PREPARATION AND CHARACTERIZATION OF STEARIC ACID BASED OLEOGEL AND OLEOGEL-IN-WATER PICKERING EMULSIONS STABILIZED BY CELLULOSE FROM COFFEE PEEL

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ABSTRACT:

This study is to prepare and determine characteristics of oleogels and an oleogel-in-water Pickering emulsion (OPEs). Soybean oil (SBO) and sunflower oil (SFO) are structured with Stearic Acid (SA) in creating oleogels. The gelation kinetics of the oleogels is determined by spectrophotometers at 560 nm and 575 nm for SFO and SBO based oleogels, respectively. Then, oleogels are stabilized with microcrystalline cellulose (MC) to prepare the OPEs at 70°C. Characterized rheology, texture evaluation and microstructure of oleogels and OPEs are observed with the use of a Leica polarizing microscope. The study finds out that SA concentration (10%), oleogel fraction of 0.44 and SBO are the optimal conditions to create the most stable OPEs system.

Keywords: Stearic acid, oleogel, Oleogel-in-water Pickering emulsion, cellulose, coffee peel.

1. Introduction

In this research, cellulose from the coffee peel (bio-based materials) was availability of natural resources. SBO were trapped within a 3-dimensional gel-network with SA that was structured by cellulose from the coffee peel could have good form and viscosity behavior. OPEs was stabilized by MC which may be used as delivery systems for many molecules (essential oil compounds...) for reduced animal fat foods.

2. Literature review

Saturated and trans-fats are the negative effects on human health. Because that excessive intake of them could result in a series of chronic disease. Therefore, food manufacturers look for alternative strategies to form lipid-based food products (commercial shortening or cake margarine) in the absence of statured and trans-fatconsumption. (Patel, 2014). Recently, the potential application of oleogels as substitution of solid fats and oleogelation, an efficient physical with viscoelastic properties (Patel, 2014 and Luo, 2019). Oleogel is dispersed system ion oil continuous phase (>90% wt of liquid oil) whose molecular interactions alter the physical properties of oil, good elastic properties and low-viscosity behavior (Patel, 2014;

Yael Cegla-Nemirovsky, 2015; Si, 2016). And the Pickering emulsions (PEs), which are stabilized by MC, starch instead of low-molecule surfactants, have received extensive attention (Shilin Liu, 2021). Currently, a new type of pickering emulsion, which is similar to solid lipid particles has been designed: oleogels are used as dispersed phase of O/W emulsions.

There are two main ways to prepare oleogels such as the hydrophobic oleogelator (waxy esters, fatty alcohol...) and the hydrophilic oleogelator (methyl cellulose (MC), xanthan gum, pectin, protein...) (Shui-zhong Luo, 2019). However, oleogelation has a major limitation in using for food products and water-soluble food polymers could be used to revolutionize the way lipid-based food products are formulated (Patel, 2014). Recently, Stearic acid cause gelation of two commonly oils, viz. sesame oil and soy bean oil (K. Pal, 2015).

OPEs are an O/W emulsion that is very suitable for replacing solid fats due to their low-calorie food, great stability and high biocompatibility (Ahmadi, Tabibiazar, Roufegarinejad, & Babazadeh, 2020; Wei & Huang, 2019). Particles such as starch, water-insoluble dietary fibers... can be used as a physical barrier preventing the agglomeration of oil droplets, which have excellent interfacial properties (Xia, Xue, & Wei, 2020). Besides, the beneficial effects of dietary fibers have been proven by many scientists, showing that MC was more suitable for OPEs.

In this article, the viscoelastic properties, the texture and bright-field microscopy of Pickering emulsion was measured by Brookfield, Texture analyze and Leica, respectively.

3. Methodology

3.1. Materials

Coffee (*Coffee arabica* L.) was collected from Lam Dong, a highland province of Vietnam. MC from the coffee peel was prepared by using the temperature-pressure method (Duy N. Dao et al., 2022). SBO and SFO were purchased from a local supermarket (Co.opXtra Linh Trung, Thu Duc City, Ho Chi Minh City). Chemical solvents (stearic acid, Xilong Scientific Co., Ltd) was of analytical grade.

3.2. Methods

Preparation of oleogels: SBO and SFO oleogels were prepared by using SA as the oleogelator. SA was dissolved in either SFO or SBO at 70^{o}C in 15 ml vials. The hot SA solution (5%-25% w/w) was cooled down to room-temperature (25^{o}C) or ice bath temperature (10^{o}C). This resulted in the formation of either cloudy suspension or organogel.

Preparation OPEs: Preliminary experiments were conducted to choose formulation (Table 1) that can obtain stable OPEs. Cellulose from coffee peel (CFCP) was dispersed in disstilled water was mixed with SBO oleogels. The cellulose dispersion and SBO oleogels were separately heated in a water bath (Memmert, Germany) at 70^{o}C for 15 min. Then the hot Cellulose dispersion was poured into the soybean oil oleogels and sonicated by a ultrasound processor (Biologics, Inc, USA) by for 4 min at 50% pressure amplitude. During mixing, the temperature was maintained at 70^{o}C using the water bath. The resulting hot emulsion was cooled in an ice bath or room-temperature (25±2^{o}C) for 15 min and then further analysis. (Tao Wu et al, 2020).

Gelation kinetics of oleogels: The microscopic structure of the developed oleogels was analyzed using a bright field microscope (DM 2500, Leica, Germany). The gelation kinetics of the oleogels were studied by spectrophotometers (UV-11, MRC, Israel). Absorbance of the molten gels was measured at 560 nm and 575 nm for sunflower oil and soy bean oil based oleogels, respectively and determine induction time (Ti), fibrillar growth time (Tf). The weight of oleogels was kept constant (5 g) for all the gels (S.S. Sagiri et al., 2014).

The morphology of the OPEs: The morphology of the OPEs was analyzed using polarized microscope (Leica, Germany).

Determination of rheology: The rheological properties of oleogels and OPEs were characterized using a rotational rheometer (Brookfield, USA) with a 40 mm diameter

aluminum plate. (Y. Xie et al., 2021).

Texture evaluation: The deformation properties (firmness and stickiness) of the developed oleogels and the OPEs were studied by performing mechanical tests using a texture analyzer (Stable Microsystems, TA-Xplus, U.K.) at room-temperature with 45° conical perspex probe (pretest: 1.0, test: 0.5, post test: 10.0 mm/s, depth: 23mm), auto force (5 g; 5 mm).

Statistical analysis: All experiments were repeated three times. Analysis of variance and significant difference ($p \leq 0.05$) between treatments were determined using LSD multiple range test by the Statgraphics Centurion XV.I software (Statgraphics Technologies, Inc, the Plains, Virginia) and the Microsoft Excel 2016.

Table 1. Formulations of oleogel-in-water Pickering emulsions

Formulations	SA Concentration	Concentration of CFCP	Oleogel fraction
	%, w/100g oil	%, w/w	φ
SA Concentration-5%	5	0.5	0.44
SA Concentration-10%	10	0.5	0.44
SA Concentration-15%	15	0.5	0.44
SA Concentration-10%	10	0.5	0.3

Table 2. Gelation parameters of the oleogels

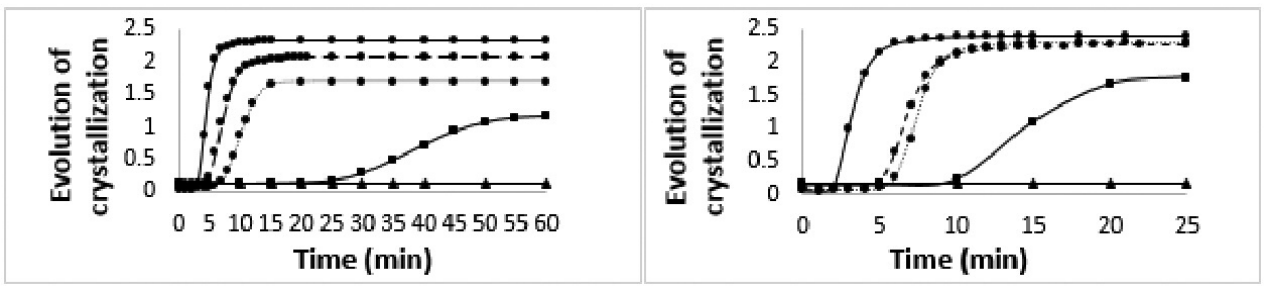
Oil	Stearic Acid Concentration	Ti (min)	Tf (min)
Sunflower oil	10%	20	30
	15%	7	8
	20%	5	7
	25%	3	5
Soy bean oil	10%	12	8
	15%	6	4
	20%	5	4
	25%	2	3

4. Results and discussion

4.1. Gelation kinetics of oleogles

Gel setting time was considered as the time required in reaching the equilibrium phase. The developed oleogels were opaque and semi-solid. This happened in the 10-25% SA soybean oil sample and the same with SFO. The oleogels are thermoreversible in nature and stable at room-temperature (Fig 5). There was a difference in oil composition (X. Liu, et al, 2007), thus creating a difference in the polarity of the oils used. This change in polarity may impact the nucleation mechanism (S.S. Sagiri et al., 2014). Thereby it affect the turbidity of oleogels during crystallization. Fig 1 shows the turbidity of different gels made up of SFO and SBO at different concentrations of SA. The developed formulations were at 70°C, the gelation kinetics were studied by measuring the absorbance of the liquid gels. During the process of heat transfer to the air of the gels, gelation was induced via crystallization of the SA fibers. This happening was

Fig 1: Gelation kinetics of: (ledf) SFO based oleogels, (right) SBO oleogels



described as the evolution of crystallization with respect to time in Fig. 1. Except for sample SA-5%, all gel samples have self-heating phase (Ti), and when reaching a certain temperature, rapid crystallization begins to appear, increasing the absorbance rapidly (small Tf). Gel setting time was considered as the time required in reaching the equilibrium phase (Ti+Tf; Table 2.). Equilibrium phase was first achieved by SBO-SA-25% and SFO-SA-25%.

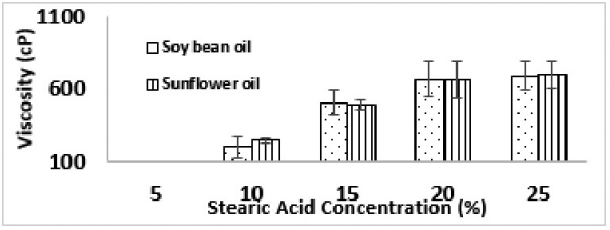
In general, the gel setting time of SFO based oleogels was larger than that of soybean oil. Formation of SA fibers with high length:width ratio was also confirmed from the light micrographs studies (Fig 6). This kind of phenomenon was observed in SA/SBO oleogels. (S.S. Sagiri et al., 2014)

4.2. Texture analysis of oleogles

The firmness and stickiness are two of the most important functional properties of commercial shortenings and structured fats. Therefore, the firmness and the stickiness of the gel samples was determined using a texture analyzer, and the results are shown in Fig. 2 (SBO) and Fig. 3 (SFO). Both figure 2 and fig. 3 showed that firmness and stickiness increased when increased SA concentrations were increased. Liquid samples of both oils (SA 5%) showed very small firmness and stickiness, which indicates that the crystallization of SA was not sufficient to solidify part of the mixture. So the conclusion that the sample of SA concentration 5% was not oleogels, due to the high mobility. This was consistent Pictographs in Fig. 5. At concentrations of SA 10% to 25%, firmness and stickness increased significantly, large-scale crystallization of SA occurred, leading to a marked decrease in fluidity. Resulting oleogles are formed at SA concentrations of 10% or more. This case was similar to the results of Shu Yang et al (2017) at the concentration of SA 20% and sunflower oil.

4.3. Viscosity properties of oleogles

Fig 4: The rheological properties of SFO based oleogels and SBO based oleogels



The rheological properties of the oleogels were shown in Fig. 4. This was the viscosity measured at 0.5rpm, representing the stationary state viscosity of oleogels. Measurements were performed on Brookfield DVT and CP. instruments. The flow behavior indices of the oleogels were suggest the pseudoplastic nature of the oleogels (Except SA-5% sample) (S.S. Sagiri et al., 2014). Similar to Texture evaluation, the trend of viscosity of oleogels also increased with SA concentration. Fig 4 shows the maximum viscosity (670 ± 125cP, SBO) at 20% SA concentration compared with other gels. The effect of SA concentration on gel viscosity was statistically significant. This is the result of solidification of SA molecules in vegetable oils.

4.4. The microscopic structure of Oleogels

As the solution was natural cooled down to room-temperature, Oleogels became opaque. Formation of oleogels was confirmed by inverted tube method (Fig 5) (S.S. Sagiri, et al , 2012).

Fig 2: Texture evaluation of SBO based oleogels

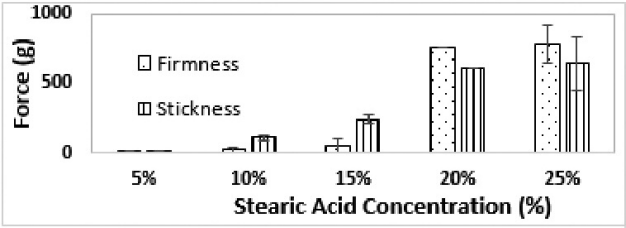


Fig 3: Texture evaluation of SFO based oleogels

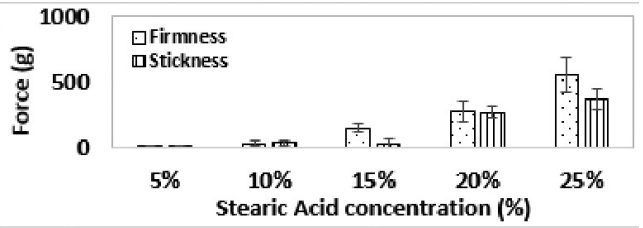


Fig 5: Pictographs of SFO based oleogels (a) and (b); SBO based oleogels (c)

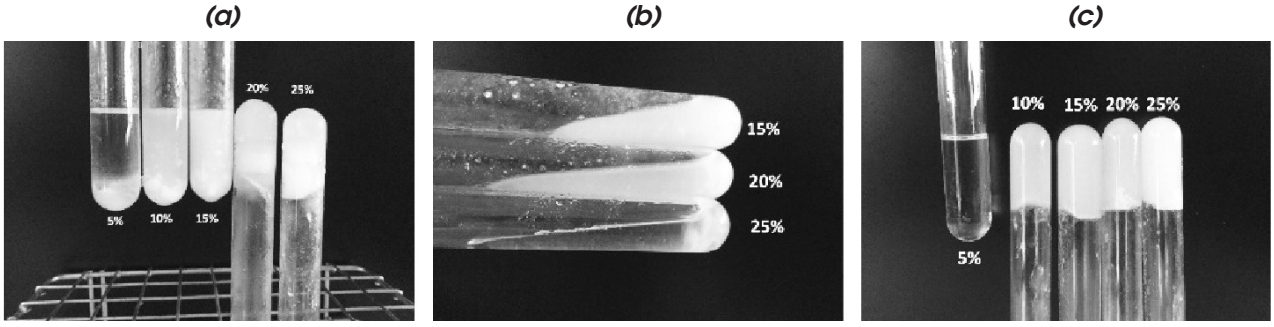
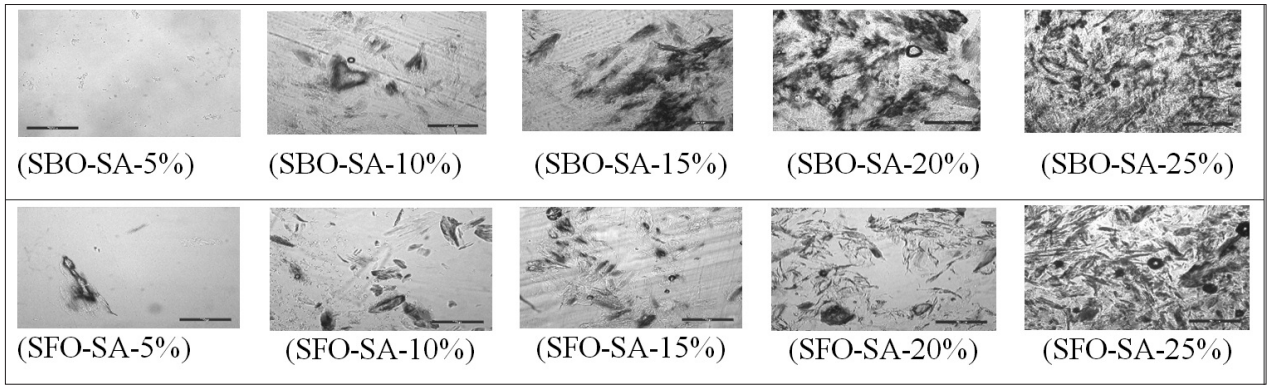


Fig 6: Light micrographs of oleogels prepared with SA



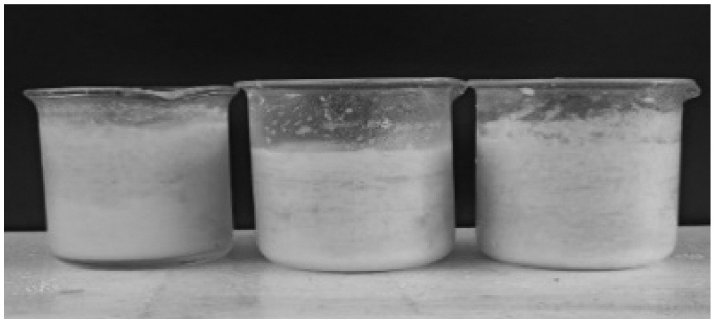
For SBO, the concentration of SA from 10% to 25% has shown high stability, representing the nature of a typical oleogel (chisel, sticky, solid). The concentration of SA in 10% was enough for the crystals to maintain the structure of the system, which was not affected by gravity flowing down when tube was inverted. The same thing happened with sunflower oil based oleogels.

Figure 6 showed the SA lattice structure in the oleogels. From left to right, the crystal density increased with increasing SA concentration. In both oils, the concentration of SA 5% was too small to maintain the texture of the sample when inverted, similar to the visual observation in Fig 5. The fiber aggregates was one-dimensional seems to have been following first-order kinetics. SA fibers were dispersed in the oils and entangled to form a coherent network. In general, low molecular organogelators yield fibrous networks by molecular self-assembly through noncovalent interactions (from SA-10% to SA-25%) (J. Danie, et al 2003 and S.S. Sagiri, et al ,2013). It is this phenomenon that increased the strength of the crystal lattice so that the hardness, stickiness and viscosity of oleogels increase as shown in Fig 2, Fig 3, Fig 4.

4.5. Preparation OPEs

All prepared emulsions were cooled rapidly in water at room-temperature or ice-bath. We selected oleogels samples with SA concentrations from 5, 10 and 15% and Soybean oil to proceed to create OPEs.

Fig 7: Image of OPEs with different concentrations of SA



In this research, an oleogel was prepared by structuring soybean oil with SA and stabilized with CFCP to prepare oleogel-in-water Pickering emulsions (OPEs). Experiments were conducted to choose formulation (Table 1) that can obtain stable OPEs. In general, the color of OPEs depends on the color of the CFCP, which is yellow. All OPEs samples are stable over a long period of time, homogenous. The Pickering stabilization mechanism was demonstrated by Polarized light microscopy images in Fig. 13.

4.6. Texture evaluation of OPEs

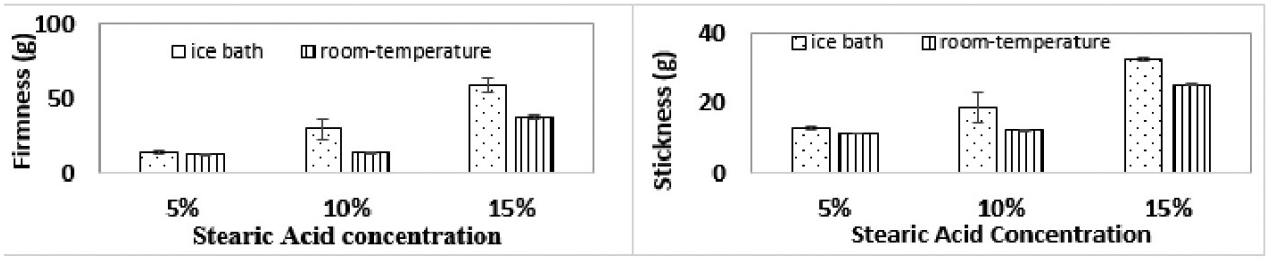
Text evaluation (firmness and stickiness) of OPEs was measured by texture analyzer (TA.XT plus). In general, from Figure 8, Figure 9 shows that all samples cooled in ice bath have higher hardness and adhesion than samples cooled at room temperature. The sudden rapid cooling from 70 □C to 10°C of the ice bath made the OPEs more stable and stiffer.

formation of an elastic gel network structure through tightly packed droplets (Boostani et al., 2020; Ye et al., 2018). This was desirable for application in fat substitutes, for using in biscuits. Viscosity results showed that OPEs samples at 10% and 15% SA concentrations were not statistically different. But at the SA concentration of 15%, there was quite high solid-liquid separation (SA solid part, liquid part: water and soybean oil) during long-term storage. As for OPEs sample at 5% SA concentration, the viscosity was too low, leading to particles settled to the bottom of the tube. This caused a breakdown of the pickering emulsion structure. Therefore, we chose a concentration of SA in oleogels of 10% for further testing.

4.8. Preparation OPEs at different oleogels fraction

Figures 9 shown the texture evaluation of OPEs at 0.44 and 0.3 oleogels fraction. Samples of OPEs at 0.44 oleogel fraction showed higher hardness and

Fig 8: Firmness (left) and stickness (right) of SBO based OPEs at 0.44 oleogels fraction



4.7. Viscosity properties of OPEs

The rheological properties of the OPEs were shown in Fig. 10. The rheological measurement results indicated that the emulsions showed shear-thinning behavior (Yunxiao Xie et al, 2021). Similar results in O/W pickering emulsions using starch particles as emulsifier (Song et al., 2015). Viscosity increased with the increase of SA concentration but no significant difference between room temperature cooling and ice bath. The emulsion exhibited a typical gel–like behavior (Yunxiao Xie et al, 2021). The enhanced tight accumulation by CFCP particles between oil droplets might enhance droplet–droplet interactions at the interface, resulting in the

Fig 9: Firmness (top) and stickiness (below) of OPEs at 0.44 and 0.3 oleogels fraction

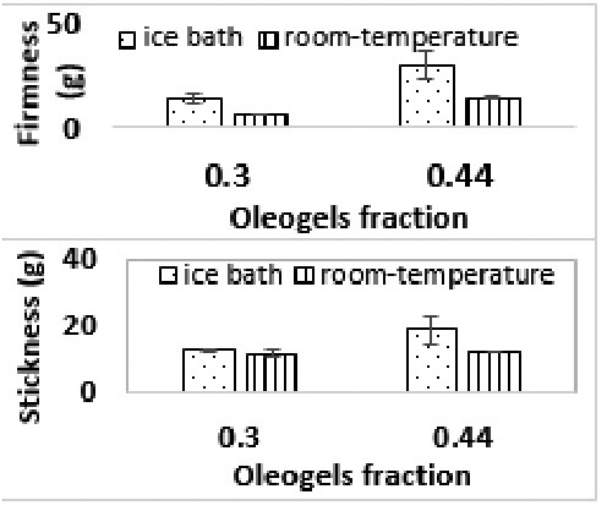


Fig 10: Viscosity of OPEs at 0.44 oleogels fraction

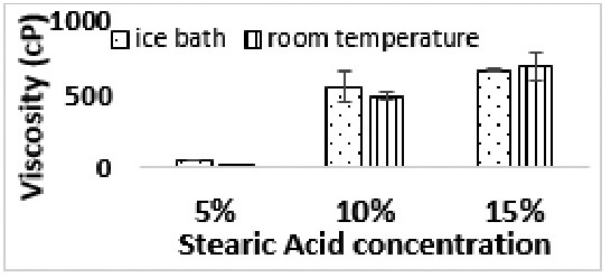
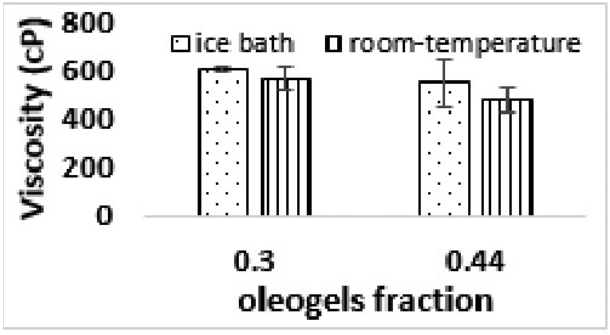


Fig 11: Viscosity of SBO based OPEs at 0.44 and 0.3 oleogels fraction



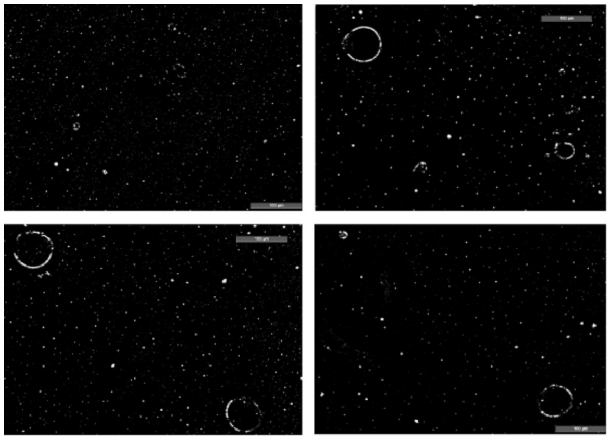
stickiness and were significantly different in ice bath cooled OPEs samples.

However, the viscosity of the OPEs samples at 0.44 and 0.3 oleogels fraction did not differ, as shown in Fig. 11. OPEs at oleogel fractions of 0.44 and 0.3 all demonstrated a shear-thinning behavior. The viscosity profiles were similar for two oleogel levels. The results were similar to the experiment of creating OPEs by Cellulose Nano Crystal, SBO and beeswax (Wenhui Qi et al, 2020).

The microstructure of OPEs is shown in the polarized light micrographs (Fig 12). The cellulose acted as a bridge between oil droplets and caused the flocculation of oil droplets (Sun & Gunasekaran, 2009).

However, the high viscosity of the sample when cooling the ice bath and storing it at low temperature

Fig 12: Polarized light microscopy images of SBO based OPEs at 0.44 (a) and 0.3 (b) oleogels fraction



prevented oil agglomeration. Figure 12 shown the uniform density distribution of cellulose particles in OPEs. However, the droplet size of OPEs with oleogels fraction 0.44 was smaller than that of oleogels 0.3.

5. Conclusions

In this study, soybean oil was structured with SA to prepare oleogel, which was then stabilized by CFCP to prepare OPEs. The prepared oleogels have shown semi-solid properties at SA concentrations from 10 to 25%, measured parameters such as viscosity, hardness, stickiness and observed by polarizing microscopy. The crystal lattice of SA was flake-like consisting of many SA molecules linked together and elongated.

Experiments to create OPEs were also conducted. The measured parameters include viscosity, hardness, stickiness, observation by polarizing microscope. The best OPEs are the most stable over the long term. We have determined the optimal conditions for good OPEs including SA concentration, vegetable oil, oleogel fraction ■

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QUÁ TRÌNH ĐIỀU CHẾ VÀ ĐẶC TÍNH CỦA OLEOGELS VÀ NHŨ TƯƠNG PICKERING OLEOGEL/NƯỚC (OPES) BẰNG VIỆC SỬ DỤNG CELLULOSE TỪ VỎ CÀ PHÊ

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TÓM TẮT:

Nghiên cứu này tiến hành điều chế và xác định các chỉ tiêu, tính chất của Oleogel và nhũ tương Pickering oleogel/nước (OPEs). Dầu đậu nành (SBO) và dầu hướng dương (SFO) được sử dụng để hỗ trợ định hình cấu trúc bán rắn bằng Axit Stearic (SA) trong việc điều chế oleogel. Động học tạo gel của oleogel được xác định bằng máy đo quang phổ UV-Vis lần lượt ở bước sóng 560 nm và 575 nm đối với các oleogel dựa trên SFO và SBO. Sau đó, oleogel được ổn định bằng cellulose từ vỏ cà phê để điều chế nhũ tương OPEs ở 70°C. Các oleogel và OPE đều được xác định các đặc trưng lưu biến, đánh giá kết cấu và quan sát cấu trúc vi mô bằng kính hiển vi phân cực Leica. Nghiên cứu cho thấy mẫu OPEs ổn định nhất có các thông số thành phần như sau: nồng độ SA (10%, w/w), tỉ lệ Oleogels/nước 0,44 và dầu thực vật sử dụng là dầu đậu nành.

Từ khoá: Axit Stearic, oleogel, nhũ tương Pickering oleogel/nước, cellulose, vỏ cà phê.