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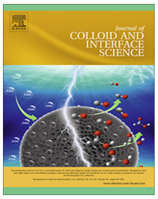


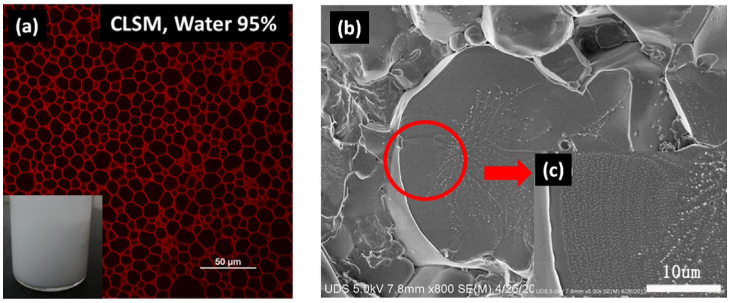
Regular Article

High internal phase water-in-oil emulsions stabilized by food-grade starch

Qiang Zhao [a], Lingxiang Jiang [a], Zhen Lian [a], Ezat Khoshdel [c], Stephan Schumm [d], Jianbin Huang [a,*], Qiqing Zhang [b,*]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China
[b] Unilever Research and Development Centre Shanghai, Shanghai 200335, PR China
[c] Unilever Research and Development Port Sunlight, Bebington CH63 3JW, UK
[d] Unilever Research and Development Vlaardingen, 3130 AC, the Netherlands

GRAPHICAL ABSTRACT



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ABSTRACT

Water in oil emulsions would be prepared by silicones (SO), modified silicones (DC8500) and a food-grade stabilizer (starch **1**). With increasing water contents, the emulsions turned from a liquid-like to gel-like behaviors with enhancing storage and loss modulus. When DC8500/SO was 1/17 with 10 wt% starch **1**, a high internal phase emulsion can be obtained with 95 wt% water content. DC8500 and SO worked as efficient emulsifiers and possessed amphiphilic property to form emulsions with water in different ratios. A food-grade starch **1** was supplied as a stabilizer which can enhance both water content and strength of emulsion when added in a low concentration. Besides, it is indicated that the food-grade starches provided potential benefit on stabilizing emulsions in very low concentration.

1. Introduction

Emulsions are mixtures of two immiscible phases, of which one phase is dispersed into the other one [1-3]. High internal phase emulsions (HIPEs) are the ones with over 74% v/v internal phase. In critical concentration of HIPE, there are uniform sphere droplets suspending in the emulsion. HIPEs are widely applied in food industries as high water concentration in emulsions reduces the cost. Many foods contain emulsified treatment during manufacturing process on some extent [4]. However, the stability of HIPE is always the challenge when construct emulsions with high water content. Besides, synthetic method to construct emulsions are expensive, time-consuming and always accompanied with pollution [5]. In order to broaden the applications of emulsification in

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* Corresponding authors.
E-mail addresses: JBhuang@pku.edu.cn (J. Huang), qiqing95936@hotmail.com (Q. Zhang).

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industry, cheap and easily acquired ingredients are requested in preparing emulsions as well.

Poly(dimethylsiloxane)s is a structure reported to be highly hydrophobic, low volatile and thermal stable which possesses the capability of low surface tension and interfacial tension [6-10]. Silicones, especially the ones with chemical modifications, are broadly used in many applications, such as emulsification and softner in personal care [11,12], demulsification in fossil oil [13,14], superwetting in agriculture and additives in foam [15-17]. DC8500 is a kind of silicones with poly(dimethylsiloxane)s and polyol structures that exhibits well performance on emulsification as amphiphiles. As siloxane in DC8500, it features low irritation to skin. Besides, DC8500 is with low price and easy to be prepared as an industrial product. So it has potential benefit to be emulsifier in further applications.

Nowadays, starches and their derivatives are common as additives in food applications, such as sauces [18,19], puddings [20], infant foods [21,22], food packages, *etc*. [23-25]. Eric Dickinson interpreted the mechanism of food-grade starch working as stabilizers in the emulsions [26]. Meanwhile, Huang et al. studied how a waxy corn starch affects the oil-in-water emulsions [27]. It was stated that the starch can enrich the oil-water interface of the emulsions as stabilizer. Hence, starch **1** was selected to be an ideal candidate to stabilize emulsion in this work. As it is a kind of corn starches modified with dodecyl group (C12) which can possess enhancing amphiphilic property by C12 and polysaccharide structures when constructing the emulsions [28]. In addition, starch **1** is renewable and abundant in agriculture, so it is ideal emulsifier to be utilized in green chemistry and industrial applications.

In this study, a HIPE was constructed by DC8500, silicones and starch **1**. Most ingredients are industrial or food grade with wide source to acquire. By ranging the ratios of each component, various emulsions with different water contents were fabricated and studied by visual observation, rheological measurement, confocal laser scan microscope (CLSM) and cryogenic-scanning electron microscope (Cryo-SEM). The mechanism of emulsion stability was explored by rheological measurement. Besides, the effect of each ingredient in the emulsions and their potential benefits in industrial applications were discussed as well.

2. Experimental section

2.1. Materials

Starch **1**, a C12 modified starch, was supplied by National Starch. Silicones (SO). DC8500 was purchased from Dow Corning. An amino-modified silicones (SO-NH_2) was purchased from Sigma-Aldrich. All the other reagents are in AR grade. Aqueous solutions were prepared using Milli-Q water of ~18.3 MΩ×cm.

2.2. Emulsions preparation

Emulsions with different water contents were prepared by mixing DC8500, SO, starch and water in different ratios. First, mixed DC8500 and SO together and then starch **1** was added as one tenth of DC8500 and SO mixture in weight. Water was added and stirred vigorously over 1 h until stable, uniform and opalescent emulsions formed. When the weight of DC8500/SO was 1/1, starch **1** was added as one tenth of DC8500 and SO mixture. After mixed and stirred with water, the samples with 40 wt% and 83 wt% water content were prepared. When the weight of DC8500/SO was 1/17, the maximum dose of water can be 95% in the emulsion.

2.3. Rheological measurement

Emulsions were assessed by dynamic rheological measurements by a Thermo Haake RS300 rheometer with cone and plate geometry (35 mm diameter, 0.105 mm cone gap). The temperature was kept at 25 °C and a water trap was used to minimize water evaporation from the sample. Frequency spectra were conducted in the linear viscoelastic regime of the samples determined from dynamic strain sweep measurements. The weight ratio of DC8500/SO was 1/1 and water content was varied. In dynamic rheology measurements, the emulsions were deformed with frequency f to give the elastic (or storage) modulus G' and viscous (or loss) modulus G''. The oscillation frequency sweep tests were conducted to be nondestructive for the emulsions, in which the stress was chosen as 1 Pa and frequency was varied exponentially.

2.4. Confocal laser scan microscopy (CLSM) observations

Emulsions with 40 wt%, 83 wt% and 95 wt% water contents were observed by CLSM. In the measurements, the oil phase was stained by Rhodamine B (red fluorescent). For CLSM observation, the stained samples were allowed for equilibrium for 24 h. A drop (about 10 μL) of the samples was sealed between two slides, ready for CLSM observation. A TCS-sp inverted confocal laser scanning microscope (Leica, Germany) was used to conduct experiments in florescence and differential interference contrast (DIC) modes. Laser Scanning Confocal images were performed on Nikon A1R-si microscope. Microstructure of emulsion samples was revealed by optical microscope and CLSM.

2.5. Cryogenic-Scanning electron microscopy (Cryo-SEM) observations

The morphologies of emulsions with 95 wt% water content was tested by Cryo-SEM. The observation was carried out with a Hitachi S-4800 FESEM scanning electron microscope equipped with liquid nitrogen cooled sample preparation and Cryo-transfer units (Gatan Alto 2500). A drop of emulsions was deposited on the aluminum specimen holder first and frozen in the slushing station with boiling liquid nitrogen. The sample was transferred to the preparation chamber under vacuum. And the preparation chamber was at −140 °C and equipped with a blade to fracture the sample. After being fractured, the sample was coated with Au and then inserted to the observation chamber. The observation chamber equipped with a SEM stage cold module held at −125 °C. After fracturing, the sample was inserted into the observation chamber to observe.

3. Results and discussion

3.1. General phase behavior

Usually, the silicones oil with hydrophilic groups can enhance the water content of emulsions as an efficient emulsifier. In this work, DC8500 was selected as the emulsifier, and the chemical structure is shown in Fig. 1. When R is -CH_3, it is silicones (SO) as shown in Fig. 1a. When R is structure shown as Fig. 1b, the modified silicones is DC8500. Obviously, SO is more hydrophobic and DC8500 exhibits more like amphiphiles due to the hydrophobic siloxane structure and hydrophilic anino polyhydroxy groups. Besides, starch **1** was chosen as stabilizer to increase the viscosity of emulsions. With SO, DC8500 and starch **1** mixing together, the high internal phase emulsions (HIPE) was prepared in good mechanical properties.

Stability of emulsions was studied by mixing SO, DC8500 and starch **1** in different concentrations. Stable emulsions cannot be formed with SO only (Fig. 1c) because SO is too hydrophobic as emulsifier. When apply DC8500 only in water stirring vigorously, stable emulsion can be acquired as shown in Fig. 1d. However, regarding the mixture of SO and DC8500 (1/1, w/w) as emulsifier, stable emulsions can only be constructed when water content

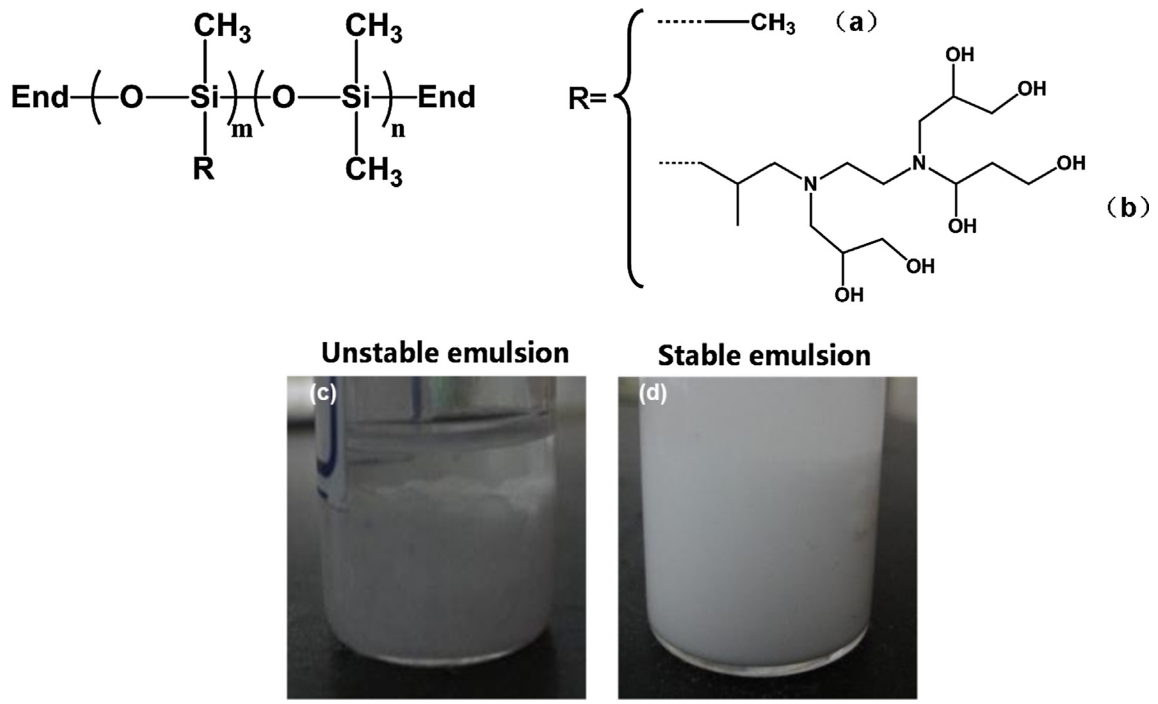

Fig. 1. Chemical structures of (a) silicones (SO) and (b) DC8500 which is modified by polyhydroxy aninofunctional branched chain. The photos of (c) unstable emulsions and (d) stable emulsions.

lowers than 20 wt%. When adding starch **1** as stabilizer, the stability and water content can be enhanced significantly, and the maximum dose of water can be up to 83 wt% in the emulsion. It is noticed that adjusting the ratio of SO and DC8500 to 1/17 (w/w), the water content can increase to 95 wt% in the emulsion.

The phase behavior study was show in Fig. 2, when SO/DC8500 was in ratio of 1/1 (w/w). Regarding the mixture of SO and DC8500 as Oil, the stability and water content in the emulsions were explored with increasing starch **1** dosages. As shown in Fig. 2, the yellow region indicates the formation of stable emulsions and the blue one shows even with more water added or stronger stirring, no stable emulsions can be acquired. Without starch **1**, the water content in emulsion can only be 20 wt%. When adding starch **1**, the water content was dramatically enhanced to 83 wt% which indicating HIPE was formed. The emulsion can be preserved stably in 6 months at room temperature. It was found that increasing the dosage of starch **1**, the water content can be enhanced in the emulsion. But when starch **1** doses up to 1 wt%, there is a plateau of water content in emulsions.

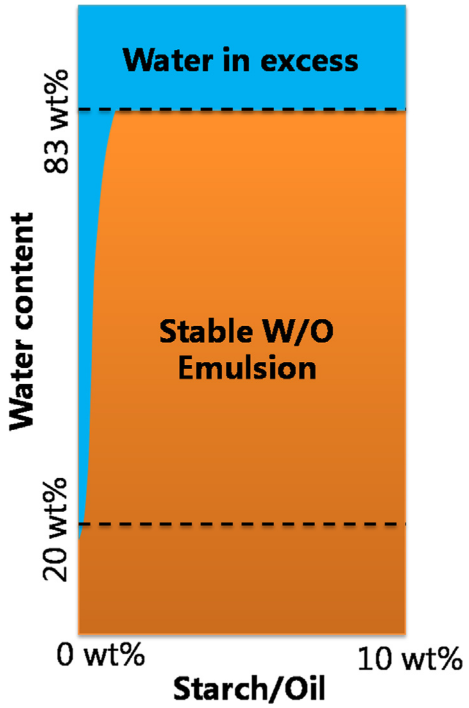

Fig. 2. Phase diagram of emulsions formation. DC8500/SO was 1/1 (w/w) and the dosages of starch **1** were various from 0 wt% to 10 wt% of the DC8500 and SO mixture.

Regarding the mixture of DC8500/SO as emulsifier and 10 wt% starch **1** as stabilizer, various emulsions were fabricated with different water contents. In Fig. 3, it is exhibited that when DC8500/SO was 1/1 (w/w), the water content can be up to 83 wt %. Increasing the ratio of SO in the emulsifier, more water can be added into the emulsions on some extent. When DC8500/SO ratio was 1/17 (w/w), the water content reached to 95 wt%. This is because adjusting the ratio of DC8500 and SO can make the amphiphilic property of emulsions changed and form stable internal phase in the emulsions. But when the SO doses up to 1/17, no stable emulsions can be built as the emulsifiers are too hydrophobic to maintain water in the emulsions.

3.2. Rheology in different proportions of SO/DC8500 and water contents

Rheological test was conducted to explore the physical properties of the emulsions as shown in Fig. 4. For 20 wt% water emulsions (Fig. 4a), both storage modulus (G') (blue[1] line) and loss modulus (G”) (pink line) relied on the frequency, and G'' was dominating the G', suggesting a liquid-like property of the emulsion. For the emulsions with 83 wt% water content (Fig. 4a), although G'

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[1] For interpretation of color in Figs. 2 and 4 the reader is referred to the web version of this article.

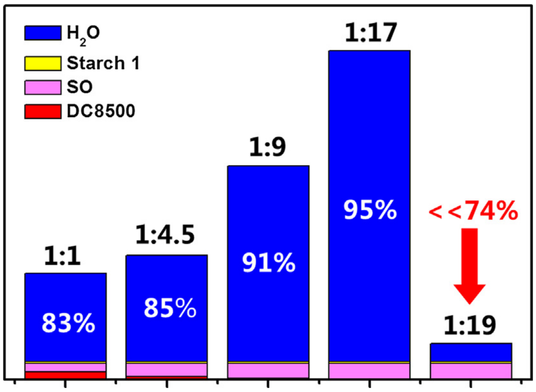

Fig. 3. Diagram of emulsions with different ratios of SO/DC8500 and the effect on water contents in emulsions. The starch **1** was dosing as 10 wt% of DC8500 and SO mixtrue.

(black line) and G'' (red line) were dependent on the frequency, G' was dominating the G" over entirely investigated frequency range, indicating a gel-like behavior of emulsion. Furthermore, amplitude sweep tests were performed on the gel-like emulsions that the frequency *f* was kept at 1 Hz and the applied stress was elevated exponentially. In Fig. 4b, before a certain stress (see the arrow), G' and G'' were independent on the stress and the deformation was close to 0. Over a certain stress, G' and G'' dropped dramatically which indicated that the sample were deformed and the gel structure was destructed (or yielded). The stress, ~150 Pa, was denoted as the yield point of emulsions, and such a high value implied a good mechanical performance. Moreover, Fig. 5a and b showed how water content gradually affected the G', G'' and the structures of emulsions. The emulsions with a higher content of water were more elastic (higher G' value) and gel-like (higher G'/G'' value). When water content was over 62 wt%, the emulsions experienced a fluid-to-gel transition and ended up as a strong gel with a high yield point.

In addition, when the ratio of DC8500/SO was 1/17 (w/w), the rheological properties of emulsions were studied. When water content was 60 wt%, the emulsion was liquid-like as G'' was dominating the G' (Fig. 6a). For water content of 95 wt% (Fig. 6a), the emulsions exhibited a gel-like behavior, which was similar to the ones of DC8500/SO at 1/1 (w/w). However, Fig. 6b showed that the yield point, ~10 Pa, which was smaller than that in DC8500/SO at 1/1. The yield point implied that the general mechanical performance deceased with both water and SO content increasing.

3.3. Microstructure

Microstructure of emulsions was revealed by optical microscopy and CLSM. The emulsions were stained oil phase by Rhodamine B (red fluorescent). There were a lot of water droplets in

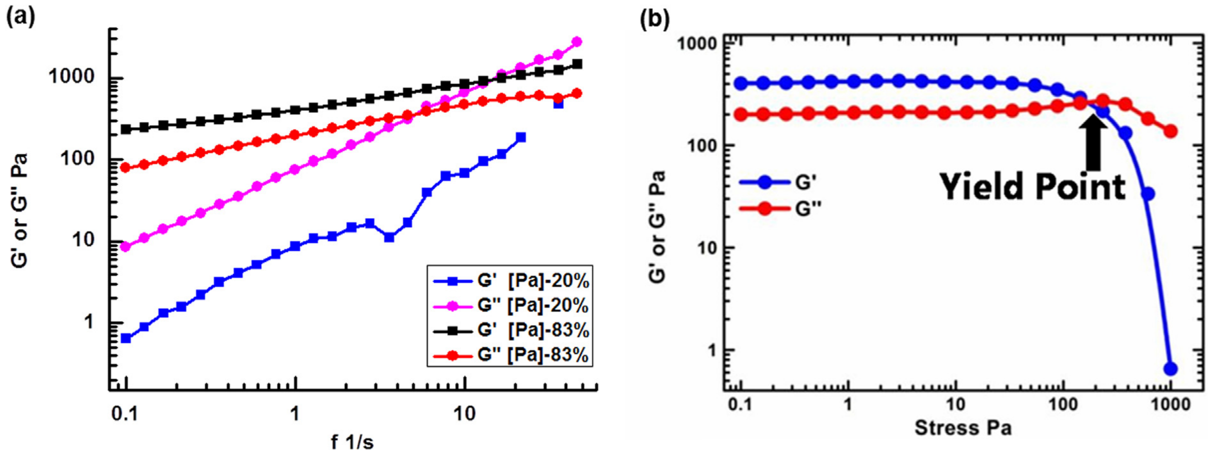

Fig. 4. (a)Oscillation frequency sweep test for 20 wt% and 83 wt% water content emulsions of which DC8500/SO was 1/1. The starch **1** was added as 10 wt% of DC8500 and SO mixtrue. (b)Amplitude sweep test for 83 wt% water content emulsions of which DC8500/SO was 1/1. The starch **1** was added as 10 wt% of DC8500 and SO mixtrue.

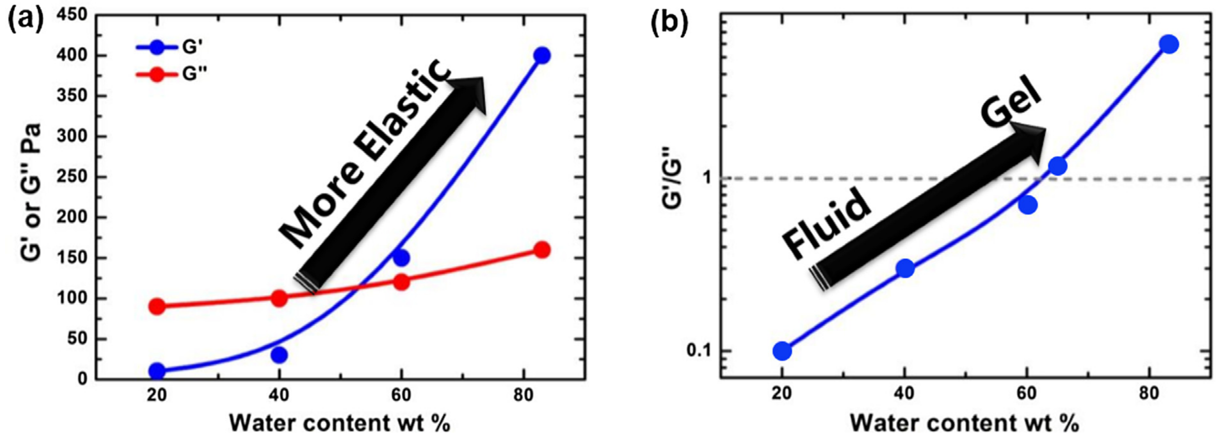

Fig. 5. (a)The G' and G'' test on emulsions with 83 wt% water content. (b)The ratio of G' and G" changed from fluid to gel behaviors. The ratio of DC8500/SO was 1/1 and the starch **1** was added as 10 wt% of DC8500 and SO mixtrue.

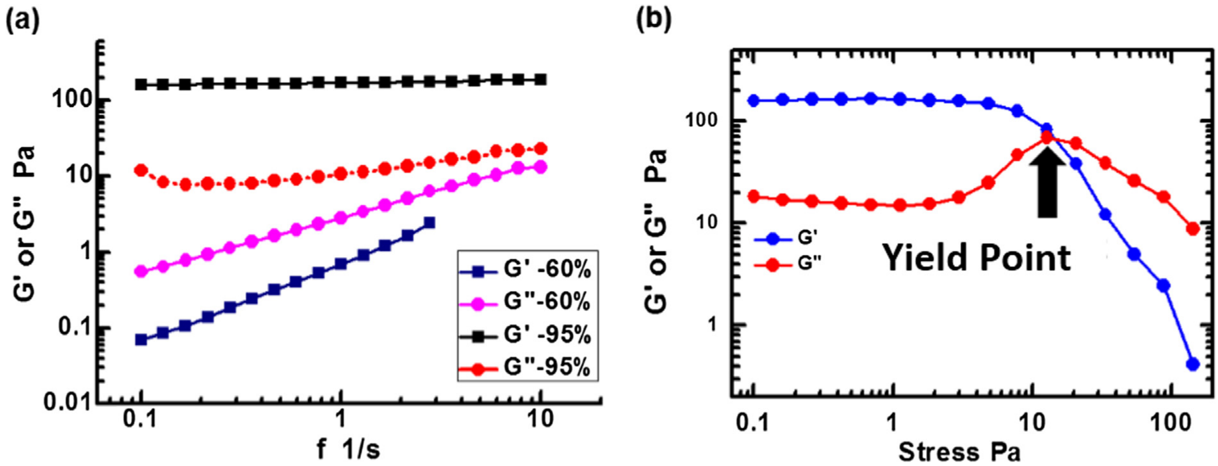

Fig. 6. (a)Oscillation frequency sweep test for 60 wt% and 95 wt% water emulsion which DC8500/SO was 1/17. (b)Amplitude sweep test for 95 wt% water emulsion which DC8500/SO was 1/17. The starch **1** was added as 10 wt% of DC8500 and SO mixtrue.

red fluorescence indicating a W/O structure of emulsions by both CLSM and optical microscopy (Fig. 7). When the water content was lower than 74 wt%, the droplets are spherical. With water dosages increasing, the droplets in emulsions grew larger and gradually turned morphologies into non-sphere. The non-spherical structures suggested a low interfacial tension between W/O phases. In addition, when the water dosed up to 95 wt%, the droplets grew into polyhedral structure because of the formation of high internal phase emulsion (HIPE), as show in Fig. 7c and f. The lower interface tension lead to an increasing size of water droplet in emulsions with higher water content. The growing droplets would tend to aggregate and the morphology of droplets become non-spherical when the water content was above 74 wt%.[29]

Meanwhile, the internal structure of the emulsion with 95 wt% water content was tested by Cryo-SEM in Fig. 8. The morphology of droplets was polyhedral with size ranging from several to one hundred micrometers. In Fig. 8b and 8c, the cross-section of the droplets revealed the distribution of starch **1** in the emulsion. The outside boundary of droplets was about two micrometers with oil phase. Most starch **1** was found in center of the droplet as shown in Fig. 8c. But the starch **1** was only suspending in water which located inside of the droplets. This was probably because of the amphiphilic property of starch **1** with C12 modified structure, which made starch **1** stable in water droplets. As a consequence, starch **1** helped maintain more water in the emulsions as a stabilizer.

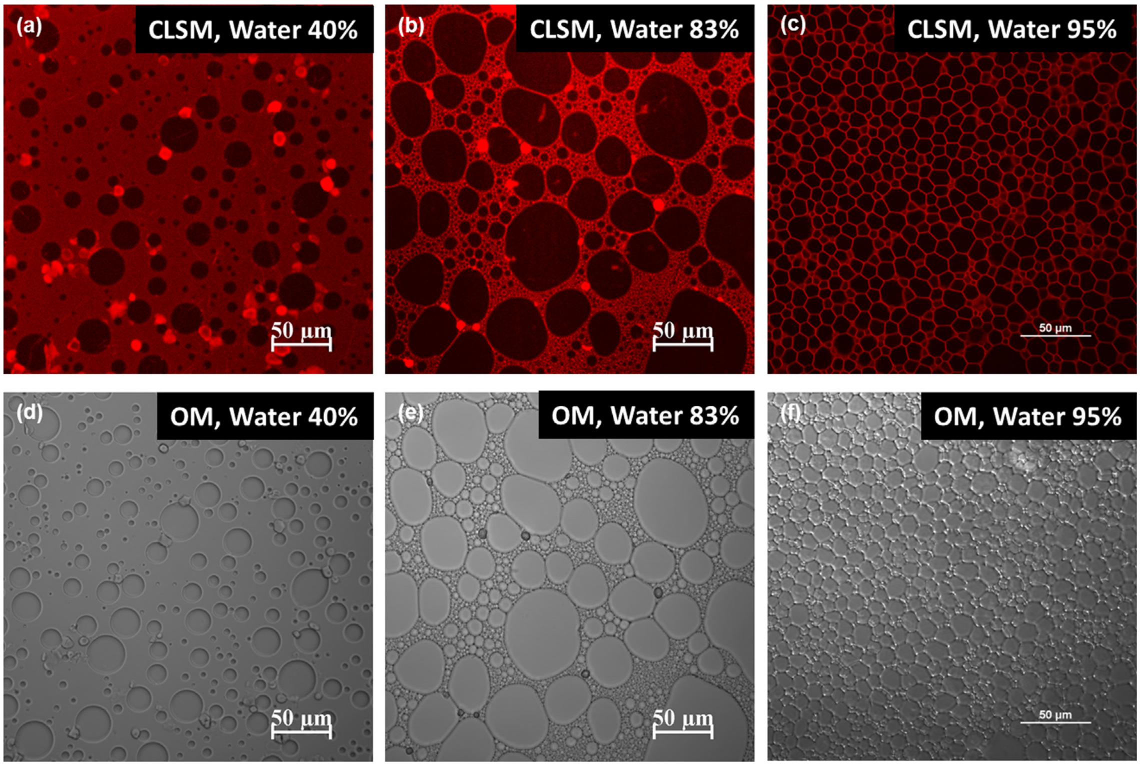

Fig. 7. Microstructure of various emulsions with different water contents (40 wt%, 83 wt%, 95 wt%) as shown by CLSM (a-c) and optical microscopy (d-f). Scale bar is 50 μm.

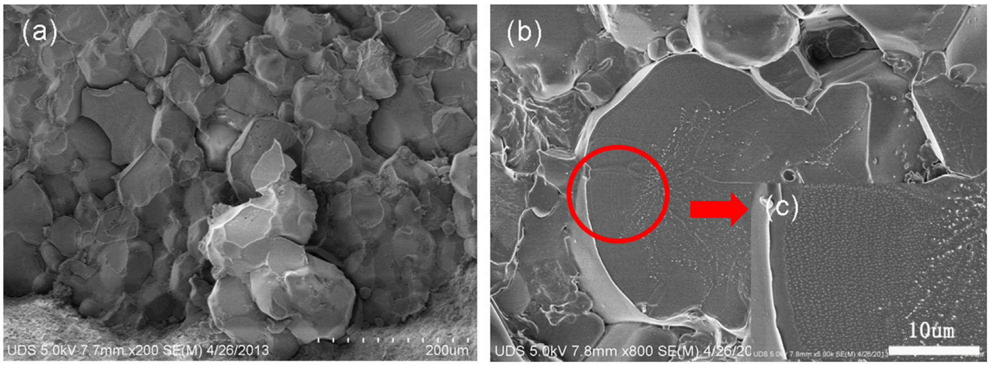

Fig. 8. Cryo-SEM images of microstructure of emulsion with 95 wt% water content. (a)Polyhedral droplets in emulsion, scale bar is 200 μm. (b)Cross-section of a droplet in the emulsion. (c)The distribution of starch **1** in water and oil phase respectively: NO starch **1** was observed in oil phase, instead of dispersing in water of droplets. Scale bar is 10 μm.

3.4. Effect of DC8500

With polyhydroxyl aminofunctional group modifying on the silicones, DC8500 showed well capability of emulsification and contributed to the formation of HIPE. Starch **1** can stable the emulsions in the water phase of emulsions. When the ratio of DC8500/SO was 1/17, HIPEs were acquired with 95 wt% water content. It is indicated that the amphiphilic property of silicones can be adjusted to construct into stable emulsions even with small amount of DC8500. As DC8500 is industrial product, C14-C15 fatty alcohol contained in the raw materials and may influence the formation of emulsions. Tetradecanol was assessed to investigate the effect of fatty alcohol. Upon addition of 5 wt% tetradecanol, the maximum water content decreased to 91 wt% in the emulsions that indicated the negative effect of fatty alcohol on formation of emulsions. On the contrary, the existence of alcohol highlighted the superior capability of DC8500 on emulsification. Some other chemical grade compounds was tested as well, such as SO-NH_2 which is amino group modified silicones (Fig. 9), no stable emulsion can be formed whether mixed with starch **1** or not. It is indicated that DC8500 exhibited superior capability on emulsification as emulsifier and exhibited potential benefit in industrial application with low price.

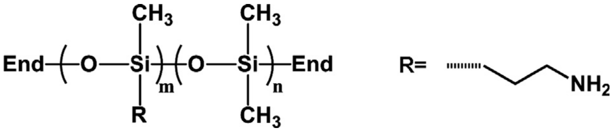

Fig. 9. The structure of aminofunctional group modifying siliconess (SO-NH_2).

3.5. Effect of starch 1

Starch **1** is a C12 modified corn starch with high effective emulsification and stabilization properties. When DC8500/SO was 1/1, the emulsions without starch **1** were formed with water content up to 20 wt%. Adding small amount of starch **1** (1 wt% of the DC8500 and SO mixtrue), the water content can significantly increase to 83 wt%. Some studied have been reported that the strength of emulsions can be enhanced by starch [30]. Rousseau et al. [31] applied starch in the emulsions and the *G*” enhanced to ~50 Pa after adding 6 wt% starch [32]. Fig. 10a showed that *G*′ increased from ~80 Pa to ~180 Pa and *G*” from ~3 Pa to ~10 Pa when 0.3 wt% starch **1** was added. Fig. 10b showed that increasing starch **1** from 0 wt% to 10 wt% enhanced the viscosity of emulsions. Because starch **1** can stably exist in the water phase as particles to increase the strength of emulsions. In addition, compared with some chemical products, the food-grade starch **1,** was cheap, friend to environment, easy to get, as well as excellent stabilization property. With starch **1** added, the emulsions can be stored for 6 months at room temperature.

4. Conclusion

Emulsions can be constructed by DC8500, SO, starch **1** and water. With increasing water contents, the emulsions encountered

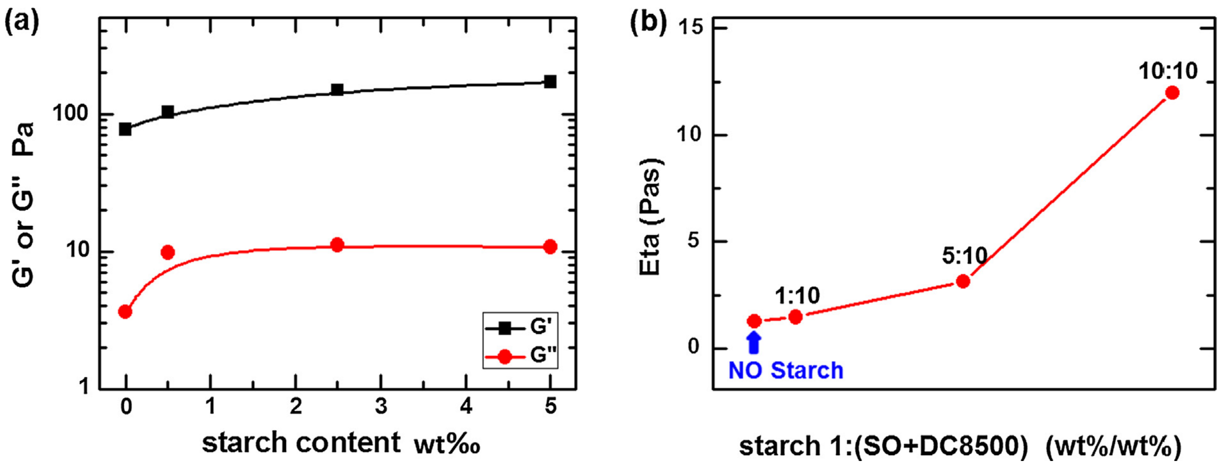

Fig. 10. The effect of starch **1** on (a) *G*′ and *G*”, and (b) viscosity with increasing dosages.

from a liquid-like to gel-like behaviors with enhancing yield point. When DC8500/SO was 1/17 with 10 wt% starch **1**, a high internal phase emulsion can be acquired with 95 wt% water content. The polyhedral droplets inside suggested a low interfacial tension exiting in the emulsion. DC8500 and SO worked as efficient emulsifiers and possessed amphiphilic property to form emulsions with water in different ratios. A food-grade starch **1** was supplied as a stabilizer which can enhance both water content and strength of emulsion when added in a low concentration. Moreover, it is indicated the food-grade starches provided potential benefit on fabricating emulsions with high water content as stablizers [2,33,34]. Compared with synthetic products, food-grade materials exhibited more advantages with renewable, low cost and non-toxicity which is ideal in more applications, such as personal care [35]. Moreover, the results contributed to the understanding of emulsions preparation with food-grade materials and the mechanism on how modified silicones and starch worked together on constructing emulsions.

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