were mixed at 8000 then 15000 rpm for 1.5 minutes each. The emulsion was then observed for its stability, microstructure, and rheological characteristics. The results showed that the emulsion was visually stable after two weeks of storage, and there was no visible creaming. The microscopic picture displayed that the changes in droplet diameter were occurred in emulsion containing 10 and 17.5% flaxseed oil. All emulsion shows shear thinning behavior with the flow behavior index, where the higher the oil ratio, the more pseudoplastic the emulsion. At 2.5 and 5% oil concentrations, emulsions' rheological characteristics are thought to be prominently influenced by Pregelatinized Waxy Rice Starch (PWRS) dispersion. At a high shear rate, the emulsions were rheopectic, where the higher the oil content, the less rheopectic properties. At the low shear rate, the emulsions showed a time-independent behavior.

Keywords Emulsion, Pregelatinized Waxy Rice Starch, Time-dependent, Rheology

1. Introduction

Emulsion - a dispersion system consisting of two immiscible liquids - is found in various foods such as ice cream, mayonnaise, dairy products, butter, etc. Protected droplets in the emulsion system are often used for various purposes, such as carrying functional agents [1], [2], encapsulating aroma and bioactive compound [3-7] and to produce healthy low-fat products [8,9].

Consumer demands for the availability of healthy food products have increased research on using natural ingredients to replace synthetic materials, including efforts to reduce or replace the use of artificial surfactants. Modified starch can be used as an alternative to minimize or even substitute synthetic surfactants. Gelatinized and pregelatinized starch has been reported to have characteristics as an emulsifier, such as waxy rice, non-waxy rice, and waxy maize starch [10,11].

The stability of the emulsion - for an extended period - is affected by all kinds of interactive factors, such as droplet size distribution, the density difference between the two phases, and the chemical integrity of the dispersed phase [12]. Emulsion rheology, besides playing a role in determining sensory perception [13] and their functional properties, also affects the stability of the emulsion. The continuous phase's viscosity affects the emulsion's stability in creaming or sedimentation [14], while the relationship between viscosity and shear rate can provide an image of the strength of the interaction between droplets [15]. Various factors determine the rheology of the emulsion, such as the dispersed droplet ratio; the structure of dispersed and continuous phase; size, type, and interactions between droplets; and continuous phase characteristics [14], [16,17]. The time-dependent rheological behavior of an emulsion is related to structural changes due to shearing, which is essential for understanding the product changes that occur during the process, so it is helpful for quality control, optimization, shelf life, and equipment design.

Rheology properties and the stability of emulsion with pregelatinized waxy rice starch (PWRS) are influenced by the degree of gelatinization, rotational speed during emulsification, type of oil, and storage conditions [11,18]. The research aimed to study the effect of oil concentration on the characteristics of the flaxseed oil emulsion stabilized with PWRS. Flaxseed oil was used as a dispersed phase since it contains high fatty acids such as ALA and other elements like protein, vitamins, and minerals, making it beneficial for health. Stability to creaming and changes in droplet size was visually observed after storage for two weeks, and the fresh emulsion was subjected to time-dependent rheological analysis, where their rheopectic behavior was described using the Weltman model.

2. Materials and Methods

2.1. Materials

Flaxseed oil was produced by Asahi and Co., LTD, and waxy rice starch (0% amylose) was produced by Matsutani Chemical Industry Co., Ltd. Pregelatinized waxy rice starch was obtained by drying the waxy rice starch dispersion layer (gelatinized at 85°C for 10 minutes) at 40°C for 12 hours at relative humidity 20%. The resulting dried flakes were ground and sieved to obtain 100 mesh pregelatinized waxy rice starch.

2.2. Emulsion Preparation

PWRS dispersion was obtained by stirring PWRS and pure water for 30 minutes. The PWRS concentration in the emulsion was 5wt%. Emulsification was carried out using IKA Ultraturrax T 25 at 8000 rpm and 15000 rpm for 1.5 minutes for each. The oil concentration was 2.5, 5, 10 and 17.5%.

2.3. Stability Emulsion

Emulsion stability was analyzed after storage for two weeks at 25°C. The creaming stability was observed visually, while the change in droplet size was observed through changes in its microstructure using a BX1 fluorescence microscope (Olympus, Tokyo, Japan).

2.4. Rheological Measurement

The HV Toki Sangyo viscometer was used to determine the rheological characteristics. 1 ml of emulsion was placed in a vessel and held for 5 minutes for temperature equilibrium. The measurements were performed at a shear rate of 9,575 to 383 s^{-1} at 10 to 260 seconds. The time-dependent rheological behavior was studied at the shear rate of 9,575; 38,3; 191,5; and 383 s^{-1} and modelled using Weltman model in the following equation:

$$\tau = A + B \ln(t) \quad (1)$$

Where τ is the shear stress, t is the shearing time, A is the constant that represents the initial shear stress, and B is a constant that describes the structure breakdown or construction rate.

The data taken at 60 seconds were used to obtain the rheological characteristics of the emulsion. The consistency coefficients and the flow behavior index were derived from the Herschel-Buckley equation:

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (2)$$

Where τ_0 is yield stress, k is consistency coefficient, $\dot{\gamma}$ is shear rate, and n is flow behavior index.

3. Result

3.1. The Stability of Emulsion

The flaxseed oil emulsion stabilized with PWRS was evaluated for its resistance against creaming and ability to maintain droplets. Flaxseed oil emulsion with PWRS after two weeks of storage is shown in Figure 1. All emulsions were stable to creaming within two weeks of storage. The microstructure of the fresh emulsion and the emulsion after two weeks is shown in Figure 2. As revealed in this figure, the higher the oil concentration, the larger the droplet size at the same PWRS concentration. After two weeks of storage at room temperature, there was a change in droplet size at oil concentrations of 10 and 17.5%. For the emulsion containing 17.5% flaxseed oil, there was a reasonably significant droplet size change, whereas, after two weeks of storage, there were droplets size of more than 100 μm, which indicates a high coalescence.

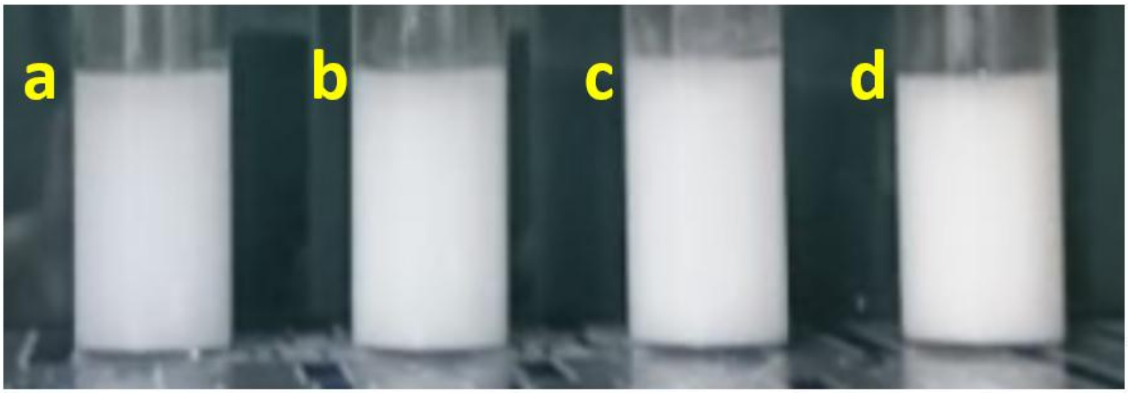

Figure 1. Visual appearance of flaxseed oil emulsion stabilized with PWRS at oil concentration of 2.5 %(a); 5 %(b); 10 % (c) and 17.5 % (d)

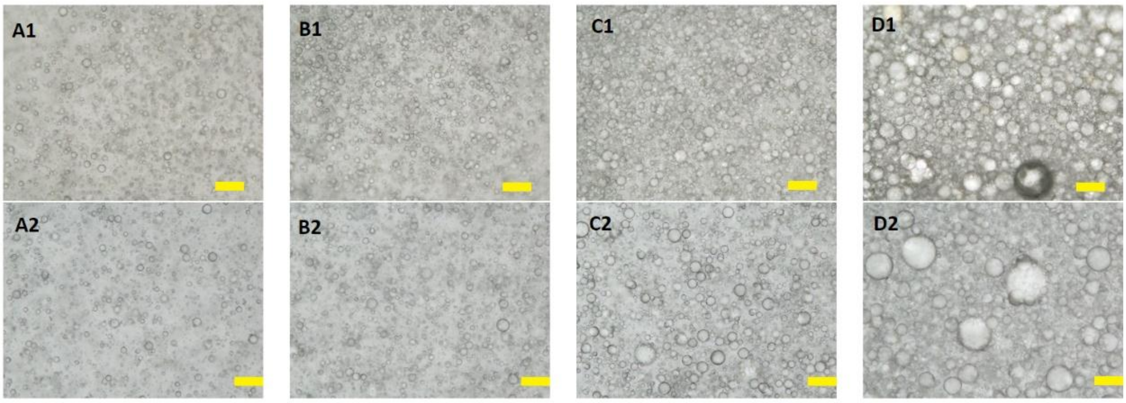

Figure 2. The microstructure of fresh emulsion (denote by number 1) and after two weeks of storage ((denote by number 2) with the oil concentration of 2.5 (A), 5 (B), 10 (C) and 17.5 % (D). Yellow bar indicates 100 μm

3.2. Rheological Properties of Emulsion

The effect of shear rate on the viscosity of flaxseed oil emulsions at different concentrations is shown in Figure 3. All emulsions behave as shear-thinning fluids. Viscosity decreases sharply at low shear rates and changes gradually at high shear rates. At the same shear rate, the emulsion viscosities with concentrations of 2.5 and 5% were not significantly different. The viscosity increased sharply at concentrations of 10 and 17.5%. At a shear rate of 38.3 s^{-1}, the viscosity of the emulsion containing oil 2; 2.5; 10; and 17.5%, respectively, were 171.8; 174.9; 220.3; and 309.1 mPa s.

The rheological constant of the emulsion is shown in Figure 4. The effect of oil concentration on the value of the consistency coefficient and flow behavior index is similar to its impact on viscosity, where the values are similar at concentrations of 2.5 and 5%. The significant differences are found at concentrations of 10 and 17.5%. The consistency coefficient at the oil concentration of 10 and 17.5% increased 1.5 times and doubled, respectively, from the value in the emulsion with 5% oil. The flow behavior index ranged from 0.645 to 0.676, with a tendency to decrease with increasing oil content in the emulsion.

3.3. Time-dependent Rheological Properties

The time-dependent rheological properties are shown in Figure 5. For all oil concentrations with shear rates of 9.575 and 38.3 s^{-1}, the rheological characteristics of the emulsion are independent-time. At a shear rate of 191.5 s^{-1}, the emulsion behavior at 10 and 17.5% oil concentrations were thixotropic, and those at a shear rate of 383 s^{-1} at all oil concentrations were rheopectic. Rheopectic behavior at a shear rate of 383 s^{-1} is modeled using the Weltman model with constant values, as shown in Table 1. The value of A, representing the initial shear stress, increases with increasing oil concentration, ranged from 26.39 to 48.83. However, the value of B, describing the construction rate, decreases with increasing oil concentration, ranged 0.63 to 0.92.

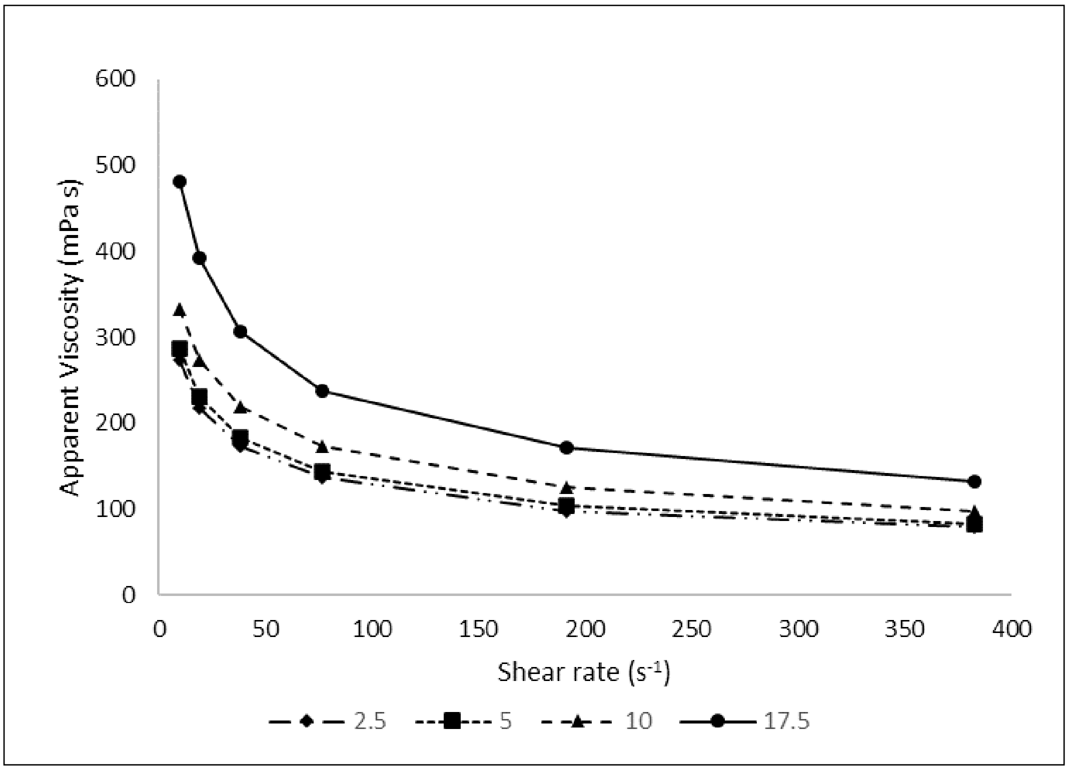

Figure 3. Shear rate dependence of the viscosity flaxseed oil emulsion at the oil concentration of 2.5 (♦), 5 (■), 10 (▲), and 17.5 (●)

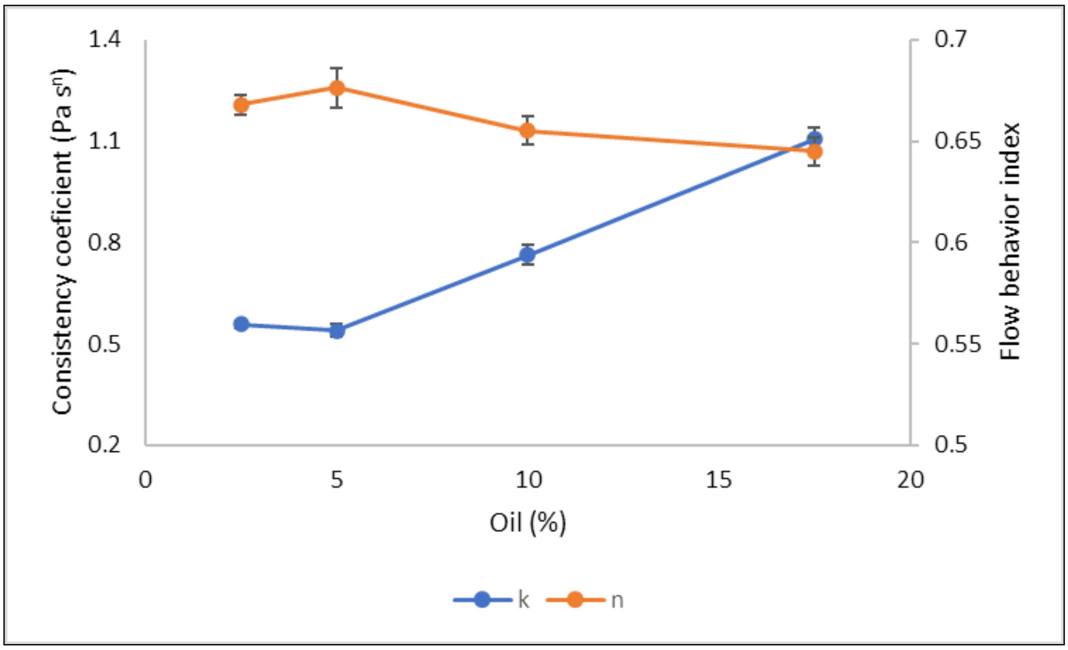

Figure 4. Consistency coefficient and flow behavior index of the flaxseed oil emulsion with PWRS at different oil concentration

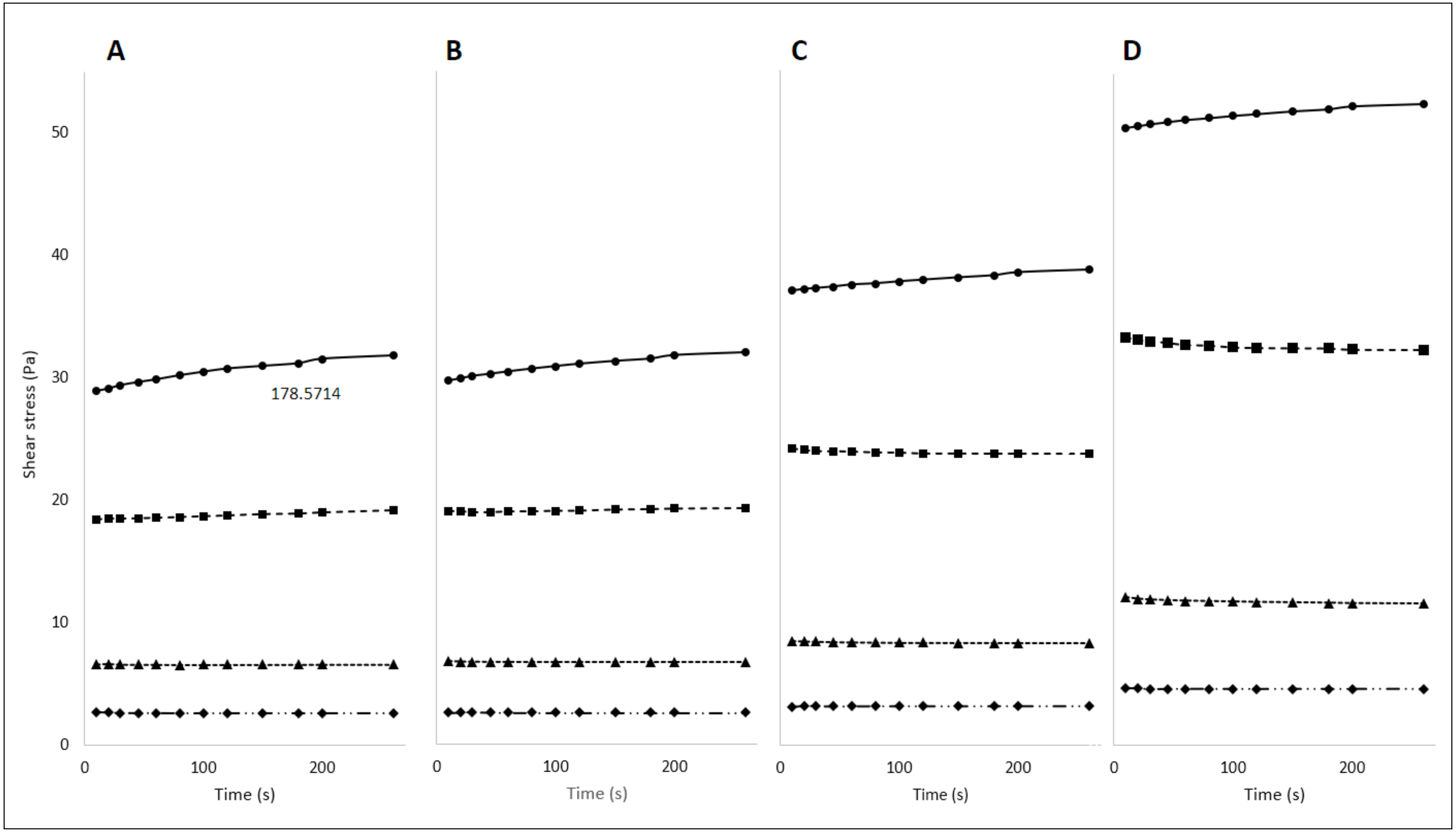

Figure 5. Time-dependent rheological properties of flaxseed oil emulsion with the oil concentration of 2.5 (A), 5 (B), 10 (C), and 17.5 (D) as a function of time at different constant shear rates (9.575 (♦), 38.3 (▲), 191.5 (■), and 383 s^{-1}(●))

Table 1. The constant of Weltman model at the shear rate of 383 s^{-1}

Oil(%)	A	B	RMSE	SE
2.5	26.39±1.89	0.92±0.31	0.23	0.24
5	27.71±1.64	0.72±0.35	0.19	0.20
10	35.56±0.68	0.52±0.24	0.18	0.19
17.5	48.83±0.22	0.63±0.25	0.17	0.18

4. Discussion

4.1. Stability of Emulsion

All emulsions show the stability on creaming after two weeks of storage. The emulsion's creaming is influenced by several factors such as the density differences between the continuous phase and the dispersed phase, the viscosity of the continuous phase, the oil ratio, the interaction between droplets, and the structure of the continuous phase [14]. Emulsions with PWRS have good stability against creaming, presumably due to several factors. Besides being caused by the high viscosity, the presence of a polymer network in the continuous phase, which hinders the movement of droplets, also plays a role in emulsion stability. In general, a small oil ratio will be more liable to creaming. The oil content in an emulsion is related to viscosity, and viscosity will affect creaming. The higher the oil content, the denser the droplets, and the higher the viscosity, lead to the slower the creaming rate [19,20]. In contrast, at low oil content, the weak flocculated network easily collapses under its weight [19].

After two weeks of storage, emulsion with PWRS did not show any creaming even at an oil content of 2.5%, presumably due to the high viscosity and a polymer network in the continuous phase. The polymer network formed in the fully gelatinized waxy rice starch redispersion process has a solid structure to resist droplets' movement.

The big droplet diameter in the emulsion containing 17.5% oil indicates a noticeable droplet diameter change. The size of droplet is related to the ease of deformation, where larger droplets will be easier to be deformed. On the other hand, droplet deformation plays an essential role in emulsion stability [21] since the deformation will develop a flat plane film which increases the van der Walls attract force [22], making it easier for coalescence. The similar result was also obtained from this study, where the larger the droplet size, the more significant the droplet size change, as shown in Figure 2. In the emulsion with 17.5% oil, large droplets were seen, indicating coalescence. Besides being affected by droplet size, the stability against coalescence is also determined by the adsorbed layer on the droplet surface [23]. In consequence, the higher oil content will have a less protective coating.

4.2. Rheological Characteristics of Emulsion

The viscosity of the emulsion increases with the increased oil concentration. Emulsion containing 2.5 and 5% flaxseed oil possessed similar apparent viscosity value, but increases sharply at higher concentrations. This result was consistent with several previous papers, which proved that the emulsion viscosity was more sensitive for higher oil ratios. The drastic increase in viscosity at high oil ratios is caused by several factors such as interactions between droplets, increased interference with normal flow, and strong colloidal interactions. [24,25]

Flaxseed oil emulsion display shear thinning behavior. According to Barnes [26,27], the rheology of an emulsion containing biopolymer is determined by several factors such as the response of the continuous phase to shear stress, droplet size distribution, internal viscosity, concentration, temperature, composition, etc. Shear thinning of an emulsion is caused by several possibilities, such as the release of the biopolymer due to the application of shear stress, the arrangement of the biopolymer with a shear field, and the interference of physical interaction that keeps the biopolymer jointly [14]. The rheological properties of emulsions with PWRS dominantly influenced by the characteristics of the continuous phase affected by the gelatinization degree [11], and shear thinning behavior was caused by the alignment of polymer with shear field.

The time-dependent rheological behavior of flaxseed oil emulsion was affected by shear rate. At low shear rates, the rheological characteristic was time independent. Otherwise, the emulsion was rheopectic at high shear rates, where the stress increases with time, indicating the emulsion's elastic deformation. This rheopectic behavior shows the structure's orientation that is related to the material's elastics strain. [28]. A similar result was found on highly concentrated water in oil emulsion [29], however in that study, the emulsion was rheopectic at a low shear rate, and time-independent at high shear rate. Rheopectic behavior indicates an increase in entanglement due to shear application. The rheopectic behavior at the high shear rate in this study was thought to be due to the arrangement occurring randomly, increasing the disruption that leads to the increase in viscosity. Amylopectin in the continuous phase, its interaction with droplets, and interactions between droplets increase viscosity with time, though causing the formation of a complex structure due to shear. On the other hand, the disturbance was low at low shear rates [30]. Table 1 shows that the smaller the oil concentration, the higher the constant B in the Weltman model, indicating a higher viscosity increase in low oil concentration. The high rise in viscosity was thought to be caused by the dominance of amylopectin, a branched polymer in the emulsion system that forms complex structure due to shearing. Emulsion with 10 and 17.5% oil behaves thixotropy at a shear rate of 191.5 s^{-1}. Greco et al. [31] stated that the thixotropy was related to viscosity reduction due to alignment and droplet deformation caused by shear rate changes. It was thought that in the emulsion with the oil content of 10 and 17.5%, the droplet deformation was more dominant compared to polymer entanglement in the aqueous phase at a shear rate of 191.5 s-1, so the emulsion behaved thixotropy.

5. Conclusions

The flaxseed oil emulsion stabilized with PWRS was visually stable against creaming within two weeks of storage. Changes in droplet size occurred in emulsions containing 10 and 17.5% oil. Emulsions are shear thinning, where the emulsion is rheopectic at high shear rates and time-independent at low shear rates. The domination of amylopectin in the emulsion system makes emulsions with lower oil concentrations exhibit higher viscosity changes with time.

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